Temporal assessment of copper speciation, bioavailability and toxicity in UK freshwaters using chemical equilibrium and biotic ligand models: Implications for compliance with copper environmental quality standards
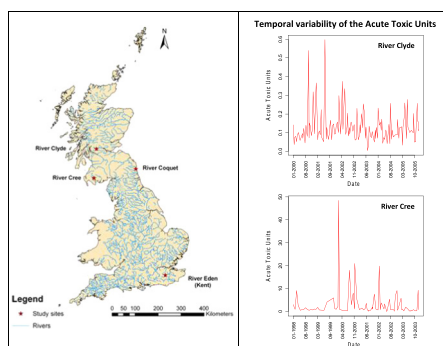
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HIGHLIGHTS

- Temporal/seasonal variations of water quality parameters may influence EQS compliance.
- Sensitive site or catchment specific EQS is important in assessing aquatic metal toxicity.
- EQS compliance evaluation for sensitive sites requires more intense sampling.

GRAPHICAL ABSTRACT

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Although significant progress has been made in understanding how environmental factors modify the speciation, bioavailability and toxicity of metals such as copper in aquatic environments, the current methods used to establish water quality standards do not necessarily consider the different geological and geochemical characteristics of a given site and the factors that affect copper fate, bioavailability potential and toxicity. In addition, the temporal variation in the concentration and bioavailable metal fraction is also important in freshwater systems. The work presented in this paper illustrates the temporal and seasonal variability of a range of water quality parameters, and Cu speciation, bioavailability and toxicity at four freshwaters sites in the UK. Rivers Coquet, Cree, Lower Clyde and Eden (Kent) were selected to cover a broad range of different geochemical environments and site characteristics. The monitoring data used covered a period of around six years at almost monthly intervals. Chemical equilibrium modelling was used to study temporal variations in Cu speciation and was combined with acute toxicity modelling to assess Cu bioavailability for two aquatic species, *Daphnia magna* and *Daphnia pulex*. The estimated copper bioavailability, toxicity levels and the corresponding ecosystem risks were analysed in relation to key water quality parameters (alkalinity, pH and DOC). Although copper concentrations did not vary much during the sampling period or between the seasons at the different sites; copper bioavailability varied markedly. In addition, through the chronic-Cu BLM-based on the voluntary risk assessment approach, the potential environmental risk in terms of the chronic toxicity was assessed. A much higher likelihood of toxicity effects

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was found during the cold period at all sites. It is suggested that besides the metal (copper) concentration in the surface water environment, the variability and seasonality of other important water quality parameters should be considered in setting appropriately protective environmental quality standards for metals.

1. Introduction

The concentration of metals and their compounds in fresh aquatic systems can vary significantly temporally and spatially, either naturally or also due to human interventions. Metal chemical forms and distribution control their mobility, bioavailability and subsequent potential for toxicity which, in turn, dictates surface water quality. Copper has received special attention in environmental regulation since it is an essential micronutrient for biological processes, which may also have adverse effects when present in excess.

Environmental regulations such as the EU Water Framework Directive (WFD) (2000/60/EC) aim to achieve good chemical and ecological status of surface water systems (EC, 2000a) using, amongst other instruments, environmental quality standards (EQS) to manage the presence of metals in the environment. The EQS of a particular pollutant or group of pollutants is defined as the level that should not be exceeded in order to protect human health and not to affect the structure and function of the aquatic environment (Janssen et al., 2000).

The early EQS values for metals, with the exception of Fe, were based on their dissolved concentrations; which did not reflect whether metals were in potentially bioavailable forms, or the seasonal variability that would affect metal bioavailability and likely toxicity over time. On the other hand, the revised Priority Substances Daughter Directive (2013/39/EU) includes annual average EQS values for nickel (4 µg l^{-1}) and lead (1.2 µg l^{-1}) that refer to their bioavailable concentrations. In the UK, the implementation of a bioavailability/DOC adjustment-based EQS for metals that are considered to be specific pollutants applies for copper (1 µg l^{-1} bioavailable Cu), zinc (10.9 µg l^{-1} bioavailable Zn) and manganese (123 µg l^{-1} bioavailable Mn) (WFD-UKTAG, 2014). Recent literature (WFD-UKTAG, 2012, 2013) has also recognised the value of adopting a bioavailability-based approach and indicates that regulatory organisations are now considering how best to account for the regional and local characteristics of surface water systems in setting EQS values. This has led to the development of several chronic biotic ligand models (BLM) that enable predicting chronic toxicity for copper, zinc (Heijerick et al., 2005; De Schamphelaere et al., 2005), lead (Nys et al., 2014) and nickel, as a function of surface water chemistry at multiple trophic levels: algae, daphnids and fish, considering a species sensitivity distribution (SSD). In addition, in order to facilitate regulatory application, user-friendly bioavailability tools have been developed to calculate the bioavailable metal concentrations for copper, zinc, nickel and manganese. In a recent publication by Arche et al. (2014), a lead-BLM-SSD-normalisation tool using a bioavailability-based approach with a species sensitivity distribution for assessing the long term hazard concentration of lead in the freshwater aquatic environment has been developed.

In addition, there are acute BLMs available for several trace elements, including copper, lead, zinc, silver and nickel. Importantly, these have mostly been developed in North America, using ecotoxicity data that fulfil USEPA Water Quality Guideline requirements (e.g. USEPA, 1996). These tend to differ from the requirements of an EQS under the WFD, particularly in relation to the taxonomic breadth of data, as they use only one trophic level. However, of great importance is the fact that in order to implement an acute bioavailable approach there is a need to derive a maximum allowable concentration considering bioavailability (MAC$_{bioavailable}$). Currently, MAC$_{bioavailable}$ values have not been derived under the WFD (Bio-met, 2014) and it is a fact that in Europe chronic BLMs have received more regulatory attention than acute models.

On the other hand, the importance and implications of the temporal variability of water quality parameters on metal bioavailability and

toxicity for the derivation of EQS has not been so far well reported. For the Cu EQS assessment through the application of a tiered-risk based approach, when no annual data was available, a lower quartile of 25% of default concentrations was used (WFD-UKTAG, 2012; Bio-met, 2014) in order to provide a precautionary, indicative compliance assessment, accounting for bioavailability. This approach gives a summary of measured data with its spread around the mean value over a year and provides a relatively conservative assessment of the EQS without considering seasonality and temporal variability in detail. The work presented here highlights the importance of local conditions and accounting for seasonal effects (temporal differences) in the bioavailable metal fractions through a systematic evaluation of four river systems in the UK (Coquet, Lower Clyde, Cree, and Eden in Kent) which exhibit markedly different geochemical characteristics.

Many biotic and abiotic factors in aquatic systems determine the amount of metal that interacts at biological surfaces and subsequently being taken up (Luoma, 1983; Allen, 2000). Water pH affects the toxicity of metals to freshwater biota although a relationship between the two has been difficult to establish. Some authors have shown an increase in metal toxicity with decreasing pH, due to an increased predominance of the free metal ion (De Schamphelaere and Janssen, 2004b); conversely other studies have shown the opposite as a consequence of reduced metal uptake due to competition with H$^+$ at cell surfaces (Janssen et al., 2003; Heijerick et al., 2002). Natural DOC, in the form of fulvic and humic acids, is an important complexing agent for copper in aquatic systems (Tipping et al., 2002) shown to have a protective effect in freshwater through reducing the chemical activity of the free metal concentration (De Schamphelaere and Janssen, 2004b; Heijerick et al., 2002). Many of the studies that have determined the toxicity of metals to freshwater biota have confounded the effects of water hardness with alkalinity and pH because an increase in calcium and/or magnesium concentration is frequently associated with an increase in alkalinity and therefore pH. However, it is important to separate the effects of water hardness and alkalinity because each variable has a different mechanism of reducing metal toxicity. Although the effect of water hardness is a function of competitively inhibiting metal uptake and hence toxicity for sensitive receptors (Heijerick et al., 2002), alkalinity directly affects metal speciation in solution through complexation with carbonate and bicarbonate ions, which reduce the free aqueous activity and thereby reduce metal bioavailability (De Schamphelaere and Janssen, 2002). It is generally accepted that neither the total nor the dissolved copper concentration in surface waters accurately represent the bioavailable metal fraction (Allen and Hansen, 1996). Rather, the activity or the free hydrated cupric ion [Cu^{2+}] is considered to be the most toxic form of this metal. Previous EQS derivations under the Dangerous Substances Directive (DSD) approach for several cationic metals (including copper and zinc) have been expressed as a function of water hardness to address the combined effect of certain cations (principally calcium and magnesium) on toxicity. It was later recognised by the US. EPA (US.EPA, 1992) that hardness was not the sole contributor to biological protection from metals exposure; and factors such as DOC, pH, alkalinity further modified the toxicity of metals and therefore needed attention for the development of predictive water-quality models.

It is rather difficult to measure the bioavailable concentration of a metal directly, so the use of appropriate models to predict the bioavailable concentration from the dissolved concentrations is attractive. The Biotic Ligand Models (BLM) incorporate elements from classic models but address the level of metal accumulation on the physiological active site of toxic action (Di Toro et al., 2001; Santore et al., 2001). The use of the BLMs in assessments of metal EQS compliance offers a more