Radioactive Contamination of the Environment due to Phosphate Fertilizer Production

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Abstract. Phosphate ore is starting material for all phosphate products and is the main source of phosphorus for fertilizer production. Prior to processing, phosphate ore contains radium and its decay products, which tends to stay in phosphogypsum produced during the wet phosphoric acid process. Most of the phosphogypsum is considered waste and is disposed at local dump sites or used as by-products. The local dump sites, containing radium are often unprotected and may be a source of contamination to surface or ground waters. Practical implications of this finding are important in view of possible environmental contamination of the area around a fertilizer plant. This study was carried out in the area of a phosphate fertilizer factory in central Croatia, within systematic radioactive measurements of the Croatian environment performed by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health in Zagreb. The purpose of this paper was to determine radium specific activity resulting from the phosphate fertilizer production and evaluate possible environmental contamination of the area. Distribution of total radium by the components of the production process was assessed from the values of the radium initial concentrations in raw material, and mean values of radium concentrations measured in waste water, trickling water from piezometers, phosphogypsum deposit and final products.

1. Introduction

The raw material used in the production of fertilizers is phosphate ore containing various amounts of naturally occurring radioactive elements. During phosphate ore processing, owing to chemical properties of radium, practically all $^{226}$Ra gets incorporated into phosphogypsum and remains in disequilibrium status when compared to radioactivity levels contained in the raw material. Most of the phosphogypsum is considered waste and is stockpiled or discharged into the aquatic environment. Potential issues of concern resulting from phosphogypsum disposal are its environmental impacts; possible increases in radionuclides in soils or in groundwater and consequential ingestion by humans through exposure routes such as drinking water and food chain. 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 [1,2].

This study was carried out in the area of a fertilizer factory located in central Croatia, which was identified as a site of significant ecological burden due to fertilizer production and disposed phosphogypsum. 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 pools by a special pipeline. The water from the pools surface is pumped back into production, which makes this a closed system [3].

Considered as a particularly sensitive ecosystem for its specific geographic location, this area has been included in an extensive monitoring program of the Croatian environment [2], carried out by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health in Zagreb for over several decades [4].

The purpose of this paper was to determine $^{226}$Ra specific activity resulting from the phosphate fertilizer production in the samples of waste water, trickling water and well water in order to assess whether ingestion of drinking water poses a health risk for the inhabitants of this area.
2. Materials and Methods

Trickling water is sampled by means of piezometers installed at the pool area. Samples of trickling water were taken as grab samples 4 and 10 m deep at the phosphogypsum and SiF deposit. Samples of well water were collected in the vicinity of phosphogypsum deposits in a nearby residential zone. All samples were collected during the period 1986 - 2003.

All liquid samples were radiochemically separated, and $^{226}$Ra was determined by alpha spectrometric measurements using silicon charged particle (ORTEC Si(Li) surface barrier) detector. The counting time for each measurement was 60,000 sec or longer.

All samples were gammaspectrometrically analysed in the laboratory using HP Ge 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%) with electronic units and gammaspectrometrical software on a personal computer. All samples were measured in Marinelli beaker, volume 1L or volume 0.1L. Measurement time was 80,000 sec or higher.

3. Results and Discussion

The phosphate ore used in the production of fertilizers contains $^{226}$Ra concentrations in dependence of the origin of the phosphate ore processed, which is usually about 900 Bq kg$^{-1}$. The $^{226}$Ra concentrations in the phosphate ore used as raw material in the investigated plant fall within the range of 500-1500 Bq kg$^{-1}$ and in waste phosphogypsum 400-1200 Bq kg$^{-1}$. 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 a tone of phosphoric acid, which represents a considerable ecological burden to the plant area.

Figure 1 shows distribution of $^{226}$Ra activity determined in waste water from the factory. Average activity value was 39.25 Bq m$^{-3}$, and altogether 50% of waste-water samples contained activity over 27.70 Bq m$^{-3}$.

![FIG: 1. $^{226}$Ra activity concentrations in waste-water](image-url)
Permeability of solid waste deposit is monitored using samples of trickling water. Figure 2 shows average $^{226}$Ra activities in trickling water collected 4 and 10 m deep at the phosphogypsum deposit, in the period 1986-2003. Maximum activity of $166 \pm 32$ Bq m$^{-3}$ was measured on March 1994 in the samples of trickling water at the depth of 4 m. Average activity value was 66.12 Bq m$^{-3}$, and altogether 50% of trickling-water samples contained activity below 62.80 Bq m$^{-3}$.

![FIG. 2. $^{226}$Ra activity concentrations in trickling-water](image)

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 and consuming the well water (Figure 3).

![FIG. 3. $^{226}$Ra activity concentrations in well-water](image)
Varied $^{226}\text{Ra}$ concentrations resulting from different $^{226}\text{Ra}$ initial activities measured in wells located in the vicinity of the phosphogypsum deposit site were relatively higher when compared to concentrations found elsewhere in the state. The mean $^{226}\text{Ra}$ concentration for well water samples was $28.9 \pm 8.5 \text{ Bq m}^{-3}$. Our study included only the wells located in a close proximity to the phosphate fertilizer plant.

4. Conclusion

In the environmental control of pollutants drinking water should be controlled for radioactive contaminants and appropriate measures should be taken whenever activity detected in water exceeds the permissible levels set up by country legislation. The results of this study indicate that $^{226}\text{Ra}$ concentrations in the well water in the area around the investigated fertilizer plant fall within tolerable limits and that the adverse health effects to the population are negligible. There is no evidence of an impact to the well water due to permeability of phosphogypsum deposit. Although our results obtained so far speak against any need for a concern about possible health risks from ingestion of drinking water, further monitoring of the phosphogypsum deposit and periodic sampling of the well water is recommended in order to evaluate possible trends in radionuclide contaminations over time.

5. References


