Identification of NORM Facilities in Bulgaria – Methodical Approach and Results

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Introduction

Methodical approach

(1) Pre-check of industry sectors based on the positive lists from IAEA and EC.

(2) Selection of available and accessible facilities or sites.

(3) Preparation of a facts finding mission. Identification of waste types of potential concern from a process analysis.

(4) Facts finding mission with in-situ measurements and sampling.

(5) Evaluation of results with exposure estimations and conclusions regarding a national positive list.

Pre-check
Macroeconomic approach – based on the international positive lists

- Extraction of rare earths from monazite
- Production of thorium compounds and manufacture of thorium-containing products
- Processing of niobium/tantalum ore
- Oil and gas production
- TiO_2 pigment production
- Thermal phosphorus production
- Zircon and zirconia industry
- Production of phosphate fertilisers
- Cement production, maintenance of clinker ovens
- Coal-fire power plants, maintenance of boilers
- Phosphoric acid production
- Primary iron production
- Tin/lead/copper smelting
- Ground water treatment

positive list specifies what activities may be subject to regulation.

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Any industry that is not on the list should be exempted from notification.

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However, EU Member States may add industrial activities to the list if the national authorities identify other activities requiring regulatory attention.

Possible industries of concern in Bulgaria in result of pre-check

- Extraction of rare earths from monazite
- Production of thorium compounds and **manufacture of thorium-containing products**
- Processing of niobium/tantalum ore
- **Oil and gas production**
- TiO_2 pigment production
- Thermal phosphorus production
- **Zircon and zirconia industry**
- **Production of phosphate fertilisers**
- **Cement production, maintenance of clinker ovens**
- **Coal-fire power plants, maintenance of boilers**
- Phosphoric acid production
- [illegible]

Out of operation

- **Tin/lead/copper smelting**
- **Ground water treatment**

Selection of facilities or sites
(for exemplary investigations)

Site	Industry
Pernik/Blagoevgrad	Drinking water utility
Eleshnitsa	Former uranium mine, treatment of mine effluent
Mezdra	Ceramics production using Zircon/Zirconia
Varna (Agropolihim)	Phosphate fertilizer production
Maritsa-Radnevo	Coal-fired power plant
Asarel-Medet, Panagyurishte	Copper ore mining and smelting
Ihtiman	Production of thoriated welding rods
Momin Prohod Hisarya, Narechenski Bani	Mineral water springs and spas
Dolni Dabnik, Pleven	Oil/gas production

Preparation of a facts finding mission. Identification of waste types of potential concern from a process analysis.

Positive lists describe industry sectors of concern

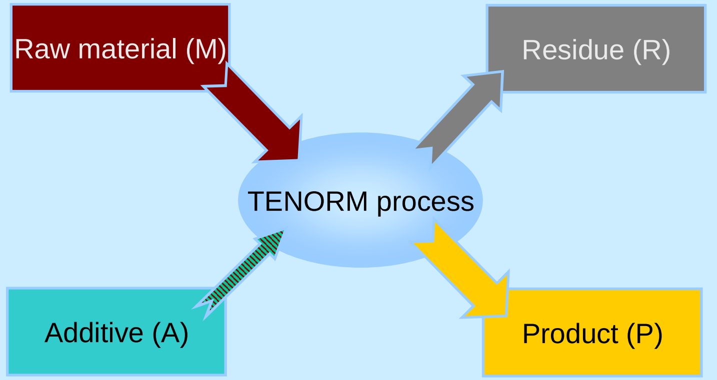
These sectors cover a wide variety of possible facilities, workplaces and waste streams

→ Facts finding must be focussed on materials of concern and workplaces related to these materials.

→ Materials of concern can be identified by a process analysis using a balance model (Fig.)

Balance model describing TENORM formation

→ The process of TENORM formation can be characterised by four parameters



The model helps …

- to identify the relevant parts of an operation based on general physical or chemical considerations,
- to select the appropriate radiation detectors (e.g., beta-sensitive devices if thermo-dust dominated by Pb-210 is expected),
- to give detailed instructions to the laboratory to which samples are sent, to use appropriate spectrometry equipment (e.g., Pb-210: 46 keV line),
- to draw conclusions on the age of residues (e.g., from the activity ratio of Ra-228 and Th-228).

Preparation of the facts-finding mission

- Detailed "industry fact sheets" were prepared and sent in advance to the site operators. They contained information about the technological processes, which typically lead to the formation of NORM, the types of radiation (γ, β) encountered, and a motivation letter describing why radiation protection may be an issue in the industry.
- As a methodical tool for the inspection teams checklists and instructions regarding on-site sampling equipment, sample storage/transportation (solid, liquid), use and calibration of radiation measuring devices as well as health and safety instructions were prepared.

2 Phosphate fertilizer production

2.1 Description of the technical process

Phosphate fertilisers are made from phosphate ores by transforming the phosphorous compounds into a more plant-available form. The raw material required for the production of phosphate fertilisers is phosphatic rock.

There are two distinct types of process, which lead to different types of wastes with different radiological properties:

- Sulphuric acid process (H_2SO_4 process)
- Nitric acid process (HNO_3 process)

They are described in the following sub-sections.

2.1.1 Sulphuric acid process

The sulphuric acid process is the standard process to turn phosphate rock into fertilizer.

Apart from the initial phosphate rock the following substances are involved: ammonia (NH_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potash salts, ammonium sulphate, ammonium phosphates, magnesium salts, dolomite, boron compounds, zinc sulphate, talcum and coating agents as additives.

Figure 2 (a) presents a simplified block flow diagram of the production of SSP in a so-called den.

In order to enable the reaction with sulphuric acid, the phosphate rock is ground in a mill and then fed into a mixer, where the phosphate rock is mixed with sulphuric acid (concentration of about 75%) at the required rate. The reaction between sulphuric acid and the fluorapatites contained in the phosphate rock proceeds in two stages. At first, the insoluble phosphate rock is converted into soluble phosphoric acid leading to the wastes of solid calcium sulphate (phosphogypsum), which is produced at an amount of 5 tons per ton phosphoric acid and usually dumped close by the processing plant, and volatile HF:

$$Ca_5F(PO_4)_3 + 5\,H_2SO_4 \rightarrow 3\,H_3PO_4 + 5\,CaSO_4 + HF$$

The second step is to mix the phosphate rock with the produced phosphoric acid, which then leads to SSP and once again HF as waste:

$$Ca_5F(PO_4)_3 + 7\,H_3PO_4 \rightarrow 5\,Ca(H_2PO_4)_2 + HF$$

After a mixing time of 1-3 minutes, the reaction mass is discharged from the mixer onto a continuously moving enclosed conveyor in a den, which has a slow moving circulating floor. The mass is held in the enclosed area for a residence time of about 20-40 minutes to enable solidification, thereby moving to the end of the den. The solidified mass is then broken up by a cutter and transferred via an enclosed conveyer to a storage pile for "curing" at least for 1 week in order to complete the reaction. Waste gases containing dust and considerable amounts of HF and SiF_4 arise from the dissolution of phosphate rock in sulphuric acid. Those waste gases are treated by wet scrubbing, from which waste water emissions arise

Facts finding mission with in-situ measurements and sampling.

No access allowed

BSS Category	Industry/Facility	NORM relevance
Oil and gas production	Several places near Pleven	Radioactive scales and sludges as residues
Production of thorium compounds and manufacture of thorium-containing products	“ELECTRODES” JSC, Ihtiman	Maybe production of thoriated electrodes; One product was purchased and analysed

Facts finding mission with in-situ measurements and sampling.

Visited sites

BSS Category	Industry/Facility	NORM relevance
Ground water treatment	Water works in Blagoevgrad (1)	Using sand filters for water purification
Zircon and zirconia industry	Techceramics-M in Mezdra (4)	Applying Zircon/Zirconia as additives in small amounts
Production of phosphate fertilisers	Agropolychim near Varna (6)	Using phosphate rocks as raw material
Coal-fire power plants, maintenance of boilers	TPP Maritsa East 2, Radnevo (7)	Production of ashes and slags as waste
Tin/lead/copper smelting	Assarel Medet, copper mine near Panaguyrishte (8)	Possible production of dusts and slags as waste

Facts finding mission with in-situ measurements and sampling.

Not visited, but samples analysed

Category	Industry/Facility	Task/NORM relevance
Spas, Mineral springs	Momin Prohod	Samples were taken by DIAL and analysed by IAF; Parameters: Alpha-particle spectroscopy: • U-238, U-234, Ra-226, Gamma-ray spectroscopy • Rn-222
	Hisarya	
	Narechenski Bani	

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Site 3: Eleshnitsa WTP (former Uranium mining)

Ambient gamma dose rates

Outside the water treatment plant	130 nSv/h
Inside the hall of the water treatment plant	90 nSv/h
At the water treatment column in the hall (face-to-face)	170 nSv/h

Site 3, Eleshnitsa:
Conclusion of radionuclide analysis

- The sludges in the lagoon and the sludge arising from the treatment process have similar activity concentrations.
- Water treatment reduces Ra-226 concentration by a factor of about 25 and uranium by two orders of magnitude.
- Ra-226 concentration of the purified water is comparable with that of drinking water. U-238 concentration is somewhat elevated but still in an interval characteristic for drinking water.
- U-238 concentration in the brook in which the purified water is discharged, is about 10 times higher than the treated water.

→ The environment is characterized by elevated levels of natural radioactivity. No further adverse effects on environment.

Site 4: Ceramic industry, TechCeramics-M (Mezdra)

Ceramic plate from Kozlodoy

Ambient gamma dose rates and Radon

- An ambient gamma dose rate <u>outside the buildings</u> and <u>inside was about 70 nSv/h</u> → <u>very low background level</u>.
- Only small amounts of materials with enhanced radioactivity.
- Company enforced strict H&S rules (wearing dust protection masks wherever dust concentrations may be high) → Additional radiation protection measures are not necessary.

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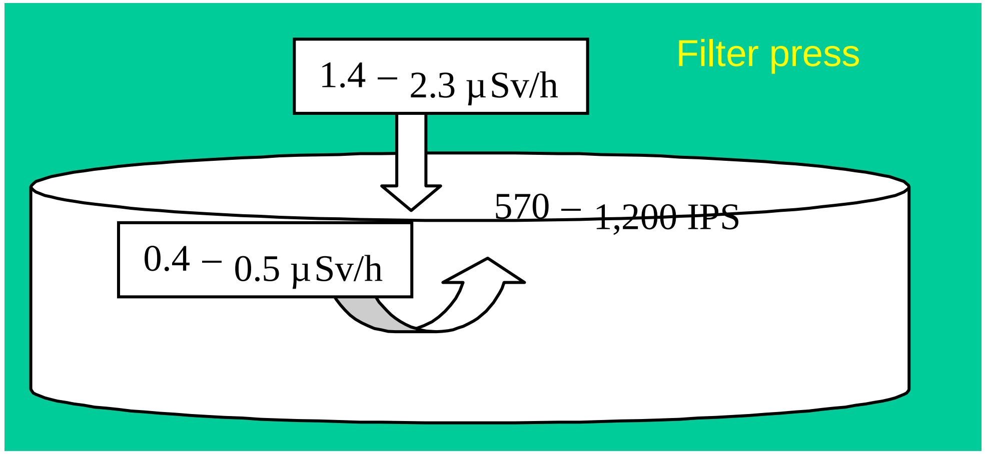
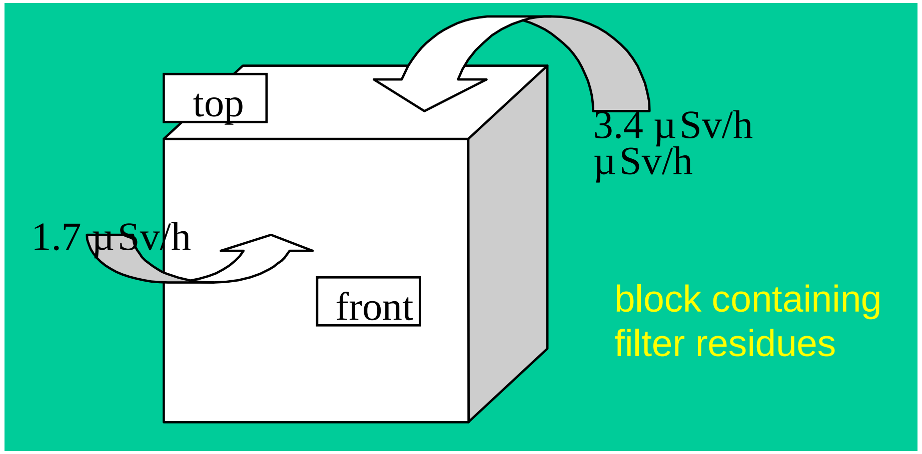
Site 6: The company Agropolychim near Varna





Ambient gamma dose rates

- empty filter press: 0.4 - 2.3 µSv/h
- concrete containers: 1.7 - 3.4 µSv/h outside of the building

- still large uncovered parts
- gamma dose rate: 250...320 nSv/h

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Site 7: Coal-fired power plant Maritsa East 2 (Radnevo)

Ambient gamma dose rates

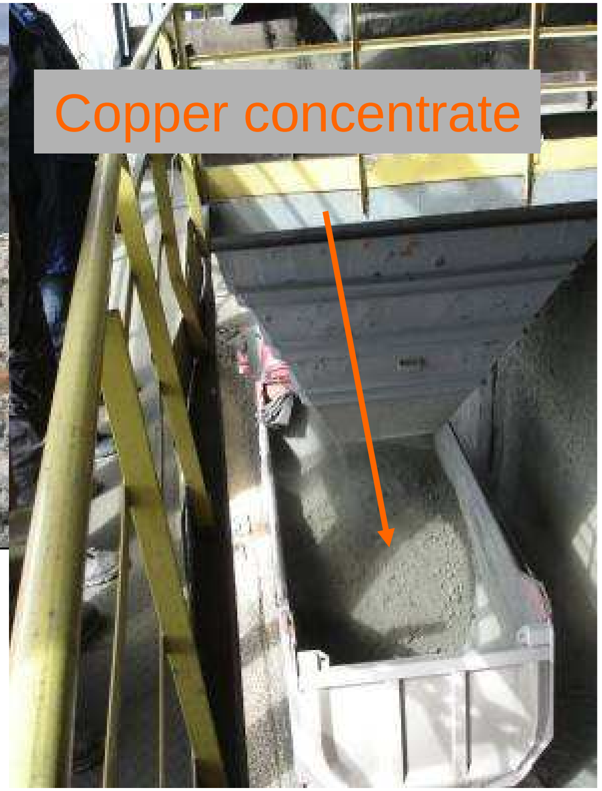
- An ambient gamma dose rate of about 60 - 80 nSv/h was registered <u>outside the buildings</u> and <u>inside</u>. This can be interpreted as a <u>very low background level</u>.

Site 7, CPP Maritsa East 2
Conclusion of radionuclide analysis

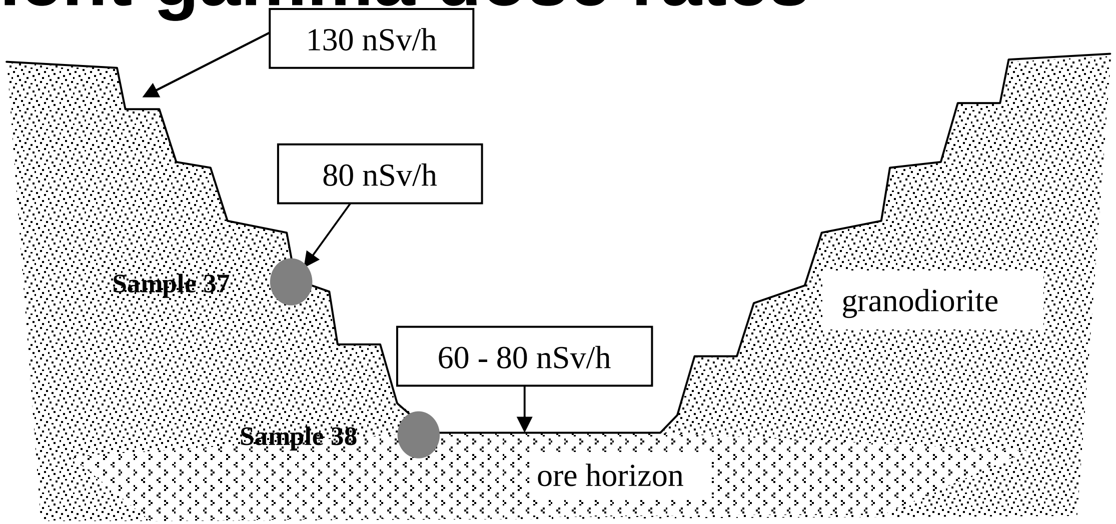
- Radioactivity of coal is about 70 Bq/kg for U-238 and Ra-226.
- Radionuclide composition of the coal varies due to the mineral admixtures (relatively high portion of mineral sands).
- After combustion radioactivity is concentrated in bottom slag and fly ash. Uranium, radium are enriched only by a factor 2
- The gypsum from the flue gas de-sulphurization has almost no radioactivity. Radon exhalation from the plasterboards can neglected.

→ activity levels do not indicate exposures of concern

Site 8: Assarel Medet open pit mine (Copper), Panagyurishte



Ambient gamma dose rates



Sites 10, 11, 12: Spa's

- Momin Prohod
- Hisarya
- Narechenski Bani

	U-238 [mBq/l]	U-234 [mBq/l]	Ra-226 [mBq/l]	Rn-222 [Bq/l]
Mineral water from Momin Prohod	550	600	213	795
Mineral water from Hisarya ("Momina salsa" spring)	135	122	11	207
Mineral water from Narechenski Bani ("Ochno Izvorche" spring)	19	22	8	62

Experience gained

- A plant may not be operational at the time of the investigation but temporarily shut down for maintenance. Raw materials and residues may therefore not be available for sampling.
- Raw materials used at the time of the site visit may coincidentally not be representative. In particular, their radiological properties may be untypical.
- Raw materials and processes may change. For example, a phosphate fertilizer plant may import raw phosphate from different sources with varying radionuclide concentrations. Dust filters may be installed in the future, which minimize airborne discharge of dust but necessitate the management of filter dust rich in Pb-210 and/or Po-210.
- The level of radioactivity in the raw materials may significantly vary between individual sites. This is particularly true for mineral water springs and spas, and natural oil or gas production sites. Therefore, even if a particular site shows no elevated level of radioactivity, this is not sufficient to draw a firm conclusion for the entire industrial sector in the country.

Evaluation of results with exposure estimations

- Objective:
  - „conservative-realistic“ to „conservative“
  - identification of most important exposure pathways
  - order of magnitude, no details!
- No standardised dose calculation approach available for Bulgaria, e.g., for
  - Consumption rates
  - Dwelling indoor and outdoor
- Reasonable assumptions must be made
- German „BMU 99“ approach used

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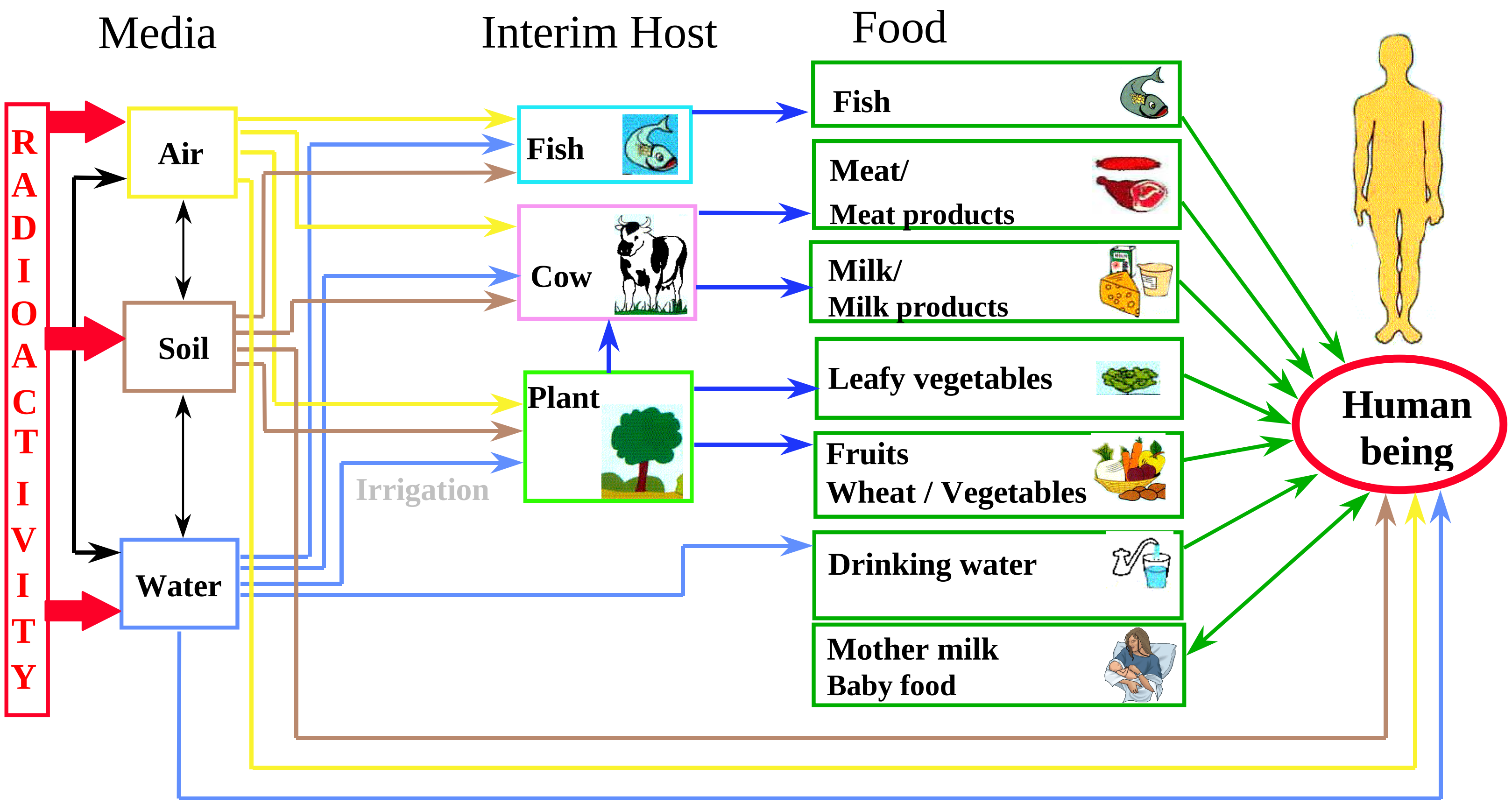
Evaluation of results with exposure estimations



Realistic assumptions regarding the behaviour of site operators and members of the public are used

General remarks

For any decision about the regulatory needs we have to distinguish:

- Existing situations at present
- Situations that may exist in future resulting from changes in the economy.

- No intention to deliver „precise“ or „absolute“ effective doses
- The objective is an indication of the order of magnitude and thus of the relevance of a given industry/scenario
- Question reduces the effective dose
  - **well below 1 mSv/a?**
  - **coming close to 1 mSv/a?**
  - **definitely exceeds 1 mSv/a?“**

Results

- Coal-fired power plants
  - No relevant doses (<< 1mSv/a)
  - Use of fly ash for construction purposes must be restricted
- P-Fertilizers
  - Workers may experience high doses (> 1mSv/a)
  - Public/Environment: Water pathway must be controlled
- Th-containing welding rods
  - Workers: doses may exceed 1 mSv/a
  - Public: not relevant
- Drinking water treatment
  - Currently not an issue, but U removal due to new WHO guideline may lead to problems
  - Don‘t use radioactive filter sands in construction materials

Results (2)

- Mine dewatering: not an issue
- Geothermal water
  - Workers: < 1 mSv/a
  - Public (future developments): > 1 mSv/a
- Non-uranium mining
  - Workers: currently not an issue, but may vary between sites
  - Public: doses < 1mSv/a (low background area)

Conclusions

- Bulgaria is a region of low background radioactivity, owing to its geology in wide parts of the country.
- The limited number of sites, which were available for the surveys makes it difficult to identify such work activities, which are really of concern regarding naturally occurring radioactivity in Bulgaria in a comprehensive fashion, but allows the conclusion that the number of industries and sites requiring regulatory attention is limited to a small number.

Conclusions

- With an expected economic growth, and possible changes in feedstocks and/or technologies of NORM industries in Bulgaria, a Positive List restricted to the current situation seems inadequate. Therefore, a Positive List has been developed, which includes a broad summary of potential NORM industries that may be of concern in Bulgaria. This ensures compatibility with the Positive List of the revised EU BSS. Furthermore, the proposed Positive List supports the administrative execution by specifying the processes and the materials, which need a regulatory attention.

Conclusion

- In summary, the investigation provided an overall picture of the Bulgarian situation with respect to NORM, and formed the basis of deriving the level of the necessary regulatory regime for work activities and materials involving NORM in Bulgaria. The methodology chosen has turned out to be practicable and adequate. It can be applied to other regions or countries, which require a systematic investigation of naturally occurring radioactivity in their industry.