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Occurrence, behavior and distribution of high levels of uranium in shallow groundwater at Datong basin, northern China

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HIGHLIGHTS

- High U groundwater occurs at the alluvial plains of Datong basin.
- Redox state, complexation and adsorption are responsible for U enrichment.
- Carboniferous and Permian sedimentary rocks have higher U contents at Datong.
- Uranyl is preferentially complexed with carbonate in groundwater.
- U in the aquifer sediments may be primarily associated with carnotite.

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ABSTRACT

Geochemical investigations of uranium (U) occurrence in the environments were conducted at Datong basin of northern China. The results suggest that U contents were generally <1 mg/kg for the igneous and metamorphic rocks, typically 2–5 mg/kg for the Carboniferous and Permian sedimentary rocks and around 3 mg/kg for sediments and topsoil, respectively. U in the Quaternary aquifer sediments may be primarily associated with carnotite from the Carboniferous and Permian coal-bearing clastic rocks around the basin. Shallow groundwater had U concentrations of <0.02–288 μg/L (average 24 μg/L), with 24% of the investigated boreholes above the WHO provisional guideline of 30 μg/L for U in drinking water. Average U concentration for surface water was 5.8 μg/L. In oxidizing waters, uranyl (UO_2^{2+}) species is dominant and strongly adsorbed onto iron (hydro)xides, while it would be preferentially complexed with carbonate in the alkaline groundwater, forming highly soluble uranyl-carbonate complexes at Datong. Under reducing conditions, uranous (U(IV)) species is ready to precipitate or bind to organic matter, therefore having a low mobility. At the study area, high U groundwater (>30 μg/L) occurs at the alluvial plains due to intermediate redox and enhanced alkaline conditions. The abnormally high levels of U in groundwater (>100 μg/L) are locally found at the west alluvial plains. By contrast, U co-precipitation with secondary carbonate minerals like $Ca_2UO_2(CO_3)_3$ in the dominant Ca–Mg–Na–HCO_3 type groundwater may prevail at the east alluvial plains. Besides, bedrocks such as Carboniferous and Permian sedimentary rocks, especially the coal-bearing strata which have higher U contents at the west mountain areas may also account for the abnormally high levels of U in groundwater.

1. Introduction

Uranium (U) is well known for its use in nuclear weapons and nuclear fuels. The element is a heavy metal and weakly radioactive, comprising three radioactive isotopes: ^{234}U, ^{235}U and ^{238}U with weight percentage of 0.0054%, 0.72% and 99.27%, respectively. U is common in nature and occurs in variable concentrations in soils, minerals, rocks and waters (Smedley et al., 2006). The chemical toxicity of U taken up via foodstuff and drinking water is more significant than its radiological risk (EFSA, 2009). Nephritis is the primary chemically induced effect of U in humans, and there has been little information about the chronic health effects of exposure to environmental U (EFSA, 2009; WHO, 2011). U is not a routinely tested element in water quality investigations. However, WHO (2011) and the US-EPA (2011) promulgated a provisional guideline value of 30 μg/L for U in drinking water.

Principal U minerals include autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10–12H_2O$), pitchblende ($U_3O_8$), uraninite ($UO_2$), coffinite ($(USiO_4)_{1-x}(OH)_{4x}$) and uranophane ($Ca(UO_2)_2SiO_3(OH)_2 \cdot 5H_2O$). Although these minerals generally are restricted in U-mineralized zones (Smedley et al., 2006), groundwater of meteoric origin is generally believed to supply U (Welch and Lico, 1998) owing to water–rock interactions. Hexavalent (U(VI)) and tetravalent (U(IV)) are the main oxidation states of U in nature waters. Under oxidizing conditions, uranyl ion (UO_2^{2+}) would be dominant at low pHs (<pH 5), while at higher pHs, $UO_2CO_3^0$ and the di- and tri-carbonate complexes predominate (Langmuir, 1978). Uranyl

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can also complex with phosphate under near-neutral pH conditions (Drever, 1997; Gorman-Lewis et al., 2008; Sanding and Bruno, 1992) and with fluoride and sulfate under acidic conditions or in mine or saline waters (Bernhard et al., 1998; Drever, 1997; Langmuir, 1978; Porcelli and Swarzenski, 2003). Uranyl species could be strongly adsorbed onto iron (hydr)oxides, clay minerals and dissolved organic matter (Hsi and Langmuir, 1985; Smedley et al., 2006; Waite et al., 1994), although desorption may occur due to competition between mineral surface sites and ligands for binding of uranyl (Bachmaf et al., 2008; Hsi and Langmuir, 1985; Villalobos et al., 2001; Wu et al., 2006). Under intermediate redox (Eh, −0.1 V–0.2 V) and neutral to alkaline conditions, the formation of highly soluble uranyl-carbonate complexes can increase dissolved U concentrations by several orders of magnitude (Langmuir, 1978). Under reducing conditions, stable uraninite will be dominant, and dissolved U concentrations in waters are kept low because of the low solubility of uraninite below roughly 10^{-4} μg/L (Langmuir, 1978) or the binding of uranous species to organic matter (Sheppard et al., 2005). Nonetheless, laboratory study suggests that formation of UO_2 nanoparticles reduced by green rusts may have significant effect on the mobility of U under iron reducing conditions (O'Loughlin et al., 2003). Many microorganisms mediate the reduction of U(VI) to U(IV) under anaerobic conditions (Wu et al., 2006).

In recent years, high levels of U in groundwater have been reported in many parts of the world, such as Germany, southern Finland and Portugal of Europe (EFSA, 2009), Japan, India, Uzbekistan and Mongolia of Asia (Nriagu et al., 2012) as well as several states of the US (ATSDR, 2013). Although we have been doing hydrogeological and hydrogeochemical studies at Datong basin of northern China for years, there has been no systematic work on the occurrence of U in the environments at Datong. This work was aimed to investigate U occurrence in the environments and understand geochemical behavior and distribution of U in shallow aquifers at the study area. It is hypothesized that the soda water (Wang et al., 2009) could favor U enrichment at Datong and regional geogenic high levels of U in groundwater have not been well documented worldwide.

2. Regional hydrogeology

Datong basin, located in the north part of Shanxi province with an area about 8700 km^2, is one of the Cenozoic faulted basins of Shanxi rift system. The Shanxi rift system is an s-shaped, NNE-trending extensional faulting system that forms asymmetric rift basins of Datong, Xin-ding, Taiyuan, Linfen and Yuncheng (Fig. 1). Originated from thermally cool Precambrian crustal segment, the Shanxi rift system developed during Mesozoic and Cenozoic Eras in response to the build-up of regional stress fields due to the collision of India and Eurasia (Xu and Ma, 1992) as well as the subduction of Pacific plate (Li, 1997). Datong has an arid climate with an average annual temperature of 6.8 °C, an average annual atmospheric precipitation in the range of 370–420 mm, and an average annual evaporation of up to 1800 mm. Sanggan River and its biggest tributary Huangshui River are the main ephemeral rivers that run through the basin from the southwest to the northeast.

The basin is surrounded by Hongtao Mountains on the west and Hengshan Mountains on the east. Bedrocks on the east and the north are mainly Neo-Archaean Hengshan metamorphic complex, including migmatite, tonalite, granodiorite and granitic gneiss, as well as mafic lenses, pegmatites and granites (Li and Qian, 1994). Ordovician carbonate, Cambrian as well as Carboniferous and Permian sedimentary rocks occur on the west and the south. Cenozoic unconsolidated sediments occur all over the basin with varying depths, which is more than 2000 m in central basin. As a common feature of inland basins, grain size of unconsolidated sediments gradually decreases from the margins to central basin. Sediment types beneath the margins are pluvial sand and gravel while in the plain areas and central basin mainly consist of pluvial–alluvial and alluvial–lacustrine interstratified sand, silt, silty clay and clay.

Quaternary alluvial, alluvial–pluvial and alluvial–lacustrine sediments constitute the major hydrostratigraphic unit from which groundwater is pumped. Quaternary aquifers occur in four groups, including phreatic aquifers in the depth <10 m, shallow semi-confined aquifers in the depth 10–50 m, medium confined aquifers in the depth 50–150 m, deep confined aquifers in the depth >150 m (Wang et al., 2009). Middle–late Pleistocene alluvial–pluvial sand and gravel in the depth <150 m is the predominant Quaternary aquifer (Han, 2008). Groundwater system is recharged mainly by precipitation, permeating groundwater from bedrocks along the mountains, leakage from rivers and reservoirs, as well as irrigation return flow (infiltrating water from irrigation) (Han, 2008; Wang et al., 2009). Evaporation and pumping are the main ways of discharge of shallow groundwater. The groundwater table altitude (Fig. 1) indicates that the mountain areas and pluvial plain areas are the natural recharge areas of regional groundwater, while the areas along the Sanggan River at central basin are the natural discharge areas.

3. Methodology

3.1. Sampling

One hundred and twenty-three rock samples were collected from the mountains around Datong basin (Fig. 1) in 2005, including magmatic and metamorphic rocks of Neo-Archaean Hengshan Complex, sedimentary rocks of Cambrian, Ordovician, Carboniferous and Permian systems, as well as Cenozoic volcanic rocks. One hundred and sixty three topsoil (0–20 cm) samples were collected in May 2010 following sampling scheme of 2 × 2 km rigid orthogonal grids. Ninety-one unconsolidated sediment samples from 5 boreholes with depth less than 25 m were collected in September 2010. The groundwater samples were mainly collected from private boreholes of villagers from shallow aquifers (depth < 50 m). For this reason, combination of orthogonal grids and locations of villages was designed as the sampling method. A total of 161 groundwater samples were collected in July and November 2011 and September 2012 all over the study area. For comparison, 5 surface water samples were also collected from reservoirs, Sanggan River and small creeks in the east mountain areas. When sampling groundwater from boreholes, care was taken to ensure that the borehole had been adequately purged before sampling and measurement. Eh, pH, electrical conductivity (EC) and temperature of water samples were in-situ determined using portable Hatch multi-parameter meters (HQ40D Field Case). The Eh values reported in this study have not been corrected to the standard hydrogen electrode (SHE) but instead can be used as relative values. Alkalinity of waters was determined by titration in 24 h after sampling. Water samples were collected in 50 mL PET bottles after passing through a 0.45 μm filter, cations and trace elements were preserved by acidification with GR grade HNO_3 (15 mol/L) to pH < 2, while anions were unpreserved.

3.2. Chemical analyses

After being air-dried, the soil samples passed through 1 mm sieve and were quartered. Soil soluble extracts in the representative subsamples were extracted using soil to water ratio of 1:5 following standard process (USDA, 1954). The extracts were preserved or unpreserved in the same way as mentioned earlier. One hundred and twenty-three rock samples, 125 soil sub-samples and 71 dried sediment samples were crushed and passed through 200-mesh sieve, and were HNO_3 and HF digested. The powered rock samples were also fused with lithium tetraborate to manufacture glass beads.

Major cations (Ca, K, Mg and Na) of water samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo Electron Corporation IRIS Intrepid II XSP). Major anions (Cl,