



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.

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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 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 countries. 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

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