THE INFLUENCE OF MUNICIPAL WASTE ON URANIUM MILL TAILINGS: A HYDROGEOCHEMICAL STUDY ON A MIXED TAILINGS SITE

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ABSTRACT

Mining and milling has taken place in Saxony and Thuringia, in eastern Germany, for over 800 years. Radioactive waste rock was dumped without regard for the environment for centuries. The area is now rather densely populated, and some of the smaller dumps and tailings have been used as municipal or industrial landfills after the uranium mine and mill closed. Ground water contamination has occurred down-gradient of an industrial disposal plant in Dresden (Saxony). To determine the source of the contamination, a multi-parameter interpretation was done using ^{234}U, ^{238}U, ^{226}Ra, ^{222}Rn, ^{2}H, ^{18}O, ^{34}S, and ^{13}C, as well as conventional hydrochemical parameters. Ground water contamination in the natural aquifer beyond the disposal site was determined to be from the tailings due to its oxidizing, acidic character and high concentrations of sulfate, uranium and heavy metals. In this case, the contamination was not caused by recent seepage water from the dump. Water currently leaching from the tailings has been modified by water draining from the superimposed waste, which has had a positive influence on the tailings. Uranium and heavy metals have been immobilized in place due to the changes in the chemical environment.

INTRODUCTION

Until 1989, the former G.D.R. was the world's third-largest producer of uranium with a total production of more than 200,000 tons. Initially, ore processing plants were located close to the mines. In the early 1960's, many of these small mines were closed down, and local processing was abandoned and replaced by centralized plants. Consequently a number of small-scale abandoned uranium mines, dumps, tailings, and remains of processing plants can be found in the federal states of Saxony and Thuringia.

In this research project, an industrial disposal plant in Dresden (Saxony) was investigated (Figure 1). Uranium ores from several deposits were processed in this plant by acidic and alkaline leaching. The tailings, including iron hydroxide sludge, were deposited without any protective layers in two dumps (dump 'A' and dump 'B') from 1950 until 1962. In the 1970's and 1980's, dump 'A' was used as a municipal waste deposit (rubbish and ashes) for the city of Dresden.

SITE CHARACTERIZATION

The study site is located at the border region of the Permian Döhlen Basin and the Dresden Cretaceous Basin ('Elbtalzone'). The intense lithified sediments (tuffaceous breccia, claystone, clay schist, conglomerates) of the Döhlen Basin dip 15 - 200 to the SW and water percolates only along joints. The confined ground water of the Permian aquifer in the Kaitzbach Valley is locally coupled to the Kaitzbach creek. The layers of the Dresden Cretaceous Basin (sandstone and finer-grained sediments) lie discordantly on the Permian. They wedge out near the tailings and at the slopes of the Kaitzbach Valley (Figures 1 and 2). The ground water flow direction is N-NE, in accordance with the slight dip of the layers (2-50) (Ullrich et al., 1994). The Quaternary formations are of local importance (Kaitzbach Valley), but do not have any influence on regional ground water movement. Kaitzbach Creek is influenced by mining, industrial, and municipal facilities.

Dump 'A' was established in a section of the Kaitzbach Creek valley (Figures 1 and 2), which was closed with two dams, partly consisting of tailings material. It consists of a layer of tailings at least 25 m thick overlain by approximately 12 m of household waste. Ashes from lignite power plants and rubble from demolished buildings lay on top. There are two water tables within the dump: one in the tailings and another above the tailings in the waste layer. The smaller dump 'B' was established in a small depression NW of the Kaitzbach Valley and consists only of tailings. Table 1 gives general information about the dumps.

Table 1. General information about dump 'A' and 'B' (Ullrich et al., 1994).

Parameter	Dump 'A'	Dump 'B'
area (ha)	23	6
total volume (10^6 m^3)	4	0.3
ash (10^6 m^3)	0.3	0.08
household waste (10^6 m^3)	1.6	-
tailings (10^6 m^3)	2.1	0.25
tailings (10^6 t)	3.4	0.4

The pollutant potential of both dumps was estimated as 10^{13} - 10^{14} Bq radium (about 1.5 kg), 1500 t uranium, 1500 t arsenic, and 10,000 t various heavy metals (Ullrich et al., 1994). Both the waste and the tailings produce highly mineralized water with elevated levels of sulfate, chloride and heavy metals. Due to the hydraulic properties of the layers, it is possible that the waste water partially flows at the interface between the waste and the tailings to the dams and then seeps further underground. Meanwhile, dilution by rain water and/or ground water complicates things further. As a result, determining the contamination source for ground water pollution can be problematic.

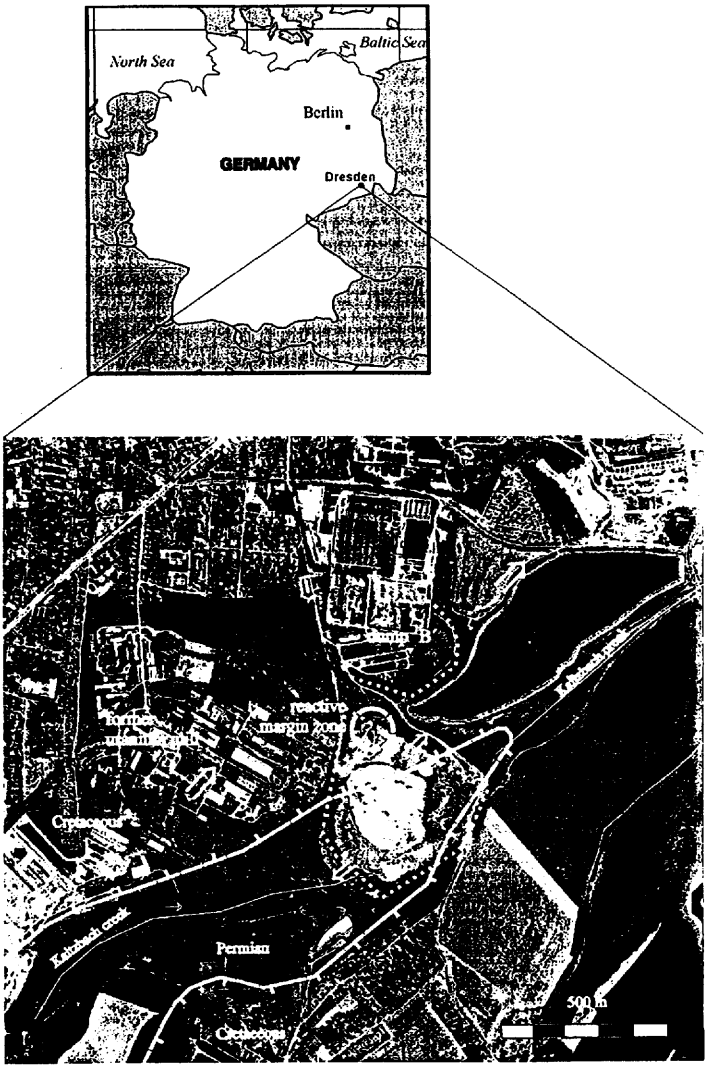

Figure 1: Location and site schematic (Photo: Landesvermessungsamt Sachsen, 1991).

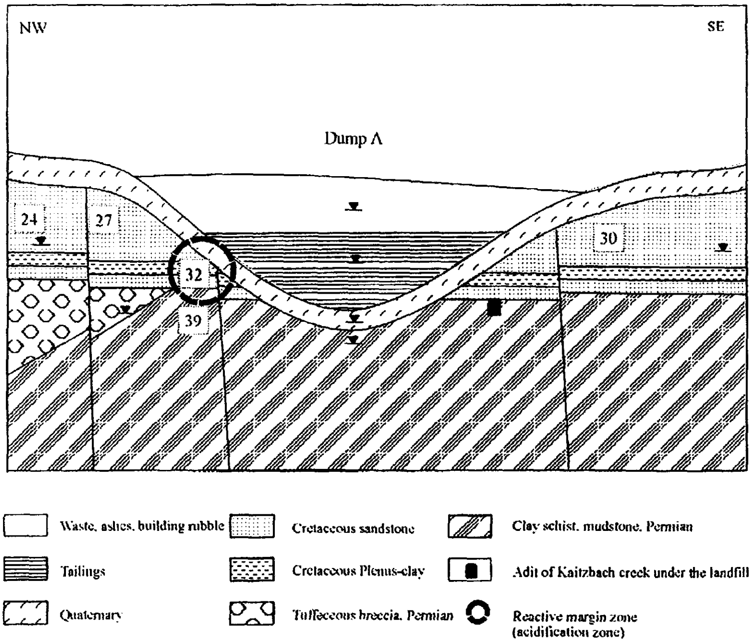

Figure 2: Schematic cross-section through the landfill (NW-SE), tritium values [T.U.] in boxes.

METHODS

Ground water samples of all relevant aquifers were taken from the incoming flow, from the landfill and from the outflow of the disposal site. The conventional chemical parameters, including heavy metals, were determined as well as the radionuclides ^{238}U, ^{234}U, ^{226}Ra, ^{222}Rn, tritium, and the stable isotopes ^{2}H, ^{18}O, ^{34}S, and ^{13}C. Uranium was measured using mass spectrometry (U_{nat}) and radium by means of liquid scintillation after filtration through 0.45 1m filters. Radon activity was determined using a Lucas cell. The measurement of low level tritium activities was done in two steps: an electrolytic enrichment of 250 mL of water, followed by J^{-} counting of the resulting 8 mL of water. Liquid scintillation counting was done with Quantulus 1220 (WALLAC GmbH). Analytical methods, detection limits and measurement errors are compiled in Table 2.

RESULTS AND DISCUSSION

The stable isotopes ^{2}H, ^{18}O, ^{34}S, and ^{13}C are more or less specific for the several ground water types (Helling and Nitzsche, 1997). The parameter $L^{34}S$ could be especially useful in distinguishing between ground water impact by waste water and tailings water. In this paper, results are reported concerning the general characteristics of the investigated ground waters as well as the radionuclides uranium, radium, radon, and tritium.

Table 2. Analytical methods with detection limits and measurement errors.

Parameter	Method	Detection limit	Measurement errors
U_{nat}	ICP-MS	0,1 1g/l	5 %
^{238}U, ^{234}U	alpha spectrometry	<0.01 Bq/l	8 %
^{226}Ra	liquid scintillation counting	0.001	8%
^{222}Rn	Lucas cell	1 Bq/l	10 %
Tritium	liquid scintillation counting	0.3 T.U.	10 %
$L^{18}O$, $L^{34}S$	delta E mass spectrometer	no statement	< 0.2 U

Hydrochemistry

The ground water of the geologic background (natural, unaffected ground water) is characterized by total dissolved solids (TDS) < 1 g/L and predominant Ca-SO_4 components. The pH of the water in the Cretaceous aquifer is about 6 due to acid rain and the limited buffering capacity of the aquifer.

The waste (household waste, ashes and building rubble) produces slightly alkaline Na-Ca-Cl-HCO_3-water with a TDS of 4-6 g/L, increased temperature (280C) and DOC as well as low Eh. The water is similar in the subjacent tailings, though the TDS and sulfate concentrations are higher. The tailings water is of the Na-Mg-SO_4-Cl-type with an uranium content up to 1 mg/L (0,5-10 Bq/L ^{238}U) at almost neutral pH, whereas a slight dilution is observed at the dams due to the influx of rain water (Table 3).

Table 3. Ground water characteristics in the region of the mixed tailings site.

Aquifer	pH	Eh [mV]	DOC [mg/L]	Conduct. [µS/cm]	Sulfate [mg/L]	U [mg/L]
Rubbish	7.2	-118	59	9200	272	0.003
Tailings	7.0	197	32	12750	6800	0.67
Cretaceous (acidified zone)	3.3	661	10	11720	27300	80.13
Dam	6.9	260	17	10700	7800	1.32
Cretaceous	6.9	302	3.3	1477	500	<0.02
Permian	6.1	335	1.4	2000	1150	1.83
German drinking water standards (TVO 1990)	6.5-9.5			2000	240	0.2

Ground water contamination caused by the waste material can be detected locally in the natural aquifers (Quaternary, Permian) near the dams. The TDS ranges up to 6 g/L and heavy metals (especially iron and manganese) also show increased concentrations. Ground water acidification (down to pH 3.3) coupled with a locally high Eh occurs in the Cretaceous aquifer in the northern part of dump 'A', the so-called *reactive margin zone* (see Figures 1 and 2). This is associated with extremely high concentrations of sulfate (up to 27 g/L), heavy metals and radionuclides (up to 80 mg/L U_{nat} resp. 1000 Bq/L ^{238}U). The source of the ground water contamination is presently being investigated and seems to be connected with the former water level of the tailings pond. No direct contamination due to the landfill is evident in the various aquifers at a distance greater than 500 m from the contamination source. However, the sulfate concentration exceeds 240 mg/L, which is the German drinking water standard (TVO 1990).

Radionuclides in the Ground Water

Results of measurements of the radionuclides (including tritium) are shown in Table 4. Ground water that is influenced by the tailings shows significantly higher uranium concentration than the background (see also Table 5).

Table 4. Isotopes in the ground waters of the study site.

Aquifer	**^{238}U [Bq/L]**	**Activity ratio $^{234}U/^{238}U$**	**^{226}Ra [Bq/L]**	**^{222}Rn [Bq/L]**	**Tritium [T.U.]**
Waste	0.03	7.3	0.035	17 - 96	24.1 - 31.8
Tailings	0.53 - 11.86	1 - 2.8	0.03 - 2.5	74 - 500	36.7 - 67.6
Dam	1.55 - 18.45	0.9 - 2.6	0.02 - 1.35	6 - 20	26.3 - 39.9
Quaternary	0.15 - 2.53	1.1 - 1.4	n.a. - 0.26	21 - 34	15.9 - 32.6
Cretaceous	0.01 - 985.5	0.9 - 2.0	n.a. - 0.4	14 - 75 (198)	24.0 - 39.5
Permian	0.05 - 22.52	0.9 - 3.7	n.a. - 0.25	35 - 250	5.8 - 55.2

n.a. = not available

Table 5. Natural background values (^{226}Ra and ^{238}U) of ground water in the study area (Helling et al., 1996).

Aquifer	**^{226}Ra [Bq/L]**	**^{238}U [Bq/L]**
Permian	<0.03	0.2-0.6
Cretaceous	0.1	0.04-0.08
Quaternary	0.08	no values
Surface water	<0.06	0.01-0.05

The maximum value occurs in the Cretaceous aquifer in the *reactive margin zone* of dump 'A' (see Table 6). This local acidification is probably derived from tailings that had been leached with sulfuric acid, resulting in a low pH (around 3.3) and a high concentration of sulfate. The pond water seeped (in a hydraulic window) through the Quaternary into the Cretaceous aquifer. The cause of the contamination is also indicated by an uranium activity ratio (^{234}U/^{238}U) near equilibrium as well as by the low radium content (radium was not mobilized during processing).

In contrast to uranium, the maximum radium concentration occurs in the tailings water and dam water (Table 4) due to altered Eh as a result of the overlaying municipal waste. The reducing, anoxic environment is also the reason for the relatively low uranium concentration and the slight increase of the uranium activity ratio in the tailings water (in comparison to the reactive margin zone). Table 6 shows the differences between the tailings water and that of the acidified zone. The enrichment of ^{234}U is attributed to both (1) the radiation damage of crystal lattices, caused by alpha emission and (2) the recoil of parent nuclides (Dickin, 1995). This effect is mostly observed under reducing conditions and is masked in an oxidizing environment (Herczeg et al., 1995).

Table 6. Ground water characteristics of the tailings and the acidification zone.

Parameter	**Tailings water Dump 'A'**	**Water from the acidification zone (Cretaceous aquifer)**
Eh	Reducing	Oxidizing
pH	slightly alkaline - slightly acidic	Acidic
^{238}U [Bq/L]	1 - 18	10 - 1000
^{234}U/^{238}U activity ratio	1.2 - 2.6	ca. 1
^{226}Ra [Bq/L]	0.09 - 25	< 0.035
^{222}Rn [Bq/L]	74 - 500	ca. 200
interpretation as	**current tailings water** (altered due to overlaid waste)	**old tailings water** (from the deposition in the 1960's)

Radon content (determined as ^{222}Rn) in the water is generally higher in relation to its radium content because radon comes from the radium-rich underground. The highest radon activity, up to 500 Bq/L, was measured in the tailings water, caused by the radium in both the tailings and the tailings water. Radon in the groundwater of the acidification zone as well as in the NE outflow of the landfill originates primarily from the natural background of radium. The radium produced by uranium decay in the *reactive margin zone* is insignificant because of the low tailings age (30-40 years). High radon concentrations of up to 1000 Bq/L were measured in the groundwater in the far field (Hochtritt, 1996). In this case, an influence of the disposal site is unlikely due to the distance of several hundred meters and the short half life of the nuclide. Kempski et al. (1997) give migration distances of some ten m for joint systems and fault bundles, only 3-4 m for porous media. The transport of radon in the natural aquifers is assumed to occur through joints and temporary channels because the elevated concentrations of radon underlie local and temporary variations in the observation wells.

Tritium

Water samples from the observation wells in the Kaitzbach valley (Quaternary and Permian aquifer) and the Kaitzbach creek have the same tritium content (about 16 T.U., see Figure 3). This indicates a possible hydraulic connection between both aquifers (the Cretaceous formation is not developed here, see also Figure 2). A mean residence time of 11 years was computed by the program MULTIS (Richter, 1995) using linear and exponential models. Tritium concentrations measured in the ground water of the Permian aquifer near the SW dam appeared to depend on the water level. This would suggest a varying mixture of: a) "old" Permian ground water [5 T.U.] with b) infiltrated precipitation and bank-filtered water from the Kaitzbach creek [14 T.U.] as well as c) seepage water coming from the dam zone [31 T.U.]. The same situation occurs in the Quaternary aquifer with 14 T.U. in case b) and 29 T.U. in case c). However, if we take the corresponding precipitation and its tritium values (taken from Freiberg, see Table 7) into consideration as input for the ground water recharge, it is obvious that precipitation makes up the main part of this ground water.

The tritium values of the Cretaceous aquifer can be explained with a linear model assuming a phreatic aquifer with increasing thickness in the direction of flow. This gives a mean travel time of 30 years for the inflowing water and 40 years for the outflowing water. The flow velocity in this table is 30 m per year.

The high tritium content in the tailings water (up to 68 T.U.) can be interpreted as tritium from precipitation during the deposition of the tailings (early 1960's). This suggests the water to be nearly stagnant in the tailings. However, a small amount of rubbish seepage water probably mixed with the tailings water, based on the fact that tritium values varied depending on the water level and due to the neutralization since deposition. The water from the dams represents a mixture of tailings water with precipitation. The resulting tritium values are in the range of 26 to 40 T.U. Water of the Quaternary measuring point at the toe of the NW dam is obviously influenced by seepage water of the tailings (36 T.U.). Tritium values in water samples from the underlying Cretaceous and Permian aquifer north of the landfill are significantly increased and are similar to values found in the tailings water. This supports the above-mentioned assumption, that the source of this contamination is infiltration from the former tailings surface water.

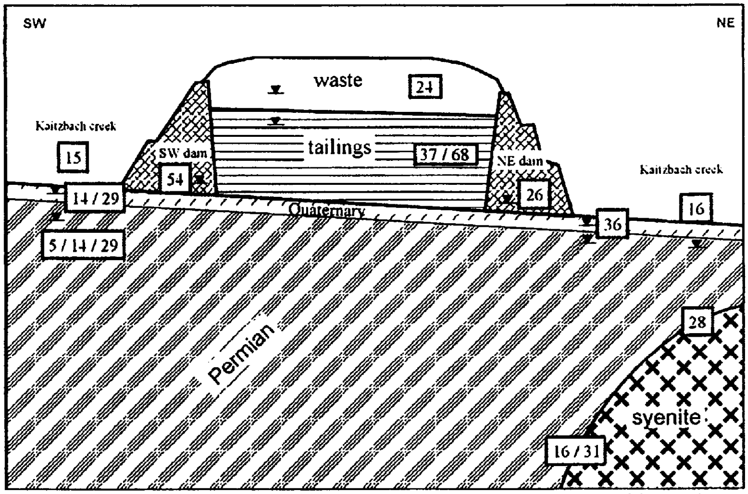

Figure 3: Schematic cross-section through Kaitzbach Valley (SW-NE); tritium values [T.U.] in boxes. For legend, see Figure 2.

Table 7. Tritium values in the ground water of the Permian aquifer in the Kaitzbach Valley near the SW dam of dump 'A' (observation well P4). Additionally, the corresponding precipitation data (quantity and tritium content) are given from Freiberg.

Month/year	**Tritium in P4 [T.U.]**	**water level in P4 [m a.s.l.]**	**Precipitation in Freiberg [mm]**	**Tritium in the precipitation in Freiberg [T.U.]**
4/94	13.7	199.03	71.9	12.6
7/95	24.5	198.88	128.7	20.4
10/96	5.8	197.77	17.1	9.4

CONCLUSIONS

At a complex disposal site, several seepage water and ground water types were investigated. To distinguish between two potential contamination sources (waste and uranium mill tailings) a multi-parameter investigation was conducted. In addition to conventional hydrochemical parameters, the radionuclides ^{234}U, ^{238}U, ^{226}Ra and ^{222}Rn and the environmental isotopes ^{2}H, ^{18}O, ^{34}S, ^{13}C were all measured.

Ground water contamination in the natural aquifer beyond the disposal site was determined to be from the tailings due to its oxidizing, acidic character and high concentration of sulfate, uranium and heavy metals. Obviously, this water has been sitting in a hydrogeological trap since neither dilution with ground water flow nor a spreading of the pollutant plume was observed.

The water in the tailings body reflects reducing, anoxic conditions as a result of the overlying waste. In this case, most of the uranium (as well as heavy metals) has been immobilized while the solubility of radium increased since these radioactive elements show a different chemical behavior. This assumption is supported by the environmental isotopes, which in some cases give a better idea of the source of the waters then the usual parameters.

The alkaline waste has had a positive influence on the tailings, immobilizing uranium and heavy metals. This effect was also observed at a similar site in the Ore Mountains (Junghans and Helling, 1998).

Further Studies and Remediation/reclamation Projects

The contamination of seepage waters by organic contaminants from the landfill should be considered. Currently, the role of humic substances in radionuclide transport are being investigated. Since there is nothing known about the long-term behavior of such complex disposal situations, column experiments should be conducted under varying conditions to find the "best" way to minimize the risk of mobilizing radionuclide, heavy metals or other pollutants.

Based on the results of chemical modeling, the dump will be kept in place. The remediation plan now includes:

- Chemical in-situ immobilization of the dam zone to create additional buffering capacity for the neutralization of acidity generated by the weathering of sulfide minerals;
- Removal and immobilization of tailings material with acid drainage potential;
- Topsoil cover on the surface of the dump and revegetation of the dams; and
- Ground water monitoring twice a year.

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