NICKEL AND ITS COMPOUNDS

This EQS dossier was prepared by the Sub-Group on Review of the Priority Substances List (under Working Group E of the Common Implementation Strategy for the Water Framework Directive).

The dossier has been reviewed by the Scientific Committee on Health and Environmental Risks (SCHER), which noted that in-depth analysis, including independent statistical analysis, of the higher-tier data made available by the nickel industry could influence the final EQS. This has since been attempted, but ongoing difference of opinion among the experts means that further consideration, including by the SCHER, is needed. The additional analysis has not yet been included in the dossier. which is essentially the version submitted to the SCHER and which therefore presents an AA-EQS for freshwaters of 2 rather than the 4 µg/l being formally proposed pending the further consideration. No sediment EQS is proposed in this dossier pending the availability of additional information.

Introduction

A European Union Risk Assessment Report (EU-RAR) is available for nickel (Ni) and four inorganic nickel compounds (Ni sulphate, Ni carbonate, Ni chloride and Ni dinitrate) (EC 2008). The risk assessment was thoroughly discussed by EU Member States in the Technical Committee for New and Existing Substances, and was approved in May, 2008. The aquatic effects assessment of nickel that is included in the EU-RAR (EU risk assessment Report) uses nickel Biotic Ligand Models (BLMs) to normalize an extensive aquatic toxicity database (which includes chronic toxicity data for 31 aquatic species) in order to remove the influence of different chemical conditions among different toxicity tests. The bioavailability normalization approach also allows the aquatic toxicity data to be normalized for site- or region-specific water chemical characteristics.

The EU-RAR also included an extensive assessment of secondary poisoning and human health.

The EU-RAR was independently reviewed by the European Commission's Scientific Committee on Health and Environmental Risks (SCHER 2009).

Section 2.8.1 of the Technical Guidance for Deriving Environmental Quality Standards (2011) recommends that the PNECs derived from the Existing Substances Regulation be adopted as Quality Standards, on the basis that the assessment and the data have undergone thorough peer review. This is the case with the Ni EU-RAR, and results from the Ni EU-RAR are relied upon in the present document almost exclusively for the derivation of Ni Quality Standards, except for sediment, where a conclusion 1 was the outcome of the RAR (conclusion 1: "There is a need for further information and/or testing"), and for calculation of the maximum acceptable concentration (MAC), which is not calculated in the EU-RAR. The data are almost exclusively from the EU-RAR, and have thus been validated as part of the development of the RAR.

After the EU-RAR received approval within Europe, the data sets were discussed at the international level within the Organization of Economic Cooperation and Development (OECD). The Ni ecotoxicity data sets used in the EU-RAR were accepted at the OECD's SIDS (Screening Level Information Data Set) Initial Assessment Meeting (SIAM 28, October 2008), as was the use of nickel BLMs to normalize the Ni ecotoxicity data.

This factsheet draws heavily upon the findings of the EU-RAR, as required by EU EQS Directive 2008/105/EC (Article 3, Paragraph 4) and the EQS Technical Guidance (EC 2011). Furthermore, the basis for incorporating bioavailability into the Ni EQS that is presented in this factsheet was supported by the SCHER review.

The aquatic effects assessment of nickel in the EU-RAR is based on the assumption that adverse effects on aquatic organisms are a consequence of exposure to the bioavailable Ni-ion, rather than the parent substances. The result of this assumption is that the ecotoxicology will be similar for all nickel substances that contribute to the formation of the Ni-ion (e.g., nickel metal, nickel sulphate, nickel chloride, nickel carbonate, nickel dinitrate, etc). The Quality Standards derived in this document will therefore be relevant for all inorganic Ni substances. Determining the EQS for Ni should be consistent with this approach. Therefore, data from soluble nickel salts are used in the derivation of chronic ecotoxicological NOEC and $L(E)C_{10}$ values.

1 CHEMICAL IDENTITY

Common name	Nickel
Chemical name (IUPAC)	Nickel
Synonym(s)	-
Chemical class (when available/relevant)	Metal
CAS number	7440-02-0
EU number	231-111-4
Molecular formula	Ni
Molecular weight ($g.mol^{-1}$)	58.7

2 EXISTING EVALUATIONS AND REGULATORY INFORMATION

Annex III EQS Dir. (2008/105/EC)	Not included
Existing Substances Reg. (793/93/EC)	List 3 (Nickel, Nickel sulphate) and 4 (Nickel carbonate, Nickel dichloride, Nickel dinitrate) / Draft Final RAR published may 2008 and finalised
Pesticides(91/414/EEC)	Not applicable
Biocides (98/8/EC)	Not applicable
PBT substances	Not investigated by EU PBT groups
Substances of Very High Concern (1907/2006/EC)	No
POPs (Stockholm convention)	No
Other relevant chemical regulation (veterinary products, medicament, ...)	No
Endocrine disrupter	Not investigated in available public literature an EU framework reports (e.g. E.C., 2007).

3 PROPOSED QUALITY STANDARDS (QS)

3.1 ENVIRONMENTAL QUALITY STANDARD (EQS)

The Generic Environmental Quality Standard for nickel is an $EQS_{bioavailable}$.

EQS	Value	Comments
Proposed AA-$EQS_{bioavailable}$ for [freshwater] [µg.l^{-1}][1]	2	**See section 7**
Proposed AA-EQS for [marine water] [µg.L^{-1}]	8.6	
Proposed MAC-EQS for [freshwater] [µg.L^{-1}]	34	**See section 7**
Proposed MAC-EQS for [marine water] [µg.L^{-1}]	34	

3.2 SPECIFIC QUALITY STANDARD (QS)

Protection objective	Unit	Value	Comments
Pelagic community (freshwater)	[µg.l^{-1}]	Covered by $EQS_{bioavailable}$	**See section 7**
Pelagic community (marine water)	[µg.l^{-1}]	8.6	**See section 7**
Benthic community (freshwater)	[µg.kg^{-1} $_{dw}$]	Under development	**See section 7**
	[µg.l^{-1}]		
Benthic community (marine)	[µg.kg^{-1} $_{dw}$]	Under development	
	[µg.l^{-1}]		
Mammalian predators (secondary poisoning)	[µg.kg^{-1} $_{biota\ ww}$]	92000	**See section 7.4**
	[µg.l^{-1}]	340	
Avian predators (secondary poisoning)	[µg.kg^{-1} $_{biota\ ww}$]	12300	**See section 7.4**
	[µg.l^{-1}]	46	
Human health via consumption of fishery products	[µg.kg^{-1} $_{biota\ ww}$]	40780	**See section 7.5**
	[µg.l^{-1}]	151	
Human health via consumption of water	[µg.l^{-1}]	20	

[1] The AA-EQS is expressed as a being equivalent to 2 µg Ni.l^{-1} after normalizing for bioavailability. This concept is explained thoroughly in Section 7. The basis for expressing a metal EQS as a function of bioavailability has been set by the case of Cd, where the AA-EQS is a function of water hardness. In the case of Ni, bioavailability is a function of pH, dissolved organic carbon, and hardness. The incorporation of bioavailability takes place in the tiered approach that is presented in Section 7.

4 MAJOR USES AND ENVIRONMENTAL EMISSIONS

4.1 USES AND QUANTITIES

The EU-RAR addressed five Ni substances: Ni metal, Ni chloride, Ni dinitrate, Ni hydroxycarbonate, and Ni sulphate.

Ni metal: The major uses of primary and secondary nickel metal in the EU for 2000 were the manufacture of stainless steel (71%), non-ferrous alloys (14%), alloy steels (5%), foundry steels (4%), and plating (4%). Other end uses, including Ni-based batteries, catalysts, and chemicals, accounted for less than 3% of total nickel use.

Ni chloride is mainly used in the plating sector (71%) and catalyst production (29%). A small but unidentified portion is also used in chemicals manufacturing.

Ni dinitrate is mainly used for the production of catalysts (50-75%) and the manufacturing of Ni-Cd batteries (10-50%) – together 92.5% of total EU production. An estimated additional 5-10% is used for other applications, including chemical pretreatment of products.

Ni hydroxycarbonate: Approximately 70% of is used for plating, 20% for catalyst production, 5% for pigment production, and lesser amounts in electronic components.

Ni sulphate: The majority of Ni sulphate is used in the plating sector (89%) and catalyst production (11%). A small, but unidentified portion is also used in chemicals manufacturing.

4.2 ESTIMATED ENVIRONMENTAL EMISSIONS

The total Ni emissions to the aquatic compartment that were estimated by the Ni EU-RAR for the EU-15, based on the inventory of emissions from the year 2000, were 157056 $kg.year^{-1}$.

Important industrial sectors discharging nickel to an off-site waste water treatment plant are the following: metal production and processing (53% of facilities), basic organic chemicals production (16%), installations for surface treatment (i.e. plating; 10%) and waste treatment installations (15%).

Industrial surface water emitters are Ni metal producers (9% of total industrial emissions), multiple steel product manufacturers (5%), Ni chemicals producers (3%), and Ni plating sites (3%).

5 ENVIRONMENTAL BEHAVIOUR

5.1 ENVIRONMENTAL DISTRIBUTION

Parameter	Value	Master reference
Water solubility ($mg.l^{-1}$)	Ni metal: Insoluble	EC 2008
	Ni chloride: 2450 $g.l^{-1}$ (20°C)	
	Ni sulphate: 625 $g.l^{-1}$ (20°C)	

	Ni dinitrate : 2385 $g.l^{-1}$ (20°C) Ni hydroxycarbonate : Ksp = 10^{-8} to 10^{-7}	
Volatilisation		
Vapour pressure (Pa)	237 at 1,453°C	EC 2008
Henry's Law constant ($Pa.m^3.mol^{-1}$)	Not applicable	
Adsorption	Not applicable	
Organic carbon – water partition coefficient (K_{OC})	Not applicable	
Kp[2]	Range: 8.9 – 256,842	EC 2008
Suspended matter – water partition coefficient ($K_{susp-water}$)[2]	Range: 5,754 – 117,490 Mean (50th percentile) = 26 303	EC 2008
Sediment – water partition coefficient (K_{sed})	Range: 2,138 – 16,982 Mean (50th percentile) = 7,079	EC 2008
Bioaccumulation	**The BCF value of 270 is used for derivation of quality standards.** **Ni does not appear to biomagnify**	
Octanol-water partition coefficient (Log Kow)	Not applicable	EC 2008
BCF (measured) [3]	270	EC 2008

5.2 ABIOTIC AND BIOTIC DEGRADATIONS

Abiotic and biotic degradation are not relevant parameters for the environmental fate of metals.

6 AQUATIC ENVIRONMENTAL CONCENTRATIONS

6.1 BACKGROUND

The concentrations of nickel in surface waters (both marine waters and freshwater) are dependent on natural and anthropogenic conditions: it is almost impossible to determine experimentally a 'natural' background concentration in Europe. Due to geochemical differences, the ambient background concentrations will differ in Europe. In addition, since the concentrations that are measured in the environment are the sum of an anthropogenic and a 'natural' source, one cannot simply distinguish the 'natural' part from the anthropogenic part. Hence, background concentrations are not measured, but estimated or determined with other methods (EC 2008).

Ni ambient concentrations in surface waters:

[2] Ranges are given indicating the high levels of variability in these parameters rather than uncertainty.

[3] Highest bioconcentration factors for *Cerastoderma edule* (marine bivalve): 26,500. BCF = 270 for all other bivalves and aquatic organisms.

Country	Value (µg.l^{-1})	Fraction	Mean, median	Reference
Finland	0.25 0.25 0.11, 0.49, 0.54 **0.33**	Not defined Not defined Not defined	Median Mean Median Average	EC 2008
Rhine (The Netherlands)	1.89 **1.2** 2.1 3.7 (3.6 – 3.8) **2.56**	Total Dissolved Total Total Total	Average	
The Netherlands	2.5, 3.5, 3.6, 5.5 **4.1** **3.3**	Not defined Total Dissolved		
Northern European Lowland	3.6	Dissolved	Mean	
Northern Sweden	0.42	Not defined	Mean	
United Kingdom	1.3, 9.0 **5.15***	Not defined	Average	
General mean value[4]	**3.3** **2.7**	**Total** **Dissolved**		
Austria	2.18	Dissolved	Mean	**Umweltbundesamt, Austria**[5]
England and Wales	2.27	Dissolved	Mean	**Data obtained from the Environment Agency of England and Wales**
Sweden*	0.89	Dissolved	Mean	**EIONET**
Rhine (Northern France)*	2.13	Dissolved	Mean	**EIONET**
General mean value	**1.35**	**Total Dissolved**	**Mean**	
Data from 23 Member States[6]	**6.71** **1.00**	**Total Dissolved**	**Mean** **Median**	**INERIS 2009**[7]

*Data affected by historical reporting limiting of 5 µg l^{-1}

Ni ambient concentrations in surface sediments:

Country	Sampling period	Ambient PEC mg Ni/kg dry wt	Min-max range (excl. outliers)	Reference
Belgium – Flanders	1999-2002	**28.0**	1.0 -77.0 mg/kg	EC 2008
France				
Artois-Picardie	1999-2001	27.2 (1)	1.0 – 58.0 mg/kg	
Rhone-Mediterranean	1992-2001	37.0 (1)	1.0 – 57.0 mg/kg	
Average:		**31.9**		

4 undefined fractions are not included

5 http://wisa.lebensministerium.at/

6 http://www.priority.substances.wfd.oieau.fr/pdf/All_metals.pdf

7 http://www.priority.substances.wfd.oieau.fr/fiche_pdf.php?determinandID=list&list=ma

COMMPS-database	1995-1996	36.2 (1)	2.0 – 99.0 mg/kg	
Germany – COMMPS	1994-1996	60.0 (1,2)	11.0 – 472 mg/kg	
The Netherlands – COMMPS	1996-1997	**42.8**	6.8 – 96.0 mg/kg	
UK – Scotland – COMMPS	1994-1996	**34.4**	7.1 – 47.6 mg/kg	
Spain – COMMPS	1996-1997	**53.7**	2.6 – 96.2 mg/kg	
Sweden	1998-1999	**25.5**	2.1 – 106 mg/kg	
EUROPE – Average		36.1		
EUROPE – Median		**33.5**		

Ni ambient concentrations in marine waters:

Type	**Value (µg.l^{-1})**	**Reference**
Estuarine and estuarine-influenced coastal waters	3.34 (range 0.26 – 3.75)	EC 2008
Open water	0.30 (range 0.14 – 3.75)	
Baltic sea	0.79 (range 0.64 – 0.81)	

7 EFFECTS AND QUALITY STANDARDS

There are several abiotic factors that influence chronic aquatic nickel toxicity. The most important of these are pH, hardness and dissolved organic carbon (DOC)(Figure 7.1). In the EU-RAR (EC 2008), the Biotic Ligand Modelling (BLM) approach was developed to incorporate "*aqueous speciation reactions and competition of cations for binding to biotic receptors*".

Several chronic BLMs have been developed and validated for different species from three trophic levels. Nickel BLMs exist for two invertebrates (*Ceriodaphnia dubia* and *Daphnia magna*), one alga (*Pseudokirchneriella subcapitata*) and one fish (*Oncorhynchus mykiss*). These models are also applied to organisms other than those for which the models were derived. Support for this cross-species extrapolation has been demonstrated by applying the *O. mykiss* BLM to another fish, i.e. *Pimephales promelas* (Deleebeeck et al. 2007a), by applying the *D. magna* BLM to other cladocerans (Deleebeeck et al. 2007b), and by applying the *P. subcapitata* BLM to other green algae species (Deleebeeck et al. 2009). Schlekat et al. (2010) demonstrated that the *C. dubia* and *D. magna* BLMs could predict Ni toxicity to other non-cladoceran invertebrates within a factor of two.

The chronic nickel BLM which is applied within the EU RAR represents a further development of these individual models by undertaking taxa-specific bioavailability corrections for each organism in the chronic ecotoxicity database. This is used to derive a site-specific species sensitivity distribution (SSD) from which the site-specific PNEC can be derived. In effect, this is equivalent to performing all of the ecotoxicity tests undertaken in waters matched to the characteristics of the site under consideration. This model has been developed and validated under the risk assessment program on nickel within the framework of the Existing Substances Regulation (793/93/EEC, EC 2008). Like chronic BLMs for copper and zinc, the NiBLM predicts chronic nickel toxicity based on aquatic abiotic factors.

The NiBLM requires data inputs for several physicochemical parameters to enable the normalisation of the complete chronic nickel dataset to the site for which those physicochemical parameters were measured. The model is relatively sophisticated and represents the most advanced state of understanding about chronic nickel ecotoxicity in freshwaters. The predictions of the NiBLM have been validated using an independent data set in waters that cover conditions in more than 80% of the surface waters in the EU. The validation ranges of the NiBLM are pH 6.5 - 8.2, an unlimited range for DOC, and 3.8 - 88 mg Ca l^{-1}. The validation exercise demonstrated that predictions of the NiBLM were within a factor of two of the ecotoxicity data. Furthermore, the findings of the risk assessment and subsequent validation of the model predictions from both mesocosm and field-based research (Peters et al. 2009) indicate that the nickel BLM is *protective* for all taxa (Section 7.2).

An approach accounting for nickel bioavailability provides an ecologically and environmentally relevant metric by which to assess potential nickel risks. Using bioavailability in a regulatory context provides an evidence-based way to assess compliance, set discharge limits and, importantly, to prioritise and rank locations at potential risk (EC 2011). The explicit ecotoxicological premise on which the BLMs are constructed provides a direct link to the goals and aims of the WFD.

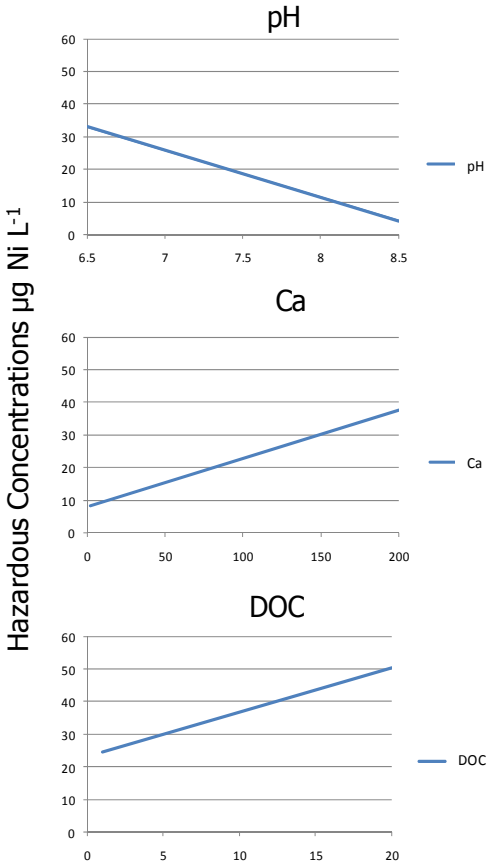

Figure 7.1. Predicted 'stylised' changes in the ecotoxicity of nickel using the Screening Nickel Tool (Section 7.1). Results are expressed as an HC_5, for pH, calcium (Ca mg.l^{-1}) and dissolved organic carbon (DOC mg.l^{-1}). Individual parameters were varied while the other two parameters remained constant (pH 7, Ca 120 mg.l^{-1}, DOC 2 mg.l^{-1}).

The EQS Technical Guidance has provided clarity on the implementation of bioavailability-based approaches for metals (EC 2011). The guidance advocates the use of a tiered approach (e.g. Figure 7.2). The first tier is the use of a generic or reference $EQS_{bioavailable}$ to which the annual average of the dissolved nickel monitoring data is compared to assess compliance. The generic $EQS_{bioavailable}$ should be protective for *all* water bodies that may be monitored and, if possible, the toxicity data should be normalised to a reference condition that is representative of reasonable worst case conditions – i.e. high bioavailability (for Ni this would be waters of relatively high pH and low DOC).

From the European Risk Assessment of nickel the bioavailability scenario that had the most sensitive conditions, as measured by the lowest PNEC, was for Lake Monate in Italy. An assessment factor of 2 was used on the HC_5 in the risk assessment and this same assessment factor has been used in the derivation of the generic Ni EQS. The PNEC for Lake Monate was 3.6 $\mu g.l^{-1}$ with a pH of 7.7, 48 mg $Ca.l^{-1}$ and 2.5 mg $DOC.l^{-1}$. The risk assessment covered the approximate range of conditions from the 10^{th} to the 90^{th} percentiles of key abiotic parameters. For the purpose of assessing compliance it is necessary to consider the *complete range* of EU water quality conditions and not just the 10^{th} to the 90^{th} percentiles of key abiotic water parameters. This is an important difference between the objectives of generic risk assessments and an EQS used for site-specific compliance assessment and permitting.

In order to define the reference conditions for the generic $EQS_{bioavailable}$ and to ensure that there is just *one* Ni EQS that is applicable to the whole of the EU it is necessary to have an understanding of the abiotic conditions that are likely to result in the greatest nickel bioavailability, or the most sensitive conditions to nickel exposures (Figure 7.1). From this understanding the NiBLM can be used to calculate the range of PNECs across all EU waters. The final reference condition selected must represent the worst case bioavailability conditions so that the generic EQS is adequately protective of all EU waterbodies, so that it can be usefully applied as a screening step within a tiered compliance assessment process (Figure 7.2). It is clear from Figure 7.1 that waters with low DOC and relatively high pH represent conditions of greatest sensitivity to nickel exposures.

Table 7.1 shows the 5^{th} and 10^{th} percentiles of PNECs derived using the NiBLM for EU datasets from England, Wales, Scotland, Sweden, Austria, Spain, The Elbe and Northern France. These have been calculated using matched data for single sites for pH, DOC and Ca. It is clear from Table 7.1 that Austrian waters are the most sensitive of those listed. Due to mixed temporal scope (i.e. different time frames of collection) of the datasets presented in Table 7.1 the percentiles of PNECs have, for all but the data from England, Wales and Scotland, been calculated using single monitoring event data, i.e. *not* annual averages. Annual averages are required by the EQS Directive and in the recent technical specification[8]. However, this is a more precautionary assessment as data extremes are still present.

Table 7.1. The 5^{th} and 10^{th} percentiles of Predicted No Effect Concentrations for EU Member States as calculated using the Nickel Screening Tool (as based on the NiBLM (Section 7.1)).

Dataset and number of samples	10^{th} Percentile	5^{th} Percentile
England, Wales and Scotland* (n = 184)#	3.31	2.93
France (n = 249)#	2.64	2.32
Austria (n = 1553)#	2.17	1.85
Spain (n =48)^	3.67	3.66
The Elbe (n =294)^	4.11	3.73
Sweden (n = 3997)#	5.60	5.04
Walloon (n = 559)^	3.18	2.91
All data (n = 6885)	**3.29**	**2.60**

*This dataset is from annual averages and annual medians
#These data have been obtained direct from Member States and EIONET
^These data are the same as those used in the EU RAR.

[8] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:201:0036:0038:EN:PDF

In a practical application of the EQS Technical Guidance the Ni PNEC reference condition selected is that condition that will ensure 95% protection of waters from the most sensitive region; in the case of nickel this is Austria. The selection of a reference condition based on a low percentile of the most sensitive region prevents the "moving target" nature of basing reference EQS on the absolute lowest value. The generic $EQS_{bioavailable}$ selected from the approximate 5th percentile of the Austrian dataset is 2 µg Ni l^{-1} (pH 8.2, DOC 2 mg.l^{-1}, Ca 40 mg.l^{-1}).

7.1 A POTENTIAL METHODOLOGY FOR THE IMPLEMENTATION OF BIOAVAILABILITY

The proposed AA EQS for Ni is an $EQS_{bioavailable}$. This is effectively the same as defining an EQS on the basis of a specific operationally defined form of a chemical, such as has been done by some Member States with several other WFD EQS, e.g. un-ionised ammonia, reactive aluminium, or free chlorine. Equally, the bioavailability-based approach is similar in terms of implementation, to that for the cadmium EQS based on hardness correction. Historically, incorporating a compliance- and permitting-based framework that accounts for bioavailability through use of BLMs has been seen as presenting some significant practical challenges to regulators (UBA 2008). There is a requirement for a practical methodology to perform full bioavailability normalisation for the site-specific conditions under consideration at each monitoring location. One way to do this is through the adoption of a tiered framework and use of a Screening Tool that mimics the BLM in a precautionary way and is simple to use (Zwolsman and De Schamphelaere 2007; Environment Agency 2009; Geoffroy et al. 2010).

The development of a Screening Tool to predict site-specific bioavailability of nickel is a practical step to help implement bioavailability-based approaches. The nickel Screening Tool has several characteristics that make this possible. The key characteristics of the nickel Screening Tool are:

- The prediction of nickel toxicity is from a limited set of input parameters - DOC, pH, and calcium;
- It is Microsoft Excel™-based and therefore readily supported by most office computer systems;
- The basis for the calculations is simple and can be incorporated into laboratory data management systems, so the tool can be automated;
- The Ni bioavailability predictions from the Screening Tool are precautionary compared to the NiBLM;
- Many thousands of samples can be processed in seconds and the outputs are all in Microsoft Excel™.

The Screening Tool has been developed from over 2000 NiBLM PNEC predictions, where DOC, calcium and pH are varied, but input parameters are fixed. The concentrations of competing cations, such as Mg, are estimated from the Ca concentration according to relationships established for European surface waters (Peters et al. 2010). Optimisation of the constants was performed by minimising the root mean squared error between the estimate and the NiBLM prediction. The Screening Tool makes predictions that are not quite as accurate, but are always precautionary when compared to the NiBLM. Importantly, the Screening Tool will perform calculations for waters that lie outside the validation range of the NiBLM (The validation ranges of the NiBLM are pH 6.5 - 8.2, an unlimited range for DOC, and 3.8 - 88 mg Ca l^{-1}). However, when pH and/or Ca data are entered outside the BLM validation range these abiotic parameters are set at the extreme of the validation range. When this occurs the Screening Tool gives a flag in the output column indicating that the result is tentative and that the physico-chemistry is outside the validation range. Furthermore, because of the improved understanding and knowledge gained through the EU-RAR on the ecotoxicology of Ni in freshwaters (Figure 7.1) it is possible to provide an indication, with the flag in the Screening Tool, as to whether the result in the output column is going to be over or underprotective. This enables the user to make an informed decision as to how to treat this site specific information, for example if the Screening Tool gives a result for a monitoring site with physico-chemistry beyond the validated NiBLM boundary conditions, but that result is overprotective and no risk is identified, there is no need for this site to advance to Tier 3.

The Screening Tool has been developed for use as an early tier in a tiered risk-based compliance framework (Figure 7.2). There are three required data fields to account for nickel bioavailability. Using the generic $EQS_{bioavailable}$ as derived above the Screening Tool calculates a bioavailability factor (BIOF). This BIOF is then applied to the monitoring data to give the bioavailable concentration of nickel at a monitoring site. This bioavailable nickel concentration is then compared to the generic EQS. The use of a BIOF means that *only* one generic nickel EQS is needed across Europe (EC 2011), provided that it is expressed as a bioavailable concentration, and is then applied within a tiered approach.

The recommended tiered approach is shown in Figure 7.2. This follows a standard risk assessment paradigm in which early tiers are conservative, but allow high relative sample throughput. As individual monitoring sites progress through the tiers in lower and lower numbers because low risk sites are screened out, the amount of effort required for assessment is proportionate to levels of potential environmental risk. The lower tiers of this assessment are generally precautionary and use the conservative generic $EQS_{bioavailabe}$, so require limited input information and technical skill for the interpretation of outputs. Indeed, Tiers 1 and 2 can be (and have been in England and Wales) automated in laboratory monitoring systems (Environment Agency 2010). This is important if adoption of a bioavailability-based compliance assessment framework for nickel is not to require any more (*and preferably less*) resource than existing approaches to compliance assessment. Therefore, focus should be on the rates of site removal at these early tiers in the compliance framework. If this is high then this operation will require very little routine resource use. The individual tiers are described in more detail below. The process undergone in Tier 4 is not discussed here and would be determined by individual Member State requirements.

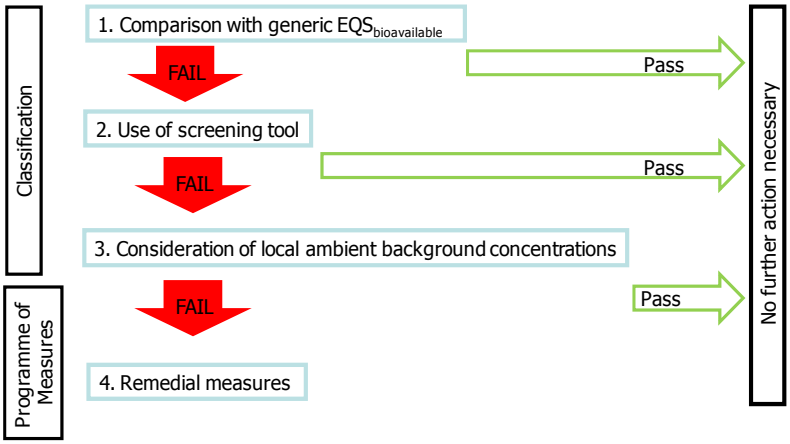

Figure 7.2. Flow diagram of the stages in a tiered compliance assessment. The red arrows indicate sites that continue through tiered process, green arrows are sites that need no longer be considered as having a potential nickel risk (Environment Agency 2009).

Tier 1. The first tier in the scheme simply considers a direct comparison of the annual average concentration from monitoring data with the generic 100% “bioavailable” nickel EQS. Although the EQS is expressed as a “bioavailable” concentration, it is compared to dissolved metal measurements. This means that the assessment is conservative and false negatives are minimised. This tier is applicable to all waterbodies that will be monitored, so that additional supporting parameters (such as pH, DOC, and Ca) are not required in order to undertake analysis in this initial tier of the assessment. Sites, or samples, failing at this tier progress to the second tier of the assessment, in which information on additional supporting parameters (pH, DOC, and Ca) are required as inputs to the screening tool. The generic $EQS_{bioavailable}$ can be precautionary as its use is part of a tiered risk-based framework. A Generic $EQS_{bioavailable}$ of 2 $\mu g.l^{-1}$ nickel is proposed as being sufficiently protective of relatively high bioavailability conditions.

Tier 2. This tier makes use of the readily available Excel™-based Screening Tool that can be embedded and automated in monitoring and assessment systems. Samples failing this screen progress to Tier 3 and the consideration of local ambient background concentrations. The Screening Tool provides a relatively precautionary estimate of nickel bioavailability, and represents a much more refined assessment of the potential for adverse effects than the generic $EQS_{bioavailable}$ applied in the first tier. This tier requires information on the site pH, DOC concentration, and Ca concentration of the waterbody, although in some cases default values may be available for some of the required input data (Environment Agency 2009). Annex 1 of this document provides an example of how the compliance and permitting can be performed in a precautionary manner if DOC data are not available.

Tier 3. This tier uses specific localised ambient natural background concentrations (ABCs). The use of waterbody or hydrometric area-specific ABCs for metals for which BLMs exist (such as nickel) is expected to be limited because of the exclusion of locations requiring attention during earlier tiers of the assessment. The relative uncertainty associated with the derivation and use of ABCs is significantly greater than uncertainty from the use of the BLMs, and therefore ABCs must only be considered after the use of the speciation-based models. Indeed, the use of backgrounds in compliance assessment using the 'added risk approach' is a pragmatic and not scientifically driven decision (EQS Technical Guidance (EC 2011)). In many cases the application of a background correction to sites which have reached this tier of the assessment is unlikely to result in a change in the conclusion of the assessment. This is especially true if bioavailability has been taken into account, due to the relatively low level of background concentrations in many parts of Europe (Environment Agency 2008). In addition, many of the measured nickel data on the EIONET Central Data Repository[9] are reported at below limits of detection or as total concentrations, rather than as dissolved concentrations. This presents a considerable difficulty when attempting to follow European Commission guidance on deriving natural background concentrations (EC 2011).

Tier 4. At this tier the failure of a site to achieve good chemical status has been clearly determined. Consideration of a programme of measures to mitigate the situation, within the appropriate cost/benefit framework, may be required. The advantage of using the bioavailability-based approach at an earlier tier is that causal factors may be identified which provide a focus for the programme of measures. A possible course of action in some cases may be the collection of additional data, for example in cases where the DOC information is based on defaults or limited information (Annex 1).

7.2 ACUTE AND CHRONIC AQUATIC ECOTOXICITY

Freshwater

Acute toxicity

Acute NiBLM models for freshwater and saltwater have not been developed.

The freshwater and marine acute data have been pooled to derive a common HC_5 of 0.067 mg/l, and a resulting common MAC = 0.0335 mg/l (see marine MAC derivation below).

Summary of the "species mean" LC/EC_{50} values (total risk approach) in mg $Ni.l^{-1}$ for freshwater organisms (n=65):

[9] http://www.eionet.europa.eu/

Taxonomic group	**Species**	**Species mean LC/EC$_{50}$ value (mg.l^{-1})**
Cyanobacteria	*Anacystis nidulans*	6.03
	Nostoc muscorum	0.20
Algae	*Ankistrodesmus falcatus*	0.31
	Chlamydomonas sp.	0.09
	Chlorella pyrenoidosa	0.41
	Chlorella sp.	1.09
	Coelastrum microporum	0.27
	Desmodesmus sp.	0.27
	Desmodesmus spinosus	0.12
	Desmodesmus subspicatus	0.36
	Pediastrum duplex	0.06
	Pseudokirchneriella sp.	0.10
	Pseudokirchneriella subcapitata	0.18
	Scenedesmus accuminatus	0.13
	Scenedesmus acutus	33.30
	Scenedesmus quadricauda	0.59
	Spermatozopsis exsultans	0.18
Annelid	*Lumbriculus variegatus*	32.00
	Tubifex tubifex	35.97
Crustacean	*Asellus aquaticus*	119.00
	Bosmina coregoni	0.30
	Ceriodaphnia dubia	0.11
	Ceriodaphnia quadrangula	0.12
	Chironomus tentans	69.50
	Cyclops abyssorum	15.00
	Daphnia hyalina	1.90
	Daphnia magna	1.85
	Eudiaptomus padanus	3.60
	Gammarus fasciatus	100.00
	Hyalella azteca	14.00
	Mesocyclops pehpeiensis	1.19
	Peracantha truncata	2.45
	Simocephalus serrulatus	0.96
Fish	*Anguilla rostrata*	13.00
	Carassius auratus	9.82
	Catla catla	14.40
	Channa punctatus	56.90
	Cyprinus carpio	2.80
	Danio rerio	100.00
	Fundulus diaphanus	46.10
	Lebistes reticulatus	19.27
	Lepomis gibbosus	8.00
	Lepomis macrochirus	21.07

Taxonomic group	Species	Species mean LC/EC_{50} value ($mg.l^{-1}$)
	Morone saxatilis	11.34
	Mystus vittatus	255.00
	Oncorhynchus mykiss	15.39
	Pimephales promelas	3.74
	Poecilia reticulata	36.00
	Puntius sophore	13.57
	Rasbora daniconius neilgeriensis	48.83
	Roccus americanus	13.60
	Roccus saxatilus	6.20
	Thymallus arcticus	8.45
	Tilapia nilotica	64.00
Insect	*Chironomus riparius*	79.50
Macrophyte	*Lemna gibba*	0.21
	Lemna minor	0.54
Mollusc	*Anodonta imbecilis*	0.19
	Helisoma trivolvis	3.20
	Jugo plicifera	0.10
	Lymnaea acuminata	4.33
	Physa gyrina	0.22
	Viviparus bengalensis	99.68
Platyhelminth	*Dugesia tigrina*	32.00
Rotifer	*Philodina acuticornis*	4.00

Given the large number and taxonomic spread of the ecotoxicity data, a statistical species sensitivity analysis of the freshwater acute data has also been performed to derive a 5th percentile Hazardous Concentration (HC_5).

Data were analysed using RIVM ETX 2.0 (http://www.rivm.nl/rvs/risbeoor/Modellen/ETX.jsp) and CSIRO Burrlioz (http://www.csiro.au/products/BurrliOZ.html) software for deriving SSDs. Figure 7.2 shows the graphical output from the ETX lognormal model fitted to the data. The HC_5 is 0.06539 $mg.l^{-1}$ (confidence interval (90%) = 0.0282 – 0.1289 $mg.l^{-1}$).

However, Anderson Darling and Cramer von Mises goodness of fit (GoF) tests are failed at all significance levels, and the Kolmogorov-Smirnov (K-S) GoF test is failed at p = 0.1 and 0.05 significance and passed at p = 0.025 and 0.01. The plot of data in Figure 7.2 suggests that this failure of GoF tests is because the lognormal model predicts a more conservative result in the lower tail. It should also be noted that, as with other statistical tests, goodness of fit tests become more powerful as the number of data points increases. However, this has the counter-intuitive effect of making it more likely that the "same" distribution will pass a GoF test if it has fewer data.

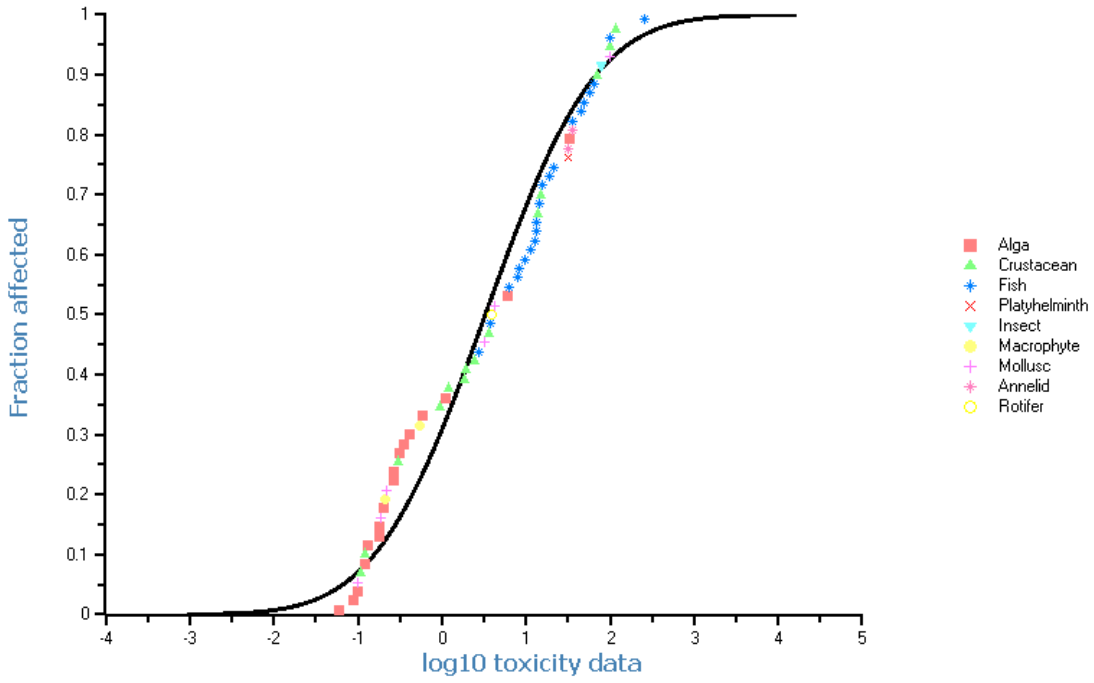

Figure 7.2 Lognormal Species Sensitivity Distribution for nickel based on n=65 acute freshwater data points generated using ETX.

The results from the Burr III analysis of the data support the results from the ETX SSD analysis (Figures 7.3 and 7.4). The HC5 from a reciprocal Weibull distribution in Burrlioz is 0.096 $mg.l^{-1}$ and the 90% confidence interval is 0.069 to 0.147 $mg.l^{-1}$. The Burrlioz analysis was performed using 1000 bootstrap resamples to determine the confidence interval around the HC5.

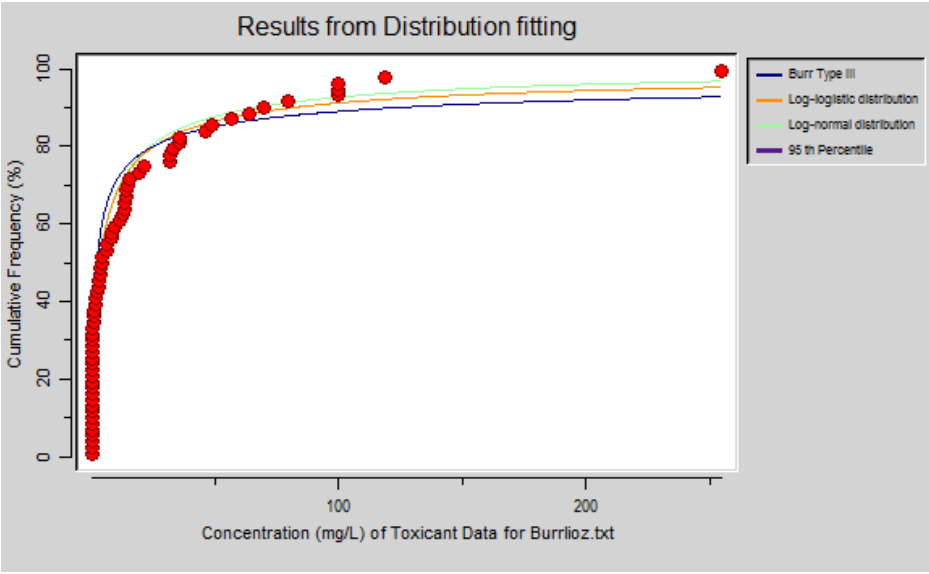

Figure 7.3 Lognormal Species Sensitivity Distribution for nickel based on n=65 acute freshwater data points generated using Burrlioz (natural scale).

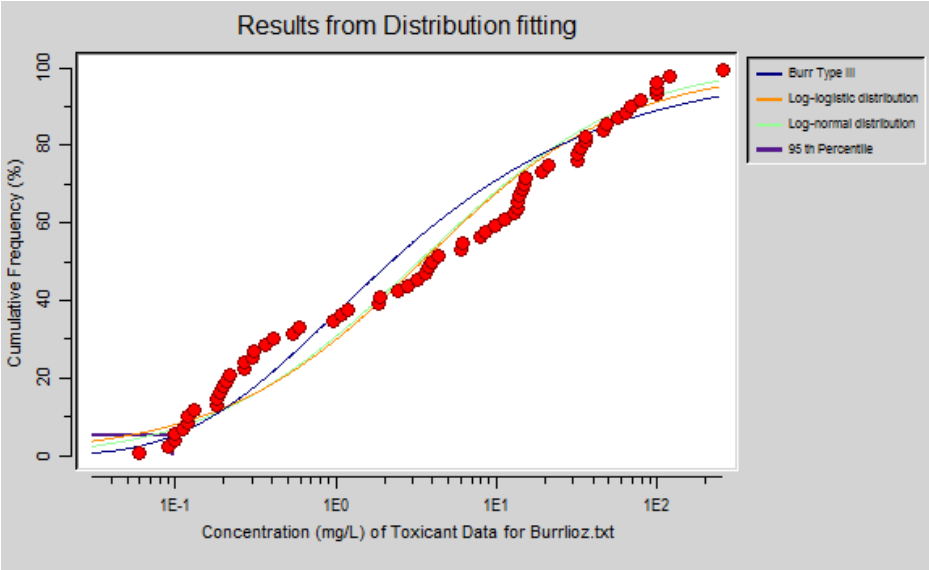

Figure 7.4 Lognormal Species Sensitivity Distribution for nickel based on n=65 acute freshwater data points generated using Burrlioz (log scale).

The following conclusions can be drawn:

1. The ETX and Burrlioz estimates of the HC_5 are similar (0.065 and 0.096 $mg.l^{-1}$ respectively), with the plots of the Burrlioz estimate showing that the fit is better than that produced by the lognormal model in ETX.

2. The lower 90th percent confidence limit from Burrlioz (0.069 $mg.l^{-1}$) is very close to the median HC_5 estimate from ETX (0.065 $mg.l^{-1}$).

3. Similar analyses of marine acute Ni data provide similar results from both ETX and Burrlioz (see marine acute toxicity section below).

4. Risk assessors in Europe are well acquainted with ETX software. Therefore a pragmatic approach to estimating the HC_5 is to use the ETX value of 0.065 $mg.l^{-1}$. Despite the relatively poor fit of the lognormal model in ETX, evidence from the Burrlioz analysis shows that this errs towards a lower value rather than a greater.

Chronic toxicity

The dataset used to derive the freshwater AA-EQS was taken directly from the EU-RAR. As stated earlier, these data sets were discussed within the Organization of Economic Cooperation and Development (OECD) and were accepted at the OECD's SIDS (Screening Level Information Data Set) Initial Assessment Meeting (SIAM 28, October 2008), as was the use of nickel BLMs to normalize the Ni ecotoxicity data. The chronic datasets are discussed in greater detail in the RAR. Derivation of the EQS is described in the RAR.

Summary of the "species mean" NOEC or EC_{10} values (total risk approach) in µg $Ni.l^{-1}$ (with most sensitive endpoint) for freshwater organisms:

Taxonomic group	Species	Most sensitive endpoint	Species mean NOEC/EC_{10} value (µg.l^{-1})
Algae	*Scenedesmus accuminatus*	Growth rate	12.3
	Desmodesmus spinosus	Growth rate	22.5
	Pediastrum duplex	Growth rate	23.8
	Chlamydomonas sp	Growth rate	27.9
	Ankistodesmus falcatus	Growth rate	28.4
	Chlorella sp	Growth rate	42.0
	Coelastrum microporum	Growth rate	46.2
	Pseudokirchneriella subcapitata	Growth rate	92.7
Higher plants	*Lemna minor*	Growth	27.9
	Lemna gibba	Growth rate	70.0
Rotifer	*Brachionus calyciflorus*	Intrinsic rate of growth	633.2
Molluscs	*Lymnea stagnalis*	Growth	6.8
	Juga plicifera	Mortality	124.0
Crustacea	*Ceriodaphnia dubia*	Reproduction	6.9
	Ceriodaphnia quadragula	Mortality	7.4
	Peracantha truncata	Reproduction	8.0
	Simocephalus vetulus	Reproduction & mortality	16.3
	Ceriodaphnia pulchella	Reproduction & mortality	16.7
	Alona affinis	Mortality	25.0
	Daphnia longispina	Mortality	27.8
	Daphnia magna	Reproduction	35.6
	Hyalella azteca	Mortality	29.0
Insects	*Clistoronia magnifica*	Mortality	66.0
	Chironomus tentans	Biomass	458.9
Hydrozoans	*Hydra littoralis*	Growth	60.0
Fish	*Brachydanio rerio*	Hatchability	40.0
	Pimephales promelas	Growth	57.0
	Oncorhynchus mykiss	Growth	134.0
Amphibians	*Xenopus laevis*	Malformation	171.6
	Gastrophryne carolensis	Mortality	184.9
	Bufo terrestris	Growth	640.0

Marine

Acute toxicity

Summary of the "species mean" LC/EC_{50} values (total risk approach) in mg $Ni.l^{-1}$ for marine organisms (n=21):

Taxonomic group	Species	Species mean LC/EC50 value ($mg.l^{-1}$)
Alga	*Macrocystic pyrifera*	2.4
	Champia parvula	0.456
	Dunaliella terteolecta	66.026
	Skeletonema costatum	2.22
Annelid	*Nereis virens*	25
Cnidarian	*Hydrodes elegans*	0.274
Crustacean	*Americamysis bahia*	0.508
	Neomysis integer	0.765
	Penaeus duorarum	112
	Pagurus logicarpus	47
	Mysidopsis intii	0.1486
Echinoderm	*Asterias forbesi*	150
Fish	*Fundulus heteroclitus*	350
	Chelon labrosus	118.3
	Atherinops affinis	26.56
	Liza klunzingeri	4.168
Mollusc	*Crassostrea virginica*	1.18
	Mya arenaria	320
	Nassarius obsoletus	72
	Haliotus rufescens	0.1455
	Mercenaria mercenaria	0.31

According to the TGD-EQS (EC 2011) marine and freshwater data should be compared statistically, an if the two dataset do not differ significantly they should be pooled.

A t-test performed on the log-transformed data yielded P = 0.24 (two tailed). Thus the two datasets do not differ significantly, and may be pooled. (For the chronic data the difference was highly significant with P = 0.0003, and pooling was thus not an option).

The resulting $HC_{5\text{-}50}$ is 0.067 mg l^{-1} with lower and upper confidence limits of 0.032 mg l^{-1} and 0.125 mg l^{-1} respectively.

The total number of species is 86. The Anderson-Darling, Cramer von Mises, and Kolmogorov-Smirnov tests for normality all failed. However, given the high number of species even a minor divergence from normality will result in statistical significance. As can be seen from Figure 7.5 assuming a normal distribution will result in a somewhat lower rather than greater estimate of HC5 than the data would actually suggest.

The SSD analysis and the resulting HC5 are therefore accepted. As marine species are well represented no extra assessment factor is applied for the marine environment.

The large number of data points for Ni across a very wide range of species (86 separate species values), and higher taxonomic groups (12) means that a large assessment factor need not be applied to this conservative HC_5. An AF of 2 is appropriate for the following reasons:

a. Tha data-set contains information on 86 species representing 12 higher taxonomic groups.
b. The proposed MAC is close to the lower confidence limit (0.032 $mg.l^{-1}$) from the conservative ETX analysis.
c. The lowest geomean in the overall acute dataset is for the alga *Pediastum duplex* (0.06 $mg.l^{-1}$), which would not be exceeded by the proposed MAC.
d. The proposed MAC of 0.034 $mg.l^{-1}$ is below individual LC/EC_{50} values for the majority of tested species even under conditions of high bioavailability.
    i. The lowest reported individual 96-h LC_{50} for a fish species is 0.35 $mg.l^{-1}$ for *Pimephales promelas* (Pyle et al. 2002). The proposed MAC is therefore below the most sensitive EC50 value for fish species.
    ii. The lowest reported individual LC_{50} for an invertebrate species is a 48-h LC_{50} of 0.013 $mg.l^{-1}$ for *Ceriodaphnia dubia* (Schubauer-Berigan et al. 1993). This result is substantially lower than all others for *C. dubia*. The geometric mean from all *C. dubia* data including the low Schubauer-Berigan et al. value (n = 15) is 0.11 $mg.l^{-1}$, and the geometric mean for tests under high pH values, where toxicity is greatest, is 0.068 $mg.l^{-1}$. The proposed MAC is therefore below the most sensitive species mean LC50 value for invertebrate species.
    iii. The lowest reported individual EC_{50} for a plant species is a 72-h EC_{50} of 0.025 $mg.l^{-1}$ for *Pseudokirchneriella subcapitata* (Deleebeeck et al. 2005). This result is reported as >0.0253 to <0.365 $mg.l^{-1}$, which is a confidence limit around an EC_{50} estimate, This is consistent with the geometric mean (n=4) of 0.1 $mg.l^{-1}$ for *P. subcapitata*. The proposed MAC is therefore lower than the most sensitive species mean EC_{50} value for plant species.

The resulting MAC for marine and freshwater is thus 0.067 mg/l:2 = 0.0335 mg/l ≈ 0.034 mg/l.

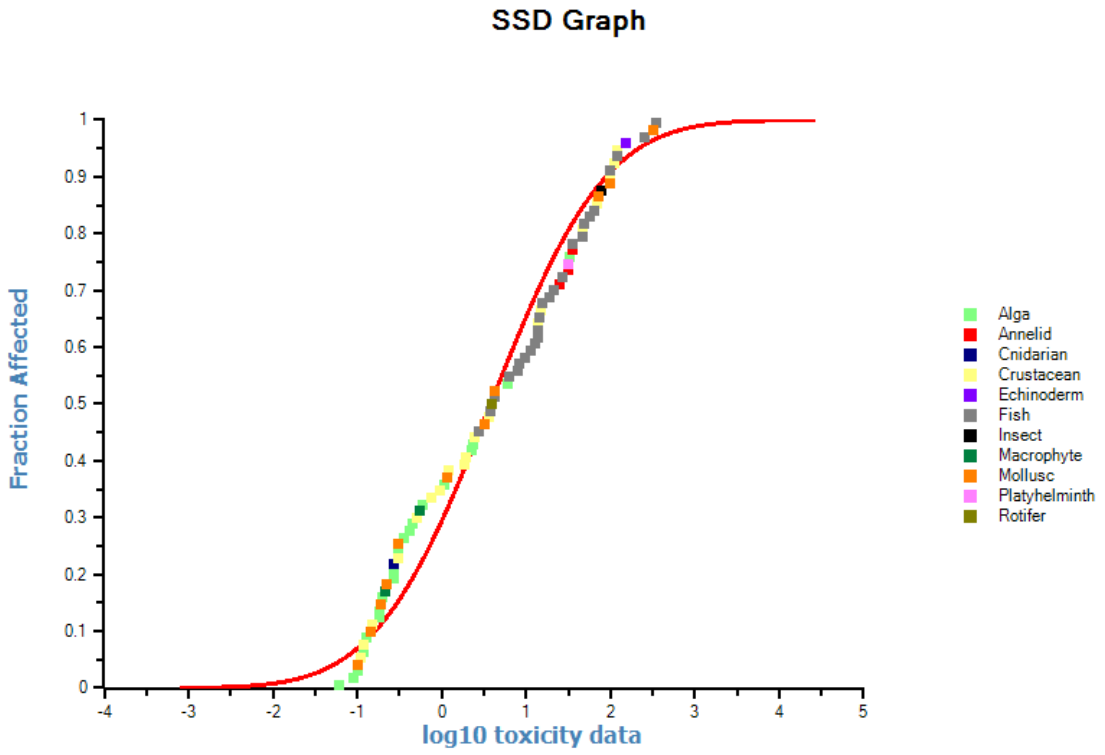

Figure 7.5. **Lognormal Species Sensitivity Distribution for nickel based on n=86 acute pooled marine and freshwater data points generated using ETX.**

Twenty one species are represented in the marine dataset, but only 7 higher taxonomic groups, where 8 are recommended in the TGD-EQS (EC 2011). Applying an SSD to the marine acute data only results in an HC5 = 0.073 mg/l, and the following additional conclusions can be drawn:

1. The ETX and Burrlioz estimates of the HC_5 differ by a factor of only approximately 2 (0.0725 and 0.142 $mg.l^{-1}$ respectively), and **are similar to the results for the freshwater acute dataset**.

2. The lower 90^{th} percent confidence limit from Burrlioz (0.087 $mg.l^{-1}$) is very close to the median HC_5 estimate from ETX (0.0725 $mg.l^{-1}$).

3. Risk assessors in Europe are well acquainted with ETX software for which the lognormal model fit is acceptable for Ni marine acute data

There could be arguments against pooling the marine and freshwater datasets. Among these are the physiological differences between the two groups of organisms concerning especially differing ion transport strategies. Also, some types of organisms occur only or almost only I either the marine or freshwater environment. For example, echinoderms occur only in saltwater and insects almost only in freshwater.. However, the datasets overlap completely, and in spite of the very great number of data the statistical analysis is highly insignificant, which is also demonstrated by the HC5-values for the two kinds of environment being very close.

Chronic toxicity

Summary of the "species mean" NOEC or EC_{10} values (total risk approach) in µg $Ni.l^{-1}$ (with most sensitive endpoint) for marine organisms:

Taxonomic group	Species	Most sensitive endpoint	Species mean NOEC/EC_{10} value (µg.l^{-1})
Algae	*Dunaliella tertiolecta*	Growth rate	17891
	Skelatonema costatum	Growth rate	316.5
	Macrocystis pyrifera	Growth	96.7
	Champia parvula	Reproduction	144
Molluscs	*Mytilus galloprovincialis*	Development	269.7
	Crassostrea gigas	Development	431
	Haliotis rufescens	Metamorphosis	36.4
Echinodermata	*Paracentrotus lividus*	Development	139
	Dendraster excentricus	Development	191
	Strongylocentrotus purpuratus	Development	335
Crustacea	*Mysidopsis bahia*	Reproduction	61
	Mysidopsis intii	Growth	45.2
Polychaetes	*Neanthes arenaceodentata*	Reproduction	22.5
Fish	*Atherinops affinis*	Survival	3599
	Cyprinodon variegatus	Growth	20760

A range of statistical options was explored for determining the HC_5 (50%) from the marine ecotoxicity data using the SSD approach. Alternatives to the preferred approach of using the lognormal distribution were required because this distribution was rejected based on Goodness of Fit tests. The alternative approaches included:

1) alternative non-rejected parametric frequency distributions (all data points)

2) log-normal distribution using a reduced data base (with exclusion of fish and dinoflagellate data based on a mechanistically based hypothesis); and

3) a non-parametric approach called "flexible kernel density estimation" (all data points).

It was concluded in the RAR that each of the above approaches had advantages and disadvantages and that no approach could be said to be scientifically and indisputably superior. A weight-of-evidence approach was used to evaluate the options, and in the RAR it was decided to take the mean from the most cautious approach of option 1 (i.e. the arithmetic mean HC_5 (50%) value of 19.9 µg.l^{-1} for all statistically valid parametric distributions) and the outcome of option 3 (i.e. the HC_5 (50%) of 14.5 µg.l^{-1} of the Kernel Density Estimation approach with optimal band width). Therefore an HC_5 (50%) value of 17.2 µg.l^{-1} is taken forward for the $PNEC_{marine}$ determination.

Based on the amount, type and nature of chronic data on marine organisms and remaining uncertainty an Assessment Factor of 2 was chosen in the RAR, which yielded a $PNEC_{marine}$ value of 8.6 µg $Ni.l^{-1}$.

7.3 SEDIMENT TOXICITY

A technical conclusion i was determined for the sediment compartment in the 2008/2009 European Union Risk Assessment for Nickel and Nickel Compounds.EU Member States and the ECB (European Chemicals Bureau) have accepted a formal testing recommendation for sediments, which was published in the Official Journal of the European Union on May 28th, 2008. To derive $PNEC_{sed}$ values, the proposed research comprises three components, including:

1. An evaluation of optimal sediment spiking techniques;

2. Generation of reliable ecotoxicity data on sediment dwelling organisms providing effect concentrations relating to bulk sediment concentrations;

3. The development of an integrated, equilibrium-partitioning based bioavailability model for normalizing the sediment effect concentrations to bioavailable sediment concentrations under both aerobic and anaerobic conditions.

A research program has been designed specifically to address these components. The U.S. Geological Survey (USGS, Columbia, Missouri, USA) has conducted ecotoxicity testing for nine benthic organisms and for eight sediment types to evaluate the bioavailability of Ni in a wide range of sediments and toxicity to a variety of benthic organisms. These data will be used to generate an integrated bioavailability model for toxicity in sediments.

The setting of an EQSsediment awaits the generation of more data and availability models.

7.4 SECONDARY POISONING

A tiered approach was developed and applied for determining risks associated with dietary Ni exposure to the aquatic food chain in the EU-RAR (EC 2008). The default approach suggested by the TGD-EQS always showed risk, even at concentrations known to be within the range of natural background concentrations. This demonstrated the need to modify the TGD-EQS default assumptions with refined approaches. Refinements in subsequent tiers included the development of species-specific $NOEC_{oral}$ values based on allometric adjustment, the quantification of absorption of dietary nickel, and adjustment of the diet of predators to more relevant combinations of prey organisms (as opposed to assuming that predators consume 100% of the same organism).

Tiered Approach for refined assessment of secondary poisoning

Tier 1: default assessment

- $PNEC_{oral}$ values were derived from reference NOAELs (from long-term studies) without species-specific modification;
- bioavailability of dietborne nickel was assumed to be 100%;
- diets were composed of one food source with a single nickel concentration.

Tier 2: correction for species specific info on $PNEC_{oral}$

Species-specific $PNEC_{oral}$ values were developed for relevant consumer organisms.

Tier 3: correction for bioavailability of the dietborne fraction

Bioavailability of dietborne nickel was incorporated into the assessment. Relative absorption factors (RAFs) were calculated from the literature for different relevant dietary components in the mammalian food chain, including a soil RAF and a comprehensive RAF used for other dietary components.

Tier 4: correction for diet composition

Use a more realistic dietary composition instead of assuming that the predator consumes only one food source containing nickel.

Food chains:

For the freshwater mammalian food chain, the European otter (*Lutra lutra*) was identified as a relevant species that will feed on fish and other aquatic biota:

freshwater → fish → European otter

For the marine mammalian food chain, the harbour seal (*Phoca vitulina*) was identified as a relevant species that will feed on fish and other aquatic biota:

seawater → fish/octopus/squid → harbour seal

The relevant food chain for evaluating secondary Ni poisoning in aquatic birds for both marine and freshwater is as follows:

freshwater → fish/mollusc → bird

PNECoral

The PNECoral for the European otter was calculated to be 2.3 mg Ni/ kg diet.

The PNECoral for the harbor seal was calculated to be 4.6 mg Ni/ kg diet.

The PNECoral for aquatic birds was calculated to be 12.3 mg Ni/kg diet.

Bioavailability correction

For Tiers 3 and 4 of the mammalian food chains, bioavailability was taken into account by applying a RAF of 0.025. This RAF value was derived from studies on humans that showed nickel sulphate absorption of 27% when administered with water compared with 0.7% when administered with food (0.7/27 = 0.025, or 2.5%).

Assimilation efficiencies of Ni will likely vary according to food type, consumer organism, and other factors. This variability is accounted for to some extent by the 10-fold assessment factor used in the derivation of the $PNEC_{oral}$, which is intended to account for interspecies variability and lab-to-field extrapolation. The interspecies variation could include differences between humans (upon which the tissue-specific RAF of 0.025 was based) or rats (upon which the soil-specific RAF of 0.039 was based) and other mammals with respect to the efficiency with which Ni from food and soil is absorbed.

To back-calculate to a critical dissolved Ni concentration that is protective of dietary exposure to predators, the refined assessment approach was used. This is the most relevant approach, and draws upon an extensive amount of information developed in the EU-RAR.

First, critical PEC_{oral} values (i.e., where PEC_{oral} = $PNEC_{oral}$) were determined for the mammalian and avian foodchains. Critical PEC_{oral} values for the freshwater and marine mammalian foodchains were 2.3 and 4.6 mg $Ni.kg^{-1}$ diet, respectively. The mammalian PEC_{oral} values represent the bioavailable fraction of dietary Ni, and they were therefore adjusted to total Ni concentrations in food using the RAF of 0.025. This yielded total PEC_{oral} values of 92 and 184 mg $Ni.kg^{-1}$ for freshwater and marine foodchains, respectively.

No information is available to determine an appropriate RAF for avian foodchains, and therefore no adjustment was made. The total PEC_{oral} value is therefore 12.3 mg $Ni.kg^{-1}$ diet. This should be considered a cautious value as it is very likely that birds do not assimilate 100% of dietary Ni.

The next step was to calculate the critical dissolved Ni concentration in water that is necessary to achieve the critical total PEC_{oral} values.

For both the mammalian and avian food chains, a Bioconcentration Factor (BCF) of 270 $l.kg^{-1}$ was used. The EU-RAR concluded that this value was appropriate to estimate tissue Ni concentrations for both fish and bivalves[10], and it therefore covers both of these dietary sources.

Applying this BCF to the total PEC_{oral} value of 92 mg $Ni.kg^{-1}$ for the mammalian food chain yields a dissolved Ni concentration of 0.340 mg $Ni.l^{-1}$ ((92 mg $Ni.kg^{-1}$) x (1 kg/270 l) = 0.340 mg $Ni.l^{-1}$), or 340 µg $Ni.l^{-1}$. This concentration is far above the highest bioavailability-normalized dissolved PNEC for direct Ni toxicity to pelagic organisms, which was determined to be 22.8 µg $Ni.l^{-1}$ (this value was calculated by applying the water quality characteristics from a low bioavailability freshwater scenario (pH = 6.9, hardness = 260 $mg.l^{-1}$ $CaCO_3$, DOC = 12.0 $mg.l^{-1}$) using the Ni BLMs).

For the marine foodchain, applying the BCF of 270 $l.kg^{-1}$ to the total PEC_{oral} value of 184 mg $Ni.kg^{-1}$ yields a dissolved Ni concentration of 0.682 mg $Ni.l^{-1}$ ((184 mg $Ni.kg^{-1}$) x (1 kg/270 l) = 0.682 mg $Ni.l^{-1}$), or 682 µg $Ni.l^{-1}$. This concentration is far above the chronic marine PNEC of 8.2 µg $Ni.l^{-1}$ that was determined in the EU-RAR.

For the avian food chain, applying the BCF of 270 $l.kg^{-1}$ to the total PEC_{oral} value of 12.3 $Ni.kg^{-1}$ yields a dissolved Ni concentration of 0.046 mg $Ni.l^{-1}$ ((12.3 mg $Ni.kg^{-1}$) x (1 kg/270 l) = 0.046 mg $Ni.l^{-1}$), or 46 µg $Ni.l^{-1}$. This concentration is nearly two times higher than the highest bioavailability-normalized dissolved PNEC for direct Ni toxicity to pelagic organisms, which was determined to be 22.8 µg $Ni.l^{-1}$. Given that the critical dissolved concentration of 46 µg $Ni.l^{-1}$ is based on 100% bioavailability, it is likely that the actual critical dissolved concentration is even higher. From this analysis which is based on the EU-RAR (EU, 2008), it can be concluded that the risks associated with dietary Ni exposure to the aquatic food chain are not the most sensitive pathway that needs to be considered for the Ni Environmental Quality Standard.

Assessment of Top Predators

The Ni EU-RAR (EC 2008) concluded that the existing information suggests that Ni does not biomagnify, but rather that it tends to exhibit biodilution, particularly when upper levels of the food chain are considered. Because the information available on Ni indicates that this metal is subject to biodilution as opposed to biomagnification, analysis of a top mammal predator is excluded from the present analysis as such a predator would be expected to be exposed to lower dietary Ni concentrations than the consumer organisms considered, e.g., the harbour seal.

Secondary poisoning of top predators	**Master reference**

[10] The EU-RAR identified a BCF of 270 $l.kg^{-1}$ based on the median of BCFs for bivalves and for fish from studies using measured whole organism tissue Ni concentrations and paired dissolved Ni concentrations (BCF = tissue concentration (mg/kg)/dissolved concentration ($mg.l^{-1}$)).

Mammalian oral toxicity	Rat / Oral / 2-generation reproductive study NOAEL : 1.1 $mg.kg^{-1}_{bw}.d^{-1}$ NOEC: 22 $mg.kg^{-1}_{bw}$ $PNEC_{oral}$: 2.3 $mg.kg^{-1}_{biota\ ww}$	EC, 2008
Avian oral toxicity	*Gallus domesticus* / Oral / 42d / Body weight NOEC: 150 $mg.kg^{-1}_{bw}.d^{-1}$ $PNEC_{oral}$: 123 $mg.kg^{-1}_{biota\ ww}$	EC, 2008

Tentative $QS_{biota\ secpois}$	**Relevant study for derivation of QS**	**AF**	**Tentative QS**
Mammalian food chain	See Section 7.3	-	Freshwater: 92 $mg.kg^{-1}_{biota\ ww}$ corresponding to 340 $\mu g.l^{-1}$ Marine: 184 $mg.kg^{-1}_{biota\ ww}$ corresponding to 682 $\mu g.l^{-1}$
Avian food chain	See Section 7.3	-	Freshwater and Marine: 12.3 $mg.kg^{-1}_{biota\ ww}$ corresponding to 46 $\mu g.l^{-1}$

7.5 HUMAN HEALTH

The derivation of a biota standard for the protection of humans from consuming fishery products is triggered for substances with specific hazardous classifications. Various nickel substances are classified as known or suspected carcinogens (e.g., Ni chloride and Ni sulphate) and as reproductive toxicants (e.g., Ni chloride and Ni sulphate). Therefore, the basis for deriving a biota standard for the protection of humans from consuming fishery products has been triggered.

The classification of Ni substances as carcinogenic is based on the inhalation pathway. This is therefore not relevant for the derivation of a biota standard, which is based on the ingestion of fish and the subsequent absorption of nickel. The most sensitive systemic effect for nickel has been shown to be the exacerbation of existing dermatitis (EU-RAR 2008). Basing the derivation of a biota standard on this endpoint would therefore be protective of less sensitive effects, such as reproductive toxicity.

The primary basis for this assessment was the Indirect Environmental Exposure to Humans Assessment (also known as Man via the Environment, or MvE) that was performed as part of the EU-RAR (EC 2008). The MvE assessment calculated a total systemic absorbed dose for people living in close proximity to industrial facilities that emit Ni to the environment. This total systemic absorbed dose considered all relevant exposure pathways, including inhalation of air, and ingestion of soil, indoor dust, drinking water, and food. Systemic doses for the regional scale were calculated by determining the reasonable worst case Ni concentrations in each exposure medium (where reasonable worst case was defined as the 90th percentile of Ni as calculated by relevant regional monitoring databases for air, dust, and soil, and as the 95th percentile of Ni as calculated in drinking water and food from regional drinking water databases and from market basket surveys), and then applying the appropriate absorption factor (30% for drinking water, 5% for soil, dust, and food). The total systemically absorbed dose based on regional background was 17.0 µg Ni.day^{-1} [0.385 (soil/dust) + 4.98 (drinking water) + 11.65 (food) = 17.0].

The most critical Derived No Effects Level (DNEL) for nickel is for the acute systemic effect of oral exacerbation of existing dermatitis via the oral route. The DNEL is 0.012 mg Ni.kg$^{-1}_{bw}$.day^{-1} (840 µg Ni.day^{-1} for a 70 kg person or 252 µg Ni.day^{-1} of absorbed dose based on 30% absorption of Ni from water under fasting conditions). The LOAEL established after provocation of patients with empty stomach is 12 µg.kg^{-1} body weight (Nielsen et al. 1999). It should be noted that this dose is the acute LOAEL for exacerbation of dermatitis in fasting patients with hand dermatitis on a 48h diet with reduced nickel content. These patients are the most sensitive of the nickel allergic population to oral elicitation. A LOAEL after repeated exposure may be lower and a LOAEL in non-fasting patients is probably higher because of reduced absorption of nickel ions when mixed in food.

The critical dose by ingestion of Ni-contaminated fish that is required to exceed the DNEL can be calculated by subtracting the total systemically absorbed dose (17 µg Ni.day^{-1}) from the DNEL expressed as absorbed dose (252 µg Ni.day^{-1}). The difference between the DNEL and the total systemically absorbed dose is 235 µg Ni.day^{-1} (DNEL (= 252 µg Ni.day^{-1}) – total systemically absorbed dose (= 17 µg Ni.day^{-1}) = 235 µg Ni.day^{-1}).

To calculate the external dose of Ni, the critical dose of 235 µg Ni.day^{-1} is divided by the appropriate absorption rate, which is 5%. This yields a critical external dose of 4700 µg Ni.day^{-1} (235 absorbed µg Ni.day^{-1} x (1 external µg Ni/0.05 absorbed µg Ni)).

The critical fish tissue concentration that is required to deliver the critical dose of Ni can be calculated by dividing the critical dose of Ni (4700 µg Ni.day^{-1}) by the daily consumption rate of fish. The daily consumption rate of fish is 0.115 kg fish.day^{-1}, and is based on the REACH R.16 guidance (Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.16: Environmental Exposure Estimation). The critical fish tissue concentration is calculated to be 40780 µg Ni.kg^{-1} tissue (4700 µg Ni.day^{-1}/0.115 kg fish tissue.day^{-1} = 40780 µg Ni.kg^{-1} fish tissue).

The Ni concentration in water that is required to cause the critical fish tissue concentration can be calculated by dividing the critical fish tissue concentration (40780 µg $Ni.kg^{-1}$ fish tissue) by the relevant bioconcentration factor (BCF). The secondary poisoning section of the EU-RAR concluded that a BCF of 270 $l.kg^{-1}$ should be used to estimate whole body Ni fish tissue concentrations. This is a cautious approach because Ni BCFs show an inverse relationship with dissolved Ni concentration (McGeer et al. 2003). This calculation results in a critical dissolved Ni concentration of 151 µg $Ni.l^{-1}$ (40780 µg $Ni.kg^{-1}$ fish tissue/ (L/270 kg) = 151 µg $Ni.l^{-1}$).

Several points need to be made on this assessment:

First, the range of reported Ni fish tissue concentrations in Europe indicates that concentrations of 40780 µg $Ni.kg^{-1}$ tissue are unlikely to be observed. Ni concentrations in edible portions of fish tissue range from 20 to 1600 µg $Ni.kg^{-1}$ tissue, with the higher concentrations observed for polluted waters (EU-RAR, Secondary Poisoning Assessment, EC 2008).

Second, the calculations above were made using a BCF based on a dissolved Ni concentration of 2 µg $Ni.l^{-1}$. The higher the dissolved Ni concentration, the lower the BCF. For a dissolved Ni concentration of 150 µg $Ni.l^{-1}$, the corresponding BCF would be 40 $l.kg^{-1}$ (log BCF = -0.424 log Ni +1.262, McGeer et al. 2003).

Given the cautious nature of this assessment which is based on the EU-RAR (EU, 2008), it can be concluded that the dietary exposure pathway of Ni-contaminated fish is not the most sensitive pathway that needs to be considered for the Ni Environmental Quality Standard.

Human health via consumption of fishery products		**Master reference**
Mammalian oral toxicity	Human/oral/exacerbation of existing dermititis LOAEL : 0.012 $mg.kg^{-1}_{bw}.d^{-1}$	Nielsen, 1999 Cited in Denmark, 2008
CMR	Nickel, metallic and alloys: Cat. 2b Nickel compounds: Cat. 1	IARC, 2009

Tentative $QS_{biota\ hh}$	**Relevant data for derivation of QS**	**AF**	**Threshold Level**	**Tentative QSbiota, hh**
Human health	LOAEL : 0.012 $mg.kg^{-1}_{bw}.d^{-1}$	1[11]	12 $\mu g.kg^{-1}_{bw}.d^{-1}$	40780 $\mu g.kg^{-1}_{bw}.d^{-1}$ corresponding to 151 $\mu g.l^{-1}$ (freshwater)

Human health via consumption of drinking water		**Master reference**
Existing drinking water standard(s)	20 $\mu g.l^{-1}$ (preferred regulatory standard)	Directive 98/83/EC

[11] Assessment factor of 1 was agreed upon because the Nielsen (1999) study is based on a highly sensitive human subpopulation.

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ANNEX 1

OPTIONS FOR USING THE NICKEL SCREENING TOOL WHEN SITE SPECIFIC DISSOLVED ORGANIC CARBON DATA ARE NOT AVAILBLE

Dissolved organic carbon (DOC) data are a required input into any bioavailability normalisation step for nickel. However, not all Member States routinely measure DOC at the locations where nickel has been measured. Therefore, this can present a considerable obstacle to the implementation of a bioavailability-based approach. This issue has been addressed in several Projects undertaken by the Environment Agency of England and Wales (Environment Agency 2009, 2010). There are several options that can be used if DOC data are absent:

I. DOC monitoring at metal compliance assessment sites;
II. Establishing default values for DOC on a localised basis; or
III. Estimating DOC concentrations from other water chemistry parameters.

These options are discussed further below.

I. DOC monitoring

Some regulatory regimes may decide to undertake increased monitoring for DOC, although there may be significant cost implications associated with such an approach. Such an approach could, in some cases, only be applied to sites which fail the first tier assessment, and following this approach is likely to reduce significantly the number of sites requiring additional monitoring.

II. Establishing DOC defaults

In the UK, as in a number of Member States, DOC which is probably the key input parameter for most BLMs, is not routinely monitored as there is no regulatory requirement to report levels of DOC (Environment Agency 2009). Financial and organisational pressures mean that there is a need to meet direct regulatory reporting requirements as a top priority. However, considerable DOC data were collected across the country in the past. Therefore, while there may be limited DOC data for waterbodies of interest from the last five years, there is considerable monitoring data for the previous 15 years. The Environment Agency has investigated the use of default DOC values as inputs to the Screening Tool and the results for nickel are shown in Figure A. It can be seen from this figure that the use of defaults provides a lower PNEC as compared to those predicted using measured DOC. Default DOC values have been set for individual waterbodies where possible, and for sites which do not have at least eight DOC measurements per year, default values are set at the hydrometric area level (Environment Agency 2009, EC 2011). The 25th percentile of the measured waterbody or hydrometric area DOC concentrations was chosen as the default as it is conservative, but not unreasonably so. Greater detail on the methodology for the calculation, validation and use of the default DOC values can be found in Environment Agency (2009). Note that the default DOC values are used as inputs to the Screening Tool at an early tier of any compliance framework. If a site does not comply when using default values then one action may be to take waterbody specific DOC measurements (Tier 4 in Figure 7.2).

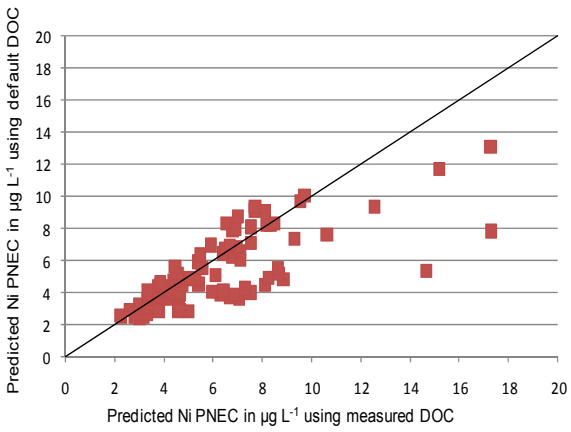

Figure A. Predicted Ni PNEC using measured and default DOC values for 100 sites in the England and Wales.

III. Estimating DOC concentrations from other water chemistry parameters

DOC concentrations do appear to co-vary with some other water quality parameters, such as colour and dissolved iron concentrations. It is possible in some instances to make estimates of DOC concentrations from such parameters (preferably using relationships derived from locally relevant data). The use of estimated DOC concentrations is not recommended for compliance assessment purposes, but may be useful for providing an indication of the potential compliance situation in cases where no DOC monitoring data are available. Figure B below shows the relationship between DOC and dissolved iron concentrations in waters from the England, Scotland and Wales

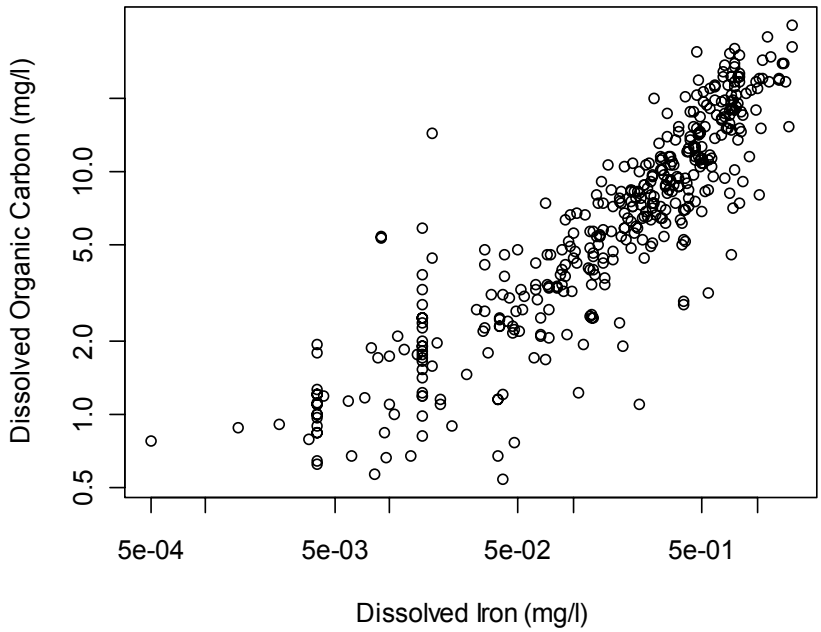

Figure B. Dissolved iron and dissolved organic carbon concentrations in 407 samples from England, Scotland and Wales.

The selection of the appropriate model for estimating DOC concentrations needs to be considered carefully in terms of its ability to appropriately identify areas where DOC monitoring is most useful for refining the assessment of site specific risks due to metals for which a bioavailability correction based on DOC can be made. An analysis of the risks based on relatively precautionary estimates of DOC concentrations can be used to identify locations, or regions, where DOC monitoring is likely to be required. If the method used to estimate DOC concentrations is too conservative (i.e. predicted DOC concentrations are much lower than actual DOC concentrations) then the screening process may not be useful because risks may be provisionally identified at a large proportion of sites, suggesting that widespread DOC monitoring is likely to be required. Figure C shows the relationship between DOC and dissolved iron for over 800 monitoring sites in Austria, along with predictions of DOC concentrations (shown as a blue line) based on a relationship between these two parameters from UK data. In this example 65% of estimates are within +/- 1 mg l^{-1} and 88% of estimates are within 2 mg l^{-1} of the true DOC concentration. Figure D shows the Ni PNECs predicted for this same dataset using the Screening Tool with measured DOC verses DOC estimated from the relationship dissolved iron. The dark line is the 1:1 relationship and hatched lines are a factor of 2. Only 1.2% of the values are out by more than a factor of 2.

The relationship between dissolved iron and DOC concentrations should not be applied in areas of anthropogenic iron contamination. It is considered to be appropriate to apply an upper limit to the concentrations of DOC which are predicted, and in this case an upper limit to the predicted DOC concentrations is set at 10 mg l^{-1} DOC. It has often been assumed that DOC concentrations cannot be predicted from other water quality properties (e.g. pH, Ca, etc.), and the relationships observed between dissolved iron and DOC were initially unexpected. The most plausible explanation seems to be that the dissolved iron concentrations observed are due to associations between iron and organic matter. Transport

of organic matter from soil horizons to surface waters may result in the transport of iron which is already associated with the organic matter, although this is speculative. “Dissolved” iron in circumneutral waters is unlikely to be present as truly dissolved material, and is more likely to be present either as Fe ions which are bound to organic matter, or as fine colloids which also tend to be associated with organic matter in natural waters.

Other methods for estimating DOC concentrations, for example from UV absorbance measurements should also be considered in cases where DOC monitoring data is not available, and analysis of DOC in some instances should be able to confirm whether or not the methods of estimation of DOC concentrations are actually applicable in any particular instances (e.g. when using UK data to estimate DOC concentrations in other regions). Approaches which rely on estimating DOC concentrations from other water quality parameters should be applied only for screening purposes, and not for classification. The identification of potential metal toxicity issues as a result of such assessments should be used as a trigger improved local monitoring of both metal concentrations and bioavailability modifying factors.

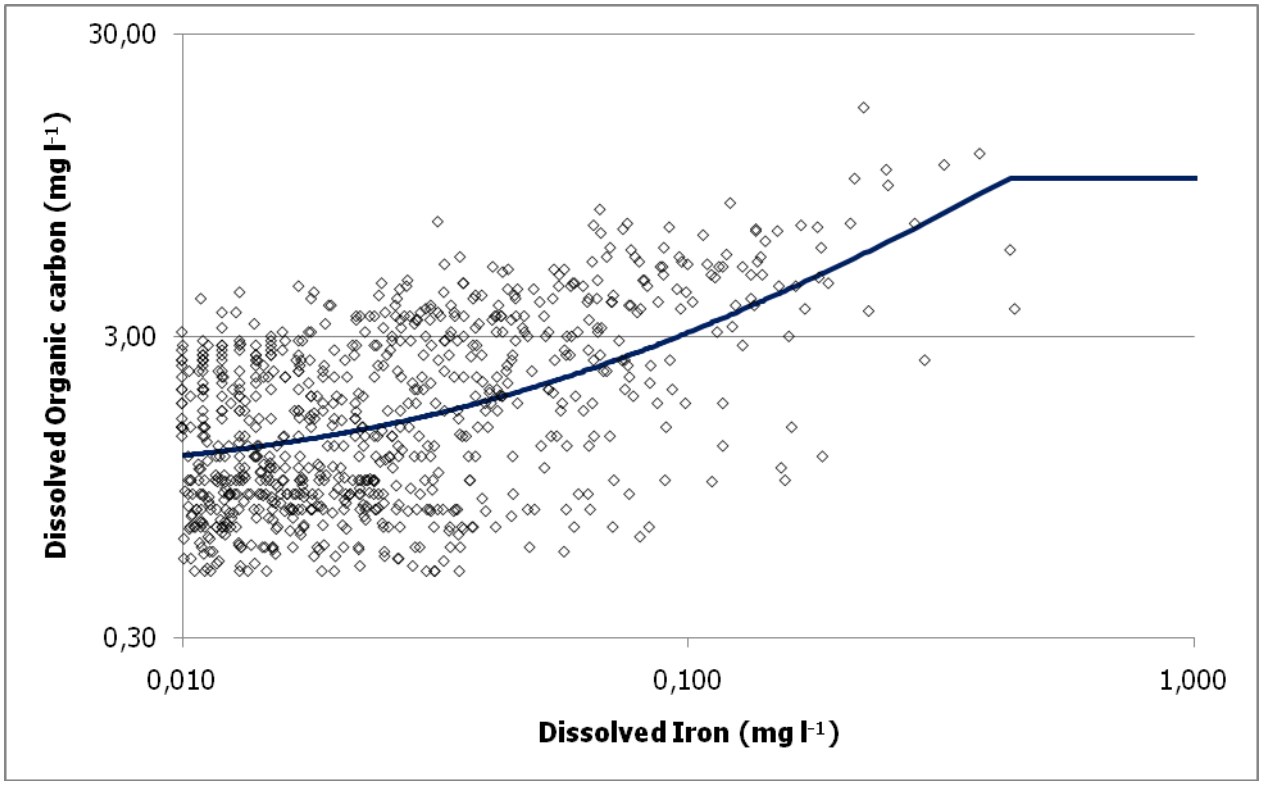

Figure C. Dissolved iron and dissolved organic carbon concentrations in over 800 samples from Austria. The line predicts DOC concentrations from dissolved iron concentrations based on a relationship derived from UK data.

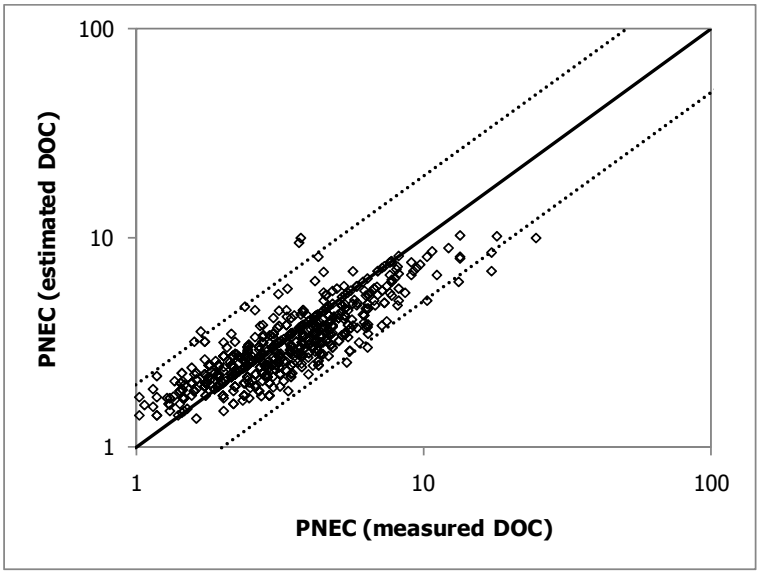

Figure D. Predicted No Effect Concentrations for nickel as calculated using matched DOC data and DOC values as estimated using dissolved iron concentrations in over 800 samples from Austria. The solid line gives the 1:1 relationship and the hatched lines are a factor of 2.