Roberta Bottino Montolar Sparovek
Jürgen Fleckenstein
Ewald Schnug

Issues of uranium and radioactivity in natural mineral waters

Issues of Uranium and Radioactivity in Natural Mineral Waters

Roberta Bottino Montolar Sparovek, Juergen Fleckenstein and Ewald Schnug [1]

Abstract

Methodical investigations on uranium (^{238}U) concentrations were conducted on 15 selected mineral waters from European sources. The samples were selected according to their radioactivity deriving from ^{226}Ra, which ranged from 3.7 to 1780 mBq l^{-1}.

The determination of ^{238}U in mineral water by ICP-QMS showed to be an efficient replacement for the laborious radiochemical method. Results obtained by both methods were in reasonable good agreement.

The U concentrations in the specimens ranged from less than the detection limit of ICP-QMS (15 ng l^{-1} ^{238}U) up to 8.6 µg l^{-1} (corresponding to 218 mBq l^{-1}). An extreme U concentration was found in a source from Moravia (Czech Republic) with 188 µg l^{-1} U corresponding to 4747 mBq l^{-1}. On an average U contributed the same amount of radioactivity to a mineral water than ^{226}Ra (range: 0-87 %). Although a daughter nuclide of the ^{238}U decay series, ^{226}Ra concentrations were not correlated. In multiple regression analysis the mineral components Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-} explained up to 99 % of the summarized radioactivity (U + ^{226}Ra) in the specimens. Chloride and potassium concentrations explained most of the variability and as a rough role of thumb it was found that twice the chloride concentration in mg l^{-1} was equal the summarized radioactivity (U + ^{226}Ra) in the investigated waters.

The results of the investigation underline the need to communicate the content of radionuclides with the customer information of natural mineral waters.

Key words: uranium, radium, radioactivity, anions, cations, mineral-waters

Zusammenfassung

Ein Beitrag zu Uran und Radioaktivität in natürlichen Mineralwässern

Uran (^{238}U) wurde mittels induktiv gekoppelter Quadrupol Plasma Massenspektrometrie (ICP-QMS) in 15, nach ihren Gehalten an ^{226}Ra ausgewählten, natürlichen Mineralwässern europäischer Herkunft untersucht. Die Bestimmung von Uran mittels ICP-QMS erwies sich dabei als effizienter Ersatz für arbeitsaufwändige radiochemische Methoden.

Die Urankonzentrationen der Mineralwässer reichten von weniger als 15 ng l^{-1} (experimentelle Nachweisgrenze der ICP-QMS) bis zu 8,6 µg l^{-1} (entsprechend 218 mBq l^{-1}). Ein extrem hoher Urangehalt von 188 µg l^{-1} (entsprechend 4747 mBq l^{-1}) wurde in einem Mineralwasser aus Mähren (Tschechien) gefunden. Im Mittel, bei allerdings großer Bandbreite von 0-86 %, trug Uran etwa in gleichem Umfang zur Radioaktivität (Uran + ^{226}Ra) der Mineralwässer bei. Obgleich Tochter der ^{238}U Zerfallsreihe, konnte keine signifikante Korrelation zwischen den Gehalten an ^{226}Ra und Uran gefunden werden.

Von den mineralischen Bestandteilen Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- und SO_4^{2-} erklärten die Gehalte an Cl^- und K^+ bereits 86-98 % der Variabilität der Radioaktivität (Uran + ^{226}Ra) der Wässer. Das Doppelte der Cl-Gehalte in mg l^{-1} entsprach näherungsweise der Radioaktivität der untersuchten Mineralwässer in mBq l^{-1}.

Die Ergebnisse unterstreichen die Notwendigkeit, die Gehalte an Uran und ^{226}Ra in die Verbraucherinformationen auf Mineralwasserflaschen aufzunehmen.

Schlüsselwörter: Uran, Radium, Radioaktivität, Kationen, Anionen, Mineralwasser

[1] Institute of Plant Nutrition and Soil Science, Ferderal Agricultural Research Centre (FAL), Bundesallee 50, 38116 Braunschweig, Germany

1 Introduction

Radionuclides are part of our natural environment. Their biological impact is mostly considered as negative (Banks et al., 1995; BEIR III, 1980; BEIR IV, 1990), but there are also sources which claim a positive effect of low radiation for life processes, called "hormesis" (Luckey, 1991) and as the active principle of a couple of spas and mineral waters (Akerblom, 1994; Franke et al., 1987; Hevesy and Paneth, 1938; Jianli et al., 1983; McNulty, 1991; West, 1954). Uranium is present in the environment as a natural element, but generally in low concentrations which may be elevated as a result of leaching from natural deposits or due to anthropogenic activities, such as mining operations, nuclear industry, industrial and medical wastes, and last but not least the use of phosphate fertilisers in agriculture (Azuoazi et al., 2001; Barisic et al., 1992; Kobal et. al., 1990; Schnug et al., 1996). Spalding et al. (1972) for instance attributed the increased U concentrations in North American rivers (~ 0.7-0.9 μg l^{-1} compared to ~ 0.1-0.2 μg l^{-1} in South American rivers (Cothern and Lappenbusch, 1983)) to the use of phosphate fertilizers in the region.

A new source of uranium contaminations in certain areas are military combat actions by which ammunition with penetrators manufactured from ^{238}U ("depleted uranium") is used. Not more than 10 % of the rounds fired during an ambush usually hit targets, but the majority get buried in the ground and becomes a potential risk for contamination of groundwater, soil and plants. Heavy firing of ammunition with depleted uranium penetrators in one area could increase the potential source of uranium contamination of groundwater by a factor of 10 to 100. While the radiation doses will be very low, the resulting uranium concentration might exceed WHO health standards for drinking water (Anonym, 2001a; UNEP, 2001). Noteworthy is also that "depleted uranium has the unusual property that it becomes more hazardous with time" (Anonym, 2001b) because of its more dangerous daughter nuclides with higher decay energies (fig. 1a and 1b).
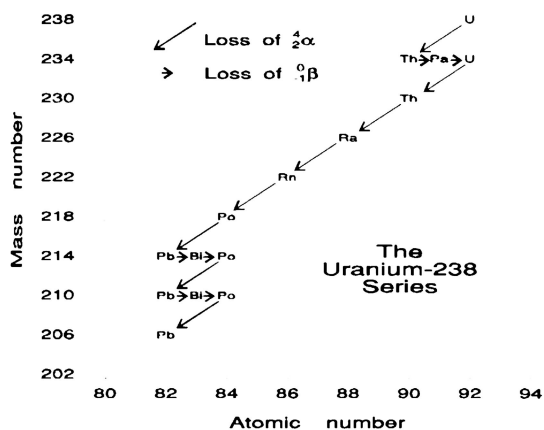
Natural uranium is a mixture of three isotopes ^{238}U, ^{235}U, and ^{234}U in the weight proportions 99.27 %, 0.72 % and 0.006 % respectively. 1μg of natural uranium has an activity of 25.28 mBq (Anonym, 2001b). Uranium can adopt in four valences: U^{3+} (III), U^{4+} (IV), UO$_2^+$ (V), and UO$_2^{2+}$ (VI), the predominant states in the environment are U (IV) and U (VI) (Fellows, 1998). This number of different valence is also one explanation for the potential toxicity of uranium in comparison to other heavy metals (Ribeira et al., 1996). Part of the decay series of ^{238}U is ^{226}Ra (fig. 1), which is considered as one of the most toxic radionuclides. This is, because radium like calcium, with which it shares the same group of the periodic system, enriches in bones causing a long lasting and therefore dangerous exposure of tissue to radiation. In uranium ores and systems without any element specific enrichment or depletion process uranium and radium occur in a relation of weights of 1 : 3*10^{-7}.

In soils the average uranium concentration ranges from 1-4 mg kg^{-1}. Mineral soils with a high content of clay can have uranium concentrations much above this average, because clay minerals have a high uranium content and the surfaces of clay minerals are prominent adsorbers for this element (Harmsen and Haan, 1980). In terms of masses water is the most significant vector for the transport of uranium (in solutions or by erosion) in the environment. The transport of uranium to natural waters occurs by diffusion or mass flow either dissolved or suspended. For information on the hydro-geochemistry of uranium the reader may refer to Drever, 1988, Garrets and Christ (1965) and Krauskopf (1979). The solubility of uranium in soils depends on many factors like for instance pH, redox potential, temperature, texture, organic and inorganic compounds, moisture and microbial activity (Anonym, 2001b; Harmsen and Haan, 1980). In the aquatic environment uranium occurs in concentrations from 0.1-10 μg l^{-1} (Brits and Smith, 1977), mainly as uranyl carbonate complexes. In confined aquifers the uranium is found in the tetravalent stage (U^{4+} (IV)) but in surface waters in the hexavalent state (UO$_2^{2+}$ (VI), Ribera, et al., 1996). Almost all tetravalent (uranous) compounds are really insoluble and are less
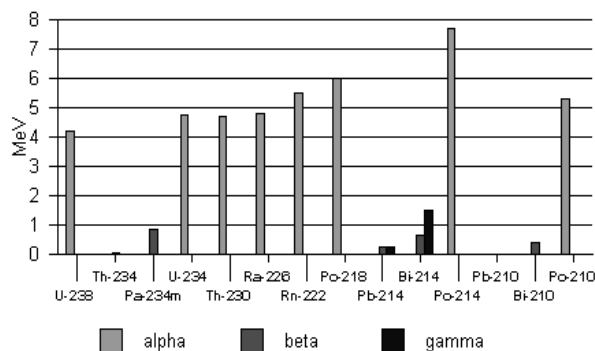

Fig. 1 a
Decay series of ^{238}U
(Anonym, 2001c)

Fig. 1 b
Average decay energy of the ^{238}U series
(Anonym, 2001b)

mobile than hexavalent (uranyl) ones. Due to the complexation reaction between ligands that are present in natural waters, this stages are the most important ones of uranium in water (Cothern and Lappenbusch, 1983; Erikson et al., 1990).

The formation of hydrolysis products increases the solubility of uranium oxides by a complex formation between a metal and one or more ligands (OH-, Cl-, CO_3^{2-}, PO_4^{3-}, F-, SO_4^{2-}, Higgo et al., 1989; Nguyen-Trung et al., 1991). The amounts of hydrolysis products in solutions is directly related to the activity of UO_2^{2+} and the pH (Harmsen and Haan, 1980). It also competes with the formation of organic and inorganic complexes (Cothern and Lappenbusch, 1983). At pH values below 4 the uranyl ion is complexed by fluorite, between pH values 4 and 7.5 by phosphate and at higher pH values complexation with carbonate to a carbonate-uranyl complex predominates (Erikson et al., 1990). In the natural environment with typical pH values around 6 or below and in the presence of oxygen, humic and fulvic acids, very stable complexes are formed.

Human and animals can be contaminated by uranium in different ways: inhalation, ingestion and contact. The inhalation is not so important as food and water, and the contact is important for the people that work directly with uranium, and in the actually days for the people that live in those places where the war is part of life. The ingestion of uranium can be through the drinking water and food chain, by animals that are contaminated and plants that are able to take up the soluble form of uranium.

Mammals have a particular high sensibility to uranium (Fellows et al., 1998). Once the uranium is in the organism, it is transferred to the extracellular fluids and transported through the blood to others organs, uranyl (UO_2^{2+}) is the soluble form transported and it forms complexes with protein and anions. The U that is not retained is eliminated by the urinary and fecal excretion, the retained in the organism has two parts: the biological is linked with mechanisms and kinetic of U's transfer for the other organs, and the physical that is linked with the emission of radioactivity.

The risks related with the exposure to uranium can be chemical and radiological. The first one is related with the binding of U to biological molecules. This risk is particular high for kidneys because of peak concentrations during the excretion process. The second one is the radiation which is of particular risk for lungs and bones. The liver and spleen are places of U accumulation. The most remarkable effect of U toxicity going along with low and medium contaminations is cancer. Compared to this mutation is a phenomenon only associated with very high U contamination of organisms. The dangers arising from the biochemical toxcity of uranium are generally considered to predominate the risks from its radioactivity (Milvy and Cothern, 1990).

According to Cothern and Lappenbusch (1983) even at low concentration levels drinking water accounts to more than 80 % of the total U ingestion and Harduin et al. (1994) underline the need to limit the uptake of soluble U compounds with waters for personal risk reduction. With the increased consumption of mineral waters, being advertised as the "better drinking water" also the relative importance of this source of radioactivity is growing.

Higher concentrations of U in ground water comes along with low pH, low adsorption capacity, lack of anions, and presence of uranium ores. In comparison to this surface waters usually show low concentrations of U because of precipitation and adsorption to bottom sediments especially at the presence of organic matter and reducing conditions (Casas et al., 1998; Harmsen and Haan, 1990; Higgo et al., 1989; Hydroisotop, 2001; Nguyen-Trung et al., 1991).

The objective of the research work reported here was:
- to check ICP-QMS as an alternative method for the radiochemical determination of [238]U,
- to investigate the U content in selected mineral waters of different [226]Ra radioactivity,
- to assess the contribution of U to the radioactive exposures to humans by mineral waters, and
- to investigate the correlations between U and other mineral constituents in mineral waters.

2 Materials and Methods

Twelve mineral waters with a range of [226]Ra activity from 3.7 to 1780 mBq l[-1] were selected in four groups (<25; ~125 ~300: > 1500 mBq l[-1] [226]Ra; tab. 1). The [226]Ra activities were taken from an official survey conducted by Gans et al. (1987).

The composition of mineral waters is considered to be site specific and thus to be long term stable (Dopchai, 2000; Stevenson, 2000), which again keeps the validity of analytical data even for later samples. Gans et al. (1987) summarized radiochemical methods which were employed in their survey for analyzing [226]Ra activity, involving direct emanation of [222]Rn, precipitation of radium by barium and enrichment of radium on poly-acryl-nitril wafers, all followed by alpha-spectroscopy.

U was analyzed in the same study according to Frindik (1980) involving the extraction by triisooctylamine, isolation via anion-exchange as hexachloro-complexe and electrochemical precipitation followed by alpha-spectroscopy.

In addition to the twelve samples selected by their [226]Ra activity three mineral waters from Czech sources and one from Turkey, the first bottled waters with an exceptional high mineral content the second water from a hot spring with a reported high [222]Rn activity of 1000 mBq l[-1] (sampled on May 24, 2001 in Davutlar: 37° 44,17′ N; 27° 17,80′ E) were included in the survey, because such waters are supposed to have a high content of radionuclides too (Sanchez et al., 1999).

In this study U was analyzed directly by means of inductively coupled quadrupole plasma mass spectrometry

Table 1
Chemical composition and [226]Ra activity of mineral waters

Water	^{226}Ra ** mBq.l^{-1}	U µg l^{-1}	Ca^{2+} mg l^{-1}	Mg^{2+} mg l^{-1}	K$^+$ mg l^{-1}	Na$^+$ mg l^{-1}	Cl$^-$ mg l^{-1}	HCO$_3^-$ mg l^{-1}	SO$_4^-$ mg l^{-1}	Σ ***
Volvic	3.7	0.39	9.9	6.1	5.7	9.4	8.4	65	6.9	112
Contrex	5.5	1.40	486.0	84.0	3.2	9.1	8.6	403	1187.0	2181
Bismark	6.3	>LLD	61.9	4.1	*4.2	10.0	14.9	193	17.0	305
Wittenseer	6.7	>LLD	0.2	5.7	1.3	9.8	17.8	243	32.0	310
Hella	7.4	>LLD	51.2	3.6	*3.2	8.2	*29.1	46	*0 .0	142
Evian	8.1	1.92	78.0	24.0	1.0	5.0	4.5	357	10.0	480
Perrier	11.5	2.62	143.0	3.4	*5.1	9.0	21.5	390	33.0	610
Vittel	23.3	0.72	91.0	19.9	4.9	7.3	*29.4	258	105.0	517
Apollinaris	118.0	0.10	100.0	130.0	20.0	410.0	100.0	1810	80.0	2650
S. Pellegrino	152.0	8.61	208.0	53.5	2.8	42.0	68.0	223	534.6	1132
Heppinger	307.0	0.23	115.9	164.8	52.7	856.0	244.7	2891	188.0	4513
Mlynsky	1780.0	0.78	*149.0	43.5	93.0	1682.0	591.1	2019	1579.0	6157
Magnesia	n.a.	>LLD	36.7	236.3	2.0	5.0	3.9	1292	25.0	1601
Mattoni	n.a.	0.29	62.4	18.0	*3.9	96.7	12.9	541	51.7	787
Saratica	n.a.	187.78	219.7	943.8	26.5	2203.0	124.2	557	8141.0	12215

n. a.   not available
*   estimated values from regression analysis
**   data by Gans et al. (1987)
***   main minerals = Σ (Ca^{2+} + Mg^{2+} + K$^+$ + Na$^+$ + Cl- +HCO$_3^-$ + SO$_4^{2-}$)

(ICP-QMS) of ^{238}U (Taylor, 2001) employing a VG-Elemental Plasmaquad 3 instrument. ICP-QMS is an analytical technique where an (usually) aqueous sample is nebulized to an aerosol which is transported into a plasma by an argon gas stream. "Inductive coupling" is the process which sustain the plasma by a cascading collision of electrons accelerated in the outer spheres of the plasma by radio frequency (typically 700 - 1500 W, ~ 27 MHz frequency) with argon atoms. In the plasma at temperatures between 7.000 - 11.000 K the elements in the sample are atomized followed by immediately ionization. Ions are representatively sampled from the plasma into the high vacuum of a quadrupole spectrometer. Quadrupoles are electromagnetic mass filters through which only ions of a pre-selected mass can pass onto a detector, where they are converted into a measurable electric current (Taylor, 2001).

The most important feature of ICP-QMS is that unlike with radiochemical (DeCamargo and Mazilli, 1996) or optical emission spectroscopy from an ICP source (ICP-OES) (Dadfarina and McLeod, 1994; Miura et al., 2000) no enrichment steps are required for the concentration range in question.

The theoretical lower limit of detection (LLD) for ^{238}U by ICP-QMS is 2ng l^{-1} (El-Himri et al., 2000), but practically the LLD was found to be 15 ng l^{-1}, which fits well with the 13 ng l^{-1} reported by UNEP (2001).

Analytical data for Ca^{2+}, Mg^{2+}, K$^+$, Na$^+$, Cl$^-$, HCO$_3^-$ and SO$_4^{2-}$ were taken from the reports of reference laboratories for the individual mineral waters (tab. 1 and Albu et al., 1997). Missing data for individual waters were estimated by regression equations calculated from the existing data

set (Ca^{2+} from SO$_4^{2-}$ (= 0.36); K from Cl$^-$ (r = 0.98); Na$^+$ from SO$_4^{2-}$ (r = 0.82; Cl$^-$ from Na (r = 0.71)). Calculated data are indicated in tab. 1.

Statistical treatments were conducted employing the SPSS 10.0 statistical package.

3 Results and Discussion

3.1 Comparison of ^{238}U determination by ICP-QMS with radiochemical analysis

For three of the mineral waters data for U by ICP-QMS conducted during this project and by radiochemistry, published by two different sources (Frindik 1980; Gans et al., 1987) were available for comparison (tab. 2). Although derived from two independent analytical methods performed in different laboratories on specimens which sampling dates are 14 to 20 years apart, the results showed a surprising good agreement (tab. 2).

The mean difference of 36% obtained in the comparison of the two independent methods is in the same range as the repetition of the determination of the ^{226}Ra activity in two mineral waters with sampling dates more than 14 years apart by basically the same analytical method but also conducted in two different laboratories (37 %; Apollinaris and Heppinger by Gans et al., 1987 and PlusMinus, 2000).

Compared to this the determination of ^{226}Ra activity in three mineral waters analyzed with one method in one laboratory on specimens of three sampling dates but in a much shorter time range (< 1 year) resulted with 43 % an even higher variation (Vichy, Vittel, Volvic by Gans et al., 1987).

Table 2
Comparison of ^{238}U concentrations in three mineral waters sampled before 1987 and analyzed radiochemical by a: Gans et al. (1987) and b: Frindik (1980) and re-sampled in 2000 and analyzed by inductively coupled quadrupole plasma-mass spectrometry (ICP-QMS)

	Radiochemistry		ICP-QMS	
	measured	calculated	measured	calculated
Source	mBq l^{-1}	µg l^{-1}	µg l^{-1}	mBq l^{-1}
Apollinaris	1.5a	0.06a	0.10	2.5
	2.0b	0.08b		
Contrex	24.0	0.96	1.40	35.0
Heppinger	1.5a	0.06a	0.23	5.8
	2.4b	0.10b		
Mean	9.0	0.36	0.58	14.4

3.2 Relation between uranium concentration and ^{226}Ra activity in natural mineral waters and contribution of uranium to radioactivity

Although a daughter nuclide of the decay series of ^{238}U and although the samples had been pre-selected by increasing ^{226}Ra activity there was no relation between ^{226}Ra activity and U concentration (fig. 1). This fits well to the findings of Banks et al. (1995) and Gans et al. (1987). The brand "Pellegrino" for instance had only 10 % of the ^{226}Ra activity of "Mlynsky" (Karlsbader Muehlbrunnen) but more than 10 times more radioactivity deriving from U. The additional analysis of a natural water from a hot spring in Western Turkey with a high activity of 1000 mBq l^{-1} ^{222}Rn yielded only a U content of 0.29 mg l^{-1}.

Yoshida et al. (1994) attributed disequilibria of the ^{238}U decay series to different U migrations on a microscale which again is different in each of the minerals in which U flow takes place. Another reason is the fact that the solubility of U is strongly dependent on the redox-potential of the medium. Mobilization takes place under oxidizing conditions and immobilization by precipitation in secondary minerals under reducing conditions (Hydroisotop, 2001). Banks et al. (1995) concluded from the weak correlation between the radionuclides that "hydrodynamic factors, complexing, pH and redox conditions and solution recoil phenomena are the major controlling factors for radioelement concentration, often masking the effect of mere radioelement concentrations in the bedrock". Beside the fact of being feed predominately by rain and the geology of a source area (Gellermann and Stolz, 1997) this is also a reason why on an average shallow ground and surface waters have a lower U content and a lower radioactivity compared to mineral waters.

In deeper zones of the earths crust heavy minerals containing radioactive nuclides are quite frequent. About 100 mineral species especially in granite rocks, contain 1 % or more U. Thus groundwater is more likely to have elevated U concentrations than surface water (Casas et al., 1998; Harmsen and Haan, 1990; Higgo et al., 1989; Hodge et al., 1973; Hydroisotop, 2001; Nguyen-Trung et al., 1991). On an average German groundwater has only 2 mBq l^{-1} radioactivity (Gellermann and Stolz, 1997; Hydroisotop, 2001; Medicine-Worldwide, 2001) and in the tap water of Braunschweig U concentrations are lower than the detection limit of the ICP-QMS.

When ascending to the earths surface water from extreme depths losses radioactivity due to the processes described by Yoshida et al. (1994). In a simplified way this process is similar to what happens in chromatography

Table 3
Radioactivity originating from ^{226}Ra and uranium in twelve natural mineral waters

Water	^{226}Ra (mBq l^{-1})	Uranium* (mBq l^{-1})	Radioactivity from ^{226}Ra + uranium (mBq l^{-1})	Radioactivity from uranium (%)	Mineral-content** (mg l^{-1})
Volvic	3.7	9.7	13.4	72	112
Contrex	5.6	35.4	40.9	86	2181
Bismark	6.3	0.0	6.3	0	305
Wittenseer	6.7	0.0	6.7	0	310
Hella	7.4	0.0	7.4	0	142
Evian	8.1	48.5	56.7	86	480
Perrier	11.5	66.2	77.7	85	609
Vittel	23.3	18.2	41.5	44	517
Apollinaris	118.0	2.5	120.5	2	2650
Pellegrino	152.0	217.7	369.7	59	1132
Heppinger	307.0	5.8	312.8	2	4513
Mlynsky	1780.0	19.8	1799.8	1	6157

*   calculated from uranium concentration (tab. 1).
**   sum of main minerals = Σ (Ca^{2+} + Mg^{2+} + K$^+$ + Na$^+$ + Cl$^-$ + HCO$_3^-$ + SO$_4^{2-}$)

where in a stream flowing through a column heavy compounds stay behind lighter ones. Increasing the flow comparable to forced pumping of a mineral water in order to increase the yield of a source, weakens the separation process and the amount of heavier radionuclides transported to the surface increases.

Considering 25.28 mBq for each μg U (Anonym, 2001b) U accounts to 0-86 % of the radioactivity of the mineral waters in this investigation (tab. 3). This figure doesn't consider ^{222}Rn, also a daughter nuclide of the ^{238}U decay series, because with a half-life time of only 3.8 days and as a gas its content may depend very much upon degassing and gas exchanges during the manufacturing process of the individual mineral waters. But its noteworthy that radioactivity from the gaseous ^{222}Rn in mineral waters may well exceed the one deriving from particular radioisotopes. Hevesy and Paneth (1938) for instance report the Rn content at source of spring water from Karlovy Vary in the Czech Republic (Mlynsky, tab. 3) with 426 Bq l^{-1}, 250 times more than the summarized radioactivity deriving from uranium and ^{226}Ra. The same authors also report on mineral spring waters of up to 40.000 Bq l^{-1}.

Relative to the radioactivity deriving from ^{226}Ra uranium added between 0 and more than 6 times extra to the radioactivity of the mineral waters (tab. 3). Considering a relation of the equivalent doses of ^{226}Ra to ^{238}U of 6.7:1 for adults and 13.3:1 for small children (Medicine-Worldwide, 2001) the average contribution of U to the radioactive exposure of humans deriving from consumption of mineral waters equals the one of ^{226}Ra.

However, regulations for radionuclides content and radioactivity in drinkable waters are scarce and inconsistent: The USA have issued a standard value of 30μg l^{-1} U for drinking water (EPA, 2000) but in its guidelines for U in drinking water the WHO recommends a limit of only 2μg l^{-1} U (WHO, 1998).

In Europe until now no critical value for radioactivity in drinking water has been established. One reason for this may be, that any kind of radioactivity, no matter if of natural or man made origin has to be considered as a thread for human health and minimizing risk means keeping the intake of radioactive substances as low as possible (Harduin et al., 1994; EZV, 2000). Unfortunately the missing of critical values is often miss-understood as an indication for a low or even zero risk level.

The results of this investigation show clearly that because of its significant contribution to the radioactivity of mineral water the U content need to be considered in risk assessments.

3.3 Relation between uranium and other inorganic constituents in natural mineral waters

The investigated waters showed a wide range in mineral composition (tab. 1). In the two specimens "Saratica" and "Mlynsky" for instance very different combinations of mineral concentrations were associated with high radioactivity: in "Saratica" a high U content came along with high concentrations in magnesium, sodium and sulphate, whereas in "Mlynsky" with a high ^{226}Ra activity potassium, sodium and chlorine concentrations were high too (tab. 1).

This is in line with the findings of Sanchez et al. (1999) who supposed mineral rich waters to have a high radioactivity because a high natural radioactivity is mainly related to mineralization in waters of underground origin.

In a multiple regression analysis the variability of Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-} explained 77 to 99 % of the variability of U and ^{226}Ra in the mineral waters (tab. 4). Excluding the two waters "Saratica" and "Mlynsky" which showed extreme values for mineral concentrations and radioactivity weakened the correlation coefficients, but still left significant amounts of variability explained by the mineral content (tab. 4).

As to expect, the exclusion of the extreme specimens "Saratica" and "Mlynsky" reduced the explained variability observed in the summarized radioactivity, but the multiple regression equations calculated for the whole set of minerals still explained 87 - 99 % (tab. 5). As a rule of thumb twice the amount of chloride content in mg l^{-1} was equal the summarized radioactivity (U + ^{226}Ra) in the investigated mineral waters. In addition figure 3 displays the relative weights (*Beta* weights) of individual minerals in the regression equations given in tab. 5. This figure reveals again the significance of halogenide and chloride concentrations in the mineral waters for their radioactivity.

The largest amount of variability of summarized radioactivity (U + ^{226}Ra) was explained by the variation of chloride and potassium concentrations in the mineral waters (fig. 2).

The fact that chloride and potassium concentrations explain so much of the variability of radioactivity in a mineral water reflects the close relation of mineral waters to the geology of their originating site: for instance Carnotite $K_2[UO_2VO_4]_2 \cdot 3H_2O$, an uranium mineral contains potassium, and feldspars and halides containing potassium and chloride are often associated with minerals containing actinides.

Table 4

Variability (%) of radioactivity originating from uranium and ^{226}Ra in natural mineral waters explained by the variability of Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-} in a multiple regression analysis

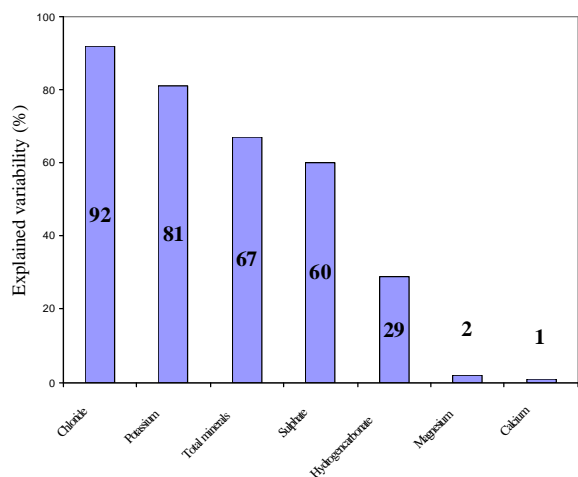|	sample set (range of radioactivity in mBq l^{-1})		
Source of radiation	0-4747	0-1800	0-367
Uranium	99.5	76.6	74.9
^{226}Ra	n.a.	99.7	97.8

Fig. 2
Variability of summarized radioactivity (uranium + ^{226}Ra) in 12 mineral waters explained by different mineral components
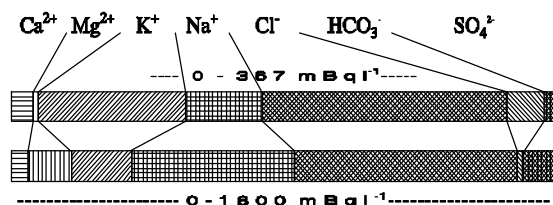

Fig. 3
Variability of summarized radioactivity (uranium + ^{226}Ra) in 12 mineral waters explained by different mineral components

Table 5
Regression equations for the concentrations of Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-} on the summarized radioactivity (uranium + ^{226}Ra) in natural mineral waters

Y = summarized radioactivity (uranium + ^{226}Ra; mBq l^{-1})	r^2 (%)
SAMPLE SET 0-1800 mBql^{-1}	
Y = 2.68 Cl^- - 33.3	9 2
Y = 6.85 Cl^- - 24.6 K^+ - 4.68	9 8
Y = 0.46 Ca^{2+} - 0.27 Mg^{2+} - 16.9 K^+ + 0.49 Na^+ + 4.9 Cl^- - 0.14 HCO_3^- - 0.071 SO_4^{2-} + 12.1	9 9
SAMPLE SET 0-367 mBql^{-1}	
Y = 1.30 Cl^- - 31.0	5 3
Y = 4.82 Cl^- - 17.0 K^+ +19.4	8 2
Y = 0.18 Ca^{2+} + 1.35 Mg^{2+} - 6.9 K^+ - 1.0 Na^+ + 5.49 Cl^- + 0.01 HCO_3^- - 0.09 SO_4^{2-} - 53.9	8 7

The regression equations given in tab. 5 were calculated to demonstrate the close relation between mineral composition and radioactivity in the waters, but they are not necessarily suitable to estimate the radioactivity of a water from its mineral composition.

4 Conclusions

The content of radionuclides and radioactivity are a characteristic feature of mineral waters. As the significance of natural mineral waters has developed from an occasionally administered remedy (Albu et al., 1997) towards a common thirst quencher replacing tap water as "the better drinking water" (Misund et al., 1999) its impact on the intake of U and radioactivity has increased too.

No matter if someone favors the idea that radioactivity is a thread or a benefit for life, in both cases information on the concentrations of radionuclides and radioactivity are essential for the customer and should be provided with the customers information and become part of the "Codex Norms for Mineral Water" (Commission du Codex Alimentarius, 1983).

Acknowledgement

156

References

Akerblom G (1994) Radon i vatten [Radon in water; in Swedish]. Forrsvaengen 3/94, pp 30-34

Albu M, Banks D, Nash H (1997) Mineral and thermal groundwater resources. London: Chapman and Hall

Anonym (2001a) United nation environment program recommends precautionary action regarding depleted uranium in Kosovo[online]. UNEP press release March 13, 2001, zu finden in <http://www.balkans.unep.ch/press/press010313.html> [zitiert im Okt.2001]

Anonym (2001b) Uranium radiation properties [online]. WISE Uranium project, zu finden in <http://www.antenna.nl/wise/uranium/rup.html> [zitiert im Okt.2001]

Anonym (2001c) Uranium a radioactive clock [online], zu finden in <http://www.atral.com/U238.html> [zitiert im Okt. 2001]

Azouazi M, Ouahidi Y, Fakhi S, Andres Y, Abbe JC, Benmansour M (2001) Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. J Environ Radioact 54: 231-242

Barisic D, Lulic S, Miletic P (1992) Radium and uranium in phosphate fertilizers and their impact on the radioactivity of waters. Water Research 26: 607-611

Banks D, Roeyset O, Strand T, Skarphagen H (1995) Radioelement (U, Th, Rn) concentrations in Norwegian bedrock groundwaters. Environ Geology 25: 165-180

BEIR III (1980) The effects on populations of exposure to low levels of ionizing radiation. Washington: Nat Acad Press

BEIR IV (1990) Health effects of exposure to low levels of ionizing radiation. Washington: Nat Acad Press

Brits RJN, Smit MCB (1977) Determination of uranium in natural waters by preconcentration on anion-exchange resin and delayed-neutron counting. Anal Chem 49:67-69

Casas L, de Pablo J, Gimenez J, Torrero ME, Bruno J, Cera E, Finch RJ, Ewing RC (1998) The role of pH and carbonate on the solubility of UO2 and uranite under normally reducing conditions. Geoch Cosmochim Acta 62: 2223-2231

Commission du Codex Alimentarius (1993) Normes Codex Pour les Eaux Minérales Naturelles. Commission du Codex Alimentarius Vol. XII, Programme mixte FAO/OMS sur les normes alimentaires (CAC/VOL. XII, 1st ed.). Organisation des Nations Unies pour l'alimentation et l'agriculture (Folio)/Organisation mondiale de la santé (WHO), Rome, 1983

Cothern CR, Lappenbusch WL, Cotruvo A (1983) Health effects guidance for U in drinking water. Health Phys 44 (Suppl 1): 377-384

Cothern, CR and Lappenbusch (1983) Occurrence of uranium in drinking water in the U.S.. Health Phys 45: 89-99

Dadfarina S, McLeod CW (1994) On-line trace enrichment and determination of uranium in waters by flow-injection inductively-coupled plasma-mass spectrometry. Appl Spectrosc 48: 1331-1336

De Camargo IMC, Mazzilli B (1996) Determination of uranium and thorium isotopes in mineral spring waters. J Radioanal Nucl Chem 212: 251-258

Dopychai A (2000) Radium-226 in Mineralwasser. ARD-Sendung "plusminus" am 11.4.2000: "Radioaktivität aus der Flasche". In: Koll H W (ed) Radioaktivität im Mineralwasser [online]. zu finden in <http://www.dr-koll.de/minwas.htm> [zitiert im Okt.2001]

Drever JI (1988) The geochemistry of natural waters. 2nd ed, Prentice-Hall

El-Himri M, Pastor A, de la Guardia M (2000) Determination of uranium in tap water by ICP-MS. Fresenius J Anal Chem 367: 151-156

Ensinger (2000) Kein Uran im Ensinger Mineralwasser [online]. Zu finden in <http://www.ensinger.de> [zitiert im Okt.2001]

EPA (2000) U. S. EPA standard for uranium in drinking water 65 FR 76707, December 7, 2000

Erikson RL, Hostetler CJ, Divine JR, Price KR (1990) A review of the environmental behavior of uranium derived from depleted uranium alloy penetrators. Pacific Northwest Laboratory

EZV (2000) Radioaktive Belastung von Mineralwasser [online]. zu finden in <http://www.ezv.de/meldungen/im_mineral-h2o_radium.html>

Fellows RJ, Ainsworth CC, Driver CJ, Cataldo DA (1998) Dynamics and transformations of radionuclides in soils and ecosystem health. Soil Sci Soc Am J, Spec Pub 52: 85-112

Franke OL, Reilly TE, Bennett GD (1987) Definition of boundary and initial conditions in the analysis of saturated ground-water bow systems: an introduction. In: JSGS Techniques of Water-Resources Investigations, Book 03, Chapter B5

Frindik O (1980) Alphaspektrometrische Methoden zur Bestimmung von Plutonium und Uran in Lebensmitteln, biologischem Material und Boeden. Karlsruhe: Bundesforschungsanstalt fuer Ernaehrung, BfE-Bericht 1980/6

Frindik O, Fischer E (1984) Uran und Thorium in einigen Mineralwaessern in der Bundesrepublik Deutschland. Z Lebensm -unters -forsch 179: 330-332

Gans I, Fusban HU, Wollenhaupt H, Kiefer J, Gloebel B, Berlich J, Porstendoerfer J (1987) Radium 226 und andere natuerliche Radionuklide in Trinkwasser und in Getraenken in der Bundesrepublik Deutschland. WaBoLu Hefte 4/1987

Garrets RM, Christ CL (1965) Solutions, minerals and equilibria. Freeman, Cooper & Co

Gellermann R, Stolz W (1997) Uran in Wässern. Z Umweltchem Ökotox 9: 87-92

Green M, Green T (1985) The good water guide. Rosendale Press, UK

Harduin JC, Royer P, Piechowski J (1994) Uptake and urinary-excretion of uranium after oral-administration in man. Radiation Protection Dosimetry 53: 245-248

Harmsen K, Haan FAM de (1980) Occurence and behaviour of uranium and thorium in soil and water. Neth J Agric Sci 28: 40-62

Hevesy G, Paneth FA (1938) A manual of radioactivity, 2nd ed. Oxford

Higgo, JJW, Falck WE, Eobkerj PJ () Sediment-groundwater systems froze the natural analogue sites of Needle's Eye and Broubster. British Geological Survey, Fluid Processes Series, Technical WE/89/40

Hodge HC, Stannard JS, Hursh JV (1973) Uranium, plutonium transplutonic elements. New-York: Springer

Hydroisotop (2001) Radium und Uran in Mineral- und Grundwässern [online]. Zu finden in <http://www.hydroisotop.de/radium.html> [zitiert Okt.2001]

Jianli N, Jinkai L, Chengzhi W, Shuqiang Q (1993) The control and protection of groundwater in fractured gneiss diving coal mining. In: Banks S B, Banks D (eds) Hydrogeology of Hard Rocks. Mem XXIVth Congress of the Int Ass of Hydrogeologists, 28 June-2 July 1993, As, Oslo, Norway, pp 259-264

Kobal I, Vaupotic J, Mitic D, Kriston J, Ancik M, Jerancic S, Skofljanec M (1990) Natural radioactivity of fresh waters in Slovenia, Yugoslavia. Environ Int 16: 141-154

Koll HW (ed) Radioaktivität im Mineralwasser [online]. zu finden in <http://www.dr-koll.de/minwas.htm> [zitiert im Okt.2001]

Krauskopf KB (1979) Introduction to geochemistry, 2nd ed, New-York: McGraw-Hill

Luckey TD (1991) Radiation hormesis. CRC Press

McNulty M (1991) The radium waters of Bath. In: Kellaway G A (ed) Hot Springs of Bath, Bath City Council

Medicine-Worldwide (2001) Radioaktivitaet im Wasser und Mineralwasser [online]. zu finden in < //http://www.m-ww.de/enzyklopaedie/strahlenmedizin/radio_wasser.html> [zitiert Okt.2001]

Milvy P, Cothern CR (1990) Scientific background for the development of regulations for radionuclides in drinking water. In: Cothern C R, Rebers P (eds) Radon, Radium and Uranium in Drinking Water. Chelsea, Michigan: Lewis Publishers

Misund A, Frengstad B, Siewers U, Reimann C (1999) Variation of 66 elements in European bottled mineral waters. Sci Total Environm 243/244: 21-41

Miura T, Morimoto T, Hayano K, Kishimoto T (2000) Determination of uranium in water samples by ICP-AES with chelating resin disk pre-concentration. Bunseki Kagaku 49: 245-249

PlusMinus (2000) Radium im Mineralwasser [online]. In: Gammy News, zu finden in <http://www.gammy.de/news/news.htm> [zitiert Okt.2001]

Ribeira D, Labrot F, Tisnerat G, Narbonne JF (1996) Uranium in the environment: Occurrence, transfer, and biological effects. Rev Environ Contam Toxicol 146: 53-89

Sanchez AM, Montero MPR, Escobar VG, Vargas MJ (1999) Radioactivity in bottled mineral waters. Appl Radiat Isot 50: 1049-1055

Schnug E, Haneklaus S, Schnier C, Scholten LC (1996) Issues of natural radioactivity in phosphates. Comm Soil Sci Plant Anal 27: 829-841

Singh NP, Wrenn ME (1987) Uptake of uranium from drinking water. Trace substance in environmental health. In: Proc Univ of Missouri's annual conf on trace substances in environmental health. (21st). 203-212

Spalding RF, Sackett WM (1972) Uranium runoff from the Gulf of Mexico. Distribution province anomalous concentration. Science 175: 629-631

Stevenson F (2000) zitiert Stueben H: Bericht ueber Radioaktivitaet in Mineralwaessern [online]. Kieler Nachrichten vom 9.7.2000. Personal communication

Taylor HE (2001) Inductively coupled plasma-mass spectrometry. London: Acad Press

UNEP (2001) Depleted uranium in Kosovo - post conflict environmental assessment. United Nations Environmental Programme, Nairobi, Kenya

West G (1994) The radon water of Badgastein. Austria. Unpublished manuscript cited in Albu et al., 1997

WHO (1998) WHO guidelines for uranium in drinking water

Yoshida H, Kodama K, Ota K (1994) Role of microscopic flow-paths on nuclide migration in sedimentary rocks - a case study from the Tono uranium deposit, Central Japan. Radiochimica Acta 66-7: 505-511