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How important is it to update the existing environmental quality standard for nickel? An example based on the UK†

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In Europe the Environmental Quality Standard (EQS) for nickel in freshwaters was set in 2013 based on the best available evidence at the time. Since then, additional information about the toxicity of nickel to aquatic organisms and the effects of water chemistry conditions on nickel bioavailability have become available, and there is much more information available about the water chemistry conditions that affect nickel toxicity in freshwaters. This study has taken the updated information about nickel ecotoxicity and bioavailability and evaluates how this could potentially affect the EQS for nickel if it was to be updated. Although the sensitivity of freshwaters to nickel based on the update is very similar to the EQS on a site-specific basis, the thresholds derived are slightly lower. A broader range of water chemistry conditions can be covered by the update than are currently covered by the existing EQS. An updated standard of 2.9 $\mu\text{g L}^{-1}$ bioavailable nickel could be derived based on the UK dataset evaluated here, which is slightly lower than the existing EQS of 4 $\mu\text{g L}^{-1}$ bioavailable nickel. Consequently, a slightly higher number of potential compliance failures would be expected based on the update. A simple and practical approach toward the incorporation of local nickel background concentrations into the compliance assessment process for sites that fail the bioavailability based EQS is also proposed. Initial assessments suggest that compliance with the existing EQS could potentially result in more than 5% of species in freshwater aquatic ecosystems being affected, but that with the exception of a very small number of cases the proportion of potentially affected species would be less than 8% of species in the ecosystem. In regions where the existing EQS is not fully implemented, particularly through limited consideration of bioavailability, the adoption of the updated standard is likely to be less beneficial than focusing on better implementation of the existing EQS. However, in regions where the existing EQS has been implemented extensively for some time the updated standard offers a refinement in terms of the coverage of a higher proportion of surface waters and a slightly higher level of protection for sensitive species than the existing EQS.

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Environmental significance

This manuscript addresses whether additional ecotoxicity data and advances in bioavailability modelling for nickel that have become available since the existing EQS was set warrant an update of the EQS. The study applies the derivation approach for bioavailability based EQS in the UK and Europe to derive a potential update of the bioavailable nickel standard based on UK water chemistry conditions, and considers the implications for compliance in the UK. It also includes an evaluation of the protectiveness of the updated standard against ecological data, and a practical approach to the consideration of background concentrations in the compliance assessment. The potential implications of maintaining the existing EQS are evaluated in terms of the fraction of the ecosystem that may be affected are also considered.

Introduction

In Europe, under the Water Framework Directive Environmental Quality Standards (EQS) are derived to ensure all surface

waters meet ‘good status’. For substances that represent a Europe-wide risk (“Priority” and “Priority Hazardous” Substances), and also substances that are national risks (“Specific Pollutants”), EQS values are derived as a single measure and are legally binding. Nickel (Ni) was identified as a Priority Substance under the WFD in 2008, which requires all EU Member States to demonstrate compliance with the EQS. In the absence of a comprehensive technical basis upon which to set an EQS for nickel and nickel compounds, the Daughter Directive (2008/105/EC) prescribed an interim EQS for nickel of

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20 $\mu\text{g L}^{-1}$. The value of 20 $\mu\text{g L}^{-1}$ was the World Health Organisation Drinking Water Value at the time and was acknowledged to have little ecological relevance.¹

In late 2009, the second review of WFD Priority Substances began. The purpose of this review was to revisit the priority status of the existing EQS and to revise the existing EQS on the basis of new data. Indeed, Recitals 6 and 7 in the Revised EQS Directive² state that “in preparing its policy on the environment, the Union is to take account of available scientific and technical data, environmental conditions in the various regions of the Union”, further that consideration should be given to “revising the EQS for some existing substances in line with scientific progress”. In 2013, an annual average bioavailability-based Ni EQS of 4 $\mu\text{g L}^{-1}$ was derived based upon ecotoxicity data collated and published in the Risk Assessment Report conducted under the Existing Substances Regulations (ESR RAR³) and used available surface water monitoring data to establish an EQS_{bioavailable}.⁴ Deriving an EQS based on a bioavailable metal concentration requires that all the ecotoxicity data are normalised to a reference water chemistry.⁵ In order for the derived EQS to provide a sufficiently high level of protection, the reference water chemistry must represent the reasonable worst-case conditions of high bioavailability that are encountered within Europe. Specifically, the EQS is required to ensure the protection of 95% of surface waters within the most sensitive region, with the region being defined, in practice, as a single Member State. The use of a high percentile avoids errors and bias associated with extreme values and avoids the need to identify the most sensitive water chemistry conditions within the entire continent. This requires that bioavailability calculations are performed for a large number of waters, and also means that the derived EQS is dependent upon the quality of the available regulatory water chemistry monitoring dataset. Notably, at the time of the 2011 Ni EQS derivation, a relatively limited amount of surface water monitoring data was available (*i.e.*, <7000 samples for the whole of Europe). The EQS for nickel in the UK is the same as that used in Europe.

This derivation approach allows a single EQS value to be applied throughout Europe, despite considerable variation in water chemistry conditions, and consequently large differences in bioavailability. In practice, this also allows the EQS_{bioavailable} to be used as a screening tier against which dissolved metal concentrations can be compared to evaluate whether an assessment of the local bioavailability is required.⁶ If compliance is not demonstrated by the screening assessment at the dissolved level, then bioavailability is considered.

The existing annual average EQS_{bioavailable} for Ni was derived over 10 years ago. Here we derive an updated standard for Ni based on the best currently available science. We evaluate the significance of any differences that are identified and assess the advantages and disadvantages associated with adopting a revised standard compared to the continued use of the existing one. We use a single regulatory monitoring dataset collected from the UK as the basis for providing a direct comparison between the existing EQS and the updated standard, in terms of the coverage of waters, the local standards for dissolved nickel at monitoring sites, and the implications for compliance

assessment against the legally binding existing EQS. We also provide discussion on the need to appropriately follow well-established guidelines and to consider new scientific evidence in periodic revisions to ensure an appropriate level of protection is maintained.

This example derivation of an updated standard for nickel is based only on data for the UK. This country has an extensive database of surface water chemistry information and because bioavailable standards have been in force for several metals for over a decade there is a good quality dataset of the supporting parameters that are required for bioavailability assessment to facilitate the sensitivity assessment for an updated standard. Furthermore, the UK includes a diverse range of water chemistry conditions that are broadly comparable to those encountered in Europe, but within a smaller area, and the overall dataset can be readily split into a number of administrative subregions. The UK therefore provides a useful example upon which to assess the potential value of an updated standard.

Given the statutory status of the existing EQS this is referred to throughout as the EQS, whereas because the potential update is a possibility only, and has not been subject to the required regulatory scrutiny, it is referred to as the updated standard.

Existing EQS

The existing EQS_{bioavailable} derived in 2011,⁴ and made statutory in 2013,² was derived from an ecotoxicity dataset of 214 chronic toxicity data points from 31 aquatic species, including algae, vascular plants, invertebrates, fish, and amphibians and includes a correction for bioavailability.³ The EQS was set as a bioavailable nickel concentration so that a single value could be applied to waters of differing degrees of nickel bioavailability. The bioavailability correction is based on a suite of Biotic Ligand Models (BLMs) that were developed for an alga,⁷ two invertebrates,^{8,9} and a fish.¹⁰ These bioavailability models are used to normalize all data that is included in the ecotoxicity database to the local conditions using the model developed for the same trophic level. As there are two models available for invertebrates, unless there is clear evidence that one of the models is more appropriate, both models are applied and the lowest predicted value (*i.e.*, most conservative) is selected for use in calculating the local EQS. The ecotoxicity dataset and bioavailability normalisation approach have been published previously.¹¹

The EQS is derived from a compilation of the entire ecotoxicity database that includes a single entry for each of the species that are represented within it to reflect the overall sensitivity distribution of the ecosystem. Each species entry is calculated as the geometric mean of all bioavailability normalised data for the most sensitive endpoint for the species. This approach is known as a Species Sensitivity Distribution (SSD), and a threshold is derived from the distribution of the data rather than from a single datapoint. From this distribution, the concentration that would be expected to affect 5% of species in the ecosystem (termed the Hazardous Concentration for 5% of species (HC5)), is derived and is defined as the ‘Local EQS’ for the specific site for which the bioavailability normalisation was



performed. Both the HC5 and the local EQS are expressed as a dissolved nickel concentration. An assessment factor is applied in deriving an EQS to take account of any residual uncertainty. Due to the large and robust body of evidence available for nickel an assessment factor of one was applied in the derivation of the existing EQS.

The Europe-wide nickel EQS_{bioavailable} was derived from calculations of nickel sensitivity in surface waters for as many sites as possible throughout Europe.⁵ This is based on their local pH, Dissolved Organic Carbon (DOC) concentration, and calcium concentration because these are the key factors in determining nickel bioavailability. Site-specific HC5 values were calculated for each site, and the EQS_{bioavailable} was set to be protective of 95% of surface waters in the most sensitive region (*i.e.* country). The sensitivity calculations could only be applied to waters that were within the operating range of the models, which, at the time of the 2011 derivation, was a pH between 6.5 and 8.2, and a calcium concentration between 2 and 88 mg L⁻¹. Consequently, the existing EQS_{bioavailable} for nickel can only be applied within these ranges of water chemistry conditions. Due to the complexity of performing the bioavailability calculations, a simplified tool (bio-met, www.bio-met.net) has been developed to provide the results of the bioavailability calculations for users, and the validity of this tool relative to the underlying evidence has been demonstrated.¹² A similar tool (M-BAT¹³) has been developed specifically for use in the UK that enables the calculation of bioavailable metal concentrations to be performed automatically within the Laboratory Information Management System when the required data for a site is available, therefore reducing the resource requirements associated with implementation.

Updated standard

The ecotoxicity database and bioavailability normalisation procedure for nickel has recently been updated and published.¹⁴ This update includes a review of the existing data, resulting in the revision or exclusion of some of the data where appropriate, as well as the review and assessment of new data that has been published since the ESR RAR. New chronic toxicity data for nickel comprised 152 results (individual EC10 or NOEC values) covering 31 species. There are an additional 24 species: algae *Chlorella* sp. (two strains), and *Navicula pelliculosa*; aquatic plant *Lemna aequinoctialis*; amphipod *Gammarus pseudolimnaeus*; annelids *Lumbriculus variegatus* and *Tubifex tubifex*; cladocerans *Daphnia ambigua*, *D. galeata*, *D. lumholtzii*, *D. pulex* and *D. similis*; hydrozoan *Hydra viridissima*; insects *Chironomus dilutus*, *Hexagenia* sp. and *Neocloeon triangulifer*; mollusc *Lampsilis siliquoidea*; rotifer *Euchlanis dilatata*; fish *Acipenser fulvescens*, *Cottus bairdi*, *Melanotaenia splendida splendida* and *Oncorhynchus tshawytscha*; and amphibians *Lithobates sylvaticus* and *Rhinella arenarum*. There are two species, *Brachydanio rerio* and *Hydra littoralis*, that are included in the database used for the existing EQS but were excluded from the final database used for calculation of the updated standard¹⁴ due to a lack of measured data being available for the tests. The exclusion of these species does not, however, reduce the degree of taxonomic representation of the dataset.

The updated freshwater Ni chronic ecotoxicity database contains 366 individual high-quality chronic ecotoxicity data for 53 different species, belonging to a diverse range of different taxonomic groups and for ecologically relevant endpoints (*e.g.* mortality, reproduction, hatching, abnormalities, and growth). There are data for primary producers (10 unicellular green algae, 1 diatom, 3 aquatic plants), invertebrates (2 amphipods, 2 annelids, 13 cladocera, 1 hydrozoan, 5 insects, 2 rotifers, 3 molluscs), and vertebrates (6 fish, 5 amphibians). Full details of the ecotoxicity database and bioavailability normalisation procedures are available.¹⁴ Since the 2011 EQS derivation there have also been developments in the modelling of nickel bioavailability, enabling predictions to be made for higher pH¹² and lower calcium¹⁵ conditions than was originally possible. These extensions are important because they can represent high bioavailability conditions and allow for the standard to cover a greater portion of EU freshwaters. There is considerably more information available for the derivation of the updated standard than was available for the existing EQS_{bioavailable}, and for this reason there is no scientific justification for increasing the assessment factor applied in deriving a standard from the value of one that was used in the derivation of the existing EQS_{bioavailable}.

The bioavailability-normalised ecotoxicity data, expressed as dissolved nickel concentrations, are compiled into a Species Sensitivity Distribution (SSD) that includes a single value for each species calculated from the averaged intrinsic sensitivity coefficient from each contributing test for the species. Importantly, there are two differences in the way that the bioavailability-normalised SSD is calculated compared to the existing EQS. Firstly, an intrinsic sensitivity coefficient has been defined for the most sensitive endpoint (equivalent to using the geometric mean of the bioavailability normalised results) for each species. The intrinsic sensitivity coefficient defines the sensitivity of each species to nickel and allows a single bioavailability model to be applied across numerous different species. Secondly, only a single bioavailability normalisation model is applied to each invertebrate species, selected based on which of the two invertebrate bioavailability models results in the lowest variability in predictions. Species for which there was not sufficient data to perform an assessment use the same bioavailability normalisation model as species from the same taxonomic group for which the analysis could be performed.¹⁴ This avoids a situation where the use of the most sensitive of two predictions could reduce the reliability of the SSD.¹⁶ However, due to concerns regarding the changes to the models that enable them to be applied to very soft waters, lower calcium conditions are not currently considered to be sufficiently robust for inclusion in the derivation of a statutory EQS. This is because much of the data in the ecotoxicity database is outwith the applicability range of the soft waters bioavailability model, and the application of this model therefore results in a step change in the predicted sensitivity to nickel when the model used is changed.¹⁵

In addition to the extension to higher pH conditions,¹² the models are also applied to lower pH and higher calcium conditions. In both of these situations the models predict lower relative toxicity, and a limited extension to the ranges is



implemented by maintaining the input pH for the calculations at the limit (pH 6.5 or 88 mg L⁻¹ calcium) but allowing the predictions to be extrapolated to pH 6.0 or a calcium concentration of 150 mg L⁻¹.

Methods

Water chemistry dataset

Water chemistry data for pH, DOC, calcium, and dissolved nickel was obtained from the Environment Agency, the Scottish Environment Protection Agency, Natural Resources Wales, and the Northern Ireland Environment Agency from 2016 to 2021. Data was only available for Scotland up to 2018 due to technical reasons. These data were then collated to provide averaged data for these parameters at each site, and sites were included in the assessment where there was data available for pH, DOC, and calcium as these are the minimum requirements for performing bioavailability calculations. Data for dissolved nickel was also included where it was available for these sites. The dataset was evaluated for its reliability and relevance to the present assessment according to the Criteria for Reporting and Evaluating Exposure Datasets (CREED) for the evaluation of environmental exposure datasets.^{17–20}

Sensitivity calculations

Calculations of the Hazardous Concentrations for 5% of species (HC5) were performed for each individual site in the UK water chemistry dataset using the approaches for the existing EQS¹² and updated standard,¹⁴ respectively. For both the existing EQS_{bioavailable} and the updated standard, the assessment was performed only for waters that were within the appropriate operating ranges of the standards (see Table 1). Any additional water chemistry parameters that are required for performing the bioavailability calculations (Mg, K, Na, SO₄, and Cl) were estimated following published empirical relationships.²¹ The HC5 values from the SSDs were calculated based on the assumption of a log-normal distribution. Additionally, an indicative compliance assessment was also performed for those sites at which dissolved nickel exposure data was available.

Indicative compliance assessment

At those sites for which there was dissolved nickel exposure data available an indicative compliance assessment was performed. This indicative compliance assessment for each site based on the ratio of the dissolved nickel exposure concentration to the local

HC5 value that was calculated for each site within the sensitivity assessment (above). This yields a Risk Characterisation Ratio (RCR) that indicates a potential cause for concern if it is greater than unity. This approach differs from the usual tiered approach for regulatory compliance assessment because it did not use the bioavailable nickel EQS or standard as a screening tier, but assessed every site at the final tier because the bioavailability corrected local HC5 values were already available.

Field evidence

A subset of the dataset of matched chemical and ecological data that has previously been used for an evaluation of the protectiveness of the EQS for zinc²² was used for samples that had dissolved nickel exposure data available. This dataset is entirely independent of the one used for the sensitivity assessment described above, and includes matched chemistry and ecology data. Predictions of the expected invertebrate community under reference conditions were calculated for each sample using RICT (v3.1.6, <https://riapplications.shinyapps.io/rictapp/>). Local HC5 values for each site were calculated following the updated standard approach,¹⁴ and quantile regression analyses were performed using an approach described previously.^{22,23} Benthic invertebrate community metrics were expressed as the Ecological Quality Ratio (EQR), which was calculated as the observed number of scoring taxa (N-Taxa) or average score per taxon (ASPT) divided by the value predicted by RICT for these metrics at each site.

Analyses of individual taxa were based on the raw abundance data reported for each sample, and samples in which taxa were absent were assigned an abundance value of 0.1 to facilitate log transformation of taxon abundance for analysis. The probability of occurrence of each taxon at sites with low nickel exposures, defined as having a bioavailable nickel concentration of <0.3 µg L⁻¹, was calculated (*i.e.* the fraction of low exposure sites at which the taxon was found) so that analyses could be focused on those taxa that were most commonly occurring following recommendations made previously.²² Analyses based on individual taxa were conducted only for those taxa with a probability of occurrence at sites with low nickel exposures of at least 0.4, and *Ancylus fluviatilis* which was the most commonly occurring mollusc at low exposure sites with a probability of occurrence of 0.38. This is due to the concern that analyses based on taxa that are not commonly occurring may give misleading results due to being absent at a large proportion of sites regardless of the presence of potential toxicants.²¹

All nickel exposures were expressed as bioavailable nickel concentrations, which were calculated as the product of the dissolved nickel concentration and a site-specific bioavailability factor for nickel.⁶ The site-specific bioavailability factor was calculated as generic bioavailable nickel concentration from the updated standard (the 5th percentile of the HC5 values for the most sensitive region) divided by the site-specific HC5 value calculated using the updated standard. Quantile regression analysis was conducted at both the 90th and 95th quantiles. The results of all quantile regression analyses were considered to be significant if the slope of the regression was both negative and statistically significant at the 95% level ($p < 0.05$).

Table 1 Applicability ranges of the existing EQS_{bioavailable} and updated standard

| | Existing EQS _{bioavailable} | Updated standard |
|----------------------------------|--------------------------------------|------------------|
| Minimum pH | 6.5 | 6.0 |
| Maximum pH | 8.2 | 8.7 |
| Minimum Ca (mg L ⁻¹) | 2.0 | 2.0 |
| Maximum Ca (mg L ⁻¹) | 88 | 150 |
| Percentage of UK sites | 64.4 | 92.4 |



Protectiveness of the existing EQS relative to the updated standard

In order to evaluate the degree of potential under-protection, the Potentially Affected Fraction (PAF) of the ecosystem was calculated assuming an exposure concentration of $4 \mu\text{g L}^{-1}$ dissolved nickel for those sites with the most sensitive water chemistry conditions based on the updated standard. This was performed for sites with site-specific local HC5 values of $3.5 \mu\text{g L}^{-1}$ dissolved nickel or lower.

Consideration of background concentrations in compliance assessment

Sites at which consideration of local background concentrations may be warranted were identified following procedures that have been outlined elsewhere.²⁴ sites where the updated standard was exceeded, the RCR value is less than 2, the local HC5 is less than $10 \mu\text{g L}^{-1}$ dissolved nickel, and the dissolved nickel concentration is less than $10 \mu\text{g L}^{-1}$ were identified as candidates for background correction. Where possible, sites were assessed for copper and zinc exposures because these are very common anthropogenic contaminants and are both widely monitored for. Sites with dissolved copper concentrations of more than $6 \mu\text{g L}^{-1}$, or dissolved zinc concentrations of greater than $30 \mu\text{g L}^{-1}$ were excluded from deriving background concentrations due to being potentially impacted as indicated by the presence of elevated levels of these other metals.

Industrial sites reporting emissions of nickel to either air or water in the E-PRTR were also identified to provide an indication of the proximity of the sites for which nickel background concentrations were required to point source emissions of nickel. Sites were considered to be in close proximity of a point source nickel emission if they were within 3 km of an E-PRTR reporting site for nickel. The sites applicable for considering background concentrations were also checked visually on a map to assess their proximity to large urban areas and major roads.

Potential surrogate sites that could be used to provide nickel background concentrations were identified from the water quality monitoring dataset. Sites that did not have high exposures of copper, or zinc, based on the same criteria as used to identify the sites for which background concentrations were required, and dissolved nickel exposures below $10 \mu\text{g L}^{-1}$ were included for this purpose. The closest potential surrogate site to sites requiring a background nickel concentration was used and the distance between them recorded.

A background corrected HC5 value was calculated by adding the local background concentration to the site-specific local HC5, and the background corrected RCR value (RCR_{bkgd}) was calculated as the local dissolved nickel exposure concentration divided by the background corrected RCR value (RCR_{bkgd}).

Results

Water chemistry dataset

The complete dataset was found to be reliable with restrictions, and relevant without restrictions for this assessment, and was found to be useable with restrictions (CREED Silver standard) for

the purpose of this study. Data on the sampling methods and sample handling procedures were not included in the dataset, information on the limits of detection were not available for all data, and no data were available for field quality control samples. However, all of the data were collected as part of routine regulatory monitoring following established accredited procedures and represents the best currently available data for this purpose. A summary of the CREED assessment, including the purpose statement, is included in the ESI S1.†

Data were available for a total of 10 443 sites, of which 3804 have data for all three of the required parameters for performing bioavailability calculations (*i.e.* pH, DOC, and calcium). Covering all UK regions. Of these 3804 sites, 2663 also have data for dissolved nickel. A summary of the ranges of water chemistry conditions for the UK as a whole and for each individual region, in terms of the 5th percentile, the median, and the 95th percentile values of pH, DOC, and calcium, are summarised in the ESI S2.†

Comparison of ecotoxicity databases

The existing EQS for nickel is not linked to any specific water chemistry conditions, because it is derived from the distribution of surface water sensitivities, although there are a relatively limited range of water chemistry conditions that can result in a local HC5 value that is equal to the EQS. Fig. 1 shows the data and fitted SSD curves for both the existing EQS and the updated standard following normalisation to the water chemistry conditions of a site with an HC5 value that is equal to the existing EQS_{bioavailable} of $4 \mu\text{g L}^{-1}$ bioavailable nickel. The local HC5 value for this site is $4.0 \mu\text{g L}^{-1}$ dissolved nickel based on the existing EQS_{bioavailable} and $2.9 \mu\text{g L}^{-1}$ dissolved nickel based on the updated standard. For this specific water chemistry (pH 7.49, DOC 0.8 mg L^{-1} , and calcium 10.4 mg L^{-1}) the local HC5 value based on the updated standard is lower than the existing EQS, although the difference is relatively minor given the considerable increase in the number of species included (53 for the updated standard compared to 31 for the existing EQS).

A comparison between the site-specific HC5 values calculated based on both the existing EQS_{bioavailable} and the updated standard is shown for all of the sites with water chemistry conditions that are within the applicability range of the existing EQS in Fig. 2. This shows that the updated standard is consistently lower than the existing EQS for the same water chemistry conditions, although this difference is always less than a factor of two. The difference between the two approaches is smallest for the most sensitive water chemistry conditions and slightly greater for less sensitive water chemistry conditions.

Coverage of UK waters

Fig. 3 shows the pH and calcium conditions of the sites that are included in the UK water chemistry dataset, along with the ranges of those water chemistry conditions that are covered by the existing EQS and the updated standard. This shows that the vast majority of the additional waters that are covered by the updated standard compared to the existing EQS_{bioavailable} have a high pH and/or a high calcium concentration. The existing EQS_{bioavailable} was estimated to be representative of



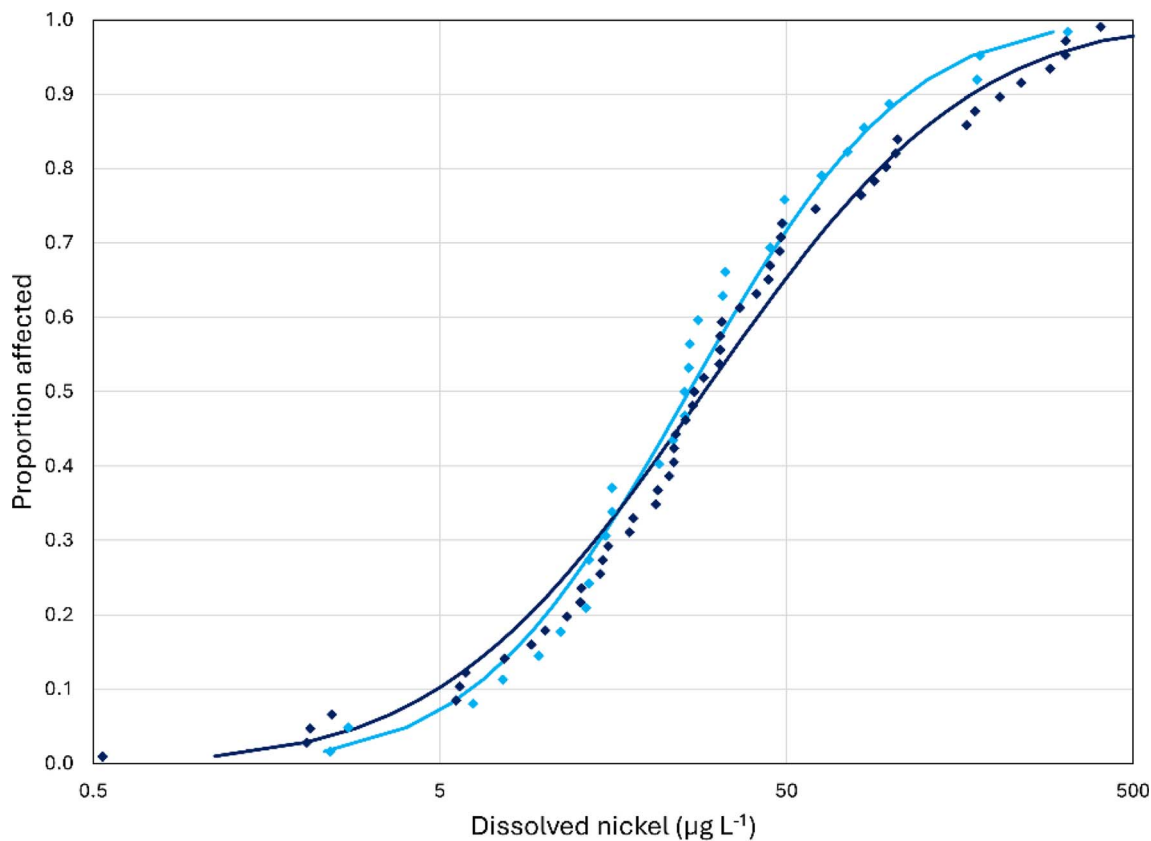


Fig. 1 Comparison of the bioavailability normalised datasets (datapoints, each one represents an individual species) and SSDs (curves) for the existing EQS (light blue, 31 species) and the updated standard (dark blue, 53 species) for a high bioavailability site where the local HC5 value based on the existing EQS is equal to the $EQS_{bioavailable}$.

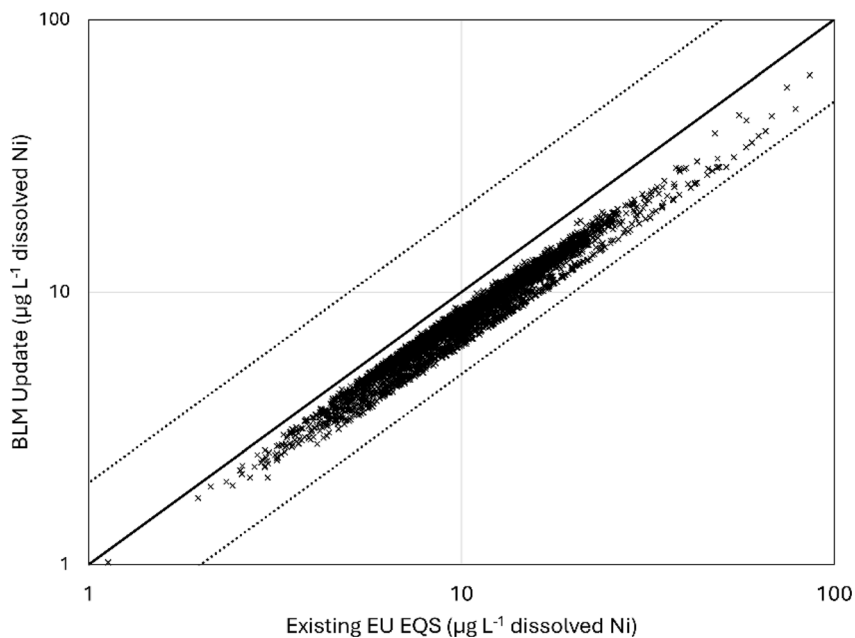


Fig. 2 Comparison between site-specific HC5 values calculated based on the existing $EQS_{bioavailable}$ and the updated standard for waters with chemistry conditions that are within the applicability range of the existing $EQS_{bioavailable}$. The solid line indicates a 1 : 1 relationship between the results and the dotted lines indicate a factor of 2 difference between them.



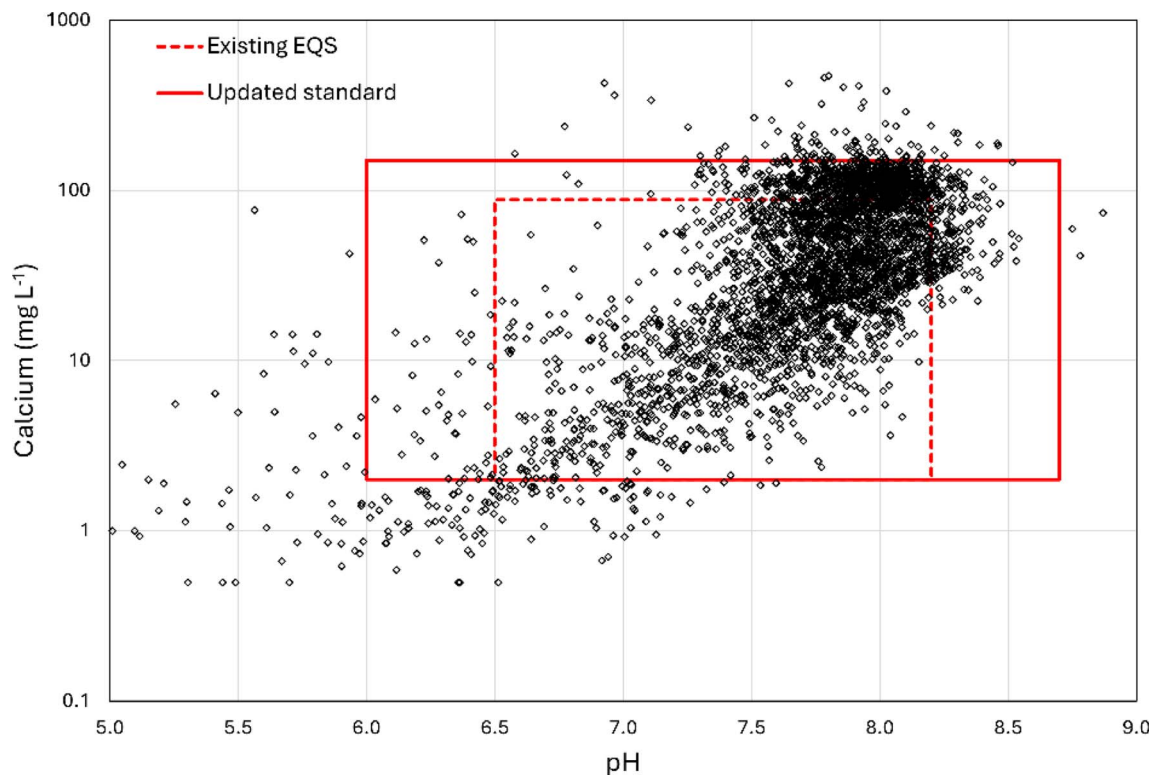


Fig. 3 pH and calcium concentrations at surface water monitoring sites in the UK dataset (points) and the ranges of conditions covered by the existing EQS (dashed red line) and the updated standard (solid red line).

approximately 64.4% of UK waters, while the updated standard is estimated to cover 92.4% of UK surface waters, indicating a substantial increase in relevance.

Sensitivity of UK surface waters to nickel

As noted above, an EQS that is set on the basis of a bioavailable metal concentration is derived from a comprehensive dataset of surface water chemistries. Whilst the same dataset has been used here for both the existing EQS_{bioavailable} and the updated standard there are potential differences due to the different ecotoxicity databases used, differences in the implementation of the bioavailability correction, and the coverage of water chemistry conditions by the two approaches. The sensitivity of the UK overall and each of the individual subregions is summarised in Table 2, along with the degree of coverage of the bioavailability models for the water chemistry conditions in each region, the distribution of site sensitivities is also shown in the ESI S3.†

Existing EQS_{bioavailable}

Of the 3804 sites that are included in the database, only 64.4% of them fall within the applicability range of the existing EQS_{bioavailable} for nickel, with the degree of coverage varying widely between the different regions (Table 2). Whilst 93% of the 525 sites in Northern Ireland were within the applicability range of the existing EQS only 5.6% of the 338 sites in Anglian region are within the range. The 5th percentile calcium concentration in Anglian region is 81.5 mg L⁻¹, which is close to

the upper limit of the calcium concentrations covered by the existing EQS_{bioavailable}, and, consequently, a very large proportion of surface waters in this region are not covered by the EQS_{bioavailable} due to high calcium concentrations. High calcium concentrations represent the greatest limitation on the application of the existing EQS_{bioavailable} in the UK.

For all UK surface waters not divided by region, the overall 5th percentile of the calculated HC5 values is 4.9 µg L⁻¹ dissolved nickel, which is slightly higher than the existing EQS_{bioavailable} (4 µg L⁻¹). This is consistent with the observation that the UK was not the most sensitive European region in the assessment that was performed to derive the EQS based on bioavailable nickel. When considering UK regional differences the North West is the most sensitive subregion, and has a 5th percentile HC5 value of 3.7 µg L⁻¹, which is very close to the existing EQS_{bioavailable} for nickel.

Updated standard

Of the 3804 sites that are included in the database, 92.4% of them fall within the applicability range of the updated standard (Table 2). The degree of coverage for the updated standard is considerably better, principally due to the higher pH and calcium concentrations that are covered. The increased coverage of water chemistry conditions results in over 87% of sites in Anglian region being within the range of the updated standard. For UK surface waters the overall 5th percentile of the calculated HC5 values is 3.9 µg L⁻¹ dissolved nickel. The North West is the most sensitive subregion, with a 5th percentile HC5



Table 2 Sensitivity of UK regions to nickel based on the existing EQS and the updated standard

| Region | Number of sites | Existing EQS | | Updated standard | |
|----------------------|-----------------|---------------------------|---|---------------------------|---|
| | | Coverage ^a (%) | 5th P HC5 ^b ($\mu\text{g L}^{-1}$ Ni) | Coverage ^a (%) | 5th P HC5 ^b ($\mu\text{g L}^{-1}$ Ni) |
| UK | 3804 | 64.4 | 4.85 | 92.4 | 3.86 |
| Anglian | 338 | 5.6 | 7.82 | 87.6 | 5.87 |
| Midlands | 544 | 52.6 | 5.03 | 94.1 | 4.21 |
| North West | 328 | 80.2 | 3.66 | 92.7 | 2.93 |
| Northern Ireland | 525 | 93.0 | 9.12 | 98.5 | 6.82 |
| Scotland | 351 | 70.9 | 6.35 | 80.6 | 5.22 |
| South East | 173 | 68.2 | 8.07 | 100.0 | 4.61 |
| South West | 452 | 69.0 | 3.91 | 95.4 | 3.00 |
| Thames | 250 | 27.2 | 8.00 | 96.8 | 4.79 |
| Wales | 315 | 71.1 | 4.35 | 78.7 | 3.40 |
| Yorkshire North East | 528 | 79.7 | 5.86 | 96.4 | 4.63 |

^a Percentage of sites in the region with water chemistry conditions that are within the operating range of the bioavailability models. ^b 5th percentile of all HC5 values ($\mu\text{g L}^{-1}$ dissolved Ni) for applicable sites within this region.

value of $2.9 \mu\text{g L}^{-1}$, which is lower than the existing EQS_{bioavailable} for nickel.

Indicative compliance assessment

There are 1827 sites with dissolved nickel exposure data that the existing EQS_{bioavailable} can be applied to, and risk characterisation ratios (RCR) are generally low, with approximately 90% of these sites having RCR values below 0.5 and only 4.1% of sites having RCR values of greater than 1 (*i.e.* potential risks to local ecosystems due to nickel toxicity). There are 2504 sites with dissolved nickel exposure data that the updated standard can be applied to, with RCRs higher than those based on the existing EQS due to the updated standard resulting in slightly lower HC5 values and being applicable to higher sensitivity waters (*e.g.* high pH). Nonetheless, compliance against the updated standard is still very high, with at least 90% of sites having RCR values below 0.65 and only 5.6% of sites having RCR values of greater than 1. A summary of the compliance assessment results as cumulative frequency distributions of the RCR values based on both the existing EQS and the updated standard is shown in the ESI S4.†

There are a total of 108 sites that the existing EQS_{bioavailable} can be applied to at which potential risks are expected based on the updated standard. Thirty-three of these sites do not result in potential risk being predicted based on the existing EQS_{bioavailable}, although the highest RCR value based on the updated standard, for a site that is not predicted to be at risk based on the existing EQS, is 1.43. The existing site-specific EQS at this site is equivalent to a dissolved nickel concentration of $14.7 \mu\text{g L}^{-1}$, the updated standard would be $10.2 \mu\text{g L}^{-1}$ dissolved nickel, and the dissolved nickel exposure concentration is $14.5 \mu\text{g L}^{-1}$.

The sites that are potentially at risk based on the updated standard are predominantly concentrated in the South West region (49.3% of sites in the region potentially at risk) and the Midlands region (23.6%), with the majority of the remaining sites that are potentially at risk located in Yorkshire and the North East (7.9%), Wales (7.1%), and Anglian (4.3%) regions.

The South West region has relatively sensitive water chemistry conditions, and has the lowest median DOC concentration of all regions (1.9 mg L^{-1}). This region also has a long history of mining activity and it is likely that the combination of sensitive waters and elevated exposures due to historic mining result in lower compliance against the updated standard.

Field evidence

This approach derives a limiting function which assumes that at low bioavailable nickel concentrations, the maximum achievable EQR value, or taxon abundance will not be limited by nickel. However, at elevated bioavailable nickel concentrations, the maximum achievable ecological quality will be limited by nickel regardless of the presence of other stressors (*e.g.* Peters *et al.* 2014). The point at which bioavailable nickel exposures are high enough to reduce ecological quality is identified by quantile regression analysis. Analyses based on benthic invertebrate community metrics EQR ASPT and EQR N-Taxa both identified a statistically significant decline (*i.e.* the slope of the quantile regression was both negative and significantly different from 0, *i.e.* $p < 0.05$) in these metrics as a function of increasing bioavailable nickel concentrations at both the 90th and 95th quantiles. Analyses based on EQR ASPT resulted in calculated EC10 values of 21.6 (95% confidence interval 14.9 to 47.4) and 22.4 (95% confidence interval 13.5 to 31.1) $\mu\text{g L}^{-1}$ bioavailable nickel at the 90th and 95th quantiles respectively ($p = 0.003$ in both cases). Analyses based on EQR N-Taxa resulted in calculated EC10 values of 3.9 (95% confidence interval 3.3 to 6.5) and 4.9 (95% confidence interval 3.2 to 7.8) $\mu\text{g L}^{-1}$ bioavailable nickel at the 90th and 95th quantiles respectively ($p < 0.001$ in both cases). The results of the analysis of EQR N-Taxa at the 90th quantile are shown in Fig. 4. The results of this analysis indicate that compliance with the updated standard of $2.9 \mu\text{g L}^{-1}$ bioavailable nickel would not be expected to result in any significant decline in the diversity of benthic macro-invertebrate taxa that are found to be present at a site relative to predicted number of taxa.



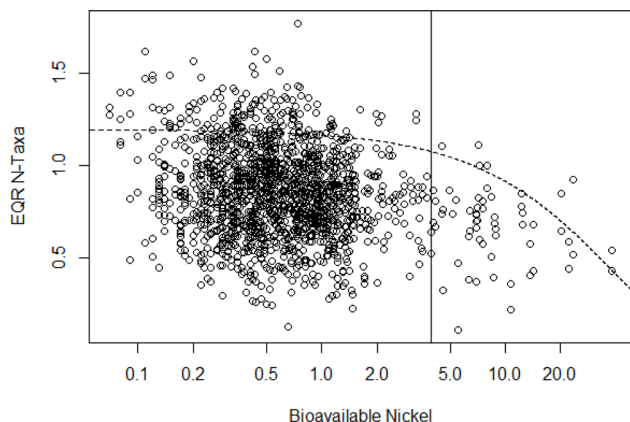


Fig. 4 Results of quantile regression analysis, at the 90th quantile, of the decline in EQR N-Taxa as a function of bioavailable nickel concentrations ($\mu\text{g L}^{-1}$). The dashed line indicates the fitted quantile regression model and the solid vertical line indicates the EC10 value derived from it.

Those taxa for which analyses were performed, and their probability of occurrence at low exposure sites, are shown in Table 3. None of the analyses performed for individual taxa at the 95th quantile resulted in statistically significant model fits. Examples of the data for the two taxa with the highest probability of occurrence at low exposure sites, *Oligochaeta* and *Elmis aenea*, are shown in the ESI S5.†

Protectiveness of the existing EQS relative to the updated standard

Fig. 5 shows the PAF at an exposure concentration of $4 \mu\text{g L}^{-1}$ dissolved nickel for the site-specific SSD calculated based on the updated standard at sites where the site-specific local HC5 is $3.5 \mu\text{g L}^{-1}$ dissolved nickel or less. The most sensitive sites have site-specific local HC5 values of approximately $2 \mu\text{g L}^{-1}$ dissolved nickel, although there are very few sites that exhibit such a high level of sensitivity. Approximately 10% of species in the ecosystem could potentially be affected by an exposure

Table 3 Probability of occurrence of taxa at sites with RCR values of less than 0.1 (occurrence), and the p value associated with the slope of the quantile regression at the 95th quantile (Q 95 p slope)

| Taxon | Occurrence | Q95 p slope |
|---------------------------------|------------|-------------|
| <i>Oligochaeta</i> | 0.832 | 0.186 |
| <i>Elmis aenea</i> | 0.815 | 0.243 |
| <i>Limnius volckmari</i> | 0.737 | 0.563 |
| Orthocladinae | 0.593 | 0.144 |
| Dicranota | 0.579 | 0.603 |
| <i>Hydropsyche siltalai</i> | 0.559 | 0.709 |
| <i>Potamopyrgus antipodarum</i> | 0.556 | 0.235 |
| <i>Rhyacophila dorsalis</i> | 0.519 | 0.197 |
| Hydracarina | 0.451 | 0.253 |
| Tanytarsini | 0.441 | 0.996 |
| <i>Hydropsyche pellucidula</i> | 0.438 | 0.630 |
| <i>Sericostoma personatum</i> | 0.404 | 0.423 |
| <i>Ancyclus fluviatilis</i> | 0.380 | 0.274 |

concentration of $4 \mu\text{g L}^{-1}$ dissolved nickel at sites with a site-specific local HC5 value of less than $2.5 \mu\text{g L}^{-1}$ dissolved nickel.

Consideration of background concentrations in compliance assessment

Over half of the sites at which potential risks are expected may be considered as marginal failures due to having RCR values that are between 1 and 2, and many of these sites also have low nickel exposures of less than $10 \mu\text{g L}^{-1}$ dissolved nickel. These sites may be relevant for the consideration of whether local background concentrations of nickel may be affecting the compliance assessment outcomes. There are 80 sites that are within the applicability range of the updated standard for which the indicative compliance assessment indicates a potential failure based on the updated standard and have RCR values of below 2.

One site in the Midlands (River Hamps – Waterhouses, Table 4) was identified as being potentially impacted by a local point source, as it was approximately 1 km from an E-PRTR emission to air from a cement works. The site had a dissolved nickel concentration of $9.2 \mu\text{g L}^{-1}$, and an RCR value of 1.14. Eight of the sites for which background concentrations were required are geographically close to anthropogenic activity (e.g., located close to the edge of small towns or villages, or close to a main road). However, none of these sites were close to a large urban area or motorway.

The distances between the sites and their nearest potential surrogate sites were between 0.1 km and 9.0 km, with an average distance of approximately 3.5 km. Although 12 of the 13 sites were within 6 km of their closest potential surrogate site, only 8 of them were within 5 km, and only 5 of them were within 3 km. Potential surrogate sites were also assessed for their proximity to E-PRTR reporting sites, and those within 3 km were not considered to be appropriate surrogate sites. The remaining sites are summarised in Table 4, in terms of their dissolved nickel exposures, local HC5 values, surrogate sites, and RCR values both before and after background correction.

Discussion

The updated standard includes considerably more data, and species, than are included in the ecotoxicity database that was used for the existing EQS, although it does not include any taxonomic groups that were not already represented. The database used for the existing EQS was already extensive, given that it includes 31 species. Despite the considerable increase in the number of individual data points and species that are included in the ecotoxicity database for the updated standard compared to the existing EQS the changes to the resulting site-specific HC5 values (Fig. 2) and the SSD overall (Fig. 1) are relatively limited. This is likely to be due to the fact that the existing EQS already includes an extensive ecotoxicity dataset that provides a good reflection of the range of sensitivities of freshwater aquatic species. However, because the updated standard includes more data it covers a broader range of individual species sensitivities, and includes both more sensitive and less sensitive data than the existing EQS. The greater range of species sensitivities covered results in the SSD curve for the



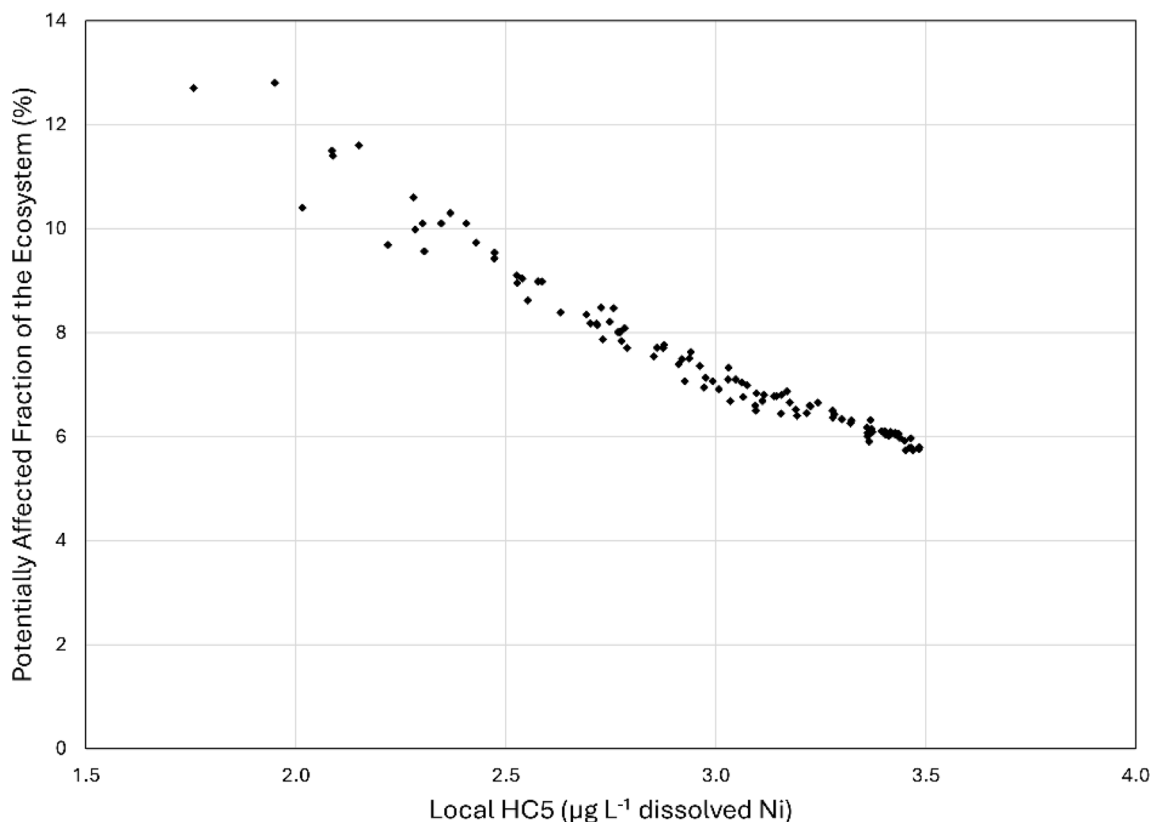


Fig. 5 Potentially affected fraction of the local ecosystem at a dissolved nickel concentration of $4 \mu\text{g L}^{-1}$ for sites with sensitive water chemistry conditions where the updated standard would be lower than the existing $\text{EQS}_{\text{bioavailable}}$ of $4 \mu\text{g L}^{-1}$.

Table 4 Background correction for sites in the UK example

| Site name | Ni^a | HC5^b | Nearest ^c (km) | $\text{Ni}_{\text{bkgd}}^d$ | RCR^e | $\text{RCR}_{\text{bkgd}}^f$ |
|--|---------------|----------------|---------------------------|-----------------------------|----------------|------------------------------|
| Cwmsychn Brook | 8.97 | 5.55 | 3.50 | 2.56 | 1.62 | 1.11 |
| Garnant at Neuadd Road Bridge | 4.94 | 3.14 | 9.00 | 1.52 | 1.58 | 1.06 |
| Nant Cedfww at Betws Rd Shwt | 3.44 | 3.11 | 0.70 | 0.74 | 1.11 | 0.89 |
| R Dwyrdd | 6.54 | 6.28 | 3.10 | 0.70 | 1.04 | 0.94 |
| River Hamps – Waterhouses | 9.15 | 8.02 | 5.30 | 2.99 | 1.14 | 0.83 |
| Cannop Brook, Newerne | 9.03 | 6.05 | 1.20 | 4.87 | 1.49 | 0.83 |
| Yorkley Slade Brook Confluence Cannop BK | 5.98 | 4.03 | 0.10 | 2.18 | 1.48 | 0.96 |
| Wye, Burbage – 500M DS of discharge | 5.53 | 4.98 | 0.40 | 1.63 | 1.11 | 0.84 |
| West Okement at Woodhall Bridge | 4.65 | 4.54 | 3.80 | 1.29 | 1.02 | 0.80 |
| West Okement at Okehampton hospital | 8.78 | 4.93 | 5.10 | 0.76 | 1.78 | 1.54 |
| Rainworth water at Robin dam bridge | 9.81 | 8.92 | 1.70 | 2.09 | 1.10 | 0.89 |
| River calder at centre vale park | 5.42 | 5.30 | 5.80 | 3.43 | 1.02 | 0.62 |
| Walsden water at Todmorden | 6.23 | 5.37 | 5.90 | 3.43 | 1.16 | 0.71 |

^a Dissolved nickel concentration at the site ($\mu\text{g L}^{-1}$). ^b Site-specific HC5 value for the site based on the updated standard ($\mu\text{g L}^{-1}$). ^c Distance to the nearest suitable surrogate site for local background derivation (km). ^d Dissolved nickel concentration at the surrogate site ($\mu\text{g L}^{-1}$). ^e Risk characterisation ratio for the site without taking account of the background concentration. ^f Risk characterisation ratio for the site after taking account of the background concentration.

updated standard being less steep, resulting in a lower HC5 value (see Fig. 1), although the four most sensitive species (8% of the dataset) in this example all have calculated EC10 values below the HC5.

A log-normal distribution has been used to fit the SSDs and derive the site-specific local HC5 values for the sites. This

approach is consistent with the approach used for the existing EQS, which also used a log-normal distribution. The example SSD for the updated standard shown in Fig. 1 meets all of the goodness-of-fit criteria used by the ETX programme at all significance levels that has been the standard approach for SSD fitting for regulatory purposes in Europe. Example SSDs are also



provided for two other waters with different water chemistry conditions (ESI†) one of which meet the goodness-of-fit criteria at all significance levels, and one of which meets the goodness-of-fit criteria at the 5% level for the Anderson–Darling and Kolmogorov–Smirnov tests, but only at the 2.5% level for the Cramer–von–Mises test. These analyses suggest that the assumption of a log-normal distribution is likely to be acceptable for site-specific SSDs calculated following the approach used for the updated standard.

However, it is appropriate to consider whether there are alternative distributions that could provide an improved fit relative to the assumed log-normal distributions. SSDtools has therefore been used to compare the goodness-of-fit of additional distributions, log–log–normal, log–logistic, log–log–logistic, and Burr type 3, and a summary of the results is provided in the ESI† along with the HC5 values calculated from the different distributions. For the three examples used the maximum HC5 value is 20% higher than the minimum HC5 value for the example shown in Fig. 1, and slightly lower for the less sensitive waters used for the other two examples. The HC5 calculated from the log-normal distributions was never either the highest or lowest HC5 value calculated by the five different distributions. In all cases the different measures of goodness-of-fit, such as the Anderson–Darling statistic or the Akaike Information Criterion can lead to different models being selected as the best fitting. It is also evident that this approach does not find a single model to provide the best fit to all of the site-specific SSDs. There are 3515 different site-specific SSDs that

are used for the derivation of the updated standard for UK surface waters, and a much larger number would be required if the approach was applied within Europe. The use of the log-normal distributions is considered to be a pragmatic choice that provides an acceptable goodness-of-fit, and a consistent distributions across all site-specific SSDs, that can be easily applied and maintains consistency with previous SSD fitting approaches used in Europe.

The updated standard also covers considerably more of the surface waters that are included in the UK dataset. The existing EQS only covers approximately two-thirds of the waters, whereas the updated standard covers over 90% of them. Importantly, high pH conditions can be particularly sensitive conditions for metals, including nickel, and the updated standard is applicable to water chemistry conditions that are more sensitive than those applicable for the existing EQS. However, the applicability ranges of the models indicated by the red rectangles on Fig. 3 (and Fig. 6) are the extremes of the applicability ranges of the individual key input parameters used by the bioavailability models. These ranges should not be taken as an indication that the models have been developed and validated for all possible conditions. This is especially so for the validation tests, which have generally been conducted on natural waters. The more uncommon water chemistry combinations such as high pH and low calcium, or low pH and high calcium (Fig. 3) are unlikely to have been tested. However, in the application of the models to surface waters, locations with these kinds of uncommon water chemistry conditions are likely to be encountered infrequently.

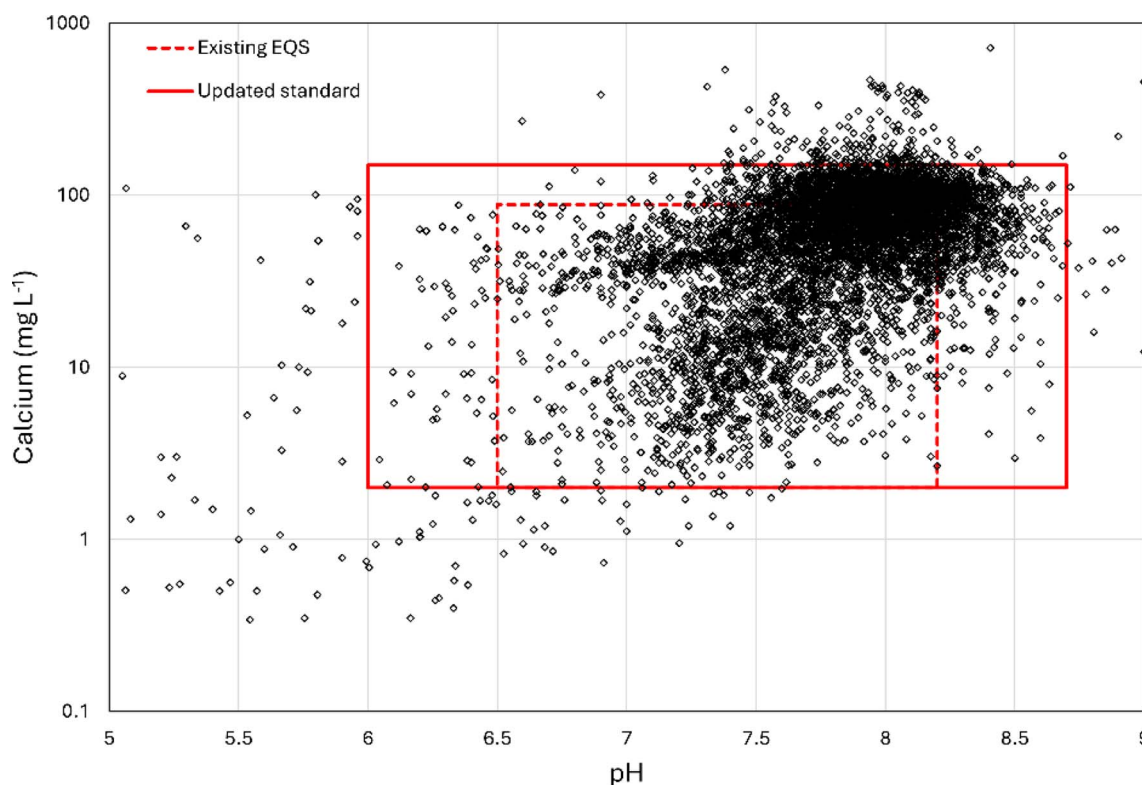


Fig. 6 pH and calcium concentrations at surface water monitoring sites in Europe (points) and the ranges of conditions covered by the existing EQS (dashed red line) and the updated standard (solid red line).



The updated standard does result in a higher proportion of potential compliance failures based on the indicative compliance assessment performed here. Whilst this is, in part, due to the inclusion of more waters and more sensitive conditions, there are also sites for which the existing EQS can be applied and is met that are expected to fail based on the updated standard. This is due to the fact that the local HC5 values calculated by the updated standard are always lower than those calculated by the existing EQS (Fig. 2).

The updated standard may provide a more accurate reflection of the true sensitivity of the overall ecosystems than the existing EQS. If the EQS is not updated to account for the improved understanding of nickel toxicity to aquatic life, there could be some degree of under-protection of aquatic ecosystems in the UK even if compliance is met to the existing EQS.

Sites with sensitive water chemistry conditions are not the only sites where there is the potential for under-protection if the EQS is not updated because, as shown in Fig. 2, all sites have lower site-specific HC5 values based on the updated standard. However, even relatively low exposures ($<4 \mu\text{g L}^{-1}$ dissolved nickel) that do not trigger further consideration of bioavailability based on the existing EQS could cause potential risks in highly sensitive waters. The EQS derivation approach aims to be protective of 95% of waters in the most sensitive region, which ensures a very high level of protection overall (98.8% based on the UK sites covered by the updated standard). Whilst just over 12% of species in the ecosystem may be affected at an exposure concentration of $4 \mu\text{g L}^{-1}$ dissolved nickel in the most sensitive waters, less than 8% of species would be affected at sites with local HC5 values equal to, or higher than, the updated standard of $2.9 \mu\text{g L}^{-1}$ dissolved nickel that would be protective of 95% of sites in the most sensitive UK region at the same exposure level (Fig. 5).

The lower site-specific HC5 values produced by the updated standard, the applicability to a broader range of water chemistry conditions, and coverage of more nickel sensitive waters ultimately result in a greater number of sites being identified as potentially at risk due to nickel. The existing European guidance on EQS implementation⁶ acknowledges that background concentrations may be important in compliance assessment, and provides some approaches for their derivation, although it does not identify where background concentrations should be applied and the derivation approaches are both complex and data intensive. Background concentrations are most likely to be relevant where surface waters are sensitive to nickel and are not significantly affected by anthropogenic influences. This example demonstrates that it is possible to identify whether a local background concentration may be required, and to derive a local background concentration if one is appropriate, using information that is readily available to assessors. This provides a practical means to further refine the compliance assessment against an EQS, although it is only likely to be applicable for a relatively small number of sites overall.

Metals are naturally ubiquitous in the environment and as environmental standards for them become lower, the possibility of the naturally occurring background concentrations contributing to the risk of non-compliance against an EQS

increases. However, the contribution of background concentrations is not relevant for any sites at which there is no predicted risk based on the EQS having taken account of bioavailability, because there is no effect on the compliance outcomes. Furthermore, because background concentrations are typically low there is a limit to the range of RCR values that could potentially be revised based on consideration of local background concentrations. Sites at which there is any significant evidence of anthropogenic disturbance are unlikely to be appropriate for the consideration of background concentrations, even if there is no evidence of nickel contamination.

Fig. 1 shows that the SSD for the updated standard covers a wider range of species sensitivities than the existing EQS, and consequently the SSD curve is less steep. Under these relatively sensitive conditions it is only the most sensitive species that are not likely to be sufficiently protected by the existing EQS. Fig. 5 suggests that this situation may be exacerbated under extremely sensitive water chemistry conditions. However, there are only two sites in the dataset for which nickel exposure data are available where the local HC5 based on the updated standard is below the existing EQS_{bioavailable} of $4 \mu\text{g L}^{-1}$, so would be identified as not at risk based on current regulatory screening approaches but are potentially at risk due to the updated standard. These two sites have RCR values based on the updated standard of 1.1 and 1.2, and both sites have a dissolved nickel exposure concentration of $3.4 \mu\text{g L}^{-1}$.

When the existing EQS was adopted it changed from a single value dissolved nickel concentration to a bioavailability based standard that was considerably lower for the majority of sites. This represented a major change both in terms of environmental protection and in terms of how it was implemented. The bioavailability based standard required a change to the way that compliance assessments were performed, and a move towards a tiered compliance assessment approach that enables the additional resources required for an assessment of bioavailability to be focused on those sites where it is required.⁶ In areas where the implementation of the existing EQS for nickel has been limited, especially in terms of taking account of site-specific bioavailability in the compliance assessment, the focus should be on proper implementation of the existing EQS. However, in countries such as the UK where the implementation of bioavailability based standards for nickel and other metals has been extensive adoption of the updated standard offers a more up to date and scientifically robust improvement that ensures a slightly higher level of ecosystem protection.

Applicability to Europe

Although this example derivation of an updated standard for nickel has been based entirely on UK data the fact that the assessment based on the existing EQS results in a 5th percentile HC5 value that is very close to the EQS of $4 \mu\text{g L}^{-1}$ bioavailable nickel suggests that similar results would likely be obtained for Europe as a whole. The most sensitive surface waters within the UK are found in the North West region, and the 5th percentile HC5 value based on the existing EQS is $3.7 \mu\text{g L}^{-1}$ dissolved nickel, indicating that the bioavailability of nickel in these



waters is similar to the very high bioavailability conditions that the existing EQS is set for. This suggests that the updated standard would be expected to result in a threshold for bioavailable nickel of approximately $3 \mu\text{g L}^{-1}$ if these developments were adopted in Europe. An important difference between this UK based example and any potential application to Europe is that smaller sub-regions of the UK have been used as the basis for identifying the most sensitive region and the dissolved nickel concentration that would be protective of 95% of surface waters within that region. The derivation of the existing nickel EQS in Europe uses individual Member States as the regions.

Fig. 6 compares the applicability range of the bioavailability models used by the existing EQS and the updated standard to the ranges of water chemistry conditions (pH and calcium concentrations) in Europe based on a published dataset of European surface water chemistry conditions.²⁵ This shows that there is a comparable situation for Europe overall to that seen for the UK (Fig. 3) in that there is a considerable number of sites with either high calcium concentrations, high pH, or both high calcium and high pH that are not covered by the bioavailability models use for the existing EQS, but would be covered by the updated standard. The coverage of these waters by the updated standard is 95.0%, whereas the coverage of these waters by the existing EQS is 59.8%.²⁵

Conclusions

The current statutory EQS for nickel in Europe was set in 2013. Since that time, a significant additional body of evidence has become available regarding the toxicity of nickel to aquatic life, and how water chemistry conditions affect nickel bioavailability. The additional information has been evaluated to identify whether there would be any potential implications associated with either updating the existing EQS in line with this additional information or maintaining the existing EQS. Given the extensive body of information that was used to derive the existing EQS the changes are relatively small, except for the fact that a much larger proportion of UK waters can now be covered by the bioavailability models. The updated standard of $2.9 \mu\text{g L}^{-1}$ bioavailable nickel results in slightly lower site-specific HC5 values, and consequently slightly higher levels of predicted risks due to nickel in the UK. Given the scope of the available information upon which the derivation of the updated standard is based there is no scientific justification for considering an assessment factor that is larger than the value of one that was used for the derivation of the existing EQS for nickel. Reducing EQS values for metals increases the likelihood of background concentrations contributing to failures, although in the case of nickel in the UK this is a relatively minor issue with very few sites being affected.

Data availability

The water chemistry data used for this article are available from the Department for Environment Food & Rural Affairs Water Quality Data Archive at [https://environment.data.gov.uk/water-](https://environment.data.gov.uk/water-quality/view/landing)

[quality/view/landing](https://environment.data.gov.uk/water-quality/view/landing). This manuscript addresses whether additional ecotoxicity data and advances in bioavailability modelling for nickel that have become available since the existing EQS was set warrant an update of the EQS. The study applies the derivation approach for bioavailability based EQS in the UK and Europe to derive a potential update of the bioavailable nickel standard based on UK water chemistry conditions, and considers the implications for compliance in the UK. It also includes an evaluation of the protectiveness of the updated standard against ecological data, and a practical approach to the consideration of background concentrations in the compliance assessment. The potential implications of maintaining the existing EQS are evaluated in terms of the fraction of the ecosystem that may be affected are also considered.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- 1 WHO, *Nickel in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality*, 2005, WHO/SDE/WSH/05.08/55, https://cdn.who.int/media/docs/default-source/wash-documents/wash-chemicals/nickel-background-document.pdf?sfvrsn=90644b9f_9#:~:text=According%20to%20the%20above%20studies,%C2%B5g%20or%20less%20from%20water.
- 2 European Commission, Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, *Official Journal of the European Union*, 2013, L266/1, <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:226:0001:0017:en:PDF>.
- 3 European Commission, *European Union Risk Assessment Report on Nickel, Nickel Sulphate, Nickel Carbonate, Nickel Chloride, Nickel Dinitrate*, Final Report May 2008, Prepared by Denmark, Danish Environmental Protection Agency on behalf of the European Union, Denmark.
- 4 European Commission, *Nickel EQS Dossier. 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)*, 2011.
- 5 European Commission, *Common Implementation Strategy. Guidance Document No. 27 – updated version 2018. Technical Guidance for deriving Environmental Quality Standards (EQS)*. 2018, accessed March 2024 from: <https://op.europa.eu/en/publication-detail/-/publication/d5b2b9b9-32fb-11e8-b5fe-01aa75ed71a1>.



- 6 European Commission, Common Implementation Strategy. Guidance Document No. 38 Technical Guidance for implementing Environmental Quality Standards (EQS) for metals, *Consideration of metal bioavailability and natural background concentrations in assessing compliance*, 2019, accessed March 2024 from: https://circabc.europa.eu/sd/a/2f0bdb9-9161-4c8d-8503-d221ab93d718/WD2019%E2%80%9338_Implementing%20the%20EQS%20DRAFT%20guidance%20WD%20meeting%202026%20Nov%20202019.pdf.
- 7 N. Deleebeeck, K. De Schamphelaere and C. Janssen, Effects of Mg^{2+} and H^+ on the toxicity of Ni^{2+} to the unicellular green alga *Pseudokirchneriella subcapitata*: model development and validation with surface waters, *Sci. Total Environ.*, 2009, **407**, 1901–1914.
- 8 K. De Schamphelaere, L. Van Laer, N. Deleebeeck, B. Muysen, F. Degryse and E. Smolders, Nickel Speciation and Ecotoxicity in European Natural Surface Waters: Development, Refinement and Validation of Bioavailability Models, *Report prepared for the Nickel Producers Environmental Research Association (NiPERA), Durham, NC, USA*, Gent University, Laboratory of Environmental Toxicology and Aquatic Ecology, Gent, Belgium, 2006.
- 9 N. Deleebeeck, K. De Schamphelaere and C. Janssen, A novel method for predicting chronic nickel bioavailability and toxicity to *Daphnia magna* in artificial and natural waters, *Environ. Toxicol. Chem.*, 2008, **27**, 2097–2107.
- 10 N. Deleebeeck, K. De Schamphelaere and C. Janssen, A bioavailability model predicting the toxicity of nickel to rainbow trout (*Oncorhynchus mykiss*) and fathead minnow (*Pimephales promelas*) in synthetic and natural waters, *Ecotoxicol. Environ. Saf.*, 2007, **67**, 1–13.
- 11 C. Nys, C. Janssen, P. Van Sprang and K. De Schamphelaere, The effect of pH on chronic aquatic Ni toxicity is dependent on the pH itself: extending the chronic Ni bioavailability models, *Environ. Toxicol. Chem.*, 2016, **35**, 1097–1106.
- 12 A. Peters, C. Nys, G. Merrington, F. Verdonck, S. Baken, C. Cooper, F. Van Assche, C. Schlekhat and E. Garman, Demonstrating the reliability of bio-met for determining compliance with Environmental Quality Standard (EQS) for metals in Europe, *Environ. Toxicol. Chem.*, 2020, **39**, 2361–2377.
- 13 UKTAG, *Metal Bioavailability Assessment Tool (M-BAT). SNIFFER*, Stirling, Scotland, 2014, <https://www.wfduk.org/sites/default/files/Media/Environmental%20standards/MBAT%20UKTAG%20Method%20Statement.pdf>.
- 14 A. Peters, C. Nys, D. Leverett, I. Wilson, P. Van Sprang, G. Merrington, G. Merrington, E. Middleton, E. Garman and C. Schlekhat, Updating the Chronic Freshwater Ecotoxicity Database and Biotic Ligand Model for Nickel for Regulatory Applications in Europe, *Environ. Toxicol. Chem.*, 2023, **42**, 566–580.
- 15 A. Peters, G. Merrington, C. Schlekhat, K. de Schamphelaere, J. Stauber, G. Batley, A. Harford, R. van Dam, C. Pease, T. Mooney, M. Warne, C. Hickey, P. Glazebrook, J. Chapman, R. Smith and R. Krasso, Validation of the nickel biotic ligand model for locally relevant species in Australian freshwaters, *Environ. Toxicol. Chem.*, 2018, **37**, 2566–2574.
- 16 A. Peters, G. Merrington, J. Stauber, L. Golding, G. Batley, F. Gissi, M. Adams, M. Binet, K. McKnight, C. Schlekhat and E. Garman, Empirical bioavailability corrections for nickel in freshwaters for Australia and New Zealand Water Quality Guideline development, *Environ. Toxicol. Chem.*, 2021, **40**, 113–126.
- 17 G. Merrington, L. Nowell and C. Peck, An introduction to Criteria for Reporting and Evaluating Exposure Datasets (CREED) for use in environmental assessments, *Integr. Environ. Assess. Manage.*, 2024, **20**(4), 975–980.
- 18 M. Hladik, A. Markus, D. Helsel, L. Nowell, S. Polesello, H. Rudel, D. Szabo and I. Wilson, Evaluating the reliability of environmental concentration data to characterize exposure in environmental risk assessments, *Integr. Environ. Assess. Manage.*, 2024, **20**(4), 981–1003.
- 19 A. Peters, M. Beking, L. Oste, M. Hamer, J. Vuaille, A. Harford, T. Backhaus, S. Lofts, C. Svendsen and C. Peck, Assessing the relevance of environmental exposure data sets, *Integr. Environ. Assess. Manage.*, 2024, **20**(4), 1004–1018.
- 20 C. Di Paolo, I. Bramke, J. Stauber, C. Whalley, R. Otter, Y. Verhaegen, L. Nowell and A. Ryan, Implementation of the CREED approach for environmental assessments, *Integr. Environ. Assess. Manage.*, 2024, **20**(4), 1019–1034.
- 21 A. Peters, G. Merrington, K. Delbeke and K. de Schamphelaere, Regulatory consideration of bioavailability for metals: Simplification of input parameters for the chronic copper Biotic Ligand Model, *Integr. Environ. Assess. Manage.*, 2011, **7**, 437–444.
- 22 A. Peters, I. Wilson, C. Cooper, A. Ryan, F. Van Assche and H. Winbow, Evaluating the Protectiveness of a Bioavailability-Based Environmental Quality Standard for the Protection of Aquatic Communities from Zinc Toxicity Based on Field Evidence, *Environ. Toxicol. Chem.*, 2023, **42**, 1010–1021.
- 23 A. Peters, P. Simpson, G. Merrington, C. Schlekhat and E. Rogevich-Garman, Assessment of the effects of nickel on benthic macroinvertebrates in the field, *Environ. Sci. Pollut. Res.*, 2014, **21**, 193–204.
- 24 I. Wilson, A. Peters, G. Merrington, E. Middleton, C. Schlekhat and E. Garman, Practical Estimation and Use of Ambient Background Concentrations in Surface Waters for Nickel in Europe, *Integr. Environ. Assess. Manage.*, 2024, accepted.
- 25 A. Peters, I. Wilson, G. Merrington, C. Schlekhat, E. Middleton and E. Garman, Assessing the Extent of Environmental Risks from Nickel in European Freshwaters: A Critical Reflection of the European Commission's Current Approach, *Environ. Toxicol. Chem.*, 2022, **41**, 1604–1612.

