

Fate of radium in river and lake sediments impacted by coal mining sites in Silesia (Poland)

Christelle Courbet¹, Małgorzata Wysocka², Loïc Martin³, Izabela Chmielewska², Michał Bonczyk²,
Bogusław Michalik², Evelyne Barker¹, Mathilde Zebracki¹, Arnaud Mangeret¹

¹*Institut de Radioprotection et de Sûreté Nucléaire, 31 avenue de la Division Leclerc, 92260 Fontenay-Aux-Roses, France, christelle.courbet@irsn.fr*

²*Główny Instytut Górnictwa, Plac Gwarków 1, 40-166 Katowice, Poland, mwysoc@igig.katowice.pl*

³*Institut de Physique du Globe de Paris, 1 rue Jussieu, 75005 Paris, France, martin@ipgp.fr*

Abstract

The Upper Silesian Coal Basin has been extensively mined since the beginning of the 20th century. Wastewaters released from Polish coal mines contain radium (Ra) in ionic form as well as in suspended matter. Although co-precipitation of Ra into radio-barite ((Ba,Ra)SO₄) has been enhanced for reducing the impact of mining activities on water quality, sediments in rivers and lakes surrounding mining sites still show relevant activities of both ²²⁶Ra (1600 y half-life) and ²²⁸Ra (5.7 y half-life) isotopes. The management of this contamination currently relies on natural attenuation.

This study focuses on assessing the long-term impact of Ra which has been trapped into river and lake sediments in the vicinity of coal mining sites in Poland. Two geochemical interfaces have been surveyed by sampling sediment, surface and pore waters downstream from coal mining sites: (1) the hyporheic zone of a river, where groundwater tends to mix with surface waters within the river bed; and (2) the water-sediment interface in a lake which was formerly used as a settling pond. Both represent redox interfaces where radium-bearing solid phases (barite, metal oxyhydroxides) can undergo various geochemical processes which have not been quantified yet.

Our preliminary results show that pore water geochemistry within the hyporheic zone of the studied river is impacted by diffuse and direct wastewater releases from an operating settling pond. A geochemical model built with JCHESS® suggests that mixing of surface waters with wastewaters favors witherite (BaCO₃) precipitation within the riverbed. Additional investigations are planned to assess the consequences of this suspected process on Ra behavior through the hyporheic zone. Moreover further investigations are performed for studying the fate of Ra trapped into BaSO₄ within pond sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation and where ²¹⁰Po (²²⁶Ra decay product) is detected into surface waters.

Key words: radium, coal mines, barite, witherite, polonium

Introduction

The Upper Silesian Coal Basin in southwestern Poland has been extensively mined since the beginning of the 20th century (Chałupnik et al. 2001). Almost 30 underground coal mines are currently operated which has led to the release of brines (Total Dissolved Solids ≈ 200 g/L) in surface waters, naturally enriched with radium (up to a few Bq/L), barium (up to several g/L) and metals (Zn, Sr, Pb, Cu, Ni, Co). Since the beginning of the 1990s, a wide range of counter-measures were taken in order to decrease the impact of mining activities on surface water quality (Leopold et al. 2007; Chałupnik & Wysocka 2008a&b). These basically consisted in reducing infiltration of meteoric waters into the underground galleries and enhancing co-precipitation of Ra into radio-barite ((Ba,Ra)SO₄). Although these actions led to the reduction of Ra releases to surface waters by 60% (Chałupnik & Wysocka 2008a&b), sediments in rivers and lakes surrounding mining sites still show relevant activities of both ²²⁶Ra (1600 y half-life) and ²²⁸Ra (5.7 y half-life) isotopes (Leopold et al. 2007).

Over many mining sites, radionuclides and heavy metals usually migrate through several water pathways as dissolved phases, colloids and suspended particles. Before these contaminants reach fast-flowing water systems, bottom sediments in streams and lakes can act as geochemical barriers and long-term sinks of radionuclides (Winde & van der Walt 2004) and heavy metals (Fuller & Harvey

2000). On the one hand in ponds and lakes, this natural attenuation results from scavenging by sedimentation and early diagenesis. On the other hand in watercourses, this attenuation is driven by dilution in fast-flowing waters and geochemical processes that occur in the hyporheic zone defined as the redox transition interface where groundwater tends to mix with surface waters (usually more oxygenated than groundwater; Gandy *et al.* 2006). Because of this attenuation, diffuse releases via groundwater from point or diffuse sources (tailings disposals, settling ponds, etc.) to adjacent water courses are difficult to monitor and quantify while it can lead to a substantial contamination of sediments by radionuclides and co-contaminants (Winde & van der Walt 2004). Understanding the way in which aquatic interfaces (like water/sediment interface in lakes or aquifer/river interface in streams) interfere on radionuclide transport through the aqueous pathway is thus of importance for assessing the impacts of radioactive substances on aquatic ecosystems and consequently human populations.

In order to contribute to the characterization effort of Polish mining sites for future radio-ecotoxicological researches, this study focuses on assessing the long-term impact of Ra which has been trapped into river and pond sediments in the vicinity of coal mining sites in Poland. Two geochemical interfaces have been surveyed by sampling sediment, surface and pore waters in the vicinity of an operating coal mining site: (1) the hyporheic zone of a river, where groundwater tends to mix with surface waters within the riverbed; and (2) the water-sediment interface in a lake which was formerly used as a settling pond. Whereas the hyporheic zone is advection-dominated, the water-sediment interface in lakes is usually diffusion-dominated. However, both represent redox interfaces where radium-bearing solid phases (barite, metal oxyhydroxides) undergo various geochemical processes which have not been quantified yet.

Methods

The vicinity of an operating underground coal mine was selected for sampling (1) the hyporheic zone of a river adjacent to a settling pond (where mine wastewaters are temporary stored before being discharged into the river), (2) the water-sediment interface in a lake which was formerly used as a settling pond by the same mine operator (from 1977 to 2002). Two field campaigns were performed: a first one in Nov. 2014 for selecting the site and undertaking preliminary water and sediment characterizations; a second one in May 2015 for further investigating the hyporheic zone and the former settling pond.

Surface water sampling was performed in both the current and former settling ponds of this site as well as into the river adjacent to the current settling pond (both upstream and downstream from the direct discharge). The hyporheic pore water was sampled into small piezometers disposed into the riverbed (2-cm wide pipes slotted over 5 cm at their bottom and installed at 0.5 meter below the water/sediment interface into the riverbed). In order to ensure that pore water samples were representative of a mixing zone between groundwater and surface waters, the pipes were installed into coarse riverbed sediments composed of sand and pebbles and were subjected to initial pumping tests in order to monitor how quickly the water level returns to the pre-pumped level. Sampling was performed when the water level into the small piezometers was higher than the river level (*i.e.* when groundwater is drained by the river). In order to check that no mixing with surface waters occurred during pore water sampling into the hyporheic zone, the small piezometers were sampled at very small rates (< 50 mL/min), more than 24 hours after their installation and initial testing, while the electrical specific conductivity of pore water was measured in line for ensuring that it was held constant. Groundwater representative of the main shallow water table connected to the river was also sampled into a piezometer located at 10 meters from the studied river, on the other river bank which is supposed to be not influenced by mining activities.

At each measurement location, pH, Eh, electrical conductivity and dissolved O₂ content were measured *in situ* with calibrated field probes. Water samples were filtrated at 0.45 µm. Laboratory characterization of filtrated surface water samples includes ICP-OES and ionic chromatography for major ion determination, ICP-MS for trace elements, liquid scintillation counting (according to Schonhofer *et al.* 2009 method) for dissolved ²²⁶Ra, ²²⁸Ra and ²¹⁰Po (daughter product of ²²⁶Ra decay) activity measurements, and acid titration for alkalinity measurement. ²²⁶Ra and ²²⁸Ra activities associated with suspended particles larger than 0.45 µm were measured onto filters by gamma

spectrometry using well-type detector. As the amount of sampled water into the hyporheic zone was too low (< 500 mL), pore water characterization did not include dissolved Ra determination and suspended matter analyses.

Sediment sampling was performed with a 3-cm wide hand corer into the former settling pond below 2 meters of surface water while it was performed with a shovel into the current settling pond and the river (at the same locations as the small piezometers). Sediment characterization includes sieve analysis, XRD for identifying the major mineralogical content, gamma spectrometry for quantifying ²²⁶Ra and ²²⁸Ra activities, X-Ray fluorescence spectroscopy with wavelength dispersive system for measuring the major oxide content, ICP-MS for trace elements, Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) and total sulfur content measurements by IR spectrometry after combustion, and moisture content measurement by gravimetric method.

Results and discussion

According to the concentrations of dissolved conservative elements measured in water samples (*i.e.* Br and Cl contents reported in fig. 1), two main end-members can be distinguished: (1) the geochemical background of non-impacted sub-surface waters on the one hand; and (2) the currently operated settling pond water to the other hand. Waters from the former settling pond and the shallow water table tend to pool with the background signature (*i.e.* subsurface waters upstream from the studied site). This observation confirms that the piezometer selected for characterizing the water table geochemistry is not impacted by mining activities. This also shows that the water of the former settling pond has been renewed since its closure in 2002 and does not correspond anymore to mine wastewater.

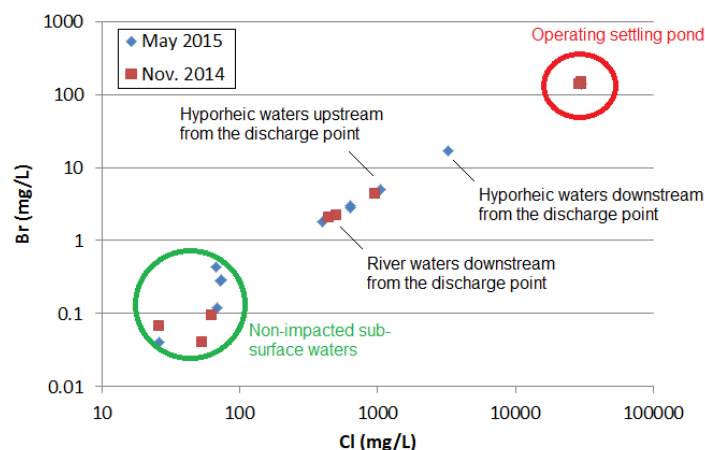


Figure 1 Dissolved Br and Cl content measured in water samples in Nov. 2014 and May 2015

All the other water samples appear to be a mix between these two end-members, especially the river waters downstream from the studied mining site and the hyporheic zone waters (both upstream and downstream from the direct discharge of the currently operated settling pond into the river). A significant redox contrast was found in May 2015 between the hyporheic zone (Eh~110 mV; O₂<2 mg/L) and the river (Eh~320 mV; O₂~9 mg/L). Additionally, the electrical specific conductivity was much higher into the hyporheic zone (up to 4400 μS/cm) than into the river water (550 μS/cm) upstream from the wastewater discharge. These observations together with the signature given by Br and Cl ratios show that groundwater within the hyporheic zone of the studied river is impacted by diffuse and direct wastewater releases from the operating settling pond. Dissolved barium was also detected into pore waters of the hyporheic zone both upstream and downstream from the wastewater discharge of the closest studied mine.

A preliminary reactive geochemical model built with JCHESS® (van der Lee 1998) tends to suggest that mixing of surface waters with wastewaters according to the mixing ratios given by these end-members tend to favor witherite (BaCO₃) precipitation (fig. 2) within the riverbed. Additional investigations are planned to demonstrate the occurrence of this process into riverbed sediments and to identify its consequences on Ra behavior through the hyporheic zone by analyzing Ra in pore waters.

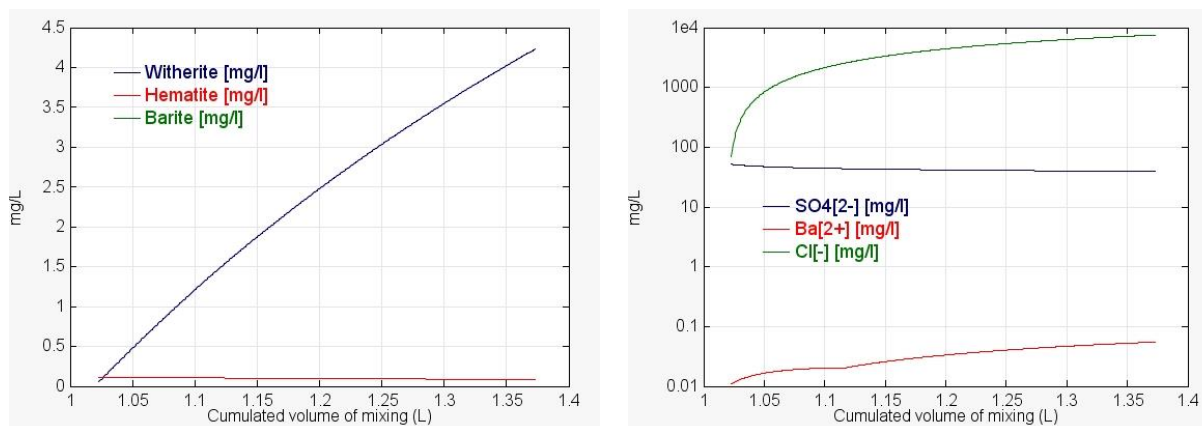


Figure 2 Simulated precipitation/dissolution of minerals (left part) and dissolved concentrations (right part) that could occur into the hyporheic zone of the studied site due to water mixing (1L of surface water with 0.4 L of settling pond water)

Regarding the former settling pond, its bottom sediments were found to be composed of mineral phases similar to that of the operating pond (barite, chlorite, illite, amorphous phases, feldspars and quartz). However a higher organic matter content was detected into the former settling pond sediments (14% of TOC). Ongoing investigations are performed to understand radium activity profiles detected into several sediment cores from this former pond. The objective of these additional works is to check the sustainable trapping of Ra into BaSO_4 in case of lake sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation. In May 2015, low dissolved ^{226}Ra (~ 0.03 Bq/L) and ^{228}Ra (< 0.01 Bq/L) activities were detected into the surface waters of this pond while high activities were measured into bottom sediments (up to 9000 Bq/kg of ^{226}Ra and 300 Bq/kg of ^{228}Ra). This observation tends to show that since the renewal of the water column into this pond (closed in 2002) natural attenuation has been favorable to the disposal of contaminated bottom sediments by limiting significantly the impact of Ra on surface water quality. However, we found a relevant total ^{210}Po activity into these surface waters (0.50 ± 0.05 Bq/L in May 2015). ^{210}Po is a short-lived (138.4 d half-life) decay product of ^{226}Ra that usually displays a complex biochemical cycling in subsurface environments due to its preferential removal by biota and rapid regeneration because of remineralization from sinking biogenic debris (Kim *et al.* 2011). Additional works are thus needed for confirming first that natural attenuation processes governing the fate of ^{210}Po grandparent (i.e. ^{226}Ra) will be sustainable in the long run (i.e. over several half-lives of ^{226}Ra) and second, quantifying the processes involved in the release of its progeny ^{210}Po toward surface waters.

Conclusion

This study reports preliminary results of water and sediment characterization aiming at understanding the fate of Ra through aqueous interfaces usually encountered in the vicinity of mining sites. In the hyporheic zone of a river, where groundwater tends to mix with surface waters, geochemistry of pore waters shows that diffuse and direct wastewater releases from an operating settling pond impacts water quality within the riverbed. A geochemical model built with JCHESS® suggests that mixing of surface waters with wastewaters favors witherite (BaCO_3) precipitation within the riverbed. Additional investigations are planned to assess the consequences of this suspected attenuation process on Ra behavior through the hyporheic zone. Moreover further investigations are performed for studying the fate of Ra trapped into BaSO_4 within lake sediments where sulfate-reducing conditions could occur with depth due to organic matter degradation and where ^{210}Po (^{226}Ra decay product) is detected into surface waters.

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References

- Chałupnik S, Michalik B, Wysocka M, Skubacz K, Mielnikow A (2001) Contamination of settling ponds and rivers as a result of discharge of radium-bearing waters from Polish coal mines, *Journ Environ Radioactivity* 54:85—98
- Chałupnik S, Wysocka M (2008a) Changes of radium concentration in discharge waters from coal mines in Poland as a result of mitigation. In: Merkel BJ, Hasche-Berger A (Eds), *Uranium, Mining and Hydrogeology*, Springer, pp. 839–850
- Chałupnik S, Wysocka M (2008b) Radium removal from mine waters in underground treatment installation. *J Environ Radioactivity* 99:1548—1552
- Fuller C, Harvey JW (2000) Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona. *Environ Sci Technol* 34:1150—1155
- Gandy CJ, Smith JWN, Jarvis AP (2006) Attenuation of mining-derived pollutants in the hyporheic zone: A review. *Sci Tot Environ* 373:435—446
- Kim G, Kim T-H, Church TM (2011) Po-210 in the Environment: Biochemical Cycling and Bioavailability. In: Baskaran M (Ed), 2011 *Handbook of Environmental Isotope Geochemistry, Advances in Isotope Geochemistry*, Springer-Verlag Berlin Heidelberg, pp. 271–284
- Leopold K, Michalik B, Wiegand J (2007) Availability of radium isotopes and heavy metals from scales and tailings of Polish hard coal mining. *J Environ Radioactivity* 94:137—150
- Schonhofer F, Chałupnik S, Wallner G, Chmielewska I (2009) Natural radionuclides in mineral water sold in Upper Silesia, Poland: Their measurement by Liquid Scintillation Spectrometry. Doses and Compliance with Regulations, *Conf on Advances in LSC, Radiocarbon 2009*, Tuscon, Arizona, USA, p 125—131
- van der Lee J (1998) Thermodynamic and mathematical concepts of CHESS. Technical Report LHM/RD/98/39, CIG Paris School of Mines, Fontainebleau, France
- Winde F, van der Walt IJ (2000) The significance of groundwater–stream interactions and fluctuating stream chemistry on waterborne uranium contamination of streams—a case study from a gold mining site in South Africa. *J Hydrology* 287(1):178—196