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# Radium isotope contamination of river water due to the coal mine activity in the Silesia region in Poland (East-Central Europe)

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## INTRODUCTION

The most dangerous threat to the quality of the Vistula River (called *a queen of Polish rivers*) water in last decades was industrial and municipal sewage from the Silesia industrial region. Contamination of the Vistula River began increasing in the 1960s, when an unrestrained development of industry and disordered development of urbanization occured. Primary pollutants in the Vistula River water are chlorides, phenols, cyanides, oils, greases, heavy metals, sulfates, and coal mud. In the beginning of the 1980s pollution increased rapidly after hard coal mines were put into operation. Chemical composition of water in the Vistula River in Cracow (about 60 km from the Silesia) is artificial. In comparison with chemical composition of seminatural river water, antropopression effect exceeds in many cases 90% (Tab. 1). However there has not been enough attention paid to the contamination of the Vistula River water by radionuclides.

The Silesia industrial region has been recognized as a natural radioanomaly since the 1970s this century. Intensive coal mining activity developed more than a hundred years ago in the Silesia region is one of the technologically enhanced natural radiation (TENR) sources there (Skubacz et al. 1992). There are 66 underground coal mines extracting approximately 150 x $10^6$ tons of coal per year. The depth of mine works varies from 350 to 1050 m. Concentration of $^{226}$Ra in the Upper Silesian brines is usually between 1 and 100 Bq dm$^{-3}$, with the maximum value 390 Bq dm$^{-3}$ (natural waters with similarly high radium concentration were also observed especially in oil fields; hot springs in Iran contained up to 330 Bq dm$^{-3}$ of $^{226}$Ra; also in a coal mine in Germany occurred radium-bearing waters with $^{226}$Ra concentration up to 63 Bq dm$^{-3}$). The isotope $^{226}$Ra is a particularly significant nuclide because of its relatively high radiotoxicity. Some of these waters contain not only radium, but barium ions as well. When mixing of such waters with other natural waters containing sulfate ions occurs, radium is coprecipitated with barium as sulfates. The $^{226}$Ra specific activities in these solids vary from 110 to even 133200 Bq kg$^{-1}$ (Lebecka et al.1986; Lebecka et al. 1994).

been estimated that mine waters ccontribute about 420 MBq of $^{226}Ra$ to the Vistula every day.

The $^{226}Ra$ concentration in river water has been investigated (Wardaszko et al. 1996; ...cka et al. 1996). The highest concentration of the radium $^{226}Ra$ in the Vistula River water observed the vicinity of the Silesia region: 0.057 Bq $dm^{-3}$ in filtered water and 190 Bq $kg^{-1}$ ash from suspended matter. Enhanced $^{226}Ra$ concentration is observed also in Cracow: [illegible] Bq $dm^{-3}$ and 40 Bq $kg^{-1}$ respectively. Cracow is located about 60 km downstream from the Silesia region. Also bottom sediments in the Vistula River are clearly enhanced (Jasińska et al. 1998; Pociask-Karteczka 1997; Pociask-Karteczka et al. 1997; Pociask-Karteczka et al. 1999).

The aim of this project was to determine the influence of weirs on the Vistula River concentration of $^{226}Ra$ in river water and the transport process of radium in the river channel.

**Area of investigations**

Large part of the Upper Silesia region is located in the Upper Vistula drainage basin. Mean annual discharge of the Vistula River in the vicinity of Silesia and in the vicinity of Cracow equals 22.7 and 96.6 $m^3 s^{-1}$ respectively. The area of the Vistula River drainage basin in Cracow is about 7,524 $km^2$.

The project was conducted in the Cracow area, where three weirs are situated. The distance between the first weir (The Kościuszko Dam) and the last one (The Przewóz Dam) is 25 km (Fig. 1).

**Data collection and analysis**

Water samples from the Vistula River were collected in 1999 during periods when water levels were different. The sampling locations (A, B, C, D) and time of sampling are presented in Fig. 1 and tables 2 and 3. Water samples were taken above a cascade of three weirs (point A) and below of the cascade (point D). Additionally, there were taken water samples by near the Kościuszko Dam at different depth.

Each rough water sample was of 1.2 $dm^3$ volume. They were stored in plastic vessels. Samples were filtered through a paper filter. Dried filters were ashed in 600°C. Those ashes, and 0.4 $dm^3$ of filtered water from each sample were taken separately for radiochemical analyses. To each fraction Pb and Ba carriers were added (1 mg and 200 μg, respectively) along with the tracer ($^{133}Ba$, 220 Bq). Ashes were wet mineralised using subsequently concentrate acids: HF, HNO3, HCl. To the last solution 0.5 g of $Na_2CO_3$ and 0.5 g of $H_3BO_3$ were added to destroy traces of sulphates and flourides. After evaporation the residue was dissolved in concentrate nitric acid and then diluted to about 40 $cm^3$ of 1 M $HNO_3$ solution.

Filtered water was acidified with nitric acid to pH~1 and evaporated to get about 40 $cm^3$. Separation of Ra and Ba from Ca, for both kind of samples, were done by co-precipitation with $PbCrO_4$ (Sunderman and Townley, 1960). Centrifuged residues were then dissolved in hot 0.1 M DTPA (di-ethylene tri-amine pentaacetic acid) solution, and then Ra was co-precipitated with barium sulphate at pH=4.5 to obtain thin, alpha spectrometric source (Sill, 1987) when the suspension was filtered. Membrane filter with pore diameter equal to 50 nm was produced by JINR Dubna (Russia). Along to the measurements on a alpha-spectrometer Silena AlphaQuattro with SBSi detectors, obtained sources were also measured on gammaspectrometer with germanium detector for the determination of chemical yield (recovery of $^{133}Ba$).

Radium is a bivalent metal with atomic number Z=88. More then 25 isotopes of radium are known, all of them are radioactive. Three of them are relatively easily detectable in nature. The most abundant in the terms of mass is: $^{226}Ra$ ($T_{1/2}$=1600 a), which belongs to uranium series. Two other belong to thorium series, they are: $^{224}Ra$ ($T_{1/2}$=3.64 d) and $^{228}Ra$ ($T_{1/2}$= 5.75 a). The $^{226}Ra$ is decaying by emission of 4.7 MeV alpha particle to $^{222}Rn$, in which subsequent decay next alpha particles occurs. The $^{226}Ra$ is an origin of gamma radiation of 186 keV, as well. The $^{224}Ra$ is alpha emitter, $^{228}Ra$ is beta emitter. The quantum intensity of 186 keV line is low, equal to 3.28%, and it might be interfered by 185 keV line of $^{235}U$. However, the daughters of $^{222}Rn$ emits a lot of intense gamma radiation. They are often used for the determination of $^{226}Ra$, but the secular equilibrium between isotopes in uranium series must be established.

**Results**

On the base of the research conducted near the Kościuszko Dam it may be stated, that the $^{226}Ra$ concentration in filtered water was little differentiated i.e. from 30±3 to 45±5 mBq dm$^{-3}$ (Tab. 2). Similar results were reported in previous years (Mietelski et al. 1998, Pociask-Karteczka et al. 1999).

The range of $^{226}Ra$ concentration in suspended matter was from 16±2 to 30±3 mBq dm$^{-3}$. The highest activity had water from the surface near the left-side spillway (sample 2; tab. 2). This value is not an effect of high radiotoactivity of suspended matter but by high amount of transported material near the water surface (0.0249 g dm$^{-3}$ of dry matter). The highest activity had suspended matter at the depth of 2 m, i.e. 2.1±04 kBq kg$^{-1}$ (sample 3; Tab. 1). For comparison: mean concentration of $^{226}Ra$ in soils is 25 Bq kg$^{-1}$ (Kathreen 1984).

On the base of the research conducted on the cascade of three weirs it may be stated, that $^{226}Ra$ concentration in filtered water was from 14±8 to 134±9 mBq dm$^{-3}$ (Tab. 3). However, in all cases $^{226}Ra$ concentration was higher than the mean value for Polish rivers, i.e. 4 mBq dm$^{-3}$ (Wardaszko et al. 1996). We do not as yet have explanation for situations, when $^{226}Ra$ concentration above cascade is significantly lower than below the cascade, for example 23.06.1999 (samples 9, 10; Tab. 3) and 29.06.1999 (samples 11, 12; Tab. 3).

The $^{226}Ra$ content in suspended material ranged from 3±0.3 to 298±15 mBq dm$^{-3}$. Low values of $^{226}Ra$ content occured during low and medium water levels, when small amount of material was transported. The highest $^{226}Ra$ contents occured during high water levels, then the amount of transported matterial is the highest (samples 8, 9; Tab. 3). The exception was sample no 7 (Tab. 3) with $^{226}Ra$ content only 12±1 mBq dm$^{-3}$ in spite of significant amount of transported material (0.4071 g dm$^{-3}$). A very low $^{226}Ra$ contents in ash in this sample is worth of attention; this is the lowest value in all investigated samples (0.034±0.004 kBq kg$^{-1}$ of ash). There was observed hundred times higher $^{226}Ra$ content in ash below cascade (0.34±0.02 kBq kg$^{-1}$). Also increase, but not so significant, was observed 27.05.1999 (low water level period). There was noted 0.76±0.04 kBq kg$^{-1}$ of ash above cascade and till 2.05±0.12 kBq kg$^{-1}$ of ash below cascade, i.e. almost a hundred times more than mean content of $^{226}Ra$ in soil. It testifies a resuspension process of radiotoxitic, bottom sediments occuring between the weirs.

The ratio of the $^{226}Ra$ activity observed in suspended material, to the activity in filtered water was lower than 1. Thus, most radium seems to be transported in soluble form. However, four results were equal or greater than 1 (samples 2,6,8,9; Tab. 3). It means, radium can be transported in insoluble form also. The $^{226}Ra$ contents in suspended material was considerably higher than $^{226}Ra$ contents in filtered water in samples taken during high water level (samples 8,9; Tab. 3). Hence, the radium in insoluble form constitues the main source of radioactivity during high water level periods.

**Conclusions**

The $^{226}Ra$ concentration in the cross section of the channel of the Vistula River is differentiated. This is a result of irregular suspend matter distribution in the river channel: there are visible concentrations of suspended material in the shape of stripes and clews. The radioactivity of this material is differentiated. Thus, streams with suspended material of various radioactivity are present in the channel of the Vistula River where the $^{226}Ra$ content exceeded mean concentration of $^{226}Ra$ in soil.

The $^{226}Ra$ concentration in filtered water in the Vistula River is higher than mean value for the Polish rivers. The lowest $^{226}Ra$ concentration in suspended material occur during low and medium water level periods, i.e. then the load of material transported by the river is low. The highest $^{226}Ra$ activity of suspended material occur during high water level periods, when the amount of transported material is high.

The resuspension of bottom sediments with high radioactivity in the sector between the weirs occurs during both high and low water levels. The present research has confirmed, that radium is transported mainly in insoluble form or very tiny particles (colloids). It has showed also another aspect of phenomena: radium in insoluble form is a main source of radioactivity during high water levels.

The cascade influence on the decrease of $^{226}Ra$ concentration in water could be a result of sedimentation process in the channel between the weirs. However the $^{226}Ra$ concentration depends not only on the input from the Silesia region but on the resuspention process in the cascade sector.

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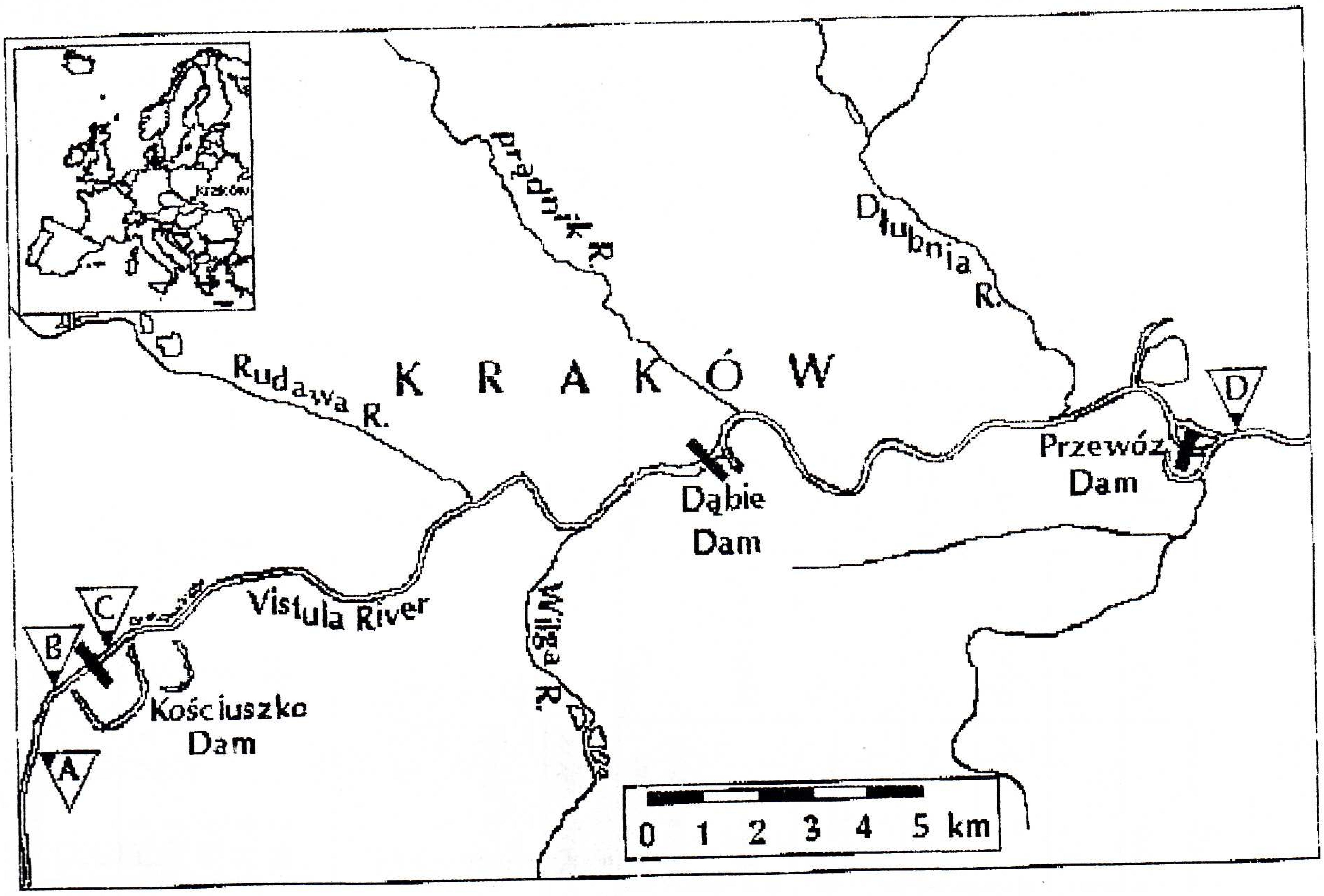
Fig. 1. Location of sampling sites (A, B, C, D)



**Tab. 1. Antropopression effect in the chemical composition of water in the Vistula River in Cracow (after Kamiński, Wróbel 1991).**

| Chemical component | Kamienica River | Vistula River | Antropopression % |
|---|---|---|---|
| | mg $l^{-1}$ | | |
| Chlorides | 4,7 | 815 | 99,4 |
| Sulphates | 16,8 | 177 | 90,5 |
| Sodium | 1,6 | 466 | 99,6 |
| Calcium | 31,9 | 113 | 71,8 |
| Magnesium | 6,7 | 56,7 | 88,2 |

**Tab. 2. $^{226}Ra$ concentrations in the Vistula River water by the Kościuszko dam (22.01.1999).**

| Sample no. | Location of sampling sites | Filtered water | | Suspended matter | | | |
|---|---|---|---|---|---|---|---|
| | | Radioche - mical yield (%) | $^{226}Ra$ (mBq $dm^{-3}$) | Dry matter (g $dm^{-3}$) | Radioche- mical yield (%) | $^{226}Ra$ (mBq $dm^{-3}$) | $^{226}Ra$ (kBq $kg^{-1}$ of ash) |
| 1 | Above a dam (Tyniec) – point A | 53.3 | 30±3 | 0.0135 | 19 | 18±3 | 1.6±0.2 |
| 2 | By the left-side spillway – point B (surface of water) | 57.9 | 39±4 | 0.0249 | 17.3 | 30±3 | 1.4±0.2 |
| 3 | By the left-side spillway – point B (depth 2 m) | 62.1 | 44±4 | 0.0128 | 9.1 | 23±3 | 2.1±0.4 |
| 4 | By the left-side spillway – point B (depth 4.5 m – bottom) | 43.5 | 40±4 | 0.0141 | 17.3 | 16±2 | 1.3±0.2 |
| 5 | By the right-side spillway – point B (depth 4.7 m – bottom) | 34.2 | 45±5 | 0.0125 | 11.1 | 17±2 | 1.6±0.2 |
| 6 | Below a dam – point C (surface of water) | 60.6 | 36±3 | 0.0169 | 13.6 | 24±2 | 1.7±0.2 |

**Tab. 3. $^{226}$Ra concentrations in the Vistula River water above and below cascade of three dams.**

| Sample no. | Date of sampling | Location of sampling sites | Filtrated water | | Suspended matter | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| | | | Radiochemical yield (%) | $^{226}$Ra (mBq dm$^{-3}$) | Dry matter (g dm$^{-3}$) | Radiochemical yield (%) | $^{226}$Ra (mBq dm$^{-3}$) | $^{226}$Ra (kBq kg$^{-1}$ of ash) | |
| 1 | 07.05.1999 | Above cascade (Tyniec) – point A | 44 | 55±3 | 0.0107 | 27 | 3.0±0.3 | 0.35±0.03 | Low water level |
| 2 | | Below cascade (Przewóz) – point D | 45.7 | 16±4 | 0.0473 | 18.1 | 16.0±1.3 | 0.41±0.03 | |
| 3 | 14.05.1999 | Above cascade (Tyniec) – point A | 18.6 | 31±3 | 0.0129 | 48.4 | 8.0±0.5 | 0.78±0.05 | Mean water level |
| 4 | | Below cascade (Przewóz) – point D | 29.4 | 47±3 | 0.0187 | 40.7 | 9.0±0.6 | 0.61±0.04 | |
| 5 | 27.05.1999 | Above cascade (Tyniec) – point A | 32.5 | 37±6 | 0.0182 | 65.6 | 12±1 | 0.76±0.04 | Low water level |
| 6 | | Below cascade (Przewóz) – point D | 20.3 | 14±8 | 0.0195 | 19.4 | 34±2 | 2.05±0.12 | |
| 7 | 19.06.1999 | Above cascade (Tyniec) – point A | 16.5 | 56±4 | 0.4071 | 5.2 | 12±1 | 0.034±0.004 | High water level |
| 8 | | Below cascade (Przewóz) – point D | 9.6 | 35±15 | 1.0513 | 22.9 | 298±15 | 0.34±0.02 | |
| 9 | 23.06.1999 | Above cascade (Tyniec) – point A | 4.8 | 27±13 | 0.4388 | 7.2 | 106±22 | 0.29±0.06 | High water level |
| 10 | | Below cascade (Przewóz) – point D | 6 | 134±9 | 0.2947 | 49.1 | 45±3 | 0.18±0.01 | |
| 11 | 29.06.1999 | Above cascade (Tyniec) – point A | 17.9 | 36±7 | 0.1451 | 18.4 | 13±1 | 0.11±0.01 | Mean water level |
| 12 | | Below cascade (Przewóz) – point D | 0.8 | 103±60 | 0.1432 | 19.4 | 23±2 | 0.20±0.02 | |
| 13 | 01.07.1999 | Above cascade (Tyniec) – point A | 11.4 | 88±21 | 0.0106 | 62.5 | 6.0±0.4 | 0.70±0.04 | Mean water level |
| 14 | | Below cascade (Przewóz) – point D | 18.7 | 57±4 | 0.016 | 24.7 | 10±1 | 0.79±0.07 | |

* *lack of measurements*

**Fig. 1. Location of sampling sites (A, B, C, D)**