Weathering and evaporation controls on dissolved uranium concentrations in groundwater – A case study from northern Burundi

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HIGHLIGHTS

- Processes controlling the environmental mobility of uranium were investigated.
- Chemical and isotope data for lake, groundwater, and rainwater were collected.
- Data from north Burundi were quantitatively interpreted using a geochemical model.
- Rock weathering and evaporation are the main controls on solute concentrations.
- Groundwater radionuclide levels can reach harmful levels in discharge zones.

GRAPHICAL ABSTRACT
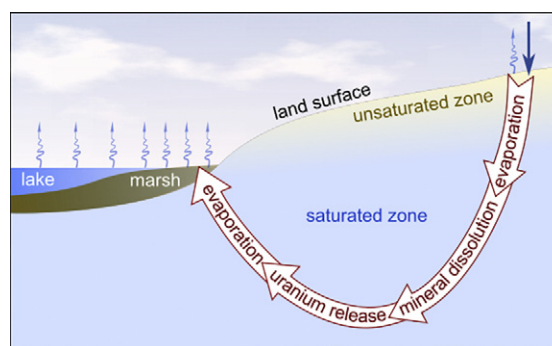
ARTICLE INFO

ABSTRACT

The potential use of groundwater for potable water supply can be severely compromised by natural contaminants such as uranium. The environmental mobility of uranium depends on a suite of factors including aquifer lithology, redox conditions, complexing agents, and hydrological processes. Uranium concentrations of up to 734 μg/L are found in groundwater in northern Burundi, and the objective of the present study was to identify the causes for these elevated concentrations. Based on a comprehensive data set of groundwater chemistry, geology, and hydrological measurements, it was found that the highest dissolved uranium concentrations in groundwater occur near the shores of Lake Tshohoha South and other smaller lakes nearby. A model is proposed in which weathering and evapotranspiration during groundwater recharge, flow and discharge exert the dominant controls on the groundwater chemical composition. Results of PHREEQC simulations quantitatively confirm this conceptual model and show that uranium mobilization followed by evapo-concentration is the most likely explanation for the high dissolved uranium concentrations observed. The uranium source is the granitic sand, which was found to have a mean elemental uranium content of 14 ppm, but the exact mobilization process could not be established. Uranium concentrations may further be controlled by adsorption, especially where calcium-uranyl carbonate complexes are present. Water and uranium mass balance calculations for Lake Tshohoha South are consistent with the inferred fluxes and show that high uranium groundwater represents only a minor fraction of the overall water input to the lake. These findings highlight that the evaporation effects that cause radionuclide concentrations to rise to harmful levels in groundwater discharge areas are not only confined to arid regions, and that this should be considered when selecting suitable locations for water supply wells.

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1. Introduction

Groundwater is often preferred over surface water as a source of potable water supply because of its favorable characteristics in terms of availability and bacteriological quality. However, the presence of natural contaminants is frequently a health risk that should be assessed in developing groundwater resources. In several cases, high natural contaminant levels have led to adverse health effects, and the arsenic problem in Bangladesh (Smedley and Kinniburgh, 2002) is probably the most well-known of these. Other elements, like fluorine, selenium, and uranium, often also occur in groundwater at concentrations above drinking water standards (Bailey et al., 2012; Ozsvath, 2009; Smedley et al., 2006). The latter is the focus of the present contribution.

Together with thorium and potassium, uranium is the main element contributing to natural terrestrial radioactivity. All naturally-occurring isotopes of uranium (^{234}U, ^{235}U, and ^{238}U) are radioactive. Of these, ^{238}U is the most abundant and has a decay chain of 18 members that finishes in ^{206}Pb (Skeppström and Olofsson, 2007). The processes affecting uranium in natural waters have been studied intensively, because of their relevance for ore formation and public health. The environmental mobility of uranium is strongly controlled by the pH and the redox state of water (Drever, 1997). Dissolved uranium occurs in the tetravalent (IV) and hexavalent (VI) oxidation states, whereby the mobility of the former is limited by the solubility of uraninite and coffinite (Langmuir, 1978). In the absence of complexing ions, U(VI) will be present as the uranyl complex (UO_2^{2+}).

The strong control of redox conditions is borne out by observations near ore bodies, for example the Okélobondo uraninite deposit in Gabon, where dissolved uranium concentrations are high in deep oxidized groundwater, but low in shallow reduced groundwater (Salas and Ayora, 2004). Similarly, near the Palmutto vein-type mineralization in Finland, uranium concentrations reach up to 765 µg/L, and display a strong correlation with the redox potential, with reduced conditions associated with lower uranium concentrations (Ahonen et al., 2004). In Manitoba, Canada, it was found that the reducing conditions in superficial uranium deposits rich in organic matter render uranium insoluble (Tixier and Beckie, 2001). On the other hand, oxidation in clay strata has been found to constitute a source of dissolved uranium to groundwater in underlying and overlying aquifers (Betcher et al., 1988).

The presence of dissolved uranium is commonly believed to be restricted to oxic conditions, yet uranium has been found to be soluble in reduced environments as well. Experimental data by Delécaut et al. (2004) suggest that total dissolved uranium concentrations on the order of 238 µg/L can occur under reducing conditions ($-450 < E_h < -200$ mV). These high concentrations were attributed to the suspected presence of colloids or U(VI) carbonate species, but complexation to organic matter was also postulated. In natural waters, Welch and Lico (1998) reported uranium concentrations of up to 550 µg/L at dissolved oxygen concentrations below 1 mg/L, demonstrating that high dissolved oxygen concentrations are not a prerequisite for high natural background concentrations.

In addition to the groundwater redox state, lithology plays a major role in controlling dissolved uranium concentrations. Asikainen and Kahlos (1979) attributed extreme concentrations, of >10,000 µg/L, found near Helsinki, Finland, to the dissolution of uranium-bearing precipitates from the fissures of the granite-dominated bedrock. In Norway, concentrations of U, as well as Th and Rn, were found to be strongly correlated to the lithologic variations, with rocks high in uranium hosting the groundwater with the highest radioelement concentrations (Banks et al., 1995).

The uranium content of igneous rocks often leads to elevated concentrations in groundwater, but uranium-bearing sedimentary rocks can be the source of high dissolved concentrations as well. In Korea, total dissolved uranium concentrations of up to 263 µg/L were found in samples obtained from hot springs discharging groundwater hosted in both granites and black shale rich in uranium (Lee et al., 2001). On

Cyprus, Charalambous et al. (2013) found that uranium concentrations were higher in groundwater from chalk and marls of marine origin than from igneous rocks. Alkinani et al. (2016) reported on dissolved uranium concentrations in water samples from an alluvial fan aquifer in Iraq, and speculated that the uranium was released from sediments in which it had become trapped under formerly reduced conditions.

While many other studies have also invariably shown a strong control of water-rock interaction (Smedley et al., 2006), the source of the uranium in groundwater cannot always be clearly established. In Jordan, for example, there was no spatial correlation between elevated dissolved uranium concentrations and uranium-enriched phosphorite deposits, nor could the high concentrations be explained by a provenance from deep geothermal waters (Smith et al., 1996). Studies of the regional distribution of dissolved uranium levels typically demonstrate a high spatial heterogeneity with concentrations spanning a wide range of values (Spalding et al., 1984). This indicates that the mobility of uranium is controlled by a suite of factors that can vary locally over short distances, complicating the interpretation of the observed patterns.

In addition to redox state and lithology, other factors such as residence time, leachability, and weathering intensity play an important role as well, and typically account for the variability within lithological units (Morland et al., 1997). Evaporative concentration has further been identified as a possible cause for increased concentrations in semi-arid regions (Welch and Lico, 1998; Leach et al., 1980; Benson and Leach, 1979). Fujii and Swain (1995) reported dissolved uranium concentrations as high as 5400 µg/L in the San Joaquin valley, USA, which they attributed to the abundance of complexing ligands such as carbonate and phosphate in waters concentrated by evaporation.

Welch and Lico (1998) contended that sorption can limit uranium concentrations during evapo-concentration. The uranyl ion can adsorb to oxyhydroxides, clay minerals and organic matter (Davis et al., 2004; Waite et al., 1994; Jurgens et al., 2010). The formation of uranyl carbonate complexes ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) as well as calcium-uranyl carbonate complexes ($Ca_2UO_2(CO_3)_3^0$ and $CaUO_2(CO_3)_3^{2-}$) have been found to limit adsorption (Hsi and Langmuir, 1985; Fox et al., 2006), and thereby increase the environmental mobility of uranium. For example, Jurgens et al. (2010) found that a rise in groundwater bicarbonate concentration in the San Joaquin Valley in California (USA) led to higher dissolved uranium concentrations, which they attributed to the formation of the neutral $Ca_2UO_2(CO_3)_3^0$ complex, and the resultant reduction of uranium sorption. Both the sorption of the uranyl ion, and the formation of the uranyl carbonate and calcium-uranyl carbonate complexes is highly dependent on pH. The effects of sorption have been successfully modelled using surface complexation models (Hsi and Langmuir, 1985; Waite et al., 1994), but the model parameters are site-specific, and this leads to uncertain predictions of uranium behavior under field conditions (Davis et al., 2004).

The maximum admissible concentration (MAC) adopted by the World Health Organization (WHO) for uranium is 30 µg/L (World Health Organization, 2011). Adverse health effects associated with uranium ingestion stem from radiological hazard as well as its toxicity, especially to the kidneys (Milvy and Cothern, 1990; Taylor and Taylor, 1997). The annual radiation ingestion dose for adults is calculated assuming a daily consumption of 2 L of water, and summing up the individual radiation contributions of ^{238}U, ^{234}U, ^{226}Ra, ^{210}Po, and ^{210}Pb. Drinking water is considered as radionuclide-free when its consumption does not lead to an annual doses ingestion of >0.1 mSv as (World Health Organization, 2011). For annual ingestion doses between 0.1 mSv and 0.3 mSv, the WHO recommends a regular observation to be able to take measures whenever the doses overcome the limit of 0.3 mSv. If drinking water produces annual ingestion doses above 0.3 mSv, the WHO guideline recommends measures to be taken, e.g. mixing with radionuclide-free water.