

**UK Technical Advisory Group  
on the Water Framework Directive**

**PROPOSALS FOR FURTHER ENVIRONMENTAL  
QUALITY STANDARDS FOR SPECIFIC POLLUTANTS**

**Final version for UKTAG**

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### PROPOSALS FOR ENVIRONMENTAL QUALITY STANDARDS FOR SPECIFIC POLLUTANTS

#### INTRODUCTION

The Water Framework Directive requires that Member States identify and set standards for 'specific pollutants'<sup>1</sup>. These are synthetic and non-synthetic toxic substances that are discharged in significant quantities into the water environment.

After consultation in 2007, the UKTAG published its recommendations for environmental quality standards (EQSs) for the following 19 specific pollutants [1]:

ammonia, arsenic, chlorine, chromium(III), chromium(VI), copper, cyanide, cypermethrin, diazinon, 2,4-dichlorophenol, 2,4-dichlorophenoxyacetic acid (2,4-D), dimethoate, iron, linuron, mecoprop, permethrin, phenol, toluene, zinc

For 11 of these pollutants, the recommended EQSs were the same as those set previously under the Dangerous Substances Directive (DSD) (76/464/EEC). This relates to:

ammonia (saltwater long-term standard only), arsenic, chlorine, copper, cyanide, diazinon (saltwater short-term standard only), 2,4-dichlorophenol, iron, permethrin, toluene (long-term standards only), zinc

Since publishing its last recommendations, the UKTAG has identified a number of potential additional specific pollutants and has developed recommendations on EQSs for 10 of these. It has also revisited the EQSs for the 11 pollutants referred to above to ensure the standards reflect the latest scientific information on their effects on the environment.

This report describes:

- (a) the basis for selecting the proposed additional specific pollutants;
- (b) the procedure used to derive proposed EQSs for these and to revise the EQSs for existing specific pollutants;
- (c) the proposed EQSs;
- (d) how the proposed standards differ from existing standards; and
- (e) an estimate of the extent of compliance with the standards.

The proposed standards are recommended for the following purposes:

- Assessing, as relevant, the ecological status or ecological potential of bodies of surface water. When one or more substances are assessed in a water body, their standards have to be met to be considered good status.

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<sup>1</sup> Pollutants covered by the list in Annex VIII, points 1–9, of the Water Framework Directive. The identification of priority and priority hazardous substances and the setting of their standards is done at the European level.

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- Identifying where action to improve water quality should be taken. Action is considered appropriate provided there is adequate confidence that an EQS is breached. Corroborating evidence of biological damage at failing sites is considered unnecessary given the process by which the standards are set.
- Calculating the degree of action needed to achieve good water quality and where that action is feasible and not disproportionately expensive. This includes bespoke action for permitting individual discharges and regional or national initiatives, such as controls on the use of chemicals or the land.
- Assessing whether a proposed new use or discharge of a pollutant poses a risk to the water environment or whether it can be accommodated without breaching the EQS for the pollutant.

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### OVERVIEW OF THE PROCESS – FROM SUBSTANCE IDENTIFICATION TO DEVELOPING PROPOSALS FOR SPECIFIC POLLUTANTS

The UKTAG has developed its recommendations in the light of the *Framework for Standards* [2], a process which reviews the scientific basis for the standard, the degree of protection it provides, its impact on those who may have to take action to secure compliance<sup>1</sup>, and a consideration of the practical aspects of using the standard.

This report covers the first steps in the *Framework for Standards* – the scientific assessment. The process is illustrated in Figure 1. The steps include:

- choosing the substances that need standards;
- deriving draft standards and subjecting their basis to peer review;
- checking the standards to see whether, technically, they can be adopted in practice as effective standards<sup>2</sup>.

This report does not cover:

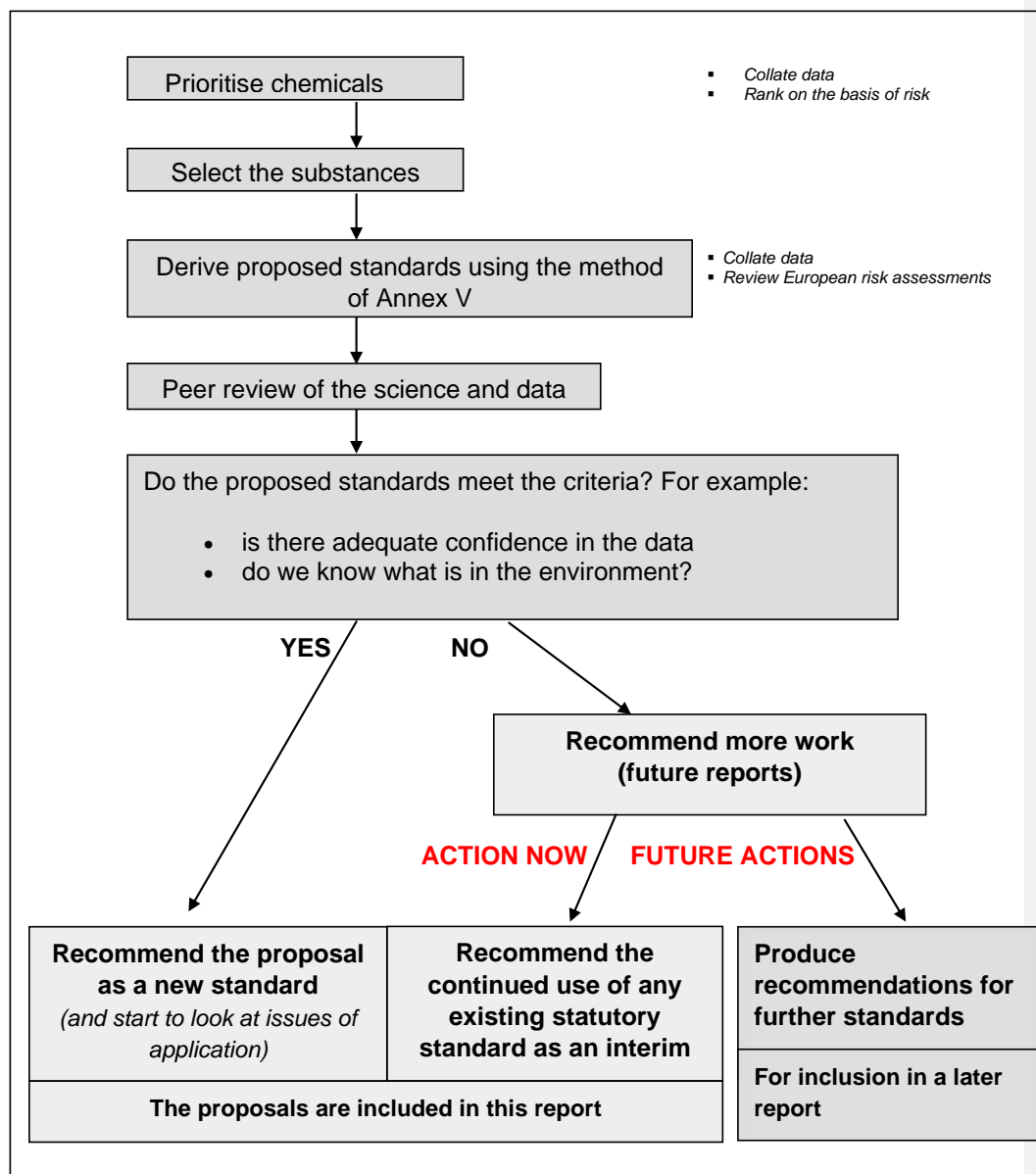
- an economic assessment of the impacts of the standards;
- a full consideration of the practical aspects of using the standards.

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<sup>1</sup> Which in this case will be part of the Regulatory Impact Assessments undertaken by the administrations.

<sup>2</sup> Examples of issues of implementation are given in [5].

**Figure 1** The process for determining recommended standards



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### **Identification of proposed new specific pollutants**

The UKTAG's starting point for identifying potential additional specific pollutants was a list of more than 300 chemicals. This list included substances covered by existing legislation, those subject to current obligations for monitoring, and substances that have emerged recently as concerns.

The substances in the list were ranked using a method consistent with European guidance agreed under the Common Implementation Strategy for the Water Framework Directive [3]. For each substance, the UKTAG considered:

- its hazardous properties – the persistence of the substance, its potential to bioaccumulate, and its toxicity;
- the potential environmental exposure to the substance – this was based on the level and pattern of use, or on data from monitoring.

Each substance was scored against these criteria. The scores were combined in an assessment of the risk to aquatic life. A rank of 1 indicates high risk and a value of 5 indicates very low risk<sup>1</sup>. Substances ranked 1 or 2 are considered as candidates for identification as specific pollutants.

Sixty-nine substances were ranked 1 or 2 through this process and their ranking was subject to peer review. The results are listed in Tables A1 (ranked 1) and A2 (ranked 2) in Annex A along with a summary for each substance of the final conclusion from the review. The peer review concluded that substances either:

- were a priority for EQS development;
- were not a priority because other work may have an influence on the potential permitted marketing and use of the substance, or because adequate controls for that substance were already in place; or
- required further investigation to improve confidence in their ranking, such as monitoring data to corroborate the occurrence of the substance in the environment in cases where the assessment of exposure was based only on data on the use of the substance.

The prioritisation and review resulted in the identification of 11 substances as possible new specific pollutants. Three of these are also under consideration at the European level as potential priority substances, ie EE2, E2 and PFOS. We have considered the remaining eight chemicals for EQS development as candidate specific pollutants. These are:

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<sup>1</sup> The prioritisation process has minimum data requirements. Where these are not met for a substance, a ranking cannot be assigned.



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benzyl butyl phthalate, carbendazim, chlorothalonil, 3,4-dichloroaniline, glyphosate, methiocarb, pendimethalin, triclosan
--

The list of substances for identifying candidate specific pollutants will be kept under review by the UKTAG.

The prioritisation process is designed for ranking pollutants that are organic chemicals rather than inorganic compounds or metals. The UKTAG will also consider other emergent substances that may pose risks to the environment, but which are not suitable for putting through the process. Thus, silver has been identified for consideration as a new candidate specific pollutant.

In its previous report, the UKTAG was unable to recommend proposals for aluminium, manganese and tetrachloroethane. It had identified these as candidates for EQS development. The UKTAG proposed that more data were collected for these substances and advised the need to consider how standards for metals could be implemented. We have reconsidered these substances for this report.

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### The process for developing the standards

The scientific methods used to derive the values proposed in this report are specified in Annex V to the Water Framework Directive and are described in detail in recent European guidance [4].

The UKTAG has evaluated 10 substances using the methods required under the Water Framework Directive. It proposes new standards for these chemicals and that they are treated as specific pollutants (Tables 1.1–1.10). These substances are:

benzyl butyl phthalate, carbendazim, chlorothalonil, 3,4-dichloroaniline, glyphosate, manganese, methiocarb, pendimethalin, tetrachloroethane (TCE) and triclosan

The UKTAG has also looked at aluminium and silver. There are no existing statutory EQSs for these chemicals. The UKTAG is unable to make recommendations at present, but may propose standards in future. It is therefore premature to propose these substances as specific pollutants.

As noted above, the UKTAG has reviewed the EQSs for the 11 specific pollutants for which, in its previous report [1], it had recommended the use of existing statutory EQSs as an interim measure<sup>1</sup>. At that time these EQSs were retained for a variety of reasons. For example, in cases where there was too much uncertainty in the science or gaps in data, new standards could not be proposed.

This report proposes updated EQSs for six of these specific pollutants (see below). In addition for diazinon (saltwater short term) and toluene (long term), existing statutory standards were previously recommended because the standards derived using the Water Framework Directive method were less stringent<sup>2</sup>. The UKTAG has reviewed the situation for these two substances and recommends using the standards derived by the Water Framework Directive method for the second river basin management plans because they reflect the best available science.

copper, cyanide, diazinon, 2,4-dichlorophenol, iron, permethrin, toluene and zinc

For the remaining three substances, arsenic, ammonia and chlorine, the UKTAG recommends maintaining the existing EQSs.

There are, in addition, a number of substances covered by the DSD that were neither scheduled as priority substances under the Water Framework Directive nor identified as specific pollutants

<sup>1</sup> These substances were implemented as specific pollutants through Directions in England, Wales and Scotland and Regulation SR 2011 No. 10 in Northern Ireland.

<sup>2</sup> Article 22.6 of the Water Framework Directive states that EQSs under the first river basin management plans should be at least as stringent as those under the DSD.

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in the earlier UKTAG report [1]. These are the List II substances. The UKTAG's priority assessment ranked these substances at a score of 3 or below using the method described in the previous section. Because the provisions of the DSD will be repealed in 2013, the UKTAG has reviewed the risks posed by these substances [5]<sup>1</sup>. The 12 substances considered are:

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

None of these substances have been identified in significant concentrations by monitoring programmes<sup>2</sup> and in addition a number are subject to controls on their marketing and use, eg fenitrothion is not approved for use as a pesticide in the UK or EU. The UKTAG therefore concludes that it is not necessary to propose these substances as specific pollutants and develop standards for these substances<sup>3</sup> once the DSD is repealed. It is therefore recommended that any extra requirements for these substances under the Water Framework Directive are repealed.

One of the substances, dichlorvos, has recently been proposed as a priority substance by the European Commission. Future requirements for this substance may be put in place at an EU level.

The DSD standards for these substances can still be used as operational values for those situations where these substances occur.

### Deriving the standards

For most substances, extensive sets of field data on chemistry and biology are not available, and the method for deriving EQSs for specific pollutants uses laboratory studies of toxicity. Difficulties in interpreting laboratory data for a few substances, for example iron, mean that an analysis of field data is the favoured approach. In other cases, matched chemical and biological data have provided supporting evidence in deriving some standards, such as for zinc.

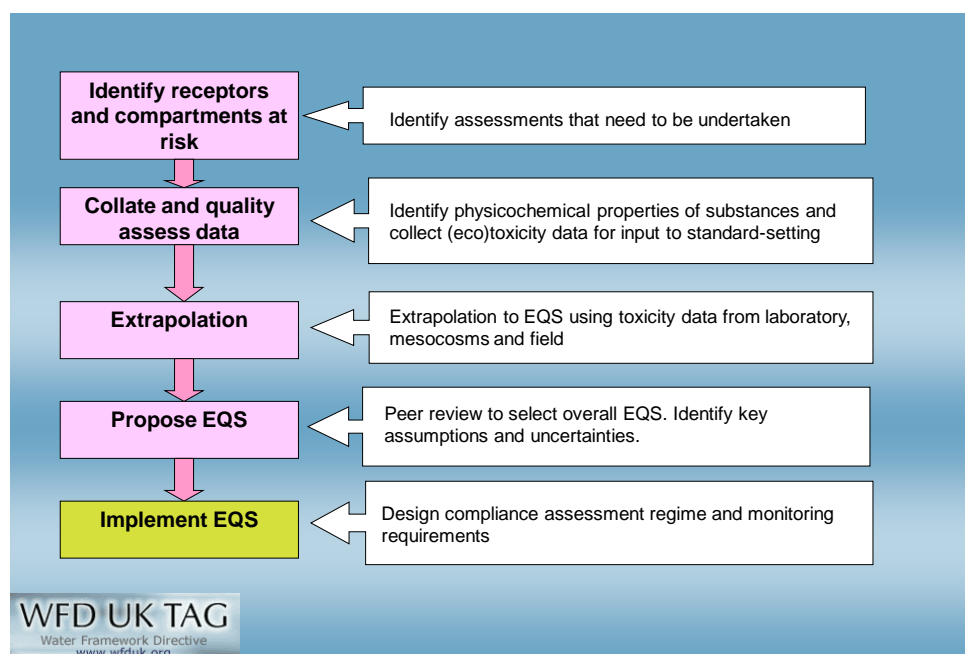
Annex B sets out the process for developing standards and the associated technical issues. The stepwise process is illustrated in Figure 2 and described below.

<sup>1</sup> Other remaining DSD List II substances that were no longer authorised for use were not included in the priority assessment. These were azinphos-methyl, demeton, omethoate, triazophos, PCSDs, sulcofuron and flucifuron. Their status has also been assessed in an annex to the review mentioned here.

<sup>2</sup> Bentazone has shown a slight drop in agricultural usage since 2006 [available at <http://pusstats.csl.gov.uk/> accessed 1 September 2011]. It was not possible to form any meaningful conclusions from monitoring data for dichlorvos, but this substance is no longer authorised for use.

<sup>3</sup> Azinphos-methyl, demeton, omethoate, triazophos, PCSDs, sulcofuron and flucifuron also do not require new standards.

**Figure 2 Steps in deriving a standard**



**Step 1:** Identify which receptors may be at risk, for example aquatic life, sediment-dwelling organisms or predatory biota.

**Step 2:** Collate information on the effects of chemical concentrations on aquatic biota. (The UKTAG uses the outputs of European risk assessments, where these are available.) Assess the quality of these data and decide which are critical to setting the predicted no-effects concentration (PNEC)<sup>1</sup>. Considerations include:

- the reliability of the toxicity data, in particular to be sure that the effects seen are of ecological relevance and that any changes are big enough to be of concern;
- the particular chemical form of the pollutant that is toxic<sup>2</sup>;
- whether naturally occurring background concentrations are likely and whether the biota would acclimatise to them<sup>3</sup>.

The last two points may also need to be considered when applying the standard, particularly those for metals (see Annex C).

<sup>1</sup> The PNEC is the concentration of a pollutant below which no harmful effects on aquatic organisms would be expected.

<sup>2</sup> For metals in particular, the toxic form and its availability may be affected by the properties of the surface waters that it is found in. In such cases, where possible, data are used to derive a standard expressed as a 'bioavailable' concentration.

<sup>3</sup> Discounting background levels as part of deriving the standard is called the 'added risk approach', whereas deriving the standard without discounting background levels is called the 'total risk approach'.

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**Step 3:** Use these data to derive PNECs, effectively extrapolating from a concentration that shows no effect on biota in laboratory experiments. This can be done by one of two methods<sup>1</sup>:

1. Deterministic extrapolation from the most sensitive species

This involves looking at the confidence in the information, in particular, the range of species for which there are toxicity data. Where the data are uncertain or limited, an allowance is made for this. Under the Water Framework Directive, this is done by starting with the lowest credible toxicity concentration for any of the biota tested and tightening it by a factor that lies between 10 and 1000. This factor is called an 'assessment factor'<sup>2</sup>. Low overall confidence in the dataset leads to a high assessment factor and tighter standards – a more precautionary approach. The result, after applying the assessment factor to the concentration that has no effect on the biota, is the PNEC<sup>3</sup>.

2. Using mathematical models

Species sensitivity distribution (SSD) models describe the number of species likely to be affected by a particular concentration, and such models can be used to estimate PNECs for those chemicals where data are plentiful. In such circumstances, the model can improve confidence in the value chosen to derive the PNEC and so reduce the value of the assessment factor (between 1 and 5) that is applied.

**Step 4:** Peer review the derived PNECs to seek confirmation that they are valid scientifically, and that the data used to derive them are sound and complete. A panel of independent scientists from the UK advises on the adequacy of the data, the extent to which these data should influence the final PNEC, and how the UKTAG should interpret the data. The results are discussed at workshops attended by members of the UKTAG, contractors undertaking some of the scientific assessments and peer reviewers.

Generally, the proposals of the UKTAG represent the consensus of the reviewers. Any differences are discussed in the technical reports [7].

The PNECs that come through this process can be recommended as the basis for the standards<sup>4</sup>. These PNECs may differ for saltwater and freshwater<sup>1</sup>. Often two PNECs are

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<sup>1</sup> For iron, a quite different approach has been adopted because of the difficulties in interpreting laboratory ecotoxicity data. In this case, the PNEC is based on an analysis of field data in a similar way to that done for ammonia and dissolved oxygen under the environmental standards programme.

<sup>2</sup> Assessment factors are applied as specified in the EU guidance and are set based on the quantity of the data and, in particular, the coverage of the biota [4].

<sup>3</sup> For example, an assessment factor of 10 means that the proposed standard will be one tenth of the value produced by the laboratory work.

<sup>4</sup> Those that do not are the subject of proposals for further work.

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provided.

The first leads to a short-term standard. The PNEC for this is based on the analysis of data from acute (short term) toxicity studies, usually lasting for hours or a few days and typically measuring effects on survival or sometimes growth of test plants and animals. The resulting standard aims to protect against intermittent or short-lived periods of exposure<sup>2</sup>.

The second PNEC leads to a long-term standard. The PNEC is derived by analysing data from chronic (long term) toxicity tests typically conducted over weeks, months or even years and often measuring effects on reproduction, growth and development. It is designed to protect against prolonged or continuous exposure.

**Step 5:** The final step is to consider the practicalities of implementing a particular standard, including analytical practicalities, or whether there is a need to account for natural backgrounds.

### Accepting a predicted no-effect concentration as a draft UK standard

As discussed above, we are required to apply assessment factors whose scale increases with the uncertainty in the data. The UKTAG notes that:

1. Large assessment factors may lead to standards that are too strict. The UKTAG takes the view that EQSs should be based on adequate data in which there is sufficient confidence, removing the need for large assessment factors.
2. In chemical risk assessment, a large assessment factor would normally trigger the generation of new data to improve the understanding of the risks and so allow a smaller factor to be used and a new PNEC to be proposed. This step may not be possible within the timetable for deriving EQSs for use in the second round of river basin management planning.

The UKTAG has proposed new EQSs only where there is sufficient scientific evidence to set those standards<sup>3</sup>. Standards are proposed when the assessment factor used in their derivation is at or below 50 or 100 for freshwater and saltwater values, respectively (for further information, see Annex B).

Where this criterion is met, the UKTAG advises that:

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<sup>1</sup> For a number of the substances considered as candidate specific pollutants, the proposed freshwater and saltwater values are identical. However this is not the case for benzyl butyl phthalate, copper, cyanide, 2,4-dichlorophenol, permethrin and zinc. For these substances, the approach taken for transitional waters will be to use the saltwater standards, which are usually more stringent. This follows the precedent set by the EU Directive on environmental quality standards for priority and priority hazardous substances (2008/105/EC).

<sup>2</sup> This can be the main issue for some chemicals, for example, pesticides.

<sup>3</sup> The UKTAG would also look to see whether a proposed PNEC is so close to the natural background that its implementation might give rise to spurious EQS failures.

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1. the PNEC is proposed now as the basis for a new UK standard;
2. the substance is used as a specific pollutant for the Water Framework Directive in the second round of river basin plans.

Where this criterion is not met, ie there is low confidence in the data and the resulting PNEC, the UKTAG recommends that:

3. any existing statutory EQS, if available, is adopted in the interim.
4. any substance covered by such a standard remains a specific pollutant for the Water Framework Directive in the second round of river basin management plans.

When failure is reported for saltwater standards derived using an assessment factor of 100, it is recommended that supporting information, including evidence of ecological damage, should be obtained before committing to expensive action.

In its previous report [1], the UKTAG was unable to make new proposals for some substances because of issues with uncertainty in the science or data. To help reduce that uncertainty, the UKTAG commissioned the generation of new toxicological data. Some of the UKTAG's proposals in this report reflect the results of these studies. Improvements in data (for example, from field monitoring) have also given an increased level of confidence to some of the proposed standards.

Sometimes, uncertainty about the PNEC is coupled with difficulties in chemical analysis. Extra toxicological data can improve confidence and thus lead to a less-stringent value. This in turn can remove the need to develop new techniques of chemical analysis. However, some proposals (indicated in Tables 1.12, 1.16 and 1.18), while based on a large body of evidence, may still demand new methods of chemical analysis.

The UKTAG will also not propose values that are around or below ckground levels.

In addition to PNECs based on the direct toxicity of a substance to organisms in water, secondary poisoning PNECs may be derived when predators or humans are likely to be exposed to the substance via the food chain. This secondary poisoning PNEC can be converted into an equivalent concentration for application in the water column. If this secondary poisoning PNEC is more stringent than the long-term water column value, the former PNEC is recommended for the basis of the EQS.

The UKTAG has also considered the relevance of the PNECs for different types of water in terms of likely exposure. For example, proposals for a saltwater EQS are not made where the use of a substance is likely to result in discharges to freshwater only, as is expected with agricultural pesticides, and where such discharges disappear before rivers reach the sea. However, the PNECs are derived for both freshwater and saltwater environments, and those values not taken forward as proposals now could still be applied as guideline operational values, if required.

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## THE PROPOSALS

This report proposes new standards for 18 substances: benzyl butyl phthalate, carbendazim, chlorothalonil, copper, cyanide, diazinon, 3,4-dichloroaniline, 2,4-dichlorophenol, glyphosate, iron, manganese, methiocarb, pendimethalin, permethrin, tetrachloroethane (TCE), toluene, triclosan and zinc.

The proposals are set out in Tables 1.1–1.18: Tables 1.1–1.10 list proposals for new specific pollutants, and Tables 1.11–1.18 list proposed revisions for some existing specific pollutants. For comparative purposes, existing EQSs for the substances, where available, are shown. The proposed EQSs apply to the water column<sup>1</sup>. Unless specified otherwise, the standards apply to unfiltered samples. The approach is consistent with that adopted at EU level for priority substances.

When they are used in classification and to decide the actions needed to secure and maintain compliance, proposals for standards are defined as summary statistics, such as an annual mean concentration or annual percentile concentration. The standard can also then be used to calculate things like limits in the permits for discharges, and the costs and benefits of new policies on the use of substances.

Long-term EQSs are expressed as annual means; the short-term values are annual 95-percentiles. Where separate short-term EQSs based on acute toxicity data are not proposed, any short-term risk is considered to be managed sufficiently through the achievement of the long-term EQSs. This is for two reasons: Firstly, because experience shows the substances, for example many metals, tend to occur continuously rather than only for short episodes. Secondly, because in securing the annual mean, there is confidence that the annual 95-percentile and all rarer percentiles are met automatically. In cases where the use of a chemical is likely to result in short episodes of exposure, such as for many pesticides, and the long-term standard may not be effective enough, a short-term standard based on acute toxicity data will be proposed.

The UKTAG recommends that where the standard is used in classification, assessment of compliance is based on data taken over one or more complete years. This ensures a balance between typical rates of sampling and the risks of declaring wrongly the sites have passed or failed.

Generally it has been shown that the achievement of the annual mean and the annual 95-percentile protects against all risks. For some chemicals and their mode of use, the use of the annual mean and annual 95-percentile may need to be augmented by extra measures to control risks that result from rare and dramatic accidents, the illegal use of a chemical or approved direct applications (see Implications for particular chemicals). In these cases, the protection that

<sup>1</sup> Of the substances evaluated, only the herbicide pendimethalin is deemed sufficiently bioaccumulative to warrant determination of a biota standard. The values presented are based on the biota standard, but are back-calculated to the equivalent concentration in water.

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achieves the annual mean and annual 95-percentile is overlaid with extra measures to control the added risks, or through the imposition of absolute limits and upper-tiers in the permits of discharges.

Further detail on the expression of standards and the assessment of compliance is given in Annex B.

Annex D sets out a summary of information for each proposed EQS listed in Tables 1.1–1.18. Each summary includes:

- the fate and properties of the substance;
- an explanation of how the PNECs were derived;
- the assessment factor used in each case;
- the proposed PNECs for freshwater and saltwater;
- initial proposals on how the standards might be used.

The detailed scientific documents detailing all aspects of the data used and the derivation of the PNECs, after consideration by the peer review panel, are available via the UKTAG [7].

<b>Table 1.1: Recommended standards for benzyl butyl phthalate (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	7.5	20
	Short-term	95-percentile	51	100
Salt	Long-term	Mean	0.75	20
	Short-term	95-percentile	10	100
The proposed saltwater long-term standard has been derived using an assessment factor of 100. Where the standard is failed, it is recommended that supporting evidence of ecological damage should be obtained before committing to expensive action.				

<b>Table 1.2: Recommended standards for carbendazim (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.15	0.1
	Short-term	95-percentile	0.7	1.0

<b>Table 1.3: Recommended standards for chlorothalonil (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.035	0.1
	Short-term	95-percentile	1.2	1.0

<b>Table 1.4: Recommended standards for 3,4-dichloroaniline (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.2	–
	Short-term	95-percentile	5.4	–

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Salt	Long-term	Annual mean	0.2	–
	Short-term	95-percentile	5.4	–

<b>Table 1.5: Recommended standards for glyphosate (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	196	–
	Short-term	95-percentile	398	–
Salt	Long-term	Mean	196	–
	Short-term	95-percentile	398	–

<b>Table 1.6: Recommended standards for manganese</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	123 µg/l bioavailable	30 µg/l dissolved
"Bioavailable" means the fraction of the dissolved concentration of manganese (that which passes through a 0.45-µm filter) likely to result in toxic effects as determined in accordance with the Metal Bioavailability Assessment Tool (M-BAT) for manganese (see Annex C).				

<b>Table 1.7: Recommended standards for methiocarb (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.01	0.01
	Short-term	95-percentile	0.77	0.16

<b>Table 1.8: Recommended standards for pendimethalin (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.1	1.5
	Short-term	95-percentile	0.58	6.0

<b>Table 1.9: Recommended standards for tetrachloroethane (TCE) (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	140	–
	Short-term	95-percentile	1848	–

<b>Table 1.10: Recommended standards for triclosan (µg/l)</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.1	–
	Short-term	95-percentile	0.28	–
Salt	Long-term	Mean	0.1	–
	Short-term	95-percentile	0.28	–

<b>Table 1.11: Recommended standards for copper</b>				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	1 µg/l bioavailable	1–28 µg/l dissolved
Salt	Long-term	Mean	2.64 µg/l dissolved,	5 µg/l dissolved

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			where DOC ≤1 mg/l	
			$2.64 + (2.677 \times ((\text{DOC}/2) - 0.5)) \mu\text{g/l}$ dissolved, where DOC >1 mg/l	
<p>"Bioavailable" means the fraction of the dissolved concentration of copper (that which passes through a 0.45-µm filter) likely to result in toxic effects as determined in accordance with the Metal Bioavailability Assessment Tool (M-BAT) for manganese (see Annex C).</p> <p>"DOC" means the annual mean concentration of dissolved organic carbon in mg/l.</p> <p>The proposed saltwater standard applies to the fraction of a water sample that passes through a 0.45-µm filter or that is obtained by any equivalent pre-treatment.</p> <p>The existing freshwater standard depends on the hardness of the water.</p>				

Table 1.12: Recommended standards for cyanide ('free' i.e. µg/l of HCN/l)				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.26	1
	Short-term	95-percentile	2.8	5
Salt	Long-term	Mean	0.052	1
	Short-term	95-percentile	0.42	5
There are analytical issues associated with these proposals.				

Table 1.13: Recommended standards for diazinon (µg/l)				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Salt	Short-term	95-percentile	0.26	0.1
No changes are proposed to the UKTAG's existing recommendations on freshwater standards for diazinon or to its recommended long-term saltwater standard.				

Table 1.14: Recommended standards for 2,4-dichlorophenol (µg/l)				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	4.2	20
	Short-term	95-percentile	140	–
Salt	Long-term	Mean	0.42	20
	Short-term	95-percentile	6	–
The proposed saltwater standards have been derived using an assessment factor of 100. Where these standards are failed, it is recommended that supporting evidence of ecological damage should be obtained before committing to expensive action.				

Table 1.15: Recommended standards for iron (ug/l)				
Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	730 µg/l total	1000 µg/l dissolved
No change is proposed to the UKTAG's existing recommended standard for iron in saltwaters.				

Table 1.16: Recommended standards for permethrin (µg/l)				
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Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	0.001	--
	Short-term	95-percentile	0.01	0.01
Salt	Long-term	Mean	0.0002	–
	Short-term	95-percentile	0.001	0.01
There are analytical issues associated with these proposals.				

**Table 1.17: Recommended standards for toluene (µg/l)**

Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	74	50
Salt	Long-term	Mean	74	40
No changes are proposed to the UKTAG's existing recommendations on short-term standards for toluene in freshwaters and saltwaters.				

**Table 1.18: Recommended standards for zinc**

Water	Exposure	Annual statistic	UKTAG proposal	Existing standard
Fresh	Long-term	Mean	10.9 µg/l bioavailable additional to bioavailable natural background	8– 125 µg/l total
Salt	Long-term	Mean	3.4 µg/l dissolved additional to dissolved natural background	40 µg/l dissolved
<p>"Bioavailable" means the fraction of the dissolved concentration of zinc (that which passes through a 0.45-µm filter) likely to result in toxic effects as determined in accordance with the Metal Bioavailability Assessment Tool (M-BAT) for zinc (see Annex C).</p> <p>"Natural background" means the concentration expected with no or only minor anthropogenic inputs (see Annex C).</p> <p>The proposed saltwater standard applies to the fraction of a water sample that passes through a 0.45-µm filter or that is obtained by any equivalent pre-treatment.</p> <p>There are analytical issues associated with the saltwater proposal.</p> <p>The existing freshwater standard depends on the hardness of the water.</p>				

In line with the established principles under the DSD and the Priority Substances Directive (2008/105/EC), the UKTAG recommends the designation of mixing zones adjacent to points of discharge. In such mixing zones, which must be restricted to the proximity of the point of discharge, concentrations of pollutants may exceed the relevant standards. The EU Common Implementation Strategy (CIS) guidance document on mixing zones provides advice to Member States on the identification of acceptable mixing zones [6].

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### THE IMPLICATIONS FOR SURFACE WATERS

#### Estimates of compliance with the proposed standards

Using the available monitoring data, the UKTAG has assessed some of the implications of applying its proposals. The assessment highlights the sites that are currently monitored which would exceed a standard. Where possible, results are given for face-value<sup>1</sup> estimates of failure and for failure based on high statistical confidence<sup>2</sup>.

The proportion of failures at face value is particularly relevant to the development of national actions and policies to improve compliance. Those with high statistical confidence imply high priority for local action.

There are few or no monitoring data available for a number of substances. This is in part due to the fact that some of the proposed specific pollutants are not covered under existing legislation, and therefore there are no specific requirements for monitoring, and because the substances have not previously been considered a threat to water quality. Where monitoring data are available, they will have been targeted at sites that are at risk because of past experience or incidents, or because of knowledge of activities in the catchment. For this reason, the proportions of failure are not necessarily representative of all rivers. However, data arising from known pollution incidents occurring at the time of the monitoring have been excluded. The periods over which data have been collected are given below.

Where possible, an assessment is also included of applying standards for metals expressed as bioavailable values, using the approach outlined in Annex C.

#### Implications for England

Table 2 gives an estimate of the number of monitored sites<sup>3</sup> in England that would not meet the new long-term standards listed in Tables 1.1–1.18.

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<sup>1</sup> Action at 50 per cent confidence involves taking no notice of statistical errors. Sometimes this is called taking action at face value. Such a policy means big risks that reported failures or passes are spurious and caused by statistical errors in sampling and analysis. An example of a face-value assessment is to work out the simple arithmetic average from 12 sample results. This is then compared with the mean standard. If the average were 12.26 and the standard were 10, this indicates failure at face value because 12.26 is worse than 10. In practice, the confidence interval around 12.26 may be 7 to 18. This range of uncertainty arises because there are only 12 samples (and there are 31 million seconds in a year), and because of errors in chemical analysis. This means that there is a strong possibility that the face-value failure is not a true failure – that the true annual average is less than 10.

<sup>2</sup>  $\geq 95\%$  confidence.

<sup>3</sup> There are 7105 surface water bodies in England and Wales and each one may contain more than one site. For example, there are 5818 river water bodies. Within these, 5920 sites in England and 900 in Wales are assessed for physicochemical parameters. Not all water bodies will be assessed for a pollutant, only those where there is a likely issue.

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In practice, the classification results from each site in a water body would be used to calculate the overall classification of a water body by taking the median result to determine the typical conditions for the water body.

The main driver for existing monitoring networks is the Water Framework Directive, but these networks may still encompass monitoring provisions for the Freshwater Fish Directive, Harmonised Monitoring<sup>1</sup>, the Oslo and Paris Convention, and the Dangerous Substances Directive. Table 2 is based on monitoring for the period 2008–2010 and includes saltwater sites. The monitoring data assessed were those with statutory sampling purpose codes<sup>2</sup>.

<b>Table 2: Specific pollutants – implications for England</b>			
Substance	Freshwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Carbendazim	0	0	6
Chlorothalonil	0	0	6
Copper (bioavailable)	see Table 3		
3,4-Dichloroaniline	0	0	8
2,4-Dichlorophenol	0	0	45
Glyphosate	0	0	15
Iron (total)	130 (32%)	49 (12%)	403
Manganese (bioavailable)	see Table 3		
Methiocarb	0	0	1
Pendimethalin	0	0	6
Triclosan	0	0	4
Zinc (bioavailable)	see Table 3		
Substance	Saltwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Copper (dissolved) <sup>(1)</sup>	81 (26%)	46 (15%)	311
2,4-Dichlorophenol	0	0	24
Glyphosate	0	0	3

<sup>1</sup> A UK scheme for special monitoring of the downstream limits of rivers.

<sup>2</sup> Data for England and Wales giving the results shown in the Tables 2 and 6 were assessed using an Environment Agency classification tool that processes information from samples with statutory sampling purpose codes of MI, MN, MP, MS and MU. Less than values in this tool are set to half the limit of detection value and the number of such values in each dataset are noted by the tool. Results for a sample point are only used if there are three or more sample results over the three-year period. The use of three years' data where possible reflects the three-year period used for classification.

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Zinc (dissolved) <sup>(2)</sup>	169 (59%)	106 (37%)	286
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## Notes to Table 2

- (1) The saltwater EQS for copper includes a correction for DOC. The compliance assessment has not been able to take this into consideration because of the limited data for DOC. The number of failures may therefore have been overestimated as the assessment does not incorporate this correction.
- (2) The zinc saltwater EQS was derived using the 'added risk' approach and, therefore, background concentrations should be used as part of compliance assessment (see Annex C). The assessment here does not take into account such concentrations and, therefore, the number of failures may be overestimated.

The implications of applying the copper, manganese and zinc standards in the freshwater environment have been reviewed by taking into account bioavailability at individual sites for which matched data are available<sup>1</sup>. Following the approach described in Annex C, the calculated bioavailable metal concentration – based on site-specific conditions – was compared with the bioavailable standard in a face-value assessment for each site. The results are shown in Table 3. For comparison, compliance of those sites against the current EQS values was also undertaken.

Table 3: Implications for England when applying bioavailable metal standards			
Substance	Freshwater sites 'not good' (face-value assessment)		Number of sites assessed
	Based on compliance with the existing EQS	Based on compliance with the proposed bioavailable EQS	
Copper	85 (12%)	35 (5%)	698
Manganese	n/a <sup>(1)</sup>	2 (1%)	156
Zinc	22 (7.5)% <sup>(2)</sup>	29 (10)% <sup>(3)</sup>	293

## Notes to Table 3

- (1) As a statutory EQS is not available for manganese, compliance with an existing standard has not been undertaken.
- (2) This value is indicative because the existing standard for zinc is expressed as total zinc, but the data used were for dissolved zinc in order to evaluate the standard for bioavailable zinc. Therefore, the figure may underestimate failure of the existing standard.
- (3) The zinc freshwater EQS was derived using the 'added risk' approach and, therefore, background concentrations should be used as part of compliance assessment (see Annex C). The assessment here does not take into account such concentrations and, therefore, the number of failures may be overestimated.

<sup>1</sup> This approach requires matched calcium, dissolved organic carbon (DOC) and dissolved metal concentrations, as well as pH data for each site. The following are relevant to the assessments for England and Wales: Where calcium values were unavailable, these were calculated by converting mean hardness bands into calcium estimates. Where DOC values were unavailable, 10 years (2000–2010) of historic DOC data were collated and a mean value was calculated per site. The availability of measured DOC values limited the number of sites that could be considered. The assessment was performed using the BLM screening tool version 28.



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Monitoring data for metals are more readily available than data for most of the organic substances, although the number of sites with dissolved zinc data is affected by the fact that the existing statutory requirement for this metal under the DSD is for total zinc<sup>1</sup>. In addition, there are over 3000 sites that have dissolved copper data, but the assessment in Table 3 is limited to those sites that have matched data for the input values required to assess bioavailability.

Table 3 shows that when bioavailable copper concentrations are compared with the proposed standards, the implications for England are less severe than when using the current standards. Within this picture, however, there may be regional differences. Our evidence shows that the number of EQS failures would fall in the north west, but there may be situations in the south east where some sites that had previously complied fail when a bioavailability-based approach is adopted. This is because the bioavailability-based approach takes account of a much wider range of physicochemical parameters than the existing approach, which considers only water hardness.

The implications assessment for England indicates a higher failure rate for iron in freshwaters compared with the situation using the current standard. It is not possible to make a true comparison as the current standard is for dissolved iron rather than the total metal. However, of 798 sites measured for dissolved iron, 0.2% failed at 95% confidence compared with 12% using the proposed value with sites measured for total iron (Table 2). Minewaters have been identified as a key source of iron and therefore may be attributed to potential EQS failures for ironwaters as one main source. Iron is also used by the water industry to treat phosphorus in water treatment works and such works are, therefore, a potential source of iron in the freshwater environment.

For salt waters, there is likely to be a significant increase in the number of sites assessed as “not good” for copper and zinc using the new standards, particularly for zinc. With the current standards, all sites assessed for zinc comply and only two out of those monitored for copper show very certain failures (0.6% of sites failing at 95% confidence). However, the predicted compliance with the proposed standards for these substances shown in Table 2 may improve when corrections for DOC for copper and background concentrations for zinc are taken into account.

The compliance rate for 2,4-dichlorophenol does not look set to change with the new standards; all sites comply.

The specific pollutants proposed by UKTAG have been selected by a process that uses available usage and monitoring data. Because the statutory monitoring data are limited for most substances, the implications assessment shown here may give an underestimate of the substances occurrence and hence underestimate the risk, particularly for substances where there is no existing statutory requirement to monitor their occurrence. However, additional

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<sup>1</sup> Which also includes particulate zinc.

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monitoring data from planned investigations or other monitoring programmes are available for some substances.

An additional source of data from England and Wales for organic substances has been generated by a survey of surface and groundwaters using gas chromatography–mass spectrometry (GC-MS). It is not possible to undertake a formal assessment of EQS compliance using these data due to the semi-quantitative nature of the results and also the fact that, in general, only one or two results are available for a site. However, the summary below provides an indication of the possible extent of the occurrence of some of the organic compounds. The data indicate, for example, that triclosan is present widely, but that widespread failures are not anticipated. For pendimethalin and benzyl butyl phthalate, occasional results are above the proposed long-term EQS values, but as they are one-off samples they are not directly comparable; that is, the limited data does not give a true reflection of what this means in terms of compliance.

- Triclosan: 105 samples contained detectable residues at concentrations above 0.01 µg/l (the reporting limit for the technique); 6 samples were above 0.1 µg/l.
- 3,4-Dichloroaniline: 18 positive detections were found with concentrations in the range 0.01–0.14 µg/l.
- Pendimethalin: 18 positive detections were found with concentrations in the range 0.01–0.26 µg/l.
- Benzyl butyl phthalate: 10 positive detections were found with concentrations in the range 1.35–12 µg/l.
- Chlorothalonil: 4 positive detections were found with concentrations in the range 0.01–0.03 µg/l.
- Tetrachloroethane: data were available for both 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane, but were restricted to groundwaters; 33 samples contained concentrations between 0.01 and 64 µg/l.

### Implications for Northern Ireland

There are limited data. The following gives an indication of the implications of the proposed standards based on the available data:

- Benzyl butyl phthalate: A limited amount of surveillance monitoring data are available covering seven months in 2009. There were four positive detections of benzyl butyl phthalate.
- Carbendazim: Surveillance monitoring data for 2008–2009 (April–March) are available for 44 sites, although not covering 12 months at most sites. There were three positive detections of carbendazim.
- 2,4-Dichlorophenol: Surveillance monitoring data for 2008–2009 are available for 20 sites for 12 months. There were four positive detections of 2,4-dichlorophenol. Quarterly monitoring was performed at the 11 OSPAR sites.
- Glyphosate: Surveillance monitoring data for 2008–2009 are available for 28 sites. There

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were 85 positive detections. Quarterly monitoring was performed at the 11 OSPAR sites.

- Tetrachloroethane: Surveillance monitoring data for 2007–2008 are available for 70 sites with less than 12 samples per site. There were no positive detections.
- Triclosan: Surveillance monitoring data for 2008–2009 are available for 16 sites. There were 45 positive detections at 14 of the 16 sites. Quarterly monitoring was performed at the 11 OSPAR sites.

There were no face-value exceedances of the proposed freshwater standards for the above substances, although data were limited in some cases.

There is a large amount of monthly and quarterly dissolved copper data (Freshwater Fish Directive sites). The samples indicate exceedance of the proposed freshwater standard, but this assumes that the dissolved concentrations are completely bioavailable. An assessment taking into account bioavailability is not possible at this time.

No data are available for chlorothalonil, cyanide, 3,4-dichloroaniline, iron, manganese, methiocarb, pendimethalin, permethrin and dissolved zinc.

### Implications for Scotland

Table 4 gives an estimate of the number of monitored sites in Scotland that would not meet the new long-term standards listed in Tables 1.1–1.18. Table 4 is based on monitoring for the period 2008–2010 and includes saltwater sites.

<b>Table 4: Specific pollutants – implications for Scotland</b>			
Substance	Freshwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Benzyl butyl phthalate	0	0	58
Chlorothalonil	0	0	8
Copper (bioavailable)	see Table 5		
2,4-Dichlorophenol	0	0	20
Iron (total)	147 (41%)	90 (25%)	359
Manganese (bioavailable)	see Table 5		
Pendimethalin	0	0	8
Permethrin	1 (5%)	0	21
Zinc (bioavailable)	see Table 5		
Substance	Saltwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Benzyl butyl phthalate	0	0	1

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Copper (dissolved) <sup>(1)</sup>	3 (2%)	0	151
Permethrin	0	0	8
Zinc (dissolved) <sup>(2)</sup>	24 (16%)	11 (7%)	151

#### Notes to Table 4

- (1) The saltwater EQS for copper includes a correction for DOC. The compliance assessment has not been able to take this into consideration because of the limited data for DOC. The number of failures may therefore have been overestimated as the assessment does not incorporate this correction.
- (2) The zinc saltwater EQS was derived using the 'added risk' approach and, therefore, background concentrations can be used as part of compliance assessment (see Annex C). The assessment here does not take into account such concentrations and, therefore, the number of failures may be overestimated.

The implications of applying the copper, manganese and zinc standards in the freshwater environment have been reviewed by taking into account bioavailability at individual sites for which matched data are available<sup>1</sup>. Following the approach described in Annex C, the calculated bioavailable metal concentration – based on site-specific conditions – was compared with the bioavailable standard in a face-value assessment for each site<sup>2</sup>. The results are shown in Table 5. For comparison, compliance of those sites against the current EQS values was also undertaken.

Table 5: Implications for Scotland when applying bioavailable metal standards			
Substance	Freshwater sites 'not good' (face-value assessment)		Number of sites assessed
	Based on compliance with the existing EQS	Based on compliance with the proposed bioavailable EQS	
Copper	2 (1.8%)	0	113
Manganese	n/a <sup>(1)</sup>	1 (1.3%)	78
Zinc	3 (2.6%)	0	116

#### Notes to Table 5

- (1) As a statutory EQS is not available for manganese, compliance with an existing standard has not been undertaken.

<sup>1</sup> This approach requires matched dissolved metal concentrations, pH and calcium and DOC concentrations for each site. Compliance assessment was not carried out where data for supporting parameters were not available. The assessment was performed using the screening tool version 28.

<sup>2</sup> Additional sites are monitored for the dissolved metal, but these sites may not have data for one or more of the supporting parameters. In addition further sites are monitored for total metal concentrations. In total an additional 212 sites for which there were copper and zinc data and 308 sites for which there were manganese data could not be assessed using this approach.

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Monitoring data are sparse for some substances in Table 4 mainly because there has been no requirement for monitoring in the past or because there are only a few localised pressures. A summary of the monitoring undertaken for each of the substances is given below:

- Benzyl butyl phthalate: Monitoring covers a subset of SEPA's surveillance network of sites located in major rivers across Scotland. There are no known sources and therefore the surveillance approach should provide a good indication of compliance. The data so far indicate that there are no failures of the proposed standard.
- 2,4-Dichlorophenol: Monitoring covers a smaller subset of SEPA's surveillance network targeting major urban rivers. There are no known sources and therefore the surveillance approach should provide a good indication of compliance. The data so far indicate that there are no failures of the proposed standard.
- Chlorothalonil, pendimethalin and methiocarb: Monitoring for certain pesticides is being carried out in a limited number of agricultural priority catchments identified as potentially at risk from pesticide pressures. This monitoring has only recently been implemented in one or two of these catchments. Our understanding of compliance with the proposed standards will improve as further monitoring is undertaken. The data so far indicate that there are no failures of the proposed standards.
- Carbendazim, permethrin, tetrachloroethane, toluene and cyanide: Monitoring is generally limited and relates to point source inputs. Environmental monitoring is no longer undertaken for some of these substances as the small number of sources are well understood and controlled.
- 3,4-Dichloroaniline and glyphosate: No monitoring is currently undertaken for these substances.
- Triclosan: No monitoring is currently undertaken for this substance. Although there is no environmental monitoring data for triclosan, an initial assessment of data from a small number of waste water treatment sites was undertaken to calculate predicted environmental concentrations. This indicated similar findings to the work undertaken in England, in that the substance is widely present, but not expected to lead to widespread failures of the standard.

Data for metals are more readily available across Scotland with monitoring sites covering a subset of SEPA's surveillance network and a large number of operational monitoring sites designed to assess the impacts of specific environmental pressures, for example mining activities. The number of sites with dissolved zinc data is affected by the fact that the existing freshwater standard is for total zinc. More generally, a risk-based approach to monitoring metals is taken whereby dissolved metal concentrations are measured only where the total metal concentrations indicate a potential compliance concern. The number of sites assessed is limited to those which have the supporting parameters' data available to estimate bioavailable concentrations.

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The implications assessment for Scotland shows a reduced number of failures in freshwaters for those metals with proposed bioavailable standards compared with the situation using the existing standards. One of the main reasons for breaches of the existing copper standards is discharges from distilleries. Further work is required in relation to background concentrations of zinc in saltwater so that the number of failures can be fully understood.

There is likely to be a substantial increase in the number of sites assessed as “not good” for iron. Only one site in Scotland (of those assessed here) breaches the current UK standard of 1000 µg/l dissolved iron. Prior to the adoption of a UK standard for iron proposed by UKTAG in the previous report [1], SEPA used an operational standard of 1000 µg/l total iron. An assessment against SEPA’s previous operational standard showed that 24% of sites would be assessed as ‘not good’ at face-value (13% of sites with 95% confidence). The proposed iron standard leads to a significant increase in the number of sites currently failing. The failures are thought to be in the main due to historical mining activities, although a more thorough assessment is required.

### Implications for Wales

Table 6 gives an estimate of the number of monitored sites in Wales that would not meet the new long-term standards listed in Tables 1.1–1.18.

In practice, the classification results from each site in a water body would be used to calculate the overall classification of a water body by taking the median result to determine the typical conditions for the water body.

The main driver for existing monitoring networks is the Water Framework Directive, but these networks may still encompass monitoring provisions for the Freshwater Fish Directive, Harmonised Monitoring, the Oslo and Paris Convention, and the Dangerous Substances Directive. Table 6 is based on monitoring for the period 2008–2010 and includes saltwater sites. The monitoring data assessed were those with statutory sampling purpose codes.

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<b>Table 6: Specific pollutants – implications for Wales</b>			
Substance	Freshwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Carbendazim	0	0	2
Copper (bioavailable)	see Table 7		
2,4-Dichlorophenol	0	0	3
Glyphosate	0	0	3
Iron (total)	20 (21%)	8 (8%)	95
Manganese (bioavailable)	see Table 7		
Methiocarb	0	0	1
Zinc (bioavailable)	see Table 7		
Substance	Saltwater sites 'not good'		Number of sites assessed
	Face value	At 95% confidence	
Copper (dissolved) <sup>(1)</sup>	3 (6%)	0	51
Zinc (dissolved) <sup>(2)</sup>	22 (39%)	6 (11%)	56

**Notes to Table 6**

- (1) The saltwater EQS for copper includes a correction for DOC. The compliance assessment has not been able to take this into consideration because of the limited data for DOC. The number of failures may therefore have been overestimated as the assessment does not incorporate this correction.
- (2) The zinc saltwater EQS was derived using the 'added risk' approach and, therefore, background concentrations can be used as part of compliance assessment (see Annex C). The assessment here does not take into account such concentrations and, therefore, the number of failures may be overestimated.

The implications of applying the copper, manganese and zinc standards in the freshwater environment have been reviewed by taking into account bioavailability at individual sites for which matched data are available. Following the approach described in Annex C, the calculated bioavailable metal concentration – based on site-specific conditions – was compared with the bioavailable standard in a face-value assessment for each site. The results are shown in Table 7. For comparison, compliance of those sites against the current EQS values was also undertaken.

<b>Table 7: Implications for Wales when applying bioavailable metal standards (face-value assessment using a tiered approach)</b>			
Substance	Freshwater sites 'not good'		Number of sites assessed
	Based on compliance with the existing EQS	Based on compliance with the proposed bioavailable EQS	

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Copper	85 (35%)	2 (1%)	243
Manganese	n/a <sup>(1)</sup>	3 (6%)	51
Zinc	36 (41%) <sup>(2)</sup>	38 (43%) <sup>(3)</sup>	88

### Notes to Table 7

- (1) As a statutory EQS is not available for manganese, compliance with an existing standard has not been undertaken.
- (2) This value is indicative because the existing standard for zinc is expressed as total zinc, but the data used were for dissolved zinc in order to evaluate the standard for bioavailable zinc. Therefore, the figure may underestimate failure of the existing standard.
- (3) The zinc freshwater EQS was derived using the 'added risk' approach and, therefore, background concentrations should be used as part of compliance assessment (see Annex C). The assessment here does not take into account such concentrations and, therefore, the number of failures may be overestimated.

Existing statutory monitoring data are sparse for most substances shown in Table 6, although additional data from planned investigations or other monitoring programmes are available in some cases (see implications section for England).

Data for metals are more readily available, although the number of sites with dissolved zinc data is affected by the fact that the existing statutory requirement for this metal under the DSD is for total zinc. In addition, there are over 850 sites that have dissolved copper data, but the assessment in Table 7 is limited to those sites that have matched data for the input values required to assess bioavailability.

The implications assessment for Wales indicates a higher failure rate for iron in freshwaters compared with the situation using the current standard. It is not possible to make a true comparison as the current standard is for dissolved iron rather than the total metal. However, of 155 sites measured for dissolved iron, 1.3% failed at 95% confidence compared to 8% using the proposed value with sites measured for total iron (Table 6). Mining is likely to be the main source of iron.

For salt waters, there is a predicted increase in the number of sites assessed as "not good" for zinc using the new standards. With the current standards, all sites assessed for zinc comply (as is also the case for copper). However, the predicted compliance with the proposed standards for zinc shown in Table 6 may improve if background concentrations are taken into account.

Table 7 shows that when bioavailable metal concentrations are compared against the corresponding standards, the implications for Wales are less severe in the case of copper. Consideration of bioavailability makes a very small difference in the case of zinc and no difference for manganese, although the indications are that compliance with the manganese standard is quite high.



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### THE RESPONSE TO FAILURE OF THE PROPOSED STANDARDS

The response to reported failures of standards for specific pollutants is part of the programmes of measures for the Water Framework Directive, and will be informed by the policies for each administration.

In the past, the environment agencies have operated with two general types of water quality standard. In some cases, there is confidence that securing and maintaining compliance is truly necessary to avoid environmental damage. In other cases, we may not have sufficient confidence that a standard has actually been exceeded.

The response to a failed standard will vary for each pollutant, but the UKTAG proposes that, in general, a consideration of action to achieve compliance for specific pollutants does not require additional and local ecological corroboration of damage<sup>1</sup>. The type of action taken will be subject to the Directive's considerations of cost effectiveness and disproportionate cost. This includes the feasibility of securing compliance and the associated degree of protection.

There are two ways in which compliance with standards might be used to take decisions. First, compliance at a particular location is used to consider action for that location (such as reviewing a permit). Second, summaries of compliance with a standard across a region or nation may lead to regional and countrywide measures (such as recommending national restrictions on the use of a chemical)<sup>2</sup>. Sites may benefit from both types of action.

In general terms, where a standard is failed, the agencies will seek to determine the cause (the reasons for failure) in a systematic way. Where this reveals a problem with, for example, a single discharge, the agencies will seek to tighten permit conditions subject to the Directive's considerations of cost effectiveness and disproportionate cost. Where there are several discharges, the Directive promotes the most cost-effective approach. Where there is a mix of point sources, diffuse sources and unknown sources, a further step will be needed to determine and apportion the main sources. This may involve monitoring and modelling, a consideration of cost-effectiveness and proportionate cost, and looking at the feasibility of securing compliance. Table 8 indicates how the substances covered by this report are used and, therefore, likely sources of environmental contamination.

The environment agencies will continue to seek to influence developments and growth in a way that manages the risk of deterioration and ensures that sustainable uses of the environment can continue and develop. They will assess the effectiveness of their efforts through the classification of water bodies and compliance with standards, and by calculating the impacts of changes in terms of movement within classes and compliance with standards.

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<sup>1</sup> Exceptions to this are shown in Tables 1.1 and 1.14.

<sup>2</sup> Such national measures have an advantage that the assessment is based on information on lots of sites and this allows the prospect of demonstrating a high confidence of need, even if the level of monitoring at each site is insufficient to show a need at any one of them.

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<b>Table 8: Major uses and likely sources of the substances for which EQSs are proposed</b>		
<b>Substance</b>	<b>Major uses</b>	<b>Likely sources in surface waters</b>
benzyl butyl phthalate	PVC plasticizer occurring in wide range of industrial and domestic products	wastewater treatment works, industrial effluents
carbendazim <sup>(1)</sup>	fungicide used in horticulture and agriculture	diffuse agricultural
chlorothalonil <sup>(1)</sup>	fungicide used in agriculture, horticulture and amenity turf	diffuse agricultural
copper	widespread occurrence in domestic and industrial applications	domestic sources (wastewater treatment works), industrial effluents, minewaters, sediments
cyanide	industrial applications and chemical intermediate	industrial effluents, wastewater treatment works
diazinon*	organophosphate insecticide, with agricultural, horticultural and veterinary uses (sheep dip)	diffuse and point source agricultural
3,4-dichloroaniline	industrial intermediate	industrial effluents, wastewater treatment works
2,4-dichlorophenol	industrial intermediate	industrial effluents, wastewater treatment works
glyphosate <sup>(1)</sup>	herbicide, including aquatic weed control	diffuse, including amenity, industrial and agricultural uses
iron	wide range of industrial and domestic applications; wastewater treatment	domestic sources (wastewater treatment works), industrial effluents, minewaters,
manganese	industrial applications (e.g. metal alloys, pigments, electrical)	industrial effluents, minewaters, domestic sources (wastewater treatment works), sediments
methiocarb <sup>(1)</sup>	carbamate insecticide and molluscicide	diffuse agricultural
pendimethalin <sup>(1)</sup>	agricultural herbicide	diffuse agricultural
permethrin <sup>(1)</sup>	pyrethroid insecticide, including some household uses	diffuse agricultural and domestic sources
tetrachloroethane	industrial solvent and intermediate	industrial effluents, wastewater treatment works
toluene	industrial solvent and intermediate	industrial effluents, wastewater treatment works

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triclosan	biocide (antibacterial); widely used in domestic products and personal care products	domestic sources (wastewater treatment works)
zinc	wide range of uses in domestic and industrial applications	domestic sources (wastewater treatment works), industrial effluents, minewaters, sediments

### Notes to Table 8

(1) Pesticide currently approved for use in the UK.

## Issues arising from reporting compliance

The Water Framework Directive advocates a “risk-based” approach to monitoring. Some locations may be judged to be at low risk based on mathematical modelling to predict chemical exposure and the absence of threats and evidence of relevant impacts. These may not need the type of chemical monitoring required for the routine assessment of compliance with EQSs<sup>1</sup>. In effect the EQS is assumed to be met.

In many cases the assessment of compliance involves using data from monitoring to make the appropriate comparison with the standard. In other cases it might involve calculations using models. These data or models will always be associated with levels of error and uncertainty, and these translate into statements of the degree of confidence that a standard has been met or has been failed.

The Water Framework Directive expects us to know and report these levels of confidence. They will be used to decide the amount of monitoring required to detect whether a particular site has failed a standard by a particular amount or deteriorated by a set amount (say 20 per cent).

The environment agencies will ensure that the confidence that the standard has been failed is considered when deciding what action to take under the programmes of measures. If there is high confidence of failure, the environment agencies would seek remedial action<sup>2</sup>. If there is a low confidence, the environment agencies would be expected to undertake more monitoring to see if the failure is confirmed with sufficient confidence, in order to assess whether such remedial action was truly necessary<sup>3</sup>.

<sup>1</sup> UKTAG Guidance (2005) 12a Guidance on the Selection of Monitoring Sites and Building Monitoring Networks for Surface Waters and Groundwater.

<sup>2</sup> Or, within the options of the Directive, set alternative objectives for water bodies.

<sup>3</sup> This might apply to expensive or controversial action. Any agreed and available low-cost measures would always be applied, even at sites where confidence of failure was low.

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In all this, national actions like controls on chemicals or the use of land may be easier to justify with high confidence because the effect of pooling hundreds of monitored sites effectively irons out the uncertainties associated with a single site.

### Refining the understanding of risks

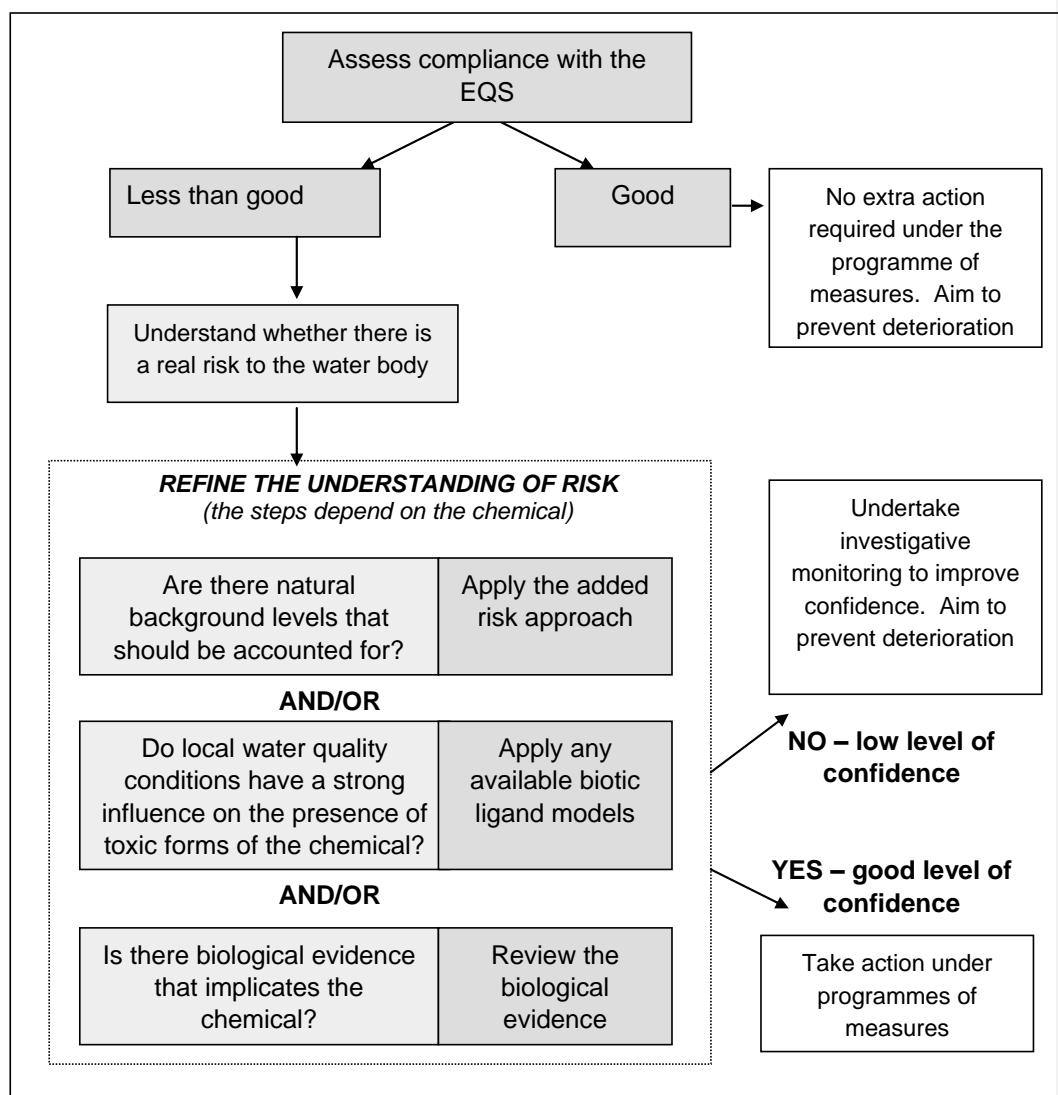
A water body cannot be declared to be of good ecological status if an EQS for a specific pollutant is failed. Where these failures are at “face-value”, there is a risk (of up to 50 per cent) that the failure is not true, but is actually a reflection of uncertainties in monitoring (false positive). There is a similar risk that failed sites are wrongly reported to have passed (false negative). Nonetheless, for a particular substance, the proportions of failed waters can lead to an accurate measure of the national position. It remains important to seek and gain high confidence of failure before taking action to improve individual sites.

Where good status is declared as an integrated result across all standards using the “one-out all-out” rule, the proportion of failed sites is heavily biased in a pessimistic direction. This bias increases with an increase in the number of standards. This fact needs to be taken into account in the framing of national targets and whether they are met. For specific pollutants, this is best done through separate targets for individual chemicals and not through statements such as “X per cent of waters fail a standard for a specific pollutant”.

Figure 3 shows:

- The activities that may be needed after an initial assessment of compliance. These activities seek to assess the level of risk and the confidence in the data, and, therefore, to determine action under the programmes of measures.
- The circumstances in which the environment agencies may be able to use biological data as a diagnostic tool to inform their advice and decision making. For example, certain pesticides can give rise to characteristic changes in biological diversity. The environment agencies can then focus attention on the substances responsible for the damage.

**Figure 3** Determining the need for action under the programme of measures



### Implications for particular chemicals

For substances where the UKTAG proposes the continued use of the existing standard, for example chlorine, the continued use of the current regimes for taking decisions in response to failure is recommended until such time as new standards are established.

### Episodes of exposure

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For substances such as pesticides, it may be useful to do additional monitoring during certain times of the year, for example when applications are most likely to occur (for example, during the spring months for foliar-applied insecticides to protect against insect damage in top fruit). In such instances, we must avoid bias when determining compliance with a standard that is expressed as an annual mean or an annual percentile. For example, if we normally take 12 samples per year, but include an additional six samples in a given month (for instance when pesticide applications are highest), all the data from that month would be used to provide an estimate of the monthly mean. This, in turn, would be used to calculate that month's contribution to the annual mean<sup>1</sup>.

Some chemicals may be deliberately released into water, for example for aquatic weed control or to control pests in farmed fish, which can give rise to a high concentration in the environment for a short period of time. This presents a challenge to balance the benefits of using such chemicals with the risks they may pose to the environment, and the circumstances under which EQSs would apply. For example, glyphosate is sometimes used in the water environment to control invasive plants. To do this it has to be discharged in concentrations that are toxic to the target plants. This means that there is a risk of exceedance. The target plants are often invasive species and their control can protect or improve the ecological quality of the water environment. Glyphosate is expected to break down quickly and so poses little risk to the wider aquatic ecosystem. Such occasional and short duration events would not be expected to affect decisions on classification.

Intermittent discharges of specific pollutants could result in concentrations in the environment that cause harm. Such concentrations may not be detected by the type of routine monitoring used to assess compliance with annual average and 95-percentile standards in the receiving water, especially where compliance with the percentile standard is based on counting failed samples and using a 'look up table' (see Annex B). In such a case, a water could be deemed compliant with the percentile even if one or two elevated (harmful) concentrations are picked up by monitoring. The agencies would follow up such events.

Where such risks exist in known discharges, the UKTAG recommends that they are managed by the controls set in permits, perhaps designing the operation of the discharge to meet a 99-percentile standard in the receiving water [8] or more extreme percentiles, and setting absolute limits on discharge quality. Where an intermittent discharge is expected to be frequent enough for the planned monitoring strategy to pick up occasional harmful concentrations, UKTAG also recommends using the parametric methods described in the relevant ISO Standard [9] to assess compliance with the percentile standards for waters.

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<sup>1</sup> Albeit with improved precision for the value for that month and improved precision in the estimate of the annual mean. Note that the annual mean standard embraces the acceptable risk of occasional and expected peak events. But none of this means that we can operate without a parallel regime for managing the risk of "out of the ordinary" peaks.

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### Metal speciation

Local variations in the physicochemical properties of a water body are known to cause changes in the distribution of species of a metal and thus affect the proportions of the forms of the metal that are toxic or benign. The assessment of compliance against a metal standard can give misleading estimates of risk if such variations are not taken into account.

Speciation models have been developed to allow a more accurate, automated way of assessing compliance with EQSs for some metals (copper, zinc, manganese). However, we may need to further refine our understanding of the risks posed by metals for those sites that appear to fail using these simple models. This is also covered in Figure 3 through, for example, the use of more detailed speciation models, the so-called biotic ligand models, the need to allow for natural backgrounds, or through the development of methods to measure the toxic forms directly by chemical analysis. The proposed full approach for assessing metals compliance is given in more detail in Annex C.

## FUTURE WORK

### Review of environmental quality standards

The approach adopted by the UKTAG has been designed to minimise levels of uncertainty that can give rise to unnecessarily stringent standards. The UKTAG has proposed standards only where the level of uncertainty is acceptable.

The UKTAG has reviewed specific pollutants for which existing DSD standards were adopted as an interim measure for the first cycle of river basin management. For these substances either new standards are proposed (Tables 1.11–1.18) or it is recommended that the existing values are maintained (for arsenic, ammonia, chlorine and iron saltwater). In the case of arsenic, working is ongoing to determine possible future proposals for this substance.

In addition, the UKTAG has reviewed substances not considered specific pollutants, but for which there are existing requirements under the Water Framework Directive. The UKTAG recommends such requirements are repealed. These substances are no longer considered as causes for concern. Should information become available in the future indicating any of these substances may be a cause for concern, then the UKTAG will re-assess the chemical in question using their risk-based prioritisation method (see earlier).

The UKTAG has not proposed new standards for aluminium or silver, which were also considered for this report. There are no existing statutory standards that can be used in the interim. The UKTAG proposes that more data are collected for these substances to get a better understanding of the risk they pose to UK waters and to enable robust standards to be derived if required.

#### *Aluminium:*

The speciation of aluminium in surface waters is complex and strongly affected by local physicochemical conditions. The UKTAG has undertaken work that focuses on ways of assessing and controlling aluminium in surface waters. We have considered aluminium speciation, potential risks based on pH banding, and available field and ecotoxicological data that may be used to inform PNEC derivation. We have developed draft guideline values for active aluminium using a weight-of-evidence approach which are being considered. Further relevant ecotoxicological data and analysis are required before PNEC values can be derived using the Water Framework Directive method.

#### *Silver:*

We have undertaken a monitoring exercise in collaboration with industry to get a better understanding of exposure to dissolved silver and possible risk [10]. The results suggested that the risk in freshwaters is low. However, the UKTAG recommends a future review of ongoing research programmes concerning risks from nanosilver in particular.

The UKTAG proposes a regular review of standards, on a six-year cycle to coincide with the river basin plans. As part of this, we will consider any emerging substances as potential



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candidates for standards derivation and the status of any substances under review from the prioritisation process (see Annex A). In addition, some substances that were ranked highly through our prioritisation process are currently being considered at European level as potential priority substances. If standards are not set at this level then we may want to consider them as future specific pollutants.

### Improving confidence through field data

The Water Framework Directive allows the modification of assessment factors where this can be justified by field data. The UK agencies have matched data for chemistry and biology<sup>1</sup> from previous monitoring campaigns and further data are also being generated under the first cycle of river basin management. These may be analysed to help inform the size of assessment factors to be applied in the extrapolation step.

This information provides an additional line of evidence about the link between chemical concentrations and biology. The UKTAG can use this to verify whether or not concentrations close to or exceeding the proposed standards appear to have an effect on biology, and where we might take a less precautionary approach than indicated by the data from laboratory studies in isolation. This approach is particularly useful if the biological sampling covers the most-sensitive taxonomic groups known to be affected by a substance.

As a rule, we cannot use this approach to identify where standards should be tightened except when we are sure that the biological data are unaffected by other chemical or physical pressures. This is because the comparison could imply wrongly that concentrations are responsible for the damage from other causes. Also, for metals, it can be difficult to take account of factors that could affect the proportions of available metal in its most toxic forms. Such factors include, for example, dissolved organic carbon, temperature, pH, suspended solids and hardness.

In the case of iron, particularly heavy reliance has been placed on the use of such field data in the derivation of a PNEC. Conventional laboratory ecotoxicity data for iron are very difficult to interpret with confidence so, for this substance, the UKTAG has applied a quantile regression approach to freshwater field data to identify the maximum concentration of total iron at which the diversity and abundance of invertebrate communities are maintained at a level consistent with good (or better) status. This threshold has then been used as the basis for the proposed EQS.

For zinc, the freshwater PNEC is based on an analysis of laboratory ecotoxicity data, but similar field evidence has been used to corroborate the UKTAG's proposal for an EQS and to justify the use of a small assessment factor.

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<sup>1</sup> Data for biological status and chemical exposure at the same time or at adjacent sites.

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The UKTAG will update its recommendations where available field data lead to different conclusions from the PNECs derived from laboratory data, where this is supported by the scientific evidence.

### **Improving the understanding of risks from metals**

An important development since the first UKTAG report [1] has been new research on metals. In particular, we have looked at ways of incorporating bioavailability into the proposed standards and the approaches used to assess compliance.

The UKTAG has worked to develop speciation models to support compliance assessments against bioavailable metal standards (see Annex C).

The speciation models will help take account of the effect of local water quality on the speciation and therefore the toxicity of metals. Work has also been undertaken on defining and taking into account natural background concentrations of metals where necessary. Guidance on how and at what stage these approaches should be used in the implementation of standards for metals is given in Annex C.

The UKTAG will continue to explore the use of models for assessing the bioavailability of metals as part of its approach to setting standards for metals and assessing compliance.

Further work is recommended to get a better understanding of the fate and behaviour of metals in the transitional zone from freshwater to fully saline waters. This is so that environmental risks in such transitional waters can be correctly classified. At this stage, the UKTAG has only proposed metal standards for marine waters where the evidence is robust.

### **Interactions with other Member States**

Other Member States, and Norway, are developing standards for specific pollutants. The German Federal Environment Agency performed an exercise in 2011 comparing the standards for specific pollutants developed by different Member States for the first cycle of river basin planning and concluded that unexpected high differences in values were observed and that harmonisation of limits was required [11]. It is possible that some variation in the values reported was due to Member States, including the UK, adopting existing DSD standards as interim measures. In addition, most of the standards would have been developed before the advent of the EU guidance [4] so it is possible that the values are based on different approaches and assumptions. However, such variations in EQSs may be an issue, for example, when considering transboundary rivers.

The UK has been involved in the development of the EU guidance and has provided information for use in the development of standards for priority and priority hazardous substances.

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The UKTAG has actively engaged with other countries in the important area of standards derivation. In particular, the UKTAG has developed close working relationships with the Republic of Ireland, Belgian, Danish, French, German and Netherlands agencies to share experience and to identify opportunities to develop standards more efficiently. The development of European technical guidance on the derivation of EQSs [4] is an important step forward because it should help promote consistency between regulatory authorities' activities. Our collaboration with others may also help identify particular causes of inconsistency between Member States.

We may find that we can use the standards proposed by other countries, particularly where they have been developed under a process that is similar to that used for the UK. Similarly, other countries may wish to use standards adopted by the UK.

### **Planned work – in summary**

- Review potential additional specific pollutants and derive any subsequent proposals for these substances.
- Where it has not been possible to recommend a standard at this stage, use additional toxicological studies to enhance confidence in the data and so provide lower assessment factors.
- Use matched biology and chemistry data from the field, where appropriate, to support future proposals.
- Consider any relevant developments for assessing metals speciation and bioavailability.
- Collaborate with other Member States to share experience and outputs.

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## ANNEX A: SUBSTANCES RANKED 1 AND 2 THROUGH THE PRIORITISATION PROCESS USED TO IDENTIFY POTENTIAL SPECIFIC POLLUTANTS

Table A1: Chemical prioritisation: substances ranked 1		
Substance	CAS number	Conclusion from peer review
Aroclor 1242	53469-21-9	Further work needed to improve confidence in the ranking
Aroclor 1248	12672-29-6	Further work needed to improve confidence in the ranking
Aroclor 1254	11097-69-1	Further work needed to improve confidence in the ranking
Aroclor 1260	11096-82-5	Further work needed to improve confidence in the ranking
Chlorothalonil	1897-45-6	Priority for EQS development
2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol [butylated hydroxytoluene (BHT)]	128-37-0	Further work needed to improve confidence in the ranking
3,4-Dichloroaniline	95-76-1	Priority for EQS development
1,2-Dichlorobenzene	95-50-1	Further work needed to improve confidence in the ranking
4-(Dimethylbutylamino)diphenylamin (6PPD)	793-24-8	Further work needed to improve confidence in the ranking
Diocetyl 3,3'-thiodipropionate	693-36-7	Further work needed to improve confidence in the ranking
Diocetyl phthalate	117-81-7 (sec-derivative, i.e. DEHP)	Captured under Annex X as DEHP

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<i>tert</i> -Dodecanethiol	25103-58-6	Further work needed to improve confidence in the ranking
Dodecylphenol, mixed isomers (branched)	121158-58-5 (mixed isomers 27193-86-8)	Further work needed to improve confidence in the ranking
<i>N,N'</i> -Ethylenebis(4,5,6,7-tetrabromophthalimide)	32588-76-4	Further work needed to improve confidence in the ranking
Hexabromocyclododecane	25637-99-4	Further work needed to improve confidence in the ranking
Mancozeb	8018-01-7	Further work needed to improve confidence in the ranking
Metamitron	41394-05-2	Not currently a priority for EQS development
Mevinphos	7786-34-7	Not currently a priority for EQS development
Nonylphenol ethoxylates		Not currently a priority for EQS development
Perfluorooctanyl sulphonic acid and its salts (PFOS)	1763-23-1	Priority for EQS development
Pendimethalin	40487-42-1	Priority for EQS development
Polychlorinated biphenyls (PCBs) (as a group or if the following individual isomers indicate greater toxicity: 28, 31, 52, 101, 105, 118, 138, 153, 156, 180)	1336-36-3	See Aroclors
Triclosan	3380-34-5	Priority for EQS development

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Table A2: Chemical prioritisation: substances ranked 2		
Substance	CAS number	Conclusion from peer review
Aniline (benzeneamine)	62-53-3	Further work needed to improve confidence in the ranking
Azinphos-ethyl	2642-71-9	Not currently a priority for EQS development
Benzamine, <i>N</i> -phenyl, styrenated	68442-68-2	Further work needed to improve confidence in the ranking
Benzyl butyl phthalate (BBP)	85-68-7	Priority for EQS development
Bisphenol A	80-05-7	Further work needed to improve confidence in the ranking
Bromoxynil	1689-84-5	Further work needed to improve confidence in the ranking
Carbendazim	10605-21-7	Priority for EQS development
Chloridazon	1698-60-8	Not currently a priority for EQS development
4-Chloro-2-methylphenoxy acetic acid (MCPA)	94-74-6	Not currently a priority for EQS development
Chlorotoluron	15545-48-9	Not currently a priority for EQS development
DDE (pp)	72-55-9	Not currently a priority for EQS development
6,6'-Di- <i>tert</i> -butyl-2,2'-methylenedi- <i>p</i> -cresol	119-47-1	Further work needed to improve confidence in the ranking
2,4-Di- <i>tert</i> -butylphenol	96-76-4	Further work needed to improve confidence in the ranking
2,6-Di- <i>tert</i> -butylphenol	128-39-2	Further work needed to improve confidence in the ranking
Dibutyl phthalate	84-74-2	Not currently a priority for EQS development
1,4-Dichlorobenzene	106-46-7	Not currently a priority for EQS development
Diquat	231-36-7	Further work needed to improve confidence in the ranking
Erythromycin	114-07-8	Further work needed to

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		improve confidence in the ranking
17 $\alpha$ -Ethinylestradiol	57-63-6	Priority for EQS development
Fenpropidin	67306-00-7	Further work needed to improve confidence in the ranking
Fluroxypyr	69377-81-7	Not currently a priority for EQS development
Galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylindeno[5,6-c]pyran)	1222-05-5	Further work needed to improve confidence in the ranking
Glyphosate	1071-83-6	Priority for EQS development
Heptachlor epoxide	1024-57-3	Not currently a priority for EQS development
Hexachlorocyclopentadiene	77-47-4	Further work needed to improve confidence in the ranking
Malachite Green	569-64-2	Not currently a priority for EQS development
Metazachlor	67129-08-2	Not currently a priority for EQS development
Methiocarb	2032-65-7	Priority for EQS development
Methyl bromide	74-83-9	Not currently a priority for EQS development
Monolinuron	1746-81-2	Not currently a priority for EQS development
17 $\beta$ -Oestradiol	50-28-2	Priority for EQS development
Paraquat	4685-14-7	Not currently a priority for EQS development
Parathion-methyl	298-00-0	Not currently a priority for EQS development
Pirimicarb	23103-98-2	Not currently a priority for EQS development
Pirimiphos-methyl	29232-93-7	Not currently a priority for EQS development
Prochloraz	67747-09-5	Not currently a priority for EQS development
Propachlor	1918-16-7	Further work needed to improve confidence in the ranking
Propiconazole	60207-90-1	Not currently a priority for EQS development
Propyzamide	23950-58-5	Not currently a priority for EQS development



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Tebuconazole	107534-96-3	Further work needed to improve confidence in the ranking
Terbutryn	886-50-0	Not currently a priority for EQS development
Tetrabromobisphenol A	79-94-7	Further work needed to improve confidence in the ranking
1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one	1506-02-1	Not currently a priority for EQS development
Thiram	137-26-8	Further work needed to improve confidence in the ranking
Triallate	2303-17-5	Further work needed to improve confidence in the ranking
Trichlorophenols	25167-82-2	Further work needed to improve confidence in the ranking

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### ANNEX B: THE PROCESS FOR DEVELOPING STANDARDS

#### Purpose of the standards

For specific pollutants, the Water Framework Directive requires that standards protect aquatic life from exposure via the water column, from exposure through the food chain, and from risks from contaminated sediments.

Unlike the priority and priority hazardous substances, there is no requirement for specific pollutants in the Water Framework Directive to consider the protection of human health from the consequences of the direct consumption of substances (from drinking water) or from the indirect consumption (for example, from eating contaminated fish). Such requirements, where they need to go further than the general protection provided by the Water Framework Directive, are managed through other procedures, such as those established under the Drinking Water Directive.

We are required by the Water Framework Directive to protect freshwater and marine habitats. Data for saltwater are sometimes sparse and so, where possible, if there are insufficient data to develop specific standards for seawater, the UKTAG proposes that data for freshwater organisms and saltwater organisms are 'pooled' and an additional assessment factor applied to address any uncertainty<sup>1</sup>.

We are required to derive standards that will protect from prolonged exposure. This is the purpose of the long-term standards. These are normally based on an extrapolation from data on chronic (or long-term) toxicity. They are typically expressed as annual mean concentrations that, if met, can ensure protection against the range of concentrations encountered in a year.

#### Using standards to classify waterbodies or permit discharges

The expression of a standard as an annual mean works because, for most substances, the statistical distribution of concentrations occurring in the environment is fairly uniform and the annual mean is well correlated with the probability that high concentrations occur within the year. Experience of monitoring shows that the upper 95-percentile<sup>2</sup> of a year's sampling results will be two or three times higher than the mean concentration. For many types of risk, measures to comply with an annual mean act also on the risks associated with the full spread of concentrations that may arise in a water body (including infrequent episodes of high exposure). However, we must live with the consequences than the annual mean is estimated far more precisely than the annual 95-percentile from a fixed degree of monitoring effort. Two or three times as much monitoring would be needed to detect the same risk of failure.

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<sup>1</sup> An additional factor of 10 is applied in line with the EU guidance [B2], which says that we should make extra allowance for the greater biodiversity of the marine environment compared with that of the freshwater environment. It is recognised that reports of failures against saltwater standards that have been derived with an AF of 100 will require a response that involves more work on establishing the damage and its cause.

<sup>2</sup> The 95-percentile is the value exceeded for 5 per cent of the time.

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Where the short-term standard is only slightly higher (2–3 times) than the long-term standard (that is the acute toxicity occurs at concentrations close to chronic exposures), then compliance with the long-term standard may not give adequate protection to peaks in exposure. For such substances, it may be necessary to use a short-term standard to protect more specifically against the high concentrations that may occur in a year. Such circumstances may arise for substances whose concentrations are trivial most of the year, but high on rare occasions.

### Short-term standards

There may be cases where substances are used or released only for short periods of time. This occurs, for example, with some pesticides. Under these circumstances, control based on meeting the annual mean concentration in the water, or even on meeting the annual 95-percentile, may not work well enough, even though compliance with these standards will usually give a good indication of risk. For such substances we might place greater reliance on the proposed short-term standards that are extrapolated from acute toxicity data, and augment our controls with those more usually associated with preventing pollution incidents.

Proposals for short-term standards are sometimes expressed as maximum allowable concentrations (MACs). Whilst this commonly used title implies that this concentration must never be exceeded, it can only practically be used if it is expressed as a percentile, for the reasons set out below.

What is meant by “allowable”? Is it that a modest exceedance of the maximum concentration is acceptable for 30 seconds over 50 years. Or is it more like moderate exceedances totalling 10 days over an average year. There is a 1.4 million-fold difference in severity between these statements.

Experience over recent decades has shown us that most decisions to protect water quality can be based successfully on samples collected 12 times per year. In some cases this is reduced to 4 and in others increased to 50. There are 31 million seconds in a year and, in most cases, taking a sample captures only one of those seconds. This means that we accept a risk of exceeding the standard and not knowing (because we don’t sample all the time). It means that a sampling rate of 12–20 samples per year is the exact mathematical equivalent of assuming that the MAC is equivalent to an annual 90- or 95-percentile.

If the MAC is used as an absolute “maximum”, serious and arbitrary errors will result. Such errors may lead to:

- a biased classification;
- wrong decisions and wasted resources on action to secure compliance.

The UKTAG suggests that the short-term standard is taken to be an annual 95-percentile.

The UKTAG recommends that serious action to improve a site requires a demonstration of 95%

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confidence that the annual mean or, if appropriate, the annual 95-percentile is failed. This applies wherever the cost of extra monitoring to confirm such confidence is trivial compared with the cost of the action to secure compliance.

For determining compliance with the annual 95-percentile, one method is to use a look-up table to give a confidence of failure. The look-up table<sup>1</sup> below (Table 9) gives the number of failed samples required in a given set of samples to give 95% confidence that a 95-percentile is failed. Other methods, for example assessing compliance with an annual mean, are based on an assumption of the statistical distribution underlying the spread of values of concentration.

<b>Table 9: Look-up table for assessing 95% confidence of failing a 95-percentile standard</b>	
Number of samples	Required number of exceeding samples
4–7	>1
8–16	>2
17–28	>3
29–40	>4
41–53	>5
54–67	>6

This approach is in line with the International Standard ISO 5667-20 Water quality –Sampling – Part 20: Guidance on the use of sampling data for decision making – Compliance with thresholds and classification systems.

### Use of standards for classification and other uses

For substances where the potential for exposure is frequent or continuous, the use of the annual average standard is the most appropriate for determining waterbody classification and for permitting discharges. Whilst it is proposed that short-term standards are described as a percentile for classification purposes and for things like setting limits in permits, it is recognised that protection against short-term acute impacts is still important. We need to look out for cases where the general controls that will meet an annual 95-percentile in the receiving water are not vulnerable to abuse or accidents. This requires the additional scrutiny provided by our procedures for guarding against pollution incidents.

It is also recommended that any face-value breach of a short-term standard expressed as a MAC should be regarded only as an indication of possible risk and trigger investigations into risks to water quality.

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<sup>1</sup> As used for 95% confidence of failure of 95-percentile standards under the Urban Waste Water Treatment Directive. Tables for other percentiles and other degrees of percentage confidence can be easily constructed.

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In the case of the annual mean or the annual 95-percentile standards for the water column, there is scope to calculate in a mathematically precise manner the extent of actions needed to secure compliance with the standard. For example, the improvements to discharges can be calculated to ensure the standard is met in a water body to a specified degree of reliability and confidence.

In summary, for the purposes of assessing compliance, that is water quality classification, the standards must be defined as summary statistics, such as the annual mean and the annual 95-percentile. This allows the correct use of statistical methods and calculation of the confidence of failure. The use of such summary statistics also allows the precise back-calculation of actions needed to secure compliance. The UKTAG has derived both long-term and short-term predicted no-effect concentrations (PNECs) where the data allow. The environment agencies have agreed that the long-term (annual average) or short-term PNECs (95-percentiles) will be used as standards, and for compliance assessment and classification, as appropriate.

### Method for deriving predicted no-effect concentrations

The method previously used to develop many standards in the UK [B1] to meet the requirements of the Dangerous Substances Directive (DSD) does not meet the requirements of the Water Framework Directive. Therefore, the UKTAG re-evaluated this approach<sup>1</sup>. The UKTAG has re-assessed any existing standards for specific pollutants that were based on the previous method and has also derived new standards for potential specific pollutants using the method specified in Annex V of the Water Framework Directive and with reference to the associated EU guidance [B2].

The process comprises the following steps:

- Step 1: collate information on the effects of concentrations on aquatic biota;
- Step 2: assess the quality and relevance of these data, and decide which are admissible;
- Step 3: use these data to derive PNECs for different biota.

Step 3 is an extrapolation that is intended to account for uncertainties in the data, including differences between laboratory and field exposures and their exposure periods, and, in particular, to account for biological species for which no toxicity data are available.

Differences occur in steps 2 and 3 between the method used previously in the UK and that now required by the Water Framework Directive. Both methods extrapolate to the PNEC by identifying the critical data on toxicology (step 2) and by applying a factor. This factor is called an assessment factor and is intended to account for uncertainties and gaps in the toxicity data.

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<sup>1</sup> The UKTAG has applied the requirements of Annex V of the Water Framework Directive as well as the Environment Agency's *Framework for Standards*. This encourages a process in which the decision about a standard includes the scientific assessment, scientific peer review and an initial consideration of how the standards may be applied (this report), and an economic assessment of its impacts (part of future regulatory impact assessments by Administrations).

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Using the Water Framework Directive method, there are two approaches to extrapolation, depending on the quantity of data available. If we have data for only a small number of species (<10), the following approach is adopted: the lowest credible no-effect concentration (that is, for the most sensitive of the species tested) is divided by an assessment factor between  $10^1$  and 1000 to convert it into a PNEC (deterministic method).

The above approach required for the Water Framework Directive is more prescriptive on the minimum amount of data needed and the size of the assessment factor used than the previous UK method. The approach usually requires the use of a larger assessment factor where there are few sets of toxicological data. This gives values that are more precautionary. The methods tend to produce similar results where we have sets of data on toxicity for a wide range of species<sup>2</sup>.

The Water Framework Directive also allows the use of mathematical models to describe the number of species likely to be affected by a concentration of a substance. These species sensitivity distribution (SSD) models are applied where data are more plentiful ( $\geq 10$  species covering at least 8 taxonomic groups). Such models are used to estimate a concentration that will protect a high proportion (typically 95 per cent) of species. An assessment factor would then be applied to this estimate, but the factor is much smaller (only 1–5) than that used in the deterministic approach. The models became increasingly accepted as a valid way of developing standards under the European Union's Technical Guidance Document [B3] and, in fact, are now preferred where there are sufficient data.

Good sets of data for a wide range of species must be available to use the modelling approach and, in practice, few substances have these. Where they do, the approach tends to yield less-stringent values than the deterministic method.

### Scientific peer review

A panel of independent scientists from the UK have reviewed the results of the scientific assessments. The panel advised on the adequacy of the data, the extent to which they should influence the final PNEC, and how the UKTAG should interpret them. The results have also been discussed at several peer review workshops.

Generally, the proposals of the UKTAG represent the consensus of the reviewers and any differences are discussed in the technical reports.

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<sup>1</sup> In some cases, a smaller assessment factor might be justified. This was the case with triclosan where the toxicity dataset on which the PNEC is based included taxa that the UKTAG expects to be particularly sensitive to this substance.

<sup>2</sup> When faced with data from a range of toxicological studies it is always possible that the lowest value, upon which a standard could be based, is actually an outlier arising from random errors. The UKTAG is content that this risk is managed by scientific peer review.

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The scientific assessment and the peer review have highlighted a number of issues. These are listed here and discussed in the next few sections:

- chemical speciation – the existence of several forms of the chemical;
- the use of field data to support data from laboratory studies;
- assessing the feasibility of PNECs as standards.

### Chemical speciation

Some chemicals can exist as different forms in the environment, but only some of those forms can be taken up and exert toxic effects. Ammonia is a well-known example, but metals can also exist as different ‘species’, only some of which are toxic. In recent years, the scientific understanding about the environmental fate and toxicity of metals has advanced considerably, and we are now at a stage where we can incorporate this new understanding into our proposals for metals.

Depending on the metal and the water conditions, many metals occur in a variety of states and some form complexes with humic acids, carbonates or sulphides. The toxicity of metals depends on their availability to be taken up by plants and animals and this can depend on the chemical form. Some forms have low toxicity whilst others are highly toxic at low concentrations. By and large, the form of most toxicological concern is the free ion (such as  $\text{Cu}^{2+}$ ), rather than any complexes it might form.

This has implications for standards for metals. First, the standard may need to be expressed in a way that takes account of local physicochemical conditions of a water body and how these vary. Second, standards based on ‘total’ concentrations might be unhelpful if much of the substance is in a non-toxic form and if the concentrations of the toxic forms are poorly correlated with the total concentration. It is sensible, in these cases at least, to aim to set the standard in terms of concentrations of the toxic ‘bioavailable’ forms. The new science has allowed the UKTAG<sup>1</sup> to do that for some important specific pollutants, namely copper, zinc and manganese..

There are some important implications of this new approach to dealing with metals (see Appendix C). The most important is to consider how to reflect the influence of local water quality conditions on metal bioavailability. The approach taken by the UKTAG is to propose standards that protect flora and fauna under conditions that favour the toxic bioavailable form of the metal. These conditions may occur in some locations, but certainly not everywhere so the UKTAG proposes to use the measured dissolved concentrations of the metals to predict how much of the metal concentration is actually in a bioavailable form. This can occasionally be 100% (that is, all the metal present is in a bioavailable form), but, more frequently, it is a much

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<sup>1</sup> In the earlier UKTAG report [1] there are separate proposals for chromium(III) and chromium(VI), reflecting their difference in toxicity. Standards for copper, manganese and zinc in this report are expressed as bioavailable values, reflecting that their toxicity to aquatic species is dependent on local physicochemical conditions of the water body.

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smaller proportion, often less than 10 or 20%. This 'modified' concentration is then used as the input to assess compliance in the usual way. Simple screening tools based on complex biotic ligand models (BLMs) are now available to undertake these modifications and to estimate the bioavailable concentration. In addition to measurements of the dissolved metal, they also use measurements (or estimates) of dissolved organic carbon, pH and calcium concentration.

### Use of field data

Most of the data on which the proposals of the UKTAG are based have been obtained from laboratory studies. Data for some substances are also available from the field or from studies using experimental ponds and streams in which environmental exposure can be linked with measured biological effects. The Water Framework Directive acknowledges that field data may be used to adjust the size of the assessment factor that is used in the extrapolation step (step 3 above).

In one case (the proposal for iron), the PNEC is based solely on an analysis of field data. This is because the available laboratory data are difficult to interpret – the UKTAG could not be sure what form of iron was responsible for the measured toxicity, and effects owing to physical fouling made the studies difficult to interpret – but field data were plentiful. Therefore after taking advice from the peer review panel, a purely field-based approach was adopted. This involved a statistical analysis of 'matched' chemical and biological data and allowed us to estimate an upper concentration at which no biological deterioration could be seen. The summary in Annex D provides more detail.

In some cases, field data were not good enough to influence the PNECs, for example where the data were too biased towards impacted sites or the chemical and biological information were poorly matched. In such sets of data there were insufficient comparisons in which the substance was at very low levels and the biological data showed no effect. This meant that the UKTAG was unable to estimate the boundary between effects and no effects with confidence and so these data were not used to inform the PNEC.

### Existing standards

The Water Framework Directive requires that standards established under the first river basin management plans are at least as stringent as any corresponding standards under the DSD. The UKTAG has reviewed the situation with respect to diazinon (saltwater short term) and toluene (long term), for which existing standards were adopted for the first cycle because of this requirement. For these substances, the UKTAG recommends using the less strict values derived using the Water Framework Directive method as a basis for proposals for the second cycle. This is because they represent the best science, and monitoring data reviewed show no issues with these two substances.

Where existing standards for a proposed substance have a non-statutory status, the newly



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derived values are considered more scientifically relevant and in line with the requirements of the Water Framework Directive methodology. As a consequence, where the PNEC derived for this report is less strict than the existing non-statutory standard, the UKTAG proposes the use of the new standard.

### Standards from European risk assessments

Some substances have been assessed already as part of the European Union's programme of risk assessments for 'existing substances' or as part of their review of plant protection products (pesticides and growth regulators) [B4,B5].

Where substances have been considered under the Existing Substances Regulation, we have used the outputs of their risk assessments in combination with any new data, if available. This helps ensure that the UKTAG gains access to all available data, but does not repeat rigorous evaluations of data that have already taken place.

The situation for reviews of plant protection products is more complicated. The assessments are confined to freshwater using data generated under particular regimes for testing the substances. The reviews do not provide a PNEC, but a way of deciding whether additional data are required. The UKTAG suggests that these assessments are insufficient as the basis for PNECs for use under the Water Framework Directive, and that a full review of such substances is needed.

### Uncertainty in data

The guidance in Annex V of the Water Framework Directive is based on a method used generally for assessing risks from chemicals [B3] and not just the environmental risks to waters.

During these risk assessments, if a risk is identified and a high assessment factor has been used, this would normally trigger the generation of more data to reduce the uncertainty in the overall process. These data then allow a better estimate of the risk before action is taken to reduce it.

Applying large assessment factors in cases where there is a lack of data can lead to proposals for standards that would be very precautionary. In some cases, this outcome can contradict the results of routine monitoring for chemicals and biology – there is no damage to the ecology even though the proposed standard is exceeded in lots of places. There are therefore anomalies between the standards and evidence from monitoring and field studies, which – given more time – should prompt the standards to be reviewed to allow a more precise assessment factor to be calculated. The UKTAG would not propose a standard where it considers there is an excessive level of uncertainty.

Bearing in mind the overall approach of the above risk assessments [B3], where a PNEC has

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high uncertainty, the UKTAG proposes that additional data are collected. Where appropriate, the UKTAG will identify studies that, if undertaken, could reduce uncertainty and result in use of a smaller assessment factor. In the interim, the UKTAG recommends continued use of the existing standards for regulatory purposes, where these exist, but that the substances should still be regarded as specific pollutants under the Water Framework Directive.

Since the previous UKTAG report [B6], the UKTAG has commissioned more data for some of the specific pollutants for which DSD standards were proposed as an interim measure. As a consequence, we have been able to reduce the uncertainty and provide new proposals using the Water Framework Directive methodology.

The assessment factors used as indicators of high uncertainty are >50 for freshwater and >100 for saltwater. The cut-off value for saltwater is higher than that previously applied [B6]. This is because the use of the new EU guidance [B2] on the derivation of standards for the Water Framework Directive leads to a minimum assessment factor of 100 being used for saltwater PNEC derivations when data are sparse (in particular, where there are no additional saltwater toxicity data for marine taxa eg echinoderms). The UKTAG recommends that while all proposals should be used as the basis for classification, those based on PNECs derived through the use of an assessment factor of 100 would prompt the retrieval of supporting information, including evidence of ecological damage, before any commitment to expensive remedial measures.

### **Sensitivity of chemical analysis**

The UKTAG has identified where there is no suitable method of chemical analysis, or where present limits of detection for routine chemical analysis are too high for its proposals. The UKTAG proposes that where there are analytical issues with derived PNECs for substances, these should not be used as a basis for not setting a standard and the value would still be recommended.

### **Accounting for natural backgrounds**

Some candidate specific pollutants occur naturally, and their concentrations in water may vary for a variety of reasons, including the nature of the local geology. The EU Directive on environmental quality standards (EQSs) for priority and priority hazardous substances (2008/105/EC) allows Member States to take account of natural background concentrations for metals and local physicochemical conditions that affect the bioavailability of metals when assessing monitoring results against the EQS.

Background concentrations apply principally to metals, and the UKTAG have only considered metals in its proposals for accounting for backgrounds. The UKTAG has considered the best methods for implementing standards for metals and suggests the tiered approach to compliance assessment outlined in Annex C.

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The UKTAG will not propose values that are below or around natural background levels.

### Standards in sediments

The UKTAG does not advocate setting mandatory standards in sediments. This is because the lack of sediment toxicity data for many substances means that sediment PNECs are subject to high uncertainty. There are also concerns over the suitability of the partitioning theory<sup>1</sup> as an approach to setting such standards to address this gap. Furthermore, there are difficulties in using measurements on sediments to provide the basis for environmental control regimes. These include the consequences for monitoring and the assessment of compliance where there is high spatial variability. This contributes to the difficulty in calculating the controls needed to secure compliance with the standards.

There may be scope to develop guideline values for sediments as opposed to mandatory or statutory EQSs. Where a PNEC for sediments has been developed, the UKTAG recommends that it can be used as a guideline. These guideline values might be part of a wider process of assessment, for example as a trigger for further evidence gathering to support a case for investigation and regulatory action.

### Standards for secondary poisoning

In some cases, the major risk to flora and fauna is through the food chain (secondary poisoning). Where this occurs, the UKTAG could propose a biota standard, to protect predators from secondary poisoning, based on residues in the flesh of prey organisms (for example, as a  $\mu\text{g/kg}$  concentration) or as a calculated equivalent concentration in water. In the latter case, where such concentrations are lower than the long-term water column standards to protect against the direct toxic effects of a chemical, the UKTAG recommends that the values based on secondary poisoning are adopted to afford the appropriate level of protection. In the proposals presented here, only the herbicide pendimethalin meets the criteria for determining a biota standard. The values presented in Table 1.8 are back-calculated from the biota standard to the equivalent concentration in water.

### References

[B1] Zabel T F and Cole S (1999). The derivation of Environmental Quality Standards for the protection of aquatic life in the UK. *Journal of the Chartered Institute of Water and Environmental Management*, 13, pp. 436–440.

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<sup>1</sup> Calculations based usually on the chemical properties of a substance that predict how much of the substance may end up in sediments and elsewhere.

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[B2] European Commission (2011). Common Implementation Strategy for the Water Framework Directive (2000/60/EC); Guidance document No. 27, Technical Guidance for Deriving Environmental Quality Standards; Technical report –2001 – 055. Available at: [http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework\\_directive/guidance\\_documents/tgd-egs\\_cis-wfd/ EN 1.0 &a=d](http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents/tgd-egs_cis-wfd/ EN 1.0 &a=d)

[B3] European Commission Joint Research Centre (JRC) (2003). Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No. 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council Concerning the placing of biocidal products on the market. Part II. EUR 20418 EN/2. Luxembourg: Office for Official Publications of the European Communities. Available at: <http://ecb.jrc.it/tgdoc>

[B4] Council regulation (EEC) No 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances. Available at: [http://ec.europa.eu/environment/chemicals/exist\\_subst/pdf/793\\_93\\_ec.pdf](http://ec.europa.eu/environment/chemicals/exist_subst/pdf/793_93_ec.pdf)

[B5] The Council Directive of 15 July 1991 concerning the placing of plant protection products on the market (91/414/EEC). Annex 1. Available at: [http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en\\_1991L0414\\_do\\_001.pdf](http://europa.eu.int/eur-lex/en/consleg/pdf/1991/en_1991L0414_do_001.pdf)

[B6] UKTAG (2008). Proposals for Environmental Quality Standards for Annex VIII Substances. Final Report January 2008 (revised June 2008) (SR1 – 2007).

## ANNEX C: THE PROPOSED APPROACH FOR IMPLEMENTING BIOAVAILABILITY-BASED METAL STANDARDS

### Background

For a number of metals, EQSs derived under previous legislation are expressed as different hardness bandings as the available data at that time indicated their toxicity to aquatic life is influenced by the hardness of the water. This is the case, for example, for the existing EQSs for copper and zinc under the DSD. Further developments in scientific understanding, however, have shown that the toxicity of certain metals is also influenced by a number of other physicochemical parameters, in particular dissolved organic carbon and pH.

Dissolved organic carbon (DOC) has been found to have a mitigating effect on the toxicity of certain metals by binding with the metal and thereby making it less available to aquatic organisms. Other parameters such as calcium and hydrogen ions may compete with the metal to bind at the site of toxic action in the organism. These effects mean that measurements of the dissolved concentration of a metal in water are not always the best indicator of the concentration available to cause toxic effects to organisms. The fraction of the measured dissolved concentration that actually results in toxic effects is known as the bioavailable fraction.

Greater understanding of the influence of the various parameters on the toxicity of metals and the ability to use this knowledge to predict the fraction of bioavailable metal present have led to a major shift in our approach to metal EQSs. The development of thresholds for metals are now based on the bioavailable fraction of the metal. This is particularly the case for copper and zinc, where the EU risk assessments undertaken in relation to the Existing Substances Regulations (ESR) took into account the bioavailability of the metals in the derivation of the PNECs.

The assessment of the bioavailability of metals has been acknowledged under the Water Framework Directive (WFD). Its daughter directive on environmental standards (Annex I, part B<sup>1</sup>) sets a precedent in implementing metal standards as it allows Member States to:

*“...when assessing the monitoring results against the EQS, take into account:*

- (a) natural background concentrations for metals and their compounds, if they prevent compliance with the EQS value, and*
- (b) hardness, pH or other water quality parameters that affect the bioavailability of metals.”*

The EU technical guidance for the development of EQSs under the WFD [C1] includes guidance on the consideration of the bioavailability of metals in the derivation of EQSs for metals where sufficient data are available.

The UK have been one of the leading Member States in the development of the approach for

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<sup>1</sup> Directive 2008/105/EC on environmental standards in the field of water policy.

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implementing bioavailability-based EQSs for metals and have been instrumental in developing the guidance at an EU level.

Bioavailability-based EQSs have been proposed for copper, zinc and manganese, and the UKTAG's approach for implementing these standards is outlined below.

### **Derivation of bioavailability-based environmental quality standards**

Environmental quality standards for copper, zinc and manganese have been derived for the freshwater environment using data that has considered effects on aquatic life under conditions of high bioavailability. These EQSs are termed bioavailable EQSs or EQS<sub>bioavailable</sub>. Because they reflect toxicity in highly sensitive areas, these EQSs are precautionary. To apply these bioavailability-based generic EQSs, the concentration of bioavailable copper, zinc and manganese at a particular site needs to be determined. The proposed approach is outlined below.

### **Accounting for bioavailability through the use of biotic ligand models and M-BAT**

After several years research in industry and academia, biotic ligand models (BLMs) have been developed that can be used to predict the toxicity of metals in aquatic systems based on the local water chemistry conditions. A number of chronic toxicity BLMs have been developed including ones for copper, zinc and manganese.

The full BLMs however are complex tools which:

- often require a number of data inputs; for example, the full copper BLM requires approximately 14 data inputs;
- can be slow to run owing to their complexity and are therefore not practical for assessing thousands of samples; and
- operate using software that is often not compatible with regulatory agency systems.

Simplified versions of the BLMs have, therefore, been developed on behalf of the regulatory agencies by wca environment. These less-complex versions provide a regulatory tool that requires only three input parameters, that is pH, calcium and DOC, and enables a more rapid consideration of bioavailability. The regulatory tool, referred to as the Metal Bioavailability Assessment Tool (M-BAT, previously referred to as the PNEC Estimator or Screening Tool) has been developed so that the outputs reflect the outputs of the 'full' BLMs as closely as possible. The M-BAT enables large numbers of samples to be run relatively quickly and has been developed to be compatible with regulatory systems so that it can be automated if required. The M-BAT currently covers copper, zinc and manganese [C2–C4].

The input data required to run M-BAT are:

- dissolved metal concentrations measured at a site;

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- pH;
- DOC concentrations; and
- calcium (Ca) concentrations.

Based on this information, M-BAT calculates the site-specific:

- bioavailable fraction (fraction of the dissolved metal that is bioavailable at that site);
- bioavailable concentration (concentration of the dissolved metal that is bioavailable and can cause toxic effects at that site); and
- PNEC (metal concentration predicted to cause no effects at that site).

The site-specific bioavailable concentration can then be compared with the  $EQS_{\text{bioavailable}}$  to assess compliance.

M-BAT can be embedded within the laboratory information systems (LIMS) of the regulatory agencies. This enables automated processing of the large amount of samples taken. However, it can also be used as a standalone tool, particularly if a limited number of sites are being considered. The high level of agreement between the results obtained from M-BAT and the full BLMs reduces the need to use the full BLMs [C3,C4].

### Boundary values

M-BAT was created based on the full BLMs developed by industry through the European ESRs<sup>1</sup> (copper and zinc) or to help meet requirements under REACH<sup>2</sup> (manganese). These full BLMs have been validated over a range of physicochemical conditions. The validated boundary conditions in each of the full BLMs are shown in Table C1 for each of the M-BAT input requirements, that is calcium concentrations, pH and DOC concentrations.

<sup>1</sup> EC Council Regulation (EEC) No. 793/93.

<sup>2</sup> EC Regulation No. 1907/2006 concerning the registration, evaluation, authorisation and restriction of chemical substances.

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**Table C1. The validated boundary conditions of the full biotic ligand models [C4,C5]**

<b>Metal</b>	<b>DOC (mg/l)</b>	<b>pH</b>	<b>Ca (mg/l)</b>
Cu	0.5–20	5.5–8.5	4–144
Zn	1–20	6–9	5–120
Mn	0.5–32	5.5–8.5	1–200

The validated ranges do not, however, cover the full range of conditions that can occur in UK waters. Therefore, it has been necessary to adapt M-BAT to operate under other conditions. This is discussed below for each of the input parameters.

### *Dissolved organic carbon*

The operational range for DOC within M-BAT has been set as 'unlimited' because the effect of DOC on metal availability is a chemical, rather than biological, one [C2]. This parameter is considered very important for the predictions of bioavailability, particularly with respect to copper and zinc. By contrast, DOC has very little influence on the toxicity of manganese to aquatic life [C4].

### *Calcium*

M-BAT operates beyond the calcium boundaries at the upper end of the range as the tool's predictions tend to be conservative.

For zinc, the EU ESR risk assessment proposed a soft-water PNEC for waters at calcium concentrations below 7 mg/l. Data gathered more recently show no compelling evidence for the need for a separate soft-water PNEC [C6]. For this reason, the zinc component of M-BAT has been set to operate down to calcium concentrations of 5 mg/l. At calcium concentrations <5 mg/l, M-BAT will perform the calculation based on a set value of 5 mg/l and will highlight and flag the result as being based on 'sensitive conditions' [C3]. For copper and manganese, calcium concentrations below the lower boundary value will also be flagged within M-BAT.

### *pH*

For pH, the boundary values arise for two reasons:

- (1) they were created to correspond to prevailing European conditions; and
- (2) the ecotoxicological tests upon which the BLMs are based cannot be conducted under more pH-extreme conditions on laboratory test organisms.

To extend the screening tools to cover other UK conditions, the UKTAG developed and tested extrapolations to allow calculations down to pH 4 for copper and zinc [C7]. Where an input value for pH is within the extended range, that is pH 4–5.5 for copper and pH 4–6 for zinc, the results in the screening tool are highlighted and flagged as being outside the validation range and therefore 'tentative'. Results from waters that are above the upper range of pH or below the



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lower range (pH <4), are flagged as being outside the validation range and are assumed to reflect 100 per cent bioavailability. This might be precautionary, but there will be opportunities in the tiered scheme (see below) to refine the assessment of risk.

Table C2 shows the resulting boundary conditions within M-BAT.

**Table C2. Boundary conditions within M-BAT**

<b>Metal</b>	<b>DOC (mg/l)</b>	<b>pH</b>	<b>Ca (mg/l)</b>
Cu	Unlimited	5.5–8.5 (pH extended down to 4)	4–144

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Zn	Unlimited	6–9 (pH extended down to 4)	5–120
Mn	Unlimited	5.5–8.5	1–200

### Input data

#### *Use of average values for the input data*

The input parameters required for M-BAT are the dissolved metal concentration, pH and calcium and DOC concentrations. For compliance assessment purposes, it is proposed that the average dissolved metal concentration should be used along with the average pH values and dissolved calcium concentrations and the median DOC concentrations [C3]. The UKTAG recognises that the average value used, for example an annual or three-year average, may vary depending on the compliance requirements and approaches used within the regulatory agencies. Where M-BAT is automated within a LIMS system, EQS compliance will be based on bioavailability-corrected results for individual samples, using the input parameters collected at the same time and location. Where M-BAT is used as a standalone tool, the average bioavailable metal concentration may be developed based on individual results or bioavailability-corrected results. Research carried out by the UKTAG [C5] has found that the final predicted bioavailable concentrations were not affected significantly by whether the input data were averaged prior to estimating bioavailability, or whether the bioavailable concentrations estimated from individual samples were averaged afterwards.

For assessments that are not related solely to compliance assessment, such as specific site investigations, individual sample results rather than averages could be used within M-BAT. The general principles about potential errors in compliance assessment and confidence of failure considerations apply to these metal assessments in exactly the same way as for any other substance.

It is possible that the receiving water for a discharge could present conditions that make the metal less bioavailable than a point further downstream. This is not relevant to classification, but is a consideration for permitting point source discharges. The UKTAG proposes that in these latter situations, the most-sensitive conditions should be used in the assessment. These conditions can easily be identified using M-BAT in conjunction with a constant measured metal concentration to identify the most vulnerable reach.

#### *Use of default data*

In cases where data on pH, calcium and DOC are not available, it may be necessary to use default data to enable M-BAT to be applied. pH has been widely monitored and so data are generally available. Where a result is missing, historical data for that site may be appropriate.

For calcium, either historical data can be used or, alternatively, the appropriate calcium input can be estimated based on relevant hardness data for the watercourse.

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To date, varying amounts of monitoring have been undertaken for DOC. In some areas of the UK only limited data are available. Because DOC may not always be monitored, the UKTAG has considered the use of default values. A method has been developed for the derivation of default DOC values that provides generally precautionary values at the water body level. These defaults are based on the 25-percentile of previously measured DOC data for that area [C8]. Hydrometric area level defaults can also be derived where data are sparse at the water body level, but do not provide such representative results. However, these defaults can be subject to a high level of uncertainty because they are based on limited data. In addition, defaults could only be derived for a small number of existing monitoring sites and we currently have a limited understanding of the variability of DOC levels in the environment. It has therefore been agreed that these defaults are not suitable for use in compliance assessment. However, as additional DOC monitoring data become available, default DOC values may be estimated with greater confidence. Until then, the UKTAG recommends the collection of DOC data alongside samples for metals analysis.

### Background concentrations

Metals occur naturally in the environment with some being essential elements for certain aquatic species. The general definition of natural background levels is the concentration that is present owing to natural and geological processes only (i.e. without man-made contributions). However, few surface waters are truly pristine, containing only 'natural' concentrations. This is recognised in the EU EQS Technical Guidance which states that 'any estimate of a background concentration will more likely be an 'ambient' background concentration (ABC), comprising both a natural geochemical fraction and a small anthropogenic fraction.

If sites fail the EQS (after taking account of bioavailability), consideration of the natural background concentration may be undertaken to further assess compliance. The 2008 Directive allows Member States to take account of such backgrounds 'if they prevent compliance with the EQS value'. Consideration of natural background concentrations might be a first step in an investigation and prior to any expensive or time-consuming remediation (see Figure C1).

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There are several methods by which a background concentration may be estimated. Potential approaches have been identified in the EU EQS Technical Guidance. The guidance notes that in freshwater, the preferred option is to determine the concentration in springs and/or waterbodies in pristine areas in the given region, e.g. headwaters. Existing data may be sparse however and other possible approaches are documented in the EU EQS guidance as noted below.

1. Determine the concentration in springs and/or waterbodies in pristine areas in the given region, e.g. headwaters (though existing data may be sparse).
2. An alternative pragmatic approach is to take the 10th percentile dissolved metal concentration of all the monitoring data available for the waterbody or region (after removing sample results with elevated concentrations from known point source discharges or pollution events).
3. Extract data from national or international databases, such as the FOREGS Geological Baseline Programme (<http://www.gsf.fi/foregs/geochem>).
4. Use modelling to estimate the contribution to surface waters from erosion
5. Adopt concentrations from deep groundwater - though the concentration may be higher here than in the surface water, for example, because of the groundwater's contact with deep lying mineral rocks or soils and subsequent dilution by rain
6. Estimate the background concentration in the water from natural background concentrations found in the sediment using equilibrium partitioning models

UKTAG has not stipulated a preferred method. However as part of the work undertaken for the development of the zinc EQS, consideration has been given to the determination of background concentrations. This has involved consideration of the distribution of metal concentrations from samples taken at unimpacted sites (remote from known point source discharges, no pollution events) and the use of a low percentile of the distribution, eg 5<sup>th</sup> and 10<sup>th</sup> percentiles to determine the background concentration (as noted in point 2 above). Where such data are limited, ambient background concentrations could be read across from an adjacent hydrometric area or data could be pooled across several adjacent hydrometric areas with broadly comparable geology, land use and hydromorphology. Reliable estimates however are dependent on a number of factors including the number of sampling points and the percentage of 'less than' values within the dataset.

The UKTAG's work on this topic has highlighted the uncertainty associated with the derivation of ABCs. It may be possible to refine ABCs as further data become available and efforts to gather such data can be targeted at sites based on risk (that is, where EQS failure is likely to be attributable to high ABCs).

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This approach involves discounting background levels as part of applying the standard. It assumes that organisms have acclimatised to natural background levels and that those backgrounds can be added to the generic EQS to derive a corrected standard that takes account of such local conditions. This is sometimes referred to as an 'added risk' approach.

As noted above background concentrations only need to be considered for those sites at which an EQS failure has been observed apart from zinc. The EQS for zinc is expressed as an EQS<sub>add</sub>, ie the EQS refers to the concentration above the natural background and therefore consideration of the background concentration needs to be made when assessing compliance.

EQS compliance is achieved when:

$$EQS_{added, bioavailable} + background\ concentration_{bioavailable} > measured\ bioavailable\ metal\ concentration$$

In practice, the background concentration only needs to be considered when the measured bioavailable concentration exceeds the EQS, i.e. the background concentration will not need to be considered for every sample/site.

### Tiered approach to metals compliance assessment

The UKTAG proposes a tiered approach for metals compliance assessment which allows a stepwise consideration of bioavailability and background concentrations in metals compliance assessment. Tiered approaches are commonly used within risk assessments. Early tiers of such frameworks are generally designed to be conservative and allow a relatively high throughput of samples/sites so that resources are only applied to situations most likely to be at risk. Individual monitoring sites progress through the tiers, but attention focuses on the riskier sites as the low risk sites are screened out. The amount of effort required to make the assessment is, therefore, commensurate with the levels of potential environmental risk.

The proposed tiered approach is illustrated in Figure C1 and discussed in more detail below<sup>1</sup>.

**Tier 1** – Compare the total dissolved metal concentration with the EQS<sub>bioavailable</sub>.

As explained earlier, this generic EQS is derived based on conditions of high bioavailability for the metal and, therefore, is the most precautionary. This tier requires the least input information and technical skill for assessment and involves a simple comparison of the total dissolved metal concentration against the bioavailable standard, (assuming 100 per cent bioavailability of the metal). If the total dissolved metal concentration does not exceed the standard, then there is no need to take account of bioavailability because the bioavailable concentration in the environment can only be lower. If bioavailability corrections are made automatically, for example as part of the LIMS, bioavailable metal concentrations may already be available for direct comparison against the bioavailable metal standard. In such cases, tier 1 is effectively

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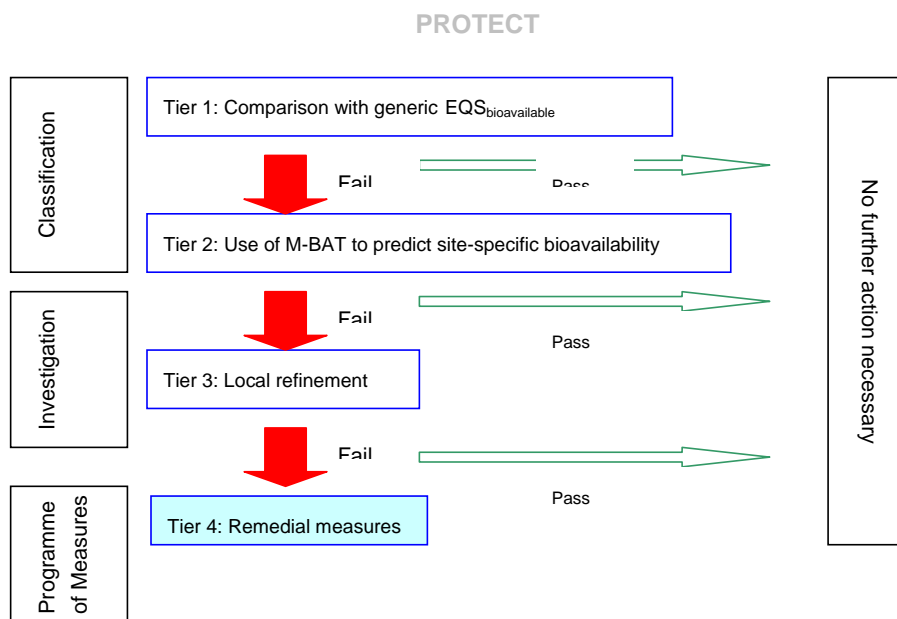
<sup>1</sup> Assessment of compliance is subject to the same considerations about taking account of sampling error and considering confidence of compliance, as described earlier in the report.

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omitted and the assessment at tier 2 is performed.

*Tier 2* – Calculate the bioavailable metal concentration using M-BAT (or the models embedded in the LIMS) using the dissolved concentrations and information on pH, calcium and DOC. Then compare the bioavailable concentration with the  $EQS_{bioavailable}$  to assess compliance. For EQSs expressed as an EQSadd, eg the zinc EQS the bioavailable background concentration for the site also needs to be determined and incorporated within the compliance assessment.

*Tier 3* – Undertake local investigations. This tier includes the use of a potential range of tools to help refine the assessment of bioavailability, such as the use of the 'full' BLMs or further sampling and analysis, particularly where default values may have been used for the input parameters, and the consideration of background concentrations. Only when these factors have been accounted for can we safely assume the EQS has been breached.



**Figure C1 Tiered approach to compliance assessment**

## References

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- [C2] Peters A, Merrington G (2012); The development and use of the copper bioavailability tool. Environment Agency: Bristol.
- [C3] Brown B, Merrington G, Crane M (2012). Implementation of copper and zinc environmental quality standards in freshwaters: accounting for bioavailability and natural backgrounds; SC080021/8e; UKTAG: Edinburgh.
- [C4] Merrington G, Peters A, Brown B (2012). The development and use of the manganese screening tool; SC080021/1g-1; UKTAG: Edinburgh.
- [C5] Comber S, Georges K (2008). Tiered approach to the assessment of metal compliance in surface waters; SC050054/SR1a; Environment Agency: Bristol.

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[C6] Peters A, Merrington G, Crane M (2012). Evaluation of the use of bioavailability corrections for zinc under low pH and low Ca conditions; SC080021/8c; UKTAG: Edinburgh.

[C7] Gardner M (2012); Desk top study to evaluate options outside BLM thresholds (low pH and low calcium issues); SC080021/8d; UKTAG: Edinburgh.

[C8] Merrington G, Peters A (2012); The importance of dissolved organic carbon in the assessment of environmental quality standard compliance for copper and zinc; SC080021/7a; UKTAG: Edinburgh.

[C9] Peters A, Merrington G, Crane M (2012). Estimation of background reference concentrations for metals in UK freshwaters; SC080021/1a; UKTAG: Edinburgh.



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## ANNEX D: DATA SHEETS BY SUBSTANCE (ALPHABETICAL ORDER)

**Comment [H1]:** Need to check contents sheet as not all included on current contents page

<b>Benzyl butyl phthalate (CAS number 85-68-7)</b>			
<b>Receiving medium and exposure</b>	<b>Assessment Factor</b>	<b>Proposed PNEC (µg/l)</b>	<b>Existing EQS (µg/l)</b>
<b>Freshwater/long-term</b>	10	7.5	20 (AA)
<b>Freshwater/short-term</b>	10	51	100 (MAC)
<b>Saltwater/long-term</b>	100	0.75	20 (AA)
<b>Saltwater/short-term</b>	50	10	100 (MAC)
<b>Recommendation:</b> The PNECs are proposed as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.			
<b>Background Information:</b>			
<b>Properties and fate in water</b>	<p>Few data are available on the mode of toxic action of BBP in aquatic organisms. However, polar narcosis is generally accepted as the primary mode of action.</p> <p>BBP has a relatively low water solubility (2.8 mg l<sup>-1</sup>) and based on its log Kow of 4.8 and log Koc of 10500 is expected to partition to sediments, suspended matter and biota in the aqueous environment. Hydrolysis and photolysis are not expected to be major fate processes for BBP and based on its Henry's law constant (0.176 Pa.m<sup>3</sup>/mol) volatilisation from water surfaces is likely to be insignificant. Biodegradation is the rate controlling process for environmental degradation of BBP. Aerobic degradation is rapid in natural water and sewage systems with degradation rates of &gt;80% reported after 14 days and 2 days in domestic sewage and river water, respectively. BBP also degrades rapidly under anaerobic conditions with 90% degradation after 8-days in municipal sewage sludge. The major degradation products of BBP are monobutylphthalate, monobenzylphthalate and phthalic acid.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>An EU Risk Assessment Report (RAR) has been compiled for BBP. As it has been proposed that RAR PNECs are used for the derivation of WFD EQSs the RAR PNECs are recommended as the proposed long term PNECs for freshwater and saltwaters. Short term PNECs have been derived based on the available data.</p> <p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for BBP, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V of the WFD.</p>		

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<p><b>Long-term PNEC for freshwaters</b></p>	<p>The lowest valid long-term freshwater data point was a 30-day NOEC (for growth and length) of 0.14 mg l<sup>-1</sup> for the fathead minnow (<i>Pimephales promelas</i>). However, given the similarity in effects in both fresh and saltwater the EU RAR combined the two data sets. In saltwater a 28-day NOEC (reproduction/growth) of 0.075 mg l<sup>-1</sup> was reported for the mysid shrimp (<i>Mysidopsis bahia</i>). This datum was generated in a GLP study under flow through conditions and was regarded by the RAR as fully valid for PNEC derivation.</p> <p>The long-term freshwater PNEC in the EU RAR was therefore based on the 28-day NOEC (for reproduction and growth) of 0.075 mg l<sup>-1</sup> reported for the mysid shrimp (<i>Mysidopsis bahia</i>) and an assessment factor of 10 applied, because of the availability of long-term data for three trophic levels and the similarity in sensitivity of trophic levels,</p> <p><b>Recommended PNEC: 7.5 µg l<sup>-1</sup> (AF 10)</b></p> <p><b>Change from existing EQS: Lower than existing non-statutory EQS of 20 µg/L</b></p>
<p><b>Short-term PNEC for freshwaters</b></p>	<p>The lowest valid short-term freshwater data point was a 72-hour EC50 (growth rate) of 0.64 mg l<sup>-1</sup> for the alga <i>Navicula pelliculosa</i>. However, given the similarity in effects in both fresh and saltwaters the EU RAR combined the two data sets. In saltwater a 96-hour LC50 of 0.51 mg l<sup>-1</sup> was reported for the shiner perch (<i>Cymastogaster aggregata</i>). This datum was generated under flow-through conditions with measured exposure concentrations and was regarded, by the RAR, as fully valid for PNEC derivation.</p> <p>Although short-term critical data were identified in the RAR, EU RARs do not usually derive intermittent (short-term) PNECs. Consequently, no short-term RAR PNEC was available to be adopted as the EQS.</p> <p>Therefore, a short-term PNEC was derived in this report by applying an assessment factor of 10 to the lowest available datum, because of the availability of reliable short-term data for at least three trophic levels and the similarity in sensitivity of trophic levels resulting in a PNEC<sub>freshwater_st</sub> of 51 µg l<sup>-1</sup> BBP.</p> <p><b>Recommended PNEC: 51 µg l<sup>-1</sup> (AF 10)</b></p> <p><b>Change from existing EQS: Lower than the existing non-statutory EQS of 100 µg/L</b></p>
<p><b>Long-term PNEC for salt waters</b></p>	<p>Long-term saltwater data for BBP were available for the 'base set' of organisms (algae, invertebrates and fish). The long-term saltwater PNEC in the EU RAR for BBP was based on the 28-day NOEC (reproduction/growth) of 0.075 mg l<sup>-1</sup> reported for the mysid shrimp (<i>Mysidopsis bahia</i>). An additional assessment factor of 10 was used compared to the freshwater long term PNEC as no long-term data was available for additional marine taxonomic groups such as echinoderms or molluscs, resulting in a PNEC<sub>saltwater_lt</sub> of 0.75 µg l<sup>-1</sup> BBP.</p> <p><b>Recommended PNEC: 0.75 µg l<sup>-1</sup> (AF 100)</b></p> <p><b>Change from existing EQS: Lower than existing non-statutory EQS of 20 µg/L</b></p>

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<p><b>Short-term PNEC for salt waters</b></p>	<p>No short-term saltwater PNEC was derived in the EU RAR for BBP. However, the lowest short-term critical data were identified in the RAR. The lowest reliable data point in the combined data set was the 96-hour LC50 of 0.51 mg l<sup>-1</sup> reported for the shiner perch. An assessment factor of 50 is proposed (ie an additional AF of 5 compared to freshwater) because in addition to reliable short-term data for at least three trophic levels, there are short-term data for an additional marine taxonomic group (molluscs). The use of such an assessment factor with the short-term saltwater data is in line with the guidance within the EU TGD (ECB 2003). This results in a PNEC<sub>saltwater_st</sub> of 10 µg l<sup>-1</sup> BBP.</p> <p><b>Recommended PNEC: 10 µg l<sup>-1</sup>(AF 50)</b></p> <p><b>Change from existing EQS: Lower than the existing non-statutory EQS of 100 µg/l</b></p>
<p><b>PNEC for secondary poisoning</b></p>	<p>The draft RAR identified the NOAEL of 50 mg/kg body weight from a rat reproduction toxicity study as most suitable for derivation of PNEC<sub>secpois.biota</sub>. The appropriate assessment factors to derive a PNEC based on a chronic NOAEL<sub>food</sub> from a mammalian study are a conversion factor of 20 and an assessment factor of 30 resulting in a PNEC<sub>secpois.biota</sub> of 33.3 mg/kg BBP in food.</p> <p>Reported BCF values for whole fish range from 188 to 663. However, the draft RAR identified a BCF of 449 in Bluegill sunfish (<i>Lepomis macrochirus</i>) as the most suitable for the estimation of secondary poisoning. Consequently, the concentration in water preventing bioaccumulation in prey to levels &gt;PNEC<sub>secpois.biota</sub> is a PNEC<sub>secpois.water</sub> of 74 µg l<sup>-1</sup> BBP.</p> <p><b>Recommended PNEC: 74 µg l<sup>-1</sup> (AF 30)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments</b></p>	<p>BBP has a log Kow value of 4.84 which is above the TGD trigger level of 3. As such sediment standards for BBP should be derived. However, it was not possible to locate data on the direct toxicity of BBP to sediment-dwelling organisms. Consequently, it was not possible, at this time, to derive a sediment PNEC.</p> <p><b>Recommended PNEC: Not derived</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>Analysis</b></p>	<p>BBP may be analysed by gas chromatography/mass spectrometry and by high-performance liquid chromatography.</p> <p>Proposed PNECs derived for BBP range from 0.75 to 51 µg l<sup>-1</sup> in environmental waters. The data quality requirements are that, at a third of the EQS total error of measurement should not exceed 50 per cent. Using this criterion, current analytical methodologies should offer adequate performance to analyse for BBP</p>
<p><b>Implementation</b></p>	<p>The current analytical capability should be adequate for compliance assessment.</p> <p>The PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty.</p> <p>When failure is reported for saltwater standards derived using an assessment factor of 100, it is recommended that supporting information, including evidence of ecological damage, should be obtained before committing to expensive action.</p>

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Carbendazim (CAS number 10605-21-7)			
Receiving medium and exposure	Assessment factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	10	0.15	0.1
Freshwater/short-term	10	0.7	1.0
Saltwater/long-term	100	0.015	0.1
Saltwater/short-term	50	0.14	1.0
<b>Recommendation:</b> <p>The freshwater long term and short term PNECs are proposed as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use. The values may be used as guideline values for operational purposes.</p>			
Background information:			
<b>Properties and fate in water</b>	<p>Values of 5.0 to 12.9 mg l<sup>-1</sup> indicate that carbendazim has low to moderate water solubility. A log K<sub>ow</sub> of 0.40–1.52, suggests that carbendazim is unlikely to significantly partition to sediments and suspended matter and/or accumulate in biota. In a study of distribution in water and sediment systems carbendazim was shown to partition into sediment, but this did not occur rapidly. Volatilisation is not expected to be an important environmental fate process for carbendazim, based on a Henry's Law constant of 3.5 x10<sup>-8</sup> Pa.m<sup>3</sup>.mole<sup>-1</sup>.</p> <p>The ready biodegradability of technical grade carbendazim in a closed bottle test according to OECD Guideline 301D was reported in the EU DAR (2000). Within 28 days 6% biodegradation was attained, and, therefore, technical grade carbendazim may not be classified as readily biodegradable.</p> <p>Bioconcentration data (as BCF values) for carbendazim is low, with values for whole fish ranging from 23 to 159 (and 380 to 460 for viscera). The one BCF value over 100 for rainbow trout was an exception and values &lt;100 were recorded in the same study for channel catfish and bluegill sunfish. Other studies have reported BCF values of 23 and 27.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for carbendazim, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Information collated for the risk assessment of carbendazim under the Plant Protection Products Directive has been considered. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.</p>		

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Long-term PNEC for freshwaters	The lowest valid long-term toxicity value for freshwater invertebrates is a 21-day No Observed Effect Concentration (NOEC) of 1.5 µg active ingredient (a.i.) l <sup>-1</sup> for effects on the reproduction of the waterflea <i>Daphnia magna</i> . Reliable long-term NOECs are available for algae, crustaceans, fish, molluscs and platyhelminths. An assessment factor of 10 could be applied to the lowest valid toxicity value, based on the EU Technical Guidance Document (TGD) methodology.
	<b>Recommended PNEC: 0.15 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: Slightly higher than existing non-statutory EQS of 0.1ug/l</b>
Short-term PNEC for freshwaters	Reliable short-term data are available for algae, amphibians, annelids, crustaceans, fish, insects, molluscs and protozoa. The lowest valid short-term toxicity value is a 96-hour LC50 of 7 µg a.i. l <sup>-1</sup> in the channel catfish yolk sac fry ( <i>Ictalurus punctatus</i> ). Based on the EU TGD methodology and a large body of reliable acute data for carbendazim, an assessment factor of 10 can be applied to the lowest valid toxicity value.
	<b>Recommended PNEC: 0.7 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: Slightly lower than existing non-statutory EQS of 1ug/l</b>
Long-term PNEC for salt waters	No long-term single species toxicity data for marine organisms are available. The absence of long-term data means that it is not possible to generate a PNEC <sub>saltwater_lt</sub> based on the saltwater data alone and it is proposed that the combined freshwater and saltwater dataset is used for the PNEC generation.
	Reliable long-term NOECs are available for algae, crustaceans, fish, molluscs and platyhelminths, but no data are available for exclusively marine taxa such as echinoderms. Therefore, based on the methodology outlined in the TGD, an assessment factor of 100 could be applied to the lowest valid freshwater chronic toxicity value.
	<b>Recommended PNEC: 0.015 µg l<sup>-1</sup>(AF 100)</b>
Short-term PNEC for salt waters	<b>Change from existing EQS: Lower than existing non-statutory EQS of 0.1ug/l</b>
	Single species short-term toxicity data for marine organisms are available for three different taxonomic groups, i.e. crustaceans, molluscs and fish. Therefore, it is proposed that the PNEC <sub>saltwater_st</sub> is based on the combined freshwater and saltwater dataset.
	The lowest valid short-term toxicity value for freshwater fish is a 96-hour LC50 of 7 µg a.i. l <sup>-1</sup> in the channel catfish yolk sac fry ( <i>Ictalurus punctatus</i> ). Since no data are available for marine taxa such as echinoderms, an additional assessment factor of 10 would also normally be applied. However, there is a large body of short-term data in the combined freshwater and saltwater dataset and there are toxicity data for saltwater molluscs. Therefore, a reduced assessment factor of 50 applied.
	<b>Recommended PNEC: 0.14 µg l<sup>-1</sup>(AF 50)</b>
	<b>Change from existing EQS: Lower then existing non-statutory EQS of 1ug/l</b>

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<b>PNEC for secondary poisoning</b>	Bioconcentration data (as BCF values) for carbendazim is low, with values for whole fish ranging from 23 to 159 (and 380 to 460 for viscera). The one BCF value over 100 for rainbow trout was an exception and values <100 were recorded in the same study for channel catfish and bluegill sunfish. Other studies have reported BCF values of 23 and 27. Therefore, on a weight of evidence basis it is considered that the TGD BCF trigger of 100 has not been exceeded and the derivation of a PNEC in whole fish for secondary poisoning of predators is not required.
	<b>Recommended PNEC: BCF&lt; 100, so PNEC not required</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for sediments</b>	The log Kow of carbendazim is 0.4-1.52 and the log Koc is 2.30-2.39, so the derivation of PNECs for the protection of benthic organisms is not required according to the TGD since the log Kow/Koc trigger value of 3 is not exceeded.
	<b>Recommended PNEC: Not required</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis</b>	For water, proposed PNECs derived for carbendazim range from 0.015 to 0.7 µg l <sup>-1</sup> . The data quality requirements are that, at one third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing gas or liquid chromatography/mass spectrometry are capable of achieving detection limits as low as 0.001 µg l <sup>-1</sup> should offer adequate performance to analyse for carbendazim.
<b>Implementation</b>	Current analytical methods are sensitive enough to assess compliance with the proposed PNECs in receiving waters. The analytical capability should be adequate for compliance assessment. Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use. The values may be used as guideline values for operational purposes

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Chlorothalonil (CAS number 1897-45-6)			
Receiving medium and exposure	Assessment factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	10	0.035	0.1
Freshwater/short-term	10	1.2	1.0
Saltwater/long-term	100	0.0035	0.1
Saltwater/short-term	10	0.36	1.0
<b>Recommendation:</b> <p>The freshwater long term and short term PNECs are proposed as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use. The values may be used as guideline values for operational purposes.</p>			
Background information:			
<b>Properties and fate in water</b>	<p>Chlorothalonil is a broad spectrum, non-systemic, organochlorine fungicide used primarily in agriculture and to a much lesser extent on managed amenity turf. It is also used in approved antifoulant products.</p> <p>Chlorothalonil is a polychlorinated aromatic compound, but it is atypical in that it does not have the high degree of persistence associated with many other chlorinated organic chemicals. This difference is attributed to the two nitrile groups which activate the molecule. Several of chlorothalonil's primary metabolites are also polychlorinated, and appear to be more persistent and more mobile than chlorothalonil. Bioconcentration of chlorothalonil in aquatic organisms is considered to be low to moderate with reported Bioconcentration Factors (BCFs) of 9.4 to 264.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for Chlorothalonil, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Information collated for the risk assessment of chlorothalonil under the Plant Protection Products Directive has been considered. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.</p>		
<b>Long-term PNEC for freshwaters</b>	<p>The lowest reliable long-term toxicity value for freshwater organisms is a NOEC of 0.35 µg l<sup>-1</sup> for rainbow trout, <i>Oncorhynchus mykiss</i>. Reliable long-term NOECs are available for algae, invertebrates and fish, and, therefore, an assessment factor of 10 has been applied.</p>		
	<b>Recommended PNEC: 0.035 µg l<sup>-1</sup> (AF 10)</b>		
	<b>Change from existing EQS: Lower than existing non-statutory EQS of 0.1ug/l</b>		

# PROTECT

<b>Short-term PNEC for freshwaters</b>	Reliable short-term data are available for algal, invertebrate and fish species, which shows that acute sensitivity to chlorothalonil is comparable across taxa. The lowest reliable short-term result is the 5-day growth inhibition (using the biomass endpoint) EC50 of 8.8 µg l <sup>-1</sup> for the diatom, <i>Navicula pelliculosa</i> with a corresponding growth inhibition EC50 (using the more relevant growth rate endpoint) of 14 µg l <sup>-1</sup> . Reliable 96-hour LC50 values of 12 µg l <sup>-1</sup> for effects of chlorothalonil on the survival of the freshwater lobster <i>Astacopsis gouldi</i> and rainbow trout <i>Oncorhynchus mykiss</i> have also been reported. To derive the short-term freshwater PNEC is proposed that an assessment factor of 10 (given the large body of acute data) was therefore applied to the 96-hour LC50 values of 12 µg l <sup>-1</sup> for <i>A.gouldi</i> and <i>O.mykiss</i> .
	<b>Recommended PNEC: 1.2 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: Slightly higher than existing non-statutory EQS of 1ug/l</b>
<b>Long-term PNEC for salt waters</b>	Long-term single species saltwater toxicity data are only available for algae and crustaceans. The most sensitive result is a 28-day NOEC of 0.83 µg l <sup>-1</sup> for the mysid shrimp, <i>Americamysis bahia</i> , but this study is not considered reliable enough to be used as the basis of a PNEC. As the saltwater toxicity data values available do not appear to differ markedly from the range obtained for corresponding freshwater species, a combined freshwater and saltwater dataset for marine effects assessment was used to derive the long-term saltwater PNEC. Therefore, the freshwater PNEC is recommended to be adopted to protect saltwater taxa. It is also proposed that an additional assessment factor of 10 is applied to account for the paucity of long-term toxicity data for marine species.
	<b>Recommended PNEC: 0.0035 µg l<sup>-1</sup>(AF 10)</b>
	<b>Change from existing EQS: Lower than existing non-statutory EQS of 0.1ug/l</b>
<b>Short-term PNEC for salt waters</b>	Reliable short-term data are available for six different taxonomic groups (algae, ascidians, crustaceans, echinoderms, fish and molluscs) including the base set of algae, invertebrates and fish. The most sensitive short-term result for saltwater species is a 96-hour shell deposition EC50 of 3.6 µg l <sup>-1</sup> for <i>Crassostrea virginica</i> . This is an unpublished study, but a further unpublished study using the same species reported 96-h EC50 values of 5.0 µg l <sup>-1</sup> supporting this sensitive result. In addition, there is a 48-hour EC50 of 6.6 µg l <sup>-1</sup> for developmental effects in the echinoderm <i>Paracentrotus lividus</i> . It is therefore recommended that a short-term saltwater PNEC should be based on effects to the mollusc <i>C. virginica</i> (3.6 µg l <sup>-1</sup> ) and an assessment factor of 10. This results in a PNEC <sub>saltwater st</sub> = 0.36 µg l <sup>-1</sup> .
	<b>Recommended PNEC: 0.36 µg l<sup>-1</sup>(AF 10)</b>
	<b>Change from existing EQS: Lower than existing non-statutory EQS of 1ug/l</b>



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<b>PNEC for secondary poisoning</b>	<p>Fish bioconcentration data (as BCF values) for chlorothalonil range from 9.4 to 264, hence the trigger of a BCF &gt;100 is exceeded and the derivation of PNECs for secondary poisoning of predators is required. The lowest relevant NOEC<sub>food</sub> is 120 mg kg<sup>-1</sup> derived from a 2-year study with dogs. Using the highest reported BCF of 264 for the calculation results in a corresponding water concentration of PNEC<sub>secpois.water</sub> = 4 mg kg<sup>-1</sup> prey / BCF (264) = 15 µg chlorothalonil l<sup>-1</sup>.</p> <p>This concentration is higher than the proposed long-term PNECs for the protection of freshwater and saltwater organisms. Therefore, if EQS are set on the basis of these PNECs the protection of predators from secondary poisoning would be included, and the derivation of additional quality standards for secondary poisoning is unnecessary.</p> <p><b>Recommended PNEC: 15 µg l<sup>-1</sup>.</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<b>PNEC for sediments</b>	<p>The TGD trigger value of a log K<sub>oc</sub> or log K<sub>ow</sub> of ≥3 is met, as reported log K<sub>ow</sub> and K<sub>oc</sub> values are in the range 2.91 – 3.05 and 2.9-3.84 respectively. However, there is only limited information with respect to experimental data on sediment toxicity for chlorothalonil and therefore no PNEC<sub>sediment</sub> can be derived.</p> <p><b>Recommended PNEC: Insufficient data</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<b>Analysis</b>	<p>For water, the lowest proposed PNECs derived for chlorothalonil is 0.0035 µg l<sup>-1</sup>. The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50%. Using this criterion, it is evident that current analytical methodologies (non-standard) employing gas chromatography (GC) with electron capture detection or off-line solid-phase extraction followed by high performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry, are both capable of achieving detection limits of 0.001 µg l<sup>-1</sup>. This should offer adequate performance to analyse for chlorothalonil in freshwater but may need further consideration in relation to the long term saltwater</p>
<b>Implementation</b>	<p>Current analytical methods are sensitive enough to assess compliance with the proposed PNECs in freshwaters.</p> <p>The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use. The values may be used as guideline values for operational purposes.</p>

# PROTECT

Copper metal (CAS number 65357-62-2)		
Receiving medium and exposure	Proposed EQS	Existing EQS
Freshwater long-term	1 µg/L	1-28 µg/l for hard waters (dependent on CaCO <sub>3</sub> /l).
Saltwater long-term	Reference PNEC = 2.64 µg l <sup>-1</sup> (dissolved) Site PNEC = 2.67 x (DOC/2 – 0.5) + 2.64 (dissolved)	5 µg l <sup>-1</sup> (AA) (dissolved)
<b>Recommendation:</b> The freshwater and saltwater PNECs are proposed as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.  A short term standard has not been proposed for copper as due to the fact it is persistent in the environment and arises from a number of sources the long term impacts are considered to be of priority.		
<b>Background Information:</b>		
<b>Properties and fate in water:</b>	Copper normally exists in solution as the cupric (2+) ion, complexed with inorganic ions or organic ligands, as insoluble precipitates, or sorbed to particulate matter. Toxicity to aquatic life depends strongly on water quality factors, especially pH, hardness, and dissolved organic carbon. The effects of these factors on speciation and availability of copper, and their interaction with biotic ligands (e.g., fish gills) and, therefore, toxicity, have enabled the development of Biotic Ligand Models (BLMs) that are the basis of PNECs derived within the voluntary risk assessment and the EQSs proposed here.	
<b>Factors affecting derivation of the PNEC</b>	<p>The UK proposal for a freshwater copper EQS is based on a voluntary risk assessment (VRA) carried out in 2008. This assessment was subjected to detailed scrutiny by Member States, TC NES and the EU's Scientific Committee (SCHER) and endorsed for use in a generic risk assessment as a result of this scrutiny. Therefore, it was decided that the PNECs derived through this process could be used as the basis for the long-term freshwater UK EQS.</p> <p>Water conditions in many UK waterbodies however are such that adopting the generic PNEC from the VRA would not be sufficiently protective to many UK waters. A more stringent UK generic EQS was therefore required, taking into account the most sensitive conditions in the UK. This does not require a wholesale review of the entire risk assessment but, rather, a correction to allow for UK conditions. The approach used to derive the PNEC however is consistent with the VRA.</p> <p>The marine dataset for Cu has both the taxonomic breadth and relevant end points to allow the use of a species sensitivity</p>	

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	<p>distribution (SSD). Due to the quality and quantity of fate and behaviour data on Cu in the marine environment it is possible for an assessment to be made on the influence of water characteristics upon Cu availability. A relationship was identified between Cu ecotoxicity to marine organisms and dissolved organic carbon (DOC) concentration. A bioavailability correction for Cu in the marine environment has thus been proposed, which is based on the complexation of Cu by DOC in seawater and has been assessed against short term toxicity tests for marine species.</p>
<b>Long-term PNEC for freshwaters</b>	<p>Water quality conditions for nearly 1000 UK sites were taken and site-specific PNECs developed for each one, taking account of bioavailability. The frequency distribution for these PNECs was then used to estimate the concentration corresponding to a value at which 95% of sites in the various UK regions (i.e. the 5%ile) would be protected.</p> <p>Variations between regions were evident and the North-West Region was identified as most sensitive, where a 5%ile of <math>0.9 \mu\text{g l}^{-1}</math> dissolved copper was found. In this particular region, around half the sites would not be adequately protected by the generic PNEC arising from the VRA.</p> <p>The proposed freshwater generic EQS for copper is therefore <math>1 \mu\text{g l}^{-1}</math> dissolved copper.</p> <p>Following a tiered approach, site specific bioavailability factors may be taken into account when assessing compliance.</p> <p><b>Recommended generic PNEC<sub>freshwater</sub> is <math>1 \mu\text{g l}^{-1}</math> dissolved Cu</b></p> <p><b>Change from existing EQS: comparable to existing EQS for low hardness waters</b></p>

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<p><b>Long-term PNEC for salt waters</b></p>	<p>There are sufficient data to allow construction of a species sensitivity distribution (SSD) using marine ecotoxicity data. Furthermore, it is possible for an assessment to be made on the influence of water characteristics upon Cu availability. Increasing dissolved organic carbon (DOC) has been shown to significantly reduce the ecotoxicity of Cu in marine water. Using the DOC correction, each individual NOEC/L(E)C10 value was normalised to a predefined DOC concentration of 0.5 mg l<sup>-1</sup> active DOC (equivalent to 1 mg l<sup>-1</sup> measured DOC in natural seawater) to construct a reference SSD from which an HC5 of 2.64 µg Cu l<sup>-1</sup> was estimated.</p> <p>An assessment factor of 1 is recommended for the derivation of the PNEC from the ecotoxicity data.</p> <p><b>Reference PNEC = 2.64 / 1 = 2.64 µg l<sup>-1</sup> dissolved Cu</b></p> <p>This PNEC is then adjusted to ambient conditions through the use of a bioavailability correction based on the concentration of DOC. The site specific PNEC, in µg l<sup>-1</sup> dissolved copper is calculated as follows:</p> $PNEC_{\text{Site Specific}} = 2.677 * \left( \frac{DOC}{2} - 0.5 \right) + 2.64$ <p><b>Recommended PNEC<sub>saltwater</sub> = Reference EQS 2.64 µg Cu l<sup>-1</sup></b></p> $PNEC_{\text{Site Specific}} = 2.677 * \left( \frac{DOC}{2} - 0.5 \right) + 2.64$ <p><b>Change from existing EQS: Reference PNEC is lower than existing EQS of 5ug/l</b></p>
<p><b>Analysis</b></p>	<p>The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 percent. It is anticipated that analytical methodologies currently employed by UK environmental regulators will be able to achieve this.</p>
<p><b>Implementation</b></p>	<p><b>Freshwater</b></p> <p>Analytical techniques are considered adequate and the proposed PNEC is not subject to excessive uncertainty.</p> <p>The PNEC<sub>bioavailable</sub> will be implemented as part of a tiered assessment framework which will include consideration of site specific water quality conditions, ie pH, calcium and DOC</p>

**PROTECT**

	<p><b>Saltwater</b> Analytical techniques are considered adequate and the proposed PNEC is not subject to excessive uncertainty. A methodology for determining appropriate DOC values to use need to be agreed upon.</p>
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## PROTECT

<b>Cyanide (free) [CAS number (HCN) 74-90-8]</b>		
<b>Receiving medium and exposure</b>	<b>Proposed PNEC (<math>\mu\text{g free CN l}^{-1}</math>)</b>	<b>Existing UK EQS (<math>\mu\text{g free CN l}^{-1}</math>)</b>
Freshwater long-term	0.26 (AF 20)	1.0
Freshwater short-term	2.8 (AF 10)	5.0
Saltwater long-term	0.052 (AF 100)	1.0
Saltwater short-term	0.42 (AF 10)	5.0
<b>Recommendation:</b>  Both the saltwater and freshwater long and short term PNECs are proposed as EQSs. The PNECs are considered suitable for use as they are not subject to excessive uncertainty. However, the analytical capability for assessing compliance may need consideration.		
<b>Background Information:</b>		
<b>Properties and fate in water</b>	<p>Cyanides are extensively used in industry and are also emitted from car exhaust fumes. They also occur ubiquitously in the environment and are found in a range of aquatic organisms such as arthropods, macrophytes, fungi and bacteria.</p> <p>Volatilisation and biodegradation are important transformation processes for cyanide in ambient waters. Hydrogen cyanide can be biodegraded by acclimated microbial cultures, but is usually toxic at high concentrations to unacclimated microbial systems.</p> <p>Cyanides are readily soluble in water where they exist in the free state (<math>\text{CN}^-</math> and <math>\text{HCN}</math>), as simple cyanides (e.g. <math>\text{NaCN}</math>), complex cyanides (organic or metal complexes) or total cyanide (all available species). Hydrogen cyanide (<math>\text{HCN}</math>) dissociates in water to give the free ion (<math>\text{CN}^-</math>) under alkaline conditions (50 per cent of both forms at pH 9.36). The <math>\text{CN}^-</math> ion has a half-life of 15 days in water; <math>\text{HCN}</math> has a tendency to volatilise from water, with a half-life measured from hours to a few days. Simple cyanides readily dissociate, as do some metal complexes (e.g. zinc and cadmium) releasing free <math>\text{CN}^-</math>. Other metal complexes containing cyanide are very stable with limited dissociation.</p> <p>Undissociated <math>\text{HCN}</math> is primarily used to determine toxicity, with <math>\text{HCN}</math> being more toxic than <math>\text{CN}^-</math>. However, <math>\text{CN}^-</math> contributes to toxicity due to formation of <math>\text{HCN}</math> at pH values up to around 8. Simple cyanides readily dissociate and hydrolyse to form <math>\text{HCN}</math> and <math>\text{CN}^-</math> and, therefore, have the same toxicity as free cyanide. Therefore, only data on free cyanide are used to set the PNECs in this report.</p>	
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for cyanide, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment so that decisions are based only on scientifically sound data. After consultation with an independent peer review group, critical data have been identified. Assessment factors have been selected</p>	

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	based on consultation and by further consideration of the available data in accordance with the guidance given in Annex V. The toxicity of the various forms of cyanide has been taken into account in the derivation and expression of the PNEC.
<b>Long-term PNEC for freshwaters</b>	<p>Fish appear to be the most sensitive taxonomic group, followed by crustaceans. The lowest reliable long-term data point is a 289-day LOEC value of 5.2 µg l<sup>-1</sup> HCN for total inhibition of spawning in the bluegill <i>Lepomis macrochirus</i>. An assessment factor of 10 could be applied to this value, but as it represents a significant effects level, an increased factor of 20 is proposed (composed of the assessment factor of 10 plus an additional factor of 2 to account for the conversion of the LOEC to a NOEC), resulting in a PNEC<sub>freshwater_lt</sub> of 0.26 µg l<sup>-1</sup> HCN.</p> <p>This PNEC is lower than the existing 1998 EQS of 1 µg l<sup>-1</sup> HCN. This was based on a value of ca. 10 µg l<sup>-1</sup> obtained from a study on the effects of cyanide on salmonid reproduction to which an assessment factor of 10 was applied.</p> <p><b>Recommended PNEC: 0.26 µg HCN/l (AF 20)</b></p> <p><b>Change from existing EQS: Lower than existing EQS of 1ug/l</b></p>
<b>Short-term PNEC for freshwaters</b>	<p>As in the long-term studies, fish and crustaceans were found to be the most sensitive taxonomic groups. The most sensitive, reliable result was a 96-hour LC50 of 28 µg l<sup>-1</sup> HCN for rainbow trout (<i>Oncorhynchus mykiss</i>). Given that good quality data are available for both fish, crustaceans and algae and that fish are the most sensitive organisms to both long- and short-term exposures to cyanide, an assessment factor of 10 is proposed. This results in a PNEC<sub>freshwater_st</sub> of 2.8 µg l<sup>-1</sup> HCN.</p> <p>In comparison to the current EQS, the proposed PNEC is 2 times lower. The 1998 EQS of 5 µg l<sup>-1</sup> HCN was based on applying an assessment factor of 10 to an LC50 of 43 µg l<sup>-1</sup> HCN obtained in a study on the same species.</p> <p><b>Recommended PNEC: 2.8 µg HCN/l (AF 10)</b></p> <p><b>Change from existing EQS: Lower than existing EQS of 5ug/l</b></p>

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<p><b>Long-term PNEC for salt waters</b></p>	<p>The data suggest saltwater organisms to be of similar sensitivity to freshwater organisms with similar effect values. Given that cyanide acts as a respiratory depressant, similar effects would be expected in both environments. Because of this, the freshwater and saltwater datasets were combined.</p> <p>As there were no high quality long-term saltwater data, the lowest reliable data point of the combined dataset is the 289-day LOEC value of 5.2 µg l<sup>-1</sup> HCN for total inhibition of spawning in the bluegill <i>Lepomis macrochirus</i>. An assessment factor of 50 could be applied to this value because there are long-term data for three freshwater trophic levels and short-term data for echinoderms and molluscs. The short-term data indicate that whilst molluscs may be sensitive to cyanide, echinoderms are of reduced sensitivity compared to crustaceans and fish.</p> <p>Therefore, given the available data in the combined dataset, a total assessment factor of 100 is proposed (including a factor of 2 to convert the LOEC to a NOEC), resulting in a PNEC<sub>saltwater_lt</sub> of 0.052 µg l<sup>-1</sup> HCN.</p> <p>This is considerably lower than the existing EQS of 1 µg l<sup>-1</sup> HCN, which was 'read across' from the freshwater EQS.</p> <p><b>Recommended PNEC: 0.052 µg HCN/l (AF 100)</b></p> <p><b>Change from existing EQS: Lower than existing EQS of 1ug/l</b></p>
<p><b>Short-term PNEC for salt waters</b></p>	<p>For the same reasons as outlined for the long-term data, the freshwater and saltwater datasets were combined for the derivation of a short-term PNEC for saltwaters. Based on the available short-term saltwater data, crustaceans appear to be the most sensitive taxonomic group.</p> <p>The most sensitive and reliable datum is a 96-hour LC50 of 4.2 µg l<sup>-1</sup> for larvae of the rock crab <i>Cancer irroratus</i>. This value is supported by a saltwater mollusc and fish study. Given that in the combined dataset reliable data are available for three trophic levels (algae, invertebrates including echinoderms and molluscs and fish) an assessment factor of 10 is proposed resulting in a PNEC<sub>saltwater_st</sub> of 0.42 µg l<sup>-1</sup> HCN.</p> <p>This is lower than the existing EQS of 5 µg l<sup>-1</sup> HCN, which was 'read across' from the freshwater EQS.</p> <p><b>Recommended PNEC: 0.42 µg HCN/l (AF 10)</b></p> <p><b>Change from existing EQS: Lower than existing EQS of 5ug/l</b></p>
<p><b>PNEC for secondary poisoning</b></p>	<p>The available data suggest that the likelihood of free cyanide to bioaccumulate in aquatic organisms is low. Accumulation through the food chain is also not expected due to the rapid detoxification of cyanide by most organisms. Because the bioconcentration factor data for free cyanide are below 100, there is no requirement to derive a PNEC for secondary poisoning.</p> <p><b>Recommended PNEC: None derived</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments</b></p>	<p>Based on the low tendency of free cyanide to adsorb to particulate materials and the knowledge that the toxicity of complex cyanides in sediments is due to the release of free cyanide in the water column, a PNEC for sediments is not relevant.</p> <p><b>Recommended PNEC: None derived</b></p>



**PROTECT**

	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis</b>	<p>It is customary to distinguish between total and free cyanide because of their differences in toxicity. Free cyanide is operationally defined as those cyanide forms that are readily oxidised to cyanogen chloride by treatment with chlorine. These forms include free cyanide plus any complex forms that readily dissociate.</p> <p>The lowest proposed PNEC derived for cyanide is 0.052 µg l<sup>-1</sup> HCN. From the literature, it can be seen that analytical methodologies provide detection limits of around 5–10 µg l<sup>-1</sup>, which suggests that they may not be adequate to analyse cyanide for compliance with the proposed PNECs.</p>
<b>Implementation</b>	<p>The freshwater and saltwater PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty. However, the analytical capability for assessing compliance may need attention as it may not be adequate.</p> <p>When failure is reported for the saltwater long term standard derived using an assessment factor of 100, it is recommended that supporting information, including evidence of ecological damage, should be obtained before committing to expensive action.</p> <p>Uncertainties associated with the long term saltwater standard could be reduced through availability of additional reliable long term saltwater studies.</p>

# PROTECT

Diazinon (CAS: 333-41-5)			
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Saltwater/short-term	10	0.26	0.1
<b>Recommendation</b> <p>The existing statutory saltwater short-term value for this substance was an used interim value for the first cycle of river basin planning. It is recommended that the proposed PNEC<sub>saltwater_st</sub> is applied for the second cycle of river basin management as its derivation reflects the best science.</p> <p>All other EQS values already established for this substance (i.e., freshwater and long-term saltwater values) would still apply.</p> <p>The PNEC is proposed as an EQSs as it is not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p>			
<b>Background Information:</b>			
<b>Properties and fate in water</b>	Diazinon is a contact organophosphorus insecticide with a wide range of agricultural and veterinary applications. It is hydrolytically stable with a half-life in natural waters of several days but undergoes microbial degradation. Diazinon is moderately lipophilic (log Kow 3.1–4.0) and so will tend to partition into sediment and biota. Its primary mode of action is through the inhibition of cholinesterases in the nervous system and invertebrates are particularly sensitive.		
<b>Factors affecting derivation of the PNEC</b>	The PNEC described are based on a technical assessment of available ecotoxicity data for diazinon, along with any data that relate impacts under field conditions to exposure concentrations. The data were subjected to rigorous quality assessment by both the authors and an independent peer review panel.		
<b>Short-term PNEC for salt waters:</b>	An assessment factor of 10, applied to a 96-hour LC50 to <i>Acartia tonsa</i> of 2.6 ug/l is recommended. This results in a PNEC of 0.26 ug/l and is justified on the assumption that, as a crustacean, <i>Acartia</i> represents a particularly sensitive taxon.		
	<b>Recommended PNEC: 0.26ug/l</b>		
	<b>Change from existing EQS: Higher than the current EQS of 0.1ug/l</b>		
<b>Analysis</b>	The data quality requirements are that, at one-third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that non-standard analytical methodologies employing extraction and preconcentration with gas chromatography mass spectrometry are capable of achieving detection limits as low as 0.5 ng/l (and potentially lower using a Nitrogen Phosphorus Detector), sufficient to quantify concentrations of diazinon at the EQS.		
<b>Implementation</b>	The PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.		

## PROTECT

<b>3,4-Dichloroaniline (3,4-DCA) (CAS number 95-76-1)</b>			
<b>Receiving medium and exposure</b>	<b>Assessment factor</b>	<b>Proposed PNEC (µg/l)</b>	<b>Existing EQS (µg/l)</b>
Freshwater/long-term	10	0.2	-
Freshwater/short-term	10	5.4	-
Saltwater/long-term	10	0.2	-
Saltwater/short-term	10	5.4	-
<b>Recommendation:</b>  The proposed freshwater and saltwater PNECs are proposed as EQSs as they are not subject to excessive uncertainty. The PNECs are in line with those derived by the EU in the Risk Assessment Report.			
<b>Background information:</b>			
<b>Properties and fate in water</b>	<p>Few data are available on the mode of toxic action of 3,4-DCA in aquatic organisms. However, polar narcosis is generally accepted as the primary mode of action.</p> <p>3,4-DCA is not expected to volatilise from the water column nor undergo hydrolysis. However, it is likely to be susceptible to photolysis with half-lives ranging from 0.4 hours to 6 days. On release to the aquatic environment it forms covalent bonds with the organic fraction of sediments and suspended matter, removing it from the water column.</p> <p>OECD biodegradation tests indicate that 3,4-DCA would not be regarded as readily biodegradable. Based on the available data the majority (&gt;90%) of 3,4-DCA released to the environment is expected to partition to the organic fraction of sediments and soils where, due to its slow degradation, it is likely to accumulate over time.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>An EU Risk Assessment Report (RAR) has been compiled for 3,4-DCA. As it has been proposed that RAR PNECs are used for the derivation of WFD EQSs, the RAR PNECs are recommended as the proposed long term PNECs for freshwater and saltwaters. Short term PNECs have been derived based on the available data. The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for 3,4-DCA, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V of the WFD.</p>		

# PROTECT

<b>Long-term PNEC for freshwaters</b>	<p>The lowest valid long-term freshwater data points are 42 and 48 day NOECs (for growth and survival) of <math>2 \mu\text{g l}^{-1}</math> in guppies and zebra fish. The long-term freshwater PNEC in the EU RAR for 3,4-DCA was therefore based on these data points with an assessment factor of 10 given the availability of long-term data for three or more trophic levels. A number of field and mesocosm studies are available for 3,4-DCA. The lowest endpoints from the available studies were MATCs of <math>8\text{--}10 \mu\text{g l}^{-1}</math> for zooplankton abundance and sediment invertebrate abundance in an outdoor stream experiment. In addition, an MATC of <math>10 \mu\text{g l}^{-1}</math> 3,4-DCA has been suggested to be protective of field populations of <i>Daphnia</i>. Therefore the proposed PNEC of <math>0.2 \mu\text{g l}^{-1}</math> would be regarded as protective of long-term exposures to 3,4-DCA in the field.</p>
	<b>Recommended PNEC: <math>0.2 \mu\text{g l}^{-1}</math> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Short-term PNEC for freshwaters</b>	<p>Freshwater short-term toxicity data are available for nine taxonomic groups including algae, annelids, bacteria, ciliates, crustaceans, fish, insects, molluscs and rotifers. The lowest valid short-term freshwater data point is a 48-hour EC50 of <math>54 \mu\text{g l}^{-1}</math> for the immobilisation of <i>D. magna</i>. The assessment factor of 10 is felt justified due to the availability of reliable short-term data for at least three taxonomic groups. This results in a <math>\text{PNEC}_{\text{freshwater\_st}} = 54 \mu\text{g l}^{-1} / \text{AF (10)} = 5.4 \mu\text{g l}^{-1}</math>.</p>
	<b>Recommended PNEC: <math>5.4 \mu\text{g l}^{-1}</math> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Long-term PNEC for salt waters</b>	<p>Long-term saltwater toxicity data are available for six taxonomic groups: algae, annelids, crustaceans, fish, molluscs and plankton. Although long term saltwater data was available the RAR noted that given the similarity in the sensitivity of freshwater and saltwater species of the same taxonomic group and the non-specific mode of action of 3,4-DCA as it is a non-polar narcotic it is proposed that the saltwater PNEC be based on the lower freshwater data, ie the saltwater and freshwater data are combined. The lowest reliable value in the saltwater data set is a 38-day NOEC (reproduction) of <math>3.2 \mu\text{g l}^{-1}</math> for the polychaete worm (<i>Ophryotrocha diadema</i>). Due to the similarity in sensitivity and the non-specific mode of action it was proposed that the assessment factor of 10 applied to the freshwater PNEC is also applied for the derivation of the saltwater PNEC.</p>
	<b>Recommended PNEC: <math>0.2 \mu\text{g l}^{-1}</math> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Short-term PNEC for salt waters</b>	<p>Short-term saltwater toxicity data are available for seven different taxonomic groups: algae, annelids, bacteria, crustaceans, fish, molluscs and rotifers. The lowest reliable short-term saltwater value is a 72-hour EC50 (growth) of <math>1100 \mu\text{g l}^{-1}</math> for <i>Phaeodactylum tricornutum</i>. However, in the combined freshwater and saltwater data set a lower 48-hour EC50 of <math>54 \mu\text{g l}^{-1}</math> is available for <i>D. magna</i>, based on immobilisation.</p> <p>Given the similarity in the sensitivity of freshwater and saltwater species of the same taxonomic group and the mode of action of 3,4-DCA as a polar narcotic it is proposed that the same assessment factor (10) be used for the freshwater short-term PNEC for the saltwater environment.</p>
	<b>Recommended PNEC: <math>5.4 \mu\text{g l}^{-1}</math> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>

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<p><b>PNEC for secondary poisoning</b></p>	<p>The EU RAR identifies a NOAEL of 30 mg/kg body weight per day 2,5-DCA from a rat oral toxicity study as most suitable for the derivation of the PNEC<sub>secpois.biota</sub>. The RAR proposes a conversion factor of 10 (to convert the dose to a concentration in food) and an assessment factor of 1000, giving:</p> <p><b>PNEC<sub>secpois.biota</sub> = (NOAEL 30 mg/kg bw x 10)/AF 1000 = 0.3 mg/kg in food</b></p> <p>(The 2,5-DCA NOAEL was chosen due to a lack of suitable data for 3,4-DCA. The EU RAR stated that due to the structural similarity of 2,5-DCA to 3,4-DCA it causes similar toxic effects such as haemolytic anaemia and methaemoglobinaemia. Consequently, 2,5-DCA was considered a suitable surrogate for 3,4-DCA (ECB 2006)).</p> <p>Reported BCF values range from 4 to 800. However, the RAR identifies a BAF of 570 for <i>Lumbriculus variegatus</i> as most suitable for PNEC derivation.</p> <p><b>PNEC<sub>secpois.water</sub> = 0.3 mg/kg prey/BAF (570)= 0.0005 mg l<sup>-1</sup> (0.5 µg l<sup>-1</sup>)</b></p> <p>This is the calculation made by the RAR. However, the AF (1000) used appears to be far too high and it could be that they have used the conversion factor incorrectly or duplicated it and added also to the AF. If this is correct the resulting PNEC<sub>secpois.water</sub> is overprecautionary and any reduction in the assessment factor would result in a higher value.</p> <p>This concentration is higher than the proposed long-term PNECs for the protection of pelagic communities in both inland and marine water bodies. Therefore, if quality standards are set on the basis of the freshwater and saltwater PNECs, the protection of predators from secondary poisoning will be covered.</p> <p><b>Recommended PNEC: 0.5 µg l<sup>-1</sup></b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments</b></p>	<p>The log Kow for 3,4-DCA is 2.7 and in theory does not meet the EU TGD criterion for the assessment of sediment dwelling organisms. However, on release to the aquatic environment 3,4-DCA forms covalent bonds with the organic fraction of sediments and suspended matter, removing it from the water column. Consequently, sediments are one of the primary sinks for environmental releases of 3,4-DCA and sediment PNECs are required.</p> <p>The EU RAR identifies the 28 day LOEC of 5 mg/kg dw of Oetken <i>et al.</i> (2000) for deformations of <i>L. variegatus</i> as the lowest reliable sediment data, but the effect was not statistically significant. However, this study did report 28-d NOECs of 5 mg/kg dw for effects of 3,4-DCA on the number and total biomass of worms. Consequently, the appropriate assessment factor for two long-term sediment values is 50 resulting in a PNEC<sub>freshwater sediment</sub>= 5 mg/kg/AF (50) = 0.1 mg/kg dw (0.04 mg/kg ww).</p> <p><b>Recommended PNEC: 0.1 mg/kg dw (0.04 mg/kg ww)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>Analysis</b></p>	<p>Proposed PNECs derived for 3,4-DCA range from 0.2 to 5.4 µg l<sup>-1</sup> in environmental waters and 0.1 mg/kg dw (0.04 mg/kg ww) in sediments. The data quality requirements are that, at a third of the EQS total error</p>

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	of measurement should not exceed 50 per cent. Using this criterion, current analytical methodologies should offer adequate performance to analyse for 3,4-DCA
<b>Implementation</b>	<p>The proposed PNECs are consistent with those proposed in the EU Risk Assessment Report for 3,4-DCA.</p> <p>The PNECs are considered suitable for use as EQSs as they are not subject to excessive uncertainty and current analytical capability should be adequate for compliance assessment purposes.</p> <p>Due to the potential for 3,4-DCA to adsorb to sediment and bioaccumulate consideration should be given as to the relevance of sediment and biota standards for this substance.</p>

## PROTECT

<b>2,4-Dichlorophenol (CAS number 120-83-2)</b>			
<b>Receiving medium and exposure</b>	<b>Assessment factor</b>	<b>Proposed PNEC (µg/l)</b>	<b>Existing EQS (µg/l)</b>
Freshwater/long-term	50	4.2	20
Freshwater/short-term	10	140	140
Saltwater/long-term	500	0.42	20
Saltwater/short-term	100	6.0	140
<b><u>Recommendation</u></b> The freshwater long term and short term PNECs are proposed as EQSs as they are not subject to excessive uncertainty. Current analytical methods are sensitive enough to assess compliance with the proposed PNECs in receiving waters.			
<b>Background information:</b>			
<b>Properties and fate in water</b>	<p>Dichlorophenol compounds are considered to act as polar narcotics in fish, with the toxicity exhibited being characterised by a convulsant action where the loss of reaction to external stimuli and/or loss of equilibrium are detected.</p> <p>The pKa (pH at which an acid compound is 50 per cent dissociated) of 7.89 for 2,4-dichlorophenol indicates that, at the pH range characterising most physiological and environmental conditions (typically pH 7–8), these compounds will exist predominately in the more toxicologically active undissociated form.</p> <p>2,4-Dichlorophenol is not expected to persist in the water column when the substance is released to the aquatic compartment. It is expected to volatilise from water surfaces and is rapidly degraded by exposure to ultraviolet light.</p> <p>2,4-Dichlorophenol is not expected to persist in the soil when the substance is released to the terrestrial compartment due to a low adsorption to organic matter (based on a log K<sub>oc</sub> of 2.54) and the processes of volatilisation and degradation.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for 2,4-dichlorophenol, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.</p>		

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Long-term PNEC for freshwaters	<p>The lowest valid reported long-term toxicity value for 'standard' ecotoxicological endpoints (e.g. growth, reproduction and mortality) is an 85 day NOEC of 100 µg l<sup>-1</sup> for effects on the survival of early life stage rainbow trout <i>Oncorhynchus mykiss</i>. The same study also reported an 85-day LOEC of 100 µg l<sup>-1</sup> for effects on the growth (as wet weight) of fry of the rainbow trout <i>Oncorhynchus mykiss</i> at the 4 weeks post swim-up stage. There was a 40% reduction in the wet weight of fry at this concentration and because the effect level is greater than 20% the TGD approach cannot be used to derive a NOEC value from the LOEC. A lower NOEC value of 0.1 µg l<sup>-1</sup> for effects of 2,4-dichlorophenol on the net spinning behaviour of larvae of the trichoptera <i>Hydropysche slossonae</i> was reported, but there were concerns about the validity of these data. Since reliable long-term NOECs are available for algae, invertebrates (including crustaceans and insects) and fish, an assessment factor of 10 could be applied to the lowest valid toxicity value resulting in a PNEC<sub>freshwater_lt</sub> of 10 µg l<sup>-1</sup>. However, in order to be protective of the effects of 2,4-dichlorophenol observed on the growth of rainbow trout <i>Oncorhynchus mykiss</i> at 100 µg l<sup>-1</sup>, it is proposed that the chronic algal and invertebrate dataset is used to derive the PNEC. The lowest reliable value for this dataset is a 21-day NOEC of 210 µg l<sup>-1</sup> for reproductive effects in the water flea <i>Daphnia magna</i>. By applying an assessment factor of 50 (for NOECs from two taxonomic groups) the resulting value would be 4.2 µg l<sup>-1</sup> 2,4-dichlorophenol.</p>
	Recommended PNEC: 4.2 µg/l (AF 50)
	Change from existing EQS: Lower than existing statutory EQS of 20ug/l
Short-term PNEC for freshwaters	<p>Reliable short-term data are available for algal, invertebrate and fish species. The lowest valid short-term data is considered to be a 48-hour EC50 of 1,400 µg l<sup>-1</sup> for effects on the mobility of the cladoceran copepod <i>Daphnia magna</i>. Since there is an acceptable short-term toxicity database for freshwater organisms, an assessment factor of 10 has been applied resulting in a PNEC<sub>freshwater_st</sub> of 140 µg l<sup>-1</sup>.</p>
	Recommended PNEC: 140 µg/l (AF 10)
	Change from existing EQS: Same as existing statutory EQS of 140ug/l



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<p><b>Long-term PNEC for salt waters</b></p>	<p>No long-term single species toxicity data for marine organisms are available. The absence of long-term data means that it is not possible to generate a PNEC<sub>saltwater_lt</sub> based on the saltwater data alone. It is proposed that the combined freshwater and saltwater dataset is used for the PNEC generation.</p> <p>The lowest valid reported long-term toxicity value for 'standard' ecotoxicological endpoints (e.g. growth, reproduction and mortality) is a 85-day NOEC of 100 µg l<sup>-1</sup> for effects on the survival of early life stages of rainbow trout <i>Oncorhynchus mykiss</i>. Reliable long-term NOECs are available for freshwater algae, invertebrates and fish but no toxicity data are available for marine taxa such as echinoderms and molluscs.</p> <p>Given that there is limited data for these marine taxa, a total assessment factor of 100 (including a factor of 10 to account for the greater uncertainty due to the limited data for marine taxa) could be applied to the lowest valid toxicity value resulting in a PNEC<sub>saltwater_lt</sub> of 1.0 µg l<sup>-1</sup>.</p> <p>However, in order to be protective of the effects of 2,4-dichlorophenol observed on the growth of rainbow trout <i>Oncorhynchus mykiss</i> at 100 µg l<sup>-1</sup>, it is proposed that the chronic algal and invertebrate dataset is used to derive the PNEC. The lowest reliable value for this dataset is a 21-day NOEC of 210 µg l<sup>-1</sup> for reproductive effects in the water flea <i>Daphnia magna</i>. By applying a total assessment factor of 500 (for NOECs from two taxonomic groups and accounting for the greater uncertainty due to the limited data for marine taxa) the resulting value would be 0.42 µg l<sup>-1</sup> 2,4-dichlorophenol.</p> <p><b>Recommended PNEC: 0.42 µg/l (AF 500)</b></p> <p><b>Change from existing EQS: Much lower than existing statutory EQS of 20ug/l</b></p>
<p><b>Short-term PNEC for salt waters</b></p>	<p>The lowest valid short-term toxicity value is a 72-hour EC50 value of 600 µg l<sup>-1</sup> for effects on the growth of the diatom <i>Phaeodactylum tricornutum</i>. Reliable short-term L(E)C50s are available for freshwater algae, invertebrates and fish but no toxicity data are available for marine taxa such as echinoderms and molluscs. Given that there is limited data for these marine taxa, a total assessment factor of 100 (including a factor of 10 to account for the greater uncertainty due to the limited data for marine taxa) should be applied to the lowest valid toxicity value resulting in a PNEC<sub>saltwater_lt</sub> of 6.0 µg l<sup>-1</sup>.</p> <p>This value is lower than the existing EQS of 140 µg l<sup>-1</sup>, which was 'read across' from the freshwater short-term value.</p> <p><b>Recommended PNEC: 6 µg/l (AF 100)</b></p> <p><b>Change from existing EQS: Much lower than existing statutory EQS of 140ug/l</b></p>

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<b>PNEC for secondary poisoning</b>	Bioconcentration factor (BCF) values – for 2,4-dichlorophenol for aquatic organisms are generally low with values for fish ranging from 3.8 to 100 at neutral pH. Higher BCFs of 282–980 have been reported for one taxonomic group, leeches, although this has been attributed to a deficiency in these organisms of the enzyme necessary for the metabolism of chlorophenols. Hence, the trigger EU Technical Guidance Document BCF of 100 is not exceeded and the derivation of a PNEC in whole fish for secondary poisoning of predators is not required.
	<b>Recommended PNEC:</b> BCF < 100, so PNEC not required
	<b>Change from existing EQS:</b> No existing standard
<b>PNEC for sediments</b>	Since the log K <sub>ow</sub> of 2,4-dichlorophenol is >3, the derivation of PNECs for the protection of benthic organisms is required. An extensive literature search for data on the toxicity of 2,4-dichlorophenol to sediment-dwelling organisms did not identify any relevant studies. As a result it is not possible to derive a PNEC <sub>sediment</sub> based on experimental toxicity data.
	<b>Recommended PNEC:</b> Insufficient data
	<b>Change from existing EQS:</b> No existing standard
<b>Analysis</b>	The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing gas chromatography/mass spectrometry (GC-MS), which are capable of achieving detection limits as low as 2–5 ng l <sup>-1</sup> , should offer adequate performance to analyse for 2,4-dichlorophenol.
<b>Implementation</b>	Current analytical methods are sensitive enough to assess compliance with the proposed PNECs in receiving waters.
	When failure is reported for saltwater standards derived using an assessment factor of 100, it is recommended that supporting information, including evidence of ecological damage, should be obtained before committing to expensive action.

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<b>Glyphosate (CAS number 1071-83-6) (also including glyphosate isopropylamine, CAS number 38641-94-0)</b>		
<b>Receiving medium and exposure</b>	<b>Proposed PNEC (ug/l)</b>	<b>Existing EQS (µg l<sup>-1</sup>)</b>
Freshwater/long-term	196	-
Freshwater/short-term	398	-
Saltwater/long-term	196	-
Saltwater/short-term	398	-
<b>Recommendation:</b> Both the saltwater and freshwater long and short term PNECs are proposed as EQSs. The PNECs are considered suitable for use as they are not subject to excessive uncertainty.		
<b>Background Information:</b>		
<b>Properties and fate in water:</b>	<p>Glyphosate-based herbicides have a broad spectrum of activity towards plants. In contrast, activity towards animals is believed to be weak because the mode of action for glyphosate is a biochemical pathway found only in plants and some micro-organisms. Glyphosate inhibits plant growth by inhibiting the production of essential aromatic amino acids through competitive inhibition of synthesis of the enzyme enolpyruvylshikimate phosphate (EPSP). This is a key enzyme in the shikimic acid pathway for the synthesis of chorismate, which is the precursor for the essential amino acids phenylalanine, tyrosine and tryptophan.</p> <p>Glyphosate is a weak organic acid and is usually formulated as a salt of the deprotonated acid of glyphosate and a cation, e.g., isopropylamine. Glyphosate is sold in many different formulations for uses ranging from agriculture and forestry, to ready-to-use products for the home and garden. To work effectively glyphosate must be mixed with a surfactant that facilitates its uptake by the plant.</p> <p>Although readily soluble in water glyphosate is readily ionized and the anion will be strongly adsorbed to sediments and soils of pH &gt; 3.5. Glyphosate degrades to natural products such as CO<sub>2</sub> and phosphate ions with degradation in terrestrial and aquatic systems occurring predominantly via microbial processes.</p> <p>Bioconcentration of glyphosate in aquatic organisms is low. Glyphosate is not suspected of being an endocrine-disrupting chemical.</p>	
<b>Factors affecting derivation of the PNEC:</b>	<p>Freshwater short and long-term laboratory data are available for eight different freshwater taxonomic groups. The toxicity of glyphosate occurs over a wide concentration range. The available short-term and long-term toxicity test data indicate that for glyphosate and its salt aquatic plants are the most sensitive taxa of those tested.</p>	

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	<p>For marine organisms, single species short-term toxicity data are available for six different taxonomic groups. However, no long-term toxicity data are available for the minimum of three saltwater taxa (algae, crustaceans and fish) required under Annex V of the WFD. Laboratory data are supplemented by freshwater and saltwater mesocosm and field data which indicate that glyphosate may not be as toxic in natural settings as in laboratory tests, due to rapid dissipation. The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for glyphosate, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.</p>
<b>Long-term PNEC for freshwaters:</b>	<p>There are sufficient freshwater ecotoxicity data to allow a PNEC to be derived by the probabilistic method from the HC5 of an SSD. Since there are no obvious differences in the sensitivity of freshwater or saltwater species of the same taxonomic group, the draft WFD Technical Guidance approach of using a combined freshwater and saltwater dataset for the freshwater and marine effects assessment has been used. An HC5 of 586.8 µg l<sup>-1</sup> was derived using a log-normal species sensitivity distribution. An assessment factor of 3 applied to the HC5 results in:</p> <p><math>PNEC_{freshwater\_lt} = 586.8 \mu g l^{-1} / AF (3) = 196 \mu g l^{-1}</math> glyphosate (rounded)</p> <p><b>PNEC<sub>freshwater\_lt</sub> by SSD =196 µg l<sup>-1</sup> glyphosate (rounded) (AF 3)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<b>Short-term PNEC for freshwaters:</b>	<p>There are sufficient freshwater ecotoxicity data to allow a PNEC to be derived by the probabilistic method from the HC5 of an SSD.</p> <p>The freshwater and saltwater datasets have been combined since there is no apparent difference in sensitivity between freshwater and marine taxa. Based on the 30 fresh- and saltwater species L(E)C50s (using geometric means where applicable) the median (i.e. 50 per cent confidence) 5th percentile cut-off value of 1988.3 µg l<sup>-1</sup> glyphosate is calculated.</p> <p>According to the draft WFD Technical Guidance the AF should normally be 10. This PNEC is essentially the same as the long-term combined freshwater and saltwater PNEC of 196 µg l<sup>-1</sup>. Examination of the dataset indicates that the acute to chronic ratio is at least 2.5 suggesting that an AF of 10 is too stringent and that a lower assessment factor is more appropriate, and therefore, an assessment factor of 5 is recommended. This results in:</p> <p><math>PNEC_{freshwater\_st} = 1988.3 \mu g l^{-1} / AF (5) = 398 \mu g l^{-1}</math> glyphosate (rounded)</p> <p><b>Recommended PNEC: PNEC<sub>freshwater\_lt</sub> by SSD =398 µg l<sup>-1</sup> glyphosate (rounded) (AF 5)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>

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<p><b>Long-term PNEC for salt waters:</b></p>	<p>Since long-term single species toxicity data are only available for algae and eelgrass, a combined freshwater and saltwater dataset for the marine effects assessment was used to derive the PNEC. The saltwater toxicity data do not differ markedly from the range of values obtained for corresponding freshwater species. If a combined dataset is used, the draft WFD Technical Guidance recommends that the AF of 1-5 applied to the HC5 estimated from the SSD should only be applied for coastal and territorial waters if the data set used to establish the SSD comprises long-term NOECs or EC10s for at least two additional typically marine taxonomic groups, other than fish, crustaceans and algae. If such data is unavailable then an additional AF of 10 should be applied to deal with residual uncertainty. However, it can be argued that the additional AF of 10 is not required for glyphosate since aquatic plants are the most sensitive taxa and data for echinoderms and molluscs are not expected to show lower toxicity values. This results in:</p> <p><b>PNEC<sub>saltwater_it</sub> = 586.8 µg l<sup>-1</sup>/AF (3) = 196 µg l<sup>-1</sup> glyphosate (rounded)</b></p> <p><b>Recommended PNEC: PNEC<sub>saltwater_it</sub> = 586.8 µg l<sup>-1</sup>/AF (3) = 196 µg l<sup>-1</sup> glyphosate (rounded)</b></p> <p><b>Change from existing EQS: No existing saltwater EQS</b></p>
<p><b>Short-term PNEC for salt waters:</b></p>	<p>Reliable short-term saltwater toxicity data are available for algae, invertebrates and fish and there is no evidence to suggest that other saltwater species (particularly those that are exclusively saltwater in distribution) would be more sensitive. Therefore, the freshwater and saltwater datasets have been combined. No additional AF is required for the saltwater short-term EQS as there are data for two additional marine taxonomic groups (molluscs and echinoderms). This results in:</p> <p><b>PNEC<sub>saltwater_st</sub> = 1988.3 µg l<sup>-1</sup>/AF (5) = 398 µg l<sup>-1</sup> glyphosate (rounded)</b></p> <p><b>Recommended PNEC: PNEC<sub>saltwater_st</sub> = 1988.3 µg l<sup>-1</sup>/AF (5) = 398 µg l<sup>-1</sup> glyphosate (rounded)</b></p> <p><b>Change from existing EQS: No existing saltwater EQS</b></p>
<p><b>PNEC for secondary poisoning:</b></p>	<p>The EU Technical Guidance Document (TGD) bioconcentration factor (BCF) trigger of 100 in whole fish is not exceeded by glyphosate so there is no need to derive PNECs for secondary poisoning.</p> <p><b>Recommended PNEC: No recommended PNEC</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments:</b></p>	<p>The TGD trigger value of a log K<sub>oc</sub> or log K<sub>ow</sub> of ≥3 is met, as the reported log K<sub>oc</sub> for glyphosate is 2.9 – 4.8 (EC 2002). No long-term sediment studies were available. Short-term data are available for studies carried out using various glyphosate formulations. These results suggest a wide range in toxicity, which may be explained by differences in organic carbon and the partitioning behaviour of glyphosate in sediment. Because of the uncertainties, short exposure periods, use of different glyphosate formulations and the wide range in toxicity values in the empirical data no PNEC<sub>sediment</sub> can be recommended.</p> <p><b>Recommended PNEC: No recommended PNEC</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>

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<b>Analysis:</b>	The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50%. Using this criterion, it is evident that current analytical methodologies (non-standard) employing coupling ion chromatography (IC) separation with inductively coupled plasma mass spectrometry (ICP-MS) detection), capable of achieving detection limits as low as 700 ng l <sup>-1</sup> , or large-volume injection in a coupled-column LC system using fluorescence detection (LC-LC-FD), capable of achieving detection limits as low as 20 ng l <sup>-1</sup> , should offer adequate performance to analyse for glyphosate.
<b>Implementation</b>	Both the saltwater and freshwater long and short term PNECs are proposed as EQSs. The PNECs are considered suitable for use as they are not subject to excessive uncertainty.

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Iron (total) (CAS number 7439-89-6)		
Receiving medium/ exposure scenario	Proposed PNEC (mg l <sup>-1</sup> ) total iron	Existing EQS (mg l <sup>-1</sup> ) dissolved iron
Freshwater/long-term	0.73	1.0
Saltwater/long-term	Existing EQS retained	1.0
<b>Recommendation:</b> The proposed freshwater PNEC is 0.73 mg l <sup>-1</sup> total iron and is proposed as an EQS. Current analytical methods are adequate to analyse iron for compliance with the proposed PNEC.		
Background Information:		
<b>Properties and fate in water:</b>	<p>Iron is a naturally occurring element that also enters the environment from industrial sources. It is an essential micronutrient and plays an important role in many life processes. In ionic form, its most common oxidation states are +2 and +3, and both Fe(II) and Fe(III) ions bond with anions or form coordination compounds.</p> <p>Iron has a potentially complex chemistry in freshwaters due to the oxidation of Fe(II) to Fe(III), and the precipitation of Fe(III) to form colloidal or fine particulate material. In addition iron may interact with dissolved organic carbon (DOC), either by direct binding of free Fe ions or through associations between DOC and precipitated forms of iron.</p> <p>Iron can also be bound to organic matter, in a manner similar to that of many other trace metals. It is often necessary for the concentrations of iron species in solution to be estimated by assuming that they are at equilibrium with a solid phase, such as ferrihydrite. The two iron ions differ in their binding affinities to humic and fulvic acids.</p> <p>These differences may be attributed principally to their charge, with Fe (III) showing much stronger binding than Fe (II), due to electrostatic effects. As a result of this, virtually all dissolved phase Fe (III) would be expected to be bound to organic matter throughout the range of pH which is relevant to natural waters. Fe (II), on the other hand, would be expected to show steadily increasing DOC binding with increasing pH, up to a maximum at around pH 7.8. Fe(III) is extensively hydrolysed in slightly acidic to neutral freshwaters, which can result in the formation of precipitates due to the low solubility of Fe(OH)<sub>3</sub>.</p> <p>While the forms of iron responsible for toxicity are difficult to determine, dissolved Fe(II) appears to be more toxic than Fe(III), although data suggest that precipitates of the latter can also contribute to toxicity through 'smothering' effects. Dissolved concentrations of metals are typically considered to be most relevant to any evidence of ecological effects. However, this may not be the case for iron, as indicated by the reviews of traditional ecotoxicity test data discussed in the EQS proposal. If the mode of action of iron is not usually exerted via chemical toxicity then other expressions of iron</p>	

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	concentration may be required. Total or particulate iron concentrations may be more relevant to ecological effects if the mode of action of iron is usually via physical effects such as smothering.
<b>Factors affecting derivation of the PNEC:</b>	<p>Many historic ecotoxicity tests are considered to have effectively tested the “toxicity” of a suspension of precipitated material, and often have limited detail on the actual exposure conditions. This means that interpretation of the results of most of the available test data is uncertain: the question of whether they show direct toxic effects or adverse effects due to precipitated material remains.</p> <p>As a result of these uncertainties this project has focused on the use of field data with matched monitoring for both ecology and chemistry. These datasets have been used to derive thresholds for iron concentrations which are consistent with the ability of benthic macroinvertebrate communities to achieve particular predefined Ecological Status objectives under the WFD.</p> <p>Two water quality standards have been set in the UK on the basis of field evidence- dissolved oxygen and ammonia- so there is a precedent.</p>



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<b>Long-term PNEC for freshwaters:</b>	<p>Analyses of data for fish, macrophyte, and diatom communities did not show any statistically significant decline in the maximum achievable ecological quality with increasing total iron exposures. Assessments based on benthic macroinvertebrate communities did show a statistically significant decline in response to increasing total iron exposures. Thresholds have been derived on both a whole macroinvertebrate community basis, for direct comparison with ecological quality standards, and also for the most sensitive fraction of the community. Thresholds have been derived for the boundary between Good and Moderate ecological status (GMB) as defined under the WFD.</p> <p>Thresholds which are not normalised for water quality conditions, for the protection of sensitive macroinvertebrate taxa and for the protection of benthic macroinvertebrate communities have been derived. The proposed thresholds are 0.73 mg l<sup>-1</sup> total iron for the protection of sensitive taxa, and 1.84 mg l<sup>-1</sup> total iron for the protection of the whole community (using community metrics agreed for use in classification under the WFD). As these thresholds are not normalised for possible differences in iron toxicity under different water quality conditions they may not necessarily be protective of iron exposures under sensitive conditions.</p> <p>Thresholds which relate directly to defined measures of ecological status under the WFD can therefore be proposed which are expected to be protective of sensitive conditions and can also be adjusted through the use of an empirical relationship between DOC concentrations, water hardness and iron toxicity to invertebrates where conditions are less sensitive. Thresholds which are normalised in this way have been derived only for the whole community and the value relating to the GMB for ecological status is 0.78 mg l<sup>-1</sup> total iron under sensitive conditions of low DOC and low hardness. This threshold is considered to be applicable to waters with a pH of greater than 7, but there is considerable uncertainty surrounding its relevance to waters of lower pH.</p> <p>The GMB thresholds derived for both the most sensitive taxa (0.73 mg l<sup>-1</sup>) and for the whole community under sensitive conditions (0.78 mg l<sup>-1</sup>) are both slightly higher than the NOEC values from the most sensitive ecotoxicity tests, but are below the LOEC values from these tests. They are therefore considered to be broadly consistent with the existing laboratory ecotoxicity data.</p> <p><b>The GMB EQS proposal is therefore: 0.73 mg l<sup>-1</sup> total iron (for the protection of sensitive taxa)</b></p> <p>Taking account of the effect of water chemistry on the sensitivity of invertebrates to iron suggests that the ability of communities to achieve good ecological status will not be compromised, even under the most sensitive water chemistry conditions. This is considered as supporting information for the proposed EQS value.</p>
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	<b>Recommended GMB EQS: 0.73 mg l<sup>-1</sup> total iron (for the protection of sensitive taxa)</b>
	<b>Change from existing EQS: Lower than existing statutory EQS</b>
<b>Long-term PNEC for salt waters:</b>	Further standards for iron in saltwater have not been considered, so it is proposed that the current value of 1 mg/l dissolved iron be retained.
	<b>Recommended PNEC<sub>saltwater_it</sub>: Existing statutory EQS of 1 mg l<sup>-1</sup> retained.</b>
<b>PNEC for secondary poisoning:</b>	In the report produced for the previous Specific Pollutant report it was noted that iron is an essential element that has been shown not to bioaccumulate in higher organisms. This is due to the organism's body regulating its requirements for iron and not storing excessive amounts. Therefore, PNECs for secondary poisoning of predators are not proposed.
	<b>Recommended PNEC<sub>Sec pois</sub>: No recommended PNEC</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for sediments:</b>	In the report produced for the previous Specific Pollutant report it noted that no sediment toxicity data were located specifically for iron. A PNEC <sub>sediment</sub> was not derived.
	<b>Recommended PNEC<sub>Sed</sub>: No recommended PNEC</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis:</b>	<p>The lowest proposed PNEC derived for iron is 0.73mg l<sup>-1</sup>. The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent.</p> <p>However, the limit of detection using ICP-OES is 0.01mg l<sup>-1</sup> for total iron, which suggests that current analytical methods should be adequate to analyse iron for compliance with the proposed PNEC.</p>
<b>Implementation:</b>	<p>Current analytical methods are adequate to analyse iron for compliance with the proposed PNEC.</p> <p>The EQS proposal is 0.73 mg l<sup>-1</sup> total iron, and is derived from analyses of the abundance of the most sensitive taxa. This approach is considered to be the most consistent with the current approach towards EQS derivation where protection of the most sensitive species is assumed to ensure the protection of ecosystem structure and function. Taking account of the effect of water chemistry on the sensitivity of invertebrates to iron suggests that the ability of communities to achieve good ecological status will not be compromised, even under the most sensitive water chemistry conditions. This is considered as supporting information for the proposed EQS value.</p>

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<b>Manganese (CAS number 7439-96-5) (including its species and salts)</b>		
<b>Receiving medium and exposure</b>	<b>Proposed PNEC (<math>\mu\text{g l}^{-1}</math> total dissolved manganese)</b>	<b>Existing EQS (<math>\mu\text{g l}^{-1}</math>)</b>
Freshwater/long-term	123 (SSD approach)	30
Saltwater/long-term	0.05 (AF 100)	na
<p><b>Recommendation:</b></p> <p>The freshwater PNEC is proposed as an EQS. The proposed freshwater long term PNEC is not subject to excessive uncertainty and analytical techniques are sufficient to assess compliance. It is derived based on conditions of high bioavailability and therefore bioavailability needs to be taken into account when assessing compliance.</p> <p>The saltwater PNEC is an order of magnitude lower than typical seawater concentrations, and is based on a very limited dataset so is not being proposed as an EQS.</p> <p>A short term standard has not been proposed for manganese as due to the fact it is persistent in the environment and arises from a number of sources the long term impacts are considered to be of priority.</p>		
<b>Background Information:</b>		
<b>Properties and fate in water:</b>	<p>Manganese is a naturally occurring and abundant Group VII element. It occurs in the environment as a result of weathering of geological material, but also from point sources arising from its use in steel manufacture and associated with coal mining. The most commonly occurring of 11 possible oxidation states are +2 (e.g. manganese chloride or sulphate), +4 (e.g. manganese dioxide) and +7 (e.g. potassium permanganate), although the latter is unstable in the environment. Most manganese salts, with the exception of phosphates and carbonates, are soluble in water. Manganese oxides are poorly soluble in water.</p> <p>In anoxic waters, <math>\text{Mn}^{2+}</math> is generated by reduction of insoluble <math>\text{Mn}^{4+}</math> species and mobilised from sediments from which it diffuses into the water column. Its solubility is controlled by the precipitation of insoluble species. In most oxygenated waters, the thermodynamically stable form of manganese is insoluble manganese oxide. Under reducing conditions it may be present as the free <math>\text{Mn}^{2+}</math> ion, as soluble inorganic complexes or, more likely, as insoluble carbonates and oxides. Organic complexation can also occur.</p>	
<b>Factors affecting derivation of the PNEC:</b>	<p>The +7 oxidation state is unstable in water, due to being a strong oxidising agent, so is only environmentally relevant near to permanganate discharge points. An EQS needs to address the presence of the +2 and +4 forms. Water quality conditions such as pH and hardness influence toxicity although the effect varies for different organisms. Bioavailability correction models for manganese have recently been developed by the International Manganese Institute for three species covering three trophic levels. These bioavailability</p>	

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	correction models will be used for correcting manganese exposure concentrations for comparison against a single generic EQS for manganese, which relates to conditions of high bioavailability.
<b>Long-term PNEC for freshwaters:</b>	<p>As long-term NOEC data are available for a variety of fish, invertebrates, and primary producers (algae and higher plants), an SSD approach is considered to be appropriate. An HC5 of <math>246 \mu\text{g l}^{-1}</math> (dissolved Mn), with a confidence interval of 62 to <math>572 \mu\text{g l}^{-1}</math>, was calculated from an SSD that meets all goodness-of-fit criteria. An analysis of field evidence, in terms of <math>\text{Mn}^{2+}</math> exposure, suggests that an assessment factor of at least 2 would be expected to ensure protection of potentially sensitive taxa, and that no changes would be observed in whole community metrics at this level of protection. Based on comparison with assessment factors applied to HC5 values in European risk assessments for metals with similar data profiles, an assessment factor of 2 is considered to be appropriate for the derivation of the PNEC from the HC5.</p> <p>The existing EQS for dissolved manganese is <math>30 \mu\text{g l}^{-1}</math>. This was derived by applying an assessment factor of 10 to the lowest reliable chronic datum available at that time, a survival LOEC of <math>320 \mu\text{g l}^{-1}</math> for brown trout fry.</p> <p><b>PNEC<sub>freshwater</sub> by SSD = <math>123 \mu\text{g l}^{-1}</math> manganese (bioavailable) (AF 2)</b></p> <p><b>Change from existing EQS: Proposed PNEC is higher than the existing non-statutory standard of <math>30 \mu\text{g/l}</math></b></p>
<b>Long-term PNEC for salt waters:</b>	<p>The effects database for marine species is considerably smaller than that for freshwater organisms. Invertebrates are sensitive to Mn in both mediums but would appear to be more sensitive in saltwaters. There are also differences in the chemistry of manganese in increasingly saline systems, and as a result of this the use of a combined dataset is not recommended.</p> <p>The most sensitive and reliable long-term toxicity values relate manganese exposure over 7–20 days to growth of Pacific oyster, <i>Crassostrea gigas</i>, and hatching of yellow crab, <i>Cancer anthonyi</i>, both resulting in a lowest observed effect concentration (LOEC) of <math>10 \mu\text{g l}^{-1}</math>. This is supported by an experiment to assess effects on settlement of oyster spat, where a NOEC of <math>20 \mu\text{g l}^{-1}</math> was estimated. An assessment factor of 2 is recommended to extrapolate to a NOEC from the LOECs of <math>10 \mu\text{g l}^{-1}</math> and another factor of 100 is recommended to account for interspecies differences in sensitivity because there are no long-term NOECs for saltwater fish or algae. Although chronic data are not plentiful, indications of a steep dose response in these studies suggest a factor no greater than 100 is required. This results in a PNEC<sub>saltwater</sub> of <math>0.05 \mu\text{g l}^{-1}</math> manganese (dissolved).</p> <p><b>Recommended PNEC<sub>saltwater</sub> = <math>0.05 \mu\text{g l}^{-1}</math> manganese (dissolved) (AF 100)</b></p> <p><b>Change from existing EQS: No existing saltwater EQS</b></p>
<b>PNEC for secondary poisoning:</b>	Manganese can be significantly bioaccumulated by aquatic biota, especially by lower trophic levels. Given the essentiality of manganese, and the fact that it is accumulated to a greater extent by primary producers than by consumers, a PNEC for secondary poisoning is not considered to be relevant.

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	<b>Recommended PNEC: Not proposed</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for sediments:</b>	Although manganese is found in sediments, there is only one study describing its toxicity to sediment-dwelling organisms. The study was not deemed suitable for PNEC derivation. It is therefore not possible to derive a PNEC <sub>sediment</sub> .
	<b>Recommended PNEC: Not proposed</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis:</b>	The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. Analytical methodologies currently employed by UK environmental regulators are capable of achieving detection limits of below 1 µg l <sup>-1</sup> . Consequently, the current analytical methods should offer adequate performance to analyse dissolved manganese for compliance purposes in freshwater.
<b>Implementation</b>	<p>The proposed freshwater long term PNEC is not subject to excessive uncertainty and analytical techniques are sufficient to assess compliance. It is derived based on conditions of high bioavailability and therefore bioavailability needs to be taken into account when assessing compliance.</p> <p>The saltwater PNEC is an order of magnitude lower than typical seawater concentrations, so is not being proposed as an EQS. Due to the limited dataset available in relation to long term effects of manganese on saltwater species.</p>

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Methiocarb (CAS number 2032-65-7)			
Receiving medium and exposure	Assessment factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	10	0.01	0.01
Freshwater/short-term	10	0.77	0.16
Saltwater/long-term	100	0.001	0.01
Saltwater/short-term	100	0.077	0.16
<b>Recommendation:</b> <p>The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use. The values may be used as guideline values for operational purposes.</p>			
<b>Background information:</b>			
<b>Properties and fate in water</b>	Methiocarb is a carbamate compound with insecticidal, acaricidal and molluscicidal activity. Methiocarb is moderately soluble and is expected to undergo some adsorption to sediment and suspended solids but it is not expected to accumulate in sediments. Volatilisation is not expected to occur, based on a Henry's Law constant of $1.2 \times 10^{-4}$ Pa.m <sup>3</sup> .mole <sup>-1</sup> at 20°C. The hydrolysis of methiocarb is pH dependent with first-order DT50s of 321, 24 and 0.21 days having been calculated at pH 5, 7 and 9, respectively. In aerobic natural water, 80% breakdown of methiocarb has been reported after 3 days. Given reported bioconcentration factor (BCF) values of 11-90, methiocarb is unlikely to accumulate in fish.		
<b>Factors affecting derivation of the PNEC</b>	The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for methiocarb. Data reviewed for the purposes of the risk assessments undertaken in relation to the Plant Protection Products Directive was included for consideration. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.		
<b>Long-term PNEC for freshwaters</b>	The lowest valid long-term toxicity value for freshwater invertebrates is a 21-day No Observed Effect Concentration (NOEC) of 0.1 µg active ingredient (a.i.) l <sup>-1</sup> for effects on the reproduction of the waterflea <i>Daphnia magna</i> . Reliable long-term NOECs are available for algae, invertebrates and fish. Therefore, based on the EU Technical Guidance Document (TGD) methodology, an assessment factor of 10 could be applied to the lowest valid toxicity value. This results in a PNEC <sub>freshwater_lt</sub> of 0.01 µg l <sup>-1</sup> .		
	<b>Recommended PNEC: 0.01 µg l<sup>-1</sup> (AF 10)</b>		
	<b>Change from existing EQS: Same as existing non-statutory EQS</b>		

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<b>Short-term PNEC for freshwaters</b>	Reliable short-term data are available for algal, invertebrate and fish species. The lowest valid acute toxicity value for freshwater invertebrates is a 48-hour EC50 of 7.7 µg a.i. l <sup>-1</sup> for the effects of technical grade methiocarb on the immobilisation of the waterflea <i>Daphnia magna</i> . Lower short-term values have been reported in non-GLP studies, but these are considered to be unreliable due to the use of field collected organisms. Based on the EU Technical Guidance Document (TGD) methodology and a large body of acute data for methiocarb, an assessment factor of 10 could be applied to the lowest valid toxicity value. This results in a PNEC <sub>freshwater_lt</sub> of 0.77 µg l <sup>-1</sup> .
	<b>Recommended PNEC: 0.77 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: Higher than existing non-statutory EQS of 0.16ug/l</b>
<b>Long-term PNEC for salt waters</b>	No long-term single species toxicity data for marine organisms are available. The absence of long-term data means that it is not possible to generate a PNEC <sub>saltwater_lt</sub> based on the saltwater data alone, and it is proposed that the combined freshwater and saltwater dataset is used for the PNEC generation. Reliable chronic NOECs are available for algae, invertebrates and fish. The lowest long-term toxicity value in the combined dataset is a 21-day NOEC of 0.1 µg active ingredient (a.i.) l <sup>-1</sup> for effects on the reproduction of the waterflea <i>Daphnia magna</i> . This is consistent with the greater sensitivity expected in insects and crustaceans given the mode of action of methiocarb. However, since no long-term data is available for marine species such as echinoderms it is proposed that an assessment factor of 100 is applied. This results in a PNEC <sub>saltwater_lt</sub> of 0.001 µg l <sup>-1</sup> .
	<b>Recommended PNEC: 0.001 µg l<sup>-1</sup> (AF 100)</b>
	<b>Change from existing EQS: Lower than existing non-statutory EQS of 0.01ug/l</b>
<b>Short-term PNEC for salt waters</b>	Single species short-term toxicity data for marine organisms are available for three different taxonomic groups, i.e. crustaceans, fish and molluscs. Therefore, it is proposed that the PNEC <sub>saltwater_st</sub> is based on the combined freshwater and saltwater dataset.
	The lowest valid short-term toxicity value for freshwater invertebrates is a 48-hour EC50 of 7.7 µg a.i. l <sup>-1</sup> for the effects of technical grade methiocarb on the immobilisation of the waterflea <i>Daphnia magna</i> . This is consistent with the greater sensitivity expected in insects and crustaceans given the mode of action of methiocarb. However, since no short-term data is available for marine species such as echinoderms it is proposed that an assessment factor of 100 is applied. This results in a PNEC <sub>saltwater_st</sub> of 0.077 µg a.i. l <sup>-1</sup> .
	<b>Recommended PNEC: 0.077 µg l<sup>-1</sup> (AF 100)</b>
<b>PNEC for secondary poisoning</b>	<b>Change from existing EQS: Slightly lower than existing non-statutory EQS of 0.16ug/l</b>
	Bioconcentration data (as BCF values) for methiocarb are low, with values for fish ranging from 11 to 90. Hence, the TGD BCF trigger of 100 is not exceeded and the derivation of a PNEC in whole fish for secondary poisoning of predators is not required.
	<b>Recommended PNEC: Not Required</b>
	<b>Change from existing EQS: No existing EQS</b>

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PNEC for sediments	Since the log Kow of methiocarb is 3.08, the derivation of PNECs for the protection of benthic organisms is required according to the TGD. However, although a sediment toxicity study is available, it is not considered appropriate for the derivation of a PNEC <sub>sediment</sub> .
	<b>Recommended PNEC: Insufficient data</b>
	<b>Change from existing EQS: No existing EQS</b>
Analysis	For water, proposed PNECs derived for methiocarb range from 0.001 to 0.77 µg l <sup>-1</sup> . The data quality requirements are that, at one third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, current analytical methodologies employing direct aqueous injection liquid chromatography/mass spectrometry (LC-MS) are capable of achieving detection limits as low as 0.005 µg l <sup>-1</sup> and do not offer adequate performance to analyse for methiocarb against all the proposed PNECs. With development however the situation should be remedied.
Implementation	<p>The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use, but the values may be used as guideline values for operational purposes. The analytical capability for saltwater environments however will need to be considered.</p>



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Pendimethalin (CAS number 40487-42-1)			
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	–	0.1	1.5
Freshwater/short-term	10	0.58	6.0
Saltwater/long-term	10	0.27	1.5
Saltwater/short-term	10	0.52	6.0
<p><b>Recommendation:</b>  The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>The proposed long-term freshwater value is driven by the biota standard converted for use in the water column as this value is below the long term standard derived based on aquatic life.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance only has agricultural use, but the values may be used as guideline values for operational purposes.</p>			
Background Information:			
<b>Properties and fate in water</b>	<p>Pendimethalin is in the dinitroaniline family of chemicals and is a selective herbicide used for the control of broadleaf and grassy weeds. Pendimethalin acts as a microtubule disruptor on pre-emergent plants. It works by inhibiting the steps in plant cell division responsible for chromosome separation and cell wall formation. Pendimethalin is used in various formulations in terrestrial systems.</p> <p>Pendimethalin has low water solubility, high hydrophobicity (log Kow = 5.2) and is stable under acidic and alkaline conditions. The limited amount of data available suggests that pendimethalin dissipates rapidly out of the water column. Pendimethalin residues are tightly bound to soil and sediment particles, the degree of sorption being dependent on the presence of organic matter. Pendimethalin is expected to moderately persist in sediment as it does not partition into the aqueous phase. Some dissipation will also occur due to biodegradation and photolysis.</p> <p>Bioconcentration of pendimethalin in aquatic organisms is high with Bioconcentration Factors in fish ranging from an 'environmentally realistic' value of 1000 (in a mesocosm study) to a 'worst case' value of 5100 (in a laboratory study).</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for Pendimethalin, along with any data that relate impacts under field conditions to exposure concentrations. Data reviewed for the purposes of the risk assessments undertaken in relation to the Plant Protection Products Directive was included for consideration. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically</p>		

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	sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V of the WFD.
<b>Long-term PNEC for freshwaters</b>	<p>The lowest valid long-term toxicity value is for freshwater algae where a 5-day NOEC of <math>3.0 \mu\text{g l}^{-1}</math> for effects on growth inhibition (using the growth rate endpoint) of the green alga <i>Pseudokirchneriella subcapitata</i> has been reported in the EU DAR (2003). Reliable long-term NOECs are available for algae, invertebrates and fish, and therefore an assessment factor of 10 can be applied resulting in a <math>\text{PNEC}_{\text{freshwater\_lt}}</math> of <math>0.3 \mu\text{g l}^{-1}</math>.</p> <p>This value is lower than the previously proposed tentative EQS of <math>1.5 \mu\text{g l}^{-1}</math> which was derived by applying an assessment factor of 2 to the algal data.</p> <p><b>Recommended PNEC: <math>0.3 \mu\text{g l}^{-1}</math> (AF 10)</b></p> <p><b>Change from existing EQS: Lower than existing non-statutory EQS of <math>1.5 \mu\text{g/L}</math></b></p>
<b>Short-term PNEC for freshwaters</b>	<p>Reliable short-term data are available for algal, invertebrate and fish species. The lowest valid short-term toxicity value is a 5-day growth inhibition (using the growth rate endpoint) EC50 values of <math>5.8 \mu\text{g l}^{-1}</math> for the diatom <i>Navicula pelliculosa</i> reported in the EU DAR (2003). The short-term toxicity database for freshwater organisms is not extensive, but does adequately indicate that algae and macrophytes are the most sensitive taxa to short-term exposure to pendimethalin. An assessment factor of 10 was therefore applied, resulting in a <math>\text{PNEC}_{\text{freshwater\_st}}</math> of <math>0.58 \mu\text{g l}^{-1}</math>.</p> <p>This value is lower than the previously proposed tentative EQS of <math>6.0 \mu\text{g l}^{-1}</math> which was based on the EC50s for growth of <math>5.8</math> and <math>6.7 \mu\text{g l}^{-1}</math> reported for the algae <i>Navicula pelliculosa</i> and <i>Pseudokirchneriella subcapitata</i>, respectively, without the application of an assessment factor.</p> <p><b>Recommended PNEC: <math>0.58 \mu\text{g l}^{-1}</math> (AF 10)</b></p> <p><b>Change from existing EQS: Lower than existing non-statutory EQS of <math>6 \mu\text{g/L}</math></b></p>

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<p><b>Long-term PNEC for salt waters</b></p>	<p>Since long-term single species toxicity data are only available for algae, a combined freshwater and saltwater dataset for the saltwater effects assessment was used to derive the PNEC. The most sensitive result is a 5-day growth inhibition (using the growth rate endpoint) NOEC for the diatom, <i>Skeletonema costatum</i>, of 2.7 µg l<sup>-1</sup> reported in the EU DAR (2003). The combined dataset indicate that algae are evidently the most sensitive taxonomic group in both freshwater and saltwater with comparable species showing similar sensitivities. Although data are not available for marine taxa such as echninoderms it is proposed that, given the mode of action of pendimethalin, assessment factor of 10 is applied without an additional factor to account for specifically saltwater species. Therefore, it is recommended that the lowest marine toxicity value is used along with an assessment factor of 10. This results in a PNEC<sub>saltwater_lt</sub> of 0.27 µg l<sup>-1</sup> which is essentially the same as the freshwater PNEC.</p> <p>This value is lower than the previously proposed tentative EQS of 1.5 µg l<sup>-1</sup> which was based on the long-term PNEC for freshwaters because of insufficient marine data to derive an EQS.</p> <p><b>Recommended PNEC: 0.27 µg l<sup>-1</sup>(AF 10)</b></p> <p><b>Change from existing EQS: Lower than current non-statutory EQS of 1.5 ug/L</b></p>
<p><b>Short-term PNEC for salt waters</b></p>	<p>Reliable short-term saltwater toxicity data are available for algae, invertebrates and fish. The most sensitive result is a 5-day growth inhibition (using the growth rate endpoint) EC50 for the diatom, <i>Skeletonema costatum</i>, of 5.2 µg l<sup>-1</sup> reported in the EU DAR (2003), which is consistent with toxicity values for freshwater species. The combined dataset indicate that algae are evidently the most sensitive taxonomic group in both freshwater and saltwater with comparable species showing similar sensitivities. Therefore, it is recommended that the lowest toxicity value for marine algae is adopted along with an assessment factor of 10 (but without the application of an additional assessment factor to account for the absence of data for groups such as echinoderms due to the mode of action of pendimethalin). This results in a PNEC<sub>saltwater_lt</sub> of 0.52 µg l<sup>-1</sup> which is consistent with the freshwater PNEC.</p> <p>This value is more stringent than the previously proposed tentative EQS of 6.0 µg l<sup>-1</sup> which was also based on the short-term PNEC for freshwaters because of insufficient marine data to set an EQS.</p> <p><b>Recommended PNEC: 0.52 µg l<sup>-1</sup>(AF 10)</b></p> <p><b>Change from existing EQS: Lower than current non-statutory EQS of 6 ug/L</b></p>

# PROTECT

<p><b>PNEC for secondary poisoning</b></p>	<p>Bioconcentration data (as BCF values) for pendimethalin for fish range from 1000 (in a mesocosm study) to 5100 (in a laboratory study), hence the trigger of a BCF &gt;100 is exceeded and derivation of PNECs for secondary poisoning of predators is required. The lowest relevant NOEC<sub>food</sub> is 50 mg kg<sup>-1</sup> derived by extrapolation from a LOEC of 100 mg kg<sup>-1</sup> from a 13-week study with rats.</p> <p>Bioconcentration of pendimethalin in aquatic organisms is high with Bioconcentration Factors in fish ranging from 1000 (in a mesocosm study) to 5100 (in a laboratory study). The mesocosm study, which used a single dose and was carried out to GLP, was considered by the EU DAR (2003) to be valid and suitable to modify the BCF in fish and invertebrates to around 1000 with a clearance time of 5.1 days (&gt;95% in 5 days) and to indicate a low potential for food chain biomagnification. However, there is a possibility that pendimethalin could be released on a more continuous basis and as a precautionary measure, it would be more appropriate to use the BCF of 5100 in the calculation of the PNEC<sub>secpois.water</sub>.</p> <p>This calculation results in a corresponding water concentration of PNEC<sub>secpois.water</sub> = 0.55 mg kg<sup>-1</sup> prey / BCF (5100) = 0.1 µg pendimethalin l<sup>-1</sup>.</p> <p>This concentration is lower than the proposed long-term PNEC for the protection of freshwater and saltwater organisms (i.e. 0.3 and 0.27 µg l<sup>-1</sup> respectively). Therefore, if quality standards are set on the basis of the proposed long-term water column it is probable that predators would not be protected from secondary poisoning.</p> <p><b>Recommended PNEC: 0.1 µg l<sup>-1</sup></b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments</b></p>	<p>The TGD trigger value of a log K<sub>oc</sub> or log K<sub>ow</sub> of ≥3 is met, as the reported log K<sub>ow</sub> is 5.2 and reported K<sub>oc</sub> values range from 6700 to 29400. There are no reliable experimental data on sediment toxicity for pendimethalin and, therefore, no PNEC<sub>sediment</sub> can be derived.</p> <p><b>Recommended PNEC: Not derived</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>Analysis</b></p>	<p>For water, the lowest proposed PNEC derived for pendimethalin is 0.1 µg l<sup>-1</sup>. The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50%. Current analytical methodologies using gas chromatography/mass spectrometry can attain low ng/l levels routinely and so will offer sufficient performance to analyse for pendimethalin.</p>
<p><b>Implementation</b></p>	<p>The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>The proposed long-term freshwater value is driven by the biota standard converted for use in the water column as this value is below the long term standard derived based on aquatic life.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not</p>

**PROTECT**

	being proposed as EQSs due to the fact this substance only has agricultural use, but the values may be used as guideline values for operational purposes.
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## PROTECT

Permethrin (CAS number: 52645-53-1)			
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	100	0.001	0.01
Freshwater/short-term	10	0.01	-
Saltwater/long-term	500	0.0002	0.01
Saltwater/short-term	50	0.001	-
<b>Recommendation:</b> The PNECs for saltwater and freshwater are proposed as EQSs however available analytical techniques may not be sufficient to enable compliance assessment.			
<b>Background Information:</b>			
<b>Properties and fate in water</b>	<p>Permethrin is a synthetic pyrethroid insecticide with a wide range of applications. It has four isomers (its <i>cis</i>- and <i>trans</i>-isomers both have two optical isomers) and is a potent neurotoxin. Permethrin is relatively nontoxic to mammals but very toxic to certain forms of aquatic life.</p> <p>In water, permethrin is hydrolytically stable but readily biodegradable. It also undergoes photolysis. In general, the degradative processes are more rapid with the <i>trans</i>-isomer and both isomers degrade to less toxic products. Permethrin is lipophilic (log Kow 3.48–6.5) and has been found to sorb strongly to sediment, where it is persistent.</p>		
<b>Factors affecting derivation of the PNEC</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for permethrin, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.</p>		

## PROTECT

<p><b>Long-term PNEC for freshwaters</b></p>	<p>As expected from the mode of action of permethrin, crustaceans and insects appear to be the most sensitive taxonomic groups.</p> <p>Based on the available data, the lowest good quality long-term NOEC is a value of 0.029 µg l<sup>-1</sup> for the stonefly <i>Pteronarcys dorsata</i>. In the study with <i>P. dorsata</i>, however, a very steep concentration response was observed with no effect at 0.029 µg l<sup>-1</sup>, but 100 per cent immobilisation at 0.042 µg l<sup>-1</sup> after 28 days [12]. However, In the same study, the caddisfly <i>Brachycentrus americanus</i> suffered 55 per cent mortality at 0.03 µg l<sup>-1</sup> (the lowest concentration tested) and no NOEC value could be determined. Since the effects level is greater than 20% the TGD approach cannot be used to derive a NOEC from the LOEC. Therefore, it is proposed that the data for <i>B.americanus</i> is used in a supporting role.</p> <p>The lowest reliable NOEC is the value of 0.029 µg l<sup>-1</sup> for the stonefly <i>Pteronarcys dorsata</i>. As good quality long-term NOECs are available for a range of taxa (crustaceans, insects and fish) and, given the mode of action of permethrin, the most sensitive organisms are represented, an assessment factor of 10 could be used to derive the PNEC:</p> <p><math display="block">\text{PNEC}_{\text{freshwater\_It}} = (0.03 \mu\text{g l}^{-1} \text{ permethrin})/\text{AF} (10) = 0.003 \mu\text{g l}^{-1} \text{ permethrin}</math></p> <p>The TGD also proposes the derivation of the PNEC from acute data with an AF of 100 if acute effect data are available that are lower than the lowest long-term NOEC. The short-term database contains two 50 per cent effect concentrations at low concentrations of permethrin (<i>Oncorhynchus mykiss</i> LC50 of 0.014 µg l<sup>-1</sup> and a <i>Daphnia magna</i> 96-hour LC50 of 0.039 µg l<sup>-1</sup>).</p> <p>Both values are likely to be outliers but, if the process were followed through, using the lowest reliable E(L)C50 (<i>Hexagenia bilineata</i> 96-hour LC50 of 0.1 µg l<sup>-1</sup>) and applying an AF of 100 would generate a PNEC of 0.001 µg l<sup>-1</sup> permethrin. These PNEC values are supported by the data from the freshwater mesocosm studies described in Section 2.6.6 which show that effects in complex natural systems may be observed at very low permethrin concentrations, which are close (with a factor &lt;5) to the PNEC based on single species tests.</p> <p>Based on the review of the available data it is proposed that the PNEC of 0.001 µg l<sup>-1</sup> derived using short-term data is applied as the long-term value. This value provides a margin of safety with respect to the significant effects of permethrin on the survival of the caddisfly <i>Brachycentrus americanus</i> at 0.03 µg l<sup>-1</sup>.</p> <p>This is 10 times lower than the existing EQS of 0.01 µg l<sup>-1</sup> total permethrin expressed as a 95th percentile. This was based on field and laboratory data that suggested levels &lt;0.01 µg l<sup>-1</sup> would be unlikely to affect aquatic invertebrates or dependent fisheries.</p> <p><b>Recommended PNEC: 0.001ug/l</b></p>
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# PROTECT

	<b>Change from existing EQS: Lower than existing EQS of 0.01ug/l</b>
<b>Short-term PNEC for freshwaters</b>	<p>The acute data show crustaceans and insects, followed by salmonid fish, to be the most sensitive taxonomic groups.</p> <p>It is recommended that the short-term PNEC is derived on the basis of a 96-hour LC50 of 0.1 µg l<sup>-1</sup> for the mayfly <i>Hexagenia bilineata</i> and guidance given in the EU Technical Guidance Document (TGD) on effects assessment for intermittent releases. Given that permethrin is a neurotoxin with a specific mode of action and that insects belong to the most sensitive organisms, a reduced assessment factor of 10 (instead of 100) is recommended in order to extrapolate from the 50 per cent acute effect level to the short-term no-effect level. This results in a PNEC<sub>freshwater_st</sub> of 0.01 µg l<sup>-1</sup>.</p> <p>The available field studies support this suggested value.</p>
	<b>Recommended PNEC: 0.01ug/l</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Long-term PNEC for salt waters</b>	<p>The data suggest that there are no obvious differences between freshwater and saltwater species from the same taxonomic groups. Because of this and the lack of marine data, the freshwater and saltwater datasets were combined.</p> <p>Therefore, the long-term PNEC for saltwater was derived on the same basis as the freshwater PNEC i.e. using the lowest reliable E(L)C50 (<i>Hexagenia bilineata</i> 96-hour LC50 of 0.1 µg l<sup>-1</sup> and applying an AF of 100 to generate a PNEC of 0.001 µg l<sup>-1</sup> permethrin .. The TGD suggests a total assessment factor of 1000 if three long-term tests are available for three taxonomic groups, with a factor of 10 applied to account for the absence of data for marine species. However, short-term tests with additional marine species are available and a reduced assessment factor of 500 is recommended. These acute marine data indicate that molluscs are one of the least sensitive groups and would be protected by the proposed PNEC<sub>saltwater_lt</sub> of 0.0002 µg l<sup>-1</sup>.</p> <p>This proposed PNEC is considerably lower than the existing EQS of 0.01 µg l<sup>-1</sup>, which was 'read across' from the long-term freshwater EQS.</p>
	<b>Recommended PNEC: 0.0002ug/l</b>
	<b>Change from existing EQS: Lower than existing EQS of 0.01ug/l</b>



# PROTECT

<b>Short-term PNEC for salt waters</b>	Crustaceans appear to be the most sensitive taxonomic group.  The lowest acute value was the geometric mean 96-hour LC50 of 0.052 $\mu\text{g l}^{-1}$ for the shrimp, <i>Americamysis bahia</i> , calculated from empirical LC50 values from a number of good quality studies. As with the freshwater PNEC, it is recommended that the PNEC be derived on the basis of general guidance given in the TGD on effects assessment for intermittent releases. Because permethrin acts specifically on the nervous system and crustaceans belong to the most sensitive organisms, a reduced assessment factor of 50 (instead of 100) is recommended in order to extrapolate from the 50 per cent acute effect level to the short-term no-effect level. This results in a PNEC <sub>saltwater_st</sub> of 0.001 $\mu\text{g l}^{-1}$ .
	<b>Recommended PNEC: 0.001ug/l</b>
	<b>Change from existing EQS: No existing EQS</b>

## PROTECT

<b>PNEC for secondary poisoning</b>	<p>The BCF data for permethrin are 4–570 for insects, 55–750 for fish and 1,900 for the oyster species <i>Crassostrea virginica</i> (see Section 2.5). Hence, the trigger of BCF &gt;100 is met and the derivation of PNECs for secondary poisoning (secpois) of predators is required.</p> <p>The two lowest reported oral NOELs are 40 and 100 mg/kg diet for hens and rats, respectively (Table 3.1). The NOEL for hens is unbounded (i.e. the highest concentration tested) and, therefore, not suitable for the assessment of secondary poisoning. The rat NOEL, however, refers to a 2-year chronic study and is relevant for PNEC derivation.</p> <p>The appropriate assessment factor to derive a PNEC based on a chronic NOEC<sub>food</sub> of a mammalian study is 30 (Table 23 of the TGD [45]).</p> <p><b>PNEC<sub>secpois_biota</sub> = NOEC<sub>food</sub> (100 mg/kg)/AF 30 = 3.33 mg/kg prey (wet weight)</b></p> <p>Reported BCF values for insects, fish and molluscs range up to 570, 750 and 1,900, respectively. Information on biomagnification of permethrin is not available but, due to its rapid metabolism and elimination from the body within a short period of time, the occurrence of biomagnification is considered unlikely (see Section 2.5). Biomagnification is, therefore, not considered in the following calculations.</p> <p>The corresponding safe concentration in water (preventing bioaccumulation in prey to levels &gt;PNEC<sub>secpois_biota</sub>) is calculated as follows:</p> <p><b>PNEC<sub>secpois_water</sub> = PNEC<sub>secpois_biota</sub>/BCF</b></p> <p>If the highest reported BCF of 1900 is used for the calculation, this results in a (lowest) corresponding water concentration of:</p> <p><b>PNEC<sub>secpois_water</sub> = 3.33/1,900 = 1.75 µg l<sup>-1</sup> permethrin</b></p> <p>This concentration is much higher than the proposed long-term PNECs for the protection of the pelagic communities in both inland and marine water bodies. Therefore, if quality standards are set on the basis of these PNECs, the protection of predators from secondary poisoning is included and the derivation of additional quality standards with particular reference to secondary poisoning is not considered necessary.</p>
	<b>Recommended PNEC: 1.75ug/l</b>
	<b>Change from existing EQS: No existing standard</b>

# PROTECT

<p><b>PNEC for sediments</b></p>	<p>Because the log Kow is &gt;3, the derivation of a PNEC for the protection of benthic communities is required.</p> <p>Two sediment studies are available and both the 10-day LC50 of 2.11 mg permethrin/kg sediment and the &gt;20-day NOEC of 0.4 mg permethrin/kg sediment are suitable for PNEC derivation. Using the chronic toxicity data and the appropriate assessment factors of 100 (chronic) for freshwater and 1,000 (chronic) for saltwater results in a PNEC<sub>sediment_freshwater</sub> of 4.0 µg permethrin/kg sediment dry weight (dw), and a PNEC<sub>sediment_saltwater</sub> of 0.4 µg permethrin/kg sediment dry weight (dw), respectively.</p> <p><b>Recommended PNEC: 4ug/kg (dw) freshwater and 0.4ug/kg (dw) saltwater</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>Analysis</b></p>	<p>The lowest proposed PNECs derived for permethrin are 0.3 ng l<sup>-1</sup> for waters and 0.4 µg/kg for sediments. The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. From the literature, it can be seen that analytical methodologies are capable of achieving detection limits in the low µg l<sup>-1</sup> order in most media, suggesting that current analytical methods would not be adequate to analyse permethrin for compliance purposes.</p>
<p><b>Implementation</b></p>	

# PROTECT

1,1,1,2-Tetrachloroethane (CAS number 630-20-6) and 1,1,2,2-tetrachloroethane (CAS number 79-34-5)			
Receiving medium and exposure	Assessment factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	10	140	n/a
Freshwater/short-term	10	1848	n/a
Saltwater/long-term	100	14	n/a
Saltwater/short-term	100	185	n/a
<b>Recommendation:</b> <p>The freshwater long term and short term PNECs are proposed as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.</p> <p>Although the saltwater PNECs are considered suitable for use as they are not subject to excessive uncertainty the saltwater values are not being proposed as EQSs due to the fact this substance is not considered an issue in saltwaters. The values however may be used as guideline values for operational purposes.</p>			
Background information:			
<b>Properties and fate in water</b>	Tetrachloroethane is a water-soluble, volatile chlorinated solvent. It is lost from water through volatilisation, but the rate at which this occurs depends on the local characteristics of the water body, ambient temperature and wind speed. Tetrachloroethane can be broken down by a number of processes; it hydrolyses in water, particularly at high pH, and can be degraded anaerobically.		
<b>Factors affecting derivation of the PNEC</b>	The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for TCE, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.		
<b>Long-term PNEC for freshwaters</b>	<p>The lowest reliable no observed effect concentration (NOEC) of 1,400 µg l<sup>-1</sup> is for growth of the fathead minnow (<i>Pimephales promelas</i>) following a 32-day exposure to TCE. Slightly higher NOECs of 4,931 µg l<sup>-1</sup> for the flagfish <i>Jordanella floridae</i> after 10 days exposure and 5,900 µg l<sup>-1</sup> for the green algae, <i>Pseudokirchneriella subcapitata</i> after 72 hours exposure have also been generated. The available evidence suggests that fish are slightly more sensitive to TCE than algae and crustaceans. Therefore, an assessment factor of 10 applied to the fathead minnow NOEC of 1,400 µg l<sup>-1</sup> is recommended following the Annex V guidance, resulting in a PNEC<sub>freshwater</sub> of 140 µg l<sup>-1</sup>.</p> <p><b>Recommended PNEC: 140 µg l<sup>-1</sup> (AF 10)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>		

# PROTECT

<b>Short-term PNEC for freshwaters</b>	Good quality data are available from acute studies with fish, algae and crustaceans, with flagfish being the most sensitive species of those tested (96-hour LC50 of 18,480 µg l <sup>-1</sup> ). As a result, a factor of 10 applied to the flagfish 96-hour LC50 is recommended, resulting in a PNEC <sub>freshwater st</sub> of 1,848 µg l <sup>-1</sup> .
	<b>Recommended PNEC: 1848 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Long-term PNEC for salt waters</b>	The absence of reliable chronic saltwater toxicity data means the saltwater PNEC is based on freshwater data. This assumes that freshwater and saltwater species share a similar distribution of sensitivities to TCE. This is considered acceptable since the non-specific mode of action of this substance should not result in systematically greater sensitivity of any particular taxonomic group. However, the greater taxonomic diversity of marine organisms compared with those living in freshwaters introduces greater uncertainty into the prediction of a saltwater PNEC. Together with the paucity of saltwater data (e.g. for echinoderms and molluscs), these considerations invite a higher safety factor to be applied. Consequently, an assessment factor of 100 applied to the fathead minnow 32-day NOEC is recommended, resulting in a PNEC <sub>saltwater lt</sub> of 14 µg l <sup>-1</sup> .
	<b>Recommended PNEC: 14 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Short-term PNEC for salt waters</b>	Although several studies with marine organisms have been reported, none were of sufficient quality to form the basis of a PNEC. As a result, a saltwater short-term PNEC is based on freshwater data. Again, this assumes that freshwater and saltwater species share a similar distribution of sensitivities to TCE. This assumption is considered acceptable given the non-specific mode of action of this substance. An assessment factor of 100 applied to the flagfish 96-hour LC50 is recommended, reflecting the high level of uncertainty associated with extrapolating from a small freshwater dataset. A PNEC <sub>saltwater st</sub> of 185 µg l <sup>-1</sup> results. Again, some of this uncertainty, and hence the size of the assessment factor, could be reduced if reliable acute toxicity data were to be generated, e.g. for marine fish, algal and invertebrate species.
	<b>Recommended PNEC: 185 µg l<sup>-1</sup> (AF 100)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for secondary poisoning</b>	TCE is not sufficiently lipophilic or bioaccumulative to warrant the development of PNECs for secondary poisoning.
	<b>Recommended PNEC: Not required</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for sediments</b>	<b>Effect on biota:</b> TCE is not sufficiently lipophilic or bioaccumulative to warrant the development of PNECs for sediments.
	<b>Recommended PNEC: Not required</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis</b>	Analytical methodologies currently employed by UK environmental regulators are capable of achieving detection limits of below 1 µg l <sup>-1</sup> . This is sufficiently sensitive to analyse TCE in water for compliance purposes.
<b>Implementation</b>	The freshwater long term and short term PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and analytical capability should be adequate for compliance assessment purposes. The saltwater PNECs are not being proposed as PNECs as

**PROTECT**

	tetrachloroethane is not considered to be an issue in saltwaters.
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# PROTECT

Toluene (CAS number: 108-88-3)			
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l )
Freshwater/long-term	10	74	50
Saltwater/long-term	10	74	40
<b>Recommendation</b> The existing statutory long-term values for this substance were used as interim values for the first cycle of river basin planning. It is recommended that the proposed PNEC <sub>it</sub> are applied for the second cycle of river basin management as their derivation reflects the best science. These would replace the interim existing values. All other EQS values already established for this substance (i.e., short-term values) would still apply.			
<b>Background Information:</b>			
<b>Properties and fate in water</b>	Toluene is widely used in manufacturing and process industries. It has low solubility in water and volatilisation is expected to be an important fate process. Whilst it is readily biodegradable at high concentrations in water, toluene exhibits a reduced degradation rate at lower concentrations.		
<b>Factors affecting derivation of the PNEC</b>	The PNECs described are based on a technical assessment of available ecotoxicity data for phenol, including those data contained in the EU Risk Assessment Report (EU RAR) compiled for toluene. The data were subjected to rigorous quality assessment by both the authors and an independent peer review panel. An EU Risk Assessment Report (RAR) has been compiled for BBP. As it has been proposed that RAR PNECs are used for the derivation of WFD EQSs the RAR PNECs are recommended as the proposed long term PNECs for freshwater and saltwaters.		
<b>Long-term PNEC for freshwaters:</b>	The lowest long-term datum was a No Observed Effect Concentration of 074 mg/l for reproduction of the water flea, <i>Ceriodaphnia dubia</i> over a 7-day exposure period. This is supported by chronic toxicity data for other taxa, allowing an Assessment factor of 10 to be applied, which would result in a PNEC of 74 µg/l.		
	<b>Recommended PNEC:</b> 74µg/l (AF 10)		
	<b>Change from existing EQS:</b> The proposed PNEC is higher than the existing EQS of 50µg/l.		
<b>Long-term PNEC for salt waters:</b>	There are too few toxicity data for marine species to derive a PNEC. However, freshwater and saltwater species from the same taxonomic group exhibit similar sensitivities and, on this basis, we can combine the freshwater and saltwater datasets. The lowest No Observed Effect Concentration for the combined dataset is a 7-day reproduction study with <i>Ceriodaphnia dubia</i> (0.74 mg/l). Since toxicity data for other taxa suggest these would be no more sensitive than <i>Ceriodaphnia</i> , an assessment factor of 10 applied this NOEC can be justified. This would result in a PNEC of 74 µg/l, the same as for the freshwater, long-term situation.		
	<b>Recommended PNEC:</b> 74µg/l (AF 10)		
	<b>Change from existing EQS:</b> The proposed PNEC is higher than the existing EQS of 40µg/l.		
<b>Analysis</b>	The lowest proposed PNEC derived for toluene is 74 µg/l. The data		

**PROTECT**

	quality requirements are that, at one-third of the EQS, the total error of measurement should not exceed 50 per cent. Analytical methodologies currently employed by UK environmental regulators are capable of achieving detection limits of below $1 \mu\text{g l}^{-1}$ which suggests that they would be adequate for assessing compliance with the proposed PNECs.
<b>Implementation</b>	These PNECs are suitable for use as EQSs because they are not subject to excessive uncertainty. Analytical capability is adequate for compliance assessment purposes. The PNECs proposed are in line with the long term PNECs derived in the EU RAR for toluene.



# PROTECT

<b>Triclosan (2,4,4'-trichloro-2'-hydroxydiphenyl ether) (CAS number 3380-34-5)</b>		
<b>Receiving medium/ exposure scenario</b>	<b>Proposed PNEC (ug/l)</b>	<b>Existing EQS (µg l<sup>-1</sup>)</b>
Freshwater short-term	0.28 µg l <sup>-1</sup> (AF 5)	-
Freshwater long-term	0.10 µg l <sup>-1</sup> (AF 10)	-
Saltwater short-term	0.28 µg l <sup>-1</sup> (AF 5)	-
Saltwater long-term	0.10 µg l <sup>-1</sup> (AF 10)	-
<b>Recommendation:</b> The PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.		
<b>Background Information:</b>		
<b>Properties and fate in water:</b>	<p>Triclosan is an antibacterial agent belonging to the chlorinated diphenyl ethers which is added to a wide range of consumer products to offer long lasting protection against bacteria, moulds and yeasts. The majority of its usage is associated with household and personal care products (e.g. toothpastes, mouthwashes, soaps and deodorants). These uses result in the substance being released to the sewerage system where there is the potential for release to the aquatic environment.</p> <p>Triclosan has a pKa of 7.9-8.1 and readily ionises at environmental pH. The substance is predominantly in its neutral form at pH 7.0 but is predominantly in its ionised form at pH 8.5. Organic molecules have been shown to be less likely to cross lipid membranes when in their ionised state which is consistent with the greater bioaccumulation found in aquatic organisms exposed to triclosan at pH below the pKa (see below). In waters above pH 8.0 the predominance of the ionised form of triclosan results in lower levels of bioaccumulation.</p> <p>Triclosan is transformed via direct photolysis and the pH-dependent dissociation of triclosan governs its susceptibility to photooxidation. Half lives of 8 and 4 days respectively have been reported for the photolysis of triclosan (using a starting concentration of 9.4 mg l<sup>-1</sup>) in freshwater and seawater (at pH of 7.0) under a low intensity artificial white light source. 2,8-Dichlorodibenzo-p-dioxin (at a level of 1%) was detected in both samples after 3 days of irradiation. In contrast, a half-life of only 41 minutes for aqueous photolysis was found in drinking water at pH 7 and 25°C, with most of the triclosan being converted to 2,4-dichlorophenol.</p> <p>In receiving waters with a pH &lt;8.0 triclosan is expected to adsorb to suspended solids and sediment based on an estimated Koc value of 9200 (determined from a log Kow of 4.76). Volatilization of triclosan is not expected to be an important fate process given an estimated Henry's Law constant of 2.4x10<sup>-7</sup> Pa-m<sup>3</sup>/mole (derived from its vapour</p>	

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	<p>pressure of <math>7 \times 10^{-4}</math> Pa, and a water solubility of <math>10 \text{ mg l}^{-1}</math>.</p> <p>Triclosan is not readily or inherently degradable in standardised screening tests like OECD 301C (MITI I) or OECD 302C (MITI II). The negative results in these tests may be a consequence of the bacterial toxicity of triclosan at the high substrate concentration required for these biodegradability screening tests. However, removal rates up to 99% have been recorded in tests using a Continuous Activated Sludge (CAS) system. In a study at a sewage treatment works triclosan was found to be susceptible to biodegradation with over 79% of the substance being degraded during a one-week survey and only 6% of the triclosan entering the plant remaining in the treated effluent. Methyl triclosan and 2,7/2,8 dibenzodichloro-p-dioxin are potential biotransformation products following treatment of triclosan at a sewage treatment plant.</p> <p>Bioconcentration factors are reported in the range 15 to 90 and 2.7 to 44 in carp (<i>Cyprinus carpio</i>) at concentrations of 3 and <math>30 \text{ } \mu\text{g l}^{-1}</math>, respectively, suggesting the potential for bioconcentration in aquatic organisms is low to moderate. However, the BCFs for zebra fish (<i>Danio rerio</i>), assessed over a five-week test period were 4157 at <math>3 \text{ } \mu\text{g l}^{-1}</math> and 2532 at <math>30 \text{ } \mu\text{g l}^{-1}</math>, indicating that there is a significant likelihood for bioaccumulation. The pH of the test media used in the studies are not known but pH differences may explain the differences in BCF values between species. This is supported by a study which reported BCF values of 3700-8700 in zebrafish exposed to triclosan at pH in the range 6-9, with the higher BCFs being reported in fish exposed to the substance at pHs of 6-7. High concentrations of triclosan have also been reported in the bile of fish exposed to the substance.</p>
<b>Factors affecting derivation of the PNEC:</b>	<p>The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for triclosan, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V of the WFD.</p>
<b>Long-term PNEC for freshwaters:</b>	<p>Lowest valid long-term toxicity value for any freshwater species is a 3-day no observed effect concentration (NOEC) of <math>0.5 \text{ } \mu\text{g l}^{-1}</math> for effects on the growth rate of the algae <i>Scenedesmus subspicatus</i>. Reliable long-term NOECs are available for algae, invertebrates and fish including a large body of data for algae which are the most sensitive taxonomic group. Based on the data available and the combined weight of evidence it presents it is considered appropriate to apply a reduced assessment factor of 5 this results in a <math>\text{PNEC}_{\text{freshwater\_lt}}</math> of <math>0.10 \text{ } \mu\text{g l}^{-1}</math> triclosan.</p> <p><b>Recommended PNEC: <math>0.10 \text{ } \mu\text{g l}^{-1}</math> (AF 5)</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>

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<b>Short-term PNEC for freshwaters:</b>	Reliable short-term data are available for algal, invertebrate and fish species. The lowest valid short-term toxicity value is a 72-hour growth rate EC50 of 2.8 µg l <sup>-1</sup> for the alga <i>Scenedesmus subspicatus</i> . There is a considerable short-term toxicity database for freshwater organisms, which shows that algae such as <i>Scenedesmus</i> are likely to be most sensitive to triclosan. An assessment factor of 10 was therefore applied, resulting in a PNEC <sub>freshwater st</sub> of 0.28 µg l <sup>-1</sup> triclosan.
	<b>Recommended PNEC: 0.28 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Long-term PNEC for salt waters:</b>	The only long-term saltwater data available is a 4-day EC25 of >66 µg l <sup>-1</sup> for effects of triclosan on the marine alga <i>Skeletonema costatum</i> . Since algae are the most sensitive freshwater taxa and marine algae are apparently not more sensitive to triclosan than freshwater species it is recommended that the freshwater PNEC is also adopted to protect saltwater taxa. It is proposed not to apply an additional assessment factor of 10 for marine species due to the antimicrobial mode of action of triclosan which indicates that organisms such as echinoderms and molluscs are likely to be less sensitive than algae. This results in a PNEC <sub>saltwater lt</sub> of 0.10 µg l <sup>-1</sup> .
	<b>Recommended PNEC<sub>saltwater lt</sub> = 0.10 µg l<sup>-1</sup> (AF 5)</b>
	<b>Change from existing EQS: No existing saltwater EQS</b>
<b>Short-term PNEC for salt waters:</b>	There are limited short-term data available for saltwater species exposed to triclosan, but the data for marine algae (the most sensitive freshwater species) do not show greater sensitivity compared to freshwater species. It is therefore recommended that the freshwater PNEC is also adopted to protect saltwater taxa. This results in a PNEC <sub>saltwater st</sub> of 0.28 µg l <sup>-1</sup> triclosan.
	<b>Recommended PNEC<sub>saltwater st st</sub> = 0.28 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: No existing saltwater EQS</b>
<b>PNEC for secondary poisoning:</b>	Bioconcentration data (as BCF values) for triclosan for fish are variable ranging from 2.7 to 90 for carp ( <i>Cyprinus carpio</i> ) and 2532-8700 for zebrafish ( <i>Danio rerio</i> ). The BCF values are dependent on the pH of the exposure medium. As the trigger of BCF values >100 is met the derivation of a PNEC for secondary poisoning of predators is required. The PNEC based on the risks of secondary poisoning to mammals and birds (3.8 µg l <sup>-1</sup> ) is higher than those derived for the protection of aquatic life and so does not influence the development of aquatic EQSs for triclosan.
	<b>Recommended PNEC<sub>sec pois</sub> = 3.8 µg l<sup>-1</sup> (AF 10)</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>PNEC for sediments:</b>	Triclosan has a log Kow of 4.76 which exceeds the TGD trigger value of a log Kow of >3, therefore a sediment quality standard is necessary. However, data on direct toxicity to sediment-dwelling organisms are limited and are insufficient to derive a PNEC.
	<b>Recommended PNEC<sub>sed</sub>: No recommended PNEC</b>
	<b>Change from existing EQS: No existing EQS</b>
<b>Analysis:</b>	For water, proposed PNECs derived for triclosan range from 0.10 to 0.28 µg l <sup>-1</sup> . The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing voltammetry, gas chromatography–mass spectrometry (GC-MS), or liquid chromatography–mass spectrometry

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	(GC-MS),capable of achieving detection limits as low as 0.5 ng l <sup>-1</sup> , should offer adequate performance to analyse for triclosan.
<b>Implementation</b>	The PNECs are suitable for use as EQSs as they are not subject to excessive uncertainty and the current analytical capability should be adequate for the purposes of compliance assessment.

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Zinc metal (divalent ion form) (CAS number 7440-66-6)				
Receiving medium and exposure	Proposed EQS (ug/l)	Existing EQS		
Freshwater long-term	10.9 µg l <sup>-1</sup> (generic PNEC based on bioavailable Zn)	CaCO <sub>3</sub>	EQS 1	EQS 2
		0–50 mg l <sup>-1</sup>	8 µg l <sup>-1</sup>	75 µg l <sup>-1</sup>
		50–100 mg l <sup>-1</sup>	50 µg l <sup>-1</sup>	175 µg l <sup>-1</sup>
		100–150 mg l <sup>-1</sup>	75 µg l <sup>-1</sup>	250 µg l <sup>-1</sup>
		150–200 mg l <sup>-1</sup>	75 µg l <sup>-1</sup>	250 µg l <sup>-1</sup>
		200–250 mg l <sup>-1</sup>	75 µg l <sup>-1</sup>	250 µg l <sup>-1</sup>
>250 mg l <sup>-1</sup>		125 µg l <sup>-1</sup>	500 µg l <sup>-1</sup>	
Saltwater long-term	3.4 µg l <sup>-1</sup> (dissolved)	40 µg l <sup>-1</sup> (AA) (dissolved)		
<b>Recommendation:</b>				
<p>Long-term standards have been derived for freshwater and saltwater and are being proposed as EQSs as they are not subject to excessive uncertainty. Analytical capabilities are adequate in relation to assessing compliance with the freshwater value but may need further consideration in relation to the saltwater value.</p> <p>The freshwater PNEC is derived based on conditions of high bioavailability and therefore bioavailability needs to be taken into account when assessing compliance.</p> <p>A short term standard has not been proposed for zinc as due to the fact it is persistent in the environment and arises from a number of sources the long term impacts are considered to be of priority.</p>				
<b>Background Information:</b>				
<b>Properties and fate in water:</b>	<p>Zinc is a naturally occurring element that exists mainly as sulphides, silicates and carbonates. Zinc plays an essential role in organisms, where its internal concentration can be regulated to a limited extent depending on the concentrations to which it is exposed. Effects of deficiency or toxicity may occur if the concentrations deviate from those that the organism can regulate.</p> <p>In water, zinc exists in the +2 oxidation state in forms that are dependent on physicochemical parameters, such as pH, hardness and the content of dissolved organic carbon. Bioavailability may be affected by organic and inorganic complexation, with anions such as chloride (Cl<sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>), and by the competition of cations (e.g. Ca<sup>2+</sup> and H<sup>+</sup>) with zinc at biological receptors.</p>			
<b>Factors affecting derivation of the PNEC:</b>	<p>The “added risk” approach is appropriate when deriving PNECs for zinc because zinc is a naturally occurring substance which organisms will have been exposed to over an evolutionary timescale. Furthermore, zinc is ubiquitous in aquatic</p>			

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	<p>environments. The added risk approach takes account of ambient background concentrations and the PNEC (<math>PNEC_{add}</math>) applies only to the additional contribution over and above the ambient background level (i.e. the value at which toxic effects occur, ignoring contributions from background concentrations). A practical consequence of this is that when assessing compliance with such an EQS it will be necessary to consider ambient background zinc concentrations at a regional, river basin, or waterbody scale.</p> <p>A <math>PNEC_{add, freshwater}</math> derived in the EU RAR for soft waters (those with a hardness <math>&lt;24 \text{ mg l}^{-1} \text{ CaCO}_3</math>) has been reassessed in a recent Environment Agency project demonstrated no clear requirement for a difference in approaches between waters with hardnesses of greater than or less than <math>24 \text{ mg l}^{-1} \text{ CaCO}_3</math>. It appears that similar principles for the competition between Zn and major cations such as Ca and Mg, and bioavailability reduction through Zn binding to DOC, can be applied across the complete range of water hardnesses in the UK.</p> <p>A research programme conducted as part of the EU RAR developed quantitative methods for taking into account the bioavailability of zinc because of water and sediment chemistry. These methods use biotic ligand models (BLMs) and the acid volatile sulfide (AVS) approach. However, the practicality of the latter correction method for compliance monitoring in the UK is unclear.</p>
<b>Long-term PNEC for freshwaters:</b>	<p>Algae appear to be the most-sensitive taxonomic group, followed by crustaceans, sponges, rotifers and fish. The key input parameters for Zn BLM are pH, DOC and Ca. The generic HC5 value was selected so as to provide 95% protection for the most sensitive region of the UK (North West England), which would ensure a high level of protection if applied on a UK basis.</p> <p>An AF of 1 is recommended in order to derive the <math>PNEC_{add}</math> from the generic PNEC value of <math>10.9 \text{ } \mu\text{g l}^{-1}</math>.</p> <p>The proposed PNEC is above the very lowest toxicity values observed under some test conditions. Field evidence does not, however suggest that freshwater algae, such as benthic diatoms, are especially sensitive to zinc toxicity.</p> <p>The existing EQSs for total zinc are banded according to water hardness, with values ranging between <math>8 \text{ and } 125 \text{ } \mu\text{g l}^{-1}</math> for the protection of "sensitive taxa". The <math>PNEC_{add, freshwater, lt}</math> derived using the SSD approach is comparable to the most stringent value from this range; the <math>PNEC_{add, freshwater, lt}</math> based on an assessment factor approach is lower.</p> <p><b><math>PNEC_{add, freshwater, lt} = 10.9 \text{ } \mu\text{g l}^{-1}</math> (AF 1)</b></p> <p><b>Change from existing EQS: comparable to existing EQS for low hardness waters</b></p>

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<p><b>Long-term PNEC for salt waters:</b></p>	<p>Based on abiotic factors, freshwater and saltwater can be regarded as different environments, each with organisms adapted to that environment. Thus, the freshwater and saltwater data in the EU RAR were not combined to derive a general <math>PNEC_{add,saltwater}</math>.</p> <p>There are 36 species NOECs (using geometric means where applicable) available to construct an SSD to estimate an HC5 for saltwaters. The median 5<sup>th</sup> percentile cut-off value of <math>6.76 \mu g l^{-1}</math> Zn is calculated with a lower 95% CL of <math>3.6 \mu g l^{-1}</math> and an upper 95% CL of <math>10.9 \mu g l^{-1}</math>. Based on comparison with assessment factors applied to HC5 values in European risk assessments for metals with similar data profiles, an assessment factor of 2 is considered to be appropriate for the derivation of the PNEC from the HC5.</p> <p><b><math>PNEC_{add,saltwater} = 6.76 \mu g l^{-1} / AF (2) = 3.4 \mu g l^{-1}</math> zinc (dissolved)</b></p> <p>This results in a PNEC that is lower than the existing EQS for dissolved Zn of <math>40 \mu g l^{-1}</math>, which was derived by applying an assessment factor of 4 to a chronic data value of <math>166 \mu g l^{-1}</math> obtained for the mysid shrimp <i>Americamysis bahia</i> (formerly <i>Mysidopsis bahia</i>).</p> <p><b>Recommended <math>PNEC_{add,saltwater} = 3.4 \mu g l^{-1}</math> zinc (dissolved)</b></p> <p><b>Change from existing EQS: Lower than existing EQS of 40ug/l</b></p>
<p><b>PNEC for secondary poisoning:</b></p>	<p>Based on data on the bioaccumulation of zinc in animals and on biomagnification, the EU RAR concludes that secondary poisoning is not relevant in the effects assessment of zinc.</p> <p><b>Recommended PNEC: Not required</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>PNEC for sediments:</b></p>	<p>According to the EU RAR, only four reliable chronic NOEC values for benthic organisms (the insect <i>Chironomus tentans</i>, the annelid <i>Tubifex tubifex</i> and the crustacean <i>Hyalomma azteca</i>) in the range of 488 – 1100 mg kg<sup>-1</sup> sediment dw are available. These benthic species represent three taxonomic groups of invertebrates with different living and feeding conditions, therefore, an assessment factor of 10 should be applied to the lowest chronic NOEC.</p> <p>This gives a <math>PNEC_{add,sediment}</math> of 49 mg zinc kg<sup>-1</sup> dw (equivalent to a <math>PNEC_{add,sediment}</math> of 11 mg zinc kg<sup>-1</sup> wet weight (ww)).</p> <p><b>Recommended <math>PNEC_{add,sediment}</math> of 49 mg zinc kg<sup>-1</sup> dw (equivalent to <math>PNEC_{add,sediment}</math> of 11 mg zinc kg<sup>-1</sup> (ww))</b></p> <p><b>Change from existing EQS: No existing EQS</b></p>
<p><b>Analysis:</b></p>	<p>The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. Analytical methodologies currently employed by UK environmental regulators are capable of achieving detection limits of below <math>1 \mu g l^{-1}</math> in freshwater however available techniques may not be sufficient for saltwater.</p>
<p><b>Implementation</b></p>	<p>To implement the proposed PNECs using the added risk approach, it would be necessary to determine background concentrations of zinc at a regional, river basin or waterbody scale. The approach for determining background concentrations</p>

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	needs to be developed. Analytical techniques for saltwater may need to be considered.
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**GLOSSARY**

CCW	Countryside Council for Wales
CIS	Common Implementation Strategy
DELG	Republic of Ireland's Department of Environment and Local Government
DOC	Dissolved organic carbon
DSD	Dangerous Substances Directive 76/464/EEC
ESR	Existing Substances Regulations
EQS	Environmental quality standard
JNCC	Joint Nature Conservation Council
LIMS	Laboratory information systems
MAC	Maximum allowable concentration
M-BAT	Metal Bioavailability Assessment Tool
NIEA	Northern Ireland Environment Agency
NOEC	No observed effect concentration
PNEC	Predicted no-effect concentration
SEPA	Scottish Environment Protection Agency
SNH	Scottish Natural Heritage
SSD	Species sensitivity distribution
TCE	Tetrachloroethane
UKTAG	The United Kingdom's Technical Advisory Group on the Water Framework Directive
WFD	Water Framework Directive