Natural radioactivity of selected bottled waters in Poland

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A b s t r a c t. Natural radioactivity has been measured in 22 different bottled waters from central and southern Poland. Although most of the investigated waters origi- nate from the Outer Carpathian Mts. (Flysch Carpathians), samples from the Kraków-Częstochowa Upland, Lublin Basin, Podlasie Depression, Silesian-Kraków Monocline, Szczecin-£ódź Basin and Sudety Mts. were also analysed. Mineralization of these waters is dominated by the HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+ ions and falls within the range from 186 mg/l to 2930 mg/l. Except for "Staropolanka 2000" and "Wielka Pieniawa", The activities of radium isotopes in all other waters are in the order of several mBq/l, with the maximum values reaching 100 mBq/l. The activities of uranium isotopes are below 75 mBq/l, with the average values of 4.9 mBq/l mBq/l and 11.7 for ^{238}U and ^{234}U, respec- tively. The calculated annual committed effective dose from uranium and radium isotopes resulting from the consumption of the investi- gated waters by teenagers and adults is lower than the recommended value of 0.1 mSv/year. However, if some of the analysed waters ("Dobrawa", "Nałęczowianka", "Polaris", "Aquarel", "Hermes", and highly mineralised waters) are used to prepare food for infants below 1 year old, then the annual committed effective dose will exceed the recommended value.

Keywords: *bottled water, radioactivity, radium, uranium, annual committed effective dose*

In decades in Poland, as in the rest recent of Europe, the bottling industry has been growing rapidly. In 2011, the amount of bottled consumed water per of the statistical consumer was 74 l; by comparison, in 1960. - only 0.4 l (Rutkowski, 2011). In 2020, consumption of bottled beverages per statistical projected at inhabitant of Europe is 259 l, 44% of which will be mineral waters (Rutkowski, 2011). According to the , same forecastsbottled water consumption in Poland will reach approximately 110 litres. addition to are valuable from a biochemical point of , Inelements that viewwater may also contain heavy and radioactive elements that may have undesirable or harmful for the organismconsequences .

In Poland, the bottling industry of natural mineral waterson natural mineral waters, spring waters and table waters", the "Act of 25 August 2006 on safety", , spring waters and therapeutic waters is subject to a number of strict regulations contained in the "Regulation of the Minister of Health of 31 March 2011 food and nutrition as amended; "Act of 9 June 2011. - Geological and Mining ", "Regulation of the Minister of Health of Law13 April 2006 on the scope of examinations necessary to determine the therapeutic properties of natural raw materials medicinaland the criteria for their assessment and the specimen of the certificate confirming these therapeutic properties of the climate, theproperties" and in "Regulation of the Minister of Health of 20 April 2010 amending the Regulation of the on the quality of water intended for human consumption". Every producer of bottled waters is isotopic obliged to have up-to-date chemical and attestation of the waters used in accordance with the current legislation. Numerous papers can be found in the literatureon the radioactivity of bottled mineral , e.g. Surbeck (1995), Bayés et al. (1996), Kralik et al. (2003), waters Somlai et al. (2002), Skwarzec et al. (2003), Chau and Michalec (2008), Wallner and Jabbar (2010). These publications concern isotope determinations of uranium, radium and lead in some bottled waters sold in Germany, Austria, Spain, Hungary and Poland. The literature related to natural radioactivity of bottled waters in Poland is rather scarce. Such works, e.g. Mielnikov et al. (2000), Chau and Fujak (2007) or Chau et al. (2007), are published in journals that are difficult to access for the average con- sumer. The lack of reliable knowledge on the conditions for the occurrence of radionuclides in natural waters of various types and the lack of information related to the actual risks arising from them create favourable conditions for issuing sometimes inaccurate opinions appearing in the media at large. The inadequate level of education of the public in this respect is further exacerbated by the difficulty of this publicising academics, who do not count publications of a popularising nature towards their academic achievements.issuein the daily press and by the rules governing the assessment of

This work, too, range ofdoes not reach a wide recipients. Nonetheless, it is significantly increasing their gro- du. This article presents the results of analyses of the uranium content and radium of selected bottled natural

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Table 1. Chemical composition and radionuclide activities of spring (Z), mineral M) and medicinal (L) . watersThe symbol TDS (.*total dissolved solids*) denotes the total mineralisation of the waters
Table 1. Natural radioactivity levels and chemical composition of the: spring waters (Z), mineral waters (M), therapeutic waters (L). TDS (total dissolved solids) denotes the total water mineralization

Exploitation Exploitation placeplace , **commercial name of bottled water** *and commercial name of bottled water*	*Chemical composition Chemical composition* [mg/l]								*Total Total* activity *activity* [mBq/l]		*Activity of isotopes Activity of isotopes* [mBq/l]					
	Ca^{2+}	Mg^{2+}	At^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	TDS	alpha	beta	^{226}Ra	^{228}Ra	^{238}U	^{234}U	$^{234}U/^{238}U$	^{40}K
Outer Carpathians *Outer Carpathians*																
Krynica, "Kryniczanka" (M)	548	114	67,3	6,7	2170	9,6	10,6	2930	96	333	73	96	2,86	3,51	1,23	211
Krynica, 'Jan' (L)	152	24,8	15,4	3,6	525	51,3	17,7	790	19	474	9	9	3,94	5,36	1,36	114
Muszyna, "Muszyna" (M)	483	51,9	47,2	6,5	1860	2,9	5,3	2450	206	284	47	45	1,72	4,67	2,72	170
Muszyna, "Muszynianka" (M)	192	129	93,2	10,1	1460	31,1	13,9	1930	55	367	44	45	4,66	10,2	2,19	290
Piwniczna, "Piwniczanka" (M)	235	121	-	17,9	1900	29,4	12,4	2314	155	592	57	39	2,2	2,09	0,95	563
Ustroń, "Ustronianka" (M)	78,6	15,6	5,8	-	291	20,6	12	423	100	161	16	<10	10,5	16,9	1,6	n.a.
Zywiec, "" Zywiec(Z)	27,8	8,2	8	-	109	-	4,6	186	2,2	53	1	29	0,61	1,66	2,72	n.a.
Krościenko nad Dunajcem, "Kinga" (M)	97,8	13,1	4,6	2,3	336	28,5	7	489	9	160	3	5	4,43	7,79	1,76	73
Tylicz, "Kropla Beskidu" (Z)	46,5	19,5	37,7	1,5	299	30,3	1,8	434	11	88	4	<10	2,8	6,45	2,28	49
Ustroń, "Laguna" (Z)	71,6	25,6	5,8	-	291	20,6	12,8	427	23	132	22	8	10	12,1	1,21	n.a.
Jura Krakowsko-Częstochowska *Kraków-Częstochowa Upland*																
Progress, "Jurassic" (Z)	67,1	36,5	9	2,5	346	37,7	8,5	507	n.a.	n.a.	12	<10	1,34	7,42	5,48	79
Lublin Trough *Lublin Basin*																
Nałęczów, "Nałęczowianka" (M)	114	23,1	12,7	5,4	496	-	8,5	696	16	183	2	16	0,81	1,19	1,47	170
Kazimierz Dolny, "Kazimierska" (M)	87,7	28,7	10	4	388	35,2	7,4	561	n.a.	n.a.	1	13	5	9,51	1,9	126
Raszyn, "Oasis" (Z)*	52,1	7,3	2,5	0,5	171	23	4,8	281	18	87	1	8	6,79	10,8	1,59	16
Precambrian platform - Podlasie lowering *Precambrian Platform - Podlasie Depression*																
Bielsk Podlaski, "Polaris" (Z)	103	16	11,3	2,9	433	-	2,8	592	40	406	20	12	4,23	4,47	1,06	93
Silesian-Cracow Monocline *Silesian-Kraków Monocline*																
Rzeniszów, "Aquarel" (M)	44,1	15,8	60	8,7	336	-	28	519	100	252	18	19	0,57	0,75	1,32	223
Rzeniszów, "Dobrawa" (M)*	55,2	29,6	1,2	0,85	287	20	5,3	402	139	67	66	10	5,1	22,8	4,47	-
Palaeozoic platform - the BasinSzczecin-Lodz *Paleozoic Platform - Szczecin-Lodz Basin*																
Włoszakowice, "Hermes" (M)	109	17	10	1,3	214	117	35,5	504	20	87	4	18	5,1	7,1	1,39	42
Warsaw, "Mazowszanka" (M)*	38,1	15,6	95	7,5	322	-	64,2	543	n.a.	n.a.	1	<10	n.a.	n.a.	n.a.	236
Sudetes *Sudety Mts.*																
Polanica, "Staro-polanka 2000" (M)	355	77,3	135	52	1865	24	8,9	2520	592	1780	525	276	7,68	2,2	2,2	1360
Polanica, "Wielka Pieniawa" (L)	232	26,1	68,5	38,7	1030	29,4	7,1	1400	625	1560	249	169	4,4	4,32	4,32	1070

Explanatory notes: n.a. - not analysed, * - bottling abandoned.
Explanations: n.a. - not analysed,- no longer bottled.*

mineral waters and spring and waters therapeutic from various geological regions of Poland (Table 1). The results of measurements were used to estimate annual effective doses caused by ingestion of the isotopes mentioned above. The measurements were taken in the laboratory of the Department of Applications Nuclear Physics at the Faculty of of Applied Physics Science and and Informatics of Technology the AGH Stanisław Staszic in Cracow.University

ANALYTICAL METHODS

In order to determine the total activity of the alpha- and beta-emitting nuclides, the mass of the initial water sample (approximately 1 kg) was reduced several times by slow evaporation. Then 8 g of the concentrated solution was collected and mixed with 12 ml of liquid scintillator (HiSafe 3). The prepared sample thus was measured with a Quantulus™ spectrometer. This spectrometer has the ability to differentiate signals from alpha and beta particles. For this purpose, calibration with standard samples is required. Standard solution for the measurement of total

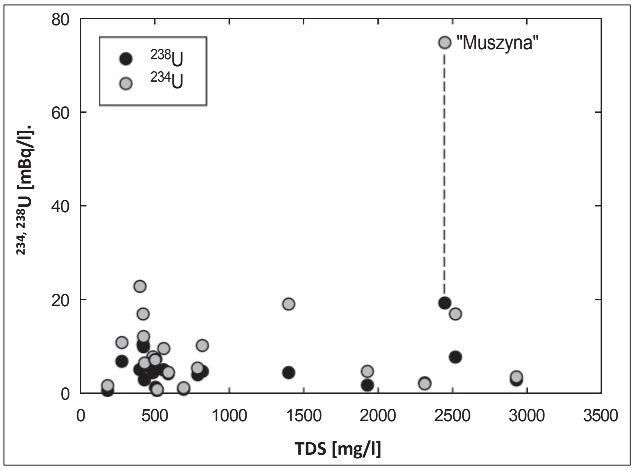

Fig. 1. Relationship between total water mineralisation (TDS) and uranium isotope activity
Fig. 1. The relationship between activities of uranium isotopes and total mineralization of the waters (TDS)

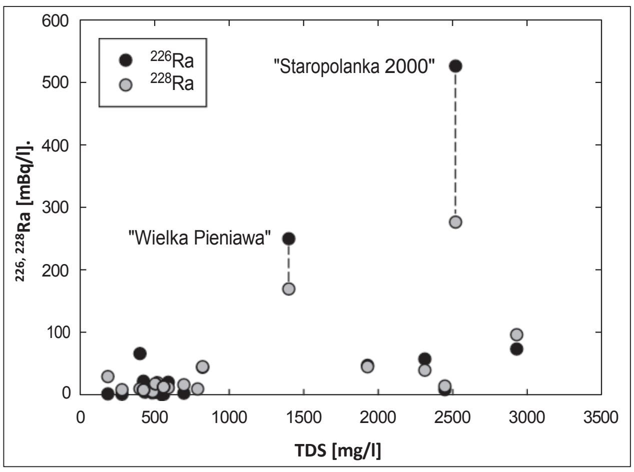

Fig. 2. Relationship between total water mineralisation (TDS) and radium isotope activity
Fig. 2. The relationship between activities of radium isotopes and total mineralization of the waters (TDS)

alpha-emitting isotope activity was prepared on the basis of the isotope ^{241}Am. The solution ^{90}Sr-^{90}Y served as a calibration standard for beta-radioactive nuclides. procedures The preparation and measurement are described in detail in Rusconi et al. (2006).

For the determination of uranium isotope activity, 5-litre water samples were used, from which uranium was co-precipitated on manganese hydroxide reduction by evaporation. The resulting precipitate, after dissolution in 9 M HCl solution, was purified using the ion-exchange technique. Finally, the uranium was precipitated with neodymium chloride (NdClafter 5-fold $_3$) and the resulting precipitate was drained on an Eichrom™ plastic mem- brane filter with a porosity of 0.1 μm. After drying, the filters were measured with a Canberra™ spectrometer with a silicon semiconductor detectorPIPS-type . The procedure used ^{232}U as an internal standard.solution

Radium isotopes were precipitated in the form of sulfate- The sample was mixed from a 2 l water sample. After separation of the interfering isotopes and chemical purification of the sample, it was mixed in a proportion of 6 ml of the final solution
+ 12 ml gel and measured with a scintillatorAlpha/Beta Scintillation Counter™ scintillation . Detailed chemical and measurement prepa- ration procedures are described in Chau Wallac 1414 Guardian liquid spectrometer(2010).

Data on the chemical composition of the tested waters were taken from the labels on the bottles.

RESULTS OF THE ANALYSES AND THEIR DISCUSSION

The chemical composition and results of radiolabelling of the analysed bottled waters are presented in Table 1. The analysed watersare natural mineral , watersspring waters and therapeutic waters. Mineralisation of the bottled waters is contained in the range 186-2930 mg/l, with individual ion contents of:
- HCO_3^- - 109-2170 mg/l;
- Ca^{2+} - 27.8-548 mg/l;
- Mg^{2+} - 7.3-129 mg/l;
- At^+ - 1.2-135 mg/l;
- K^+ - 0.5-52 mg/l;
- SO_4^{2-} - 2-117 mg/l;
- Cl^- 1.8-64.2 mg/l.

Table 1 shows that the total activities alpha- and beta-radionuclide for all studied waters except for "Staropolanka 2000" and "Wielka Pieniawa" are lower than the maximum permissible levels recommended by WHO (WHO, 2008), equal to 0.5 Bq/l and 1 Bq/l respectively. The high levels of radioactivity in the Sudetic mineral waters are related to the geological structure (lithology and tectonics) of the water-bearing formations in this region. The natural radioactivity of bottled waters from other regions of the country is low. Uranium isotope activities are in the range of a few to a few tens of millibecquerels per litre, while radium isotope activities do not exceed 100 mBq/l. In the case of the studied waters, no correlation is observed between uranium or radium activity and their overall mineralisation (cf. Fig. 1-2). eitherNo such correlations are observed for individual ionic constituents .

Measurement data also indicate that in most of the studied waters, isotope ^{40}K activity accounts for more than 50% of the total betapromie- nuclide activity. However, due to its negligible radiological harmfulness, this isotope is neglected in considerations related to the estimation of annual effective loading doses.

ANNUAL EFFECTIVE DOSE

The annual effective loading dose D [mSv/year] (referred to also hereafter as annual) dosedue to absorption of radionuclides contained in water can be estimated using the following formula:

$$D = \sum_i V \cdot e_i(g) \cdot w_i \quad (1)$$

where

$e_i(g)$ - effective loading dose due to absorption of the i-th isotope with activity 1 Bq for a person of age group g expressed in Sv/Bq,

w_i - concentration of the ith isotope in a given water [Bq/l],

V - average amount of water consumed by a person in a given age group g per year [l].

Values of $e_i(g)$ are provided in the "Beginning of the Council of Ministers of 18 January 2005 on dose limits for ionising radiation". Most misconceptions about the harmfulness of radionuclides contained in water are due to incorrect inter- pretation of the above formula. First of all, the effective dose is determined for an annual periodaccounting . This means that consumption of water with increased radioactivity for a shorter period (e.g. during spa treatment) does not necessarily result in exceeding the annual effective dose. An important factor influencing the dose the annual is isotopic parameters. As indicated by a few studies, it (!) intake of water with the given is very difficult (if at allage possible) .to determine this figure for individual groups

In the study, annual doses were estimated for three categories - infants under 1 year, adolescents (12-17 years) and adults (?17 years). It was assumed that infants consume 365 litres of water . The results of the estimates for per yearthis age category are illustrated in Fig. 3. As can be seen from the data presented, in the category, infantalmost all the waters exceed tested the permissible annual intake. Therefore, natural mineral waters should not be used for cooking and preparing meals for infants.

In the adolescent and categoriesadult , was assumed annual consumption at the statistical mean, i.e. 74 l/year. Estimated doses The annual doses are shown in Fig. 4, where through the figure a line indicates the recommended acceptable dose level of 0.1 mSv/year. In both age , with an annual consumption of 74 l of water, the annual doses levelscategoriesare below the permissible . The exceptions are "Staropolanka 2000" in the 12-17 years . categoryIt estimated isthat an adult drinks, in various forms, about 2 l of water per day, i.e. about 730 l per year. This is an amount that leads to

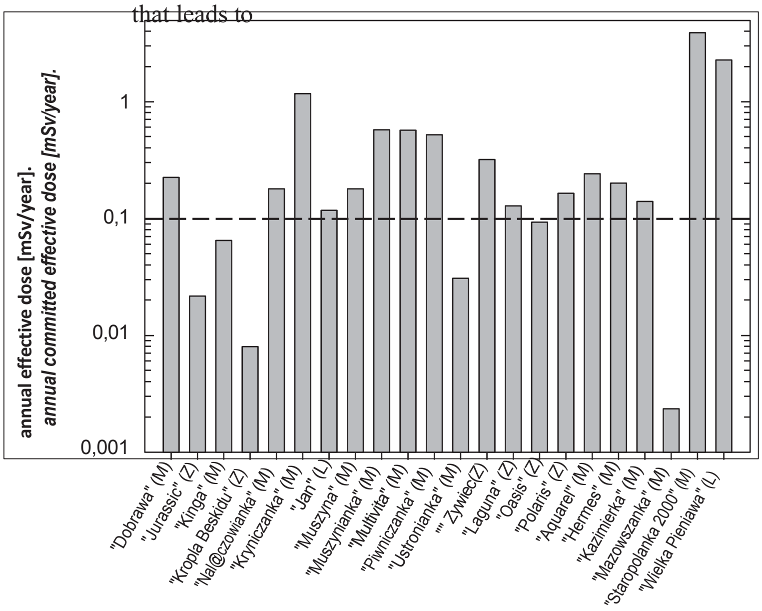

Fig. 3. Annual burden dose to infants resulting from water consumption of 365 l/year. The dotted line indicates the acceptable level. For designations Z, M, L, see Table 1.

Fig. 3. Annual dose rate for infants resulting from intake of the waters at the level of 365 l/year. Dashed line denotes the recommended level. Symbols Z, M, L - as in Table 1.

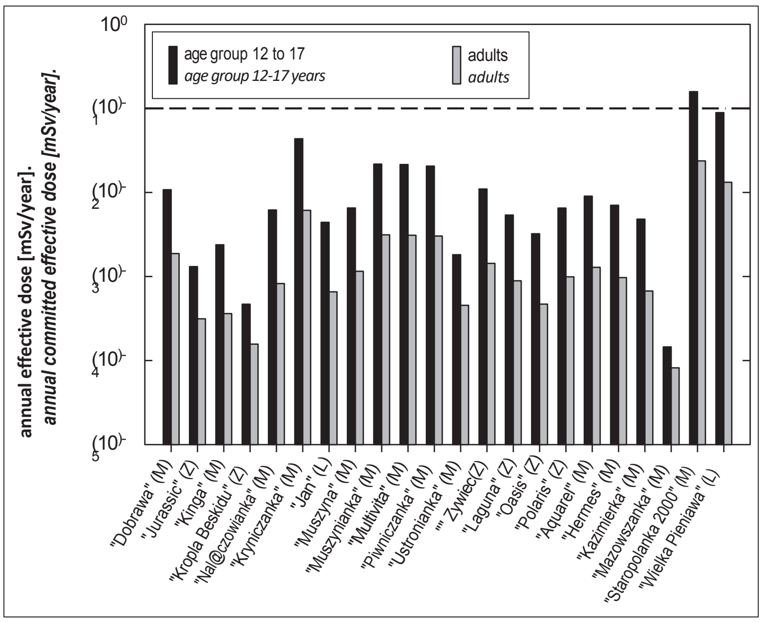

Figure 4: Annual burden dose for the 12-17 age group and adults with an assumed intake of 74 l/year. The dashed line indicates the acceptable level. For designations Z, M, L, see Table 1.

Fig. 4. Annual dose rate for teenagers 12-17 years old and adults resulting from intake of 74 l/year of the waters. Dashed line represents the permissible level. Symbols Z, M, L - as in Table 1.

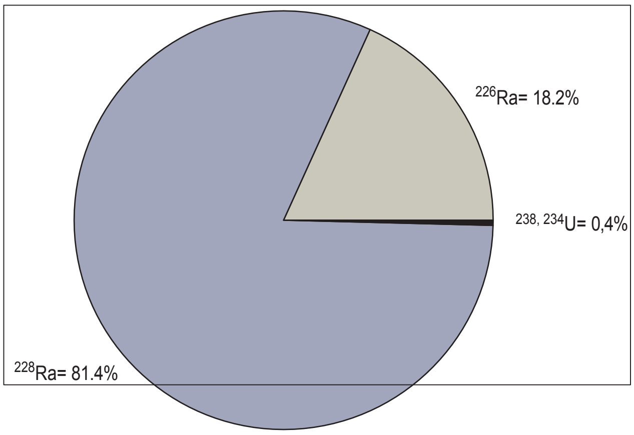

Fig. 5. Uranium and radium isotope contributions to the annual effective dose for adults resulting from absorption of isotopesoral

Fig. 5. Contribution of uranium and radium isotopes to the annual dose rate for adults resulting from intake of the bottled waters

ten times higher annual doses than those determined for the statistical . averageSimple calculations show that with this amount of consumed water, "Kryniczanka",the permitted annual doses may be exceeded for
"Muszynianka", "Multivita" and "Piwniczanka" in the 12-17 categoryyears , and for obvious reasons for "Staropolanka 2000" and "Wielka Pieniawa". However, remains an open questionthe structure of the water . consumed It is hard to imagine that highly mineralised waters are used to make tea, coffee or soup. It would therefore seem conclude that a consumption of 730 litres of mineral water per year is unlikely. Therefore, any estimates made for such a quantity are more or less inflated, depending on individual preferences. Finally, it should be reasonable to clearly emphasised that exceeding the norms for radioactivity in consumed water by 100% results in only a 3% increase in the total annual dose received from all sources by the population in Poland.

Figure 5 shows the shares of the individual isotopes in the annual dose for adults. The largest contribution to the dose is ^{228}Ra (over 81%), followed by ^{226}Ra (about 18%). In contrast, the contribution of both uranium isotopes is minimal and does not exceed 0.5%.

CONCLUSIONS

The results of studies on natural radioactivityradiological of bottled waters available in retail chains in the Cracow area confirm earlier opinions that these waters pose practically no threat to the statistical consumer. Increased activity of some isotopes, mainly radium isotopes, related to geological structure (lithology and tectonics) . isotope activities is observed in waters of the Sudety regionUranium in all studied waters are negligibly small and contribute negligibly to the annual effective doseloading . For some brands, an increase in the amount of water consumed may lead to exceeded the recommended annual dose being in the 12-17 category. However, this only ,becomes apparent when the amount of water consumed is 730 litres per year. The average citizen, even in countries with highest therates, does not drink this amount of water, even of one type. The results of the study show that, from a radiological point of view, most of the tested bottled waters (even the weakly mineralised ones) should not be given to infants under one year of age.

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