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Importance of redox interface regarding the fate and behaviour of radium in surface water impacted by NORM

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Abstract. Usual approach to remove radium from industrial wastewater consists in the co-precipitation of radium with barium. Although barite is being known as a highly insoluble phase, it is also suspected to be dissolved under sulphate-reducing conditions. Our study focused on the interactions occurring at the water-sediment interface of a former settling pond operated by the coal mining industry of the Upper Silesia Coal Basin (USCB), Silesia, Poland. Based on sediment composition and pore water analysis our results provided new insight for studying the fate and behaviour of radium in a NORM storage reservoir evolving towards a natural ecosystem.

Introduction

Extraction operations are known to increase the transfer of pollutants to the surrounding environment and the present challenge is to develop green mining strategies. It concerns not only the production stage but also the remediation operations and the associated waste management. Many questions arise from past activities, especially regarding the effectiveness and the long-term sustainability of the remediation works. Among these questions is the fate of diffusive and advective transport of pollutants at redox interfaces¹.

Radium is one of the specific contaminant of NORM industries, including uranium mining, coal activity, oil and gas production. Co-precipitation of radium (Ra) with barium (Ba) into radio-barite is usual approach to remove Ra from industrial wastewater. Barite is considered as one of the main Ra-bearing phases in natural and anthropogenic systems. Although barite is frequently cited as a highly insoluble phase under oxidizing conditions, it is also suspected to be dissolved under sulphate-reducing conditions²⁻⁵. This process questioned the long-term sustainability of Ra-waste storage in barite.

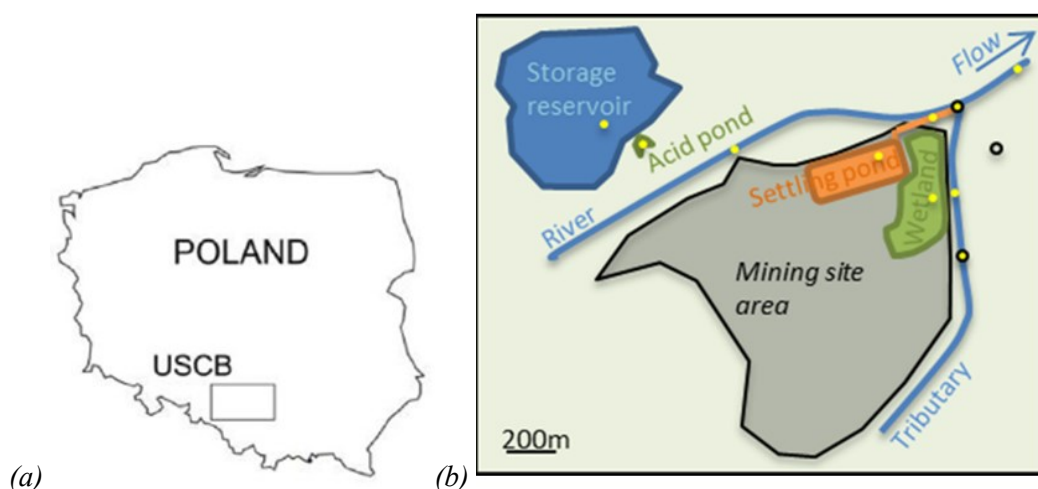


FIG. 1: Localization of the Upper Silesian Coal Basin (USCB) in Poland (a) and scheme of the coal mining area including the pond identified as "storage reservoir" (b); sampling points were illustrated by yellow dots.

The Upper Silesian Coal Basin (USCB) is situated in the southern part of Poland and it represents one of the sites of interest for the European network in radioecology (<https://radioecology-exchange.org/content/upper-silesian-coal-basin>). Deriving from underground coal mining activities, brines containing high concentrations of Ra (up to 300 Bq L⁻¹) and Ba are mixed with underground waters containing sulphate ions SO₄²⁻ allowing the removal of Ra and Ba from waters by co-precipitation in settling ponds⁶. As a result, much of the Ra isotopes are trapped into radio-barite, *i.e.*, (Ba,Ra)SO₄, in the bottom deposits of the settling ponds⁶. When the mine wastewater stop being discharged, the settling ponds are used as storage reservoirs for NORM wastes; the present study focused on one of them.

Since 2013 several sampling campaigns were performed by IRSN and GIG to study Ra behaviour in the vicinity of former and ongoing coal mines⁷. The previous results evidenced the occurrence of mixing processes between two source terms represented by the composition of the mine wastewater and the hydro-chemical background⁷.

The present study focused on a former settling pond, especially on the water-sediment interface as it constitutes an active boundary of redox modification. The settling pond was used by the local coal mining operator from 1977 to 2002. Since the settling pond is unused, it serves as a storage reservoir (*FIG. 1*). The renewal of surface waters allowed its return into a natural ecosystem. This shallow water reservoir is situated in the floodplain of the Upper Vistula River; its surface area is about 0.36 km² and the water depth is ~ 2 m. The pond and its surrounding environment are presently characterized by abundant aquatic and terrestrial fauna and flora. As such, the pond provides an analogue of long-term situation of Ra-rich waste storage.

1. Material and methods

2.1 Samplings

Two sampling campaigns were performed in May 2016 and 2018, allowing the collection of water and sediment from the storage reservoir (*FIG. 1*). Several methods were deployed on site and numerous analyses were dispatched between the laboratory units of GIG (Katowice, Poland) and IRSN (Fontenay-aux-Roses, France). The methods used for sample collection and analysis were briefly described below.

At the sampling point (*FIG. 1*), several liters of surface water were collected in 5 L PET bottles using a peristaltic pump at three different depths, *i.e.*, at 1.6, 0.8 and 0.2 m of a total water depth of 1.8 m. Water was then filtered through cellulose acetate membrane of 0.45 µm porosity (Sartorius).

In addition, sediment coring was performed at the sampling point using a sediment sampler (Uwitec hammer type). The sediment was retrieved by extrusion from the PVC tube crystal of 8.6 cm inner diameter. The core length was 32 cm and the sediment was subsampled every 2 cm in depth, leading to the collection of 16 solid samples.

2.2 Sediment analysis

Sediment samples were oven dried at 55°C then crushed and milled to granulation < 1 mm and homogenized.

The activity concentration of Ra-226 was determined by gamma-spectrometry, using Canberra high-purity germanium detector of 50% relative efficiency at GIG laboratory, and following the recommendations described elsewhere⁸. Flat cylindrical containers made of

polypropylene (10 mm of height, 35 mm of diameter) were filled with samples and tightly sealed. Two weeks waiting period was applied in order to reach secular equilibrium between Ra-226 and its progenies. The spectrometric system was calibrated by use of certified reference material corresponding to the tested sample matrix. The activity concentration of Ra-226 was determined directly using 186.2 keV line with correction to uranium interference (U-235 at 185.7 keV), and through its daughters (Bi-214 at 609.3 keV, Pb-214 at 295.2 and 351.9 keV). Activity expressed in Bq kg⁻¹ of dry matter and uncertainty was calculated at $\pm 2 \sigma$.

The total organic carbon content (TOC) was calculated by subtracting total inorganic content (TIC) from total carbon content (TC); TIC and TOC were determined by IR spectrometric method coupled to high temperature combustion method at GIG laboratory.

The determination of barium oxide (BaO) content was performed by X-ray fluorescence method with wavelength dispersion WD-XRF at GIG laboratory; the analysis was carried out in ash samples which were obtained after combustion in a furnace at 815 °C.

Additionally mineral composition of sediment was analyzed by XRD method at GIG laboratory; mineral composition of the sediment was tested by the powder X-ray diffraction (XRD) method and D8 Discover Bruker diffractometer was used.

The content of TOC and BaO, and the mineral composition expressed in % of total dry sample sediment and the associated analytical uncertainty didn't exceed 10 %.

2.3 Liquid analysis

At GIG laboratory the filtered surface water was analyzed for Ra-226 activity concentration laboratory following the liquid scintillation procedure⁹, and the Br and Cl anions were determined by ion chromatography according to the procedure PN-EN ISO 10304-1:2009.

The vertical profiles of iron (Fe), manganese (Mn) and barium (Ba) were determined in the sediment pore water at mm-resolution using the technique of diffusive equilibration in thin-films¹⁰, *i.e.*, DET (DGT Research Ltd). The constrained DET probe containing 75 small wells (1x1x18 mm) was filled with gel made of 98.5 % agarose. The probe was oxygen-degassed prior to the deployment by vigorous nitrogen-bubbling.

After 20 h of deployment within the sediment, the DET probe was retrieved and composite samples were prepared by gathering 3 pieces of gel before being eluted in 6 mL of HNO₃ 1 M (Suprapur, Merck). Analysis was performed using ICP-OES at IRSN (ICAP 7600 DUO Thermo-Fisher).

Microelectrodes were used to determine the vertical profiles of O₂ and H₂S concentrations in the sediment pore water at mm-resolution¹¹ (microsensors 100 μm-diameter; Unisense, Denmark). Microsensors were vertically inserted in the sediment core at 20–500 μm step using a motor-controlled micromanipulator coupled to a pico-ammeter.

2. Results and discussion

3.1 Ra and Ba-enrichment

In the coal mining area including the studied pond, early results evidenced the occurrence of mixing processes between two source terms represented by the composition of mine wastewater and the hydro-chemical background⁷, including both surface (river, tributary) and sub-surface water (sub-surface land). Although being not discussed before⁷, the characteristics of the ancient settling pond were shown to be included in the natural pool due to the continuous renewal of surface water through the present study (*FIG. 2a*). In the plots of Ba vs. Cl and Ra vs. Cl concentrations (*FIG. 2bc*), the deviation in Ba/Ra concentration from the

theoretical mixing curve highlighted a Ba/Ra-enrichment in the pond. This Ba/Ra-enrichment of the surface water was attributed to the sediment contribution by diffusion processes.

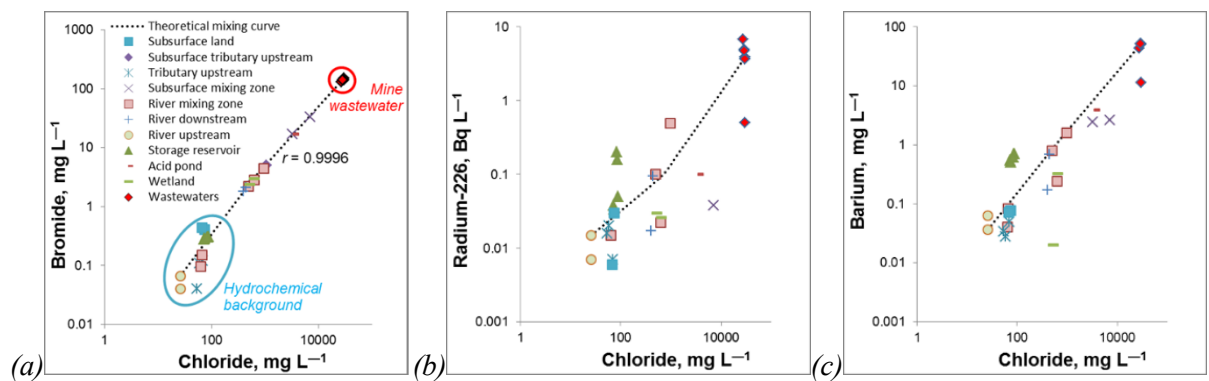


FIG. 2: Plots of Br vs. Cl (a), Ra vs. Cl (b) and Ba vs. Cl (c), which were modified from [10]; data for the studied pond were added and were illustrated by green triangles (“storage reservoir”).

3.2 Sediment composition

Coupling the visual aspect of the sediment core to the geochemical characteristics (TAB. 1), three distinct sediment units were distinguished:

- (1) The top unit (0–4 cm) was olive-green coloured, it displayed relatively high content in TOC (8.4–8.5 %), BaO (2.1–2.2 %) and Ra (4.4–4.5 kBq kg⁻¹): it was considered being representative of the recent inputs from terrigenous origin occurring after 2002 ;
- (2) The middle unit (6–10 cm) displayed intense black colour, it was characterized by the highest content of TOC (17.6–17.9 %), Ba (4.6–5.0 %) and Ra (10.9–11.6 kBq kg⁻¹): it was attributed to the Ra-rich waste deposited during the 1977–2002 period corresponding to the mine wastewater discharges ;
- (3) The bottom unit (below 16 cm) was characterized by grey-limy material, displaying the lowest content of TOC (2.4–3.9 %), Ba (0.05–0.14 %) and Ra (0.11–0.38 kBq kg⁻¹), and being attributed to the local geochemical background representative of sediment deposited before mining operation, *i.e.*, before 1977.

Table I: Sediment characteristics.

Depth cm	Ra-226 \pm Bq/kg		BaO	TOC	Quartz	Amorphous substance	Feldspars	Illite muscovite Content in %	Kaolinite	Chlorite	Total sulphur	Barite
0–2	4360	130	2.12	8.5	48	30	9	6	4	2	0.72	2
2–4	4510	150	2.24	8.4	46	31	10	6	3	3	0.76	2
4–6	6430	180	2.95	10.7	50	32	5	5	3	3	1.14	3
6–8	11650	350	4.6	17.9	48	31	8	4	3	2	1.86	5
8–10	10890	350	5.01	17.6	43	33	9	5	4	2	1.92	6
10–12	4520	250	2.56	10.1	41	40	7	5	3	1	1.67	3
12–14	660	30	0.25	14.4	19	41	4	6	11	3	1.70	0.25
14–16	395	18	0.16	5.7	25	30	6	6	21	4	0.36	0.25
16–18	381	16	0.14	3.9	26	28	7	6	21	5	0.20	0.25
18–20	250	15	0.11	3.4	41	30	11	5	6	2	0.12	<0.25
20–22	158	5	0.07	3.2	49	31	8	5	3	1	0.11	<0.25
22–24	143	8	0.06	3.1	48	30	10	4	3	1	0.08	<0.25
24–26	145	9	0.06	2.9	49	30	8	6	3	3	0.06	<0.25
26–28	118	7	0.06	2.8	47	31	8	7	3	3	0.06	<0.25
28–30	133	6	0.06	2.9	57	29	5	5	3	1	0.06	<0.25
30–32	119	10	0.05	2.4	58	28	5	5	3	1	0.04	<0.25

The remaining layers of sediment, *i.e.*, 4–6 and 10–16 cm (*TAB. 1*), didn't clearly exhibit characteristics suitable to the present classification. The lack of classification was identified as being a consequence of the 2-cm vertical resolution during the core subsampling step (sediment layers 4–6 cm and 10–12 cm) and the absence of available description of the study site before its use as a settling pond (sediment layers 12–14 cm and 14–16 cm).

Based on the mineralogical composition (*TAB. 1*), the maximum of barite content (5–6 %) coincided with the highest Ra activity concentration in sediment (6–10 cm), that was coherent with the Ra removal process from surface water. It was noticed that both amorphous substances (28–41 %) and quartz (19–58 %) represented the main sediment phases within the whole sediment. The sediment composition was roughly in accordance with the characteristics of the USCB geological context¹² as it is dominated by sandstones, conglomerates, limestones, dolomites and sands.

3.3 Pore water chemistry

The vertical resolution profiles of dissolved O₂ and H₂S displayed a pronounced evolution along the sediment depth, highlighting the physicochemical changes within the sediment pore water (*FIG. 4ab*). The oxygen consumption was total below the first mm of the water-sediment interface, indicating a rapid and intensive bacterial respiration¹³. The increasing H₂S concentration below 7 cm depth was representative of an upward flux of sulphide related to sulphate reduction and followed by sulphide re-oxidation¹⁴.

The vertical profiles of Fe, Mn and Ba displayed a top-bottom gradient of concentration, highlighting an upward diffusive flux across the water-sediment interface (*FIG. 5*). However the release of these elements into the overlying water was limited by scavenging mechanisms in the interfacial anoxic/oxic boundary between water and sediment (*FIG. 4a*).

In the sediment pore water the remobilization of Fe, Mn and Ba was attributed to the occurrence of early diagenetic processes¹³. The Fe/Mn distributions were similar (*FIG. 5ab*), the peaks observed at 5 cm depth were attributed to the reductive dissolution of Fe/Mn oxy-hydroxides.

The coincidence of Ba release with the increase of Fe/Mn concentrations suggested that Ba distribution was controlled by the reductive dissolution of Fe/Mn oxy-hydroxides. The

pronounced Ba peak at 3 cm of depth was attributed to a transient diagenetic signal where the reduction of Ba oxides proceeded faster than its diffusion¹⁴.

The absence of a clear Ba release in the sulphate reduction zone below 6 cm (FIG. 4b, 5c) suggested that the Ba distribution within the sediment pore water was not controlled by an eventual dissolution of pure (or impure) barite phase^{4,5,14}.

Below 7 cm the decrease of Fe/Mn coincided with the production zone of sulphide (FIG. 4b), suggesting the re-precipitation of Fe/Mn into sulphide minerals (*i.e.*, pyrite) or other crystalline and amorphous phases (*i.e.*, mackinawite).

Comparing to Fe/Mn distribution, Ba downward diffusion was not followed by re-precipitation process since the high Ba ion radius probably prevented it from mineral-sulphide incorporation¹⁴.

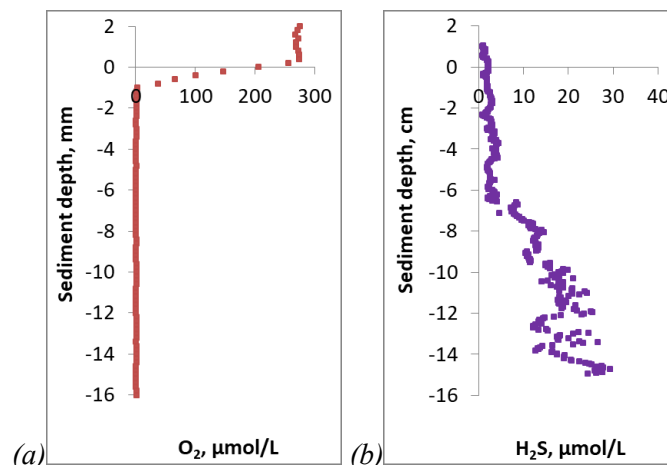


FIG. 4: Vertical profiles of dissolved (a) O_2 and (b) H_2S concentrations in the sediment pore water (the depth of sediment was expressed in mm and cm).

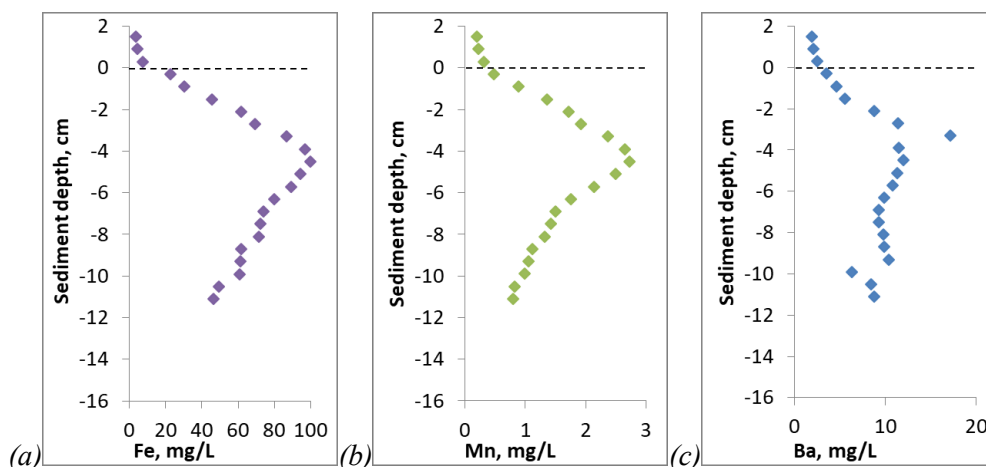


FIG. 5: Vertical profiles of (a) Fe, (b) Mn and (c) Ba concentrations in the sediment pore water (the water-sediment interface was represented by a dashed line at depth 0).

Conclusion

The study of the water composition in the former settling pond revealed an enrichment in Ba and Ra which was attributed to solute discharge by diffusion from the sediment. The vertical profile of Ba which is an analogue of Ra clearly displayed an upward diffusive flux across the water-sediment interface. The return of the settling pond into a natural ecosystem was accompanied by the establishment of early diagenetic sequence, due to the renewal of the

surface water. In future, flux and geochemical calculations should help to better constrain the mobility and behaviour of radium within the sediment.

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