# Investigations at the former sites of raw phosphate processing in Germany

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**Abstract.** Raw phosphates have been processed in an industrial scale in Germany approximately since the middle of the 19th century. During the centuries, huge amounts of residues with high mass specific activities have been accumulated. Within the framework of a historical study, we have determined the accumulated radionuclide inventory from 1865 to 2005. The consumption amounts to approx. 150 million tons raw phosphates (corresponds to approx. $2.22*10^{14}$ Bq U-238) with a fraction of national production of approx. 1 million tons. A production of approx. 3 million tons of elemental phosphorus (calcium silicate slag: $3.6*10^{13}$ Bq Ra-226) and approx. 12 million tons of phosphoric acid (phosphogypsum: $2.7*10^{13}$ Bq Ra-226) had been achieved. In the next step, we have looked for the former sites with legacies of the raw phosphate processing industry. 92 sites of former production of phosphate fertilizers, 3 sites of former production of elemental phosphorus and 10 sites of former production of phosphoric acid had been identified. Some of them were selected for more detailed researches regarding the accumulated radionuclide inventory and on-site/laboratory radiological investigations.

***KEYWORDS: NORM, raw phosphates, phosphogypsum, calcium silicate slag, legacies, sites, dump***

## 1. Introduction

Raw materials are extracted in Europe in considerable quantities since the early Middle Ages. As a result of past mining, beneficiation and industrial processing of raw materials, residues with elevated activity concentrations of natural radionuclides arose. Parts of these residues are found nowadays also in the environment (NORM legacies).

By order of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety in Germany, the TÜV SÜD Industry Services was assigned to carry out investigations under a research project to develop concepts for the identification and estimation of NORM legacies in Germany. The TÜV SÜD was supported by the "Gesellschaft für Anlagen- und Reaktorsicherheit (GRS) mbH", the University of Wuerzburg, Geological Institute and the Federal Office for Radiation Protection (scientific steering).

The project was carried out in 6 parts. Part 3b [1] treats the industrial legacies of the phosphate ores processing in depth. Some important results from part 3b are presented in [2].

The paper [2] presents data on properties of phosphate minerals and phosphate rocks, fundamental principles on the technology applied for raw phosphate processing (beneficiation of phosphate rocks to concentrates, the wet and thermal process of raw phosphate digestion), on the formation of residues and by-products as well as on typical average mass-related activities. Fig. 1 shows the generation of

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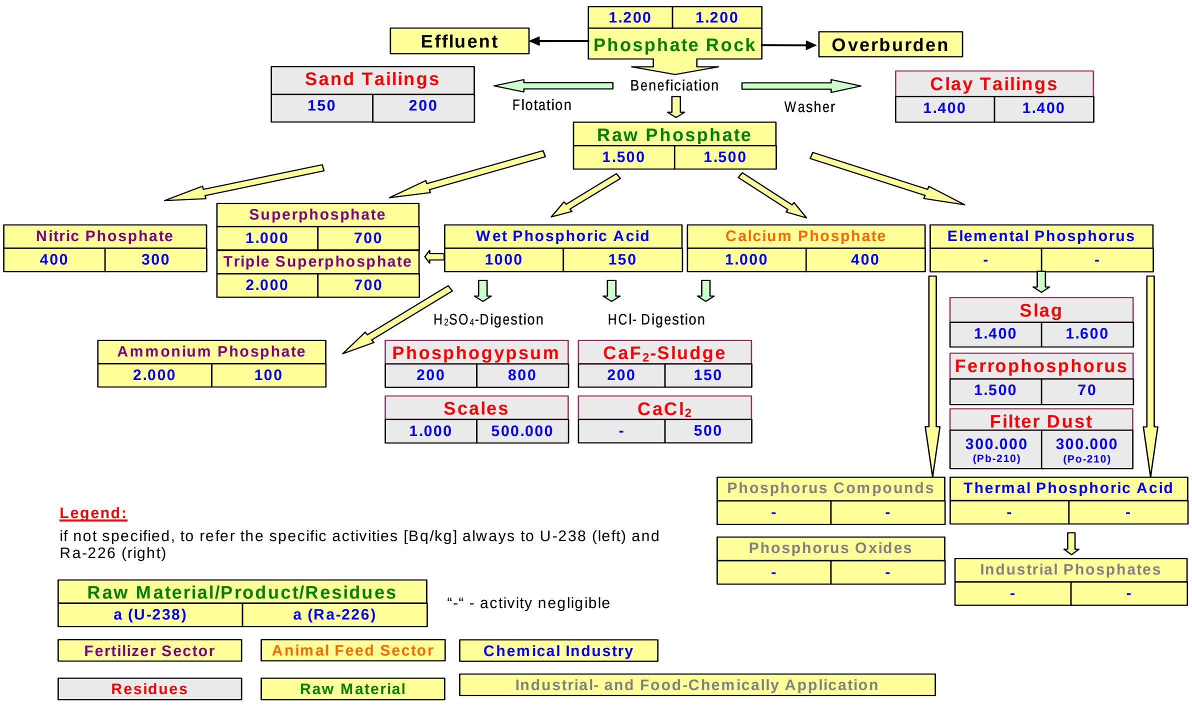
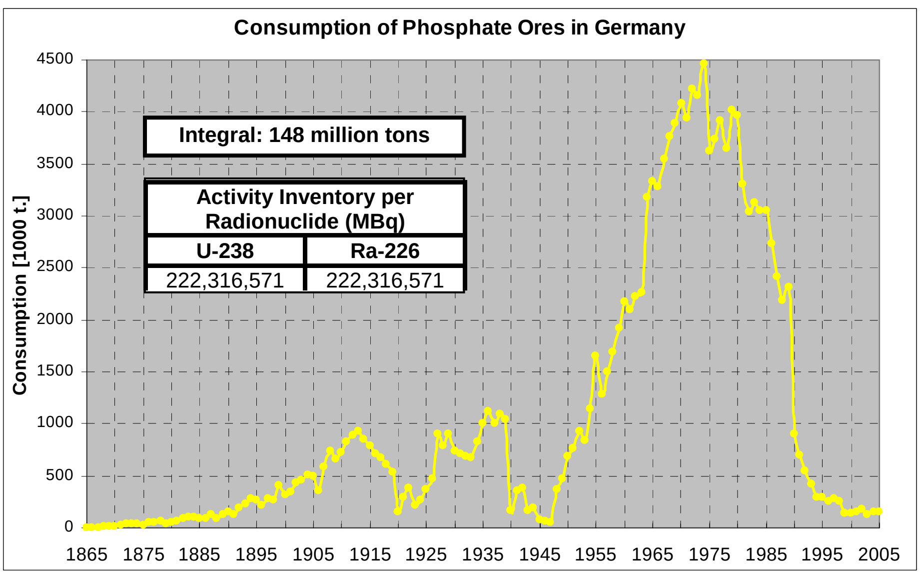
radiologically important products and residues resulting from the processing of raw phosphates including the typical average mass-related activities (taken from [2]). The shown mass-related activities are the result of extensive literature studies and own measurements.

**Figure 1:** Flow chart of generation of radiologically important products and residues resulting from the processing of raw phosphates, giving the typical average mass-related activities [Bq/kg] [2]




As a result of a very comprehensive historical investigation regarding industrial sites, national production, import, export and use of raw phosphates as well as the production of elemental phosphorus, phosphoric acid and phosphate fertilizers we determined the time dependent course of the consumption of raw phosphates (approx. 150 million tons of raw phosphates with a fraction of national production of 0.75 million tons), the production of elemental phosphorus (approx. 3 million tons) and the production of phosphoric acid (approx. 12 million tons) in Germany. Fig. 2 shows as example the consumption of raw phosphate in Germany in the time period from 1865 to 2005 (taken from [2]).

**Figure 2:** Consumption of raw phosphate in Germany in the time period from 1865 to 2005 [2]



The activity inventory of resulting residues from the electro-thermal digestions of raw phosphates for the production of elemental phosphorus in Germany was calculated for the period from 1900 to 2005.

The production of approx. 3 million tons of elemental phosphorus generated calcium silicate slag with an activity inventory of $3.1*10^{13}$ Bq U-238 and $3.6*10^{13}$ Bq Ra-226, ferrophosphorus with an activity inventory of $7.1*10^{11}$ Bq U-238 and $3.3*10^{10}$ Bq Ra-226, filter dust with an activity inventory of $7.1*10^{13}$ Bq Pb-210 and Po-210, offgas with an activity inventory of $3.1*10^{12}$ Bq Pb-210 and $9.4*10^{12}$ Bq Po-210 and effluent with an activity inventory of $4.2*10^{10}$ Bq Pb-210 and $5.7*10^{11}$ Bq Po-210.

Also the activity inventory of resulting residues from the production of phosphoric acid in Germany was calculated for the period from 1936 to 2005.

The production of approx. 12 million tons of phosphoric acid generated phosphogypsum with an activity inventory of $6.8*10^{12}$ Bq U-238 and $2.7*10^{13}$ Bq Ra-226 and effluent with an activity inventory of $1.9*10^{13}$ Bq U-238 and $2.3*10^{12}$ Bq Ra-226.

## 2. Aims and methodology

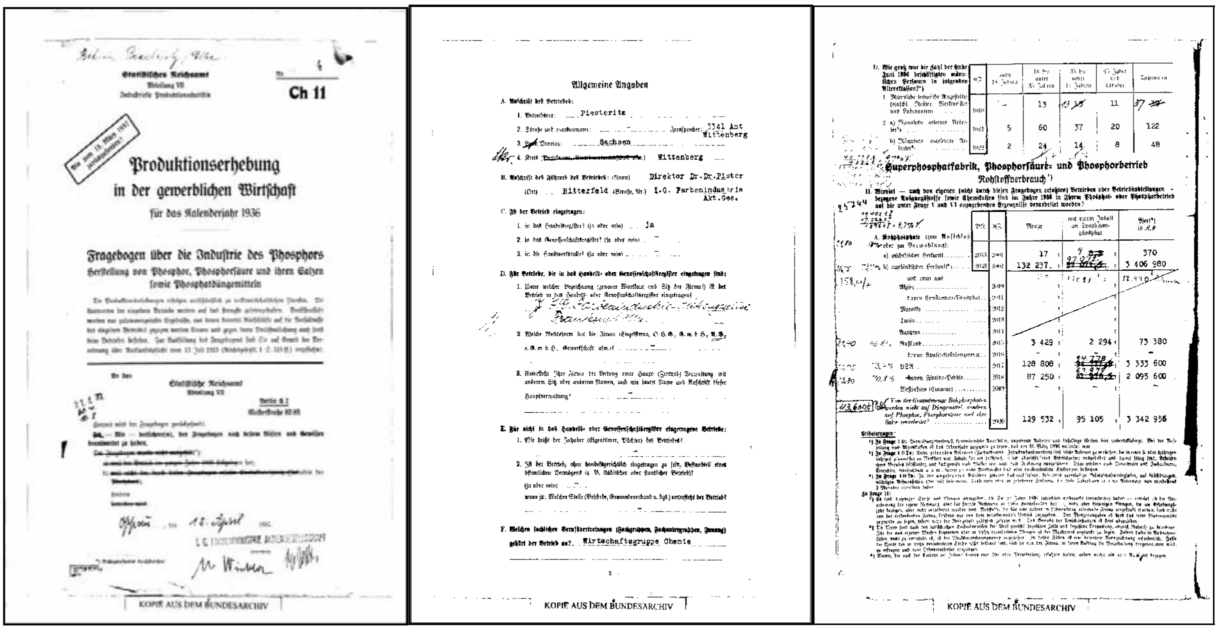
As a result of part 3b [1] of the project, we realized that during the centuries, in which raw phosphates were industrially processed in Germany, huge amounts of residues with high mass specific activities were accumulated.

In the next step (part 4b [3] of the project), the former sites with legacies of the raw phosphate processing industry were investigated. In particular, the researches were focused on finding out where the residues exist nowadays and which amounts and activities are involved in this respect.

In order to determine the former industrial locations, amounts and activities of legacies of the raw phosphate processing, we carried out historical investigations regarding production of elemental phosphorus, phosphoric acid and phosphate fertilizers.

A main part of the project consists of compiling the knowledge and data from historical archives regarding a relatively large historical time period. Fig. 3 gives an example for this.

**Figure 3:** Documents from the archives (“Bundesarchiv” in *Berlin*): industry of phosphorus in 1936, “I. G. Farbenindustrie” (factory *Piesteritz*), pages 1, 2 and 4 [4]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Produktionserhebung in der gewerblichen Wirtschaft für das Kalenderjahr 1936

Fragebogen über die Industrie des Phosphors

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## 3. Results

### 3.1 Historical investigations

In archives and literature 92 sites of former production of phosphate fertilizers, 3 sites of former production of elemental phosphorus and 10 sites of former production of phosphoric acid were identified.

As an example, the 3 sites of former production of elemental phosphorus were *Bitterfeld, Piesteritz* and *Knapsack/Hürth.*

In the beginning of the 20th century, Germany was one of the leading countries of the world regarding the production of phosphorus, starting in *Bitterfeld* in 1900 and in *Piesteritz* on the river Elbe in 1927. Although the phosphorus furnaces were dismantled in 1946, the production of phosphorus was later continued in new built plants, commissioned in *Bitterfeld* at the latest in 1949 and in *Piesteritz* in 1951. Both plants are now decommissioned.

After the World War 2, on the territory of the Federal Republic of Germany, in Knapsack/Hürth, red elemental phosphorus was produced by means of big electrical phosphorus furnaces. The first furnace with a capacity of 10 MW started up on the 26th of January 1953. In the plant in *Knapsack*, the production of phosphorus was ceased at the beginning of the 1990ies.

Table 1 shows details about the production at the old German sites of production of elemental phosphorus *Bitterfeld* and *Piesteritz* in 1936.

**Table 1:** Details about production at the old German sites of production of elemental phosphorus Bitterfeld and Piesteritz in 1936 [4]

| **company** | I. G. Farbenindustrie Aktiengesellschaft | |
|---|---|---|
| **place** | **Bitterfeld** | **Piesteritz** |
| **street** | Äußere Zörbigerstr. | . |
| **land/province** | Sachsen (a) | Sachsen (a) |
| **district** | Bitterfeld | Wittenberg |
| **employees at the end of December 1936** | 287 | 512 |
| **use of raw phosphate of domestic origin [t]** | - | 17 |
| **use of raw phosphate of foreign origin [t]** | 10,433 | 132,237 (b) |
| **production of elemental phosphorus [t]** | 1,605 | 17,440 |
| **thereof processed at phosphorus oxides [t]** | 383 | 17,301 |
| **thereof processed at phosphorus compounds [t]** | 599 | - |

(a) nowadays Sachsen-Anhalt, (b) hereof 3429 t from Russia, 128.808 t from USA (hereof 87.250 t Florida-pebble)

### 3.2 Investigations on-site

For more detailed researches regarding the accumulated radionuclide inventory and on-site/laboratory radiological investigations, some of the sites had been selected. In the following, examples will be described:

**"Chemische Fabrik Budenheim KG", (*Budenheim* near *Mainz*)**

Estimated accumulation of phosphogypsum: 2 million tons; in recent time, underground disposal of residues; company did not permit measurements on the factory premises, therefore the measurements were made around the factory fence: 200 nSv/h on one location (double background).

**"Chemische Werke vorm. H. & E. Albert, Wiesbaden" (*Mainz-Amöneburg*)**

Phosphogypsum: 11,000 t in 1936; company did not permit measurements on the factory premises, therefore measurements around the factory fence: 120 nSv/h on two locations (slightly increased background value).

**Industrial site *Bitterfeld*, among others “I.G. Farben AG”**

In the past, slag, sludge and effluent were mostly deposited in pits on the factory premises; later (since 1974), calcium silicate slag has been recycled as insulating material and as road grit; latterly, the residues were placed in underground disposals investigations of streams: no contamination.

**Industrial site *Piesteritz* , among others. “I.G. Farben AG”**

Ferrophosphorus: 3.000 t in 1936, calcium silicate slag: 130.000 t in 1936; no knowledge about the residues before 1945; dumping and recycling of residues (insulating material, road grit) after 1945.

**Phosphogypsum dump “Guano Werke” (*Nordenham*)**

Phosphogypsum resulting from the fertilizers production has been deposited from 1964 to 1967: on average 290 Bq/kg Ra-226, 360 Bq/kg Pb-210, < 6 Bq/kg U-238, max. 102 nSv/h (background 89 nSv/h); the radium activity in the ground-water is higher in the down-stream flow (Ra-226: 30 mBq/l, Ra-228: 80 mBq/l) than in the up-stream flow (Ra-226: < 10 mBq/l, Ra-228: 20 mBq/l).

**Above-ground disposal “*Knapsack-Hürth*”**

1975 to 1992: dumping of $6.5*10^6$ tons of calcium silicate slag and $6*10^6$ tons of gypsum.

Fig. 4 shows the individual positions of the investigated sites on a map of Gwermany.

**Figure 4:** Positions of selected sites for detailed investigations

### 3.3 Investigations in detail

As an example for investigations in detail, the phosphogypsum dump “Guano Werke” (*Nordenham*) was choosen for this paper.

The Superphosphorus Plant in *Nordenham* (“Superphosphatfabrik Nordham”) was founded on the 22nd of November 1906 and produced fertilizer. In 1956 the plant was sold to the “Guano Werke AG” which belongs to the “BASF AG” company since 1969. The production was ceased in 1987 and the industrial ground was also remediated.

Nowadays there exists only a dump on which from 1964 to 1967 approximately 300,000 tons of phosphogypsum from the fertilizer production (probably by means of phosphoric acid produced in the own plant) were deposited. Florida phosphat was mainly processed. No information regarding the fate of residues from other years of production are available at date.

The dump belongs nowadays to the town of Nordenham. Fig. 5 shows the dump in a non-remediated state and Fig. 6 shows clearly the present recultivated state.

**Figure 5:** Photo of the phosphogypsum dump in *Nordenham* in 1984 [5]

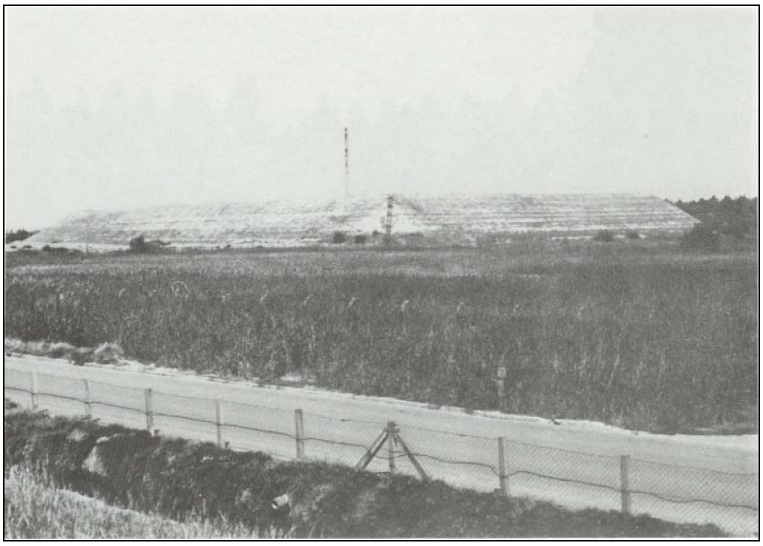
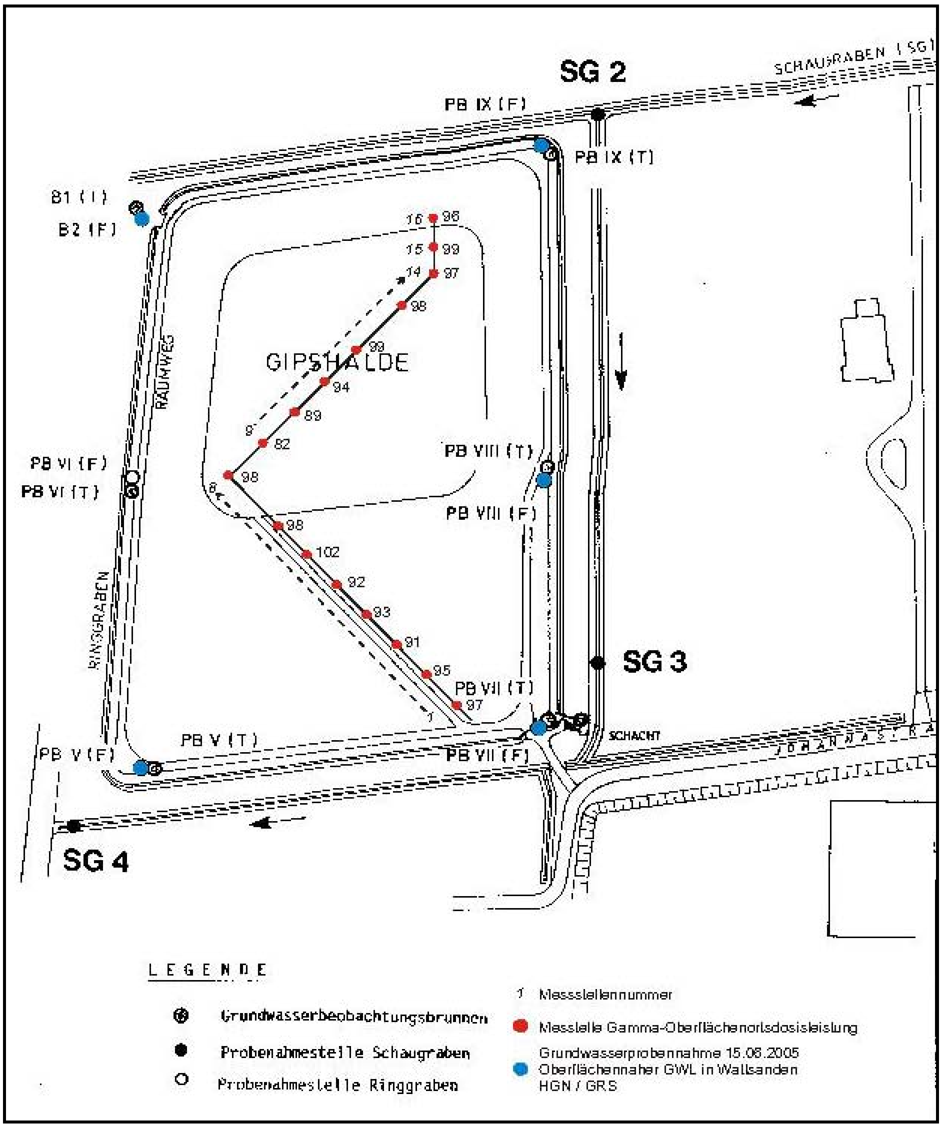


**Figure 6:** Recultivated phosphogypsum dump in Nordenham at the time of the radiological investigations

The gamma radiation dose rate was measured at 16 measuring points. The measuring points are presented in Fig. 7.

**Figure 7:** Location of phosphogypsum dump in Nordenham with measuring points (red points: gamma radiation dose rate, blue points: sampling of the ground-water)




The sampling of material on the dump itself was not regarded as reasonable because of the advanced remediation and the covering already made. According to investigations made in 1985 (before the remediation) the average Ra-226 activity was of 290 Bq/kg, the Pb-210 activity 360 Bq/kg and the U-238 activity < 6.2 Bq/kg [5].

At 5 sampling points along the edge of the”phosphogypsum dump”, ground-water samples were taken from the near-surface aquifer. The locations of sampling are marked in Fig. 6 by blue points. The sampling took place on the 15th of June 2005.

The locations for sampling of the ground-water B 2 F and PB 5 F are in the up-stream flow, while all other are situated in the down-stream flow.

Table 2 shows the measurement results of the gamma radiation dose rate (measuring points see Fig. 7). Table 2 contains also details on vegetation and slope. The background is of 89 nSv/h and the maximum measured has been of 102 nSv/h.

**Table 2:** Gamma radiation dose rate on single locations at the phosphogypsum dump in Nordenham

| Measuring point corresponding to Fig. 7 | Gamma radiation dose rate (nSv/h) | vegetation | slope |
|---|---|---|---|
| 1 | 97 | Grass | Moderate steep |
| 2 | 95 | Grass | Moderate steep |
| 3 | 91 | Grass | Moderate steep |
| 4 | 93 | Grass | Moderate steep |
| 5 | 92 | Grass | Moderate steep |
| 6 | 102 | Grass | Moderate steep |
| 7 | 98 | Grass | Moderate steep |
| 8 | 98 | Grass | Flat |
| 9 | 82 | Grass | Flat |
| 10 | 89 | Grass | Flat |
| 11 | 94 | Grass | Flat |
| 12 | 99 | Grass | Flat |
| 13 | 98 | Grass | Flat |
| 14 | 97 | Grass | Flat |
| 15 | 99 | Grass | Flat |
| 16 | 97 | Grass | Moderate steep |
| background | 89 | . | . |

Table 3 shows the activity of the taken ground-water samples.

**Table 3:** Activity of samples from ground-water at the phosphogypsum dump in Nordenham

| point of sampling | activity [Bq/l] | | | | | | |
|---|---|---|---|---|---|---|---|
| | U-238-series | | | Th-232-series | | U-235-series | K-40 |
| | U-238 | Ra-226 | Pb-210 | Ra-228 | Th-228 | U-235 | |
| B 2 F | *< 0.14* | *< 0.01* | *< 0.06* | 0.03 ± 0.02 | 0.02 ± 0.01 | *< 0.02* | 2.98 ± 0.06 |
| PB 5 F | *< 0.20* | *< 0.05* | *< 0.06* | 0.02 ± 0.01 | 0.008±0.004 | *< 0.01* | 0.36 ± 0.02 |
| PB 7 F | *< 0.14* | 0.04 ± 0.01 | *< 0.06* | 0.07 ± 0.02 | 0.02 ± 0.01 | *< 0.02* | 1.39 ± 0.06 |
| PB 8 F | *< 0.12* | 0.02 ± 0.01 | *< 0.07* | 0.08 ± 0.02 | 0.02 ± 0.01 | *< 0.03* | 0.93 ± 0.06 |
| PB 9 F | *< 0.16* | 0.02 ± 0.01 | *< 0.06* | 0.08 ± 0.02 | 0.02 ± 0.01 | *< 0.02* | 1.21 ± 0.06 |

The radium activity in the ground-water is higher in the down-stream flow (Ra-226: about 20 to 40 mBq/l, Ra-228: about 70 to 80 mBq/l) than in the up-stream flow (Ra-226: < 10 mBq/l, Ra-228: about 20 to 30 mBq/l). Ra-228 shows always higher values than Th-228. Due to the fact that radium is enriched in phosphogypsum (compare Fig. 1), we can consider it as a sign for the entry of radionuclides from the dump body in the ground-water aquifer.

## 4. Conclusion

NORM legacies were distributed during the time in the environment or are deposited until now (partly hidden) concentrated in places in the environment or in industrial and residential areas. With the aid of historical investigations even today the identification of locations with relevant amounts and activities is possible. However, the situation is complicated by an ambiguous legal basis for NORM legacies.

**Acknowledgements**

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