MEASUREMENTS OF ^{226}Ra, ^{222}Rn AND URANIUM IN UKRAINIAN GROUNDWATER USING ULTRA-LOW-LEVEL LIQUID SCINTILLATION COUNTING

A. V. ZELENSKY, M. G. BUZINNY and I. P. LOS'

Ukrainian Research Center for Radiation Medicine, Melnikova 53, 254050 Kiev, The Ukraine

ABSTRACT. More than 50,000 drilled wells supply ~22% of the Ukrainian population with drinking water. Geologically, more than 30% of the Ukrainian territory is situated on the Ukrainian shield with elevated levels of Rn, Ra, and U in groundwater. Technical advantages of the Quantulus 1220™ liquid scintillation spectrometer allowed us to start a nationwide program focusing on drinking water originating from drilled wells that may be rich in natural radionuclides. Since 1988, ~1500 groundwater samples have been analyzed for ^{222}Rn, ^{226}Ra, ^{238}U and ^{234}U. ^{222}Rn was measured by mixing a 10-ml water sample with 10 ml of toluene-based cocktail in a plastic or glass vial. Besides direct measuring, ^{226}Ra and U were determined after evaporating a 50–100 ml water sample. To determine ^{238}U and ^{234}U separately, a 1-liter water sample was concentrated and ^{238}U was extracted in a toluene-based cocktail with tributylphosphate. Minimum detectable activities were: ^{222}Rn, 0.05 Bq liter^{-1}; ^{226}Ra, 0.04 Bq liter^{-1}; ^{234}U and ^{238}U, 0.08 Bq liter^{-1}. The population-weighted average concentration for ^{222}Rn was 164 Bq liter^{-1}, for ^{226}Ra, 0.26 Bq liter^{-1} and for ^{238}U, 0.75 Bq liter^{-1}. The maximum concentrations were 2660, 5.2 and 21 Bq liter^{-1}, respectively. The ratio of ^{234}U to ^{238}U varied from 0.7 to 5.

INTRODUCTION

The Chernobyl accident attracted public attention to all sources of radiation exposure. Estimates of the incident's consequences must account for natural sources of radiation exposure. This is especially important in relocating inhabitants from accidentally contaminated provinces elsewhere in the Ukraine.

An important source of natural radioactivity exposure is ^{226}Ra and ^{222}Rn in drinking water, as over 20% of the Ukrainian population consumes well water. Because of the great variability of natural and artificial sources of radioactivity in the Ukraine, studies of human exposure must encompass the range of geologic and physiographic provinces. Our studies of regional geology and of ^{222}Rn concentration in dwellings have shown that the highest activities of natural radionuclides occur in the granitic Ukrainian Crystalline Shield (UCS) (Fig.1), where about 30% of the Ukrainian population live.

We have measured ^{222}Rn, ^{226}Ra and ^{238}U in groundwater sources since 1988 with a low-background Quantulus 1220™ liquid scintillation (LS) counter. We have also measured ^{222}Rn in 1500 samples, and determined gross alpha activity and concentrations of ^{238}U and ^{226}Ra in 520 samples.

METHODS

We sampled water from drilled wells and water pipes that are partially or fully supplied by water from drilled wells. ^{222}Rn measurements were performed using plastic vials (Wallac Oy, Turku, Finland) and glass vials (Wheaton). Initially, ^{222}Rn measurements were performed in plastic vials with a domestic dioxane-based scintillator, GS-8, and Optiphase HiSafe™ 2 (Wallac Oy), in sample/scintillator ratios of 1/19 and 2/18, respectively.

Most samples were measured with the domestic toluene-based scintillator, GS-1; 10 ml of scintillator were mixed in a vial with 10 ml of water. To check possible leakage of ^{222}Rn from counting vials, we prepared 20 reference sources from water with ^{222}Rn concentration of 300–400 Bq liter^{-1} (10 samples in plastic and 10 samples in glass vials). Samples were measured after each 6 h for 1 week.

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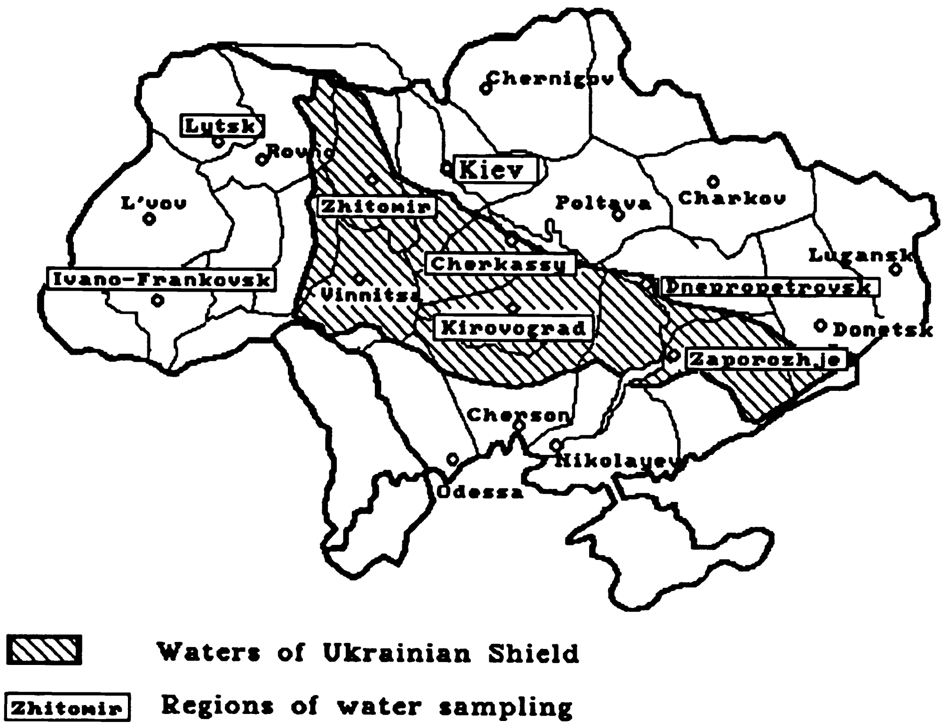

Fig. 1. Ukrainian Crystalline Shield groundwaters and regions of water sampling

Calibration and choice of optimal pulse-shape analysis (PSA) level were performed with a liquid standard solution of $^{226}RaSO_4$ with an activity of 2 Bq per sample. For measurement in plastic and glass vials with the toluene-based scintillator, GS-1, the PSA level was 60. For measurement in plastic vials with scintillators, GS-8 and OptiPhase HiSafe™ 2, the PSA level was 85. For a 20-min measurement, minimum detectable activities for each procedure were 0.05, 0.5 and 0.25 Bq liter^{-1}, respectively.

For ^{226}Ra and ^{238}U measurements, we use the method of Salonen (1989, 1990). The sample was prepared for counting first by evaporation of 50 ml of sample in a Teflon-copper 20 ml vial (Wallac Oy), then dissolving the residue in 1 ml of 0.5 M HCl, finally adding 19 ml of OptiPhase HiSafe™ 3 (Wallac Oy) to the vial. The sample was measured immediately after preparation and again after 1 month of equilibrium establishment. ^{226}Ra concentration was determined from the peak of ^{214}Po. U concentration was determined by subtraction of ^{226}Ra and daughters from the gross α count. Samples were calibrated with standard solutions $^{226}RaSO_4$ and $U(NO_3)_3$. The PSA level was chosen at 130. Minimum detectable activity (MDA) for a 100-min measurement was 0.04 Bq liter^{-1}. We also measured the ratio $^{238}U/^{234}U$. To do this, we concentrated (by evaporation) 500–1000 ml of water sample, acidified with 0.5 M HNO_3, to 2–5 ml. Then we mixed the solution with 4 ml of extraction mixture, prepared with 25% TBP in a GS-1 scintillator. We shook the mixture for 5–10 min to transfer activity into the organic phase. After a 20- to 30-min phase separation, the organic phase was separated and placed in a counting vial.

We developed a Matlab program (The MathWorks, Inc.) for spectra processing. The measurement spectrum was approximated by normal distribution curves. For 100-min measurements and considering 30% error for concentration and ratio values, MDA was 0.08 Bq liter^{-1}.

RESULTS AND DISCUSSION

Tables 1, 2 and 3 summarize the average and maximum concentrations of the radionuclides, measured in water samples from a drilled well. Average concentrations in UCS water are 5–10 times higher than concentrations in water from regions outside the UCS. The arithmetic mean of ^{222}Rn in regions located on the UCS was 261 Bq/liter^{-1}, and outside the UCS, 37 Bq/liter^{-1}. The arithmetic mean obtained from all data was 102 Bq/liter^{-1} (Fig. 2, Table 4). We found maximum ^{222}Rn concentrations in the Cherkassy region (2660 Bq liter^{-1}). For UCS regions, the proportions of drilled wells in which ^{222}Rn exceeds 100, 500 and 1000 Bq liter^{-1} are 40, 15 and 8.4%, respectively. For regions outside the UCS, the amount of wells with concentrations >100 Bq liter^{-1} is 7.5%, whereas concentrations >500 Bq liter^{-1} were not found. We calculated these proportions by averaging the same proportions for each region. In areas on the UCS, the arithmetic means for ^{226}Ra and U were 0.64 and 2.43 Bq liter^{-1}, respectively, that is, ~6 and 8 times higher than the same average means for areas outside the UCS.

The permissible concentration of ^{226}Ra for drinking water in the Ukraine is 2 Bq liter^{-1}, higher than that in the USA (0.185 Bq liter^{-1}) or the value recommended by the World Health Organization (0.111 Bq liter^{-1}). The proportions of drilled wells in areas on the UCS with ^{226}Ra concentrations exceeding 0.185, 0.4 and 2 Bq liter^{-1} are 43.8, 29.7 and 8.3%, respectively.

Maximum concentrations of U were found in the Zaporozhje region. The maximum U concentration of 21.2 Bq liter^{-1} corresponds to a $^{238}U/^{234}U$ ratio of 1.5. About 17% of wells yield a U concentration exceeding 2.5 Bq liter^{-1}, which corresponds to ~100 g of natural U, the permissible toxicity level in drinking water recommended by Wrenn (1985).

We recently began measuring $^{238}U/^{234}U$ ratios. From 37 results, the average ratio was 1.9 ± 0.75, with minimum and maximum ratios of 0.7 and 5. Figure 3 shows three typical α spectra obtained after U measurement, extracted from water samples. Energy resolution is ~350 kev for an energy of 5 MeV.

TABLE 1. Average and Maximum Concentrations of ^{222}Rn (Bq liter^{-1}) in Groundwater

Location	No. of samples	Arithmetic mean	Geometric mean	Standard deviation	Maximum
UCS					
Kiev	390	247	56	349	1155
Kirovograd	133	264	164	153	493
Zhitomir	547	75	30	112	844
Cherkassy	81	611	101	846	2661
Zaporozhje	69	106	41	118	1217
Average		261	78		
Outside the UCS					
Lutsk	45	27	4.7	64	195
Ivano-Frankovsk	90	30	17	25	65
Chernigov	72	28	20	15	62
Average		37	21		

TABLE 2. Average and Maximum Concentrations of ^{226}Ra (Bq liter^{-1}) in Groundwater

Location	No. of samples	Arithmetic mean	Geometric mean	Standard deviation	Maximum
UCS					
Kiev	196	0.37	0.23	0.44	3.5
Kirovograd	158	0.38	0.16	0.55	3.57
Zhitomir	28	1.38	0.72	1.23	4.1
Cherkassy	35	0.18	0.13	0.20	1.01
Zaporozhje	32	0.91	0.62	0.73	5.23
Average		0.64	0.37		
Outside the UCS					
Ivano-Frankovsk	16	0.06	0.056	0.024	0.11
Lutsk	39	0.13	0.12	0.05	0.26
Average		0.10	0.09		

TABLE 3. Average and Maximum Concentrations of U (Bq liter^{-1}) in Groundwater

Location	No. of samples	Arithmetic mean	Geometric mean	Standard deviation	Maximum
UCS					
Kiev	196	1.04	0.68	1.10	6.3
Kirovograd	158	1.05	0.46	1.73	10.5
Zhitomir	28	4.2	2.3	3.76	12.3
Cherkassy	35	0.53	0.39	0.59	3.0
Zaporozhje	32	5.32	3.12	4.81	21.2
Average		2.43	1.39		
Outside the UCS					
Ivano-Frankovsk	16	0.18	0.17	0.07	0.34
Lutsk	39	0.40	0.37	0.16	0.77
Average		0.29	0.27		

TABLE 4. Average Concentrations of ^{222}Rn, ^{226}Ra and U (Bq liter^{-1}) from All Data

Nuclide	No. of Samples	Arithmetic mean	Geometric mean
^{222}Rn	1536	102	26
^{226}Ra	520	0.38	0.19
U	520	1.13	0.57

Table 5 shows resident population-weighted concentrations, calculated on the basis of average concentrations in regions on and outside the UCS. The ^{222}Rn dose is calculated only for intake with ingested water. The dose factor for ^{222}Rn inhalation from water is 0.003 mSv yr^{-1} Bq liter^{-1}. Measurements were performed in buildings supplied by water with a ^{222}Rn concentration of 1000–

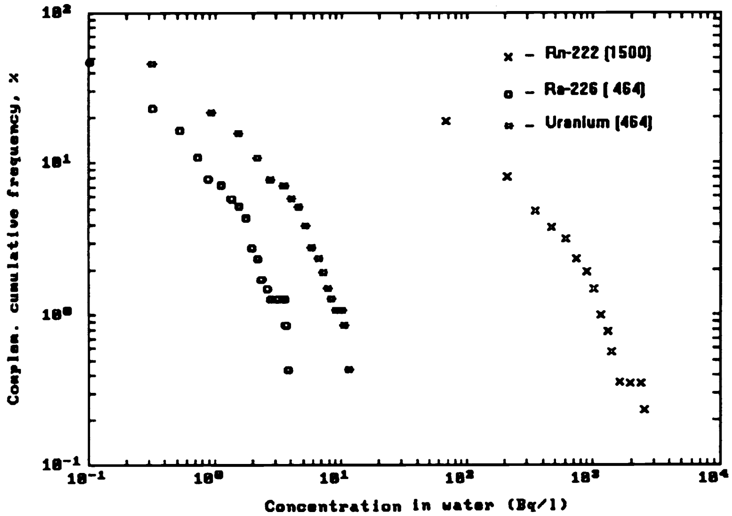

Fig. 2. Complementary cumulative frequency distribution of ^{222}Rn, ^{226}Ra and U in groundwater of the Ukraine

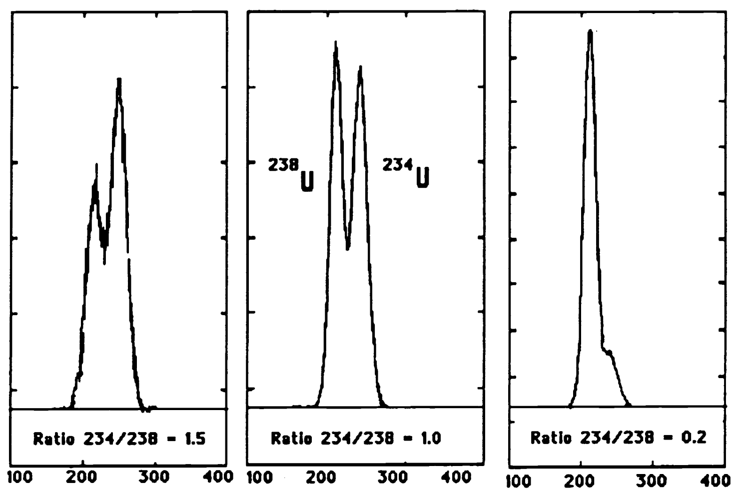

Fig. 3. Spectra of extracted U with various $^{238}U/^{234}U$ ratios

2000 Bq liter^{-1}. The ^{222}Rn transfer factor from water in air is 1×10^{-4}, and coincides with data systematized by UNSCEAR (1988). Taking into account the inhalation of ^{222}Rn, the total annual effective dose equivalent from ^{222}Rn in water will be 0.41 mSv, that is, 4 times higher than the total dose from U and ^{226}Ra (Table 5).

It is interesting to compare doses of ^{222}Rn, ^{226}Ra and ^{238}U from drinking water with internal doses from the Chernobyl accident (Table 6). As average individual annual doses from the Chernobyl event change with time, we compared population doses (Zelensky 1993) and calculated lifetime individual doses (70 yr). Chernobyl doses of internal exposure were calculated on the Lindel scheme (1960). Doses of ^{222}Rn, ^{226}Ra and ^{238}U in water were 10–100 times higher than internal doses from all Chernobyl radionuclides.

TABLE 5. Population-Weighted Average Concentrations of ^{222}Rn, ^{226}Ra and U in Groundwater and Corresponding Effective Dose Equivalents

Nuclide	Effective dose equivalent rate* $\left(\frac{mSv\ yr^{-1}}{Bq\ liter^{-1}}\right)$	Arithmetic mean for UCS area (Bq liter^{-1})	Arithmetic mean for areas outside the UCS (Bq liter^{-1})	Population-weighted arithmetic mean (Bq liter^{-1})	Effective dose equivalent (mSv yr^{-1})
^{222}Rn	0.001	261	37	164	0.104
^{226}Ra	0.25	0.64	0.1	0.26	0.065
U	0.053	2.43	0.29	0.93	0.05
Total					0.219

*Effective dose equivalent rate for ^{222}Rn is from UNSCEAR (1988), and for ^{226}Ra and U from Naturally Occurring Radiation in Nordic Countries–Recommendations (1986). For U, the effective dose equivalent was calculated for the $^{238}U/^{234}U$ ratio, 1.9.

TABLE 6. Comparison of the Doses due to Ingestion of ^{222}Rn, ^{226}Ra and U with Groundwater and Internal Doses from the Chernobyl Accident

		Doses of ^{222}Rn, ^{226}Ra and U in groundwater			Internal doses from the Chernobyl accident	
Location	Population (× 1000)	Annual effective dose equivalent (mSv)	Lifetime dose* (mSv)	Collective dose* (man Sv)	Lifetime dose (mSv)	Population dose** (man Sv)
Kiev	4542	0.39	27.6	125,465	2.37	10,755
Zhitomir	1545	0.23	15.8	24,404	7.09	10,950
Cherkassy	1532	1.18	82.5	126,390	2.18	3345
Kirovograd	1240	0.34	23.6	29,259	1.45	1797
Zaporozhje	2081	0.62	26.0	89,654	1.03	2135
Ivano-Frankovsk	1424	0.07	5.7	7131	1.11	1585
Lutsk	1062	0.08	5.2	5999	1.00	1065

*Lifetime, collective and population doses were calculated for a 70-yr life span
**Zelensky, Buzinny and Los' (1993)

CONCLUSIONS

LS α/β spectrometry is the most appropriate method for measuring natural ^{222}Rn, ^{226}Ra and U in groundwater; its sensitivity allows direct measurement of Rn concentrations. ^{226}Ra and U measurements require preliminary concentration of >50 ml of water sample. The greatest average and maximum concentrations were found in UCS groundwater; they average ~6–8 times higher than those for areas outside the UCS. The most significant dose contributor to the Ukrainian population is ^{222}Rn (0.104 mSv yr^{-1}) ingested with drinking water; the additional inhalation dose is ~0.41 mSv yr^{-1}. Population doses during the 70-yr post-accident period due to ingestion of Rn, Ra and U are ~10–100 times greater than internal doses from all Chernobyl radionuclides. These data will simplify development of the radiation protection strategy and population relocation from contaminated areas.

Results of this study have aided in establishing minimum permissible radionuclide levels for drinking water: 100 Bq liter^{-1} for ^{222}Rn, 0.4 Bq liter^{-1} for ^{226}Ra and 4 Bq liter^{-1} for U. Investigation of the radionuclides, ^{228}Ra, ^{210}Pb and ^{210}Po, is needed to obtain complete information about the exposure of the Ukrainian population to natural radioactivity from drinking water.

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