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Technical Article

Radionuclide Contamination of Surface Waters, Sediments, and Soil Caused by Coal Mining Activities in the Ruhr District (Germany)

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Abstract. The discharge of highly mineralised mine waters with enhanced ^{226}Ra and ^{228}Ra activity concentrations has affected creeks, rivers, sediments, soils, and plants along the Lippe River and its tributaries. ^{226}Ra activity concentrations were elevated in all water samples receiving mine water, with activity concentrations gradually decreasing with increased distance from the colliery due to dilution and chemical precipitation of radium with barium. Increased concentrations of radium and radium decay products were also measured in sediments and flood-affected soils. The sediments show an enrichment of ^{226}Ra up to a factor of 750, while the contaminated soils "only" reach a factor of 10. In aquatic plants, a 4-fold increase in ^{226}Ra activity concentrations was measured downstream of the discharge points. The contamination of the river banks and adjacent floodplain with radium is responsible for enhanced gamma dose rates, which, along with the incorporation of soil by playing children, provide potential radiation exposure to the public.

Key words: Coal mining; Lippe River; radium; Ruhr District; sediments; soils, sequential extraction; surface waters

Introduction

One of the biggest problems of underground coal mining is highly mineralised mine water, which frequently contains enhanced activity concentrations of two radium isotopes: ^{226}Ra and ^{228}Ra. The increased concentrations of radium are caused by displacement of Ra from adsorptive sites in the aquifer by other ions, and can occur even if the radium concentrations in the aquifer strata are moderate (Wiegand and Feige 2002). This process is enhanced in high ionic strength mine waters. Wiegand (in press) calculated that, under normal sandstone aquifer conditions (30 Bq/kg ^{226}Ra in the rock), a ^{226}Ra mobilisation rate of only 3% is sufficient to produce a relatively high ^{226}Ra concentration of 10 Bq/L in the ground water.

This paper summarizes a PhD thesis (Schmid 2001), focusing on the ^{226}Ra aspects. The thesis was a regional investigation of radionuclide release of hard and brown coal mining activities in the Ruhr District and in the Cologne basin (Feige and Wiegand 1999). Other recent studies showing the radionuclide distribution in the environment due to mining activities include Schneider et al. (2001) and Vrecek and Benedik (2002). The investigations of Chalupnik et al. (2001), conducted in the Upper Silesia coal basin (Poland), are especially comparable to this study. In both the Ruhr District and Upper Silesia coal basin, coal measures of the same stratigraphical record are mined, and the chemical compositions of the mine waters are very similar. In addition, Pluta and Trembaczowski (2001) observed remobilisation of radium from pond sediments in Upper Silesia by reductive processes. Paridaens and Vanmarcke (2001) investigated a small creek in Belgium, along with its sediments and river bank soils, which were all contaminated by radium due to phosphate ore processing. Clulow et al. (1998) conducted a thorough study of ^{226}Ra contamination of Elliot Lake in Ontario (Canada), where uranium mining and milling operations have contaminated surface waters and sediments. The authors of that study also investigated radium transfer into fish.

About 40 millions m³ of mine water are pumped from underground mines in the Ruhr district in the state of North Rhine Westphalia, Germany, and about 5% of this is highly mineralised (Wedewardt 1995). The water is discharged to several creeks that flow into small rivers like the Lippe, Emscher, and Fossa Eugeniana. Along the Lippe River and its tributaries, two collieries, the Auguste Victoria and the Bergwerk Lippe, discharge their effluent water. Water, sediment, river bank soil, and flora were sampled along the lower course of the Lippe and its tributary, Sickingmühlenbach Creek (Figure 1), and analysed for radium and radium decay products. Sampling points LW1 and LW2 are not contaminated by mine water, being upstream of where the Auguste Victoria colliery discharges into Sickingmühlenbach Creek, and were used to establish background levels. LW3 is located in the creek shortly before it reaches the Lippe. LW4 and all other sampling sites are downstream of this confluence. The Bergwerk Lippe colliery has non-point discharges at two additional points between LW6 and LW8.

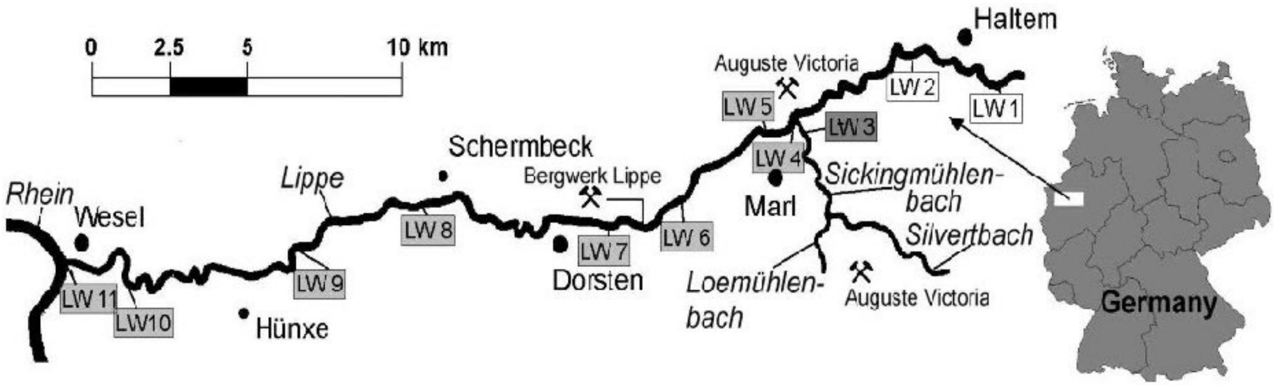

Figure 1. The locations of surface water sampling sites along the Lippe River; white boxed sample numbers: uncontaminated, light grey: contaminated, dark grey: strongly contaminated

Methods

Monthly, from May 1998 to June 1999, 124 water samples were collected from Sickingmühlenbach Creek and the Lippe River. At LW3, a 24 hr measurement was done; each hour, a sample was taken. All water samples were analysed on-site for pH, Eh, electrical conductivity (EC), and temperature. The samples were membrane filtered (0.45 µm) and HNO_3 was added. They were analysed using a radon emanation technique for ^{226}Ra, ICP-OES for Na, K, Mg, Ca, Sr, Ba, Mn, Fe, S, and ion-selective potentiometry for Cl (Kellner et al. 1998; Nölte 2002; Schmid 2001). This study focuses on the analytical results for ^{226}Ra, Ba, Sr, Na, Cl and EC.

Within the investigation area, 27 sediment and 18 soil samples were taken from a depth of up to 5 cm. Sediment samples were taken from the boat and from the riverside using a bottom-grab. This study shows only the results of investigations at the Lippe River and Sickingmühlenbach Creek with 22 sediment and 6 soil samples. Oven-dried (105°C) samples were used to determine the particle size distribution and to separate the <2 mm fraction, which was analysed using gamma-ray spectroscopy (N-type Ge-Detector) and x-ray diffraction (XRF) (X-LAB 2000, Spectro), (Gilmore and Hemingway 1995; Heckel et al. 1991; Schmid 2001; Van Grieken et al. 2003). Na, K, Mg, Ca, Ba, Al, Si, P, Fe, Mn, Ti, As, Cd, Cr, Cs, Cu, Ni, Pb, Sn, Sr, Te, Th, U, V, Zn and Zr were analysed using XRF; the Ba and Sr concentrations are reported here. Similarly, using gamma-ray spectrometry, ^{7}Be, ^{40}K, ^{60}Co, ^{137}Cs, ^{208}Tl, ^{210}Pb, ^{212}Pb, ^{214}Pb, ^{212}Bi, ^{214}Bi, ^{226}Ra, ^{228}Ac, ^{228}Th, ^{230}Th, ^{234}Th, ^{234}Pa, ^{235}U, ^{241}Am were analysed but only the ^{226}Ra, ^{228}Ra and ^{210}Pb values are discussed in this study.

The ratio of ^{228}Ra and ^{226}Ra is an indicator of the age of the sediments (Zielinski et al. 2001). Assuming that the ^{228}Ra/ ^{226}Ra ratio of the mine water is stable, the age can be calculated using the different half-lives of the radionuclides. The initial activity concentration (r_0) is determined by fresh radiobaryte precipitates from the discharge point: ^{228}Ra = 15150 Bq/kg, ^{226}Ra = 32480 Bq/kg. The age was calculated by:

$$\text{age} = \frac{\ln\left(\dfrac{a_0\,{}^{228}\text{Ra}}{a_1\,{}^{228}\text{Ra}}\right)}{\lambda\,{}^{228}\text{Ra}}\text{ , where}$$

$$a_{0(228)} = r_0 * a_{1(226)}\text{ , } r_0 = \frac{a_0^1({}^{228}\text{Ra})}{a_0^1({}^{226}\text{Ra})}\text{ and}$$

a_0^1 = the initial activity concentration of the water

$r_0 = {}^{228}\text{Ra}/{}^{226}\text{Ra}$ ratio of initial activity concentrations of the source

a_0 = initial activity concentration of the sample

a_1 = actual measured activity concentration

λ = decay constant

A 6-step sequential extraction was applied to selected samples to determine the kind of chemical bonding (Table 1) (Zeien and Brümmer 1989; Zeien 1995).

The gamma dose rate was determined at 120 sites along both waterways using a handheld gamma-ray scintillometer. In addition, 25 plants (*Myriophyllum ssp. heterophyllum*) were collected (without roots) by boat and from the riverside. The plant samples were washed ultrasonically and oven-dried (105°C), then hackled and analysed using gamma-ray spectrometry (Schmid 2001).

A limit of quantitation (LOQ), defined as three times the limit of detection (LOD), was used as an indication of significance, but concentrations and activity concentrations that are below LOQ but higher than LOD are nevertheless included in this paper.

Radionuclide Distribution in Surface Waters

In this paper, all activity concentrations represent the arithmetic mean for the investigation period (n=14). The ^{226}Ra activity concentrations of both background

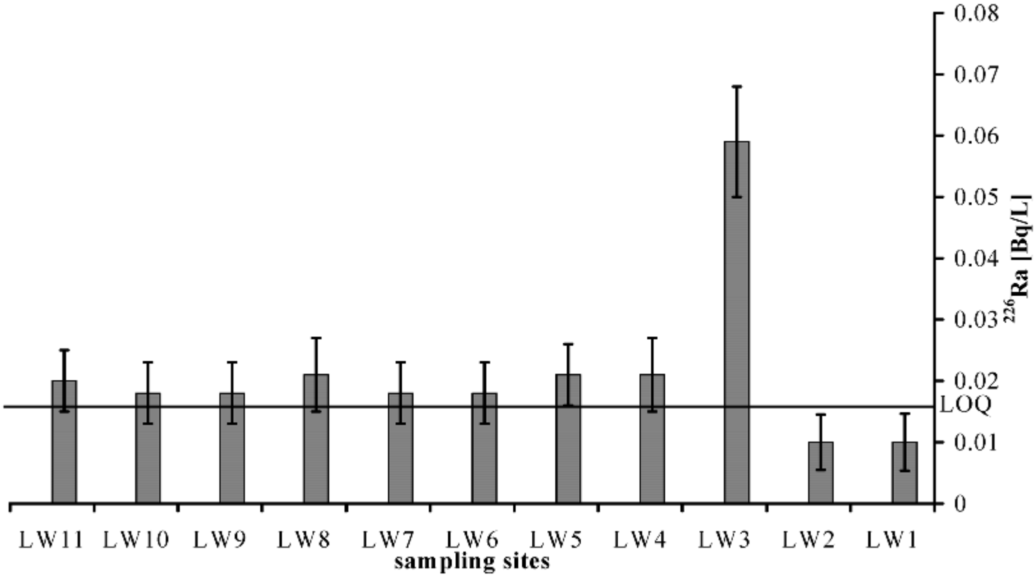

Figure 2. Mean ^{226}Ra activity concentrations (n=14, with standard deviation) of the water samples along the Lippe River (limit of quantitation (LOQ) = 0.015 Bq/L).

Table 1. The steps of the sequential extraction used in this study (Zeien and Brümmer 1989; Zeien 1995)

Fraction	Solvent	Time	Remarks
Mobile	1 m NH_4NO_3	24 h	
Exchangeable	1 m NH_4Ac, pH 6	24 h	
Mn oxides	0.1 m NH_2OH-HCl, 1 m NH_4Ac, pH 6	50 min	
Organic	0.025 m NH_4EDTA, 1 m NH_4Ac, pH 4.6	100 min	
Amorphous Fe oxides	0.2 m NH_4Ox, pH 3.25	4 h	in the dark
Crystalline Fe oxides	0.1 m ascorbic acid 0.2 m NH_4Ox, pH 3.25	70 min	T = 96°C
Residual			

sites (LW1 and LW2) were below the (LOQ) of 0.01 Bq/L (Figure 2). Site LW3, located close to the mine water discharge point in Sickingmühlenbach Creek, had a high activity concentration with an average value of 0.059 Bq/L and a maximum of 0.163 Bq/L. Downstream of LW3, the mean activity concentrations were lower, but above the LOQ. The strong decrease of ^{226}Ra activity concentrations, from 0.06 Bq/L down to approximately 0.02 Bq/L, is due to dilution and the chemical precipitation of radium with barium, forming radiobaryte, which was proven by XRD (Wiegand in press). Along with the radium concentrations, the electrical conductivity and all analysed elements (Na, K, Mg, Ca, Sr, Ba, Mn, Fe, S, Cl) increase sharply at LW3, and then decrease downstream from there (Table 2).

In addition to this regional change in radium activity in the surface waters, the activity concentrations vary temporally as well (Figure 3). In part, this is due to different mining depths and the amount of accumulated mine water. But mainly, the collieries take advantage of low night rates for electrical power, resulting in more pumping and discharging of mine waters at night. There was no rainfall or other meteorological influence during sampling. This is important for the classification of the measured waters at LW3, where sampling was generally conducted during the day. A seasonal change (i.e. parallel to water table fluctuations) was not observed.

Radionuclide Distribution in Sediments

The location of the sediment samples is compiled in Figure 4. Samples LS1 to LS4 were collected upstream of where Sickingmühlenbach Creek meets the Lippe, and represent background conditions. Sites LS5 and LS6 were located at Sickingmühlenbach Creek near the discharge point. All of the other sites were from further downstream along the Lippe River before it meets the Rhein at Wesel. Between LS11 and LS12, the Bergwerk Lippe colliery discharges mine water into the Lippe River.

As shown in Table 3, the ^{226}Ra activity concentrations in non-contaminated sediments (LS1-4) vary between approximately 10 and 50 Bq/kg, similar to observations by Barth et al. (1998). Extremely high radium activity concentrations were measured in the Sickingmühlenbach Creek sediments (LS5 and LS6),

Table 2. Mean concentrations of Ba, Sr, Na, and Cl (n=14) and the electrical conductivity (EC) of water samples collected along the Lippe River. The sample marked in grey is from Sickingmühlenbach Creek.

Sampling point	EC [mS/cm]	Ba [mg/L]	Sr [mg/L]	Na [mgL]	Cl [g/L]
LW1	1.4	0.4	2.1	147	0.4
LW2	1.4	0.5	2.1	150	0.4
LW3	6.2	1.5	14.3	882	3.2
LW4	2.3	0.7	4.0	298	0.9
LW5	1.8	0.7	3.0	221	0.7
LW6	1.9	0.7	3.0	227	0.7
LW7	1.9	0.7	2.9	236	0.7
LW8	2.0	0.7	2.9	239	0.7
LW9	1.8	0.6	2.7	224	0.7
LW10	1.7	0.6	2.6	208	0.6
LW11	1.6	0.6	2.6	198	0.6

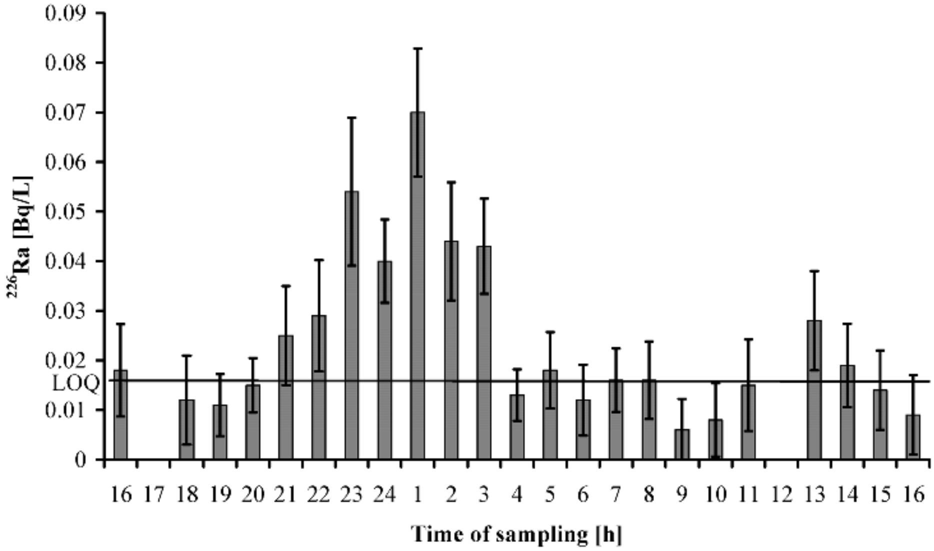

Figure 3. Short term measurements of ^{226}Ra activity concentrations (with 2σ-error) at sampling site LW3 on 22 and 23 September 1999 (limit of quantitation (LOQ) = 0.015 Bq/L)

up to 15,000 Bq/kg for ^{226}Ra and 6,480 Bq/kg for ^{228}Ra. At the confluence of the Sickingmühlenbach and the Lippe (LS7), the activity concentration of ^{226}Ra in the Lippe increased to 425 Bq/kg, 15 times the background values upstream. Similar levels were found in the vicinity of Polish coal mines (Chalupnik et al. 2001). The activity concentrations decreased downstream to site LS11, but then the influence of the Bergwerk Lippe colliery increased ^{226}Ra from 109 Bq/kg to 365 Bq/kg at LS12 (Table 3). The next strong increase in ^{226}Ra was observed at LS16, where the activity concentrations increased from 266 Bq/kg to 441 Bq/kg (Table 3). This was likely caused by seepage from the Bergwerk Lippe colliery as well. The two anomalies in the sediments at LS12 and LS16 can hardly be identified in the water samples (Figure 2, Table 2). The ^{226}Ra activity concentration is slightly increased in LW8 (Figure 2), corresponding approximately with LS18 (Figures 1, 4). The ^{226}Ra levels and EC in LW8 are enhanced (Table 2). Following the sediment contamination, the water samples at LW7 should show enhanced concentrations as well because this sampling point corresponds to LS13, where the sediments are clearly contaminated. But LW7 shows only a slight increase in Na, which suggests that the discharge of the Bergwerk Lippe colliery was higher and more important some years ago.

The activity concentration continues to decrease until it reaches background levels at LS22, where the significant drop is due to the influence of the Rhein River, which dilutes the contaminated water.

Differences in the ^{226}Ra / ^{228}Ra ratio are due to their different half-lives. Since ^{226}Ra has a half-life of 1600 years, contamination will persist for a long time. The half-life of ^{228}Ra is much shorter (5.7 years), and therefore contamination vanishes after some decades. The ratio ^{226}Ra / ^{228}Ra can be a good indicator for the

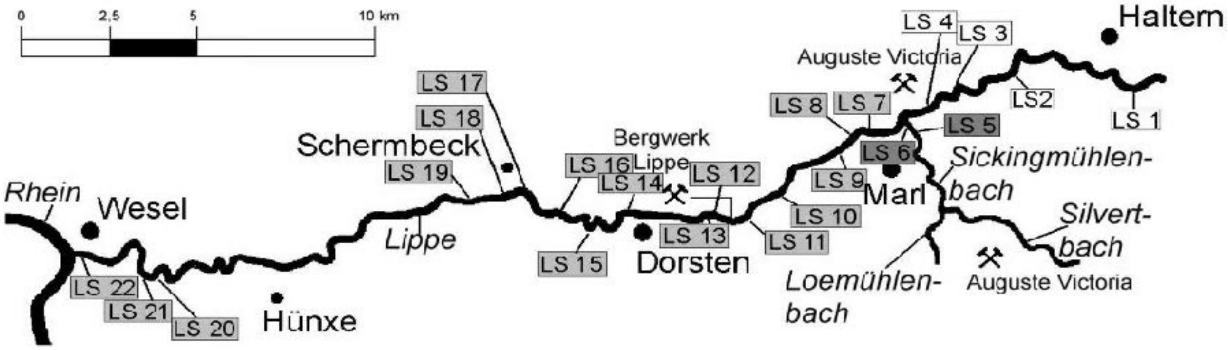

Figure 4. Location of the sediment sampling sites along the Lippe River; colour of the boxed sample numbers: white = uncontaminated, light grey = contaminated, dark grey = strongly contaminated

time when the contamination occurred, if initial ^{226}Ra and ^{228}Ra activity concentrations are known. Table 3 shows the calculated age of the sediments. The samples LS5 and LS6 from the Sickingmühlenbach are very young due to the strong radium deposition. Further downstream in the Lippe River, the age of the sediment samples increases up to 7.8 years. Because of sampling depths up to 5 cm and sediment redistribution along the river, the ages vary.

^{210}Pb activity concentrations can also be used to indicate the age of radium contamination (Table 3). This nuclide increases with a half-life of 22 years, subsequent to the decay of ^{226}Ra. For example, the highly contaminated samples LS5 and LS6 are young (^{226}Ra/^{210}Pb = 98) compared to older contamination like LS14 (^{226}Ra/^{210}Pb = 2.7). However, estimating age using the ratio of ^{226}Ra/^{228}Ra is more reliable than the ^{226}Ra/^{210}Pb method because the determination of ^{228}Ra is more accurate than that of ^{210}Pb.

Good positive correlations between the radium nuclides and the geochemically similar cations Ba and Sr are obvious from Table 3. The correlation coefficients were 0.99 for ^{226}Ra vs. Ba, 0.94 for ^{226}Ra vs. Sr, 0.84 for ^{228}Ra vs. Ba and 0.87 for ^{228}Ra vs. Sr.

Chemical Bonding of Radionuclides in Sediments

About half of the sampled sediments were sequentially extracted (Table 1). Figure 5 presents the proportional distribution of ^{226}Ra for the seven different fractions. Focusing on the mobile fraction (radium attached to surfaces of mineral grains), it seems that this component increases with increased distance from the discharge point. The lowest value of the mobile fraction was determined at background site LS3 (4%). Downstream, the fraction increases from LS7 (5%) to LS11 (13%). Downstream of LS11, the fraction increases again from 5% (LS12) to 36% (LS22). However, if the proportional values of the different fractions (Figure 5) are transferred into absolute ^{226}Ra activity concentrations, the impression of an increase in the mobile fraction with increased distance from the contamination is corrected (Figure 6). The mobile fraction is more or less constant along the Lippe River, but the residual fraction shows high variability: With increased distance from the discharge point, the ^{226}Ra levels decrease significantly. The residual fraction represents the ^{226}Ra that is precipitated as radiobaryte (Ra,Ba SO_4). As long as oxic conditions prevail, this fraction is highly immobile (Wiegand and Feige 2002). The sum of the other five fractions behaves similarly to the residual fraction, though this trend is not as obvious.

The distribution of the different fractions in the sediments of Sickingmühlenbach Creek (Figure 7) underlines the importance of determining the chemical bonding of contaminants in sediment samples. In these highly contaminated sediments, 99% of the ^{226}Ra has precipitated as radiobaryte immediately after the reduced Ra-rich mine waters were discharged into the sulphate-containing creek. This effect is also underlined by the unusually high values for Ba in these sediment samples: 56.8 wt-% (LS5) and 36.6 wt-% (LS6) (Table 3). Furthermore, the fraction of radium that is available for uptake by plants (the mobile fraction) is more or less the same within the contaminated sediments, and nearly independent of the total ^{226}Ra activity concentrations of the sediment. Only the reference sampling site for background conditions (LS3) has a clearly lower mobile fraction activity concentration (Figure 6).

Distribution of Radionuclides in River Bank Soils

At three sampling sites, the influence of floods on the contamination of the river bank soils was investigated (Figure 8). LB1 is upstream of the confluence of Sickingmühlenbach Creek and the Lippe River, and is used as a reference point for background conditions. The activity concentrations of ^{226}Ra, ^{228}Ra and ^{210}Pb, as well as the concentrations of Ba and Sr and the gamma dose rate for LB1, LB2, and LB3 are provided in Table 4. LB2-1 and LB3-1 are located directly at the riverside, while LB3-2 is 3 m from the riverbed, and LB2-2 and LB3-3 are from an area not influenced by flooding about 30 m from the river.

Table 4 clearly shows that the concentrations of the radionuclides and elements as well as the dose rates decrease as the distance to the river increases.

Table 3. Mean activity concentrations of ^{226}Ra, ^{228}Ra, and ^{210}Pb and mean concentrations of Ba and Sr (with 2σ instrumental standard deviation) of the sediments along the Lippe River. The age of the sediments was calculated using the ^{226}Ra/^{228}Ra ratio, unless the activity concentrations were too low to allow this.

Sampling point	^{226}Ra [Bq/kg]	^{228}Ra [Bq/kg]	^{210}Pb [Bq/kg]	Ba [mg/kg]	Sr [mg/kg]	Age [years]
LS1	42.7	16.9	35.2	1041	185	-
	± 0.8	± 1.5	± 4.7	± 51	± 9	
LS2	53.8	27.5	48.9	13939	233	-
	± 0.9	± 2.1	± 6.5	± 6	± 11	
LS3	9.9	6.3	6.1	208	34	-
	± 0.4	± 0.9	± 3.1	± 11	± 2	
LS4	10.4	6.7	12.2	267	54	-
	± 0.4	± 0.9	± 2.9	± 13	± 3	
LS5	15,000	6,480	153	567,900	41,510	0.6
	± 18	± 35	± 65	± 28300	± 2070	
LS6	10,990	5,671	47.6	366,200	17,430	0
	± 91	± 24	± 28	± 18200	± 895	
LS7	425	187	147	9762	1006	0.5
	± 3.0	± 6.0	± 13	± 492	± 50	
LS8	353	141	89.0	8745	625	1.3
	± 2.6	± 4.8	± 11	± 436	± 31	
LS9	331	59.7	118	7834	521	7.8
	± 2.2	± 3.3	± 11	± 392	± 26	
LS10	211	59.2	54.0	4019	267	4.1
	± 1.6	± 2.8	± 8.2	± 202	± 13	
LS11	109	43.4	35.8	2253	191	1.3
	± 1.2	± 2.4	± 6.2	± 111	± 10	
LS12	365	99.3	124	8134	561	4.4
	± 0.7	± 1.2	± 3.6	± 406	± 28	
LS13	367	146	104	7270	503	1.3
	± 2.6	± 5.0	± 12	± 362	± 25	
LS14	296	66.0	111	7013	600	6.0
	± 2.1	± 3.2	± 9.3	± 351	± 30	
LS15	266	76.5	98.2	5482	417	4.0
	± 2.0	± 3.3	± 8.5	± 274	± 21	
LS16	441	163	147	8624	840	1.9
	± 3.0	± 5.5	± 13	± 431	± 42	
LS17	204	79.9	64.7	4221	359	1.4
	± 1.8	± 3.4	± 8.0	± 211	± 18	
LS18	130	29.0	37.0	3626	235	6.0
	± 1.3	± 1.9	± 5.8	± 183	± 12	
LS19	146	61.6	41.3	3710	311	0.8
	± 1.4	± 2.8	± 7.3	± 186	± 16	
LS20	71.0	27.8	31.1	1769	184	1.4
	± 1.0	± 1.9	± 5.1	± 87	± 9	
LS21	97.6	59.4	32.6	2700	210	-
	± 12	± 2.1	± 5.7	± 135	± 11	
LS22	34.8	15.0	14.6	644	79	-
	± 0.7	± 1.3	± 3.7	± 32	± 4	

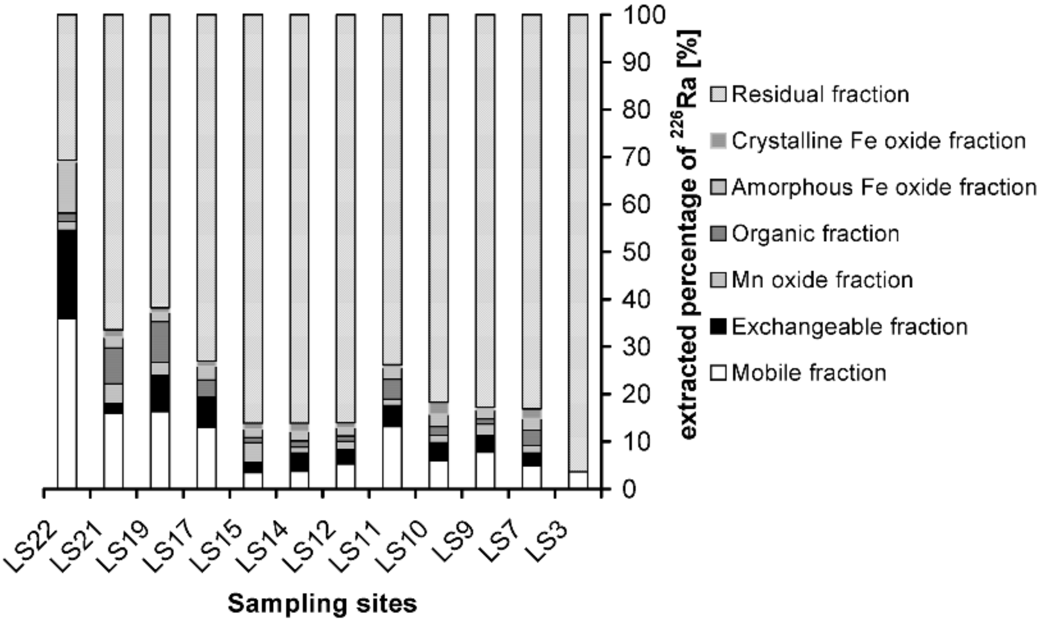

Figure 5. Proportional distribution of different types of chemical bonding for ^{226}Ra in sediments of the Lippe River (for location of sampling sites, see Figure 4)

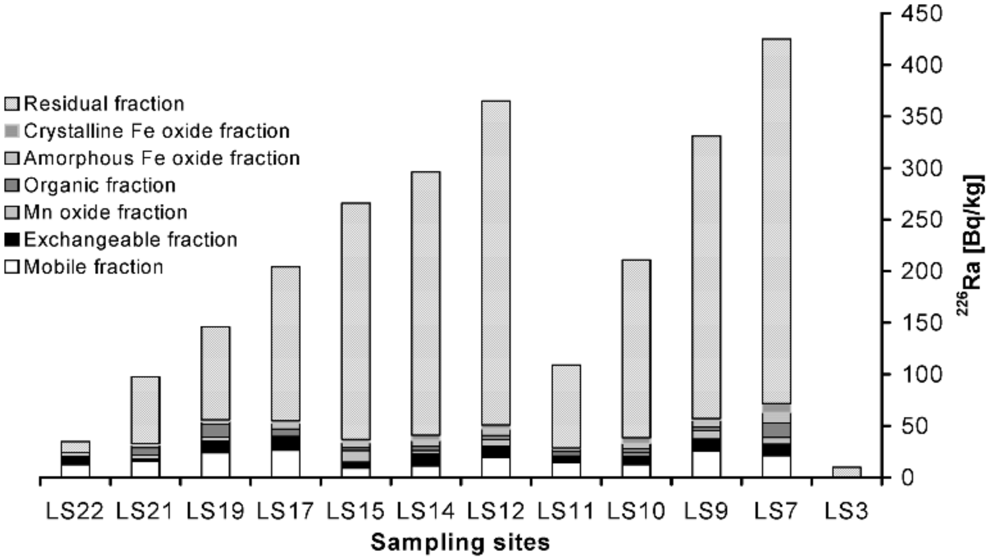

Figure 6. Activity concentrations of ^{226}Ra in seven different fractions of sediments of the Lippe River (for location of sampling sites, see Figure 4)

Obviously, the high activity concentrations close to the river are due to more frequent flooding events and to longer periods of inundation. Very similar results were published by Paridaens and Vanmarcke (2001) for contaminated river bank soils near a phosphate facility in Belgium.

Radionuclide Uptake by Plants

To investigate the transfer of radionuclides from sediments, a common aquatic plant (*Myrophyllum ssp. heterophyllum*) was sampled along the Lippe River (Figure 9). In non-contaminated samples (PF1, PF2, PF4), the ^{226}Ra activity concentrations of *Myrophyllum* were about 20 Bq/kg in dried plants. Subsequent to the inflow of the Sickingmühlenbach Creek, the ^{226}Ra activity concentrations of the plants increased significantly, reaching maximum values of 78 Bq/kg at PF18, an increase in ^{226}Ra activity concentrations up to a factor of 4. In contrast to the regional distribution of ^{226}Ra in sediments, the aquatic plants show similar ^{226}Ra activity concentrations downstream from the Sickingmühlenbach (Figure 9). This finding is in accordance with the results shown

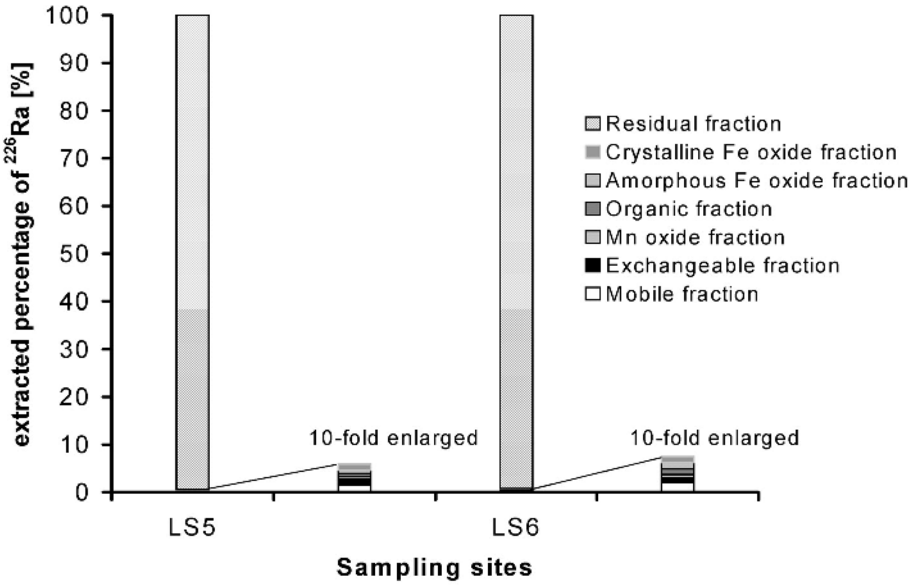

Figure 7. Proportional distribution of different types of chemical bonding for ^{226}Ra in Sickingmühlenbach Creek sediments (for location of sampling sites LS 5 and LS 6, see Figure 4)

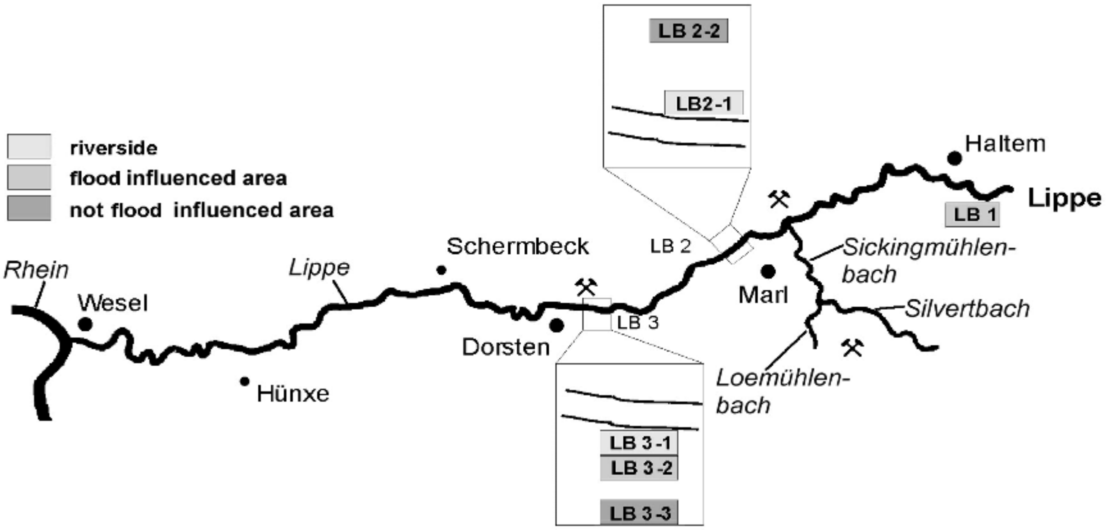

Figure 8. Locations of soil sampling sites along the Lippe River

Table 4. Radionuclide (^{226}Ra, ^{228}Ra, ^{210}Pb) and element (Ba, Sr) concentrations (with 2σ instrumental standard deviation) and gamma dose rates of soil samples at sampling site LB2 and LB3

Sampling point	^{226}Ra Bq/kg	^{228}Ra Bq/kg	^{210}Pb Bq/kg	Ba mg/kg	Sr mg/kg	dose rate nSv/h	Remark
LB2-1	659 ± 17	188 ± 10	34.6 ± 2.6	9.806 ± 490	866 ± 43	180	r
LB2-2	94.0 ± 2.5	38.3 ± 2.3	13.5 ± 1.1	1.330 ± 67	178 ± 9	160	nfa
LB3-1	521 ± 3.2	187 ± 5.7	114 ± 13	13,400 ± 670	958 ± 48	300	r
LB3-2	393 ± 2.6	104 ± 4.1	124 ± 11	8,719 ± 438	647 ± 34	200	fa
LB3-3	66.6 ± 1.1	35.5 ± 2.5	65.4 ± 7.7	1,552 ± 75	159 ± 8	140	nfa

r: riverside, fa: flood influenced area, nfa: not flood influenced area

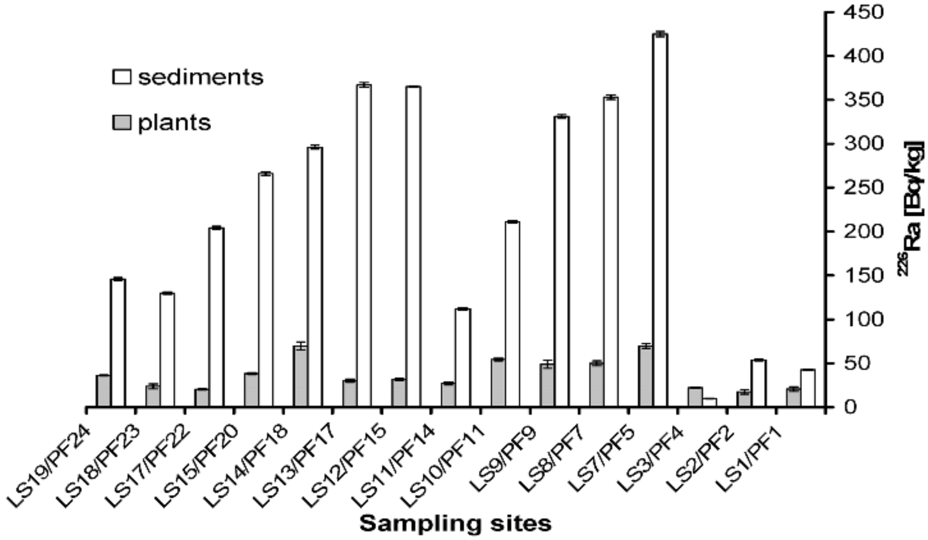

Figure 9. Activity concentrations of ^{226}Ra in plants (*Myrophyllum ssp)* and assigned sediments (with 2σ-error) from the Lippe River (for location of sampling sites, see Figure 4)

Risk Assessment

This study followed the radium pathway, starting at its source (the mine water discharge points) and ending in temporal "inter-sinks" like river sediments, occasionally flooded soils, or plants. Based on these findings, the surface waters have no direct impact on radiation exposure since due to the high salinity of the water, it is not used as drinking water. The sediments show the highest radium activity concentrations of the investigated types of samples, but like the surface water, they are not a direct source of radiation to humans as long as they stay in the river bed. Most of the radium in the sediment is firmly fixed in the lattice of radiobaryte. However, if anoxic conditions develop, radiobaryte can be reduced, and Ra and Ba can be remobilised (Pluta and Trembaczowski 2001).

Under the prevailing oxic conditions, the sediments can contribute to the radiation exposure of humans if they are exposed to the atmosphere. This can happen if the water table drops, if the contaminated sediments are eroded and redistributed on to the river banks by natural processes, or if the sediments are exposed during river restoration. Increased radiation exposure due to enhanced gamma dose rates results and ingestion or inhalation of ^{226}Ra, ^{228}Ra are a threat if no measures against inhalation are taken, especially for restoration workers.

The exposed sediment and the river bank soils that receive radium by temporal flooding, pose the greatest risk to the public. The highest radium activity concentrations were measured in samples taken close to the river (Figure 10). Maximum values up to 6000 nSv/h were determined above parched creek sediments, exceeding the values found by Biesold et al. (1996) in the legacies of the East-German uranium mining (maximum of 4600 nSv/h). High gamma dose rates, up to 1700 nSv/h, were determined at the confluence of the Sickingmühlenbach and the Lippe. This is comparable to the gamma dose rates measured at sedimentation installations, dumps, and lagoons of the former East-German uranium mining industry (Biesold et al. 1996). The gamma dose rates are still elevated further downstream (Figure 10). As expected, further from the riverside, the gamma rate decreases. Germany's Radiation Protection Commission considers levels of 300 nSv/h and higher as "radiologically significant". This level was reached twice along the Lippe, and frequently along Sickingmühlenbach Creek.

To calculate the potential effect on the public, exposure time along the riverside was divided into likely (50 h/a) and unlikely (400 h/a) conditions (Penfold et al. 1999). For both, calculations were made with an average gamma dose rate of 600 nSv/h, which was the mean value of 26 measuring sites directly at the riverside. The likely scenario leads to a maximum dose rate of 0.3 mSv/a, and an average dose rate of 0.03 mSv/a (Table 5). In the worst case scenario, the maximum dose rate increases to 2.4 mSv/a, and the average dose rate increases to 0.24 mSv/a (Table 5).

A much higher potential risk is caused by the ingestion of contaminated river bank soils by children. Children are allured by rivers or creeks like the Sickingmühlenbach, and were observed frequently during sampling. Children commonly ingest contaminated water or soils while playing. Again, the calculations of the effective dose rates were divided into a likely and unlikely scenario. The likely scenario was calculated with 1% of the maximum concentrations (^{226}Ra: 15,000 Bq/kg, ^{228}Ra: 6,500 Bq/kg), while the unlikely (worst case), was calculated with the total amount. The latter scenario requires that the chemical bonding of Ra in the soil is weak, i.e. all of the Ra is soluble (which was not true, see Figures 5, 7) and assumes that 200 mg/d of contaminated soil is ingested 240 days a year (EPA 1997). Ingestion coefficients, relative to age, from a radiation protection directive (BMU 2001) were used. Using these parameters, a child 2 to 7 years old would receive a likely maximum effective dose of 0.06 mSv/a for ^{226}Ra and 0.15 mSv/a for ^{228}Ra, and in the worst case scenario, up to 5.8 mSv/a (^{226}Ra) and 15.5 mSv/a (^{228}Ra) (Table 5).

Evaluating increased radiation exposure due to radium enrichment in aquatic plants is more difficult. These plants are not used for production of foods, but radionuclide transfer along the food chain, which was not investigated, could be important. The transfer of radium from the contaminated river bank soils into terrestrial plants like grass, which were sampled and analysed by Schmid (2001), was small (compared to aquatic plants) and was observed only directly along the riverside. Since no agriculture or dairy farming was practised at the investigated sites, subsequent radiation exposure does not need to be considered at the moment but it has to be avoided in the future by the communities in the investigated areas.

Due to the high gamma dose rates and the possible ingestion of contaminated soil, the extremely contaminated regions should be fenced to prevent access by children and fishing enthusiasts. Furthermore, the contaminated areas should be examined more carefully and classified relative to the risk of radiation exposure to the public, and this should be done before river restoration commences.

To avoid additional contamination by radionuclides, radium should be precipitated underground (a project to do so is planned), as has been done in Poland (Chalupnik et al. 2000). Last but not least, the public

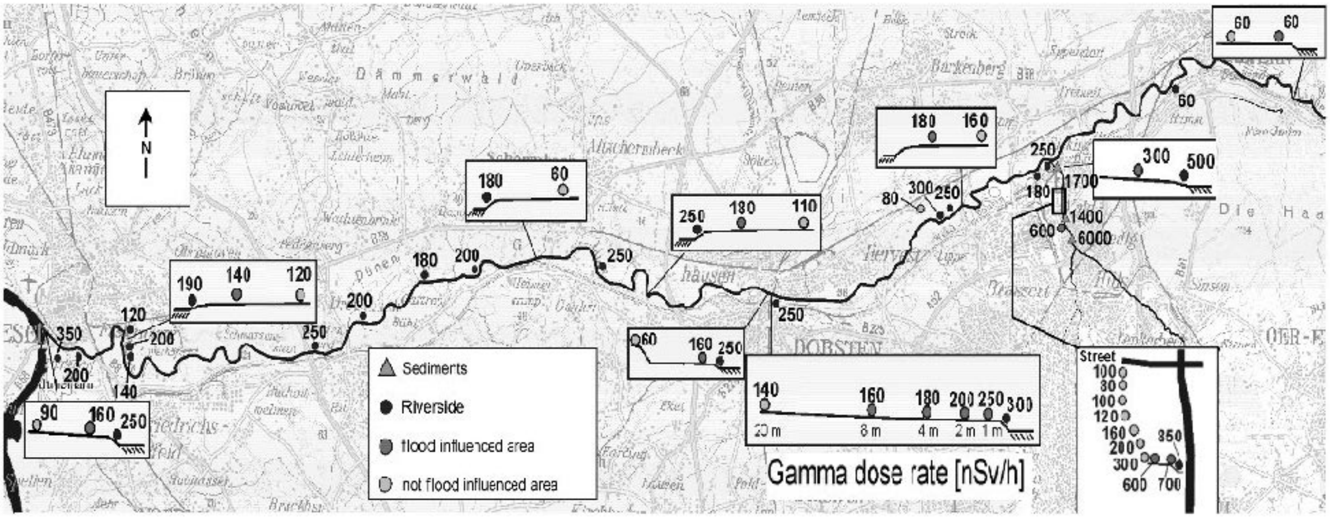

Figure 10. Gamma dose rates along the Lippe River

Table 5. Effective dose rates for the public due to (1) gamma dose rates and (2) ingestion by playing children

1. External Exposure	Assumed exposure time [h/a] and gamma dose rate [nSv/h]	
	likely: 50 h/a	likely: 400 h/a
	0.3 mSv/a (at 6000 nSv/h)	2.4 mSv/a (at 6000 nSv/h)
	0.03 mSv/a (at 600 nSv/h)	0.24 mSv/a (at 600 nSv/h)
2. Ingestion of 200 mg/d contaminated soil	Duration of stay: 240 d/a (age of children given as indices; ad=adults)	
	likely (1% of total Ra):	unlikely (total Ra):
	150 Bq/kg ^{226}Ra; 65 Bq/kg ^{228}Ra	15,000 Bq/kg ^{226}Ra; 6,500 Bq/kg ^{228}Ra
	$^{226}Ra_{2-7}$: max. 0.06 mSv/a	$^{226}Ra_{2-7}$: max. 5.8 mSv/a
	$^{228}Ra_{2-7}$: max. 0.15 mSv/a	$^{228}Ra_{2-7}$: max. 15.5 mSv/a
	$^{226}Ra_{7-12}$: max. 0.04 mSv/a	$^{226}Ra_{7-12}$: max. 3.8 mSv/a
	$^{228}Ra_{7-12}$: max. 0.10 mSv/a	$^{228}Ra_{7-12}$: max. 10.2 mSv/a
	$^{226}Ra_{12-17}$: max. 0.03 mSv/a	$^{226}Ra_{12-17}$: max. 2.9 mSv/a
	$^{228}Ra_{12-17}$: max. 0.07 mSv/a	$^{228}Ra_{12-17}$: max. 7.7 mSv/a
	$^{226}Ra_{ad}$: max. 0.01 mSv/a	$^{226}Ra_{ad}$: max. 1.4 mSv/a
	$^{228}Ra_{ad}$: max. 0.04 mSv/a	$^{228}Ra_{ad}$: max. 4.35 mSv/a

should be informed about the levels of contamination and any planned remediation.

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