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Toxicity of aqueous vanadium to zooplankton and phytoplankton species of relevance to the athabasca oil sands region

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ABSTRACT

Vanadium (V) is an abundant trace metal present in bitumen from the Athabasca Oil Sands (AOS) region in Alberta, Canada. The upgrading of bitumen can result in the production of large volumes of a carbonaceous material referred to as petroleum coke that contains V at elevated levels compared to the native bitumen. Previous studies have shown that coke has the capacity to leach ecotoxicologically relevant levels of V into water it contacts, yet limited data are available on the toxicity of aqueous V to planktonic organisms. Therefore, this study set out to evaluate the acute and chronic toxicity of V (as vanadate oxyanions) to freshwater zooplankton and phytoplankton species that are either commonly-used laboratory species, or species more regionally-representative of northern Alberta. Four cladoceran (2-d and 21-d tests) and two algal (3-d tests) species were exposed to V to obtain both acute and chronic toxicity estimates. Acute V toxicity (LC50s) ranged from 0.60 mg V/L for *Ceriodaphnia quadrangula* to 2.17 mg V/L for *Daphnia pulex*. Chronic toxicity estimates (EC50s) for cladoceran survival and reproduction were nearly identical within species and ranged from a low of 0.13 to a high of 0.46 mg V/L for *Daphnia dentifera* and *D. pulex*, respectively. The lack of sublethal V toxicity in daphnia suggests a direct mechanism of toxicity through ion imbalance. Growth inhibition (EC50) of green algae occurred at concentrations of 3.24 and 4.12 mg V/L for *Pseudokirchneriella subcapitata* and *Scenedesmus quadricauda*, respectively. Overall, cladocerans were more sensitive to V than green algae, with survival of the field-collected *D. dentifera* being approximately 2.5 to 3.5 times more sensitive to acute and chronic V exposure than the standard test species *D. pulex*. However, there were no significant differences in V toxicity between the field-collected cladocerans *Simocephalus serrulatus* and *C. quadrangula*, compared to the respective standard species *D. pulex* and *Ceriodaphnia dubia*. Similarly, there were no significant differences in sensitivity to V in the two algal species evaluated. Based on V concentrations reported in laboratory-generated coke leachates, zooplankton survival could be adversely impacted under conditions of chronic leachate exposure if V concentrations in the environment exceed 0.1 mg/L. Furthermore, toxicity thresholds from commonly-used planktonic test species would likely have sufficed for derivation of a V water quality guideline (WQG) for protection of local aquatic communities near oil sands operations, but the new data presented here on V toxicity to more regionally-representative species will strengthen the database for WQG derivation.

1. Introduction

The Canadian oil sands, located in northern Alberta, rank third globally in terms of proven oil reserves, following only behind Saudi Arabia and Venezuela (Allen, 2008; National Energy Board, 2013). Within this area, the Athabasca Oil Sands (AOS) region is the largest of three bitumen deposits in Alberta and has been estimated to contain 170 billion barrels of bitumen, a viscous hydrocarbon (Allen, 2008). The Alberta Energy Regulator (AER) predicts continued growth in bitumen production over the next decade (AER, 2015). The bitumen extraction and upgrading processes used by some oil sands companies produce large volumes of liquid and solid by-products, predominately in the form of oil sands process-affected water (OSPW) and petroleum coke (Allen, 2008; AER, 2015; Scott and Fedorak, 2004). Following a no-release practice, substantial amounts of these products have been accumulating on-site of some oil sands companies and their eventual reclamation and/or utilization are of importance to the industry.

Syncrude Canada Ltd. (SCL) upgrades bitumen to a lighter more valuable synthetic crude oil through the operation of three fluid cokers. Fluid coking uses high temperatures to increase the hydrogen to carbon

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(H:C) ratio of bitumen through the removal of carbon (Zubot et al., 2012). Annually, SCL can generate up to 2 million tons of coke, with an overall coke production across the entire oil sands industry reaching 90 million tons at the end of 2014 (Alberta Energy Regulator, 2015; Fedorak and Coy, 2006; Scott and Fedorak, 2004). Currently, operators are required to store petroleum coke on-site because it is viewed as a potential future energy resource, similar to medium grade coal (Baker, 2007; Fedorak and Coy, 2006). However, coke impurities such as high sulfur content (6–7 wt%), low combustibility and availability of cheaper energy sources, prevent its current use (Furimsky, 1998; Scott and Fedorak, 2004; Small et al., 2012a). With the vast volumes of coke being produced, some companies may eventually face challenges with available storage capacity. Initially, oil sands coke was thought to be biologically inert, however, recent studies have found coke to affect microbial processes and to leach certain metals (e.g., V, Ni, Cu, Mn, and Mo) when it is exposed to water and weathering processes (Fedorak and Coy, 2006; Puttaswamy et al., 2010; Squires, 2005).

Treatment approaches to mitigate OSPW toxicity have been directed at removing the bitumen-derived organic fractions, including naphthenic acids (NAs) and other acid-extractable organic compounds that are mostly responsible for toxicity. Chemical oxidation of NAs in OSPW by ozone effectively removes up to 95% of the NAs and attenuates OSPW toxicity to *Vibrio fischeri* and *Chironomus dilutus*, as well as reduces steroidogenic effects in human cell lines (Anderson et al., 2012; Gamal El-Din et al., 2011; He et al., 2010; Scott et al., 2008). However, full-scale treatment of the approximately 1 billion m^3 of OSPW stored on-site at the AOS may be impractical (Scott et al., 2008). Consequently, activated carbon (AC) has also been investigated as a treatment option for OSPW, but it too would be expensive to obtain and use on an industrial scale of this magnitude (Small et al., 2012a, 2012b). Therefore, petroleum coke, which is high in carbon (> 80 wt%) and available in large supply on-site, has been proposed as an option to treat OSPW in an engineered facility (Small et al., 2012a; Zubot et al., 2012). In appropriate applications, petroleum coke can remove complex organic compounds with higher molecular weight and low solubility from OSPW resulting in a reduction in acute toxicity over a shorter time frame than untreated OSPW (Gamal El-Din et al., 2011; Pourrezaei et al., 2014a, 2014b; Small et al., 2012a, 2012b; Zubot et al., 2012).

While most metals do not appreciably leach into water that is in contact with coke, increased concentrations of V have been observed in coke leachates and coke-treated OSPW (Small et al., 2012a, 2012b; Puttaswamy et al., 2010; Squires, 2005). However, Zubot (2011) reported that leached V will decline with prolonged coke-water residence times due to predicted adsorption of V onto metal hydroxides that will be present within saturated coke deposits. The V leached from coke is primarily V(V) which is favored under the more alkaline pH conditions of OSPW (pH 8–9). The presence of V in petroleum coke is not surprising given it is a highly abundant trace metal in crude oil where it forms organic porphyrin complexes. Bitumen from the AOS contains one of the greatest concentrations of V in the world, an estimated 220 mg/kg (Moskalyk and Alfantazi, 2003; Ventura et al., 2015; Zubot et al., 2012). When bitumen is upgraded, V is removed and enriched into coke at concentrations of up to 1226 mg/kg, therefore making it the most elevated metal in coke (Zubot et al., 2012). Several studies have documented the leaching of coke upon contact with water, potentially generating ecotoxicologically relevant V concentrations (Puttaswamy et al., 2010; Puttaswamy and Liber, 2011; Small et al., 2012b; Squires, 2005; Zubot et al., 2012). For example, V can be released into leachates at concentrations greater than the 7-d median lethal concentration (LC50) for the aquatic invertebrate, *Ceriodaphnia dubia* (Puttaswamy et al., 2010). In addition, the amount of V that leached from coke in an 18-month lysimeter study resulted in V concentrations > 1000 µg/L (Puttaswamy et al., 2010). Typically, median background levels of aqueous V in freshwater ecosystems are reported within the range of 0.5–2.4 µg/L (Hirayama et al., 1992; Rehder, 1992).

The release of V from petroleum coke suggests that coke leachates could expose aquatic ecosystems of northern Alberta to relatively high concentrations of V, depending on how the coke leachate is generated, stored and handled prior to discharge. However, the limited V toxicity data available in the peer-reviewed literature presently prevents the development of appropriate water quality guidelines (WQGs) for the protection of aquatic life. Furthermore, future development of site-specific guidelines or objectives for V will become a priority if oil sands companies want to discharge process water containing V into the natural aquatic ecosystems of northern Alberta. To address this data gap, this study set out to characterize the acute and chronic toxicity of V to freshwater planktonic organisms for which limited data were available. In addition, the study aimed to determine whether species more regionally representative of northern Alberta were more or less sensitive to V than more conventional (standard) test species. These data will be useful to assess the ecological risks that V in Syncrude coke leachates would pose to the biota in receiving environments of the AOS region.

2. Materials and methods

2.1. Source and culturing of test organisms

Standard test organisms, *Daphnia pulex* and *Pseudokirchneriella subcapitata*, were obtained from in-house cultures maintained at the Toxicology Centre, University of Saskatchewan (U of S), Saskatoon, SK, Canada. Culturing procedures followed general guidelines described elsewhere (Environment Canada, 1990a, 1992a). Daphnids were maintained in groups of 25–30 adults in 2-L glass jars in environmental chambers at 23 ± 1 °C under a 16:8 h light: dark photoperiod. Water renewals occurred three times weekly and daphnids were fed a daily diet of green algae, *P. subcapitata*. Regionally-relevant test species were either collected from a reference pond on Syncrude's mine site or were purchased based on species most representative of the region. Field-collected zooplankton from Syncrude's Test Pond 1 included *Daphnia dentifera, Simocephalus serrulatus* and *Ceriodaphnia quadrangula*. The green algae, *Scenedesmus quadricauda*, was identified as a regionally-representative green algal species based on its reported presence and abundance in a local reference lake, Mildred Lake (Hayes, 2006). This alga was purchased from the Canadian Phycological Culture Centre (CPCC) at the University of Waterloo, ON, Canada. Stock cultures were incubated on a rotary shaker at 100 rpm in an environmental chamber at 24 ± 1 °C under continuous lighting (3000–4000 lx) and maintained in log-phase growth in 1-L Erlenmeyer flasks containing 250 ml of axenic nutrient media (Environment Canada, 1992a).

2.2. Test material and dilution water

The test chemical, sodium metavanadate ($NaVO_3$, anhydrous, min. 96% pure), was obtained from Strem Chemicals Inc., Newburyport, MA, USA. Concentrated stock solutions were prepared for toxicity tests by dissolving sodium metavanadate in ultrapure water (Barnstead NANOpure, 18.2 MΩ-cm) in 1-L, acid-washed, glass volumetric flasks. Stock solutions were then diluted with appropriate volumes of dilution water to achieve the target V concentrations for the different treatments.

The dilution water used for all toxicity tests was reconstituted water prepared to mimic the general characteristics of the Athabasca River (ARW) in terms of conductivity, hardness, and alkalinity, based on field data from various local sampling sites generated by the Regional Aquatics Monitoring Program (RAMP, 2011). To achieve target values, carbon-filtered, bio-filtered municipal water from the City of Saskatoon, was diluted with approximately 30% reverse osmosis (RO) water. This water was then aerated for a minimum of 24 h prior