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Uranium theoretical speciation for drinking water from private drilled wells in Sweden – Implications for choice of removal method

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ABSTRACT

Elevated concentrations of uranium (U) from natural sources have been measured in drinking water from private drilled wells in Sweden and many other countries world-wide. Although U is a radioactive element, radioactivity is not the main concern, but rather chemical toxicity, e.g. kidney damage. Uranium chemistry is complex and U in water has a very high tendency to form complexes with other compounds. Since speciation is crucial for the properties of U, and therefore the removal efficiency, this study determined theoretical U species in drinking water from private drilled wells using the geochemical model Visual MINTEQ. The drinking water samples used in modelling were from two datasets: (1) 76 water samples selected from a previous survey of 722 wells; and (2) samples of drinking water from 21 private wells sampled in May 2013. The results showed that neutrally charged U complexes dominated in the pH range 6.7–7.8, which is common in private drilled wells. This has important implications for removal method, since charge is an important factor for U removal efficiency. In the alkaline pH range, one of two calcium-UO_2 carbonate complexes dominated and calcium (Ca) concentration proved to be a key factor determining the Ca-UO_2 carbonate complex formed: the neutral $Ca_2UO_2(CO_3)_3^0(aq)$ or the negative $CaUO_2(CO_3)_3^{2-}$. Complexes with organic carbon (C) varied greatly in the acidic range, indicating that it is crucial to measure organic C content in the water since it is critical for the dissolved organic matter (DOM)-UO_2 complex formation. Therefore before U removal method is selected, some crucial parameters for complex formation should be measured. Based on our results, such measurements should include pH, Ca, alkalinity and organic C concentration, as these determine the type of complexes formed and their charge.

1. Introduction

Elevated concentrations of uranium (U) have been measured in drinking water in several countries throughout the world (Kurttio et al., 2002; Orloff et al., 2004; Ek et al., 2008; Prat et al., 2009; Stalder et al., 2012). Uranium is a naturally occurring element in bedrock which is released to groundwater upon weathering of minerals. Uranium can also be enriched in groundwater from anthropogenic sources; from mill tailings of U mines, the use of depleted U for military devices (DU ammunition), or from phosphate fertilizers, which are often associated with U.

Uranium exists in five different oxidation states but only U(+IV) and U(+VI) are relevant for the groundwater. Uranium(+VI), which dominates in oxic conditions, is the mobile form of the element, while the reduced form U(+IV) precipitates as a solid phase, e.g. as uraninite (UO_2). Uranium can also be removed from the groundwater by sorption to solid surfaces in the subsurface environment. When dissolved in the aqueous phase, U(+VI) is commonly associated with oxygen in the uranyl ion (UO_2^{2+}), which has a high tendency to form complexes with other ions. The pH, proportion of complex-forming ions in the water and CO_2 pressure decide the type of complexes formed. Uranium chemistry is complicated, Langmuir (1978) identified 42 different aqueous species in thermodynamic calculations. Complexes with dissolved organic matter (DOM) and Ca-uranyl carbonate complexes were not considered in the calculations, but have recently been shown to be crucial for U speciation in water (Bernhard et al., 1996, 2001; Fox et al., 2006; Gustafsson et al., 2009; Prat et al., 2009). DOM-UO_2 complexes have been considered in some previous studies, but mainly in connection with U transport in the subsurface environment (Artinger et al., 2002; Ranville et al., 2007; Yang et al., 2012). These complexes are still omitted from many speciation calculations and are assumed to be of minor importance in the alkaline pH range (Fox et al., 2006; Ranville et al., 2007; Prat et al., 2009). However, Gustafsson et al. (2009) included dissolved organic C (DOC) in their simulation of U species and showed the

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dominance of DOM-UO_2 complexes at pH < 7.2 under atmospheric CO_2 pressure. When the partial CO_2 pressure (P_{CO2}) in that study was increased 10-fold, the pH threshold at which DOM-UO_2 complexes dominated decreased to 6.6, illustrating that carbonate species are stronger complex-forming ligands. The first studies to show evidence of the Ca-uranyl carbonate complexes were those by Bernhard et al. (1996, 2001), who used time-resolved-laser-induced fluorescent spectroscopy (TRLFS) to confirm the thermodynamic calculations. They found that the complexes $Ca_2UO_2(CO_3)_3^0$(aq) and $CaUO_2(CO_3)_3^{2-}$ influenced U speciation significantly in the pH rage 6–10 in calcium- and uranium-rich water, a finding later confirmed by others (Kalmykov and Choppin, 2000; Dong and Brooks, 2006; Fox et al., 2006; Geipel et al., 2008; Gustafsson et al., 2009; Prat et al., 2009). Moreover, Prat et al. (2009) suggested that these complexes could be less toxic than other species, since they found no clear association between chronic U exposure and cancer risk in studies of Finns using drinking water with high U concentrations obtained from drilled wells.

Around 1.2 million of the 9 million people in Sweden permanently use drinking water from private drilled wells and about the same numbers of people occasionally use private water supplies in their holiday cottage. In a study by the Swedish Geological Survey (SGU) and Swedish Radiation Safety Authority (SSM) which measured radioactive elements, fluoride (F) and selected metal in drinking water from 722 private drilled wells throughout Sweden, it was found that 17% of wells had U concentrations exceeding the recommended guideline value (Ek et al., 2008). The guideline defined by the Swedish Board of Health and Welfare is 15 $\mu g\,L^{-1}$ and this value was originally adopted by WHO, but the latter has recently increased its provisional guideline value to 30 $\mu g\,L^{-1}$ (WHO, 2004, 2011). This change has been criticised as failing to protect children, susceptible individuals and those with long-term exposure (Frisbie et al., 2013).

In contrast to users of municipal drinking water, households with private wells do not pay a fee for their water and are therefore responsible for checking water quality and for treatment of contaminated water. However, a recent survey showed that few well owners check their water quality every three years, as recommended by the Swedish Board of Health and Welfare (Karlsson, 2010). It is not the radioactive properties of U which are the major concern, but rather the chemical toxicity, e.g. damage to the kidneys (Kurttio et al., 2002; Svensson et al., 2005).

The objective of the present study was to estimate the U species in drinking water from private drilled wells using the geochemical model Visual MINTEQ, ver. 3.0 (Gustafsson et al., 2009). In general, previous studies have used synthetic water samples and have often not considered all relevant species in their speciation calculations. Only Prat et al. (2009) simulated drinking water, but the 10 water samples used in that study had pH > 7.9, whereas most drinking water from drilled wells in Sweden has a lower pH. A clear understanding of the U species occurring in drinking water is highly relevant in selecting treatment strategy for contaminated water and in risk assessments.

2. Materials and methods

2.1. Water samples

In the study, two datasets on water samples were evaluated for dominant U species: (1) selected wells sampled in the study by SGU/SSM (Ek et al., 2008) and (2) well water sampled in May 2013.

2.1.1. Water samples in dataset 1 – SGU/SSM survey

Of the 722 private wells sampled throughout Sweden in the SGU/SSM survey, 76 were selected for inclusion in simulations with the MINTEQ model. The selection criteria were for samples to have a minimum uranium concentration of 15 $\mu g\,L^{-1}$, i.e. the guideline value set by the Swedish Board of Health and Welfare for private wells, and analytical data on all elements of importance for U complex formation. All of the chemical compounds included in the model do not have significance for forming complexes with U, they were included for the reason of competition amongst the elements. One important chemical constituent that was not measured in the survey was total organic carbon (TOC) and therefore a concentration of 1 $mg\,L^{-1}$ was set for all samples. This low concentration can be expected in waters originating from Swedish bedrock and has been confirmed by measurements in drilled boreholes (Lindquist and Nilsson, 2010).

Before sampling, the water samples in the SGU/SSM survey were flushed for 15–60 min, depending on depth of the well, size of the pressure vessel and installation. The U concentration and other metals were analysed by ICP-MS in the laboratory at SGU on unfiltrated samples since it was the water quality at consumption that was of interest. The alkalinity was estimated by titration with 0.02 M HCl down to pH 5.4.

The concentrations of other elements were analysed at accredited laboratories by standard methods, as reported by Ek et al. (2008).

2.1.2. Water samples in dataset 2 – sampled in May 2013

The important parameter of TOC in the water was not measured for the samples in dataset 1 and therefore a new set of samples was collected within Siljansringen, in the county of Dalarna, in May 2013. This location was selected since the geology and U species vary within small distances in the area (Löv, 2012). A subset of 21 private drilled wells was selected from a list of 700 wells sampled in previous surveys by the County Board in Dalarna. All these wells had a U concentration that exceeded the guideline value in the previous surveys. Five had a filter installed for removal of radioactive elements and those wells were sampled before and after the filter. The sampling procedure and analytical methods were similar to those described above for dataset 1.

2.2. Uranium speciation

Uranium speciation was simulated with Visual MINTEQ 3.0, which was originally coded by the U.S. Environmental Protection Agency (EPA) and has been further developed by Gustafsson (2013). The formation constants used in the modelling were the default values given in Visual MINTEQ 3.0 (Table 1), which originate from Guillamont et al. (2003). The constants for the two Ca-uranyl carbonate complexes, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3^0$(aq), originate from Dong and Brooks (2006). For the speciation with organic matter, the Stockholm Humic Model (SHM) was used and 70% of the DOC was set as fulvic acid, a value used previously in groundwater chemistry modelling (Gustafsson et al., 2009).

Ionic strength was set to be calculated for each sample by the model from the measured concentrations of ions in the water. The partial CO_2 (pCO_2) pressure was set to atmospheric pressure (0.00038 atm), as it was assumed that equilibrium with the atmosphere was reached. However, since pCO_2 pressure is an important parameter in determining the U species formed, the simulation was also conducted at an eight-fold higher pCO_2 pressure for five samples with pH varying between 6.3 and 8.0. This higher pCO_2 pressure was a rough estimate of the pressure at a depth of around 70 m, which is the average depth of the wells studied.

For dataset 1, no information about the temperature was provided and therefore it was set to 5 °C, since this is the average groundwater temperature in Sweden. A sensitivity analysis by Löv (2012) showed that the temperature has very little effect on the U species formed in the temperature range commonly found