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^{226}Ra IN DRINKING WATER IN THE REPUBLIC OF CROATIA

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Owing to its exceptional radiotoxicity ^{226}Ra in drinking water may directly affect human health. Its presence was investigated in several categories of drinking water in Croatia: well water, tap water from several municipal water supply systems and bottled mineral water. The method of ^{226}Ra determination was alpha-spectrometric measurement after radiochemical separation. The ^{226}Ra content in all investigated categories of waters are below the legislative level permissible for human health.

Key terms:
derived concentration, health risk, natural radioactivity, radioactive contamination, radiotoxicity

The discovery that radium is hazardous to humans resulted from its wide application in early research into radioactivity, in the field of medicine, and in industry. Radium has also been identified as a major environmental pollutant. Pollution of water and soil with radium has been reported world-wide (1). Since many different transport mechanisms and exposure routes make environmental radiation dose more difficult to assess than radium contamination of the workplace, concern for the general public and for the environment took longer to develop (2-5).

The radium isotope of greatest concern is ^{226}Ra. It has always attracted special attention from the viewpoint of the health risks associated with its presence in public drinking water. Namely, ^{226}Ra is characterized by great radiotoxicity, »bone seeking« ability and a long half-life (1622 years). As an alpha emitter it has a high potential for causing biological change (6-9).

Although there is some metabolic discrimination against radium because of its high mass number, it tends to follow the same metabolic pathways as calcium. In human exposure the critical pathway for radium is ingestion through food chains or drinking water. Once deposited in bone tissue it continually irradiates the human skeleton for many years and is a potential inducer of bone sarcoma

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(6, 8). The most important aspect of radium protection is the prevention of its entry of radium into the human body (10, 11).

Radiation exposure of a population may increase significantly through drinking water intake (12). Estimates of the ^{226}Ra water content make part of the studies dealing with the global distribution of radium in nature. The occurrence of radium, its natural distribution and concentration in drinking water are strongly influenced by the geological setting, water flow cycles and interaction with the environment. They should therefore be considered on a regional basis. According to extensive studies carried out in different parts of the world ^{226}Ra concentrations in water vary over a wide range (2, 12-19).

In general, drinking water supplies make use of ground-water sources. Surface waters (well and river waters) can also constitute a major source of local drinking water supplies.

Radium in ground-water can arise from natural sources, i.e. from the interactions of ground-water and radium bearing materials like rocks, soil, ore bodies, etc. (1, 17). It can also arise indirectly from man's exploitation of the radioactive mineral uranium, thorium, etc. as part of the nuclear fuel cycle (2, 20). In contrast to the relatively high and widely varying ^{226}Ra concentrations in ground-waters, surface water displays a rather low and narrow range of radium concentrations.

From the point of view of radium contamination surface waters are greatly jeopardized by the technological activity of man; wastes from uranium and phosphate milling and uranium mine drainage water continue to be the most important local sources of radium in surface water (2, 21, 22).

The purpose of this study was to determine specific activity of ^{226}Ra in samples of drinking water from several locations in the Republic of Croatia, in order to provide guidelines for regulatory revision in case of an enhanced ^{226}Ra activity.

MATERIAL AND METHODS

The presence of ^{226}Ra in drinking water was investigated in samples of well water, tap water from public water supply systems and bottled mineral water.

Well water samples were collected in the vicinity of a phosphate fertilizer plant and at several randomly selected locations in Croatia. The greatest number of samples came from locations close to deposits of phosphogypsum, by-product from phosphate fertilizer production.

Tap water was sampled from public water supply systems in several towns. A large number of samples were taken from locations in the city of Zagreb. One litre samples were collected daily and an aliquot of pooled sample per month was analysed radiochemically.

Samples of bottled mineral water were randomly collected from two mineral water springs. In all samples ^{226}Ra was determined after radiochemical separation,

by alpha spectrometric measurements using Si(Li) surface barrier detector ORTEC (23). The counting time for each measurement was 60,000 s or longer.

RESULTS AND DISCUSSION

The well water samples collected in the vicinity of phosphogypsum deposits were of special interest due to possible contamination of and an enhanced risk to the local population using the well water.

Figure 1 shows ^{226}Ra activity concentration in samples of well water collected at the location closest to a phosphogypsum deposit. Variability of ^{226}Ra concentrations resulted from different initial activities of the feedstock used in the process of phosphate fertilizer production. The observed frequency distribution of all samples was normal.

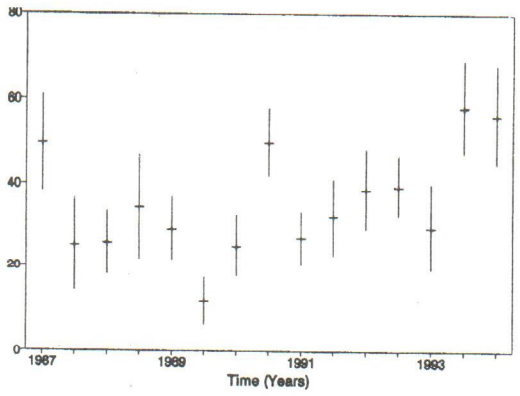

Figure 1 *^{226}Ra activity in samples of well water close to a phosphate fertilizer plant*

Figure 2 shows relative frequencies of ^{226}Ra specific activities measured in all samples of well water and the related theoretical function of distribution. The data fit a normal distribution, but not too well. The observed frequency distribution is skewed to the right (skewness: 0.0158, $t = 9.108$, $P<0.01$). Mean value was 33.5±14.7 Bq m^{-3}. The range of all values 52.35 Bq m^{-3}.

Figure 3 shows ^{226}Ra activity in tap water samples from the public water supply system for the city of Zagreb. The mean values were lower than those for well water by one order of magnitude. They were also of the order of magnitude corresponding to the low level of detection (LLD) of the instrument, that is 1.2 Bq m^{-3}; range of LLD value 0.49 Bq m^{-3}. The mean value of ^{226}Ra in public water

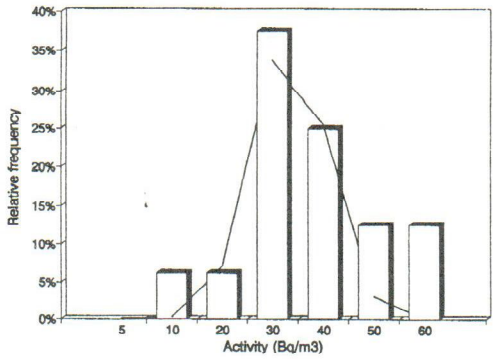

Figure 2 *Relative frequencies of ^{226}Ra activities in samples of well water*

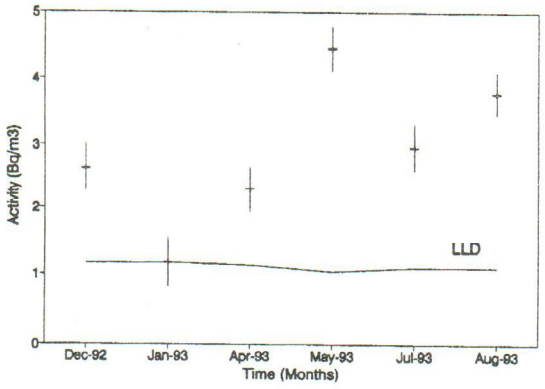

Figure 3 *^{226}Ra activity in tap water in the city of Zagreb*

supply systems in the city of Zagreb and several major urban centres in Croatia was 2.1±1.4 Bq m^{-3}. All the values followed a normal distribution pattern as can be distinctly seen on the normal probability plot in Figure 4; deviations from normal distribution were minimal.

The ^{226}Ra specific activities in samples from the tap water system were lower than those for well water samples by one order of magnitude. Higher values measured in well waters were due to the fact that our investigation included only the wells situated in the close proximity of the phosphate fertilizer plant, which were used by the population living in a nearby residential zone. Those were rather shallow wells. For the sources supplying water to the public tap water system

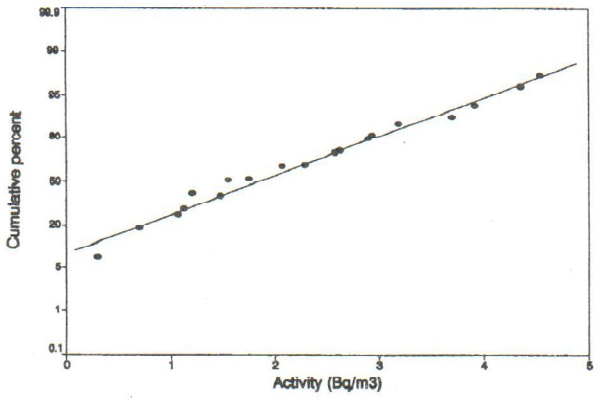

Figure 4 *Normal probability plot of ^{226}Ra in tap water*

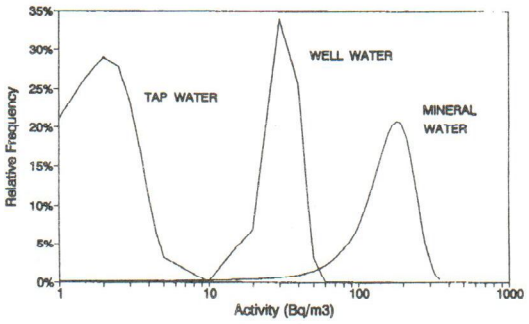

Figure 5 *Frequency distribution of ^{226}Ra activities in well water, tap water and mineral water*

locations were carefully selected. They were of different depth. According to our data, ^{226}Ra activity measured in them was more than satisfactory, particularly in comparison to the values for other European countries. In Germany ^{226}Ra activity varied from 1.1 to 12.6 Bq m^{-3} (5, 18, 19), in USA from 1.55 to as much as 629 Bq m^{-3} (14). As recent literature data show, these waters need to be treated before they are allowed into the water supply system (24). ^{226}Ra activity in the wells is directly related to the soil; its quality and composition are prerequisites of terrestrial activity. This is particularly meaningful in respect to mineral water sources which are found to be several times more active than other water sources (13, 15, 25).

The samples of mineral waters for the study were collected from two mineral water springs in Croatia. Their activity was higher than of well water samples or of those coming from the public drinking water supply system. The values corresponded to literature data for bottled mineral water for several countries (1, 11, 25). In bottled mineral water widely consumed in several countries radium concentrations range from 55 to 500 Bq m^{-3} (1).

Figure 5 shows a normal frequency distribution of ^{226}Ra specific activity in well water, tap water and mineral water. The observed relative frequency of ^{226}Ra activity in our mineral water samples has a normal distribution, mean value 183.0±94.0 Bq m^{-3}. The range for all mineral waters is 202,0 Bq m^{-3}. Positions of separate distribution curves and their relations in the logarithmic scale of activity are given to stress the difference in the order of magnitude for each water category.

Environmental pollution control should involve control of drinking water for radioactive contaminants. Measures should be taken if the activity detected in water exceeds the permissible levels as set up by a country's legislation.

By the U.S. Public Health Service standards for drinking water the maximum contaminant level for radium was first specified at 111 Bq m^{-3}. This standard has been subsequently increased to 185 Bq m^{-3} by the Regulations on Radionuclides which were issued by the Environmental Protection Agency (EPA), as part of the National Interim Primary Drinking Water Regulations (2, 19, 26-28).

The latest guideline activity concentration for ^{226}Ra as recommended by the World Health Organization (29) is 1 Bq L^{-1}. It assumes an intake of two litres of water daily, for one year and corresponds to a dose of 0.1 mSv from one year's intake, which is less than 5 per cent of the natural dose (2.4 mSv y^{-1}).

The legislation presently valid in the Republic of Croatia includes the former Federal Act on radiation protection and nuclear energy, with accompanying regulations. The Croatian legislation is based on the latest IAEA recommendation taking 1000 Bq m^{-3} as the maximum permissible level for ^{226}Ra in drinking water which is a derived concentration for a group of individuals (30).

Table. *Ratio of maximal ^{226}Ra activities and derived concentrations (DC) as specified by legislation*

Water category	Maximal activity Bq·m^{-3}	DC %
Well water	58.0	5.8
Tap water	4.5	0.4
Mineral water	303.1	30.3

The Table shows the ratio of maximal activities for different water categories and derived concentration for drinking water per group of individuals in a population. Mineral water is most active, its maximum radioactivity exceeding 30 per cent of the derived concentration for drinking water. Its minimum value is 10 per cent of the derived concentration, which is two times higher than the maximum value measured in the drinking water supply system. It should be stressed, however, that in Croatia mineral water has not been included in the existing legislation

on drinking water and has not been taken into consideration as a distinct category of water in general.

Under normal environmental conditions, the relative contribution of drinking water to the total ^{226}Ra intake by a standard man is minor; only about 10 per cent of radium uptake is due to drinking water. This, of course, may not be true of the sites having water with a high ^{226}Ra concentration.

Well water, tap water and bottled mineral water generally consumed by the population should be subject to regular control in order to safeguard the health and prevent possible risks from ^{226}Ra activities in the waters. In Croatia, samples of well water and tap water showed acceptable ^{226}Ra concentrations; the highest activity was measured in mineral water.

CONCLUSION

According to the results of the study the specific activity of ^{226}Ra measured in samples of drinking water in Croatia poses no risk for the general population. Maintaining regular control of drinking water is necessary, especially at locations close to industrial plants. Those are possible sources of an enhanced natural activity and therefore may be hazardous to the population groups using water from nearby local wells.

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Sažetak

^{226}Ra U PITKOJ VODI HRVATSKE

Zbog svoje izuzetne radiotoksičnosti, ^{226}Ra u pitkoj vodi može izravno utjecati na ljudsko zdravlje. U radu je opisano istraživanje specifične aktivnosti ^{226}Ra u pitkoj vodi Hrvatske, i to: u uzorcima bunarskih voda, uzorcima vodovodnih voda u nekoliko gradova Hrvatske i u mineralnim vodama. ^{226}Ra je određen alfa-spektrometrijskim mjerenjem nakon radiokemijske separacije. Istraživanje je pokazalo da je količina ^{226}Ra u svim ispitivanim kategorijama voda ispod razine koju zakonska regulativa smatra tolerantnom po zdravlje čovjeka.

Ključne riječi:
izvedena koncentracija, prirodna radioaktivnost, radioaktivna kontaminacija, radiotoksičnost, rizik za zdravlje

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