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ALUM SHALES CAUSING RADON RISKS ON THE EXAMPLE OF MAARDU AREA, NORTH-ESTONIA

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The Maardu area is among the most polluted regions in Estonia. Past pollution here comes mainly from the phosphorite mining and processing. Waste hills at Maardu contain some 73 million tonnes of alum shale comprising over two million kg of uranium, which leaches into the surface and ground waters and enters the Gulf of Finland. High radon concentrations up to 10 000 Bq/m^3 *have been recorded on the outcrops of alum shale and they are dangerous to human health.*

Introduction

Estonia, the northernmost of the Baltic States, is situated on the southern slope of the Fennoscandian Shield in the northwestern part of the East-European Craton. Estonian nature is variegated and rather well protected. Biological diversity is high.

In the National Environmental Strategy, approved by the Estonian Parliament on March 12, 1997 [1] nearly 40 significant environmental problems were identified. Among priority environmental problems, past pollution resulting from industrial, agricultural and military activities in the former Soviet Union were mentioned. The problems of the past pollution had high priority also in the new environmental strategy compiled for the years up to 2030, and approved by the Estonian Parliament on February 14, 2007 [2]. The Maardu area in northern Estonia is one of the most polluted locations in the Republic (Fig. 1). This is particularly due to long-term phosphorite mining and processing in the region.

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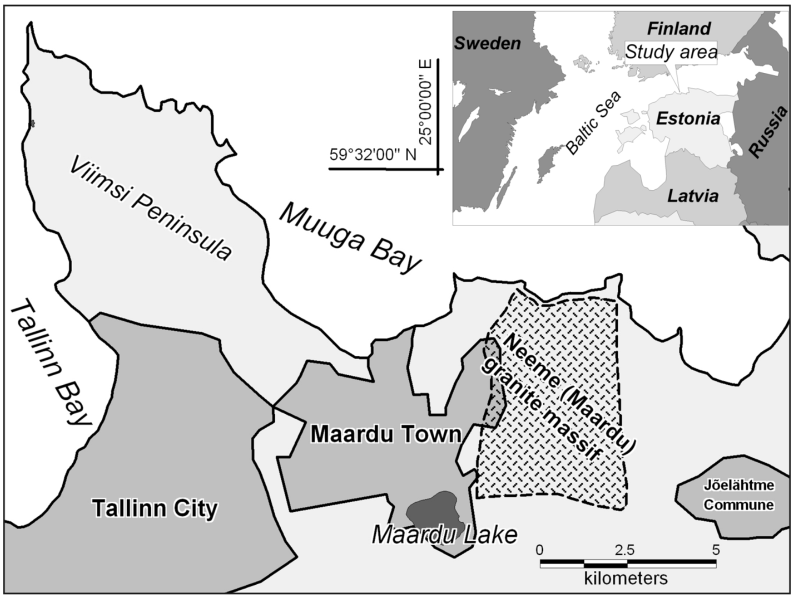

Fig. 1. The location of the study area.

The origin of chemical degradation and contamination of the environment, including soil, water and air is complicated. The principal factors causing contamination in the Maardu area are pollutants leaching out from phosphorite traps. On the outcrops of alum shale (Dictyonema argillite, Dictyonema "shale"), radon emissions are sporadically dangerous.

Geological setting

In this paper environmental situation in the surroundings of Maardu town and in the western part of Jõelähtme commune will be analysed. Geostructurally, the area is located on the north-western border of the Russian Platform. Here the crystalline basement, made up of magmatic and metamorphic rocks, is overlaid by sedimentary bedrock. The bedrock is covered with soft Quaternary deposits. In the crystalline basement, which is a continuation of the southern Finland Svecofennian orogenic belt, the metamorphic and magmatic rocks of the Lower Proterozoic Jägala complex as well as the intrusive porphyry-like potassium granites of the Neeme massif can be distinguished. The upper surface of the basement is some 150 metres below the sea level. The majority of the metamorphic rocks are made up of biotite, quartz-feldspar and mica amphibole gneisses and amphibolites. The upper part of the basement has suffered heavy chemical weathering down to a depth of 20 m, forming a clay-like crust [3].

The sedimentary cover formed of Neoproterozoic and Palaeozoic rocks, is 100–150 m thick and follows the topography of the basement surface. The

Kotlin sedimentation of the Vendian (Ediacaran) complex (ca 540–610 million years old) is represented by clastic rocks (sandstone, siltstone, claystone). The Cambrian rocks (ca 490–540 million years old) are also prevailingly sandstone, siltstone and claystone. The thickness of the Ordovician rocks in the area under consideration is around 60 metres. The Lower Ordovician rocks (ca 470–490 million years old) are tremendously diversified. One can find the phosphatic Obolus sandstone, including brachiopod bivalves and fragments, radioactive alum shale, glauconite-rich gray bentonite clay and glauconitic sandstone. The Middle Ordovician rocks (ca 460–470 million years old) in the area are represented by ca 15–20-metre-thick carbonate rocks [4].

Alum shale is rich in uranium and other valuable microelements (Mo, V, Th, Ra). During the opencast mining of phosphorite at Maardu, radioactive alum shale (average uranium content 80–120 g/t, maximum 300–450 g/t) was deposited in waste dumps. In 1989, opencast mining at Maardu was carried out in an area of 6.36 km^2. Waste hills at Maardu contain 73 million tonnes of alum shale. If there were only the possible minimum content of uranium, 30 g per tonne of alum shale, then 2.19 million kg of uranium would leach into the surface and ground waters [5].

Brief history of the phosphorite mining

The first written data available on the use of Obolus phosphate rocks date from the 19th century. In 1861, C. Schmidt stressed the significance of Obolus sandstone as a possible raw material in the manufacture of artificial fertilisers, which is easy to enrich through sifting [6]. The best sites for excavating the rock were located west and northeast of the town of Maardu, near Iru Village close to the Pirita River and at Ülgase near the coast of the Gulf of Finland. The Iru site was discovered during World War I while digging trenches and ammunition storages for the artillery.

In 1920, the joint-stock company Estonian Phosphorite was founded by Estonian agricultural activists with the aim to mine phosphate rock. A mine and an enrichment plant were established in Ülgase at the expense of the company. The capacity of the facilities was planned to be 4,000 tonnes of ground phosphate rock per year; it was reached in 1936. The height of the underground passages was 1.3–1.6 m. The phosphate ore was broken off by hand and delivered by horizontal workings to the Ülgase enrichment plant, established in a klint terrace over Hõbemägi. The portion of the ground and sieved phosphate concentrate meant for export was carried out via the port at the Koljunuki Cape. In 1938 the enrichment plant burnt down, but already in 1939 the joint-stock company Estonian Phosphorite started building a new factory. After the war the plant was enlarged. The highest annual output reached 850 000 tonnes of raw material, most of which was used for producing an uneffective fertilizer – phosphorite meal. At the end of 1955, a sulphuric acid plant started operating and in 1956 a superphosphate plant was launched. In 1965 underground mining was stopped and a complete transition to open-pit mining took place [7]. In order to use the limestone obtained as a by-product of open-pit mining, a crushed-stone plant was put into operation.

In Soviet times the plant was turned into a powerful chemical enterprise Estonian Phosphorite, where millions of tonnes of phosphate ore were mined and 15 different kinds of goods produced. It resulted in a high pollution of the air and water and overturning the soils. After Estonia regained its independence, the green movements started protesting against hazardous emissions into the atmosphere, and the plant was closed down in 1991 [8].

Self-burning of the alum shale (Dictyonema argillite)

Scientific research into spontaneous combustion of alum shale was spurred on by frequent events of self-ignition in the heaps of caprock of the Maardu phosphate rock mine. In transition from underground to open-pit mining in 1965, a 4–5 metre-thick layer of alum shale, found in the composition of caprock, was thrown in a heap together with other caprocks. This brought along a constant stream of ever new spontaneous combustion and burning sites in the Maardu quarry heaps (Fig. 2). In some places between the hills of surface layer mine waste, the temperatures in the heap occasionally exceeded 500 ºC.

Spontaneous combustion can occur in heaps that are both a few months as well as over 20 years old (Fig. 2). Spontaneous heat generation and combustion is usually most intense in 3–5-year-old heaps. In 1990, at the

Fig. 2. Alum shale with clear traces of burning after 20 years of mining. Photo by Madis Metsur.

average temperature of the heap, an estimated 520.3×10^3 tonnes of oxygen were spent on oxidizing the rocks buried in the heap. This equals to 6.6% of the annual oxygen output of Estonian forests during a 7-month vegetation period. The amount of gases emitted from burning shale was estimated as: $SO_2 = 10^4$ t and $CO_2 = 73.3\times10^3$ tonnes [9].

The extreme leaching of several components by the water filtrating through the heap, and their dispersion in the mine and in the groundwater, is also connected to the oxidation of shale. Per one square kilometre of the Maardu heap, an average of 1646.4 t of dissolved minerals was leached and dispersed in surface and groundwater. Of that amount, 72.9% was made up of ion SO_4^{-2}, 12.8% Ca^{+2}, 11.3% Mg^{+2}, 1.1% K^++Na^+ and the rest were various micro-components. The leaching from the heap is not directly dependent on the amount of water flowing through the heap, but rather on the intensiveness of the oxidation process of the rocks. The Maardu heap is a source of pollution, which will keep polluting the surface and ground water for a very long time (Fig. 3). The effluent of the Maardu mine and plant, which was directed into the sea via Kroodi Brook, delivered up to 20.18 million m^3 of water with very different levels of pollution into Muuga Bay each year. The amount of dissolved minerals delivered into the sea reached up to 38.4×10^3 t annually [9].

Fig. 3. Maardu phosphorite opencast 20 years after mining. Uranium is leaching into the water bodies. Photo by Madis Metsur.

The main negative environmental impacts caused by the spontaneous combustion of alum shale are:

1) the destruction and hindered development of flora on burning sites as well as the accumulation of damaging agents into the plants;
2) the anaerobic degradation of kerogen near the burning sites, bringing about a danger of organic pollution;
3) the quickening of the transport of heavy metals from the cooled burning sites in the extent of various magnitudes [10].

Influence on the ecological situation of Lake Maardu

Lake Maardu, which is surrounded on the north and east by former phosphorite open pits, is situated 15 km east of Tallinn, on the Viru-Harju limestone plateau near the Tallinn – St. Petersburg highway (Fig. 1). In the vicinity, there is a densely populated industrial town of Maardu. The lake attracts numerous holiday-makers and fishermen, but its ecological situation is rather bad. The lake has a surface area of about 1.7 km^2, its maximum depth is 3 m and catchment area 23 km^2.

Waste water from the phosphorite open pit has been conducted into the lake since 1972. The heavily polluted water from the northern open pit was diverted elsewhere in 1987, and phosphorite mining was terminated in 1991. Due this anthropogenic influence, Lake Maardu is among the most heavily polluted lakes in Estonia and the concentrations of Ca, Mg, SO_4, F, Mn, Ni, Cu, Zn and Mo in the water exceed the safe limits for inland waters up to several hundred-fold [11].

The main source of pollution in Lake Maardu has been the mining of phosphorite in the vicinity. Millions of tonnes of crushed deposits have been buried in the waste dumps of the Maardu open pit, comprising in some places up to 38% of alum shale. Under normal weathering conditions shale is easily oxidizing, and even spontaneous heating and ignition has taken place [12]. These processes lead to an annual leaching of 1500 tonnes of mineral matter per a square kilometre of waste dump, the resulting waste water being discharged into the lake and causing a drastic change in the sedimentation pattern [13].

Radioactivity and radon emissions

The main natural source of radiation in Estonia is radon. It concentrates in indoor air and its density differs from region to region. The main source of elevated indoor radon concentrations is the inflow of radon-bearing soil air. Therefore, knowledge of the concentration of radioactive elements – above all uranium – in rocks and soils is urgently needed to identify radon prone regions, areas and sites.

Immediately after World War II, research into the concentration of uranium and thorium in the bedrock of Estonia together with the studies of alum shale (Lower Ordovician Pakerort Stage) and phosphorite (to a lesser extent) were undertaken. As a result of these investigations, the Sillamäe region in North-East Estonia with the average concentration of uranium in alum shale 300 g/t, was deemed a suitable area to refine uranium. These investigations were top secret [14].

Extensive, but often indirect investigations of radon in the bedrock and soils began in 1958 in association with geological mapping at a scale of 1:200 000. Estonian uranium deposits were deemed nonviable in the 1960s, but investigations of uranium continued irregularly until the beginning of the 1970s.

In conjunction with prospecting for phosphorite deposits, determination of uranium and thorium concentrations in the alum shale and phosphorite was ubiquitous during 1972–1986.

Investigations specifically aimed at determining the concentration of uranium, thorium and potassium in Estonian soils began in 1985 in conjunction with systematic geochemical mapping of topsoil and subsoil. Indoor radon was first measured in 1985-1990 in the basement or on the ground floor of dwellings [15]. In 1995 the Estonian Radiation Protection Centre started systematic investigations jointly with the Swedish Radiation Protection Authority.

When compiling the radon risk map of Estonia at a scale of 1:500,000 [16] it appeared that on almost 33% of land area the content of radon (Rn) in soil air exceeds the safe limit for unrestricted construction (50 kBq/m^3). In such high Rn risk areas the concentration of Rn in the soil air ranges from 50 to 400 kBq/m^3, reaching occasionally 2100 kBq/m^3. In the indoor air of 33% of dwellings the concentration of Rn exceeds the permissible limit (200 Bq/m^3) and reaches 2000 Bq/m^3, in a few cases even 10,000 Bq/m^3 [17]. In high Rn risk regions, there is a good positive correlation between the content of Rn in soil air and indoor air of the dwellings in these areas.

According to the geological setting of Estonia, the major sources of Rn are the following:

1) Alum shale and Obolus sandstone (phosphorite) with a high concentration of Rn. These Lower-Ordovician rocks of subhorizontal bedding crop out in the North-Estonian Klint (escarpment) and in the slopes of buried valleys. Clasts and fines of radioactive rocks occur in variable concentrations in the Quaternary deposits all over Estonia;
2) Granitoidal material rich in U, Th and K transported to Estonia from the outcrop areas of crystalline basement rocks in Finland and the Gulf of Finland by glaciers;
3) Some varieties of Devonian sand- and siltstones with elevated concentrations of U (>3–4 g/t).

The areas with the highest concentrations of radon are located in the klint belt in Northern Estonia: right in the limits of the outcrop of alum shale and phosphorite, in the areas between the marine terraces and on the slightly sloping plains below them reaching towards the sea, but also in a number of places on the plains situated on the klint, where Maardu town is also located.

By direct measurements, the Rn content in the soil air of the heaps in the former Maardu phosphate mine is rather low and homogeneous, varying between 25–34 kBq/m^3. The Rn content computed after the U (Ra) content is also homogeneous, but nearly 12 times higher than by direct measurements, and varies between 218–625 kBq/m^3. This indicates that the aeration conditions in the heaps are very good and, hence, these are areas at high risk from radon. In Maardu area radon in soil air exceeds the safe limit for unrestricted construction (50 kBq/m^3). Radon is highly radioactive and carcinogenic element causing mutations, firstly lung cancer.

Conclusions

During the Soviet occupation not much attention was paid to the nature protection problems. Chemical industry and mining of phosphorites left behind heavy contamination in the Maardu area. Nowadays the pollution load is thoroughly monitored. However, up to now the radioactivity level in the region is high and radon emissions pose a threat to human health. New risks will probably arise if a deep granite mine will be opened in the Maardu area.

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