Coal mining activity and radium isotope contamination of river water in Silesia, Poland

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Abstract The aim of this research was to determine the relative proportions of soluble and nonsoluble radium in river waters in the Silesia region of Poland and its vicinity. Samples were collected in May 1997 from the Vistula River at seven different locations, and from six tributaries during medium river level conditions. Samples were filtered, and separate analyses were conducted on the liquid and solid phases. Radium was separated by co-precipitation (with $PbCrO_4$ and $BaSO_4$). The thin sources obtained were analysed by alpha-spectrometer with silicon detectors, and by low-background gamma spectrometer (the recovery of radium was controlled by Ba-133 tracer). The highest activity of Ra-226 in the water samples was 334±11 mBq l^{-1}, whereas the lowest result was 0±1 mBq l^{-1}. These results suggest that radium is transported in soluble form (or as very tiny particles).

INTRODUCTION

The Upper Silesia industrial region has been recognized as a natural radio-activity anomaly since the 1970s. A major source of radiation in this area results from coal mining activity, which was introduced more than a hundred years ago. Mine workings range from 350 to 1050 m in depth. There are 66 underground coal mines extracting 150×10^6 tons of coal per year. Water pumped from the mines, and the coal, contain significant quantities of Ra-226. The radionuclide concentrations in coal samples vary greatly in the Silesia region: Ra-226 concentrations ranged from 0 to as high as 121 Bq kg^{-1} (Wysocka & Skowronek, 1991). One of the most serious problems met by coal extraction in Upper Silesia in Poland is the presence of water of very high salinity in geological strata. The concentration of Ra-226 in the Upper Silesian brines generally is between 1 and 100 kBq m^{-3}, with a maximum value of 390 kBq m^{-3}. Because the volume of saline water drained by underground mine workings is as high as 91 000 m^3 day^{-1}, the total activity of Ra-226 reaches 306 MBq day^{-1}. The presence of barium ions in saline water has an important effect on the environmental behaviour of radium because it causes co-precipitation of radium and barium sulphates. Therefore, radium present in water containing radium and barium ions is always precipitated out and forms radioactive deposits of $BaSO_4$ and $RaSO_4$ through either the spontaneous or controlled mixing of natural waters. The concentrations of Ra-226 in these deposits are very high, ranging from 110 to as high as 133 200 Bq kg^{-1}. Radioactive deposits precipitate mainly in pipes and mine channels and therefore most of them remain in the underground environment. In two mines a technology of underground purification of radium and barium has been implemented. Nevertheless, wastewaters released by a few mines contain more radium than is acceptable by Polish regulations. The radioactivity is directly discharged to the river water through waters pumped from mines. Radium carried by these waters is diluted in waters of the Vistula and other rivers.

In previous work we studied radium activity in Vistula River sediments by gamma spectrometric measurements (Pociask–Karteczka et al., 1997). The aims of this project were: (a) to determine the relative proportions of soluble and nonsoluble radium in river waters, and (b) to test an alpha spectrometric method of radium determination.

AREA OF INVESTIGATION

The Upper Silesia region is located in the southern part of Poland (Fig. 1). The mean annual discharge of the Vistula River close to the Silesia coal fields, and in the vicinity of Krakow, is 22.7 and 96.6 $m^3 s^{-1}$, respectively. Inflow to the Vistula River includes a few Carpathian rivers (and also the Dunajec River) with relatively good-quality water and the Przemsza, Chechlo Gostynia, and other rivers from Silesia with very polluted water, including water pumped from mines.

METHODS

Water samples from the Vistula River and its tributaries were collected in May 1997 (Fig. 1). The Dunajec River water, which is not affected by the coal mines, was analysed to determine the natural level of radium in water. The sampling locations are described in Table 1. At the time of sampling, the discharge of the rivers was a little enhanced but still moderate. The volume of each water sample was two litres, and the samples were put into plastic bottles. Samples were acidified immediately after arriving at the laboratory. They were initially filtered using a paper filter and then again using a membrane filter (pore diameter 0.7 μm). The dried membrane filters were analysed with a gamma-ray spectrometer for Ra-226 and Ra-228 (←Ac-228). Then these filters, and the residues from the paper filters, were ashed at 600°C. The ashes and 0.5 dm^3 of filtered water from each sample were taken separately for radiochemical analyses.

The Pb and Ba carriers (1 mg and 200 μg, respectively) were added with a radiochemical tracer (Ba-133, 55 or 220 Bq per sample). Ashed sediments were wet mineralized using concentrated acid solutions (HF, HNO_3, HCl) and then transferred to a dilute HNO_3 solution. The separation of Ra and Ba from Ca for all the samples was done by co-precipitation with $PbCrO_4$ at a pH of between 3 and 4 (Sunderman & Townley, 1960). The centrifuged residues were dissolved in hot 0.1 M DTPA solution, and then co-precipitated with 100 μg of barium sulphate at pH 4.5 to obtain a thin alpha spectrometric source (Fig. 2).

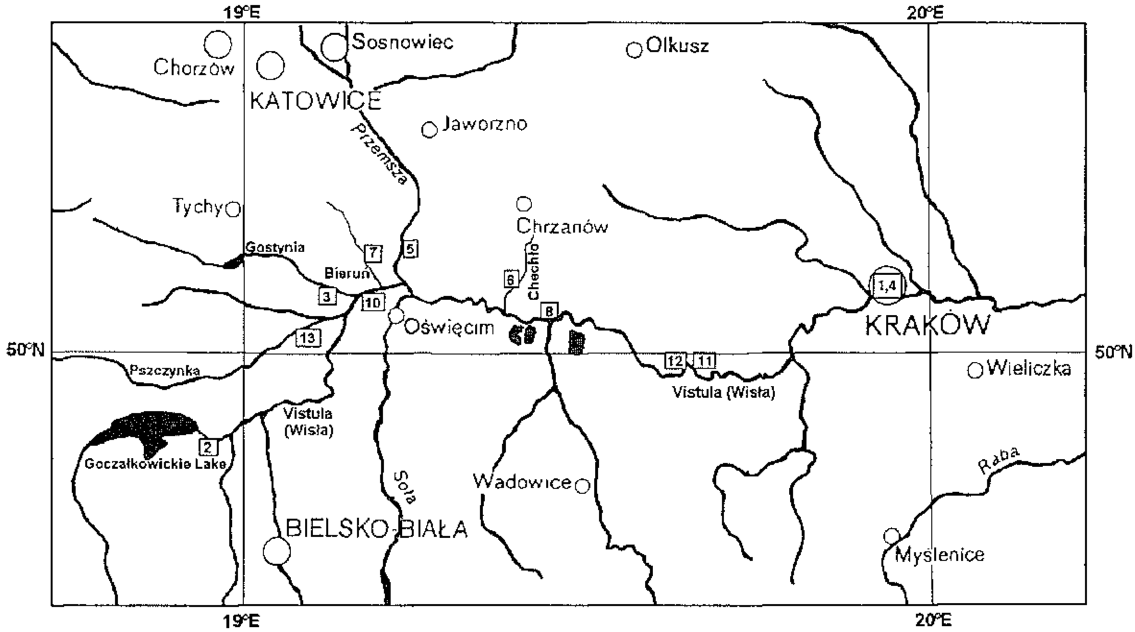

Fig. 1 The location of sampling sites in southern Poland.

The original co-precipitation method was simplified. We did not prepare barium sulphate seed suspensions (Sill, 1987). Instead, we used a membrane filter with a very small (50 nm) pore diameter produced by JINR Dubna (Russia). In addition to the measurements on an alpha-spectrometer, the sources obtained were also analysed on a gamma-spectrometer to measure the chemical yield (recovery of Ba-133) and determine Ra-228 (←Ac-228). The chemical yields achieved for the samples are

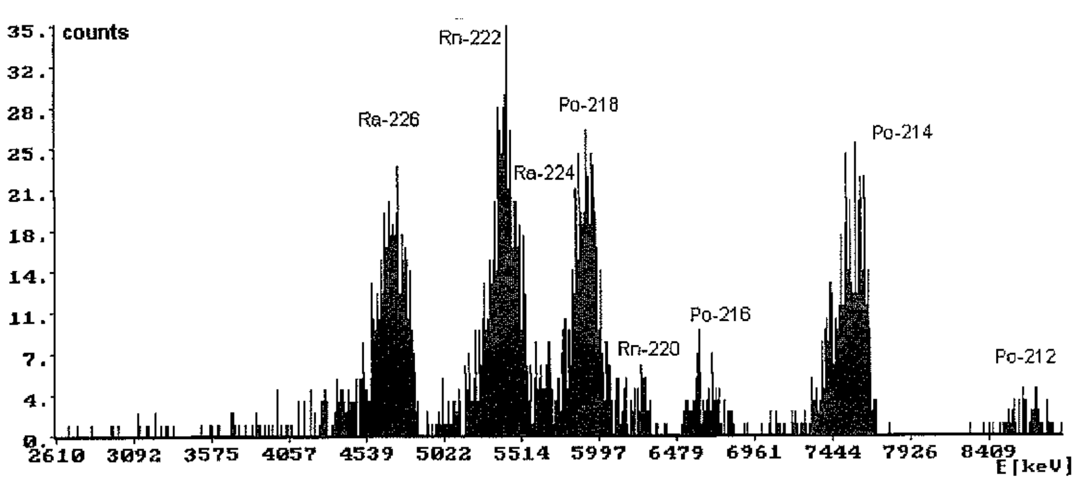

Fig. 2 Example of the radium alpha spectrum for the Vistula River water (sample no. 12); volume 0.5 dm^3, measurement time 117 h, detector SBSi 300 mm^2; source preparation: co-precipitation with $BaSO_4$; Ra-226 activity determined: 0.071±0.003 Bq dm^{-3}.

Table 1 Details of the samples.

Sample no.	Location	Chemical yield (%): Water	Filtered sediment	Mass of ash of filtered sediment (g)
1	Vistula at Kraków	10.4	2.3	0.0378
2	Vistula at Goczalkowice, below the dam	26.8	2.3	0.0265
3	Gostynia, below the Czeczott coal mine	27.8	20.9	0.2228
4	Vistula at Kraków	37.5	2.6	0.0356
5	Pszemsza near Chelmek	11.5	4.5	0.0720
6	Chechlo stream	25.6	19.1	0.0099
7	Bieruñ stream	16.0	14.7	0.1689
8	Vistula at Zator	7.3	<1	0.0520
9	Dunajec at Nowy Targ	10.1	<1	0.0448
10	Vistula at Nowy Bieruñ	4.9	3.3	0.1698
11	Vistula at Łączany, below the dam	16.6	1.1	0.0342
12	Vistula at Łączany, above the dam	18.5	11.6	0.0198
13	Pszczynka	17.2	<1	0.0299

presented in Table 1. The yields were generally low. The best recovery was 38% for a water sample and 21% for a sediment sample. However, after finishing the analyses described here, our laboratory took part in an intercalibration run for radium determination in water (Narbutt & Fuks, 1998). We successfully used the method described here (the only modification was in the pH value for $PbCrO_4$ precipitation, which was adjusted in the intercalibration run to between 4 and 5), and we achieved higher recoveries (mean value 44%, range 35–51%).

RESULTS

The concentration of radium for both kinds of samples of water and sediment are expressed as the activity per unit of water volume, i.e. in Bq l^{-1}, in Table 2. In addition, the last column of Table 2 contains the results for Ra-226 in sediment samples presented as the concentration in ashed material.

The highest activity of Ra-226 in a water sample was 334±11 mBq l^{-1} (sample no. 7, Bieruñ). The second-highest result was 244±7 mBq l^{-1} (sample no. 3, Gostynia). The lowest result was 0±1 mBq l^{-1} for sample no. 9 (Dunajec). Other low results for Ra-226 in water, 2±1 mBq l^{-1} and 3±1 mBq l^{-1}, were obtained for samples no. 5 (Pszemsza) and 13 (Pszczynka), respectively. For the remaining water samples, the Ra-226 activity ranged from 12±3 mBq l^{-1} to 71±3 mBq l^{-1}. The Ra-226 value on a coarse filter is generally lower than that of the water sample. The highest activity (calculated per unit of volume of the original water sample), 65±4 mBq l^{-1}, was obtained for sample no. 10 (Vistula, near Nowy Bieruñ), which reveals a moderate level of radium activity in the water itself. The samples with the highest Ra-226 content in water (nos 3 and 7) also possess enhanced levels of radium activity stopped on a coarse filter: 41±2 mBq l^{-1} and 20±1 mBq l^{-1}, respectively. However, sample no. 5 (Pszemsza), which has one of the lowest values of radium in water, has an enhanced level of Ra-226 in suspended matter: 29±2 mBq l^{-1}. This feature could be the result of several different processes,

Table 2 Results of the radium concentration measurements.

Sample no.	Water:		Filtered sediment:		
	^{228}Ra (gamma) (Bq l^{-1})	^{226}Ra (alpha) (Bq l^{-1})	^{228}Ra (gamma) (Bq l^{-1})	^{226}Ra (alpha) (Bq l^{-1})	^{226}Ra (alpha) (Bq kg^{-1} of ash)
1	0.4±0.1	0.012±0.003	2.7±0.7	0.003±0.001	40±13
2	0.2±0.1	0.013±0.001	0±0.2	0±0.001	<19
3	0±0.2	0.244±0.007	0.4±0.1	0.041±0.002	92±4
4	0±0.2	0.034±0.002	2.9±1	0.002±0.001	28±14
5	1.8±0.4	0.002±0.001	0.5±0.2	0.029±0.002	200±14
6	0±0.2	0.015±0.001	0±0.2	0.007±0.001	350±50
7	0±0.2	0.334±0.011	0.3±0.1	0.020±0.001	60±3
8	0±0.2	0.052±0.004	–	–	–
9	2.0±0.6	0.0±0.001	–	–	–
10	0±0.2	0.057±0.003	0±0.2	0.065±0.004	190±12
11	1.6±0.4	0.053±0.002	0.7±0.3	0±0.001	<15
12	0.5±0.1	0.071±0.003	0±0.2	0.005±0.001	125±25
13	0+0.2	0.003±0.001	–	–	–

– not determined because of low chemical yield.

and we do not as yet have a final explanation for it. The Ra-226 activities of suspended matter retained by a coarse filter, calculated as the specific activities expressed in Bq kg^{-1} of ashed matter, show enhanced levels for samples no. 6 (350±50 Bq kg^{-1}, Chechlo), no. 5 (200±14 Bq kg^{-1}, Pszemsza), no. 10 (190±12 Bq kg^{-1}, Vistula at Nowy Bieruñ), and no. 12 (125±25 Bq kg^{-1}, Vistula at Łączany above the dam). The water samples corresponding to all these samples showed low or moderate activities. The calculated activities of Ra-226 in the remaining sediment samples are less than 100 Bq kg^{-1}. The ratio of the Ra-226 activity observed in material retained on a coarse filter, to the activity in water, ranges from 0 to 15, but only two results are greater than 1. Thus, most radium seems to be transported (at medium water levels) in soluble or very tiny (<0.7 μm) particles (colloids).

Gamma spectrometric results for Ra-228 for most samples and especially for the filtered sediment, were very near the detection limits of the spectrometer used, and therefore their credibility is low. However, these results are presented in Table 2 with the Ra-226 results.

The results for the smaller suspended matter, i.e. that retained on 700 nm membrane filters, are not presented because zero values were obtained for alpha spectrometric measurements on all of them. A few very small non-zero values, with large errors, were obtained for those samples for gamma spectrometric measurements for Ra-226. However, the lack of confirmation of those results from alpha spectrometric measurements discourages us from presenting them.

Generally, the observed Ra-226 activities confirmed the results obtained by other investigators in previous years. For example, the concentration of Ra-226 in filtered water collected in 1993 at Krakow was reported to be 0.035 Bq l^{-1} and the same value was found by other authors as the average value for the years 1994–1996. In our work, we obtained results of 0.012 and 0.034 Bq l^{-1} (samples 1 and 4, respectively) (Pociask–Karteczka *et al.*, 1997; Wardaszko *et al.*, 1996; Wysocka *et al.*, 1996).

CONCLUSION

There are many anthropogenic sources that contribute to human radiation doses. The input from coal mines strongly affects the natural environment, not only in the Upper Silesia region, but in downstream areas, also, via aquatic transport. The water ecosystem of rivers and channels are mainly affected. The method applied here can be used for the determination of the radium isotope content of water samples, but the method should be improved to increase the chemical yield. The results obtained suggest that at medium (not high) river levels, radium is transported in soluble form or as very tiny particles. Further investigations are planned to study the role of dams in radium transport through the upper Vistula River.

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