

# Uranium isotopes as a tracer of groundwater transport studies

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**Abstract** The activity concentrations of  $^{234}\text{U}$  and  $^{238}\text{U}$  in thermal groundwater, deep well water and river water samples from Central Poland were determined. Concentration of  $^{234}\text{U}$  and  $^{238}\text{U}$  in the examined waters varied from  $<0.013$  (LLD) to  $16.8\text{ mBq/dm}^3$  and from  $<0.013$  (LLD) to  $45.5\text{ mBq/dm}^3$  respectively. The highest uranium activity concentrations were measured in the thermal groundwater from Mszczonow and Cieplice, while the lowest were observed in thermal ground water from Uniejow and Poddebice. In thermal groundwater from Skierniewice, uranium activity concentrations were below lower limit of detection ( $0.013\text{ mBq/dm}^3$ ). The  $^{234}\text{U}/^{238}\text{U}$  activity ratio varied from 0.37 (Cieplice) to 1.30 (Poddebice well water).

**Keywords** Uranium radionuclide ·  $^{234}\text{U}/^{238}\text{U}$  activity ratio · Alpha spectrometry · Thermal groundwater

## Introduction

Uranium chain radionuclides are usually used for a wide range of applications in the Earth Sciences. The  $^{234}\text{U}/^{238}\text{U}$  activity ratio is used as a geochemical tool to investigate transport and flow relationships in major hydrological reservoirs, groundwater pattern and it is highly useful for interpreting timescales of weathering. In rocks older than a few million years,  $^{234}\text{U}/^{238}\text{U}$  activity ratios should be in secular equilibrium [1]. Many studies on  $^{238}\text{U}$  and  $^{234}\text{U}$  in natural waters indicate that these isotopes occur in a disequilibrium state and that, with a few exceptions, water samples contain

higher  $^{234}\text{U}$  activities than  $^{238}\text{U}$  [2–4]. The higher activity of  $^{234}\text{U}$  in waters is the result of the  $^{234}\text{U}$  atom displacement from the crystal lattice after  $^{238}\text{U}$  decay and recoil of the formed  $^{234}\text{Th}$  nuclide, which after two consecutive decays finally form the  $^{234}\text{U}$  nuclide. It allows  $^{234}\text{U}$  to be more mobile during the weathering of rocks by atmospheric water. The recoil  $^{234}\text{U}$  atoms are liable to be oxidized to the hexavalent stage and can be leached into the water phase more easily than its parent nuclide  $^{238}\text{U}$ . The oxidation of U(IV) to U(VI) is an important step in leaching into water, because compounds of U(VI) have a higher solubility in water [2, 3, 5, 6]. The uranium isotope ratio is also influenced by other factors: the age of the rocks, rock type and climate difference [1]. This fact has been successfully applied for geological tracing or the characterization of geochemical processes.

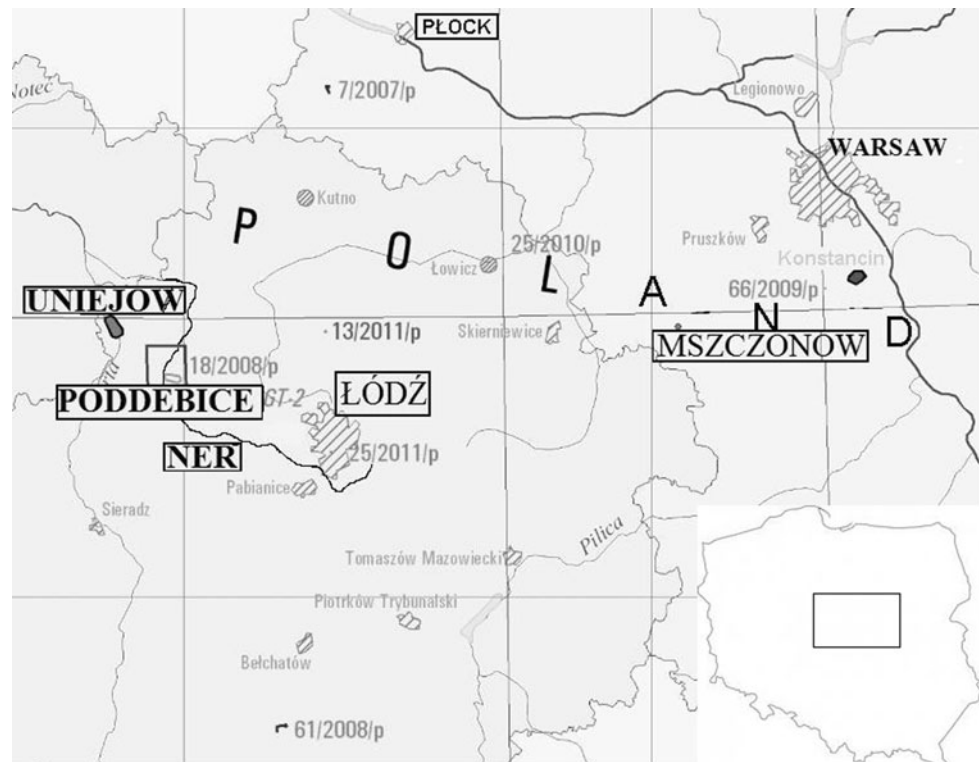
In the same way, the  $^{235}\text{U}/^{238}\text{U}$  isotope ratio (natural value  $7.25 \times 10^{-3}$ ) has been used for the identification of anthropogenic pollution scenarios [7, 8].  $^{235}\text{U}$  is a key isotope in nuclear fuel manufacture and reprocessing, and any deviation from the expected natural isotope ratio in environmental samples is an indication of contamination from nuclear activity. Large increases in the  $^{236}\text{U}/^{238}\text{U}$  isotopic ratio represent have been used as a clear indicator of the presence of irradiated uranium [8, 9].

Average  $^{238}\text{U}$  and  $^{234}\text{U}$  activity concentrations in surface and ground water are in the range from 1 to  $20\text{ mBq/dm}^3$  [10]. A major source of uranium is seawater, where its average concentration of  $^{238}\text{U}$  equal to  $41.5\text{ mBq/dm}^3$  [11]. The highest uranium activity concentrations were detected in the drinking water in a private well in Finland –  $150\text{ Bq/dm}^3$  [12].

The uranium activity ratio can be measured in diverse matrices by radiometric, mass spectrometry and alpha spectrometry methods. Advances in the methods of uranium activity ratio determination have been recently overviewed [13–15].

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**Fig. 1** Location of sampling collection sites



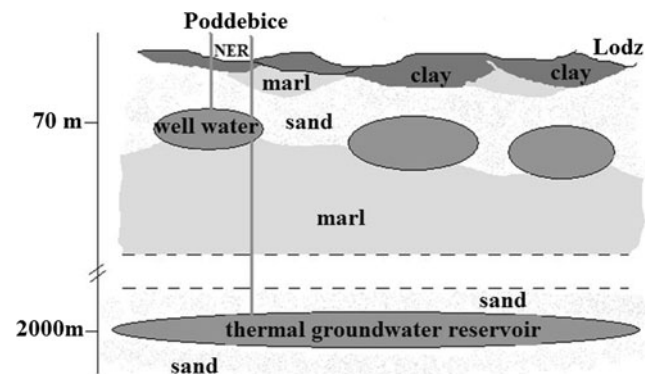
Recently we have found significant differences in the some natural radionuclide activity concentrations in deep well water samples (including thermal groundwater) originating basically from the same Lower Cretaceous geological formation [16]. Since the salinity of these samples differs also substantially one possible explanation for this phenomenon is the possible infiltration of surface water to these underground reservoirs. Special attention has been devoted to a newly exploited source of the thermal groundwater from Poddebice close to the city of Łódź. In very close vicinity of this thermal groundwater source lying 2,000 m below ground level, there are two other important water sources: an underground water reservoir (70 m below surface) used as a source of municipal drinking water, and the Ner river. The Ner river flows mostly through the rural area, and the main source of uranium in its water should be the dissolved uranium from fertilizers.

Therefore, it seems to be interesting to compare the uranium activity ratio in the selected water samples in order to detect the possible vertical transport of the surface water to the deep underground thermal water reservoir.

## Experimental

### Study area

Samples of thermal groundwater, groundwater and surface water was collected from different sites from central Poland (Fig. 1).



**Fig. 2** Sites of samples collection in Poddebice

In the case of Poddebice, the water samples were taken from three water sources:

- The Ner river
- Well municipal water (70 m below surface)
- Thermal groundwater reservoir (2,000 m) as is shown in Fig. 2.

Ten litres of each water sample were collected in polyethylene bottles with screw caps. All samples were acidified to  $\text{pH} \approx 2$  directly after collection. As the water samples presented complete clarity, filtering of the samples was considered unnecessary.

For the Poddebice sites, several soil samples from different levels of the bore-hole were also taken for uranium radionuclides analysis.

**Table 1** The results of <sup>234</sup>U and <sup>238</sup>U activity in International Atomic Energy Agency (IAEA) samples

| Sample | <sup>234</sup> U   |                        | <sup>238</sup> U   |                        |
|--------|--------------------|------------------------|--------------------|------------------------|
|        | IAEA value (Bq/kg) | Measured value (Bq/kg) | IAEA value (Bq/kg) | Measured value (Bq/kg) |
| 1      | 0.04 ± 0.00        | <LLD                   | 0.04 ± 0.00        | <LLD                   |
| 2      | 1.30 ± 0.03        | 1.29 ± 0.02            | 0.70 ± 0.02        | 0.69 ± 0.02            |
| 3      | 0.47 ± 0.01        | 0.47 ± 0.02            | 0.31 ± 0.01        | 0.29 ± 0.02            |

Radiochemical method

Uranium isotopes were co-precipitated from water samples with hydrated manganese dioxide by a method described elsewhere [17–19].

Hydrated manganese dioxide was dissolved in 50 mL of 3% H<sub>2</sub>O<sub>2</sub> in 1 M HCl solution and evaporated to dryness. The residue was dissolved in 50 mL of 9 M HCl and was passed through the anion exchangeable resin Dowex 1X8 (50–100 mesh, Cl<sup>-</sup> form). Each column was first conditioned by 50 mL 9 M HCl. Under this condition, uranium is adsorbed by the resin, whereas thorium and other elements are passed with the solution and discarded [20]. Then the column was washed with 20 mL of 9 M HCl to eliminate residual thorium traces. Cations of U<sup>+4</sup>, U<sup>+6</sup> and Fe<sup>+3</sup> were retained on the column. Iron ion was eluted with 25 mL of 8 M HNO<sub>3</sub>. The remaining uranium was eluted in two portion: with 25 mL of 8 M HNO<sub>3</sub> and with 50 mL deionized water, and the total collected solution was evaporated. After evaporation the solid residue containing uranium was dissolved in 0.75 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> solution and then it was transferred to an electrolytic cell. Uranium isotopes (<sup>234</sup>U and <sup>238</sup>U) are electrodeposited on a stainless steel disc at a current density of 1.2 A/cm<sup>2</sup> for 1.5 h. Fifteen minutes before

ending the electrolysis, 0.5 mL NH<sub>4</sub>OH solution was added to the electrolyte to complete the uranium deposition on the disk. The disk with uranium was washed with deionized water and acetone.

The activity concentrations of uranium isotopes were determined using an α spectrometry system with PIPS detector (Canberra Packard). Lower limit of detection, for 300,000 s counting time, were equal to 0.013 mBq/dm<sup>3</sup> for each of the uranium isotopes.

The activity concentrations of <sup>238</sup>U via its daughter <sup>234</sup>Th in the soil samples were determined by gamma spectrometry with HPGe detector using its principal γ-line 63.3 keV.

Quality assurance of the elaborated method

The accuracy of the developed method for uranium determination was evaluated by checking the activity concentration of <sup>234</sup>U and <sup>238</sup>U in two Standard Reference Materials: IAEA Soil 327, IAEA Phosphogypsum 434 and IAEA water samples distributed for intercomparison measurements—CU-2010-03. The average uranium recovery was almost quantitatively (varied from 92 to 100%). The results for intercomparison measurements—CU-2010-03 are presented in Table 1.

Results and discussion

Activity concentration of uranium isotopes in Poddebice region

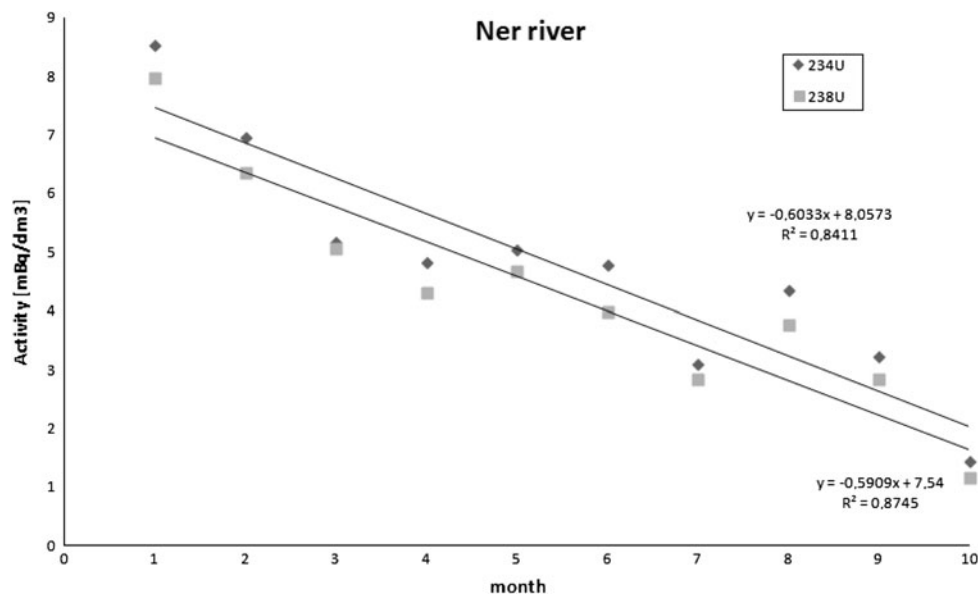
The activity concentration of <sup>234</sup>U and <sup>238</sup>U in the water samples taken from three sources around the geothermal bore-hole of Poddebice in different months of 2011 are presented in Table 2.

**Table 2** Activity concentration of <sup>234</sup>U and <sup>238</sup>U in thermal groundwater, well water and river water from Poddebice (mBq/dm<sup>3</sup>)

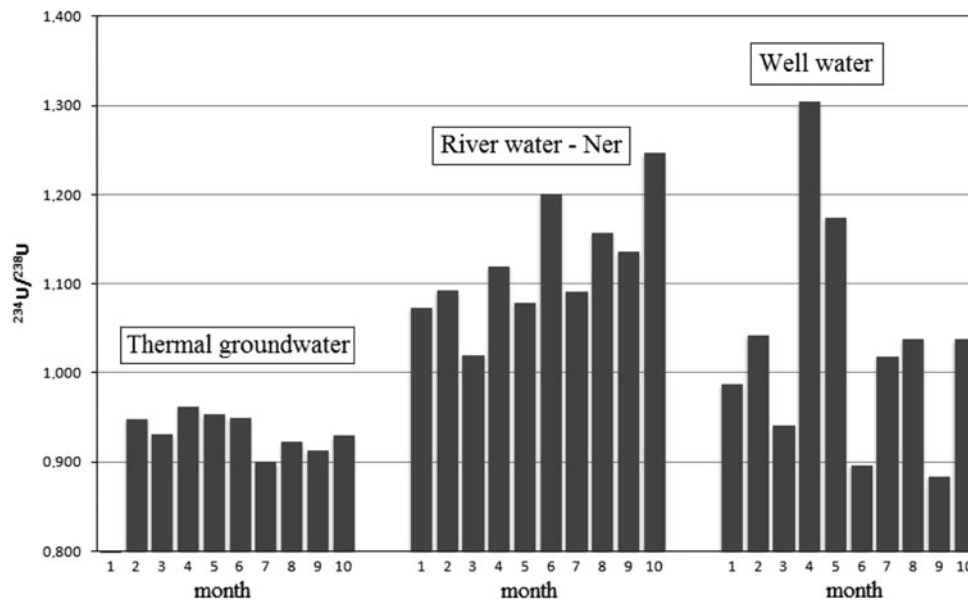
| Months    | Geothermal reservoir |        |                  |        | River water-NER  |       |                  |       | Well water Poddebice |       |                  |       |
|-----------|----------------------|--------|------------------|--------|------------------|-------|------------------|-------|----------------------|-------|------------------|-------|
|           | <sup>234</sup> U     |        | <sup>238</sup> U |        | <sup>234</sup> U |       | <sup>238</sup> U |       | <sup>234</sup> U     |       | <sup>238</sup> U |       |
| January   | na                   |        | na               |        | 8.54             | ±0.19 | 7.96             | ±0.18 | 4.12                 | ±0.13 | 4.17             | ±0.13 |
| February  | 0.151                | ±0.025 | 0.159            | ±0.026 | 6.95             | ±0.17 | 6.36             | ±0.16 | 1.29                 | ±0.07 | 1.23             | ±0.08 |
| March     | 0.110                | ±0.021 | 0.119            | ±0.022 | 5.16             | ±0.15 | 5.05             | ±0.14 | 0.79                 | ±0.06 | 0.83             | ±0.06 |
| April     | 0.102                | ±0.020 | 0.106            | ±0.021 | 4.83             | ±0.16 | 4.31             | ±0.15 | 1.19                 | ±0.07 | 0.92             | ±0.06 |
| May       | 0.168                | ±0.026 | 0.176            | ±0.027 | 5.03             | ±0.14 | 4.66             | ±0.14 | 0.97                 | ±0.07 | 0.82             | ±0.07 |
| June      | 0.087                | ±0.020 | 0.092            | ±0.021 | 4.78             | ±0.15 | 3.98             | ±0.14 | 1.73                 | ±0.12 | 1.92             | ±0.13 |
| July      | 0.037                | ±0.012 | 0.041            | ±0.013 | 3.09             | ±0.12 | 2.83             | ±0.11 | 1.65                 | ±0.08 | 1.62             | ±0.08 |
| August    | 0.049                | ±0.014 | 0.053            | ±0.014 | 4.35             | ±0.14 | 3.76             | ±0.13 | 0.45                 | ±0.04 | 0.43             | ±0.04 |
| September | 0.064                | ±0.014 | 0.071            | ±0.015 | 3.23             | ±0.11 | 2.84             | ±0.10 | 0.62                 | ±0.05 | 0.70             | ±0.05 |
| October   | 0.123                | ±0.019 | 0.132            | ±0.020 | 1.43             | ±0.07 | 1.15             | ±0.06 | 0.85                 | ±0.05 | 0.82             | ±0.05 |

na Not analyzed

**Fig. 3** Activity concentration of  $^{234}\text{U}$  and  $^{238}\text{U}$  in the Ner river



**Fig. 4** Uranium isotopic ratio ( $^{234}\text{U}/^{238}\text{U}$ ) in thermal groundwater, deep well water and river water from Poddebice



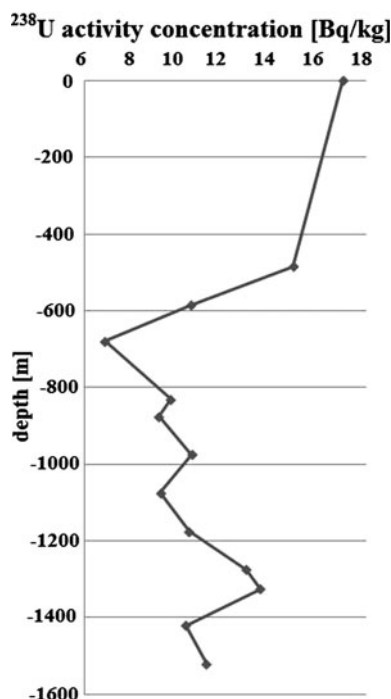
The lowest activity concentration of  $^{234}\text{U}$  and  $^{238}\text{U}$  were found in the thermal groundwater samples, and varied from 0.087 to 0.168 mBq/dm<sup>3</sup> and from 0.092 to 0.176 mBq/dm<sup>3</sup> for  $^{234}\text{U}$  and  $^{238}\text{U}$  respectively. As expected, the highest contents of uranium isotopes were found in the river water, from the Ner, as a result of additional anthropogenic uranium input from agricultural application of phosphoric fertilizer [21]. In this water activity, concentrations varied from 1.43 to 8.54 mBq/dm<sup>3</sup> and from 1.15 to 7.96 mBq/dm<sup>3</sup> for  $^{234}\text{U}$  and  $^{238}\text{U}$  respectively.

The slight seasonal decrease of uranium concentration in the Ner river, connected with periods of rain, can be also

observed (Fig. 3). Similar levels of  $^{238}\text{U}$  activity concentration and its seasonal fluctuation were observed for other Polish main rivers [21, unpublished data].

$^{234}\text{U}/^{238}\text{U}$  isotopic ratio in Poddebice region

As was mentioned, the interesting information concerning mutual transfer between underground and surface water can be obtained from a comparison of  $^{234}\text{U}/^{238}\text{U}$  activity ratio in these water samples. The results of the seasonal fluctuations of  $^{234}\text{U}/^{238}\text{U}$  in water samples from Poddebice are shown in Fig. 4.



**Fig. 5** Uranium-238 activity concentration profile for the Poddebice bore-hole

In thermal groundwater from Poddebice, the activity ratio of  $^{234}\text{U}/^{238}\text{U}$  was the lowest with an average value  $0.935 \pm 0.021$ , and practically does not change seasonally.

In deep well water exploited from 70 m below ground level, the uranium isotope activity ratio changed from 0.9 in June to 1.30 in April.

As was mentioned, most groundwater samples have  $^{234}\text{U}/^{238}\text{U}$  activity ratio above 1. An excess of  $^{234}\text{U}$  is explained by  $\alpha$ -recoil of  $^{234}\text{Th}$  into solution and by preferential leaching of  $^{234}\text{U}$  from soil [22, 23]. However this phenomenon plays a role for water reservoirs with adjacent rock with a higher concentration of uranium, for example granitic minerals. It should be mentioned that  $\alpha$ -recoil mechanism is efficient when dissolution rates are low and the residence times of adjacent water in contact with the rock are very long. Such conditions do not exist in the case of Poddebice thermal groundwater, which has a temperature of about 60 °C, and a sandy soil environment with very low uranium content. The profile of the uranium activity concentration in the Poddebice bore-hole is shown in Fig. 5.

As is evident from Fig. 5, uranium surface soil activity is equal to 17 Bq/kg, whereas for the deeper sandy geological formation, which surround the thermal groundwater reservoir, this activity concentration decreases to very low values of  $\approx 11$  Bq/kg.

In this case, the dissolution rate of both uranium isotopes is higher and the input of  $^{234}\text{U}$  recoil directly to the

**Table 3** Activity concentration and activity ratio of uranium isotopes in the water samples from central Poland

|                      |                        | Activity (mBq/dm <sup>3</sup> ) |                  | $^{234}\text{U}/^{238}\text{U}$ |
|----------------------|------------------------|---------------------------------|------------------|---------------------------------|
|                      |                        | $^{234}\text{U}$                | $^{238}\text{U}$ |                                 |
| Geothermal reservoir | Mszczonow              | $13.32 \pm 0.26$                | $15.98 \pm 0.29$ | 0.83                            |
|                      | Skierniewice           | <0.013                          | <0.013           | –                               |
|                      | Uniejow                | $0.39 \pm 0.04$                 | $0.54 \pm 0.04$  | 0.75                            |
|                      | Poddebice <sup>a</sup> | $0.12 \pm 0.03$                 | $0.13 \pm 0.03$  | 0.94                            |

<sup>a</sup> Average from ten month in 2011 year

solution is negligible. However, because of very low uranium concentration in the surrounding soil, leachable uranium radionuclides in the time scale of these processes (the dozen thousands of years) are exhausted and there is no renewal of material (uranium) exposed to water weathering. Then, such water would be expected to evolve to have values of  $^{234}\text{U}/^{238}\text{U}$  ratio below unity even up to 0.3 as presented in models by Anderson et al. [24] or Rihs et al. [25].

This data clearly show lack of any water transport from the surface water to thermal groundwater reservoir. However, such transfer from the Ner river to the underground municipal water is possible.

Uranium activity concentration in thermal groundwater samples from Central Poland

Lower values of  $^{234}\text{U}/^{238}\text{U}$  activity ratio were also observed for the geothermal waters in other places in Central Poland. The results are presented in Table 3.

As shown in Table 3, the activity concentration of  $^{234}\text{U}$  and  $^{238}\text{U}$  in water samples varied in a wide range, from <0.013 to 16.84 mBq/dm<sup>3</sup> and from <0.013 to 45.47 mBq/dm<sup>3</sup>, respectively. The highest uranium activity concentrations were measured in thermal groundwater from Mszczonow and Cieplice, whereas the lowest uranium activities were found in thermal ground water from Uniejow and Poddebice.

The values of  $^{234}\text{U}/^{238}\text{U}$  activity ratio below 1 confirm basically the same hydro geochemical conditions for all these thermal groundwater reservoirs in Central Poland. Similarly, lower values of uranium activity ratio for most geothermal waters are reported by Osmond and Cowart [4].

## Conclusions

$^{234}\text{U}$  and  $^{238}\text{U}$  activity concentrations were determined in the water samples (river water, deep well water and thermal groundwater) collected from Central Poland. Uranium activity concentrations in the analyzed waters varied in a

wide range. On the basis of the measured values, the uranium activity ratio ( $^{234}\text{U}/^{238}\text{U}$ ) was calculated. In deep well water and river water, uranium activity ratio ( $^{234}\text{U}/^{238}\text{U}$ ) was higher than 1 (from 1.06 to 1.20), while in thermal groundwater it was lower than 1 (from 0.75 to 0.95). A comparison of the average uranium isotopic ratio in the well water from Poddebice (1.06) and river water from the Ner (1.09) show possible infiltration of surface water to this reservoir.

The lower  $^{234}\text{U}/^{238}\text{U}$  ratios in the geothermal water are caused by the fact that the majority of both uranium isotopes come from the uranium present in low concentrations in the adjacent rocks and its relatively quick dissolving at higher temperatures leads to its exhausting from the surface layer of rocks contacting with water. Therefore, the input of the recoil  $^{234}\text{U}$  atoms is negligible. The remarkably lower  $^{234}\text{U}/^{238}\text{U}$  data for thermal groundwater in the Poddebice region in comparison with data for surface and well water in this region, clearly show lack of any water transport from the surface water to this reservoir.

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