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# Contamination of settling ponds and rivers as a result of discharge of radium-bearing waters from Polish coal mines

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**Abstract**

Saline waters from underground coal mines in Poland often contain natural radioactive isotopes, mainly $^{226}Ra$ from the uranium decay series and $^{228}Ra$ from the thorium series. Approximately 40% of the total amount of radium remains underground as radioactive deposits, but 225 MBq of $^{226}Ra$ and 400 MBq of $^{228}Ra$ are released daily into the rivers along with the other mine effluents from all Polish coal mines. Technical measures such as inducing the precipitation of radium in gobs, decreasing the amount of meteoric inflow water into underground workings, etc. have been undertaken in several coal mines, and as a result of these measures, the total amount of radium released to the surface waters has diminished by about 60% during the last 5–6 years. Mine water can have a severe impact on the natural environment, mainly due to its salinity. However, associated high levels of radium concentration in river waters, bottom sediments and vegetation have also been observed. Sometimes radium concentrations in rivers exceed 0.7 kBq/m$^3$, which is the permitted level for waste waters under Polish law. The extensive investigations described here were carried out for all coal mines and on this basis the total radium balance in the effluents has been calculated. Measurements in the vicinity of mine settling ponds and in rivers have given us an opportunity to study radium behaviour in river waters and to assess the degree of contamination. Solid waste materials with enhanced natural radioactivity have been produced in huge amounts in the power and coal industries in Poland. As a result of the combustion of coal in power plants, low-radioactive waste materials are produced, with $^{226}Ra$ concentration seldom exceeding a few hundreds of Bq/kg. A different situation is observed in coal mines, where, as a result of precipitation of radium from radium-bearing waters, highly radioactive deposits are formed. Sometimes the radioactivity of such materials is extremely high; precipitates from coal mines

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may have radium concentrations of 400 000 Bq/kg — equivalent to 3% uranium ore. Usually, such deposition takes place underground, but sometimes co-precipitation of radium with barium takes place on the surface, in settling ponds and in rivers. Therefore management of solid waste with technologically enhanced natural radioactivity (TENR) is a very important subject. 

*Keywords:* Radium; Coalmines; Rivers; Contamination; Poland

## 1. Enhanced natural radioactivity

The presence of natural radioactivity in uranium mines was known from early times. In other types of mines (such as for coal or phosphate), enhanced levels of natural radioactivity have been observed, but unfortunately this problem is not so well recognised.

The enhanced levels of gamma radiation in Polish coal mines were discovered in the early 1960s (Saldan, 1965) and regular investigations were started in the 1970s (Tomza & Lebecka, 1981). These studies concentrated on radium-bearing waters and radioactive deposits. In one coal mine in Poland, the radium concentration ($^{226}Ra$) in a precipitate reached 400 kBq/kg and this has the same activity as 3% U ore. Similar problems in the Ruhr Basin were reported by Gans (Gans et al., 1982), who also found high radium concentration in waste waters from coal mines. Natural radioactivity enhanced by effluents from the phosphate industry has been investigated in Brazil (Paschoa & Nobrega, 1981). Very high radium concentrations have been found in the USA in waste brines from the oil and gas industry (Maksimovic & Movrey, 1994). As a result of radium precipitation from such waters in pipes etc., highly radioactive scales are formed. A similar situation has been observed in the Romanian oil industry (Sandor & Peic, 1996), which caused contamination of the natural environment.

The Upper Silesian Coal Basin (USCB) is located in the southern part of Poland and there are about 50 underground coal mines. The total water outflow from these mines is about 800 000 $m^3$/day. The salinity of these brines is far higher than that of ocean water. The total amount of salt (total dissolved solids — TDS) carried with mine waters to the rivers is about 10 000 tonnes/day. The commonest ions in these brines are $Cl^-$ and $Na^+$ with concentrations up to 70 and 40 g/l respectively, and these waters usually contain several grams per litre of $Ca^{2+}$ and $Mg^{2+}$ and significant amounts of other ions (Tomza & Lebecka, 1981). Waters with high radium concentration occur mainly in the southern and central parts of the coal basin, where coal seams are overlain by a thick layer of impermeable clays (Rozkowski & Wilk, 1992). These saline waters cause severe damage to the natural environment, mainly due to their high salinity (sometimes $>200$ g/l), but also their high radium concentration, reaching 390 kBq/$m^3$ (Skubacz, Lebecka, Chalupnik & Wysocka, 1990).

Investigation by Tomza and Lebecka (1981) showed that the concentration of radium in water is correlated with its salinity. As the salinity of mine waters usually increases with depth, waters with higher radium concentration occur in deeper levels. Two different types of radium-bearing water were found in coal mines (Skubacz et al., 1990). One type (type A) contains high concentrations of radium and barium, but no sulphate ions, whilst the other (type B) has very low barium but high radium and sulphate. From type A waters radium is easily co-precipitated with barium sulphate when mixed with other natural waters containing sulphate ions. For radium-bearing type B waters, there is no co-precipitant for the radium and therefore precipitation does not occur. Further investigation (Lebecka, Chalupnik, Lukasik & Wysocka, 1993) showed that radium-bearing waters released from coal mines sometimes cause widespread contamination of both small and larger rivers in their vicinity. This contamination is caused by radium being present in ionic form in water as well as in suspended matter. Highly radioactive deposits are formed by co-precipitation of barium and radium as sulphates from radium-bearing type A waters (Tomza & Lebecka, 1981). This process results in reduction of the total activity released into rivers because part of the radium remains in the underground mine workings. Precipitation of barium and radium sulphates in underground mine workings takes place either spontaneously or as a result of the applied treatment procedure which aims to reduce the radium concentration in waste waters below the permitted level (Decree, 1989).

In the past, the highest concentration of $^{226}$Ra in discharge waters from a single coal mine in USCB was 25 kBq/m$^3$ (Skubacz et al., 1990). According to Polish regulations, waters with a $^{226}$Ra concentration over 0.7 kBq/m$^3$ should be treated as waste with enhanced natural radioactivity (Decree, 1989). Such waters were released from 10 out of the 66 underground hard coal mines in Poland, in which radium-bearing waters were originally dumped via settlement ponds into the natural environment. Type A waters were originally discharged from 7 coal mines (now 3). The total activity of $^{226}$Ra released with these waters is about 30 MBq per day. Although Type B waters were discharged from only 3 mines, the total output of $^{226}$Ra is higher than for Type A waters — approximately 225 MBq per day (Lebecka et al., 1994). The occurrence of enhanced natural radioactivity in Polish coal mines is a potential radiation hazard for mining crews. In the mining industry in Poland, monitoring of the radioactivity of mine waters and precipitates, as well as $\gamma$ doses, has been obligatory since 1989. The monitoring system provides an opportunity to obtain a complete picture of the influence of an individual mine on the natural environment.

## 2. Applied methods and instrumentation

### 2.1. Measurements of radium isotopes in waters

Radioactivity of waters from coal mines is mostly from the radium isotopes — $^{226}$Ra from the uranium series and $^{228}$Ra from the thorium. A method of chemical separation of radium, developed by Goldin (Goldin, 1961), has been modified for liquid scintillation counting (Chalupnik & Lebecka, 1990, 1993). Radium is co-precipitated with barium in the form of sulphates and this precipitate is mixed with liquid gelling scintillator. The prepared samples were measured by a low background liquid scintillation spectrometer (QUANTULUS, Wallac Oy, Finland). This counter has $\alpha/\beta$ separation with an anti-coincidence shield, which enables measurements of $^{226}$Ra concentration above 3 Bq/m$^3$ with simultaneous measurements of $^{228}$Ra (LLD = 30 Bq/m$^3$) and $^{224}$Ra (LLD = 50 Bq/m$^3$). In addition, the procedure enables the simultaneous preparation of $^{210}$Pb, which can be separated from the radium isotopes at the last stage of analysis and also measured in the LS spectrometer with a detection limit of 20 Bq/m$^3$. Radium standards were supplied by Amersham.

### *2.2. Measurements of $\gamma$-emitting natural nuclides in solid samples*

Solid samples (deposits from settlement ponds, river beds, soils, solid wastes, ash) mainly contain radionuclides from the uranium and thorium decay series, $^{40}$K and sometimes $^{137}$Cs (from the Chernobyl disaster). For these measurements, a $\gamma$-spectrometry system was used — it comprises an HPGe detector (45%, PGT), multichannel analyser with built-in computer (CANBERRA) and the GENIE-PC software for spectrum analysis (CANBERRA). This instrumentation enables measurements of $^{226}$Ra concentration (LLD as low as 1 Bq/kg), $^{228}$Ra and $^{224}$Ra, $^{40}$K and other natural and artificial nuclides (Lebecka et al., 1996) at similar levels. Calibration has been achieved using certified materials from IAEA and EPA.

## 3. Investigations of the contamination of the natural environment, caused by the coal mining industry

The assessment of the total activity of radium released from all coal mines in Upper Silesia with waste water was based on:

- determination of radium isotopes in waters released by all coal mines;
- the amount of water released by individual mines.

### *3.1. Analysis of outflows from Polish coal mines*

Radium-bearing waters from coal mines are discharged into settling ponds on the surface and later into rivers. In some cases, radium isotopes are co-precipitated with barium in these ponds or adsorbed on the bottom sediments.

Samples of discharged waters were taken from each settlement pond. We found that the amount of $^{226}$Ra released with saline waters to the rivers is approximately 225 MBq per day (75 GBq/year) and for $^{228}$Ra 400 MBq/day (145 GBq per year). These values were calculated from the radium concentrations as measured and from data for the amounts of water expelled from the mines.

In outflows from settlement ponds for 87% of Polish coal mines, the $^{226}$Ra concentration exceeds 0.008 kBq/m$^3$, in 25% the $^{226}$Ra concentration is higher than 0.1 kBq/m$^3$ and in 8% the concentration exceeds the permitted level — i.e. 0.7 kBq/m$^3$ (Decree, 1989).

Enhanced concentrations of radium in rivers can be observed many kilometres downstream of the discharge points. This is mainly true for radium-bearing type B waters, because radium is not easily precipitated. The highest value of $^{226}Ra$ concentration was as high as 1.3 kBq/m$^3$ — in a small stream near its junction with the Vistula River. Consequently, more extensive investigations were undertaken in this area.

### 3.2. Monitoring of contamination of surface settling ponds

In order to investigate the behaviour of radium in such an environment, it is necessary to carry out detailed analyses of waters and deposits from the different settling ponds. The main purpose of such a pond is to allow mechanical suspensions to settle, but additionally deposition of radium takes place there. Two settling ponds were chosen for comparison and both of these settling ponds are located in the catchment area of the Vistula River (Table 1). Into the first one, Rontok, type A waters are discharged but then released directly to the Vistula. The second reservoir, Bojszowy, is used as a settling pond for type B waters from which the outflow is into the Gostynka River, a small tributary of the Vistula.

## 4. Rontok reservoir

The use of this pond started in 1977. Since then about 72 million cubic meters of saline waters were pumped into the reservoir from the "SILESIA" Coal Mine. The concentration of the suspended load varied from 0.3 to 2.4 g/dcm$^3$. The total amount of the suspension, deposited in the pond, was calculated as 100 000 m$^3$ (about 150 000 tons). Type A waters (with radium and barium ions) were discharged into the pond during this period. The activity ratio between the two radium isotopes $^{226}Ra$:$^{228}Ra$ was about 2 : 1. Early discharge was about 10 000 m$^3$, but since 1998 the discharge of water is much smaller, only 5600 m$^3$/day. The inflows of sulphate-rich groundwater are small but numerous and therefore precipitation of $BaSO_4 + RaSO_4$ occurs in the pond. In pond bed deposits, the concentration of radium isotopes is clearly enhanced. The outflow is directly into the Vistula.

Currently, there is less co-precipitation of radium and barium in the pond, because of the two factors: the lower radium content in waters during recent years (now

Table 1
Radium concentration in water samples from Rontok

| Rontok | Radium concentrations | |
|---|---|---|
| | $^{226}Ra$ (kBq/m$^3$) | $^{228}Ra$ (kBq/m$^3$) |
| Average | 6.81 | 1.65 |
| Median | 6.88 | 1.73 |
| Max. | 20.5 | 2.60 |
| Min. | 0.18 | 0.23 |

$\sim$2.5 kBq/m$^3$ of $^{226}$Ra, but up to 15 kBq/m$^3$ before), coupled with a reduction in volume to about one half. It means that the total amount of radium in waste water, dumped into the pond, is several times lower than it was 4 to 5 years ago.

## 5. Bojszowy reservoir

The second settling pond is the Bojszowy reservoir, into which saline, radium-bearing waters from two mines are released. The inflow from the "Czeczott" coal mine is about 15 000 m$^3$/day whilst from the "Piast" mine, the discharge is even bigger — roughly 20 000 m$^3$/day. In both cases the type of water is the same (B type – no barium only radium and sulphate ions). The activity ratio between $^{226}$Ra: $^{228}$Ra is 1 : 2, the reverse of Rontok. Due to the absence of barium, no precipitation of radium in the pond can be observed. Nevertheless, measurements of the radium content in bottom sediments showed enhanced concentrations of radium isotopes up to several hundred Bq/kg as a result of sorption of radium.

The pond was used from 1980, and about 227 million m$^3$ of waters have been discharged into the reservoir. The pond waters are released into the small river Gostynka, a tributary of the Vistula.

### *5.1. Rontok reservoir — Radium-bearing waters*

The radium input for the Rontok reservoir was assessed as approximately 9.5 GBq/year. However, there was twice as much water (10 000 m$^3$/day) discharged from the mine prior to 1998 and the average radium concentrations were slightly different: for $^{226}$Ra — 3.20 kBq/m$^3$ and for $^{228}$Ra — 1.43 kBq/m$^3$.

We found during preliminary investigations that the average radium concentrations in outflows were higher than the corresponding values for inflows. This is thought to result from the de-watering of deeper horizons (where waters with higher radium concentrations occur) during the night, because of the lower energy costs. The results for radium concentrations in waters from the pond (Table 1) support this conclusion. For instance, the maximum value of $^{226}$Ra concentration was found to be 20 kBq/m$^3$ in the reservoir.

### *5.2. Radium in bottom sediments*

The contamination of bottom sediments in Rontok and the soil in adjacent areas was monitored. Sampling of sediments from the bottom of the pond was done on a $50 \times 50$ m grid, and the thickness of the layer of sediments was measured at each sampling point. After drying, samples were measured and the concentrations of the natural radionuclides calculated. The same procedure was applied to soil samples. Mine management restoration of the Rontok area is planned to be undertaken within a few years so an investigation of this pollution is critical.

We found that the maximum radium content in sediments occurred near the outlet of the pipeline that transported water from the mine to the settling pond. The total activity of radium isotopes ($^{226}Ra+^{228}Ra$) here was 55 kBq/kg. On average, however, the radium content was much lower, and the distribution of radium was very non-uniform. In some places, the radium concentration in sediments was the same as in the earth's crust (25 Bq/kg), as can be seen in Table 2.

Concentrations of radium isotopes are below 350 Bq/kg for $^{226}Ra$ and 230 Bq/kg for $^{228}Ra$ in about 35–40% of the area of the pond. These levels are close to or below the maximum permitted levels and no remedial action needs to be taken. In contrast, in the southern-east part of the pond, near the mine discharge point, the thickness of the sedimentary deposit is approximately 1.2 m and it is here that the maximum concentrations of radium were found. Taking all these data into account, we were able to assess the total amount of deposits in the settling pond as well as the mass balance of radium isotopes in the deposits (Table 3).

## 6. Bojszowy reservoir — Radium-bearing waters

The waters released from two coal mines into the Bojszowy reservoir are both of type B with $^{228}Ra$ activities higher than $^{226}Ra$. The average values of radium concentrations in discharges from the Piast Mine were ca. 4.1 kBq/m$^3$ for $^{226}Ra$ and about 7.2 kBq/m$^3$ for $^{228}Ra$. Corresponding values for inflows from the Czeczott Mine were lower, 3.2 kBq/m$^3$ for $^{226}Ra$ and 4.9 kBq/m$^3$ for $^{228}Ra$. These are average values for the last two years.

The assessment of the radium concentrations ($^{226}Ra+^{228}Ra$) in inflows to the Bojszowy settling pond gives us an annual activity of about 124 GBq. This is 55% of the total amount of radium carried in waters from all the coal mines of Poland

Table 2
Radium in bottom sediments from Rontok

| Rontok | Radium in sediments | |
|---|---|---|
| | $^{226}Ra$ (Bq/kg) | $^{228}Ra$ (Bq/kg) |
| Average | 5110 | 1410 |
| Median | 1190 | 593 |
| Max. | 49 200 | 6390 |
| Min. | 67 | 62 |

Table 3
Assessment of the amount of sediment in Rontok and total radium activity in the deposits

| Area of the pond (m$^2$) | Volume of deposits (m$^3$) | Amount of water (m$^3$) | Total activity of $^{226}Ra$ (Bq) | Total activity of $^{228}Ra$ (Bq) | Amount of radium in the pond $^{226}Ra+^{228}Ra$ (Bq) |
|---|---|---|---|---|---|
| 360 000 | 113 000 | 262 000 | $240\times10^9$ | $74\times10^9$ | $314\times10^9$ |

(Skubacz et al., 1993). We calculated the average radium concentrations in waters discharged to the pond as 3.6 kBq/m$^3$ for $^{226}$Ra and 6.2 kBq/m$^3$ for $^{228}$Ra.

The reservoir water and bottom sediments were sampled in 1996. The grid was the same ($50 \times 50$ m) as for the Rontok settling pond. The results of the analyses of radium concentrations in 42 water samples are shown in Table 4.

It can be seen that the distribution of radium in water in Bojszowy is more uniform than in the Rontok settling pond. The main reasons seems to be a more stable radium content in the inflows and the type of the water, from which radium is removed only by sorption, because there is no carrier (barium ions) for co-precipitation of radium.

The average radium concentration in outflows from the settling pond were similar to the values at inflow — 3.5 kBq/m$^3$ for $^{226}$Ra and 6.0 kBq/m$^3$ for $^{228}$Ra. This means that only small amounts of radium are deposited on the bottom. Moreover, the total concentration of radium isotopes in waters released to the Gostynka stream is about 10 kBq/m$^3$, which is more than 10 times greater than the permitted level for waste water. A significant improvement of the situation will be achieved very soon, thanks to the construction of an underground treatment plant for mine waters in the Piast Colliery (Chalupnik, 1999).

By comparing the results of radium analysis of inflows and outflows from the Bojszowy reservoir to the Gostynka River, we calculated that only 2.9% of the $^{226}$Ra and 3.3% of $^{228}$Ra activities remain in the pond and are sorbed onto bottom sediments.

More than 95% of the radium is discharged with the saline waters into the Gostynka River. The influence of this discharge is obvious. Upstream from the discharge point the concentration of radium isotopes is very low, below 0.1 kBq/m$^3$, a value typical of groundwater and river waters in Poland (Wardaszko & Grzybowska, 1996). Downstream from the discharge point there is a rapid increase of radium content. Usually during winter and spring, when water levels in the river are higher, the concentration of radium does not exceed 0.7 kBq/m$^3$. However, during summer, the concentrations of $^{226}$Ra in the Gostynka River vary within the range 0.5–0.7 kBq/m$^3$, whilst for $^{228}$Ra the concentrations are higher and range at about 1.0–1.3 kBq/m$^3$. The total activity of radium isotopes in this river can be as high as 1.5–2.0 kBq/m$^3$ (Wysocka, Lebecka & Chalupnik, 1997). Additionally, a proportion of the radium (several relative percent) is adsorbed onto bottom

Table 4
Radium concentration in water samples from Bojszowy

| Bojszowy | Radium concentrations | |
|---|---|---|
| | $^{226}$Ra (kBq/m$^3$) | $^{228}$Ra (kBq/m$^3$) |
| Average | 3.45 | 6.95 |
| Median | 3.34 | 6.76 |
| Max. | 5.21 | 8.32 |
| Min | 2.12 | 4.67 |

sediments, but most of the radium is transported into the Vistula. In this big river, the radium concentration in water decreases as a result of dilution and further adsorption (Wardaszko & Grzybowska, 1996; Wysocka et al., 1997).

### 6.1. Bottom sediments

Bottom sediments were sampled at the same sites that waters were taken. Boreholes were drilled into the bottom of the settling pond and cores of sediments collected and analysed by $\gamma$-spectrometry. Sediments from Bojszowy showed $^{226}$Ra concentrations in the range 95–950 Bq/kg, and $^{228}$Ra from 124 up to 1705 Bq/kg (Wysocka et al., 1997). It is characteristic of these samples that in almost all cases the activities of $^{228}$Ra and $^{224}$Ra were close to equilibrium, and very often the concentration of $^{226}$Ra was only slightly lower than the $^{228}$Ra content. This implies that the sediments are relatively old, at least a few years. It also means that the adsorption in such places is very slow. It is only in a very few places and far from the banks that we found these "young" deposits. Results are shown in Table 5.

Based upon these measurements, the balance of radium in bottom deposits in the settling pond was calculated (Table 6). We assumed that the distribution of radium isotopes in the bottom sediments was uniform, and so we used the average concentrations of both radium isotopes for our calculations.

The results of these considerations show that the total activity of $^{226}$Ra, accumulated in bottom sediments during the 19 years of operation of the Bojszowy reservoir, is ca. 66 GBq, and the corresponding value for $^{228}$Ra is about 100 GBq. The annual rate of deposition is about 3.5 GBq for $^{226}$Ra and 5.8 GBq/year for $^{228}$Ra. This is only 7% of the annual discharge of radium with waters into the settling pond. Earlier calculations (Wysocka et al., 1997) gave lower rates of deposition — about 4% per year, but those assessments were not very accurate,

Table 5
Radium in bottom sediments from Bojszowy

| Bojszowy | Radium concentrations | |
|---|---|---|
| | $^{226}$Ra (kBq/m$^3$) | $^{228}$Ra (kBq/m$^3$) |
| Average | 414 | 627 |
| Median | 406 | 628 |
| Max. | 950 | 1710 |
| Min. | 95 | 124 |

Table 6
Assessment of the amount of deposits in Bojszowy and total radium activ1ity in deposits

| Area of the pond (m$^2$) | Volume of deposits (m$^3$) | Amount of water (m$^3$) | Total activity of $^{226}$Ra (Bq) | Total activity of $^{228}$Ra (Bq) | Amount of radium in the pond $^{226}$Ra + $^{228}$Ra (Bq) |
|---|---|---|---|---|---|
| 160 000 | 240 000 | 262 000 | $66 \times 10^9$ | $100 \times 10^9$ | $166 \times 10^9$ |

because they did not take into account the large uncertainties in the parameters measured.

### *6.1.1. The comparison of radium deposition in both settling ponds*

The above results can be used to describe the radium behaviour in both settling ponds and rivers and can be used to attempt to correlate them with the chemical composition of the radium-bearing waters (Table 7). In the case of the Bojszowy reservoir, the rate of deposition of radium is very low, only about 4–7% of the total activity being adsorbed in bottom sediments per year. The distribution of radium in the sediments is rather uniform and therefore calculation of the radium balance in sediments was relatively easy. At least 90% of the radium is discharged into the Gostynka River and later to the Vistula. This leads to the contamination of river water a long way from the discharge point.

The Rontok settling pond is quite different. The rate of deposition is much higher, because of the different type of water, i.e. type A with elevated barium content. The assessment of the deposition rate for radium was also difficult. Calculations made in two different ways gave different results. Taking into account the measurement of radium concentrations in the inflows, we obtained a value of about 350 GBq for the whole period of operation. Another method of calculation, based on the amount of radium in the bottom deposits and measurements of radium concentrations in the outflows, gave a result almost three times higher at 810 GBq. In the latter case, the average concentration of radium isotopes in waters released to the pond during the whole period of operation was roughly 10 kBq/m$^3$. This relates to a deposition of about 39% (more reliable and accurate) and contrasts with the 90% calculated using the first approach. The main uncertainties in the calculations are connected with the sampling method and the properties of the de-watering system in the mine, i.e. the grab sampling from the inflow with a strong variability of radium content leads to significant errors in the assessment.

### *6.1.2. Radium in the Vistula catchment*

The discharge of radium-bearing waters firstly into settling ponds and then into rivers causes contamination of the river waters. Enhanced radium concentrations are

Table 7
Radium balance in the Bojszowy and Rontok settling ponds[a]

| Settling pond | Area (m$^2$) | Volume of deposits (m$^3$) | Total amount of radium discharged into pond (GBq)[a] | Amount of radium deposited in the pond (GBq)[a] | Deposition Rate (%) |
|---|---|---|---|---|---|
| Bojszowy | 160 000 | 240 000 | 2356 | 166 | 7 |
| Rontok | 360 000 | 110 000 | 350[b] | 314 | 90[b] |
| | | | 810[c] | | 39[c] |

[a] Total activity of $^{226}$Ra + $^{228}$Ra.

[b] Assessment made on a basis of measurements of radium concentration in inflows to the pond.

[c] Assessment made on a basis of measurements of radium concentration in outflows to Vistula and amount of radium, deposited in the pond.

mainly observed in the Vistula River, into which most of the radium-bearing type B waters are discharged at approximately 180 MBq of $^{226}$Ra and 375 MBq of $^{228}$Ra per day. High concentrations of $^{226}$Ra (0.035 kBq/m$^3$) were observed in the Vistula River in Cracow, 80 km downstream from Upper Silesia (Fig. 1). The markers in the diagram show the concentrations of radium in the discharge waters from the mines. Some mine waters are not discharged directly into the Vistula River, but enter through its tributaries. The 7-km bar represents the outflow from the Rontok reservoir (type A waters), whilst the 40-km marker shows the confluence with the Gostynka River, through which waters are introduced from the Bojszowy reservoir (type B — from two mines). Another contaminated tributary enters at the 44 km marker.

The influence of each inflow can be seen very clearly. There is a clear difference in behaviour between type A input (fast precipitation) compared with type B tributaries.

The situation in the vicinity of the Oder River is different. The coal mines in this area produce mainly type A waters, whilst the amount of radium discharged into the

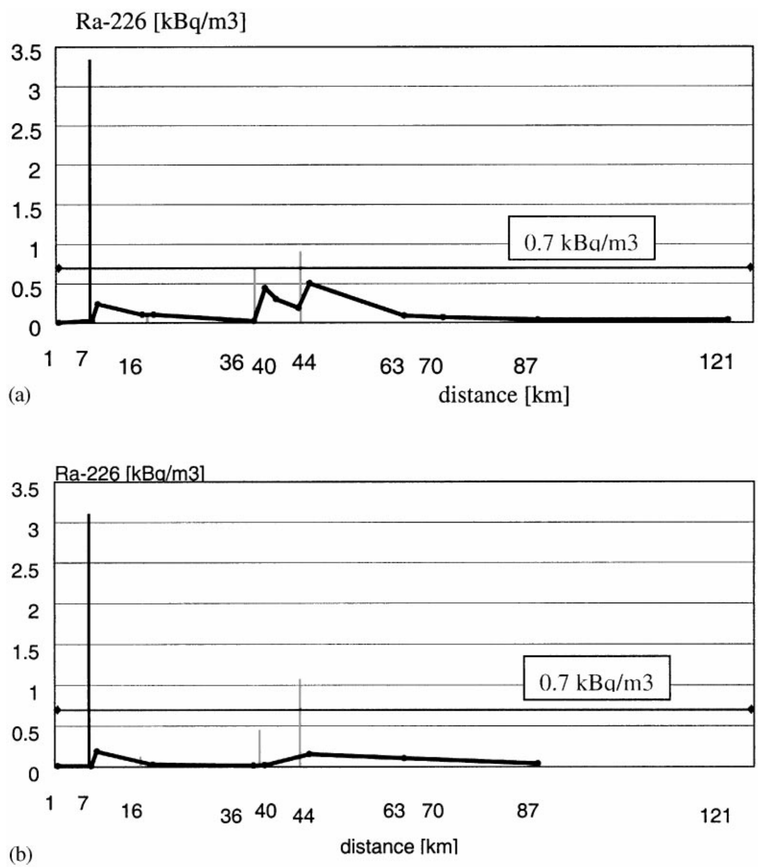


Fig. 1. Radium in the Vistula River during the (a) summer, and (b) autumn and winter.

Oder is much lower, about 20 MBq per day of $^{226}$Ra and 10 MBq per day of $^{228}$Ra. As a result, the concentrations of radium in the Oder are below 0.1 kBq/m$^3$.

Concentrations of radium isotopes in some rivers in Upper Silesia are clearly higher than natural levels. In comparison with data from other locations, the concentrations of radium isotopes in the rivers of the USCB are significantly higher. The increased concentrations of radium in these river waters are caused solely by mine waters.

Owing to the release of radium-bearing mine waters from the coal mines, there is a contamination of the river waters. As a result, radium concentrations in some small rivers exceeds the permissible level for waste waters. Therefore development and application of purification methods are necessary and further efforts are needed to reduce the contamination of rivers, particularly the Vistula River and its tributaries.

In one of the small tributaries of the Vistula, concentrations of radium isotopes in the Gostynka River change from 0.006 kBq/m$^3$ above the settling pond discharge point to 0.635 kBq/m$^3$ ($^{226}$Ra) below, whilst the corresponding figures for $^{226}$Ra are 0.01 kBq/m$^3$ to 0.99 kBq/m$^3$. The radium concentrations in water samples from that settling pond varied from 2.4 to 4.2 kBq/m$^3$ for $^{226}$Ra and from 3.5 to 7.0 kBq/m$^3$ for $^{228}$Ra. Polish regulations indicate that waters from both the reservoir and from the Gostynka River should be treated as waste with enhanced natural radioactivity. Therefore, treatment methods within the coal mines are of critical importance.

## 7. Conclusions

- The underground mining of coal sometimes causes a significant enhancement of natural radioactivity in the environment. This is mainly the result of the release of radium-bearing waste waters from the coal mines, as well as the storage on the surface of solid waste products with enhanced natural radioactivity. This phenomenon is observed not only in the Upper Silesian Coal Basin (USCB) but also in Germany and in other countries.
- In Upper Silesia, the annual release of radium in mine waters to the natural environment can be assessed at about 75 GBq of $^{226}$Ra and approximately 145 GBq of $^{228}$Ra.
- We found that different types of radium-bearing waters (A and B) have different impacts on the natural environment. Not only is the range of transport and contamination of the river waters greater for type B brines but there is also the possibility of further migration of radium. Radium adsorbed on bottom sediment from Type B waters is probably far more mobile than radium precipitated as barium and radium sulphates from Type A waters. This problem needs further investigation.
- A significant proportion of the radium released with mine water into settling ponds on the surface is transported to rivers. This method of contamination of the natural environment is very important in the catchment area of Poland's biggest river, the Vistula.

- In certain settling ponds, significant amounts of radium isotopes have accumulated during their operation. There is an increase of $\gamma$ dose rates in the vicinity of such ponds and contamination of the banks of these reservoirs.
- Until now the same regulations governing the mining industry have been applied to such reservoirs and the dose equivalent limit for miners is much higher than for the general public. Problems may arise when the mines are closed because local authorities would have to undertake ground reclamation or removal of deposits with enhanced natural radioactivity. Moreover, a much lower dose limit, 1 mSv per year, is applicable to the general public.

Owing to the fact that the problem of radioactive contamination of the natural environment is only partly covered by Polish regulations, actions must be undertaken to resolve this problem.

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