**UK Technical Advisory Group** 

on the Water Framework Directive

# **PROPOSALS FOR ENVIRONMENTAL QUALITY STANDARDS FOR ANNEX VIII SUBSTANCES**

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# PROPOSALS FOR ENVIRONMENTAL QUALITY STANDARDS FOR ANNEX VIII SUBSTANCES

### INTRODUCTION

The United Kingdom's Technical Advisory Group on the Water Framework Directive (UKTAG) is developing environmental standards for the Directive.

The UKTAG is a partnership of environment and conservation agencies<sup>1</sup>. It was formed to provide technical advice to the UK's government administrations and their agencies. The UKTAG also includes representatives from the Republic of Ireland.

This is a technical report by the UKTAG intended for an audience that is familiar with how water quality standards are set and used. It outlines the UKTAG proposals and describes the role the proposals could play. The proposals would help focus efforts to protect the water environment.

This report is an update of a version issued for consultation and it takes account of the comments from the consultation. The report will be sent to the administrations of the devolved governments, and to the environment and conservation agencies. The UKTAG expects that the final standards will be used to help develop policy, and to guide the Directive's first cycle of River Basin Management Plans.

The approach to the adoption and implementation of proposals like those of the UKTAG might vary for each country within the UK, depending on present and proposed legislation, and on policy in each country. This is a matter for Ministers to decide; it is subject to the normal policy-making considerations of the administrations and their agencies. Some of these agencies have been designated as Competent Authorities under the legislation that transposed the Water Framework Directive into UK law.

<sup>&</sup>lt;sup>1</sup> Countryside Council for Wales (CCW), Natural England, Environment Agency (for England and Wales), Environment & Heritage Service (Northern Ireland) (EHS), Joint Nature Conservation Council (JNCC), Scottish Environment Protection Agency (SEPA), ), Scottish Natural Heritage (SNH), Republic of Ireland's Department of Environment and Local Government (DELG)

# THE NEED FOR STANDARDS

#### The Water Framework Directive

The Directive sets out objectives that include:

- prevent deterioration of the status of all surface water and groundwater bodies;
- protect, enhance and restore all bodies of surface water and groundwater with the aim of achieving good surface water status and good groundwater status by 2015.

The Directive requires Environmental Quality Standards (EQS) for polluting substances. These standards are thresholds which, if exceeded, could result in adverse effects on ecosystems<sup>1</sup>; they will supersede some of the standards from other legislation.

#### **Priority and Priority Hazardous Substances**

As envisaged by the Water Framework Directive, certain substances that are regarded as the most polluting were identified in 2001 as Priority and Priority Hazardous Substances by a Decision of the European Parliament and the Council of Ministers. For these substances, Environmental Quality Standards will be determined at the European level and these will apply to all Member States. Priority and Priority Hazardous Substances are not covered in this report. This report deals only with substances whose standards may be derived by each Member State.

Environmental Quality Standards for Priority Substances and Priority Hazardous Substances are criteria for the assessment of Good Chemical Status for bodies of surface water. These standards form part of a proposal by the European Commission for an Article 16 Daughter Directive that is currently under consideration by the Council of Ministers and the European Parliament. Action to meet the requirements embodied in the standards will be part of River Basin Management Plans.

#### **Specific Pollutants**

The Water Framework Directive requires that Member States identify and develop standards for 'Specific Pollutants'<sup>2</sup>. These Specific Pollutants are the subject of this report.

<sup>&</sup>lt;sup>1</sup> And for substances defined as Priority Substances, human health as well. Human health must also be considered as part of the managing of groundwater bodies.

<sup>&</sup>lt;sup>2</sup> Section 1.2.6 in Annex V of the Water Framework Directive

The Water Framework Directive provides an indicative list of such pollutants<sup>1</sup>. Specific Pollutants are defined as substances that can have a harmful effect on biological quality, and which may be identified by Member States as being discharged to water in "significant quantities"<sup>2</sup>.

#### **Existing Standards**

We already have standards for substances under the Dangerous Substances Directive. In time, the Water Framework Directive will take over the provisions of the Dangerous Substances Directive<sup>3</sup>.

In effect, most of the substances identified in List I for the Dangerous Substances Directive will be called Priority Substances or Priority Hazardous Substances under the Water Framework Directive. Generally, candidates for Specific Pollutants will come from List II of the Dangerous Substances Directive, or they will be chemicals identified as emerging issues.

As part of the development of its proposals, the UKTAG will review the existing standards for substances that are candidates for Specific Pollutants to assess whether a new standard is required.

#### About this report

This report describes work by the UKTAG to develop the standards for candidate Specific Pollutants. Failure of standards can indicate where action may be required. Standards are also used to calculate the degree and type of action needed to achieve compliance.

Developing standards takes time and resources. The work of the UKTAG is being done in phases, taking batches of substances in turn. This report describes the procedure for setting standards, and gives the UKTAG proposals for standards for the first set of substances.

Work has focussed on the development of thresholds that are called Predicted No Effect Concentrations<sup>4</sup> (PNEC). Further steps are needed before these can be adopted as final Environmental Quality Standards. These steps include consultation by the administrations on how the standards are to be implemented.

<sup>&</sup>lt;sup>1</sup> At Annex VIII

<sup>&</sup>lt;sup>2</sup> See the description of quality elements in Section 1.1 and 1.2 of Annex V of the Water Framework Directive.

<sup>&</sup>lt;sup>3</sup> The Dangerous Substances Directive will be repealed in 2013

<sup>&</sup>lt;sup>4</sup> The Predicted No Effect Concentration is the concentration of a pollutant below which no harmful effects on aquatic organisms would be expected.

#### Classification

Surface water bodies will be assigned to one of the Directive's five ecological status classes – High, Good, Moderate, Poor or Bad. The standards for Specific Pollutants will contribute to ecological status – where a standard is failed the water body cannot be classed as Good.

(Under the Dangerous Substances Directive, Member States are not obliged to classify water bodies on the basis of the water quality standards<sup>1</sup> – Member States are expected to set controls on discharges and emissions in order to meet the standards, and to put in place plans to reduce pollution).

The UKTAG intends in 2008 to consult on its proposals for classifying water bodies. The response to a failed standard will vary for each pollutant, but the UKTAG proposes that as a rule, the classification for Specific Pollutants would not depend on a step which involves additional and local ecological corroboration of impact. Also, for most standards, the consideration of the need for action to secure compliance would not require additional and local ecological corroboration of damage. The type of action actually 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.

In the first cycle of River Basin Planning under the Water Framework Directive, part of the monitoring will focus on sites where the environment agencies believe there is a risk of pollution by Specific Pollutants or candidate Specific Pollutants. The UKTAG proposes that this be done using the guidance it has issued<sup>2</sup>.

<sup>&</sup>lt;sup>1</sup> For Scotland, a limited set of Dangerous Substances is used in the present classification of water quality

<sup>&</sup>lt;sup>2</sup> UKTAG Guidance (2005) 12a) Guidance on the Selection of Monitoring Sites and Building Monitoring Networks for Surface Waters and Groundwater.

### THE PROCESS FOR DEVELOPING THE STANDARDS

The UKTAG has developed its proposals by using the method specified in Annex V of the Water Framework Directive.

This has been done in the light of the Environment Agency's *Framework for Standards,* a process which reviews the scientific basis for the standard, the degree of protection it provides, its impact<sup>1</sup>, and a consideration of the practical aspects of using the standard. The *Framework for Standards* separates these steps so that we can see their importance, and so that, as far as possible, the process is consistent across different standards.

This report covers the first steps in the *Framework for Standards* – the scientific assessment. These steps include a peer review of the science, and address some of the issues of implementation<sup>2</sup>. The process is illustrated in Figure 1. It covers:

- choosing the substances that need standards;
- deriving a draft standard;
- checking the standard to see whether, technically, it can be adopted in practice as an effective standard.

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.

#### Choosing the substances for standards in Phase 1

The UKTAG first established a list of polluting substances that might be considered as Specific Pollutants. This list, containing more than three hundred chemicals, includes substances covered by existing legislation, those subject to current obligations for monitoring, and some substances that have emerged recently as potential concerns, for example, flame-retardants.

The substances in the list were ranked on a scale of 1 to 5 using the method agreed by the UKTAG (Annex A). Categories 1 and 2 are seen as priorities for the development of standards. The substances in these categories are listed in Annex A.

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

<sup>&</sup>lt;sup>2</sup> Examples of these are in [2]

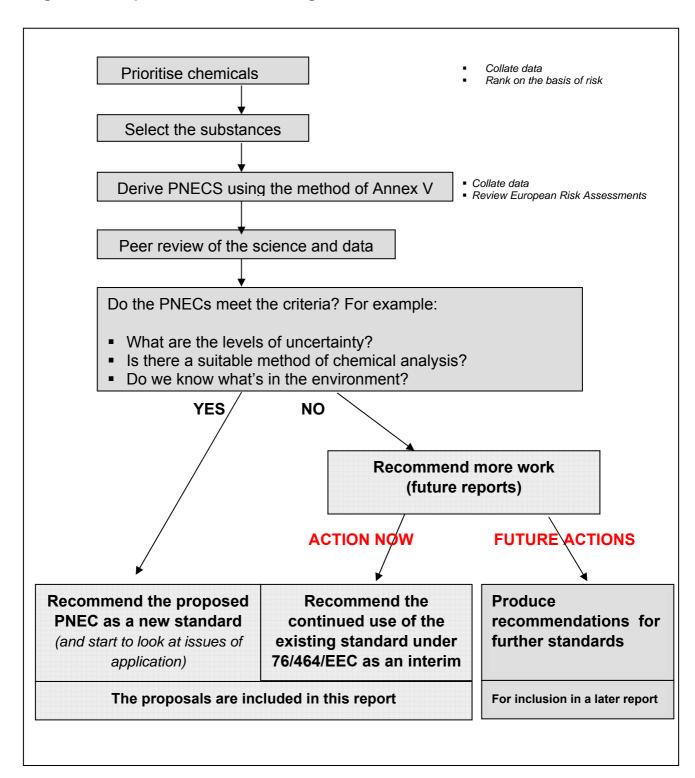


Figure 1: The process for determining standards

Because of the requirements for data, the setting of priorities took a long time. The UKTAG identified 33 substances for early consideration. These included substances that feature most often in the permit conditions for discharges to water across the UK. The UKTAG suggests that this means that these substances are associated with widespread risk, and that they are "discharged to water in significant quantities". The UKTAG also included a number of other substances that are considered to pose risks.

So far, the UKTAG has evaluated 18 substances. These are:

2,4-D<sup>1</sup> (ester and non-ester); 2,4-dichlorophenol; ammonia; arsenic; chlorine; copper; chromium; cyanide; cypermethrin; diazinon; dimethoate; iron; linuron; mecoprop; permethrin; phenol; toluene; and zinc.

This report proposes new standards for 9 of these substances (Table 1: Part A) and that the standards are treated for the Water Framework Directive as Specific Pollutants:

2,4-D (ester and non-ester); chromium; cypermethrin; diazinon; dimethoate<sup>2</sup>; linuron; mecoprop; phenol; and toluene.

This report also proposes as an interim measure the continued use of the existing standards<sup>3</sup> for the 9 substances in Table 1: Part B. These substances are also defined as Specific Pollutants under the Water Framework Directive. The UKTAG proposes that the use of these standards be extended to parts of the UK that do not have existing statutory controls. The substances are:

2,4-dichlorophenol, ammonia, arsenic, chlorine, copper, cyanide, permethrin, iron and zinc.

Because ammonia is a common pollutant the UKTAG proposes that it should be a Specific Pollutant. Historically the concentration of the un-ionised ammonia<sup>4</sup> has been used as the part that demonstrates toxic effects. The UKTAG has in a previous report also proposed standards for total ammonia for High, Good, Fair, and Poor Status [3].

There are extensive data on total ammonia and un-ionised ammonia in fresh waters and it is clear from these that standards proposed by the UK for total ammonia [3] are sufficient to cover the protection provided by the existing standard for un-ionised ammonia. The UKTAG suggests that for freshwaters the requirements for un-ionised ammonia are provided by the use of its proposals on total ammonia, and that meeting these will meet the requirements for ammonia as part of Good Status.

<sup>&</sup>lt;sup>1</sup>2,4-dichlorophenoxyacetic acid (known as 2,4-D)

 <sup>&</sup>lt;sup>2</sup> For dimethoate, we have recommended the adoption of the new standard produced using the European Union's Technical Guidance Document. The values so generated are close to existing standards.
 <sup>3</sup> And the controls and policies for these substances

<sup>&</sup>lt;sup>4</sup> Unionised ammonia  $(NH_3)$  exists in equilibrium in water with a fraction based on the ammonium ion. The un-ionised ammonia is usually calculated from the total ammonia, the pH and temperature.

In salt waters, the UKTAG proposes the continued use the existing salt water standard for un-ionised ammonia.

The UKTAG has looked at aluminium, manganese and tetrachloroethane. There are no existing Environmental Quality Standards for these and the UKTAG is unable to make recommendations at present, but may propose standards in future. These substances should not yet be defined as Specific Pollutants under the Water Framework Directive.

The remaining substances in the starting set of 33 candidates include those covered by the Dangerous Substances Directive but which are not scheduled as Priority Substances under the Water Framework Directive. These are mainly List II Substances under Dangerous Substances Directive. The UKTAG has assessed the priority of the List II Substances: they were ranked at category 3 or below using the method described in Annex A. As a result, the UKTAG advises that the existing Environmental Quality Standards and controls need not be reviewed and should continue to be used.

The substances concerned are listed in Table 1: Part C. They should not be treated as Specific Pollutants under the Water Framework Directive. This advice covers:

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

The UKTAG suggests that existing measures and policies for these substances will deliver progressive reductions without the need for further action at this time. This situation will be reviewed before the repeal of Dangerous Substances Directive in order to identify substances that are still being discharged in significant quantities. In this case the UKTAG will bring forward proposals for the derivation of Environmental Quality Standards.

#### **Deriving the standards**

In its report on the standards set specifically to support Good Ecological Status [3] the UKTAG was fortunate in some instances to have access to sets of chemical data, with matched biological data, that covered much of the UK. This allows an approach to setting standards, for example, for phosphorus and ammonia<sup>1</sup>, that avoided the need to rely mainly on laboratory studies, and the requirement to extrapolate the results of such studies to environmental waters. The availability of such data also provides standards that have the correct properties for use in the assessment of compliance, and in deciding action to improve water quality [3].

<sup>&</sup>lt;sup>1</sup> Used for total ammonia in the Phase 1 report but suitable for un-ionised ammonia

In other cases for its first report [3], the UKTAG was able to conclude that work for other Directives met the requirements for Good Ecological Status under the Water Framework Directive.

For substances that are candidates for Specific Pollutants, the method specified for deriving standards relies much more on laboratory studies of toxicity. Although field data can play a part, extensive sets of data on chemistry and biology are not generally available. Annex B sets out the process and the technical issues. Briefly, this is:

**Step 1**: Collate information on the effects of chemical concentrations on aquatic biota. (The UKTAG has adopted the precedent set for the Priority Substances of taking PNECs from European Risk Assessments, where these are available).

**Step 2**: Assess the quality of these data, and decide which are critical to setting the PNEC, including:

- the reliability of the toxicity data;
- the particular chemical form that is toxic;
- whether naturally occurring backgrounds are likely and whether the biota would acclimatise<sup>1</sup>. This will need to be considered when applying the standard.

**Step 3**: Use these data to derive PNECs for different biota. This can be done by one of two methods:

1. Selecting a concentration that shows no effect on biota in laboratory experiments.

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 concentration shown to have no effect on any of the biota, and tightening it by a factor that lies between 1 and 1000. The factor is called an Assessment Factor, or Safety Factor. Low overall confidence leads to a high Assessment Factor and tighter standards - a more precautionary approach. The result, after applying the Factor, is the PNEC (the proposed standard).

The UKTAG notes that small sets of data require the use of large Assessment Factors<sup>2</sup>. This will lead to standards that are overly protective or precautionary where the small set of data includes the most sensitive biota.

<sup>&</sup>lt;sup>1</sup> Discounting background levels as part of applying the standard is called the Added Risk Approach, where applying the standard without discounting background levels is called the Total Risk Approach.

<sup>&</sup>lt;sup>2</sup> Assessment Factors are used to scale the standard will be one tenth of the value produced by, say, the laboratory work.

#### 2. Using mathematical models

Species Sensitivity Distribution Models describe the number of species likely to be affected by a particular concentration and such models can be used to suggest standards for those chemicals where data are plentiful. In such circumstances the model can improve confidence in the PNEC and so reduce the value of the Assessment Factor that is applied.

**Step 4**: Peer review of the derived PNECs to seek confirmation that they are valid scientifically, and that the data used to derive them are sound and complete.

**Step 5**: Recommend PNECs for each substance. These PNECs may differ for saltwater and freshwater<sup>1</sup>. Often two standards are provided. The first is a short-term standard, usually expressed as a Maximum Allowable Concentration (MAC) and based on the analysis of data on acute (short-term) toxicity.

The second standard is a long-term standard, usually expressed as an Annual Average. It is derived by analysing data from chronic (long term) toxicity tests and, in some cases, from field data. The long-term value also covers long-term or continuous exposure.

The short-term standard aims to protect against intermittent or short-lived periods of exposure<sup>2</sup>. They are often used in the assessments associated with particular incidents. They are not normally used in the context of routine monitoring and compliance assessment because, for most chemicals, the short-term risk is managed sufficiently through the achievement of the long-term standards<sup>3</sup>.

To these steps, the UKTAG suggests we add for the future:

**Step 6**: Compare the results of the work for the UK with that done by other Member States.

<sup>&</sup>lt;sup>1</sup> For a number of the specific pollutants the fresh water and saltwater values are identical However this is not the case for Cr(VI), diazinon, and toluene. For these substances the approach adopted taken for transitional waters will be to utilise the saltwater standards which are usually more stringent. This follows the precedent set by the draft EU Priority Substances Daughter Directive. <sup>2</sup> This can be the main issue for some chemicals, for example, pesticides

<sup>&</sup>lt;sup>3</sup> As discussed later (page 42), where a Maximum Allowable Concentration is used in classification, or within policies on water quality planning to decide actions like conditions in permits, the UKTAG recommends that the compliance statistic is a 95-percentile over one or more complete years.

#### Accepting a PNEC as a draft UK standard

As discussed above, the Directive's method sets out Assessment Factors whose scale increases with the uncertainty in the data. The UKTAG notes that:

- (a) Large Assessment Factors may lead to standards that are very precautionary. The environment agencies take the view that regulatory standards should be based on adequate data in which there is sufficient confidence
- (b) Analytical techniques may not be sensitive enough to quantify contamination at the level of the PNEC<sup>1</sup>. (Effective monitoring requires methods of chemical analysis that are sufficiently sensitive to assess compliance with the proposed standards).
- (c) In the context of 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 standard to be proposed. This step may not be possible in the process and timetable for deriving standards for the first round of River Basin Plans for the Water Framework Directive.

In its proposals therefore, the UKTAG has at this stage proposed new standards in the first round of River Basin Plans only where there is sufficient scientific evidence to set a standard. (For further information see "Uncertainty in data" in Annex B).

The UKTAG has analysed key gaps where new work would help reduce uncertainty. The UKTAG proposes that these gaps are filled by generating data. The UKTAG will make new proposals if evidence becomes available that reduces the level of uncertainty, or if improvements in scientific data (for example, from field monitoring) increase confidence in our proposed standards.

In summary, the UKTAG will propose a new standard if there is:

- adequate confidence in the data<sup>2</sup>;
- a suitable method of chemical analysis: reliable detection of the chemical, and sound estimation of concentrations in environmental waters.

<sup>&</sup>lt;sup>1</sup> In some cases the level of pollution in the environment can be estimated by mathematical modelling. Such models can also be used to suggest the action needs to comply with standards even in cases where there a no reliable methods of chemical analysis that can detect low concentrations in the water environment.

<sup>&</sup>lt;sup>2</sup> The particular Assessment Factors used for the UKTAG's proposals are listed in Annex C.

Where these criteria are met, the UKTAG advises that:

- 1) the PNEC is proposed now as a new UK standard;
- 2) the substance is used as a Specific Pollutant for the Water Framework Directive in the first round of River Basin Plans.

Where we have reviewed the data but these criteria are not met , the UKTAG advises that :

- 3) the existing standard is adopted in the interim as a UK standard;
- 4) the substance is used as a Specific Pollutant for the Water Framework Directive in the first round of River Basin Plans;

In other cases the UKTAG recommends:

- 5) the continued use existing standards and controls under other Directives for the period covered by the first round of River Basin Plans;
- 6) further work by the UKTAG to establish whether substances in Table 1 Part C are still being discharged in significant quantities. Where this is the case UKTAG will develop new standards in accordance with the Annex V of the Water Framework Directive. This work will be described in future reports.

# THE PROPOSALS

#### Proposals for the first set of substances

The report proposes new standards for nine polluting substances: 2,4-D; chromium; cypermethrin; diazinon; dimethoate; linuron; mecoprop; phenol; and toluene. These are in Table 1: Part A. Part A includes the proposal (discussed above) to adopt the UKTAG total ammonia standards [3] as a surrogate for un-ionised ammonia in fresh waters. The UKTAG suggests that these substances are used as Specific Pollutants in the first round of River Basin Plans. For comparative purposes, the existing standards are shown.

Annex C sets out a summary of information for each new standard listed in Table 1 (Part A). 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 documents, considered by the peer review panel, are available on the UKTAG web-site.

Table 1 also lists in Part B those substances for which the UKTAG proposes the use of existing controls and standards<sup>1</sup> for the first round of River Basin Plans. The UKTAG has reviewed these chemicals according to the requirements of the Water Framework Directive and the criteria set out earlier in this report. Lack of adequate data precludes the UKTAG from proposing new standards at this stage. The UKTAG recommends that these substances should still be considered as Specific Pollutants in the first round of River Basin Plans. These chemicals are 2,4-dichlorophenol, ammonia(un-ionised)<sup>2</sup>, arsenic, chlorine, copper, cyanide, iron, permethrin, and zinc.

There is no existing statutory standard for iron. It is proposed that the present nonstatutory standard<sup>3</sup> used for England and Wales should be used for the first round of River Basin Plans, and applied in Scotland and Northern Ireland.

<sup>&</sup>lt;sup>1</sup> For some substances there are no existing standards. This applies to aluminium, tetrachloroethane and manganese. UKTAG will consider how these substances may be regulated in future

<sup>&</sup>lt;sup>2</sup> The existing salt water un-ionised ammonia standard will be maintained because the UKTAG Phase 1 Standards report did not set standards for ammonia in other waters

<sup>&</sup>lt;sup>3</sup> The existing standard, contained in Circular 7/89, has non-statutory status in England and Wales. It does not apply in Scotland or Northern Ireland.

For copper, an industry-led voluntary risk assessment is in preparation. This has not yet been agreed. The UKTAG proposes that the existing standards are retained in the interim.

These standards would apply to the water column. The UKTAG has made no proposals for standards for sediments or biota. Standards in sediments and other issues are discussed in Annex B.

Part C of Table 1 lists substances where the UKTAG proposes, without further review, the continued use of the existing standards for List II Substances under the requirements of the Directive on Dangerous Substances. The substances cover: bentazone; biphenyl; 4-chloro-3-methylphenol; chloronitrotoluenes; 2-chlorophenol; dichlorvos; fenitrothion; malathion; 1,1,1-trichloroethane; 1,1,2-trichloroethane; triphenyltin; and xylene (m, p and o). The substances have been ranked using the method described in Annex A and are not considered a problem in the UK at present.

The standards for these substances (Part C of Table 1) will remain in force until the driving legislation (the Dangerous Substances Directive and the Freshwater Fisheries Directive) is repealed in 2013. The environment agencies will continue to address any failures of the standards in their own right.

Although meeting these standards will contribute to achieving the objectives of the Water Framework Directive, such action will not be included as Programmes of Measures under the Water Framework Directive until or unless the substances are established as Specific Pollutants,.

The UKTAG anticipates that a review of these substances (Table 1: Part C) will be completed before the repeal of their Directives. This review will establish whether the substances are still discharged in significant quantities, and so lead to a decision on whether new standards are required.

Proposals for the addition of further Specific Pollutants will depend on additional research and development. It is unlikely that further substances will be added to the UK list until the second round of River Basin Planning. Such substances will be subject to review and consultation.

The UKTAG is developing its proposals for the classification of water bodies under the Water Framework Directive. This will be the subject of consultation in 2008. The approach on how to apply the exemptions under the Water Framework Directive has yet to be finalised. Such exemptions are allowed on grounds of technical infeasibility or excessive cost.

In Table 1, the PNECs defined as Maximum Acceptable Concentrations are listed with a compliance statistic that is a 95-percentile<sup>1</sup>. The UKTAG recommends that such a compliance statistic, actually a 95-percentile over one or more complete years, is used in cases where the standard is used in classification, or where it is used within policies on water quality planning to decide actions like conditions in permits, or controls on the use of chemicals<sup>2</sup>.

This report has proposed no new standards for metalloids and metals like arsenic, copper and zinc. This was due in part to the need for additional work to reduce uncertainty by looking further at how to take account of the natural background<sup>3</sup>. In the case of chromium the UKTAG judges that it is unnecessary to take account of background concentrations. The only sources of chromium(VI) are anthropogenic; while for chromium(III) the naturally occurring background levels do not approach the levels thought to be toxicologically relevant. This means that for chromium the UKTAG proposes the Total Risk Approach<sup>4</sup> for assessing compliance.

Table	Table 1 (Part A): Proposals for standards						
Water	Exposure	Compliance Statistic	<b>Our proposal</b> (*no change from existing standard)	Existing standard			
PART /	A: Specific Poll	utants for which	new standards are prop	oosed under WFD			
2,4-D (j	ug/l)						
Fresh and	Long-term	Annual mean	0.3	40 (acid) 1 (ester)			
salt	Short-term	95-percentile	1.3	200 (acid) 10 (ester)			

<sup>&</sup>lt;sup>1</sup> As discussed in Annex B

<sup>&</sup>lt;sup>2</sup> Such a definition of the Maximum Acceptable Concentration is a technical requirement for standards where routine sampling is used to assess compliance, or where permit conditions are calculated as those needed to meet an environmental standard in the receiving water [1,9].

<sup>&</sup>lt;sup>3</sup> This is the Added Risk Approach. It is discussed further in Annex B

<sup>&</sup>lt;sup>4</sup> The Total Risk Approach assumes that any sources of a substance, including those arising naturally, contribute towards the potential failure of the standard (Annex B)

Total A	mmonia (mg/l)	(7)			
Fresh	Long-term 90%ile	Lowland High alkalinity	0.6*	0.6	
		Upland low alkalinity	0.3	0.6	
Chrom	ium(VI) (µg/l di	ssolved)(2)			
Fresh	Long-term Annual mean 3.4		3.4	5–50 (1)	
	Short-term	95-percentile	Not available	-	
Salt	Long-term	Annual mean	0.6	15	
	Short-term	95-percentile	32	-	
Chromium(III) (μg/l dissolved) …(2)					
Fresh	Long-term	Annual mean	4.7	-	
	Short-term	95-percentile	32	-	

Cyperr	nethrin (ng/l)			
Fresh	Long-term	Annual mean	0.1	0.2
	Short-term	95-percentile	0.4	2.0
Salt	Long-term	Annual mean	0.1	0.2
	Short-term	95-percentile	0.41	2.0
Diazino	on (µg/l) …(3)			
Fresh	Long-term	Annual mean	0.01	0.03
	Short-term	95-percentile	0.02	0.1
Salt	Long-term	Annual mean	0.01	0.03
	Short-term	95-percentile	0.1*	0.1
Dimeth	oate (µg/l)(4	)		
Fresh	Long-term	Annual mean	0.48	1.0
	Short-term	95-percentile	4.0	-
Salt	Long-term	Annual mean	0.48	-
	Short-term	95-percentile	4.0	-
Linuro	n (µg/l)			
Fresh	Long-term	Annual mean	0.5	2
	Short-term	95-percentile	0.9	20
Salt	Long-term	Annual mean	0.5	2
	Short-term	95-percentile	0.9	-

Месор	rop (µg/l) <sup>1</sup>			
Fresh	Long-term	Annual mean	18	20
	Short-term	95-percentile	187	200
Salt	Long-term	Annual mean	18	20
	Short-term	95-percentile	187	200
Phenol	(µg/l)			
Fresh	Long-term	Annual mean	7.7	30
and salt	Short-term	95-percentile	46	300
Toluen	e (µg/l) (3)			
Fresh	Long-term	Annual mean	50*	50
	Short-term	95-percentile	380	500
Salt	Long-term	Annual mean	40*	40
	Short-term	95-percentile	370	400

<sup>&</sup>lt;sup>1</sup> New ecotoxicological data was acquired during the Stakeholder Review process. These data were subsequently evaluated and a further peer review process undertaken. The conclusions from this exercise were that the values shown should be proposed for Mecoprop. See the data summary sheet in Annex C and full PNEC report for more information.

Table 1	(Part B): Pr	oposals for sta	ndards (continued)	
Water	Exposure Compliance Statistic		Our proposal (*no change from existing standard)	Existing standard
	: Specific Pol bosed for use	lutants - Reviewe	d substances for which	existing standards
2,4-dich	lorophenol (µ	g/l)		
Fresh	Long-term	Annual mean	20*	20
Salt	Long-term	Annual mean	20*	20
Ammon	ia (un-ionised	l) (µg/l)(8)		
Salt	Long-term	Annual mean	21*	21
Arsenic	(µg/l dissolve	ed)		
Fresh	Long-term	Annual mean	50*	50
	Short-term	95-percentile	-	-
Salt	Long-term	Annual mean	25*	25
	Short-term	95-percentile	-	-
Chlorin	e (µg/l)	-		
Fresh	Long-term	Annual mean	2 *(Total Available Chlorine)	2 (Total Available Chlorine)
	Short-term	95-percentile	5 *(Total Available Chlorine)	5 (Total Available Chlorine)
Salt	Short-term	95-percentile	10*(Total Residual Oxidant)	10 (Total Residual Oxidant)
Copper	(µg/l dissolve	d)(1)		
Fresh	Long-term	Annual mean	1-28 *(1)	1-28 (1)
Salt	Long-term	Annual mean	5*	5

Cyanide ("Free" i.e. μg/l of HCN/l)							
Fresh	Long-term	Annual mean	1*	1			
and salt	Short-term	95-percentile	5*	5			
Iron (mg	Iron (mg/l dissolved) (5)						
Fresh	Long-term	Annual mean	1*	1			
Salt	Long-term	Annual mean	Annual mean 1*				
Permeth	rin (µg/l)(6)						
	Long-term	95-percentile	0.01*	0.01			
Zinc (µg	Zinc (µg/l) (1)						
Fresh	Long-term	Annual mean	8–125* (1)	8–125 (1)			
Salt	Long-term	Annual mean	40*	40			

Water	Exposure	Compliance	Our proposal	Existing standard
		Statistic	(*no change from existing standard)	
		for which existin ot Specific Polluta	g standards are propos ints	ed without further
	one (µg/l)	-		
Fresh	Long-term	Annual mean	500*	500
Salt	Long-term	Annual mean	500*	500
Biphen	yl (µg/l)	·		
Fresh	Long-term	Annual mean	25*	25
Salt	Long-term	Annual mean	25*	25
4-Chlor	o-3-methylpho	enol (µg/l)		
Fresh	Long-term	Annual mean	40*	40
Salt	Long-term	Annual mean	40*	40
Chloror	nitrotoluenes	(total) (µg/l)		
Fresh	Long-term	Annual mean	10*	10
Salt	Long-term	Annual mean	10*	10
2-Chlor	ophenol (µg/l)			
Fresh	Long-term	Annual mean	50*	50
Salt	Long-term	Annual mean	50*	50
Dichlor	vos (µg/l)			
Fresh	Long-term	Annual mean	0.001*	0.001
Salt	Long-term	Annual mean	0.04*	0.04
	Short-term	95-percentile	0.6*	0.6
Fenitro	thion (µg/l)			
Fresh	Long-term	Annual mean	0.01*	0.01
Salt	Long-term	Annual mean	0.01*	0.01
Malathi	on (µg/l)	•		•
Fresh	Long-term	Annual mean	0.01*	0.01
Salt	Long-term	Annual mean	0.02*	0.02
1,1,1-Tr	richloroethane	(μg/l)		
Fresh	Long-term	Annual mean	100*	100
Salt	Long-term	Annual mean	100*	100
1,1,2-Tr	richloroethane	- (μg/l)		
Fresh	Long-term	Annual mean	400*	400
Salt	Long-term	Annual mean	300*	300
Triphen	nyltin (total) (µ	g/l)		

Fresh	Short-term	95-percentile	0.02*	0.02	
Salt	Short-term	95-percentile 0.008* 0.008		0.008	
Xylene (total) (µg/l)					
Fresh	Long-term	Annual mean	30*	30	
Salt	Long-term	Annual mean	30*	30	

Environmental Quality Standards apply will apply to all designated water bodies, but in keeping with existing provisions under the Dangerous Substances Directive and the EU proposal for a Priority Substances Daughter Directive 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 standard provided that they do not affect the compliance of the rest of the body with those standards. The EU may develop additional guidance on mixing zones.

Unless specified otherwise all the above standards are expressed in terms of concentrations from unfiltered samples. This could overestimate the level of risk because not all of the substance may be in a form that can be taken up by biota. The approach is consistent with that adopted for standards proposed under Annex X of the Water Framework Directive, and with that used already for standards for the Dangerous Substances Directive.

- (1) For zinc and copper, the existing standard depends on the hardness of the water. The existing statutory zinc standard is expressed as total metal.
- (2) For chromium we propose a Total Risk Approach as natural background levels are not significant
- (3) The UK must continue to comply with the standards set under the Dangerous Substances Directive until its repeal in 2013. Where the work of the UKTAG has derived a more stringent standard than the existing standard under the Dangerous Substances Directive, the new standard will be applied. In the case of the long term standards for toluene, and the short-term standards for diazinon in saltwater, the UKTAG has derived less stringent standards than those in place under the Dangerous Substances Directive. However, the standards under the Dangerous Substances Directive must be applied until 2013, at which point the UKTAG recommends that these standards for toluene and diazinon should be relaxed, where there is scientific evidence that the appropriate level of environmental protection is maintained.
- (4) For dimethoate, the UKTAG recommends the adoption of the new standard derived using the European Union's Technical Guidance Document. The UKTAG will look to gain more data to enable a reduced Assessment Factor, to support the second cycle of River Basin Plans.
- (5) The current standard of 1 mg/l dissolved iron applies only to England and Wales
- (6) Expressed as a 95-percentile in the original report
- (7) In Fresh waters UKTAG recommends the adoption of the total ammonia standard from the UK Environmental Standards and Conditions (Phase 1) report dated August 2006. UKTAG believes that this approach will provide an effective level of protection for both total and unionised ammonia in freshwaters.
- (8) In salt waters UKTAG recommends the continued adoption of the current unionised ammonia standard

# THE IMPLICATIONS FOR RIVERS

#### Our estimates of compliance with the proposed standards

The UKTAG has assessed some of the implications of applying its proposals using the available monitoring data. These implications are discussed below, highlighting:

- the sites which are currently monitored that would exceed a standard;
- the number of rivers that might be reported as less than Good status.

For England and Wales, this is mainly new failure: the waters meet the existing standards but would fail the new standards. For Scotland, SEPA has identified failures for existing and new standards.

Current monitoring is often targeted at sites that are at risk because of past experience or incidents, or knowledge of activities in the catchment. Therefore the results reflect sites where the probability of failure is higher than average: the proportions of failure are not necessarily representative of all rivers.

#### Implications for England and Wales

Table 2 gives an estimate of the number of monitored sites in England and Wales that would not meet the new standards in Table 1 (Part A). Results are given for face-value<sup>1</sup> estimates of failure and for estimates of failure where there is at least 95-percent confidence of failure.

The main purposes for existing monitoring networks are for the Freshwater Fish Directive, Harmonised Monitoring<sup>2</sup>, the Oslo and Paris Convention, and the Dangerous Substances Directive. Table 2 is based on monitoring over the past three years, and includes salt water sites.

<sup>&</sup>lt;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.

Table 2: Implications for England and Wales						
Substance	P	er cent of	monitored fre	eshwater	sites Not	Good
	England		Number of	Wa	ales	Number of
	Face Value	95% confidence	sites monitored	Face value	95% confidence	sites monitored
2,4- dichlorophenol	0.4	0.0	509	0	0.0	23
Chromium	5	2	2424	7	2	236
Cypermethrin	21	1.9	316	19	0	257
Diazinon	4	1.7	485	8	1	247
Dimethoate	0.0	0.0	348	0.0	0.0	200
Linuron	0.2	0.0	480	0	0	67
Mecoprop	2.0	0.1	619	0.0	0.0	78
Phenol	1.6	0.3	681	17	6	103
Toluene	2	0.0	378	0.0	0.0	67
	P	er cent of	monitored salt water sites Not			Good
	Eng	land	and Number of	Wales		Number of
	Face value	95% confidence	sites monitored	Face value	95% confidence	sites monitored
2,4- dichlorophenol	0	0	77	-	-	0
Chromium	21	3	788	10	2	105
Cypermethrin	6	0	16	-	-	0
Diazinon	5	0	88	-	-	0
Dimethoate	0.0	0	114	-	-	0
Linuron	0.0	0	72	-	-	0
Mecoprop	1.4	0	73	-	-	0
Phenol	0	0	64	29	0	24
Toluene	0.0	0	111	0	0	3

#### Implications for Northern Ireland

There are limited data. The indications are:

- Chromium: a limited amount of data on dissolved chromium are available.
- Cypermethrin: an assessment is not possible because of limits of detection. Biological monitoring of upland areas has identified a few problems which may be due to cypermethrin.
- Diazinon: 61 sites are monitored and some have occasional samples that exceed the concentrations in the annual mean standards. One site appears to exceed the annual mean standard itself.
- Phenol: 50 sites monitored. There is no indication of a significant issue.
- Toluene: there are no data.
- 2,4-dichlorophenol: at present there are no monitoring data. This substance has been detected in effluents from waste water treatment works. It may also enter the water environment as a breakdown product of herbicides, particularly from soils.
- 2,4-D: for the last 18 months this substance has been analysed at the downstream end of certain rivers – the OSPAR sites<sup>1</sup>. Whilst the values meet the proposed standards, the sampling stations are well downstream of likely areas of application. The possible effects of dilution, breakdown and uptake suggest these data are not a good estimate of compliance in rivers generally.
- Dimethoate: this substance has also been also analysed at OSPAR sites. The location of the sampling stations and low sampling frequency means that these data do not provide a good estimate of compliance generally.
- Linuron has been detected at environmentally significant levels in private water supplies and in surface waters. For the last 18 months, it has been analysed quarterly at the OSPAR sites. Linuron has not yet been positively detected. These data should be treated with caution as they are located well down stream of areas of application.
- Mecoprop: limited data indicates some potential for exceedence of the proposed standards. Values up to 2.1ug/l have been recorded at abstraction points. Mecoprop has also been detected in effluents from wastewater treatment works.

<sup>&</sup>lt;sup>1</sup> Those sample points at the downstream ends of major rivers that are monitored for the purposes of the Oslo and Paris Convention – OSPAR sites

A survey has been conducted of the Derg catchment. Mecoprop was detected at concentrations just below  $1\mu g/l$ .

Mecoprop has been detected at the OSPAR sites. This suggests that problems may exist in those parts of the catchment bordering the areas of application.

#### Implications for Scotland

The assessment has been carried out for freshwater rivers. There are limited data. The number of river sites monitored for 2,4-D, cypermethrin, dimethoate, linuron, mecoprop, phenol and toluene are particularly sparse: monitoring for these parameters in the past was generally carried out only where there were known sources.

Table 3 expresses the results in terms of river length rather than number of sites.

Table 3: Implications of meeting proposed standards at sites in monitoring networks in Scotland				
Substance	Per cent of r Good	River length monitored		
	Face value	(km)		
2,4-D	0 0		-	
Chromium	2 1		899	
Cypermethrin	0 0		13	
Diazinon	0	0	234	
Dimethoate	0	0	-	
Linuron	0	0	-	
Mecoprop	0	-		
Phenols	0	5		
Toluene	0	0	-	

Whilst SEPA currently has limited monitoring data for many of these substances, some are used in Scotland. Mecoprop, for example, is thought to be widely used as a pesticide. Future monitoring will be targeted at water bodies potentially at risk. Cypermethrin has been detected in some of the groundwater samples taken at sites at risk from sheep dip.

A cypermethrin-based product is used as a bath treatment for the control of sea lice in marine cage salmon farms. SEPA has derived operational standards for cypermethrin and these are used to regulate the use of this chemical in marine fish farms. It has not yet been possible to assess the implications of the proposed standards for cypermethrin for this industrial sector. This may require further consideration, particularly on mixing zones.

### THE RESPONSE TO FAILURE OF THE PROPOSED STANDARDS

The response to reported failures of standards for Specific Pollutants will be 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, the environment agencies have felt they needed to confirm first that there is a real risk to the environment at the location covered by the failure<sup>1</sup>.

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 depend on a step which involves additional and local ecological corroboration of damage. 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. Second, summaries of compliance with a standard across a region or nation may lead to regional and countrywide measures<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 causes. This may involve monitoring and modelling, a consideration of cost-effectiveness and proportionate cost, and looking at the feasibility of securing compliance.

The environment agencies will continue to seek to control 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.

<sup>&</sup>lt;sup>1</sup> Given that a general risk has been established through the development of the standard.

<sup>&</sup>lt;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.

#### Issues stemming from reporting compliance

Water Framework Directive advocates a "risk-based" approach to monitoring. Locations that may be judged to be at low risk on grounds of the absence of threats, and to show no of evidence of relevant impacts. These may not require the type of chemical monitoring required for the assessment of compliance with Environmental Quality Standards<sup>1</sup>.

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>.

#### Refining the understanding of risks

The failure of an Environmental Quality Standard for a Specific Pollutant would not be consistent with reporting Good Ecological Status. The details about how water bodies will be classified and reported have not yet been decided but Figure 2 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.

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

<sup>&</sup>lt;sup>2</sup> Or, within the options of the Directive, set Alternative Objectives for water bodies

<sup>&</sup>lt;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.

Figure 2 includes circumstances in which the environment agencies may be able to use biological data 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.

The assessment of compliance can give misleading estimates of risk if local variations in water quality lead to changes in the distribution of species of a metal beyond the norms covered in setting the standard. Such changes in distribution may alter the toxicity of a metal by affecting the proportions of the forms of the metal that are toxic or benign. Again this is covered in Figure 2 through, for example, the use of speciation models, or through the development of methods to measure the toxic forms directly by chemical analysis.

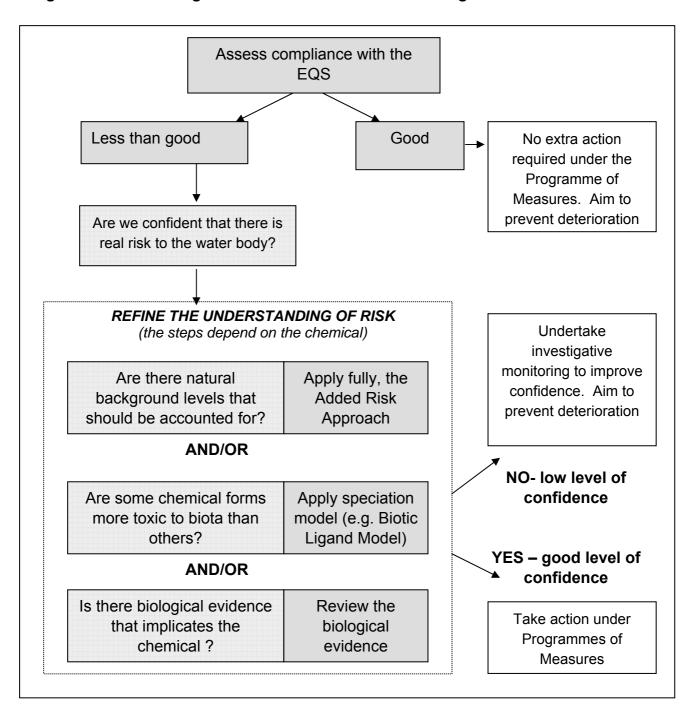


Figure 2: Determining the need for action under the Programme of Measures

#### Implications for particular chemicals

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

For compliance assessment in general, the environment agencies will assess pass or fail against the standard and assign a level of confidence to that statement. As noted above the UKTAG proposes that as a rule, the consideration of the need for action to achieve compliance for Specific Pollutants would not depend on a step which involves additional and local ecological corroboration of damage. The type of action actually taken would be subject to the Directive's considerations of cost effectiveness and disproportionate cost.

There may be cases where decisions in response to a reported failure of certain standards may be improved by reference to direct evidence of the local biological impacts. The details of this will be developed by the environment agencies. It might include cases where the damage took the form of rare incidents.

For substances such as the sheep-dip chemicals, cypermethrin and diazinon, it may be useful to do additional monitoring during certain times of the year, when treatment and applications are most likely to occur. 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 would 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>.

<sup>&</sup>lt;sup>1</sup> Albeit with improved precision for the value for that month.

# **FUTURE WORK**

#### Substances for which there are no existing standards

UKTAG has proposed no new standards for aluminium, manganese or tetrachloroethane. There are no existing standards that can be used in the interim. The UKTAG proposes that more data are collected for these substances.

#### Aluminium:

The PNEC for aluminium may be best expressed as a particular form of aluminium that is the toxicologically relevant form of the metal<sup>1</sup>. It is difficult to measure or quantify this form aluminium in the environment. The UKTAG is undertaking research on the options.

#### Manganese:

The background levels of manganese are much higher than the PNECs emerging from the research and these high levels appear to cause no problems to the ecology of rivers. The UKTAG advises that a need to consider carefully how a standard for manganese could be implemented, how the background levels of naturally occurring manganese can be taken into account.

#### Tetrachloroethane:

The PNEC for tetrachloroethane attracted a large Assessment Factor because there is low confidence in the data. The UKTAG recommends additional testing to produce data from which a PNEC could be proposed.

#### Iron:

Although there are operational standards for iron, they apply only to England and Wales. There is a question about the relative importance of dissolved iron, and the physical effects of iron-rich deposits in causing impacts on biota. This needs to be addressed.

#### Improving the approach for certain metals

The UKTAG has recommended no new standards for metalloids and metals - arsenic, copper, zinc, etc. This was due to the need for additional work to reduce uncertainty by:

<sup>&</sup>lt;sup>1</sup> And because the proportion of the reactive form cannot easily be calculated from the concentration of total aluminium

- a) understanding the effect of local water quality on speciation<sup>1</sup> the forms of the metal present in water and how these vary, and the toxicity of the different forms;
- b) looking further at how to take account of the natural background, for example, by adopting an Added Risk Approach, and generating sufficient scientific confidence that there is a real issue in the environment.

Several projects are underway to support this.

#### Improving confidence through field data

The Water Framework Directive allows the modification of the Assessment Factors where this can be justified by field data. The UK agencies have large amounts of matched data on chemistry and macro-invertebrates that can be analysed for this purpose. Research has compared the data collected for a number of substances including the dissolved concentrations for cadmium, chromium, copper, iron, nickel, lead and zinc [7].

This information provides extra evidence about the link between chemical concentrations and biology. The UKTAG can use this to verify whether or not concentrations of metals close to or exceeding 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. This approach is justified if the biological sampling covers the most sensitive taxonomic groups affected by a substance<sup>2</sup>.

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

This consideration of matched chemical and biological data indicates changes in biology at concentrations that, for most substances, are within an order of magnitude of the PNECs based on laboratory data. Some, for example, chromium, are very close. Given the assumptions underlying the analysis, the indications are that the PNECs suggested by laboratory data are broadly consistent with field data.

<sup>&</sup>lt;sup>1</sup> Speciation: metal speciation is important in assessing the potential toxicological impact. The chemical and physical properties of a species of metal depend on its oxidation state and the proportions of species can vary with the local water quality. A good estimate of the concentrations of key species is important to evaluate the potential risk presented by the metal. Such estimates can be based on chemical analysis, or calculations, or both

<sup>&</sup>lt;sup>2</sup> The analysis of matched chemical and biological data relies on data for benthic invertebrates that, for some substances, are not the most sensitive taxa.

Two exceptions are zinc and iron<sup>1</sup>. Here the laboratory-based PNECs appear too precautionary. For zinc, this may be because the most sensitive ecological group, algae, is not part of the biological sampling from the field: the PNEC for laboratory data is based on data on toxicity to algae.

The UKTAG will update its recommendations where the 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

The UKTAG has investigated the use of Biotic Ligand Models for copper and zinc to support a tiered approach to compliance assessment, as illustrated in Figure 2. This will help take account of the effect of local water quality on the speciation and therefore the toxicity of metals.

The UKTAG will continue to explore the use of Biotic Ligand Models as part of its approach to setting standards for metals and assessing compliance. It will also look at methods of estimating directly, concentrations of the toxicologically relevant form of a metal.

Work is progressing on the use of the Added Risk Approach to take account of natural background concentrations when assessing compliance with some standards for metals. In particular the UKTAG is assessing methods for defining Background Reference Conditions for metals for different geochemical regions in the UK. Until that work is complete the UKTAG cannot recommend suitable background values.

### Standards for other substances

The UKTAG has described how it will set priorities for the development of standards (Annex A). The substances selected will reflect national and regional concerns. The standards will be developed over the first cycle of River Basin Planning.

#### Interactions with other Member States

Other Member States, and Norway, are developing standards for Specific Pollutants. The UKTAG anticipates that during 2008 that there will be an opportunity to compare the proposals in this report with those from other Member States.

<sup>&</sup>lt;sup>1</sup> For which the UKTAG is not at present proposing new standards

We may find that we can also use the standards developed by these other countries particularly where they have been developed under a process that is similar to that used for the UK. For instance the Republic of Ireland is using the same contractors as the UKTAG to support the development of standards. The Republic of Ireland is also considering whether it could adopt standards proposed by the UKTAG.

The UKTAG has also developed working relationships with Belgian, French, German and Netherlands agencies, to share experience and to identify opportunities to develop standards more efficiently.

## **Review of Environmental Quality Standards**

The approach adopted by UKTAG has been designed to minimise levels of uncertainty that may give rise to unnecessarily stringent standards. The UKTAG has developed standards where only where the level of uncertainty is acceptable. For example standards have not normally been proposed when the Assessment Factor (or Safety Factor) is larger than 50.

Where there negotiations are pending in the EU process of Risk Assessment the UKTAG has not set standards for the substances concerned. In addition the UKTAG has commissioned a number of ecotoxicological studies to reduce some of the Assessment Factors.

The UKTAG proposes a regular review of standards, on a six year cycle to coincide with the River Basin Plans.

#### Planned work – in summary

- developing proposals for standards for the remaining substances on the list of candidates for Specific Pollutants;
- developing a position on sediment standards in the light of European discussions (as noted above and in Annex B);
- work on the Added Risk Approach. This involves a method for estimating background concentrations, and of a way of using these in assessing compliance;
- work on how field data might be used to check estimates of PNECs;
- where it has not been possible to recommend a standard at this stage, additional toxicological studies to enhance confidence in data and so provide lower Assessment Factors.

# **ANNEX A: SETTING PRIORITIES FOR DERIVING STANDARDS**

The Water Framework Directive leaves Member States to select Specific Pollutants. It indicates that they should be pollutants from the list of substances in Annex VIII which have a harmful effect on biological quality elements, and which those States have identified as being discharged to water in "significant quantities"<sup>1</sup>. There are many potential Specific Pollutants.

A formal process of setting priorities proved time-consuming, and the UKTAG therefore identified 33 candidates for immediate consideration. These include substances in List II of the Dangerous Substances Directive<sup>2</sup>. They also include substances for which there is no UK standard but which are recognised as posing a risk because they feature most often in the permit conditions for discharges. This usually means that these substances are associated with widespread risk, and that they are "discharged to water in significant quantities". The UKTAG also included in this exercise a number of other substances considered to pose risks, but not particularly from permitted discharges.

The starting point for selecting the 33 candidates was a list of more than three hundred chemicals. This list includes substances covered by existing legislation, those subject to current obligations for monitoring, and substances that have emerged recently as concerns – flame retardants, for example.

The substances in the list were ranked using a method agreed by the UKTAG<sup>3</sup> that is consistent with CIS IMPRESS (Common Implementation Strategy, IMPRESS Working Group) Guidance. For each substance, the UKTAG considered:

- the hazard the persistence of the substance, its potential to bioaccumulate, and its toxicity;
- data on exposure (based either on the level and pattern of use, or on data from monitoring).

Each substance was scored against these criteria for hazard and exposure. The scores were combined in an assessment of the risk to aquatic life. A rank of 1 indicates high risk and a rank of 5 indicates very low risk. A refinement uses modelling to estimate whether a substance will occur in the aquatic environment.

<sup>&</sup>lt;sup>1</sup> See description of quality elements in section 1.1 and 1.2 of Annex V.

<sup>&</sup>lt;sup>2</sup> List II substances included in the list are those that have statutory reporting requirements. Therefore boron, vanadium and cyfluthrin have been excluded after confirming that they were unlikely to pose a risk. <sup>3</sup> For details on the methodology, see [8]. A description of the prioritisation of the full list of chemicals and

results will be given in 'Prioritisation of chemicals for consideration under the WFD standards derivation programme'.

Substances ranked 1 or 2 are considered for inclusion on the UK's list of candidates for Specific Pollutants. For some of these substances, it is better to do more monitoring than to start developing standards now. Substances that score 3–5 will not normally go forward as candidates for Specific Pollutants, unless there are special reasons for including them. Such reasons might be that they are List II Substances under the Dangerous Substances Directive, or that they are known to cause problems.

The UKTAG subjected its findings from this analysis to peer review on whether the development of a PNEC was the most suitable course of action. Alternatives might include changes in the marketing and use of chemicals.

This process has identified 64 substances as potential Specific Pollutants. These are given in Table A1 (Rank 1) and Table A2 (Rank 2).

All chemicals have a unique CAS (Chemical Abstracts Service) registry number. This is given in Tables A1 and A2 to help remove the possibility of ambiguity about the identity of the chemicals.

Table A1: Chemical prioritisation: substances ide	ntified as Rank 1*
Substance	CAS No.
Aroclor 1242	53469-21-9
Aroclor 1248	12672-29-6
Aroclor 1254	11097-69-1
Aroclor 1260	11096-82-5
benzyl butyl phthalate (BBP)	85-68-7
bisphenol A	80-05-7
tert-butyl methyl ether (MTBE)	1634-04-4
Chlorothalonil	1897-45-6
2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol [butylated hydroxytoluene (BHT)]	128-37-0
6,6'-di- <i>tert</i> -butyl-2,2'-methylenedi- <i>p</i> -cresol	119-47-1
3,4-dichloroaniline	95-76-1
4-(dimethylbutylamino)diphenylamin (6PPD)	793-24-8
dioctadecyl 3,3'-thiodipropionate	693-36-7
dioctyl phthalate	117-81-7 ( <i>sec</i> -deriv, i.e. DEHP)
tert-dodecanethiol	25103-58-6
dodecylphenol, mixed isomers (branched)	
N,N'-ethylenebis(4,5,6,7-tetrabromophthalimide)	32588-76-4
Glyphosate	1071-83-6
Hexabromocyclododecane	25637-99-4
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8- hexamethylindeno[5,6- <i>c</i> ]pyran	1222-05-5
Mancozeb	8018-01-7
Mevinphos	7786-34-7
nonylphenol ethoxylates	
Pendimethalin	40487-42-1
Styrene	100-42-5
Triallate	2303-17-5
Triclosan	3380-34-5
vinyl chloride (chloroethylene)	75-01-4

\* Final rankings are subject to peer review

Table A2 Chemical prioritisation: substances in	dentified as Priority 2*
Substance	CAS No.
aniline (benzeneamine)	62-53-3
azinphos-ethyl	2642-71-9
Bromoxynil	1689-84-5
Carbendazim	10605-21-7
4-chloro-2-methylphenoxy acetic acid (MCPA)	94-74-6
DDE (pp)	72-55-9
2,6-di- <i>tert</i> -butylphenol	128-39-2
1,2-dichlorobenzene	95-50-1
1,4-dichlorobenzene	106-46-7
1,3-dichloropropene	542-75-6
Diquat	231-36-7
17a-ethinyloestradiol	57-63-6
Ethylbenzene	100-41-4
Fluroxypyr	69377-81-7
Heptachlorepoxide	1024-57-3
Hexachlorocyclopentadiene	77-47-4
Malachite Green	569-64-2
Metamitron	41394-05-2
Methiocarb	2032-65-7
methyl bromide	74-83-9
octylphenol ethoxylates	
17β-oestradiol	50-28-2
Paraquat	4685-14-7
parathion-methyl	298-00-0
perfluorooctanyl sulphonic acid and its salts (PFOS)	1763-23-1
Pirimicarb	23103-98-2
Pirimiphos-methyl	29232-93-7
polychlorinated biphenyls (PCBs)	1336-36-3
Prochloraz	67747-09-5
Propachlor	1918-16-7
Propiconazole	60207-90-1
Propyzamide	23950-58-5
Tebuconazole	107534-96-3
Terbutryn	886-50-0
1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-	1506-02-1
naphthyl)ethan-1-one	
Thiram	137-26-8

\* Final rankings are subject to peer review

# **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 the risks from contaminated sediments.

Unlike the Priority Substances 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).

We are required by the Water Framework Directive to protect freshwater and marine habitats. Data for salt water are sometimes sparse and so, where possible, if there are insufficient data to develop specific standards for seawater, the UKTAG proposes that the freshwater standard be applied to the salt water column.

We are required to derive standards that will protect from prolonged exposure – longterm standards. These are normally based on an extrapolation from data on chronic (or long-term) toxicity. They are typically expressed as annual mean concentrations.

The expression of a standard as an annual mean concentration also gives a measure protection against higher concentrations. This is because, for most substances, the annual mean is well correlated with the probability that high concentrations occur. For many types of risk, measures to comply with an annual mean act also on the full spread of concentrations that may arise in a water body.

However, for some substances, it may be necessary to set a standard to protect more specifically against high concentrations. Sometimes this is achieved by using as a standard the annual 95-percentile that corresponds to the annual mean<sup>1</sup>.

There may be cases where substances are used or released only for short periods. This occurs, for example, with 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, even though compliance with these standards will give a good indication of risk. In this case we might also have to develop and use standards based more directly on acute toxicity.

<sup>&</sup>lt;sup>1</sup> Typically this will be two or more times greater than the annual mean. The 95-percentile is the values exceeded for 5 per cent of the time.

The UKTAG suggests that such standards based on acute toxicity might be expressed as an absolute limit for the purpose of designing controls on premises or on the use of chemicals. Such controls would be set up to prevent accidents or misuse that would otherwise cause immediate damage like fish kills.

For the annual mean and an annual percentile, compliance can be assessed from a set of representative samples taken over a calendar year or a number of years<sup>1</sup>. For the annual mean and a percentile (but not the absolute limit), the result can be expressed as the statistical confidence that the standard has been failed (or achieved).

In the case of the annual mean or the 95-percentile standards for the water column, there is scope to calculate exactly, the extent of actions needed to secure compliance. 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.

The UKTAG has derived both long-term and short-term PNECs where the data allow. The environment agencies have agreed that long-term (annual average) PNECs will be used as standards, and used for compliance assessment and classification.

The environment agencies have agreed that the short term PNECs, expressed as Maximum Allowable Concentrations, will be used as values to trigger investigations or further monitoring in the event of exceedances. They will not be used generally for classification, but where they are used, the Maximum Acceptable Concentrations will be treated as 95-percentiles that cover one or more whole years.

#### Method for deriving Predicted No Effect Concentrations

The method previously used to develop many standards in the UK [3,6] is regarded by the UKTAG<sup>2</sup> as not meeting the requirements of the Water Framework Directive. Therefore, for this report, the UKTAG re-evaluated this approach and reassessed existing standards<sup>3</sup>.

<sup>&</sup>lt;sup>1</sup> There may also be increasing scope to use mathematical models to make estimates of compliance.

<sup>&</sup>lt;sup>2</sup> This was the result of peer review

<sup>&</sup>lt;sup>3</sup> The UKTAG has applied the requirements of Annex V of the Directive as well as the Environment Agency's *Framework for Standards* [1]. 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).

The first stages of any method comprise the following steps:

- Step 1: collate information on the effects of concentrations on aquatic biota;
- Step 2: assess the quality of these data, and decide which are critical;
- Step 3: use these data to derive Predicted No Effect Concentrations (PNEC) for different biota.

Step 3 is an extrapolation that is intended to account for uncertainties in the data, including 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; it is a measure of the degree of certainty (or consistency) in the data.

If the critical data suggest that a particular concentration has an effect, this might be divided by an Assessment Factor between 1 and 1000 to convert it into a PNEC. A low Assessment Factor (10, or less) is applied where there is a higher degree of confidence. The overall result is that where data are fewer and less consistent, the resultant PNEC is more stringent.

The approach required for the Water Framework Directive is more prescriptive on the minimum amount of data needed, and the size of the Assessment Factor to be used. The approach usually requires the use of a larger Assessment Factor where there are few sets of toxicological data. Overall this gives stricter values. The methods tend to produce similar results where we have sets of data on toxicity for a wide range of species<sup>1</sup>.

The 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 models are called Species Sensitivity Distribution (SSD) Models. Such models are seen as being used to extrapolate to a concentration that will protect a high proportion (typically 95 per cent) of species. The models are increasingly accepted as a valid way of developing standards under the European Union's Technical Guidance Document [4].

<sup>&</sup>lt;sup>1</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 happy that this risk is managed by scientific peer review.

Good sets of data for a wide range of species must be available in order 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 method based on the selection of critical data to which an Assessment Factor is then applied.

### Scientific peer review

Three independent scientists from the UK and other Member States have reviewed the results of the scientific assessments. The reviewers advised on the adequacy of the data, and how the UKTAG should interpret them. The results have also been discussed at three workshops.

Generally, the proposals of the UKTAG represent the consensus of the reviewers. Differences are discussed in the technical reports [2].

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

- chemical speciation;
- the use of field data;
- assessing the feasibility of PNECs as standards.

#### **Chemical speciation**

Certain chemicals exist in water in a range of forms, depending on and varying with aspects of water quality. For example, ammonia occurs as un-ionised ammonia and as the ammonium ion. The un-ionised form is much more toxic. The distribution of these species of ammonia depends strongly on pH and also on temperature.

Metals also occur in various forms. 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.

This has implications for standards. First, the standard may need to be expressed in a way that takes account of local conditions of water quality 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 forms.

The understanding of speciation has influenced the work of the UKTAG. For chromium, there are separate proposals for chromium(III) and chromium(VI), reflecting the difference in toxicity.

# 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 experimental ponds and streams. However, the scientific peer reviewers felt that these data were not good enough in some cases to influence the PNECs. This was where the data were biased towards impacted sites. 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.

The 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). Earlier<sup>1</sup>, this report explained that the UKTAG commissioned research to investigate the relationship between data from chemical monitoring and the biological quality of watercourses. This tended to support the PNECs based on laboratory data but indicated that some PNECs might be over-precautionary. These PNECs need further consideration. In the interim the UKTAG has proposed the continued use of the existing established standards.

# **Existing standards**

The Water Framework Directive requires that new standards are at least as stringent as the standards for the Dangerous Substances Directive. As a consequence, where the PNEC derived for this report is less strict than the existing standard, the UKTAG proposes continued use of the existing 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 the European Union's review of plant protection products (pesticides and growth regulators) [5].

The former has resulted in PNECs for chromium that already conform to the method described in Annex V of the Water Framework Directive, and which have already undergone extensive peer review. The UKTAG has used these PNECs in its own proposals.

<sup>&</sup>lt;sup>1</sup> Page 35

The situation for reviews of plant protection products is more complicated. The assessments were 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 do not fulfil the requirements of its work, and that a full review of such substances is needed.

#### Uncertainty in data

The guidance in Water Framework Directive Annex V is based on a method used generally for assessing risks from chemicals and not just the environmental risks to waters. The guidance is described in the European Union's Technical Guidance Document [4].

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. It has not yet been possible to gather more ecotoxicological data under the timetables set for the Water Framework Directive and the first round of River Basin Plans. The UKTAG has been able to analyse only the data from the scientific literature and commercial sources.

A lack of data produces uncertainty in some of the UKTAG assessments. Applying large Assessment Factors in these cases can lead to proposals for standards that are very precautionary. In some cases this outcome can contradict the results of routine monitoring for chemicals and biology – there is no damage to ecology even though the proposed standard is exceeded in lots of places. There are therefore anomalies between the standards and evidence from monitoring and filed studies, which – given more time- should prompt the standards to be reviewed to allow a more precise safety factor to be calculated.

Bearing in mind the overall approach of the Technical Guidance Document [4], where a PNEC has high uncertainty, the UKTAG proposes that additional data are collected. 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. This affects the proposals in this report for 2,4-dichlorophenol, chlorine, cyanide, iron, permethrin, copper, and ammonia.

## 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 for such substances the present standards and policies are retained in the interim but that the substances are still adopted as Specific Pollutants under the Water Framework Directive. This affects the proposals for ammonia, chlorine, cyanide, iron and permethrin.

## Compliance assessment - background concentrations and chemical availability

Some candidate Specific Pollutants occur naturally, and the concentrations in water may vary for a variety of reasons, including the nature of the local geology. The proposal by the European Union for the Daughter Directive on Priority Substances allows Member States to take account of natural background concentrations when assessing compliance. In addition it may be necessary to take account of the biological availability of certain substances, especially metals.

The UKTAG suggests the following tiered approach:

1. Total and Added Risk Approaches

The Total Risk Approach assumes that all sources of a substance, including those arising naturally, contribute towards the potential failure of the standard.

The Added Risk Approach discounts natural background concentrations. It assumes organisms acclimatise to these. Only the amounts of a pollutant added from anthropogenic sources contribute to failure of the standard.

The Added Risk Approach assumes that the PNECs are based on test organisms that have not adapted to natural background concentrations. Its use requires prior assessment of the variation in the natural background concentration at a local or on regional scale. It also assumes that the step change in water quality that is represented by failure of the standard is equally damaging whether or not there is a natural background level.

2. Availability

For metals, it is usually the case that only the chemically available, and subsequently bioavailable, fraction is important<sup>1</sup>. This suggests that a standard should be expressed in terms of such a fraction<sup>2</sup>.

<sup>&</sup>lt;sup>1</sup> As opposed to the values reported from the chemical analysis for the total metal. The available form might be one of a number of forms present

<sup>&</sup>lt;sup>2</sup> This is especially important where there is no simple relationship between the total amount of metal and the fraction present in the bioavailable form

Biotic Ligand Models have recently been developed for a range of metals including copper and zinc. These models enable the prediction of the ecotoxicologically relevant metal concentration at a site. This prediction is based on a combination of the physico-chemical properties of the water column, and ecotoxicological data. The models open up the possibility of expressing the standards in terms of the available form.

The UKTAG advises that the Total Risk Approach is adopted for all man-made pollutants such as pesticides. An Added Risk Approach, and the use of Biotic Ligand Models, where available, may be best for metals like zinc and potentially metalloids such as arsenic.

#### **Standards in Sediments**

The UKTAG does not advocate setting mandatory standards in sediments. 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 of high spatial variability. This contributes to the difficulty in calculating the controls needed to secure compliance with the standards.

This stance reflects the limited availability of toxicological data and the consequent uncertainty in standards. There are also concerns over the suitability of partitioning theory<sup>1</sup> as an approach to setting such standards.

This approach reflects the views of European Union's Scientific Committee on Toxicity, Eco-toxicity and the Environment on the development of standards for its Priority List. A new European working group has been established to consider the development of new EQ standards. UK will co chair this group and we will watch closely developments in this area.

There may be scope to develop guideline values as opposed to mandatory or statutory Environmental Quality Standards. 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 that supports a case for further investigation and regulatory action.

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

## Conclusions

As a consequence of the discussion in this section, the UKTAG has in this report proposed new standards for 9 substances and that these substances be used as Specific Pollutants under the Water Framework Directive. These are: 2,4-D, chromium; cypermethrin; diazinon; dimethoate; linuron; mecoprop; phenol; and toluene (Table 1: Part A). In addition the UKTAG also includes a proposal to adopt the total ammonia standard earlier work [3] as a surrogate for un-ionised ammonia<sup>1</sup> in fresh waters.

Although PNECs have been derived for the other substances, the UKTAG has not proposed them as new UK standards because:

- more data are needed;
- there is inadequate sensitivity in analytical techniques. In some cases this arises because a high Assessment Factor leads to a stringent standard.

The UKTAG recommends that existing standards continue for 2,4-dichlorophenol, unionised ammonia(saltwater), arsenic, chlorine, copper, cyanide, iron, permethrin and zinc but that these substances are still treated as Specific Pollutants for the Water Framework Directive.

The UKTAG makes no recommendation at this time for new standards for aluminium, tetrachloroethane or manganese. There are no established standards in current use for these substances.

Twelve List II Substances under the Dangerous Substances Directive were not reviewed because the substances were assessed to have low priority. The UKTAG recommends the continued use of the existing standards under the Dangerous Substances Directive and that these substances are not adopted as Specific Pollutants.

The UKTAG proposes further research and data gathering for candidate Specific Pollutants where there is currently too much uncertainty to derive a suitable standard, so that one can be set for future rounds of River Basin Plans. This work will be the subject of a future report.

<sup>&</sup>lt;sup>1</sup> The concentration of the un-ionised ammonia fraction is a function of the total ammonia concentration, the pH value and temperature of the water under consideration. This parameter is normally calculated from these values.

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

2,4-Dichloroph	enoxya	cetic acid (2,4-D	)	
Receiving mediu exposure		Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term		10	0.3	40 (acid), 1 ester)
Freshwater/shor	t-term	10	1.3	200 (acid), 10 (ester)
Saltwater/long-	term	10	0.3	40 (acid), 1 (ester)
Saltwater/short	-term	10	1.3	200 (acid), 10 (ester)
Recommendatio	<u>n</u>			·
not subject to exc	essive u		nmental Quality Standa current analytical capa sessment	
Background Info	rmation	:		
Properties and fate in water	water c		adsorbed to sediment	will mostly remain in the . Bioconcentration of
Factors affecting derivation of the PNEC	The PNECs described are based on a technical assessment of ecotoxicity data for 2,4-D, its salts and esters, along with any data that relate impacts under field conditions to exposure concentrations. Analysis of the data showed no compelling evidence for differences in toxicity of these different chemical derivatives and so the data can be combined for PNEC derivation. The data were subjected to quality assessment by the authors and an independent peer review panel.			
Long-termEffect on biota: The lowest valid long-term toxicity value is an estimated 60-day No Observed Effect Concentration (NOEC) of for the effects on the aquatic macrophyte M. sibiricum. Reliable term NOECs are also available for algae, invertebrates and fish.		city value is an ation (NOEC) of 3.3 μg/l ricum. Reliable long-		
	<b>Recommended PNEC:</b> PNEC <sub>freshwater_lt</sub> of 0.3 $\mu$ g 2,4-D/l (after applying an Assessment Factor of 10)			
	<b>Change from existing EQS</b> : This value is appreciably lower than the existing EQS of 40 $\mu$ g/l for 2,4-D acid and 3 times lower than the existing EQS of 1.0 $\mu$ g/l for 2,4-D esters			
Short-term PNEC for freshwaters:	inverte is a 14- <i>sibiricu</i> freshwa	brate and fish spe day growth EC50 <i>m</i> . There is a cons ater organisms, wh	short-term data are avected side and the lowest valid s of 13 $\mu$ g/l for the macrosiderable short-term tox nich shows that macrop be amongst the most s	hort-term toxicity value ophyte <i>Myriophyllum</i> icity database for hytes such as
	<b>Recommended PNEC:</b> PNEC <sub>freshwater_st</sub> of 1.3 $\mu$ g 2,4-D/I (after applying an Assessment Factor of 10)			
	existing	•		eciably lower than the lower than the

Long-term PNEC for salt waters:	<b>Effect on biota</b> : Long-term freshwater and saltwater data have been combined to derive the PNEC. No saltwater macrophyte (e.g., saltmarsh plant) data are available and there is no evidence from the available long-term saltwater data to suggest that other saltwater species (particularly those that are exclusively saltwater in distribution) would be more sensitive. It is therefore recommended that the freshwater PNEC is adopted to protect saltwater taxa.
	Recommended PNEC: PNEC <sub>saltwater_lt</sub> of 0.3 µg 2,4-D/I
	<b>Change from existing EQS:</b> This value is appreciably lower than the existing EQS of 40 $\mu$ g/l for 2,4-D acid and lower than the existing EQS of 1.0 $\mu$ g/l for 2,4-D esters
Short-term PNEC for salt waters:	<b>Effect on biota:</b> Reliable short-term saltwater toxicity data are available for algae, invertebrates and fish. No saltwater macrophyte (e.g., saltmarsh plant) data are available and there is no evidence from the available short-term saltwater data to suggest that other saltwater species (particularly those that are exclusively saltwater in distribution) would be more sensitive. It is therefore recommended that the freshwater PNEC is adopted to protect saltwater taxa.
	Recommended PNEC: PNEC <sub>freshwater_st</sub> of 1.3 µg 2,4-D/I
	Change from existing EQS: This value is lower than the existing EQS of 200 $\mu$ g/l for 2,4-D acid and the existing EQS of 10 $\mu$ g/l for 2,4-D esters
PNEC for secondary poisoning:	<b>Effect on biota:</b> The bioconcentration factor (BCF) trigger of 100 in whole fish is not exceeded by 2,4-D acid or 2,4-D salts or butoxyethyl ester, so there is no need to derive PNECs for secondary poisoning. Although the estimated BCF for the 2-ethylhexyl ester is 5600, no calculation for secondary poisoning is required as the half-life in natural water is 6.2 hours, which is lower than the trigger of 12 hours.
	Recommended PNEC: none recommended
	Change from existing EQS: no change
PNEC for sediments	A sediment quality standard should not be required for 2,4-D because the log Kow for the acid and salts do not exceed the trigger value in the Technical Guidance Document [4] of a log Kow of >3, and the more hydrophobic esters have a short half-life. Data on direct toxicity to sediment-dwelling organisms were not found.
	Recommended PNEC: none recommended.
	Change from existing EQS: not applicable
Analysis	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 chromatography-mass spectrometry (GC-MS), capable of achieving detection limits as low as 10 ng/l, should offer adequate performance to analyse for 2,4-D.
Implementation	Determination of pass or failure can then be based on comparison with the PNEC, including a consideration of sampling error

2,4-Dichloroph	enol	
Receiving medium and exposure		Existing EQS (µg/l )
Freshwater/lon	g-term	20
Freshwater/sho	ort-term	No proposal
Saltwater/long	g-term	20
Saltwater/shor	t-term	No proposal
Recommendation         PNECs derived according to the Annex V methodology are unsuitable for use as         Environmental Quality Standards because they are subject to excessive uncertainty. This         uncertainty would be reduced by undertaking additional ecotoxicity testing, which could         lead to a change in the proposed PNECs.         It is recommended that the existing freshwater and saltwater long-term Environmental         Quality Standards are retained. EQSs for 2,4-dichlorophenol were described in a report         published by the Environment Agency in 1997 (Environment Agency 1997).		
Background Infe		
Properties and fate in water	erties and Dichlorophenol compounds are considered to act as polar narcotics in	
Long-term PNEC for freshwaters:	c for applying a safety factor of 10 (to account for extrapolation to a no-	
Short-term PNEC for freshwaters:	No shor	t-term standards are proposed

Long-term PNEC for salt waters:	Given the limited data on the toxicity of 2,4-dichlorophenol to saltwater organisms (including the absence of reliable long-term toxicity data), it was proposed that the EQSs set for the protection of freshwater life should also be adopted as tentative values for the protection of saltwater life. This was justified by the fact that the available data on the toxicity, fate and behaviour of 2,4-dichlorophenol was similar under both freshwater and saltwater conditions.
Short-term PNEC for salt waters:	No short-term standards are proposed

#### Reference:

Environment Agency (1997) Proposed Environmental Quality Standards for 2-, 3- and 4-Chlorophenol and 2,4-Dichlorophenol in Water. Environment Agency technical Report P46/i688

Ammonia		
	Proposed EQS	
Receiving medium and exposure	'High'	'Good'
Freshwater – upland and low alkalinity	0.2 mg/l (total, as a 90%ile)	0.3 mg/l (total, as a 90%ile)
Freshwater – lowland and high alkalinity	0.3 mg/l (total, as a 90%ile)	0.6 mg/l (total, as a 90%ile)
Saltwater/long-term	21 µg/l (un-ionised,	as an annual mean)
Saltwater/short-term	No proposal	

#### Recommendation

In the Phase 1 Standards report, standards for total ammonia have been developed on the basis of ammonia conditions associated with macro-invertebrate communities at High and Good Status. Although technical PNECs for unionised ammonia have been investigated using the Annex V methodology, analysis suggests the outcomes (risk of failure and levels of protection) are broadly similar. For this reason, and to avoid confusion, we propose to defer to the Phase 1 standards for total ammonia. Further work will be done during the first cycle of River Basin Management Plans to confirm that the proposed values also protect communities of freshwater fish, though this seems likely from the comparison with present standards.

The Phase 1 Standards report does provide equivalent standards for saltwaters. Proposals for long –term saltwater standards developed according to the Annex V methodology were subject to high uncertainty and could not be quantified using current analytical methods. For this reason, we propose to retain existing long-term standards for the protection of saltwater organisms. No short-term standards are proposed.

#### **Background Information:**

•	
fate in water	Ammonia is hazardous due to its toxic and sub-lethal impacts on fish and macro-invertebrates. It is a decay product of nitrogenous organic wastes and of the breakdown of animal and vegetable wastes. Sewage effluent from treatment works is a major source of ammonia in rivers. Agricultural diffuse sources of ammonia are also important. It comprises two principal forms: the ionised ammonium ion $(NH_4^+)$ and un-ionised ammonia $(NH_3)$ . The toxicity of ammonia to fish is attributable mainly to the un-ionised NH <sub>3</sub> molecule. The proportion of un-ionised ammonia increases with increasing temperature and pH, but decreases with increasing salinity. At pH 8.5, the proportion of un- ionised ammonia is approximately 10 times that at pH 7.5 and, for every 9°C increase in temperature, the proportion of un-ionised ammonia approximately doubles.

Arsenic		
Receiving medi exposure		Existing EQS for Total Dissolved Arsenic ( $\mu$ g/I )
Freshwater/lon	g-term	50
Freshwater/sho	rt-term	No proposal
Saltwater/long	-term	25
Saltwater/shor	t-term	No proposal
PNECs derived a comply with the 'r and saltwater long described in WR	ccording t no deterio g-term En c's 1992 re	proposed PNECs to the Annex V methodology cannot yet be implemented. To ration' principle, it is recommended that the existing freshwater vironmental Quality Standards are retained. These are eport to the Department of Environment (WRc 1992) which ater and saltwater EQSs previously proposed by Mance <i>et</i>
Background Info	ormation:	
Properties and fate in water	Arsenic is a naturally occurring element but also enters the environme from anthropogenic sources. Under aerobic conditions, the pentavaler form As(V) predominates over the less thermodynamically stable trivalent form As(III). Arsine (–3) and elemental arsenic occur only under strongly reducing conditions and are rarely found in surface waters.	
	Whereas As(III) is thought to act by binding to sulfhydryl groups in proteins, As(V) competes with phosphorus to affect oxidative phosphorylation. Indeed, phosphorus can offset the toxicity of arser Arsenic can also occur as organic compounds, but these are less to than the inorganic forms.	
Long-term PNEC for freshwaters:	a 16-we assessn EQS of	hwater EQS is based on an LC10 of 0.14 mg l <sup>-1</sup> as obtained in ek study on bluegill sunfish ( <i>Lepomis macrochirus</i> ). An nent factor of 2 was applied to this value resulting in a rounded <b>50 μg l<sup>-1</sup> total dissolved arsenic</b> expressed as an annual concentration.
Short-term PNEC for freshwaters:	No shor	t-term standards are proposed
Long-term PNEC for salt waters:	96-hour concent an 18-ho of 20 wa an extre	protection of saltwater life, the lowest acute effect values were a LC50 of 508 $\mu$ g l <sup>-1</sup> for copepod ( <i>Acartia clausi</i> ) and a ration of 577 $\mu$ g l <sup>-1</sup> observed for arrested spore development in our study on red alga <i>Plumaria elegans</i> . An assessment factor as applied to these values because the available data covered amely small range of biota. This resulted in an EQS of <b>25 <math>\mu</math>g l<sup>-1</sup> asolved arsenic</b> expressed as an annual average ration.

Short-term PNEC for salt waters:	No short-term standards are proposed

References:

WRc (1984) Proposed Environmental Quality Standards for List II substances in Water. Arsenic. WRc Technical Report TR 212. WRc Plc, Frankland Road, Wilts SN5 8YR

WRc (1992) Revised Environmental Quality Standards for Arsenic in Water. Final Report to the Department of the Environment, WRc Report No: DoE 2633/1. WRc Plc, Frankland Road, Wilts SN5 8YR

Chlorine		
Receiving med	ium and exposure	Existing EQS (µg/I )
Freshwater/long-term		2 (TAC)
Freshwat	er/short-term	5 (TAC)
Saltwate	er/long-term	No proposal
Saltwate	er/short-term	10 (TRO)
Recommendatio	n	
EU Risk Assessment Reports (EU RARs) have been compiled for chlorine and hypochlorite. The UK is committed to the use of PNECs derived through this process as the basis for Water Framework Directive Annex X EQSs. However, these cannot yet be implemented and so it is recommended that the existing freshwater and saltwater Environmental Quality Standards are retained. These are described in the 1994 UK EQS report (NRA 1994) where the freshwater standards were expressed as total available chlorine (TAC) and a saltwater short-term standard as total residual oxidant (TRO). The long-term standard for freshwater was derived from data relating to the toxicity of chloramine, since it was found to be more persistent in the environment than free chlorine (HOCI).		
Background Info	ormation:	
Following dissolution chlorine (Cl <sub>2</sub> ) but, at h hypochlorite (OCl <sup>-</sup> ) pr chlorine is present as present as OCl <sup>-</sup> . Chlo The species of primal available chlorine (FA acid and the hypochlo chloride. The main removal pa degradation (e.g. rea- volatilisation and pho bioaccumulation of ch chlorinated organic by Hypochlorous acid is Consequently, across (6.5–7.2), chlorine is plays a role in the spe pronounced impact th sensitive to chlorine a		eactive gas that dissolves readily in water. in water, the main species at pH <2 will be higher pH values, hypochlorous acid (HOCI) and redominate. At 25 C and pH 7, 70 per cent of s HOCI and, at pH 8, 80 per cent of the chlorine is brine can also form toxic compounds with amines. any concern here are those determined as free AC), which is the concentration of hypochlorous orite ion, excluding other chlorine compounds and athways for chlorine species in water are abiotic action with other chemicals present in the water), otolytic reactions. Biodegradation and hlorine species are not important and only by-products would be bioaccumulated to any extent. a more toxic than the hypochlorite ion. s the pH range most usually found in freshwaters likely to be in its most toxic form. Temperature also eciation of chlorine, although it has a less han pH. Aquatic organisms tend to be more at higher temperatures and so added care may be orine is present in heated water discharges.

Long-term PNEC for freshwaters:	Chloramine is a product resulting from the reaction between chlorine and naturally occurring amines. A 15-week study reported that exposure to 3.4 µg l <sup>-1</sup> total chloramine significantly reduced the number of offspring produced by the shrimp <i>Gammarus</i> sp. and, therefore, an <b>EQS of 2 µg l<sup>-1</sup> TAC</b> expressed as an annual average concentration was proposed to protect freshwater aquatic life from continuous exposure to chlorine.
Short-term PNEC for freshwaters:	The short-term standard was based on a 48-hour $LC_{50}$ of 9.3 µg $\Gamma^1$ TAC for mayfly ( <i>Isonychia</i> sp.). An assessment factor of 2 was considered adequate because there was a large dataset on the acute effects of chlorine (decreasing the uncertainty in ensuring protection of the most sensitive species); the available data also indicated a relatively small acute to chronic ratio, and free chlorine (HOCI) is not persistent. This resulted in an <b>EQS of 5 µg <math>\Gamma^1</math> TAC</b> expressed as a maximum allowable concentration. However, data for fish suggested that some avoidance behaviour and depressed activity might occur at this concentration.
Long-term PNEC for salt waters:	A saltwater long-term standard was not proposed due to a lack of chronic exposure data for chloramines and bromamines.
Short-term PNEC for salt waters:	The standard derived for marine waters was expressed as total residual oxidant (TRO), i.e. the sum of both 'free' and 'combined' residual oxidant including both chlorine and bromine compounds. The early life stages of fish were found to be particularly sensitive to chlorine. For the larvae of both plaice ( <i>Pleuronectes platessa</i> ) and sole ( <i>Solea solea</i> ), an LC50 of 28 $\mu$ g l <sup>-1</sup> TRO was reported. Based on the relatively large dataset on acute effects combined with the relatively short persistence time of free residual oxidants in marine water, an assessment factor of 2 was applied to this value to give an EQS of 10 $\mu$ g l <sup>-1</sup> TRO, expressed as a maximum allowable concentration.

Reference: NRA (National Rivers Authority now the Environment Agency) (1994) Proposed Environmental Quality Standards for Chlorine in Fresh and Marine Waters. R&D Note 332.

Chromium				
Receiving medi exposure		Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/I)
		Chro	mium(VI)	
Freshwater/long	g-term	3	3.4	Range from 5–50 depending on hardness
Saltwater/long	-term	10	0.6	15
Saltwater/short	t-term	10	32	No standard
		Chro	mium(III)	
Freshwater/long	g-term	10	4.7	No standard
Freshwater/sho	rt-term	10	32	No standard
Recommendatio	<u>n</u>	· · ·		
Chromium(VI):				
	oes not r cale.	leed to consider l	d when applying PNEC background levels at a	
•	r			
Properties and fate in water	Chromium occurs naturally but also enters the environment from anthropogenic sources. In surface waters, chromium exists in two oxidation states, 3+ (III) and 6+ (VI), but the more thermodynamically stable state is Cr(VI). Almost all the Cr(VI) in the environment arises from human activities. Conversion from Cr(VI) into Cr(III) can be slow, depending on the prevailing conditions that can stabilise Cr(III). Chromium readily sorbs to sediments although the high water solubility of Cr(VI) limits the extent to which this occurs. Chromium(III) is less toxic than Cr(VI) and its low solubility in water limits its availability. PNECs for Cr(VI) and Cr(III) are considered separately.			
Factors affecting derivation of the PNEC	The PNECs described are based on a technical assessment of available ecotoxicity data for chromium, along with any data that relate impacts under field conditions to exposure concentrations.			
	An EU Risk Assessment has been compiled for chromium. Toxicity data taken from the EU Risk Assessment Report (EU RAR) were not subjected to additional quality assessment as both the authors and an international advisory forum of EU experts had already assessed these.			

	In the EU RAR, a total risk approach has been adopted as almost all hexavalent chromium [Cr(VI)] in the environment is of anthropogenic origin and natural background levels of Cr(VI) are, therefore, negligible.
	Long-term studies with freshwater invertebrates do not show any clear influence of water chemistry on Cr(VI) toxicity. Although relationships between hardness and toxicity have been described for divalent metal cations, the fact that the chromium species here are oxoanions means that their toxicity may be less influenced by water chemistry. Detailed relationships between the behaviour of chromium and environmental factors were not developed in the EU RAR and the UKTAG agrees that the data do not warrant normalisation of chromium toxicity for water quality parameters.
	PNECs for Cr(III) were developed in the EU Risk Assessment Report but only for the protection of freshwater organisms, due to a lack of salt water toxicity data. There are no existing Environmental Quality Standards specifically for Cr(III).
Chromium(VI)	
Long-term	Effect on biota:
PNEC for freshwaters:	There are sufficient long-term data to construct a Species Sensitivity Distribution Model (SSD) and to estimate a threshold based on the lower 5-percentile from the model fitted to the ranked No Observed Effect Concentrations (the HC5). In accordance with the Annex V methodology, an Assessment Factor of 3 is applied to the HC5.
	This was the agreed approach in the EU Risk Assessment Report and, although a PNEC may also be derived using the deterministic (Assessment Factor) approach, the value from the SSD model has been applied here.
	<b>Recommended PNEC:</b> 3.4 $\mu$ g/l (after applying an Assessment Factor of 3)
	<b>Change from existing EQS:</b> the proposed PNEC corresponds to the lower end of the range of values covered by the existing standard
Short-term PNEC for freshwaters:	None proposed: The long-term freshwater PNEC was derived using the Species Sensitivity Distribution Model (SSD) while the short-term PNEC estimated using Assessment Factors. The result is that the short-term standard is stricter than the long-term. This is not acceptable and since a long-term PNEC is of greater utility, a short-term standard is not recommended.
Long-term	Effect on biota:
PNEC for salt waters:	The lowest available No Observed Effect Concentration of 4–6 $\mu$ g/l in <i>Mytilus edulis</i> is unbounded (in other words it was the highest concentration tested) and consequently is unsuitable for PNEC derivation. The next lowest value, a 2-week No Observed Effect Concentration of 6 $\mu$ g/l for mortality in <i>Nereis arenaceodentata</i> , was regarded as valid for PNEC derivation in the EU Risk Assessment Report. Since reliable long-term data are also available for five other taxa, an Assessment Factor of 10 can be justified

	<b>Recommended PNEC:</b> 0.6 µg/l (after applying an Assessment Factor of 10)			
	<b>Change from existing EQS:</b> The existing EQS for the protection of marine organisms is higher, at 15 $\mu$ g/l dissolved chromium.			
Short-term	Effect on biota:			
PNEC for salt waters:	A 96-hour LC50 of 0.32 mg/l obtained with <i>Callinectes sapidus</i> is the basis for the derivation of the PNEC. An Assessment Factor of 10 is considered adequate to extrapolate to the PNEC because good quality data are available for algae, crustaceans and echinoderms. Although acute data for salt water fish are lacking, chronic data indicate they are unlikely to be the most sensitive group. In addition, the resulting PNEC will be in the range of the lowest No Observed Effect Concentrations obtained for species with a short life cycle such as algae and crustaceans.			
	<b>Recommended PNEC</b> : 32 $\mu$ g/l (applying an Assessment Factor of 10)			
	Change from existing EQS: No existing EQS			
Chromium(III)				
Long-term PNEC for freshwaters:	<b>Effect on biology:</b> The lowest reliable chronic No Observed Effect Concentration values are 0.05 mg/l for rainbow trout ( <i>Oncorhynchus mykiss</i> ) and 0.047 mg/l for <i>Daphnia magna</i> , from studies using soft water. Long-term toxicity data are available for representatives of at least three different taxonomic groups, permitting the use of an Assessment Factor of 10.			
	<b>Recommended PNEC:</b> 4.7 $\mu$ g/l (after applying an Assessment Factor of 10)			
	Change from existing EQS: No existing EQS			
Short-term	Effect on biology:			
PNEC for freshwaters:	The lowest EC50 of 0.32 mg is reported for <i>Selenastrum capricornutum</i> biomass gain over 96 h. Given the availability of data for a number of taxa, an Assessment Factor of 10 applied to the EC50 of 0.32 mg/l for <i>Selenastrum capricornutum</i> is recommended			
	<b>Recommended PNEC:</b> 32 $\mu$ g/l (including an Assessment Factor of 10)			
	Change from existing EQS: No existing EQS			
Chromium(VI) ar	nd Chromium(III)			
Analysis	The lowest proposed PNEC derived for chromium is 0.6 µg/l. Current analytical methodologies are able to discriminate between chromium(VI) and chromium(III), although chromium(III) is routinely estimated by subtraction of chromium(VI) from total chromium concentrations. Detection limits as low as 15ng/l are achievable. Since the data quality requirements are that at one-third of the EQS total measurement error should not exceed 50 per cent, they should offer adequate performance to analyse for the lowest PNEC (salt water/long- term) derived according to the European Union's Technical Guidance Document [4].			

Implementation	The favoured thermodynamic state for Cr is Cr (VI) in oxygenated waters above pH 5. However, biotic and abiotic factors may counteract this tendency and can reduce Cr (VI) to Cr (III). These factors include enzymatic reduction in organisms, oxidation of dissolved organic carbon and any ferrous ions present.
	Thus chromium present in environmental waters will be a mix of VI and III oxidation states. Work undertaken by Comber and Gardner1 in the Humber catchment indicated that about half the chromium present is in the VI state.
	Background levels of chromium in the environment in most areas of the UK are estimated to be well below 1µg/l.
	We expect that Environmental Quality Standards for chromium(VI) will be more widely used than for chromium(III). The Total Risk approach will be applied in the first instance where Environmental Quality Standards for chromium are implemented,. In the event of failures an Added Risk Approach could be useful but an appreciation of Cr(III) natural background concentrations would be required over a defined range of geographical scales.
	In order to ensure that regulatory action is targeted on those locations where there is a real risk to biota, the UKTAG proposes a tiered approach to compliance assessment. The underlying principle behind this tiered approach is that an initial assessment is made based on measurements of total, dissolved chromium concentrations (that which passes through a 0.45 µm filter) to exclude particulate-bound residues. If these were included, the level of risk would be over-estimated. Any sites where the dissolved environmental concentration is less than the PNEC for either chromium(VI) or chromium(III) are clearly deemed to have passed the EQS. The others cases are not necessarily failures however. That can only be determined through additional effort that examines concentrations of the individual species of chromium and, in the case of chromium(III), the local background conditions.
	Assuming that there would be greater interest in controlling chromium(VI) than chromium(III), the UKTAG recommends focusing initially on assessing compliance with the PNEC for chromium(VI).

<sup>&</sup>lt;sup>1</sup> S. Comber and M. Gardner, *Journal of Environmental Monitoring*, 2003, **5**, 410-413

Copper	
Receiving medium and exposure	Existing EQS for dissolved copper (µg/l)
Freshwater / long term	
Hardness bands: 0–50 mg CaCO <sub>3</sub> /I 50–100 mg CaCO <sub>3</sub> /I 100–250 mg CaCO <sub>3</sub> /I >250 mg CaCO <sub>3</sub> /I	1 6 10 28
Freshwater/short term	No proposal
Saltwater/long term	5
Saltwater/Short term	No proposal

#### Recommendation

A voluntary EU Risk Assessment Report is being compiled for copper. The UK is committed to the use of PNECs derived through this process as the basis for Water Framework Directive Annex VIII EQSs. However, there remain some issues about the implementation of these PNECs as standards and so it is recommended that, at least in the interim, existing freshwater and saltwater Environmental Quality Standards are retained.

The EQS values reported in 1984 (WRc 1984) were for dissolved copper and the freshwater standards were banded according to water hardness.

Background Information:		
Properties and fate in water	Copper occurs naturally in the environment, usually as compounds, but it is also widely used in industry and household goods. It normally exists in solution as the cupric (2+) ion, complexed with inorganic ions or organic ligands, as insoluble precipitates, or sorbed to particulate matter. Although the cuprous (1+) ion can also occur, it is unstable in aqueous media.	
	The form present influences toxicity and, in turn, depends strongly on water quality factors such as pH, hardness, and the availability of inorganic and organic ligands. The effects of these factors on speciation and availability of copper, and their interaction with biotic ligands (e.g., fish gills) and, therefore, bioavailability are now well understood, and this has enabled the development of Biotic Ligand Models that are the basis of PNECs derived within the voluntary risk assessment.	
Long-term PNEC for freshwaters:	Standards proposed by the European Inland Fisheries Advisory Commission (EIFAC) were adopted as annual average concentrations for the protection of freshwater fish. Because the available data for other freshwater life were limited and varied in nature, the EIFAC EQS values were also used for the protection of other aquatic life.	
Short-term PNEC for freshwaters:	No standard proposed	

Long-term PNEC for salt waters:	Only one chronic toxicity datum was available on which to base a marine standard: an effects concentration of 54 $\mu$ g/l was obtained in a life-cycle test on the mysid shrimp, <i>Mysidopsis bahia</i> . Acute toxicity data indicated that another crustacean, <i>Acartia tonsa</i> , and embryo of the summer flounder, <i>Paralichthys dentatus</i> , were more sensitive. Therefore, an assessment factor of 10 was applied to the shrimp datum resulting in a saltwater standard of 5 $\mu$ g/l expressed as an annual average concentration.
Short-term PNEC for salt waters:	No standard proposed

Reference: WRc (1984) Proposed Environmental Quality Standards for List II substances in Water. Copper. WRc Technical Report TR 210. WRc Plc, Frankland Road, Wilts SN5 8YR

Cyanide		
Receiving medium and exposure		Existing EQS for "free" cyanide (µg/l )
Freshwater/long-term		1
Freshwat	er/short-term	5
Saltwate	er/long-term	1
Saltwate	er/short-term	5
Recommendatio	'n	
uncertainty becau assessment facto sensitivity) if they complies with the standards for "fre until these difficul	use of a lack of reliable ors making the resulting were adopted as EQS Annex V methodology e" cyanide, developed ties can be resolved.	nodology are associated with a high degree of e ecotoxicity data. This requires the use of large g PNECs difficult to implement (analytical ss. For these reasons, a robust standard that cannot yet be implemented and existing in 1998 (Environment Agency 1998) are proposed
Background Info	1	
Properties and fate in water	Cyanides occur ubiquitously in the environment. 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. Cyanides are readily soluble in water where they exist in the free state (CN <sup>-</sup> and HCN), as simple cyanides (e.g. NaCN), complex cyanides (organic or metal complexes) or total cyanide (all available species). Hydrogen cyanide (HCN) dissociates in water to give the free ion (CN <sup>-</sup> ) under alkaline conditions (50 per cent of both forms at pH 9.36). The CN <sup>-</sup> ion has a half-life of 15 days in water; HCN has a tendency to volatilise from water, with a half-life measured from hours to a few days. Simple cyanide are very stable with limited dissociation; metal complexation can reduce bioavailability. Cyanide acts as a respiratory depressant and can inhibit aerobic metabolism. Free cyanide ions can also pass though the gill membranes. Undissociated HCN is primarily responsible for toxicity, with HCN being more toxic than CN <sup>-</sup> . However, CN <sup>-</sup> contributes to toxicity due to formation of HCN at pH values up to around 8. Simple cyanides readily dissociate and hydrolyse to form HCN and CN <sup>-</sup> and, therefore, have the same toxicity as free cyanide.	

Long-term PNEC for freshwaters:	Chronic toxicity data were limited to algae, crustaceans and fish with significant sub lethal effects, particularly effects on the reproductive physiology and growth of fish. A reasonably extensive and reliable dataset indicated effects of cyanide on salmonid reproduction at around 10 $\mu$ g l <sup>-1</sup> . However, effect concentrations as low as 5 $\mu$ g l <sup>-1</sup> were also reported in two other studies, though the effects observed were difficult to interpret. An assessment factor of 10 was applied to the salmonid reproduction value resulting in a freshwater EQS of <b>1</b> $\mu$ g l <sup>-1</sup> expressed as an annual average.
Short-term PNEC for freshwaters:	The short-term freshwater standard was based on fish data, as fish appeared to be the most sensitive group of organisms. The lowest credible acute effects concentration for free cyanide was a 96-hour LC50 of 43 $\mu$ g l <sup>-1</sup> for the rainbow trout <i>Oncorhynchus mykiss</i> . To this an assessment factor of approximately 10 was applied to give a maximum allowable concentration of <b>5.0</b> $\mu$ g l <sup>-1</sup> .
Long-term PNEC for salt waters:	Given the limited data on the toxicity of cyanide to saltwater organisms it was proposed that the EQS set for the protection of freshwater life should also be adopted as a tentative value for the protection of saltwater life.
Short-term PNEC for salt waters:	Given the limited data on the toxicity of cyanide to saltwater organisms it was proposed that the EQS set for the protection of freshwater life should also be adopted as a tentative value for the protection of saltwater life.

Reference: Environment Agency (1998) Proposed Environmental Quality Standards for Cyanide in Water. Environment Agency R&D Technical Report P41.

Cypermethrin				
Receiving medium and exposure		Assessment Factor	Proposed PNEC (ng/l)	Existing EQS (ng/l)
Freshwater/long	-term	1	0.1	0.2
Freshwater/shor	t-term	10	0.4	2.0
Saltwater/long-	term	1	0.1	0.2
Saltwater/short-	-term	10	0.41	2.0
Recommendatio	<u>n of use</u>	of proposed PN	<u>ECs</u>	
are not subject	t to exce	essive uncertainty	nvironmental Quality Sta and, with some develop ance assessment purpo	ment, analytical
Background Info	rmation	1:		
fate in water	of applications. Cypermethrin rapidly degrades in soil and sediment, with hydrolysis and photolysis playing major roles in the degradation. Cypermethrin is highly hydrophobic as indicated by its very low water solubility. Taking this into account and the related high lipoaffinity (reported log Kow values = $3.76 - 5.54$ ), this indicates a strong tendency to sorb to sediment and accumulate in aquatic biota. This also contributes strongly to losses of cypermethrin from the water column. Given the physicochemical properties of cypermethrin, long-term exposure of biota in the water column is unlikely except where there are continuous releases. Episodic exposures e.g. resulting from accidental overspray or spillages are more likely.			
Seasonal monitoring	For substances such as the sheep-dip chemicals, cypermethrin and diazinon, it may be useful to do additional monitoring during certain times of the year, when treatment and applications are likely to occur. In such instances we must avoid bias when determining compliance with respect to a standard that is expressed as an annual mean or an annual percentile. For example if we would normally take 12 samples per year, but include an additional six samples in a given month, we would take all the data from that month to provide a monthly mean. This, in turn, would be used to calculate the correct contribution to the annual mean.			
Factors affecting derivation of the PNEC	No additional comments			

Long-term	Effect on biota:
PNEC for freshwaters:	The most sensitive and reliable long-term toxicity value is a No Observed Effect Concentration of 0.1 ng/l for expression of milt by male Atlantic salmon ( <i>Salmo salar</i> ). This is a significant endpoint because it could lead to reduced fertility. Reliable data are also available for algae and invertebrates, and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng/l. This helps elininate much of the uncertainty involved in estimating a PNEC and so an Assessment Factor of 1 is recommended.
	<b>Recommended PNEC:</b> 0.1 ng/l (after applying an Assessment Factor of 1)
	Change from existing EQS: similar to the existing EQS of 0.2 ng/l
Short-term	Effect on biota:
PNEC for freshwaters:	Reliable short-term data are available for algal, invertebrate and fish species. The most sensitive and reliable short-term toxicity values are a 96-hour LC50 of 4 ng/l for the mayfly <i>Cloeon dipterum</i> and the amphipod <i>Gammarus pulex</i> . Since amphipods were identified as amongst the most sensitive organisms in mesocosm tests, with effects at less than 30 ng/l, a reduced Assessment Factor of 10 (instead of the default value of 100) applied to the LC50 is proposed.
	<b>Recommended PNEC:</b> 0.4 ng/l (after applying an Assessment Factor of 10)
	<b>Change from existing EQS:</b> lower than the existing EQS of 2 ng/l, reflecting the availability of new data showing high sensitivity of invertebrates to short-term exposure to cypermethrin
Long-term	Effect on biota:
PNEC for salt waters:	Given the absence of long-term data for both algae and fish it is not appropriate to generate a PNEC based on the salt water data alone. However, since the long-term data for salt water crustaceans indicate similar sensitivities to freshwater crustaceans and given the specific mode of action of cypermethrin it is proposed that the combined freshwater and salt water dataset be used for the PNEC generation.
	The most sensitive and reliable long-term toxicity value in the combined data set is a No Observed Effect Concentration of 0.1 ng/l for expression of milt by male Atlantic salmon. Since data are also available for algae and invertebrates and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng/l, an Assessment Factor of 1 is recommended.
	Recommended PNEC: 0.1 ng/l (including an Assessment Factor of 1)
	Change from existing EQS: similar to the existing EQS of 0.2 ng/l.
Short-term	Effect on biota:
PNEC for salt waters:	Reliable short-term data are available for invertebrate and fish species. The lowest valid acute toxicity value is a 96-hour Low Observed Effect Concentration of 4.1 ng/l for lethality of nauplii of the copepod <i>Acartia</i> <i>tonsa.</i> The use of a reduced Assessment Factor of 10 is justified because of the availability of data for exclusively marine species.

	Recommended PNEC: 0.41 ng/l (including an Assessment Factor of 10)
	Change from existing EQS: lower than the existing EQS of 2 ng/l
PNEC for secondary poisoning:	<b>Effect on biology:</b> Bioconcentration data (reported as bioconcentration factors (BCF), the ratio of concentrations inside and external to test organisms) for cypermethrin for invertebrates and fish range from 31-238 and 84-1200, respectively. Hence the trigger of BCF greater than 100 is met and PNECs to protect against secondary poisoning of predators is required.
	The calculated PNEC of 2.78 $\mu$ g/l (for secondary poisoning) is much higher than the proposed long-term PNECs for the protection of the pelagic communities in both inland and marine water bodies, and so does not influence the development of water column Environmental Quality Standards for cypermethrin.
	Recommended PNEC: None recommended
	Change from existing EQS: no change
PNEC for sediments	Since the log Kow of cypermethrin is greater than 3 the derivation of PNECs for the protection of benthic organisms is required. The resulting PNEC for freshwater sediments of 0.2 $\mu$ g/kg (dry weight) is higher than the other long-term and short-term PNEC values.
	Recommended PNEC: None recommended.
	Change from existing EQS: Not applicable
Analysis	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 non-standard analytical methodologies employing gas chromatography-mass spectrometry, capable of achieving detection limits as low as 15 pg/l, should offer adequate performance to analyse for cypermethrin. However, some development will be necessary to achieve these sensitivities in routine analysis.
Implementation	Because it is highly lipophilic, there is a tendency for cypermethrin to sorb to suspended solids. Care will need to be taken to exclude such solids from samples taken for compliance assessment (e.g. by avoiding taking samples during periods of high flow) because otherwise environmental concentrations will be over-estimated. Determination of pass or failure of the standard can then be based on comparison with the PNEC, including a consideration of sampling error.

Diazinon				
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)	
Freshwater/long-term	10	0.01	0.03	
Freshwater/short-term	10	0.02	0.1	
Saltwater/long-term	1	0.01	0.03	
Saltwater/short-term	10	0.26	0.1	

#### Recommendation

These PNECS are suitable for use as Environmental Quality Standards because they are not subject to excessive uncertainty and, with some development, analytical capability should be adequate for compliance assessment purposes

The proposed PNEC<sub>saltwater\_st</sub> is higher (less stringent) than the existing saltwater short-term EQS. Therefore, to comply with the 'no deterioration' principle, it is recommended that the existing saltwater short-term EQS is retained.

Background Information:				
Properties and fate in water	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.			
Factors affecting derivation of the PNEC	The PNECs 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.			
Long-term PNEC for freshwaters:	Effect on biota:			
	Recent studies have revealed significant reductions in olfactory responses of male Atlantic salmon ( <i>Salmo salar</i> ) following 30 minute exposure to 0.3 $\mu$ g/l diazinon, with a No Observed Effect Concentration (NOEC) of 0.1 $\mu$ g/l. These data are supported by similar NOECs for reproduction in the crustaceans <i>Ceriodaphnia dubia</i> , <i>Daphnia magna</i> and <i>Gammarus pseudolimnaeus</i> . The standard Assessment Factor of 10 applied to the Atlantic salmon NOEC of 0.1 $\mu$ g/l is recommended.			
	<b>Recommended PNEC:</b> 0.01 µg/l (after applying an Assessment Factor of 10)			
	<b>Change from existing EQS</b> : This is similar to the existing EQS of 0.03 $\mu$ g/l for sheep dip insecticides (combined concentrations of diazinon, chlorfenvinphos, propetamphos, coumaphos, and fenchlorphos).			

Short-term PNEC for freshwaters:	Effect on biota:	
	The lowest reliable effects concentration is a 96-hour LC50 of 0.2 $\mu$ g/l to the freshwater shrimp <i>Gammarus fasciatus</i> . The specific mode of action of diazinon, coupled with the indications that this species is likely to be amongst the most sensitive taxa, allows a reduced Assessment Factor (10) to be applied.	
	<b>Recommended PNEC:</b> 0.02 $\mu$ g/l (after applying an Assessment Factor of 10)	
	<b>Change from existing EQS:</b> This concentration is 5 times lower than the existing EQS of $0.1 \mu g/l$ for sheep dip insecticides (combined concentrations of diazinon, chlorfenvinphos, propetamphos, coumaphos, and fenchlorphos).	
Long-term PNEC for salt waters:	Effect on biota:	
	In the absence of reliable chronic salt water toxicity data, a salt water PNEC may be based on freshwater data. However, an Assessment Factor of 10 applied to the lowest freshwater chronic No Observed Effect Concentration (NOEC) (0.1 $\mu$ g/l for olfactory responses in Atlantic salmon) is considered adequate. This is because evidence from acute tests suggests that long-term NOECs generated for these salt water taxa would not be lower than those already available. This results in a PNEC of 0.01 $\mu$ g/l, identical to that for freshwater.	
	<b>Recommended PNEC</b> : 0.01 $\mu$ g/l (after applying an Assessment Factor of 10)	
	<b>Change from existing EQS:</b> This is similar to the existing EQS of 0.03 $\mu$ g/l for sheep dip insecticides (combined concentrations of diazinon, chlorfenvinphos, propetamphos, coumaphos, and fenchlorphos.	
Short-term	Effect on biota:	
PNEC for salt waters:	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:</b> The proposed PNEC is higher than the existing EQS (0.1 $\mu$ g/l) and so, under the no deterioration principle, the current EQS is recommended for adoption	
	Change from existing EQS: no change	
PNEC for secondary poisoning:	Effect on biota:	
	PNECs based on the risks of secondary poisoning to mammals and birds (0.06 $\mu$ g/l) are higher than those derived for the protection of aquatic life and so do not influence the development of Environmental Quality Standards for diazinon.	
	Recommended PNEC: none recommended	
	Change from existing EQS: no change	

PNEC for sediments	Since the log Kow of diazinon is greater than 3 the derivation of PNECs for the protection of benthic organisms is required. The resulting PNEC for freshwater sediments of 0.2 µg/kg (dry weight) is higher than the other long-term and short-term PNEC values.		
	Recommended PNEC: none recommended.		
	Change from existing EQS: not applicable		
Analysis	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 most stringent EQS. However, some method development will be necessary to realise this sensitivity in routine analysis.		
Implementation	Because it is highly lipophilic, there is a tendency for diazinon to sorb to suspended solids. Care will need to be taken to exclude such solids from samples taken for compliance assessment (e.g. by avoiding taking samples during periods of high flow) because otherwise environmental concentrations will be over-estimated Determination of pass or failure can then be based on comparison with the PNEC, including a consideration of sampling error.		
	The short-term PNEC for salt waters is greater than the existing EQS of $0.1 \ \mu g/l$ for sheep dip insecticides (combined concentrations of diazinon, chlorfenvinphos, propetamphos, coumaphos, and fenchlorphos). Therefore, the current EQS for diazinon is recommended to avoid deterioration in status.		

Dimethoate			
Receiving medium and exposure	Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term	50	0.48	1.0
Freshwater/short-term	500	4.0	-
Saltwater/long-term	50	0.48	-
Saltwater/short-term	500	4.0	-

## Recommendation

Although the Assessment Factors are large, additional testing would probably result in standards that were less stringent than the existing standard. Under these circumstances, the 'no deterioration' principle would apply and the existing EQS would be adopted. Since the proposed PNEC is close to the existing standard, the UKTAG recommends proceeding with the PNEC as the EQS.

Current analytical capability should be adequate for compliance assessment purposes.

Background Info	Background Information:		
Properties and fate in water	Dimethoate is an organophosphate insecticide used to kill mites and insects systemically and on contact. It is not expected to persist in the water column or in soil due to biodegradation The low log Koc values of 1.26-1.56 indicate that dimethoate will not strongly sorb to soils, but would be subject to leaching. Dimethoate is unlikely to bioconcentrate in fish given typical bioconcentration factors (BCF) values of less than 6.		
Factors affecting derivation of the PNEC	Laboratory data are supplemented by freshwater mesocosm data which confirm the sensitivity of crustaceans to dimethoate. Dimethoate has been shown to disrupt reproductive function in mammalian species. Although the pathogenesis of dimethoate-induced reproductive toxicity remains to be determined, a reduction in serum testosterone levels is thought to play an important role. Data for snails indicates that there may be endocrine-mediated effects in egg production and development but this needs to be substantiated.		
	The PNECs described are based on a technical assessment of available ecotoxicity data for dimethoate, 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.		
Long-term	Effect on biota:		
PNEC for freshwaters:	The lowest valid long-term toxicity value for freshwater invertebrates is a 21-day No Observed Effect Concentration (NOEC) of 24 $\mu$ g a.i. /l for effects on the growth of the water flea <i>Daphnia magna</i> . Although reliable long-term NOECs are also available for algae, invertebrates and fish, and therefore an assessment factor of 10 could be applied to the lowest valid toxicity value, this would result in a higher PNEC <sub>freshwater_lt</sub> than certain short-term toxicity data. This potential discrepancy has been addressed by the application of an assessment factor of 50		

	<b>Recommended PNEC:</b> PNEC <sub>freshwater_lt</sub> of 0.48 $\mu$ g dimethoate /I (after applying an Assessment Factor of 50)			
	<b>Change from existing EQS</b> : This value is similar to the existing EQS of 1.0 ug /l			
Short-term	Effect on biota:			
PNEC for freshwaters:	Reliable short-term data are available for algal, invertebrate and fish species. The lowest valid short-term toxicity value for freshwater invertebrates is a 48-h EC50 of 2000 $\mu$ g a.i. /l for the effects of dimethoate on the immobilisation of the water flea <i>Daphnia magna</i> . Lower short-term toxicity values have been reported in non-GLP <sup>1</sup> studies but these are considered to be unreliable. Given the issues with the reliability of the data from the non-GLP studies a larger precautionary assessment factor of 500 applied to the lowest valid toxicity value has been adopted			
	<b>Recommended PNEC:</b> PNEC <sub>freshwater st</sub> of 4.0 $\mu$ g dimethoate /I (after applying an Assessment Factor of 500)			
	Change from existing EQS: There is no current EQS			
Long-term	Effect on biota:			
PNEC for salt waters:	No long-term toxicity data for marine organisms are available and a combined freshwater and saltwater dataset is proposed used for PNEC generation. Reliable long-term NOECs are available for freshwater algae, invertebrates and fish, and therefore an assessment factor of 10 could be applied to the lowest valid toxicity value. However, the use of this factor along with the would result in a higher PNEC <sub>freshwater_lt</sub> than certain short-term toxicity data. This discrepancy has been addressed by the application of an assessment factor of 50			
	<b>Recommended PNEC</b> : PNEC <sub>saltwater It</sub> of 0.48 $\mu$ g dimethoate /I (after applying an Assessment Factor of 50)			
	Change from existing EQS: There is no current EQS			
Short-term	Effect on biota:			
PNEC for salt waters:	Single species toxicity data are available for five different marine taxa, but all were of low or uncertain reliability. Therefore, it is proposed that the PNEC <sub>saltwater_st</sub> is based on the combined freshwater and saltwater data set.			
	The lowest valid short-term toxicity value for freshwater invertebrates is a 48-h EC50 of 2000 $\mu$ g a.i. /l for the water flea <i>Daphnia magna</i> . Lower short-term toxicity values have been reported in non-GLP studies but these are considered to be unreliable. Given the issues with the reliability of the data from the non-GLP studies a larger precautionary assessment factor of 500 applied to the lowest valid toxicity value has been adopted			
	<b>Recommended PNEC:</b> PNEC <sub>freshwater_st</sub> of 4.0 $\mu$ g dimethoate /I (after applying an Assessment Factor of 500 )			

<sup>&</sup>lt;sup>1</sup> Good Laboratory Practice - a Quality Assurance scheme for biological testing to assure the integrity of data

	Change from existing EQS: There is no existing EQS
PNEC for secondary poisoning:	Effect on biota:
	Bioconcentration data (as BCF values) for dimethoate for the majority of aquatic organisms are low with values for fish ranging from 1 to 6. Hence the BCF trigger of 100 is not exceeded and the derivation of a PNEC in whole fish for secondary poisoning of predators is not required
	Recommended PNEC: none recommended
	Change from existing EQS: no change
PNEC for sediments	Since the log Kow of dimethoate is <3 according to the Technical Guidance Document [4] the derivation of PNECs for the protection of benthic organisms is not required
	Recommended PNEC: none recommended.
	Change from existing EQS: not applicable
Analysis	The data quality requirements are that, at 1/3 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-mass spectrometry (GC-MS), capable of achieving detection limits as low as 50 ng/l, should offer adequate performance to analyse for dimethoate
Implementation	Analytical capability is adequate for compliance assessment purposes. Determination of pass or failure of the standard is based on comparison with environmental concentrations, including a consideration of sampling error.
	Although the Assessment Factors are large, additional testing would probably result in standards that were less stringent than the existing standard. Under these circumstances, the 'no deterioration' principle would apply and the existing EQS would be adopted. Since the proposed PNEC is close to the existing standard, the UKTAG recommends proceeding with the PNEC as the EQS.

Iron			
Receiving medium and exposure		Existing EQS for Total Dissolved Iron (mg/I)	
Freshwater/long-term		1	
Freshwate	er/short-term	No proposal	
Saltwate	r/long-term	1	
Saltwater	r/short-term	No proposal	
cannot yet be imp saltwater long-ter In 1988, EQSs we (filterable) iron we	ccording to the Anne plemented. It is theref m Environmental Qua ere proposed for iron ere subsequently ado	x V methodology are subject to high uncertainty and fore recommended that the existing freshwater and ality Standards are retained. (WRc 1988) and statutory standards for dissolved opted for the protection of freshwater and marine life, standards were reviewed in 1998 (WRc 1998) but	
Background Info	ormation:		
Properties and fate in water	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. Iron can exist in numerous chemical and physical forms that are dependent on water quality conditions, and ferrous [Fe(II)] ions are oxidised to the ferric [Fe(III)] species under most environmental conditions. Insoluble ferric species are stabilised in colloidal form by adsorption to natural organic compounds. Colloidal or microparticulate forms of iron are often measured as 'dissolved' iron. The adverse effects of iron are influenced by the chemical form present pH and dissolved organic concentrations. 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.		
Long-term PNEC for freshwaters:	Field data were the basis for the derivation of standards. In the 1998 review freshwater field studies reported evidence for biological effects at concentrations of filterable iron around or even below the statutory EQS, although it was possible that other substances may have contributed to the effects seen. Therefore, the statutory standard of 1.0 mg $\Gamma^1$ filterable iron expressed as an annual average was retained for the protection of freshwater life.		
Short-term PNEC for freshwaters:	No short-term standards are proposed		

Long-term PNEC for salt waters:	There were no new saltwater field data available for use in the 1998 update, and laboratory toxicity data published since the 1988 report showed similar effect concentrations to those reported previously. Therefore, an annual average of 1.0 mg l <sup>-1</sup> filterable iron for the protection of saltwater life was retained.
Short-term PNEC for salt waters:	No short-term standards are proposed

## References:

WRc (1988) Proposed Environmental Quality Standards for List II substances in Water. Iron. WRc Technical Report TR 258. WRc Plc, Frankland Road, Wilts SN5 8YR

WRc (1998) Revised Environmental Quality Standards for Iron in Water. Final Report to the Department of the Environment, Transport and the Regions, WRc Report No: DETR 4471 (P). WRc Plc, Frankland Road, Wilts SN5 8YR

Linuron				
Receiving medium and exposure		Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l)
Freshwater/long-term		2	0.5	2.0
Freshwater/shor	t-term	10	0.9	20
Saltwater/long-	term	2	0.5	2.0
Saltwater/short-	-term	10	0.9	-
Recommendatio	n			
	essive u	ncertainty and ana	onmental Quality Standa alytical capability should	•
Background Info	rmation	:		
Properties and fate in water Factors affecting	<ul> <li>Linuron is a selective, systemic herbicide absorbed principally through the roots but also through the foliage, with translocation in the xylem. It inhibits photosynthesis by blocking electron transport which leads to the production of a range of powerful oxidants causing rapid destruction of plant cells.</li> <li>Linuron degrades moderately rapidly in water and based on a log Kow of 2.83 it will mostly remain in the water column, rather than be adsorbed to sediment. Bioconcentration in aquatic organisms is low.</li> <li>Freshwater algae and macrophytes are the most sensitive taxa. Long-</li> </ul>			
derivation of the PNEC	term toxicity data for saltwater species are only available for macrophytes. Laboratory data are supplemented by freshwater mesocosm data which confirm the high sensitivity of algae and macrophytes to linuron. These allow small assessment factors to be justified. There are indications that linuron is a potential vertebrate (fish and mammals) endocrine disruptor where it may act as an androgen receptor antagonist.			
Long-term	Effect	on biota:		
PNEC for freshwaters:	The lowest reliable long-term laboratory test result is an EC10 of 1.0 $\mu$ g a.i./l for the macrophyte <i>Ceratophyllum demersum</i> . Long-term data are also available for algae, invertebrates and fish. Vascular plants such as <i>C. demersum</i> are expected to be sensitive to linuron, so it is unlikely that substantially more sensitive species will be found. In addition, exposure of a wide variety of organisms in well-performed microcosm and mesocosm studies produced a lowest NOEC of 0.5 $\mu$ g/l after continuous exposure.			
	<b>Recommended PNEC:</b> PNEC <sub>freshwater_lt</sub> of 0.5 $\mu$ g linuron/I (after applying an Assessment Factor of 2)			
	-	e from existing EC I by a factor of 4-fo	<b>QS</b> : This value is lower the	nan the existing EQS of

Short-term	Effect on biota:
PNEC for freshwaters:	Reliable short-term toxicity data are available for algae, invertebrates and fish. The lowest short-term value is a 24-h EC50 of 9.0 $\mu$ g a.i./l for inhibition of photosystem II in the macrophyte <i>Elodea nuttallii</i> . Since there is a considerable short-term toxicity database for freshwater organisms which shows that macrophytes such as <i>Elodea</i> are likely to be amongst the most sensitive to linuron, an assessment factor of 10 rather than 100 can be justified
	<b>Recommended PNEC:</b> PNEC <sub>freshwater st</sub> of 0.9 $\mu$ g linuron/l (after applying an Assessment Factor of 10)
	Change from existing EQS: This value is lower than the existing EQS of 20 $\mu g/l$
Long-term	Effect on biota:
PNEC for salt waters:	Long-term toxicity data for saltwater organisms are only available for two macrophyte species. The absence of long-term data for algae, invertebrates and fish means that it is not possible to generate a PNEC <sub>saltwater_lt</sub> based on the saltwater data alone; a combined freshwater and saltwater dataset is used for the PNEC generation.
	The lowest long-term laboratory test result is a 5-week EC10 of 1.0 µg a.i./l for inhibition of photosystem II in the macrophyte <i>Ceratophyllum demersum</i> . The argument used in the Technical Guidance Document [4] for an additional assessment factor of 10 in saltwater systems to account for greater biodiversity should not apply to linuron because macrophytes such as <i>Ceratophyllum</i> are likely to particularly sensitive. Therefore maintaining the freshwater assessment factor of 2 may be justified
	<b>Recommended PNEC</b> : PNEC <sub>saltwater_lt</sub> of 0.5 $\mu$ g linuron/l (after applying an Assessment Factor of 2)
	<b>Change from existing EQS:</b> This value is slightly lower than the interim guideline of 2.0 $\mu$ g/l in the existing EQS report, which was 'read across' from the freshwater long-term value
Short-term	Effect on biota:
PNEC for salt waters:	Acute toxicity data for marine organisms are available for bacteria, algae, crustaceans, fish and molluscs, with algae being the most sensitive group. The highly specific mode of action of linuron strongly suggests that a saltwater PNEC should be similar to one set on the basis of more extensive data for freshwater plants. Therefore the use of the 24-h growth EC50 of 9.0 $\mu$ g a.i./l for the macrophyte <i>E. nuttallii</i> and application of an assessment factor of 10 is recommended
	<b>Recommended PNEC:</b> PNEC <sub>saltwater_st</sub> of 0.9 $\mu$ g linuron/l (after applying an Assessment Factor of 10)
	Change from existing EQS: There is no current EQS
PNEC for	Effect on biota: Bioconcentration data (as BCE values) for linuron for aquatic organisms
secondary poisoning:	Bioconcentration data (as BCF values) for linuron for aquatic organisms are low with values for fish ranging from 38-49. Hence the BCF trigger of 100 in whole fish is not exceeded and the derivation of PNECs for secondary poisoning of predators is not required

	Recommended PNEC: none recommended		
	Change from existing EQS: not applicable		
PNEC for sediments	The log Kow of linuron lies between 2.76 and 3.0, which is on the borderline for requiring the derivation of PNECs for the protection of benthic organisms. However, there is no evidence from microcosm and mesocosm studies to suggest that sediment-dwelling organisms (invertebrates and decomposers) are directly affected at concentrations near those that affect photosystem II in plants. Therefore derivation of a sediment PNEC is not recommended.		
	Recommended PNEC: none recommended.		
	Change from existing EQS: not applicable		
Analysis	The data quality requirements are that, at 1/3 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-mass spectrometry (GC-MS), capable of achieving detection limits as low as 5 ng/l, should offer adequate performance to analyse for linuron.		
Implementation	These PNECS are suitable for use as Environmental Quality Standards because they are not subject to excessive uncertainty and analytical capability should be adequate for compliance assessment purposes		

Месоргор				
Receiving medium and exposure		Assessment Factor	Proposed PNEC (μg/l)	Existing EQS (µg/l)
Freshwater/long	j-term	10	18	20
Freshwater/shor	t-term	100	187	200
Saltwater/long-	term	10	18	20
Saltwater/short	-term	100	187	200
Recommendatio	n			
	essive u	ncertainty and ana	onmental Quality Standa alytical capability should	
Background Info	rmation	:		
Properties and fate in water	Mecoprop is a phenoxypropanoic acid with potent auxin activity in bioassays and in treated sensitive plants. The compound is directly toxic to susceptible plants without metabolic activation and induces a series of morphological and physiological effects. Mecoprop is not expected to persist in surface waters when released to the aquatic compartment. However, the Environment Agency have identified mecoprop as a potential substance of concern in groundwater, which may require development of a specific PNEC. Mecoprop is not expected to persist in soil when released to the terrestrial compartment since it readily biodegrades (with reported half- lives in soil ranging from 3 to 21 days depending upon soil type and conditions). Mecoprop will also readily leach from soil and may also be lost in run-off following field applications. Mecoprop is not expected to bioaccumulate in aquatic organisms.			
Factors affecting derivation of the PNEC	Freshwater macrophytes are more sensitive to both technical grade mecoprop and mecoprop formulations than algae, invertebrates and fish.			
	<ul> <li>Long-term laboratory data are available for four different freshwater taxonomic groups, including algae, crustaceans, fish and macrophyle Freshwater short-term toxicity data are available for four taxonomic groups, including algae, crustaceans, fish and macrophytes. For ma organisms single species short-term toxicity data are available for four different taxonomic groups (algae, crustaceans, fish and molluscs).</li> <li>Long-term toxicity data are available for two different saltwater taxa (algae and molluscs). Laboratory data are not supplemented by freshwater or saltwater mesocosm data.</li> </ul>		fish and macrophytes. for four taxonomic acrophytes. For marine are available for four rish and molluscs). rent saltwater taxa	

Long-term PNEC for freshwaters:	<b>Effect on biota:</b> The lowest valid no observed effect concentration (NOEC) value is from an industry generated study This complied with the OECD code of Good Laboratory Practice (GLP) <sup>1</sup> and assessed the long-term toxicity of mecoprop to macrophytes. This recorded a 7-day NOEC of 180 μg acid equivalents (a.e.) I <sup>-1</sup> for effects of MCPP-p DMA on the macrophyte <i>Lemna minor,</i> which, based on mecoprop's mode of action, is considered to be the most sensitive taxonomic group. Since reliable long-term NOECs are available for algae, crustaceans and fish an assessment factor of 10 has been applied to the lowest valid toxicity value. <b>Recommended PNEC:</b> 18 μg/l (after applying an Assessment Factor of
	10)
	<b>Change from existing EQS</b> : This is lower than the existing EQS of 20 $\mu$ g/l.
Short-term PNEC for freshwaters:	<b>Effect on biota:</b> Reliable short-term data are available for algal, macrophyte, invertebrate and fish species. The lowest reported valid toxicity value is a 7-day EC50 of 18700 µg a.e. I <sup>-1</sup> for effects of MCPP-p-DMA on the growth of the macrophyte <i>Lemna minor</i> .
	<b>Recommended PNEC:</b> 187 µg/l (after applying an Assessment Factor of 100)
	<b>Change from existing EQS:</b> This is lower than the existing EQS of 200 $\mu$ g/l.
Long-term PNEC for salt waters:	<b>Effect on biota:</b> There are limited long-term toxicity data for marine organisms with data being available only for algae and molluscs. The absence of long-term data for both crustaceans and fish means that it is not appropriate to generate a PNEC <sub>saltwater_lt</sub> based on the saltwater data alone. Therefore, it is proposed that the combined freshwater and saltwater dataset is used for the PNEC generation. The lowest long-term value from the combined dataset is a 7-day NOEC of 180 µg a.e. I <sup>-1</sup> for effects of MCPP-p DMA on the growth of the macrophyte <i>Lemna minor</i> . Since a large body of long-term data is available for freshwater and saltwater organisms, an assessment factor of 10 can be applied.
	<b>Recommended PNEC</b> : 18 µg/l (after applying an Assessment Factor of 10)
	<b>Change from existing EQS:</b> This value is lower than the existing EQS of 20 $\mu$ g/l which was 'read across' from the freshwater long-term value.
Short-term PNEC for salt waters:	<b>Effect on biota:</b> The limited reliable short-term toxicity data for marine organisms means that it is not appropriate to derive the PNEC <sub>saltwater_st</sub> based on the saltwater data alone. Therefore, it is proposed that a combined freshwater and saltwater dataset is used for the PNEC generation. The lowest valid short-term toxicity value from the combined dataset is a 7-day EC50 of 18700 µg a.e. I <sup>-1</sup> for effects of MCPP-p-DMA on the growth of the macrophyte <i>Lemna minor</i> .
	<b>Recommended PNEC:</b> 187 $\mu$ g/l (after applying an Assessment Factor of 100)

<sup>&</sup>lt;sup>1</sup> Good Laboratory Practice - a Quality Assurance scheme for biological testing to assure the integrity of data

	<b>Change from existing EQS</b> : This value is lower than the existing EQS of 200 $\mu$ g/l which was 'read across' from the freshwater short-term value.
PNEC for	Effect on biota:
secondary	Bioconcentration data (as BCF values) for mecoprop for the majority of
poisoning:	aquatic organisms are low with a value of 3 reported in whole fish. Hence the trigger of 100 in the Technical Guidance Document [4] BCF
	is not exceeded and the derivation of a PNEC in whole fish for
	secondary poisoning of predators is not required.
	Recommended PNEC: none recommended
	Change from existing EQS: no change
PNEC for	Since the log Kow of mecoprop is >3 the derivation of PNECs for the
sediments	protection of benthic organisms is required. However, field studies
	indicate that in a water sediment matrix mecoprop remains in the water
	column. No information on the toxicity of mecoprop to sediment dwelling
	organisms was located so no PNEC <sub>sediment</sub> could be derived. <b>Recommended PNEC:</b> none recommended
	Change from existing EQS: not applicable
	The data quality requirements are that, at 1/3 of the EQS, total error of
Analysis	measurement should not exceed 50%. Using this criterion, it is evident
	that current analytical methodologies (non-standard) employing gas
	chromatography-mass spectrometry (GC-MS), capable of achieving
	detection limits as low as 0.0025-1.25 pg/l, should offer adequate
	performance to analyse for mecoprop.
Implementation	These PNECS are suitable for use as Environmental Quality Standards
	because they are not subject to excessive uncertainty and analytical
L	capability should be adequate for compliance assessment purposes

Permethrin			
Receiving medium and exposure		Existing EQS (μg/Ι )	
Freshwater/long-term		0.01 (95%ile)	
Freshwater/short-term		No proposal	
Saltwa	ater/long-term	0.01 (95%ile)	
	iter/short-term	No proposal	
Recommendatio	on		
Environmental Q Current analytica This uncertainty of change in the pro- expect short term it is more approp Until the uncertai saltwater long-ter	uality Standards because I methods also lack the re- would be reduced by addi oposed PNECs. Because n episodic exposure rather riate to express the stand nty is addressed, it is reco rm Environmental Quality	methodology are unsuitable for use as they are subject to excessive uncertainty. equired sensitivity for compliance monitoring. tional ecotoxicity testing, which could lead to a of the use patterns of permethrin, we would r than continuous exposure. For these reasons, ards as 95%iles than long-term means.	
Background Infe	· · · · ·	pofing agents, including permethrin.	
Properties and fate in water	applications. It has four two optical isomers) and non-toxic to mammals to In water, permethrin is halso undergoes photoly more rapid with the tran	ic pyrethroid insecticide with a wide range of isomers (its <i>cis</i> - and <i>trans</i> -isomers both have d is a potent neurotoxin. Permethrin is relatively but very toxic to aquatic life. hydrolytically stable but readily biodegradable. It sis. In general, the degradative processes are as-isomer and both isomers degrade to less toxic	
Long-term PNEC for freshwaters:	<ul> <li>products. Permethrin is lipophilic (log Kow 3.48–6.5) and has been found to sorb strongly to sediment, where it is persistent.</li> <li>Laboratory and field toxicity data were used to derive a standard. From the data, it was unlikely that levels of total permethrin below 0.01 μg l<sup>-1</sup> would adversely affect either aquatic invertebrate populations or dependent fisheries. For the protection of aquatic life, therefore, an EQS of <b>0.01 μg l<sup>-1</sup> total permethrin</b> expressed as a 95th percentile was proposed.</li> </ul>		
Short-term PNEC for freshwaters	No standard proposed		
Long-term PNEC for salt waters	freshwater life but the re	e invertebrates was smaller than that for eported toxicity data were generally comparable. the protection of freshwater life was also used water life.	
Short-term PNEC for salt waters	No standard proposed	al Quality Standards for List II substances in Water.	

Reference: WRc (1988) Proposed Environmental Quality Standards for List II substances in Water. Mothproofing Agents. WRc Technical Report TR 261. WRc Plc, Frankland Road, Wilts SN5 8YR

Phenol				
Receiving medium and exposure		Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/l )
Freshwater/long-term		10	7.7	30
Freshwater/short-term		10	46	300
Saltwater/long-term		10	7.7	30
Saltwater/short		10	46	300
not subject to exc assessment purpo Since phenol toxic	e suitable essive un oses. city is not of the sta	significantly and an significantly affe	ronmental Quality Standar nalytical capability is adeque ected by site-specific cond on comparison with envirous f sampling error.	uate for compliance
Background Info	ormation:		· •	
Properties and fate in water	Phenol is widely used in manufacturing and process industries. It is a moderately water-soluble substance that is readily biodegraded in the aqueous environment and may also be lost through photo-degradation.			
Factors affecting derivation of the PNEC	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 phenol. The data were subjected to rigorous quality assessment by both the authors and an independent peer review panel.			
Long-term PNEC for freshwaters:	<b>Effect on biota:</b> The most sensitive species from a reliable study was the fish, <i>Cirrhina mrigala</i> , following an exposure period of 60 days and resulting in a No Observed Effect Concentration of 77 $\mu$ g/l. This is supported by similar concentrations based on studies of the effects of phenol on growth of rainbow trout and common carp. Because representatives of algae, crustaceans and fish are available in the chronic dataset, an Assessment Factor of 10 applied to this No Observed Effect Concentration is recommended.			
	10)		<b>27.7 μg/l (after applying an</b> <b>EQS:</b> 4 times lower than the	
Short-term PNEC for freshwaters:	The low of 460 µ the most occurs a need for PNECs. acute LO Recom	g/l for guppy ( <i>P</i> t sensitive taxon at much lower co a substantial ma These factors in C50 can be justifi mended PNEC: from existing E	im, by a considerable marg oecilia reticulata). There is a omic group to phenol and t ncentrations than acute toxi argin between the long-term indicate an Assessment Fact ied as the basis for a PNEC 46 µg/l (including an Asses EQS: about 6 times lower the	evidence that fish are hat chronic toxicity city. This suggests the and short-term for of 10 applied to this sement Factor of 10)

Long-term PNEC for salt waters:	<b>Effect on biota:</b> Marine taxa appear to share a similar distribution of sensitivities to their freshwater counterparts and so the two datasets can be combined. The lowest No Observed Effect Concentration (NOEC) available in the combined freshwater and salt water database is the same as used for the derivation of the PNEC (60-day NOEC of 77 $\mu$ g/l in the fish species, <i>Cirrhina mrigala</i> ). According to Annex V, the NOEC of 77 $\mu$ g/l would normally be divided by an Assessment Factor of 100. However, additional short-term tests are available for freshwater species that also occur in salt waters (annelids and molluscs). Reproduction tests with salt water and freshwater rotifer species indicate these taxa are not the most sensitive to phenol. It therefore seems unlikely that long-term tests with representatives of these additional taxonomic groups would result in lower chronic toxicity data than that obtained for fish. Consequently, a reduced Assessment Factor of 10 applied to the fish NOEC of 77 $\mu$ g/l is justified, resulting in the same PNEC as that in freshwater. <b>Recommended PNEC</b> : 7.7 $\mu$ g/l (after applying an Assessment Factor of 10) <b>Change from existing EQS</b> : 4 times lower than the existing EQS of 30
Short-term	μg/l. Effect on biota:
PNEC for salt waters:	There are no reliable short-term data for saltwater fish so the freshwater and salt water datasets were combined. As a result, the lowest acute effect concentration is the 96-hour LC50 of 460 $\mu$ g/l for guppy ( <i>Poecilia</i> <i>reticulata</i> ). We recommend that the PNEC is based on an Assessment Factor of 10 applied to the guppy 96-hour LC50. This factor is justifiable on the assumption that fish are the most sensitive species and that there is a substantial acute to chronic toxicity ratio for fish, encouraging a substantial margin between short-term and long-term PNECs for phenol. <b>Recommended PNEC</b> of 46 $\mu$ g/l (including an Assessment Factor of 10) <b>Change from existing EQS</b> : about 6 times lower than the existing EQS
Anghaig	of 300 μg/l The lowest proposed PNEC for phenol is 7.7 μg/l. The data quality
Analysis	requirements are that, at one-third of the EQS, the total error of measurement should not exceed 50 per cent. Current analytical methodologies provide detection limits as low as 0.05 $\mu$ g/l, which suggests that they would be adequate for assessing compliance with the proposed PNECs for water.
Implementation	These PNECs are suitable for use as Environmental Quality Standards because they are not subject to excessive uncertainty and analytical capability is adequate for compliance assessment purposes. Since phenol toxicity is not significantly affected by site-specific conditions, determination of pass or failure of the standard is based on comparison with environmental concentrations, including a consideration of sampling error.

Toluene		1		
Receiving medium and exposure		Assessment Factor	Proposed PNEC (µg/l)	Existing EQS (µg/I )
Freshwater/long-term		10	74	50
Freshwater/short-term		10	380	500
Saltwater/long	-term	10	74	40
Saltwater/short-term		10	370	400
Recommendatio	n			
not subject to exc assessment purpo The proposed lon Environmental Qu	essive ur oses. g-term Pl uality Star d that the	NECs are higher NECs are higher Indards. Therefor existing freshwa	nalytical capability is add	e existing long-term o deterioration' principle,
Background Info	ormation			
Properties and fate in water	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.			
Factors affecting derivation of the PNEC	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.			
Long-term PNEC for freshwaters:	Effect on biota: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 ug/l.Recommended PNEC:The proposed PNEC is higher than the existing EQS (50 ug/l) and so, under the no deterioration principle, the current EQS is recommended for adoption.			
Change from existing EQS: No change				
Short-term PNEC for freshwaters:	<ul> <li>Effect on biota:</li> <li>The lowest effect concentration was a 48-hour LC50 of 3.78 mg/l for <i>Ceriodaphnia dubia</i>. As crustaceans are the most sensitive species with respect to long- and short-term exposure, and because toluene acts non-specifically by narcosis, a reduced Assessment Factor (10) is recommended to extrapolate from this 50 per cent effect level to a short-term no effect level.</li> <li>Recommended PNEC: 380 μg/l (including an Assessment Factor of 10)</li> </ul>			

	<b>Change from existing EQS:</b> The proposed PNEC is 1.5 times lower than the existing EQS of 500 $\mu$ g/l.
Long-term PNEC for salt waters:	<ul> <li>Effect on biota:</li> <li>There are too few toxicity data for marine species to derive a PNEC.</li> <li>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</li> <li>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 ug/l, the same as for the freshwater, long-term situation.</li> <li>Recommended PNEC: The proposed PNEC is higher than the existing EQS (40 ug/l) and so, under the no deterioration principle, the current EQS</li> </ul>
	is recommended for adoption.
	Change from existing EQS: none
Short-term PNEC for salt waters:	<b>Effect on biota:</b> Crustaceans are the most sensitive taxonomic group for both marine and freshwater species with the lowest valid acute effects being nearly identical (LC50 of 3.78 mg/l for the freshwater crustacean <i>Ceriodaphnia</i> <i>dubia</i> and LC50 of 3.70 mg/l for the marine crustacean <i>Crangon</i> <i>franciscorum</i> ). As a result, the salt water data is used for the derivation of the short-term PNEC.
	As crustaceans are the most sensitive species with respect to long- and short-term exposure, and because toluene acts nonspecifically by narcosis, a reduced Assessment Factor (10) is recommended to extrapolate from the 50 per cent acute effect level to the short-term no effect level.
	<b>Recommended PNEC</b> of 370 ug/l (including an Assessment Factor of 10)
	<b>Change from existing EQS</b> : slightly lower than the existing EQS of 400 $\mu$ g/l.
Analysis	The lowest proposed PNEC derived for toluene is 40 $\mu$ g/l. The data quality requirements are that, at one-third of the EQS, the total error of measurement should not exceed 50 per cent. Current analytical methodologies provide detection limits in the ng/l range, which suggests that they would be adequate for assessing compliance with the proposed PNECs.
Implementation	These PNECS are suitable for use as Environmental Quality Standards because they are not subject to excessive uncertainty and analytical capability is adequate for compliance assessment purposes. Since toluene toxicity is not affected by site-specific conditions, determination of pass or failure of the standard is based on comparison with environmental concentrations, including a consideration of sampling error. Long-term PNECs for freshwater and salt water: because the PNEC estimated here is greater than the existing EQS (50 and 40 ug/l respectively), use of the current EQS for toluene is recommended to avoid deterioration in status.

Zinc			
Receiving medium and exposure	Existing EQS (µg/I )		
Freshwater/long-term:			
0–50 mg l <sup>-1</sup> CaCO <sub>3</sub> 50–100 mg l <sup>-1</sup> CaCO <sub>3</sub> 100–250 mg l <sup>-1</sup> CaCO <sub>3</sub> >250 mg l <sup>-1</sup> CaCO <sub>3</sub>	8 50 75 125		
Freshwater/short-term	No proposal		
Saltwater/long-term:	40 (dissolved)		
Saltwater/short-term	No proposal		
An EU Risk Assessment Report is being compiled for zinc. The UK is committed to the use of PNECs derived through this process as the basis for Water Framework Directive Annex VIII EQSs. However, there remain some issues about the implementation of these PNECs as standards, and short-term standards will also need to be developed. We recommend that, at least in the interim, existing freshwater and saltwater Environmental Quality Standards, developed in 1984 (WRc 1984) are retained. The EQSs were revised in 1992 (WRc 1992) but the modified proposals were never adopted .			
Background Information:			
fate in water silicates and carbona where its internal con depending on the co deficiency or toxicity that the organism ca state in forms that de pH, hardness and th Bioavailability and to complexation, with a ), and by the compet biological receptors.	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.In water, zinc exists in the +2 oxidation state in forms that depend on physico-chemical parameters, such as pH, hardness and the content of dissolved organic carbon. Bioavailability and toxicity may be affected by organic and inorganic complexation, with anions such as chloride (CI-) and carbonate (CO32- ), and by the competition of cations (e.g. Ca2+ and H+) with zinc at biological receptors. To account for these factors, proposals for EU PNECs are based on the use of Biotic Ligand Models.		

Long-term PNEC for freshwaters:	The standards proposed in the 1984 report and subsequently adopted for the long-term protection of freshwater life were banded according to water hardness (ranging between <b>8 - 125 ug/l total zinc</b> as annual averages, see above). The European Inland Fisheries Advisory Commission (EIFAC) originally proposed the values for the protection of salmonid and cyprinid fish in waters other than those designated as European Community fisheries.
	Because the toxicity of zinc to fish has a logarithmic linear relationship with water hardness, it was recommended that EQS values for intermediate hardness should be calculated by simple linear interpolation between the relevant hardness-related values.
Short-term PNEC for freshwaters:	No standard proposed
Long-term PNEC for salt waters:	Chronic data for marine species were limited to invertebrates, though acute data were also reported for fish. The lowest acute value was a 96-hour LC50 of 166 $\mu$ g l <sup>-1</sup> for the larvae of the mollusc <i>Mercenaria mercenaria</i> , which was identical to the chronic value obtained for the Mysid shrimp, <i>Mysidopsis bahia</i> . An assessment factor of 4 was applied to this chronic value because of the possibility of other invertebrates with greater sensitivity to zinc and the likelihood of increased toxicity of zinc to invertebrates at low salinities. This resulted in a long-term saltwater <b>EQS of 40 µg l<sup>-1</sup> dissolved zinc</b> expressed as an annual average.
Short-term PNEC for salt waters:	No standard proposed

References:

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