2023

Quality assessment of curative mud deposits in Estonia

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TERE KK field of curative mud and mud treatment

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Report

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Haapsalu, 2023

Version 10.05.23

The field of curative mud and mud treatment of
the Centre of Excellence in Health Promotion and Rehabilitation (TERE KK)
Quality Assessment of Curative Mud Deposits in Estonia 2022–2023
Funded by:
European Regional Development Fund (Project No 2014–2020.5.04.19–0372)
Responsible person: Galina Kapanen

Cover photo: Curative mud sampling in Haapsalu Tagalaht Bay (19 May 2022). Photo by Galina Kapanen

Recommended citation:
Kapanen, G.; Künnis-Beres, K.; Vaasma, T.; Eenlo, H.; Terasmaa, J.; Vandel, E. 2023. Quality assessment of curative mud deposits in Estonia 2022–2023. TERE KK, Haapsalu.

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→ Annotation

TERE KK (Centre of Excellence in Health Promotion and Rehabilitation) is a knowledge transfer centre operating under the Haapsalu College of Tallinn University, focusing on research, development, dissemination of information, and promotion of knowledge-based entrepreneurship in the field of curative mud and mud treatment, and exercise capacity. TERE KK has been operating in Haapsalu for almost ten years, and during this time has seen a rise in curative mud-related entrepreneurship and development in Estonia.

So far, neither the world nor Estonia have developed common normative standards to assess the quality of curative muds with complex and variable composition. TERE KK, under the leadership of experts in the field of curative mud, in cooperation with the Ministry of Social Affairs and the Health Board, prepared a draft regulation on curative mud under the Public Health Act: 'Requirements for natural mud and peat used in balneological procedures, their handling and labelling'. In order to ensure the quality of curative mud in Estonia's curative mud deposits, it is important to carry out monitoring and testing in accordance with the new draft curative mud regulation.

The study of curative mud identifies the current state of curative mud deposits in Estonia (in 2022), changes in the last decade, and the necessary information on the quality of curative mud.

Between 2022 and 2023, Stage I of the quality assessment was carried out, sampling three active deposits of curative mud: Haapsalu Tagalaht Bay, Käina Bay, and Värska Bay. Stage II of the study covers the Mullutu-Suurlaht Bay and Ermistu Lake deposits, where there has been no active extraction of curative mud in recent years. The timing of the activities of Stage II of the quality assessment is being specified, subject to funding availability. A total of 64 curative mud samples were collected in 2022. For the first time, the contents of hazardous substances such as phenols, petroleum products, and pesticides, in curative mud were investigated. Organic and mineral matter content, grain size, curative mud microbiology and heavy metal content were also examined. A total of 1,649 measurements/analyses were made.

Comparisons with previous data suggest that organic matter concentrations have been stable in both lake sediments (Värska Bay) and marine sediments (Haapsalu Tagalaht Bay and Käina Bay) over the last decade. The curative mud samples were found to have a relatively low microbiological contamination, indicating their cleanliness. The average concentration of C10–C40 petroleum products in Haapsalu is 42 mg/kg, in Värska 118.6 mg/kg. In the Käina curative mud, all petroleum products are below the limit of quantification (LoQ). Phenol concentrations are below LoQ (0.05 mg/kg) in all three deposits, except in Värska, where 4-methylphenol averaged 0.5 mg/kg. Pesticides found in five samples from Värska were dichlorodiphenyldichloroethylene (DDE, p,p) 1.7 mg/kg and dichlorodiphenyltrichloroethane (DDT) 4.2 mg/kg per sample. In all other sediment samples, pesticide levels were below the limit of quantification. Average concentrations of heavy metals in curative mud have decreased between 2013–2014 and 2022 and do not exceed the target value.

An important part of ensuring the consistency of the data on curative mud is the conduct of the planned study. The results of the study will allow curative mud-related entrepreneurship in Estonia to comply more easily with the new requirements described above.

1 Terms of reference

The Centre of Excellence in Health Promotion and Rehabilitation of Tallinn University Haapsalu College (TERE KK www.terekk.ee) is a knowledge transfer centre promoting research, development, dissemination, mediation, and application of knowledge in the field of curative mud and mud treatment and exercise capacity, as well as the development of knowledge-based entrepreneurship, which has been operating in Haapsalu for almost ten years. During this period, Estonia has seen a resurgence of business-oriented research and development in the field of curative mud. It is important to ensure that Estonian companies can operate on a level playing field in market conditions, which supports companies in providing the products and services of curative mud in Estonia and in export markets.

Throughout its history, Estonia's curative mud has been an important economic sector in Estonian tourism, which is why ensuring and maintaining good quality of curative mud and mud treatment is still relevant today (Terasmaa *et al.*, 2015). The sustainable and skillful use of curative mud offers a more natural alternative to synthetically produced, imported medical or cosmetic products with a higher environmental footprint, as curative mud is used as a local natural resource.

Today, while there are requirements for the marketing, storage, and use of curative mud, there are no requirements for the criteria needed to ensure its safety, such as the maximum levels of dangerous chemicals and microbes. Therefore, there is currently no legal basis to declare the curative mud contaminated and require its decommissioning. TERE KK, under the leadership of experts in the field of curative mud, in cooperation with the Ministry of Social Affairs and the Health Board, has prepared a draft regulation on curative mud under the Public Health Act: 'Requirements for natural mud and peat used in balneological procedures, their handling and labelling' (määruse eelnõu TERE KK, 2021). From the point of view of ensuring the quality of curative mud, the TERE KK experts in the field of curative mud consider it important and necessary to carry out monitoring and testing of criteria to ensure the safety of curative mud in Estonia's curative mud deposits as part of the new draft curative mud regulation.

2 Background information

What is considered to be curative mud depends on the regional context. For example, internationally, according to Gomes *et al.* (2013) generic definition of curative mud, or a peloid means a mature mud or mud suspension or dispersion with curative or cosmetic properties. It consists of a complex mixture of solid (fine grained materials of geological and/or biological origin) and liquid (mineral or sea water) substances and organic compounds commonly arising from some biological metabolic activity (*Ibid.*).

The term 'curative mud' has been in use in Estonia for a very long time, with 'peloid' and 'therapeutic mud' also used as synonyms. Estonia's curative mud is defined under two categories (Veinpalu & Veinpalu, 1976):

- → Sea mud, or peloid, which is composed of various marine mineral materials and contains more than 5% organic matter by weight of the total dry matter.
- → Lake mud, or sapropel, is freshwater sediment consisting of either clastic, organic or carbonate matter, with at least 35% organic matter by weight of the total dry matter.

Estonia's coastal bays and lakes contain large quantities of lake mud (sapropel) and sea mud (peloid), which is formed by the sedimentation of sand, mud, and clay particles and the sedimentation of decomposed organic matter that has lived there or been transported from the catchment to the bottom of the water body (Luha, 1946; Heinsalu & Veski, 1991).

There are five mud deposits in Estonia: Haapsalu, Käina, Värska Bay, Mullutu-Suurlaht Bay and Lake Ermistu (Figure 1), which were actively studied at the end of the last century (see Chapter 4 for more information on the general characterisation of the area).

Figure 1. Estonia's curative mud deposits.

In Estonia, mud is extracted from areas where there is a high risk of environmental contamination. The study *'Marketing, storage, and use of curative mud'* (Ravimuda turustamine ..., 2012) by the Health Board suggests that quality indicators for assessing the health safety of curative mud need to be further investigated and established. In this regard, between 2013 and 2014, a comprehensive examination was conducted on the surface sediments of curative mud, encompassing the collection of samples from all five officially recognized curative mud deposits in Estonia: Haapsalu Tagalaht Bay, Käina Bay, Mullutu-Suurlaht Bay, Lake Ermistu, and Värska Bay deposit (Terasmaa *et al.*, 2015).

The main environmental pollutants are persistent organic pollutants, bacterial infections, and heavy metals (Miko *et al.*, 2007). There are no normative standards for assessing the quality of complex and variable-formulation curative mud either in the world or in Estonia.

Although there are requirements for the marketing, storage, and use of curative mud, there are currently no requirements for safety criteria such as the permitted levels of dangerous chemicals and microbes. There is therefore currently no legal basis for declaring mud contaminated and prohibiting its use. TERE KK, in cooperation with the Ministry of Social Affairs and the Health Board, has provided the necessary input to the draft 'Requirements for natural mud and peat used in balneological procedures, their handling and labelling', based on the results of the 2013–2014 study. This draft replaces Regulation No 28 of the Minister of Social Affairs of 4 February 2002 'Health requirements for the marketing, storage, and use of curative mud' (which is no longer in force).

The aim of the quality requirements is to ensure that the mud used in balneological procedures is fit for purpose and to exclude the classification of other material as curative mud or peat for use in balneological procedures.

The draft regulation 'Requirements for natural mud and peat used in balneological procedures, their handling and labelling' consists of nine sections:

• § 1 of the draft regulation sets out the scope of the regulation, which is to lay down requirements for the health safety and handling of sea mud, lake mud, and peat used in balneological procedures.

• § 2 of the draft defines the new terms used in the regulation.

• § 3 of the draft sets out the requirements for the quality of sea mud, lake mud, and peat.

• § 4 of the draft sets limits for microbiological quality parameters in curative mud and peat.

• § 5 of the draft lays down the conditions for the storage of curative mud and peat.

• § 6 of the draft sets out the requirements for the labelling of curative mud and peat.

• § 7 of the draft sets out the requirements for the using of curative mud and peat.

• § 8 of the draft lays down the conditions under which the producer of curative mud and peat and the provider of the balneological treatment will be subject to safety inspections.

• § 9 will be entry into force of the regulation.

This draft curative mud regulation sets out the following requirements:

→ The provider of the balneological procedure must ensure the microbiological safety of the new batch of curative mud or peat before using it;

→ The producer of the curative mud or peat must have data on the content of hazardous substances in the curative mud or peat. Data on the content of hazardous substances in curative mud and peat must not be older than ten years;

→ The content of heavy metals (Pb, Cd, Sn, Zn, Hg), petroleum products (C10–C40 hydrocarbons sum), phenols and total pesticides is determined in the curative mud and peat. The assessment of the non-compliance of the content of hazardous substances in the curative mud or peat is based on the Regulation of the Minister of the Environment under § 83 of the Water Act, which establishes limit values for the content of hazardous substances in soil;

→ Data on the content of hazardous substances in curative mud and peat must not be older than ten years.

The choice of parameters will be based on the characteristics of curative mud and peat. For example:

- the presence of mineral particles with a grain size of more than 1.0 mm is not allowed in sea and lake mud;
- in curative mud and peat, the proportion of particles of 0.1–1.0 mm in size can be up to 3% in sea mud, 2% in lake mud, and 2% in peat;
- for organic matter content, the organic matter content in dry matter is taken into account, where it must be more than 5% in sea mud, more than 35% in lake mud, and more than 90% in peat;
- in terms of microbiological quality parameters, the regulation governs the presence of two indicator bacteria *Escherichia coli, Clostridium perfringens* and one pathogen *Staphylococcus aureus*.

Conducting the planned study is an important part of ensuring the consistency of the data for the monitoring of the curative mud. The results of the quatily assessment will also greatly facilitate compliance for companies in providing the products and services of curative mud in Estonia.

3 Project objective and schedule

Experts in the field of curative mud in TERE KK consider it important and necessary to ensure the quality of curative mud in Estonian curative mud deposits. It is therefore recommended that monitoring and testing should be carried out in accordance with the new criteria and requirements of the draft curative mud regulation to ensure the safety of curative mud for human use.

The objectives of the quality assessment study are:

1) to identify and map the state of Estonia's curative mud deposits in 2022;
2) to identify changes in the composition of the curative mud (last decade);
3) to provide businesses with the information they need for the use and product development of curative mud in terms of its quality.

By using the draft regulation 'Requirements for natural mud and peat used in balneological procedures, their handling and labelling', to analyse the following high-quality requirements:

- → the mineral composition of curative mud, its particle size and organic component;
- → the content of petroleum products (C10–C40 hydrocarbons sum);
- → the phenolic content;
- → the content of total pesticides;
- → the content of bacterial indicators and pathogens;
- → the content of heavy metals (Cd, Cr, Cu, Pb, Ni, Zn, Sr, Sn, Hg).

The study is planned to be carried out in two stages (Table 1). Between 2022 and 2023, it is planned to carry out Stage I of the quality assessment, sampling three active deposits of curative mud: Haapsalu Tagalaht Bay, Käina Bay, and Värska Bay. Stage II of the study covers the Mullutu-Suurlaht Bay and Lake Ermistu deposits, where there has been no active extraction of curative mud in recent years. The timing of this study is being specified, subject to funding availability.

Table 1. The research sampling and analysis plan: Stage I (2022–2023).

Mineral deposits	Number of sample points	Bacterial indicators and pathogen content, number of samples	Mineral and organic matter, number of samples	petroleum products, number of samples	pesticides, number of samples	phenols, number of samples	Heavy metals (Cd, Cr, Cu, Pb, Ni, Zn, Sr, Sn)	Heavy metals: Hg
Stage I								
Käina Bay	20	10	20	5	5	5	24	13
Gulf Tagalaht in Haapsalu	24	12	24	5	5	5	20	13
Värska Bay	20	10	20	5	5	5	13	13
Stage I in total:	**64**	**32**	**64**	**20**	**15**	**15**	**55**	**33**

4 General description of the study area

The majority of the Estonian curative mud sites in use and used in the past are located in relatively shallow sea bays (Haapsalu, Käina, Mullutu-Suurlaht, Voosi, etc.) and in lakes (Värska Bay, Lake Ermistu, Lake Kahala). During the quality assessment, samples are taken from three active curative mud deposits: Haapsalu Tagalaht Bay, Käina Bay, Värska Bay (Figure 1).

4.1 Haapsalu Tagalaht Bay

Haapsalu Gulf (58°97’94”N, 23°58’28”E) (Figure 2) is a part of Strait Sea (in Estonian Väinameri Sea), which has several peninsulas that divide it into smaller gulfs, varying in width between 2–4 km. The forebay is followed by the semi-enclosed shallow Haapsalu Tagalaht Bay. The back parts are formed by Tahu Bay and Saunja Bay (Ramst, 1983; Kask *et al.*, 1996; Kask & Kask, 2012). The geomorphology of Haapsalu Bay is mainly characterised by a surface relief of carbonate rocks and glacial sediments, with marine sediments occurring along the sea bay.

4.2 Käina Bay

Käina Bay (58°48’19’’ N, 22°47’11’’ E) (Figure 2) is located between the southeast coast of Hiiumaa and Kassari Island and is a part of the Strait Sea, about 10 km² in size. The shores of the bay have been shaped by the last ice age and are covered by marine sediment and various deposits. The bay is shallow with a maximum depth of 1 metre. Around Käina Bay, the marine sediments are variable and the shores are covered with different types of soil. There are sands, silts, pebbles, and fine-grained sediments, the latter mainly in the western part of the bay. The shores are predominantly covered with glaized carbonate loams, marshy carbonate soils and swampy peaty soils, bog soils and saline coastal soils, the latter being more common on Kassari Island. Käina Bay receives little freshwater inflow as most of the water flows out of the bay. The influx of freshwater increases in the second half of summer and reaches its maximum in autumn (Kask, Ermann *et al.*, 1997).

4.3 Värska Bay

Värska Bay (57°57'30 "N 27°37'26 "E) (Figure 2) is located in south-eastern Estonia, Põlva County, and is part of Lake Peipsi. The bay is shaped like an elongated flooded valley with Värska stream at its mouth. The width of the mouth of the bay is 1.3 km wide and extends northwards for 5 km. The surrounding slopes are weakly indented and the terrain is mainly composed of a variety of sands on unsorted glacial sediments. The bottom of the bay is mainly composed of brown sapropel, formed over millennia, with the remains of vegetation and lake organisms. The oldest sediments in the lake are up to 10,000 years old and lie on a peat layer underlain by Devonian sandstone (Põldvere, 2003). In addition to curative mud, mineral water is also an important mineral resource in the Lake Peipsi basin.

4.4 Curative mud deposits and reserves

Mud extraction in deposits is regulated by the Earth’s Crust Act (Maapõueseadus, 2016), which divides a deposit into several parts. Based on the Earth’s Crust Act:

> ‘Mineral deposit means the body or a part of the body of mineral resources delimited and explored by geological investigation or geological exploration and registered in the environmental register, together with the interbeds. Extraction of mineral resources means the operations performed for preparation of the removal of mineral resources from the natural state, removal of mineral resources from the natural state as well as transport and initial processing of the extracted mineral matter within the boundaries of the mining claim and the mine service plot. The state owns bedrock mineral resources and mineral resources in public water bodies. The natural body of bedrock, sediments, liquid or gas which is not registered belongs to the state and immovable property ownership does not extend thereto, unless the purpose of use of the immovable requires this. If a permit is required in order to remove mineral resources in state ownership from the natural state, the extracted mineral matter generated upon mining on the basis of the permit belongs to the holder of the permit; upon mining without the permit, the extracted mineral matter belongs to the state. A permit for the extraction of lake mud or sea mud is issued for up to 15 years.’

In accordance with the Earth’s Crust Act, mineral resources may be extracted from the part of a mining claim, which is determined as as the part of the natural resource designated for extraction or mining with a mining permit. The registered mineral resources (mineral reserves) is divided into proved reserves and probable reserves, depending on the extent of the research detail. In the area adjacent to the deposit, predicted reserves may also be defined. Proved reserves are mineral resources for which the extent of research detail provides data for extraction and exploitation. Probable reserves are mineral resources for which the level of research detail allows an assessment of the prospectivity of the resources and guides further geological exploration. Proved and probable reserves are classified as economic (hereinafter active) or potential economic (hereinafter potential) on the basis of their possibilities of use.

According to the Regulation nr 28 of the Minister of Social Affairs ‘Health requirements for the marketing, storage, and use of curative mud’, (RT I, 28, 393, 2002) the curative mud can be marketed and used only if its deposits have been registered under the Earth’s Crust Act (Maapõueseadus, 2016).

As of 31 December 2021, there are three deposits in Estonia where sea mud is the main resource (Käina Bay, Haapsalu Tagalaht Bay, Mullutu-Suurlaht Bay) with a total reserve of 2,536,500 tonnes, and two deposits where lake mud is the main resource (Värska Bay and Lake Ermistu) with a total reserve of 1,679,800 tonnes (Table 2). In 2021, a total of 1,032 tonnes of sea mud were extracted in Estonia, no lake mud was extracted. Compared to 2013, when a total of 705 tonnes of mud was extracted from five lake and sea mud deposits, i.e. Käina Bay, Haapsalu Tagalaht Bay, Värska Bay, Mullutu-Suurlaht Bay, and Lake Ermistu, the amount extracted is higher.

Table 2. Active and passive (location in Figure 2) proved reserves of Estonia's curative mud deposits, 1,000 tonnes (2021) (Roosalu, 2022).

	Proved reserves of Estonia's curative mud (1,000 t)	
Deposit	Active (economic)	Passive (potential economic)
Käina	308	1546
Haapsalu	181.1	50.8
Mullutu-Suurlaht	918.8	83
Total sea mud	1407.9	1679.8
Ermistu	63.9	0
Värska	1064.7	0
Total lake mud	1128.6	0
TOTAL	2536.5	1679.8
Estonia's curative mud IN TOTAL		**4216.3**

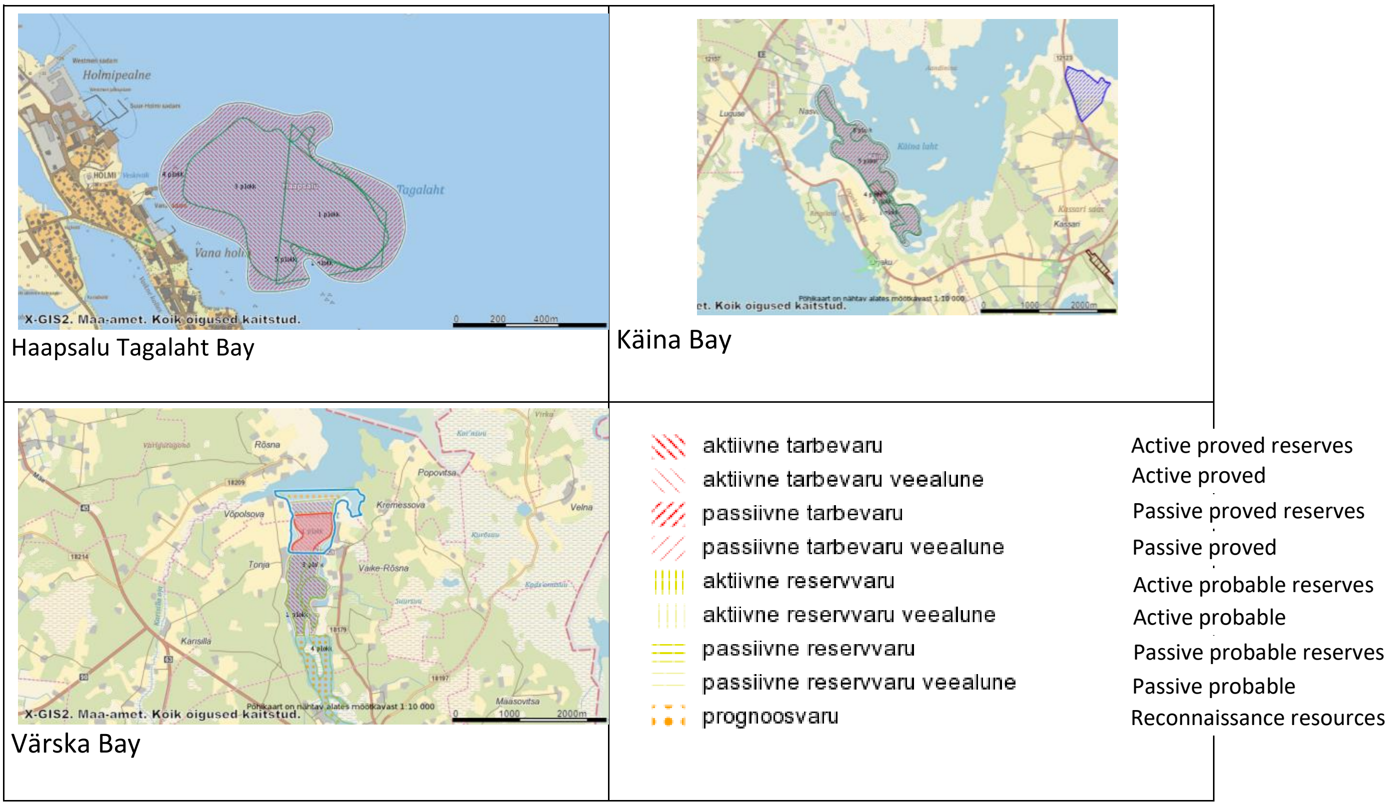


Figure 2. Location and active and passive reserves of examined curative mud deposits (Maardlad, 2023).

4.5 Previous research on Estonian curative mud

The first comprehensive research of Estonian curative mud was conducted by Professor K. Schlossmann, a microbiology professor at the University of Tartu, titled 'Estonian curative sea-mud and seaside health resorts' (Schlossmann, 1939). In addition to investigating and describing physical, chemical, and microbiological properties of Estonian curative mud, the research also emphasised the components of curative mud that have a direct effect on the skin when applied to the body.

Already in the 19th century, research on the curative mud of Haapsalu Bay began and several scientific papers have been written (for an overview see Tuulik, 2015; Kask, Talpas *et al.*, 1997). Although the organic and humic composition of the Haapsalu curative mud has generally been studied, less attention has been paid to the inorganic properties of the mud (Kask & Kask, 2012).

The use of the Värska Bay sediment as curative mud became a topical issue in 1969, following studies by the Geological Survey of Estonia and the construction of a Värska sanatorium (Tassa, 1976). Numerous investigations have been conducted, with the latest in-depth one occurring in the year 2000 (Ramst & Kask, 2000).

The curative mud of Käina Bay has been less studied, but there have been several other studies of both the geology and the natural conditions of the area. From the first half of the last century, radioactive studies of mud are known, and also in the 1960s, E. Türi determined the thickness of the mud layer and analysed it lithologically. The most recent in-depth studies date back to 1997, when the reserves of a number of Estonian curative mud deposits were inspected (Kask *et al.*, 1996; Kask, Talpas *et al.*, 1997).

The database of the surface sediments of curative mud 2013–2014 contains 145 curative mud sapling points analysis details from five curative mud deposits, which have been thermogravimetrically analysed and quantified for organics, minerals, and carbonates, as well as for major potentially toxic heavy metals (Pb, Ni, Zn, Cu, Cr, Cd) and non-metals. An estimate of changes in sediment quality is given. The results of the study by Terasmaa *et al.* (2015) confirm that the concentrations of potentially toxic heavy metals do not exceed the target values established in the Estonian curative mud deposits, above which the soil is considered contaminated, but in some places they do exceed the target value, which is the limit for good soil status. Based on the low content of heavy metals, the ecologically cleanest sediments can be found in Käina Bay. Spatial variability is highest in Mullutu-Suurlaht Bay, while the lithological composition is most homogeneous in the lake mud deposits. Lake Ermistu is the most organic-rich, while Käina Bay has the most mineral-rich mud. Compared to the 1990s, the organic matter content in sediments from 2013–2014 has rather increased in sea bays (mostly in Haapsalu Bay), while the organic matter content in lake mud deposits has remained the same or decreased slightly.

In 2018, in addition to mapping the surface sediments in two deposits – Värska Bay and Haapsalu Tagalaht Bay in Haapsalu – the total sediment composition was also studied (Kapanen & Terasmaa, 2018*a*). The aim was to specify the thickness of the mud layer at the extraction site in the active deposit and to investigate the change in lithological composition at the extraction sites of the Haapsalu Bay and Värska Bay curative mud. The study confirms a mud body thickness of at least 8 m in Värska Bay. Compared to previous data, it can be concluded that the organic matter content in the Värska lake sediment has decreased to 38% and thus the sediment has become richer in minerals. In Haapsalu Tagalaht Bay, the organic matter content of the curative mud has increased. There was more of it in the upper layer than in the lower layer. This trend refers to a deterioration in the ecological status of the bay – increasing nutrient loads, as well as algae and vegetation blooms.

Climate change, such as increased precipitation, can both strengthen and weaken the effects of eutrophication and work against measures to improve the status of water bodies.

In 2018, a pilot study was carried out to determine the levels of polycyclic aromatic hydrocarbons (PAHs) (Kapanen & Terasmaa, 2018*b*). The list of priority hazardous PAHs includes 16 compounds, including naphthalene, azenaphthene, azenaphthylene, anthracene, fluorene, fenanthrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(b)fluoranthene, chrysene, fluoranthene, pyrene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene. So far, benzo(a)pyrene (BaP) has been the most commonly used substance to assess the overall levels of PAHs in the environment and in food. The pilot study examined the curative mud in Haapsalu Tagalaht Bay and Estonian balneological peat (OÜ Loodusmark). The sampled PAH values were below the Helsinki Commission (HELCOM) Good Environmental Status (GES) limits. The most prevalent PAHs were BaP at 0.053 mg/kg per dry matter in curative mud and 0.027 mg/kg per dry matter in balneological peat.

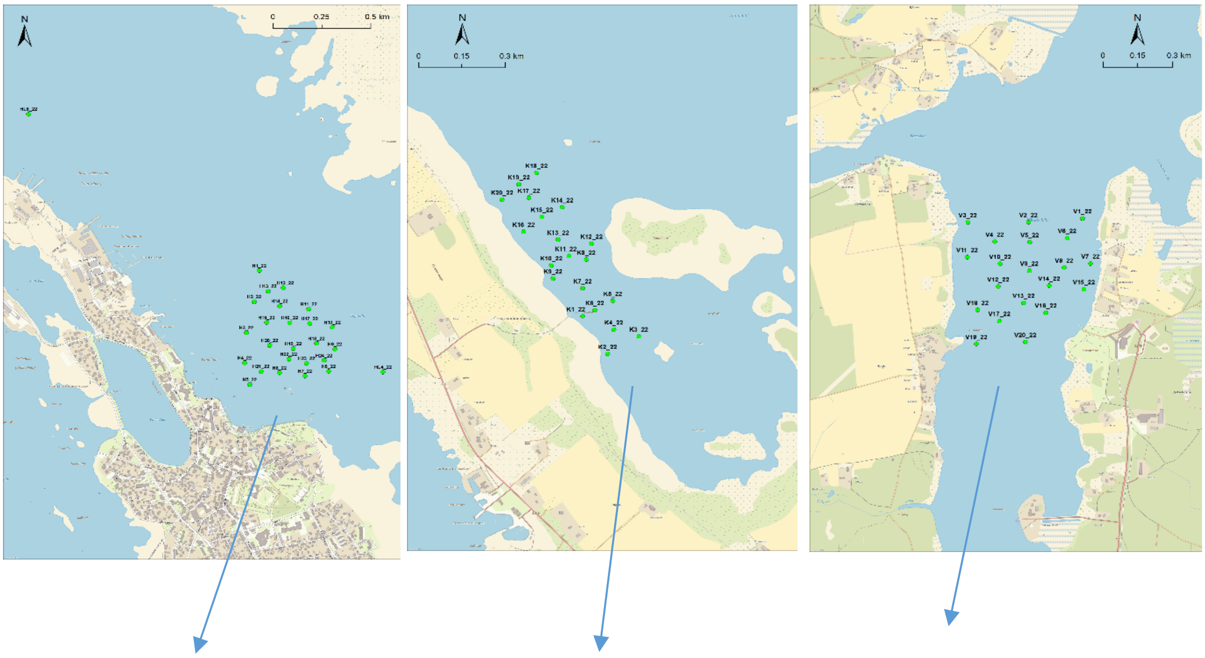
5 Methodology of Stage I of the project

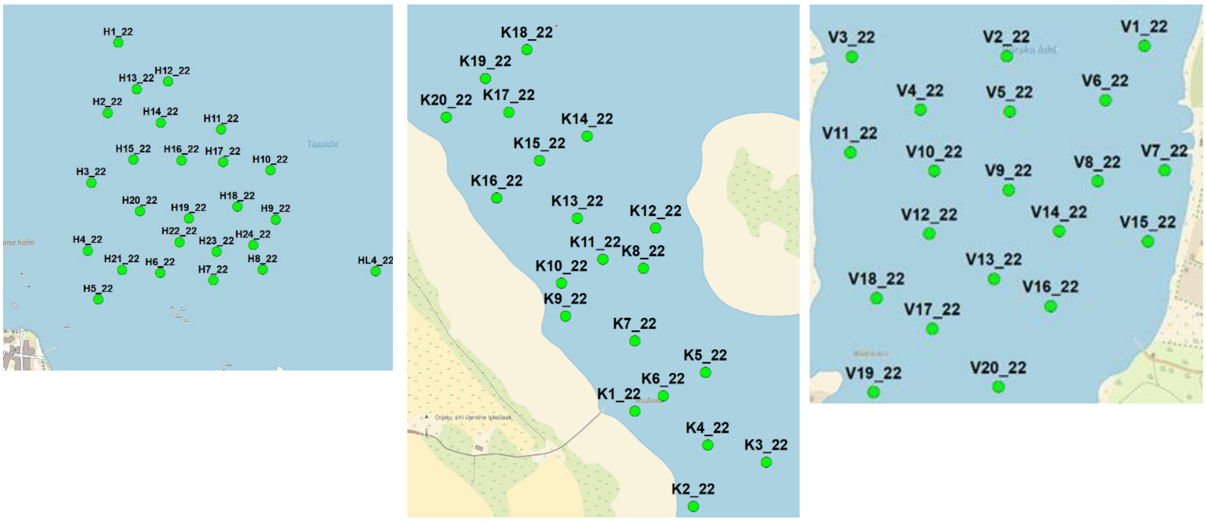
In the present study, samples were collected from the mud deposits of Haapsalu Tagalaht Bay, Värska Bay, and Käina Bay (Table 1, Figures 2, 3).

5.1 Sampling

Fieldwork was carried out in Haapsalu Tagalaht Bay, Värska Bay, and Käina Bay in the period May–June 2022 (Figure 3). Samples were collected from Haapsalu Tagalaht Bay from 0.7 to 2.3 metres below the water surface. Samples were collected from 0.3 to 0.75 metres below the water surface in Käina Bay and from 1.5 to 2.6 metres in Värska Bay. Samples were collected from 24 points in Haapsalu Tagalaht Bay on 19 May 2022. Käina Bay was sampled from 20 points on 30 May 2022 and Värska Bay was sampled from 20 points on 6 June 2022.

The samples were taken from a boat using a grab sampler (~ 0.7 L). The collected samples were packed in 1 litre grip bags and stored in a portable refrigerator at +4°C until arrival at the laboratory of the Tallinn University, School of Natural Sciences and Health (TLU LTI) or the Estonian Environmental Research Centre (EKUK). Sampling points were recorded with a GPS Garmin GPSMap 60CSx. The sediment samples were dried in a Telstar LyoAlfa 10 freeze dryer.





Haapsalu Tagalaht Bay | Käina Bay | Värska Bay

Figure 3. Sampling points for curative mud in Haapsalu Tagalaht Bay, Värska Bay, and Käina Bay mud deposits (2022).

5.2 Lithology

The water content, organic and mineral matter, carbonate content in the sediment was estimated using loss on ignition (LOI) analysis at 100°C, 550°C and 950°C, respectively (Heiri *et al.*, 2001; Santisteban *et al.*, 2004; Rosenmeier, 2005) in a total of 64 samples in the TLU LTI laboratory using the standard method. The Precisa prepASH 340 thermogravimeter was used for the analysis.

Grain size analysis of the curative mud was carried out by Tiit Vaasma in the laboratory of the Institute of Ecology at Tallinn University. In order to determine the grain size of the curative mud, six (randomly selected) samples of wet mud (about 100 ml) were first extracted from the samples collected from each deposit, in a total of 15 samples. The grain size distribution was determined by wet sieving on a Vibratory Sieve-Shaker ‘Analysette 3’. The sieving process finds the ‘sieving radius’ of the particles (Last & Smol, 2001). Six metal-tipped sieves with diameters of 36 µm, 63 µm, 125 µm, 250 µm, 500 µm, and 1,000 µm were used for sieving (Table 3). To break down the sediment, 10 mm diameter agate beads were placed on the sieves. The water and sample from all the sieves were collected in a 10 L container (a total of about 10 L of water was used for sieving). The material was sedimented in a 10 L container with water. The sifted and sedimented material was collected in pre-weighed and labelled tubes. The collected material was dried at 95°C to a constant weight and then the proportion of each fraction in the sample was determined. Pressurised water and ultrasonic baths were used to clean the sieves.

Table 3. Grain size distribution and material.

Size (mm)	Size (µm)	Descriptive Term
>512	< –9	Boulder
256...512	–8...–9	
128...256	–7...–8	Pebble
64...128	–6...–7	
32...64	–5...–6	Very coarse gravel
16...32	–4...–5	Coarse gravel
8...16	–3...–4	Medium gravel
4...8	–2...–3	Fine gravel
2...4	–1...–2	Very fine gravel
1...2	0...–1	Very coarse
0,5...1	1...0	Coarse sand
0,25...0,5	2...1	Medium sand
0,125...0.25	3...2	Fine sand
0,063...0,125	4...3	Very fine sand
0,032...0.063	5...4	Silt
0,016...0,032	6...5	
0,008...0.016	7...6	
0,004...0,008	8...7	
0,002...0,004	9...8	Clay
< 0,002	>9	

5.3 Hazardous substances

In Estonia, the Water Act (RT I, 22.02.2019, 1, 2019) regulates the maximum permissible concentration of hazardous substances. Regulation nr 26 of the Minister of the Environment of 28 June 2019 'Limit values for the content of hazardous substances in soil' (Keskkonnaministri Määrus nr 26, 2019), the respective targets and limits can be found in Annex 1.

5.3.1 Microbiology

Microbiological mud samples were collected from a total of 32 points: 12 samples from Haapsalu Tagalaht Bay, 10 samples from Käina Bay, and 10 samples from Värska Bay.

Microbiological analyses of curative mud were carried out at the Laboratory of the Health Board at the end of May and beginning of June 2022 (within one to two days after sampling). The presence of the indicator bacterium for faecal pollution, *Escherichia coli (E. coli*), and the sporogenic soil/sediment bacterium (potential pathogen) *Clostridium perfringens (Cl. perfringens*) per g of sample were analysed. The standard NMKL 95:2009 method used for the detection of *E. coli* is qualitative and gives the presence or absence result. In the *Cl. perfringens* analysis method EVS-EN ISO 7937:2004 , both viable vegetative bacterial cells and spores present in the test sample are cultured at 37°C for 24 hours, i.e. the maximum possible abundance is obtained. Since *E. coli* does not normally reproduce outside the thermophilic organism and *Cl. perfringens* is a strict anaerobe in nature, it is likely that the abundances of both bacteria will decrease during the handling of the curative mud.

5.3.2 Petroleum products

Analyses for heavy metals, phenols, and pesticides were commissioned from the Estonian laboratory, Eurofins Environment Testing Estonia OÜ.

Petroleum products (C10–C40) were analysed at Eurofins Environment Testing Estonia (Tallinn) (EP and EP C272) laboratories, 15 samples in total. The standard methodology was used for the determination (EVS-EN ISO 16703, 2004; SFS-EN ISO 9377-2, 2000).

In Estonia, the Water Act (RT I, 22.02.2019, 1, 2019) regulates the maximum permissible concentration of petroleum products. Regulation nr 26 of the Minister of the Environment of 28 June 2019 'Limit values for the content of hazardous substances in soil' (Keskkonnaministri Määrus nr 26, 2019) states that in Estonia the limit value for petroleum products in residential land is 500 mg of petroleum products per 1 kg of soil. On industrial land, the permitted limit for petroleum products is 5,000 mg/kg. Petroleum products include kerosene, diesel, petrol, various fuel oils, but petroleum can also be used to produce plastics, paints, insecticides, and synthetic fabrics (Robinson, 2012). The limits of quantification (LoQ) are given in Table 4.

Table 5: Petroleum products (C10–C40 sum), the limits of quantification of analysis method (LoQ) (dw – dry weight/dry matter).

Petroleum products (C10–C40 sum)	mg/kg dw
C10-C21	20
C21-C40	20
C10-C40	20

5.3.3 Phenols

Phenols were analysed at Eurofins Environment Testing Estonia (Tallinn) (EP and EP L272), 15 samples in total. The standard methodology was used to quantify (ISO 14154:2005, 2019); 13 different phenols were analysed. The LoQ are given in Table 5.

Table 5. The limits of quantification (LoQ) of phenols (dw – dry weight/dry matter).

	Phenols	LoQ mg/kg dw
1	Phenol	0.05
2	2-methylphenol	0.05
3	3-methylphenol	0.05
4	4-methylphenol	0.05
5	2,3-dimethylphenol	0.05
6	2,4-dim	0.05
7	2,5-dim	0.05
8	2,6dim	0.05
9	3,4dim	0.05
10	2,3,5-Trimethylphenol	0.05
13	2,4,6-trim	0.05
12	3,4,5-trim	0.05
13	4-Ethylphenol/3,5-Dimethylphenol	0.05

5.3.4 Pesticides

Pesticides were determined at Eurofins Food & Feed Testing Sweden laboratory (LW 1977), Lindköping, Sweden, using the standard methodology (Rashid *et al.*, 2010), with a total of 15 samples. The LoQ are given in Table 6.

Table 6. The limits of quantification (LoQ) of pesticides (dw – dry weight/dry matter).

Pesticides	Limit of quantification	
Aldrin	2	µg/kg dw
Aldrin/Dieldrin (sum)	2	µg/kg dw
Chlordane (sum)	1	µg/kg dw
Chlordane, alpha-	1	µg/kg dw
Chlordane, gamma-	1	µg/kg dw
DDD, o,p'-	1	µg/kg dw
DDD, p,p'-	1	µg/kg dw
DDE, o,p'-	1	µg/kg dw
DDE, p,p'-	1	µg/kg dw
DDT (sum)	3	µg/kg dw
DDT, o,p'-	1	µg/kg dw
DDT, p,p'-	1	µg/kg dw
Dichloroaniline, 3,4-	2	µg/kg dw
Dieldrin	2	µg/kg dw
Endosulfan (sum)	2.5	µg/kg dw
Endosulfan, alpha	2	µg/kg dw
Endosulfan, beta-	2	µg/kg dw
Endosulfansulfate	1	µg/kg dw
Endrin	2	µg/kg dw
HCH, alpha-	1	µg/kg dw

Pesticides	Limit of quantification	
HCH, beta-	1	µg/kg dw
HCH, delta-	1	µg/kg dw
HCH, gamma- (Lindane)	1	µg/kg dw
Heptachlor	1	µg/kg dw
Heptachlorepoxide, cis-	1	µg/kg dw
Heptachlorepoxide, trans-	1	µg/kg dw
Hexachlorobenzene	1	µg/kg dw
Pentachloroaniline	1	µg/kg dw
Pentachloroaniline/Quintozene	1	µg/kg dw
Pentachlorobenzene	1	µg/kg dw
Quintozene	1	µg/kg dw

5.3.5 Heavy metals

A total of 55 samples of heavy metals (Cd, Cr, Cu, Pb, Ni, Zn, Sr, Sn, Hg) were analysed at Eurofins Environment Testing Estonia (Tallinn) (EP and EP L272). The standard methodology (EVS-EN 16171 :2016) was used for the quantification. The laboratory LoQ are given in Table 7. All results are presented in dry weight/dry matter (dw).

Table 7. The limits of quantification (LoQ) of measured heavy metals (dw – dry weight/dry matter).

Metals		mg/kg dw
Cadmium	Cd	0.2
Chromium	Cr	1
Copper	Cu	2
Mercury	Hg	0.04
Nickel	Ni	1
Lead	Pb	1
Tin	Sn	3
Strontium	Sr	1
Zinc	Zn	3

6 Results and conclusions

For the quality assessment, samples were collected from a total of 64 sites: 24 sample points in Haapsalu Tagalaht Bay, 20 sample points in Käina Bay, and 20 sample points in Värska Bay. Compared to the previous study (2013–2014) there were fewer sample points, but for the first time markers such as phenols, petroleum products, and pesticides have been investigated. In total, 1,649 measurements/analyses were carried out.

6.1 Lithology

The samples from the Värska curative mud are all fine-grained: rich in clay/silt, with up to one-third – generally less than one-third, mainily very fine and fine (Figure 4, original data in Annex 2.1).

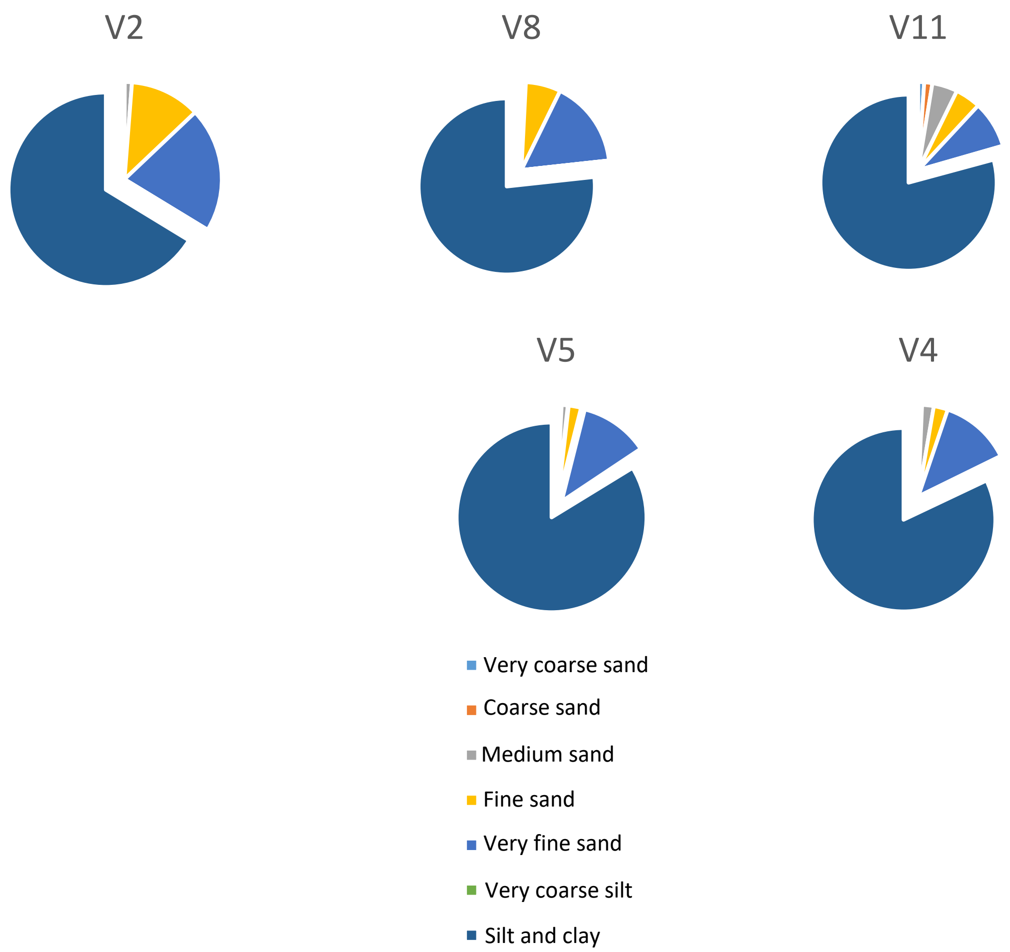


Figure 4. Grain size analysis of the Värska curative mud (sample point locations can be seen in Figure 3).

The samples from the Käina curative mud are all fine-grained: rich in clay/silt with up to a third of the fine-grained sand (Figure 5, original data in Annex 2.1). Samples K6 and K8 stand out, with 43% and 49% of fine-grained sand, respectively. Very little coarse-grained sand can also be found in the mud: for example, samples K8 and K11.

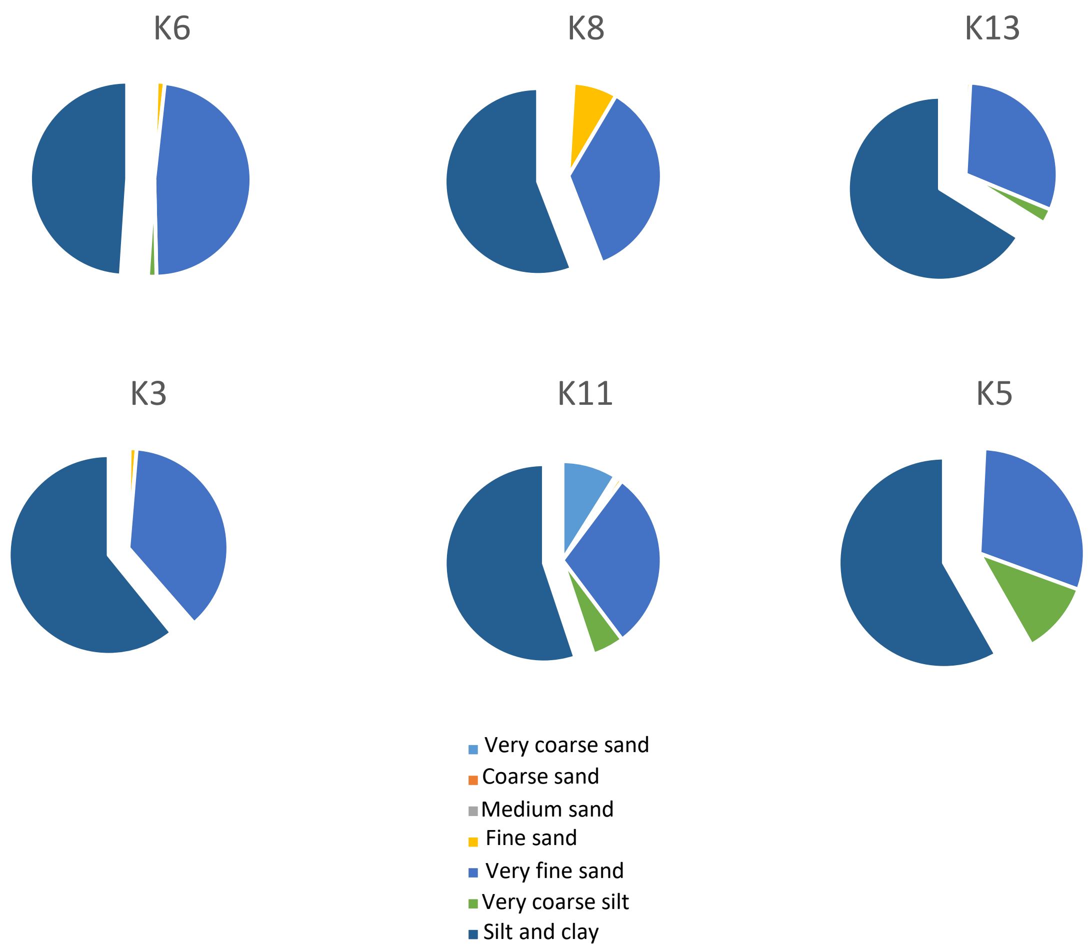


Figure 5. Grain size analysis of the Käina curative mud (sample point locations can be seen in Figure 3).

The Haapsalu curative mud samples are all fine-grained: rich in clay/silt (Figure 6, original data in Annex 2.1).

The Haapsalu deposit has an average organic matter content of 11.6%, a mineral content of 83.6%, and a carbonate content of 4.4% (Figures 7, 8). Compared to the 2013–2014 study, the average carbonate content in the Haapsalu curative mud has increased and the mineral content has decreased slightly. The proportion of organic matter has remained the same (Table 11).

Comparing the three curative mud deposits, Käina has the lowest organic matter (5.5%) and carbonate content (2.1%) and the highest mineral content (92.3%) (Figures 7, 8). Compared to the previous study, the organic matter content of Käina curative mud has decreased and the mineral content has increased slightly. The proportion of carbonates remains the same.

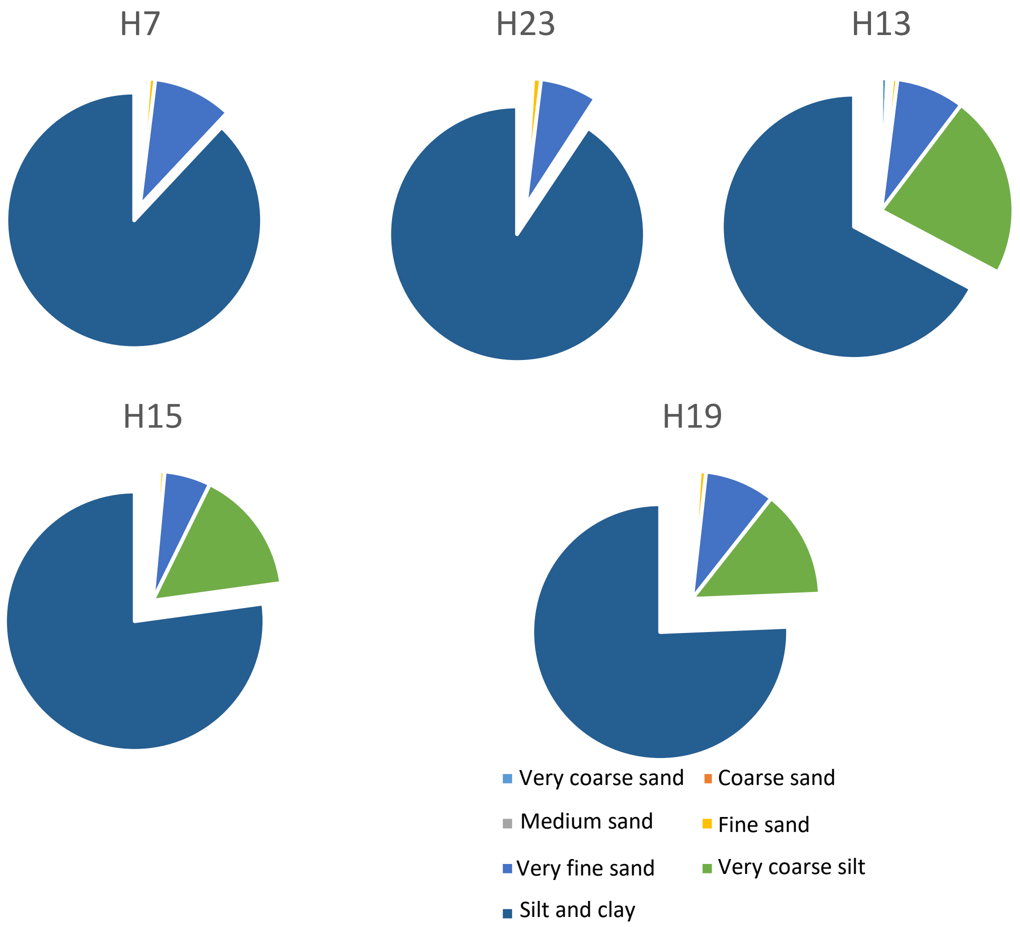


Figure 6. Grain size analysis of the Haapsalu curative mud (sample point locations can be seen in Figure 3).

The lithology of the Värska curative mud has not changed significantly compared to the results of the 2013–2014 study. On average, sediment samples contain 37.3% organic matter (2014 – 38.8%), minerals 58% (2014 – 57.5%), and carbonates 4.8% (2014 – 3.7%).

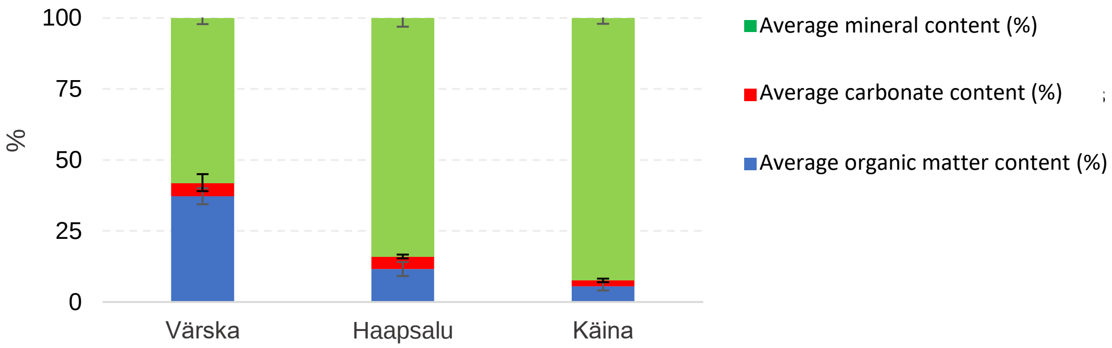


Figure 7. Percentage average organic, mineral, and carbonate contents of the sample points of the curative mud deposit (2022).

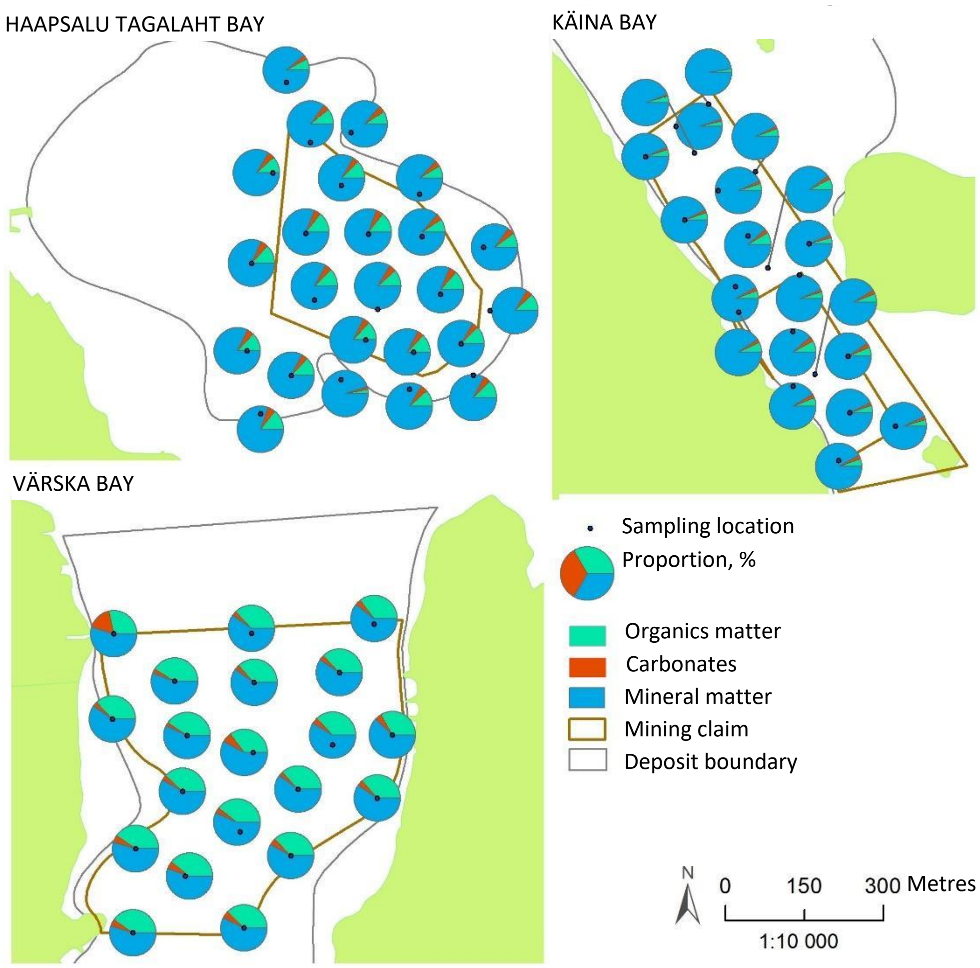


Figure 8. Spatial distribution of mineral, organic, and carbonate content (%, dry weight/dry matter) of the curative mud by deposit (2022).

6.2 Hazardous substances

The current study analysed the microbiology of the muds and the content of petroleum products, pesticides, phenols, and heavy metals in three different Estonian curative mud deposits. Samples were taken from an area of active mud reserve.

6.2.1 Microbiology

The examined curative mud samples proved to be fairly clean microbiologically – the indicator bacterium for faecal pollution, *E. coli*, was absent in all samples analysed, while *Cl. perfringens* was present in nine out of 32 samples (Table 8, Figure 3). The majority of *Cl. perfringens* positive samples occurred in Haapsalu Bay: sample H2 had 710 CFU (colony forming units, which mostly coincide with the number of viable bacterial cells)/g sediment and samples H4, H5, H6, H10, and H18 had *Cl. perfringens* abundance > 1,500 CFU/g sediment. The remaining six samples had a *Cl. perfringens* abundance of < 10 CFU/g sediment (a result of < 10 CFU/g also indicates cases when the bacterium is not present at all in the sample).

Cl. perfringens was found in three of the ten mud samples taken from the Käina Bay: samples K2 and K4 had 750 CFU/g sediment and sample K15 had 380 CFU/g sediment. In the other microbiologically analysed samples (K6, K8, K9, K12, K16, K19, K20), *Cl. perfringens* was found to be < 10 CFU/g sediment.

Mud samples taken from Värska Bay for microbiological analysis all had *Cl. perfringens* abundances of < 10 CFU/g sediment.

Table 8. Microbiology (*E. coli* and *Cl. Perfringens*) in the samples of curative mud tested (CFU – colony forming units, which mostly coincide with the number of viable bacterial cells). The samples were taken in 2022. Sample marking: H – Haapsalu Tagalaht Bay; K – Käina Bay; and V – Värska Bay.

Sample marking	*Escherichia coli*: Occurrence/1 g	*Clostridium perfringens* CFU/1 g
H2	Does not occur	710
H4	Does not occur	> 1500
H5	Does not occur	> 1500
H6	Does not occur	> 1500
H7	Does not occur	< 10
H8	Does not occur	< 10
H10	Does not occur	> 1500
H12	Does not occur	< 10
H16	Does not occur	< 10
H18	Does not occur	> 1500
H19	Does not occur	< 10
H20	Does not occur	< 10
K4	Does not occur	750
K6	Does not occur	< 10
K8	Does not occur	< 10
K9	Does not occur	< 10
K12	Does not occur	< 10
K15	Does not occur	380
K16	Does not occur	< 10
K19	Does not occur	< 10
K20	Does not occur	< 10
K20	Does not occur	750
V1	Does not occur	< 10
V3	Does not occur	< 10
V5	Does not occur	< 10
V7	Does not occur	< 10
V9	Does not occur	< 10
V11	Does not occur	< 10
V13	Does not occur	< 10
V18	Does not occur	< 10
V19	Does not occur	< 10
V20	Does not occur	< 10

Clostridia are strictly anaerobic bacteria to which oxygen is toxic. Under unfavourable environmental conditions, they sporulate, i.e. they form thick and very resistant spores that can tolerate oxygen. Thus, the spread of *Cl. perfringens* can be explained by the fact that the sites where viable clostridia were present in the samples must have been permanently or periodically anaerobic. In case of Käina Bay (where data are available on the oxygen content of the water), it appears that sampling points K2 and K4, where *Cl. perfringens* (750 CFU/g) was detected, had a lower oxygen content at the time of sampling (6.9 and 6.8 ppm, respectively) than the other sampling points in the study area (7.1–12.8 ppm).

Samples from Haapsalu Tagalaht Bay containing *Cl. perfringens* (H2–H5) were concentrated in an area where, based on heavy metal analyses, there was a relatively homogeneous composition of sediment/mud, i.e. sedimentary bed with similar characteristics and influences (see Table 9a), which suggests that the oxygen regime was also similar.

Table 9. Analytical results for *Cl. perfringens* and heavy metals in Haapsalu Tagalaht Bay: a) sample points H2–H5; b) sample point H6.

a) Points H2–H5

Sample marking	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Tin	Strontium	Zinc	*C. Perfringens*
	(mg/kg dw)									PMÜ/g
H2	0,75	35	23	-	27	19	<3	39	76	710
H3	0,62	37	23	-	31	18	<3	41	78	-
H4	0,6	39	24	-	31	19	<3	41	81	> 1500
H5	0,57	36	22	0,1	31	18	<3	43	77	> 1500
Average	**0,64**	**37**	**23**		**30**	**19**		**41**	**78**	
STDV	*0,1*	*1,7*	*0,8*		*2,0*	*0,6*		*1,6*	*2,2*	

b) Point H6

Sample marking	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Tin	Strontium	Zinc	*C. Perfringens*
	(mg/kg dw)									PMÜ/g
H6	<0,2	11	6	<0,04	7,3	4,4	<3	12	22	> 1500

At the same time, *Cl. perfringens* > 1,500 CFU/g of sediment was also detected at sampling point H6, which was significantly cleaner than the adjacent area in terms of heavy metals (see Table 9b).

As the heavy metal content of sediments primarily reflects the anthropogenic load, it can be seen that there is no clear link between the *Cl. perfringens* levels and human impact, and that it is the internal conditions of the water body, including the level of eutrophication, that determine the spread of this bacterium more than any human activity. Human activity may contribute to eutrophication but not cause the *Cl. perfringens* pollution.

6.2.2 Petroleum products

The Haapsalu curative mud contains on average 29.7 mg/kg of C21–C40 petroleum products, Värska samples – 91 mg/kg (results summarised in Annex 2.2). C10–C40 concentrations averaged 42 mg/kg in Haapsalu and 118.6 mg/kg in Värska, while C10–C21 concentrations averaged 29.3 mg/kg in Värska and below LoQ (20 mg/kg) in Haapsalu. In the Käina curative mud, all petroleum products were below LoQ. Original data can be found in Annex 2.2.

6.2.3 Pesticides

For pesticides, the average concentrations of dichlorodiphenyldichloroethylene (DDE, p,p) and dichlorodiphenyltrichloroethane (DDT) were found to be 1.7 µg/kg and 4.2 µg/kg samples, respectively, in the five Värska points. In all other sediment samples, pesticide concentrations were below the limit of quantification (see Annex 2.3 for a summary of the results).

6.2.4 Phenols

Phenol concentrations are below LoQ (0.05 mg/kg) in all three curative mud deposits, except in Värska, where 4-methylphenol averaged 0.5 mg/kg.

6.2.5 Heavy metals

The results of the heavy metal in all three deposits of curative mud indicates that the concentrations of these metals fall within the permissible limits (except for point H11) set by the regulation 'Limit values for the content of hazardous substances in soil' (Keskkonnaministri Määrus nr 26, 2019) (Table 10, Figure 9, 10).

Table 10. Suggested limits of quantification for heavy metals in soil (Keskkonnaministri Määrus nr 26, 2019) (mg/kg, dw (dw – dry weight/dry matter)).

Element	Target value	Limit value on residential land	Limit value on industrial land
Cd	1	5	20
Cu	100	150	500
Cr	100	300	800
Hg	0.5	2	10
Ni	50	150	500
Pb	50	300	600
Sn	10	50	300
Sr	-	-	-
Zn	200	500	1,000

Heavy metal analysis did not detect tin (Sn) in the samples, which may be due to the fact that laboratory LoQ was 3 mg/kg dw, i.e. all samples were below the limit of quantification.

All three deposits of the curative mud are characterised by strontium (Sr) content. Higher concentrations of zinc (Zn) are found in Käina Bay; zinc (Zn) and copper (Cu) in Haapsalu Tagalaht Bay; strontium (Sr) and chromium (Cr) in Värska Bay and Haapsalu Tagalaht Bay (Figure 9). Zn content in the curative mud is most characterised by an average of 73.3 mg/kg in Haapsalu Tagalaht Bay, 35.3 mg/kg in Käina Bay, and 72.9 mg/kg in Värska Bay, but the amount of Zn in Käina Bay is more than twice lower than in the other deposits.

Apart from Zn, the samples from Haapsalu Tagalaht Bay, Käina Bay, and Värska Bay contained the highest average concentrations of Sr (35.8 mg/kg, 17 mg/kg, and 26.8 mg/kg, respectively), for which the target value in soil is not yet regulated (Figure 11).

The average concentration of Cr in the curative mud samples Haapsalu Tagalaht Bay is 32.8 mg/kg, in Käina Bay – 15.4 mg/kg, and in Värska Bay – 23.7 mg/kg.

Copper (Cu) does not exceed the target value (100 mg/kg) in any of the studied deposits (Figure 9). The highest Cu concentrations were found in Haapsalu Tagalaht Bay and Värska Bay (maximum 25 mg/kg), although the average remained at 20.8 mg/kg and 20.9 mg/kg, respectively. The lowest Cu content was found in Käina – 8.71 mg/kg on average.

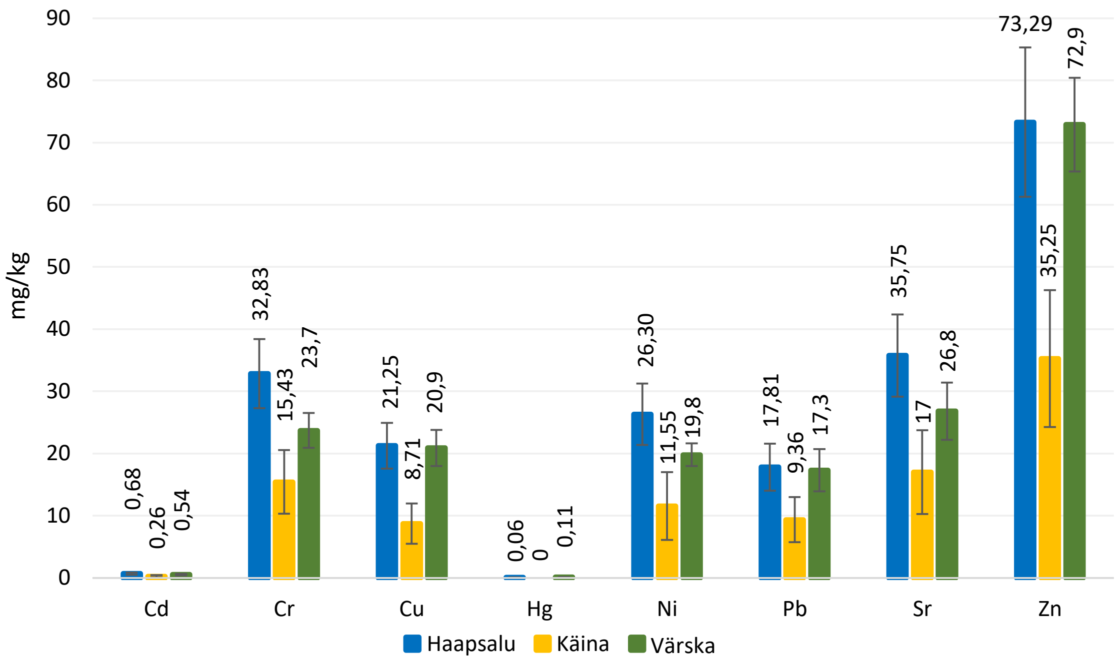


Figure 9. Average heavy metal concentrations (mg/kg dw (dry weight or dry matter)) in the Värska deposit in 2022.

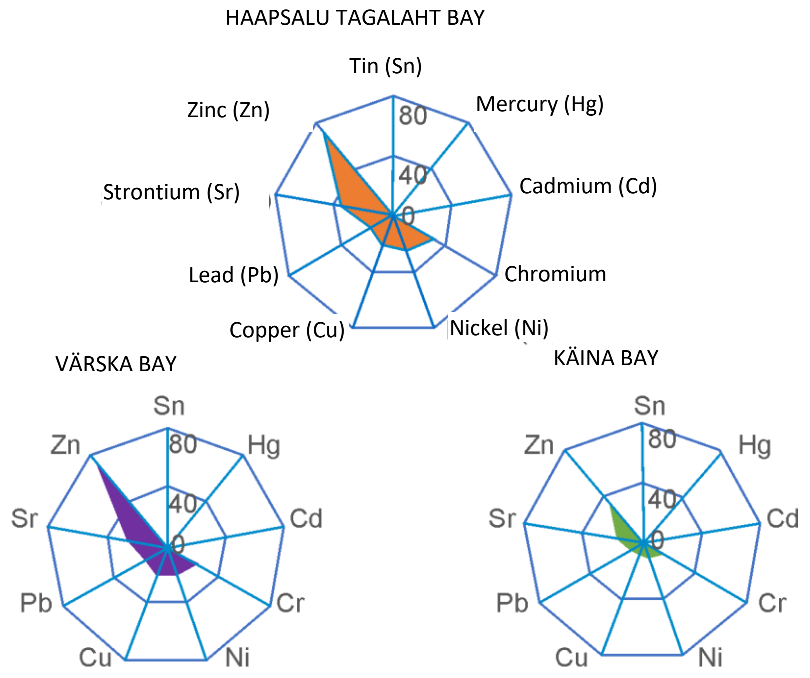


Figure 10. Average heavy metal concentrations (mg/kg dw (dry weight or dry matter)) in the examined curative mud sample points.

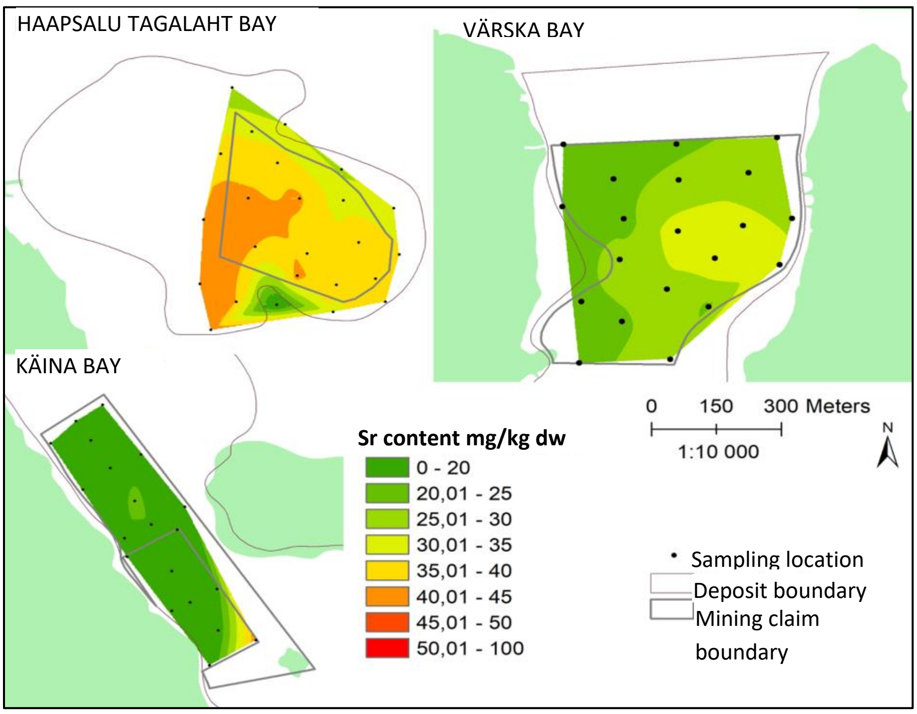


Figure 11. Strontium concentrations (mg/kg dw (dry weight or dry matter)) in the Haapsalu, Käina, and Värska deposits (2022).

Lead (Pb) concentrations are low in all the curative mud deposits examined (Figure 12). The highest levels of Pb were found in the central part of Haapsalu Tagalaht Bay deposit of curative mud, where they reached 26 mg/kg, which is below the soil target value (50 mg/kg dw). The average Pb concentration in Haapsalu Tagalaht Bay is 17.4 mg/kg.

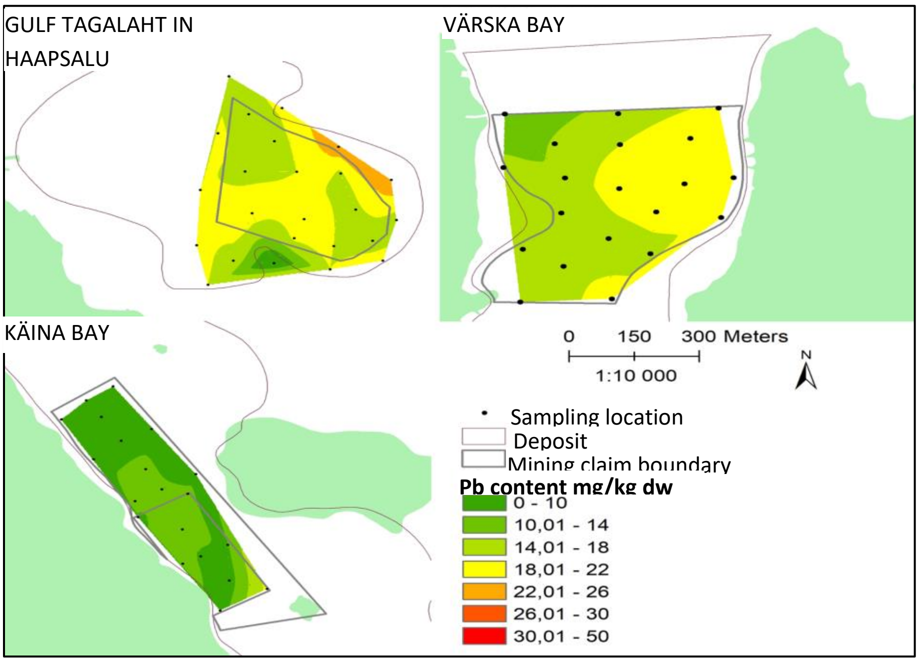


Figure 12. Lead concentrations (mg/kg dw (dry weight or dry matter)) in the Haapsalu, Käina, and Värska deposits (2022).

The highest concentrations of nickel (Ni) were detected in Haapsalu Tagalaht Bay, where they reached 31 mg/kg at sites H3, H4, and H5 (with average Ni concentration 25.8 mg/kg) (Figure 13). Nevertheless, the samples there do not exceed the soil target value (50 mg/kg dw). In Käina Bay, the average Ni content in almost the entire deposit was 11.55 mg/kg and in Värska Bay 19.8 mg/kg.

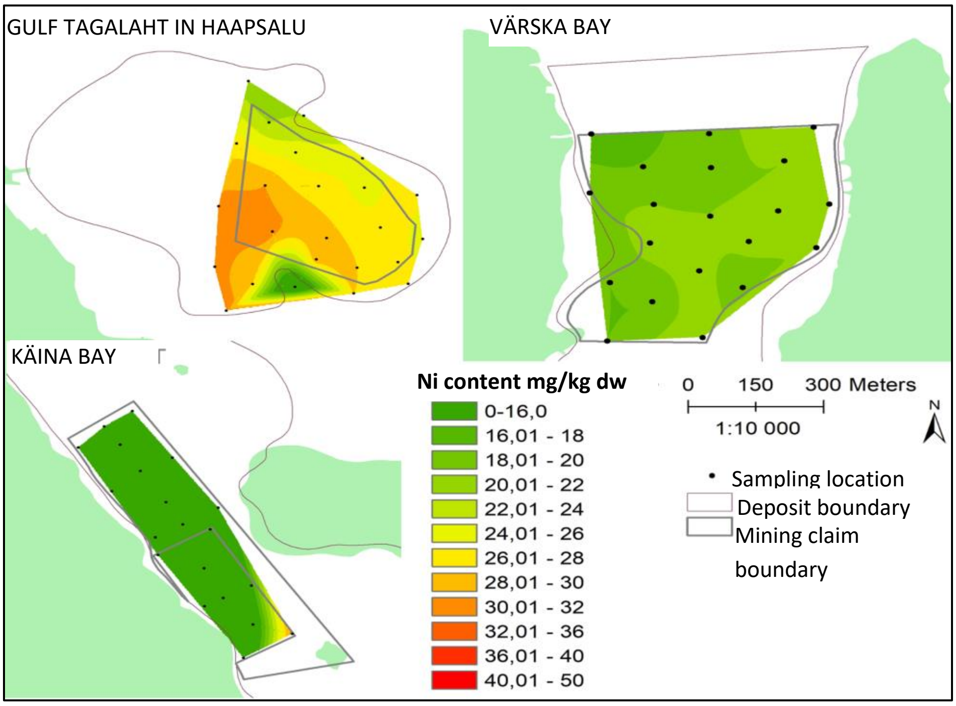


Figure 13. Nickel concentrations (mg/kg dw (dry weight or dry matter)) in the Haapsalu, Käina, and Värska deposits (2022).

On average, cadmium (Cd) does not exceed the target value (1 mg/kg dw) in any of the studied deposits. The highest concentrations were found in Haapsalu Tagalaht Bay (maximum 1.1 mg/kg and median 0.7 mg/kg). In Värska Bay, the maximum Cd value is 0.68 mg/kg. In Käina Bay, the Cd concentration was the lowest, averaging 0.33 mg/kg.

In general, the lowest concentrations of heavy metals are found in Käina Bay, while the maximum values show a high variability (Figures 9, 10).

Mercury (Hg) is a naturally occurring toxic heavy metal in the environment. The content has increased due to discharges of wastewater and the burning of fossil fuels (coal). The amount of mercury released into the environment has been significantly limited over time, but concentrations are still high. Mercury is most directly discharged to water via chlor-alkali industry and power plants, metallurgy, waste management, batteries, measuring and control equipment (e.g. thermometers), lamps, electronics, etc. The release of mercury into the atmosphere is also a major concern, as it can be transported very far from the source. Mercury (Hg) does not exceed the target value (0.5 mg/kg dw) in any of the studied deposits. In Käina Bay, the Hg concentrations are below the laboratory LoQ (0.04 mg/kg) in all samples. The highest concentration of Hg was found in Värska Bay, where it reached 0.13 mg/kg, with an average of 0.11 mg/kg. In Haapsalu Tagalaht Bay, the average Hg concentration was 0.07 mg/kg.

Interestingly, the spatial distribution of heavy metals in the different deposits is not at all related to the organic and mineral content of the sediments, but coincides with the carbonate content.

6.3 Changes in the composition of curative mud formulations over time

As all the deposits have been subjected to mud composition studies in the past, this provides a good opportunity to compare the results and draw conclusions about the direction and causes of change. However, it should be noted that the number of samples taken, their locations, and methods have changed over time. Particular attention needs to be paid to the methods used to determine heavy metal concentrations, as these have changed over time and, therefore, the heavy metal data from older studies could be less accurate. Therefore, the best overview of changes in the state of deposits is provided by the organic content of sediments (Terasmaa *et al.*, 2015).

Comparing the organic contents of the 1990s, from 2013–2014, and the results of the last study, we can see a trend of change in the last decades (Table 11). As indicated in the table, there has been a decrease in the average organic matter content in lake sediments (Värska Bay) compared to the 1990s, while all marine sediments have become more organic-rich during the same period (2013–2014). However, the results from 2022 demonstrate that over the past decade, the organic matter content has remained stable in both lake sediments (Värska Bay) and marine sediments (Haapsalu Tagalaht Bay and Käina Bay). Organic matter levels in marine sediments are still significantly lower than in lakes. In general, the trends for minimum and maximum values are similar. However, it should be noted that in Värska Bay, there has been a slight increase in the maximum organic content by a few percentage points (from 45.7% to 48.3%). Minimum concentrations have decreased compared to the past. While in the past there was a very strong trend towards an increasingly organic sediment, today, the organic content has stabilised.

Table 11. Change in the mean (Average), minimum (Min), and maximum (Max) organic matter content (%) of the curative mud Haapsalu Tagalaht Bay, Värska Bay and Käina Bay deposits for the periods 1995–1997, 2013–2014, and 2022. A green arrow indicates a decrease, a red arrow an increase, and a yellow arrow stability (change < 1%).

Deposit	Organic matter								
	Average (%)			Min (%)			Max (%)		
	1995–97	2013–14	**2022**	1995–97	2013–14	**2022**	1995–97	2013–14	**2022**
Haapsalu Tagalaht Bay	8.1 ↑	11,7 →	**11.6**	7 →	7,2 ↓	**3.2**	9,2 ↑	14,9 →	**14.6**
Värska Bay	41,2 ↓	38.3 →	**37.3**	40,7 ↑	36,4 ↓	**28.3**	41,6 ↑	45,7 ↑	**48.3**
Käina Bay	4,8 ↑	6,5 →	**5.5**	2 →	3,1 ↓	**2,4**	7.5 ↑	13,4 ↓	**8.5**

Comparing the results of the current study for heavy metals with those of 2013–2014, we can see a change in trends over the last decade (Table 12). However, as mentioned earlier, it is important to consider that the number of samples, the locations where they are taken, and the methods used may have changed over time, as may the methodology used to quantify them. In the current study, we have used the ICP (inductively coupled plasma) method to determine heavy metals, but previously, in the study for 2013–2014, we used an XRF (X-ray fluorescence) instrument, which did not give as accurate results and were mainly used to investigate the matrix of elements. The ICP method is renowned for its high sensitivity and accuracy, and it is widely used in a variety of fields such as environmental and food analysis, medical diagnosis, metallurgy, and geochemistry.

Table 12 shows the concentrations of heavy metals in the curative mud of Haapsalu Tagalaht Bay, Värska Bay, and Käina Bay from 2013–2014 (Terasmaa *et al.*, 2015) and in 2022. By way of comparison, the following elements are listed: chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), strontium (Sr), and zinc (Zn).

Average concentrations of heavy metals in curative mud have generally decreased between 2013–2014 and 2022. One of the reasons for this is the difference in heavy metal analysis methods and equipment, as mentioned above. The most significant changes in heavy metals were the following:

> In Haapsalu Tagalaht Bay: the Cu concentrations decreased from an average of 38.6 mg/kg from 2013–2014 to an average of 20.8 mg/kg in 2022. The Zn levels also decreased from an average of 135.8 mg/kg from 2013–2014 to an average of 72 mg/kg in 2022. The Ni levels have remained the same at around 25 mg/kg.
>
> In Värska Bay: the Ni concentrations decreased from an average of 43.8 mg/kg from 2013–2014 to an average of 19.8 mg/kg in 2022; Zn shows a larger decrease: from 2013–2014 the maximum reaches 72.9 mg/kg and the annual average 168.2 mg/kg, in 2022, the maximum is 203.2 mg/kg and the annual average 83 mg/kg.
>
> In Käina Bay: the Cu concentrations have remained about the same: from an average of 8.7 mg/kg from 2013–2014 to 9.1 mg/kg in 2022. The Ni concentrations increased from an average of 1 mg/kg from 2013–2014 to an average of 28.5 mg/kg in 2022. A larger decrease was shown for Sr: an average of 113.7 mg/kg from 2013–2014, and an average of 68.4 mg/kg in 2022.

Overall, the heavy metal concentrations in the curative mud have fallen and do not exceed the target level. The highest concentrations of heavy metals are found in Haapsalu Tagalaht Bay and Värska Bay, while Käina Bay has generally lower concentrations.

Table 12. Mean (Avrg), minimum (Min), and maximum (Max) concentrations of heavy metals in curative muds from deposits for 2013–2014 (Terasmaa *et al.,* 2015) and 2022 (current study).

Element		Cr		Cu		Ni		Pb		Sr		Zn	
		2013–14	**2022**	2013–14	**2022**	2013–14	**2022**	2013–14	**2022**	2013–14	**2022**	2013–14	**2022**
Haapsalu Tagalaht Bay	Avrg	78.2	**32.2**	38.6	**20.8**	24.3	**25.8**	28.8	**17.4**	146.6	**35.2**	135.8	**72**
	Min.	30.2	**13**	0	**6**	0	**7.3**	10	**4.4**	103.8	**12**	36.9	**22**
	Max.	105.8	**39**	44.8	**25**	28.5	**31**	40	**26**	173.1	**43**	184.7	**84**
Värska Bay	Avrg	57.7	**23.7**	46.9	**20.9**	43.8	**19.8**	48.9	**17.3**	82.2	**82.2**	168.2	**72.9**
	Min.	0	**18**	29.9	**15**	28.5	**16**	30	**13**	51.9	**20**	110.8	**59**
	Max.	75.5	**27**	59.7	**25**	57	**22**	60	**22**	121.1	**35**	203.2	**83**
Käina Bay	Avrg	21.6	**15.4**	9.1	**8.7**	1	**28.5**	11.4	**9.4**	113.7	**68.4**	50.8	**35.3**
	Min.	0	**7.9**	0	**4.2**	0	**5.3**	10	**4.1**	103.8	**13**	18.5	**17**
	Max.	45.3	**30**	14.9	**18**	14.3	**31**	20	**19**	121.1	**43**	73.9	**61**

→ Summary

The purpose of establishing high-quality requirements for natural mud and peat used in balneological procedures is to ensure that the mud used in balneological procedures is suitable for use and to exclude the classification of other unsuitable material as curative mud or peat used in balneological procedures. The objectives of the current quality assessment are: 1) to identify and map the state of Estonian curative mud deposits in 2022; 2) to identify changes in the composition of curative mud (last decade); 3) to provide companies with the information necessary for the use and product development of curative mud regarding the quality of the curative mud.

For the quality assessment, samples were collected from a total of 64 sites: 24 sample points in Haapsalu Tagalaht Bay, 20 sample points in Käina Bay, and 20 sample points in Värska Bay. Compared to the previous study (2013–2014), there were fewer sample points, but for the first time, hazardous substances such as phenols, petroleum products, and pesticides were investigated in curative mud. In addition, lithology analyses, microbiology, and the heavy metal content analysis were carried out. Over 1,600 measurements/analyses were conducted in total.

Samples from the three curative mud deposits examined were found to be microbiologically quite clean – the indicator bacterium *E. coli,* which is indicative of fecal contamination, was absent in all samples analysed, while *Cl. perfringens* was present in nine out of 32 samples. The majority of *Cl. perfringens* positive samples were found in Haapsalu Bay, where viable clostridia were found in six out of 12 sediment samples, and in five of them the value was higher than 1,500 CFU/g in the sediment. In Käina Bay, the bacterium was found in moderate levels in three out of ten sediment samples. In Värska Bay, the abundance of *Cl. perfringens* was less than 10 CFU/g of sediment in all samples.

Unlike the recognized indicator bacterium *E. coli*, which is commonly found in the intestines of warm-blooded animals and serves as an indicator of fecal contamination, *Cl. perfringens* as a bacteria reflects more the oxygen regime and eutrophication levels of a water body rather than the sanitary microbiological condition of the sediment/mud.

Comparisons with previous data suggest that organic matter concentrations have been stable in both lake sediments (Värska Bay) and marine sediments (Haapsalu Tagalaht Bay and Käina Bay) over the last decade. Organic matter levels in marine sediments are still significantly lower than in lakes.

The results of the heavy metal analysis (Cd, Cr, Cu, Pb, Ni, Zn, Sr, Sn, Hg) confirm that the concentrations of heavy metals found in all three deposits of curative mud are within the permitted limits (except for H11) of the target value and the limit value established in the regulation 'Limit values for the content of hazardous substances in soil' (except for H11). Average concentrations of heavy metals in curative mud (Cr, Cu, Ni, Pb, Sr, Zn) have decreased compared with 2013–2014 and 2022. One reason for this is the differences in the methods and equipment used to determine heavy metals. The highest concentrations of heavy metals are found in Haapsalu Tagalaht Bay and Värska Bay, while Käina Bay still has generally lower concentrations.

Of the petroleum products, the Haapsalu curative mud contains an average of 29.7 mg/kg of C21–C40, Värska 91 mg/kg. The average C10–C40 content in Haapsalu is 42 mg/kg, in Värska 118.6 mg/kg.

The average C10–C21 content in Värska was 29.3 mg/kg, while in Haapsalu the contents were below LoQ (20 mg/kg dw). All petroleum products in the Käina curative mud are below the LoQ. Phenol concentrations are below LoQ (0.05 mg/kg dw) in all three deposits, except in Värska, where 4-methylphenol averaged 0.5 mg/kg. Pesticides found in five samples from Värska were dichlorodiphenyldichloroethylene (DDE, p,p) 1.7 mg/kg and dichlorodiphenyltrichloroethane (DDT) 4.2 mg/kg per sample. In all other sediment samples, pesticide levels were below the limit of quantification.

It is important to continue with the quality assessment of curative mud and to carry out Stage II of the study.

The curative mud related entrepreneurs must have data on the content of hazardous substances in the curative mud or peat. If curative mud or peat does not meet the specified requirements, the reasons for the non-compliance must be identified and the necessary measures taken to remedy the non-compliance. Maintaining aquatic ecosystems is essential for the use and conservation of the curative mud resources.

In conclusion, the circular economy and curative mud are essential for a sustainable future, and the integration of these two areas can help to create greener and more resource-efficient economic models.

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→ ANNEXES

→ Annex 1. Limit values for hazardous substances in soil

(Regulation nr 26 of the Minister of the Environment of 28 June 2019 ‘Limit values for the content of hazardous substances in soil’ (Keskkonnaministri Määrus nr 26, 2019)).

No	Substance name /CAS[1] number		Target value, mg/kg	Limit value on residential land[2], mg/kg	Limit value on industrial land[3], mg/kg
1.	Mercury (Hg)[4]		0.5	2	10
2.	Cadmium (Cd)[4]		1	5	20
3.	Lead (Pb)[4]		50	300	600
4.	Zinc (Zn)[4]		200	500	1,000
5.	Nickel (Ni)[4]		50	150	500
6.	Chromium (Cr)[4]		100	300	800
7.	Copper (Cu)[4]		100	150	500
8.	Cobalt (Co)[4]		20	50	300
9.	Molybdenum (Mo)[4]		10	20	200
10.	Tin (Sn)[4]		10	50	300
11.	Barium (Ba)		500	750	2000
12.	Selenium (Se)		1	5	20
13.	Vanadium (V)		50	300	1,000
14.	Antimony (Sb)		10	20	100
15.	Thallium (Tl)		1	5	20
16.	Beryllium (Be)		2	10	50
17.	Uranium (U)4		1	5	20
18.	Fluorine (ion)		450	1200	2000
19.	Arsenic (As)		20	30	50
20.	Borium (B)		30	100	500
21.	Cyanides (CN-exclusive)		5	50	100
22.	Benzene	71-43-2	0.05	0.5	5
23.	Ethylbenzene	100-41-4	0.1	5	50
24.	Toluene	108-88-3	0.1	3	100
25.	Styrene	100-42-5	1	5	50
26.	Xylenes		0.1	5	30
27.	Monocyclic aromatic hydrocarbons (sum)		1	10	100
28.	Hydroxybenzene and isomers of cresol and dimethylphenol (sum)		1	10	100
29.	Biphasic phenols (sum of pyrocatechol, resorcinol, hydroquinone and their derivatives concentrations)		1	10	100

No	Substance name /CAS[1] number		Target value, mg/kg	Limit value on residential land[2], mg/kg	Limit value on industrial land[3], mg/kg
30.	Phenols (each compound below)		0.1	1	10
	Hydroxybenzene	108-95-2			
	O-cresol	95-48-7			
	M-cresol	108-39-4			
	P-cresol	106-44-5			
	2,3-dimethylphenol	526-75-0			
	2,4-dimethylphenol	105-67-9			
	2,5-dimethylphenol	95-87-4			
	2,6-dimethylphenol	576-26-1			
	3,4-dimethylphenol	95-65-8			
	3,5-dimethylphenol	108-68-9			
	Pyrocatechol	120-80-9			
	Resorcinol	108-46-3			
	Hydroquinone	123-31-9			
	2-naphthol	135-19-3			
31.	Chlorophenols (any compound)		0.05	0.5	5
32.	MTBE (methyl tert-butyl ether)	1634-04-4	1	5	100
33.	Petroleum products (hydrocarbons C10–C40, sum)		100	500	5,000
34.	Anthracene	120-12-7	1	5	50
35.	Chrysene	218-01-9	0.5	2	20
36.	Phenanthrene	85-01-8	1	5	50
37.	Naphthalene	91-20-3	1	5	50
38.	Pyrene	129-00-0	1	5	50
39.	Methyl and dimethyl derivatives of naphthalene (each compound)		1	4	40
40.	Acenaphthene	83-32-9	1	4	40
41.	Benzo(a)pyrene	50-32-8	0.1	1	10
42.	PAHs (polycyclic aromatic hydrocarbons, sum)		5	20	200
43.	1,2-dichloroethane	107-06-2	0.1	2	50
44.	Trichloromethane (chloroform)	67-66-3	0.1	1	25
45.	Hexachloroethane	67-72-1	1	10	100
46.	Chlorinated aliphatic hydrocarbons (all compounds not specifically mentioned in this list)		0.1	5	50
47.	PCBs (polychlorinated biphenyls, sum)	1336-36-3	0.1	5	10
48.	Organochlorine aromatic compounds (each compound)		0.1	0.5	30
49.	Organochlorine aromatic compounds (sum)		0.2	5	100

No	Substance name /CAS[1] number		Target value, mg/kg	Limit value on residential land[2], mg/kg	Limit value on industrial land[3], mg/kg
50.	Aliphatic amines		50	300	700
51.	2,4-D	94-75-7	0.05	0.5	2
52.	Aldrin	309-00-2	0.1	1	5
53.	Dieldrin	60-57-1	0.05	0.5	2
54.	Endrin	72-20-8	0.1	1	5
55.	Isodrine	465-73-6	0.1	1	5
56.	DDT	50-29-3	0.1	0.5	5
57.	Hexachlorocyclohexanes (each isomer)		0.05	0.2	2
58.	Trichlorobenzene		2	5	50
59.	Hexachlorobenzene	118-74-1	2	5	25
60.	Synthetic plant protection products (sum of active substances)		0.5	5	20

1 CAS: *Chemical Abstracts Service*

2 For the purposes of § 18[1] of the Land Cadastre Act, residential land includes residential land and other land for such purposes not included in industrial land under this regulation.

3 Industrial land within the meaning of § 18[1] of the Land Cadastre Act includes land with the following purposes:

- production land, including land under agricultural buildings and workshops and land used for the storage and servicing of machinery, but excluding land under production buildings, warehouses, and storage complexes for the food industry;
- mining land;
- land for landfill;
- transport land;
- national defence land;
- off-purpose land, including technogenic contaminated land;
- from commercial land, only the land underneath petrol stations, communications installations, and mass communications and technical installations.

4 For the purposes of applying a limit value for a hazardous substance, natural background concentrations of metals and their compounds may be taken into account if they do not allow compliance with the target value.

→ Annex 2. Results of the analysis in 2022

○ Annex 2.1. Analysis of the grain size of curative mud

(Haapsalu Tagalaht Bay – H; Käina Bay – K; Värska Bay – V).

		Sample	**H7**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.3**
Coarse sand	0.5	500	**0.4**
Medium sand	0.25	250	**0.5**
Fine sand	0.125	125	**0.8**
Very fine sand	0.063	63	**10.0**
Very coarse silt	0.036	36	**0.0**
Silt and clay	<0.036	<36	**88.0**
			100.0
		Sample	**H23**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.2**
Coarse sand	0.5	500	**0.3**
Medium sand	0.25	250	**0.5**
Fine sand	0.125	125	**1.0**
Very fine sand	0.063	63	**7.2**
Very coarse silt	0.036	36	**0.2**
Silt and clay	<0.036	<36	**90.6**
			100.0
		Sample	**H13**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.7**
Coarse sand	0.5	500	**0.2**
Medium sand	0.25	250	**0.4**
Fine sand	0.125	125	**0.6**
Very fine sand	0.063	63	**8.3**
Very coarse silt	0.036	36	**22.4**
Silt and clay	<0.036	<36	**67.3**
			100.0

		Sample	H15
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.4**
Coarse sand	0.5	500	**0.2**
Medium sand	0.25	250	**0.3**
Fine sand	0.125	125	**0.6**
Very fine sand	0.063	63	**5.8**
Very coarse silt	0.036	36	**15.6**
Silt and clay	<0.036	<36	**77.2**
			100.0
		Sample	**H19**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.2**
Coarse sand	0.5	500	**0.3**
Medium sand	0.25	250	**0.5**
Fine sand	0.125	125	**0.8**
Very fine sand	0.063	63	**8.9**
Very coarse silt	0.036	36	**13.7**
Silt and clay	<0.036	<36	**75.7**
			100.0
		Sample	**K13**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.0**
Medium sand	0.25	250	**0.1**
Fine sand	0.125	125	**0.7**
Very fine sand	0.063	63	**30.5**
Very coarse silt	0.036	36	**2.6**
Silt and clay	<0.036	<36	**66.1**
			100.0
		Sample	**K8**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.2**
Coarse sand	0.5	500	**0.1**
Medium sand	0.25	250	**0.6**
Fine sand	0.125	125	**7.6**
Very fine sand	0.063	63	**35.6**
Very coarse silt	0.036	36	**0.1**
Silt and clay	<0.036	<36	**55.8**
			100.0

		Sample	**K6**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.1**
Medium sand	0.25	250	**0.3**
Fine sand	0.125	125	**1.3**
Very fine sand	0.063	63	**47.9**
Very coarse silt	0.036	36	**1.4**
Silt and clay	<0.036	<36	**49.0**
			100.0
		Sample	**K5**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.0**
Medium sand	0.25	250	**0.2**
Fine sand	0.125	125	**0.6**
Very fine sand	0.063	63	**29.8**
Very coarse silt	0.036	36	**11.2**
Silt and clay	<0.036	<36	**58.2**
			100.0
		Sample	**K11**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**8.9**
Coarse sand	0.5	500	**0.2**
Medium sand	0.25	250	**0.4**
Fine sand	0.125	125	**0.7**
Very fine sand	0.063	63	**29.5**
Very coarse silt	0.036	36	**5.1**
Silt and clay	<0.036	<36	**55.1**
			100.0
		Sample	**K3**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.0**
Medium sand	0.25	250	**0.2**
Fine sand	0.125	125	**1.1**
Very fine sand	0.063	63	**37.3**
Very coarse silt	0.036	36	**0.6**
Silt and clay	<0.036	<36	**60.8**
			100.0

		Sample	**V2**
Name	Size, mm	Sieve, µm	Proportion, %
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.0**
Medium sand	0.25	250	**1.2**
Fine sand	0.125	125	**11.7**
Very fine sand	0.063	63	**20.8**
Very coarse silt	0.036	36	**0.0**
Silt and clay	<0.036	<36	**66.3**
			100.0
		Sample	**V8**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.0**
Coarse sand	0.5	500	**0.1**
Medium sand	0.25	250	**0.7**
Fine sand	0.125	125	**6.4**
Very fine sand	0.063	63	**16.0**
Very coarse silt	0.036	36	**0.0**
Silt and clay	<0.036	<36	**76.7**
			100.0
		Sample	**V11**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**1.1**
Coarse sand	0.5	500	**1.5**
Medium sand	0.25	250	**4.7**
Fine sand	0.125	125	**4.7**
Very fine sand	0.063	63	**8.6**
Very coarse silt	0.036	36	**0.3**
Silt and clay	<0.036	<36	**79.2**
			100.0
		Sample	**V4**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.2**
Coarse sand	0.5	500	**0.5**
Medium sand	0.25	250	**2.1**
Fine sand	0.125	125	**2.5**
Very fine sand	0.063	63	**12.5**
Very coarse silt	0.036	36	**0.2**
Silt and clay	<0.036	<36	**82.0**
			100.0

		Sample	**V5**
Name	Size, mm	Sieve, µm	**Proportion, %**
Very coarse sand	1	1,000	**0.2**
Coarse sand	0.5	500	**0.6**
Medium sand	0.25	250	**1.0**
Fine sand	0.125	125	**2.1**
Very fine sand	0.063	63	**11.7**
Very coarse silt	0.036	36	**0.6**
Silt and clay	<0.036	<36	**83.7**
			100.0

○ Annex 2.2. Petroleum products in curative mud (2022)

Standard methodology used for quantification (EVS-EN ISO 16703, 2004; SFS-EN ISO 9377-2, 2000), LoQ – limit of quantification, mg/kg dw (dry weight or dry matter).

		Total hydrocarbons: Nonpolar TPH (mg/kg dw)		
LoQ:		**20**		
ID	Deposit	**C10–C21**	**C21–C40**	**C10–C40**
H2	Haapsalu	<20	35	49
H4	Haapsalu	<20	34	46
H7	Haapsalu	<20	29	41
H9	Haapsalu	<20	30	45
H13	Haapsalu	<20	26	37
H17	Haapsalu	<20	24	34
K3	Käina	<20	<20	<20
K6	Käina	<20	<20	25
K8	Käina	<20	23	38
K12	Käina			19
K13	Käina			19
K14	Käina			19
K15	Käina			19
K16	Käina			19
K17	Käina			19
V1	Värska	28	77	110
V3	Värska	<20	48	63
V9	Värska	25	110	140
V12V13	Värska	31	110	140
V18V19	Värska	33	110	140

○ Annex 2.3. Pesticides in curative mud (2022)

Standard methodology Rashid *et al.*(2010), LoQ – the limits of quantification of analysis method (dw – dry weight or dry matter).

		Phenolic compounds (mg/kg dw)												
LoQ		0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
ID	Deposit	**Phenol**	**2-methylphenol**	**3-methylphenol**	**4-methylphenol**	**dimethylphenol**	**2,4-dim**	**2,5-dim**	**2,6dim**	**3,4dim**	**Trimethylphenol**	**2,4,6-trim**	**3,4,5-trim**	**Dimethylphenol**
H1	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
H4	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
H6	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
H8	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
H14	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
H21	Haapsalu	0	0	0	0	0	0	0	0	0	0	0	0	0
K1	Käina	0	0	0	0	0	0	0	0	0	0	0	0	0
K2	Käina	0	0	0	0	0	0	0	0	0	0	0	0	0
K9	Käina	0	0	0	0	0	0	0	0	0	0	0	0	0
K16	Käina	0	0	0	0	0	0	0	0	0	0	0	0	0
K20	Käina	0	0	0	0	0	0	0	0	0	0	0	0	0
V4V5	Värska	0	0	0	0.17	0	0	0	0	0	0	0	0	0
V6V7	Värska	0.06	0	0	1.1	0	0	0	0	0	0	0	0	0
V10V11	Värska	0	0	0	0	0	0	0	0	0	0	0	0	0
V15	Värska	0	0	0	0.33	0	0	0	0	0	0	0	0	0
V16V17	Värska	0	0	0	0.76	0	0	0	0	0	0	0	0	0