High levels of uranium in groundwater of Ulaanbaatar, Mongolia

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ABSTRACT

Water samples collected from 129 wells in seven of the nine sub-divisions of Ulaanbaatar were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using Clean Lab methods. The levels of many trace elements were found to be low with the average concentrations (ranges in brackets) being 0.9 (0.1–7.9) μg/L for As; 7.7 (0.12–177) μg/L for Mn; 0.2 (0.05–1.9) μg/L for Cd; 16 (0.1–686) μg/L for Zn; 0.7 (0.1–1.8) μg/L for Se; -0.1 (-0.02–0.69) μg/L for Cd; and 1.3 (0.02–32) μg/L for Pb. The levels of uranium were surprisingly elevated (mean, 4.6 μg/L; range <0.01–57 μg/L), with the values for many samples exceeding the World Health Organization’s guideline of 15 μg/L for uranium in drinking water. Local rocks and soils appear to be the natural source of the uranium. The levels of uranium in Ulaanbaatar’s groundwater are in the range that has been associated with nephrotoxicity, high blood pressure, bone dysfunction and likely reproductive impairment in human populations. We consider the risk associated with drinking the groundwater with elevated levels of uranium in Ulaanbaatar to be a matter for some public health concern and conclude that the paucity of data on chronic effects of low level exposure is a risk factor for continuing the injury to many people in this city.

1. Introduction

Uranium is both radioactive and a chemical toxin and the role that radiation versus chemical effects play in its toxicology remains enigmatic. Heightened interest on the environmental toxicity of uranium has been raised by two recent developments: (a) the global drive toward low-carbon energy which has rekindled interest in nuclear power and associated radioactive wastes from past, current, and future plants, and (b) its growing use as depleted uranium (DU) military in munitions (Melo and Burkart, 2011). A third important factor from exposure perspective, and the one receiving the least attention, is the increasing worldwide consumption of groundwater. Recent studies point to the fact that groundwater in many parts of world is contaminated with uranium from natural and industrial sources (EFSA, 2009; ATSDR, 2011). Exposure to uranium from drinking water is growing rapidly as more people increasingly rely on groundwater as their primary source of water (ESS, 2010). Mongolia is an example where exposure of a large number of people to uranium risk is linked to increased exploitation of groundwater resources (WHO, 2005a).

Mongolia’s water resources are very limited, fragile and stressed by variability across the regions and Mongolia is generally classified as one of the countries with limited water availability (Batnasan, 2003). The country is far from seas and oceans and almost all the rivers are frozen into riverbeds for five months in the year and hence essentially unavailable. This forces most of the population to draw heavily on the groundwater sources. In addition, there are few rivers in the steppe and semi-arid areas of the country where dry patches and river beds fill only during the uncommon rainfalls. Recent droughts add to Mongolia’s environmental woes related to water quantity and quality. A survey in 2003 found that 372 rivers and streams, 1158 springs and water sources and 537 lakes and ponds had dried up permanently. Population pressures are contributing to declining water flows in many rivers including Rivers Tuul, Haraa, and Herlen, and promoting increasing reliance on groundwater sources for drinking water. As groundwater levels fall with increased use, some wells and springs dry up completely, especially in March and April (Batnasan, 2003). The uneven distribution of water, over-exploitation and weather conditions have a strong influence on water quality leading to high levels of total dissolved solids (TDS) and an enrichment of many minor and trace elements in local groundwater resources.

Although groundwater is being intensively exploited in Mongolia, limited studies have been done to ascertain the quality of the water from this source. While groundwater samples from some parts of Mongolia have been analyzed for arsenic and some trace metals (UNICEF, 2004), we have not been able to find any data on uranium concentration in groundwater of Mongolia. This study was aimed at

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generating the first set of accurate data on uranium in groundwater of Ulaanbaatar where more than 40% of the country lives. It is hypothesized that exposure to high levels of U in groundwater is an undocumented hazard in both Ulaanbaatar and other parts of the country.

2. Methodology

Low density linear polyethylene bottles used in sample collection were decontaminated by repeated soaking in 6 M, followed by 2 M nitric acid and then with Milli-Q water (Nriagu et al., 1993). Water samples were collected during the summer of 2011 from seven of the nine sub-divisions that make up the city of Ulaanbaatar. Project staff were trained to use set protocols to minimize sample contamination during collection. Samples were collected from the pipe out of the well, and where this was not possible, samples were obtained from a tap that was not equipped with any point-of-use device. The water was run for at least 2 min to flush out the piping system. Gloved hands were used in opening, rinsing, filling and capping the sample bottles. 0.5 mL ultrapure nitric acid was added to the 50 mL water sample immediately after collection. The bottle was double-bagged (each in a zip-lock bag and then with other samples in a larger zip-lock plastic bag) and then stored in a cooler box until returned to the lab.

A different aliquot of each well water sample was collected and used in pH measurement. The following supplementary information were also obtained for each well: type (drilled or dug), age, type of casing, depth, location (address and GPS coordinates), and use of well water (private, communal, camp, or business).

All samples were kept in refrigerator (under 4 °C) and subsequently transported in a cooler box to the University of Michigan where they were analyzed. Samples were collected in June and July, 2011 and analyzed in early August, 2011. All samples were analyzed unfiltered.

2.1. Instrumental analysis

Uranium and other trace metals were measured in the samples using an Inductively Coupled Plasma Mass Spectrometer (ICP–MS; Agilent 7500c, Agilent Technologies, Palo Alto, CA) equipped with a quadrupole analyzer and octopole collision/reaction cell that can be pressurized with either a hydrogen (H₂) or helium (He) reaction gas. Sample was injected at the rate of 0.4 mL/min using a peristaltic pump. Carrier Ar gas at rate of 1.2 L/min through a Babington-style nebulizer was input into a Peltier-cooled double-pass spray-chamber at 2 °C. The 1.0 L/min auxiliary Ar and 12.0 L/min plasma gas Ar were added for a total of 14.2 L/min separated from nickel cones. The ICP–MS was tuned under standard settings by running the manufacturer’s recommended tuning solution containing 10 μg/L of Li, Y, Ce, Tl, and Co (Agilent internal standard mix) for resolution and sensitivity. Interference levels were reduced by optimizing plasma conditions to produce low oxide and doubly charged ions (formation ratio of <1.0%) and residual matrix interferences were removed using the collision/reaction processes in the Octopole Reaction System. In view of the multi-element functionality of the ICP–MS, the analytical conditions were optimized to measure the following elements (in addition to U): Al, Co, Mn, Zn, As, Se, Cd and Pb. Selection of the suite of elements analyzed was based on whether certified values were given for them in the standard reference materials used in the study.

A series of rigorous analytical quality control measures were employed in the analysis. All samples were handled in Class 100 (sample handling and processing) and 1000 (instrumental analysis) Clean labs. Any plasticware that contacted samples was acid-washed (cleaned, soaked in 6 M (24 h) and 2 M (24 h) nitric acid) prior to use. Accuracy and precision were measured by means of certified reference materials, including QMEQA508U-01 human urine (Institut National de Santé Publique du Québec, INSPQ) and spiked standard solution (Agilent Technologies).

Samples for which a contaminant was detected but the concentration was below the analytical detection limit was assigned a value of one-half the detection limit. The analytical detection limit was calculated as the concentration of the element which gave a detectable signal above the background noise at greater than the 99% confidence level, and the detection limit was calculated as the mean of blanks plus 3 times the standard deviation of the mean.

2.2. Accuracy, precision and detection limits

Appropriate Standard reference materials (SRMs) were measured to determine validity of the calibration curves. Accuracy was measured using the SRMs and spiked standard solutions. Milli-Q water served as a blank (1 blank per 10 samples).

Precision (reproducibility) was ascertained using within-day replicate analysis of SRMs and samples. The Relative Standard Deviation (RSD; % RSD = SD/χ of the replicate values × 100; χ is mean value) was calculated to give an indication of sample preparation, sample aliquoting and analytical precision. Replicates of SRMs each day provided an indication of within-day precision.

In general, the detection limit (DL) is the concentration of the analyte which gives a detectable signal above the background noise at greater than the 99% confidence level (and with the multiplier for number of samples being 3) so that:

\[ \text{DL} = 3SD/c \times C. \]

For U, multiple determinations of a blank (as Milli-Q water) are analyzed. The mean and SD are calculated, with the results in amount of U (μg/L; ppb), so the calculation for DL is simply:

\[ \text{DL} = 3SD. \]

This calculated DL is the theoretical method detection limit, or TMDL. The Practical MDL (PMDL) is 5 times the TMDL. For samples that had U less than the TMDL, the TMDL is used to calculate the concentration in the sample and are reported as less than this concentration.

3. Results

The average recovery rates of U from the spiked standard solution and standard reference material (QMEQA508U) were 103.8 ± 6.0% (n = 3) and 93.5 ± 3.6% (n = 3), respectively (Table 1). Variability, as measured by the % RSD of within-day analyses of the spiked standard solution and QMEQA508U ranged from 3.5 to 3.9% RSD (Table 1). The theoretical and practical method detection limits for U quantification were 0.035 and 0.160 μg/L, respectively (Table 1). These were all within the set tolerable ranges for the method used. In addition, we generally achieved good recovery rates for the other trace metals in NIST 1640 reference water, multi-solution spikes and QMEQA508U-01 reference urine sample (Table 1).

Total concentrations of uranium in water samples analyzed varied from 0.01 μg/L to 57 μg/L and averaged 4.6 μg/L (Table 2). The distribution of the concentrations is shown in Fig. 1. We found that the uranium levels in 5.4% of the samples exceeded 15 μg/L, while 10% of the samples exceeded 10 μg/L uranium. There were marked differences in levels of uranium in different parts of the city (Table 2). The highest uranium concentrations were found in Bayangol (18.6 μg/L) and Bagakhangai (11.3 μg/L) and the lowest levels were measured in Sukhbaatar (2.4 μg/L) and Chingeltei (1.6 μg/L). The two areas with the highest uranium concentrations are far removed from each other whereas the areas with the lowest levels are contiguous.

The depths of wells sampled varied from 3 m to over 300 m, and averaged 55 m. The relationship between uranium concentration and well depth can provide important clues on origin of the uranium in the water samples. Logistic regression of uranium concentration...
with depth resulted in an $r^2$ value of 0.018 and p-value of 0.129, indicating that depth is not a predictor of U concentration in waters of wells sampled for this study.

### 4. Discussion

An original goal of this project was to assess the extent of arsenic contamination since a recent UNICEF (2004) report had hinted that groundwater samples in Ulaanbaatar had elevated levels of this element. This study found the arsenic concentrations in groundwater of this city to be very low—mean value was only 0.9 μg/L with the range being ≤0.1 to 7.9 μg/L (Table 2). We had sought arsenic and found uranium instead in the groundwater. The discrepancy between our data and the previously published results is not surprising; the UNICEF study used a colorimetric method in measuring arsenic which did not have the sensitivity to quantify the low arsenic contents in the samples reliably. The levels of other trace metals in Ulaanbaatar's groundwater were also very low with the average concentrations (ranges in brackets) in samples analyzed being 7.7 (0.12–177) μg/L for Mn; 0.2 (<0.05–1.9) μg/L for Co; 16 (<0.1–686) μg/L for Zn; 0.7 (<0.1–1.8) μg/L for Se; <0.1 (<0.02–0.69) μg/L for Cd; and 1.3 (<0.02–32) μg/L for Pb (Table 2). These values are well below the WHO (2005b) guidelines for these elements in drinking water (Table 2) and lower than the results of other published studies. There were significant differences in the distributions of these elements in various parts of Ulaanbaatar (Table 2). In this connection, it should be noted that although the average Al concentration was 102 μg/L, the values in the Bagakhangai sub-division (209 μg/L average) mostly exceed the US EPA guideline for Al in drinking water (100–200 μg/L) and that many samples from Sukhbaatar sub-division also exceed the US EPA's guideline (Table 2). The distribution and possible effects of elevated levels of aluminum in these two sub-divisions need further attention.

We were surprised by the elevated levels of uranium in Ulaanbaatar’s groundwater (Table 2). Most (65%) of the samples had U concentrations in the range of 2–10 μg/L, 10% of the samples had over 10 μg/L, and less than 25% of the groundwater samples analyzed had U concentrations below 2 μg/L (Fig. 1). Typical concentration of U in uncontaminated groundwater in many parts of the world is <1.0 μg/L, although values in excess of 1000 μg/L water have been reported (EFSA, 2009; ATSDR, 2011). It is suspected that the uranium is derived naturally from leaching of local rocks and soils because elevated concentrations were in both highly developed areas of the city and sections heavily populated with “gers” (Mongolian traditional dwellings). The study by Markowitz et al. (2008) detected uranium in sand and soil samples from Ulaanbaatar with the concentration reaching 350 μg/g in one sample from a dry lake bed. Uranium concentrations in groundwater can vary considerably depending on the mineralogical and geochemical composition of the soil and rock, chemical composition of the water, and the residence time of groundwater in the soil and bedrock. A study of the aquifer chemistry of uranium can provide critical information in characterizing the uranium risk and planning possible risk management measures.

High levels of uranium in groundwater may be more common than is generally realized and the discovery is following the usual pattern of “the more you look, the more you find” which has marked the trajectory of other toxic metals (such as lead, mercury and arsenic) of global concern. Prior to 1980 or so, uranium in drinking water was rarely measured except when contamination from industrial sources was suspected (ATSDR, 2011). Studies since then, especially in recent years, have increasingly revealed high levels of uranium in drinking water in many parts of the world. A recent survey by the European Food Safety Authority (EFSA) found that “drinking water and mineral waters can, depending on the local geology, have in some cases uranium contents which could be sufficient to endanger consumer health” (EFSA, 2009). Average U concentration in 5474 tap water samples from various European countries was found to be 2.2 μg/L and values above the WHO guideline (15 μg/L) were reported from Germany, France, Sweden, and Switzerland (EFSA, 2009). A large drinking water study in the U.S. performed under the National Uranium Resource Evaluation (NURE) program found average U content of 28,000 domestic water samples to be 2.5 μg/L (USGS, 2006; ATSDR, 2011); the levels

<table>
<thead>
<tr>
<th>Region</th>
<th>Al</th>
<th>Mn</th>
<th>Co</th>
<th>Zn</th>
<th>As</th>
<th>Se</th>
<th>Cd</th>
<th>Pb</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayangan (n=4)</td>
<td>22</td>
<td>3.2</td>
<td>0.4</td>
<td>19.3</td>
<td>0.6</td>
<td>0.2</td>
<td>&lt;0.02</td>
<td>0.7</td>
<td>18.6</td>
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<tr>
<td>Bagakhangai (n=4)</td>
<td>208.6</td>
<td>53.8</td>
<td>0.7</td>
<td>16.7</td>
<td>0.6</td>
<td>1</td>
<td>&lt;0.02</td>
<td>1.1</td>
<td>11.3</td>
</tr>
<tr>
<td>Bayanzurkh (n=19)</td>
<td>67.5</td>
<td>4.5</td>
<td>0.2</td>
<td>52.8</td>
<td>1.4</td>
<td>0.7</td>
<td>0.1</td>
<td>0.4</td>
<td>3.7</td>
</tr>
<tr>
<td>Chingeltei (n=5)</td>
<td>7.4</td>
<td>8.2</td>
<td>0.1</td>
<td>30.3</td>
<td>0.6</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Songino Khairkhan (n=55)</td>
<td>122</td>
<td>8.6</td>
<td>0.2</td>
<td>3.9</td>
<td>0.8</td>
<td>0.8</td>
<td>&lt;0.02</td>
<td>2.9</td>
<td>4.6</td>
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<tr>
<td>Khan Uul (n=11)</td>
<td>21.7</td>
<td>1.7</td>
<td>0.1</td>
<td>28.9</td>
<td>1.8</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Sukhbaatar (n=27)</td>
<td>148.8</td>
<td>4.7</td>
<td>&lt;0.05</td>
<td>6.7</td>
<td>0.7</td>
<td>0.2</td>
<td>0.1</td>
<td>1</td>
<td>2.4</td>
</tr>
<tr>
<td>City-wide (n=129)</td>
<td>101.7</td>
<td>7.7</td>
<td>0.2</td>
<td>16.4</td>
<td>0.9</td>
<td>0.7</td>
<td>&lt;0.02</td>
<td>1.3</td>
<td>4.6</td>
</tr>
<tr>
<td>Range</td>
<td>0.37–668</td>
<td>0.12–176.6</td>
<td>&lt;0.05–1.9</td>
<td>&lt;0.1–685.9</td>
<td>&lt;0.1–7.9</td>
<td>&lt;0.1–1.8</td>
<td>&lt;0.02–0.69</td>
<td>&lt;0.02–32.1</td>
<td>&lt;0.01–57.2</td>
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<tr>
<td>WHO guidelines</td>
<td>500</td>
<td>50</td>
<td>5</td>
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<td>10</td>
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<td>USEPA guidelines</td>
<td>50–200</td>
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<td>5</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>15</td>
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</tbody>
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were \( \geq 14 \mu g/L \) in 2228 water supplies and \( \geq 20 \mu g/L \) in 979 water supplies (ATSDR, 2011). Analysis of 55,000 groundwater samples in the U.S. showed average U content of 4.8 \( \mu g/L \) (range, 0.01–946 \( \mu g/L \)) (USGS, 2006), States with high levels of uranium in their groundwater include South Dakota, Nevada, New Mexico, California, Wyoming, Texas, Arizona, and Oklahoma (ATSDR, 2011). Other countries where high levels of uranium have been reported in groundwater include Japan (Kuwahara et al., 1997), India (Kumar et al., 2006; Singh et al., 2008), Western Uzbekistan (Kawabata et al., 2006), Inner Mongolia, China (Guo et al., 2010), Finland (Kurttio et al., 2002), Norway (Frengstad et al., 2000), Greece (Katsyrianis et al., 2007), Canada (Mao et al., 1995), and Australia (Appleyard, 1984). This short list of countries reporting elevated levels of uranium should serve to point the search light on the vast number of countries where uranium in groundwater has never been measured.

Two factors have controlled much of the scientific inquiry on the health effects of uranium exposure: (i) Prior to the late 1990s, the environmental toxicology of uranium was assessed purely in terms of the radiological properties of its isotopes and most of the then established high threshold and guideline values were based on radioactive hazard serve; and (ii) the Gulf War syndrome and the concern that it is causally linked to exposure to depleted uranium (McCain, 2006; Melo and Burkart, 2011). As a consequence, serious studies on the chemical toxicity of uranium were stifled until recent research began to increasingly suggest that this should be the matter for much more concern for human and ecosystem health. Naturally occurring uranium is comprised of an isotopic mixture containing a dominant amount of \( ^{238}U \) (99.284% by weight) and very small amounts of \( ^{234}U \) (0.711%) and \( ^{235}U \) (0.005%); in terms of radioactivity, the isotopic mixture is 49% \( ^{238}U \), 2% \( ^{235}U \), and 49% \( ^{234}U \) which yields a very low specific activity of 0.68 \( \mu Ci/g \) (ATSDR, 2011). Although there is potential for the carcinogenicity of uranium, since it emits primarily alpha radiation, no conclusive evidence has been found that natural uranium in groundwater produces cancer in humans and neither the International Agency for Research on Cancer (IARC) nor the US EPA has listed uranium in the natural environment as a carcinogen. With few exceptions, however, studies of genotoxicity of uranium in various types of eukaryotic cells in vitro have yielded positive results (ATSDR, 2011).

One should regard the risk associated with ingesting groundwater with elevated levels of uranium in Ulaanbaatar to be a matter for public health concern. Some of the concentrations we found exceeded the WHO (2005b) guideline for U in drinking water of 15 \( \mu g/L \). A large number of the samples had U concentrations that exceeded the recent German national maximum level for uranium in natural mineral waters, spring waters and table waters of 10 \( \mu g/L \), as well as the German guideline of only 2 \( \mu g/L \) for waters used in preparing infant food (EFSA, 2009). Need for some concern also stems from studies in other countries which have reported adverse health effects associated with exposure to uranium concentrations in the range found in groundwater of this city. Impairment of kidney function deserves special attention since human and animal studies point to the fact that the kidney is the primary target organ for uranium (ATSDR, 2011; WHO, 1998, 2001, 2005b; UBA, 2005). A number of epidemiological studies have reported strong associations between elevated levels of uranium in drinking water and biomarkers indicative of renal dysfunction including urine levels of albumin, \( \beta \)-microglobulin, glucose levels, alkaline phosphatase, and \( \gamma \)-glutamyl transferase (Kurttio et al., 2002, 2006; Limson Zamora et al., 1998, 2009; Mao et al., 1995; Seldén et al., 2009). These studies did not always find overt signs of nephrotoxicity in the exposed cases. Kidney dysregulation was characterized by damage to the proximal convoluted tubules, with possible involvement of the glomerulus at high U doses (COT, 2006). Exposures where these changes have been reported are in the range of U concentrations found in groundwater of Ulaanbaatar.

Other studies of populations exposed to elevated levels of uranium in their drinking water have reported small but significant increases in diastolic and systolic blood pressure among adults (Kurttio et al., 2006). Bones are the secondary target organ of uranium toxicity and since the majority of absorbed uranium is stored in bones (Jiang and Aschner, 2009; ATSDR, 2011). A study of adults in an area of Finland with elevated uranium levels in drinking water (0.002–1920 \( \mu g/L \)) found a significant association between elevated serum type I collagen carboxy-terminal telopeptide (CTX) levels (biomarker of bone resorption) and levels of uranium in water (Kurttio et al., 2005). A nonsignificant association was also observed between increased osteocalcin levels (biomarker of bone formation) and uranium levels in drinking water. These associations were found only in men but not women (Kurttio et al., 2005) at concentrations in the range found in Ulaanbaatar. Reproductive impairment by U is viewed with increasing concern following a recent study that found alterations in ovarian folliculogenesis in mice at very low doses (\( \geq 0.00039 \) mg U/kg/day) in the drinking water (Raymond-Whish et al., 2007). Maternal exposure to uranium during pregnancy has induced fetotoxicity, teratogenicity, and reduced neonatal viability in mice (Domingo et al., 1989; Paternain et al., 1989). Uranium also showed estrogenic properties at very low doses in mice (Raymond-Whish et al., 2007).

Recent systematic reviews have found no human studies on the reproductive, developmental, neurotoxicological, immunological and genotoxicological effects of low-level exposure to uranium in drinking water (ATSDR, 2011; WHO, 1998, 2001, 2005b; UBA, 2005). The absence of any information on effects of prenatal and childhood exposures to
uranium should be of particularly worrisome and the recent suggestion (ATSDR, 2011) that children and adults may respond similarly to uranium in the environment should be considered as fallacious. The special vulnerability of children to U in drinking water was emphasized by Kersting et al. (1998). In that study, a 3-month old infant who weighs 6.1 kg on average and consumes 780 mL water that contains 15 μg/L, would result in uranium exposure that exceeds the tolerable intake rate of 0.6 μg/kg.b.w. per day set by the WHO (2005b). From their kinetic model, Kersting et al. (1998) estimated that the exposure of an infant consuming water with uranium concentration of 15 μg/L would be up to 3 times higher than the exposure of adults on the body weight basis. While there are uncertainties associated with the calculations by Kersting et al. (1998), it is significant to note that uranium absorption is believed to be more effective in infants than in adults, possibly leading to a higher internal dose (EFSA, 2009).