Radium isotopes and 222Rn in Austrian drinking waters

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The activity concentrations of the Ra isotopes, 226 Ra and 228 Ra, as well as of 222 Rn were measured in Austrian tap waters. Rn was extracted into a mineral oil cocktail not miscible with water and measured by liquid scintillation counting using pulse-shape analysis for α/β -separation. Ra isotopes were co-precipitated with BaSO₄ or concentrated by filtration through an element specific filter. EDTA solution was used to redissolve the precipitate as well as to release the Ra from the filter. After mixing with a cocktail, the EDTA solution was measured by liquid scintillation counting, too. From our results the effective ingestion doses for adults and 3 months old babies were calculated.

Introduction

Measurement of naturally occurring radionuclides in groundwater is important for environmental and public health studies. The source of the radionuclides dissolved in the water is the surrounding bedrock; in geological settings rich in uranium, like, e.g., granite, also higher activity concentrations of the uranium series radionuclides like 226Ra and 222Rn are expected. However, it is well known that the different radionuclides are not in radioactive equilibrium with each other due to differences in mobilization from the rock and water chemistry. So, e.g., radon activities can be three to five orders of magnitude higher than U or Ra activities, probably due to absorption of the U and Ra to the host rock, while the gaseous Rn is diffusing along microcristalline imperfections into the interstitial waters.1,2

With regard to radiation protection the uranium series nuclides 222 Rn and 226 Ra (both α -emitters with half-lifes of 3.8 days and 1600 years, respectively) and the thorium series nuclide ²²⁸Ra (a weak β -emitter with a half-life of 5.7 years) are expected to give the highest contributions to the effective dose from ingestion of water. ²²⁸Ra has a clearly higher dose conversion factor of 0.66 μ Sv/Bq for adults and 31 μ Sv/Bq for 3 months old babies, compared to the 226Ra numbers of $0.28 \mu\text{Sv/Bq}$ for adults and $4.7 \mu\text{Sv/Bq}$ for babies (the radiotoxicity of the α -emitting ²²⁴Ra (half-life 3.64 days), the 228 Ra progeny, and its daughter products is small because of their extremely short half-lives).³ Radon can lead to exposures by being ingested and also by being inhaled after having been released from the water into indoor air during water usage as, e.g., washing or cooking. Dose from uranium itself usually is neglectable, but it is a very toxic heavy metal and, therefore, has to be regulated; the maximum levels are between 10 and 30 μ g/l.^{4,5} The radiotoxicity of ²¹⁰Pb and especially of 210Po is comparable or even higher than that of the Ra isotopes, but their activity

concentrations in water usually are rather low. 232Th, the precursor of $228Ra$, is only very seldom found in water because it easily precipitates and adsorbs to the sediment; the same holds for the other thorium isotopes.

The European Commission Drinking Water Directive (98/93/EC) from 1998 does not give maximum activity concentrations for the respective nuclides but sets a maximum effective dose of 0.1 mSv-y^{-1} from ingestion of tap water for the general public; however, radon and radon daughters were explicitly excepted from this regulation. Not before December 2001 the EC published a Recommandation [K(2001) 4580] concerning radon and its long-lived daughters: the countries were asked to define an action level higher than 100 Bq/l 222 Rn for public supplies depending on the national situation; for concentrations higher than 1000 Bq/l (the action level for private wells) remedy actions are justified from the point of radiation protection. This EC recommendation has also given reference maximum concentrations of 0.1 Bq/l for 210Po and 0.2 Bq/l for $210Pb$.

The aim of this work was to give a first overview about the radiological situation of Austrian tap waters. While data on the ²²²Rn and ²²⁶Ra contents of different spring and well waters in Austria⁶ and elsewhere^{1,7,8} exist, until now there has been a clear lack of data concerning the isotope 228 Ra. Using a QuantulusTM 1220 (Wallac Oy, Finland) ultra low-level liquid scintillation counter with α/β -separation capability, both radium isotopes can be determined simultaneously after apropriate chemical isolation. Though fully aware of the radiotoxicity of 210Pb and 210Po we concentrated on the radium isotopes and $222Rn$, as we expected them to give the largest contribution to the effective dose due to higher activity concentrations in the water samples compared to 210Pb and 210Po. Furthermore, for radium determination sample collection was very easy (see below) and could be done by volunteers. Samples were taken randomly from all over Austria.

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Experimental

Sampling and methods

Samples were collected randomly by students and volunteers mainly from the public drinking water supplies; only a few were from private wells. 1–2 liter water was filled into PET- (polyethylenterephthalat), PE- (polyethylen) or glass bottles; the bottles were filled completely so that the remaining gas phase was as small as possible in order to prevent the radon from escaping into the air pocket. Radon analysis was done as soon as possible, in a few cases, however, Rn measurement was not possible due to longer transport ways or longer storage times before the sample came to the laboratory.

7 ml of radon absorbing mineral oil scintillator (NEF-957A, Packard BioScience) not miscible with water was filled into a LSC vial (volume 20 ml). 10 ml of water were pipetted from the bottom of the bottle and transferred to the LSC vial by dipping the pipette into the cocktail and letting the water flow under it; this procedure prevents loss of radon as far as possible. After shaking and waiting for about 2 hours for ingrowth of the 222Rn daughter products, the sample was measured by liquid scintillation counting using pulse-shape analysis for separation of the α - and β -spectrum. The counting efficiency is 300% for ²²²Rn and its two α emitting daughters 218Po and 214Po. The blank value in the counting region of interest is (0.19 ± 0.04) cpm, corresponding to 1 mBq of 222 Rn.

The radium isotopes ²²⁶Ra from the ²³⁸U-series and 228 Ra from the 232 Th-series were determined by sulfate co-precipitation. $8-10$ The sample was acidified with 10 ml concentrated nitric acid and then reduced to about 150–200 ml by evaporation. After cooling a pH value of 2–3 was adjusted by adding NaOH solution. After adding 19 mg $Ba(NO_3)$, carrier, the sulfate was precipitated from the boiling solution by adding about 6 ml of 1M H_2SO_4 . The precipitate was centrifuged and washed neutral, after that it was dissolved in 5 ml of 0.25M alkaline EDTA. The solution volume was reduced by evaporation to 2–3 ml; the sample solution was mixed with the cocktail HiSafe III (Wallac Oy) and measured after a cooling time of 2–3 hours.

Alternatively, in a few samples the radium isotopes were isolated by filtration of the acidified sample (resulting solution $0.2M$ HNO₃) through the element specific Radium Rad Disks (3M Empore 3291).¹¹ Radium was eluted from the filter with 0.25M alkaline EDTA; again the sample volume was reduced by evaporation before mixing with the cocktail.

For both methods the chemical yields were found between 95 and 100% by multiple processing of subsamples from a standard solution with known ²²⁶Ra activity concentration. The counting efficiency for 226Ra was 100% , the counting efficiency for $228Ra$ was determined with a standard solution $(^{228}Ra$ separated from a 232Th solution by ion-exchange) and found to be $(57±3)\%$ ¹⁰

Both the coprecipitation and the filtration method isolated not only the radium isotopes, but also the 210Pb and, therefore, would be a perfect method for measuring these nuclides simultaneously. However, for lead sorption effects at least on PE-bottles had been reported when not acidifying the water at the moment of sampling.¹² Also 40% of our samples showed $210Pb$ values lower than expected from the measured ²²²Rn activities, again demonstrating the importance of sample stabilization by acidifying. The radium concentration in the sample is not affected by sorption effects and so justified the cheap sampling by volunteers with forfeiture of information about the 210Pb content.

The blank count-rate for both methods was 0.15 \pm 0.04 cpm and 1.5 \pm 0.1 cpm for ²²⁶Ra and ²²⁸Ra, respectively (the given errors are 3σ -errors). The lower limit of detection (LLD) calculated after CURRIE¹³ for 226 Ra is 1 mBq per sample (counting time 1000 min), and for 228Ra the LLD is about 4.5 mBq per sample.

Results and discussion

Table 1 shows the results of our measurements. The 222 Rn activity concentrations are given in Bq/l, the radium concentrations are in mBq/l.

Radon-222

Only two samples showed values higher than 100 Bq/l 222Rn: St. Stefan am Walde (Mühlviertel) 644 Bq/l, and Schönfeld bei Drosendorf (Waldviertel) 119 Bq/l, both situated in the Bohemian Massif. Activity concentrations of 12 samples were between 10 and 99 Bq/l. The corresponding sampling sites were in the Bohemian Massif (Langschlag, Waidhofen/Thaya, Gastern), in the sourroundings of the famous radon spa Badgastein (Salzburg), and in gneiss areas in Carinthia (Eberstein, Hermagor); Mainburg and Feldkirch are in the Flysch Zone where in contrast to our results usually very low 222Rn concentrations are measured. 30 samples showed ²²²Rn values smaller than 10 Bq/l.

We expect to find much more tap waters with ²²²Rn activity concentrations of about 100 Bq/l and more when investigating especially the Mühl- and Waldviertel (Bohemian Massif) more thoroughly.

Table 1. ²²²Rn activity concentrations (in Bq/l) and ²²⁶Ra and ²²⁸Ra activity concentrations (in mBq/l) in Austrian tap water

Sample	Date	Volume, 1	$\sqrt{222}$ Rn, Bq/l	$\sqrt{226}Ra$, mBq/l	$\sqrt{228}Ra$, mBq/l
Steiermark					
Graßnitzberg	2001-10-28	1		1.8 ± 0.3	≤ 5
Graz	2002-02-23	2.2	9.3 ± 0.1	$1.1 + 0.1$	
Irdning	2001-10-28	1.59		1.9 ± 0.2	
Knittelfeld	2001-12-27	1		6.4 ± 0.4	≤ 8
Leibnitz	2002-02-23	1.57	68.4 ± 0.5	2.7 ± 0.2	
Loipersdorf	2002-02-03	1	3.69 ± 0.08	6.8 ± 0.4	≤ 5
Spital/Semmering	2002-02-03	2		3.4 ± 0.2	
Tirol					
Innsbruck	2002-02-07	1	5.43 ± 0.06	< 0.5	
Lienz	2001-11-25	1		0.7 ± 0.3	
Pettneu	2002-01-05			6.4 ± 0.4	
St. Anton	2002-03-16	1.58		2.6 ± 0.2	
Vorarlberg					
Dornbirn	2002-02-05		$2.28 + 0.03$	2.1 ± 0.3	
Feldkirch	2001-12-25		13.79 ± 0.07	5.2 ± 0.4	\leq 5
Lauterach	2001-12-24		6.45 ± 0.05	2.7 ± 0.3	
Lech	2002-03-15	1.58		2.4 ± 0.2	

Table 1. Continued

Radium-226

 226 Ra activity concentrations higher than 10 mBq/l were found in 6 samples: Waidhofen/Thaya 111 mBq/l, Eberstein 48 mBq/l, Hermagor 38 mBq/l, the drinking water in the healing gallery in Badgastein 32 mBq/l, Eisgarn 30 mBq/l and Freistadt 19 mBq/l. These sampling sites are situated in the Bohemian Massif with the exception of Eberstein and Hermagor (gneiss areas in Carinthia) and Badgastein (radon spa in Salzburg); it should be emphasized that the 32 mBq/l value was only found in the drinking water in the healing gallery, the 226 Ra concentration in water from the public water supply was much lower (about 6 mBq/l). The well in the healing gallery had been used mainly by workers in the gallery and was closed a few years ago (the water was also bearing high uranium levels).

In the samples from the healing gallery and from Waidhofen/Thaya the high 226Ra values were correlated with high 222 Rn concentrations (80 and 43 Bq/l, respectively), also in the above mentioned samples from Carinthia 222Rn levels were 10 and 17 Bq/l, i.e., higher than in the majority of our samples. Concerning the Eisgarn sample, 222Rn could not be measured due to a longer storage time before it was brought to the laboratory; from our measured value of (40 ± 1) mBq/l ^{210}Pb we could calculate a preceeding ^{222}Rn concentration of 93 Bq/l; however, this is only an estimate as we do not know whether we got hold of the whole amount of ²¹⁰Pb (the sample was not acidified, see above) nor are we able to distinguish between supported and unsupported ²¹⁰Pb. On the other hand, samples from St. Stefan am Walde and Schönfeld/Drosendorf with ²²²Rn levels of 644 and 119 Bq/l, respectively, showed rather low 226 Ra concentrations of about 8 and 3 mBq/l. Also samples from Langschlag, Badgastein and Leibnitz (^{222}Rn) concentrations between 44 and 68 Bq/l) showed only low 226Ra values.

Radium-228

 228 Ra from the thorium series was found in only 2 samples originating from Kamegg (Bohemian Massif) and Forstau (Salzburg) with 10 and 16.8 mBq/l, respectively; both samples were derived from private wells. For 24 samples "smaller than" values were given; this was due to higher 210Pb levels (mostly a consequence of elevated 222Rn concentrations) or rather long-lived chemoluminescence raising the background in the 228Ra region and so leading to higher LLDs.

It should be mentioned that 232Th had not been found in any of our samples; if present in water thorium would also be coprecipitated with $BaSO₄$ and its relatively low α -energy of 4.0 MeV would be easily recognizable in the α -spectrum. In the B-spectrum from Forstau we saw a clear contribution from 234Th and 234Pa, indicating elevated uranium levels. This was not surprising as nearby occurrence of uranium ore is reported.

Dose calculation

Table 2 summarizes the effective annual doses for adults and 3 months old babies calculated from our measurement results. Only samples with 222Rn activity concentrations >10 Bq/l and 226 Ra levels >20 mBq/l as well as the samples containing 228Ra were listed. The dose conversion factors used are given in Table 3.3,14

Sample	Adults			Babies (3 months old)		
	222Rn	226 Ra	^{228}Ra	222Rn	226 Ra	^{228}Ra
Eberstein	0.12	0.010	< 0.004	0.30	0.058	< 0.064
Hermagor	0.07	0.008	< 0.002	0.18	0.046	< 0.032
Eisgarn		0.006			0.035	
Kamegg	0.06	0.001	0.005	0.16	0.006	0.081
Langschlag	0.32	0.0004	< 0.004	0.78	0.002	< 0.064
Schönfeld/Dros.	0.86	0.0005		2.00	0.003	
Waidhofen/Th.	0.31	0.022	< 0.002	0.8	0.127	< 0.032
Freistadt	0.01	0.004	< 0.003	0.04	0.023	< 0.048
St.Stefan a. W.	4.72	0.0015	< 0.008	11.2	0.009	< 0.129
Badgastein	0.37	0.001	< 0.003	0.8	0.006	< 0.048
Leibnitz	0.50	0.0005		1.2	0.003	
Forstau		0.002	0.008		0.012	0.130

Table 2. Effective dose from ingestion (in mSv/y)

Table 3. Dose conversion factors (in uSv/Bq) (UNSCEAR 1993, ICRP 1993)

		226 Ra	
Adults:	0.01	0.28	0.66
Babies (3 months):) 07		21

The 222Rn dose conversion factors given by UNSCEAR are higher than the ones given by the National Research Council $(USA)^{15}$ by a factor of 3. While the latter also stated that there is no scientific reason using different conversion factors for different age groups, the UNSCEAR value for babies is 7 times higher than the value for adults. This means that our calculation using the UNSCEAR factors is rather conservative. The assumed drinking water consumtion was 730 l/y and 250 l/y for the two respective age groups (adults and 3 months old babies).

Within our samples only St. Stefan am Walde was relatively near to the EC interaction level (for private wells) of 1000 Bq/l giving an estimated annual ingestion dose of 4.7 mSv for adults (11.2 mSv/y for babies); the dose from the Schönfeld/Drosendorf sample is 0.86 mSv/y (2.0 mSv/y for babies), while all other samples ($\langle 70 \text{ Bq}/1222 \text{Rn} \rangle$ contribute less than 0.5 mSv per year (<1.2 mSv/y for babies).

It should be further noted that it has been estimated that 1000 Bq/l of 222 Rn in tap water will increase the indoor radon concentration by 100 Bq/m^3 , $14,15$ leading to an inhalation dose of about 1.6 mSv/y.

No sample with radium doses for adults near or higher than the dose limit of 0.1 mSv/y was found. The highest values were 0.02 mSv/y and 0.01 mSv/y derived from the 226 Ra concentration for the samples from Waidhofen/Thaya (Waldviertel) and Eberstein (Carinthia), respectively; all other values were lower by at least one order of magnitude, and also doses from 228Ra were clearly lower. However, due to the fact that for the radium isotopes the dose conversion factors for babies are considerably higher than for adults, for this

age group the derived annual effective ingestion doses are also higher despite lower water consumption: we found 0.127 mSv/y from 226Ra in the Waidhofen sample and 0.058 and 0.046 mSv/y in the samples from Carinthia, as well as 0.035 mSv/y in Eisgarn (Waldviertel). This means that about 40 mBq/l ^{226}Ra will produce 50% of the annual intake limit for babies. Effective ingestion doses for babies of 0.08 and 0.13 mSv/y from 228 Ra were calculated for the Kamegg (Waldviertel) and Forstau (Salzburg) samples. In the case of 228Ra an activity concentration of only 13 mBq/l will produce 100% of the annual intake limit from water consumption for babies.

Conclusions

Liquid scintillation counting is a tool well suited for the measurement of 222 Rn as well as of the Ra isotopes ²²⁶Ra and ²²⁸Ra due to α / β -separation by pulse-shape analysis; the radium isotopes were separated by coprecipitation or filtration through an element specific filter.

In our first survey of tap water samples taken randomly from all over Austria, maximum effective doses from ingestion of 222 Rn were 5 mSv/y for adults and 11 mSv/y for 3 month old babies; the calculation was rather conservative using the dose conversion factors given by UNSCEAR.

With regard to 226 Ra all samples gave doses for adults clearly lower than the EC limit of 0.1 mSv/y. When calculating the respective doses for babies one sample was found exceeding this maximum value. ²²⁸Ra was only detected in two out of 63 samples; while the effective dose for adults was far below the limit given in the EC Directive, for babies one sample was near to the limit while the second sample exceeded it. Therefore, special attention must be paid to $228Ra$ as in the case of this nuclide for babies an activity concentration of only 13 mBq/l will produce 100% of the annual intake limit from water consumption.

Further investigations of drinking water will concentrate on the area of the Bohemian Massif with its granite bedrock and will also include the measurement of the radon progeny ^{210}Pb and ^{210}Po in order to get realistic figures of the sum doses from water consumption.

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