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Radioactive contamination in Croatia by phosphate fertilizer production

Tomislav Bituh*, Gordana Marovic[1], Zdenko Franic[1], Jasminka Sencar[1], Maja Bronzovic[1]

Institute for Medical Research and Occupational Health, Radiation Protection Unit, Ksaverska cesta 2, HR-10000 Zagreb, Croatia

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ABSTRACT

The contents of natural radionuclides (radium, uranium and potassium) were measured in the area of a phosphate fertilizer factory in central Croatia, as a part of extended and still ongoing monitoring program of radioactive contamination of human environment in Croatia that is performed by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health in Zagreb. Activity concentrations in all analysed media (waste water, trickling water from piezometers, phosphogypsum deposit and final products) considerably fluctuated, especially in phosphogypsum and waste water. Mean ^{226}Ra activity concentration in waste phosphogypsum was measured to be 483 ± 190 Bq kg^{-1}. Based on that value, it was estimated that 4 million m^3 of phosphogypsum that have been deposited up to now contain about 4.3×10^{12} Bq, i.e. about 200 g of ^{226}Ra. However, effective dose for an adult that would be incurred by consumption of water from nearby wells was estimated to be 5.3 ± 1.3 μSv. The results show that ^{226}Ra activities cause effective doses, which are below the recommended maximum as the estimated annual ^{226}Ra effective dose does not exceed 0.1 mSv as recommended by the World Health Organization.

1. Introduction

The raw material used in the production of fertilizers is phosphate ore, which usually contains various amounts of naturally occurring radioactive elements. The phosphate industrial operations can be divided into the mining and milling of phosphate ores and the manufacture of phosphate products by either the wet process or the thermal process. Wet process plants produce phosphoric acid, the starting material for ammonium phosphate and triple super phosphate fertilizers. In that process, phosphogypsum is produced as waste or a by-product. Thermal process plants produce primarily high-grade phosphoric acid and produce slag as waste. During phosphate ore processing, practically all ^{226}Ra gets incorporated into phosphogypsum [1–3] since the chemical properties of radium are equivalent to those of calcium that is major constituent of gypsum [4]. Incorporated ^{226}Ra remains in disequilibrium status when compared to radioactivity levels contained in the raw material. Most of phosphogypsum is considered to be waste that is either stockpiled or discharged into the aquatic environment. Potential issues of concern resulting from phosphogypsum disposal are its environmental impacts; i.e. possible increases in radionuclide concentrations in soil or groundwater and consequential ingestion by humans through exposure routes such as drinking water and food chain [5–7]. Once deposited in bone tissue, ^{226}Ra has a high potential for causing biological damage through continuous irradiation of human skeleton over many years and may induce bone sarcoma [8–12].

This study was carried out in the area of a fertilizer factory located in central Croatia. Due to fertilizer production and disposed phosphogypsum the area has been identified as a site of significant ecological burden. The storage of phosphogypsum is organized in the floodplain of a river, some 5 km southward of the factory site. Waste gypsum, generated in the production is mixed with water and transported from the factory to ponds by a pipeline system. The water from the surface of the ponds is pumped back into production, which makes a closed system [13–15].

Considered as a particularly sensitive ecosystem for its specific geographic location, this area has been included in an extensive radioecological monitoring program of the Croatian environment, which has been carried out for several decades by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health, Zagreb, from 1948 to 2003 [16].

It should be mentioned that until recently regulators in Croatia have paid little attention to the radiation protection issues associated with these sites and the legislation regarding the protection of public and workers against natural sources of radiation is therefore still rather vague and incoherent.

The purpose of this paper is to determine activity concentrations and pathways of natural radionuclides, i.e. ^{238}U, ^{226}Ra, ^{228}Ra and ^{40}K with special attention to ^{226}Ra resulting from phosphate fertilizer production in the samples of waste water, trickling water and well water in order to assess a health risk for the population

* Corresponding author. Tel.: +385 1 4673188; fax: +385 1 4673303.
E-mail addresses: tbituh@imi.hr (T. Bituh), marovic@imi.hr (G. Marovic), franic@imi.hr (Z. Franic), jsencar@imi.hr (J. Sencar), mvrtar@imi.hr (M. Bronzovic).
[1] Tel.: +385 1 4673188, fax: +385 1 4673303.

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Table 1
Activity concentration of natural radionuclides in phosphate ore

Radionuclide	Mean (Bq kg^{-1})	Median (Bq kg^{-1})	Maximum (Bq kg^{-1})	Minimum (Bq kg^{-1})
^{226}Ra	$(1.27 \pm 0.36) \times 10^3$	1.35×10^3	1.65×10^3	7.37×10^2
^{228}Ra	9.38 ± 1.88	8.64	1.25×10^1	7.69
^{238}U	$(1.55 \pm 0.74) \times 10^3$	1.62×10^3	2.53×10^3	4.46×10^2
^{40}K	$(4.09 \pm 2.88) \times 10^1$	2.55×10^1	9.06×10^1	2.22×10^1

and occupationally exposed workers as well as whether ingestion of drinking water from the wells in the area poses a health risk for the local inhabitants.

1.1. The plant and deposition site

The Mineral Fertilizer Factory is the only fertilizer, carbon black and bentonites, manufacturer in Croatia. The Phosphate Fertilizer Plant is the largest Croatian fertilizer manufacturer, built in the settlement with more than 10,000 inhabitants while approximately 35,000 inhabitants live in the surrounding area of 10 km radius. The first plants of the industrial complex for the manufacture of fertilizers, which had a capacity of 739,000 tons per year, were built in agricultural centre of Northern Croatia in 1968, owing to an industrial tradition dating back to 1938, to the vicinity of oil and gas wells. With the start-up of the up-to-date complex of plants built in the second phase in 1984, the capacity of the fertilizer factory was increased to 1.9 million tons per year, and consists of intermediates production plants, final products plants and two energy production plants. In the production of phosphoric acid by the wet dehydrate process, around 5 tons of phosphogypsum are generated per tone of P_2O_5 [14,15,17]. The chemical reaction for the process is (Eq. (1)):

$$[Ca_3(PO_4)_2]_3CaF_2 + 10H_2SO_4 + 2H_2O \rightarrow 6H_3PO_4 + 10CaSO_4 \· 2H_2O \downarrow + 2HF \quad (1)$$

In the process, ^{238}U generally stays in the phosphoric product, while the daughter ^{226}Ra concentrates in phosphogypsum [4,18].

In the investigated plant the storage of phosphogypsum is located 5 km southward of the plant site. The storage size is 43 ha. The site is clearly seen on Google Earth (45°26′38.67″N and 16°44′40.76″E). Total capacity of ponds is 20 million m^3, but up to now only 4 million m^3 of phosphogypsum have been accumulated.

1.2. The raw materials

In order to make nutrients available to the plant, the fertilizers are produced in such way that they are either water-soluble or citrate-soluble. Different fertilizers are produced in the investigated fertilizer plant, each of them contain nitrogen, phosphorus and potassium as nutrients (N–P–K), and many other micronutrients. The natural gas is used for ammonia production as a source of N_2. Sulphuric acid and nitric acid are used as acids for rendering the raw phosphate ore, as a source of P_2O_5. Phosphate rock is the main source of phosphorus for fertilizer production. It can be of sedimentary origin (the deposits spread almost throughout the world, but especially in Morocco and Florida), volcanic origin (the principal deposit of this type is found in the Kola Peninsula), or biological origin (the accumulated droppings of marine birds are recombined with calcium from the underlying rock to give tricalcium phosphate). Like any other geological material found in nature, it contains various amounts of naturally occurring primordial radionuclides. The utilization of phosphate rock in fertilizers redistributes these natural radionuclides and may be responsible for some environmental contamination and further exposure of the public. Muriate of potash (KCl and K_2SO_4) as a source of K_2O is added to the mixture [4,19–22].

2. Materials and methods

The fertilizers manufactured by the Fertilizer Company are derived from the phosphate ores of sedimentary origin, imported mostly from Northern Africa. Determination of radioactive contamination required analyses of different types of samples. The samples of phosphate ore and muriate of potash were collected at warehouses from the top surface of the piles. The representative sample was taken from the mixture of aggregate samples. Phosphogypsum was collected at deposition site (also from the mixture of aggregate samples) and from filters at phosphoric acid production, inside the plant. The sampling frequency depended on incoming frequency of new raw materials.

Trickling water is sampled by means of piezometers installed at the pond area. Samples of trickling water were taken as grab samples 4 and 10 m deep at the phosphogypsum deposit. Samples of well water collected from five wells in the vicinity of phosphogypsum deposits in a nearby residential zone. All samples were collected one-to-three times per year during the period 1993–2006.

Soil samples were collected once a year, from uncultivated surfaces, close to phosphogypsum disposal pond. Three layers of soil, taken from the depths of 0–5, 5–10 and 10–15 cm were analysed. Samples were taken with a coring tool of known diameter (φ = 10 cm). Ten cores from a total surface area of 1 m^3 were taken and composed to make a single sample. Samples were then spread on plastic sheets, and allowed to dry at room temperature for several days. Stones and roots were discarded; samples were ground to pass a mesh size of 2 mm, dried at 105 °C for 3 days, and calcinated at 450 °C [23].

All liquid samples were radiochemically separated [24], after which ^{226}Ra was determined by alpha-spectrometric measurement using silicon charged particle detector, i.e. partially depleted PIPS detector with active area of 450 mm^2 and alpha resolution for ^{241}Am of 19 keV. The counting time for each measurement was 60,000 s or longer.

All the samples (soil, row material, waste and trickling water and well water) were also gammaspectrometrically analysed in the laboratory using HPGe and/or Ge (Li) detector (resolution 1.78 keV on 1.33 MeV ^{60}Co, relative efficiency 16.8%; resolution 1.56 keV on 1.33 MeV ^{60}Co, relative efficiency 18.7%). Samples were stored into Marinelli beakers of 1 L or 0.1 L in volume. Measurements were taken after an aging period to allow the re-establishment of the conditions of secular equilibrium between ^{226}Ra and its short-lived decay products. Measurement time was 80,000 s or higher.

3. Results and discussion

It is known that the composition of the ores varies considerably with their origin and that high phosphate contents usually correspond to high uranium content [15]. The phosphate ore used in the production of fertilizers typically contains ^{226}Ra in the concentrations of about 1271 ± 363 Bq kg^{-1}, depending on the origin of the phosphate ore processed. The results of gammaspectrometric measurements of the ore raw material used by the plant are shown in Table 1.

Table 2
Activity concentrations of natural radionuclides in waste phosphogypsum

Radionuclide	Mean (Bq kg^{-1})	Median (Bq kg^{-1})	Maximum (Bq kg^{-1})	Minimum (Bq kg^{-1})
^{226}Ra	$(4.83 \pm 1.90) \times 10^2$	4.24×10^2	7.72×10^2	3.09×10^2
^{228}Ra	4.74 ± 0.99	4.57	6.22	3.59
^{238}U	$(7.67 \pm 1.32) \times 10^1$	8.50×10^1	8.94×10^1	5.62×10^1
^{40}K	$(4.04 \pm 3.94) \times 10^1$	2.45×10^1	1.07×10^2	6.24

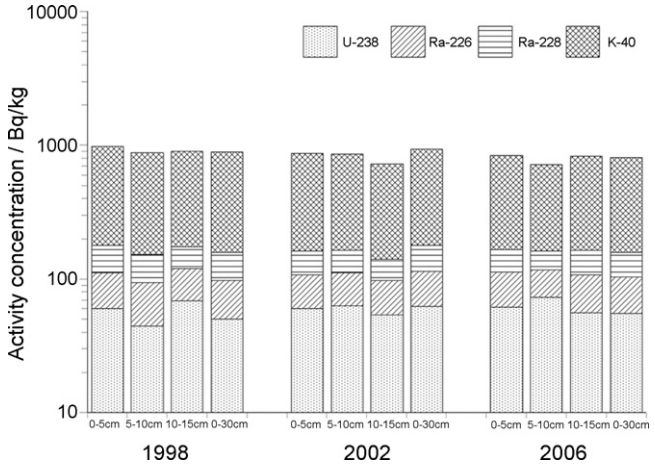

Fig. 1. Activity concentrations of natural radionuclides: ^{238}U and ^{226}Ra, ^{228}Ra and ^{40}K in uncultivated soil.

As can be seen, activity concentrations of all analysed radionuclides considerably fluctuated, which has been especially true for ^{226}Ra activity concentrations that varied from 737 to 1650 Bq kg^{-1}. Regarding waste phosphogypsum, the activity concentrations in grab samples collected annually are presented in Table 2.

Knowing values from ^{226}Ra concentration, measured in raw material and assuming that most of ^{226}Ra is incorporated in phosphogypsum, it is possible to calculate total annual amount of ^{226}Ra accumulated in deposited waste. It is estimated that about 4 tons of phosphogypsum are obtained as waste material per tone of phosphoric acid, which represents a considerable ecological burden to the area surrounding the plant.

Mean data from Tables 1 and 2 can be used to calculate ratios of activity concentrations of respective radionuclides in the raw material, i.e. phosphate ore and in the waste. The estimated ratios are 0.61, 0.50, 0.05 and 0.99 for ^{226}Ra, ^{228}Ra, ^{238}U and ^{40}K, respectively. Knowing these values it is straightforward to estimate the total annual amount of respective radionuclides accumulated in deposited waste. Also, using the data given in Table 2, defining a relationship between the activity and the mass of the material, it was possible to calculate the activity and therefore the mass of each radionuclide accumulated in 4 million m^3 of phosphogypsum that have been deposited up to now. Multiplying specific activity of the given radionuclide with its average activity concentration in phosphogypsum, mass of each radionuclide can be calculated. For ^{226}Ra ($t_{1/2}$ = 1600 year) 1 kg of phosphogypsum contains 2.1×10^{-8} g of this radionuclide. As the density of phosphogypsum is ca. 2.1–2.3 g cm^{-3}, 4 million m^3 of phosphogypsum that is deposited up to now contain about 195–197 g of ^{226}Ra. Analogously it is estimated that deposited phosphogypsum contains 5.7 mg of ^{228}Ra, 60 tons of ^{238}U and 1.4–1.5 tons ^{40}K.

In order to study radionuclide transfer from phosphogypsum into soil, ^{238}U, ^{226}Ra, ^{228}Ra and ^{40}K activity concentrations in uncultivated soil samples collected close to the phosphogypsum disposal pond were analysed. As shown in Fig. 1 average concentrations of these radionuclides were quite constant up to the investigated depth.

Comparison of the results obtained for the presence of radionuclides in non-fertilized soil samples and in the phosphogypsum waste from plant production is shown as follows:

- Activity concentrations of ^{226}Ra in phosphogypsum samples were about 10 times higher than its levels in soil samples as ^{226}Ra content in soil samples varied from 43.3 to 51.6 Bq kg^{-1} average being 48 ± 3 Bq kg^{-1}. For comparison, average world-wide ^{226}Ra content in the regular soil of cultivated fields not tilled with phosphogypsum is 48 Bq kg^{-1} [20,21]. Activity concentrations of ^{238}U in phosphogypsum samples were of the same order of magnitude (77 ± 13 Bq kg^{-1}) as in uncultivated soils close to the phosphogypsum disposal pond (59 ± 14 Bq kg^{-1}).
- Due to the technological process, activity concentrations of ^{40}K were about 13 times lower in phosphogypsum samples (40 ± 39 Bq kg^{-1}) when compared to soil samples (688 ± 68 Bq kg^{-1}), independent of the acquisition location.

Fig. 2 shows distribution of naturally occurring radionuclides (^{226}Ra and ^{226}Ra) determined in waste water from the factory. Waste gypsum, generated in the production is subsequently mixed with water and transported from the factory to pools by a special pipeline. The water from the pools surface is pumped back into production, which makes this a sort of a closed system. ^{226}Ra activity concentrations measured in waste water varied from 12.5 to 79.6 Bq m^{-3} (average 37.5 ± 20.6 Bq m^{-3}, median 29.5 Bq m^{-3}) while ^{228}Ra activity concentrations varied from 7.4 to 45.4 Bq m^{-3} (average 23.4 ± 13.3 Bq m^{-3}, median 18.9 Bq m^{-3}).

The permeability of solid waste deposit was monitored using samples of trickling water. In order to ensure the highest possible accuracy of the data on ^{226}Ra behaviour in trickling waters, the samples were collected at several different depths. Trickling water activity concentration ratio was calculated from the samples concurrently taken from the closest 4 and 10 m deep piezometers, i.e. a very small diameter water wells. More than 70% of the trickling water samples collected 4 m deep contained higher ^{226}Ra activities

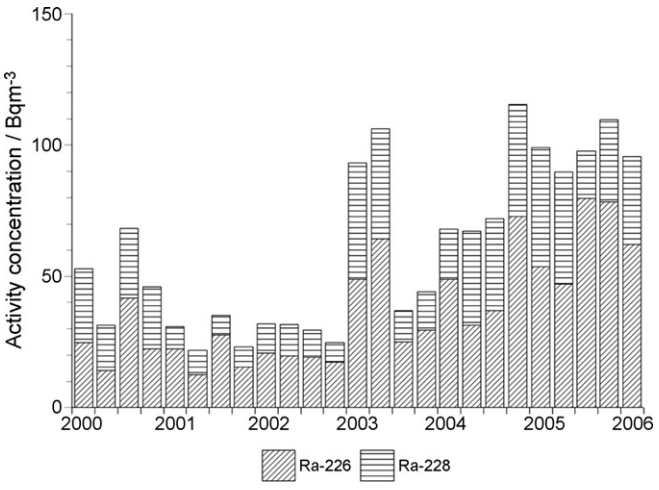

Fig. 2. Activity concentrations of ^{226}Ra and ^{228}Ra in waste water.

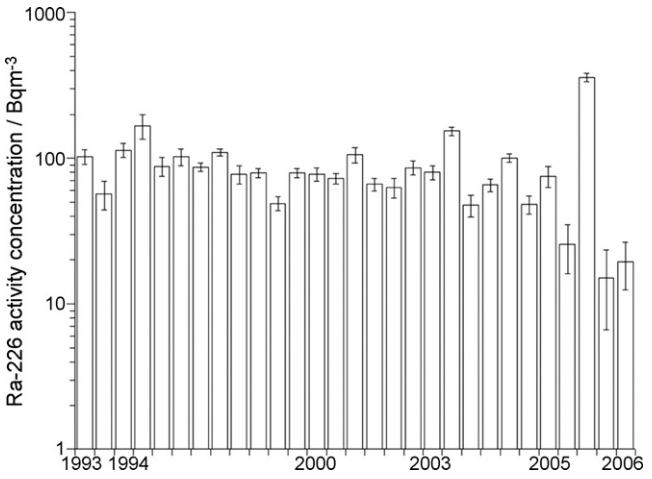

Fig. 3. Average activity concentrations of ^{226}Ra in trickling water at the phosphogypsum deposit.

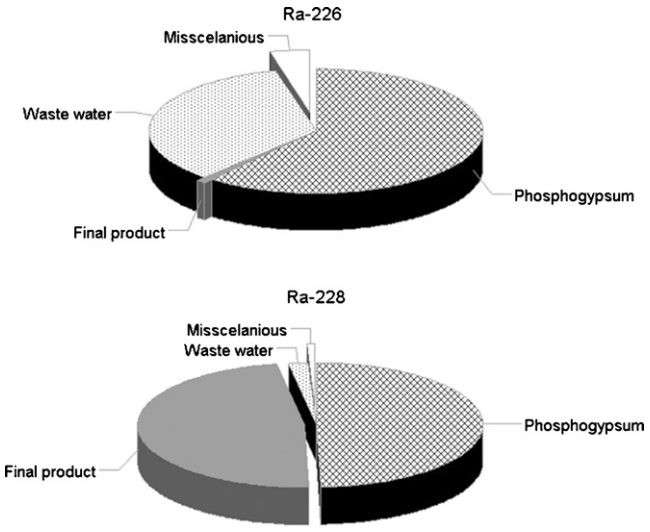

Fig. 5. Contribution of ^{226}Ra and ^{228}Ra activity concentrations in the raw material regarding the components of the production process: by-products, final product and waste and unspecified portion.

than those located deeper in the soil. Fig. 3 shows average values of ^{226}Ra activities in trickling water at the phosphogypsum deposit during the period 1993–2006, based on one-to-three samplings conducted over a 1-year period at both depths.

The ^{226}Ra activity concentrations measured in trickling water varied from 15 to 356 Bq m^{-3} (average 88 ± 60 Bq m^{-3}, median 79 Bq m^{-3}). Maximal activity concentration of 356.3 Bq m^{-3} was measured in the samples of trickling water in 2005.

Fig. 4 shows activity concentration of naturally occurring ^{226}Ra and ^{228}Ra in final products, which varied from 7.0 to 10.8 Bq kg^{-1} (average 9.4 ± 1.8 Bq kg^{-1}, median 10.5 Bq kg^{-1}) for ^{226}Ra and from 8.2 to 19.5 Bq kg^{-1} (average 12.3 ± 5.1 Bq kg^{-1}, median 9.2 Bq kg^{-1}) for ^{228}Ra.

Using the data on the initial ^{226}Ra and ^{228}Ra activity concentrations in the raw material and the mean activity concentrations in waste water (trickling water from piezometers and waste water from the factory), phosphogypsum deposit and final products, it is possible to illustrate graphically the distribution of total ^{226}Ra and ^{228}Ra by the components of the production process. Fig. 5 shows the distribution of total mean ^{226}Ra and ^{228}Ra activity concentrations contained in the raw material by the components of the production process: by-products, final product and waste as well as unspecified portion calculated on the basis of mean values.

The samples of well water collected in the vicinity of phosphogypsum deposit were of particular significance in order to assess possible contamination and an enhanced risk to the population living in this area, consuming the well water. ^{226}Ra activity concentrations measured in wells located in the close proximity of the phosphogypsum deposit site are shown in Fig. 6. These activity concentrations were higher when compared to concentration found elsewhere in Croatia (mean = 17.0 Bq m^{-3}) [25].

The mean ^{226}Ra activity concentration in well water samples was 25.8 ± 6.5. Relatively high variability of ^{226}Ra activity concentrations of well water can be explained by different ^{226}Ra initial activities [26,27].

Using mean ^{226}Ra activity concentration in well water it is straightforward to estimate the effective dose from ^{226}Ra that would be received by an adult member of local population which are drinking well water. Effective dose resulting from water ingestion over a certain period of time depends on the activity of radionuclides and on the quantity of ingested water. Therefore, the dose can be expressed as (Eq. (2)):

$$E = CD_{CF}A \quad (2)$$

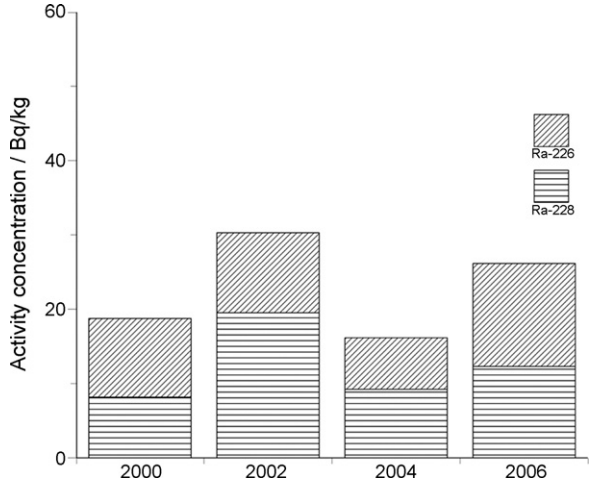

Fig. 4. Activity concentration of ^{226}Ra and ^{228}Ra in final products.

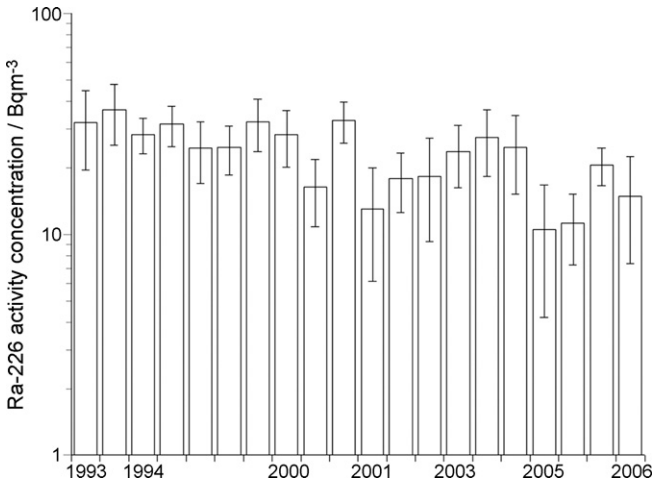

Fig. 6. Activity concentration of ^{226}Ra in well water.

where E is the effective dose (Sv), C total annual *per capita* ingestion of well water (L), D_{CF} dose conversion factor for ^{226}Ra, i.e. effective dose per unit input, which converts the ingested activity to effective dose, which for an adult member of population equals 2.8×10^{-7} Sv Bq^{-1} [11,27] and A means annual specific activity of ^{226}Ra in water (Bq L^{-1}).

The effective dose assessment is based on an assumed intake of 2 L of water daily during the period of 1 year. The results show that ^{226}Ra activities produce effective doses that are below the recommended maximum as the annual ^{226}Ra effective dose (5.3 ± 1.3 μSv) does not exceed 0.1 mSv whereas recommended by the Croatian legislation and the World Health Organization [27–29]. Namely, according to the WHO recommendations the annual effective dose from consumption of water should not exceed 5% of the average effective dose from of all natural sources (2.4 mSv), i.e. it should not be higher than 0.1 mSv.

4. Conclusion

Four million cubic meter of phosphogypsum deposited up to now at the investigated site contain about 195–197 g of ^{226}Ra, 5.7 mg of ^{228}Ra, 60 tons of ^{238}U and 1.4–1.5 tons of ^{40}K. However, the results of this study indicated that well water in the area around the investigated plant contained ^{226}Ra within tolerable limits and that the adverse health effects to the population are negligible. There is no evidence of any impact on the well water of the area due to permeability of phosphogypsum deposit. Although measurements provide no reasons for concern about a health risk from drinking water in this area, it is recommended that periodic sampling of the well water should be conducted to evaluate possible trends in radionuclide contamination over time.

Regarding the soil samples, the results of this study provide no evidence for an increase of activities of natural radionuclides in soil samples close to the phosphogypsum disposal pond, compared with the soil samples taken from uncultivated area on location.

Consequently, estimated annual ^{226}Ra effective dose that an adult member of the population would receive by consuming 2 L water daily from nearby wells of 5.3 ± 1.3 μSv does not exceed 0.1 mSv as recommended by WHO. Therefore, it can be argued that the impact of phosphogypsum disposal pond on the environment radioactivity of the area and resulting health effects is negligible. For the time being, the results of this study indicate that ^{226}Ra concentrations in the well water of the area around the investigated fertilizer plant fall within tolerable limits and that the risk of adverse health effects to the population is low.

However, further monitoring of the phosphogypsum deposit and periodic sampling of the well water of the area will be continued. Drinking water should be controlled for radioactive contaminants in order to be able to take appropriate measures whenever activity detected in water exceeds the permissible levels set up by country legislation.

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