Water Quality Benchmarks, the Modifying Effect of Organic Matter on Uranium Toxicity and Why this Matters

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Abstract

The 2011 Canadian uranium water quality guidelines (CWQGs) do not consider toxicity modifying factors. However, more recent data than considered in those CWQGs provide further evidence that dissolved organic carbon (DOC) reduces uranium bioavailability and toxicity. Determinations of site-specific uranium water quality benchmarks must consider the modifying effects of DOC as well as other factors including hardness and pH; when predictions of uranium toxicity based on water quality parameters are possible, the uranium CWQGs will need to be revised. The modifying effects of DOC (and other key physico-chemical variables) have implications for regulatory permitting, effluent management or treatment, and decommissioning.

1. Introduction

Uranium, atomic number 92, is a metallic element in the actinide series of the periodic table that has weakly radioactive isotopes. The primary concern for uranium in the aquatic environment is not radioactivity but rather possible chemical toxicity [1], which is primarily a function of exposure water quality and feeding regime as well as exposure duration [2].

The Canadian Council of Ministers of the Environment (CCME) in 2011 [3] published generic Canadian water quality guidelines (CWQGs) that are intended to provide a conservative level of protection from uranium chemical toxicity to all regions of Canada and all aquatic organisms in those regions of Canada. Specifically, as noted in the document [3 (page 1)], "when ambient concentrations are below the CWQG, adverse effects are not expected to occur in the aquatic environment."

The 2011 uranium CWQGs were derived following a protocol developed by CCME in 2007 [4]. This protocol notes (page I-2) "In the derivation of the guideline value, the influence of exposure and toxicity-modifying factors (ETMFs) (such as pH, temperature, hardness [Ca, Mg], organic matter, oxygen, other substances) is incorporated to the extent possible, provided that the scientific information to do so is available". ETMFs were not considered in the 2011 CWQG for uranium; however, new information suggests that they should be in future and should certainly be considered for the development of site-specific benchmarks. This paper briefly reviews the available evidence in support of this contention, using organic carbon as an example, and answers the "So what?" question for why this matters (see Section 4, below).

2. Evidence for Organic Matter as an ETMF in the 2011 CWQG Document

The CCME 2011 CWQG document [3] notes that abiotic conditions (page x) "such as pH, hardness, alkalinity and natural organic matter" influence uranium bioavailability and toxicity. However, it is also noted (page xi) "No quantitative relationship could be established between any of these factors and the toxicity of uranium, so no modifications or adjustments were made to the data."

Section 8.14 (pages 21-22) of the CWQG document [3] states, "NOM [natural organic matter] has the potential to bind the toxic (free ion) forms of a metal and hence reduce toxicity." Two studies are cited as indicating that an increase in NOM can decrease uranium toxicity [5,6]. However, it is concluded that this is not enough information "to reliably adjust or normalize toxicity data for this variable", and that one of the studies involved a freshwater bivalve not native to Canada with testing performed at a higher temperature than found in Canadian waters. Thus the CWQG for uranium is presently not adjusted for NOM.

3. Other Evidence for Organic Matter as a Uranium ETMF

A publication cited in the CWQG document but not relative to ETMFs provides additional evidence for the role of organic matter (and other factors) in modifying uranium bioavailability and toxicity. This publication [7] comprises a review of available information, which concludes that there is reasonable evidence to indicate that uranium bioavailability is reduced by complexation with organic compounds, such as humic substances (e.g., uranyl fulvate), as well as inorganic ligands (e.g., uranyl carbonate or uranyl phosphate).

The effectiveness of dissolved organic carbon (DOC) at complexing uranium is well documented [8,9]. Three recent publications from Australia [10,11,12] provide convincing evidence that DOC reduces uranium bioavailability and toxicity in freshwater aquatic environments primarily due to a decrease in the free uranyl ion (UO_2^{2+}) through complexation with DOC. These studies assessed three Australian tropical freshwater species (a fish, a hydra, and a green alga), and an ubiquitous Euglena. Uranium toxicity was decreased by up to 20-fold with 20 mg/L DOC compared to DOC-free test waters.

Predictive models were developed for each of these test organisms that can be used to predict uranium toxicity at a given uranium and DOC concentration. The importance of site-specific characterization of DOC was emphasized, as DOC from different sources may differ in its composition and/or capacity to bind uranium or other metals (e.g., differences in proportions and types of fulvic and humic acids).

Data demonstrating that DOC reduces uranium toxicity are now available for 5 Australian freshwater species; reanalyses of 46 existing toxicity data sets indicate that toxicity is reduced by about 5-10% per mg/L of DOC [13]. In Australia, water quality benchmarks for uranium are being revised and will likely consider the modifying effect of DOC per the formula: DOC-modified WQG = WQG + (WQG[DOC*slope]) [13]; there is no reason this cannot also be done in Canada.

4. So What?

So why is it important that the bioavailability and toxicity of uranium can be reduced by DOC? Because natural waters typically contain varying levels of DOC and this will affect the concentrations at which uranium will be toxic. The CWQGs, which do not consider the modifying effects of DOC, provide two types of information: (i) measured concentrations below the CWQGs indicate no reasonable possibility of bioavailability or toxicity; and, (ii) measured concentrations above the CWQGs indicate the possibility, <u>not the probability</u>, of bioavailability and toxicity. The more DOC in an aquatic ecosystem, the higher measured uranium water concentrations have to be above the CWQG for bioavailability and toxicity to be possible.

If CWQGs are exceeded, then site-specific benchmarks can be set taking into account the DOC in the receiving waters. This principle also applies to other key water quality variables that have been shown to affect uranium bioavailability and toxicity (e.g., pH, hardness; [2,14]). These answers to the “So what?” question have implications for regulatory permitting, effluent management or treatment, and decommissioning.

5. Conclusions and Recommendations

Because ETMFs such as DOC are not incorporated into the CWQG for uranium, this benchmark is almost certainly overly conservative. Thus, exceedances must be treated with caution since they do not definitively indicate that toxicity will occur under site-specific conditions. As noted in [4] (2007; Part II, Section 2-1) “incorporation of ETMFs will result in a range of situation-specific guidelines”. As emphasized by Cheng et al. [2], site-specific conditions need to be not only considered when evaluating potential for uranium chemical toxicity, but (page 8) “it is imperative that we continue to improve our understanding of the factors influencing the speciation, bioavailability and toxicity of U in the aquatic environment.” Such studies in Canadian waters with Canadian species are notable by their absence; they should not be – this is a major future research imperative.

Another major future research imperative is extension of the biotic ligand model (BLM) to predict acute and chronic uranium toxicity in freshwaters based on water chemistry and considering dietary exposure [15]. Previous studies have noted the to-date unrealized potential of the BLM to describe uranium toxicity [16,17]. Given that uranium is a metal and that the importance of water chemistry in controlling bioavailability and toxicity of metals is well recognized [18-20], the modifying effects of DOC (in addition to other factors such as pH, hardness) should not be overlooked and should be considered in developing site-specific water quality benchmarks

6. References

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