

# using science to create a better place

## Proposed EQS for Water Framework Directive Annex VIII substances: aluminium (inorganic monomeric)

Science Report: SC040038/SR1  
SNIFFER Report: WFD52(i)

The Environment Agency is the leading public body protecting and improving the environment in England and Wales.

It's our job to make sure that air, land and water are looked after by everyone in today's society, so that tomorrow's generations inherit a cleaner, healthier world.

Our work includes tackling flooding and pollution incidents, reducing industry's impacts on the environment, cleaning up rivers, coastal waters and contaminated land, and improving wildlife habitats.

The UK Technical Advisory Group (UKTAG) supporting the implementation of the Water Framework Directive (2000/60/EC) is a partnership of UK environmental and conservation agencies. It also includes partners from the Republic of Ireland. This report is the result of research commissioned and funded on behalf of UKTAG by the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER) and the Environment Agency's Science Programme.

**Published by:**

Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury, Bristol, BS32 4UD  
Tel: 01454 624400 Fax: 01454 624409  
[www.environment-agency.gov.uk](http://www.environment-agency.gov.uk)

ISBN: 978-1-84432-651-8

© Environment Agency/SNIFFER

February 2007

All rights reserved. This document may be reproduced with prior permission of the Environment Agency and SNIFFER.

The views expressed in this document are not necessarily those of the Environment Agency.

Further copies of this report are available from:

The Environment Agency's National Customer Contact Centre by emailing [enquiries@environment-agency.gov.uk](mailto:enquiries@environment-agency.gov.uk) or by telephoning 08708 506506.

**Author(s):**

Crane M, Atkinson C, Comber S and Sorokin N

**Dissemination Status:**

Publicly available

**Keywords:**

inorganic monomeric aluminium, Water Framework Directive specific pollutants, predicted no-effect concentrations freshwater, saltwater

**Research Contractor:**

WRc plc, Frankland Road, Blagrove, Swindon Wiltshire, SN5 8YF  
Tel: +44 1793 865000

**Environment Agency's Project Manager:**

Stephanie Cole/Lindsey Sturdy, Chemicals Science

**Collaborator(s):**

Scottish Environment Protection Agency (SEPA)  
Scotland & Northern Ireland Forum for Environmental Research (SNIFFER)  
Environment and Heritage Service (EHS)

**Science Project Number:**

SC040038

**Product Code:**

SCHO0407BLVS-E-E

# Science at the Environment Agency

Science underpins the work of the Environment Agency by providing an up-to-date understanding of the world about us and helping us to develop monitoring tools and techniques to manage our environment as efficiently as possible.

The work of our Science Group is a key ingredient in the partnership between research, policy and operations that enables us to protect and restore our environment.

The Environment Agency's Science Group focuses on five main areas of activity:

- **Setting the agenda:** To identify our strategic science needs to inform our advisory and regulatory roles.
- **Sponsoring science:** To fund people and projects in response to the needs identified by the agenda setting.
- **Managing science:** To ensure that each project we fund is fit for purpose and that it is executed according to international scientific standards.
- **Carrying out science:** To undertake the research ourselves by those best placed to do it – either by our in-house scientists or by contracting it out to universities, research institutes or consultancies.
- **Providing advice:** To ensure that the knowledge, tools and techniques generated by the science programme are taken up by relevant decision-makers, policy makers and operational staff.

Steve Killeen

Head of Science

# Use of this report

The development of UK-wide classification methods and environmental standards that aim to meet the requirements of the Water Framework Directive (WFD) is being sponsored by the UK Technical Advisory Group (UKTAG) for WFD on behalf of its members and partners.

This technical document has been developed through a collaborative project, managed and facilitated by the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER), the Environment Agency and the Scottish Environment Protection Agency (SEPA) and has involved the members and partners of UKTAG. It provides background information to support the ongoing development of the standards and classification methods.

Whilst this document is considered to represent the best available scientific information and expert opinion available at the stage of completion of the report, it does not necessarily represent the final or policy positions of UKTAG or any of its partner agencies.

# Executive Summary

The UK Technical Advisory Group (UKTAG) has commissioned a programme of work to derive Environmental Quality Standards (EQSs) for substances falling under Annex VIII of the Water Framework Directive (WFD). This report proposes predicted no-effect concentrations (PNECs) for aluminium using the methodology described in Annex V of the Directive. EQSs for aluminium have been proposed previously but never adopted.

The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for aluminium, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.

Where possible, PNECs have been derived for freshwater and saltwater environments, and for long-term/continuous exposure and short-term/transient exposure. If they were to be adopted as EQSs, the long-term PNEC would normally be expressed as an annual average concentration and the short-term PNEC as a 95th percentile concentration.

The feasibility of implementing these PNECs as EQSs has not been considered at this stage. However, this would be an essential step before a regulatory EQS can be recommended.

## **Properties and fate in water**

Aluminium is a naturally abundant element but also enters the environment from anthropogenic sources such as drinking water and wastewater treatment.

It is found as a variety of forms, depending on pH, alkalinity, temperature, dissolved organic carbon, dissolved inorganic carbon and anion concentration. Hydroxides are the most common form occurring in water but the chemistry of aluminium becomes more complicated due to the presence of organic and inorganic ligands, which compete for complexation with the hydroxide ion ( $\text{OH}^-$ ).

Inorganic monomeric forms of aluminium are of particular importance as these are the most toxicologically active species. At  $\text{pH} < 5.5$ , the free ion ( $\text{Al}^{3+}$ ) becomes the prevalent form, along with the inorganic monomeric complexes [ $\text{AlF}$ ,  $\text{Al}(\text{OH})_x$  and  $\text{Al}(\text{SO}_4)$ ]. The increased availability at this pH is reflected in higher toxicity. At  $\text{pH} 6.0\text{--}7.5$ , solubility declines due to the presence of insoluble  $\text{Al}(\text{OH})_3$ ; although precipitation of aluminium hydroxides onto fish gills is a significant mode of toxic action. At higher pH ( $\text{pH} > 8.0$ ), the more soluble  $\text{Al}(\text{OH})_4^-$  species predominate, which again increases availability. In algae, aluminium interferes with intracellular phosphorus metabolism or glucose metabolism early in the glycolytic pathway.

### **Availability of data**

Short-term freshwater toxicity data are dominated by fish and crustaceans. Long-term data are fewer, describing toxicity to algae and fish. Algae, followed by fish appear to be most sensitive.

Short-term and long-term saltwater toxicity data are available for three taxonomic groups (crustaceans, annelids and fish). Nearly all the available data are based on nominal concentrations and are, therefore, unsuitable for PNEC derivation. Only one study with saltwater organisms was based on measured aluminium concentrations.

'Total' aluminium is an unsuitable way of describing aluminium toxicity because little of the aluminium present is likely to be in a toxicologically active form. From a toxicological perspective, it is more relevant to express toxicity in terms of concentrations of inorganic monomeric aluminium. However, this precludes the use of toxicity data that are expressed as total aluminium. Such data cannot be used to predict toxicity in the field without additional information on the water chemistry to estimate aluminium speciation which is rarely available.

### **Derivation of PNECs**

Although there is a theoretical basis for a pH effect on speciation and toxicity and evidence suggesting differences in toxicity to some species at different pH, data are insufficient to warrant setting PNECs for separate pH bands.

As with other metals, the 'added risk' approach could be considered appropriate when deriving PNECs for aluminium because it is a naturally occurring substance to which organisms will have evolved tolerance. However, as the PNEC is being derived on the basis of a measure of 'available' (inorganic monomeric) aluminium, there is no need to adopt the added risk approach. The use of a speciation-based PNEC is more ecologically relevant than using added risk and removes the need to determine a background aluminium concentration at a regional scale, river basin or even local scale.

#### Long-term PNEC for freshwaters

The lowest reliable effect concentration is a 4-day EC30 of 7 µg l<sup>-1</sup> (inorganic monomeric Al) for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6. Reliable long-term (lt) data are also available from experiments with fish, but not for invertebrates. Thus, an assessment factor of 50 is recommended to account for the uncertainty in extrapolating to other taxa for which there are no data. However, a further factor of 3 is recommended. This is because the 4-day exposure period is short in absolute terms (even though it is a chronic exposure with respect to unicellular algae) and it is necessary to extrapolate from the reported EC30 to a no-observed effect concentration (NOEC). Applying these factors results in a PNEC<sub>freshwater\_lt</sub> of 0.05 µg l<sup>-1</sup> monomeric Al.

#### Short-term PNEC for freshwaters

The lowest reliable short-term (st) effect concentration is a 120-hour LC50 of 51–54 µg l<sup>-1</sup> for Atlantic salmon (*Salmo salar*) at pH 4.4. Lower toxicity was seen at higher pH values. However, applying the guidance given in Annex V of the WFD would result in a short-term PNEC that is lower (i.e. more stringent) than the long-term

PNEC. This cannot be defended toxicologically and so a preferred approach is to base the short-term PNEC on the 4-day algal EC30 used as the basis for the long-term PNEC and to apply a smaller assessment factor. Therefore, two assessment factors are again recommended: a factor of 3 to extrapolate to a NOEC and one of 10 to extrapolate to the PNEC. This results in a  $PNEC_{\text{freshwater\_st}}$  of  $0.25 \mu\text{g l}^{-1}$  monomeric Al.

#### PNECs for saltwaters

The available data for inorganic reactive aluminium are too limited to allow even a tentative conclusion to be drawn on the comparative sensitivity of the different saltwater taxonomic groups or to base a PNEC on these data. Instead, it is recommended that both the long-term and short-term saltwater PNECs are based on their freshwater counterparts. However, an additional assessment factor (10) is recommended to account for the possibility that greater taxonomic diversity in the marine environment makes it likely that some marine taxa may be more sensitive than the most sensitive freshwater taxa. This results in a proposed  $PNEC_{\text{saltwater\_lt}}$  of  $0.005 \mu\text{g l}^{-1}$  monomeric Al and a  $PNEC_{\text{saltwater\_st}}$  of  $0.025 \mu\text{g l}^{-1}$  monomeric Al.

#### PNEC for secondary poisoning

There are some indications of bioaccumulation of aluminium in biota, though it is often unclear whether body residues describe systemic uptake or merely binding to the surface of the organism. Applying the Annex V guidance to available data on bioaccumulation and toxicity to birds and mammals results in a  $PNEC_{\text{secpois}}$  of  $0.4 \mu\text{g l}^{-1}$  inorganic monomeric Al.

#### PNEC for sediments

There are insufficient data to derive a sediment PNEC for aluminium and the use of equilibrium partitioning to estimate a value based on aquatic toxicity data cannot be justified for metals.

### Summary of proposed PNECs

Receiving medium/exposure scenario	Proposed PNEC ( $\mu\text{g l}^{-1}$ monomeric Al)	Existing EQS
Freshwater/long-term	0.05	None adopted
Freshwater/short-term	0.25	None adopted
Saltwater/long-term	0.005	None adopted
Saltwater/short-term	0.025	None adopted
Secondary poisoning	0.4	None adopted

#### **Analysis**

Expressing PNECs in terms of inorganic monomeric aluminium places additional demands on the methods used to monitor compliance. This has resulted in the development of methods to determine 'reactive' aluminium, which comprises the inorganic monomeric species. The most well-established method is oxine extraction, which provides a limit of detection of around  $1 \mu\text{g l}^{-1}$  aluminium using graphite furnace atomic absorption spectrometry (GFAAS) and  $5 \mu\text{g l}^{-1}$  using inductively coupled plasma mass spectrometry (ICP-MS).

Current analytical methodologies are not yet sufficiently sensitive to be used for assessing compliance with any of the proposed PNECs in receiving waters, although they may be adequate for monitoring compliance with consent limits on point source discharges.

### **Implementation issues**

Before PNECs for aluminium can be adopted as EQSs, it will be necessary to address the following issues:

1. A method for predicting concentrations of inorganic monomeric aluminium from measured concentrations of total aluminium will be necessary to permit use of the proposed PNECs in deriving consent conditions for point source discharges. Research is underway to assess whether or not such a method is feasible. If it is, consent setting and compliance assessment will almost certainly require information about local water chemistry.
2. If assessment of compliance in receiving waters is required, an extraction and analytical method for inorganic monomeric aluminium would need to be developed and trialled.
3. Because there is no existing EQS, an interim EQS cannot be adopted while these issues are resolved. Therefore, the recommendation is not to set a standard, at least until further investigations have been undertaken.

# Contents

<b>Use of this report</b>	<b>4</b>
<b>Executive Summary</b>	<b>5</b>
<b>Contents</b>	<b>9</b>
<b>1. Introduction</b>	<b>11</b>
1.1 Properties and fate in water	11
<b>2. Results and observations</b>	<b>13</b>
2.1 Identity of substance	13
2.2 PNECs proposed for derivation of quality standards	13
2.3 Hazard classification	14
2.4 Physical and chemical properties	15
2.5 Environmental fate and partitioning	16
2.5.1 Aluminium speciation	20
2.5.2 Options for deriving standards	20
2.6 Effects data	23
2.6.1 Toxicity to freshwater organisms	24
2.6.2 Toxicity to saltwater organisms	30
2.6.3 Toxicity to sediment-dwelling organisms	34
2.6.4 Endocrine-disrupting effects	34
2.6.5 Mode of action of aluminium	34
<b>3. Calculation of PNECs as a basis for the derivation of quality standards</b>	<b>35</b>
3.1 PNECs for freshwaters	35
3.1.1 PNEC for deriving an annual average concentration	35
3.1.2 PNEC for deriving a maximum allowable concentration	37
3.2 PNECs for saltwaters	40
3.2.1 PNEC for deriving an annual average concentration	40
3.2.2 PNEC for deriving a maximum allowable concentration	41
3.3 Derivation of PNECs by the TGD probabilistic approach (SSD method)	42
3.4 Derivation of existing EQSs	42
3.5 Derivation of PNECs for sediment	42
3.6 Derivation of PNECs for secondary poisoning of predators	42
3.6.1 Mammalian and avian toxicity data	42
3.6.2 PNECs for secondary poisoning of predators	45
<b>4. Analysis and monitoring</b>	<b>46</b>
<b>5. Conclusions</b>	<b>48</b>
5.1 Availability of data	48
5.2 Derivation of PNECs	48
5.2.1 Long-term PNEC for freshwaters	48
5.2.2 Short-term PNEC for freshwaters	49
5.2.3 PNECs for saltwaters	49

5.2.4	PNEC for secondary poisoning	49
5.2.5	PNEC for sediments	49
5.3	Analysis	50
5.4	Implementation issues	50
<b>References &amp; Bibliography</b>		<b>51</b>
<b>List of abbreviations</b>		<b>58</b>
<b>ANNEX 1</b>	<b>Data quality assessment sheets</b>	<b>60</b>

# 1. Introduction

The UK Technical Advisory Group (UKTAG) supporting the implementation of the Water Framework Directive (2000/60/EC)<sup>1</sup> is a partnership of UK environmental and conservation agencies. It also includes partners from the Republic of Ireland. UKTAG has commissioned a programme of work to derive Environmental Quality Standards (EQSs) for substances falling under Annex VIII of the Water Framework Directive (WFD). This report proposes predicted no-effect concentrations (PNECs) for aluminium using the methodology described in Annex V of the Directive. EQSs for aluminium have been proposed previously but never adopted.

The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for aluminium, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data.<sup>2</sup> Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V. The feasibility of implementing these PNECs as EQSs has not been considered at this stage. However, this would be an essential step before a regulatory EQS can be recommended.

This report provides a data sheet for aluminium (inorganic monomeric).

## 1.1 Properties and fate in water

Aluminium is a naturally abundant element but also enters the environment from anthropogenic sources such as drinking water and wastewater treatment. It is found as a variety of forms depending on:

- pH
- alkalinity
- temperature
- dissolved organic carbon (DOC)
- dissolved inorganic carbon
- anion concentration.

Hydroxides are the most common form occurring in water. However, the chemistry of aluminium becomes more complicated due to the presence of organic and inorganic ligands, which compete for complexation with the hydroxide ion (OH<sup>-</sup>).

Inorganic monomeric forms of aluminium are of particular importance as these are the most toxicologically active species. At pH <5.5, the free ion (Al<sup>3+</sup>) becomes the prevalent form, along with the inorganic monomeric complexes [AlF, Al(OH)<sub>x</sub> and Al(SO<sub>4</sub>)]. The

---

<sup>1</sup> *Official Journal of the European Communities*, **L327**, 1–72 (22/12/2000). Can be downloaded from [http://www.eu.int/comm/environment/water/water-framework/index\\_en.html](http://www.eu.int/comm/environment/water/water-framework/index_en.html)

<sup>2</sup> Data quality assessment sheets are provided in Annex 1.

increased availability at this pH is reflected in higher toxicity. At pH 6.0–7.5, solubility declines due to the presence of insoluble  $\text{Al}(\text{OH})_3$ , though precipitation of aluminium hydroxides onto the gills of fish is a significant mode of toxic action. At higher pH (pH >8.0), the more soluble  $\text{Al}(\text{OH})_4^-$  species predominates, which again increases availability. In algae, aluminium interferes with intracellular phosphorus metabolism or glucose metabolism early in the glycolytic pathway.

## 2. Results and observations

### 2.1 Identity of substance

Table 2.1 gives the chemical name and Chemical Abstracts Service (CAS) number for the species of interest.

**Table 2.1 Species covered by this report**

Name	CAS Number
Aluminium (metal)	7429-90-5
Aluminium sulfate	10043-1-3
Aluminium oxide	1344-28-1
Aluminium hydroxide	21645-51-2
Aluminium fluoride	7784-18-1

### 2.2 PNECs proposed for derivation of quality standards

Table 2.2 lists proposed PNECs, obtained using the methodology described in the Technical Guidance Document (TGD) issued by the European Chemicals Bureau (ECB) on risk assessment of chemical substances [78], and existing EQSs obtained from the literature.

Section 2.6 summarises the effects data identified from the literature for aluminium. The use of these data to derive the values given in Table 2.2 is explained in Section 3.

**Table 2.2 Proposed PNECs as basis for quality standard setting (inorganic monomeric aluminium, unless otherwise stated)**

PNEC	TGD deterministic approach (AFs) ( $\mu\text{g l}^{-1}$ )	TGD probabilistic approach (SSDs) ( $\mu\text{g l}^{-1}$ )	Existing EQSs ( $\mu\text{g l}^{-1}$ )
Freshwater short-term	0.25	NA	<u>UK [1]</u> 10.0 (pH $\leq$ 6.5) (MAC) 25.0 (pH $>$ 6.5) (MAC)
Freshwater long-term	0.05	NA	<u>UK [1]</u> 15.0 (pH $>$ 6.5) (AA)  <u>Environment Ontario<sup>3</sup></u> 15.0 (pH 4.5–5.5) At pH $>$ 5.5–6.5 no increase of more than 10% above natural background concentrations of acid soluble inorganic

<sup>3</sup> <http://www.ene.gov.on.ca/>

PNEC	TGD deterministic approach (AFs) ( $\mu\text{g l}^{-1}$ )	TGD probabilistic approach (SSDs) ( $\mu\text{g l}^{-1}$ )	Existing EQSs ( $\mu\text{g l}^{-1}$ )
			aluminium. 75.0 (total aluminium at pH >6.5–9)  <u>European Inland Fisheries Advisory Commission (EIFAC) [2]</u> This takes water hardness (Ca) and DOC into account: 30.0 (Ca <2 mg l <sup>-1</sup> , pH 4.5–5) 75.0 (Ca <2 mg l <sup>-1</sup> , pH 5–6) 60.0 (Ca >2 mg l <sup>-1</sup> , pH 4.5–5) Where DOC >10 $\mu\text{g l}^{-1}$ or Si:Al >13: 30.0 (Ca >5 mg l <sup>-1</sup> , pH 5–6) 100 (Ca >5 mg l <sup>-1</sup> , pH >6) 1,000 (total aluminium; Ca >10 mg l <sup>-1</sup> , pH 6.5–8)
Saltwater short-term	0.025	NA	<u>UK [1]</u> 25.0 (MAC)
Saltwater long-term	0.005	NA	<u>UK [1]</u> 15.0 (AA)
Freshwater sediment short-term	ND	ND	NA
Freshwater sediment long-term	ND	ND	NA
Saltwater sediment short-term	ND	ND	NA
Saltwater sediment long-term	ND	ND	NA
Secondary poisoning	0.4	NA	NA

AA = annual average

AF = assessment factor

MAC = maximum allowable concentration

ND = no data

NA = not applicable

SSD = species sensitivity distribution

If a generic added risk approach is taken, a median background concentration for UK rivers of 6.0  $\mu\text{g l}^{-1}$  [3] could be added to the values given in Table 2.2.

## 2.3 Hazard classification

Table 2.3 gives the R-phrases (Risk-phrases) and labelling for the species of interest.

**Table 2.3 Hazard classification**

R-phrases and labelling	Reference
Aluminium (powder/metal): R15, contact with water liberates extremely flammable gas	[4]
Aluminium sulfate: no data	[4]
Aluminium oxide: not classified	[4]
Aluminium hydroxide: not classified	[4]
Aluminium fluoride: not classified	[4]

## 2.4 Physical and chemical properties

Table 2.4 summarises the physical and chemical properties of the species of interest.

**Table 2.4 Physical and chemical properties of aluminium compounds of interest**

IUPAC chemical name	Aluminium	Aluminium sulfate	Aluminium oxide	Aluminium hydroxide	Aluminium fluoride
Synonyms	None	None	Alumina	Aluminium hydrate, aluminium trihydrate, hydrated alumina	Aluminium trifluoride
CAS Number	7429-90-5	10043-1-3	1344-28-1	21645-51-2	7784-18-1
Molecular formula	Al	Al <sub>2</sub> O <sub>12</sub> S <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	AlH <sub>3</sub> O <sub>3</sub>	AlF <sub>3</sub>
Molecular weight	26.98 [5]	342.14 [6]	101.94 [7]	78.00 [5]	83.98 [5]
Appearance	Tin-white, malleable, ductile metal with bluish tint [5]	White, lustrous crystals, piece, granules or powder [5]	White crystalline powder [5]	White amorphous powder [5, 6]	White hexagonal crystals [6]
Melting point	660°C [5]	770°C (with decomposition) [8]	ca. 2000°C [9]	300°C [8]	1291°C [10]
Boiling point	2327°C [5]	On long boiling of aqueous solution, insoluble basic salt precipitates [5]	2980°C [11]	-	NA – sublimates at 1272°C [5]
Vapour pressure	The metal is an involatile solid at normal temperatures	Essentially zero [12]	1 mmHg at 2158°C [13]	-	1 mmHg at 1238°C [10]
Water solubility (mg l <sup>-1</sup> )	Insoluble [7]	Soluble in 1 part water [5]	Insoluble in water [5]	Insoluble in water [6]	5590 mg l <sup>-1</sup> at 25°C [5]

IUPAC chemical name	Aluminium	Aluminium sulfate	Aluminium oxide	Aluminium hydroxide	Aluminium fluoride
Soil–water partition coefficient (log K <sub>p</sub> )	NA	NA <sup>1</sup>	NA	NA	NA <sup>1</sup>

<sup>1</sup> Will dissociate in most waters to form predominantly insoluble hydroxy species. Hence a partition coefficient is not relevant.

## 2.5 Environmental fate and partitioning

Table 2.5 summarises the information obtained from the literature on the environmental fate and partitioning of aluminium.

**Table 2.5 Environmental fate and partitioning of aluminium**

Property	Value	Reference
Abiotic fate	Aluminium is the most abundant metallic element. Because of its high reactivity, it is always found combined with other elements. The high charge/radius of Al <sup>3+</sup> in aqueous solutions means that the ion forms hydroxo complexes. Because of its amphoteric character, aluminium reacts with both mineral acids and strong alkalis.	[14]
Speciation	<p>Aluminium is found as a variety of polymorphs and hydrated species. All four aluminium halides (fluoride, chloride, bromide and iodide) are known, together with a wide range of other compounds including sulfides and oxides. Aluminium forms octahedral complexes with a variety of neutral ligands and also with fluoride ions. The forms of aluminium present in the environment depend on many factors, especially pH, alkalinity, temperature, dissolved organic carbon, dissolved inorganic carbon and anion concentration. This includes ionic salts, complexes and a limited number of covalent compounds. In aqueous solutions, aluminium chemistry is characterised by the speciation of aluminium hydroxide, which is strongly influenced by pH. In natural waters, the chemistry of aluminium becomes more complicated due to the presence of alternative ligands, both organic and inorganic, which compete for complexation with the hydroxide ion (OH<sup>-</sup>).</p> <p>The main species of total aluminium measured in a water sample are:</p> <ul style="list-style-type: none"> <li>• inorganic monomeric forms [labile aluminium, Al<sup>3+</sup>, AlF, Al(OH)<sub>x</sub>, Al(SO<sub>4</sub>)];</li> <li>• organic monomeric forms (Al-org, dissolved, colloidal);</li> <li>• polymeric complexes [Al<sub>n</sub>(OH)<sub>m</sub>, polymeric, colloidal];</li> <li>• aluminium hydroxide colloids and precipitates and clays (Al<sub>n</sub>Si<sub>m</sub>, polymeric, colloidal).</li> </ul>	[15] and following

Property	Value	Reference
Hydrolytic stability	<p>Aluminium, as a metal, is insoluble in water.</p> <p>The water solubility of aluminium sulfate is 313 g l<sup>-1</sup> in cold water and 983 g l<sup>-1</sup> in hot water. Aluminium sulfate may be hydrolysed to form sulfuric acid and a variety of aluminium hydroxide species. The predominant form, and hence solubility, will depend on the pH of the water.</p> <p>Aluminium oxide is practically insoluble in water, at 0.98 µg l<sup>-1</sup>. Aluminium hydroxide is almost insoluble in water and the water solubility of aluminium fluoride is 5,590 mg l<sup>-1</sup>.</p>	
Photostability	Not applicable.	
Distribution in water/sediment systems (active substance)	<p>Aluminium exists in natural waters in a number of species, including dissolved and particulate forms. Dissolved species may be categorised as complexed with free aluminium ions (Al<sup>3+</sup>), inorganic ions (e.g. hydroxide) and complexes with naturally occurring organic substances (including humic and fulvic acids). Particulate forms comprise colloidal precipitates, divided alumino-silicate minerals and suspended particles. The proportion of dissolved aluminium that exists as free ions is small at the pH value of most natural waters.</p> <p>Aluminium concentrations in most freshwaters are generally low due to the low solubility of aluminium at pH values between 5 and 8. Outside this pH range, solubility (and hence availability) increases markedly. This leads potentially to two types of biological effects that could arise from aluminium in surface waters:</p> <ul style="list-style-type: none"> <li>• the action of dissolved material in acid or alkaline waters;</li> <li>• the action of insoluble aluminium at more neutral pH values (5–8).</li> </ul> <p>Detected aluminium concentrations are lower in seawater than in freshwater. A possible reason for this is that colloidal aluminium particles are consolidated in seawater such that material too fine to be removed by filtration is greatly reduced in the oceans. For example, aluminium present upstream of the turbidity maximum in the freshwater zone of the Ems estuary was rapidly removed from solution on mixing with seawater. The underlying process responsible for this was suggested to be the adjustment of new equilibrium between suspended matter of marine and riverine origin.</p> <p>One mechanism of aluminium transport is the dissociation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Microbial activity in the soil leading to the degradation of H<sub>2</sub>CO<sub>3</sub> causes concentrations of carbon dioxide (CO<sub>2</sub>) in the soil that are highly oversaturated with respect to the solubility of atmospheric CO<sub>2</sub>. Dissociation of H<sub>2</sub>CO<sub>3</sub> at high CO<sub>2</sub> partial pressures produces H<sup>+</sup></p>	[79]

Property	Value	Reference
	concentrations capable of solubilising particulate aluminium and the formation of $\text{HCO}_3^-$ , which may serve as a mobile anion and facilitate transport of this aluminium. However, these solutions may be exposed to atmospheric conditions such as soil solutions being transported to surface waters or lake turnover. Under these circumstances, $\text{CO}_2$ will de-gas resulting in an increase in pH, removal of $\text{HCO}_3^-$ and hydrolysis of aluminium.	
Distribution in water and sediment systems (metabolites)	No metabolites, so not applicable.	
Degradation in soil	Aluminium in soil, present due to weathering of natural minerals, can become mobilised under acidic conditions that typically follow atmospheric acid deposition in high elevation watersheds.	
Background concentrations	Workers at WRc measured monomeric inorganic aluminium concentrations in 20 UK rivers ( $n = 47$ samples; pH 7.3–8.7) in 1997 and reported the following summary values ( $\mu\text{g l}^{-1}$ ): mean = 8.58; standard deviation = 10.25; median = 5.91; range = 0.18–46.7.	[77]
Biodegradation	Elemental aluminium does not degrade in the environment. In the trivalent oxidation state, aluminium can complex with electron-rich species.	[16]
Partition coefficients (log Kow)	Not applicable.	
Bioaccumulation BCF	Bioconcentration of aluminium in fish is a function of the water quality (e.g. pH and total organic carbon). Estimated steady-state bioconcentration factors (BCFs) for aluminium in brook trout ( <i>Salvelinus fontinalis</i> ) were 215 at pH 5.3, 123 at pH 6.1 and 36 at pH 7.2. These BCFs are inversely related to pH. The maximum BCFs were 232 at pH 5.3, 153 at pH 6.1 and 46 at pH 7.2. When transferred to water of the same pH but with no added aluminium, the brook trout eliminated aluminium from tissues more rapidly at pH 5.3 than at 6.1 and 7.2.	[17]
	In Atlantic salmon ( <i>Salmo salar</i> ), steady state BCFs of 76 and 364 were reported after a 60-day exposure to aluminium at pH 5.5.	[19]
	A BCF of 155 has also been reported in rainbow trout ( <i>Oncorhynchus mykiss</i> ) gill tissue after a 3-day exposure to aluminium.	[20]
	A BCF of 0.13 to 0.5 in the whole body for the snail <i>Helix</i>	[16]

Property	Value	Reference
	<i>aspersa</i> has been reported.	
	Steady-state BCF values as high as 14,000 have been reported in <i>Asellus aquaticus</i> after a 20-day exposure to aluminium. However, much of the accumulation was due to passive adsorption of aluminium onto the cuticle. Therefore, these BCFs are not representative of the internal concentration of aluminium and overestimate accumulation in this species.	[21]
	A steady state BCF of 19,000 has been reported for the gut tissue of the freshwater snail <i>Lymnaea stagnalis</i> . However, the gut of the snail contains mucus that has a high affinity for metals such as aluminium. The mucus can be excreted and may be a primary route for the removal of metals from the snails. It was reported that mucus may have remained during the analysis of the gut and so this BCF may overestimate the accumulation of aluminium in this species.	[22]

Aluminium sulfate is the form of aluminium most likely to be released in point discharges from water treatment plants or from paper and pulp industry sites where it is used as a flocculant.

However, the fate of aluminium in the environment will depend on local conditions. In catchments subject to acidification, there is the potential for a diffuse input into watercourses through the mobilisation of aluminium under acidic conditions in the soil after both wet and dry deposition.

Aluminium oxide is a raw material in the manufacture of aluminium and aluminium fluoride is a significant inorganic monomeric species where fluoride ions are abundant. Aluminium hydroxide species constitute a large proportion of dissolved aluminium and are therefore responsible for most of the complex chemistry of the inorganic monomeric species of aluminium in water. The toxicity of aluminium will therefore depend substantially upon this species. The terminology used in this report is as shown in Table 2.6.

The presence of aluminium in waters may have effects other than direct toxicity to organisms. An important aspect of aluminium chemistry in acidic surface waters is its role as a pH buffer. The presence of aluminium in a lake can increase its base-neutralising capacity (BNC); aluminium BNC can be comparable in magnitude to hydrogen ion and inorganic carbon BNC. The BNC is defined by the amount of a strong base required to increase the pH of a litre of aluminium solution to 8.3.

The speciation of aluminium is complex and poses important issues with respect to the basis for standard setting. The technical issues, technical options for developing standards and the preferred approach from a scientific viewpoint are summarised below.

**Table 2.6 Terminology used in this report**

Term	Synonyms	Aluminium species
Total monomeric Al	Free monomeric Al Reactive Al Fast reactive Al Labile Al Non-labile monomeric Al	Inorganic and organic monomeric aluminium species
Inorganic monomeric Al	Monomeric inorganic Al species; also referred to as labile monomeric aluminium	Inorganic species: free Al, F <sup>-</sup> and SO <sub>4</sub> <sup>2-</sup> complexes and some hydroxides
Organic monomeric Al	Monomeric alumino-organic complexes; also referred to as non-labile monomeric aluminium	Simple monomeric organic species, e.g. Al citrate and Al humate complexes of low molecular weight
Acid soluble Al		Polymeric Al Colloidal Al Particulate Al Al hydroxides (unfiltered sample)
Total Al	All species present in a sample	Monomeric Al (inorganic and organic) Polymeric Colloidal Particulate Clays

### 2.5.1 Aluminium speciation

The chemical speciation of aluminium in natural waters regulates its mobility, chemical availability and toxicity, with pH being the main controlling factor.

At pH values less than 5.5, the free ion (Al<sup>3+</sup>) becomes the prevalent form, along with the inorganic monomeric complexes [AlF, Al(OH)<sub>x</sub> and Al(SO<sub>4</sub>)]. Given the increased availability at this pH, toxicity is also enhanced.

At pH values between 6.0 and 7.5, the solubility of aluminium is at its lowest due to the presence of insoluble Al(OH)<sub>3</sub>. Although a lack of solubility generally indicates that chemical availability (and hence toxicity) is minimised, precipitation of aluminium hydroxides onto the gills of fish is a significant mode of toxic action. At higher pH values (greater than 8.0) the more soluble Al(OH)<sub>4</sub><sup>-</sup> species predominates, which again increases availability. More information on aluminium speciation and the influence of pH can be found in the UK EQS document [1].

### 2.5.2 Options for deriving standards

Toxicity data for aluminium may be expressed in terms of concentrations of free and reactive concentrations, total aluminium or sometimes in terms of 'dissolved' or filterable concentrations. Three approaches for deriving standards can be recognised:

1. Toxicity of aluminium is associated with its free (Al<sup>3+</sup>) and reactive forms, usually the inorganic monomeric fraction. For this reason, it makes sense to set the standard on inorganic monomeric aluminium because this provides the most direct cause-effect

relationship. However, as shown later, this precludes the use of many published toxicity data, which are expressed only in terms of total aluminium concentrations. Although uncertainty about the significance of the measured concentrations is removed, greater uncertainty is introduced as a result of the effective loss of data for many species.

2. An alternative approach, which would make use of these data, is to base the standards on total aluminium concentrations. This has the advantage of involving a much larger dataset. However, toxicity data based on total concentrations incorporate both the active/toxic aluminium fraction as well as the bound unavailable fraction. Furthermore, the proportion of active to total aluminium does not remain constant due to varying amounts of complexing agents (e.g. clays and organic materials) excreted by test organisms during toxicity testing. There are further difficulties in assessing compliance with such a standard – measures of total aluminium include aluminium-containing clay particles as well as colloidal and dissolved species. These are unlikely to be available to organisms and do not influence toxicity. As a result, they can greatly overestimate the available aluminium concentration, which may, in turn, increase the incidence of false positives in compliance.

Laboratory data based on total aluminium concentrations cannot be used to predict toxicity in the field without additional information on the water chemistry to estimate the Al speciation which, in practice, is not often available.

3. The final approach is to supplement toxicity data expressed in terms of reactive aluminium with modelled predictions of reactive concentrations from other toxicity studies.

It is theoretically possible to utilise toxicity data expressed in terms of total aluminium concentrations by predicting the inorganic monomeric fraction using data on total concentrations and information on water quality and chemistry. However, this would provide only an instantaneous estimation of the inorganic monomeric fraction as the proportions change in relation to external factors and timescales. The concentration of inorganic monomeric aluminium is affected by:

- hydrolysis of the free ion, according to the pH of the medium, to give inorganic hydroxy species (this is very rapid – less than seconds – but these species are still essentially monomeric and can dissociate to  $\text{Al}^{3+}$  easily);
- complexation of a proportion of the inorganic forms by organic complexing agents to produce organic monomeric aluminium (this probably occurs in a few minutes or less; dissociation of the complexes is possible, e.g. in response to a pH reduction);
- coagulation of hydroxy species to form colloids (this takes tens of minutes to a few hours; these forms are not strictly monomeric and, since they have already precipitated might pose less of a toxicological risk, but can dissociate to give monomeric forms that might pose a risk);

- ripening of coagulated hydroxy species to form aged precipitate (this occurs over several hours to days; these forms are more stable and less likely to release monomeric Al by reverse reactions);
- mineralisation of ripened forms to inert clay type minerals (this occurs over days).

Consequently, at any given time the proportion of inorganic monomeric metal can vary. The specific rates of the transformation reactions are not known other than in the general relative terms as highlighted above. Rates depend on water quality characteristics (e.g. pH, suspended matter, DOC concentration, type of DOC, temperature, conductivity, alkalinity, silicate, fluoride and phosphate concentrations), so the rates can be expected to differ for different waters.

The advantages and disadvantages of each approach are set out in Table 2.7. Based on the available information, the most robust and defensible approach is to base the standard on the inorganic monomeric forms of aluminium using data where these reactive forms have been measured (Option 1). This is the approach used in this report. However, it will be important to perform an implementation analysis to anticipate the implications for compliance assessment and setting of discharge permits. This may provide impetus for further work such that Option 3 can be realised.

**Table 2.7 Advantages and disadvantages of setting standards based on the various aluminium species**

Option	Data availability	Toxicological robustness	Issues for compliance assessment	Availability of models
1. Base EQS on reported reactive [Al]	+	high	<ul style="list-style-type: none"> <li>• Requires new sample extraction technique</li> <li>• May be difficulties in translating into discharge limits</li> <li>• Confounding factors mean that analysis provides only instantaneous assessment of reactive [Al]</li> </ul>	NA
2. Base EQS on total [Al]	+++	low	<ul style="list-style-type: none"> <li>• Current compliance assessment regime could continue</li> <li>• Risk of false positives</li> </ul>	NA
3. Base EQS on reactive [Al], combining reported values (as in option 1) + modelled values	++	high	<ul style="list-style-type: none"> <li>• As Option 1</li> </ul>	<ul style="list-style-type: none"> <li>• Models at research stage and may be difficult to gain acceptance of assumptions made</li> <li>• Outputs could have a considerable effect on final decision</li> </ul>

## 2.6 Effects data

A summary of the mode of action for this substance can be found in Section 2.6.5.

Data collation followed a tiered approach.

First, critical freshwater and saltwater data were compiled from existing EQS documents. Further data published after derivation of the current UK EQS were then retrieved from the US Environmental Protection Agency (US EPA) ECOTOX database.<sup>4</sup>

As data on sediment-dwelling organisms and mammalian or avian chronic oral toxicity are not usually available in ECOTOX, further data were sought from ScienceDirect®<sup>5</sup> and Web of Science®.<sup>6</sup>

In addition, data were also sought from:

- World Health Organization (WHO) *Environmental Health Criteria (EHC) 194: Aluminium* [14];
- US EPA Integrated Risk Information System (IRIS) database;<sup>7</sup>
- Hazardous Substances Data Bank (HSDB®) database of the US National Library of Medicine [7].

Toxicity data for aluminium in sediments were not found.

In this report, as in the earlier UK EQS document [1], efforts have concentrated on identifying studies in which inorganic monomeric aluminium concentrations have been measured as there appears to be no satisfactory way of predicting the concentration of these toxic species from measurements of either total or dissolved aluminium [3].

Several factors can influence the availability or toxicity of aluminium to aquatic organisms including:

- pH;
- dissolved organic carbon, silicon and calcium concentrations.

Calcium has been reported to compete with available aluminium for binding sites at the gill surface of acid-stressed fish, thus reducing toxicity [23, 24]. However, other reports have indicated no such ameliorating effect [25]. Dissolved organic carbon in the form of humic acids has also been shown to reduce the effects of aluminium by complexation and subsequent reduction in bioavailability [26, 27]. In addition, silicon (present as silicic acid) has been reported to reduce toxicity by binding with available aluminium [28, 29].

The pH of a waterbody can have a significant effect on aluminium speciation and toxicity. In the UK EQS document [1], an analysis of the effects of pH on aquatic toxicity is reported. By plotting effect concentrations against pH for all available biological species

---

<sup>4</sup> <http://www.epa.gov/ecotox/>

<sup>5</sup> <http://www.sciencedirect.com/>

<sup>6</sup> <http://scientific.thomson.com/products/wos/>

<sup>7</sup> <http://www.epa.gov/iris/index.html>

data, toxicity was found to be greatest at pH 5.5–6.5. Toxicity to algae was greatest at pH 6, while in salmonid and non-salmonid fish, toxicity peaked at around pH 4.5–5.5. At lower and higher pH levels, toxicity was less pronounced in these organisms. Based on the available data, the EQS identified two pH ranges ( $\leq 6.5$  and  $>6.5$ ) for toxicity. Highest toxicity was observed at pH values below 6.5, with an average effect concentration (for all organisms) of  $1,380 \mu\text{g l}^{-1}$  [1]. Lower effect concentrations were seen at higher pH with an average effect concentration of  $10,440 \mu\text{g l}^{-1}$ . Consequently, the UK EQS set two quality standards for pH: one relating to effects below pH 6.5 and one relating to effects above pH 6.5.

These assessments of the influence of pH in the UK EQS report [1] were based on all available data regardless of quality. Over 100 data points were used in this analysis, but when standards were finally set only 21 ‘critical’ data points were identified. There was also considerable variability and some contradictions in the range of effects concentrations within the pH groupings and the statistical significance, if any, of the difference in effects between pH bands was not reported. There is a theoretical justification for selecting pH 6.5 as a threshold as, above this value, aluminium speciation shifts from  $\text{Al}_3^+$  to  $\text{Al}(\text{OH})_3$  and  $\text{Al}(\text{OH})_4^-$ . However, the limited amount of toxicity data available for monomeric aluminium mean that it is difficult to confirm this empirically. As a result, PNECs in this report have been derived from the most sensitive data, though data in both pH bands are discussed.

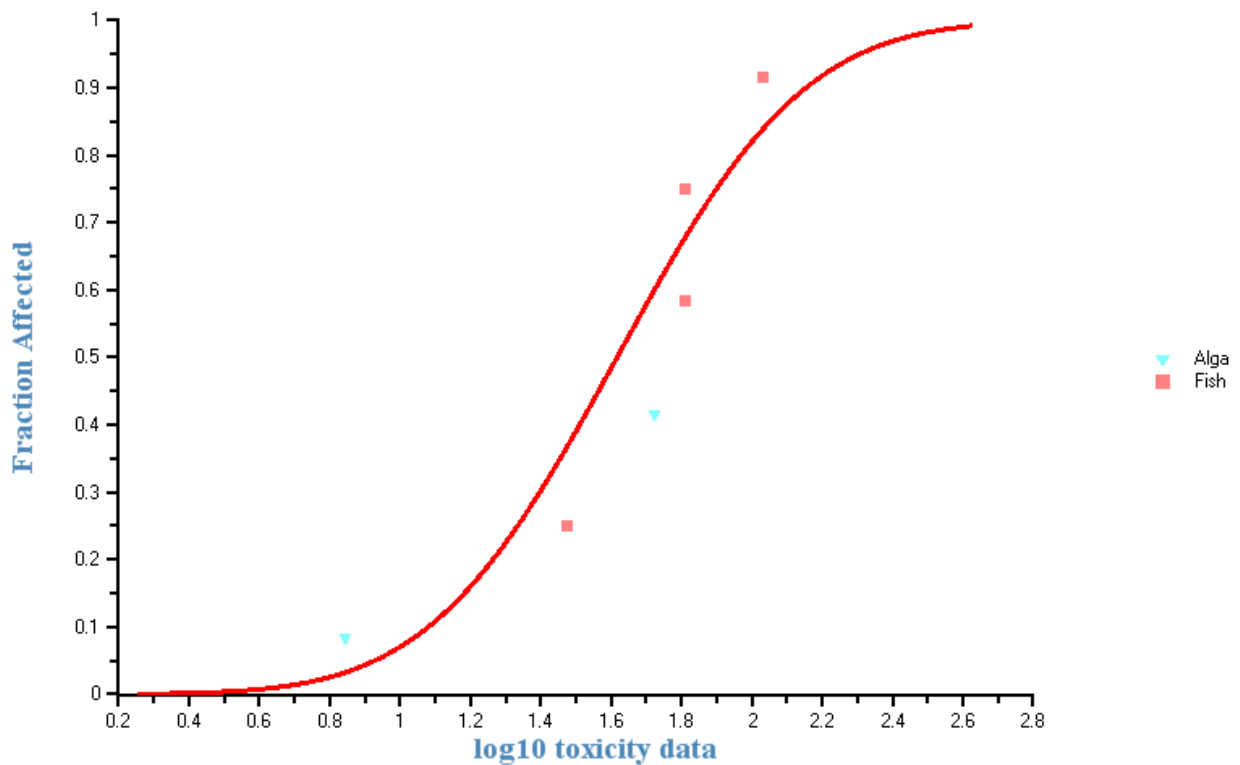
### 2.6.1 Toxicity to freshwater organisms

Most of the short-term toxicity data are available for fish (20 data points) and crustaceans (12 data points). The long-term toxicity dataset is relatively limited with a total of only 27 data points available. Most of the long-term toxicity data are for algae (15 data points) and fish (11 data points).

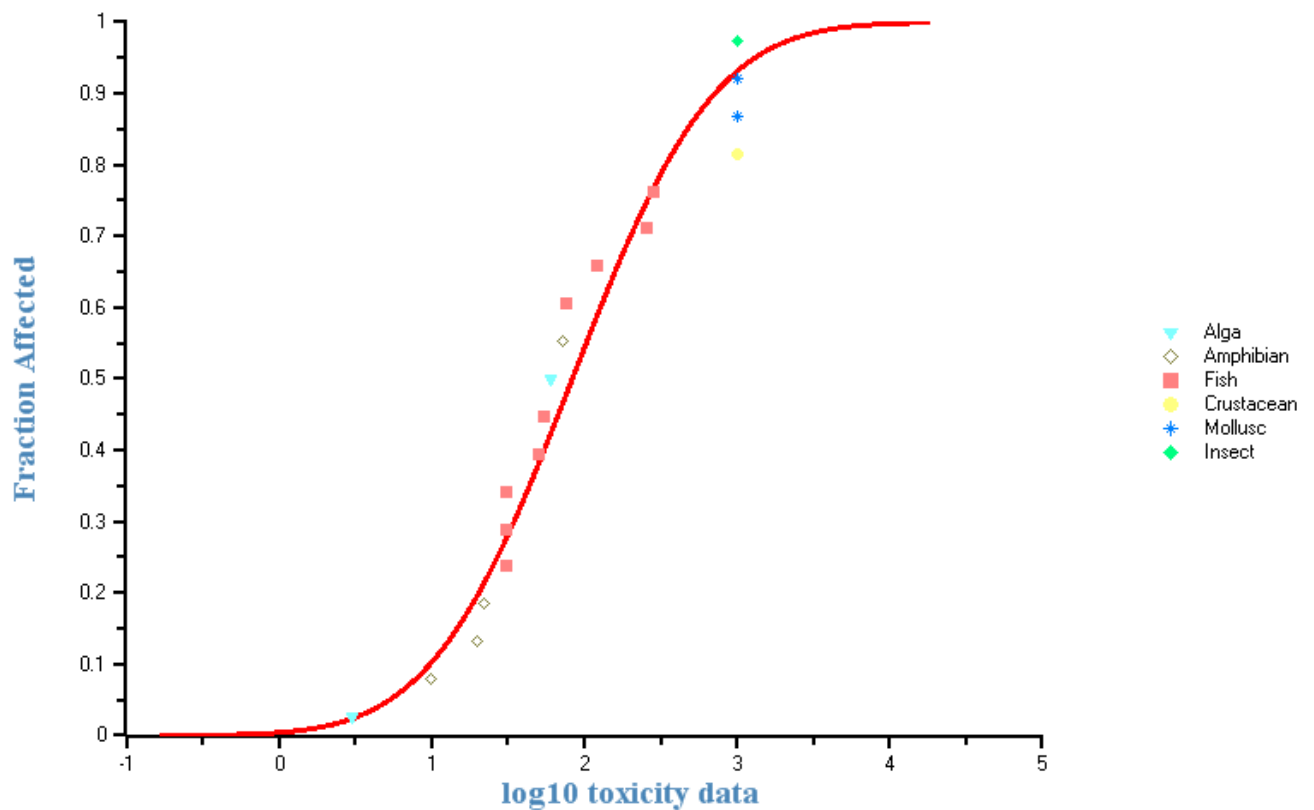
A preliminary analysis of the relative sensitivity of the species tested (i.e. not taking into account the quality of the available studies) indicates that algae, followed by amphibians and fish are most sensitive, with short-term effect concentrations reported as low as  $3.0 \mu\text{g l}^{-1}$ . Salmonid fish are more sensitive than non-salmonid fish, with the lowest long-term effect concentrations reported as 29.7 and  $402 \mu\text{g l}^{-1}$ , respectively.

Diagrammatic representations of the available freshwater data (cumulative distribution functions) for inorganic monomeric aluminium are presented in Figures 2.1 and 2.2. These diagrams include all data regardless of quality and provide an overview of the spread of the available data. These diagrams are not species sensitivity distributions and have not been used to set the aluminium PNECs. The lowest critical freshwater data for aluminium are presented in Tables 2.8 and 2.9.

**Figure 2.1** Cumulative distribution function of freshwater long-term data ( $\mu\text{g l}^{-1}$ ) for measured monomeric aluminium



**Figure 2.2** Cumulative distribution function of freshwater short-term data ( $\mu\text{g l}^{-1}$ ) for monomeric aluminium



**Table 2.8 Most sensitive long-term aquatic toxicity data for freshwater organisms**

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
<b>pH &lt;6.5</b>									
Aluminium chloride	<i>Chlorella pyrenoidosa</i>	Algae	EC30	Growth inhibition	4 days	7 (in mono Al)	pH 6; 22°C	1	[30]
Aluminium chloride	<i>Chlorella pyrenoidosa</i>	Algae	EC30	Growth inhibition	4 days	53 (in mono Al)	pH 5.5; 22°C	1	[30]
Aluminium fluoride	<i>Chlorella vulgaris</i>	Algae	NOEC	Population growth rate	3 days	1,678 (nominal)	pH 4.5; 26°C	3	[31]
Aluminium fluoride	<i>Chlorella vulgaris</i>	Algae	LC50	Population growth rate	3 days	8,393 (nominal)	pH 4.5; 26°C	3	[31]
Aluminium chloride	<i>Salmo trutta</i>	Fish	NOEC	Mortality	6 weeks	29.7–35.1 (in mono Al)	pH 5.2; 12–14°C; hardness 2 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[32]
Aluminium chloride	<i>Salmo trutta</i>	Fish	NOEC	Mortality	6 weeks	64.8–83.7 (in mono Al)	pH 5.2; 12–14°C; hardness 16.8 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[32]
Aluminium chloride	<i>Salmo trutta</i>	Fish	LC100	Mortality	6 weeks	64.8–83.7 (in mono Al)	pH 5.2; 12–14°C; hardness <1.4 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[32]
Aluminium sulfate	<i>Salmo salar</i>	Fish	NOEC	Mortality	60 days	71 (total Al)	pH 5.5; 8°C; hardness 3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[33]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LOEC (15% mortality)	Mortality	60 days	124 (total Al)	pH 5.5; 8°C; hardness 3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[33]
Not stated	<i>Salmo trutta</i>	Fish	LC27	Mortality	30 days	108 (in mono Al)	pH 4.5–5.4; 10°C; hardness 1 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[34]
<b>pH &gt;6.5</b>									
Aluminium fluoride	<i>Chlorella vulgaris</i>	Algae	LC50	Mortality	15 days	125,895 (nominal)	pH 6.8; 26°C	3	[31]
Aluminium fluoride	<i>Chlorella vulgaris</i>	Algae	NOEC	Population growth rate	15 days	33,572 (nominal)	pH 6.8; 26°C	3	[31]
Aluminium nitrate	<i>Asellus aquaticus</i>	Crustaceans	LC10	Mortality	15 days	500 (nominal)	10°C	3	[21]

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
Aluminium nitrate	<i>Lymnaea stagnalis</i>	Molluscs	Significant effect	Behaviour	14 days	300 (total Al)	pH 7.0; 17–21°C	3	[35]
Aluminium sulfate	<i>Dugesia etrusca</i>	Flatworms	Significant effect	Mortality	6 days	500 (total Al)	pH 6.8; 20°C	3	[36]
Not stated	<i>Oncorhynchus mykiss</i>	Fish	LC50	Mortality	28 days	560 (total Al)	pH 7.4; 13°C; hardness 104 mg l <sup>-1</sup> CaCO <sub>3</sub>	4	[37]

<sup>1</sup> See Annex 1.

LOEC = lowest observed effect concentration

NOEC = no observed effect concentration

EC30 = concentration effective against 30% of the organisms tested

LCx = concentration lethal to X% of the organisms tested

**Table 2.9 Most sensitive short-term aquatic toxicity data for freshwater organisms**

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
<b>pH &lt;6.5</b>									
Not stated	<i>Chlorella pyrenoidosa</i>	Algae	EC50	Growth rate	48 hours	3 (in mono Al)	pH 6.2; hardness 28 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[29]
Aluminium chloride and fluoride	<i>Chlorella vulgaris</i>	Algae	-	Effects on Physiology	4 hours	8,393 (nominal)	pH 5.65 (4.5–6.8); 26°C	3	[31]
Acid digested Al metal	<i>Hyalella azteca</i>	Crustaceans	LC50	Mortality	96 hours	>1,000 (in mono Al)	pH 4–5.5; 20–25°C; hardness 15.3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[38]
Acid digested Al metal	<i>Amnicola pisidium</i>	Molluscs	LC50	Mortality	96 hours	>1,000 (in mono Al)	pH 4–5.5; 20–25°C; hardness 15.3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[38]
Acid digested Al metal	<i>Pisidium compressum</i>	Molluscs	LC50	Mortality	96 hours	>1,000 (in mono Al)	pH 4–5.5; 20–25°C; hardness 15.3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[38]
Acid digested Al metal	<i>Enallagma</i> sp.	Insects	LC50	Mortality	96 hours	>1,000 (in mono Al)	pH 4–5.5; 20–25°C; hardness 15.3 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[38]
Aluminium chloride	<i>Daphnia magna</i>	Crustaceans	LC50	Mortality	48 hours	320 (nominal)	pH 6.5; 18–20°C; hardness 2.45 mg l <sup>-1</sup> CaCO <sub>3</sub>	3	[39]
Aluminium wire dissolved in HCl	<i>Bufo americanus</i>	Amphibians	-	Reduced hatching success	8–12 days	10 (in mono Al)	pH 4.14; 6–24°C; hardness 1.9 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[40]
Aluminium wire dissolved in HCl	<i>Rana sylvatica</i>	Amphibians	-	Reduced hatching success	11 days	20 (in mono Al)	pH 4.14; 10–24°C; hardness 1.9 mg l <sup>-1</sup> CaCO <sub>3</sub>	2	[40]
Aluminium nitrate	<i>Bufo bufo</i>	Amphibians	No effect	Hatching success and survival	13 days	22 (in mono Al)	pH 6.0	1	[41]
Aluminium sulfate	<i>Esox lucius</i>	Fish	~50%	Mortality	10 days	300 (nominal)	pH 4.2; 15°C	3	[42]
Aluminium sulfate	<i>Rutilus rutilus</i>	Fish	>50%	Mortality	10 days	100 (nominal)	pH 4.2; 15°C	3	[42]
Aluminium sulfate	<i>Oncorhynchus mykiss</i>	Fish	NOEC	Mortality	96 hours	50 (total Al)	pH 4.3	3	[43]

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	120 hours	51 (in mono Al)	pH 5.2; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	120 hours	54 (in mono Al)	pH 5.2; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	96 hours	76 (in mono Al)	pH 4.8; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	120 hours	122 (in mono Al)	pH 4.8; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	120 hours	259 (in mono Al)	pH 4.5; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
Aluminium sulfate	<i>Salmo salar</i>	Fish	LC50	Mortality	140 hours	284 (in mono Al)	pH 4.5; 10°C; hardness 4.4 $\text{mg l}^{-1}$ $\text{CaCO}_3$	1	[44]
<b>pH &gt;6.5</b>									
Acidified Al	<i>Chlorella pyrenoidosa</i>	Algae	EC50	Population growth	48 hours	60 (in mono Al)	pH 7.0; hardness 28 $\text{mg l}^{-1}$ $\text{CaCO}_3$	2	[29]
Aluminium chloride	<i>Chironomus plumosus</i>	Insects	LC50	Mortality	96 hours	30,000 (nominal)	pH 7.0; 20°C	2	[45]
Aluminium nitrate	<i>Bufo bufo</i>	Amphibians	No effect	Hatching success and survival	13 days	73 (in mono Al)	pH 6.0	1	[41]
Not stated	<i>Gastrophryne carolinensis</i>	Amphibians	LC50	Mortality	7 days	50 (total Al)	pH 7.4; 22°C; hardness 195 $\text{mg l}^{-1}$ $\text{CaCO}_3$	4	[37]
Not stated	<i>Carassius auratus</i>	Fish	LC50	Mortality	7 days	150 (total Al)	pH 7.4; 22°C; hardness 194 $\text{mg l}^{-1}$ $\text{CaCO}_3$	4	[37]
Aluminium sulfate	<i>Oncorhynchus mykiss</i>	Fish	NOEC	Mortality	96 hours	91 (total Al)	pH 8.7	3	[43]
Aluminium chloride	<i>Lepomis machrochirus</i>	Fish	No effect	Mortality	96 hours	31–75 (in mono Al)	pH 7.5	2	[46]
Aluminium chloride	<i>Ictalurus punctatus</i>	Fish	No effect	Mortality	96 hours	31–75 (in mono Al)	pH 7.5	2	[46]
Aluminium chloride	<i>Pimephales promelas</i>	Fish	No effect	Mortality	96 hours	31–75 (in mono Al)	pH 7.5	2	[46]

<sup>1</sup> See Annex 1.

NOEC = no observed effect concentration

EC50 = concentration effective against 50% of the organisms tested; LC50 = concentration lethal to 50% of the organisms tested

## 2.6.2 Toxicity to saltwater organisms

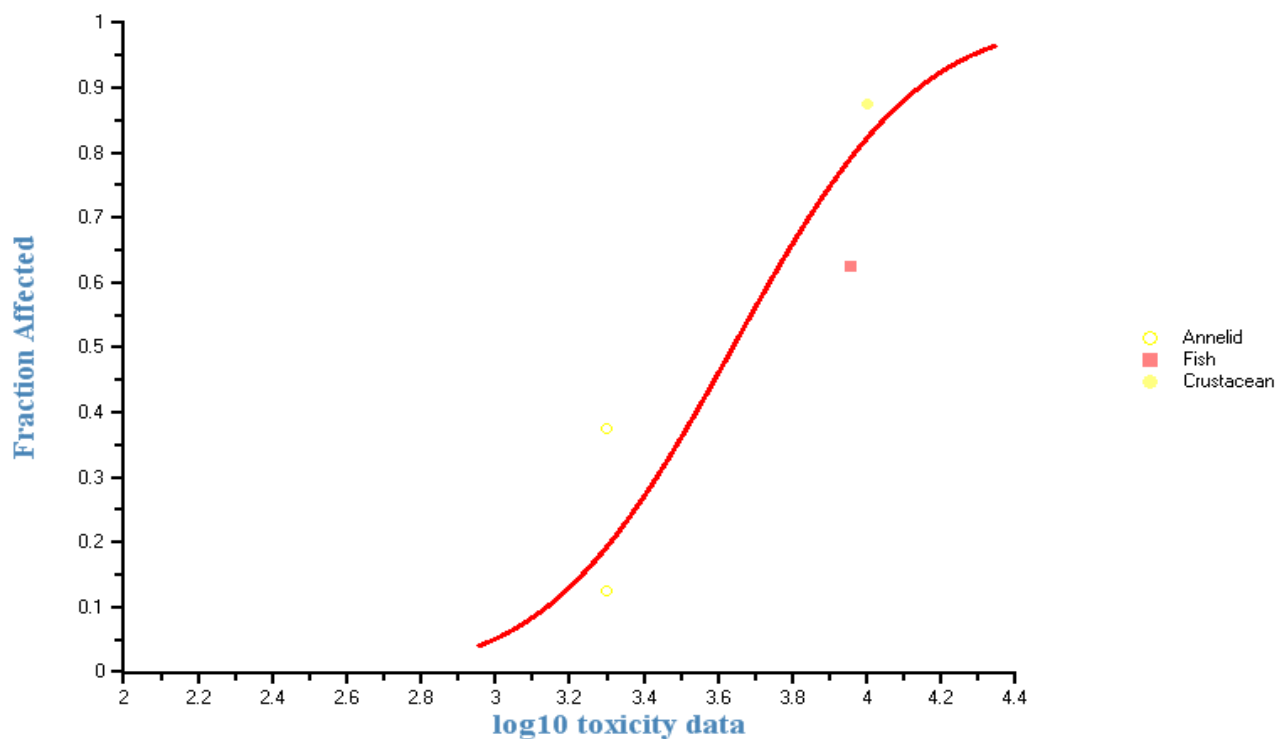
Short-term saltwater toxicity data from single species tests are available for three taxonomic groups, i.e. crustaceans, annelids and fish. No short-term toxicity data for algae were found. Long-term saltwater data from single species tests are also available for three taxonomic groups, i.e. crustaceans, annelids and fish. Data from field studies with saltwater organisms were not found.

The short-term toxicity dataset is relatively limited with a total of only 27 data points available. Most of the short-term toxicity data are available for fish (18 data points) and crustaceans (8 data points). The long-term toxicity dataset is very limited, with a total of only 4 data points available.

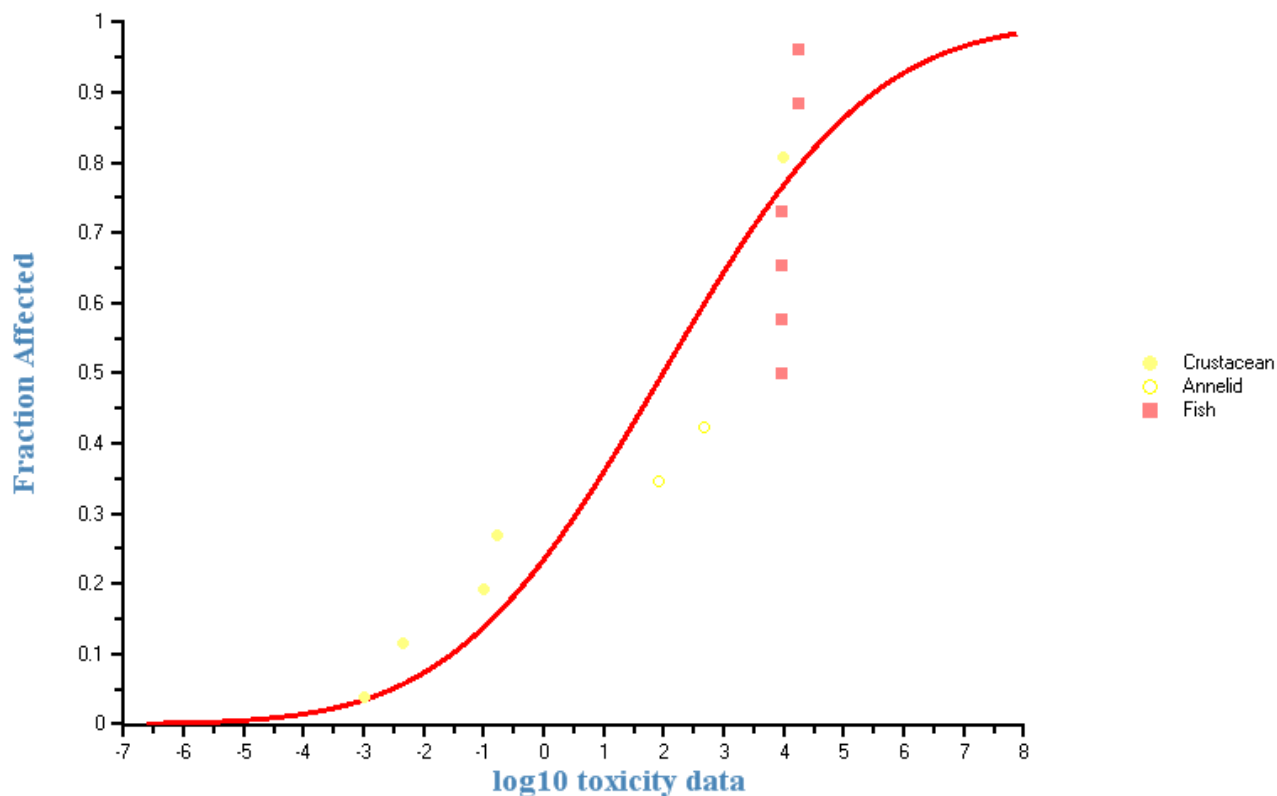
A preliminary analysis of the relative sensitivity of the species used in short-term tests (i.e. not taking into account the quality of the available studies) indicates that crustaceans, followed by annelids, are the most sensitive species, with short-term effect concentrations reported as low as 0.0045 and 480  $\mu\text{g l}^{-1}$ , respectively. The long-term dataset is too limited to allow even a tentative conclusion to be drawn on the comparative sensitivity of the taxonomic groups. Table 2.10 provides an overview of saltwater toxicity data and Section 3.1.2 a more detailed discussion of the available data.

Diagrammatic representations of the available saltwater data (cumulative distribution functions) for aluminium are presented in Figures 2.3 and 2.4. These diagrams include all data regardless of quality and provide an overview of the spread of the available data. These diagrams are not species sensitivity distributions and have not been used to set the aluminium PNECs. The lowest critical saltwater data for aluminium are presented in Tables 2.10 and 2.11.

**Figure 2.3** Cumulative distribution function of saltwater long-term data ( $\mu\text{g l}^{-1}$ ) for aluminium



**Figure 2.4** Cumulative distribution function of saltwater short-term data ( $\mu\text{g l}^{-1}$ ) for aluminium



**Table 2.10 Most sensitive long-term aquatic toxicity data for saltwater organisms**

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration (days)	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
Aluminium chloride	<i>Capitella capitata</i>	Annelids	NOEC	Mortality	7	2,000 (nominal)	pH 7.6–8	3	[47]
Aluminium chloride	<i>Neanthes arenaceodentata</i>	Annelids	NOEC	Mortality	7	2,000 (nominal)	pH 7.6–8	3	[47]
Aluminium chloride	<i>Cancer anthonyi</i>	Crustaceans	LC50	Mortality	7	>10,000 (dissolved Al)	pH 7.8; 20°C; salinity 34‰	2	[48]
Aluminium chloride	<i>Cynoscion nebulosus</i>	Fish – salmonid	NOEC	Mortality	14	9,000 (nominal)	ND	3	[49]

<sup>1</sup> See Annex 1.

NOEC = no observed effect concentration

LC50 = concentration lethal to 50% of the organisms tested

ND = no data

**Table 2.11 Most sensitive short-term aquatic toxicity data for saltwater organisms**

Test substance	Species	Taxonomic group	Endpoint	Effect	Test duration	Conc. ( $\mu\text{g l}^{-1}$ )	Comments	Reliability index <sup>1</sup>	Reference
Aluminium sulfate	<i>Myxicola infundibulum</i>	Annelids	Behaviour	Withdrawal activity affected	ND	84 (nominal)	ND	3	[50]
Aluminium chloride	<i>Ctenodrilus serratus</i>	Annelids	LC50	Mortality	96 hours	480 (nominal)	pH 7.6–8	3	[47]
ND	<i>Penaeus japonicus</i>	Crustaceans	LC50	Mortality	96 hours	0.001 (nominal)	28–30°C; salinity 32–35‰	3	[51]
ND	<i>Penaeus japonicus</i>	Crustaceans	LC50	Mortality	96 hours	0.0045 (nominal)	28–30°C; salinity 32–35‰	3	[51]
ND	<i>Penaeus japonicus</i>	Crustaceans	LC50	Mortality	96 hours	0.1 (nominal)	28–30°C; salinity 32–35‰	3	[51]
ND	<i>Artemia salina</i>	Crustaceans	LC50	Mortality	96 hours	0.17 (nominal)	28–30°C; salinity 32–35‰	3	[51]
Aluminium chloride	<i>Cynoscion nebulosus</i>	Fish – salmonid	LC50	Mortality	7 days	18000 (nominal)	ND	3	[49]
Aluminium chloride	<i>Sciaenops ocellatus</i>	Fish – non-salmonid	NOEC	Mortality	11 days	9000 (nominal)	pH 6.1–7.5	3	[49]
Aluminium chloride	<i>Fundulus similis</i>	Fish – non-salmonid	NOEC	Mortality	11 days	9000 (nominal)	pH 6.1–7.5	3	[49]
Aluminium chloride	<i>Cyprinodon variegatus</i>	Fish – non-salmonid	NOEC	Mortality	11 days	9000 (nominal)	pH 6.1–7.5	3	[49]
Aluminium chloride	<i>Cyprinodon variegatus</i>	Fish – non-salmonid	LC50	Mortality	9 days	18000 (nominal)	pH 5.5–6.7	3	[49]
Aluminium chloride	<i>Fundulus grandis</i>	Fish – non-salmonid	NOEC	Mortality	11 days	18000 (nominal)	pH 5.1–6.8	3	[49]

<sup>1</sup> See Annex 1.

NOEC = no observed effect concentration

LC50 = concentration lethal to 50% of the organisms tested

ND = no data

### **2.6.3 Toxicity to sediment-dwelling organisms**

No sediment toxicity data for aluminium were found.

### **2.6.4 Endocrine-disrupting effects**

No information was found to suggest that aluminium causes endocrine-disrupting effects.

### **2.6.5 Mode of action of aluminium**

Information on the toxic mode of action of aluminium is available for algae and fish. The mode of action differs between these two taxonomic groups.

In algae, two main modes of action for monomeric aluminium have been postulated. The first is thought to be interference with intracellular phosphorus metabolism through possible reaction with phosphate reserves or by affecting intracellular phosphatase activity [30]. The second is the inhibition of glucose metabolism early in the glycolytic pathway through complexation of free aluminium with cytoplasmic phosphate [59]. The environmental pH is an important factor in these reactions. However, evidence on whether low pH contributes to, or reduces, effects in algae is conflicting. For reactions with phosphorus metabolism, increased hydrogen ions at low pH are reported to compete for ligand sites and reduce the toxic effects of aluminium [30]. For effects on the glycolytic pathway, however, low pH results in complexation of competing hydrolysis and precipitation reactions, and increased toxicity. This is due to the availability of greater concentrations of free aluminium ( $Al^{3+}$ ), which then compete with calcium and magnesium active transport systems, resulting in greater internal Al concentrations [59].

In fish, the mechanism of toxicity is reported to involve both the surface interaction of aluminium at the gill epithelium and the subsequent increase of internal aluminium in the cells of the gill [15]. These effects are pH-mediated. At low environmental pH, aluminium comes into contact with the more alkaline microenvironment of the gill surface and precipitates out due to the formation of low solubility aluminium species. This results in a number of cellular effects, including:

- disruption of gill epithelium barrier properties leading to losses of electrolytes, haemoconcentration and impaired delivery of oxygen to body tissues [1];
- growth of aluminium polymers on the gill surface;
- increased mucus secretion leading to clogging of the intercellular spaces and hypoxia [60].

# 3. Calculation of PNECs as a basis for the derivation of quality standards

## 3.1 PNECs for freshwaters

### 3.1.1 PNEC for deriving an annual average concentration

Only limited long-term freshwater data could be found. In studies where  $\text{pH} \leq 6.5$ , only fish and algal data could be located. In studies with  $\text{pH} \geq 6.5$ , data are available for algae, invertebrates and fish.

#### *Data for pH <6.5*

Few long-term data are available for algae. Only two studies could be located, one of which is of poor quality. The lowest reported effect concentration is a 4-day EC30 of  $7 \mu\text{g l}^{-1}$  (inorganic monomeric Al) for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6 [30]. A higher EC30 of  $53 \mu\text{g l}^{-1}$  (inorganic monomeric Al) was reported at pH 5.5. This study was carried out with replication and chemical analysis of the aluminium species. Consequently, it is regarded as valid for PNEC derivation. The only other long-term data for algae are NOEC and LC50 data for *Chlorella vulgaris* [31]. The lowest reported value in this study is a 3-day NOEC of  $1,678 \mu\text{g l}^{-1}$  total aluminium at pH 4.5. No chemical analysis was carried out in the study and, consequently, it is not possible to estimate the fraction of labile aluminium in the test system. This study is regarded as unsuitable for PNEC derivation.

No long-term data could be located on the effects of aluminium on freshwater invertebrates at  $\text{pH} \leq 6.5$ .

A small number of chronic fish studies are available. The available data suggest relatively high sensitivity in these organisms. Buckler *et al.* [33] investigated the effects of aluminium on Atlantic salmon (*Salmo salar*) at pH 5.5. No mortality was observed at a concentration of  $71 \mu\text{g l}^{-1}$  total aluminium after a 60-day exposure. However, 15 per cent of larvae died when exposed to  $124 \mu\text{g l}^{-1}$  total aluminium for the same duration. Based on the available data, these values could be regarded as a no observed effect concentration (NOEC) and a lowest observed effect concentration (LOEC), respectively. Both concentrations are expressed as total aluminium, with labile aluminium reported to be present at 70–80 per cent of the total filtered aluminium concentration. However, the table of data showing analytical results does not reflect this statement and the actual proportion of labile aluminium cannot easily be obtained from the data. Consequently, this study is treated as supporting information only.

The lowest reliable fish data are reported from a 6-week study with brown trout (*Salmo trutta*) exposed to aluminium at pH 5.2 at different concentrations of calcium. At a concentration of  $29\text{--}35 \mu\text{g l}^{-1}$  (inorganic monomeric Al), no effect on fish mortality was observed at  $2 \text{ mg l}^{-1} \text{ CaCO}_3$  [32]. At  $16 \text{ mg l}^{-1} \text{ CaCO}_3$ , the no-effect concentration was

64.8–83.7  $\mu\text{g l}^{-1}$  (inorganic monomeric Al). However, the same concentration caused 100 per cent mortality when hardness was reduced below 2  $\text{mg l}^{-1}$   $\text{CaCO}_3$ . The study is considered of good quality, but because no details on replication are available, it is regarded as valid with restrictions. However, it remains the lowest good quality data point for fish.

In addition to the above data, 27 per cent mortality was observed in brown trout (*Salmo trutta*) sac fry exposed to 108  $\mu\text{g l}^{-1}$  (inorganic monomeric Al) in waters with a low calcium content and pH of 4.5 or 5.4 [34]. Although this study measured labile aluminium concentrations, there is no information on replication and so it should be treated as valid with restriction and used to support the 6-week brown trout study highlighted above.

All other long-term fish data are of lower sensitivity than the studies reported above.

#### *Data for pH >6.5*

Only one study could be located on the long-term effects of aluminium on algae at pH greater than 6.5. In a 15-day study with *Chlorella vulgaris* exposed to aluminium at pH 6.8, a NOEC and LC50 of 33,572 and 125,895  $\mu\text{g l}^{-1}$  total aluminium, respectively, were reported [31]. However, the reported NOEC is not statistically significant and no chemical analysis was carried out in this study. Consequently, it is regarded as unsuitable for PNEC derivation.

A small number of long-term studies are available for invertebrates exposed to aluminium at pH greater than 6.5. However, none of the studies reported standard endpoints and none measured inorganic monomeric aluminium. In a 50-day bioaccumulation study with the crustacean *Asellus aquaticus*, only 10 per cent mortality was observed in organisms exposed to a nominal concentration of 500  $\mu\text{g l}^{-1}$  total aluminium [21]. No analysis of inorganic monomeric aluminium was carried out. Consequently, this study is not regarded as suitable for PNEC derivation.

Campbell *et al.* [35] reported a significant effect on the behaviour of the freshwater snail (*Lymnaea stagnalis*) after a 14-day exposure to 300  $\mu\text{g l}^{-1}$  total aluminium at pH 7. However, the analysis of total aluminium does not allow estimation of inorganic monomeric concentrations and so these data are not suitable for PNEC derivation. In addition to the data for crustaceans and molluscs, data are available for the flatworm *Dugesia etrusca* [36]. A six-day exposure to 500  $\mu\text{g l}^{-1}$  total aluminium at pH 6.8 resulted in significant mortality of the exposed organisms. However, concentrations are reported as total aluminium, there is no mention of replicates and the endpoints are reported as 'days of planarian death' with no mention of the number of individuals dying. Consequently, this study is not regarded as suitable for PNEC derivation. No other long-term invertebrate data are available.

The only other long-term data available for pH >6.5 are from a long-term study with rainbow trout (*Oncorhynchus mykiss*). Birge [37] reported a 28-day LC50 of 560  $\mu\text{g l}^{-1}$  at pH 7.4 in a semi-static test system with rainbow trout. However, based on the chemical analysis method (graphite furnace), these data probably relate to total aluminium concentration. Consequently, they are not suitable for deriving PNECs for inorganic monomeric aluminium.

### *PNEC for an annual average concentration*

The most sensitive reliable datum on which to base a long-term freshwater PNEC is a 4-day EC30 of  $7 \mu\text{g l}^{-1}$  for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6 [30]. This value can be converted into an EC10 of  $2.3 \mu\text{g l}^{-1}$  by dividing by a factor of 3 as described in the TGD. An assessment factor of 50 is then justified to estimate a PNEC because there are no reliable long-term data for invertebrates.

$$\text{PNEC}_{\text{freshwater\_lt}} = 2.3 \mu\text{g l}^{-1} \text{ monomeric Al/AF (50)} = 0.05 \mu\text{g l}^{-1} \text{ monomeric Al}$$

This is likely to be a conservative estimate as the available evidence suggests that toxicity declines at higher pH values, as does the availability of the monomeric aluminium species. If a generic added risk approach is taken, a median background concentration for UK rivers of  $6 \mu\text{g l}^{-1}$  [3] could be added to this value.

### 3.1.2 PNEC for deriving a maximum allowable concentration

#### *Data for pH <6.5*

Few short-term data are available for algae. Only two studies could be located, one of which is unsuitable for PNEC derivation and the other of which should be regarded as supporting data. The lowest reported effect concentration is a 48-hour EC50 of  $3 \mu\text{g l}^{-1}$  (monomeric Al) for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6.2 [29]. Higher EC50 values are reported for higher and lower pH values. This appears to be a well performed study, with chemical analysis of monomeric aluminium species. However, the algae were exposed in hard water with few complexing agents and there is no mention of replication. In addition, chronic studies with the same species, performed with replication and chemical analysis of the aluminium species, indicate lower sensitivity (4-day EC30 of  $7 \mu\text{g l}^{-1}$ ) [30]. Consequently, this short-term study is used only as supporting information in the PNEC derivation. The only other short-term data for algae are 4-hour studies with *Chlorella vulgaris* designed to investigate the effects of aluminium on algal physiology [31]. The lowest concentration causing effects on physiology is a nominal value of  $8,393 \mu\text{g l}^{-1}$  (total Al). No chemical analysis was carried out in this study and, consequently, it is not possible to estimate the fraction of labile aluminium in the test system. Therefore, this study is regarded as unsuitable for PNEC derivation.

Although the UK EQS document [1] contains a graph that identifies more than 20 invertebrate data points, its authors proceed to review only one data point in the text, i.e. for *Daphnia magna*. In addition, this datum is based on nominal concentrations and so should not be regarded as suitable for PNEC derivation.

Very few invertebrate data have been published since this EQS and none are of suitable quality (analysis only of total aluminium, or non-standard endpoints were used). Consequently, further data were sought from studies published before the EQS. Review of these showed that very few of the studies with invertebrates included analysis of inorganic monomeric aluminium. The only study available that indicated the measurement of this aluminium species is a report of 96-hour LC50 values for several benthic invertebrates at pH 4–5.5 [38]. Tests with *Hyalella azteca* (scud), *Amnicola pisidium* (gastropod), *Pisidium compressum* (bivalve) and *Enallagma* sp. (Damselfly) indicated low sensitivity in these species, with LC50s reported to be above the highest concentration tested of  $1,000 \mu\text{g l}^{-1}$  in all organisms [38]. However, the study appears to estimate inorganic monomeric concentrations based on total aluminium analysis, though

it does proceed to compare the results of the study directly with field measured values of inorganic monomeric aluminium. Given the uncertainty in the analysis, these data are used as supporting information only.

Few studies have been published since the UK EQS in which fish were found to be more sensitive than indicated by the EQS document. One study of relevance to UK waters is a test with pike and roach exposed to aluminium over a range of pH values (pH 4–6) [42]; pike (*Esox lucius*) were less sensitive than roach to the effects of both pH and aluminium. After a 10-day exposure, significant mortality (~50 per cent) occurred at a concentration of 600  $\mu\text{g l}^{-1}$  (total aluminium) and pH 4.5, whereas at pH 4.2 only 300  $\mu\text{g l}^{-1}$  (total aluminium) was required for similar mortality. In contrast, roach (*Rutilus rutilus*) showed >50 per cent mortality at a pH of 5.2 and an aluminium concentration of 100  $\mu\text{g l}^{-1}$  (total aluminium) (controls appeared unaffected at this pH). These data show lower sensitivity of roach and pike in comparison with salmon. No chemical analysis was carried out for this study and all effects were based on nominal concentrations and modelling of aluminium speciation. Therefore, these data are not used in the PNEC derivation.

The lowest reliable short-term fish study is that reported by Roy and Campbell [44], in which Atlantic salmon (*Salmo salar*) were exposed to aluminium at different pH values (pH 4.5, 4.8 and 5.2) for 96–120 hours. The lowest LC50 values were reported after a 120-hour exposure to 51–54  $\mu\text{g l}^{-1}$  (inorganic monomeric aluminium) at pH 4.5. At lower pH values, toxicity decreased with 120-hour LC50s of 122 and 259  $\mu\text{g l}^{-1}$  (inorganic monomeric aluminium) at pH 4.8 and 4.5, respectively. This study is well-documented, with replication and analysis of monomeric aluminium (inorganic monomeric aluminium was modelled based on measured monomeric Al data). Consequently, it is regarded as valid without restriction for PNEC derivation.

In addition to the fish data, short-term studies are also available for amphibians. Clark and LaZerte [40] reported that concentrations as low as 10–20  $\mu\text{g l}^{-1}$  aluminium affected the hatching success of the American toad (*Bufo americanus*), and wood frog (*Rana sylvatica*) after an 8–12 day exposure at pH 4.14. The study was of reasonable quality with measured aluminium concentrations and modelled inorganic monomeric concentrations. However, there was no replication. In addition, the pH levels at which toxicity occurred also caused significant effects on hatching success without the presence of aluminium. The presence of aluminium did increase toxic effects beyond those caused by pH alone, but the high sensitivity of these species is likely to be due to additional stress from pH and not to aluminium exposure alone. For this reason, this study has been treated as supporting information only.

After publication of the UK EQS [1], studies were carried out in the UK with the common toad to establish the sensitivity of indigenous amphibians. Eggs of the common toad (*Bufo bufo*) were exposed to aluminium for 13 days (fertilisation to 96-hours post hatch) at pH 6 [41]. Nominal exposure concentrations ranged from 0–320  $\mu\text{g l}^{-1}$ , but measured inorganic monomeric aluminium concentrations reached a maximum of 22  $\mu\text{g l}^{-1}$ . No adverse effects on hatching success, larval survival or development were observed up to the highest concentration tested (22  $\mu\text{g l}^{-1}$  inorganic monomeric aluminium). This was a well-conducted study with measured aluminium concentrations and is regarded as valid for PNEC derivation.

#### Data for pH >6.5

Very few short-term algal data are available for pH greater than 6.5. The lowest reported effect concentration is a 48-hour EC50 of 60  $\mu\text{g l}^{-1}$  (inorganic monomeric Al) for growth of the alga *Chlorella pyrenoidosa* exposed at pH 7 [29]. This appears to be a well-performed study, with chemical analysis of monomeric aluminium species, although the algae were exposed in hard water with few complexing agents and there is no mention of replication.

Only one short-term invertebrate study is available for this pH range. Tests with larvae of the chironomid *Chironomus plumosus* indicate low sensitivity, with a 96-hour LC50 of 30,000  $\mu\text{g l}^{-1}$  (nominal concentration) at pH 7 [45]. However, there was no chemical analysis of Al speciation. The authors of this study speculate that, at pH 7, the prevailing form of aluminium in the test would have been  $\text{Al}(\text{OH})_4^-$ . This study is not regarded as suitable for PNEC derivation, though it does provide indicative information of the relative insensitivity of insect compared with other taxa.

Many more data are available for fish exposed to aluminium at pH >6.5. However, there are few standard effect concentration data available. Most data relate to no-effect concentrations, reflecting the lower toxicity of aluminium at these pH ranges. The only LC50 value available for fish at this pH range is a value of 150  $\mu\text{g l}^{-1}$  total aluminium for the goldfish (*Carassius auratus*) exposed for 7 days [37]. However, this study is based on total concentrations and so is not suitable for PNEC derivation.

Heming and Blumhagen [43] investigated the effects of aluminium at various pH levels on the survival, plasma acid-base and electrolyte states of rainbow trout (*Oncorhynchus mykiss*) over 96 hours. At pH 7.8, there was no effect on survival of the fish at a concentration of 900  $\mu\text{g l}^{-1}$  aluminium. At higher pH (pH 8.7), however, 50 per cent mortality was recorded in the absence of aluminium. This study makes no mention of replication and aluminium was measured as total only. Consequently, it is not regarded as suitable for PNEC derivation.

A similar lack of effect is reported for bluegill sunfish (*Lepomis macrochirus*), channel catfish (*Ictalurus punctatus*) and fathead minnow (*Pimephales promelas*). No mortality was observed at pH 7.5 after a 96-hour exposure to nominal concentrations of aluminium of up to 400  $\mu\text{g l}^{-1}$  [46]. Total and monomeric aluminium were measured and inorganic aluminium was estimated to be similar to total monomeric Al. Consequently, it is estimated that the inorganic monomeric concentrations would have ranged from 31–75  $\mu\text{g l}^{-1}$ . This is a well-documented study with replication and chemical analysis, and is regarded as suitable for PNEC derivation.

In addition, short-term data are available for amphibians. The lowest reliable data are for eggs of the common toad (*Bufo bufo*) exposed for 13 days (fertilisation to 96-hours post hatch) to aluminium at pH 7.5 [41]. Nominal exposure concentrations ranged from 0–320  $\mu\text{g l}^{-1}$ , but measured inorganic monomeric aluminium concentrations reached a maximum of only 73  $\mu\text{g l}^{-1}$ . No adverse effects on hatching success, larval survival or development were observed up to the highest concentration tested (73  $\mu\text{g l}^{-1}$  inorganic monomeric aluminium). This is a well-conducted study with measured aluminium concentrations and is regarded as valid for PNEC derivation.

The only other datum for amphibians in this pH range is a 7-day LC50 of 50 µg l<sup>-1</sup> total aluminium in the narrow mouthed toad (*Gastrophryne carolinensis*) exposed at pH 7.4 [37]. However, there was chemical analysis only of total aluminium so inorganic monomeric aluminium could not be estimated. Therefore this value is not included in the PNEC derivation.

#### *PNEC for a maximum allowable concentration*

The most sensitive reliable datum on which to base a short-term freshwater PNEC is the 4-day EC30 of 7 µg l<sup>-1</sup> for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6 [30], which was also used to derive the long-term freshwater PNEC. Use of this value is justified because:

- a 4-day study lies on the boundary between ‘short-term’ and ‘long-term’ tests for algae;
- there is supporting evidence from other algal studies;
- this is the best quality algal study available for monomeric aluminium.

An EC30 value of 7 µg l<sup>-1</sup> can be converted into an EC10 of 2.3 µg l<sup>-1</sup> by dividing by a factor of 3. An assessment factor of 10 is then justified to estimate a short-term PNEC because the critical datum is an EC10 and there are sufficient data to suggest that algae are the most sensitive taxonomic group.

$$\text{PNEC}_{\text{freshwater\_st}} = 2.3 \mu\text{g l}^{-1} \text{ monomeric Al/AF (10)} = 0.23 \mu\text{g l}^{-1} \text{ monomeric Al}$$

This is likely to be a conservative estimate as the available evidence suggests that toxicity declines at higher pH values, as does the availability of the monomeric aluminium species. If a generic added risk approach is taken, a median background concentration for UK rivers of 6 µg l<sup>-1</sup> [3] could be added to this value.

## 3.2 PNECs for saltwaters

Short-term toxicity data for saltwater organisms are available for three different taxonomic groups, i.e. crustaceans, annelids and fish. Long-term toxicity data are also available for crustaceans, annelids and fish, but the taxonomic coverage of available saltwater data is poor. However, of more concern is the fact that nearly all the available data are based on nominal concentrations and are therefore unsuitable for PNEC derivation. Only one study with saltwater organisms could be found that is based on measured aluminium concentrations and is of sufficient quality for PNEC calculation. A summary of the available data is presented below.

### 3.2.1 PNEC for deriving an annual average concentration

Long-term toxicity data are available for three taxonomic groups, i.e. crustaceans, annelids and fish. No data are available for marine algae. The limited long-term toxicity dataset does not allow firm conclusions to be drawn on the comparative sensitivity of the taxonomic groups.

Long-term data for marine invertebrates (annelids and crustaceans) indicate low sensitivity, with effect and no-effect concentrations ranging from 2,000 to >10,000 µg l<sup>-1</sup>. The polychaete worms *Capitella capitata* and *Neanthes arenaceodentata* were most

sensitive, with 7-day NOECs of 2000 µg l<sup>-1</sup> in both species [47]. However, no chemical analysis was carried out in this study and so the contribution of different aluminium species to toxicity could not be identified. Consequently, these data are not regarded as suitable for PNEC derivation.

The only other long-term invertebrate datum available is a 7-day LC50 of >10,000 µg l<sup>-1</sup> for embryos of the yellow crab *Cancer anthonyi* [48]. The concentrations in this study were measured and the study appears to be valid, although conducted using a non-standard method. However, because the final result is an unbounded NOEC, it should be used only as supporting information.

The lowest reported long-term data point is a 14-day NOEC of 9000 µg l<sup>-1</sup> for the salmonid fish *Cynoscion nebulosus* [49]. No details are provided on the form of aluminium used and the experiments were based on nominal concentrations. This study is therefore regarded as unreliable and is excluded from the PNEC assessment. No other high quality long-term saltwater fish data are available.

The lack of reliable long-term saltwater toxicity data means that an annual average concentration must currently be based upon the freshwater PNEC (*Chlorella pyrenoidosa* EC10 of 2.3 µg l<sup>-1</sup> with an assessment factor of 50), with an additional assessment factor of 10 to account for potentially greater sensitivity of saltwater biota for which data are unavailable.

**PNEC<sub>saltwater\_lt</sub> = 2.3 µg l<sup>-1</sup> monomeric Al/AF (50 × 10) = 0.005 µg l<sup>-1</sup> monomeric Al**

### 3.2.2 PNEC for deriving a maximum allowable concentration

Short-term toxicity data are available for three taxonomic groups, i.e. crustaceans, annelids, and fish. No short-term data are available for algae. As with the long-term dataset, none of the short-term values are based on measured concentrations, so none are suitable for PNEC derivation.

The lowest reported toxicity data points for short-term exposure to aluminium are 96-hour LC50s of 0.001 and 0.0045 µg l<sup>-1</sup> for *Penaeus japonicus* [51]. These data are by far the lowest values in the whole aluminium dataset (saltwater and freshwater). However, no chemical analysis was carried out in this study and the test pH was not reported. Consequently, these values are not suitable for PNEC derivation.

The next lowest reported data points are 96-hour LC50s of 0.1 and 0.17 µg l<sup>-1</sup> for *Penaeus japonicus* and *Artemia salina*, respectively [51]. However, neither of these studies report measured concentrations nor the form of aluminium used. Consequently, they are not suitable for PNEC derivation.

In addition to the above studies, Ward [50] reported that a concentration of 84 µg l<sup>-1</sup> affected the withdrawal activity of the polychaete *Myxicola infundibulum*. However, there are no experimental details available to help assess the quality of the study and so it is not included in the PNEC derivation.

The lowest short-term data point for a salmonid fish is a 7-day LC50 of 18000 µg l<sup>-1</sup> in the speckled trout (*Cynoscion nebulosus*) [49]. Lower short-term data points exist for non-salmonid fish. Pulley [49] reported 11-day NOECs of 9,000 µg l<sup>-1</sup> for redfish (*Sciaenops*

*ocellatus*), killifish (*Fundulus similis*) and sheepshead minnow (*Cyprinodon variegatus*). However, none of these fish studies report the form of aluminium used and all concentrations are reported as nominal. Therefore, none of the fish data are included in the derivation of a PNEC.

The lack of reliable short-term saltwater toxicity data means that a maximum allowable concentration PNEC must currently be based upon the freshwater PNEC (*Chlorella pyrenoidosa* EC10 of 2.3 µg l<sup>-1</sup> with an assessment factor of 10), with an additional assessment factor of 10 to account for potentially greater sensitivity of saltwater biota for which data are unavailable.

$$\text{PNEC}_{\text{saltwater\_lt}} = 2.3 \mu\text{g l}^{-1} \text{ monomeric Al/AF } (10 \times 10) = 0.023 \mu\text{g l}^{-1} \text{ monomeric Al}$$

### 3.3 Derivation of PNECs by the TGD probabilistic approach (SSD method)

The minimum number of long-term toxicity data (at least 10 NOECs from eight taxonomic groups) is not available. Therefore, the species sensitivity distribution (SSD) approach cannot be used for PNEC derivation.

### 3.4 Derivation of existing EQSs

While the data involved and gathered in the 1998 report [1] on proposed EQSs for aluminium in water can be used, the existing EQSs themselves were never adopted.

### 3.5 Derivation of PNECs for sediment

No data on the toxicity of aluminium in sediments could be found for algal, invertebrate or fish species. Therefore no PNECs were derived for Al in sediment.

### 3.6 Derivation of PNECs for secondary poisoning of predators

#### 3.6.1 Mammalian and avian toxicity data

The WHO published an EHC document for aluminium in 1997 [14]. Given the detailed review and quality assessment that is carried out for such a document, this source was assumed to contain the most sound and scientifically accurate data available at that time. Consequently, it is used as a primary data source for this report. In addition, data in literature published after the EHC were also sought, but further reliable or relevant values were not found. Therefore, the data detailed in Table 3.1 all originate from the WHO EHC194 [14].

**Table 3.1 Most sensitive mammal and bird oral toxicity data relevant for the assessment of secondary poisoning**

Study and result	Details
<b>Sub-chronic toxicity to mammals</b>	
<p>Gomez <i>et al.</i> 1986 [52] Cited in WHO 1997 [14] <b>Sub-chronic LOAEL</b> <b>= 104 mg kg<sup>-1</sup> bw d<sup>-1</sup></b> <b>Sub-chronic NOAEL</b> <b>= 52 mg kg<sup>-1</sup> bw d<sup>-1</sup></b></p>	<p>Female Sprague-Dawley rats received aluminium nitrate in their drinking water for 28 days at corresponding doses of 1, 26, 52 or 104 mg Al kg<sup>-1</sup> body weight (bw) day<sup>-1</sup> (ten per group). This is considered a well-conducted study, which examined a wide range of endpoints including clinical signs, food and water consumption, growth, haematological and serum analyses, tissue and plasma concentrations of aluminium and histopathology. The NOAEL and LOAEL were based on mild histopathological changes in the spleen and liver of the top dose group and a dose-dependent accumulation of aluminium in the spleen, heart and gastrointestinal tract.</p>
<b>Chronic toxicity to mammals</b>	
<p>Domingo <i>et al.</i> 1987 [53] Cited in WHO 1997 [14] <b>Chronic LOAEL</b> <b>= 261 mg kg<sup>-1</sup> bw d<sup>-1</sup></b> <b>Chronic NOAEL</b> <b>= 52 mg kg<sup>-1</sup> bw d<sup>-1</sup></b></p>	<p>Female Sprague-Dawley rats received aluminium nitrate in their drinking water for 100 days at corresponding doses of 0, 26, 52 or 261 mg Al kg<sup>-1</sup> bw day<sup>-1</sup>. This is considered a well-conducted study, which examined a wide range of endpoints including clinical signs, food and water consumption, growth, haematological and serum analyses, tissue and plasma concentrations of aluminium and histopathology. The NOAEL and LOAEL were based on significantly decreased body weight gain and decreased food consumption in the top dose group.</p>
<p>Katz <i>et al.</i> 1984 [54] Cited in WHO 1997 [14] <b>Chronic NOAEL</b> <b>= 70 mg kg<sup>-1</sup> bw d<sup>-1</sup></b></p>	<p>Beagle dogs received sodium aluminium phosphate in their diet for 6 months at corresponding doses of 118, 317, or 1,034 mg kg<sup>-1</sup> bw day<sup>-1</sup> for males and 112, 361 or 1,087 mg kg<sup>-1</sup> bw d<sup>-1</sup> for females (four animals per group). The study period is considered to be sub-chronic exposure for dogs and the group size was considered to be rather small. Clinical signs, food and water consumption, organ and body weights, haematological and serum analyses, urinalysis, ophthalmologic examinations, tissue and plasma concentrations of aluminium and histopathology were examined. The NOAEL was based on significantly decreased food consumption in the top dose females, but no other effects were observed.</p>
<p>Although the two chronic studies above may strictly be defined as sub-chronic exposure, no other true chronic (i.e. ≥2 year) studies were identified. Similarly, although aluminium is not thought to be carcinogenic, no specific carcinogenicity studies were available.</p>	
<b>Effects on reproduction of mammals</b>	
<p>The EHC monograph [14] states that ‘the limited number of studies are not able to provide adequate information on reproductive toxicity’ for aluminium in mammals. However, some information is available from studies on the rat, as discussed below.</p>	

Study and result	Details
Domingo <i>et al.</i> 1987 [55, 56] Cited in WHO 1997 [14] <b>LOAEL = 13 mg kg<sup>-1</sup> bw d<sup>-1</sup></b>	Rats were intubated/incubated with aluminium nitrate 60 days before mating at corresponding doses of 0, 13, 26 or 52 mg Al kg <sup>-1</sup> bw day <sup>-1</sup> for males and 14 days before mating for virgin females. Pregnant animals were then dosed (same doses) from 14 days gestation to 21 days of lactation. No effects were observed on fertility, litter size, or intrauterine or postnatal offspring mortality. The LOAEL was based on a dose-dependant delay in pup growth in all treatment groups, although it is unclear as to whether this effect is a true developmental effect rather than maternal or paternal toxicity.
<b>Embryotoxicity and teratogenicity</b>	
<p>Studies to assess the potential developmental toxicity of aluminium are also limited. It is thought that the form of aluminium and presence of any organic chelators are significant influencing factors [14].</p> <p>A developmental LOAEL of 75 mg Al kg<sup>-1</sup> bw d<sup>-1</sup> during gestation days 9–13 has been reported [14]. However, details and the source of this value are not available (presumed to be in rats via intraperitoneal administration).</p>	
<b>Neurotoxicity to mammals</b>	
<p>The EHC monograph [14] states that aluminium is considered to be neurotoxic to experimental animals and that species variation exists. However, no studies are available that provide clear NOAELs or LOAELs.</p>	
<b>Sub-chronic toxicity to birds</b>	
Hussein <i>et al.</i> 1988 [57] Cited in WHO 1997 [14] <b>Sub-chronic NOAEL = 0.05% Al in diet (0.5 mg kg<sup>-1</sup> diet)</b>	Japanese quail ( <i>Coturnix coturnix japonica</i> ) were fed diets containing 0.05, 0.1, 0.15 and 0.3% aluminium, as aluminium sulfate for 4 weeks. The NOAEL was based on significantly decreased egg production, temporarily reduced eggshell-breaking strength and food consumption at 0.1%; and significantly decreased body weight gain, temporarily reduced eggshell-breaking strength and food consumption at 0.15%. At 0.3%, all the above effects were permanent.
<b>Long-term toxicity to birds</b>	
Wisser <i>et al.</i> 1990 [58] Cited in WHO 1997 [14] <b>Chronic LOAEL = 0.15% Al in diet (1.5 mg kg<sup>-1</sup> diet)</b>	White leghorn laying hens were fed diets containing 0, 0.15 or 0.3% aluminium for 17 weeks. The LOAEL was based on significantly depressed fertility and chick body weight at 0.15% and these effects plus significantly reduced total egg production and feed consumption at 0.3% aluminium. Egg hatchability was unaffected.
<p>No studies are available on the potential effects of aluminium on avian reproduction or development, or on potential carcinogenicity or other toxicity.</p>	

LOAEL = lowest observed adverse effect level

NOAEL = no observed adverse effect level

### 3.6.2 PNECs for secondary poisoning of predators

A fuller dataset is available on aluminium toxicity to mammals than to birds (Table 7.1). The most sensitive mammalian LOAEL in Table 3.1 is 13 mg Al kg<sup>-1</sup> day<sup>-1</sup> for rat reproduction [55, 56]. The appropriate assessment factor to derive a PNEC for secondary poisoning (secpois) based on a chronic NOEC<sub>food</sub> from a 90-day mammalian study is 90 (Table 23 of the TGD [78]). This assessment factor will be applied to these data, even though they are a LOAEL because they are more sensitive than chronic data for rats and beagles (to which an assessment factor of only 30 would be applied).

$$\text{PNEC}_{\text{secpois.biota}} = \text{NOEC}_{\text{food}} (13 \text{ mg Al kg}^{-1}) / \text{AF} (90) = 0.144 \text{ mg Al kg}^{-1} \text{ prey (wet wt)}$$

Reported reliable BCF values for fish range up to 364 [19]. The concentration in water to prevent bioaccumulation in prey to levels greater than PNEC<sub>secpois.biota</sub> can therefore be calculated as follows:

$$\text{PNEC}_{\text{secpois.water}} = 0.144 \text{ mg Al kg}^{-1} \text{ prey} / \text{BCF} (364) = 0.0004 \text{ mg l}^{-1} \text{ Al} = 0.4 \text{ } \mu\text{g l}^{-1} \text{ Al}$$

## 4. Analysis and monitoring

Numerous methods [61–69] may be employed to determine total aluminium in environmental samples including water. They include:

- graphite furnace atomic absorption spectrometry (GFAAS)
- flame atomic absorption spectrometry (FAAS)
- neutron activation analysis (NAA)
- inductively coupled plasma atomic emission spectrometry (ICP-AES)
- inductively coupled plasma mass spectrometry (ICP-MS)
- spectrophotometry using absorbance and fluorescence detection
- phosphorimetry
- chromatography
- gas chromatography equipped with an electron capture detector (GUECD).

GFAAS and FAAS are the techniques (Methods 202.1 and 202.2) recommended by the US EPA for measuring low levels of aluminium in water and wastewater [65]. Detection limits of 100  $\mu\text{g}$  of aluminium  $\text{l}^{-1}$  of sample and 3  $\mu\text{g}$  of aluminium  $\text{l}^{-1}$  of sample are obtained using the FAAS and GFAAS techniques, respectively [65].

Spectrophotometry and GUECD have also been employed to measure low-ppb (11  $\mu\text{g}$   $\text{l}^{-1}$ ) levels of aluminium in water [15]. More recently, ICP-MS has more generally been applied to the analysis of waters and wastewaters, offering limits of detection of around 5  $\mu\text{g}$   $\text{l}^{-1}$  aluminium. Flow injection systems using absorbance [70] and fluorescence detection [71] have also been used to monitor aqueous aluminium levels in the field and in the laboratory, with detection limits as low as 0.3  $\mu\text{g}$   $\text{l}^{-1}$ . Ion chromatography using spectrophotometric detection and on-line preconcentration gives an effective detection limit  $<1$   $\mu\text{g}$   $\text{l}^{-1}$  in aqueous samples.

The realisation of the importance of aluminium speciation with respect to toxicity has resulted in the development of methods to determine 'reactive' aluminium, which comprises the inorganic monomeric species. The most well-established method is oxine extraction (based on a principle established by Barnes [72]), which provides a limit of detection of around 1  $\mu\text{g}$   $\text{l}^{-1}$  aluminium using GFAAS and 5  $\mu\text{g}$   $\text{l}^{-1}$  using ICP-MS and a precision better than 5 per cent relative standard deviation.

In biological samples, the ubiquitous nature of aluminium contamination is a major problem encountered in the analysis of aluminium by all methods except accelerator mass spectroscopy (AMS) using radioactive  $^{26}\text{Al}$ . A variety of analytical methods have been used to measure aluminium levels in biological materials, including AMS, GFAAS, FAAS, NAA, ICP-AES, ICP-MS and laser ablation microprobe mass analysis (LAMMA) [73–75]. Front-end separation techniques such as chromatography are frequently coupled with the analytical methods. Typical limits of detection are in the order of 2  $\mu\text{g}$   $\text{l}^{-1}$  using GFAAS [76].

The lowest proposed PNEC derived for aluminium is 0.005  $\mu\text{g}$   $\text{l}^{-1}$  monomeric inorganic aluminium for fresh- and saltwaters. The data quality requirements are that, at a third of

the EQS, total error of measurement should not exceed 50 per cent. Analytical methodologies provide detection limits of around 1–5 µg l<sup>-1</sup>, which suggests that current analytical methodologies do not offer adequate performance to analyse aluminium for compliance with the PNECs for water.

# 5. Conclusions

## 5.1 Availability of data

Short-term freshwater toxicity data are dominated by fish and crustaceans. Long-term data are fewer, describing toxicity to algae and fish. Algae, followed by fish, appear to be most sensitive.

Short-term and long-term saltwater toxicity data are available for three taxonomic groups, i.e. crustaceans, annelids and fish. Nearly all the available data are based on nominal concentrations and are, therefore, unsuitable for PNEC derivation. Only one study with saltwater organisms was based on measured aluminium concentrations.

'Total' aluminium is an unsuitable way of describing aluminium toxicity because little of the aluminium present is likely to be in a toxicologically active form. From a toxicological perspective, it is more relevant to express toxicity in terms of concentrations of inorganic monomeric aluminium. However, this precludes the use of toxicity data that are expressed as total aluminium. Such data cannot be used to predict toxicity in the field without additional information on the water chemistry to estimate aluminium speciation, which is rarely available.

## 5.2 Derivation of PNECs

Although there is a theoretical basis for a pH effect on speciation and toxicity and evidence suggesting differences in toxicity to some species at different pH, data are insufficient to warrant setting PNECs for separate pH bands.

As with other metals, the 'added risk' approach could be considered appropriate when deriving PNECs for aluminium because it is a naturally occurring substance to which organisms will have evolved tolerance. However, as the PNEC is being derived on the basis of a measure of 'available' (inorganic monomeric) aluminium, there is no need to adopt the added risk approach. The use of a speciation-based PNEC is more ecologically relevant than using added risk and removes the need to determine a background aluminium concentration at a regional scale, river basin or even local scale.

The proposed PNECs are described below and summarised in Table 5.1.

### 5.2.1 Long-term PNEC for freshwaters

The lowest reliable effect concentration is a 4-day EC30 of  $7 \mu\text{g l}^{-1}$  (inorganic monomeric Al) for growth of the alga *Chlorella pyrenoidosa* exposed at pH 6. Reliable long-term data are also available from experiments with fish, but not for invertebrates. Thus, an assessment factor of 50 is recommended to account for the uncertainty in extrapolating to other taxa for which there are no data. However, a further factor of 3 is recommended because:

- the 4-day exposure period is short in absolute terms, even though it is a chronic exposure with respect to unicellular algae;
- it is necessary to extrapolate from the reported EC30 to a NOEC.

Applying these factors results in a  $PNEC_{\text{freshwater\_lt}}$  of  $0.05 \mu\text{g l}^{-1}$  monomeric Al.

### 5.2.2 Short-term PNEC for freshwaters

The lowest reliable short-term effect concentration is a 120-hour LC50 of  $51\text{--}54 \mu\text{g l}^{-1}$  for Atlantic salmon (*Salmo salar*) at pH 4.4. Lower toxicity was seen at higher pH values. However, applying the guidance given in Annex V of the WFD would result in a short-term PNEC that is lower (i.e. more stringent) than the long-term PNEC. This cannot be defended toxicologically and so a preferred approach is to base the short-term PNEC on the 4-day algal EC30 used as the basis for the long-term PNEC and to apply a smaller assessment factor. Therefore, two assessment factors are again recommended:

- a factor of 3 to extrapolate to a NOEC;
- one of 10 to extrapolate to the PNEC.

This results in a  $PNEC_{\text{freshwater\_st}}$  of  $0.25 \mu\text{g l}^{-1}$  monomeric Al.

### 5.2.3 PNECs for saltwaters

The available data for inorganic reactive aluminium are too limited to allow even a tentative conclusion to be drawn on the comparative sensitivity of the different saltwater taxonomic groups or to base a PNEC on these data. Instead, it is recommended that both the long-term and short-term saltwater PNECs are based on their freshwater counterparts. However, an additional assessment factor (10) is recommended to account for the possibility that greater taxonomic diversity in the marine environment makes it likely that some marine taxa may be more sensitive than the most sensitive freshwater taxa.

This results in a proposed  $PNEC_{\text{saltwater\_lt}}$  of  $0.005 \mu\text{g l}^{-1}$  monomeric Al and a  $PNEC_{\text{saltwater\_st}}$  of  $0.025 \mu\text{g l}^{-1}$  monomeric Al.

### 5.2.4 PNEC for secondary poisoning

There are some indications of bioaccumulation of aluminium in biota, though it is often unclear whether body residues describe systemic uptake or merely binding to the surface of the organism. Applying the Annex V guidance to available data on bioaccumulation and toxicity to birds and mammals results in a  $PNEC_{\text{secpois}}$  of  $0.4 \mu\text{g l}^{-1}$  inorganic monomeric Al.

### 5.2.5 PNEC for sediments

There are insufficient data to derive a sediment PNEC for aluminium and the use of equilibrium partitioning to estimate a value based on aquatic toxicity data cannot be justified for metals.

**Table 5.1 Summary of proposed PNECs**

Receiving medium/exposure scenario	Proposed PNEC ( $\mu\text{g l}^{-1}$ monomeric Al)	Existing EQS
Freshwater/long-term	0.05	None adopted
Freshwater/short-term	0.25	None adopted
Saltwater/long-term	0.005	None adopted
Saltwater/short-term	0.025	None adopted
Secondary poisoning	0.4	None adopted

### 5.3 Analysis

Expressing PNECs in terms of inorganic monomeric aluminium places additional demands on the methods used to monitor compliance. This has resulted in the development of methods to determine 'reactive' aluminium, which comprises the inorganic monomeric species. The most well-established method is oxine extraction, which provides a limit of detection of around  $1 \mu\text{g l}^{-1}$  aluminium using GFAAS and  $5 \mu\text{g l}^{-1}$  using ICP-MS.

Current analytical methodologies are not yet sufficiently sensitive to be used for assessing compliance with any of the proposed PNECs in receiving waters, though they may be adequate for monitoring compliance with consent limits on point source discharges.

### 5.4 Implementation issues

Before PNECs for aluminium can be adopted as EQSs, it will be necessary to address the following issues:

1. A method for predicting concentrations of inorganic monomeric aluminium from measured concentrations of total aluminium will be necessary to permit use of the proposed PNECs in deriving consent conditions for point source discharges. Research is underway to assess whether or not such a method is feasible. If it is, consent setting and compliance assessment will almost certainly require information about local water chemistry.
2. If assessment of compliance in receiving waters is required, an extraction and analytical method for inorganic monomeric aluminium would need to be developed and trialled.
3. Because there is no existing EQS, an interim EQS cannot be adopted while these issues are being resolved. Therefore, the recommendation is not to set a standard, at least until further investigations have been undertaken.

# References & Bibliography

1. Dixon E, Whitehouse P, Gardner M and Mitchell R, 1998 *Proposed Environmental Quality Standards for aluminium in water*. Draft R&D Technical Report P43. Medmenham, Buckinghamshire: WRC.
2. Howells G, Dalziel T R K, Reader J P and Solbé J F, 1990 *EIFAC water quality criteria for European freshwater fish: report on aluminium*. *Chemistry and Ecology*, **4**, 117–173.
3. Dixon E and Gardner M J, 1998 *Reactive aluminium in UK surface waters*. *Chemical Speciation and Bioavailability*, **10**, 1–7.
4. European Chemicals Bureau (ECB), 2005 *European Chemical Substances Information System (ESIS)* [online]. Version 3.40, July 2005. Available from: <http://ecb.jrc.it/existing-chemicals/> [Accessed 31 January 2007]
5. Budavari S, O'Neil M J, Smith A, Heckelman P E and Kinneary J F., 1996 Editors *The Merck Index: An Encyclopaedia of Chemicals, Drugs, and Biologicals* (12th edn.). Rahway, NJ: Merck & Co., Inc.
6. Lide D R, 2000 Editor *CRC Handbook of Chemistry and Physics: a ready reference book of chemical and physical data* (81st edn.). Boca Raton, FL: CRC Press.
7. Division of Specialized Information Services (SIS) of the US National Library of Medicine (NLM), 2005 *Toxicology Data Network (TOXNET®): Hazardous Substances Data Bank (HSDB®)* [online]. Bethesda, MD: SIS. <http://toxnet.nlm.nih.gov/> [Accessed 31 January 2007]
8. Weast R C, 1989 Editor *CRC Handbook of Chemistry and Physics: a ready reference book of chemical and physical data* (69th edn.). Boca Raton, FL: CRC Press.
9. Windholz M, Budavari S, Blumetti R F and Otterbein E S, 1983 Editors *The Merck Index: An Encyclopaedia of Chemicals, Drugs, and Biologicals* (10th edn.). Rahway, NJ: Merck & Co., Inc.
10. Lewis R J, 1999 Editor *Sax's Dangerous Properties of Industrial Materials* (10th edn.). Volumes 1–3. New York: John Wiley & Sons.
11. International Labour Office (ILO), 1983 *Encyclopaedia of Occupational Health and Safety*. Volumes I and II. Geneva: ILO.
12. Mackison, F W, Stricoff R S and Partridge L J, 1981 Editors *Occupational Health Guidelines for Chemical Hazards*. DHHS (NIOSH) Publication No. 81-123, National Institute for Occupational Safety and Health (NIOSH)/Occupational Safety and Health Administration (OSHA). Washington: US Government Printing Office.

13. Sax N I, 1984 Editor *Dangerous Properties of Industrial Materials* (6th edn.) New York: Van Nostrand Reinhold.
14. World Health Organization (WHO), 1997 *Environmental Health Criteria 194: Aluminium*. International Programme on Chemical Safety (IPCS). Geneva: WHO. Available from: <http://www.who.int/ipcs/publications/ehc/en/> [Accessed 31 January 2007]
15. Dixon E, Whitehouse P, Gardner M and Mitchell R, 1998 *Proposed Environmental Quality Standards for aluminium in water*. Draft R&D Technical Report P43. Medmenham, Buckinghamshire: WRC-NSF.
16. Agency for Toxic Substances and Disease Registry (ATSDR), 1996 *Toxicological profile for aluminium*. Atlanta, GA: ATSDR, US Department of Health and Human Services.
17. Cleveland L and Buckler D R, 1991 *Residue dynamics and effects of aluminium on growth and mortality in brook trout*. *Environmental Toxicology and Chemistry*, **10**, 243–248.
18. Brooks A W, White K N and Bailey S E, 1992 *Accumulation and excretion of aluminium and iron by the terrestrial snail Helix Aspersa*. *Comparative Biochemistry and Physiology*, **103**, 577–583.
19. Murungi J I and Robinson J W, 1992 *Uptake and accumulation of aluminium by fish: the modifying effect of added ions*. *Journal of Environmental Science and Health*, **A27**, No. 3, 713–719.
20. Goossenaerts C and Grieken R V, 1988 *A microanalytical study of the gills of aluminium exposed rainbow trout (Oncorhynchus mykiss)*. *International Journal of Environmental Analysis and Chemistry*, **34**, 227–237.
21. Elangovan R, Ballance S, White K N, McCrohan C R and Powell J J, 1999 *Accumulation of aluminium by the freshwater crustacean Asellus aquaticus in neutral water*. *Environmental Pollution*, **106**, No. 3, 257–263.
22. Elangovan R, White K N and McCrohan C R, 1997 *Bioaccumulation of aluminium in the freshwater snail Lymnaea stagnalis at neutral pH*. *Environmental Pollution*, **96**, No. 1, 29–33.
23. MacDonald D G, Walker R L and Wilkes P R H, 1983 *The interaction of environmental calcium and low pH on the physiology of the rainbow trout (Salmo gairdneri)*. *Journal of Experimental Biology*, **102**, 141–155.
24. McWilliams P G and Potts W T W, 1978 *The effect of pH and calcium concentrations on gill potentials in the brown trout (Salmo trutta)*. *Journal of Comparative Physiology*, **126**, 277–286.
25. Alstad N E W, Kjelsberg B M, Vollestad L A, Lydersen E and Poleo A B S, 2005 *The significance of water ionic strength on aluminium toxicity in brown trout (Salmo trutta L.)*. *Environmental Pollution*, **133**, No. 2, 333–342.

26. Gundersen D T, Bustaman S, Seim W K and Curtis L R, 1994 *pH, hardness and humic acid influence aluminium toxicity to rainbow trout (Oncorhynchus mykiss) in weakly alkaline waters*. Canadian Journal of Fisheries and Aquatic Science, **51**, 1345–1355.
27. Peuranen S, Keinanen M, Tigerstedt C and Vuorinen P J, 2003 *Effects of temperature on the recovery of juvenile grayling (Thymallus thymallus) from exposure to Al+Fe*. Aquatic Toxicology, **65**, No. 1, 73–84.
28. Camilleri C, Markich S J, Noller B N, Turley C J, Parker G and van Dam R A, 2003 *Silica reduces the toxicity of aluminium to a tropical freshwater fish (Mogurnda mogurnda)*. Chemosphere, **50**, No. 3, 355–364.
29. Helliwell S, Batley G E, Florence T M and Lumsden B G, 1983 *Speciation and toxicity of aluminium in a model freshwater*. Environmental Technology Letters, **4**, 141–144.
30. Parent L and Campbell P G C, 1994 *Aluminium bioavailability to the green alga Chlorella pyrenoidosa in acidified synthetic soft water*. Environmental Toxicology and Chemistry, **13**, No. 4, 587–598.
31. Rai L C, Husaini Y and Mallick N, 1998 *pH-altered interaction of aluminium and fluoride on nutrient uptake, photosynthesis and other variables of Chlorella vulgaris*. Aquatic Toxicology, **42**, No. 1, 67–84.
32. Sadler K and Lynam S, 1988 *The influence of calcium on aluminium-induced changes in the growth rate and mortality of brown trout, Salmo trutta*. Journal of Fish Biology, **33**, 171–179.
33. Buckler D R, Cleveland L, Little E E and Brumbaugh W G, 1995 *Survival, sublethal responses and tissue residues of Atlantic salmon exposed to acidic pH and aluminium*. Aquatic Toxicology, **31**, 203–216.
34. Reader J P, Dalziel T R K and Morris R, 1988 *Growth, mineral uptake and skeletal calcium deposition in brown trout, Salmo trutta, yolk fry exposed to aluminium and manganese in soft acidic water*. Journal of Fish Biology, **32**, 607–624.
35. Campbell M M, White K N, Jugdaohsingh R, Powell J J and McCrohan C R, 2000 *Effect of aluminum and silicic acid on the behaviour of the freshwater snail Lymnaea stagnalis*. Canadian Journal of Fisheries and Aquatic Science, **57**, No. 6, 1151–1159.
36. Calevro F, Filippi C, Deri P, Albertosi C and Batistoni R, 1998 *Toxic effects of aluminium, chromium and cadmium in intact and regenerating freshwater planarians*. Chemosphere, **37**, No. 4, 651–659.
37. Birge W J, 1978 *Aquatic toxicology of trace elements of coal and fly ash*. In Department of Energy (DOE) Symposium Series Energy and Environmental Stress in Aquatic Systems (Augusta, GA, 1977), edited by J H Thorp and J W Gibbons, **48**, 219–240. Springfield, VA: DOE.

38. Mackie G L, 1989 *Tolerances of five benthic invertebrates to hydrogen ions and metals (Cd, Pb, Al)*. Archives of Environmental Contamination and Toxicology, **18**, No. 1/2, 215–223.
39. Havas M, 1985 *Aluminium bioaccumulation and toxicity to Daphnia magna in soft water at low pH*. Canadian Journal of Fisheries and Aquatic Science, **42**, 1741–1748.
40. Clark K L and LaZerte B D, 1985 *A laboratory study of the effects of aluminium and pH on amphibian eggs and tadpoles*. Canadian Journal of Fisheries and Aquatic Science, **42**, 1544–1551.
41. Sims I, Dixon E and Whitehouse P, 1997 *The toxicity of aluminium to early life stages of the common toad (Bufo bufo)*. WRc report to the Environment Agency CO 4349.
42. Keinanen M, Peuranen S, Nikinmaa M, Tigersted C and Vuorinen P J, 2000 *Comparison of the responses of the yolk-sac fry of pike (Esox lucius) and roach (Rutilus rutilus) to low pH and aluminium: sodium influx, development and activity*. Aquatic Toxicology, **47**, No. 3/4, 161–179.
43. Heming T A and Blumhagen K A, 1988 *Plasma acid-base and electrolyte states of rainbow trout exposed to alum (aluminium sulphate) in acidic and alkaline environments*. Aquatic Toxicology, **12**, 125–140.
44. Roy R and Campbell P G C, 1995 *Survival time modelling of exposure to juvenile Atlantic salmon (Salmo salar) to mixtures of aluminium and zinc in soft water and low pH*. Aquatic Toxicology, **33**, 155–176.
45. Fargasova A, 2001 *Winter third- to fourth-instar larvae of Chironomus plumosus as bioassay tools for assessment of acute toxicity of metals and their binary combinations*. Ecotoxicology and Environmental Safety, **48**, 1–5.
46. Palmer R E, Klauda R J and Lewis T E, 1988 *Comparative sensitivities of bluegill, channel catfish and fathead minnow to pH and aluminium*. Environmental Toxicology and Chemistry, **7**, 505–516.
47. Petrich S M and Reich D J, 1979 *Effects of aluminium and nickel on survival and reproduction in polychaetous annelids*. Bulletin of Environmental Contamination and Toxicology, **23**, 698–702.
48. MacDonald J M, Shields J D and Zimmer-Faust R K, 1988 *Acute toxicities of eleven metals to early life-history stages of the yellow crab Cancer anthonyi*. Marine Biology, **98**, 201–207.
49. Pulley T E, 1950 *The effect of aluminium chloride in small concentration on various marine organisms*. Texas Journal of Science, **2**, 405.
50. Ward J A, 1977 *Chemoreception of heavy metals by the polychaetous annelid Myxicola infundibulum (Sabellidae)*. Comparative Biochemistry and Physiology Part C: Toxicology and Pharmacology, **58**, No. 2, 103–106.

51. Elsebae A A, 1994 *Comparative susceptibility of the Alareesh marine culture centre shrimp *Panaeus japonicus* and the brine shrimp *Artemia salina* to different insecticides and heavy metals*. Alexandria Science Exchange, **15**, No. 3, 425–435.
52. Gomez M, Domingo J, Llobet J, Tomas J and Corbella J, 1986 *Short-term oral toxicity study of aluminium in rats*. Archives of Pharmacology and Toxicology, **12**, 145–151.
53. Domingo J, Llobet J, Gomez M, Tomas J and Corbella J, 1987 *Nutritional and toxicological effects of short-term ingestion of aluminium by the rat*. Research Communications of Chemical Pathology and Pharmacology, **56**, 409–419.
54. Katz A, Frank D, Sauerhoff M, Zwicker G and Freudenthal R, 1984 *A six-month dietary toxicity study of acidic sodium aluminium phosphate in beagle dogs*. Food Chemistry and Toxicology, **22**, 7–9.
55. Domingo J, Paternain J, Llobet J and Corbella J, 1987 *Effects of oral aluminium administration on perinatal and postnatal development in rats*. Research Communications of Chemical Pathology and Pharmacology, **57**, 129–132.
56. Domingo J, Paternain J, Llobet J and Corbella J, 1987 *The effects of aluminium ingestion on reproduction and postnatal survival in rats*. Life Science, **41**, 1127–1131.
57. Hussein A, Cantor A and Johnson T, 1988 *Use of high levels of dietary aluminium and zinc for inducing pauses in egg production or Japanese quail*. Poultry Science, **67**, 1157–1165.
58. Wisser L A, Heinrichs B S and Leach R M, 1990 *Effect of aluminum on performance and mineral metabolism in young chicks and laying hens*. Journal of Nutrition, **120**, 493–498.
59. Folsom B R, Popescu N A and Wood J M, 1986 *Comparative study of aluminum and copper transport and toxicity in an acid-tolerant freshwater green alga*. Environmental Science and Technology, **20**, 616–620.
60. Poleo A B S and Hytterod S, 2003 *The effect of aluminium in Atlantic salmon (*Salmo salar*) with special emphasis on alkaline water*. Journal of Inorganic Biochemistry, **97**, No. 1, 89–96.
61. Ermolenko L V and Dedkov Y M, 1988 *Photometric determination of aluminum in water with the sulfonitrazo DAF reagent*. Journal of Analytical Chemistry of the USSR, **43**, 815–820.
62. Gardiner P E and Stoeppler M, 1987 *Optimisation of the analytical conditions for the determination of aluminium in human blood plasma and serum by graphite furnace atomic absorption spectrometry. Part 2. Assessment of the analytical method*. Journal of Analytical Atomic Spectrometry, **4**, 401–404.
63. Gosink T A, 1975 *Rapid simultaneous determination of picogram quantities of aluminum and chromium from water by gas phase chromatography*. Analytical Chemistry, **47**, 165–168.

64. Jones P, Ebdon L and Williams T, 1988 *Determination of trace amounts of aluminium by ion chromatography with fluorescence detection*. Analyst, **113**, 641–644.
65. Kopp J F and McKee G D, 1978 *Methods for chemical analysis of water and wastes*. Cincinnati, OH: US Environmental Protection Agency.
66. National Institute for Occupational Safety and Health (NIOSH), 1984 *Aluminum and compounds: methods 7013 and 7300*. In NIOSH Manual of Analytical Methods Volume 5 (3rd edn.), 173-1. Washington, DC: US Government Printing Office.
67. Pastor E, Pablos F D and Ariza J L G, 1987 *Determination of nanogram amounts of aluminium and indium with 4,4'-oxalybis(hydrazonomethyl)dirosorcinol*. Analyst, **112**, 1041–1045.
68. Tapparo A and Bombi G G, 1990 *Ion chromatographic determination of trace amounts of aluminium with on-line preconcentration and spectrophotometric detection*. Analytica Chimica Acta, **238**, 279–284.
69. Woolfson A D and Gracey G M, 1988 *Methods for the determination of trace aluminium contamination in dialysis fluids*. Journal of Clinical Pharmacology and Therapy, **13**, 243–248.
70. Benson R L, Worsfold P J and Sweeting F W, 1990 *On-line determination of residual aluminum in potable and treated waters by flow-injection analysis*. Analytica Chimica Acta, **238**, 177–182.
71. Carrillo F, Perez C and Camara C, 1992 *Sensitive flow-injection-spectrofluorimetric method to determine aluminium(III) in water*. Analytica Chimica Acta, **262**, 91–96.
72. Barnes R B, 1975 *The determination of specific forms of aluminum in natural water*. Chemical Geology, **15**, 177–191.
73. Maitani T, Kubota H and Hori N, 1994 *Distribution and urinary excretion of aluminium injected with several organic acids into mice: relationship with chemical state in serum studied by the HPLC-ICP method*. Journal of Applied Toxicology, **14**, 257–261.
74. Owen L M W, Crews H M and Bishop N J, 1994 *Aluminium uptake from some foods by guinea pigs and the characterization of aluminium in in vivo intestinal digesta by SEE-IP-MS*. Food Chemistry and Toxicology, **32**, 697–705.
75. Landeghem G F V, D'Haese P C and Lamberts L V, 1994 *Quantitative HPLC/ETAAS hybrid method with an on-line metal scavenger for studying the protein binding and speciation of aluminum and iron*. Analytical Chemistry, **66**, 216–222.
76. Alderman F R and Gitelman H J, 1980 *Improved electrothermal determination of aluminum in serum by atomic absorption spectroscopy*. Clinical Chemistry, **26**, 258–260.

77. Gardner M J, 1989 *A manual of analytical quality control in water industry laboratories*. Report NS30. Medmenham, Buckinghamshire: WRc.
78. European Commission Joint Research Centre (JRC), 2003 *Technical Guidance Document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No. 1488/94 on risk assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market*. Part II. EUR 20418 EN/2. Luxembourg: Office for Official Publications of the European Communities. Available from: <http://ecb.jrc.it/tgdoc> [Accessed 31 January 2007]
79. van Beusekom J E E and de Jonge V N, 1994 *The role of suspended matter in the distribution of dissolved phosphate, iron and aluminium in the Ems estuary*. *Netherlands Journal of Aquatic Ecology*, **28**, 383–395.

# List of abbreviations

AA	annual average
AES	atomic emission spectrometry
AF	assessment factor
AMS	accelerator mass spectroscopy
BCF	bioconcentration factor
BNC	base-neutralising capacity
bw	body weight
CAS	Chemical Abstracts Service
DOC	dissolved organic carbon
EC50	concentration effective against 50% of the organisms tested
ECB	European Chemicals Bureau
ECx	concentration effective against X% of the organisms tested
EHC	Environmental Health Criteria
EIFAC	European Inland Fisheries Advisory Commission
EQS	Environmental Quality Standard
FAAS	flame atomic absorption spectrometry
GFAAS	graphite furnace atomic absorption spectrometry
GLP	Good Laboratory Practice (OECD)
GUECD	gas chromatography equipped with an electron capture detector
HSDB	Hazardous Substances Data Bank
ICP-MS	inductively coupled plasma mass spectrometry
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure and Applied Chemistry
LAMMA	laser ablation microprobe mass analysis
LC50	concentration lethal to 50% of the organisms tested
LCx	concentration lethal to X% of the organisms tested
LOAEL	lowest observed adverse effect level
LOEC	lowest observed effect concentration
lt	long term
MAC	maximum allowable concentration
NA	not applicable
ND	no data
NOAEL	no observable adverse effect level

NOEC	no observed effect concentration
OECD	Organisation for Economic Co-operation and Development
PNEC	predicted no-effect concentration
SSD	species sensitivity distribution
secpois	secondary poisoning
SEPA	Scottish Environment Protection Agency
SNIFFER	Scotland & Northern Ireland Forum for Environmental Research
st	short term
TGD	Technical Guidance Document
UKTAG	UK Technical Advisory Group
US EPA	US Environmental Protection Agency
WFD	Water Framework Directive
WHO	World Health Organization

# ANNEX 1 Data quality assessment sheets

Identified and ordered by reference number (see References & Bibliography).

Data relevant for PNEC derivation were quality assessed in accordance with the so-called Klimisch Criteria (Table A1).

**Table A1 Klimisch Criteria\***

Code	Category	Description
1	Reliable without restrictions	Refers to studies/data carried out or generated according to internationally accepted testing-guidelines (preferably GLP**) or in which the test parameters documented are based on a specific (national) testing guideline (preferably GLP), or in which all parameters described are closely related/comparable to a guideline method.
2	Reliable with restrictions	Studies or data (mostly not performed according to GLP) in which the test parameters documented do not comply totally with the specific testing guideline, but are sufficient to accept the data or in which investigations are described that cannot be subsumed under a testing guideline, but which are nevertheless well-documented and scientifically acceptable.
3	Not reliable	Studies/data in which there are interferences between the measuring system and the test substance, or in which organisms/test systems were used that are not relevant in relation to exposure, or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which is not convincing for an expert assessment.
4	Not assignable	Studies or data which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature.

\* Klimisch H-J, Andreae M and Tillmann U, 1997 *A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data*. Regulatory Toxicology and Pharmacology, **25**, 1–5.

\*\* OECD Principles of Good Laboratory Practice (GLP). See:

[http://www.oecd.org/department/0,2688,en\\_2649\\_34381\\_1\\_1\\_1\\_1\\_1,00.html](http://www.oecd.org/department/0,2688,en_2649_34381_1_1_1_1_1,00.html)

<b>Reference number</b>	<b>21</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Asellus aquaticus</i>
Life stage of the test species used	Adults
Holding conditions prior to test	Held for 15 days in 'standard snail water'
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Aluminium nitrate
Source of the test substance	Not stated
Type and source of the exposure medium	'Standard snail water'
Test concentrations used	five (0–500 µg l <sup>-1</sup> )
Number of replicates per concentration	5
Number of organisms per replicate	60
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Measured and expressed as totals.
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Bioconcentration study measuring total aluminium. Bioaccumulation aspects appear valid, but the mortality data are less suitable for PNEC derivation.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>25</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo trutta</i>
Life stage of the test species used	1 year old
Holding conditions prior to test	Not stated
Source of the test organisms	Hatchery bought

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Acidic aluminium stock
Source of the test substance	Not stated
Type and source of the exposure medium	Tap water
Test concentrations used	One concentration with three residence times prior to exposure (1, 30 and 90 minutes)
Number of replicates per concentration	None
Number of organisms per replicate	50
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Inorganic monomeric Al. Calculated using a model based on total concentrations
Measurement of water quality parameters	pH, temperature, conductivity
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Endpoint comment	Only one concentration tested and toxicity had to be estimated from graphs. The shortest (most toxic) LT50s occurred at lowest reactive aluminium concentration. LT50 of 15–20 hours at 200–300 µg l <sup>-1</sup> and LT50 of 60–70 hours at 500–600 µg l <sup>-1</sup> . However, the lowest LT50s related to the shortest residence time prior to exposure.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>27</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Thymallus thymallus</i>
Life stage of the test species used	One year old
Holding conditions prior to test	Held for 2 weeks in tap water
Source of the test organisms	Purchased from fishery

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Aluminium sulfate exposed in conjunction with iron
Source of the test substance	Merck, technical grade
Type and source of the exposure medium	Tap water
Test concentrations used	One concentration at two temperatures (3 and 13°C)
Number of replicates per concentration	1
Number of organisms per replicate	24
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Not stated: appears to be calculated using modelling software
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Exposure in conjunction with iron. Only one test concentration used. 50% mortality at 13°C, but no mortality at 3°C. No mention of analysis.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>28</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Mogurnda mogurnda</i>
Life stage of the test species used	Fry
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Follows previously published method
Form of the test substance	Aluminium
Source of the test substance	Analytical grade
Type and source of the exposure medium	ASTM water
Test concentrations used	Eight concentrations ranging from 0 to 4,000 $\mu\text{g l}^{-1}$
Number of replicates per concentration	3
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Labile aluminium
Measurement of water quality parameters	Temperature, pH and salinity
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Appears to be a valid study although conducted using a non-standard system. Effect concentrations reported as labile Al, but available Al estimated using modelling. Consequently, study regarded as reliable with restriction.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>29</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Chlorella pyrenoidosa</i>
Life stage of the test species used	Cells
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	48-hour exposure
Form of the test substance	Al in HNO <sub>3</sub>
Source of the test substance	Not stated
Type and source of the exposure medium	Freshwater
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	2–5 x 10 <sup>4</sup> cells ml <sup>-1</sup>
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Measured and expressed as total and labile Al.
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	A short paper that does not include some ancillary information, but the study appears to have been performed well.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>30</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Chlorella pyrenoidosa</i>
Life stage of the test species used	Population
Holding conditions prior to test	Growth medium at 22°C
Source of the test organisms	Laboratory culture

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium chloride
Source of the test substance	Analytical grade (Fisher Scientific)
Type and source of the exposure medium	Amyloid precursor protein (APP) growth medium, without complexing materials
Test concentrations used	Up to five (0–400 µg l <sup>-1</sup> )
Number of replicates per concentration	3
Number of organisms per replicate	10 <sup>5</sup> cells per ml
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Yes – expressed as inorganic monomeric Al
Measurement of water quality parameters	pH, temperature
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Appears to be a valid study with chemical analysis of exposure concentration.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>1</b>

<b>Reference number</b>	<b>31</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Chlorella vulgaris</i>
Life stage of the test species used	Population
Holding conditions prior to test	Not stated
Source of the test organisms	Laboratory culture

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium fluoride and chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Culture medium
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	The effects data are based on nominal concentrations. Consequently the AI species cannot be identified.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>32</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo trutta</i>
Life stage of the test species used	Adults
Holding conditions prior to test	Held for 7 days
Source of the test organisms	Commercial hatchery

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Freshwater from fish farm
Test concentrations used	Four (0–81 µg l <sup>-1</sup> total Al)
Number of replicates per concentration	Not stated
Number of organisms per replicate	20
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured and expressed as inorganic monomeric Al
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Endpoint comment	Study appears to be valid, with valid endpoints. However, there is no data on replication.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>33</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo salar</i>
Life stage of the test species used	Larvae
Holding conditions prior to test	Held overnight
Source of the test organisms	Commercial hatchery

<b>Information on the test design</b>	
Methodology used	Previously published method
Form of the test substance	Aluminium sulfate
Source of the test substance	Analytical grade (Fisher Scientific)
Type and source of the exposure medium	Freshwater
Test concentrations used	Five (0–264 µg l <sup>-1</sup> )
Number of replicates per concentration	2
Number of organisms per replicate	15
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured and expressed as totals. Labile Al estimated
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Study appears to be valid, with valid endpoints. However, the report states that labile Al was measured but all effect concentrations are reported as totals. Labile Al is reported to be 70–80% of the total filtered concentration. However, the table showing this data does not reflect this statement. Consequently, this study should be treated as supporting information only
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>34</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo trutta</i>
Life stage of the test species used	Yolk fry
Holding conditions prior to test	Held in continuously flowing dechlorinated tap water
Source of the test organisms	Commercial hatchery

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Not stated
Source of the test substance	Analytical grade
Type and source of the exposure medium	Dechlorinated tap water
Test concentrations used	Various
Number of replicates per concentration	Not stated
Number of organisms per replicate	25–30
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured – inorganic monomeric Al
Measurement of water quality parameters	pH, conductivity and temperature
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	A valid study with measured concentrations. However, it was not run to a standard method and there is no mention of replication.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>35</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Lymnaea stagnalis</i>
Life stage of the test species used	Adult
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium nitrate
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured and expressed as totals.
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	No standard endpoints measured. Only total aluminium measured.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>36</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Dugesia etrusca</i>
Life stage of the test species used	Adults
Holding conditions prior to test	Held in stream water at 20°C
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Previously published method
Form of the test substance	Aluminium sulfate
Source of the test substance	Analytical grade (Sigma)
Type and source of the exposure medium	Stream water
Test concentrations used	Seven (0–1,500 µg l <sup>-1</sup> )
Number of replicates per concentration	Not stated
Number of organisms per replicate	5
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Measured and expressed as totals.
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Endpoint comment	Total aluminium measured and effects reported as 'days of planarian death'
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>37</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Oncorhynchus mykiss</i> , <i>Carassius auratus</i> , <i>Gastrophryne carolinensis</i> and <i>Gastrophryne carolinenseis</i>
Life stage of the test species used	Eggs
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Freshwater
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Measured and expressed as totals.
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Total aluminium measured, not relevant to monomeric Al. Few data to assess endpoints
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unknown</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>4</b>

<b>Reference number</b>	<b>38</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Hyalella azteca</i> , <i>Amnicola pisidium</i> , <i>Pisidium compressum</i> and <i>Enallagma</i> sp.
Life stage of the test species used	Adults
Holding conditions prior to test	Not stated
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Metallic aluminium (acid digested)
Source of the test substance	Not stated
Type and source of the exposure medium	Natural surface water
Test concentrations used	Seven (0–1,000 µg l <sup>-1</sup> )
Number of replicates per concentration	3
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Measured and expressed as totals. Inorganic monomeric Al estimated
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Study is of reasonably good quality with replicates and chemical analysis. However, the study appears to estimate inorganic monomeric concentrations based on total aluminium analysis, though it does go on to directly compare the results of the study with field measured values of inorganic monomeric Al. Given the uncertainty in the analysis, these data are used as supporting information only.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>39</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Daphnia magna</i>
Life stage of the test species used	Mature
Holding conditions prior to test	18–20°C; 14 L; 10-day photoperiod; fed <i>Scenedesmus</i> daily and brewers' yeast every other day
Source of the test organisms	Laboratory culture

<b>Information on the test design</b>	
Methodology used	48-hour lethality test
Form of the test substance	Aluminium chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Lake water
Test concentrations used	0.02, 0.32 and 1.02 mg l <sup>-1</sup> Al at pH 6.5, 5.0 or 4.5, and 2.5 or 12.5 mg l <sup>-1</sup> Ca
Number of replicates per concentration	3
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	At pH 6.5 and high calcium, most daphnids survived for the duration of the test. At pH 6.5 and low calcium, 0.02 mg l <sup>-1</sup> Al caused little mortality, with 50% mortality at the two higher concentrations. At pH 4.5 and 5.0, almost all daphnids died at both Ca and all Al concentrations.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>40</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Bufo americanus</i> and <i>Rana sylvatica</i>
Life stage of the test species used	Spawn
Holding conditions prior to test	Not stated
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Non-standard, but well described
Form of the test substance	Aluminium metal (acid dissolved)
Source of the test substance	Not stated
Type and source of the exposure medium	Deionised water with addition of major ions
Test concentrations used	Six (0–200 µg l <sup>-1</sup> )
Number of replicates per concentration	None
Number of organisms per replicate	>100 eggs
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Measured as total Al, and inorganic fraction modelled
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Chemical concentrations measured and inorganic monomeric fraction modelled. The pH at which effects of Al occurred was also toxic to organisms without Al. Therefore, the high sensitivity of the organisms could be due to additional pH stress.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>41</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Bufo bufo</i>
Life stage of the test species used	Eggs
Holding conditions prior to test	Not stated
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Non-standard, but well described
Form of the test substance	Aluminium nitrate
Source of the test substance	Reagent grade (BDH Ltd)
Type and source of the exposure medium	Blended ground water
Test concentrations used	Eight (0–320 µg l <sup>-1</sup> )
Number of replicates per concentration	3
Number of organisms per replicate	20 eggs
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Measured as inorganic monomeric Al
Measurement of water quality parameters	Temperature, pH, conductivity
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Well-presented study, with relevant measurement of chemical concentrations
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>1</b>

<b>Reference number</b>	<b>42</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Esox lucius</i> and <i>Rutilus rutilus</i>
Life stage of the test species used	Yolk-sac fry
Holding conditions prior to test	Not stated
Source of the test organisms	Field collected adults used to obtain fry

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium sulfate
Source of the test substance	Merck
Type and source of the exposure medium	Lake water
Test concentrations used	Five (0–600 µg l <sup>-1</sup> )
Number of replicates per concentration	2
Number of organisms per replicate	10–20
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Nominal
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Not stated
Endpoint comment	Data based on nominal concentrations
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>43</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Oncorhynchus mykiss</i>
Life stage of the test species used	Adults
Holding conditions prior to test	Fresh water
Source of the test organisms	Hatchery

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Aluminium sulfate
Source of the test substance	Not stated
Type and source of the exposure medium	Freshwater
Test concentrations used	Five (0–9.1 mg l <sup>-1</sup> )
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Total Al
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	No mention of replication and analysis of total aluminium only
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>44</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo salar</i>
Life stage of the test species used	Juvenile
Holding conditions prior to test	Held in soft water for 2 weeks prior to testing
Source of the test organisms	Hatchery bought

<b>Information on the test design</b>	
Methodology used	Non-standard, but well described
Form of the test substance	Aluminium sulfate
Source of the test substance	Not stated
Type and source of the exposure medium	Reconstituted soft water
Test concentrations used	Various
Number of replicates per concentration	2
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured as monomeric Al, and inorganic fraction modelled
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Well-presented study, with relevant measurement of chemical concentrations
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>1</b>

<b>Reference number</b>	<b>45</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Chironomus plumosus</i>
Life stage of the test species used	Larvae
Holding conditions prior to test	Not stated
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Aluminium chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Tap water
Test concentrations used	Twenty (1–250 mg l <sup>-1</sup> )
Number of replicates per concentration	3
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Nominal
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Reasonably good study, but with no chemical measurement, making reliability questionable
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>46</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Lepomis macrochirus</i> , <i>Ictalurus punctatus</i> and <i>Pimephales promelas</i>
Life stage of the test species used	Juvenile
Holding conditions prior to test	Held for 4–7 days prior to testing
Source of the test organisms	Hatchery bought

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Aluminium chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Blended deionised water and well water
Test concentrations used	Five (0–400 µg l <sup>-1</sup> )
Number of replicates per concentration	2
Number of organisms per replicate	10–15
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Measured total and total monomeric Al
Measurement of water quality parameters	Temperature, pH
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Reasonably good study, with chemical measurement. Inorganic monomeric estimated to be similar to total monomeric Al.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>47</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Capitella capitata</i> , <i>Ctenodrilus serratus</i> and <i>Neanthes arenaceodentata</i>
Life stage of the test species used	Mature
Holding conditions prior to test	Not stated
Source of the test organisms	Laboratory culture

<b>Information on the test design</b>	
Methodology used	96-hour and 7-day LC50 for all species 28-day reproduction of <i>C. serratus</i>
Form of the test substance	Aluminium chloride
Source of the test substance	Not stated
Type and source of the exposure medium	Filtered natural seawater
Test concentrations used	Up to 2 mg l <sup>-1</sup> in acute tests 0.01, 0.1, 0.5, 1.0, 1.5 and 2.0 mg l <sup>-1</sup>
Number of replicates per concentration	10 ( <i>C. capitata</i> acute and <i>C. serratus</i> acute and chronic tests) 20 ( <i>N. arenaceodentata</i> acute tests)
Number of organisms per replicate	5 ( <i>C. capitata</i> acute and <i>C. serratus</i> acute and chronic tests) 1 ( <i>N. arenaceodentata</i> acute tests)
Nature of test system (static, semi-static or flow-through, duration, feeding)	Not stated
Measurement of exposure concentrations	No
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	<i>C. capitata</i> and <i>N. arenaceodentata</i> were unaffected in acute tests. 96-hour LC50 of 0.48 mg l <sup>-1</sup> for <i>C. serratus</i> . <i>C. serratus</i> reproduction NOEC of 0.1 mg l <sup>-1</sup>
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>48</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Cancer anthonyi</i>
Life stage of the test species used	Embryo and larvae
Holding conditions prior to test	Stored in continuous flowing seawater at 17–20°C for 2 weeks
Source of the test organisms	Field collected

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Chloride salt
Source of the test substance	Not stated
Type and source of the exposure medium	Filtered natural sea-water
Test concentrations used	Six concentrations ranging from 0.01 to 1000 mg l <sup>-1</sup>
Number of replicates per concentration	5
Number of organisms per replicate	50–100
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Dissolved aluminium
Measurement of water quality parameters	Temperature, pH and salinity
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Appears to be a valid study although conducted using a non-standard system. Organism also insensitive
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

<b>Reference number</b>	<b>49</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Fundulus grandis</i> , <i>Fundulus similes</i> , <i>Cyprinodon variegatus</i> and <i>Cynoscion nebulosus</i>
Life stage of the test species used	Not stated
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Not stated
Measurement of exposure concentrations	Not stated
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Insufficient data to assess study
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>50</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Myxicola infundibulum</i>
Life stage of the test species used	Not stated
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Aluminium sulfate
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Not stated
Measurement of exposure concentrations	Not stated
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	Insufficient data to assess study
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>51</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Panaeus japonicus</i> and <i>Artemia salina</i>
Life stage of the test species used	Larvae and adults
Holding conditions prior to test	Not stated
Source of the test organisms	Not stated

<b>Information on the test design</b>	
Methodology used	Not stated
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Marine water
Test concentrations used	Various
Number of replicates per concentration	Replicated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Not stated
Measurement of exposure concentrations	No
Measurement of water quality parameters	Not pH
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Endpoint comment	No information on test pH and no analysis
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Unreliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>3</b>

<b>Reference number</b>	<b>60</b>
-------------------------	-----------

<b>Information on the test species</b>	
Test species used	<i>Salmo salar</i>
Life stage of the test species used	1 year old
Holding conditions prior to test	Held in tap water for 4 days prior to testing
Source of the test organisms	Hatchery bought

<b>Information on the test design</b>	
Methodology used	Non-standard
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Tap water
Test concentrations used	One concentration with three residence times prior to exposure (1, 30 and 90 minutes) and three pH conditions from 5.8 to 9.5.
Number of replicates per concentration	None
Number of organisms per replicate	25
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Inorganic monomeric Al analysed
Measurement of water quality parameters	pH, temperature, conductivity
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Endpoint comment	Only one concentration tested. LT50s of 120–180 hours reported of 100–120 µg l <sup>-1</sup> at pH 5.6. No mortality occurred at pH 9.5. The single concentration and lack of replication make this study supporting information only.
Study conducted to GLP	Not stated

<b>Reliability of study</b>	<b>Reliable</b>
<b>Relevance of study</b>	<b>Relevant</b>
<b>Klimisch Code</b>	<b>2</b>

We are The Environment Agency. It's our job to look after your environment and make it **a better place** – for you, and for future generations.

Your environment is the air you breathe, the water you drink and the ground you walk on. Working with business, Government and society as a whole, we are making your environment cleaner and healthier.

The Environment Agency. Out there, making your environment a better place.

Published by:

Environment Agency  
Rio House  
Waterside Drive, Aztec West  
Almondsbury, Bristol BS32 4UD  
Tel: 0870 8506506  
Email: [enquiries@environment-agency.gov.uk](mailto:enquiries@environment-agency.gov.uk)  
[www.environment-agency.gov.uk](http://www.environment-agency.gov.uk)

© Environment Agency/SNIFFER

All rights reserved. This document may be reproduced with prior permission of the Environment Agency and SNIFFER.