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Using risk-ranking of metals to identify which poses the greatest threat to freshwater organisms in the UK

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ABSTRACT

Freshwater aquatic organisms face the challenge of being exposed to a multitude of chemicals discharged by the human population. The objective of this study was to rank metals according to the threat they pose to aquatic organisms. This will contribute to a wider Chemical Strategy for freshwater which will risk-rank all chemicals based on their potential risk to wildlife in a UK setting. The method involved comparing information on ecotoxicological thresholds with measured concentrations in rivers. The bioconcentration factor was also considered as a ranking method. The metals; Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn, were analysed using this approach. Triclosan and lindane were used as comparative organic pollutants. Using a range of ranking techniques, Cu, Al and Zn came top of the list of concern, with Cu coming first.

1. Introduction

As society has developed over the last 60 years, so has the consumption of chemicals, so that now over 100,000 chemicals are in use worldwide (Holt, 2000). As the various chemical industries have developed, this has led to an increase in freshwater contamination by chemicals over time (Schwarzenbach et al., 2006). There are serious questions to ask concerning whether we will ever be able to obtain sufficient information to evaluate the safety of all of these chemicals in the environment using current approaches (Sumpter, 2009). The issue of thousands of pharmaceuticals, and more recently also nanoparticles, appears to overwhelm our capacity to assess the risk to wildlife from exposure to chemicals, especially if we proceed on a 'chemical- by-chemical' basis. To date no approach has unanimous support when it comes to the risk assessment of chemicals in the aquatic environment, different methods have their own advantages and disadvantages (SEC(2011) 1544). Nevertheless, we are not short of information; in 2012, Chemical Abstracts Service (CAS) reported nearly one million articles, out of which nearly half covered research at the interface of chemistry and biology, indicating that there is a wealth of knowledge available in the subject area of chemical and biological science to help us assess risk (ACS, 2013).

Thus, given the inevitably modest budgets available for environmental study, which chemicals should we focus on, or regulate, in order to best protect our aquatic environment? Environmental research funding is not necessarily a rational or objective process, as funding organisations (and their reviewers) are influenced by fashion, novelty or political imperatives. This subjective process could leave us with considerable knowledge on some chemicals whilst others remain unstudied (Anastas et al., 2010; Grandjean et al., 2011). However if fish, as an example of aquatic wildlife, could vote, which chemical would they indicate as their greatest concern?

Globally it has been recognised that there is a need to develop a better understanding and management strategy with regards to the risk of chemicals to human health and the environment (Anastas et al., 2010). Deciding which chemicals are of most concern is a global challenge and has been highlighted as one of the top research questions needing to be answered by the Society of Environmental Toxicology and Chemistry (SETAC) (Brooks et al., 2013). The safeguarding of freshwater ecosystems is an increasing challenge as domestic and industrial demands on water resources

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grow and we continue to be in an era of water scarcity (Postel, 2000) with the potential for extreme low flow events, which may occur more frequently as a consequence of climate change.

In theory, this objective to protect aquatic organisms is not dissimilar to that used in the EU Water Framework Directive (WFD), which governs hazardous, or priority, substances. The main objective of the Priority Substances Directive of the EU (EC, 2008) is protecting wildlife and humans from harmful effects of chemicals identified as priority substances in surface waters, and to monitor trends in the concentrations of these chemicals. It does this through setting environmental quality standards (EQS) for a number of chemical pollutants, below which no harmful effects are expected to wildlife, or humans. This study will hopefully support that effort.

The objective of this study was primarily to rank metals in the water column on the basis of risk to aquatic wildlife. Metals are natural elements and some are essential for life. The discharge of metals from industry and domestic sources has drastically increased the input and release of metals into aquatic ecosystems (Wood et al., 2012a). Certain forms of metals, when present at sufficiently high concentrations, are toxic (Luoma, 1983).

The proximity between reported effect concentrations and measured river water concentrations was the approach used in this ranking assessment. The ranking of metals based on their bioconcentration factor (BCF) was also considered as an additional ranking method. While BCFs for metals have been reported as being variable and an insufficient measure of risk (Chapman et al., 1996), the bioconcentration of a chemical can be a useful indicator of chemical exposure to aquatic organisms and a prerequisite of adverse effects (Franke et al., 1994).

As the overall objective of the larger study, of which this paper is a part, is to compare the risk from different types of chemicals, two organics substances were also examined as test cases. Might the risk from metals turn out to be trivial compared to some key organics of concern? Triclosan is an antimicrobial agent found in soaps, deodorants, skin creams and plastics which we have been using in our homes since the 1960's (Price et al., 2010). Triclosan was selected as some scientists have argued that for the environment it is the most hazardous personal care product on the market (Brausch and Rand, 2011; von der Ohe et al., 2012). Designed to act as an insect neurotoxin, γ-hexachlorocyclohexane (γ-HCH), also known as lindane, has been banned for agricultural use around the world since 2009 (UNEP, 2005). It has been identified as a priority hazardous substance by the European Commission in the Water Framework Directive (2000/60/EC) and hence a water quality standard exists for it.

Previous studies have looked at the effects of one chemical on multiple species (Enick and Moore, 2007; Qu et al., 2013) or the effects of a single class of a chemicals on a range aquatic organisms, (Gerhardt, 1993; Van Sprang et al., 2009). The approach used here was to compare a range of different chemicals and examine their effects on a range of different species, in order to rank the risk they represent. It is the hope of the authors that this direct approach to chemicals risk-ranking might prove illuminating and aid regulators and scientists about where to focus their concerns and efforts.

2. Methods

2.1. Rationale

Whilst isolated industries and particular environmental circumstances can damage wildlife, these local situations were not the focus of this research. This study focused on to what degree a chemical might be of widespread concern. Only exposure in the UK was considered, so only measured UK river concentrations were used; however, the same approach could equally be applied to other counties. With respect to exposure to chemicals from the domestic population, the UK could be considered one of the most exposed countries in the developed Western world (Keller et al., 2014). In order to observe how some well-known organic pollutants might compare in terms of concern with the metals, lindane and triclosan were also studied, using the same methodology as for the metals. This methodology could be viewed as a first tier ranking which considers harmful exposure for an organism via the water column. There are many environmental factors that can modify the potential risk posed by a chemical in the aquatic environment, such as acidity and dissolved organic matter content (Gensemer and Playle, 1999; Sciera et al., 2004), which, depending on the factor and the chemical, could be protective or cause an increase in the toxicity of the chemical. Some of these factors have been explored in this paper; others will be explored in the development of the second tier methodology. These additional factors are referred to here as moderating factors. Bioconcentration of a chemical was considered by using the bioconcentration factor (BCF) as an additional ranking method, which could produce a different ranking order and thus the chemical identified as of most concern.

For all chemicals, publications were searched using a series of key words over the period Nov 2012–July 2013 (Table S1). The Web of Knowledge contains data on 23,000 scientific journals from 1900 to the present day, which can be considered representative of scientific work that has been peer reviewed and thus considered a reliable source of information. The two main categories of information required from the literature search were the effects of a chemical on aquatic organisms and the concentration of a chemical in the aquatic environment of the UK.

2.2. Environmental toxicity information gathering

With regards to the reported effects data, for these to be entered into our ecotoxicity database, only studies with measured concentrations, rather than nominal, were included. It was also considered essential that laboratory ecotoxicity studies included a description of experimental conditions, such as temperature, pH and hardness. A range of effect measurements were present in the literature including LOEC, EC50, LC50, acute toxicity and chronic toxicity. For this study, a wide range of species and endpoints were considered, to ensure that a representative picture of species and possible effects was obtained. The endpoints used included mortality, growth inhibition and changes to gene expression. In these aquatic toxicological studies, bacteria, daphnids and fish were the most commonly used test species. Species which are relevant to the UK were preferred, but failing that, common test species were used i.e. species which have been approved as standard test species (Farre and Barcelo, 2003).

Data on the bioconcentration (BCF values) of each chemical was also collected through the literature search. McGeer et al., 2003 provide a review of bioconcentration for a selection of metals (Ag, Cd, Cu, Hg, Ni, Pb, Zn) and hence, this paper, with others, was used as a reference source for BCF values.

References were reviewed per chemical, using key search terms (Table S1), also reviews, cross-referencing and consensus within the literature on which were the most sensitive organisms and endpoints for a chemical were noted. Data were added to the database until the median value didn't change significantly with the addition of new data.

Fig. S1 details the methodology process as a flow chart. Table S1 details the number of papers from the literature and Table S2 provides the actual number of these papers used to provide the toxicity data as well as the number of data points for each chemical together with accompanying reference list.

The aim of the literature search on each chemical was to get an overall impression of the effects of a chemical on a range of aquatic organisms. It was not possible during this study to review every single paper present in the literature on metals, lindane or triclosan (Table S1); doing so would be a monumental task.

2.3. Environmental concentration information gathering

For the chemicals studied, only measurements of concentrations made in the UK were collected. These included total measured river water concentrations reported in literature publications, but also total measured river water concentrations obtained from other available databases. These other databases included the Forum of European Geological Surveys (FOREGS, now EuroGeoSurveys) (Salminen et al., 2005; De Vos W., 2006) and Environment Agency WIMS data (1990–2012) (WIMS, 2013). No single data source provides an ideal balance of measurements from around the country. Measurements of concentrations reported in the scientific literature often focus on locations believed to be hot spots, such as rivers receiving mine waste contaminated with metals, whilst the FOREGS database focuses on second order, drainage basins and the WIMS data contains many entries where the concentrations were found to be below the limit of detection. These non-detects were included in the study by reporting them as half the LOD.

2.4. Risk analysis

Using the data collected for this project, each chemical was initially analysed using three ranking approaches (see below), based either on water exposure or bioconcentration. In the future, using the database that has been collated, the chemicals could be analysed further as the ranking methodology develops. This study describes how they have been considered at this first tier of development.

2.4.1. Ranking of chemicals based on exposure via the water column

The individual effect concentrations and measured river water concentrations for each chemical were plotted. This method creates two sub-sets of data, the effect data and the measured river water concentration data. It is the proximity of these two data sets which indicates the degree of concern posed by a chemical. All measured water data were plotted, thus in some cases there were outliers which may represent concentrations which are found at localised polluted sites, such as at mine sites.

The possibility exists that some values from ecotoxicity and river water concentration studies or datasets are wrong and cannot be repeated. To reduce the influence of any erroneous data, the degree of separation between the median effect concentration and the median river water concentration was the first method used for ranking chemicals on the basis of risk (equation (1)). The median of all the effect data used in the study (including all species and all endpoints) and the median of all the measured river data were calculated to provide an initial comparison.

$$\text{Risk} = \frac{mW}{mT} \tag{1}$$

Where mW is the median river water concentration (μg/L) and mT is the median effect concentration (μg/L).

This value can be described as a risk ratio, which can be used to rank concern, the larger the value, the greater the concern. The chemicals were ranked according to this risk ratio.

2.4.2. Ranking of chemicals based on exposure via the water column: A precautionary approach

Given the wide range of concentrations that could occur in rivers as a consequence of the uneven distribution of population and variation in flow in the country, it seems reasonable to fix the median environmental concentration as one of the comparators. However, a precautionary approach would be to use the 5%ile ecotoxicity concentration and compare this with the median river water concentration (equation (2)). This second ranking approach uses the same risk ranking principle, in this case comparing the distance i.e. the fold-difference between the 5%ile effect concentration and the median river water concentration to assess whether a chemical is of potential concern or not.

$$\text{Risk} = \frac{mW}{5\%ileT} \tag{2}$$

Where mW is the median measured river water concentration (μg/L) and $5\%ileT$ is the 5th percentile effect concentration (μg/L).

2.4.3. Ranking of chemicals based on Bioconcentration Factor (BCF)

The BCF is a unitless value calculated by dividing "steady-state" wet tissue concentration by "steady-state" water concentration of a particular substance (Chapman et al., 1996). By using only the BCF as a ranking tool, without any reference to toxic concentrations, a third, different ranking order with regards the threat posed by chemicals to aquatic wildlife can be produced. The BCF is an established ratio, thus values were collected from the literature and the median values used as a comparison between chemicals. The greater the BCF, the greater the concern based on this ranking methodology.

3. Results and discussion

There is a great deal of information available in the literature on metal toxicity (Brix et al., 2011); studies reporting impacts of metals on the environment have been published since the 1960's. We conclude from this that it really ought to be possible to rank the aquatic risk posed by metals. Some 250,000 papers have been published on the toxicity of the metals we investigated (Table S1).

The chemicals have been ranked and discussed based on the risk they present to aquatic wildlife. Table S3 is a summary of the ranking order and risk ratios obtained from all three methods.

3.1. Ranking of chemicals based on exposure via the water column

3.1.1. Ranking of metals

The threat of metals as an individual class of chemicals was first considered. When the data for all the metals were compared, it can be seen that some overlap between environmental concentrations and concentrations that cause effects on aquatic organisms occurs for all metals except As (Fig. 1). The difference between the median river water and effect values was relativity small (about 10-fold) for metals of most concern, such as Cu, Al, Zn, but was larger (about 10,000-fold) for metals of less concern, such as Cr, Ag and Hg (Fig. 1). When ranking the metals by comparing the median river water and median effect concentrations, Cu, Al, Zn and Ni emerge as posing the greatest risk. When using the 5%ile effect concentration as a comparison to median river water concentrations, Al, Cu, Ni and Zn appear as the metals of greatest concern (Fig. 2).

Concentrations of Cu measured in UK rivers range between 0.02 μg/L and 133 μg/L, with a median concentration of 4.7 μg/L. The lowest reported concentration which has harmful effects on freshwater organism is 2.5 μg/L; periphyton (algae) experience a 57–81% reduction in productivity at this concentration (Leland and

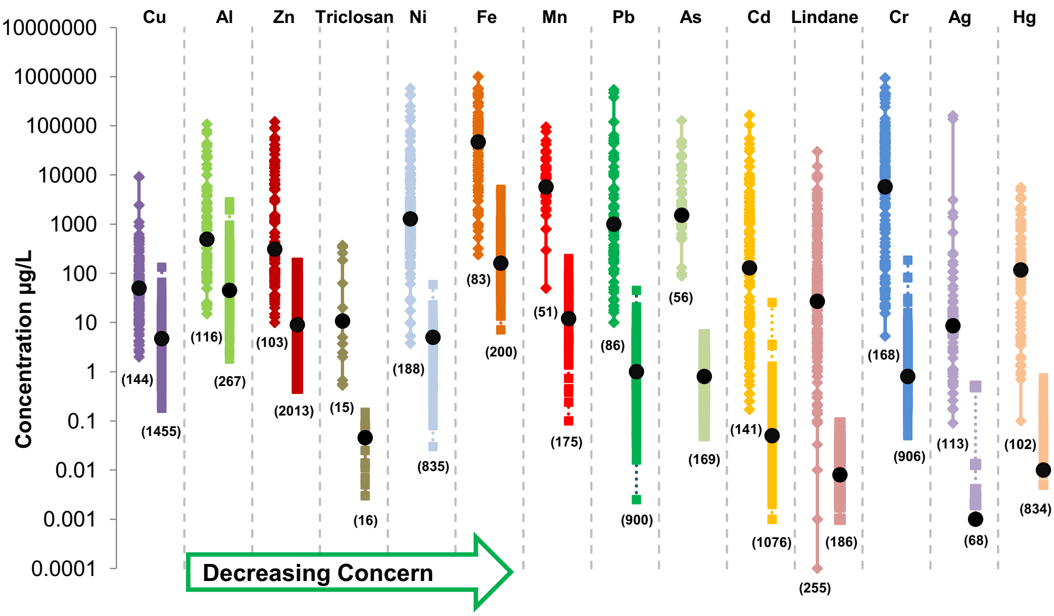

Fig. 1. – Ranking of metals, lindane and triclosan based on the difference between the median effect (left hand vertical line of each pair: diamonds) and river water concentrations (squares). The median values are plotted as black circles. The numbers in brackets represent the number of data points per data set.

Carter, 1985), with *Oncorhynchus mykiss* (Rainbow trout) being affected at 2.8 µg/L (Hansen et al., 2002). Cu toxicity is moderated by dissolved organic carbon (DOC); as binding of Cu to the DOC reduces its uptake into aquatic organisms and thus the toxicity of Cu is reduced (Wood et al., 2012a). Thus, the impact DOC would have on the ranking of Cu and other metals should be a moderating factor to consider.

Zinc has been ranked here as the third or fourth metal of potential concern to freshwater ecosystems in the UK. The median river water concentration of Zn is 9.0 µg/L, with a range of 0.46–160 µg/l. *Lemna gibba* (duckweed) appears to be a sensitive species, with a reported EC50 of 10 µg/l (Okamura et al., 2012). *Oncorhynchus mykiss* (Rainbow trout) were also reported to be affected at low concentrations, with evidence of a decrease in survival at concentrations between 20 and 289 µg/l (Mebane et al., 2012). Gardner et al. (2012) reported in their study on chemicals present in sewage effluent that the median concentrations of total Cu and Zn are found in the UK were 8.3 µg/L and 30.9 µg/L respectively (Gardner et al., 2012), which as expected are higher than median river concentrations.

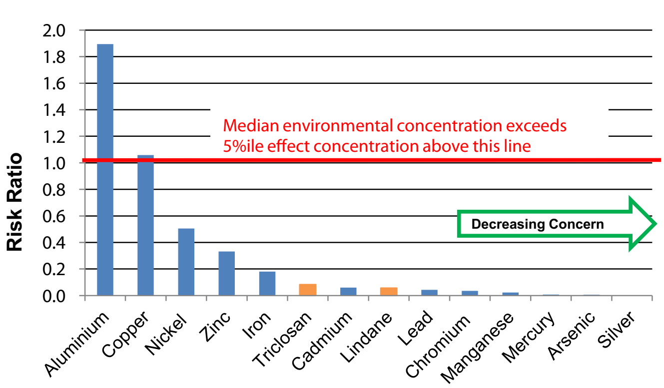

Fig. 2. – Ranking of chemicals (metals, lindane and triclosan) based on the difference between the 5%ile effect concentration and the median river water concentration. When the river water concentration exceeds the 5%ile effect concentration (risk ratio >1) this suggests a current danger to aquatic organisms.

Aluminium appeared in first or second place in order of risk to the environment when water chemistry is not considered (Figs. 1 and 2). Al has mainly been studied in relation to its toxicity in acidic waters (Baker and Schofield, 1982). To aquatic organisms, monomeric Al species are the most toxic species (Driscoll and Schecher, 1988). These species of Al are found at pH levels < pH6 and >pH8.5. Below pH6, cations (Al^{3+}, $AlOH^{2+}$, $Al(OH)^{2+}$) are present in the dissolved phase and their solubility increases with decreasing pH. In alkaline conditions the anion $Al(OH)^{4-}$ dominates (Gensemer and Playle, 1999; Wood et al., 2012b). In the UK, freshwaters are on average found to be of a neutral pH (Neal, 2002). However, any increase in sources of anthropogenic acidification gives cause for concern with regards Al toxicity to freshwater organisms (Poleo et al., 1991). Natural causes of fluxes in pH, such as during periods of snowmelt and anthropogenic acidification, can alter the speciation of Al and have been a major concern to freshwater biota (Andren and Rydin, 2012). The FOREGS project states a pH range of 6.1–8.5 with an average pH of 7.9 in UK waters, although lower pH levels (pH 3.9–6) have been reported in the literature (Tipping et al., 1998; Tipping, 2005; Tipping and Carter, 2011). The effect and exposure data included in this study encompass studies conducted at any pH level. If the risk ratio is re-calculated based only on effect and exposure data between the pH range of 6–8.5, the median effect concentration would be 1904 µg/L whilst the median river concentration is 35.1 µg/L, giving a risk ratio of 0.018, compared to 0.091 when pH is not considered. Al toxicity is also impacted by temperature, DOC and hardness (Neville and Campbell, 1988), which can reduce the toxicity of Al (Wood et al., 2012b). Therefore, whilst Al can have harmful effects on freshwater organisms, this is very closely associated with pH levels. Because these conditions are now uncommon in the UK, Al would drop down our level of concern in a second tier analysis.

Both approaches used to rank metals based on exposure via the water column result in the same top four chemicals of concern. Although the approach of comparing the effect concentration and the river water concentration uses a straightforward methodology, Cu, Zn and Ni have also been identified by others, using different approaches, as the metals posing the highest risk to aquatic wildlife

(Arambasic et al., 1995; Khan and Nugegoda, 2007). There is little to choose between the degree of concern for Cu, Zn and Ni. By using the median, which has less statistical variability, the metal of greatest concern based on water exposure is Cu.

3.1.2. Comparing metals to key organic pollutants

As an initial, and admittedly preliminary, step towards comparing the potential risk of metals with those of other chemicals, triclosan and lindane were ranked, using the same methodology as for the metals. When compared using the median data, triclosan and lindane are ranked fourth and eleventh, respectively (Fig. 1). Using the 5%ile effect concentration approach, the two organic pollutants were of similar or greater risk to aquatic wildlife (Fig. 2). It was interesting to note that using this approach triclosan appeared to be a greater threat to aquatic wildlife than most metals.

3.1.3. Ranking of chemicals based on Bioconcentration Factor (BCF)

The bioconcentration factor is the ratio of the chemical concentration in an aquatic organism to the concentration in the water. The median BCF of each chemical considered in the current study is plotted in Fig. 3. They were calculated from BCF values reported in the literature for a range of organisms. A chemical with a BCF of 2000 is considered to be bioaccumulative and a BCF of 5000 is considered very bioaccumulative, according to guidelines in Annex XIII of the REACH Regulation 1907/2006 (EC, 2006). The higher the BCF value, the more concern is associated with the chemical. Thus, Hg exceeds the very bioaccumulative value of 5000 with a BCF of 6000, Zn and triclosan exceed the 2000 benchmark with median BCF of 4000 and 3100, respectively (Fig. 3). Once BCF is considered, Hg becomes the chemical ranked highest and triclosan moves up the ranking order. Although the ranking order has changed, Cu remains a chemical of concern and is in the top half of the ranking. It should be recalled that a chemical which bioconcentrates is not necessarily hazardous (Vijver et al., 2004), and hence the final ranking would need to include an assessment of toxicity.

Mercury is found at very low concentrations in UK waters, with a range of 0.005–0.75 μg/L. It is present in freshwater in three main forms; the inorganic forms of metallic Hg^0, inorganic Hg^{2+} and the organic methylmercury [MeHg(I)] (Wood et al., 2012b). Hg in this study represents all forms of Hg. However, [MeHg(I)] is highly toxic, especially to the developing nervous system, and it accumulates in the food web, whereas the toxicity of the other forms is considerably lower. Thus, comparing total Hg values in the water column with effect concentrations could under-represent risk. The EU WFD has recently set EQS values for concentrations in biota where an EQS based on water concentrations is not considered protective enough, for Hg the EQS value of 0.05 μg/L in water has been supplemented with the in biota standard of 20 μg/kg fresh weight. Sources of natural Hg include geothermal and volcanic activity, while anthropogenic sources range from the combustion of fossil fuel in power plants to various types of manufacturing and production processes such as metal and cement facilities, incineration and mining (Pirrone et al., 2010). Although the emissions of Hg have been reduced in Europe, the [MeHg(I)] levels in freshwater fish remain high (Lepom et al., 2012), and hence Hg is still of considerable concern for aquatic wildlife in the UK (Jurgens et al., 2013).

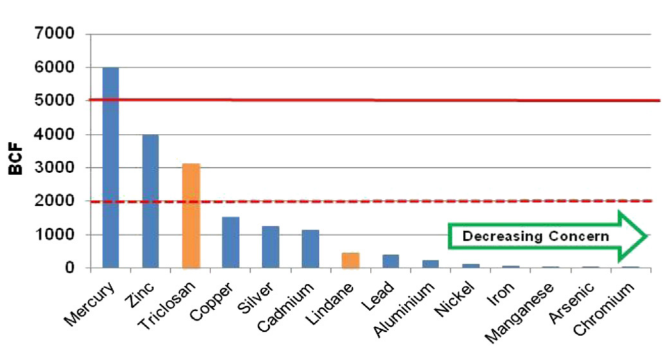

Fig. 3. – Ranking of chemicals based on the median Bioconcentration Factor (BCF). A chemical with a BCF of 2000 is considered to be bioaccumulative (red dashed line) and a BCF of 5000 is considered very bioaccumulative (red line).

Unfortunately, metal BCF values have been reported as being highly variable between organisms (Franke, 1996; Luoma and Rainbow, 2005). McGeer et al., 2003 reported that it is virtually impossible to derive a meaningful BCF value that is representative for each metal. However, this study plans to compare different classes of chemicals, which will include a range of organic and inorganic substances. The BCF model was developed to describe neutral and lipid soluble organic substances (McGeer et al., 2003), thus to make an unbiased and balanced comparison, the same data for all substances should be compared. The BCF ranking demonstrates that changes occur to the chemicals of most concern based on the ranking method used, highlighting that there are other ways to prioritise chemicals.

3.2. Moderating factors

Taking data straight from the literature regardless of ecological relevance, species, test conditions and endpoints, has allowed all possible effects to be considered, and the median concentration that produces these effects to be compared against typical UK river concentrations. This has provided an unbiased view of what a chemical's potential threat to the environment might be. However, as the methodology is further developed, it will be important to consider moderating factors which might increase or decrease a chemical's proposed ranking.

It has been known for decades that water chemistry factors will play a critical role in determining bioavailability and hence toxicity of metals; these factors include pH, hardness, and DOC. When all these factors are known, speciation and biotic ligand models (Di Toro et al., 2001) can be used to assess the most realistic exposure and risk at a particular river location. It should be noted that in most cases the bioavailable toxic species of a metal account only for a proportion of the total, so risks tend to decrease.

Mortality is one of the most frequently used endpoints in toxicity studies. However, physiological and behavioural responses to a toxicant are more sensitive, and in terms of response time, they are among the first reactions against toxicant stress at sub-lethal concentrations. In this study we have tried to remove inaccuracies which occur when only including LC50 results, to ensure that the full range of chemical impacts were taken into account. Part of the challenge will be determining, from these endpoints, which ones are of major concern to the actual function of the population, and which are of only negligible impact. For example, if the effect of a chemical was inhibition of reproduction, this would be considered of great ecological relevance. In contrast, effects on expression of some genes, without any obvious adverse consequences, would be considered mild effects, and of minor relevance. By considering a wide range of endpoints rather than just visual observable toxicity, a more precautionary assessment can be made of the impact that a chemical is having on an individual or population (Burgess et al., 2013). Moderating factors would need to be reviewed in a final analysis, although a danger of subjectivity must be acknowledged whilst doing so.

4. Conclusions

Many might argue that trying to risk rank all chemicals, or simply examples of different classes of chemicals, is impractical and unrealistic. However, few would deny that this would be highly desirable if it were possible. This study does not set out to be the final and definitive analysis of chemical risk. It merely utilizes the vast amount of information we have available now to examine how chemicals could be ranked based on current knowledge. The method described here suggests it is possible to use our approach and the corroboration between the results of this analysis and those carried out by others, at least on metals, gives strong support to this approach. Whilst merely comparing metals one against another on the basis of aquatic risk is not novel, comparing metals with organic contaminants would be. In due course, other pesticides, pharmaceuticals, biocides, surfactants, POPs and nanoparticles will be included in the comparison. At this stage of this risk ranking exercise it would appear that the historic focus by environmental scientists and regulators on metals has been entirely justified on the basis of the proximity of effect and river water concentrations for aquatic organisms. We believe it is noteworthy that a personal care product, such as triclosan, was ranked as a higher risk than many metals. At this stage, Cu, Al, Zn, Ni and triclosan appear to be the chemicals of most concern, with Cu being of most concern.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2014.07.008.

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