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# Uranium dispersion from U tailings and mechanisms leading to U accumulation in sediments: Insights from biogeochemical and isotopic approaches

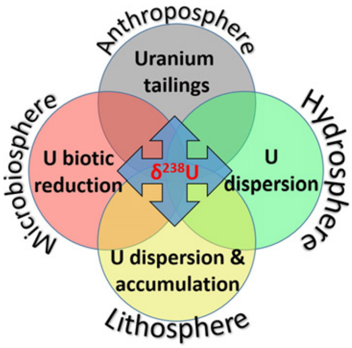
Duc Huy Dang [a],*, Wei Wang [a], Philip Pelletier [b], Alexandre J. Poulain [b], R. Douglas Evans [a,c]

[a] School of the Environment, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada
[b] Biology Department, University of Ottawa, 30 Marie Curie, Ottawa, ON K1N 6N5, Canada
[c] Water Quality Center, Trent University, 1600 West Bank Drive, Peterborough, ON K9L 0G2, Canada

## HIGHLIGHTS

- Application of radiogenic isotopes (U-Pb) for age dating of ore deposit
- Model of U-Pb isotopes for identification of U accumulation mechanisms
- Uranium accumulation by dispersion of tailings, biotic reduction and adsorption
- Bioavailable organic matter as the driving force of U biotic reduction
- Microbial abundance reveals role of specific bacteria in U sedimentary accumulation

## GRAPHICAL ABSTRACT



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## ABSTRACT

Uranium contamination is a worldwide problem that grows proportionally to human demands for energy and armory. Understanding U cycling in the environment is of eminent interest, mostly concerning ecosystems directly impacted by point sources. In Bow Lake (Ontario, Canada), which is located adjacent to a former U mine, exceptionally high concentrations of U are related to U dispersion from tailings and biogeochemical processes such as biotic reduction and adsorption. This has been shown by a U-Pb isotope composition model. In this study, we use U isotope fractionation ($\delta^{238}U$) to highlight U cycling and the role of bacteria (*Geobacteraceae* and sulfate-reducing bacteria) in affecting U cycling. Bacteria affected U cycling directly via biotic U reduction and indirectly via reductive dissolution of carrier phases. All the processes are interconnected through diagenetic reactions with the supply of bioavailable organic matter being the primary driving force of the diagenesis. This study is the first to use multiple biogeochemical and isotopic approaches to track U cycling from a contamination point source to U storage in lake sediments.

## 1. Introduction

Uranium contamination of natural ecosystems is a serious and growing problem as a result of increasing demands for U for various modern applications (e.g., power generation, atomic and depleted U weapons).

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* Corresponding author.
*E-mail address:* huydang@trentu.ca (D.H. Dang).

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More than 4300 mines around the world have generated a billion cubic meters of tailings, leading to potential radiation hazards and contamination of surrounding environments by multiple toxic elements (Abdelouas, 2006). The use of depleted U in military purposes has also led to contamination of specific sites (weapons testing sites, war fields) (Oliver et al., 2007). While the extraction and use of U has the potential for its dispersion in the environment, some biogeochemical processes, including (bio)adsorption, (bio)precipitation and (bio)reduction, can restrict U mobilization in surface/ground waters and aquifer sediments (Bopp et al., 2010; Finneran et al., 2002; Mkandawire, 2013; Newsome et al., 2014; Stylo et al., 2015; Wall and Krumholz, 2006). These processes have been used for in situ remediation of U contamination, mostly by biotic reduction (Alessi et al., 2014; Bopp et al., 2010; Boyanov et al., 2011). For this purpose, electron-donors, such as ethanol, lactate, or short-chain fatty acids (SCFAs: formate, acetate, proprionate, butyrate), are often added to stimulate bacterial activity (Anderson et al., 2003; Bopp et al., 2010; Holmes et al., 2002; Lovley et al., 1993; Tokunaga et al., 2008). In natural environments, these bioavailable molecules are by-products of hydrolytic and fermentative breakdown of natural organic matter (OM) by specific bacteria (e.g., *Clostridium* and *Bacillus* spp.). Hence, metal- and sulfur-reducing bacteria (e.g., *Geobacter*, *Shewanella* and *Desulfovibrio* spp.) couple the oxidation of these fermentative products to reduce metals and sulfate. Several bacteria have been reported to have the capacity to reduce U(VI) to U(IV), e.g., *Desulfovibrio*, *Geobacter*, *Pseudomonas* and *Salmonella*, *Shewanella* spp. (Wall and Krumholz, 2006 and references therein), all of which are anaerobes.

Organic matter plays a major role in the control of bacterial growth and subsequent metal immobilization. The fraction of the OM that can be easily used by soil and sediment microorganisms consists of dissolved OM or leachable particulate OM (or labile OM) (Guigue et al., 2015; Strosser, 2010). It is generally accepted that OM availability to heterotrophic bacteria depends on the OM composition and molecular size as well as the OM origin; the decomposition rate of phytoplankton-derived OM is faster than other OM compounds (Amon and Benner, 1996). Bacterial growth efficiency is also greater with low-molecular-weight (LMW) OM than high-molecular-weight (HMW) OM (Amon and Benner, 1996). A simple method to extract this bioavailable OM pool uses hot water; the extracted OM can then be characterized by mass spectroscopy (Oni et al., 2015; Schmidt et al., 2014).

Five uranium isotopes have half-lives longer than $10^5$ years, but $^{235}$U and $^{238}$U are the most common isotopes with the longest half-lives. $^{232}$Th, $^{235}$U and $^{238}$U decay to $^{208}$Pb, $^{207}$Pb and $^{206}$Pb, respectively and changes in isotopic ratios of parents/daughters allow age determination of geological materials (Holmes, 1911). Recent instrumental developments allow determination of U isotopic composition which has been used previously as a paleo-proxy in rocks, shales, modern and ancient sediments, ferro/manganese crusts and nodules (Goto et al., 2014; Kendall et al., 2013; Romaniello et al., 2013; Weyer et al., 2008) and also as a technique to monitor U mobility in various environments: ground waters (Murphy et al., 2014; Shiel et al., 2013), fjords (Holmden et al., 2015; Noordmann et al., 2015), seawater (Andersen et al., 2016; Noordmann et al., 2015; Rolison et al., 2017). Uranium isotope composition ($\delta^{238}$U) has been used as well to assess U removal during remediation operations (Bopp et al., 2010; Stylo et al., 2015). Both abiotic and biotic reduction leads to U immobilization but it seems that only enzymatic reduction results in U isotopic fractionation (Stirling et al., 2007; Stylo et al., 2015). For the two most abundant U isotopes, U(VI)-to-U(IV) reduction leads to a preferential accumulation of the heavier $^{238}$U in the reduced species (Bigeleisen, 1996; Dang et al., 2016; Moynier et al., 2013; Noordmann et al., 2015; Stirling et al., 2007; Weyer et al., 2008) while adsorption on Mn/Fe oxides tends to preferentially scavenge the lighter $^{235}$U onto adsorbent surfaces (Brennecka et al., 2011; Dang et al., 2016; Goto et al., 2014).

In ecosystems directly impacted by pollution sources (e.g., air, soils, surface and ground waters in the vicinity of point sources from mining sites and tailings), it is essential to keep track of pollutant dispersion and the biogeochemical mechanisms controlling pollutant cycling. The potential to use U isotope compositions to track sources and processes controlling U mobility is promising but requires extreme care due to potentially variable isotope fractionation (Dang et al., 2016) of the possible sources of U each of which could have different initial isotopic compositions (i.e., geological background vs. enriched ore bodies (Varga et al., 2009)). Therefore, multiple approaches are required to explore the environmental consequences of U mining, to contribute to the understanding of U cycling and to provide a novel isotopic methodology to track U sources and processes controlling U mobility. This study focuses on Bow Lake (Ontario, Canada) and examines the biogeochemical processes controlling U dispersion from a U mining site to the lake water and sediments using (i) geochemical characterization, (ii) isotope composition of C, N, Pb and U, (iii) molecular analysis of labile and bioavailable OM and (iv) DNA extraction and bacterial functional gene quantification.

## 2. Materials and methods

### 2.1. Study site

Bow Lake (45°00′50″N, 77°56′20″W) is located in Hastings County, Ontario, Canada. The lake is small and narrow with a long fetch and an approximate length of 3 km and a maximum depth of 13 m (Kraemer and Evans, 2012). Located on the northeastern side of the lake (Fig. 1) is the site of the Madawaska Mine (formerly Faraday Mine) operated in the mid-1950s to mid-1960s and from 1976 to 1982 (Ontario Ministry of the Environment, 2003). Since the cessation of mining and milling operations, monitoring of catchment discharge indicated elevated concentrations of $^{226}$Ra and U run-off/leaching from the site and mobilization of metals from the sediments (Ontario Ministry of the Environment, 2003). Several decades after the mine closure, U remains bioavailable in Bow Lake as high U concentrations in biota (fish, invertebrates, and zooplankton) have been recorded (Kraemer and Evans, 2012). The geological background of the Bow Lake area is mainly Precambrian bedrock, glaciofluvial outwash and deltaic deposits (Barnett, 1985). The ore minerals from the Madawaska Mine are predominantly uraninite-uranothorite with a U/Th ratio of approximately 2 (Bedell and Schwerdtner, 1981). The metals are confined to the pegmatite whose formation (fractional crystallization of magma) dates from the Precambrian Eon (Mesoproterozoic era) (Masson and Gordon, 1979). The ore grade averaged 0.07–1% $U_3O_8$ (Bedell and Schwerdtner, 1981).

The Bow Lake water column has shown a seasonal redox stratification (Ontario Ministry of the Environment, 2003); higher U, Mn and Fe concentrations were found in bottom water than in surface water, such stratification was more noticed in the east side than in the midst of the lake and diminishes with turnover in the fall.

### 2.2. Sampling and sample preparation

Sediments from the middle of Bow Lake (hereafter referred to as 'pelagic sediment samples') were collected using an Ekman grab at 10 locations along the lake (Fig. 1). Sub-samples of the sediments were immediately transferred to 150-mL HPDE bottles, tightly closed and stored in a cooler for transport to the lab. At the same time, surface water samples were also collected at each location using clean 500-mL HDPE bottles that had been previously soaked with 1 M $HNO_3$, rinsed twice with 18 MΩ water in the lab and with lake water several times in the field. Shoreline sediments (6 sites, sampled along the lake shore, hereafter referred to as 'littoral sediment samples') and 'soil samples' (6 sites) were collected with a steel shovel. These samples were treated in the same way as the pelagic sediments.

Within a few hours after sampling, all water samples were filtered (0.2 μm, Nylon filter, Sartorius) then acidified ($HNO_3$, 0.2% v/v), and the sediments were freeze-dried. The certified reference uranium