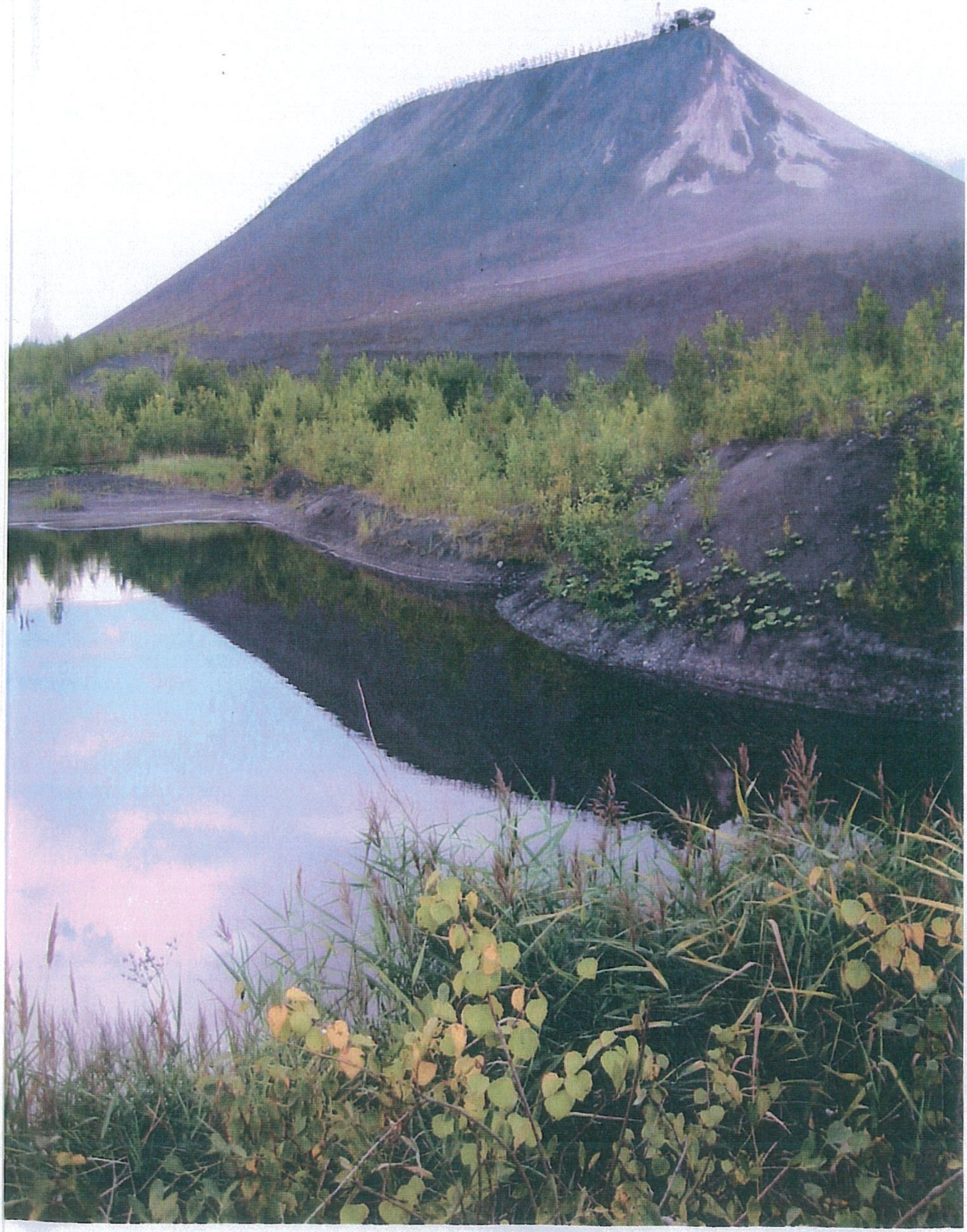

NGI

Estonia, the oil shale industry

Risk based environmental site assessment of landfills

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Estonia, the oil shale industry

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Executive Summary and Conclusions

The Norwegian Geotechnical Institute and The Norwegian Geological Survey established a joint venture with The Institute of Geology at Tallinn University of Technology. The purpose of the venture was to establish a working group for investigating the environmental conditions, under the framework of the EU landfill directive, and how this will affect the existing and future landfilling of the oil shale waste in Estonia. The project is financed and controlled by the Royal Norwegian Ministry of Foreign Affairs in cooperation with the Royal Norwegian Embassy in Tallinn. The project management also includes The Geological Survey of Estonia and The Institute of Chemical Physics and Biophysics, Tallinn, Estonia..

The largest industrially used oil-shale basin in the world is located in north-eastern Estonia. About 900 million tons of oil-shale has been excavated since World War I. About 80 % is used for generating electricity by incineration and the rest to generate shale oil by retorting. More than 300 millions tons of waste, ashes, are placed in huge landfills.

An inventory of landfills revealed that there were a total of 45 landfills with waste comprised of semi-coke, ash and enriched host rocks. The following sites were selected for detailed investigations:

- Kiviõli, two semi-coke landfills
- Kohtla-Järve, one semi-coke and one ash landfill
- Kukruse, one burnt and one unburnt landfill formed as a result of oil shale enrichment
- Narva, two ash landfills

Field investigations included survey of surface soil, drilling of monitoring wells, sampling and analysis of soil, groundwater and surface water for both inorganic and organic compounds. Modelling of groundwater and transport of contaminants were performed for Kiviõli, Kohtla-Järve and Narva.

The EU landfill directive requires bottom sealing and a collection system for leachate If necessary, the leachate from the landfill must be treated. None of investigated landfills have bottom sealing. However, the directive accepts a risk assessment to evaluate the extent of the contamination. If the risk assessment determines that a landfill with no bottom sealing poses no potential hazard to soil, groundwater, or surface water recipients the EU requirements may be reduced accordingly. Alternative remedial measures may be proposed to improve the standard of the landfills.

The semi-coke wastes of today at Kiviõli and Kohtla-Järve are characterised as non-hazardous because a few elements exceed the maximum limit for inert waste set by the EU requirements. However, the real leachate at the landfills, especially at Kohtla-Järve, contains several organic contaminants classifying it as hazardous. This is believed to be due to the fuss (tar), a hazardous waste from the torting process, which was deposited in the landfill up to few years ago.

The semi-coke landfills at Kiviõli and Kohtla-Järve do not meet the EU standard. According to transport groundwater modeling, a considerable part of the landfill leachate enters the groundwater flow as diffusive loss. For Kohtla-Järve untreated toxic leachate is also contaminating the nearby surface water recipients. The possible spreading of dust from the landfills combined with emissions to nearby remedial areas are not adequately studied yet.

The risk assessment of the diffusive loss to the groundwater, 100% at Kiviõli and about 50% at Kohtla-Järve, is not expected to cause any harmful effects to the environment. This spreading of the contaminated groundwater may be utilized as a remedial measure by the processes of natural attenuation. The 50% of the leachate entering the channels at Kohtla-Järve may be treated before being discharged or the infiltration may be improved for utilizing the natural groundwater attenuation processes. The industries involved should propose an industrial area of influence, where a certain contamination is contained and is acceptable.

It is necessary to improve the understanding of the toxicity of the leachate before the best and most economical treatment technology can be recommended.

Alternatively, the existing landfills can be abandoned and closed according to the required remedial measures and new landfill sites can be located and developed according to the EU landfill directive for non-hazardous wastes.

The programme for the monitoring the possible spreading of contaminants including redesign of the monitoring wells, should be tailored according to where the spreading may occur. The deep wells, where contaminants are detected, should be abandoned and closed, as these are expected in short sircuiting of deep groundwater by contaminated groundwater from the upper layers.

At Narva the filter and the cyclone ashes are both classified as non-hazardous waste as a few elements exceed the limit for inert waste. Due to the high incineration temperature there are no organic compounds in the wastes. However, according to ecotoxicological tests the leachate is classified as very toxic which is probably due to the very high alkalinity. Most of the leachate from the two ash landfills at Narva is classified according to the water balance as diffusive loss, since the leachate is entering into the groundwater underneath the landfills.

The landfills at Narva do not meet the EU landfill requirements. However, groundwater modelling shows that this leachate/groundwater flow is merging upwards into the channels and ponds, surrounding the landfills. This surface water is being recirculated for the hydraulically ash transport to the landfills. Some of the contaminated groundwater flow is entering into the Narva reservoir. According to the monitoring wells and studies in the Narva Reservoir, this groundwater flow does not cause any contamination.

At Narva it is necessary to upgrade the groundwater model with more calibration data to improve the water balance. Better documentation of the possible health effects from the dust spreading of ash by wind is recommended.

The hot Kukruse landfill is, because of no generation of contaminated groundwater, a special case and is not found to cause any risk of contamination to the environment.

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1. INTRODUCTION

1.1 Background

The largest industrially used oil-shale basin in the world is located in north-eastern Estonia, see Fig. 1.1-1. The exploitation of the basin started during World War 1, and since then about 900 million tons of oilshale has been excavated. After mining and enrichment, the spent oils-shale rock and the waste amounts to about 130 millions tons. About 90 % is used for generating electricity (96 % of the Estonian electricity demand) and the rest is for oil production. These activities are a major national environmental concern and have resulted in severe pollution of air, soil, sediments, the sea, surface- and groundwater. In addition, the Baltic Sea is the ultimate sink for many of the contaminants.

The power plants generate large quantities of waste bottom ash and fly ash. This waste is typically deposited in huge landfills or ponds in the vicinity of the power plants. The semi-cooking process, which extracts the oil, generates various solid wastes, which are then placed in huge semi-cokelandfills.

The wastes contain trace metals, semi-volatiles, polycyclic aromatic hydrocarbons, oil fractions, phenolic compounds, sulfides, and more.

An assessment of the leaching and spreading of the contaminants from the landfills and the toxicological effects at the receptors represent a highly challenging project. The investigations are done with the aim of executing a risk assessment. This will conclude with a waste management strategy including a proposal for remedial measures of existing landfills and a new technology for depositing the waste.

The study will follow the guidelines given in the EU landfill directive. The EU recommends assessing the environmental risk according to the "Risk Assessment for Contaminated Sites in Europe" where national guidelines are given priority. For Estonia, it is proposed to use the Norwegian Risk Assessment guidelines for Landfills (2003). All EU established standards and procedures for fieldwork and laboratory procedures (CEN-tests) will be followed.

1.2 Scope of work

A proper inventory of all waste sites, both abandoned and landfills in operation, related to the oil-shale industry in Estonia have been executed. Sufficient data and information is collected from all sites for classification and ranking with regard to existing and potential contamination.

Based on the inventory survey, typical landfills are chosen as demonstration sites where the detailed investigations and risk assessment will be carried out with the following objectives:

- Investigate and quantify the hydrologeological and geochemical processes occurring within the landfills, resulting in leachate generation.
- Assess the extent and spreading of windblown ash and its fallout to surrounding soils.
- Assess groundwater flow and contaminant transport
- Quantify the toxic hazards
- Assess the overall environmental risk with the landfills as they are today.
- Assessment of the landfills related to the EU landfill directives
- Propose remedial action to reduce the environmental risk to an acceptable level.

1.3 Project organization

The project is controlled and financed by the Royal Norwegian Ministry of Foreign Affairs. The project management consist the Norwegian Geotechnical Institute and the Norwegian Geological Survey. The local management and coordination is executed by the Institute of Geology at the Tallinn University of Technology.

To execute the project work in Estonia the following institutions and persons have participated:

Institute of Geology at Tallinn University of Technology, Liidia Bityukova (project coordinator), Leo Vallner, Tomas Metslang, Katrin Erg, Rina Klaas.

Institute of Chemical Physics & Biophysics, Anne Kahru, Lee Põllumaa, Kaja Kasemets, Angela Ivask.

Geological Survey of Estonia, Valter Petersell, Andreas Schmied.

In addition various services have been required from:

Drilling and installation of monitoring wells: BalRock OÜ

Chemical analysis: The Norwegian Geotechnical Institute (NGI) (leaching tests), Chemical Laboratory of The Geological Survey of Estonia, Hydroisotop GMBH (Germany), ACME Laboratory (Vancouver, Canada).

1.4 Project schedule

The project has been divided into the following phases:

- Project Planning
- Review of oil shale industry, wastes, etc.
- Inventory survey of landfills
  - Collecting data and reconnaissance
  - Reporting and ranking
  - Field Investigations
  - Monitoring wells
  - Field sampling and measurements
- Analysis and laboratory tests
- Project assessment
  - Contamination and modelling
  - Risk Assessment
  - Remediation strategy and recommendations
  - Reporting

The activities and the survey is illustrated in the Fig. 1.4.1

The project started 1 of May 2002 and all work except for the final report was completed within 31.12.2003. The report was completed 1. of November 2004.

2 ESTONIAN OIL SHALE AND OIL SHALE INDUSTRY

The general processes of the oil shale industry is illustrated in Fig. 2.1

2.1 Deposit occurrence, oil shale mining and processing

The Baltic Oil Shale basin is located in the northwestern border of the East European Platform. The deposit is continuous from northeastern Estonia to northwestern Russia (Fig. 1.1.1).

The area of the Baltic oil shale basin is approximately 50,000 km^2. The Estonian oil shale ***(kukersite-***from the locality name) (Kattai et al., 2000) is geologically related to Middle Ordovician. The Kukruse formation is presented by deposits of the upper part of Uhaku Regional Stage and Kukruse Regional Stage. The richer kukersite layers are located in the lower part of Kiviõli Member of the Kukruse Stage (Kattai et al., 2000). This is according to the last stratigraphical scheme of Ordovician beds (Nõlvak, 1999) Kukruse Stage related to the Upper Ordovician.

The kukersite shale occurs in two deposits: the Estonia deposit and the Tapa deposit.

- The Estonia deposit is located in north-east Estonia, is approximately 3,000 km^2, and the oil shale comprises there up to fifty laterally continuous kukersite seams having thickness from several cm to 0.9 m (Kattai and Lokk, 1998). The oil shale commercial bed consists of six kukersite seams A, B, C, D, E and F_1 and five thin interbedded limestone beds between them. The total thickness of commercial beds of oil shale varies in limits from 2.7 to 2.9 m in the northern part of the central and eastern areas of Estonian deposits, and up to 1.6 m to the south and west deposits. Among the interbeds the thickest are the beds A/B and C/D, at 18 and 22 cm, respectively.
  The total reserves of oil shale in Estonia are estimated to about 5,000 Mt of which 1,500 Mt is accessible (mineable) active reserve (Veiderma, 2002). Annual consumption (31 Mt) was at its height in 1980 (Kattai and Lokk, 1998 (Fig. 2.1), and is now 12-13 Mt/y (Adamson and Jostov, 2002).

- The Tapa deposit is located in the southwestern part of Baltic oil shale basin. Its area is 1,150 km^2. The oil shale lies under the surface at depths from 50 to 160 m, more than 2.3 m. It is currently unexploited (Kattai and Lokk, 1998).

The oil shale is mined in open casts and underground mines. As usual, the mining in open casts is carried out up to depths of 20 m. The underground mines reach 10-65 m under the surface (Kattai et al., 2000). According to the data by Kattai (Kattai et al., 2000) in 1998 oil shale was mined in three open casts and six underground mines. In 2004 the oil shale was mined in two quarries and two mines.

The oil shale mining area is located in northeastern Estonia (Ida-Virumaa County). The exploration of oil shale was started in the beginning of the last century and from 1950 the oil shale was used as a source for electrical power generation. The total volume of mined oil shale reached 872 Mln.t in 1998 (Kattai et al., 2000).

Up to 80 % of the mined shale is used by the power plants at Narva, Kohtla-Järve and Sillamäe. Chemical factories consume about 19 % of the mined oil shale for the production of shale oil and many chemical products (phenol products, antiseptics, antifreeze). Around 1 % is used by "Kunda-Nordic Tsement" (http://www.ep.ee/tarbijani/index.html).

The mining and processing of approximately 10^3 Mln.t of oil shale is accompanied by accumulation of about 300 Mln. m^3 of different types of waste (mining waste, semi-coke and ash) that leads to the environmental pollution in this region. The volume of the waste formed as the residue after oil shale enrichment before the processing is approximately 94 Mln. m^3, the semi-coke waste-70-80 Mln. m^3 and they cover about 180-200 Ha and with landfills reaching heights of up to 120 m. The ash waste volume is about 1,2 Mln. m^3, covers approximately 1000 Ha and is accumulated in the form of the plateaus.

2.2 Chemical and mineralogical composition oil shale

The main components of oil shale are the organic matter (content ranges from 10-15 up to 50-60%, carbonate minerals (20-70 %) and clastic minerals (15-60 %) (Bauert and Kattai, 1997). The main minerals of oil shale are presented by calcite, dolomite, illite, microcline, orthoclase, gypsum, pyrite and accessory minerals (Pets, 1998). Dilaktorsky and Galibina (1955) determined in the kukersite, secondary to the main minerals, limonite, hydromica, muscovite, zircon, tourmaline, leucoxene, glauconite, rutile, anatas. Consequent study of the mineralogical composition by Utsal (Utsal, 1984) and Vingissar (Vingisaar et al., 1984) determined the occurrence of chlorite, feldspar, siderite and pyrite.

The average chemical composition of oil shale ash from the Estonian deposit is: SiO_2-31 %, Al_2O_3-8.2 %, Fe_2O_3-5.9 %, CaO-39.5 %, MgO-4.8 %, SO_3-5.0 %, K_2O-4.2 %, Na_2O-0.3 % (Urov and Sumberg, 1992; Jefimov et al., 1995, 1996). The content of ash is 46.5 %, CO_2-18 %, organic matter 35.5 %, calorific values 13.0 MJ/kg, oil yield 23.0 %, natural dampness 7 %, and S-1.7 %.

The kerogen in the Estonian Ordovician kukersite has a marine origin (Hutton, 1995; Lille et al., 2002; 2003). According to the data by Urov and Sumberg (1992), the average elemental composition of organic matter of oil shale from the Estonian deposit is the following: C-77.3 %, H-9.8 %, O-10.8 %, N-0.4 % and S-1.7 %. The H/C ratio is 1.5 and oil yield is 66 %.

3 CLIMATE AND TOPOGRAPHY

3.1 Climate

The main factor influencing the climate of Estonia and in the whole of Europe is the Atlantic Ocean (in particular the North-Atlantic Stream). Estonia is located in a transition zone from maritime to continental climate. The active cyclonic activity in the northern part of the Atlantic Ocean determines a high variability of the weather, causes strong winds, high precipitation and abrupt fluctuations in temperature in Estonia. The annual average temperature in Estonia is between 4.3 °C and 6.5 °C. The average air temperature in central and east Estonia in January is –6° to –7 °C. The coldest month is February. The average temperature in July varies between 16.0 °C to 17.4 °C. The coldest areas are located on the uplands, the warmest on the coasts of shallow inland seas. Estonia is located in a region of humid climate, where the amount of precipitation exceeds the total evaporation. The annual average precipitation varies between 550 and 800 mm. Areas with the highest precipitation are located on the uplands and at a distance of 30–60 km from the western coast. The annual average of the relative air humidity is 80–83%. The annual average wind speed in the inland parts of country is less than 4 m/s; on the coasts of the open seas it is more than 6 m/s and speed of storm winds is more than 15 m/s. The intensity of snow cover in Estonia is very variable on the territory of country. The average duration of snow cover during winter is 75–135 days (http://www.estonica.org).

3.2 Topography

Estonia is located in the northwest of the East-European Plain. Its territory is about 45,000 km^2 and is very flat. The main part of the uplands of Estonia are usually 75–100 m above sea level (a. s. l.), the average absolute height is 50 m (Fig. 3.2). The highest point in Estonia and the Baltic States (Suur Munamägi Hill) is 318 m and located in the south Estonia. The main topographical forms in Estonia are the uplands, plateau-like areas, lowlands with depressions and valleys. Two erosional uplands are located in Estonia: Pandivere in northern and Sakala in southern Estonia. They have a relatively thin Quaternary cover and their appearance depends on the bedrock topography. The Harju and Viru plateaus are located in northern Estonia. They are about 30–70 m above sea level. The relief of the Viru Plateau is formed by artificial hills - oil shale waste landfills and ash hills. The lowlands cover nearly half of the Estonian territory and their absolute height is less than 50 m above sea level. As a rule their relief is mostly flat and a swampy. In the northwestern and northeastern Estonia the North Estonian Klint is located along the seacoast. The highest point of the North Estonian Klint is located at Ontika and has a height 56 m above sea level.

The Estonian topography has landforms that are formed more than 300 million years and were re-opened during more recent erosion. The Pleistocene glaciers formed the current topography of Estonia. The deposition of Quaternary deposits made the surface topography even flatter. After the ice retreated, a compensatory land rise began and it continues now in northwest Estonia, reaching 2-3 mm per year (http://www.estonica.org).

4 DESCRIPTION OF LANDFILL AND CHARACTERISATION OF OIL SHALE WASTE

The exploration of Estonian oil shale deposits was started in 1919. The open cast and underground mining cover now an area of approximately 900 km^2. Most of mined oil shale is used for producing electricity, shale oil and other raw compounds. The plants using oil shale as raw material are sited in the mining region. The industrial waste and waste after oil shale enrichment were stored in this area. Today in the oil shale mining region and in its nearest surroundings (Fig. 4.) there are 45 waste landfills (Table 4).

4.1 Methods

The distribution and estimation of the volume of wastes is based on a similar previous study (Беляев, 1992), topographic maps at the scale of 1:50 000

(Pulkovo, 1942) adjusted in 1982, raster maps of Estonia at the scale of 1:10 000 composed in 1997-1998, and earlier published papers as well as archive material. The contours and height of waste landfills marked on the raster maps were controlled and specified during fieldwork. The height and volume of the waste landfills closed before 1990 were determined by ordinary levelling (Беляев, 1992), therefore these data were taken as basis. For the landfills where the storing was finished after 1990 or those that are are currently in use, the height was determined by GPS (as the difference between the data measured on the top and on the bottom of the landfill). The review of the ash landfills (plateaus of the Baltic and Estonian PP), as well as the estimation of the volume of ash, is based on published materials and statistical reports from the power plants. The coordinates of the landfills were determined during the fieldwork by GPS and raster maps, using also the topographic maps adjusted in 1982.

4.2 Oil shale mining waste

The volume and composition of the wastes formed as a result of oil shale mining depends on the oil shale mining technology. The volume of mined oil shale in the mines and quarries of the Estonia oil shale deposit are presented in Table 4.2. Considering the setting of the commercial beds, different mining technologies have been used. Until the 1970s, the limestone interbeds were removed by selective mining or manually. Together with limestone and kerogenous limestone in waste landfills also accumulated some amount of oil shale. The data about the pattern rock are approximate, they formed up to 40% of the productive seam and its total organic matter content there was 8-14%. In the quarries (Vanamõisa, Pavandu, Viivikonna) the host rock were disposed with overburden rocks, the separation of waste was not made. The hosted rock from mines was removed by special conveyors and stored in waste landfills. These were usually 40-50 m high and the inclination of their slopes was about 30° (angle of repose).

In the 1960s, the plants for enrichment were built near main underground mines and the Aidu quarry, while smaller underground mines (Kukruse, Sompa, etc.) were closed. In Viivikonna, Sirgala and Narva quarries, large-scale selective mining was carried out. The enrichment of oil shale is performed by gravity method using heavy magnetite suspensions. The extracted material of the productive bed is crushed to the particles with a grain size of <300 mm and the fine particles (0-25 mm) are separated by sieving. During enrichment from the coarse fraction (diameter >25 mm), kukersite concentrate (25-125 mm) and limestone are separated. The limestone lumps are the tailings, which in 1998 formed about 38% of the explored productive bed material. The tailings contain 6-12 % organic matter (Воолма и др., 1981). Now the landfills of hosted rock and waste after oil shale enrichment cover more than 336.5 ha and their volume is about 94 Mln. m^3. Annually 3.0-3.5 million tonnes (1.7-2 Mnl.m^3) of wastes are formed.

In 2002, oil shale was mined at Estonia and Viru underground mines and enrichment plants operated there. In Aidu and Narva quarries, the oil shale is explored by selective method and hosted rocks disposed together with overbuden rocks. Kukersite is a spontaneously combustible rock. In the 1960s there were several occasions when spontaneous ignition of kukersite in waste landfills of hosted rock rich in kukersite occurred, e.g. at Sompa, Sompa-4, Jõhvi and Kukruse mines. At Kukruse the burning has continued up to now. The results of investigations show that in order to avoid spontaneous combustion the peaks of landfills must be levelled and their height must not exceed 40 m (Эпштейн, 1967).

4.3 Oil shale waste utilisation in northeast Estonia

Two ways of oil shale utilisation developed in Estonia: producing the raw materials for shale oil production and chemical industry, and raw material for the energy industry (production of electricity and thermal energy). The oil shale thermal processing was carried out mainly in Kiviõli and Kohtla-Järve. Already before World War II simultaneously with the extension of shale oil production, the transfer of power plants to combustion of oil shale began (Püssi, Kiviõli).

After World War II, the oil shale was widely used for producing electricity and thermal energy in Kohtla-Järve, Kohtla-Nõmme and Ahtme. The Baltic PP (capacity 1,400 MW) was launched in 1965 and the Estonian PP (capacity 1,600 MW) in 1973.

The oil shale used for technological and energy purposes has different qualities. Lump oil shale with average calorific value more than 10 MJ/kg is used for oil shale retorting. For energy purposes, all oil shale fractions with a average calorific value more than 6 MJ/kg is used. (http//www.ep.ee/). The calorific value of oil shale is tested by bomb method (Петерселлъ и др., 1992). The quality of trade oil shale (delivered to the clients from mines or quarries) is subject to regular control. The volume of trade oil shale for the above purposes is presented in Table 4.3.1.

Shale oil production in northeast Estonia began before World War II, but after that in addition to fuel oils also the production of impregnation oils, calcined petroleum coke, lacquers, mastics, phenols and other raw compounds was started. Besides Kiviõli and Kohtla-Järve, in 1980 shale oil production was initiated at the Estonian PP in Narva, but there the semi-coke formed is burnt together with oil shale and tailings are not formed, excluding it from the present study. The technologies applied at thermal oil shale processing early and at present time are presented in Table 4.3.2. In Kiviõli and Kohtla-Järve three main methods were used: tunnel ovens, chamber ovens and vertical retorts (Jefimov, 2000). In recent years only the retorts have been applied for oil shale thermal processing. Formerly the process was performed at a temperature of up to 500-600 °C, but now the temperature has been raised to 700-800 °C.

All methods of oil shale thermal processes lead to formation of oil and concentrated water rich in phenols. The retorting residues (semi-coke) were delivered in bogies to the semi-coke depositories where they were stored. The empty containers were washed with water. The composition of semi-coke obtained by different processing methods and stored at the depositories is presented in Table 4.3.3. In recent years, semi-coke is transported to the depositories by trucks instead of bogies, thus the polluted water is not pumped to semi-coke landfills any more. During last two decades the amount of the semi-coke formed as a result of oil shale retorting was approximately 1-2 million tonnes per year. To this amount could be also added the fuss formed at thermal processing which was also stored in waste landfills until the last years. Fuss, which is mechanical mixture of heavy fractions of oil, fine particles of coke and water of variable composition, forms 0.7-1.6 % of semi-coke's mass. During the last years fuss was sent to Kunda Cement Plant where it was used for heating. The semi-coke waste landfills now cover approximately 175.4 Ha, have a volume of 83.4 Mnl.m^3, and their height reaches 116 m (Table 4).

4.4 Waste resulting from electricity and thermal energy production

At the thermal power plants, crushed trade oil shale is used. Oil shale is combusted at high temperature (1,000-1,200° C), at which the oil shale organic matter is completely burned and the main carbonate minerals forming the mineral part of oil shale (calcite and dolomite) are destroyed. In the results of oil shale consumption, ash is formed that is partly fractionated. The finer and lighter ash particles volatilise and are mostly caught in cyclones or electric filters. These ash fractions form fly ash. Most of the ash, the so-called furnace ash or furnace slag, falls into the lower part of the oven and is pumped from there by pressurised water along metal pipes to waste landfills (plateaus). On these plateaus ash is deposited in a shallow (1-2 m) basin. The water is passed through additional sedimentation basins and is then repeatedly used.

Fly ash is used for liming of acid soils, producing cement and building materials (blocks), etc. The furnace ash is not used.

A large amount of free CaO is formed as a result of carbonate mineral destruction causing high alkaline environment. The water used for transportation of ash and ash deposition at the depository is not sufficient for neutralising the free CaO. The results of studies show that after 24 years free CaO is still present in the tailings (Воолма и др., 1981). The concentration of free CaO in the tailing varies (Table 4.4), but it is found in the whole vertical section of the depository. A decrease in free CaO in the lower beds of the depository was not observed. Simultaneously, many microelements (As, Br, Pb, Sb, Zn and others) concentrate in the fine ash fractions, especially those caught by electric filters (Pets at al., 1985).

In northeast Estonia the ash of power plants is stored in a total of 8 ash landfills, from these the present study does not include those in Kunda and Sillamäe. The ash landfills cover a total of 13,922 ha and their volume is 118.5 Mln.m^3 (Table 4). The Baltic and Estonian PP annually produce total 5-6 Mln.t of ash.

5 INVENTORY OF LANDFILLS

To establish the most representative and important landfills for detailed investigations a survey of all landfills has been executed. This involved reconnaissance and collection of specific data according to a questionnaire for each landfill.

5.1 Selection criteria for waste landfills investigation

A total of 45 landfills were identified and classified. The results of the inventory are listed in Table 4.

The different landfills were divided into three groups on the basis of their composition:

- landfills of host rock and formed as a result of oil shale mining and landfills of tailings formed as a result of oil shale enrichment; burnt and unburnt
- semi-coke landfills;
- ash landfills (plateaus) of thermal power plants.

Below follows a more detailed description of the three landfill categories.

5.1.1 The landfills of host rocks and tailings formed as a result of oil shale enrichment

The landfills of host rock and tailings formed in the result of oil shale enrichment are most widely distributed (total 33). As was indicated above (Chapter 4.2), they consist of pieces of limestone and kerogenous limestone, containing also some lumps of non-separated limestone and kukersite or pieces of pure kukersite accidentally delivered there by transportation. Spontaneous ignition and burning has occurred on 27% of such landfills. The wastes, which have not spontaneously ignited, yet have obviously very little impact on the environment. The environmental impact of the landfills that were burning was not investigated. Therefore, for more detailed investigations the waste landfill of Kukruse mine was selected where spontaneous ignition has occurred. This waste landfill is especially representative because it ignited last and the inside combustion continues even today, 22 years after its spontaneous ignition. For the comparison of environmental impact of burned and unburned waste, the waste landfill Kukruse 2, which had not spontaneously ignited, was also selected for the study.

5.1.2 Semi-coke landfills

Semi-coke landfills are the most hazardous for the environment. The semi-coke and fuse consist the water rich in oil products and phenols. The polluted water is formed on the account of infiltrating precipitation; previously to this was added the water used for washing of bogies. The upper surface of the landfills is porous and uneven, more than 30-40% of the precipitation fallen on the landfills' surface infiltrates. The semi-coke landfills are located in areas with different geological and hydrogeological conditions. The semi-coke landfills in Kiviõli are partly located on alvars and partly above the abandoned Kiviõli underground mine. The semi-coke landfill of Kohtla-Järve is situated outside the northern boundary of the oil shale distribution area, where the bedrock limestone and the groundwater of the Ordovician aquifer are covered by till and 2-5 m thick layer of glaciolacustrine silt. Taking into account the different age of landfills formation and differences in geology and hydrogeology of place of deposition these semi-coke landfills were selected for more detailed investigations.

5.1.3 The ash landfills of thermal power plants

The ash landfills of thermal power plants are rather similar and their influence on the environment is moderate. From the geological point of view they are situated under different conditions. Some of them are located on alvars, others in the areas where the thickness of the Quaternary cover is 3-5 m that is important from the viewpoint of hydrogeological conditions. The high alkalinity of ash leads to the formation of alkaline subsoil and groundwater. Depending on the pH values of the subsoil water formed on the account of precipitation, different elements are leached out from both ash and soils.

The first (the oldest) ash plateau of the Baltic PP was selected for more detailed investigations, since it is among the biggest and oldest ash landfills and the chemical composition of these wastes has been previously investigated.

5.2 Selection of landfills

The following landfills have been selected for detailed investigations.

The Narva site:

AS „Narva Elektrijaamad"
Sepa Street, 4
20306 Narva
ESTONIA

Contact person:
Environmental Protection Department Manager
Mr. Arvo TORDIK
Ph. +372 71 66 107
arvo.tordik@ nj.energia.ee

The Kiviõli site

Kiviõli Keemiatööstus OÜ
Turu Street, 3
43125 Kiviõli
ESTONIA

Contact person:
Head of Environmental Department
Mr. Eugen NÕMMISTE
Ph. +372 33 59 606

The Kohtla-Järve site

Viru Keemia Grupp
Järve küla tee, 14
30328 Kohtla-Järve
ESTONIA

Contact person:
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6 CLASSIFICATION OF WASTES AND LEACHATE

6.1 Type of wastes

Big samples (up to 20 kg) of the different types of waste were collected in summer 2002. Totally four samples of semi-coke and three samples of ash were studied. Fresh semi-coke from Kiviõli (sample KV-F) was taken from the new (western) part of western landfill (I) where it was transported by the lorry directly from the chemical factory. The “middle” semi-coke sample in Kiviõli (sample KV-M) was taken from the old (eastern) part of the western landfill (I) where it was transported by trucks approximately 20 years earlier. "Old" semi-coke (sample KV-O) was collected from the eastern landfill (II) located in Kiviõli next to the road Tallinn-Narva. These wastes are already at least 40 years old.

The fresh semi-coke sample from Kohtla-Järve (KJ-F) was also taken from the new landfill where it is transported now by the lorry from the chemical factory. The ash was (sample KJ-A) taken from the ash landfill where it was transported from the Kohtla-Järve power station.

The samples of ash from power station were taken from the filter (sample N-AF) and cyclone (sample N-AC) of the Baltic Power Plant. The samples were sieved to <2 mm using nylon screening and the fraction less than 2 mm was used for analyses.

The obtained results of ICP-MS measurements and organic compounds determination are showed in Tables 6.1.1.1-6.1.1.3 and 6.1.2.

6.1.1 Semi-coke

The chemical composition of the studied samples of semi-coke collected from waste landfills in Kiviõli showed the stable content of chemical elements that are mostly entered in clastic minerals (Table 6.1.1.1). Small differences were observed for Ca, Al, S and organic carbon (TOC) contents. The highest contents of Al and TOC and the lowest values of Ca and S were determined in semi-coke from the older (eastern) waste landfill (sample KV-O). The semi-coke from Kohtla-Järve (KJ-F) has the higher content of Al, K and TOC content and the lowest content of Ca relative the samples of semi-coke from Kiviõli. Content of S and other main elements are similar in semi-coke from Kohtla-Järve and semi-coke from Kiviõli but S content is much lower in old semi-coke from Kiviõli.

The contents of the main part of trace elements in the semi-coke samples from Kiviõli are higher in the semi-coke taken from the older waste landfill (sample KV-O). There the higher level of As, Ba, Ce, Cr, Cu, Dy, Ga, Gd, Nd, Pb, Pr, Sc, Sm, Th, U, V, W, Y and Yb is observed. The highest contents of trace elements from the studied samples of semi-coke were revealed in fresh semi-coke from Kohtla-Järve (KJ-F). It is characterised by the highest contents of Ag, As, Ba, Ce, Co, Eu, Ga, Gd, Ho, La, Mn, Mo, Nd, Ni, Pr, Sb, Sc, Sm, Th, Tm, V, Y and Zn.

The studied samples of semi-coke are different in content of organic compounds (Tables 6.1.1.2 and 6.1.1.3). The contents of sum PAH are similar in the "middle" semi-coke from Kiviõli (KV-M) (3.90 mg/kg) and from Kohtla-Järve (KJ-F) (4.47 mg/kg). In these samples the PAH are represented practically by the full spectrum of studied PAH compounds (Acenaphthen, Fluoren, Phenanthren, Anthracen, Fluoranthen, Pyren, Benzo[a]anthracen, Chrysen, Benzo[b]fluoranthen, Benzo[k]fluoranthen, Indeno(123-cd)pyren, Benzo[ghi]perylen). In the KV-M sample Dibenz[ah]anthracen was also revealed. From the determined PAH Phenanthren, Fluoranthen and Pyren have the highest concentrations. Much lower contents of PAH were determined in fresh (KV-F) and old (KV-O) semi-coke from Kiviõli (0.51 mg/kg and 0.46 mg/kg accordingly). In the latter the low contents of Fluoren, Phenanthren, Anthracen, Fluoranthen, Pyren and Chrysen respectively are a little bit higher than the analytical detection limits (0.01 mg/kg) were revealed. In fresh semi-coke from Kiviõli (KV-F), the Naphthalene (0.5 mg/kg) and Fluoranthen (in the trace content - 0.01 mg/kg) are determined.

The highest content of sum oil products was revealed in fresh semi-coke from Kohtla-Järve (KJ-F) (0.26 mg/kg). BenzeneBenzene (0.06 mg/kg), Toluene (0.09 mg/kg), Ethylbenzene (0.02 mg/kg) and m+ρ-Xylene (0.09 mg/kg) are present there. Sum oil products is much lower (0.1 mg/kg) in the fresh semi-coke from Kiviõli (KV-F) (Benzene 0.01 mg/kg, Toluene 0.03 mg/kg and m+ρ-Xylene 0.06 mg/kg) and in “middle” semi-coke (sum is 0.06 mg/kg) from Kiviõli (KV-M) (Toluene 0.02 mg/kg and m+ρ-Xylene 0.03 mg/kg) and less than the analytical detection limit (0.01 mg/kg) in the oldest semi-coke from Kiviõli (KV-O).

The fresh semi-coke from Kohtla-Järve (KJ-F) is characterised by a high content of phenols (9.40 mg/kg). This content is more than in ten times higher than in the fresh semi-coke from Kiviõli (KV-F) (0.85 mg/kg) and in many times higher than in "middle" semi-coke from Kiviõli (KV-M) (0.14 mg/kg). In the oldest semi-coke from Kiviõli content of phenols is less than analytical detection limit (0.01 mg/kg). In both fresh semi-coke from Kiviõli and Kohtla-Järve the phenols are presented by 4-Methylphenol (0.33 mg/kg and 4.60 mg/kg), 3,4-Dimethylphenol (0.05 mg/kg and 0.31 mg/kg), 2,3-Dimethylphenol (0.25 mg/kg and 1.90 mg/kg) and 2,4-Dimethylphenol (0.22 mg/kg and 2.60 mg/kg), respectively. In the "middle" semi-coke (KV-M) only 2,4-Dimethylphenol was determined.

6.1.2 Ash

Ash samples from Narva were selected from filter and cyclone. The ashes that accumulated there are presented by the finest fractions of the ash produced in the results of oil shale burning. According to many publications these samples have the highest concentrations of the trace elements and are the most harmful for the environment and health. The ash stored in the landfills has less risk for the environment.

The ash was analysed only for inorganic components because the high temperature of oil shale combustion gives no chances for organic compounds to be saved in the ash.

Comparison of composition of ash from Narva (Table 6.1.2), shows that ash on the filter (N-AF) has a little bit higher content of elements that are entered in clastic minerals in oil shale (Al, Ti, K, Na, P and S) and much lower content of Ca. Ash on the filter (N-AF) is also characterised by higher contents of many trace elements relatively to cyclone ash (N-AC): Ag As, Bi, Cd, Ce, Co, Cr, Dy, Ga, Gd, La, Mo, Nd, Ni, Pb, Pr, Sb, Sc, Sm, Tb, Th, U, V, W, Y, Yb and Zn. The ash from Kohtla-Järve (KJ-A) that is represented by courser fraction (< 2 mm) has the lowest contents of Ca (18.45%) relatively to the finest fractions of ashes from Narva PP. In ash from Kohtla-Järve (KJ-A) the contents of Ba, Bi, Cd, Ce, Cu, Gd, Dy, Er, Eu, La, Nd, Ni, Pb, Pr, Sb, Sc, Sm, Sr, Tb, Th, Tm, W, Y, Yb and Zn are lower than in both samples of fine fractions of ash from Narva. At the same time it could be indicated that all three ashes have similar values of trace elements contents and in the distribution of trace elements in the ashes having different grain-size composition big differences are not observed.

Study of organic compounds in ash from Kohtla-Järve showed small amounts of oil products there (Toluene 0.03 mg/kg and m+ρ-Xylene0.05 mg/kg). It could be caused by presence of the mixture of semi-coke in the ash that contains these compounds.

6.1.3 Burned oil shale waste from Kukruse

For the study of wastes after oil shale enrichment that are self-burned, the waste landfill of the mine Kukruse 2 was selected for study. Traditionally starting from the beginning of oil shale exploration these waste were stored in the form of pyramidal cone that formed in the result of transportation of waste to the top by trucks. The deposition of waste that had considerable amount of organic matter and pyrite in the form of cones led to spontaneous self-combustion of waste. The self-combustion of waste in Kukruse landfills started in 1967 and continues until now. The borehole on the slope of Kukruse waste landfill (35 m from top to bottom) was drilled during June 2003. The core was sampled with density of one average sample per meter and analysed by ICR-MS and XRD techniques. Three samples from the following intervals of the core (8.4-8.6 m, 11.6-11.8 m and 19 m) were taken for the study of organic compounds (PAH, oil products and phenols). The photo of the core and its short description are presented on Table 6.1.3.1. The results of chemical and mineralogical analysis are shown in Fig. 6.1.3 and in Table 6.1.3.2.

The chemical composition of waste is relatively stable. The concentration of main and trace elements vary. The level of element concentration is similar to the contents in unburned oil shale. The content of CaO varies from 14.17% up to 41.58%, MgO from 1.89 up to 4.24%, Fe_2O_3 from 3.43 up to 7.49 %. The content of clastic minerals ranges in the limits of 20 % up to 86.6 %. The trace element contents are relatively stable and typical for oil shale. Some increase in heavy metals contents (Ag, Co, Cu, Mo, Ni and Pb) is observed on the depth of 5 m. On this depth, it was revealed a decrease of CaO and higher contents of clastic minerals.

Content of calcite is on average approximately between 40-60 % and increases in the waste down through the depth of the well. The content of quartz and dolomite range in the limits respectively from 1.5 % up to 41.9 % and from 2.7 % up to 20.3 %. It decreases in the waste for both minerals to the depth of the well. The illite content is relatively stable and is on average of about 20 %. The gypsum was revealed in the upper part of section (from the surface up to depth of 5m), on the depth of 15m and in the deeper part of the well (21-23 m). Its content varies in wide limits (1.3-28 %) in the upper part of the well and is low (3.6-5.1 %) in deeper part.

The samples taken for the study of organic compounds are characterised by high contents of dry residue – up to 100% (Table 6.1.3.2). The phenols were detected at the upper samples by 17 and 50 mg/kg. At the deepest depth, 19 m, 0.85 mg/kg phenols were detected. Similarily with BTEX higher concentrations were detected in the upper samples at the depth 8.5 and 11.7 m, see Table 6.1.3.2.

The temperature inside the landfill is measured from 63°C at 2 m to 96° C at 23 m depth. This high temperature will have special effects on the organic compounds. Some are expected to slowly disappear by degradation, volatility and diffusion

No PAH were detected in the waste samples.

6.2 Leaching test

The concentration of chemical elements and organic compounds was tested in leachates from the solid waste samples. Leaching test was carried out in the Environmental Laboratory of the Norwegian Geotechnical Institute (NGI) according to the procedure described in EN 12457 (OJ 16.7.1999). The ratio from liquid to solid (L/S) of 10 to 1 was used.

The leaching test used the subsamples of four different types of waste collected in summer 2002. Totally seven samples (4 of semi-coke and three samples of ash) were tested. The samples for the leaching test were dried at 95 °C. The split of dried sample (200 g) was put into a dark glass bottle, 1,800 ml of Millipore water was added and the sample was mixed during twenty-four hours. The leach was filtered under vacuum and pH and electric conductivity was measured in the solution. The subsamples for the ICP-MS and organic compounds measurement were taken from each leach and preserved according to the procedures described earlier. In the leachates of ash from Narva were determined only inorganic components.

6.2.1 Semi - coke

The leachates from semi-coke in Kiviõli have different pH values. It is highest in leachates from fresh semi-coke (pH=12.54), and decreases in leachates from middle semi-coke (pH=11.22) and from semi-coke taken from the old (eastern) semi-coke waste landfill (pH=8.47) (Table 6.2.1.1). The values of electric conductivity range in the limits from 10.4 µS/cm to 1.39 µS/cm in the leachates, extracted from semi-coke in Kiviõli. The total mineralisation of leachates from the Kiviõli semi-coke range in very wide limits. It is extremely high (15,760.44 mg/l) in fresh semi-coke and gradually increases in leachates from "middle" semi-coke (203.29 mg/l) to the oldest semi-coke (34.08 mg/l) stored more than 40 years ago (Table 6.2.1.2).

The leachates of semi-coke from Kohtla-Järve are alkaline and have high values of pH (12.38) similar to leach from fresh semi-coke in Kiviõli. They are also characterised by relatively high values of electric conductivity (8.54 µS/cm). The total mineralisation of leachates from semi-coke in Kohtla-Järve (1,269.61 mg/l) is approximately ten times lower than in leachates from fresh semi-coke from Kiviõli, but several times higher than in leachates from waste stored in waste landfill more than 20 years ago.

The extractability of studied elements is very different for semi-coke waste stored at different times (Table 6.2.1.2). There is a very strong correlation of concentration of many elements in the leachates depending on the time of storage. As we can see from Fig. 6.2.1 a sharp decrease is observed for Ag, As, Au, B, Ba, Be, Bi, Br, Ca, Ce, Cl, Cr, Cs, Fe, K, Li, Mo, Na, Pb, Rb, S, Se, Sr, V, Yb and Zn from fresh semi-coke to the oldest waste taken from the eastern waste landfill (II). The content of elements in leachates from Kohtla-Järve semi-coke is less than the elements' content in the leachates from fresh semi-coke in Kiviõli and higher than in the leachates from semi-coke stored in Kiviõli more than 20 years ago.

The contents of organic compounds for each compound in the leachates from all samples of semi-coke from Kiviõli are less than analytical detection limits (0.01 µg/l for PAH, 0.5 µg/l for oil products and 0.5 µg/l for phenols) (Table 6.2.1.3). Only in one case in extract from fresh semi-coke in Kiviõli, was Fluoranthen (0.014 µg/l) revealed. The study showed that leachability of organic compounds from Kohtla-Järve semi-coke is low. A 24-hour leaching test of material from the Kohtla-Järve landfill resulted in PAH of 0.2 µg/l (0.2 µg/l of Naphthalene), BTEX - 2.1 µg/l (2.1 µg/l of TolueneToluene) and phenols less than 0.5 µg/l. All these concentrations are much lower than PLVs. The semi-coke waste is therefore not expected to be the source of the observed contamination in the subsurface.

6.2.2 Ash

In the studied leachates of ashes there is neither a difference in the pH values nor in the values of electric conductivity (EC). The very high pH was determined in all three leachates extracted from ashes. In the leachates from ash from Kohtla-Järve, pH is 12.44. In both leachates from samples of Narva ashes, pH values are similar (12.73 in leach from ash from the filter and 12.72 from ash from the cyclone). The EC is the highest (15.55 µS/cm) in leachates from Narva ash from the filter. The lower values of EC were determined in the leach from Kohtla-Järve ash (7.52 µS/cm) and Narva ash from the cyclone (12.75 µS/cm, respectively). The highest total mineralisation (2,461.01 mg/l) is in the leachates from the ash taken from the filter in the Baltic Power Plant, a little less (1,846.08 mg/l) in extracts from the ash taken from the cyclone in BPP. The leachates from the ash from Kohtla-Järve Power Plant are less mineralised (987.42 mg/l). The main contribution to mineralisation of ash leachates is made by potassium and calcium. The leachates from ash from the Kohtla-Järve Power Plants have the higher level of Al, Si, Ga, Na, Li, Cs, Rb, Co, Mn, V and Zn. This group of elements is typical for the clastic components of oil shale and it could be explained taking into account the coarser grain size composition of ash from Kohtla-Järve relative to fine fractions of ash from Narva. Comparison of leachates from the filter and the cyclone showed the higher concentrations of the elements in leachates from the filter relative to the cyclone. In the leachates from the cyclone, increase of Al, B, Fe, Ni, Sc, Si, Sr and Te content was determined.

6.3 Classification of wastes

The wastes have been classified according to the Criteria and procedures for the acceptance of wastes.(EU, 2002). The maximum acceptable leaching limits for the three classes, inert, non-hazardous and hazardous wastes are shown in Table 6.2.1.2 for inorganics. The limits are in mg/kg leached substance. To make the eluat concentrations in µg/l to mg/kg the concentrations must be divided by 100. For organics Table 6.2.1.3 show the leaching of the organic compounds. The limits for BTEX and phenols are respectively 6 and 1 mg/kg and for the PAH there are no limit determined yet. None of the eluats are exceeding these limits for inert waste.

The Table below shows that some of the elements for the fresh Kiviõli semi-coke and the ashes from Narva exceed the limits for inert waste and will be classified as non-hazardous wastes. The other wastes are classified as inert wastes. Fig. 6.3 shows the different elements for the varios wastes.

Sample	Elements which exceed limits		
	Inert	Non-Hazardous	Hazardous
Kiviõli, fresh semi-coke	As, Ba, Mo, Se	None	None
Kiviõli, <20 years semi-coke	None	None	None
Kiviõli, <40 years semi-coke	None	None	None
Kohtla-Järve, fresh semi-coke	Se	None	None
Kohtla-Järve, ash from powerplant	None	None	None
Narva, ash from filter	Cr, Hg, Mo, Se	Se	None
Narva, ash from cyclone	Cr, Hg, Se	None	None

6.4 Soil quality

With reference to the Estonian soil quality (KKMm, RTL, 1999) guidelines all the wastes are within the limits for Industrial areas for both inorganics and organics. Comparing with the Canadian soil quality guidelines (CSoQGs, 2004), which is often used for comparison, the wastes from Kiviõli and Kohtla-Järve and the cyclone ash from Narva are also within the limits for residential areas. The ash from the filter at Narva is exceeding the limit for both industrial and residential areas for Arsenic.

7 GEOLOGICAL SETTING OF THE SELECTED SITES

Three rock complexes overlying each other can be distinguished in northeast Estonia:

- the Quaternary cover,
- the sedimentary cover (Neoproterosoic Vendian and Palaeozoic Cambrian and Ordovician sedimentary rocks),
- the Proterozoic crystalline basement.

7.1 Quaternary geology

The Quaternary cover consists mostly of the glacial, glaciolacustrine and glaciofluvial deposits of Pleistocene age. The glacial deposits are mainly represented by tills, while the glaciolacustrine (Baltic Ice Lake and local ice lakes) and glaciofluvial deposits comprise mostly clays, silts and sands, seldom gravel. The Holocene deposits (marine, lacustrine, alluvial clays, silts and sands, seldom gravel) have patchy distribution (Geology..., 1997). Bog deposits are widely distributed. The Quaternary deposits contain the crushed boulder remnants as well as fine particles of the crystalline basement rocks and ores exposed on the seafloor of the Gulf of Finland. In southern Finland and southern Karelia these were delivered to northeast Estonia by the continental glaciers. After melting of the continental glacier most of this material was partly sorted and deposited on the bedrock surface as till of variable thickness. The development of lakes and mires started. Part of the mires have passed the stages of fen and transitional mire and reached the bog stage.

7.2 Basic geology

The rocks of the crystalline basement are represented by the schists and gneisses having the variable mineral and chemical composition and acid to ultrabasic intrusive rocks. Alkaline rocks are present as well (Koistinen ..., 1996; The Geochemical..., 1992).

The Vendian and Palaeozoic sedimentary rocks overlay the crystalline basement, forming sub-parallel beds following the surface of the crystalline basement and slightly dipping southward (ca 3 m per km). In northeast Estonia the sedimentary cover is presented by Vendian and Cambrian and Lower Ordovician terrigenous (clays, siltstones and sandstones) and Middle and Upper Ordovician carbonate rocks. The total thickness of terrigenous rocks is 160-190 m. The terrigenous rocks were deposited in a shallow sea with regular water salinity and they consist mainly of quartz, feldspar, micas and clay minerals (kaolinite, illite and some chlorite and montmorillonite). Carbonate minerals are missing or occur in small amounts (Viiding et al., 1983). The minerals rich in microelements occur dispersedly, mainly as varieties resistant to weathering (zircon, monazite, xenotime, apatite).

In the lowest part of the section the Ordovician deposits, there are various terrigenous rocks. The Lower Ordovician terrigenous complex (the Obolus sandstone, Dictyonema argillite, clay and glauconitic sandstone (clay)) discordantly overlay the Cambrian sedimentary rocks. These rocks are exposed in the klint and the valleys cutting the latter. The Dictyonema argillite and Obolus sandstone (phosphorite) are rich in many trace elements (Table 7.2). These rocks and oil shale influenced considerably the concentration of trace elements in the Quarternary cover of northeast Estonia (Loog and Petersell, 1994; Petersell, 1991).

The Ordovician carbonate rocks (limestone, dolomite, marlstone and domerite) crop out under the Quaternary cover to the south up to the southern boundary of the oil shale deposit. In the Upper and Middle Ordovician carbonate rocks, the beds of oil shale (kukersite) occur, which form the Estonia and Tapa oil shale deposits. These rocks were deposited in shallow sea with normal water salinity.

After the Devonian period the Estonian territory went through a very long continental period, which lasted approximately 400 million years. At the end of the non-deposition (probably continental) period the territory was uplifted and intensively eroded.

7.3 Kiviõli site

7.3.1 Quaternary surface soil

The Kiviõli investigation area is flat, very slightly dipping to the north. The ground surface elevation ranges from 45 to 51 m a.s.l.

The investigation area covers approximately 10 km^2 and is located on the north Estonian limestone plateau (Fig. 7.3.1a). Its northern boundary is 8 km to the south of the klint. In its southern part there are semi-coke landfills formed as a result of oil shale processing at the Kiviõli Chemical factory. Southeast of the investigation area, underground oil shale mining has taken place. The thickness of the Quaternary deposits in Kiviõli area is variable, reaching 4 m in the northwest, while in the southeast and central part it is only 0.5–2 m (Fig. 7.3.1b). The volume of information about the thickness of the Quaternary covers under the semi-coke landfills, as well as in the southern part of the investigation area is limited. At first the thickness of the natural Quaternary cover was 0.5–3 m, but it has been considerably changed in the result of oil shale mining, formation of waste depositories and building of the town. The ground surface has been leveled and various oil shale producing wastes have been stored there. In the northern part of the investigation area, in vicinity of the semi-coke landfills and in the south (in the area of dwelling houses) the rocks are presented prevailingly (up to 50-70%) by loam or sandy loam. The particles of crystalline rocks do not exceed 30%. Small fragments of Dictyonema argillite are found as well.

Northwest of the investigation area, tills are overlain first by an up to 3 m thick bed of glaciolacustrine clay and silt, and these in turn by fen peat. According to the geological map in the southern part (to the south of the Tallinn-Narva road) the natural till bed is often covered with technogenous soils – the wastes of oil shale production and processing.

The humus horizon has thickness from 20 cm (on clay) up to 30-40 cm (on till). On the distance of ca 200 m around the old semi-coke landfill, the soils have the admixture of semi-coke brought from the landfill by water or wind. In this area the formation of humus horizon has started and supporting gras, bushes and trees.

7.3.2 Hydrogeological conditions

The hydrogeological section of the area near the waste landfill Kiviõli is presented by the following units:

1. Quaternary aquifer (Q)
2. Keila-Kukruse aquifer (O_3kl-O_3kk)
3. Uhaku aquitard (O_2uh)
4. Lasnamäe–Kunda aquifer (O_2ls-O_2kn)
5. Lower Ordovician aquitard (O_1)
6. Ordovician-Cambrian aquifer (O_1pk-$Є_1$ts)

The natural hydrogeological regime is disturbed by Kiviõli underground mining, which was closed in 1986. After closing of the mine the mining water is discharged into Purtse River. The water level in the closed underground mines is approximately 43-44 m a.s.l.

1. The Quaternary aquifer (Q) is presented in general by peat, clayey and sandy loam and moraine. The thickness of these deposits is low- from 0.5 up to 4 m. By this reason the water filling of the quaternary deposit has a very local character. The infiltration properties are low. The infiltration coefficient varies in the limits of 0.0n-1m/d. By the reason of low thickness of quaternary deposits the rainfall and melted snow filters directly to the carbonate rocks of Kukruse Stage or accumulates in the boggy areas where the infiltration is limited by the clay and loam with very low infiltration properties.

2. Keila-Kukruse aquifer (O_3kl-O_3kk). The aquifer is presented by very fissured limestone. The thickness of limestone is 3-12 m; the depth of deposition is 0.5-4 m from the surface. The aquifer is not under pressure. The water table has the depth 1-2 m in the northern part of studied area and increase up to 10-12 m (43-45 m a.s.l.) to the south. The specific yield is 1-5 l/sec/m, the coefficient of infiltration varies from 10 up to 25 m/d. The high jointing of the carbonates causes their high water filling. The amplitude of water table variation has not increased 1.5 m during the year. The chemical composition of water is hydrocarbonate with high content of calcium and magnesium ions. The water of this aquifer is not protected from the pollution.

3. *Uhaku aquitard (O_2uh).* The deposits of aquitard are presented by the clayey limestone and marl with thickness of about 15 m. The observation showed that in the north, in case of depth of bedding near the surface and high fissure of deposits, the aquitard may be related to the aquifer. Unfortunately the infiltration properties of this aquitard are not studied in detail. Usually the infiltration coefficient is low (less than 1m/d) but in some places it may rise up to 5-10 m/d.

4. *Lasnamäe–Kunda aquifer (O_2ls-O_2kn)* is represented by limestone, domerites and dolomites with thickness of 20 m. The depth of bedding is 20-25 m from the surface. The average water table depth is 2-3.5 m in the north of the studied area and increases in the south combining with groundwater of the Keila-Kukruse aquifer in the area of underground mining (43-45 m a.s.l.). The amplitude of water table variation is up to 1.5 m/y. The aquifer is under pressure in some places.

5. *Lower Ordovician aquitard (O_1)* is presented by glauconite clay and Dictyonema shale. The thickness of aquitard varies in the limits of 4-6 m and it is located at the depth of 46-48 m from the surface, that is from 1 up to 4 m a.s.l, approximately.

6. *Ordovician-Cambrian aquifer (O_1pk-Є$_1ts$).* The deposits are presented by the sand and siltstones and lie at the depth of 45-50 m under ground surface. The thickness of the aquifer is up to 30 m. The water is under pressure. The specific yield is up to 0.3 l/sec/m. The piezometric level is determined as 35-40 m from the sea level (Põhjavee…, 1999). The data about the quality and water table variation is absent. The difference in piezometric level of Lasnamäe–Kunda aquifer showed that Lower Ordovician aquitard protect well the water of this aquifer from the inflow of pollutants. The water from this aquifer is used for the water supply of Kiviõli.

7.4 Kohtla-Järve site

7.4.1 Quaternary surface soil

The relief of the Kohtla-Järve investigation area is flat, with very slight dip to west or southwest. The natural Quaternary cover rests upon the undulating surface of the MiddleOrdovician carbonate rocks. Its thickness is variable: 1-2 m in the northeast of the area, generally increasing towards southeast up to 5 m and more. In the centre of the investigation area, peat occurs in a shallow depression of NW-SE orientation. The ground surface elevation is 46-52 m a.s.l.

The investigation area covers approximately 16 km^2 and is situated on the north Estonian limestone plateau at a distance of 3-4 km from the klint on the north (Fig. 7.4.1a). In the northern part of Kohtla-Järve area there is farmland. In its eastern part on the territory of Kohtla-Järve town are located semi-coke landfills formed as a result of oil shale retorting in Kohtla-Järve Chemical factory and the ash landfill formed as a result of oil shale burning at Kohtla-Järve power plant. Northeast the investigation area is Nitrofert Ltd., which produces nitrogen fertilisers. The volume of information about the thickness of the Quarternary cover under the waste landfills is limited. The initial thickness of Quaternary deposits was 1.5-3 m and it increased towards southwest (Fig. 7.4.1b). In the results of ground surface levelling for the formation of the waste depositories, the thickness of the Quaternary cover was changed. Above carbonate rocks usually lies till up to 2 m in thick. Till is rich in carbonate. Where the fine-grained material (mainly loam) forms 50–70 %, the share of crystalline rocks reaches 20 %. Small fragments of Dictyonema argillite are found as well. South of the investigation area (ca 2/3 of the whole territory) the till is overlain by local ice deposits (silt, sand and clay). Silts prevail in the area to the west of waste landfills, while sands are common at the western and southern boundary of the investigation area. The thickness of fen peat reaches up to 1.5 m. At first peat located in the southern part of present location of semi-coke landfill, but it is not known whether it was left under the landfill or removed.

In the surroundings of the ash landfill and westward of the semi-coke landfill the natural deposits have been disturbed due to ground surface levelling, mixing with technogenous soils or covering with the latter. The thickness of the topmost technogenous layer often exceeds 1 m, it consists of mainly the ash to which carbonate breakstone or gravel has been added.

The thickness humus horizon varies from 10-15 cm (on the sand) to 30-40 cm (on silt and till). On technogenous deposits the humus horizon are absent.

7.4.2 Hydrogeological conditions

The natural hydrogeological regime is disturbed by oil shale mining in mines "Kohtla", "Kava" and "Sompa" and quarry "Aidu". In 2001, the underground mines were closed and pumping water from these mines is stopped. The depression in the result of water pumping reaches in diameter several km. Now the water level is rising.

The hydrogeological section of this region is represented by the following units:

1. Quaternary aquifer (Q)
2. Lasnamäe–Kunda aquifer (O_2ls-O_2kn)
3. Lower Ordovician aquitard (O_1)
4. Ordovician-Cambrian aquifer (O_1pk-$Є_1$ts)

Under these units the regional Cambrian clay ($Є_1$ln) that is the regional aqitard lie.

1. *Quaternary aquifer (Q).* The aquited aquifer deposits are presented by tills, loam, clay and sand. The thickness of these reaches several meters and is variable on the territory. The water filling of the deposits depends on the lithological composition. On the areas of location of the clayey loam and clay the formation of the bogs is observed. The infiltration coefficient ranges mainly from 0.05 up to 1.3 m/d. Through the quaternary deposits the infiltration of the rainfall and surface water into the underlying aquifers takes place.

2. *Lasnamäe–Kunda aquifer (O_2ls-O_2kn)* lies in the NW part of area under quaternary deposits. In the SE it is covered by fissured carbonate rocks of Uhaku and Kukruse Stages. Stratigraphically the aquifer is presented by the Lasnamägi, Aseri and Kunda Stages these have the total thickness 20-23 m.. The depth of bedding varies from 2.7 m from the surface on the north from the semi-coke waste and landfills, up to 10 m to the south from them. The rocks are presented by dolomite and limestone, very fissured in the upper part of the section. The infiltration properties are characterised by the following parameters: the coefficient of infiltration varies from 0.7 up to 9.2 m/d and the specific yield is from 0.11 up to 1.61 l/sec/m. The static level of water table varies from 1.57 up to 5.14 m. The amplitude of its variation is 1-3.5 m during the year, depending on the season. The water supply of this aquifer takes place as at the inflow of the water from the areas located outside this region by infiltration of the surface water. In the north part of the territory, the aquifer is non-pressured, in the south part of the area the aquifer is under the high pressure is 10-15 m. The general mineralisation ranges from 0.12 up to 2.35 g/l, increasing in the direction of waste landfills. In groundwater near the semi-coke landfills (well 600), the phenols (up to 8.7 mg/l) and oil products (up to 5.1 mg/l) were determined (Razgonjajev, 1992). The composition of water is hydrocarbonate with high content of sulphate, potassium and sodium ions. In the north-eastern part of the territory the increase of Cl- content and near the semi-coke waste landfills- the increase of SO_4^{-2} content is observed. Near the waste landfills, the potassium content reaches 1,000 mg/l (well 600, data of the year 2003). The groundwater flow in the location of the waste landfills has a westerly direction. The results of the experimental testing of the infiltration have not showed the direct relation between the underlying water aquifer, but the results are incomplete.

3. *Lower Ordovician aquitard (O_1)* is presented by glauconite clay and Dictyonema shale. The thickness of aquitard varies in the limits of 4-5 m, it lies on the depth of 6-26 m up to sea level.

4. *Ordovician- Cambrian aquifer (O_1pk-$Є_1ts$).* The deposits are presented by the weakly cemented fine-coarse sandstones of Pakerort and Tiskre Stages. The depth of bedding of the aquifer from the ground surface is approximately 27 m on the north and up to 40 m on the south. The thickness of the water-bearing deposits varies from 14.5 up to 17.7 m. The aquifer is characterised by the following properties: the coefficient of infiltration varies from 0.77 up to 5.7 m/d,

the specific yield is from 0.09 up to 0.82 l/sec/m. The main source of the water recharge for this aquifer is located outside the studied area, but to a small degree it takes the local recharge. It is confirmed by not very significant increase in the water table level, which is observed approximately in a month after the intensive precipitation of the rainfall. The aquifer is under pressure. The hight of the pressure to the north is 12-13 m and 30-32 m to the south. The piezometric level is located at the depth of 6-16 m from the ground surface and 37-43 m from the sea level. The general mineralisation of water varies from 0.12 up to 0.9 g/l. The chemical composition of water is variable, mainly it is hydrocarbonate-sulphate but in some wells it has a high concentration of chlorine, magnesium, calcium, potassium and sodium ions. The water from the well located on the bottom of waste landfill has the high concentration of potassium (1,925 mg/l) in 2003. The groundwater flow in the area of the waste landfills has north-westerly direction to the north Estonian klint. The amplitude of water table fluctuation is 2-3 m during the year.

7.5 Kukruse site

7.5.1 Quaternary surface soil

The relief of Kukruse investigation area is flat, gently undulating. The ground surface elevation is 65-74 m a.s.l. To the east of the waste landfill there is somewhat lower area, which might be due to post-mining ground surface collapse.

The Kukruse investigation area covers 3 km^2. It is situated on north Estonian limestone plateau at a distance of 12 km to the south of the klint. In the central part of the investigation area is the waste landfill of Kukruse oil shale mine, which is still burning. In the investigation area, oil shale has been mined by the underground method, as a result the ground surface has collapsed up to 1 m in some places. The thickness of the Quaternary deposits is 2-4 m and they lie on the carbonate rocks of the Jõhvi and Kukruse Stages of the Upper Ordovician.

On the Kukruse area the carbonate bedrocks are usually covered by till rich in carbonates. The fines fractions of till are represented mostly by loam or sandy loam, forming 50-70 %. The coarsest fraction of till is represented by fragments of bedrocks, mainly carbonate rocks. The share of rounded crystalline rocks reached up to 50%. In the eastern part of the investigation area the till has the thickness up to 2 m and lies on the glaciolacustrine fine sands and silts. The humus horizon has similar thickness about 25-35 cm as on till.

7.5.2 Hydrogeological conditions

The hydrogeological section of the Kukruse area is presented by the following units (Savitski and Savva, 2001):

1. Quaternary aquifer (Q)
2. Keila-Kukruse aquifer (O_3kl-O_3kk)
3. Uhaku aquitard (O_2uh)
4. Lasnamäe-Kunda aquifer (O_2ls-O_2kn)
5. Lower Ordovician aquitard (O_1)
6. Ordovician-Cambrian aquifer (O_1pk-$Є_1$ts)

The studied Kukruse area is located at a former underground mining area and observation wells are absent there. The description of hydrogeology of this area is based on the data of the wells that are located outside the western border of this area (Puurkaevude kadaster, 2003) and on the data by Savitskaja (1999) and Savitski and Savva (2001).

1. Quaternary aquifer (Q). The aquifer deposits are presented in general by sandy loam and moraine (or till). The thickness of the deposits varies between 2-4 m. The infiltration properties are low, usually <0.5 m/d.

The water filling deposits are absent or they are present only in the rainy period. As a result of oil shale mining, the water table is lowered and located on the depth lower than 5 m from the surface. The infiltration of the rain- and melted water through the quaternary deposits into the underlying Keila-Uhaku aquifer takes place.

2. Keila-Kukruse aquifer (O_3kl-O_3kk). The water filling rocks of the aquifer are presented by very fissured and in some places also by karsted limestone. The thickness of this bench is up to 16 m, depth of bedding is 2-4 m from the surface. The aquifer is not under pressure. The water table lies at the depth of 4 -10 m from the surface. By the reason of closing of mines located to the south from the studied area, slow increase of the water table has taken place.

3. Uhaku aquitard (O_2uh). The aquitard deposits are presented by clayey limestone and marl with thickness of about 14 m. The depth of bedding is 10-16m from the surface.

4. Lasnamäe-Kunda aquifer (O_2ls-O_2kn). The water bearing rocks of the aquifer are presented by fissured limestone, dolomitic limestone and dolostone of Lasnamägi, Aseri and Kunda Stages. The aquifer thickness is about 20-24 m and its bedding lies at the depth of 44-47 m a.s.l. The water of this aquifer is under pressure in some places. The pressure and raise of the water table increase to the south of the studied area.

5. Lower Ordovician aquitard (O_1). The aquitard deposits are presented by clayey glauconite sandstone and Dictyonema schale. The thickness of the aquitard is 3-4m and it is the regional aquitard. The depth of the aquitard is 52-56 m from the surface and 14-18 m a.s.l.

6. Ordovician-Cambrian aquifer (O_1pk-Є$_1ts$). The water filling rocks are presented by slightly cemented sandstones of Lower Ordovician Pakerort Stage and Lower Cambrian Tiskre Formation. The thickness of the aquifer is approximately 20 m. The depth of the aquifer is 56-76 m from the surface and +14- -6 m a.s.l. The water is under pressure. The piezometric level of the aquifer is 35-40 m a.s.l., the coefficient of infiltration varies from one up to 5 m/d. The water is related in general to HCO_3' - Mg-Ca type. The total water mineralisation is mainly 0.4-0.6 g/l. The water from this aquitard is used for the supply of the habitants in this region.

7.6 Narva site

7.6.1 Quaternary surface soil

The Narva investigation area covers approximately 100 km^2, and the ground surface elevation is mainly up to 32 m, in places even 36 m above sea level (a.s.l.) The North-Estonian klint continues in northwest-southeast direction and divides the investigation area into two: smaller fore-klint lowland and larger limestone plateau.

The Narva investigation area is situated between the Gulf of Finland in the northwest, the Narva River in NE and Narva Reservoir and ash fields of the Baltic Power Plant (PP) in the south (Fig. 7.6.1). Its southwest boundary passes through Laagna village. On the fore-klint lowland the bedrocks are covered with till and the deposits of different Baltic Sea stages (Ancylus Lake, Litorina Sea and Limnea Sea). Their total thickness is mainly 10-15 m, in some places even more. The above deposits in fore-klint lowland are represented by silts and fine, mainly quartz sands, forming beach ridges and dunes. On the limestone plateau the bedrocks are covered by till, 0.1-0-3 m thick in the north and 3-4 m at the southern boundary of the investigation area. To the southwest of the klint there is an alvar, where most of Narva town is situated. On the alvar the limestone is covered with partly washed till, which in places is poor in clay (silt) or resembles shingle (poorly sorted gravel). The thickness of these friable deposits seldom exceeds 0.3-0.4 m, reaching 0.5-1 m only in the hollows of the bedrock surface. South from alvar the till consists 40-60% of fine fraction presented by loam or sandy loam, the coarse-grained material consists of fragments of bedrocks (mainly carbonate rocks). The share of rounded crystalline rocks reached up to 40 %. In lower parts of the ground surface are the glaciolacustrine deposits (sand, silt and clay). Their thickness is usually less than 2-3 m and they are distributed on several square kilometres.

The southern part of the Narva investigation area is over moist, which has led to paludification. The peat has patchy distribution, its thickness being more than 1 m, presumably up to 3 m, but there is no reliable information about it. In the area of the Baltic PP the thickness of till reaches 2.5 m and in the area of the ash fields (to the south of the power plant) it is 2-4 m. At the southern boundary of area the till is in places covered with the glaciolacustrine deposits.

The thickness of humus horizon is different. On sands and clays it may reach 10-15 cm, on tills and alvars – up to 30-40 cm, in the area of the fore-klint lowland the humus horizon is absent in some places.

7.6.2 Hydrogeological conditions

The hydrogeological situation close to the Baltic power station is influenced by the Narva reservoir and channel network located around the power station.

The hydrogeological section of the area near the Baltic Power station is presented by:

1. Quaternary aquifer (Q)
2. Lasnamäe–Kunda aquifer (O_2ls-O_2kn)
3.Lower Ordovician aquitard (O_1).
4. Ordovician-Cambrian aquifer (O_1pk-$\mathrm{Є}_1$ts)

1. Quaternary aquifer (Q)
The Quaternary cover in this area is represented by glacial deposits and varies in composition including sand, sandy loam, till, varved clay and gravel. The position of the loam and clay in the lower part of quaternary deposits leads to the formation of large boggy areas. Very often lie under the peat very plastic and fluid-plastic clays. The infiltration and drainage properties are very low. The infiltration coefficient of the sediments ranges from 0.0 up to 2-3 m/d. The thickness of the peat, sand and moraine varies in wide limits (from 0 up to 3-5 m). The total thickness of the quaternary deposits reaches 5-6 m. The water-bearing deposits are located in the area of the Baltic Power station locally. By the reason of low thickness in some places of quaternary deposits, the melted snow and rainfall filters directly to the carbonate rocks.

2. Lasnamäe–Kunda aquifer (O_2ls-O_2kn). This aquifer includes three horizons-Lasnamägi, Aseri and Kunda, and is presented by limestone and dolomites, which are weathered, fissured and karstified in the upper part. The depth of the uppermost part of aquifer ranges from 4 m up to 20 m. The thickness of the aquifer is about 20 m and decreases in the northern direction. The infiltration properties are characterised by the following parameters: infiltration coefficient from one up to 20-30 m/day, specific yield from 0.0 up to 5-10 l/sec/m. The high variation of the infiltration properties depends on the intensity of fissuration and karstification of the carbonate rocks. The water table level is located at the depth of 1-5 m from ground surface. The amplitude of its variation is approximately 0.5-1 m during the year and depends on the seasons. On the base of the chemical composition water relates to the hydrocarbonate type with the high content of calcium and magnesium ions. The general mineralisation reaches up to 600-700 mg/l. The hardness of water is 6-10 mg-equal/l.

3. Lower Ordovician aquitard (O_1). The aquitard deposits are presented by glauconite clay and sandstone and Dictyonema shale. The thickness of the aquitard is 2-3 m and it is on the depth of 22-27 m from the ground surface.

4. Ordovician-Cambrian aquifer (O_1pk- $Є_1ts$)

This aquifer lies under the *O_1* aquitard. The water-bearing deposits are presented by the fine-coarse sandstone cemented to different degrees. The aquifer lies at the depth of 25-30 m, the thickness is about 20 m. It is a pressured aquifer. The piezometric level has the depth 5-10 m from ground surface and 22-26 m a.s.l. The aquifer is characterised by the following properties: infiltration coefficient from 3.5 up to 15 m/day, specific yield of wells is from 0.4 up to 2 l/sec/m.

8 FIELD AND LABORATORY METHODS

8.1 General

The first stage of the project included the geological program and field observations for the future choice of the object of the study. The purpose of this investigation was the identification of all landfills on the localities, more precise definition and correction of the data about the volume and height of the different types of the waste in the landfills. These results were used to determine sampling placement and density as well as the optimal location of monitoring wells. The groundwater flow direction was determined by calculation of the unit change in hydraulic head between piezometric levels (the hydraulic gradient) and use of the previously obtained data (Razgonjajev et al., 1992).

After that, the sampling procedures, including the placement of monitoring wells into the aquifer were initiated. Sampling wells were selected in those areas where only a few or no data of earlier studies existed (for example near the waste landfills in Kiviõli). In Kohtla-Järve the placement of wells was determined taking into account the groundwater flow direction. For the additional well sampling, the wells belonging to the monitoring network of Viru Keemia Group and the Geological Survey of Estonia were used when sufficient background information was available.

8.2 Boring and monitoring wells

For the sampling of groundwater, both existing wells and new wells were used. New wells were drilled on the territories of landfills in order to obtain the samples from new sites. 18 wells were drilled in the frame of the project (they are marked as RA- wells in the Table 8.2). Six wells were drilled through the waste landfills in order to carry out the special Slug test and twelve other wells were drilled at different distances from the landfills. The construction of the wells drilled for slug testing is showed on the Fig. 8.2. All wells were drilled with use of a truck-mounted rotary rig; the diameter of wells is 11.3 cm. Each well (2-3 lowest m) was equipped with a plastic (PVC) filter with horizontal sloths. The radius of gravel pack is 15 cm. The upper 1 m was finished/completed by the casing-pipe and cemented. Cores from the holes were placed on the surface, described and sampled (see the Tables 9.2.2.1-9.5.2). In one studied area (Narva) the wells are located on the very hard soil, in general on the artificial dike. In Kohtla-Järve, the wells were located next to waste landfills. The maximum distance from waste landfills was about 600 m, the closest one was drilled directly on the bottom of waste landfills. In Kiviõli the wells were drilled at the different distances from the waste landfills (starting from the bottom of waste landfills up to 400-500 m from them) (see Figures 7.3.1a, 7.4.1a and 7.6). The depth of wells depended on the depth to the water aquifer and on the thickness of the sediments covered by the carbonate rocks. Special drilling was carried out through the landfill Kukruse where the self-burning processes regularly take place. This waste landfill was drilled on the slope from the top to the depth of 23 m. The core from the hole was taken out on the surface, described and sampled (Table 9.4.1.1). The photos of this core are presented in the same table.

The geographic coordinates for all wells were determined using GPS- Garmin GPS 76, as well as the altitude of wells and water level in the wells.

8.3 Sampling methods and preparation

8.3.1 Well sampling

After boring, the water from the drilled wells was pumped. The samples of water from these wells were taken approximately several weeks after drilling and stabilization of the initial water level in the wells. The groundwater from selected wells directly before the sampling was intensively pumped using electrical pumps. One to three well volumes were removed prior to sampling.

8.3.2 Water sampling

The water samples from the different types of sampling sites including channels, outflow of mines water and wells drilled into bedrocks, are presented according to its availability. From channels, the water was taken by simply scooping up the water in a glass bottle. Prior to the collection of the representative sample, the wall were pumped or if the volume of water in the well was very limited for the collection of water, the plastic sampler with R=35.6 mm and length 1 m was used. Immediately after sampling, the water was prepared for the laboratory analyses. Samples were subdivided into the subsamples for the different types of analyses. The temperature, O_2 concentration (O_2 and O_2 saturated) were measured in the field in the untreated water samples two times a year by MARVET JUNIOR. The pH, conductivity, alkalinity and $NH_4{}^-$ were measured in the Chemical Laboratory of the Geological Survey of Estonia within two days after water sampling (Table 8.2). During the period after sampling and before the measurements, the samples were refrigerated at 4-5 °C.

The content of DOC (dissolved organic carbon), organic compounds (phenols-sum and 14 compounds separately), BTEX (sum and 11 compounds) and PAH (sum and 18 compounds) were determined in Hydroisotop GmbH (Germany), and major and trace elements in ACME Laboratory (Vancouver, Canada). The shipping of samples was carried out within two-three days after sampling. Special express firms (FedEx Express and CB-Terminal) were used for the shipping of samples.

8.3.3 Water sample preparation

After stabilisation the following subsamples were taken:

- A 500-millilitre (ml) was unfiltered and unpreserved for the major ions (including Ca, K, Na, S).
- 100-ml was filtered through a 0.45 mm filter and acidified with 0.5 ml ultra-pure concentrated nitric acid HNO_3 till pH=2 for the trace elements measurements by ICP-MS analyses.
- 100-ml for the analyses of dissolved organic carbon (DOC) was preserved using NaN_3.
- 500-ml was unfiltered and unpreserved in a dark glass bottle for the analysis of (sum and separate compounds) phenols.
- 500-ml was unfiltered and preserved with $CuSO_4$ in a dark glass bottle for the analysis of (sum and separate compounds) oil products (BTEX)
- 1000-ml was unfiltered and preserved with $Na_2SO_3*5H_2O$ and hexane in a dark glass bottle for the analysis of PAH (sum and separate compounds)
- 1000-ml was unfiltered and unpreserved in a dark glass bottle within 24 h. for the ecotoxic test.

The water preliminary acidified by ultra-pure concentrated nitric acid HNO_3 till pH=2 was analysed for concentration of 72 elements by ICP-MS.

8.3.4 Sub- and topsoil sampling and preparation

The samples of core (subsoil) were taken directly after drilling. For the analysis of inorganic compounds, average samples (about 1kg) were removed for each one m of core. Approximately 1.5 kg of the sample was put into a dark glass bottle for the analysis of PAH, BTEX and phenols. The samples were frozen at –18 °C and stored until the analyses.

The topsoils were collected from three areas: Kiviõli, Kohtla-Järve and Narva. The sampling density depended on the size of studied area. In Kiviõli, the sampled area was approximately 4×3 km, the selected density of sampling was one sample per 0.5 km^2. In Kohtla-Järve the area was 25 km^2 approximately, and selected density of sampling was also one sample per 0.5 km^2. In Narva, the sampled area was approximately 100 km^2, the selected density of sampling was one sample per 1 km^2. Two samples were taken at each tenth site: topsoil from the upper soil horizon with depth 0-10 cm and subsoil (bottom soil horizon samples, usually at an approximate depth of 50-75 cm). The comparison of element distribution and calculation of ratio between these two soil horizons permitted the estimate of the accumulation of elements in upper soil horizon.

For the soil sampling survey, the same complete set of field equipment (the steel tube with volume of about one litre) as for the international project Baltic Soil Survey was used. The sampling was carried out according to the sampling instructions from NGU (Reimann et al., 2000). The samples were one litre in volume. All soil samples were air dried and sieved to <2 mm using nylon screening at IG at TUT. Before the analyses, the samples were crushed by the agate mill.

The topsoils samples were analysed for the total of 54 elements by ICP-MS analysis using two techniques of soil preparation prior to the element measurements:

1. The elements were determined in the sample after aqua regia digestion for low to ultra-low determination. A 0.5 g split was leached in hot (95 °C) aqua regia then analysed by ICP-MS.
2. The near-total determination of elements used a strong 4-acid digestion. A 0.25 g split of the sample pulp was digested in a 4-acid solution (HNO_3, $HClO_4$, HF and HCl) at high temperature and then analysed by ICP-MS.

8.3.5 Vegetation sampling and preparation

For sampling of the vegetation, the roots of meadowsweet (*Filipendula ulmariain Latina,* Angervaks in Estonian) were selected as the most informative in the sense of elements accumulation. From each studied area five samples of vegetation were taken. The samples of this perennial (annual) plant were washed by water, then dried at room temperature (at GSE) and pulverised to 100 mesh.

The surface and groundwater were analysed by ICP-MS ultratrace analysis. The samples with anomalous levels of dissolved compounds (they were indicated in requirements for the analysis) required additional treatment (dissolution) and analyses.

A 0.5 g split of vegetation sample was wet-ashed in HNO_3, digested in aqua regia and analysed for the same elements suites as in group of other samples after aqua regia digestion by ICP-MS.

8.3.6 The measurements of the groundwater properties

- The temperature and O_2 concentration (total in ppm and saturated in %) measurements were carried out in the field by the MARVET JUNIOR equipment.
- The electric conductivity of the water was measured in the Chemical laboratory of the Geological Survey of Estonia by the conductivity meter HANNA HI 8033. The precision of measurement is 0.1 μS/cm.
- The alkalinity of water was measured in the Chemical laboratory of the Geological Survey of Estonia according to the procedure described in (Unificated…, 1978).
- Measurements of organic compounds (PAH, phenols, BTEX and DOC) were carried out in Hydroisotop GmbH (Schweitenkirchen, Germany).

9 RESULTS OF FIELD AND LABORATORY INVESTIGATIONS

9.1 A general overview

A general overview of the soil, groundwater conditions and the contamination is given to introduce the present situation.

9.1.1 Surface soil

The distribution and range of trace elements illustrate the regional natural geochemical landscape. Its gives the possibility to estimate natural hazards and present the areas with potential health risk. The complex study of geochemistry of different natural geological objects (surface- and groundwater, soils, streams, vegetation) permit assessment of the influence of hydro- and geological processes on the affect of movement, dissolution and concentration, bioavailability of potentially toxic elements. Sometimes the toxic effect could be reached as a result of the combination of several factors for different chemical elements.

The topsoil has very inhomogeneous composition and consists of a mixture of weathered minerals and varying amounts of organic matter. For the general characterisation of studied soils, map distributions were used for of insoluble residue (calculated as the sum of the following oxides: Si, Al, K, Na and Ti), CaO as one of the main component of oil shale and loss-in-ignition (for the characterisation of organic matter level. The maps of distribution of these components in the surface soils of Kohtla-Järve area are showed on the Figures 9.2.1.1 a, b and c). Soils can be contaminated as result of contact with pollutants from different sources (airborne emission, leachates) and depends also from such factors as pH, ion exchange capacity, contents of organic matter and forms of mobility of elements. The effect of the lithological composition of soil and bedrock on groundwater quality is very often complicated. The impact of the bedrock composition is often stronger that the environmental factors.

9.1.2 Subsoil conditions

The analysis of the element concentration and organic compounds in the boreholeholes was carried out for the estimation of spreading of the contaminants. The subsoil may play very important role in the regulation of the movement of contaminants from the surface into underlying beds and water aquifers. Depending on the composition, they can be the subsurface barriers and reduce significantly the movement of contaminants in the case of the deposits characterised by very low infiltration properties.

9.1.3 Hydrogeochemistry and contamination

The groundwater in the Estonian Oil Shale Basin generally meets the requirements of the Drinking Water Standard of Estonia (EVS 663, 1995. Joogivesi), and directive 98/83/EC on the quality of water intended for human consumption (Perens et al., 1999). In the areas close to oil shale mining the shallow groundwater is often polluted, especially near the landfills of semi-coke and ash.

The quality of water from the Ordovician aquifer is variable. Besides the landfills the oil shale mining leads to high variability in the groundwater regime and chemical composition of groundwater. The pollution is caused by two main factors: leaching of sulphate, iron, manganese and other ions from the host rocks (presented by carbonate rocks karstified and cavernous in the upper part of section), and pollution as a result of oil shale mining. As indicated by Erg and Punning (Erg and Punning, 1994) the complex influence of natural factors and infiltration of drainage water through overburden deposits back to mines and pits leads to increase in general mineralisation that may be twice as high as one that usually characterises an Ordovician water aquifer. Concentrations of Na, Ca, Cl and SO_4 are also much higher (Erg and Punning, 1994). Intensive increase in sulphate ion concentration (up to 60 times) may be probably caused by several processes: the sulphates are partly transformed into atmospheric precipitation, and pumped out mine water partially flowing back to the depression (Erg et al., 2001)

As numerous regular observations of the chemical composition of groundwater showed in the oil shale basin area, the main aquifers are found chemically polluted in this region. A study of wells in the rural areas surrounding towns showed that of the 173 wells sampled, 95 % were high in sulphate, 91 % were contaminated by oil products, 60% by phenol derivates and the water in 53 % of wells did not meet the microbiological standards (Erg et al., 2001). It was estimated that depending on local hydrogeological conditions and on seasonal variation, 5 to 56 m^3 of water (average 14,5 m^3) must be pumped out per every ton of mined oil shale. Almost all pumped-out water (96-97%) is directly discharged either into the Gulf of Finland, the Narva River or Lake Peipsi. The calculations (Erg and Punning, 1994) have shown that because of a high permeability of surface rocks, approximately 15% of the pumped out mine water may infiltrate back into mines.

The pollution of the environment around oil shale processing plants and semi-coke landfills by organic compounds is a serious problem for this region. According the data of Viru Keemia Group AS in 1993-1997, the annual influx of volatile phenols into Kohtla River was about 24 t, their concentration in leachates from semi-coke landfills ranging from 1 up to 206 mg/l (the average value 41 mg/l). The main volatile phenols are presented by phenol (hydroxybenzene) and its methyl derivates (2-, 3-, and 4-methylphenols (Kundel and Liblik, 2000). As groundwater monitoring in northeastern Estonian Industrial Region (Otsa and Tamm, 1998) showed shallow groundwater (Ordovician aquifer O_2ls-O_2kn) from wells close to semi-coke hills contain up to 4,900 mg/l naphta products in the lower Ordovician-Cambrian (O_1pk-$Є_1$ts) aquifer up to 3,430 µg/l. In the wells that are situated 0.5 km from semi-coke hills, the concentration increases up to 17 µg/l. It was found that groundwater of the upper aquifer is polluted at the distance of 200-300 m from the semi-coke hills. Ba, B and Fe had the highest organic concentrations.

In the River Purtse the content of oil-hydrocarbons varies between 32-2700 µg/l and up to 2330 µg/l in the mouth of the River Kohtla. The content of phenols in River Purtse varies between 2-760 µg/l, in water of River Kohtla it varies between 278-24000 µg/l (Loigu et al., 1998). The concentration of volatile phenols in the mine water was determined up to 3-4 µg/l.

9.1.4 Groundwater

Trace element analyses were carried out on groundwater in order to understand water/mineral interactions under different geological conditions, their effect on solutions transport, mineral weathering, and to trace and estimate the direction and intensity of pollution based on the geochemical data. The chemical composition of groundwater depends on many factors in general; precipitation, hydraulic conductivity, properties and composition of host rock, and hydrogeological conditions.

The investigation of groundwater was carried out in the area of the oil shale basin at Kiviõli on the west to the town of Narva on the east. The main geological units in this region are presented by Quaternary deposits (silty clay, gravel and sand), Ordovician carbonate rocks (in general limestone) and Cambrian silty-clayey deposits. The depth of the water aquifer varies from several meters (Quaternary aquifer) to several tens of meters (Ordovician-Cambrian aquifer).. Groundwater was sampled from different wells (40) from depths between 3.0 and more than several tens of meters below the soil surface.

9.1.5 Air emission

The emission of organic pollutants (volatile phenols) in the atmosphere from leachates from semi-coke landfills was also observed. The concentration of phenols in the air close to the pounds varies within 4-50 μg/m^3. Between ponds the limit is 21-50 μg/m^3 during the ice-free period, depending on their background values and many meteorological factors.

The atmospheric emission from oil shale combustion is observed near the power stations. Yearly emission of gases in 2000 reached ten thousands t (about 9,000 t for NOx, 70,000 for SO_2 and about 10 Mt for CO_2) (Eesti Energia, 2002) Particulate emission in 2000 was approximately 47,000 t (Eesti Energia, 2002). The enrichment by many trace elements (as example, Sb, U, Tl, Cr and others) was determined in different fr.actions of fly ash fractions (Pets et al., 1985; Häsänen et al., 1997).

9.2 Kiviõli

9.2.1 Surface soil

Table 9.2.1 provides a review on the concentration of microelements in the upper 5 cm soil layer in the Kiviõli investigation area and their concentration levels as compared with average concentrations of the Earth's crust and the humus horizon of Estonian soils.

The geochemical background of this area is due to the concentration and distribution of main and microelements in the glacial, glaciolacustrine and glaciofluvial deposits. In these deposits occur different amounts of crystalline basement rocks originating from the Finnish territory, with the concentration of microelements close to the average concentration of the Earth's crust (The Geochemical..., 1992). The high concentration of Ca and Mg is due to the presence of Ordovician carbonate rocks. The associations of elements characteristic of the Dictyonema argillite and phosphorite rich in microelements (Mo-U-V and P-Y-REE-U-Sr) (Table 9.2.1) are only weakly expressed.

Increased or high concentration of As, Cu, Hg, Mo, Pb, U and Zn in the upper layer of soil is characteristic for Kiviõli area. Mo and U are probably related to the Dictyonema argillite and phosphorite, but others are that volatilised during the combustion of oil shale. In the Kiviõli area, the concentration of Hg and Pb more than twice exceeds the average concentration of the humus horizon of Estonian soil and are even higher than the average respective concentrations in the Narva area (Table 9.5.1.1). The above results show that the technological processing of oil shale at a temperature of up to 800-850 °C, too, causes the pollution of surrounding area with readily volatile heavy metals. The concentration and distribution of As, Hg and Pb in the soil of the surroundings of the Kiviõli Chemical Plant and its semi-coke landfills (Fig. 9.2.1.1-9.2.1.3), also support the above conclusion. The samples in which the concentration of the observed elements was low taken from between the semi-coke landfills and the samples with decreased concentrations from the surroundings of the semi-coke landfills have been collected from the fines of the semi-coke entirely or partly scattered by precipitation. These deposits are constantly relocated and washed by precipitation.

Presently there are no reliable data about the concentration of heavy metals in semi-coke. The results of analyses of heavy metals made of the aqueous solution of semi-coke show that several elements (As, Ba, Cu, Mo, Pb, Zn) are intensely washed out of semi-coke, whereas in older semi-coke landfills the outwash occurs less intensely. This also explains the lower concentration of heavy metals in the semi-coke fines scattered in the surroundings of the landfills.

9.2.2 Subsoil

In ***Kiviõli area*** , see Fig. 7.3.1b the Quaternary deposits are thin and consist of moraine: siltstone and clay. The upper layer of the topsoil (as a rule having the thickness approximately 0-0.5 m) was excluded from the sampling. The Quaternary deposits were sampled from the depth of 0.5 up to 5.5 m depending on their thickness and depth. It should be indicated that in some interval (usually 0.5 m) between the Quaternary deposits and underlying carbonate rocks (presented in this area by limestone) the section is presented by a mix of Quaternary deposits and pieces of limestone. This part of section was also excluded from the sampling. The sample from the well RA-KV-1 was taken from the depth of 4.5-5.5 m because of semi-coke waste above. There was taken one average sample per hole and only in one case (well RA-KV-4) was the composition of Quaternary deposits in two similar samples was analysed. The samples are similar in lithology, the siltstone is very dense, fine and looks like clay (Table 9.2.2.1). The siltstone from borehole RA-KV-1 and RA-KV-2 has grey (green-grey) colour, the samples from RA-KV-3 and RA-KV-4 are brown and grey-brown. The siltstone from the upper part of the boreholehole RA-KV-4 is clayey relative to the sample from the lower part of this boreholehole. The analysed samples have in general similar content of dry residue. The measured values of the dry residue range between 82.4 to 70.3 %. Only the sample from the upper part of boreholehole RA-KV-4 has more organic material (dry residue is 43.4 %) and is characterised by lower density relative to the sample from the lower part of section. It may be related to the higher content of the topsoil in the sample composition because this boreholehole was drilled on the border of the field that is used for agricultural needs.

The analyses of the organic compounds are showed in the Table 9.2.2.2. The results are presented in mg/kg of dry matter. As we can see, the soil from the Kiviõli boreholes are characterised by low concentration of PAH. The studied samples have the contents of these compounds, as a rule is less than detection limits. In the sample from the well RA-KV-1, located directly at the bottom of the new waste landfill, they were not determined. In the siltstones from the wells RA-KV-2 and RA-KV-3, the minimal contents of Pyren and Phenanthren were determined. From seven measured BTEX compounds, only the content of m+ρ-Xylene was measured in the samples from RA-KV-2, RA-KV-3 and RA-KV-4. The maximum values (0.05 mg/kg) of m+ρ-Xyleneare observed in the lowest part of the section of the well RA-KV-4 located on the maximum distance (about 600 m) from the new waste landfill. It could be noticed that m+ρ-Xylene(one from two BTEX) in content of 2.7 µg/l was determined in the groundwater from this well. From the whole set of PAH only one 4-Methylphenol was determined in the soil from RA-KV-4 (content 0.083 mg/kg). The obtained data showed that the inflow of the organic contaminants into the soil is observed up to the depth of 4.5 m, but the measured values of the pollutants show it has very limited and selective trace characters. All determined values of the organic compounds in the soils are less than PLV's in Estonia for the soil of industrial and living areas.

The chemical composition of studied soils and contents of trace elements were determined for the same samples. 46 main and trace elements concentrations were determined after digestion of the samples by aqua regia and a 4-acid solution (HNO_3, $HClO_4$, HF and HCl) using ICP-MS analyses (Table 9.2.2.1). After the digestion of the samples by aqua regia the silicate minerals are mainly dissolved. The content of the main elements in the studies soils is typical for the quaternary deposit, with the exception of the sample from the boreholehole RA-KV-1. The high values of Ca indicate the high content of carbonate bindings in the sample. It is possible to take into account the high thickness of the semi-coke covering the quaternary deposits. Comparison with the background values of the elements calculated for the continental crust and greywackes according to the data by Wedepohl (1995) showed the similarities in the elements content there and in the studied soil. The contents of Ce, Dy, La, Mo, Pr, Sm, Th, V and Y are close to maximum or increase with the background values for the elements. It may be caused by two reasons: by the admixture of the pieces of Dictiynema shale that is characterised by the high values of these elements in the moraine or by the pollution of the soils by the groundwater.

9.2.3 Hydrogeochemistry, groundwater and contamination

In the vicinities of **Kiviõli,** nine wells from two water aquifers were sampled. The wells drilled in the frame of this project that opened the upper part of the upper Keila-Kukruse aquifer (RA-KV-1, RA-KV-2, RA-KV-3 and RA-KV-4), were used for sampling of the groundwater from this aquifer, see Fig. 7.3.1b. The depth of these wells varied from 3m up to 7m. The samples of pore wastewater were taken from the wells drilled through the landfills. Sampling of the deeper groundwater in this region (Ordovician-Cambrian aquifer) was carried out from the wells, which are used for industrial water supply for the Kiviõli factory (wells K-6, K-9 and K-2309). The depth of these wells is approximately 75 m. The obtained data are showed in Tables 8.2, 9.2.3.1 and 9.2.3.2.

The groundwater of the *Keila-Kukruse* aquifer (O_3kl-O_3kk) is characterized by very changeable chemical composition, main hydrogeochemical parameters and has higher mineralisation relative to the water of Ordovician-Cambrian aquifer. All samples of groundwater are alkaline and their pH varies within wide limits. The variability of the studied parameters is shown on the Figures 9.2.3.1-9.2.3.4. The water samples from this water aquifer were taken from the depth of several meters. The wells were located on the different distance from the waste landfills. The wells RA-KV-1 and RA-KV-4 are located near the new landfill. This storage of semi-coke waste was started in 1951 and is still in operation. The wells RA-KV-2 and RA-KV-3 are located near the second waste landfill where the storage of waste was finished in 1968. The total mineralisation of the water from Keila-Kukruse aquifer varies from 894 up to 2,730 mg/l. The content of dissolved organic carbon ranges from 5.9 up to 35 mg/l (Table 9.2.3.2). The decrease of distance of well location to the waste landfill is accompanied by increases of pH (from 7.2 up to 12.8) and bicarbonate (alkalinity) (from 153 up to 3,514 mg/l). Especially high values (pH of 12.8 and alkalinity of 3,514 mg/l) were estimated in the groundwater taken from the well RA-KV-1, drilled directly on the bottom of waste landfill. The values of ammonium (NH_4^-) also increased regularly depending on the distance from the waste landfill and are in contrast with the sulphate content. The samples from this aquifer have values of electric conductivity from 2,295 up to 15,130 µS/cm, several times higher relative to the water from the Ordovician-Cambrian aquifer. The elevation of electric conductivity values in the water indicate the increase of the total mineralisation there and inflow of waters with high content of dissolved compounds. The content of dissolved oxygen is found to be from 3.2 up to 5.2 ppm, the percentage of saturated O_2 26 to 45. Relatively to the Ordovician-Cambrian aquifer, the groundwater of the Keila-Kukruse aquifer is characterized by relatively higher values of trace elements. The elements analysed showed a significant increase in contents of Al, Ca, Co, Cr, Mn, Rb, S, Sb, Si, U and W, and to a less degree As, Li, P, Sr and Re, with high pH values. The higher values of Al, Ca, Si and Sr indicate the dissolution of carbonate and hydrolyse of alumosilicate minerals of the hosted rocks. The principal differences in the distribution of the values between the groundwater from the well located near the old waste landfills and more new ones were not observed. At the same time, a trend between the regularities in the values of main parameters and distance from the waste landfills may be noted.

The waters from the wells drilled through the new semi-coke waste landfill (RA-KV-5 through the upper part of the landfill and RA-KV-6 on the bottom of the landfill) are characterized by the chemical composition and special values of the measured parameters. As we can see from the Tables 9.2.3.1 and Figure 9.2.3.2 the porous wastewater from these wells has very high values of total mineralisation (3,863.2. and 3,989.7 mg/l), and extremely high pH values

12.5 and 10.2 accordingly. The content of dissolved carbon in the water from the upper well is the highest from the studied waters (49 mg/l), at the same time the content of dissolved carbon in water from lower well (11 mg/l) is close to the average for the waters from Keila-Kukruse water aquifer. The electric conductivity values are 10,540 and 8,730 µS/cm, respectively, and show very high contents of dissolved electrolytes in these waters. Alkalinity of these waters is 1,845 and 473 mg/l. The content of dissolved oxygen measured in water of the above-mentioned wells is relatively close 1.8 and 2.2 ppm, and the percentage of saturated oxygen (16 and 18 accordingly) is lower than in the water of other wells from Keila-Kukruse aquifer. The reduced O_2 concentrations and saturated O_2 indicates the increase of the organic pollution of the water. The concentrations of trace elements in porous waters exceed as a rule their concentrations in groundwater in both aquifers. As we can see from the Table 9.2.3.1, increased concentrations are observed for Al, Be, Br, Ce, Cl, Cr, Cs, Fe, Cd, K, La, Li, Mo, Nb, Nd, Ni, P, Rb, S, Se, Sn, V, W and Y. Extremely high values were determined for As, Br, Cl, Fe, Ga, K, Li, Na, P, Rb, Se, V, W and Y.

Two small streams (channels) located at the foot of the slopes of the landfills were draining water and leachate from the landfill (samples KV-CH1 and KV-CH2). The chemical composition and the main parameters are similar to the pore wastewater sampled from the wells drilled through the waste. The total mineralisation there is high, 3,563 and 5,895 mg/l, and in one case demonstrated the highest values for the water in Kiviõli. The waters from channels have pH values lower than in groundwater and close to the neutral ones that suggests the influence on their composition of the recent meteoric water and possibly water mixing processes. The electric conductivity values of 9,500 and 6,330 µS/cm are slightly lower in comparison with the values for the pore water from waste, indicating the intensive extraction of the dissolved compounds (electrolytes). These waters are characterized by the lowest alkalinity of water samples from this region. The values of ammonium (NH_4^-) are close to average for the water of Keila-Kukruse aquifer in this area.

The waters from the diches have trace elements (Ba, Br, Fe, K, Li, Na, Rb, S and V) content similar to porous water being higher in comparison with water from the Keila-Kukruse and Ordovician-Cambrian aquifers. The increase of the same elements was determined also in the groundwater from the well RA-KV-1 drilled on the bottom of the eastern (older) part of the western (new) landfill in Kiviõli. This indicate leaching of these elements from the semi-coke and confirmed by the result of leaching test of the semi-coke samples and by the chemical data, obtained in the result of treatment of Kiviõli semi-coke by aqua regia. As we can see (Table 6.1.1.1), the regular (from fresh to old semi-coke) decrease in contents of the same group of the elements in the semi-coke samples, indicate the loss of these elements from semi-coke in the result of long-term leaching.

The distribution of *organic pollutants* in the water of this area is presented in Table 9.2.3.2. The sum of concentrations of PAH in the studied groundwater from Keila-Kukruse aquifer in Kiviõli ranges from 0.117 up to 0.561 µg/l. The larger spectrum of PAH presented by Fluoranthen, Pyren, Benzo[a]anthracen, Chrysen, Benzo[b]fluoranthen, Benzo[k]fluoranthen, Benzo[a]pyren and Indeno(123-cd)pyren is observed in water from the well RA-KV-1 located directly on the slope of the new waste landfill. The sum of PAH there is 0.152 µg/l. In the water taken at a distance of approximately one km from this landfill the sum concentration is very similar, 0.155 µg/l, but is mainly Phenanthren and Fluoranthen. In the groundwater taken from the wells near the old waste landfill, the sum content of PAH is 0.561 µg/l (well RA-KV-3). PAH there are presented only by Phenanthren. In the well RA-KV-4 the sum of PAH is 0.117 µg/l, composed Fluoren, Phenanthren and Pyren. The sample of the waste pore water (RA-KV-5) has the sum of PAH values 1.22 µg/l in the upper well drilled through the waste landfill. The PAH there are presented by the naphthalene group: mainly by Naphthalene and also by 1-Methylnaphthalin and 2- Methylnaphthalene. In the water from the lower well (RA-KV-6), the PAH was not determined. The trace values of pyren were determined in the water from the channel (the sample KV-CH1 collected on the slope of the new waste landfill). In mine water there were determined very small amounts Fluoren (0.018 µg/l) and Phenanthren (0.026 µg/l).

In the shallow groundwater from Keila-Kukruse aquifer from the wells drilled around the waste landfills, the sum of BTEX varies in the limits from 9.5 up to 5.7 µg/l. In four wells from the whole measured spectrum of oil products there was determined Toluene and m+ρ-Xylene, 3+4-Ethyltoluene in the wells RA-KV-2 and RA-KV-3. In pore water, only Styrol was measured in the water from the well RA-KV-6.

From all studied waters, phenols were determined only in the groundwater of Keila-Kukruse aquifer in the wells RA-KV-1 and RA-KV-2. The sum concentrations of phenols there are 4,763 µg/l and 20 µg/l, respectively. In the well RA-KV-1, the high concentrations of Phenol (2,032 µg/l), 2+3-Methylphenol (2,313 µg/l), 2.4+2.5-Dimethylphenol (235 µg/l) and 4-Methylphenol (183 µg/l) prevailed. The estimated values exceed the PLV. The phenols in the well RA-KV-2 are presented by the larger spectrum of phenols but their concentrations are much lower relatively to water from the RA-KV-1. They are 2.9 µg/l for Phenol, 4.9 µg/l for 2+3-Methylphenol, 3.9 µg/l for 2,4+2,5-Dimethylphenol, 3.1 µg/l for 2,6-Dimethylphenol, 2.9 µg/l for 3,4-Dimethylphenol, 1.4 µg/l for 2,3-Dimethylphenol, and 1.3 µg/l for 3,5-Dimethylphenol. The last four phenols are absent in the water from the well RA-KV-1. On the Fig. 9.2.3.5 the concentration of sum PAH and BTEX in the groundwater of Keila-Kukruse depending on the distance from the waste landfill are showed. In the distribution of sum of PAH and BTEX, a relation between their contents and the distance of the wells from the waste landfill was not observed.

The groundwater from the deep *Ordovician-Cambrian aquifer* (O_1pk-Є$_1ts$) is characterized by low mineralisation and stable pH values (from 7.6 to 7.8). The total mineralisation varies from 285 up to 1,094 mg/l with electric conductivity in the range of 820 to 2,000 µS/cm. The electric conductivity values demonstrate the abundance of dissolved electrolytes in the groundwater. In the samples from the Ordovician-Cambrian aquifer, the range of the electric conductivity is typical for the non-polluted water. The one of the main characteristics of the groundwater is the content of dissolved organic matter (DOC). In the groundwater from the Ordovician-Cambrian DOC content varies from 0.5 up to 3.3 mg/l. Oxygen is among the aggressive gases and under influence of O_2 the destruction and dissolution of minerals take place. Unfortunately, it was not possible to measure the values of O_2 in the studied wells from this aquifer because the waters were pumped from the depth to the surface for sampling. The alkalinity measured for the groundwater from the Ordovician-Cambrian aquifer is stable and ranges from 232 till 323 mg/l. The water of this aquifer is characterized by the concentrations of the chemical elements very similar to the average values for the non-polluted groundwater. At the same time the water has different total mineralisation and content of the main chemical elements. The sample taken from the well KV-9 has total mineralisation (1,094.3 mg/l) three times higher than in other wells (285.2 and 292.7 mg/l). The concentrations of Ba, Fe, K, Mg, Na, and Sr there are in average three times higher, the concentrations of Br, Cl and Rb are approximately 6-10 times higher, relatively to other wells. It could be caused by local pollution in the result of inflow of water from Keila-Kukruse water aquifer that is confirmed by the chemical analyses of water composition in Geological Survey of Estonia.

In the samples taken from the Ordovician-Cambrian aquifer, no PAH compounds and no phenols were detected. High concentrations of Toluene in content of 4 µg/l and 12.9 µg/l of m+ρ-Xylene were detected in this aquifer.

9.3 Kohtla-Järve

9.3.1 Surface soil

The concentration of microelements in the upper 5-cm soil layer in the Kohtla-Järve investigation area and their comparison with the average concentration in the Earth's crust and the humus horizon of Estonian soils are shown in Table 9.3.1.

The geochemical background in this area is very complicated. The till that is located under the topsoil in the north-eastern part of the area, influences on the elements distribution. Glacial siltstone, clay and sand that are present at most parts of the studied territory have more important influence on the elements distribution. In the southwestern part of the territory, where peat lies under the topsoil, and on the areas around the waste landfills, where technogenous soil is located in topsoil, volatile elements and elements associated with ash prevail.

On the formation of the background's values, the elements association of Dictyonema shale and phosphorite were not an influence. The increase of Ca and Mg contents in the topsoil of this area are caused by occurrence of technogenous material rich in carbonate. The distribution of CaO, LOI (loss in ignition) and IR (insoluble residue as sum SiO_2, Al_2O_3, TiO_2, K_2O and Na_2O) is shown on the Figure 9.3.1a,b and c. The same geochemical maps were used for the general characterisation of the soil and interpretation of trace elements in correlation with the main components of the soil in all studied regions.

In the topsoil of Kohtla-Järve, the increase of As, Cd, Cu and Pb concentrations are revealed. High positive correlation was determined also with Sb and Zn, at the same time their contents are lower than in the Narva and Kiviõli topsoil. The obtained data shows that the elements migrate with ash forming result of combustion of oil shale. In Kohtla-Järve topsoil, As and Hg contents are two to three times higher than the average values calculated for soil of northeastern Estonia (Petersell et al., 1994) and in the humus horizon of Estonia. Especially high enrichment of elements' relative average values for the Narva area is observed (Table 9.5.1.2). The obtained data showed that in the result of oil shale retorting the temperature 800-850 °C, the soil pollution by the volatile heavy metals takes place. Usually the pollution is caused by the transportation of the volatile fine fraction of waste rich in heavy metals and with dust from the dried waste landfills. This is in accordance with As, Hg and Pb distributions (Fig. 9.3.1.2-9.3.1.4). The maximum pollution is observed near the Kohtla-Järve Chemical factory and west from the semi-coke landfill (mainly near the semi-coke landfill), and at the area of peat's location.

It could be noticed that the increase of Pb content is observed at technogenous deposits locations. At the same time the content of Hg there is minimal. This is caused by the high content of Pb and the low content of Hg in the ash of the Kohtla-Järve Heating Plant that has been used for about 10 years, and has not yet polluted the atmosphere by the volatile elements.

The information about the heavy metal contents in semi-coke is very limited. The data about elements contents in the leachates showed that some elements (As, Ba, Cu, Mo, Pb, Se, Sr, Zn) are extracted from semi-coke intensively. The waste water and precipitation water flowing down the waste landfill accumulated in the channels located around the waste landfill. They are rich in heavy metals. The polluted water has the flow direction to the west. At the time of high stand of water (in spring and autumn) it floods large areas.

9.3.2 Subsoil

In ***Kohtla-Järve area***, the thickness of the quaternary cover is higher than in Kiviõli. The boreholes of four wells were also sampled. The Quaternary deposits are presented by more clayey sediments. The varve clays and the clayey siltstones prevailed there. Visually the clays are very dense and heavy. It leads to problems during the drilling because the holes of the wells closed very quickly during the removing of the equipment for the core sampling. The subsoil has in general green-grey colour but in some wells (RA-KJ-1 and RA-KJ-4) the colour of the soil was brown and yellow (Table 9.3.2.1). They are characterised by higher similarities in lithological composition than in Kiviõli because the average samples were taken from the larger interval of the sections. The distance of the well from the waste was different. The closest one was the well landfill of the well RA-KJ-1, it is located on the distance approximately 100 m, the wells RA-KJ-2 and RA-KJ-3 about 300 m and the well RA-KJ-4 on the distance about 700 m from the waste landfill. The thickness of topsoil in this district is very low and as a rule does not exceed 0.2-0.3 m. The samples from the well RA-KJ-3 have the smell of organic compounds.

The sampling and preparation of the samples for the analysis of the organic compounds is the same as indicated below. The results of the organic compounds measurements are showed in the Table 9.3.2.2 in mass concentration (mg/kg of dry matter). The analysed soils have very similar lithological composition. The dry residue content varies there from 70.3 up to 86.6%, the content of organic matter ranges in the limits from 0.29 up to 2.24% that is typical for the clayey sediments. From the studied set of PAH in the analysed subsoil only Phenanthren, Fluoranthen and Pyren were determined in the soil from wells RA-KJ-1, RA-KJ-3 and RA-KJ-4. The soil from RA-KJ-4 is polluted by all three PAH and is characterised by the highest summary values of these compounds. At the same time the observed level of pollution is very low and several times is less than PLV in Estonia for the soil of industrial and living areas. From the measured BTEX in the soils Toluene and m-ρ-Xylene were determined. TolueneToluene has the values 0.017-0.019 mg/kg DR and is found in the soil from RA-KJ-1 and in the sample from the upper part of RA-KJ-3. The contamination by the m-ρ-Xylene is more extended and it was estimated in the soil from wells RA-KJ-1, RA-KJ-3 and RA-KJ-4. The contents of other PAH and BTEX are very low and less than analytical detection limits.

The contents of phenols in the subsoil were determined only in trace values. Only in the samples from the upper part of the soils from RA-KJ-3 the content of 2,4-Dimethilphenol reaches 0.066 mg/kg DR. It could be noticed that the soils from Kohtla-Järve are the same as from Kiviõli and are characterised by the identical complex of organic pollutants (Phenanthren, Fluoranthen and Pyren from PAH, Tolueneand m-p-Xylene from BTEX) that permits to indicates that this set is typical for the region and depends on the specifics of technology of oil shale reworking in this region. At the same time, the samples from Kohtla-Järve showed rather high concentration of the compounds and the range varies more between different wells. Totally the values of these pollutants are very low and the soils do not accumulate the contaminants.

It is likely that the subsoils from Kohtla-Järve protected the infiltration of the pollution to the aquifers from the surface.

The results of chemical analyses of the subsoils from Kohtla-Järve are shown in the Table 9.3.2.1. The distribution of main elements is typical for the quaternary deposits. These sediments do not include the admixture of carbonates and are related to the typical varved clays.

9.3.3 Hydrogeochemistry and groundwater

18 wells and two channels around the waste landfills in Kohtla-Järve were sampled. The distance from the wells to the waste landfill fluctuated from 0 m (samples collected directly from the wells drilled through the waste landfill) to 700 m. Six wells were drilled in the frame of the project (RA-KJ-1 to RA-KJ-6). The wells 600 and 601, 602 and 603, 608 and 609, 610 and 611, 622 and 623 are grouped in pair (Razgonjajev et al., 1992). The distance between them is not more than several m and the wells are drilled through the different aquifers (the shallower ones up to Lasnamäe–Kunda (O_2ls-O_2kn) and the deeper ones up to Ordovician-Cambrian aquifer (O_1pk-$\text{Є}_1$ts). The depth of the shallow wells is approximately 20-25 m, the deeper ones - approximately 40 m. The wells drilled in the frame of this project are shallow (depth ranges from 5.7 m up to 9.5 m), into the open upper part of the Lasnamäe–Kunda aquifer. The sample KJ-CH-1 was taken from the channel flowing around the waste landfill where the waste is presented by ash, the water sample KJ-CH-2 was taken from the channel around the semi-coke landfill. The depth of the channels is several meters. The variability of the studied parameters is shown on the Table 8.2. The concentrations of elements are presented in Table 9.3.3.1 and organic compounds in Tables 9.3.3.2 and 9.3.3.3

The pH values of the sampled water are very changeable. The water from Lasnamäe–Kunda aquifer has pH values from 7.0 (wells 608, 610) up to 11.0 (well 622). The water of the Ordovician-Cambrian aquifer is characterised by close to neutral pH values. It ranges from 7.0 up to 8.2. Only in the well 601 that is located near the contact of ash and semi-coke landfills, where the water is alkaline, does the pH increase up to 11.9.

The total mineralisation of the water of Lasnamäe–Kunda aquifer is higher (the highest one is in the well 622 and the lowest one is in the well 616) than in the Ordovician-Cambrian aquifer (ranges from 192 mg/l in the well 623 up to 3,038 mg/l in the well 601).

The water from the upper Lasnamäe–Kunda aquifer has higher alkalinity and electric conductivity relatively to water from the deeper Ordovician-Cambrian aquifer. So the electric conductivity in the water from the shallow well from each pair is higher from two (wells 610/611) up to ten times (wells 622/623) in comparison with the water taken from the deeper water aquifer. The alkalinity measured for water from Lasnamäe–Kunda aquifer ranges from 1678 mg/l (well 601) up to 402 mg/l (well 620). Very low alkalinity (48.8 mg/l) in water of this aquifer was measured in the well 616. The range of the electric conductivity is from 7990 μS/cm (in the well 601, closest to the waste landfill) up to 327 μS/cm (well 616).

The values of O_2 in the studied wells from the Lasnamäe–Kunda aquifer are lower or close to values estimated for the Ordovician-Cambrian aquifer. The content of dissolved oxygen is found from 0.09 up to 6.8 ppm in water of Lasnamäe–Kunda aquifer and from 2.3 to 7.3 ppm for the Ordovician - Cambrian aquifer. The percentage of saturated O_2 (based on the data measurements in May, 2003) is in the range of 8-56 and 19-60 respectively. The samples from wells 616 and 620 are not a typical for this area and have higher content of dissolved oxygen (10.1-10.5 %) and a very high percentage of saturated O_2 (90-91). They have also low values of electric conductivity and alkalinity that indicates lower pollution of water in these wells.

Content of dissolved organic matter (DOC) is higher in wells penetrating the Lasnamäe–Kunda aquifer and located near to the waste landfills. The highest values of DOC were revealed in the well 622 (214 mg/l) and RA-KJ-3 (100 mg/l). In the wells that are situated on the long distance from the waste landfills, the content of DOC is as a rule less than 10 mg/l.

The pore water has the highest alkalinity (4118 and 3364 mg/l), the electric conductivity of 16320 to 14480 μS/cm, and the ammonium (NH_4^-) 288 and 132 mg/l. The DOC content in the higher well is 473 and much lower in the lower well (19 mg/l).

Two water samples were taken from the channels situated near to the ash landfill (sample KJ-CH-1) and near to the semi-coke waste landfill (sample KJ-CH-2). They have the highest values of pH (12.5 and 11.8), the electric conductivity (12490 and 7670 μS/cm) and alkalinity (2220 and 1071 mg/l). Estimated values are close to the data obtained for the contaminated waters collected from the Ordovician-Cambrian aquifer from the well 601 near to the semi-coke landfills. DOC content in water from the channels is characterised by the changeable values. The DOC content in the sample KJ-CH-1 is 50 mg/l and the water from the channel around the semi-coke landfill has the highest DOC content (530 mg/l) from the sampled waters. Both samples of channel water have high total mineralisation (4,087.1 mg/l in KJ-CH-1 and 3,981.7 mg/l KJ-CH-2). The contents of dissolved oxygen and saturated oxygen measured in channel waters are very different, 6.9 and 0.8 ppm and 75 and 11 % accordingly.

The concentrations of chemical elements in groundwater from Kohtla-Järve are shown in Table 9.3.3.1. The concentrations of Al are 2-3 times higher, As, 10-40 times higher, Br - up to 20 times higher, Cl - up to 20 times higher in groundwater of the Lasnamäe–Kunda aquifer relative to the deeper Ordovician-Cambrian aquifer. The concentrations of Fe and Rb are very variable. At the same time the values of B and Ba are higher for the Ordovician-Cambrian aquifer. The concentration of trace elements in porous water (RA-KJ-5 and RA-KJ-6) are similar to the contents in channel waters and characterised by extremely high concentrations of Al, A, Ba, Br, Ca, Cl, Cr, Cs, Fe, P, Rb, Re, S, Sb, Zn and Sr relative to groundwater from both aquifers. The extremely high enrichment of water was revealed for Al, Br, Ca, Cl, Cs, P, Rb and Sr.

It could be noticed that the chemical composition of groundwater of the Lasnamäe–Kunda aquifer collected from the shallow and deeper wells is very similar. There was no correlation between the composition and the depth of sampling indicating active water exchange.

The content of organic compounds in the groundwater in Kohtla-Järve is shown in the Table 9.3.3.2 The PAH concentration in groundwater in Kohtla-Järve is characterised by its low level. The sum concentration of PAH ranges from the contents lower than the analytical detection limits (the wells 616, RA-KJ-1, RA-KJ-2 and KJ-RA-3) up to 24.3 µg/l (the well 602). The PAH are presented mostly by Naphthalene, in two wells (RA-KJ-4 and 610) Phenanthren was also revealed in small amounts. The large spectrum of PAH (Naphthalene, Acenaphthen, Fluoren, Phenanthren, Anthracen, Fluoranthen, Pyren and Chrysen) is determined there, but the sum is low (10.55 µg/l). The PAH values in wells 602, 620 are higher than PLV in Estonia. In groundwater of the deeper Ordovician-Cambrian aquifer, the PAH contents are less than analytical detection limits (0.01 µg/l). The highest values of PAH were revealed in porous waters. In the well RA-KJ-5, the sum of PAH is 628.4 and in RA-KJ-6 it is 461.4 µg/l. PAH are presented by 9 and 6 compounds, respectively. These values exceed the PLV in 62 and 46 times, respectively. The water from the channels around the ash landfill is characterised by the relatively low contents of PAH, 0.322 µg/l in sample KJ-CH-1. The PAH content in KJ-CH-2 (19 µg/l) is higher than PLV in two times.

The oil product content varies in wide limits. In the groundwater of the Lasnamäe–Kunda aquifer from the deeper wells, the content of BTEX ranges from 220 µg/l (well 610) to 21 µg/l (well 616). In the shallow wells is also very variable, from 349.8 µg/l (well RA-KJ-3) to 1.7 µg/l (well RA-KJ-4). The water of Ordovician-Cambrian aquifer is characterised by the low contents of BTEX, 48.2 µg/l in the well 601, closest to the semi-coke landfill, and 3.3 µg/l in the well 603. From the studied BTEX, Bensol, TolueneToluene, Ethylbensol, m+ρ-Xylene and o-Xylene prevail. All BTEX values measured in these wells are less than PLV.

The extremely high values of BTEX that many times exceed the PLV were revealed in porous water and water from the channel located near to the semi-coke landfill (2,229 µg/l in sample KJ-CH-2). In porous water from the well RA-KJ-5, the sum of BTEX reaches 19,543 µg/l and in the well RA-KJ-6 it was determined as 1,213 µg/l. In these samples, the full set of the measured oil products in water was determined.

The high pollution of groundwater in this region by phenols is shown in (Table 9.3.3.3). It depends strongly on the distance from the semi-coke landfill and the depth of the water aquifer. In the contaminated water, there is a large spectrum of the studied phenols, but the most hazardous, mobile and chemically active group of them (2,3-Dimethyl-, 2,6 Dimethyl-, 3,4 Dimethyl-, 3,5 Dimethyl-phenols) prevails. In the groundwater of the Lasnamäe–Kunda aquifer from the deeper wells, the high contents of phenols many times exceeded the PLV determined in the wells closest to the semi-coke landfill. The highest values were estimated in the wells RA-KJ-2 (82,235 μg/l) and 601 (2,231 μg/l). The high values of phenols were revealed in the well 602 (914.1μg/l), one of the wells closest to the semi-coke waste landfill. The water of the Ordovician-Cambrian aquifer from the well 601 located near the waste landfill is also very contaminated by phenols (2,027 μg/l). The highest contamination by the phenols is observed in porous water and in water from the channel around the waste landfill (KJ-CH2). There the sum of phenols reaches 93,395 μg/l and 87,430 μg/l in the wells RA-KJ-5 and RA-KJ-6, accordingly. In the sample KJ-CH2 it is 68,469 μg/l. These concentrations exceed the PLV in hundred times.

It was revealed that the intensity and extension of groundwater contamination by organic pollutants in waste landfills depends on the depth of the water aquifer. So in the groundwater samples collected in the same place (wells 600, 601), but from the different aquifers, the content of PAH decreases from 6.8 to less than 0.01 μg/l, sum of BTEX from 134.9 to 48.2 and phenol from 559 up to 227 μg/l.

9.4 Kukruse

9.4.1 Subsoil

In the ***Kukruse area*** the Quaternary deposits were sampled from three wells. The wells RA-KK-1-1 and RA-KK-1-2 are located near the burned waste landfills close to the highway Tallinn-Narva, ref. Chp. 6.1.3. The placement of these wells was chosen on expected groundwater flow direction. The groundwater flow direction is oriented from the south to the north. The well RA-KK-1-1 is located north of the Kukruse landfills. The well RA-KK-1-2 is located to the south and this is like a background well. The well RA-KK-2 is located close to the waste landfill Kukruse 2 where the waste is represented by residue after oil shale enrichment that did burn. The core from these well is represented by grey and green-grey siltstone (Table 9.4.1.2). In the wells RA-KK-1-2 and RA-KK-2 quaternary deposits are presented by clay. They are heavy and dense. The content of dry residue in the studied soil varies from 82.6 up to 86.8 % and the organic matter ranges from 0.73 to 2.93 %.

The results of organic compounds measurements are shown in the Table 9.4.1.2 in mg/kg DR. In the distribution of organic compounds, the large difference between the wells is observed. The PAH were only detected in the samples from the upper part of well RA-KK-1-1 with 0.12 mg/kg of mostly 3-rings PAHs.

BTEX were determined in the northern well RA-KK-1-1 in both samples (lower and upper) and in the sample of well located near Kukruse 2. From the BTEX in the core of well RA-KK-1 Toluene (only in upper part of section) and m-ρ-Xylene were determined. In the soil from RA-KK-2 the low content of Ethylbenzene was also observed.

Phenols are not detected in the soil samples. The obtained results in the distribution of organic compounds showed that the soils near the waste landfills are very slightly contaminated by the very similar set of PAH and BTEX. The measured concentrations are very low and very slightly elevated over the analytical detection limits.

The data about the chemical composition of the studied soil are presented in the Table 9.4.1.1 and illustrated in Fig. 9.4.1.1. The chemical composition of these soils is characterised by the values of elements typical for the clays and fine siltstone. For the specific feature the increase of values of As, Ce and Mo in these soils could be related. The comparison of the values obtained for the samples after full digestion and after digestion by aqua regia showed the relatively lower level of ratio for the elements that are mainly included into carbonate minerals (Sr, Ba, K, Na, S) or REE elements (Yb, Er, Eu).

The average values of the main part of elements are in the background values calculated for the clays, but at the same time the elevated concentrations of As, Ce and Mo are revealed that increased the background values in average two times and could be related to the specific features of the soil in these regions.

9.4.2 Hydrogeochemistry, groundwater and contamination

The water of the Keila-Kukruse aquifer near the waste landfill Kukruse 1 (burnt) has pH of 8.0 to the south from the waste landfill (the well RA-KK-1-2) and alkaline pH (10.1) to the north from it (the well RA-KK-1-1) (Table 8.2). The electrical conductivity value (577 µS/cm) and the alkalinity (103.7 mg/l) of groundwater from the well RA-KK-1-1 are not high. These values are similar to the values measured in water from the well RA-KK-2, Kukruse 2 (unburnt) (713 µS/cm and 231.8 mg/l respectively). The total mineralisation of water in the well RA-KK-1-1 is 286.0 mg/l, in the RA-KK-1-2 it is 117.9 mg/l and in the RA-KK-2 it is 288.2 mg/l.

Having the similar values of the total mineralisation, the waters taken from the landfill Kukruse I and Kukruse II are characterised by the different complexes of the main chemical elements (Table 9.4.1.1). The water from RA-KK-2 is characterised by the higher values of Mg, Ca and S relatively to RA-KK-1-1. The water from the wells drilled to the south and to the north from Kukruse I is very different in the sets of the trace elements. In water of the well RA-KK-1-1 there are higher contents of Al, B, Br, Cl, Co, Cu, Ga, K, Li, Mo, Na, Ni, Pb, Rb, Se and V, relative to water from RA-KK-1-2. This could be caused by the differences in the extractability of waters with different pH values and also by the pollution of waters in the well drilled on the north from the waste landfill by the elements extracted from burned oil shale.

The differences in the distribution of the measured organic compounds were revealed for waters from the wells located near the landfills Kukruse I and Kukruse II (Table 9.4.1.2). No organic compounds were detected in the groundwater from the well RA-KK-2. In the water from the well RA-KK-1-1 PAH (sum is 0.664 µg/l) and oil products (sum is 41.6 µg/l) were determined. The compounds naphthalene and Xylene are dominating.

9.5 Narva

9.5.1 Surface soil

The geochemical background of soils in the Narva area is due to the concentration and distribution of main and microelements in the glacial, glaciolacustrine and glaciofluvial deposits. The latter contain different amounts of crystalline basement rocks originating from the Finnish territory, with the concentration of microelements close to the average concentration of the Earth's crust (The Geochemical…, 1992), but the crushed fragments of Dictyonema argillite and phosphorite rich in microelements are present as well.

The elements characteristic of the Dictyonema argillite and phosphorite are reflected in the geochemical composition of soil, forming associations characteristic of Dictyonema argillite (Mo, U, in places As and Pb) and phosphorite (P, Y, REE, U, Sr) (Table 7.2). In addition to the above elements, the pollution with microelements resulting from the combustion of oil shale in the Baltic PP also affects the geochemical composition of soil. It is distributed via the atmosphere on one hand (volatile elements emitted from the chimneys and of the tailings), and by solid ultra-alkaline combustion wastes on the other hand.

At the combustion of pulverised oil shale, many microelements concentrate in fly ash. Most of them are captured by grit-arresters, but very fine fractions, including the microelement compounds (monoelements) penetrate the grit-arresters and volatilise. These fractions rich in many microelements (Table 9.5.1.2 emitting into the atmosphere pollute the surrounding environment. During the combustion of pulverised oil shale, As, Hg, Pb, Cu, Ni, Zn and some other elements concentrate and volatilise as monoelements or their chemical compounds. Up to now, only few analyses of the trade oil shale and different fractions of the ash of power plants have been made and for certain elements (Cd, Hg) the results are of questionable reliability. However, the results show that the total concentration of the elements under discussion in the ash fractions is much smaller than it should be. Hg, As, Pb, Cu, Zn and others readily volatilised when combusted at high temperatures. The "deficit" of the above elements in the ash fractions is reflected in the upper layer of soil, where the concentration of the same elements has increased (Table 9.5.1.1, Fig. 9.5.1.1-9.5.1.4-11.3.3). The figures show that the concentration of As, Cd and Pb volatilised during the combustion of oil shale increases to the north of the power plant, i.e. in the prevailing wind direction. The chimneys of the power plants are high (up to 120 m), therefore the pollution is carried to long distances and dispersed. The sharp decrease in the pollution level in the coastal area of the Gulf of Finland is suspicious. In this area are spread the sands and silts of different Baltic Sea stages poor in clay fraction, and the precipitation washes the pollutants to deeper beds. For example, in 1992-1994 in Olgino village an annually average of 24 g of solid matter rich in Cd, Cu, Pb and other elements fell on 1 m² of ground surface (Table 9.5.1.2), and in 1992-1993 in Narva-Jõesuu ca 9 g of solid matter which contained Cd 26 ppm and Pb 329 ppm fell on 1 m² of ground surface (Petersell et al., 1994). Moving away from the power plant, on one hand the concentration of solid particles in the atmosphere decreases, and on the other hand the concentration of elements in the solid matter increases.

In the oil shale ash, too, the concentration of some elements (K, Ca, As, Cu, Sr, Mo, U etc.) is much bigger than in the soil of the surroundings of the depositories. With very strong winds the elements are partly carried to the surrounding areas; among these K and CaO cause the formation of ultra-alkaline conditions in the waste depository as well as in its surroundings and outwash with precipitation of many microelements from the depositories.

The utilisation of oil shale for producing electricity causes pollution of soils with several microelements, the extent and environmental impact of which are still unclear. Although the concentration of pollutants in the soils is below the maximum permissible concentrations established in Estonia, the increase in concentrations in the upper layer of soil is obvious. It influences the bodies of water, vegetation (both directly and via the soil) and humans via the atmospheric pollution.

9.5.2 Subsoil

Two average samples of core were selected for the analyses from the boreholehole drilled near the Baltic power Plant in the frame of this project. One sample (SR-N-1) was taken from the upper part of the boreholehole from the interval 0-1.1 m and the second one from the deeper interval between 1.1 and 4.5 m. The lithology of these subsoils is different: in the upper part the sediments are presented by dark-yellow sandy soil and on the depth are grey-green clay and siltstone, very typical for this area. The chemical composition of sampled subsoil is showed in Table 9.5.2. It is typical for such kind deposits and reflected mostly the variation of their lithology and grain-size composition. The contents of trace elements are very close to the average data for the earth crust (Wedepohl, 1995), only some enrichment of both samples by As (up to two times) was revealed.

9.5.3 Hydrogeochemistry and groundwater

Eleven water samples were studied in Narva region, ten of them were taken from wells. Two wells (N-7 and RA-N-1) penetrated the Quaternary aquifer. Two wells (RA-N-2 and RA-N-3) were drilled through the ash plateau and there were taken the samples of porous (infiltration) water. In five wells (N-1/2, N-6/1, N-45/2, N-46/1 and N-46/2), the water samples from the O_2ls-O_2vl aquifer were collected. One sample (N-8) was taken from the Ordovician-Cambrian aquifer and one (N-CH) from the channel located near the eastern (II) ash plateau. Taking into account the very high temperature of oil shale combustion it was proposed practically full destruction of organic compounds under this temperature. By this reason the analysis of groundwater was limited by the study of the inorganic compounds. The data set of chemical analyses is showed in Table 9.5.3.

The pH values of water from the Quaternary aquifer vary from 6.3 (well 7) to the south from the ash plateau II up to 7.8 (well RA-N-1) to the north (Table 5.2). The electrical conductivity values are 780 µS/cm and 318 µS/cm, respectively. The greater differences are observed for alkalinity (430.1 mg/l and 152.4 mg/l) and the values of ammonium (NH_4^-) (8.61 mg/l and <0.05 mg/l). The content of dissolved oxygen is found from 3.6 (well 7) up to 9.3 ppm (well RA-N-1). The content of saturated O_2 (based on the data of measurements in February 2003) is much higher (67 %) in the well RA-N-1 compared to the well 7 (27 %). The total mineralisation of water of the Quaternary aquifer is 96.5 mg/l (in well RA-N-1) and 211.0 mg/l (well 7).

The water of the O_2ls-O_2vl aquifer is characterised by stable and neutral values of pH, it varies from 6.6 up to 6.8. The increase of pH values (up to 8.2) was observed only in water from the well N-46/1. The water of this aquifer demonstrated stable levels of electrical conductivity values (ranges between 2230 µS/cm and 2390 µS/cm), alkalinity (varies from 546 mg/l to 817 mg/l) and contents of dissolved and saturated oxygen. The total mineralisation of the water of the O_2ls-O_2vl aquifer is between 390.9 mg/l and 992.7 mg/l. The obtained values of electrical conductivity that demonstrate the abundance of dissolved electrolytes in the groundwater showed the relatively high content of dissolved inorganic compounds in the water of this aquifer.

The highest studied parameters were observed in the porous (infiltration) water from the ash plateau and in water from the channel. The formation of the porous water that was sampled from the wells drilled through the ash plateau took place in the result of infiltration of the waters from the pounds located on the top of the plateau for the preliminary sedimentation of the ash pumped there. The water in channels is formed as a result of the result of inflow of the water from the plateau and precipitation. The pH values measured in these samples were extremely high, up to 13.0. The total mineralisation varies from 1,657 mg/l in the upper well (RA-N-2) up to 7,558 mg/l in the channel. The porous waters from the upper well and water from the channel are similar in the values of electrical conductivity (31,260 µS/cm and 34,540 µS/cm respectively) and alkalinity (8,311 mg/l and 7,610 mg/l) and are characterised by low contents of the values of ammonium (NH_4^-) (0.73 and 1.34 mg/l). The content of dissolved oxygen is 9.2 ppm in the upper well RA-N-2 and 10.2 ppm in the channel. In the lower well RA-N-3 it is only 4.8 ppm, typical for regular groundwater. The content of saturated O_2 (based on the data of measurements in May, 2003) is relatively high (93 %) in the well RA-N-2. In the channel it is 79 %, reflecting the influence of precipitation on the composition of water.

In comparison with groundwater in other studied regions, the water filtered through the ash plateau and accumulated in the channels in Narva is characterised by the highest total mineralisation, electrical conductivity values and alkalinity.

The concentrations of chemical elements determined in water in the Narva region are shown in Table 9.5.3. It could be pointed out that the main differences in composition of water of Quaternary and Ordovician aquifers are observed in the distribution of main elements. The water of the O_2ls-O_2vl aquifer has the highest values of Ba, Ca, K, Na and Sr, relative to the upper aquifer. The contamination of water leads to increased content of many trace elements in water. So, in contaminated porous waters and water in the channel the concentration of Al, Cd, Cr, Cs, Cu, Ga, Cd, K, Li, Mo, Na, Pb, Rb, Re, Se, Sr, Tl and W gradually increased. The highest enrichment relative to average values for groundwater of this region is observed for Cs, Ga, Li, Mo, Pb, Rb, Se (more than 100 times), Al (more than 20 times) and Cu (up to ten times. The estimated values exceed the PLV for the groundwater several times (up to ten).

10 STREAM SEDIMENTS

Three samples of stream sediments were taken in order to study in them the distribution of chemical elements and in two of them also organic compounds were also determined. The sampling was carried out in winter season when the river and the brook were covered by ice. One sample (SS-Narva) was collected from the bottom (depth 0.5 m) of the brook that flows in the village area at the distance of approximately 200 m from the ash plateau of the Baltic Power Plant.

Two samples of stream sediments (SS-ER-1 and SS-ER-2) were taken from the bottom of the Erra River to the north from the semi-coke waste landfills in Kiviõli at the distance of 500 m (SS-ER-1) and (SS-ER-2) 700 m from them. The sample SS-ER-1 was collected up-stream of the Erra River relative to the point of sampling of the sample SS-ER-2. The depth of sampling was 0.5 and 1.0 m respectively. All three samples were presented by very fine black or dark brown silt and had intensive smell.

The stream sediments from Kiviõli have the lower LOI values relative to the sediment from Narva brook. At the same time, the stream sediment from Narva is characterised by higher contents of numerous measured trace elements that may indicate the pollution of the stream sediments in the brook (Table 10.1). The elements could be extracted from the ash or transported and accumulated with the finest fractions of ash the short distance from the ash plateau. The stream sediment SS-Narva has the higher contents of Ag, Ba, Ce, Cr, Cu, Dy, Er, Eu, Ga, La, Mo, Nd, Ni, Pr, Sb, Sc, Th, U, W, Y and Yb in comparison with the stream sediments taken from Erra River. The stream sediments from Kiviõli are similar in composition of main elements. The highest differences are observed in contents of organic carbon that ranges from 21.5 up to 19.3%, iron from 8.32 up to 4.82% and CaO from 11.05 up to 5.22% in the SS-ER-2 and SS-ER-1, respectively. The sample SS-ER-1 is characterised by higher contents of practically all measured elements (except Fe, Mn, Ba and Sr) relatively to sample SS-ER-2.

From the measured organic compounds the PAH and oil products in small amounts were revealed in sample SS-ER-2 (Table 10.2). The PAH in stream sediment SS-ER-2 are presented by Acenaphthen (0.01 mg/kg on the dry matter, Acenaphthylen (0.02 mg/kg), Fluoren (0.14 mg/kg), Phenanthren (0.03 mg/kg), Anthracen (0.04 mg/kg), Fluoranthen (0.02 mg/kg) and Pyren (0.01 mg/kg). In sample SS-ER-1, only oil products were determined. From oil products in studied samples, only m+ρ Xylene as revealed in concentrations of 0.024 nd 0.022 mg/kg in samples SS-ER-1 and SS-ER-2, respectively. Other organic compounds have concentrations less than analytical detection limits.

11 VEGETATION SAMPLES

During the study in the time frame of the project, 15 samples were collected (5 from Kiviõli, Kohtla-Järve and Narva) of roots of meadowsweet (*Filipendula ulmaria*) (Fig. 11) that is widespread in the whole Estonia and is a well-known indicator plant. The choice of meadowsweet was due to the experience of colleagues from the Geological Survey of Estonia (Enel, 2000a, Enel, 2000b, Enel, 2003) that indicated this plant as the good indicator of elements accumulation. The plants were collected where possible in the same sampling points where the soil was sampled. The root samples were washed and dried at the room temperature then pulverised and used for the chemical analyses. The total concentration of elements was determinated by ICP-MS method in the solution after wet-ashing in HNO_3 and digestion in aqua regia. The excluding of the ashing procedure at the high temperature permitted determination of the concentration of the volatile elements, which have a tendency to evaporate at high temperature. The main aim of the testing of large numbers of elements in the roots was to estimate the differences in the elements distribution and combinations of elements that have the tendency to accumulation in the roots of plants growing in the areas with different types of pollution as a result of oil shale reworking.

Comparison of the elements concentration with the average level of elements in the soils in these regions permitted the assessment of the level of accumulation of elements and revealed the most bioactive elements.

The soils in the humus horizon at the studied areas near Kiviõli, Kohtla-Järve and in the south of Narva area are presented mainly by the Brown type (K0+1) and parent deposits by till. The comparison of the contents of elements was carried out based on the average (geometrical mean) data calculated for this soil type in the Geochemical atlas of the humus horizon of Estonian soil (Petersell et al., 1997). The elements distribution and range of elements values in the plants collected in the different areas are shown in Table 11. The concentrationsof Ca, Mg and P in the all sets of plants are higher that in soils in 1.2, 1.5 and 3 times that is typical for such bioactive elements. The average values of Cu, Hg, Mo in plants are significantly higher relative to contents of these elements in soils. Average values of Zn in plants are close to average values in the topsoil. Zn concentration is a little smaller in roots of plants collected in Kohtla-Järve and its values increased in plants from Narva region. The increase of content of Zn, Cu, Mn, Cd, Ba and Tl in the roots of plants collected near the Power Plant in Narva and to the north from them (in the prevailing wind direction) was revealed. Some increase of contents of Pb, Ag, Ni, Co, Mn, Th, La and Ba in the roots of meadowsweet sampled to the north from old landfill in Kiviõli is observed. In the plants sampled near the semi-coke waste landfill in Kohtla-Järve, the enrichment by Mo, Cu, Zn and U was determined.

12 GROUNDWATER FLOW MODELLING

12.1 Initial data

Three detached models of steady-state groundwater flow for areas with significant ash or semi-coke landfills in Kiviõli, Kohtla-Järve and at Narva have been created. The Visual MODFLOW v.3.1 code is the basic software for the models. The 3D models were constructed using a rectangular uniform grid with initial spacing of 125 m on the horizontal plane.

<u>Maps and elevations.</u> The Soviet military maps at the scale 1: 25.000 made in 1960 to 1963 were used as a topographic base for modelling. These maps have been based on a rectangular co-ordinate system called 'Pulkovo 1942' and, therefore, the co-ordinate system of the models is the same. A conversion of the Pulkovo system to the contemporary world system is possible by the help of existing special software. The interval between the relief contours is 2.5 m on the maps mentioned.

The elevations of ash landfills in Kohtla-Järve and at Narva were determined for modelling using heights measured by the local survey units. The model heights for the ash landfills in Kiviõli were obtained from the Base Map of Estonia as well as some estimations made by a GPS device.

Data from 34 borings made by the Geological Survey of Estonia and by the enterprise Viru Geoloogia in the Kohtla-Järve and Narva study areas in former times were applied to the modelling. The heights of these boreholeholes had been levelled with exactness 0.01m. In addition, information was used from the 10 borings carried out under the management of Dr. L. Bityukova in 2003. The X, Y, and Z coordinates of latter borings were estimated by a GPS device. All borings mentioned above are situated in marginal parts of ash landfills.

Bitmap image files (. BMP) of the Base Map of Estonia were incorporated into models as site maps. The Base Map (a satellite photomap) compiled at scale 1: 50,000 in 1993 was not detailed enough for constructing the models needed (intervals between contour lines were 20 m, the drainage network was poorly detailed, etc.). However, this coloured map was suitable for enhancing the vizualition of the model.

The hydraulic conductivity of layers modelled has been estimated by former pumping tests for only a few points in the study areas. None the less, the conductivity of regional units was predominantly specified at the current modelling on the basis of data and experience get by previous basinwide hydrogeological modelling (Vallner 2003, 2002, 1996). In each study area two slug tests have been made under the management Dr. L. Bityukova to determine the conductivity of ash or semi-coke. The bottom seam of ash landfills was characterised by one of these tests. Another test was carried out about 10 m higher than the lower test point. The results of testing the higher points were used for modelling. The transversal conductivity of layers is ten times less than their lateral conductivity in Kohtla-Järve and Narva models. The anisotropy of the layer conductivity was not specified at the Kiviõli model.

The riverbed conductance for assigning the river boundary conditions was estimated accordingly to the experience of former investigations and modelling of the groundwater runoff (Vallner 2003, 2002, 1997, 1996a, 1996b, 1980, and 1976).

Water stage in the drainage network and Narva Reservoir has been estimated accordingly to topographic maps used for modelling. The elevations of the groundwater table and the heads along layer boundaries have been given on the basis of former basinwide modelling (Vallner 2003, 2002, 1966b). The heights of the groundwater table measured in borings by the Geological Survey of Estonia and Viru Geoloogia were used as calibration targets during modelling.

The groundwater recharge was given as the net infiltration (total groundwater recharge minus evaporation from the zone of saturation or capillary fringe) onto the ground surface. It was estimated on the basis of former investigations (Vallner 2003, 1997, 1996b, 1980).

12.2 Hydrogeological units modelled

Due to the similarity of the hydrogeological conditions in northeast Estonia all three models enfold the same hydrogeological units. They are from top to bottom as follows:

<u>The technogeneous deposits (tQ_{IV})</u> are the ash and semi-coke of oil shale. They have been stored as landfills which relative height is up to 100 to 120 m in Kiviõli and Kohtla-Järve. A plateau has been formed by ash stored in the study area of Narva. The lower portion of ash and semi-coke storages with the thickness up to 10 to 20 m in Kiviõli and Kohtla-Järve and the ash plateaus at Narva contains heavily polluted water (Vallner 1996a, 1994; Vallner and Sepp 1993). Besides of ash and semi-coke the landfills or seams of other technogenous residuals (gangue, building refuse etc.) occur in study areas but they are not considered at the current modelling.

<u>Quaternary deposits (Q)</u> consisting predominantly of glacial till covered by glaciolacustrine sand and sandy loam or varved clay in places form the uppermost water bearing layers (Perens and Vallner). Their thickness ranges from 0.5 to 30 m. In boggy areas the uppermost portion of Quaternary deposits is represented by a peat layer which thickness usually does not exceed 3 m. Water table conditions prevail in Quaternary deposits. The lateral conductivity of Quaternary deposits is mostly 0.1 to 3 m/day, but the transversal conductivity of varved clay may be less than 10^{-4} m/day.

<u>The Ordovician aquifer system (O)</u> lies directly beneath the Quaternary cover. In model areas the O system is represented by diverse Middle and Lower Ordovician limestones with clayey interbeds. Their total thickness is 10 to 50 m. The limestones are fissured and heavily karstified. Therefore, they can easily become polluted. The upper portion of the carbonate bedrock belongs stratigraphically to the Kukruse Stage (O_3kk) comprising the commercially exploited (mined) oil shale (kukersite) seams. The total thickness of the commercial bed of kukersite is about 2.5 m. The Kukruse Stage is underlyed by the Uhaku Stage (O_2uh) consisting of argillaceous limestones with marly intercalations which form a local aquitard in places. The lateral conductivity of the carbonate bedrock usually changes from 2 to 20 m/day and the storage coefficient is between 10^{-6} to 10^{-3} m/day depending on the degree of fissuration and karstification. The transversal conductivity of the local aquitards is 10^{-5} m/day or even less. In these places where the thickness of the Quaternary cover does not exceed a couple of metres the uppermost portion of the carbonate bedrock belongs to the unsaturated zone. The saturated zone of the carbonate bedrock lying on a local or regional aquitard is in water table conditions. The average specific yield of the unconfined portion of the bedrock is 0.02 to 0.05. Under an aquitard the bedrock layers are confined. The water of the O aquifer is mostly polluted and not suitable for drinking in study areas.

The Ordovician regional aquitard ($O_{aquitard}$) enfolds the lowermost portion of the Ordovician layers in model areas. They consist of limestones, marls, siltstones, clays and argillites with total thickness from 2 to 10 m. The transversal conductivity of the aquitard is 10^{-7} to 10^{-5} m/day. This aquitard prevents spreading of polluted water from O aquifer downward to a certain extent.

The Ordovician-Cambrian aquifer system (O-Є) is represented by fine-grained sandstone and siltstone with total thickness about 20 m. This confined aquifer system being mostly unpolluted, is a significant source for public water supply in northeast Estonia. Its lateral conductivity is 2 to 4 m/day. The well yields are predominantly 400 to 600 m^3/day per 10 to 15 m of drawdown. The storage coefficient is 2.5×10^{-5} to 6×10^{-3}; the specific yield of the aquifer drained is 0.12 to 0.14. Due to the intensive water extraction the regional head depressions have been formed with centres southward from Kohtla-Järve and in Slancy (Russian Federation). Water moves toward the local centres of the head depression in the study areas.

The Lükati-Lontova regional aquitard (Є$_1$lk-Є$_1$ln) with the thickness of 70 m consists of siltstones and clays which transversal conductivity is 10^{-6} to 10^{-9} m/day in study areas. The intensity of downward flows penetrating this aquitard is very small. Therefore, the lower impermeable boundary of the models under consideration has been made congruent with the upper surface of the Lükati-Lontova regional aquitard.

Under the Lükati-Lontova aquitard lays the Cambrian-Vendian aquifer system on the crystalline basement (Perens and Vallner 1997). Neither has been incorporated into the models.

12.3 Kiviõli model

Model area. The Pulkovo 1942 co-ordinates of the rectangular Kiviõli model area are: lower left corner: X = 5494500, Y = 6581000; upper right corner: X = 5499500, Y = 6584500. The area measures 4,500 m from west to east and 3,500 m from north to south. Before the start of industrial operations the topography of the area was flat with absolute elevations between 45 to 55 m. The solid residuals of oil shale processing (semi-coke) have been landfilled in the central part of the model area (Fig. 12.3.1). The absolute elevation of two main landfills reaches 120 to 130 m. Between main landfills is situated a lower one with top elevation about 65 m. The area of man-made landfills has been surrounded halfway from the northwest, north, and northeast by the Koljala Creek and its branches. In the southern part of the area are situated abandoned oil-shale mines and opencast pits drained by ditches. The local drainage basis for the channel network and upper aquifers is Purtse River remaining 1 to 3 km eastward from the model area.

Model layers and boundary conditions. The model consists of 6 layers, which are from top to bottom as follows (Fig. 12.3.2-4):

The 1st layer enfolds the semi-coke inside borderlines of landfills described. The hydraulic conductivity assigned to semi-coke is 0.5 m/day. Outside the semi-coke landfills to the layer belong the Quaternary deposits represented predominantly by till. In the northwest part of the area a seam of varved clay lay on the till. The average conductivity given to the Quaternary deposits is 2.5 m/day. The layer is unconfined. Its significant portion has been dried up due to the impact of channel network' and mine drainage. The Constant Head boundary conditions were assigned along the northern and partially western and eastern borders of the 1st layer. Boundary conditions were not specified for the remaining portion of layer borders. In the last case was supposed that the groundwater stage depends predominantly on the drainage impact of underlying layers and can be estimated by modelling. The net infiltration reaching 60 mm/year was given on the top of the 1st layer.

The 2nd layer serves as an arbitrary tool. It is necessary for creating a semi-pervious screen beneath the 1st layer. Without such of screen the water table elevation modelled would be significantly lower than measured one in semi-coke landfills To the 2nd layer belong the lowermost seams of semi-coke compressed by the weight of overlying layers, lower portion of Quaternary deposits and uppermost seams of carbonate bedrock. The conductivity of the 2nd layer is 10^{-6} to 10^{-5} m/day in the area of semi-coke landfills and their vicinity. In the remained area the conductivity changes from 0.005 to 0,1 m/day. The boundary conditions of the 2nd layer are the same as in the 1st layer. The 2nd layer is considered as confined-unconfined at modelling.

The 3rd layer enfolds the Kukruse Stage and upper seams of the Uhaku Stage. In the southern part of the model area the oil-shale commercial bed has been excavated. The former opencast pits and mines have been abandoned and partially or completely filled with water at present. Accordingly to an oral information get from Dr. V. Petersell, an underground cracking of oil shale was carried out in the southwest portion of the 3rd layer in the Soviet era. This experiment failed and the bedrock layers were heavily polluted by oils and phenols. To prevent the underground spreading of this pollution the water table is kept at the absolute elevation of 40 m by a ditch system in southwest corner of the 3rd layer. This situation as well the general distribution of groundwater head in carbonate bedrock was taken into account at assigning the boundary conditions of 3rd layer. Because of mine draining described the 3rd layer is considered as unconfined-confined at modelling. The conductivity of the layer ranges from 0.1 to 8 m/day.

The 4th layer represents the lower portion of the confined Ordovician aquifer system. The Constant Head conditions have been given along layer boundaries. The conductivity is 4 m/day.

The 5th layer conforms to the Ordovician regional aquitard which conductivity is 10^{-5} m/day in the study area. Because of such low conductivity and small value of the lateral head gradient (0.001 in average) the flows across the borders of the 5th layer are insignificant and they can be neglected at modelling. Therefore, the boundary conditions were not specified for the layer border and, consequently, the latter is considered as a no flow boundary by Visual MODFLOW (Neumann's type of boundary conditions: lateral flux across the layer border is zero). The groundwater head can be calculated for the 5th layer by modelling.

The 6th layer enfolds the Ordovician-Cambrian aquifer system. Its conductivity is 2.5 m/day. In the study area this aquifer system is exploited by 10 boreholed wells with a total extraction rate reaching 80 m^3/day. The head depressions caused by groundwater pumping do not exceed 1 m. The main source of the public water supply for the study area is the underlying Cambrian-Vendian aquifer system.

12.3.1 Groundwater flow

Modeling results at the Kiviõli site show that local precipitation recharges the groundwater approximately 1,500 m^3/day. The topmost elevations of the groundwater table, reaching 55m a.s.l., are situated in southern portions of all three semi-coke landfills (Fig. 12.3.3-4). Thus, the thickness of the unsaturated zone is 70-80 m in the central part of both larger landfills. Inside the small landfill to the south, the thickness of the unsaturated zone does not exceed 10 m. In the 1st model layer, the water moves generally towards the Uuemõisa and Koljala Creeks. However, only 600 m^3/day of this water reaches the creeks. About 700 m^3/day of the water, formed by infiltration, flows downward through the 2nd model layer into the 3rd layer which represents the carbonate bedrock comprising the oil-shale commercial bed (Fig. 12.3.5). Due to an intensive draining by a ditch network, the 3rd layer is in confined-unconfined conditions. Therefore, the 1st model layer is dried up in the southern part of the study area.

Groundwater particle tracking carried out as a part of the flow modeling shows that the fluxes formed in the southern portion of the western semi-coke landfill move northward at a distance from 250 to 750 m. The flow velocity is 8-12 m/year. After the northward movement, these flows bend downward and intrude into the 3rd model layer. Due to the general trend of the water movement in the 3rd layer, the downward flows coming from the 1st layer change their course sharply and start to move in a southeast direction toward the abandoned oil-shale mine. The flow velocity here has increased to 20-40 m/year in the 3rd layer.

The water forming in the eastern big semi-coke landfill flows radially. Some of this flow diverts sharply from their previous course, too. As described above, they bend downward and move together with other flows in the 3rd layer toward the abandoned mine. A portion of water flows out from the landfill toward the right branch of the Koljala Creek. The flow velocity is up to 50 m/year in this case.

The heavily drained 3rd model layer (Fig. 12.3.5) gains water from the 1st layer through the 2nd layer and from the underlying 4th model layer (the lower portion of the Ordovician aquifer system). The amount of the total inflow from above is 700 m^3/day and from below 7,300 m3/day. The outflow into the draining network is about 7,700 m^3/day. 500 m^3/day flows downward into the 4th model layer (the Silurian-Ordovician regional aquitard). The water moves mainly to the southeast at 20-40 m/year in the 3rd layer.

The 4th model layer is recharged mainly through its lateral boundaries. The lateral inflow coming mostly from the west and southwest is about 7,100 m^3/day. From the overlying 3rd layer comes 500 m^3/day. The main outflow, about 7,300 m^3/day, goes upward into the intensively drained 3rd layer.

The 6th model layer (the Ordovician-Cambrian aquifer system) chiefly gains water through its lateral boundaries. The downward flux from the overlying 5th model layer is only about 20 m^3/day. The water moves in the northeast direction.

12.4 Kohtla-Järve model

Model area. The co-ordinates of the rectangular model area are: lower left corner: X = 5511500, Y = 6584000; upper right corner: X = 5515500, Y = 6588500. The area is 4,000 m from west to east and 4,500 m from north to south. Before the start of industrial operations the topography of the area was flat with absolute elevations between 47 to 67 m. The oil shale ash and semi-coke have been piled in the central part of the model area (Fig. 12.4.1). The absolute top elevation of this landfill reached 176 m in 2003. A natural groundwater divide is situated on the east border of the study area. The ash and semi-coke landfill is drained by a surrounding network of ditches. The water collected by the ditches mostly flows into Kohtla Creek, which is a branch of Purtse River. In the period of floods, the excessive ditch water is pumped via a pipeline into a branch of Pühajõgi River in the northeast portion of the study area.

Model layers and boundary conditions. The model consists of 5 layers (Fig. 12.4.2-3). The Constant Head boundary conditions have been assigned to outer borders of the 1st, 2nd, 3rd, and 5th layer.

The 1st layer enfolds the ash and semi-coke landfills. Their hydraulic conductivity is 0.1 m/day. The outside of the landfill borders on the Quaternary deposits consisting predominantly of till. The uppermost seams of the carbonate bedrock have been included in the layer. The average hydraulic conductivity of this layer portion is 5 m/day. The 1st layer is unconfined. The net infiltration given on the 1st layer top is 60 mm/year.

The 2nd layer represents the lower seams of ash and semi-coke piles. Their transversal conductivity is 10^{-6} m/day. Outside the ash landfill, the upper seams of the carbonate bedrock belong to this layer. Their average conductivity is 5 m/day. The 2nd layer creates a resistance partially impeding the downward flux from overlying ash and semi-coke. The layer type is confined-unconfined.

The 3rd layer consists of diverse fissured and karsted limestones with clayey interbeds from the Uhaku Stage to the Kunda Stage, which belong to the Ordovician aquifer system. Their conductivity is 4 m/day. The layer is confined.

The 4th layer enfolds the Ordovician regional aquitard. Its transversal conductivity is 10^{-5} m/day. The boundary conditions have not been specified along outer borders of the layer.

The 5th layer represents the Ordovician-Cambrian aquifer system with lateral conductivity of 3 m/day. This confined aquifer system is used for the public water supply in the Kohtla-Järve region.

12.4.1 Groundwater flow

The total infiltration from precipitation at the Kohtla-Järve site is about 2,800 m^3/day. The direct infiltration into the ash landfill is about 300 m^3/day. The topmost elevation of the groundwater table reaches about 69 m in the central part of the ash landfill (Fig. 12.4.1). In the ash, the thickness of the unsaturated zone amounts to 110 m (Fig. 12.4.2-3). The water in the ash landfill flows in radially. However, the flows moving 100-200 m eastward at first bend downward and intrude through the 2nd layer into the 3rd model layer (the Ordovician aquifer system). There they change their course abruptly and start to move westward. From the water formed in ash or semi-coke, about 150 m^3/day is drained by a network of ditches in close vicinity to the landfill. Almost the same amount of water flows laterally from ash or semi-coke into a portion of the 1st layer surrounding the landfill. These flows pass under the ditch and stream network. In ash, the water flow velocity is generally less than in Kiviõli – about 3-4 m/year. The flow from stored ash and semi-coke directly downward into the 3rd model layer is quite small, averaging 12 m^3/day.

The 3rd model layer (the Ordovician aquifer system) is recharged mainly by the downward total flow, which comes from the overlying 2nd layer (Fig. 12.4.4). The amount of this flow is about 6,400 m^3/day. The inflow through the lateral boundaries gives 2,300 m^3/day. The water stored moves mainly westward; the heads decrease from 53-62 m on eastern border of the study area to 45 m on the western border. The velocity of these lateral fluxes is remarkable – up to 50-90 m/year. Due to the impact of the drainage network, a portion of water rises up from the 3rd layer and is drained between the ash landfill and western border of the study area. The amount of this flow is 3,500 m^3/day. The downward flow from the 3rd layer into the 4th layer (the Ordovician regional aquitard) reaches 200 m^3/day.

The 5th model layer (the Ordovician-Cambrian aquifer system) is recharged mainly by downward flow coming from the overlying regional aquitard. This flow amounts to 200 m^3/day. The inflow through the lateral borders is 100 m^3/day. All the water stored flows out through western and southern lateral borders of the layer. The heads decrease from 44 m in the northeast corner of the study area to 40-42 m on its western and southern borders. The velocity of the groundwater flow is 2-4 m/year in the Ordovician-Cambrian aquifer system.

12.5 Narva model

The Model area. The coordinates of the quadratic model area are: lower left corner: X = 5558000, Y = 6578000; upper right corner: X = 5565000, Y = 6585000. The side length of the model area is 7,000 m. The natural ground surface is flat with absolute elevations between 25 to 32 m. The main drainage base for surface water and shallow groundwater is Narva Reservoir bounding the study area from the southeast (Fig. 12.5.1). In the central part of the model area, the oil shale ash stored forms two rectangular plateaus. Their sizes are about 1.7 x 2.2 km and the absolute elevations of the top surface reach from 30 m up to 64 m. On the top surface of the plateaus, a number of large ponds occur which have been formed by water used for transporting ash. The ash plateaus are drained by surrounding channels. Two sedimentation basins with sizes of 0.6 x 1.7 km bound the ash plateaus from the south. The water is recirciled for hydraulic transport of the waste. When the amount of water inside the ponds and channels is too high, this water is discharged into the Narva River system, after treatment.

The Model layers and boundary conditions. The Narva model consists of 4 layers (Fig. 12.5.2-4).

Inside the borders of the ash plateaus, the 1st layer enfolds a bed complex consisting of ash and underlying Quaternary deposits. The conductivity of this complex changes from 0.01 to 0.05 m/day. Outside of the ash plateaus, the 1st layer belongs to the Quaternary deposits, which consist predominantly of peat, glaciolacustrine sand, sandy loam (varved clay), and underlying till. The total thickness of these seams reaches 10-20 m in places. The prevailing conductivity value of sandy deposits does not exceed 1.5 m/day. However, the transversal conductivity of clayey Quaternary deposits is mostly less than 0.01 m/day and, therefore, they form a confining bed for the underlying 2nd model layer. The River boundary condition has been assigned to the southeast portion of the layer border conforming to Narva Reservoir. The Constant Head conditions have been given to the remained border portion of the 1st layer. In the areas of ash plateaus, the Constant Head boundary conditions have been assigned to the ponds mentioned above. The net infiltration changes from 20 to 300 mm/year in the 1st unconfined model layer.

The 2nd layer represents the confined Ordovician aquifer system (Fig. 12.5.5). The average lateral conductivity of the carbonate bedrock is 3 m/day in the study area, The Constant Head boundary conditions have been established along layer borders.

The 3rd layer includes the Silurian-Ordovician regional aquitard. Its transversal conductivity is 10^{-5} m/day. The boundary conditions have not been specified along outer borders of the layer.

The 4th layer enfolds the Ordovician-Cambrian aquifer system which lateral conductivity is 3 m/day. The Constant Head boundary conditions have been assigned to the layer outer borders. The groundwater moves in the southeast direction – toward a head depression centre in Slancy, Russian Federation.

12.5.1 Groundwater flow

The total infiltration from precipitation is at the Narva site about 5,100 m^3/day. The inflow through the lateral borders of the 1st layer and the river leakage reaches only 1,600 m^3/day. The rising inflow from the 2nd model layer exceeds 22,000 m^3/day. Such comparatively significant rising flow is caused by the locality of the study area on the shore of Narva Reservoir, which has a large draining capability. Here the deep groundwater flows bend upward to be drained in the channel network and large surface water bodies. In the ash storage, the water is formed mainly by the inflow from ponds which are situated on the top surface of the plateau (Fig. 12.5.1). An additional recharge is taking place at the cost of direct infiltration from precipitation. The total inflow into the ash plateaus is about 13,700 m^3/day. At that, the infiltration from precipitation gives 400 m^3/day. Elevation of the groundwater table changes from 58-48 m in the eastern plateau to 30-28 m in the western plateau. A portion of stored water flows from ash directly into the channels and ponds surrounding the plateaus. This outflow from the plateaus amounts to 1,800 m^3/day. Another portion of the outflow from the plateaus which passes under the channels and ponds and intrudes into the remaining portion of the 1st layer is 2,700 m^3/day. According to the results of groundwater particle tracking, the velocity of the lateral outflow changes from 2-5 m/year to 25-40 m/year (Fig. 12.5.2-4). The downward outflow from ash into the underlying 2nd model layer (the Ordovician aquifer system) reaches 9,200 m^3/day.

The portion of the 1st model layer laying outside the ash plateaus used for recirculation and discharge into the Narva River system.by the man-made network of channels and ponds surrounding the ash plateau. This outflow reaches 27,000 m^3/day. The outflow into the underlying 2nd layer is about 4,000 m^3/day. The total downward flow from the 1st layer (including the ash plateaus) into the 2nd layer, amounts to 13,200 m^3/day. The velocity of downward flows change from 0.1 to 1.0-1.5 m/years.

The 2nd model layer representing the aquifer system of the Ordovician carbonate bedrock is recharged by the downward flow which comes from the overlying 1st model layer and reaches 13,200 m^3/day (Fig. 12.5.5). About 70 % of this inflow originates from the eastern ash plateau. About 11,400 m^3/day of groundwater flows into the 2nd layer, mainly through its western lateral border. The total inflow into the 2nd model layer is 24,600 m^3/day. Due to the intensive inflow from the eastern ash plateau beneath the latter an area of increased groundwater heads has been formed in the 2nd layer. There the heads ranges from 31 to 57 m. Under the western ash plateau the heads are between 26-29 m. In the 2nd layer beneath the ash plateaus, groundwater moves laterally in radial directions at velocities from 4 to 40 m/year. The amount of this flow is 8,100 m^3/day.

The main outflow from the 2nd layer reaches 22,000 m^3/day and tends upward into the 1st model layer in the area of the sedimentation ponds (Roheline järv) and Narva Reservoir to the south and southeast of the ash plateaus. The downward flow in the 3rd model layer (the Ordovician regional aquitard) is comparatively small – not more than 200 m^3/day. The total outflow from the 2nd model layer, including the flow through lateral borders, is about 24,600 m^3/day.

The duration of moving of a groundwater particle from the sedimentation ponds on the surface of ash plateaus to the draining network surrounding the plateaus ranges from 20 to 150 years. The shorter moving times occur when the particle penetrates the upper ash seams, only. If the particle must penetrate the ash, underlying Quaternary deposits, and carbonate bedrock of the 2nd model layer, then the moving time will be remarkable longer. It is necessary to point out that in reality, the moving times of groundwater particles can be still longer because of dispersion phenomena at infiltration.

In the 3rd model layer enfolding the Ordovician regional aquitard, a downward flow prevails. It comes from the overlying Ordovician aquifer system and goes into the underlying 4th layer (the Ordovician-Cambrian aquifer system). Due to the very low transversal conductivity of the regional aquitard, the downward flow is about 200 m^3/day, only. The time needed for a water particle to penetrate the regional aquitard in transversal direction ranges from 70 to 100 years. The flow velocity is 0.04-0.06 m/year. Consequently, the polluted water of ash plateaus has not yet reached the Ordovician-Cambrian aquifer system.

The downward flow is the main recharge source for the Ordovician-Cambrian aquifer system. No more than 100 m^3/day of groundwater.flows through its western lateral border. In the Ordovician-Cambrian system,, the water moves mainly in southeast direction – towards the mighty intake of Slancy, Russian Federation. The lateral outflow through the eastern and southern borders of the 4th model layer amounts to 300 m^3/day. The heads decrease from 27-28 m in the northwest corner of the study area to 25 m in the southeast corner.

13 CONTAMINANT TRANSPORT MODELLING

The modelling of contaminant transport was performed using the mass transport model MT3D, a computer model for simulation of advection, dispersion and chemical reactions of contaminants in groundwater flow systems in three dimensions. The model uses a mixed Eulerian-Lagrangian approach to the solution of the advective-dispersive.reactive equation, based on a combination of the method of characteristics (MOC). The advective-dispersive-reaction equation describes the transport of miscible contaminants in groundwater flow systems.

The chemical reactions used in the MT3D transport model were equilibrium-controlled linear sorption and first-order irreversible decay. Sorption refers to the mass transfer process between the contaminants dissolved in groundwater (solution phase, K_{mob}) and the contaminants sorbed on the porous medium (solid phase, K_{sorb}). It is generally assumed that equilibrium conditions exist between the solution-phase and solid-phase concentrations and that the sorption reaction is fast enough relative to groundwater velocity so that it can be treated as instantaneous. The functional relationship between the dissolved and sorbed concentrations is called the sorption isotherm. The linear sorption isotherm assumes that the sorbed concentration ($\hat{C}$) is directly proportional to the dissolved concentration (C):

$$\hat{C} = K_d * C$$

where

K_d = the distribution coefficient, L^3M^{-1}.

The retardation factor is defined as

$$R = 1 + (\rho_b / \theta)\, K_d$$

where

ρ_b = the bulk density of the porous medium, ML^{-3}
θ = the porosity of the porous medium, dimensionless

The retardation factor is used to calculate the `retarded' flow velocity ($V_{R(i)}$of each chemical species according to the following formula:

$$V_{R(i)} = \tilde{V}_{.}\ R_i$$

where

$V_{R(i)}$ = Retarded Flow Velocity of Species i (in units of L/T)
V = Average Linear Groundwater Flow Velocity (in units of L/T)
R_i = Retardation Coefficient of Species i (unitless)

The retarded flow velocity is used to calculate the advective transport of each species.

The biodegradation is described using the equation:

$$c_t = c_0 \cdot e^{-\tau\, t_{1/2}}$$

where

c_t = concentration at time t
c_0 = the original concentration
$t_{1/2}$= the time required for the concentration to decrease to one-half of the original value
$\tau = \ln 2 / t_{1/2}$

The species parameters used for the MT3D transport model are listed in the table below:

Species	Concentration (mg/l)	$t_{1/2}$	R	K_d (1/mg/L)	K_mob (1/day)	K_sorb (1/day)
napthalene	1	258	13	3.1	0.003	0
BTEX	18	300	6	1.26	0.002	0
phenol	125	7	2	0.25	0.099	0

The Kiviõli and Kohtla-Järve areas were chosen for transport modeling of organic compounds.

13.1 Results from transport modeling

13.1.1 Kiviõli

The transport modelling was performed by placing a constant concentration of phenol in each of two landfills, one to the west and one to the east. A steady-state simulation was then run for a 100-year period with output times of 10, 50 and 100 years.

The results show that the pollution follows the local groundwater flow from each landfill. The horizontal extent of the spreading is different for each landfill, as shown in Fig. 13.1.1.1. From the landfill in the west the phenol pollution spreads towards the northwest. On the east landfill, the phenol pollution spreads in the surface layer to the northeast domain limits, covering a larger area.

The downward spreading of the pollution is restricted by the semi-pervious layer 2 as shown in the west-east transect through both landfills in Fig. 13.1.1.2. Similarly, north-south profiles through the west and east landfills in Figs. 13.1.1.3 and 13.1.1.4 respectively, show the limited downward penetration of the phenol pollution.

13.1.2 Kohtla-Järve

The transport modelling was performed by placing a constant concentration of phenol in the ash and semi-coke landfill. A steady-state simulation was then run for a 100-year period with output times of 10, 50 and 100 years.

The results show that the pollution follows the local groundwater flow from the landfill. The spreading of the pollution is towards the north and northwest model domain, as shown in Fig. 13.1.2.1.

The vertical spreading of the pollution extends down to layer three as shown in the west-east profile through both landfills in Fig. 13.1.2.2. Similarly, a north-south profile through the landfill in figure Fig. 13.1.2.3., shows the downward penetration of the phenol plume into layer 3.

14 ECOTOXICOLOGICAL INVESTIGATION

14.1 Materials and methods in ecotoxicological testing

14.1.1 Description of samples

The solid phase samples originated from Kiviõli (KV), Kohtla-Järve (KJ) and Narva (N) investigation areas, altogether 4 oil-shale semi-cokes of different age: KJ-F, KV-F, KV-M & KV-O and 3 oil-shale combustion ashes: N-AF, N-AC, KJ-A were sampled in autumn 2002. The samples were not pre-dried (dry weight percentage was from 58 to 74). Before toxicity testing samples were sieved (d=2 mm) and extracted with water as described below and leachates (eluates) were studied for the toxicity. The data of chemical analysis of the waste eluates apply for the leachates prepared separately (by L. Bityukova in Norway) from the same semi-cokes and ashes and using essentially the same method. The samples are described in Table 14.1.

Aquatic samples (groundwater, channel water, waste pore water; altogether 20 samples) originated from Kohtla-Järve (12 samples), Kiviõli (7 samples) and Kukruse (1 sample) investigation areas and were sampled from May till September 2003. The samples are described in Table 14.1.

Leachates (eluates) from the solid waste samples for the toxicity testing were made in OÜ EcoLabor (Tallinn, Estonia) according to DIN 38414-SH. The ratio of 1 part of dwt + 10 parts of distilled water was used for the extraction. Extraction was performed in glass bottles on a shaker for 24 h at room temperature. After shaking slurries were settled and supernatant was filtered through paper. The leachates (eluates) for the chemical analysis of the solid waste samples were prepared in Norway by L. Bityukova using essentially the same method. The extracts for the toxicity testing were stored at +4°C till analysis.

14.1.3 Preparation of suspensions and extracts from the solid phase samples for the flash assay

1,5 g of solid sample was added to 15 ml of water (purified by MilliQ equipment) and shaken on the rotary shaker for 24 h (200 rpm in the dark, 25°C). After that 300 mg of NaCl was added to each suspension to adjust the salinity of the sample to 2%.

14.1.4 Toxicity assays

The different tests are characterized in Table 14.2.

Photobacterial tests

In the Microtox test the *Vibrio fischeri* NRRL-B 11177 strain was used. A commercial *Vibrio fisheri* 3902 Reagent was used (Aboatox, Turku, Finland). The freeze-dried reagent was reconstituted with 12.5 ml of 2% NaCl, incubated at 4°C for 20 minutes and used for testing. The inhibition of luminescence of photobacteria during 15-minutes incubation time was used as toxicity endpoint. The testing was performed at 15°C, essentially as described earlier (Kahru, 1993). 2% NaCl solution served as sample diluent and a control. The measurements were made on 1253 Luminometer (ThermoLabsystems, Helsinki, Finland) connected to a personal computer (PC), and calculation of INH% and EC50 values was performed by means of standard software (ThermoLabsystems, Helsinki, Finland). As the test diluent (2% NaCl) is not buffered (i.e. the original pH of the samples will contribute to the net toxicity of the sample), all (alkaline) samples were also studied after adjustment of pH to neutral, in order to determine to what extent is the toxicity of the original sample caused by unfavorable pH.

The Solid-Phase Flash-Assay of suspensions and respective extracts was performed at ambient temperature using 1251 Luminometer (ThermoLabsystems; Finland) connected to PC and operated by Multiuse software (ThermoLabsystems) as described in Lappalainen et al. (1999) and Põllumaa et al. (2000). The inhibition of luminescence of photobacteria during 30-seconds of incubation time was used as toxicity endpoint. 2% NaCl solution was used as a sample diluent. The results were calculated online: the peak height from 0 to 5 seconds (P) and signal at 30 seconds (S) were measured, and the 30-second INH% was calculated as 100*[1-(S/P)]. The pH of the samples was not adjusted before the toxicity testing.

ToxScreen Assay

ToxScreen™ test (CheckLight Ltd., Qiryat-Tivo'n, Israel) is a novel semi-specific assay for the aquatic toxicity screening. The assay uses naturally luminescent marine bacterium *Photobacterium leiognathi* and could be performed in two sensitizing buffers: one (pro-organic buffer) favors the detection of organic toxicants and the other (Pro-Metal buffer) cationic heavy metals (Ulitzur et al., 2002). We used only pro-organic buffer. All alkaline samples were analyzed after adjustment of pH to neutral. The reagents were reconstituted and samples handled as described in Ulitzur et al. (2002). The inhibition of the photobacteria during 30 min of incubation was used as a toxicity endpoint. Measurements were performed in two parallels at ambient temperature (20-25°C) using ThermoLabsystems 1251 luminometer. Data reduction was performed using the Multiuse software

Toxkit microbiotests

The toxicity testing was performed according to the standard operational procedures (SOP) of the Toxkits. As the respective SOPs do not include the adjustment of pH of the samples to neutral, the pH was not adjusted. Test plates with *Daphnia magna* neonates (Daphtoxkit F™ magna) were incubated for 48 hours at 20°C in the dark, and the immobilization of the organisms after exposure to the toxicants was used as the toxicity endpoint. Daphnia test followed OECD 202 standard procedure. Test samples and controls (sample diluent included in the test kit) were analyzed in four replicates (à 4*5 test organisms).

Test plates with *Thamnocephalus platyurus* larvae (Thamnotoxkit F™) were incubated at 25°C for 24 hours in the dark, and their mortality was used as the toxicity endpoint. Test samples and controls (sample diluent included in the test kit) were analyzed in triplicate (à 3*8 test organisms).

The test cuvettes with the protozoan *Tetrahymena thermophila* (Protoxkit F™) were incubated at 30°C for 24 hours in the dark, and their growth inhibition (reflected by the reduction of food) was used as a toxicity endpoint by measuring the turbidity of the incubation medium at 440 nm. Test and control samples (bidistilled water) were analyzed in duplicate.

The procedure for the 72 h algal growth inhibition tests was slightly modified compared to SOP for Algaltoxkit F™. Namely, the algal cells were de-immobilized from algal beads (see SOP for AlgaltoxKit F) and pre-grown in a sterile growth medium included in the test kit (25-27°C, 6000-8000 lux) for 3-4 days and then used as an inoculum for the toxicity testing. 20 ml glass test vials with 5 ml of test volume were continuously shaken (100 rpm) and illuminated from below during 72h of exposure time. Test samples were analyzed in triplicate and the control samples in 8 parallels. Analogously to Algaltoxkit F™ SOP, our testing followed OECD 201 standard procedure. In addition to optical density measurements (OD670; used for the quantification of algal biomass), ethanol-extracted chlorophyll fluorescence was measured. For the extraction of chlorophyll 200 µl ethanol was added to 50 µl of algal suspensions in 96-well microplates. After addition of ethanol the plates were shaken for 3 hours in the dark and the fluorescence was measured (excitation 440 nm, emission 670 nm, Fluoroscan Ascent, ThermoLabsystems, Finland). Algal growth medium (mineral salt medium buffered to pH=8) was used as sample diluent and control.

14.1.5 Quantification of the toxicity, toxic units (TU)

The toxicity of the leachates and water samples was measured as EC50 or LC50 (%), i.e. concentration of the sample (%) that either kills 50% of the test organisms (in this case it is called half-lethal concentration, LC50) of reduces the growth rate or bioluminescence etc of test organisms (in this case it is called half-effect concentration, EC50). For the analysis of toxicity, samples (leachates or wastewaters) were exponentially diluted (2-fold, 4-fold, 8-fold etc.) and each dilution analyzed for the effect. The L(E)C50 values were calculated from the concentration-effect curves using the respective software (see above).

The L(E)C50 values were converted to TU values as follows:

$$TU=100\%/L(E)C50$$

Accordingly to arbitrary scale proposed by Persoone et al. (1993) the samples were classified by average or maximum TU obtained by battery. In our case we used data of 4 tests: Crustaceans (*Thamnocephalus*), algae (*Selenastrum*), protozoa (*Tetrahymena*) and Microtox test (*Vibrio fischeri* performed on neutralized samples) (Table 14.3)

In according to the value of maximum / average TU the samples were classified as follows:

Maximum TU obtained by the battery	Classification	
<1 TU	**not toxic**	☺
≥1 – 10 TU	**toxic**	☠
≥10 – 100 TU	**very toxic**	☠☠
≥100 TU	**extremely toxic**	☠☠☠

14.1.6 Microbiological assays

Within 1-3 days after arriving in the laboratory the water samples were streaked on microbiological agar plates (Petri dishes). Two media were used: LB medium (a rich medium) for evaluation of total heterotrophic bacteria and on mineral medium M9 containing 2.5 mM phenol, for evaluation of phenol-degrading bacteria. LB plates with bacteria were incubated at room temperature for 2 days and M9 plates about 1 week at room temperature before evaluation of growth. In Tables the growth is evaluated as follows:

-	No growth
+	Detectable growth but very small colonies
++	Clearly detectable growth
+++	Good growth
++++	Very good growth

Agarized LB medium contained (per 1 L) Bacto-tryptone 10 g, Bacto Yeast Ectract 5 g, NaCl 5 g and 15 g of agar. Agarized M9 medium contained (g/L): NaCl - 0.5; Na_2HPO_4 - 6.0; KH_2PO_4 - 3.0; NH_4Cl - 1.0; $MgSO_4*7H_2O$ - 0.49; $CaCl_2*2H_2O$ - 0.015. To M9 medium following microelements were added (mg/L in the final medium): $FeSO_4*7H_2O$ - 5; $CaCl_2*2H_2O$ - 5; $MnSO_4*5H_2O$ - 2; $CoCl_2*6H_2O$ - 0.5; $ZnSO_4*7H_2O$ - 2; $CuCl_2*5H_2O$ - 0.5; $Na_2MoO_4*2H_2O$ - 0.5. Phenol (2.5 mM in the final medium) was not sterilized and was added to the sterile medium from the concentrated stock (50 mM). 1.5% agar (in the final medium) was used.

14.2 The ecotoxicological hazard evaluation

The toxicity of the aqueous samples or aqueous leachates (eluates) of the solid waste samples was analyzed using a battery of 5 ecotoxicological tests with organisms representing different trophic levels (crustaceans, protozoa, algae and bacteria) and the particle-bound toxicity was analyzed using the Solid-Phase Flash-Assay. The water leachates of solid phase samples (semi-cokes and ashes) were investigated in parallel with two different crustaceans (*Daphnia magna* and *Thamnocephalus platyurus*) and as the toxicities were found to be similar (data not shown), only *Thamnocephalus* was used for studying toxicity on water samples as this test needs less sample amount. The results of novel ToxScreen Assay are provided and can be used as early warning signal of toxicity, but in the current study ToxScreen data were not used for scoring of the final toxicity (i.e., were not included into the decision making set of tests of the ecotoxicological battery) as ToxScreen tests operates with sensitized testing system. Table 14.3 characterizes ecotoxicological hazard of aqueous leachates (eluates) of 7 solid-phase samples: 4 oil-shale semi-cokes of different age: KJ-F, KV-F, KV-M & KV-O and 3 oil-shale combustion ashes: N-AF, N-AC, KJ-A originating from Kohtla-Järve, Kiviõli and Narva investigation areas and 20 water samples: 2 channel waters KJ-CH1 and KJ-CH2; 4 waste pore waters RA-KJ-5, RA-KJ-6, KV 7 and KV8; 13 groundwaters KJ1-KJ6, KJ9-KJ10, KV1-2, KV5-6 and Ku2 originating from Kohtla-Järve, Kiviõli and Kukruse investigation areas. The toxicities of individual ecotoxicological tests were expressed in toxic units (TU) and final toxicity of the sample was evaluated by using data of 4 ecotoxicological tests of different trophic levels (crustaceans *Thamnocephalus platyurus*, algae *Selenastrum capricornutum*, protozoa *Tetrahymena thermophila* and bacteria *Vibrio fischeri*) whereas two different scoring methods were used: 1) the average toxicity (Avg Tox) and 2) the maximum (highest) toxicity (MaxTox), i.e. the toxicity to the most sensitive species in the battery.

Solid wastes of oil shale combustion ashes and semi-cokes were designated as soils and in their chemical evaluation used Estonian permitted limit values (PLV) for industrial area soils (Environmental Ministry of Estonia, 1999; Tables 14.4, 14.5 and 14.6.). The leachates (eluates) of solid wastes studied were designated as surface waters and the chemical evaluation used Estonian permitted limit values (PLV) for surface- and groundwaters (Environmental Ministry of Estonia, 1999; Tables 14.4, 14.5 and 14.6.).

One of possible causes for toxicity of oil shale wastes and surface and groundwaters of the area could be the phenolic compounds. In our previous studies we showed the toxicity of eight main phenolic compounds to photobacteria, crustaceans, algae and protozoa (Kahru et al, 2000) and relying on these data (Table 14.7), concentration of phenolic compounds in the samples of the current study and their toxicity and assuming the additive toxicity of individual phenolic compounds, we calculated the theoretical impact (i.e. how many % of the total toxicity could be due to the phenolic compounds) of phenolic compounds on the net toxicity of the samples (Table 14.7.)

According to both (AvgTox and MaxTox) evaluation approaches 3 *extremely toxic* samples were found from Kohtla-Järve investigation area: 2 waste pore waters RA-KJ-5, RA-KJ-6 and channel water KJ-CH2 (Table 14.8). All these samples were very alkaline (pH >13!) but the toxicity was not caused by the high alkalinity as the neutralization did not change the toxicity in the Microtox test (Table 14.3). NB! The Microtox test was preformed on not neutralized (original pH) samples and neutralized samples in parallel, as according to the DIN 38 421/34 this test requires the prior neutralization of the samples but according to Environmental Canada (1999) the samples have to be tested without adjusting the pH (i.e. the whole toxicity package should be analyzed).

According to MaxTox index 8 samples were classified as *very toxic*, 12 as *toxic* and 4 as *not toxic* and by AvgTox index 6 as *very toxic*, 7 as *toxic* and 11 as *not toxic* (Table 14.8). According to both ecotoxicological evaluations (Avg Tox and MaxTox) the not toxic samples were found among groundwater samples: all 4 not toxic samples (MaxTox) were groundwater samples and 10 out of 11 not toxic samples (AvgTox) were groundwater samples. In addition to groundwater samples the old (aged) semi-coke waste leachate from Kiviõli (KV-O) proved not toxic by AvgTox index (Table 14.3).

The particle-bound toxicity of semi-cokes and ashes (altogether 7 samples) was analyzed using the Solid-Phase Flash-Assay. All solid waste samples analyzed except one ("old" semi-coke from Kiviõli study area) were toxic, partly due to the high alkalinity (data not shown).

14.2.1 The ecotoxicological hazard in Narva investigation area

Two solid-phase samples were studied for ecotoxicity: filter and collector ashes from Narva power plant (N-AF and N-AC). Both samples were classified as *very toxic* by both ecotoxicological indices (Tables 14.3 and 14.4). The alkalinity (pH=12.9, high concentration of mineral salts characterized by conductivity >10000 µS/cm, 1834 and 1705 ppm Ca in N-AF and N-AC leachate, respectively) are realistic contributors to the toxicity of these samples. The impact of alkalinity to the toxicity of these eluates was proven by the fact that toxicity was reduced for 120-160 times (from 234-253 TU till 1.6-1.9 TU; Table 14.3 & 14.4) after neutralization of the samples in Microtox test. As the organic compounds shoud be fully burned in the combustion process (organic carbon content of the samples was 0.02%), these samples were not studied for organic compounds like phenols, PAHs and BTEX. The concentration of heavy metals in these two ash samples did not exceed the permitted limit values (PLV) for residential area soils (Environmental Ministry of Estonia, 1999). However, in the aqueous eluate of N-AF the PLV for the groundwater (Environmental Ministry of Estonia, 1999) was exeeded 1.9 times for Cr and 3 times for Hg, in N-AC leachate the PLV value for Hg was exceeded by 2.7 times (Table 14.4). The water-extracted heavy metals could partly explain the toxicity of waste eluates to algae and crustaceans.

14.2.2 The ecotoxicological hazard in Kohtla-Järve investigation area

Two solid-phase samples: fresh semi-coke KJ-F and combustion ash KJ-A; two surface water samples KJ-CH1 and KJ-CH2 from channels surrounding the ash-landfills (designated as channel waters); two waste porewater samples RA-KJ-5 and RA-KJ-6; and eight groundwater samples KJ-600, 601, 602, 608, 610, 622, RA-KJ-2 and RA-KJ-3; altogether 14 samples were studied for ecotoxicity from Kohtla-Järve investigation area (Table 14.3 and 14.5).

Both ecotoxicological indices classified 3 samples as *extremely toxic* – two waste pore waters (RA-KJ-5, RA-KJ-6) and one channel water (KJ-CH2). The high alkalinity (pH>13) was not the reason for the toxicity of these samples as the toxicity reduction was not found after neutralization of these samples in Microtox test. Also, it was shown that theoretically phenols (87-96 ppm) could explain only 8…11% of the net toxicity of these samples. Although the PAH levels in these samples exceeded PLV for groundwater for 2...63 times and BTEX values exceeded the values for groundwater for 12…195 times (Table 14.5) they could still not be at these concentrations reasons for the toxicity of samples towards Microtox tests bacterium. Namely, the EC50 value in Microtox test for benzene is 531 ppm, toluene 33 ppm and xylene 97 ppm (Kahru, 1993; Table 14.7) whereas the highest BTEX value was 19 ppm (RA-KJ-5). The Microtox EC50 values for more water-soluble PAHs range from 1.9 ppm (naphthalene) till 0.48 ppm (phenanthrene) (Loibner et al., 2004; Table 14.7) but the highest concentrations in the most polluted sample RA-KJ-5 were 0.5 ppm of naphthalene and 0.01 ppm for phenanthrene (Table 9.3.3.2 or 9.3.3.3).

Also, microbiological studies showed practically no growth of bacteria (Table 14.5), most probably due to the high toxicity of these samples.

Altogether three samples: two groundwaters KJ-600 and KJ-622 and one channel water KJ-CH1 were classified as *very toxic* according to MaxTox index, but AvgTox index classified KJ-CH1 to *toxic* class. The reason for toxicity of KJ-CH1 is probably high alkalinity (pH=13.2, conductivity 11240 μS/cm as after neutralization of the samples the toxicity to Microtox decreased 174 times (till 0.9 TU). It was calculated that 18% of toxicity could be explained by phenols. Also, the sample KJ-CH1 was microbiologically sterile, i.e. growth of bacteria was not detected. Groundwater sample KJ-600 was neutral and in KJ-622 the slight alkalinity (pH=9.3) was not the reason for the toxicity, but the calculations showed that phenols (16.9 and 13.8 ppm, respectively) may explain respectively 37 and 11% of total toxicity. For total PAHs PLV values for groundwater were not exceeded and were only slightly exceeded for total BTEX (1.3 till 1.7-fold, Table 14.5).

Altogether six samples: four groundwaters (KJ-601, KJ-602, KJ-610, RA-KJ-2) and two aqueous leachates (eluates) of solid wastes (KJ-F and KJ-A) were classified as *toxic* according to MaxTox index, and AvgTox index classified 3 of them KJ-602, KJ-610, RA-KJ-2 as *not toxic*. The toxicity of eluates KJ-F and KJ-A and groundwater KJ-601 could be explained by alkalinity (pH 12.3; 12.9 and 11.5, conductivity 4440, 7600 and 1400 μS/cm, respectively), but not by phenolic compounds, PAHs or BTEX content. Also, in the groundwater KJ-601 abundant growth of heterotrophic bacteria and phenol degraders was observed.

Two groundwaters KJ-608 and RA-KJ-3 by MaxTox index and 5 groundwaters (KJ-608, RA-KJ-3, KJ-602, KJ-610 and RA-KJ-2) by AvgTox index were classified as *not toxic*.

14.2.3 The ecotoxicological hazard in Kiviõli investigation area

Three semi-cokes KV-F, KV-M and KV-O (respectively fresh, medium and old); one groundwater sample from mine (Ka); two waste porewater samples RA-KV-5 and RA-KV-6; and four groundwater samples from existing monitoring wells (KV-6, KV-9) or drilled risk assessment wells (RA-KV-1 and RA-KV-2), altogether 10 samples were studied for ecotoxicity from Kiviõli investigation area (Table 14.3 and 14.6). The growth of both heterotrophic bacteria and phenol degraders was absent (RA-KV-1, RA-KV-5 and RA-KV-6) or poor (KV-6, KV-9, RA-KV-2) (Table 14.6). Absence of growth could be caused either by high toxicity (polluted sample) or absence of growth substrate (very clean sample).

Altogether three samples: groundwater RA-KV-1, waste pore water RA-KV-5 and eluate prepared from fresh semi-coke KV-F and were classified as *very toxic* according to MaxTox index, and AvgTox index classified leachate KV-F as *toxic*. The toxicity of these samples could be explained by high alkalinity (pH 13, 13.2 and 12.5; conductivity 10000, 12000 and 5600) as the toxicity was reduced after neutralization 124, 21 and 126-fold till 1.4, 5 and 3.3 TU; respectively) whereas till 11% of toxicity was explained by phenols (Table 14.6).

Altogether six samples: semi-coke eluates KV-M and KV-O, minewater SH, groundwaters KV-6, RA-KV-2 and waste pore water RA-KV-6 were classified as *toxic* according to MaxTox index, and AvgTox index classified four of them (KV-O, KV-6, RA-KV-2 and Ka) as *not toxic*. Their pHs ranged from 7.2 to 10.5, whereas pH of 9.9 and 10.5 (samples KV-M and RA-KV-6) was not the cause of their toxicity. Thus, the toxicity of these samples is probably caused by not identified compounds.

Groundwater Ki2 was classified as *not toxic* by both indices, AvgTox index classified in addition 4 more samples as *not toxic:* groundwaters KV-6, KV-9, RA-KV-2 and SH as well as eluate from old semi-coke KV-O.

14.2.4 The ecotoxicological hazard in Kukruse investigation area

From this area only one sample was studied: groundwater KK-1/1 that was classified as *not toxic* by both indices used (Table 14.4)

14.3 Summary of ecotoxicological results

Summary of the ecotoxicological risk assessment results obtained during this project is provided in Table 14.9.

Within the framework of this project altogether **14 groundwater samples** were studied covering regions of Kohtla-Järve, Kiviõli and Kukruse. For the ranking of samples according to their toxicity, all samples were classified by two indices: by average toxicity (AvgTox) and by the most sensitive test results (MaxTox) of the battery of 4 tests (crustaceans, bacteria, algae, protozoa).

From **Kohtla-Järve** area altogether 8 samples were studied out of which 5 groundwater samples were classified as *not toxic* at least by one classification index used. Only one groundwater sample KJ-600 was classified by both toxicity classification indices as *very toxic*. The average toxicity of this groundwater sample was 10.6 TU and its pH was neutral (Tables 14.3 & 14.5). The sample contained 17 ppm of phenols explaining 37% of the toxicity of this sample, and as the pH was neutral, the alkalinity (that is typical cause of toxicity of oil-shale region wastewaters) was not the reason of the toxicity. Despite of the toxicity, the microbiological studies showed the presence of heterotrophic and phenol-degrading bacteria in sample KJ-600 indicating the possibility for natural attenuation in case of favorable temperature and oxygen concentrations.

From **Kiviõli area** 4 groundwater samples and 1 minewater were studied. 4 samples out of 5 could be considered *not toxic* (Table 14.6). Only One, RA-KV-1 was *toxic* to *very toxic* depending on the classification index used. Sample RA-KV-1 was taken from Keila-Kukruse aquifer risk assessment well and had average toxicity of 13.9 TU. Toxicity could be explained by high pH as neutralization reduced the toxicity in Microtox test 124 times (from 169 to

1.4 TU). Also, 2.4 ppm of phenolic compounds in this groundwater explains 11% of toxicity in Microtox test (Table 14.7).

The groundwater sample from **Kukruse** risk assessment well KK-1/1 was *not toxic* (Table 14.4).

The **solid wastes** studied (3 oil-shale combustion ashes and 4 semi-cokes) did not contain priority pollutants in hazardous concentrations (the levels did not exceed even the permitted limit values for living areas). At the same time, the laboratory aqueous leachates (eluates) of these waste samples (1 part of solid sample was extracted with 10 parts of water) proved *toxic* to *very toxic* (Table 14.4). Water eluates of **oil shale combustion ashes from Narva** (N-AF and N-AC) were alkaline (pH 12.9) and high average toxicity (15.7 TU). The neutralisation of the eluates decreased the toxicity to photobacteria about 123...160-fold, till practically not toxic value (1.7 TU). The leachate of NA-F contained 385 ppb of Cr and 5.9 ppb of Hg and the leachate of NA-C contained 5.4 ppb of Hg that exceeds the Estonian PLV for groundwater. However, these concentrations of metals are still too low to cause harm to the test organisms used in the current study. Water eluate of **Kohtla-Järve oil shale combustion ashes** (KJ-A) was also very alkaline (pH=12.9) but its toxicity was lower (4.5 TU) compared to Narva ashes. The toxicity of eluate of KJ-A to photobacteria was reduced 63-fold after neutralization but the neutralized eluate remained still toxic (2.5 TU).

The average toxicity of water eluates of **semi-cokes** (0.9-4.8 TU Table 14.5 &14.6) was lower than that of the ashes (4.5-15.8 TU), whereas the toxicity of semi-coke eluates was dependent on age of the semi-coke (Fig 14.2) that was shown by us also earlier with different samples of fresh and aged semi-cokes (EERC, 2003). In the current project the effect of aging was studied on three semi-coke samples from Kiviõli area: fresh, 20-years old and 40-years old semi-coke (KV-F, KV-M and KV-O, respectively).

The analysis of the chemical composition of the aqueous eluates and comparison that with the toxicity data showed that the reduction of the toxicity was parallel to the decrease of the concentration of mineral salts (reduction of the conductivity from 5600 uS/cm in case of fresh semi-coke to 357 μS/cm in case of 40-years old semi-coke). The conductivity data were in accordance with data on concentration of Ca (decrease from 14 000 ppm to 26 ppm) and respective decrease of pH (from 12.5 to 8). The toxicity reduction of semi-coke water eluates during aging was probably also due to the reduction of water-extractable toxic sulfur compounds in aged semi-coke (on toxicity of sulfur compounds, see Kahru et al., 1997), that is in accordance with decrease of sulfur in aged samples (0.99, 0.21 and 0.01 ppm in KV-F, KV-M and KV-O, respectively). Analogous results on decrease of sulfur compounds (especially in the form of sulfide that is most toxic of them) were obtained in research on oil-shale semi-coke environmental hazard (EERC, 2003).

Toxicity of fresh semi-cokes. The semi-coke samples (incl. fresh semi-coke) did not contain priority pollutants in hazardous concentrations, (Tables 14.5 and 14.6) and according to the chemical analysis semi-coke is classified as non - hazardous waste. However, the eluate of Kohtla-Järve fresh semi-coke (KJ-F) was classified as *toxic* and eluate of Kiviõli fresh semi-coke (KV-F) from *toxic* to *very toxic* depending on the index used (Table 14.3). The toxicity of KJ-F and KV-F to photobacteria was respectively 20 and 127-fold reduced after its neutralization but still remained toxic (4 and 3.3 TU, respectively). Thus, we showed that the toxicity of semi-coke aqueous eluates was mostly due to their alkaline pH, but there are other currently not known contributors to the toxicity that need to be further studied. It should be mentioned that the toxicity of eluates of fresh semi-coke to aquatic organisms was also the main reason for the classification of the fresh semi-coke as environmentally hazardous waste (EERC, 2003).

However, the eluates of old (aged) semi-coke were practically harmless to aquatic organisms. As the main reasons of the toxicity of fresh semi-coke (high alkalinity caused by high calcium content and probably also sulfide content) decrease while the semi-coke is stored in the open air (currently leached by rainwater to the surrounding soils and groundwater), then controlled aging may be an option for reducing the toxicity of that harmful waste.

Summing up, it may be concluded, that in case of oil-shale combustion ashes as well as semi-cokes the main reason for water-extractable toxicity is high alkalinity and high concentration of mineral salts (Fig.14.3). The toxic effect of sulfur compounds (especially sulfide; Kahru et al, 1997; EERC, 2003) could also be a realistic cause for the toxicity to aquatic organisms.

In addition to the laboratory-prepared eluates of semi-cokes the current project also studied the **natural aquatic leachates of semi-cokes sampled** from channels surrounding the Kohtla-Järve ash (from local power plant) landfill KJ-CH1 and semi-coke landfill KJ-CH2. KJ-CH1 had average toxicity of 9.5 TU and was classified as *toxic*. It contained 2.6 ppm of phenols (exceeding 13 times the PLV for groundwater) that explained 18% of its toxicity to photobacteria. The toxicity of this sample was mainly caused by high alkalinity (pH 13.2), as after neutralization the toxicity was reduced 174-fold till *not toxic* (0.9 TU). The growth of bacteria, probably due to high pH was not found.

The other channel water sample KJ-CH2 was *extremely toxic* (average toxicity 104 TU). 96 ppm phenols in this sample exceeded the PLV values for groundwater 480-fold explaining, however, only 9% of toxicity. Also, the alkalinity was not responsible for toxicity (data of Microtox test). As in previous channel water KJ-CH1, the heterotrophic as well as phenol-degrading bacteria were not found. The different pollutant levels and toxicity of the samples KJ-CH1 and KJ-CH2 show that the water in the channel is heterogenous.

In addition to channel waters also the **porewater** of semi-cokes was studied. For that, 2 special boreholeholes were drilled in Kohtla-Järve semi-coke landfill (higher RA-KJ-5, possibly near the fuss-deposition and lower RA-KJ-6) and 2 boreholeholes in Kiviõli most recent semi-coke landfill (higher RA-KV-5 and lower RA-KV-6). The ecotoxicological test battery classified Kohtla-Järve landfill porewaters RA-KJ-5 and RA-KJ-6 as *extremely toxic (*average toxicities 111 TU and 184 TU, respectively). The PLVs for groundwater were exeeded for PAHs, BTEXs and phenols for 63, 195 and 480 fold, respectively but only 8-11% of the toxicity of these samples could be explained by phenolic pollutants. Despite of the relatively high levels of BTEX and PAHs, these concentrations are not toxic in acute toxicity assay like Microtox. The porewaters were very alkaline (pH 13), but the toxicity to photobacteria was not reduced after neutralization. Thus, the toxicity of porewaters RA-KJ-5 and RA-KJ-6 may be caused by other contaminants, e.g., originating from nearby fuss-deposit.

Compared to Kohtla-Järve semi-coke mountain porewaters, the Kiviõli semi-coke porewaters RA-KV-5 and RA-KV-6 were by order of magnitude less toxic: average toxicity 11.3 and 2.8 TU, respectively. Despite of the high toxicity (11.3 TU) RA-KV-5 did not contain any key pollutants in hazardous concentrations. Also, the high alkalinity (pH 13.1) of this sample did not explain all the toxicity, as after the neutralization the toxicity was considerably reduced (21-fold) but the sample still remained toxic (5 TU).
Therefore, the reasons for the toxicity of these samples need to be found out in the future studies.

15 EU - LANDFILLS AND DIRECTIVES

In the EU today the following directives/guidelines are applied to assessing landfills:

1. Directive on the landfill of waste, 26. April 1999 (EU, 1999).
2. Descision on establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex 2 to Directive 1999/31/EC, Dec. 19, 2002.

According to the landfill directive the following basic requirements shall be covered:

- Characterization of waste
- Controll of waste prior to landfilling.
- The waste shall be treated before landfilling. Possible environmental adverse effects and pretreatments shall be initiated before landfilling.
- Double bottom sealing is required for hazardous and non-hazardous waste, can be fulfilled by natural and artificial barriers.
- Single bottom sealing for inert wastes
- Collection of leachate and treatment if necessary.

- Surface sealing may be required if necessary to prevent leachate formation
- Removal of gas (only applicable sanitary landfills)
- Financial guarantee to terminate the landfill properly and to follow up the environmental monitoring for 30 years after closure.

If, on the basis of an assessment of environmental risks, it can be established that the landfill poses no potential hazard to soil, groundwater, or surface water the requirements above can be reduced accordingly. It is also possible to propose remedial measures in order to improve the situation.

Most countries in EU have developed their own similar guidelines for the risk assessment. For this case, the Norwegian guideline for risk assessment of landfills is used (SFT, 2003a).

15.1 Environmental risk assessment of landfills.

The risk assessment is divided into three steps:

Step 1 - Characterization of waste and leachate

Chemical analysis of waste and leachate from leachate tests or real leachate from the landfill. Characterization of waste (inert, non-hazardous, hazardous) according to "Descision on establishing criteria and procedures for the acceptance of waste at landfills" (EU, 2002). If the real leachate concentrations (in the field) exceed the threshold values as shown below it is recommended to do ecological tests and/or to go to next step.

Parameters (selected)	Treshold values, ug/l
Zn	35
Pb	1.9
Cd	0.2
Ni	5
Cr	6.3
As	2
Hg	0.01
BTEX	0.2
Phenols	0.5
PAH	2

Step 2 – Characterization of the transport

Establish the water balance for the landfill, to determine the magnitude of the diffusive transport, classified as the part of the total leachate which is not collected. Establish the hydrogeology and the groundwater flow. The diffuse leakage of the infiltration shall preferably be less than 5 %. If excessive, the effects on the recipients must be investigated.

Step 3. Characterization of the recipient.

The recipient can be the soil, groundwater or surface water outside the natural limitation of the landfill. Investigation must document the spreading of contaminants to these media and ecotoxicological testing of surface water if necessary.

To define the recipients for major industries with landfills it is important to define an acceptable area of influence, which is a part of the overall contaminated industrial site. Depending on the local conditions it is the industry which should propose the area of influence to the environmental and local authorities.

This is only a very brief outline of the most important issues in the guideline.

16 ENVIRONMENTAL RISK ASSESSMENT OF LANDFILLS

None of the investigated landfills meet the new EU environmental requirements (EU,1999). In order to assess the actual environmental impact of the landfills an environmental risk assessment is performed for all four sites according to the outline in Chapter. 15.

16.1 Kiviõli

16.1.1 Waste characterization

Testing of the old, medium and fresh semi-coke waste and their leachates showed very low concentrations of both organic and inorganic contaminants. According to EU classification (EU, 2002) based on batch leaching testing the waste is inert except for As, Ba, Mo and Se (see tables 6.2.1.2 and 6.2.1.3).

Comparing the threshold values in Chp. 15 with the RA-KV-5 leachate, most of the parameters exceed the limits, therefore requiring ecotoxicological testing.

A comparison of the pore water waste samples from the landfill, RA KV-5 and -6 to the laboratory leachates, shows that porewater and leachates from fresh semi-coke have similar concentrations of elements and organic compounds. The pH of leachate from fresh waste and the waste pore water is extremely high, 12.5- 12.9. The ditch water is near to neutral due to delution from rainwater. Hardly any organics are detected in the leachates, both in the batch test and in the field. The tox tests show the leachates to be very toxic to toxic.

The semi-coke waste is today, according to EU classification (EU, 2002), a chemically inert waste. However, according to the ecotoxicity, it is hazardous due to acute toxicity to aquatic organisms.

16.1.2 Transport characterization

The modelling from Chapter 12. 3.1 showed that about half of the contaminated leachate/groundwater from the landfills drains into the shallow layers northwards and in the direction of the river Erra. The organic compounds, PAHs, BTEX and phenols are detected in the shallow well (RA KV -4) in low concentrations to the north of the landfill.

The modeling showed that underneath the landfill, the upper two natural soil layers are so pervious that the other half of the groundwater flow and possibly the contaminant transport is moving vertically into the the third layer. After 250 to 750 m northwards the groundwater flow bends downwards to the 3. layer and continues to move in southeast direction towards the old mining area.

According to the water balance, all of the infiltration from the landfill, can be defined as diffuse as none is being directly collected.

Based upon the borings, sampling data and the modelling data, it is belived that the transport of contaminants in the groundwater will vanish and disappear. During a timespan of 100 years PAH and BTEX are being degraded and retarded and are unable to move out of the landfill. Only phenols are able to move into the upper layers (see fig. 13.2 to 13.4). However, most of the inorganics in the leachate, like the heavy metals, are expected to be transported more rapidly into the third layer.

Analysis of groundwater from one of the deep water supply wells shows the presence of BTEX and PAH compounds. According to the contaminant transport modelling and in general the physiochemical properties of the organics, this is not possible due to the expected retardation and degradation.

The surface soil contamination of the industrial area is within the permissible limits, set by the Estonian government.

Due to very high diffuse transport of contaminants and the fact that the contaminant transport is not under control it will be important to document what is really taking place and what is the actual groundwater transport to the old mine and to Erra River.

16.1.3 Characterization of the recipients

The following recipients are present:

- surface water
- groundwater from the deep aquifer
- surface soil
- air
- plants, vegetation

Surface water

The surface water in the ditches close to the landfill is diluted by rainwater. No ecotoxicological testing has been done but comparison with the Norwegian fresh water quality standards (SFT, 1997) show that except for Cr, concentrations exceeded the very contaminated level. Pore water/leachate inside the landfill was chemically comparable to the ditch water. Ecotoxicological tests classified the porewater as very toxic. Two sediment samples from the Erra River (see Table 10.1 and 10.2) were insignificantly contaminated.

The borings, away from the landfills, showed the presence of organics and heavy metals in both the soil and the groundwater.

The water in the ditches was not treated before discharging to the environment.

Groundwater

The detected BTEX compounds in the deep Ordovician-Cambrian aquifer cannot have been transported by natural groundwater flow. It is most likely due to short-sircuiting of contaminated surface water or shallow groundwater flow along the wells, which are not properly sealed.

The surface soil

Some increase of As, Cu, Hg, Mo, Pb, U and Zn concentrations in the upper layer was observed, probably caused by natural background, presence of Dictyonema argillite and phosphorite in the underlying rocks or spreading through air by volatile particles from the oil shale combustion. The surface soil contamination of the industrial area is within the permissible limits set by the Estonian government.

Plants and vegetation

Some increase of Pb, Ag, Ni, Co, Mn, Th, La and Ba is observed in the roots of meadowsweet sampled to the north of the old landfill when compared to other samples of vegetation.

16.1.4 The conclusion of the risk assessment

Considerable improvements like improving the process of torting and minimized the amount of water into the landfill, have been made over the years to reduce the spreading of contaminants

The risk assessment and the ecotoxicological testing concludes that the contaminant situation at the semi-coke landfills is not acceptable according to the EU landfill directive. The main reason is that the diffuse groundwater discharge is about 100 % and that the effluent leachate is toxic.

There are, hovever, favourable conditions at the landfill which can be utilized to improve the situation considerably:

- The assumed risk of groundwater contamination is uncertain due to the retardation and dilution of the contaminants (natural attenuation).
- The natural upper layers underneath the landfills may be utilized as a barrier and drainage with pumping to reduce the diffuse spreading and collect the leachate for treatment.
- The waste is chemically characterized as non-hazardous
- Only a few contaminants are leaching and spreading into the environment.

Some important questions remain to be answered:

1. What is the natural and acceptable industrial area of influence, where a certain degree of contamination is acceptable for different environmental media. This concerns the surface soil contamination (residential vs industrial areas), groundwater transport both to depth and to what extent outside the landfill, and effect on the recipients (natural attenuation).
2. What is the real source/causes of the toxicity of the leachate?. (this study indicates a summary effect of pH, organic compounds and trace elements).
3. What is the composition, toxicity & mutagenicity of the fuss
4. What is the effect of spreading of pollutants through air?

16.1.5 Proposed remedial measures

Whether the owner wants to finish or continue the operation of the existing landfills, the landfill is a permanent source of contamination continuously generating new leachate.

<u>Existing landfills:</u>

1. Monitoring of natural attenuation (MNA) may be the solution to the contaminated and diffuse groundwater transport.
2. To reduce/eliminate the diffuse loss of leachate by establishing a combination of ditches, relif wells horizontal and vertical around the foot of the landfill to pump/extract the leachate/contaminated groundwater to treatment plant.
3. To reduce infiltration and possible spreading to air, the landfill can be covered by planting grass/plants/bushes.
4. The existing well design must be controlled, especially the deep ones for possible leaks of contaminated groundwater from the upper horizons.

All of these proposed remedial measures will require detailed investigation and studies.

<u>New landfill:</u>

Establish a new landfill designed and built according to the new EU-directives for landfills for non-hazardous wastes. This involves double bottom sealing with a leachate collection system and effluent treatment.

16. 2 Kohtla- Järve

16.2.1 Waste characterization

The semi-coke waste is very similar to the Kiviõli semi-coke in chemical composition and leaching characteristics. Chemically most of the parameters are classified as inert according to the EU standard (EU, 2002), except for Ba, Se, and Zn (see Tables 6.2.1.2 and 6.2.1.3). The only organic detected in the toluene is toluene. The alkalinity is extremely high and the leachate is toxic. Assessing the risk by comparing to the threshold values (ref. Chap. 15) with leachate from the landfill (channel water or the waste pore water RA KJ-5 or -6)), most of the parameters are excessively exceeding the limits, especially the organic compounds, while the leaching test showed hardly any organics. The pH is very high and the leachate is classified as toxic according to the ecotoxicological tests (see table 14.5).

The semi-coke landfill contains also a residue from the distillation process called fuss (tar), which has been deposited since the beginning of the operation until some years ago. This fuss contains high concentrations of most of the organics, PAH, BTEX and phenols. This is expected to be one reason for the high concentrations in the field leachate compared to the laboratory testing of the “pure” semi-coke waste.

The semi-coke waste as it is today is nearly a chemically inert waste according to EU classification (EU, 2002), but ecotoxicological tests show it is toxic.

The ash from the power plant is according to the EU classification (EU, 2002) classified as an inert waste, but the alkalinity is extremely high (12.9) and it is also tested to be toxic.

16.2.2 Transport characterization

The groundwater originating from the landfill flows downward and radially out to the channels surrounding the landfills and into the subsurface. About half of the infiltration drains to the channels and the other half to the subsurface (ref. chap. 12.4.1). This indicates that, according to the water balance of the landfill, the diffusive loss to groundwater and the subsurface is about 50 %. A part of the leachate, which drains into the channels, may also contribute to the infiltration of contaminants to the subsurface. This possibility is not allowed for in the groundwater modelling.

The subsurface flow penetrates the quartenary layer and reaches the Ordovician unconfined upper aquifer system (third layer) through the upper aquitard with a smaller portion reaching into the deeper Ordovician-Cambrian aquifer system (fifty layer) (see Fig. 12.4.3). In the upper layers the flow is to the east and is turning towards the west into the deeper layers (see fig. 12.4.1 and 12.4.4).

The transport modeling shows that the phenol contaminants which are the most mobile, only move as deep as the third layer. It is expected that the groundwater transport of contaminants will cease due to natural attention (combination of degradation and various chemical processes).

The upper Ordovician aquifer system, has been found to be contaminated by organic compounds (like BTEX and phenols) in high concentrations more than 300 m from the landfill. One of the two deep wells into the deeper Ordovician-Cambrian aquifer system, also show high concentrations of both BTEX and phenols (see table 9.3.3.3, well 601). However, the transport modelling shows that the organic contaminants would, after 100 years, only reach halfway into the upper aquifer (see Fig. 13.6 and 13.7).

16.2.3 Recipient characterization

The following recipients are present:

- surface water
- Ordovician groundwater,
- Ordovician-Cambrian groundwater aquifer,
- surface soil
- air
- plants, vegetation

Surface water
The channels along the landfill are expected to drain the leachate to the surface water system of Kohtla-Järve. Phenol is detected far downstream both in the Kohtla and the Purtse rivers. The analysis of the samples and from the channels near the two landfills are shown in Tables 9.3.3.1, 9.3.3.2 and 9.3.3.3. The sample from the channel near the semi-coke landfill and show extremely high consentrations of PAH, BETX and Phenol and is extremely toxic. The other analysis from the channel near the ash landfill are toxic with low to moderate concentrations.

Ordovician groundwater
The groundwater underneath the landfill down to layers 2, 3 and 4 is a major recipient of contaminated pore water from the landfill. There is limited data on the contaminant spreading (the plume) to the depth, but the modeling indicates that due to natural attenuation processes the contaminants vanish and disappear.

Ordovician-Cambrian aquifer
The detected BTEX and phenol compounds in the deep Ordovician-Cambrian aquifer cannot have been transported by natural groundwater flow. This will, according to the modelling take several hundered years. It is most likely due to short sircuit of contaminated surface water during floods or shallow

contaminated groundwater flow along the well, which may not be properly sealed.

If, on the contrary, this is caused by groundwater transport, this can be a serious threat to the future utilization of this groundwater resource.

Surface soil
The pollution of soil by volatile elements and elements associated with ash was documented in this area. The maximum pollution by As, Hg and Pb is observed near the Kohtla-Järve Chemical factory and west of the semi-coke landfill. The surface soil contamination of the industrial area is within the permissible limits, set by the Estonian government.

Air
According to the observations (Otsa et al., 2004) the average daily content of SO_3 in the air in 2003 in Kohtla –Järve was 70.9 $\mu g/m^3$ (PLV is 125 $\mu g/m^3$). PLV is according to (RT I 1998, 41/42 624). The daily average content of O_3 was estimated as 65 $\mu g/m^3$, the maximum value was 115.1 $\mu g/m^3$ and O_3 content in the air of Kohtla-Järve exceeded PLV 102 times during 2003. The daily contents of H_2S during the 2003 was within the limits of PLV (8 $\mu g/m^3$) and exceeded this values four times during the year. The daily ammonia (NH_3) contents was higher than PLV (40 $\mu g/m^3$) three times during the year.

The daily contents of NO and NO_2 do not exceed the PLV. The maximum values observed during the year of 2003 were 27.2 $\mu g/m^3$ and 57.6 $\mu g/m^3$ respectively.

One hour's NO_2 maximum value was 100.2 $\mu g/m^3$, that is less than the PLV (300 $\mu g/m^3$). The daily average contents of CO (0.77 $\mu g/m^3$), non-methane hydrocarbons (NMHC)(0.17 $\mu g/m^3$) and formaldehyde (46 $\mu g/m^3$) were less than PLV (3 $\mu g/m^3$, 2 mg/m^3 and 50 $\mu g/m^3$ respectively). The daily average content of PM_{10} (particulate matter less than 10μm) was also less than PLV (75 $\mu g/m^3$). The maximum values were estimated to 59.2 $\mu g/m^3$.

The pollution of air by phenol is monitored regularly. The daily average content of phenol exceeded the PLV (3 $\mu g/m^3$) 68 times during 2003. The maximum value was 29 $\mu g/m^3$. This contamination in the ambient air is primarity caused by emission from the smoke stacks.

Plants and vegetation
In the roots of plants sampled near the semi-coke waste landfill, enrichment of Mo, Cu, Zn and U was documented.

16.2.4 The conclusion of the risk assessment

Considerable improvements have been made over the years to reduce the spreading of contaminants like improving the process of torting, minimized the amount of water into the landfill and terminated landfilling of fuss.

The conclusion of the risk assessment and the toxicological testing is that the contaminant situation at the landfills is not acceptable according to the EU landfill directive. This is mainly due to the fact that about 50 % of the infiltration is diffusive loss to the groundwater spreading and the field leachate is both toxic and chemically hazardous.

There are hovever, favourable conditions at the landfill, which can be utilized to improve the situation:

- The diffusive contaminant spreading to groundwater may be limited due to natural attenuation.
- The natural upper layers underneath the landfills can be better utilized as a barrier to reduce the possible diffusive loss to the subsurface via the channels.
- The wastes of today are chemically characterized as non-hazardous, but are toxic.

Some important questions remain to be answered:

1. What is the natural and acceptable industrial area of influence (where a certain degree of contamination is acceptable for different environmental media)? This concerns the surface soil contamination (residential vs industrial areas), groundwater transport both to the depth and to what extent outside the landfill and effect on the recipients (natural attenuation).
2. What is the real source/causes of the toxicity of the leachate? (this study indicates an summary effect of pH, organic compounds and trace elements).
3. What is the composition, toxicity & mutagenicity of the fuss.
4. Are the channels along the landfills a source and pathway for spreading contaminants to the subsurface? Shall this leaching of contaminated water be terminated or encouraged?
5. What is the surface soil contamination in the residential areas?
6. Is there anything that can be done to remove the fuss deposits in the landfill?

16.2.5 Proposed remedial measures

Weather the owner wants to finish or continue the operation of the existing landfills, the landfill is a permanent source of contamination continuously generating new leachate.

Existing landfills:

1. Monitoring of natural attenuation (MNA) may be the solution to the contaminated and diffuse groundwater transport
2. Reduce/eliminate the possible diffuse loss of leachate from the channels by establishing impervious linings and if necessary to improve the drainage, combine the channels with more channels, relif wells horizontal and vertical around the foot of the landfill for draining to treatment plant.
3. Alternatively, improve the infiltration from the channels to utilize the groundwater flow for natural attenuation.
4. To reduce rainwater infiltration and possible spreading to air to cover by planting grass/plants/bushes, alternatively combined with a thin soil cover
5. The existing well design must be controlled, especially the deep wells, for possible leaks of contaminated groundwater from the upper horizons.

Al of these proposed remedial measures will require detailed investigation and studies.

New landfill :

Establish a new landfill designed and built according to EU-directives for landfills for non-hazardous wastes. This involves double bottom sealing with leachate collection system and effluent treatment

16.3 Kukruse

16.3.1 Waste Characterization

Two landfills in Kukruse have been assessed, Kukruse 1 which is burned due to self-combustion and Kukruse 2 which is not burnt,. These are landfills of host rock and tailings formed as a result of oil shale enrichment. Both the landfills are cone shaped and covered by dense vegetation of grass and some bushes/trees. They were closed for several yeas ago.

The boring into Kukruse 1 revealed high temperatures in the range of 63° C to 96 °C from top to bottom. The waste contained no PAH but 0.15 to 0.19 mg/kg BETX and 50 mg/kg phenols. Most of the organic contaminants are located in the upper part of the landfill. Due to the high temperatures in the landfill there is hardly any infiltration of precipitation. It is therefore no moisture and groundwater which can generate any leachate. It is therefore difficult to classify the waste and the landfill according to the EU procedure (EU, 2002).

The Kukruse 2 waste has not been investigated and it is expected to contain very low consentrations of organic contaminants.

16.3.2 Transport characterization

This unique situation with hardly any groundwater flow in the Kukruse 1 landfill results in no groundwater transport of contaminants out of the main landfill, neither to the sides nor vertically down under the landfill. Because of the high temperature there will be transport to air by diffusion due to the volatility of the organic compounds.

The boring downstream Kukruse 1, (KK-1) shows only PAH and BTEX in the surface sample above the groundwater level (see Table 9.4.1.2). This is probably due to spill of waste on the surface or from the outer edge of the landfill. Phenols are not present due to volatility and degradation. The organic compounds in the groundwater (no phenols) are therefore expected to originate from the surface and not from the landfill. This shallow groundwater with a plume of PAH and BTEX is expected to reach at a maximum 50 m away from the landfill in the silty till and possibly the aquifer below.

The boring downstream Kukruse 2, into clayey moraine shows BTEX in a sample above the groundwater which has no contaminants. This may indicate that there is no contaminantion spreading in this direction. It is not investigated if contaminants may be transported vertically downwards below the landfill.

16.3.3 Resipient characterization

Kukruse 1: The limited contaminant groundwater flow is not expected to reach any recipients like surface water or groundwater wells. The ecotoxico-logical testing of the groundwater from the downstream well was not toxic.

It is expected that most of the organic contaminants in the landfill will eventually disappear by diffusion and volatilization to air. Most of these contaminants are expected to be degraded in air because of photo-oxydation. Some resettlement to the nearby terrain of the more persisent contaminants may occur.

Kukruse 2: There is insufficient data for assessing the overall transport of contaminants from this landfill.

16.3.4 The conclusion of the risk assessment

The burned landfill Kukruse 1 is not an environmental risk for the ground-water. Diffusive spreading of small amounts of organic compounds to air will take place from the landfill over many years. Some will be degraded and some will resettle to ground surface.

For the unburned landfill Kukruse 2 there is not sufficient data available for doing a risk assessment.

16.4 Narva

16.4.1 Waste characterization

The main types of ashes from the filter and the cyclone have been characterized by analysis and leaching tests(see Table 6.2.1.2). The filter ash is classified as a non-hazardous waste as Se, Mo, Hg and Cr exceed the limit for inert waste. The cyclone waste is also classified as a non-hazardous waste as Se and Hg exceed the limits for inert waste. The pH of the leachates is both measured to 12.9. However, the alkalinity is not a classification parameter (EU, 2002).

The ecotoxicological tests showed that both of the laboratory leachates are very toxic. Additional testing proved that the toxicity in both leachates may be due to the high alkalinity, conductivity and the content of calcium. The analysed pore water in the landfill (see table, 9.5.3) which can be considered as a more real leachate does not exceed any of the limits for inert waste.

Due to the very high temperatures during the combustion of the oil shales, all organic compounds are incinerated and destroyed in the ashes.

16.4.2 Transport characterization

Large amounts of water are being used to hydraulically transport the ash to the landfills (~14.000 m^3m/day). This causes the mounding (build-up) of the high groundwater table in the landfills, the leachate and the groundwater is exerting a considerable head and gradient to the subsurface groundwater flow. According to information and the modelling, the following percentage of this flow is being distributed within the area:

- 20-30 % is draining directly into the channels
- Most of the remaining infiltrated leachate is draining into the Quaternary and the Ordovician aquifer (layer 1 and 2) as diffusive leakage (see fig. 12.5.2 to fig. 12.5.5).
- Most of this contaminated groundwater flow is moving upwards and drains into the surrounding channels, (see fig. 12.5.2 to fig. 12.5.5). A part of this groundwater flow, flows into the Narva reservoir, (see fig. 12.5.4 and layer 1 and 2).
- Only a small amount is continuing to the deeper layers of the aquifer, the Cambrian layer (see Chap. 12.5.1)

A part of the water balance at the site, must include the considerable lateral inflow of groundwater from the outside (first and seconfd layer). This is feeding and diluting the groundwater flow under the landfills and drains upward into the channels with the contaminated flow from the landfills.

The leachate entering into the groundwater flow changes its chemical composition due to several processes like dilution, dispersion, sorption and mineralization. Comparing the leachate consentations (pore water) with the channel consentrations (see Table 9.5.3), enrichment has occurred for Al, Hg, Cl, Cs, Ga, Mo, P, Si, Br, and Ni. However, none of the important environmental inorganic contaminants, like heavy, metals are reaching any high concentrations. The pH is near neutral. When reaching the channels, considerable dilution is taking place. The groundwater flow to the Narva reservoir is according to the monitoring wells neutral and not contaminated. In general, the groundwater is expected to be cleaned during this groundwater flow before it merges into the surface water.

Acording to the the groundwater modeling, the groundwater flow reaching the deeper Ordovician-Cambrian aquifer is small and may take 100 years. The diluted plume may therefore, due to various retardation processes, never reach this aquifer. In addition there are no environmentally serious contaminants detected in the plume.

16.4.3 Recipient characterization

The following recipients are present:

- Surface water (channels, ponds and Narva reservoir)
- Groundwater aquifers
- Surface soil
- Air
- Plants and vegetation

Surface water
The channel and pond water surrounding the landfills is mostly groundwater flow which includes the flow from the landfills and clean groundwater flow entering from the outside.

The total flow from the channels into the Narva Water Reservoir is about 25.000 m^3/day, with low concentrations of the environmental contaminants. It is a considerable flow, but the reservoir is also large resulting in a huge dilution factor and very low bulk concentrations. The results from the Estonian – Russian joint monitoring on Narva Water Reservoir (Narva, 2003), showed that the water quality is good, taking the most important parameters into account.

The deeper groundwater aquifers
These are not expected to be influenced by the industrial activities.

The surface soil
In the Narva vicinity this is being effected by wind erosion from the landfills combined with air emission from the smokestakes. The concentration of As, Cd and Pb, volatilized during the combustion of oil shale, increases to the north of the power plant, i.e. in the direction of the prevailing wind.

Air
According the observations (Otsa et al., 2004) the average daily contents of SO_2 and NO_2 the air in Narva during 2003 were less than PLV (125 $\mu g/m^3$ and 300 $\mu g/m^3$ accordingly) (RT I 1998, 41/42 624). The daily average content of formaldehyde exceed the PLV (50 $\mu g/m^3$) eight times and H_2S four times during the year of 2003 (PLV is 8 $\mu g/m^3$). The maximum determined value for H_2S was 10 $\mu g/m^3$.

Plants/vegetation
The increase of contents Zn, Cu, Mn, Cd, Ba and Tl in the roots of plants collected near the Power Plant in Narva and to the north from them (in the prevailing wind direction) was documented.

16.4.4. The conclusion of the risk assessment

The filter and cyclone ashes are nearly classified as inert wastes except for a few parameters being non-hazardous. However, the leachate from the leaching tests, are classified as very toxic which is due to the very high pH and alkalinity.

As there is no bottom sealing, most of the leachate is being transported by the groundwater flow from the landfills, into the subsurface. Due to the groundwater gradient the flow merges upwards into the surface water channels and ponds around the landfills. The dilution in the recipient is considerable and the concentrations are very low and are not expected to cause any environmentally adverse effects.

The deep water aquifer is according to the groundwater modelling not expected to be contaminated from the groundwater transport.

Even if there are certain unanswered questions, the overall conclusion is that the landfills are acceptable as they are with respect to the construction, operation and impact of the landfills.

It is recommended to revise the ongoing extensive monitoring program at Narva.

Some important questions remain to be answered:

1. More documentation is need for understanding the chemical evolution of the leachate and the natural attenuation from the landfill via the groundwater to the channels and ponds.
2. More documentation and modelling is needed regarding effects to the Ordovician –Cambrian aquifer, the water balance of the landfills and how much flow is entering directly into the Narva reservoir as groundwater flow.
3. What is the health effect of ash spreading by wind ?

16.4.5 Proposed remedial measures

No remedial measures are necessary.

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List of Figures:

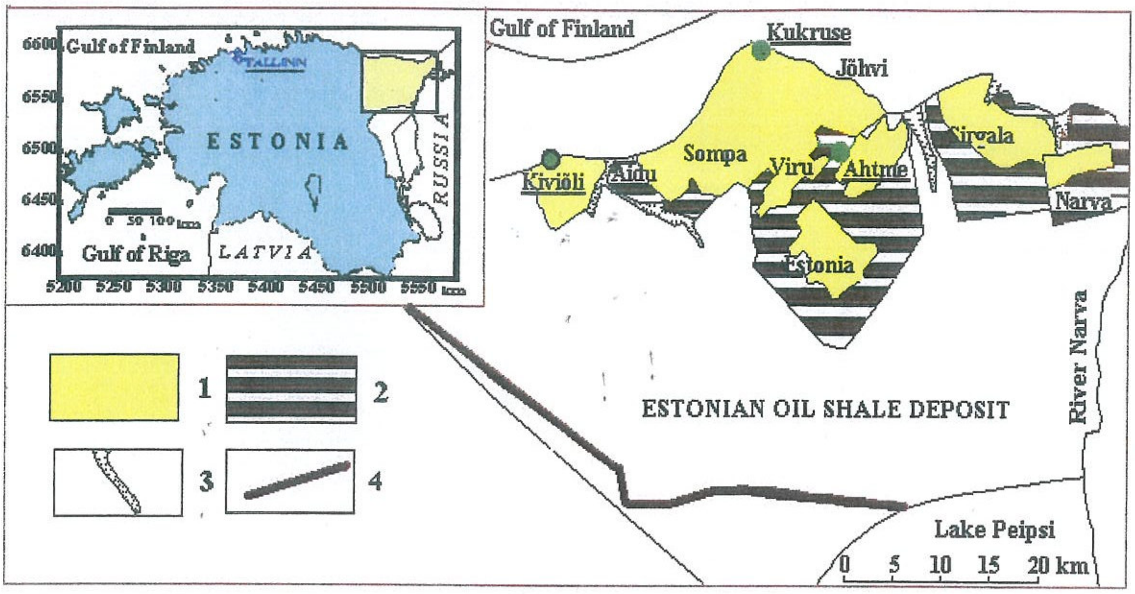


Fig. 1.1.1 Location map of Estonia oil shale deposit.
According Bauert and Kattai (Geology…, 1997) and Erg (2003). Legend: 1- oil shale underground and surface mines; 2 – claims and names of underground and surface mines; 3 – buried valley; 4 – recent erosional boundary of oil shale.

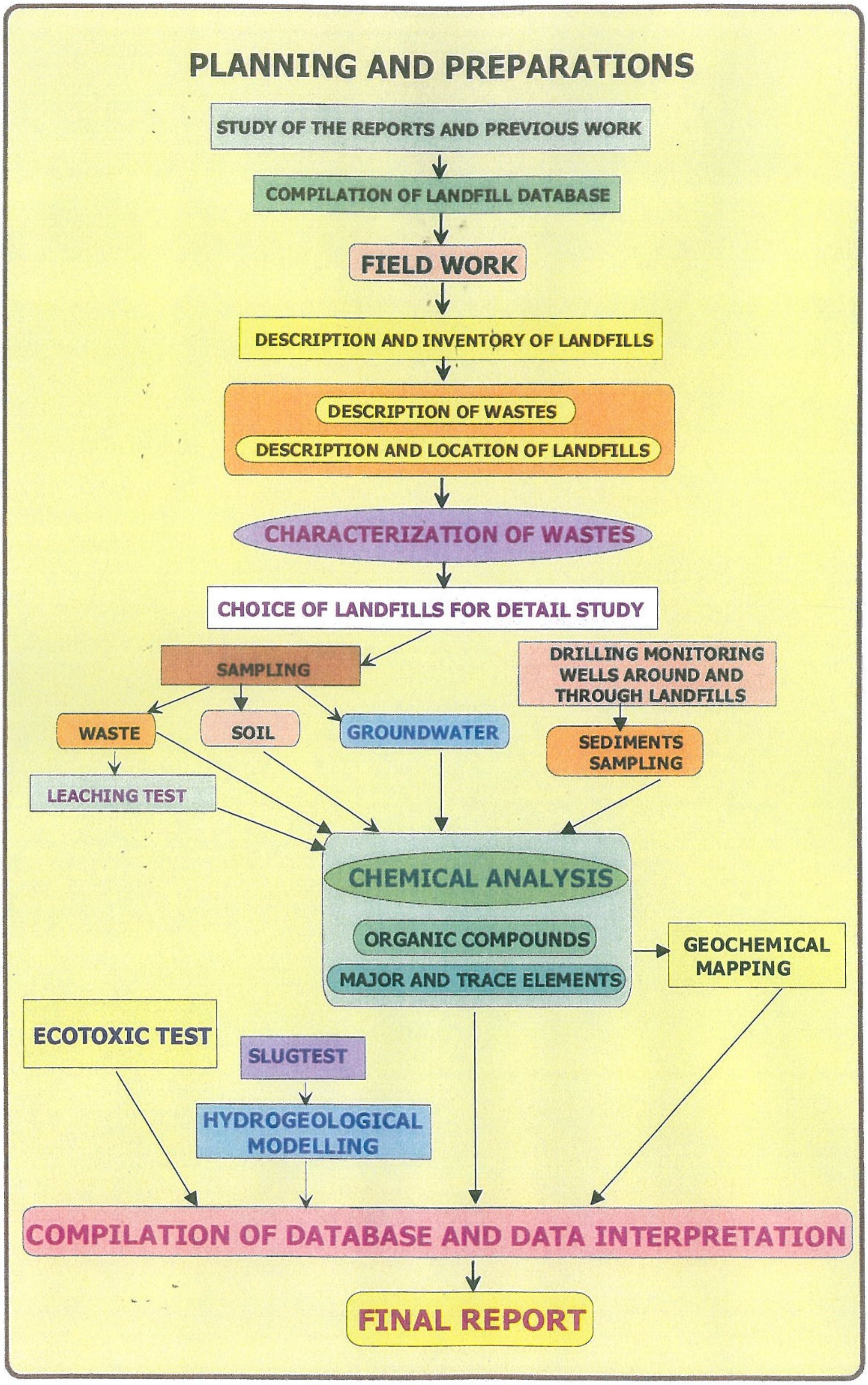


Fig. 1.4.1 Outline of project activities

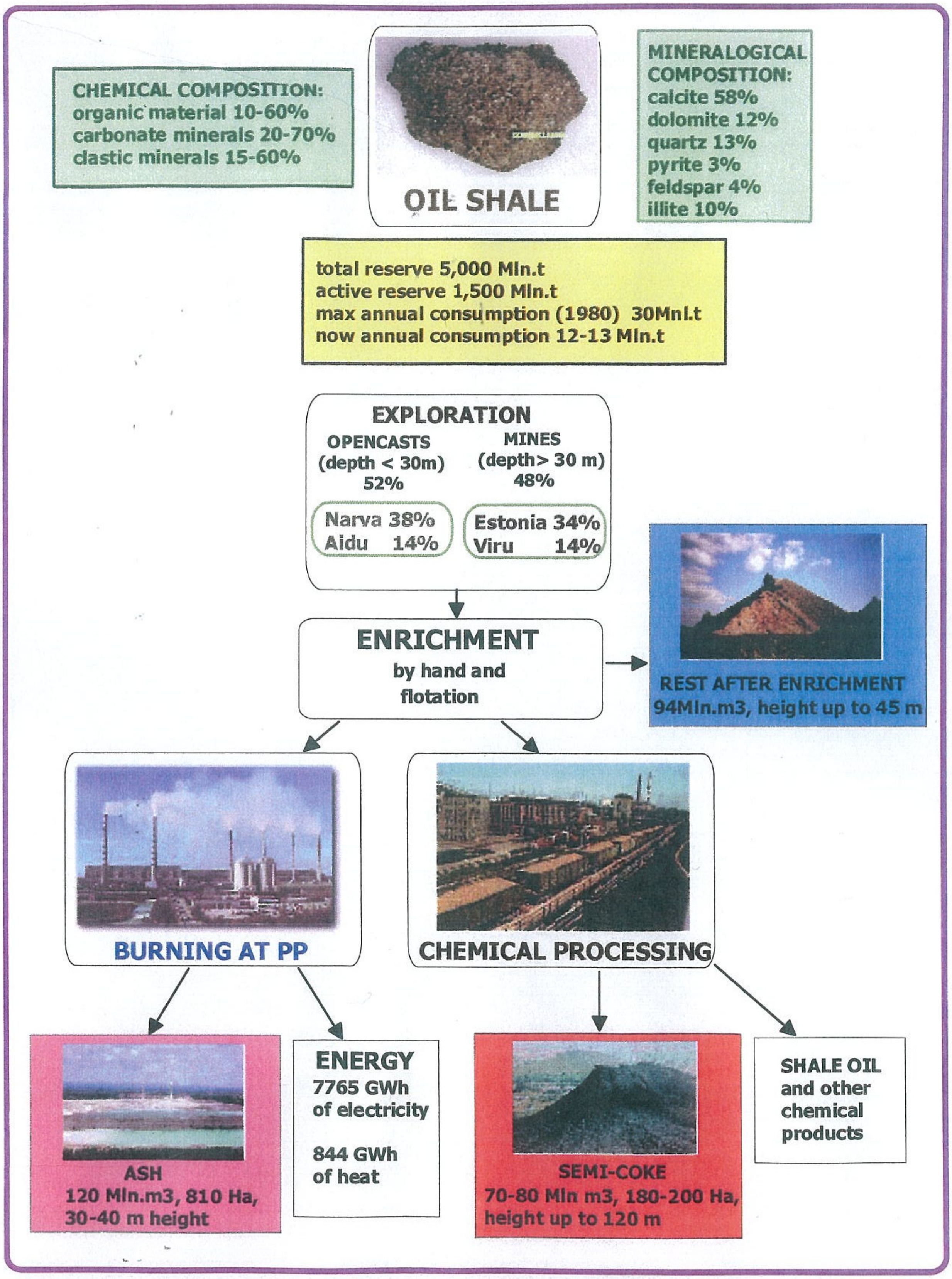


Fig. 2.1 General data about composition, exploration and processing of Estonian oil shale

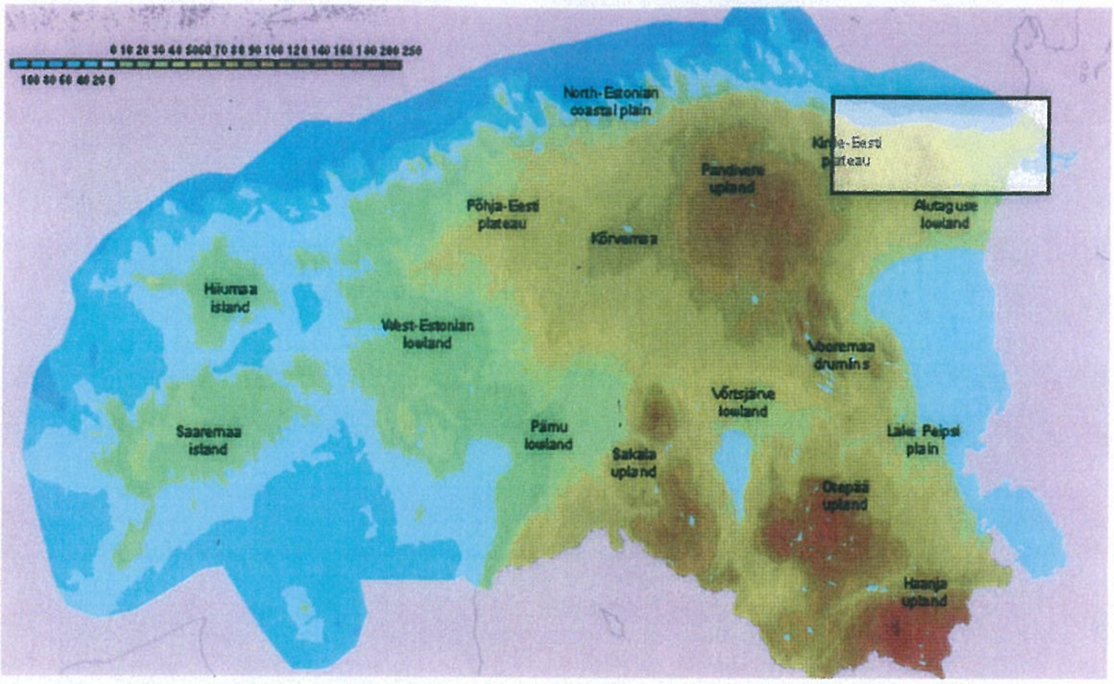


Fig. 3.2 Relief of Estonia. Studied area is showed in the box.

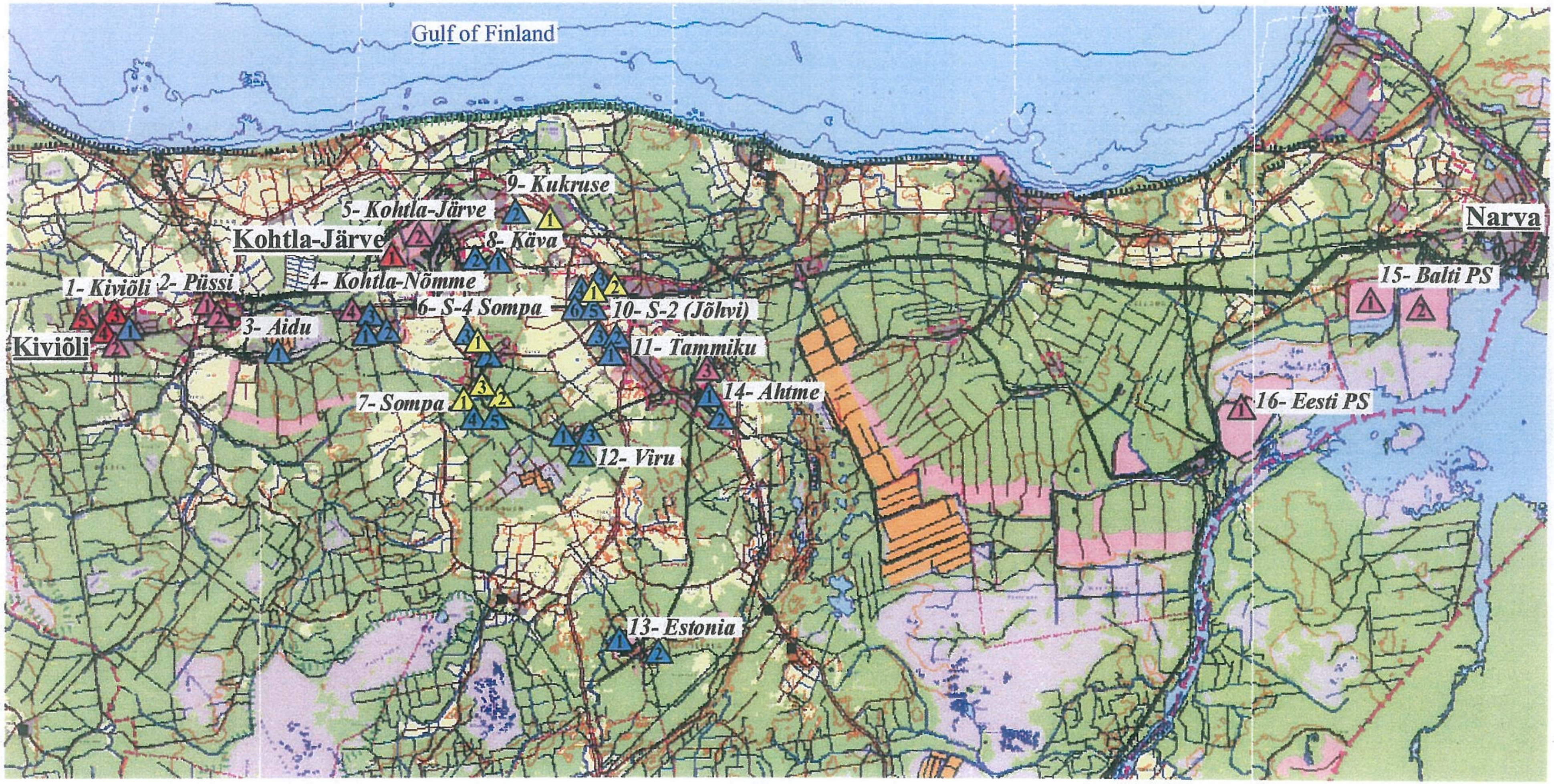


Fig. 4 Studied area and location of landfills

Legend: 1 - Kivioli - main groups of the waste mounds. ▲ - semi-coke mounds; ▲ - mounds of the rest after oil shale enrichment; ▲ - mounds of the rest after oil shale enrichment, self-burned; ▲ - ash mounds and plateau. Numbering according to Table 2.1. Kiviõli - main towns

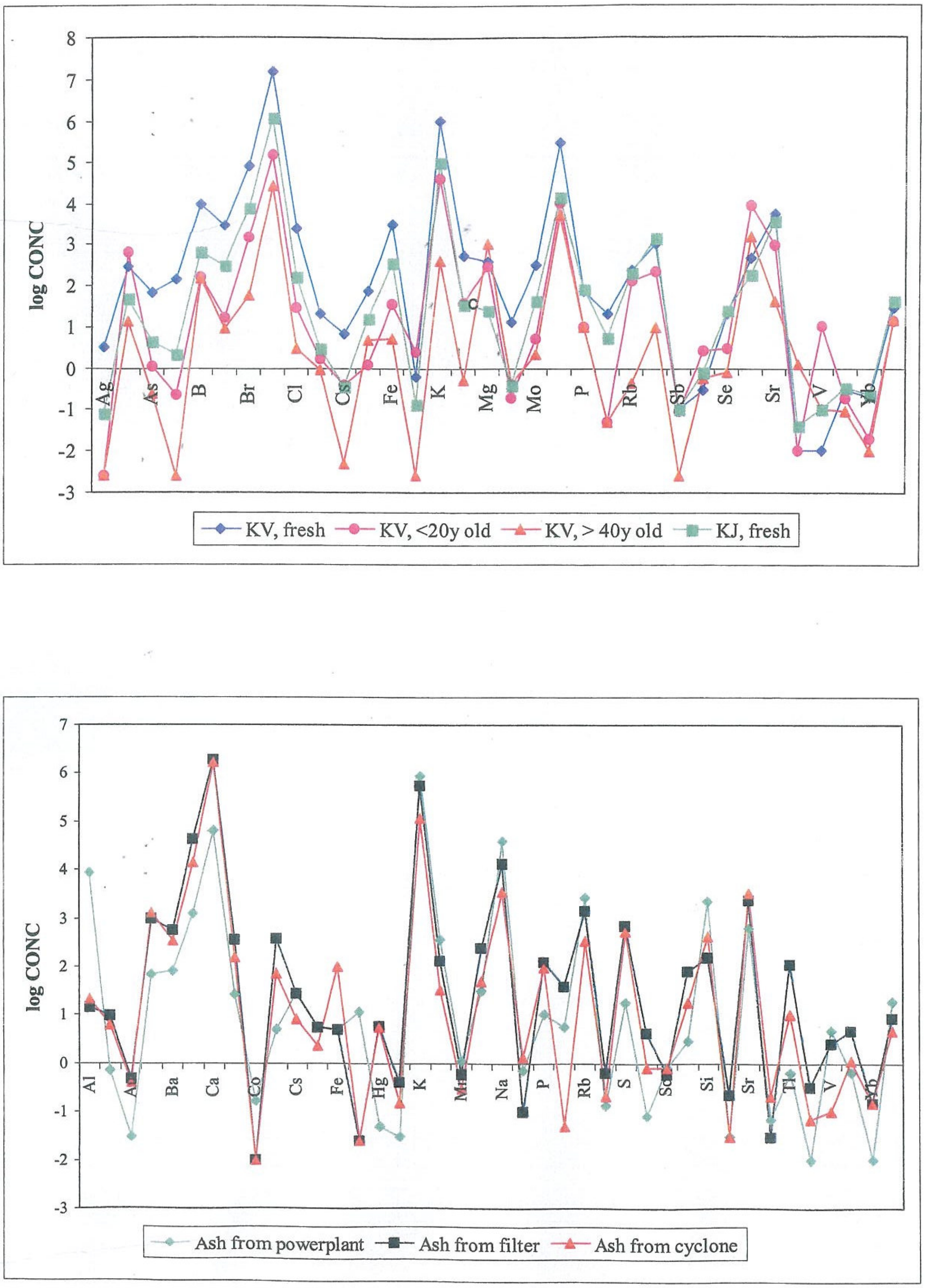


Fig. 6.3.1 Elements in the leachates of different types of waste

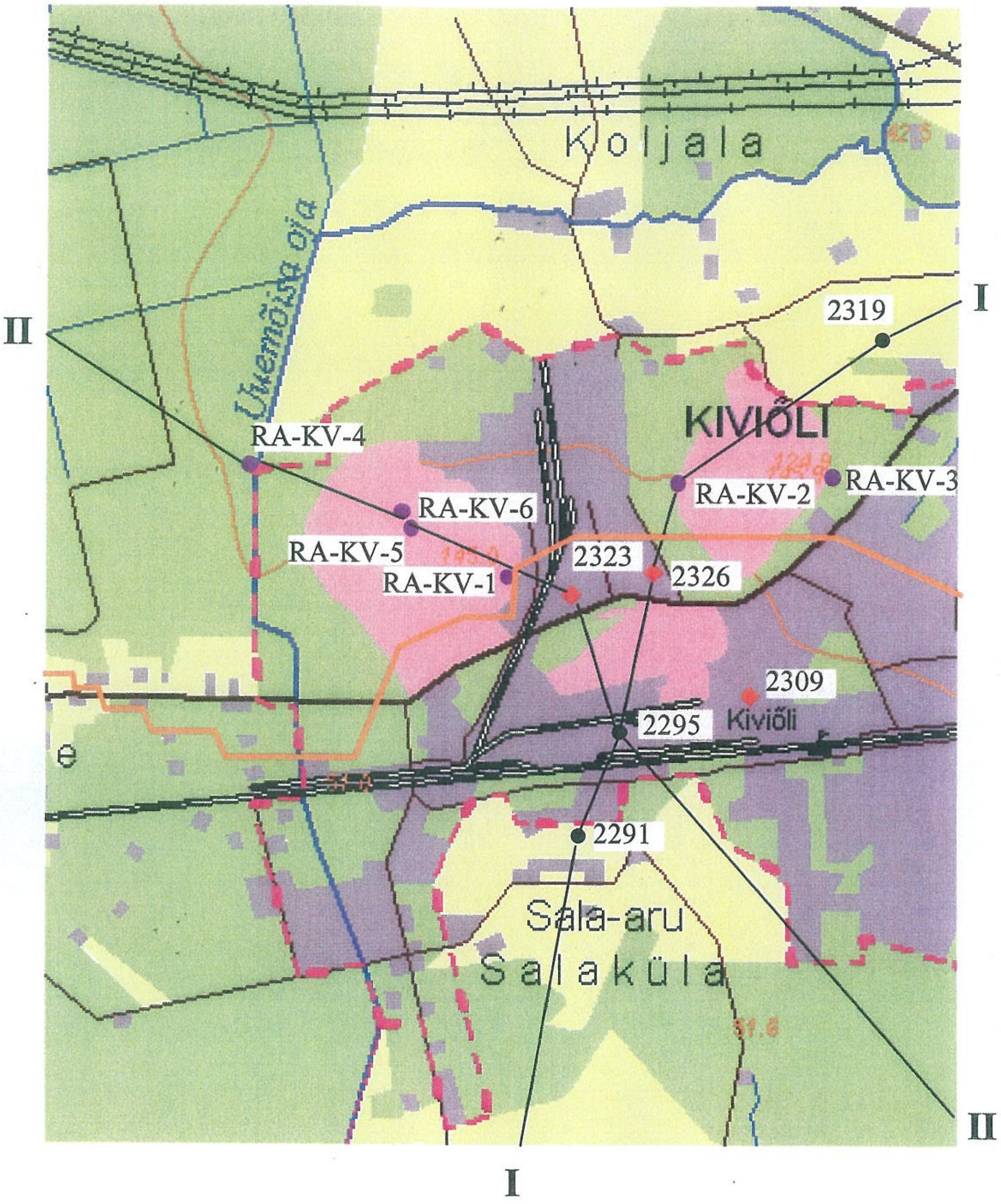
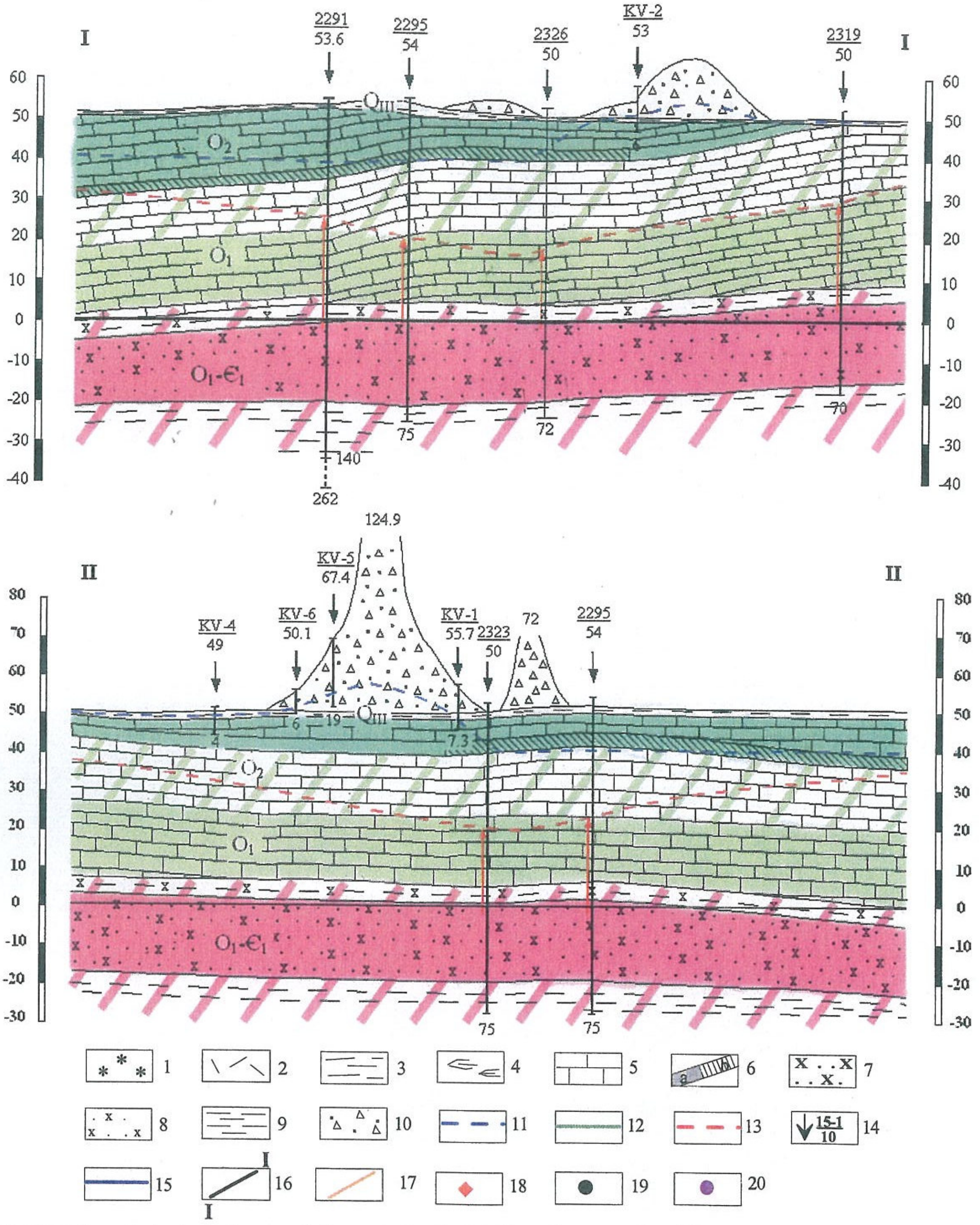


Fig. 7.3.1a Location of wells and geological sections of Kiviõli area



Explanation: 1- technical ground; 2- peat; 3- glacial lake siltstone, clay (Q); 4- clay moraine (Q); 5- carbonate rocks (limestone, marlstone, dolomite) (O_1+O_2 carbonate water complex); 6- oil shale (a- bed; b- outputted); 7- glauconite sandstone and Dictyonema oil shale (O_1, carbonate water complex and Ordovician-Cambrian aquifer; 8- sandstone and siltstone (O_1+C_1, Ordovician-Cambrian aquifer; 9- Cambrian clays; 10- ash and semi-coke mounds, altitude (m); 11- groundwater table; 12- static water table of carbonate water complex; 13- static (for Narva area) and dynamic (data on 2000 for Kiviõli and on 2003 years for Kohtla-Järve) water table of Ordovician-Cambrian aquifer; 14- borehole (well), number, altitude (m), depth (m); 15- water table of Narva reservoir (above sea level); 16- line of cross-section; 17-area there oil shale is outputted; 18- sampled wells; 19- wells used for the compilation of geological sections; 20- wells drilled in the frame of the project.

Fig. 7.3.1b Geological sections of Kiviõli area

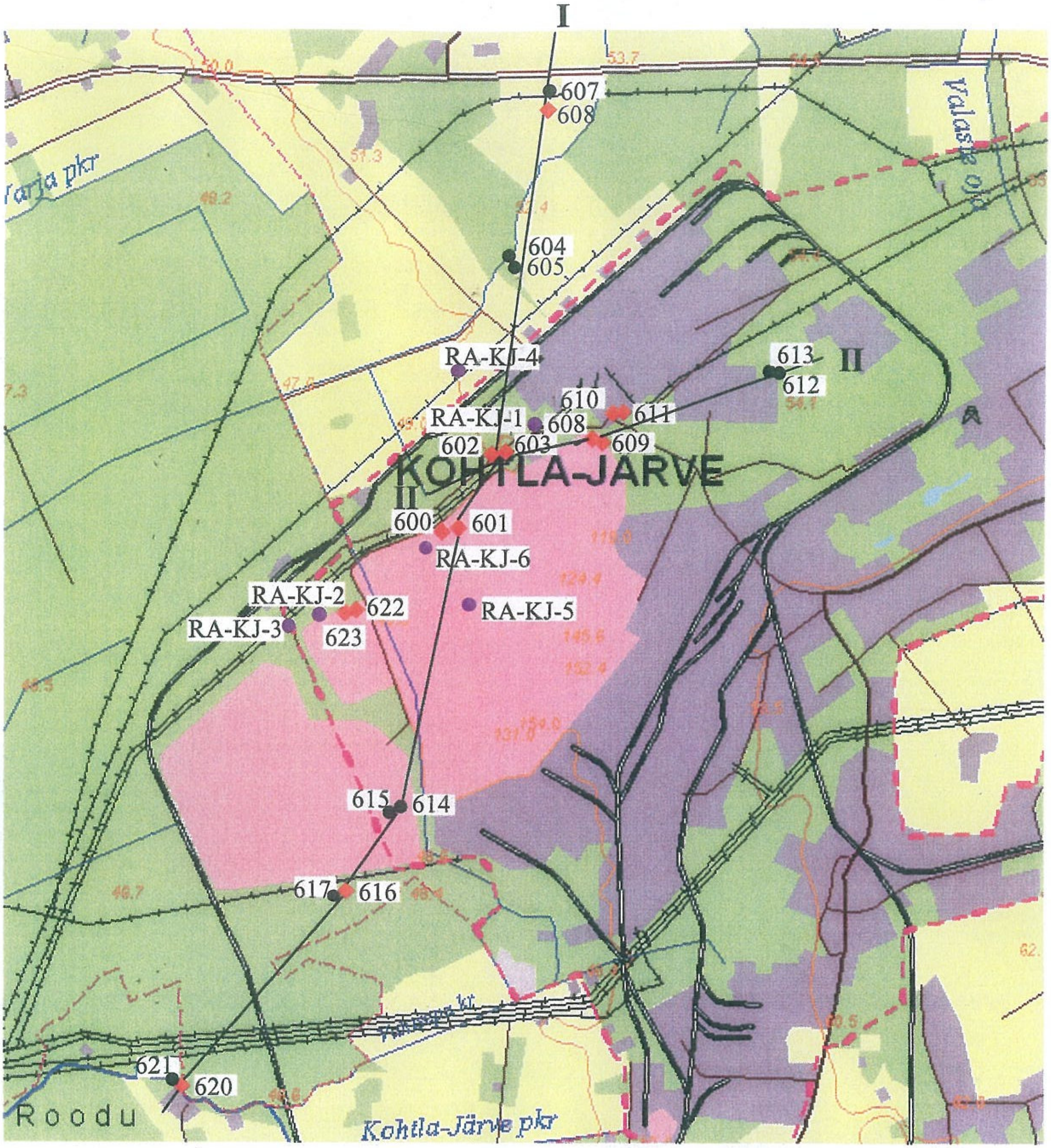


Fig. 7.4.1a Location of wells and geological sections of Kohtla-Järve area. See explanation on the Fig. 7.3.1b

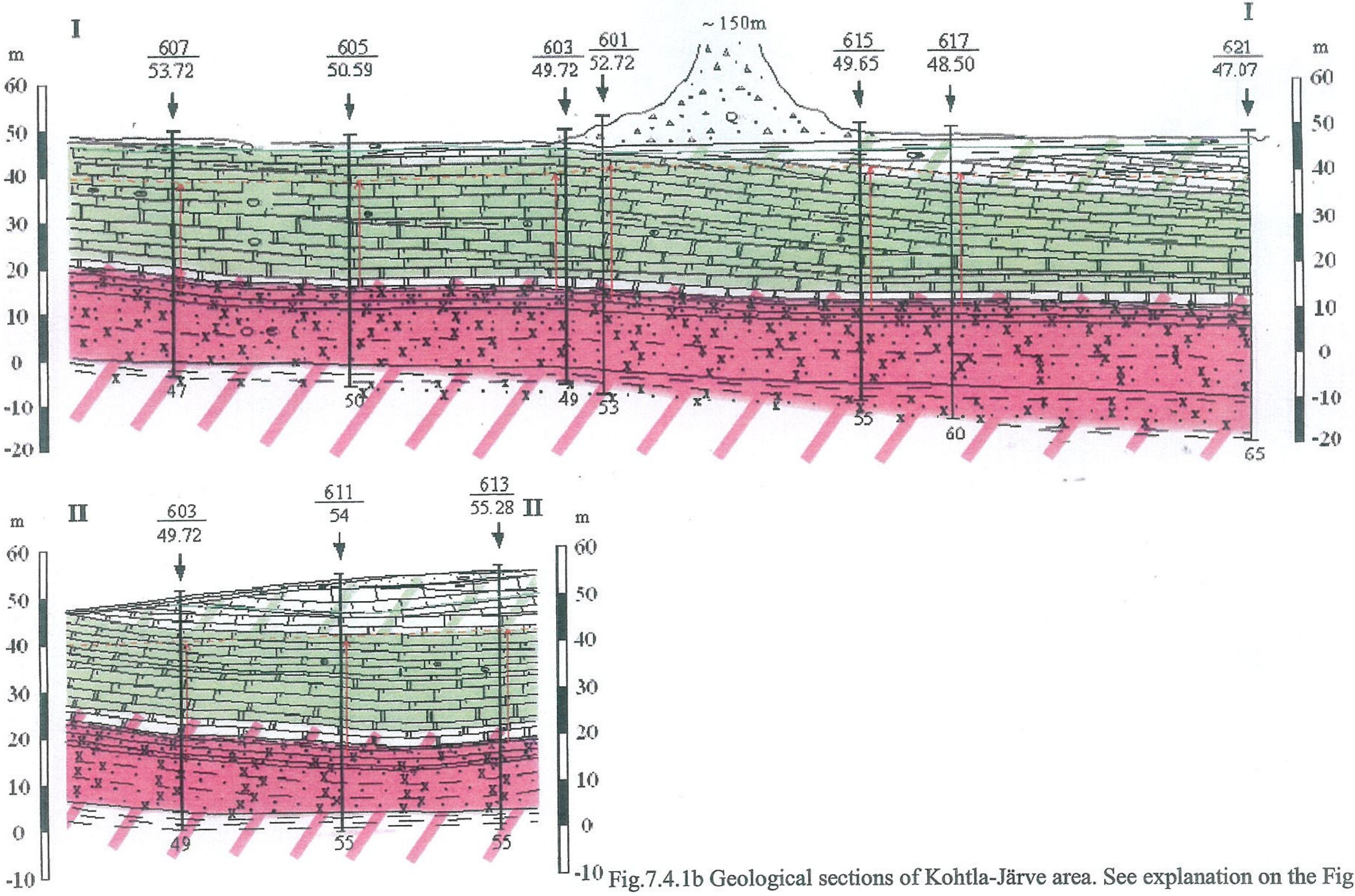


Fig.7.4.1b Geological sections of Kohtla-Järve area. See explanation on the Fig.7.3.1b

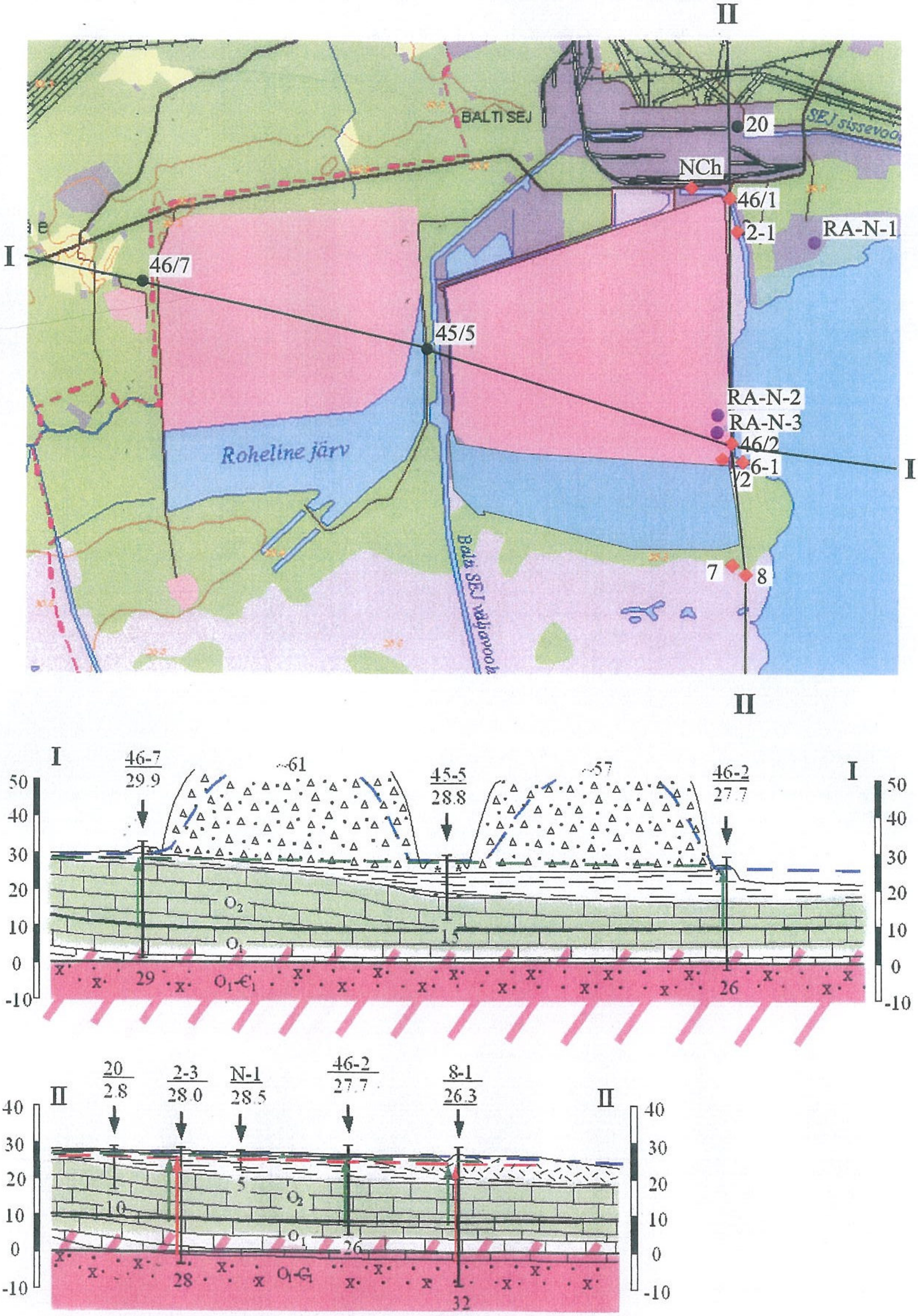
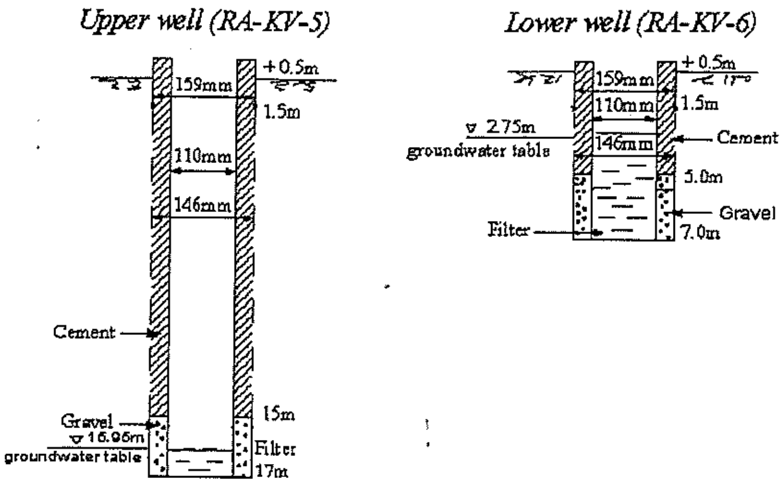


Fig. 7.6.1 Location of wells and geological sections of Narva area
See explanation on the Fig.7.3.1b

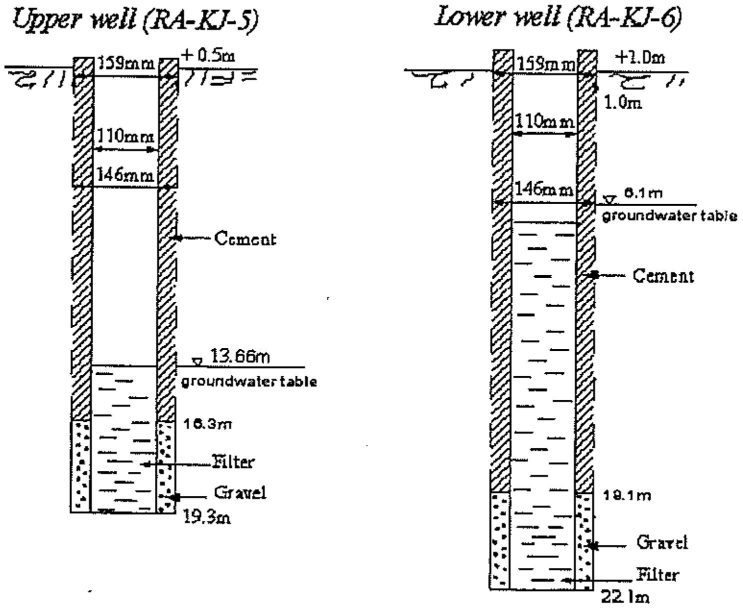
Kiviõli semi-coke landfill



Upper well (RA-KV-5)

Lower well (RA-KV-6)

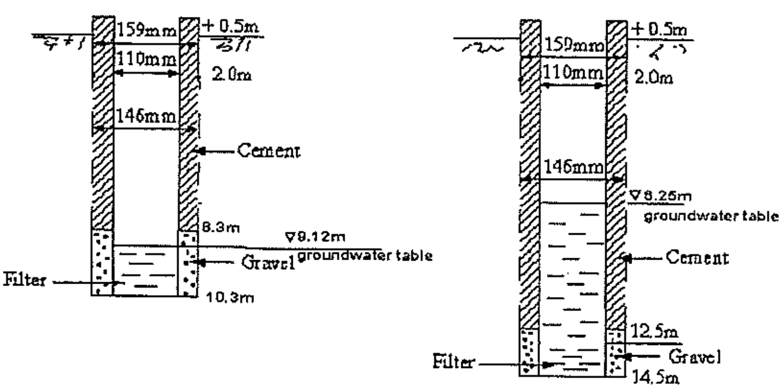
Kohtla-Järve semi-coke landfill



Upper well (RA-KJ-5)

Lower well (RA-KJ-6)

Narva ash plateau



Upper well (RA-N-2)

Lower well (RA-N-3)

Fig. 8.2 Construction of the monitoring wells drilled for slug test. Scale 1:200

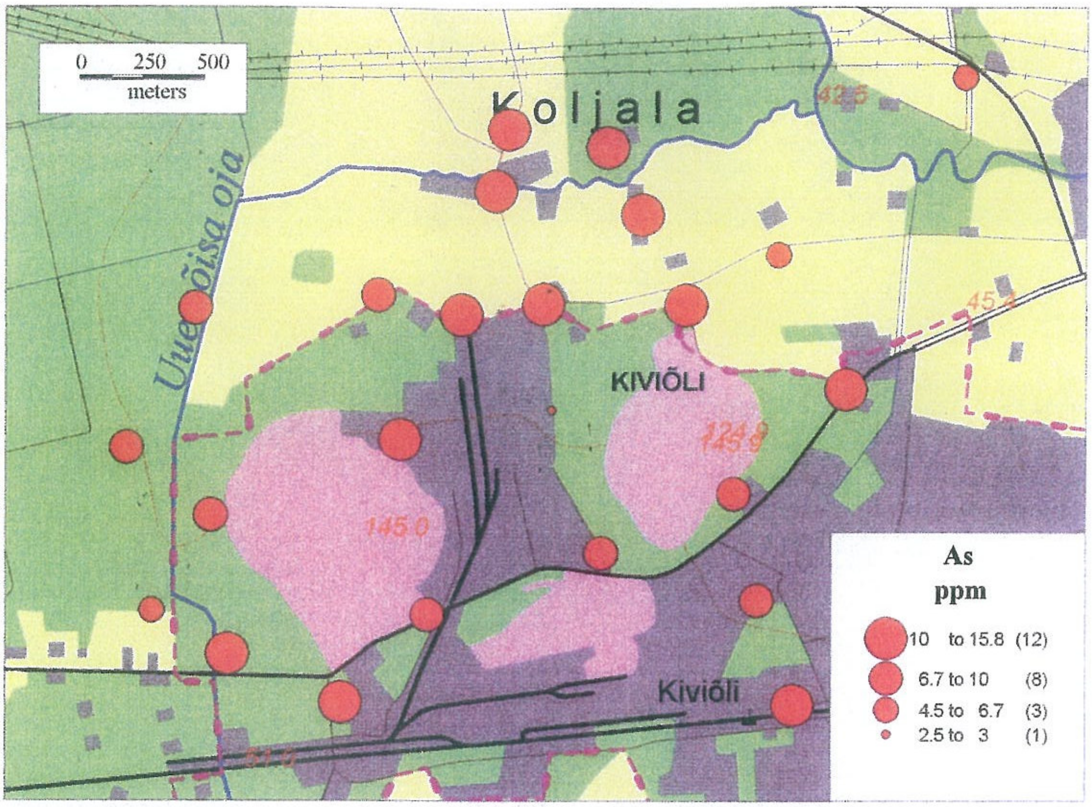


Fig. 9.2.1.1 As in topsoil in Kiviõli area

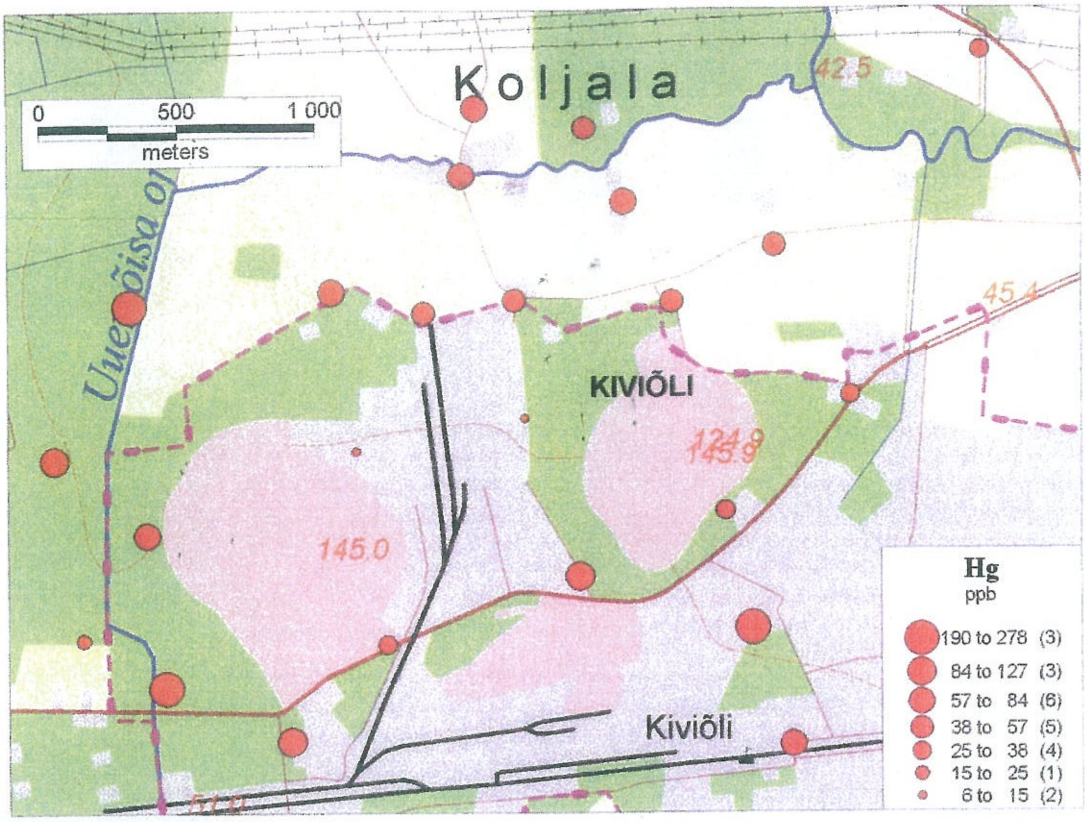


Fig. 9.2.1.2 Hg in topsoil in Kiviõli area

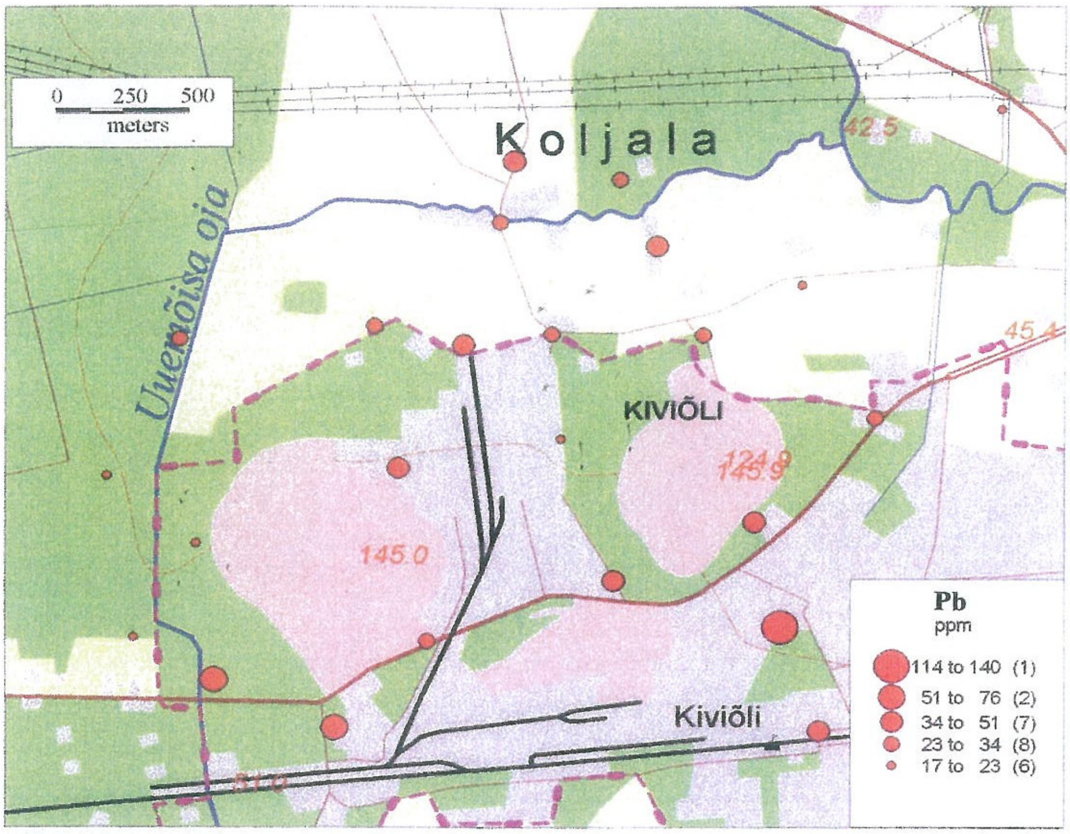


Fig. 9.2.1.3 Pb in topsoil in Kiviõli area

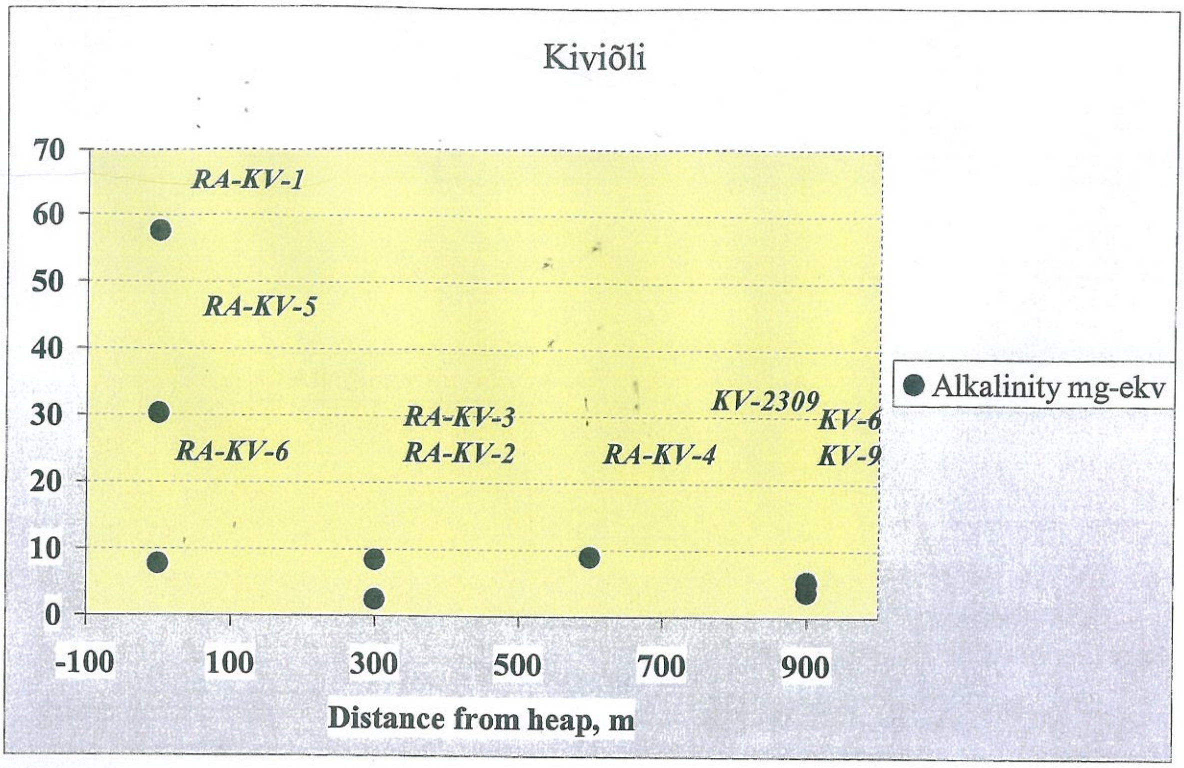


Fig. 9.2.3.1 Alkalinity values in the groundwater from the wells in Kiviõli

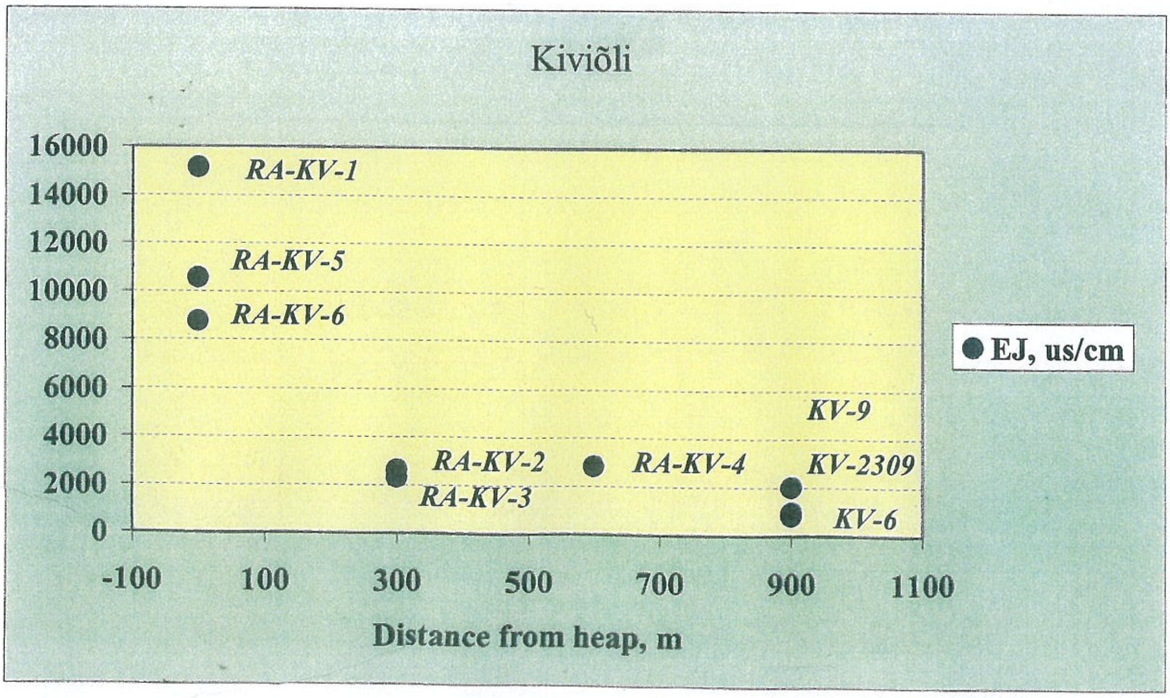


Fig. 9.2.3.2 Electric conductivity values in the groundwater from the wells in Kiviõli

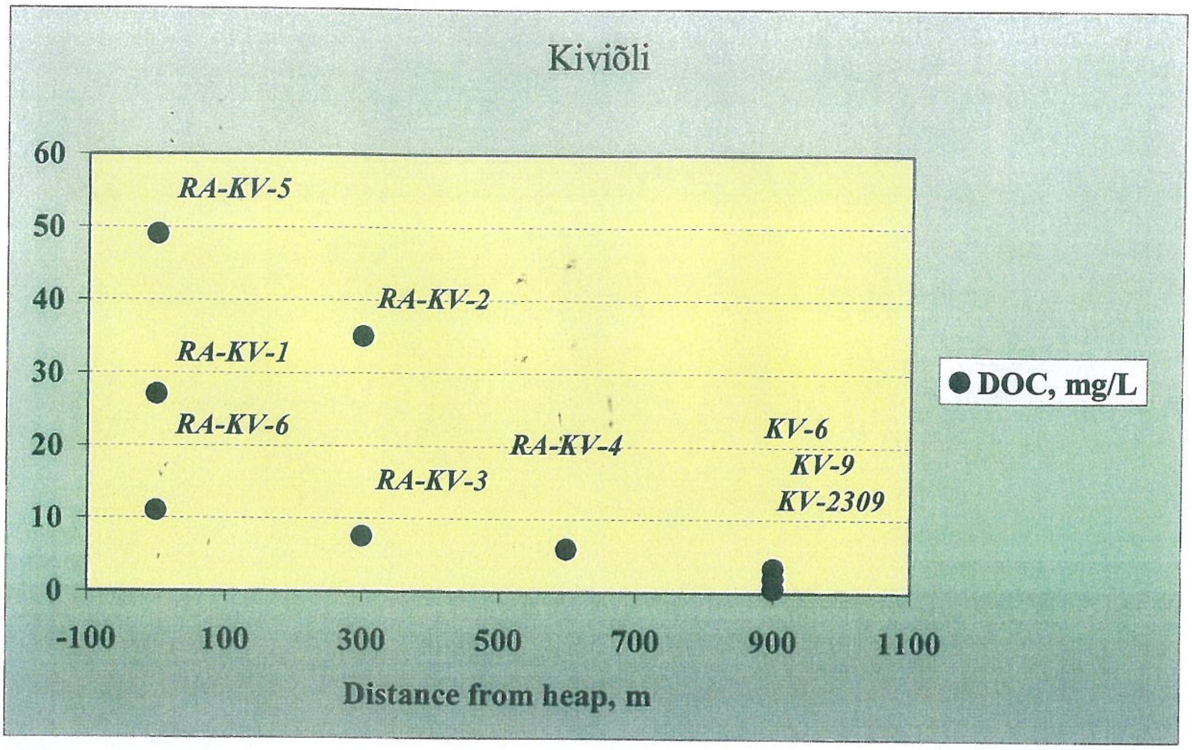


Fig. 9.2.3.3 DOC values in groundwater from the wells in Kiviõli

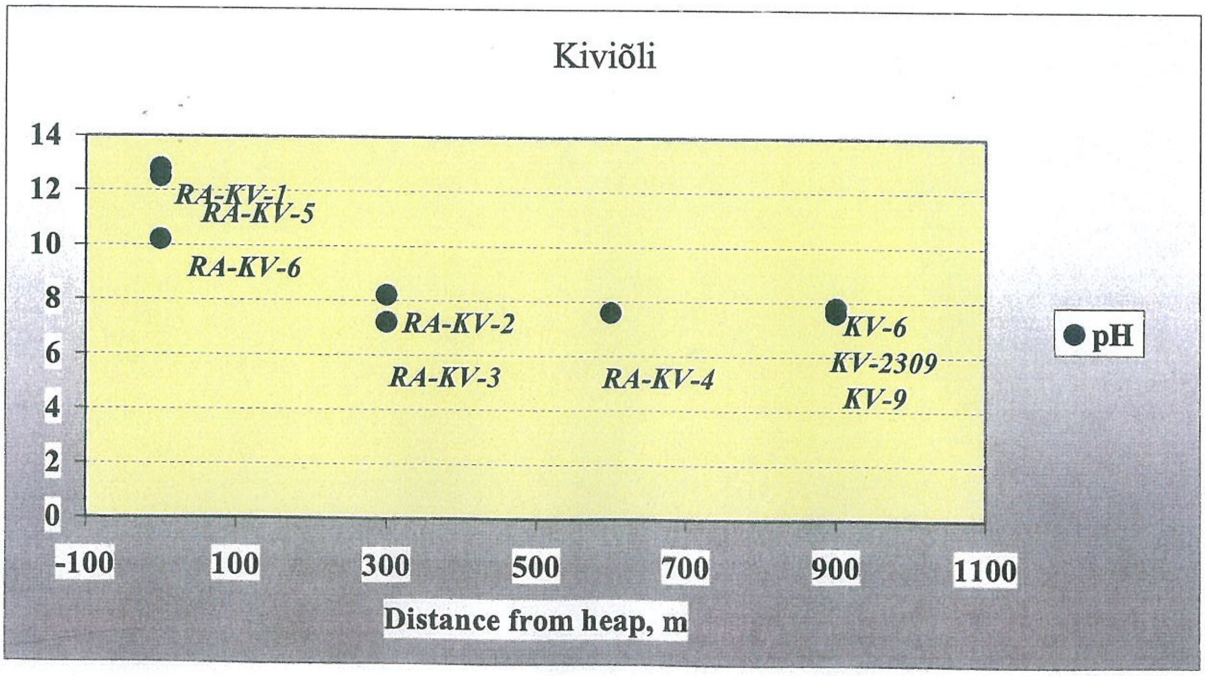


Fig. 9.2.3.4 pH values in groundwater from the wells in Kiviõli

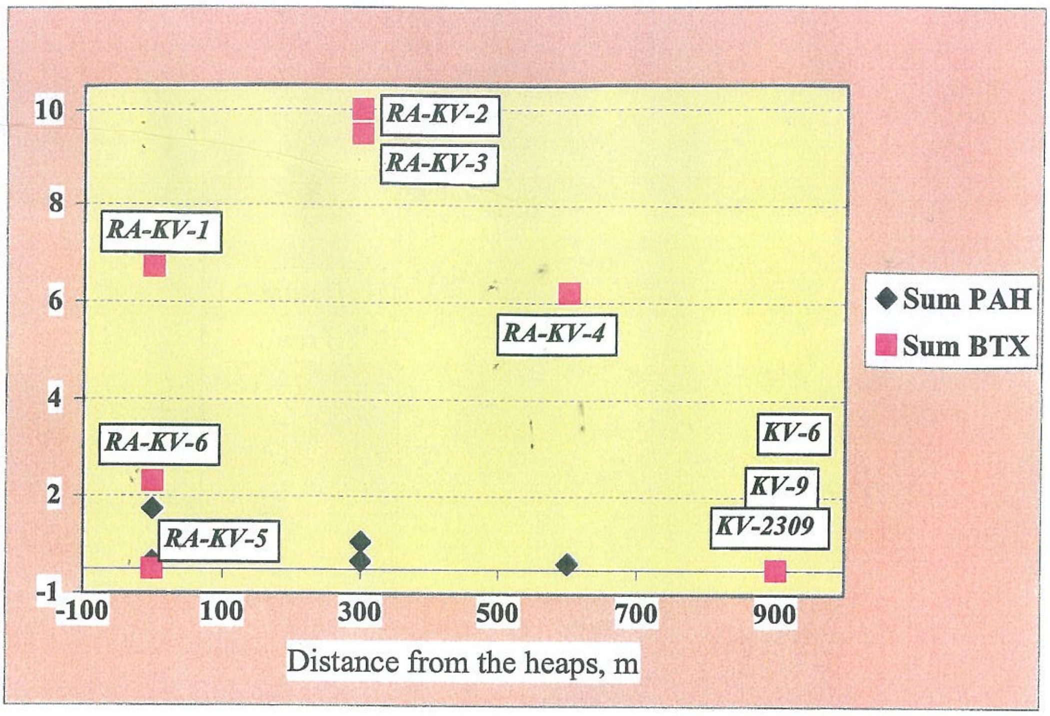


Fig. 9.2.3.5 PAH and BTX (μg/l) in groundwater from wells in Kiviõli

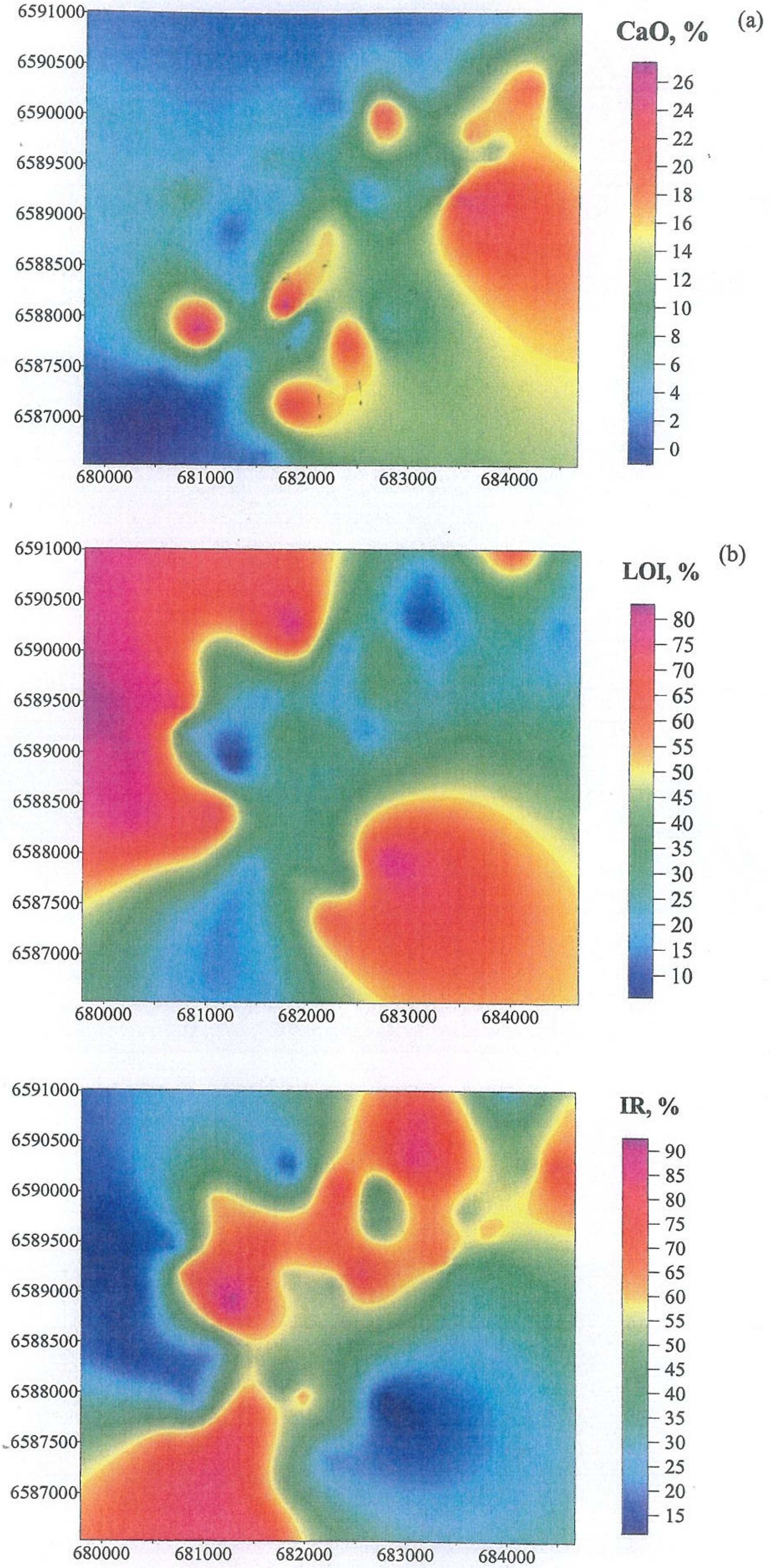


Fig. 9.3.1.1 CaO (a), LOI (b) and IR (c) in topsoil in Kohtla-Järve area

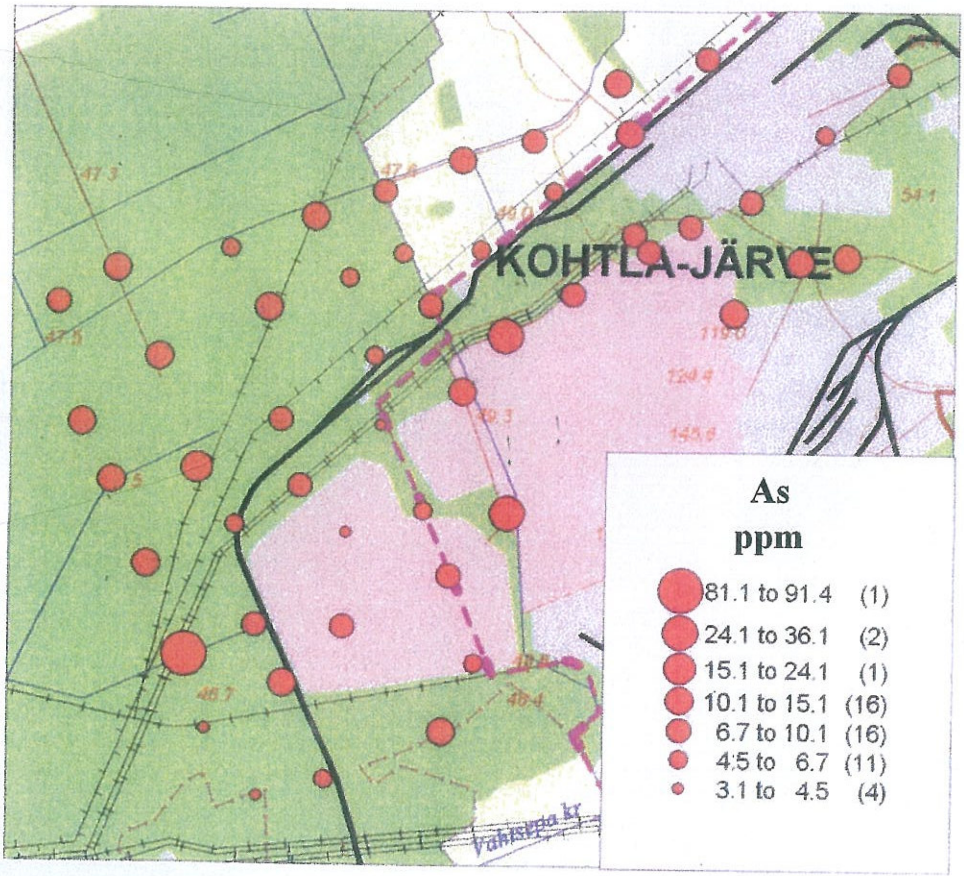


Fig. 9.3.1.2 As in topsoil in Kohtla-Järve area

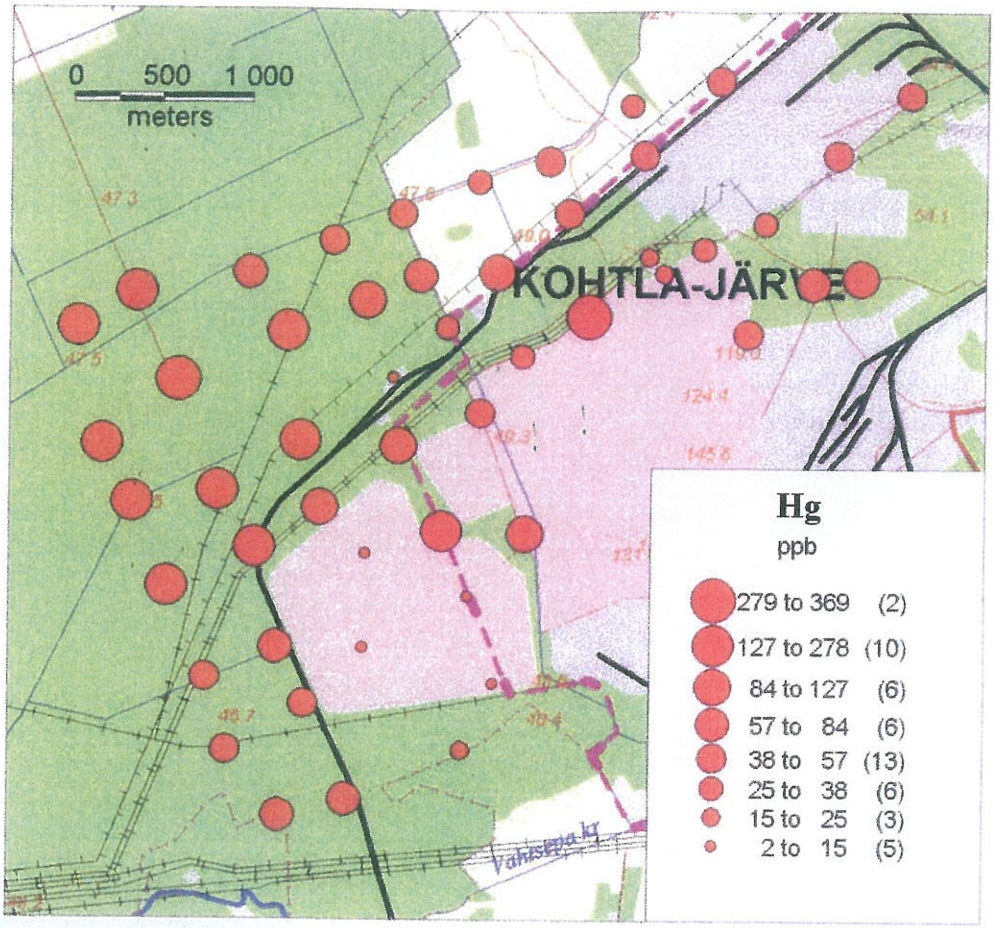


Fig. 9.3.1.3 Hg in topsoil in Kohtla-Järve area

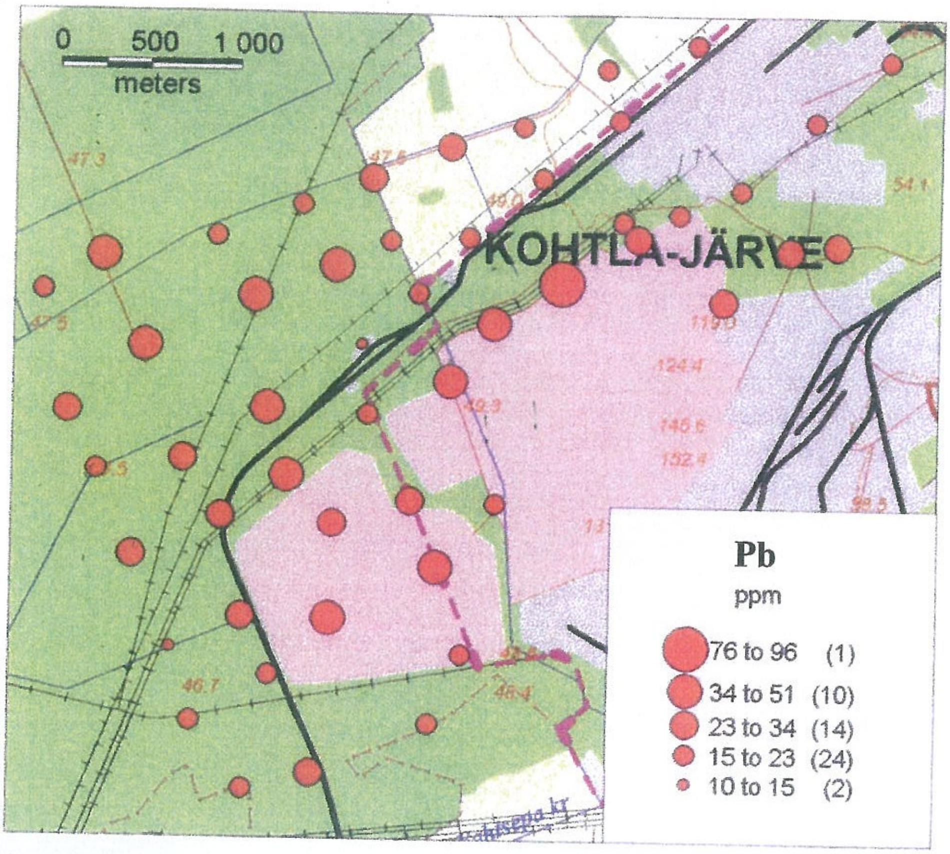


Fig. 9.3.1.4 Pb in topsoil in Kohtla-Järve area

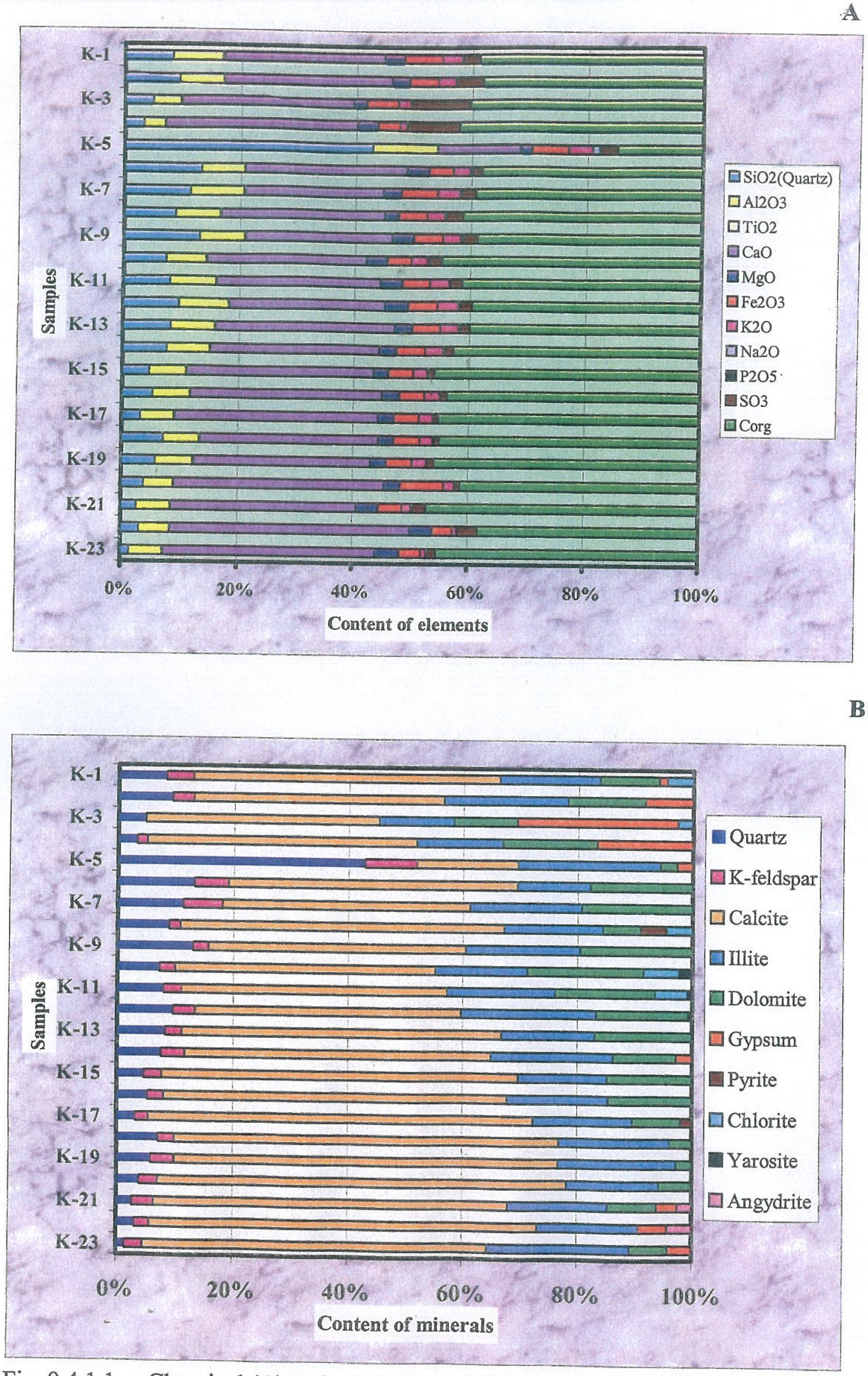


Fig. 9.4.1.1 Chemical (A) and mineralogical (B) composition of the burned oil shale from Kukruse waste heap

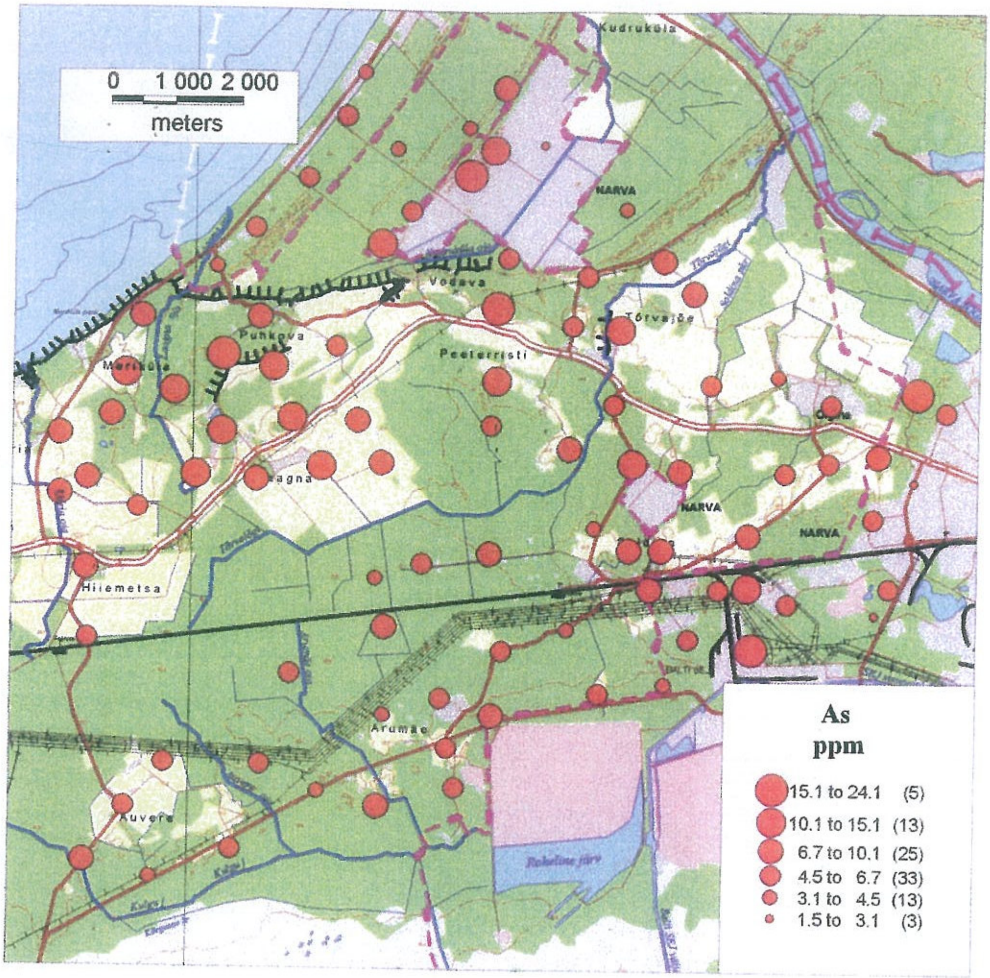


Fig. 9.5.1.1 As in topsoil in Narva area

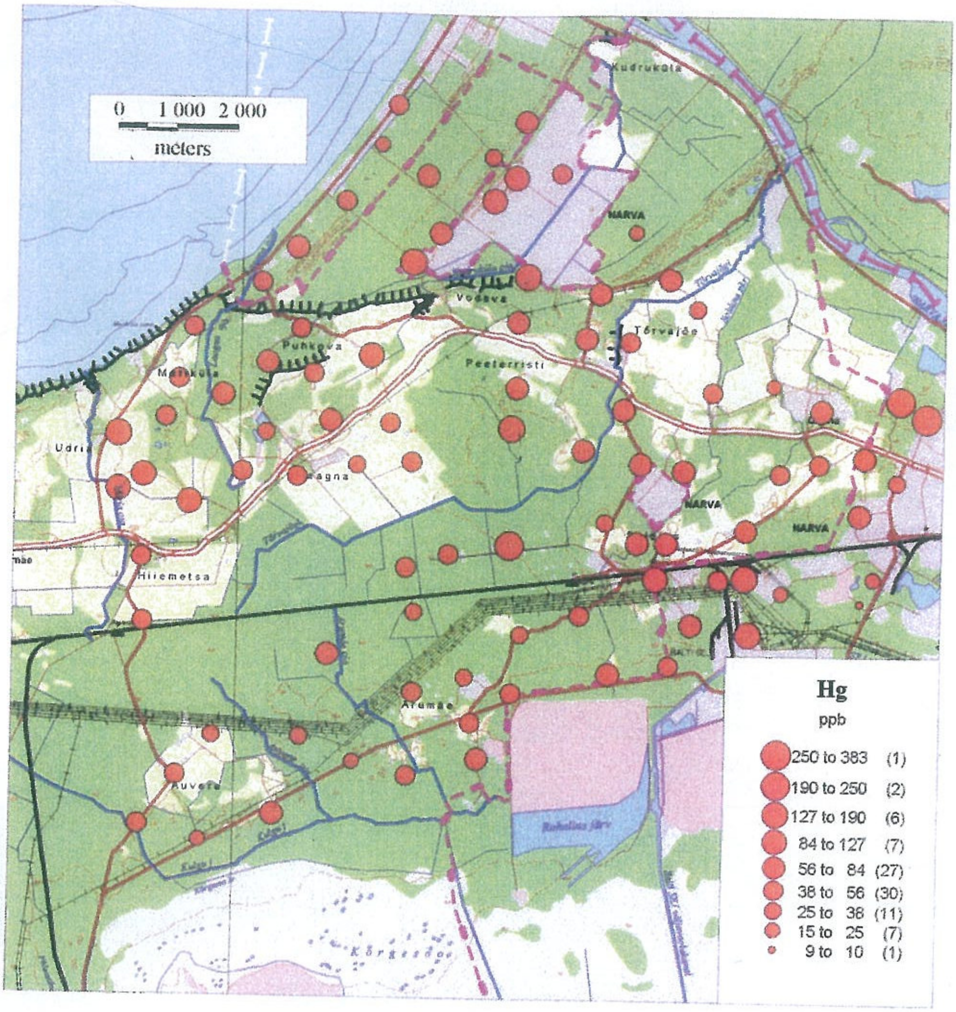


Fig. 9.5.1.2 Hg in topsoil in Narva area

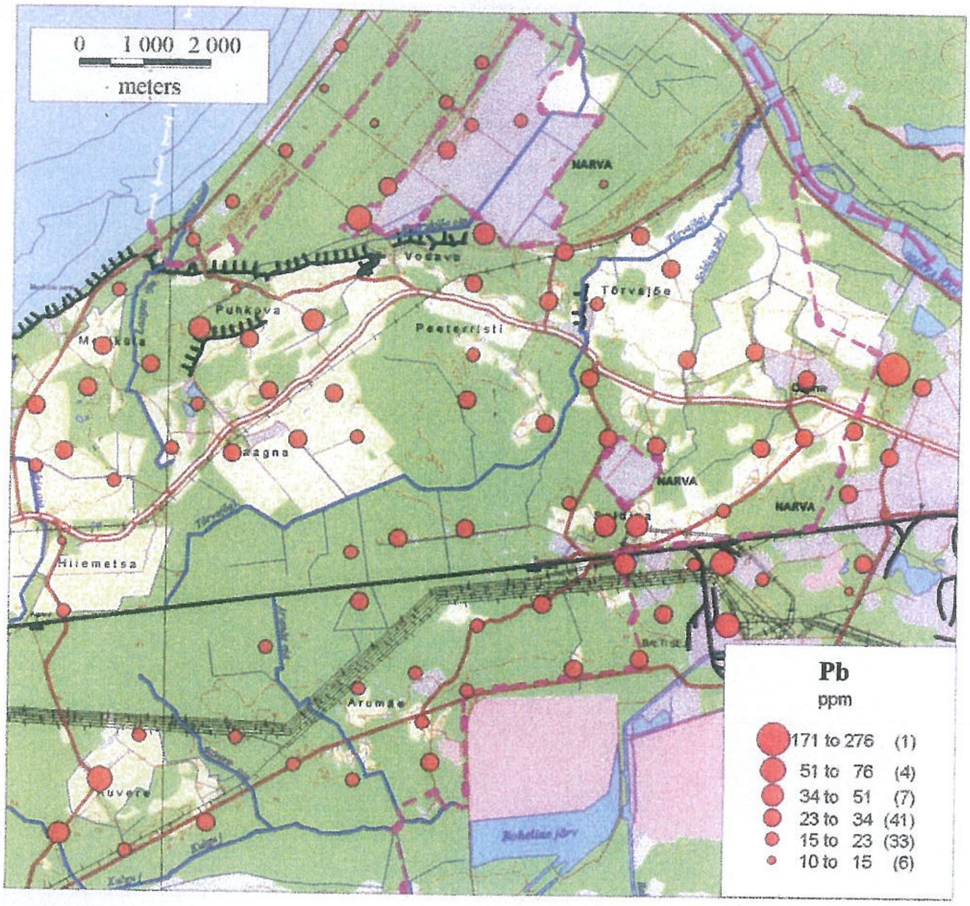
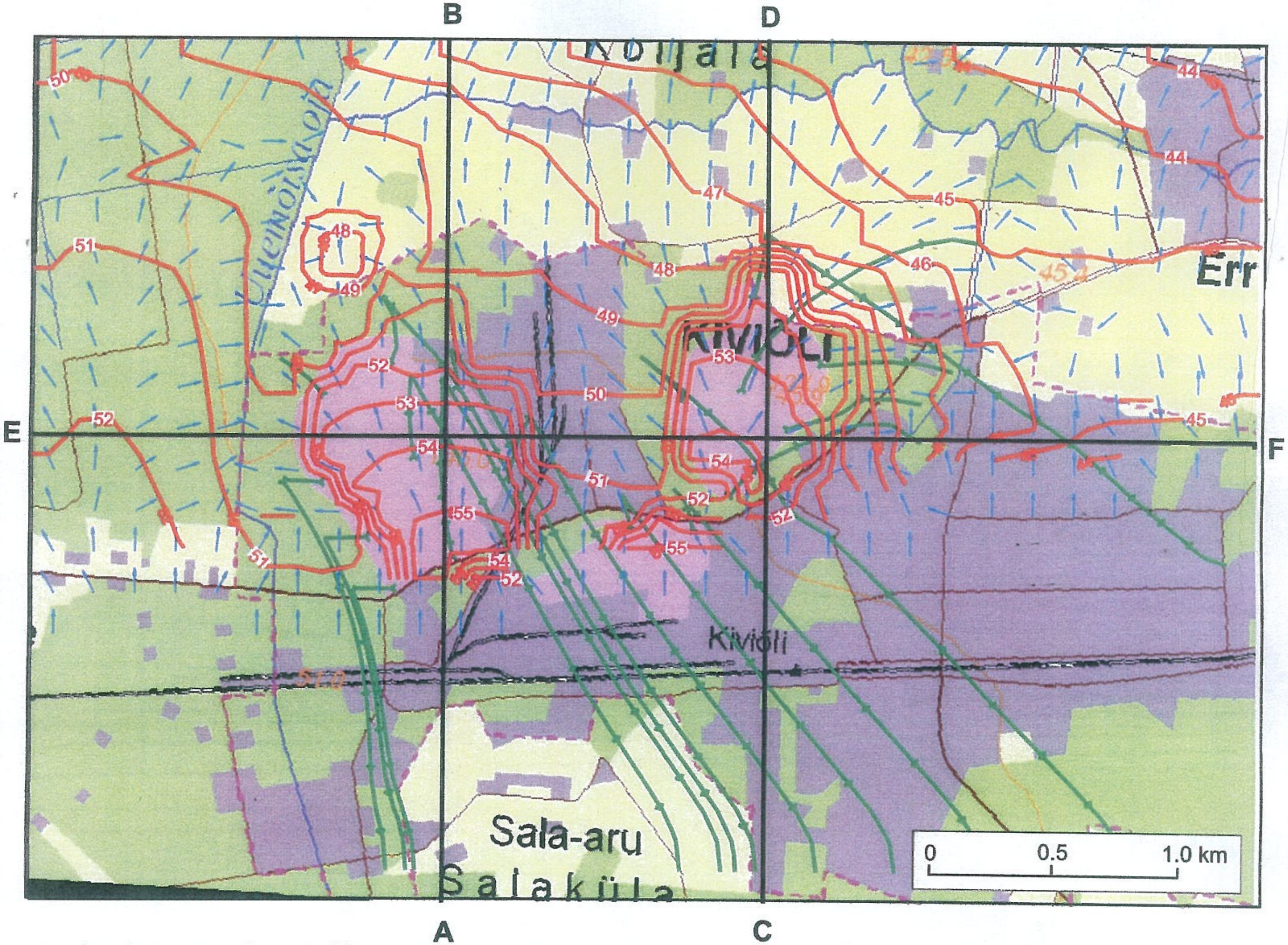


Fig. 9.5.1.3 Pb in topsoil in Narva area

Fig. 11 The meadowsweet (*Filipendula ulmaria*)



The distance between markers (green arrows) on a pathline is equal to 10 years of the groundwater movement. The pink areas on the map are the semi-coke landfills

Fig 12.3.1 Groundwater table (red isolines showing the absolute elevation, m), flow directions (blue arrows), and pathlines (green) for the upper layer of the Kiviõli model.

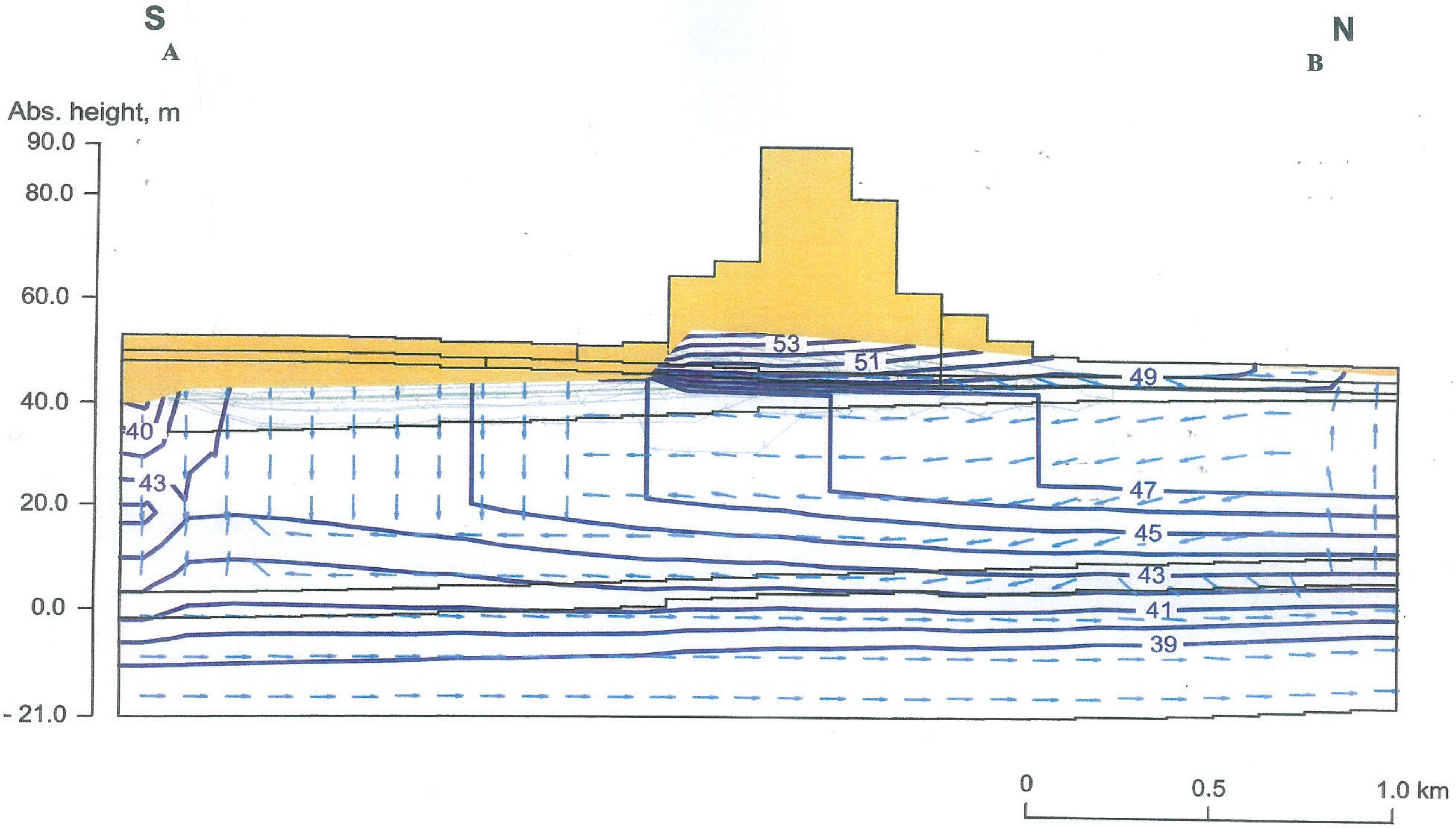


Fig 12.3.2 Groundwater head (dark blue isolines showing the absolute elevation, m), flow directions (blue arrows), and pathlines (green) for the section A-B of the Kiviõli model

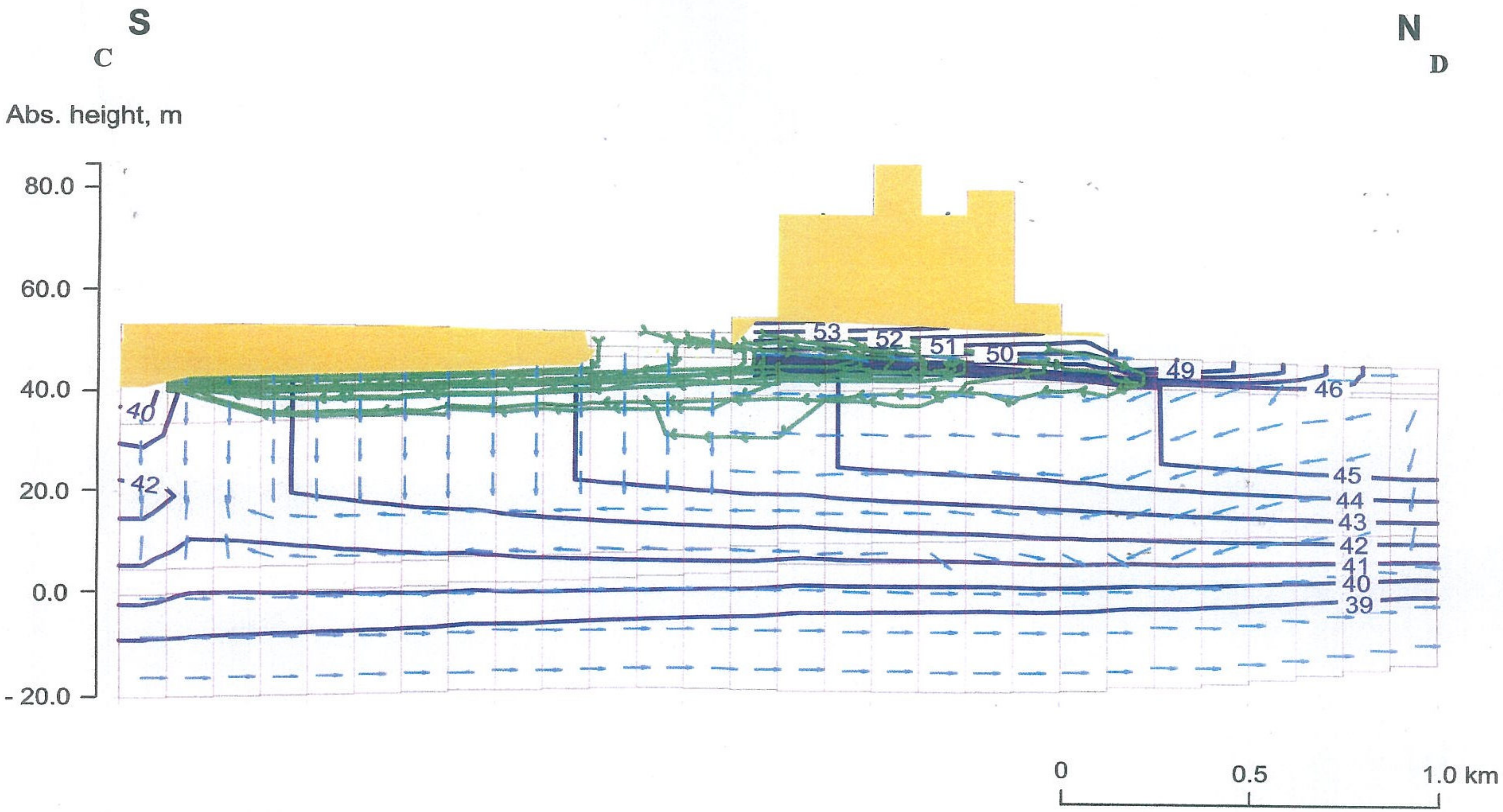


Fig.12.3.3 Groundwater head, flow directions and pathlines for the section C-D of the Kiviõli model. For explanation of signs see Fig. 12.3.2. The distance between markers (green arrows) on a pathline is equal to 10 years of the groundwater movement. The unsaturated zone is yellow

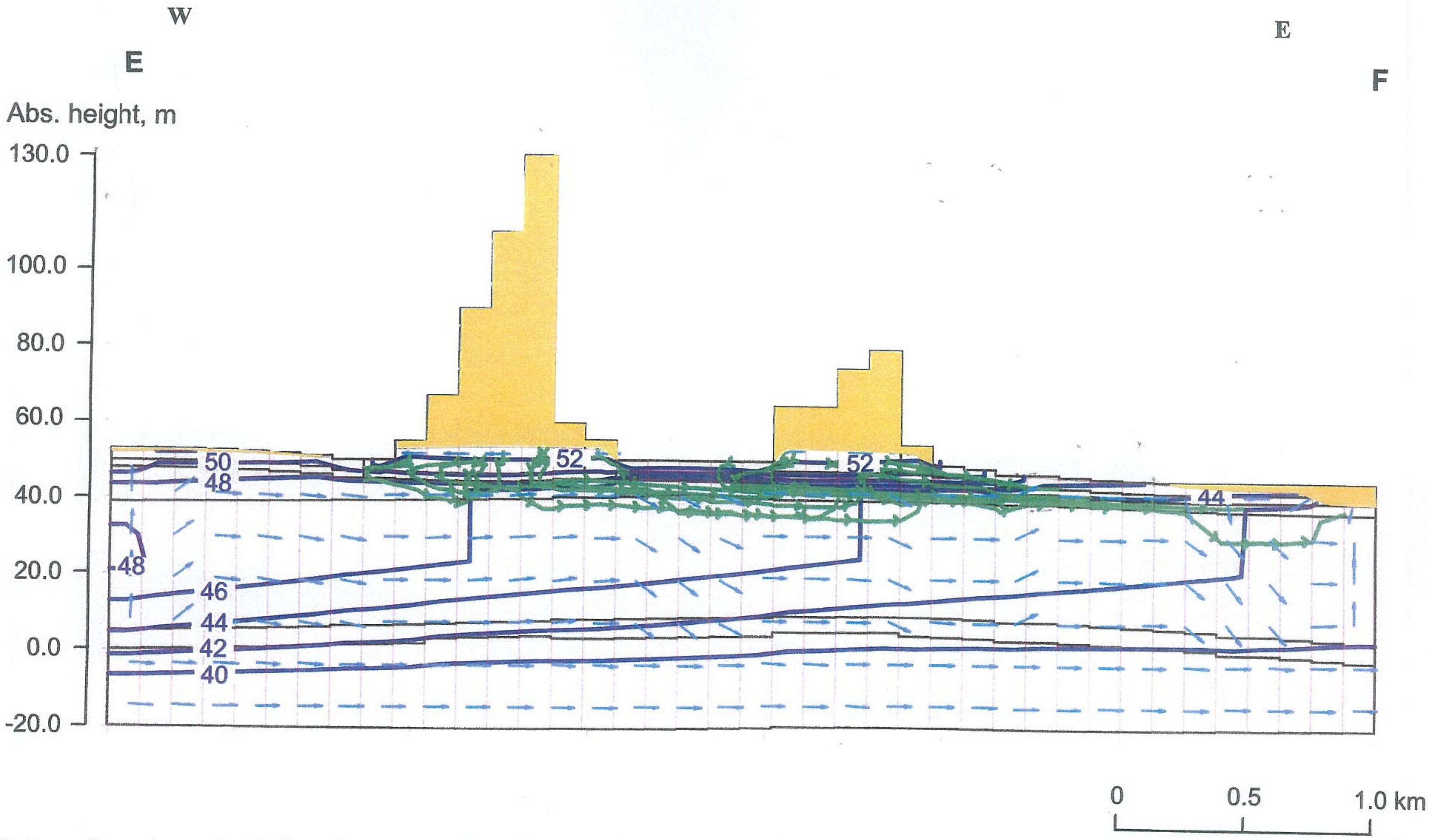


Fig.12.3.4 Groundwater head, flow directions, and pathlines for the section E-F of the Kiviõli model. For explanation of signs see Fig. 12.3.2

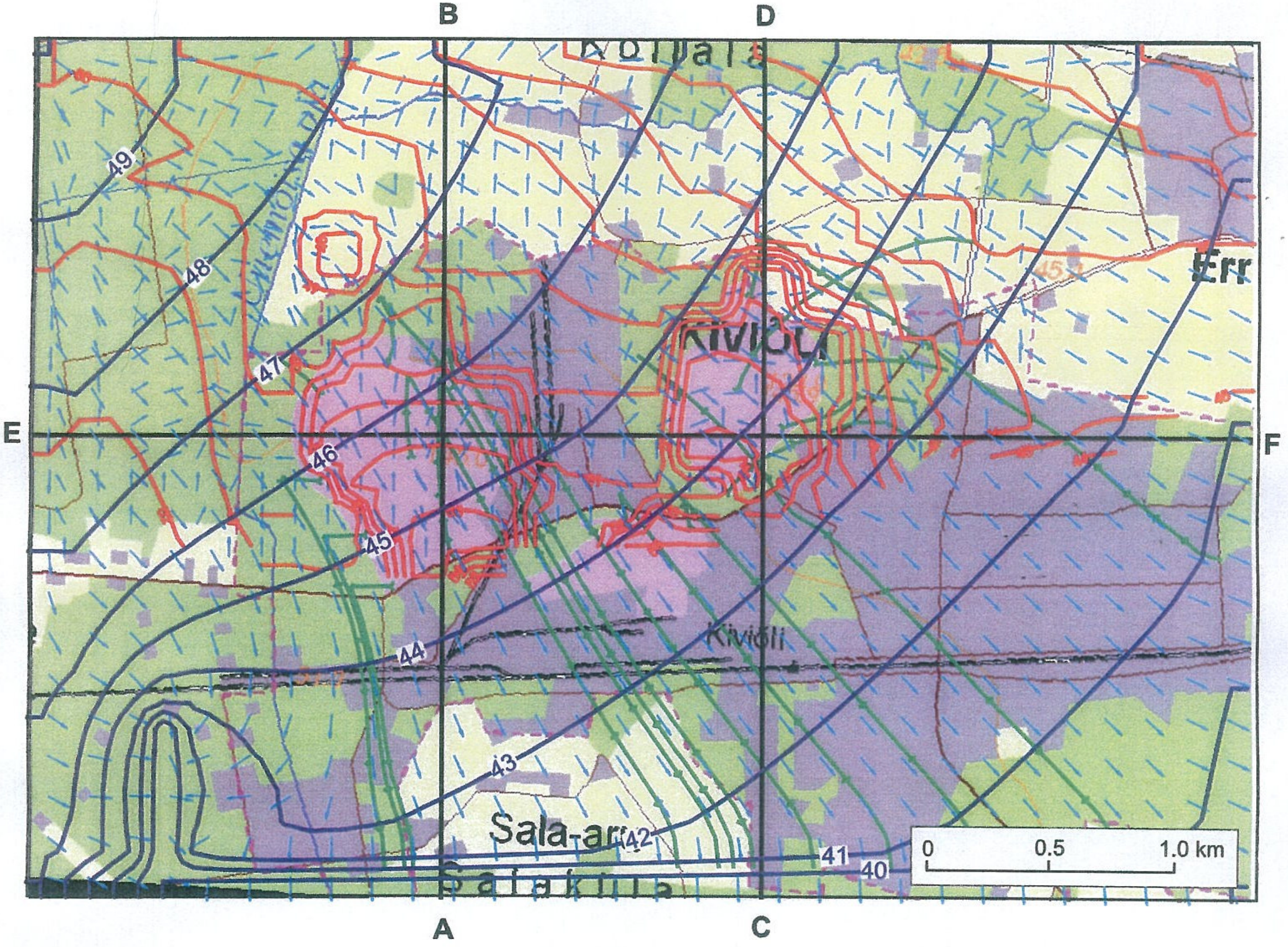
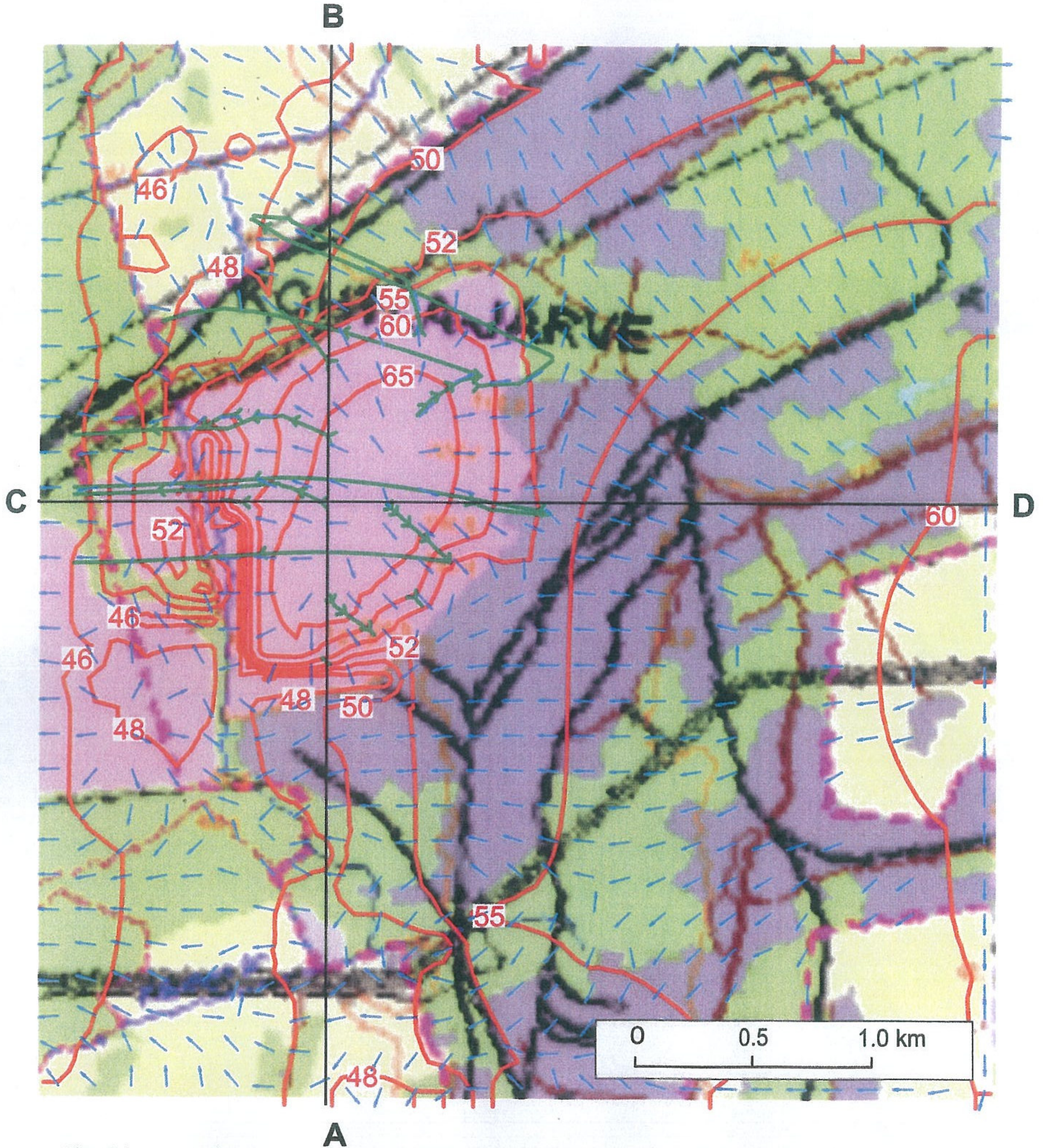


Fig 12.3.5 Groundwater head (dark blue isolines showing the absolute elevation, m), flow directions, and pathlines for the 3rd layer (the Ordovician carbonate bedrock) of the Kiviõli model. For explanation of signs see Fig. 12.3.1



The pink areas on the map are the ash and semi-coke heaps. For explanation of signs see Fig. 12.3.1

Fig 12.4.1 Groundwater table, flow directions, and pathlines for the upper layer of the Kohtla-Järve model

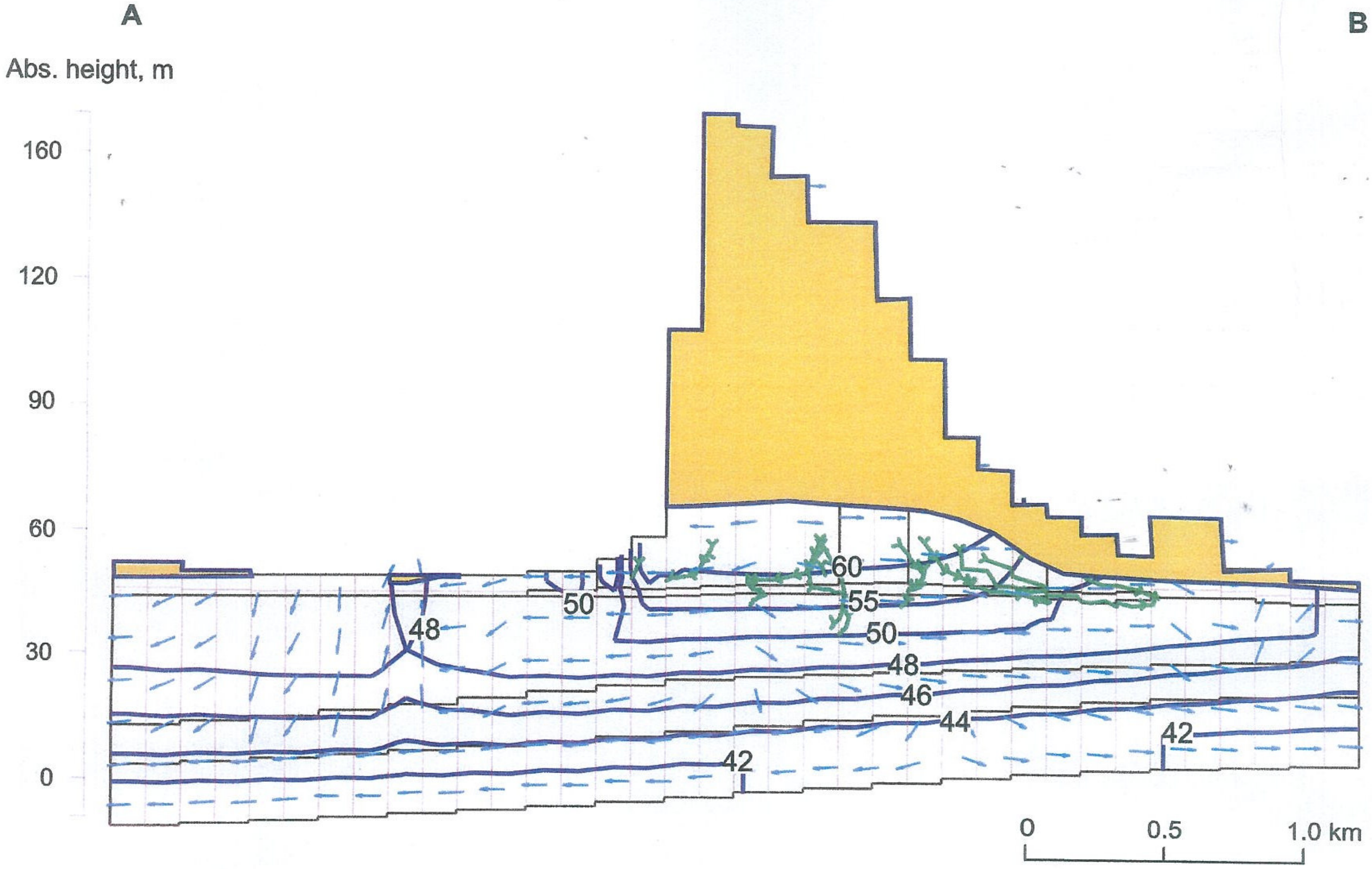


Fig.12.4.2 Groundwater head, flow directions, and pathlines for the section A-B of the Kohtla-Järve model. For explanation of signs see Fig. 12.3.3

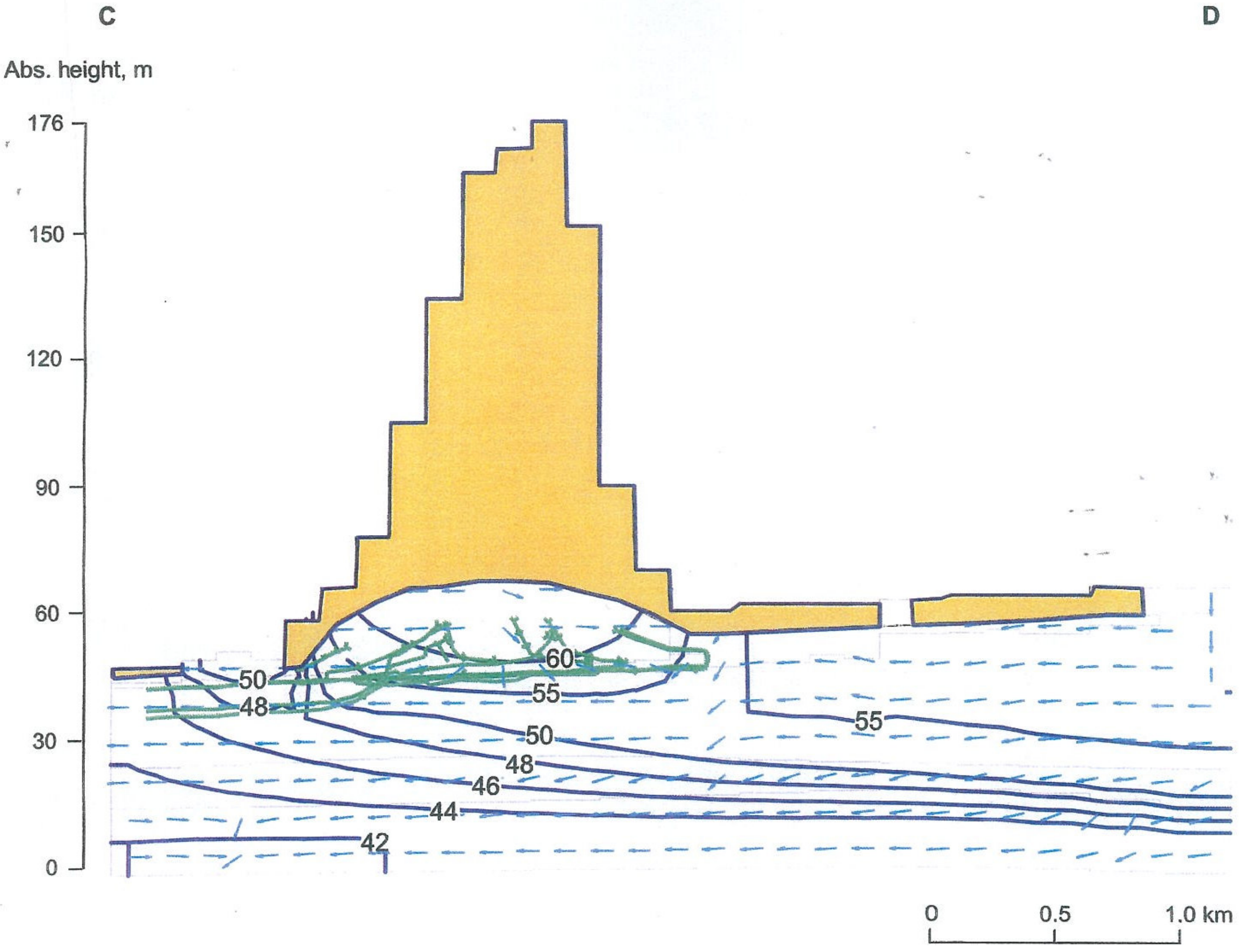
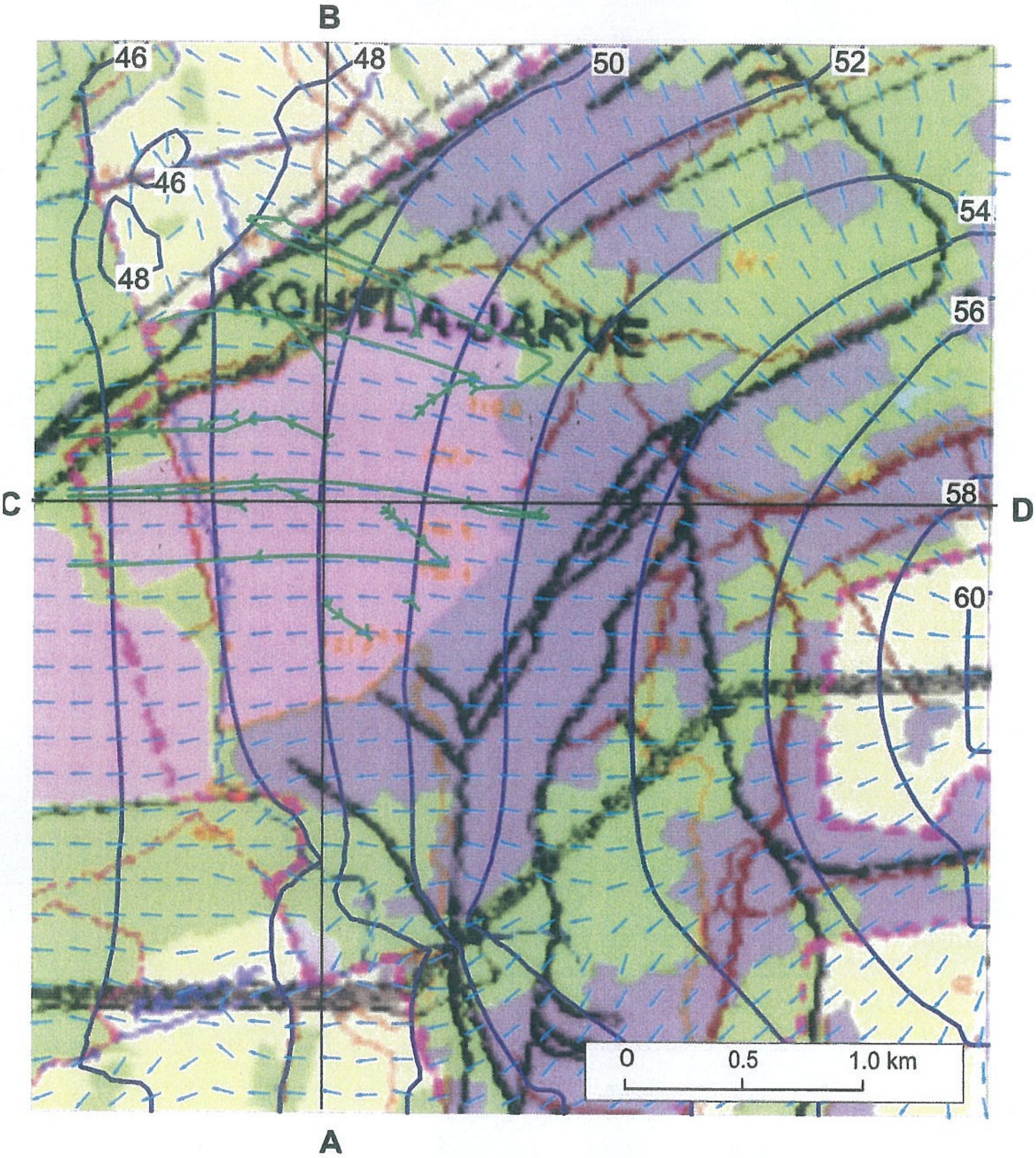
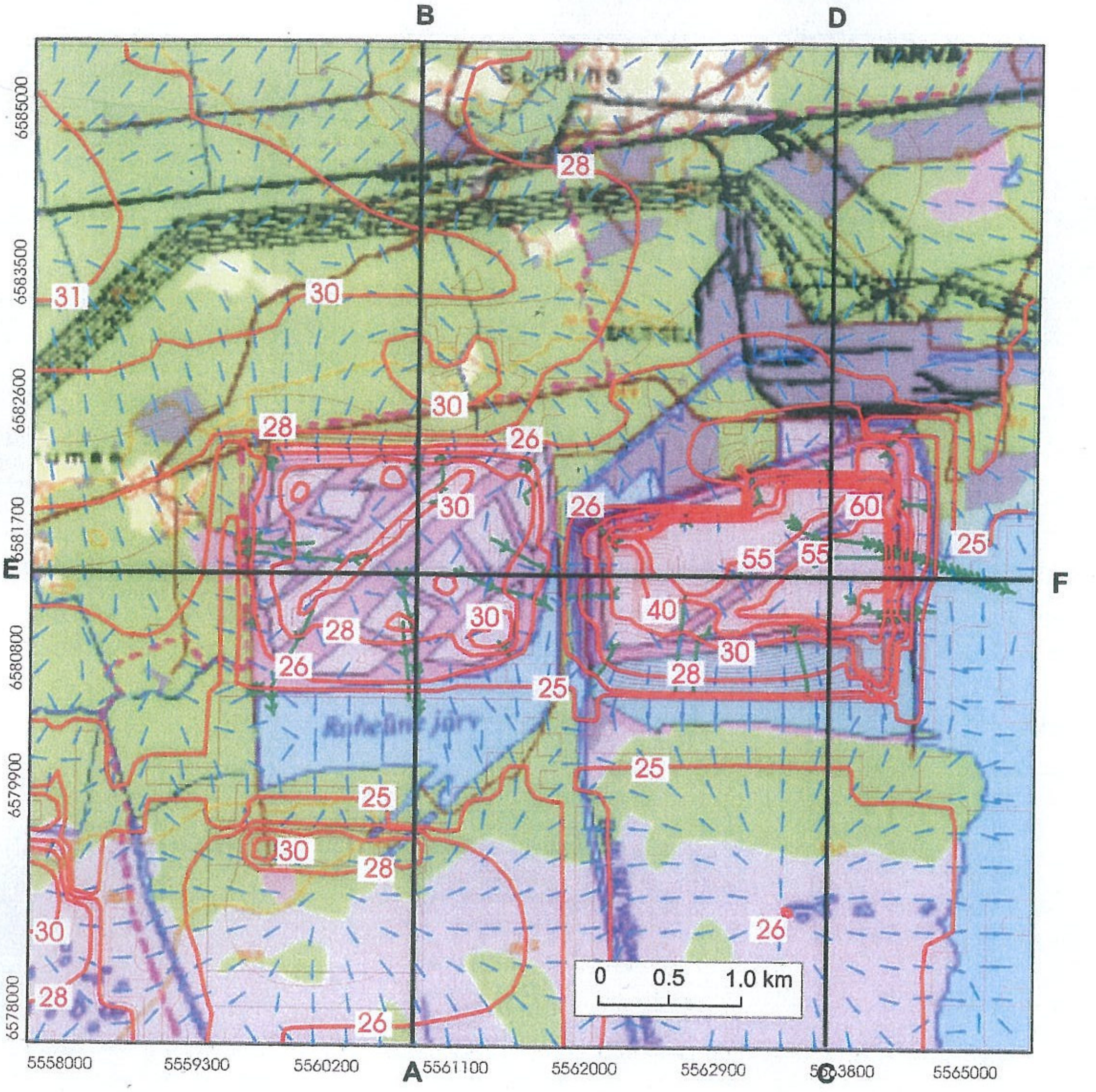


Fig.12.4.3 Groundwater head, flow directions, and pathlines for the section C-D of the Kohtla-Järve model. For explanation of signs see Fig. 12.3.3



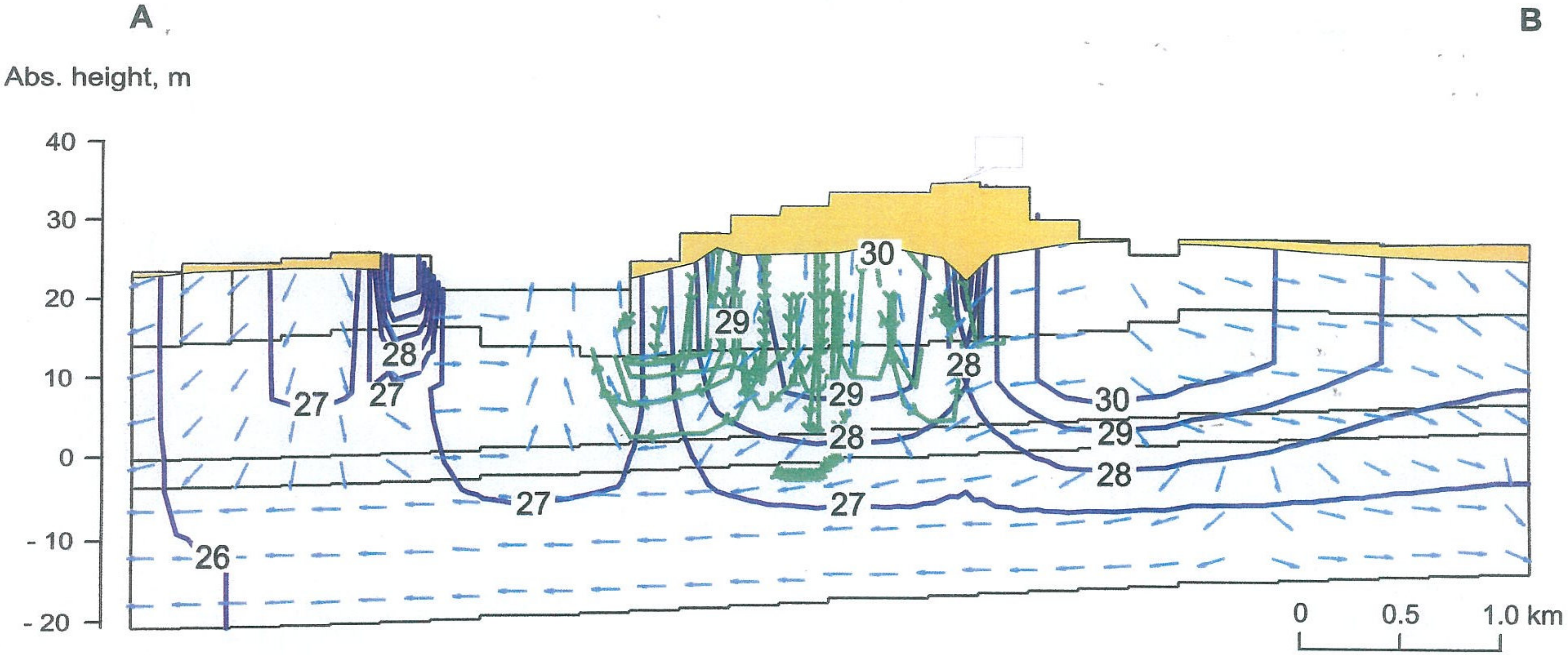
For explanation of signs see Fig. 12.3.1 and 12.3.5

Fig.12.4.4 Groundwater head, flow directions, and pathlines for the 3rd layer (the Ordovician carbonate bedrock) of the Kohtla-Järve model



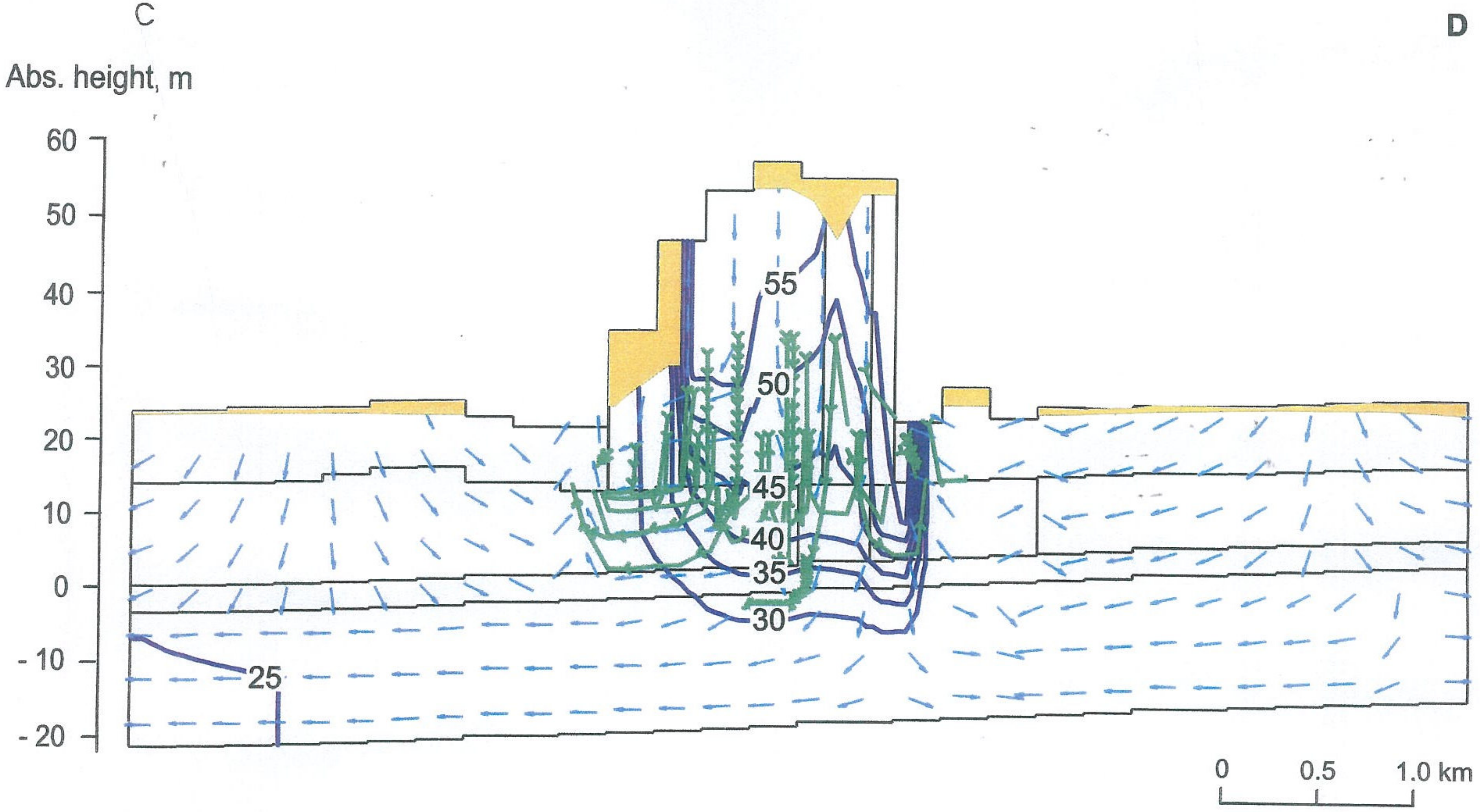
The pink areas on the map are the ponds on the upper surface of ash plateaus. For explanation of signs see Fig. 12.3.1.

Fig.12.5.1 Groundwater table, flow directions, and pathlines for the upper layer of Narva model



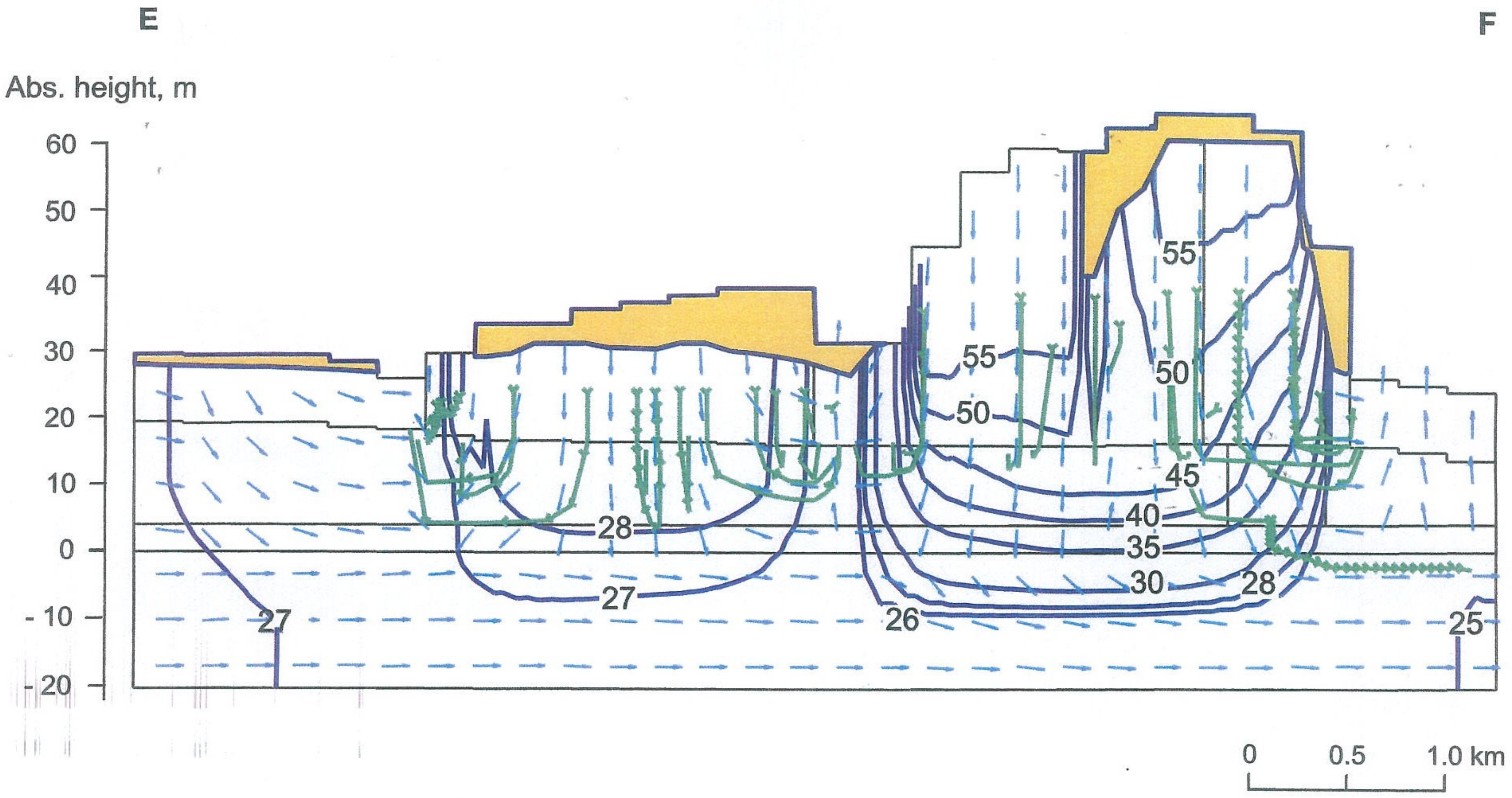
For explanation of signs see Fig. 12.3.3

Fig.12.5.2 Groundwater head, flow directions, and pathlines for the section A-B of the Narva model



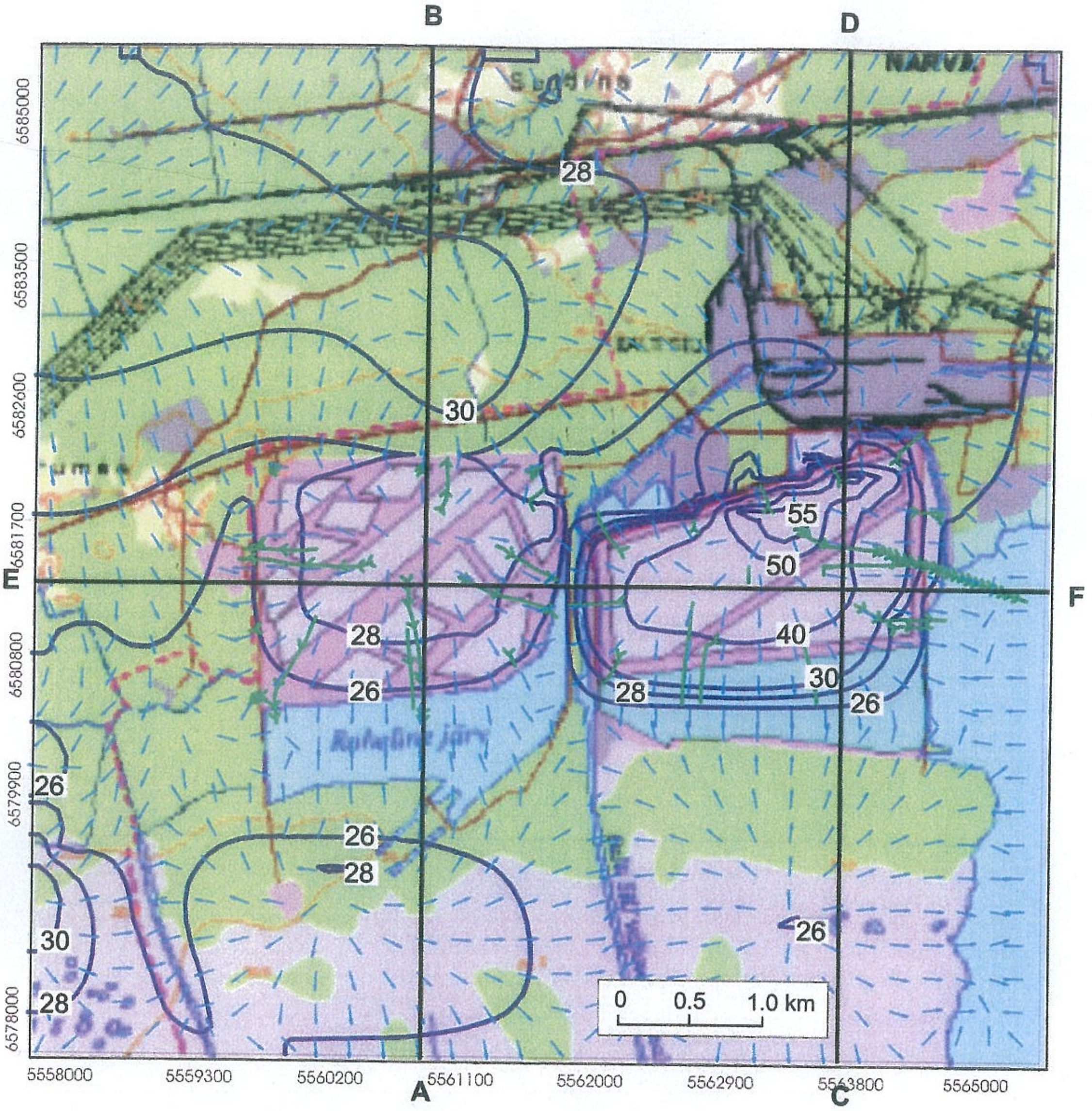
For explanation of signs see Fig. 12.3.3

Fig.12.5.3 Groundwater head, flow directions, and pathlines for the section C-D of the Narva model



For explanation of signs see Fig. 12.3. 3

Fig 12.5.4 Groundwater head, flow directions, and pathlines for the section E-F of the Narva model



For explanation of signs see Fig. 12.3.1 and 12.3.5.

Fig.12.5.5 Groundwater head, flow directions, and pathlines for the 2nd layer (the Ordovician carbonate bedrock) of the Narva model

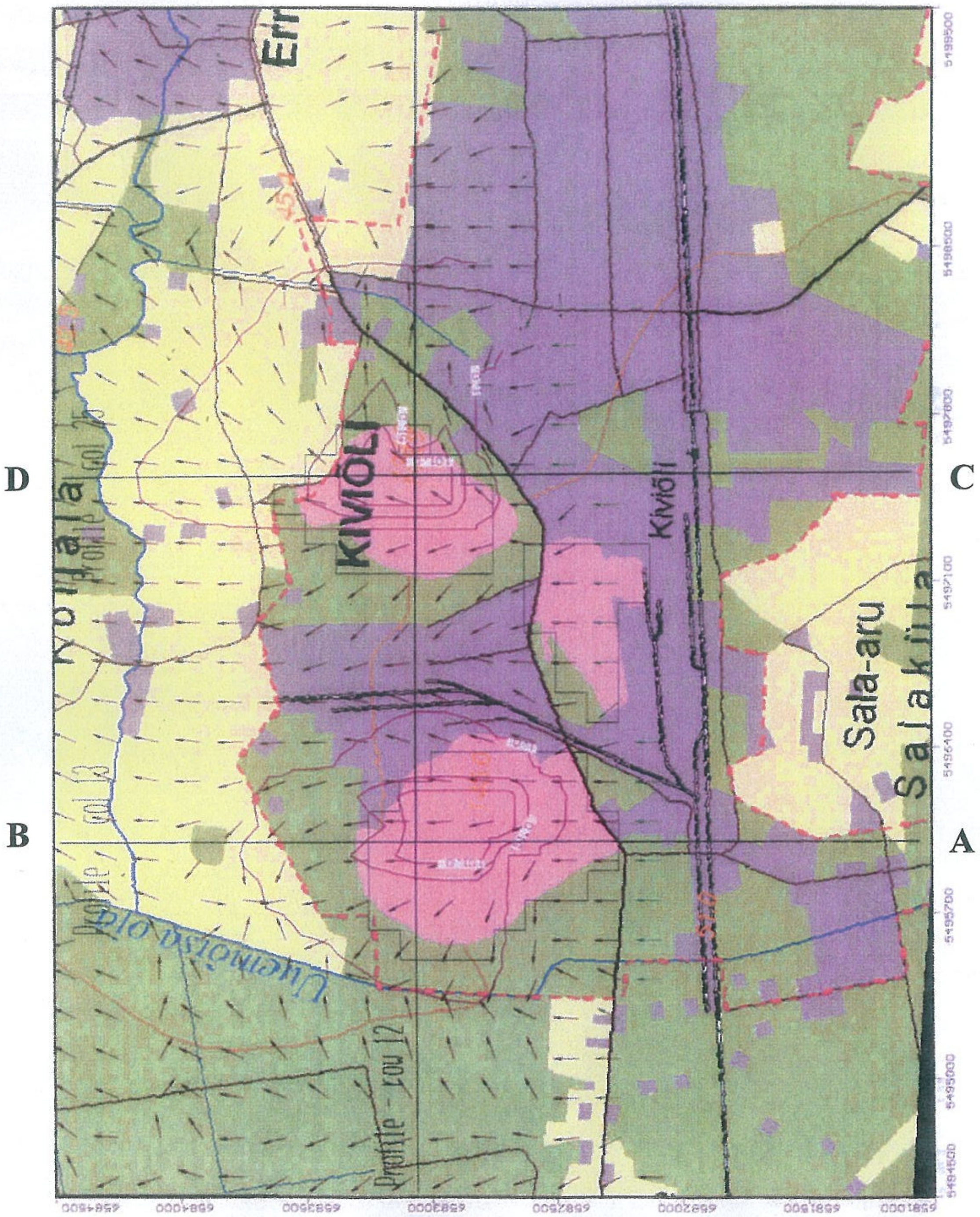


Fig. 13.1.1.1 Kiviõli landfills. Extend of phenol plume in upper layer (lilac contour lines)

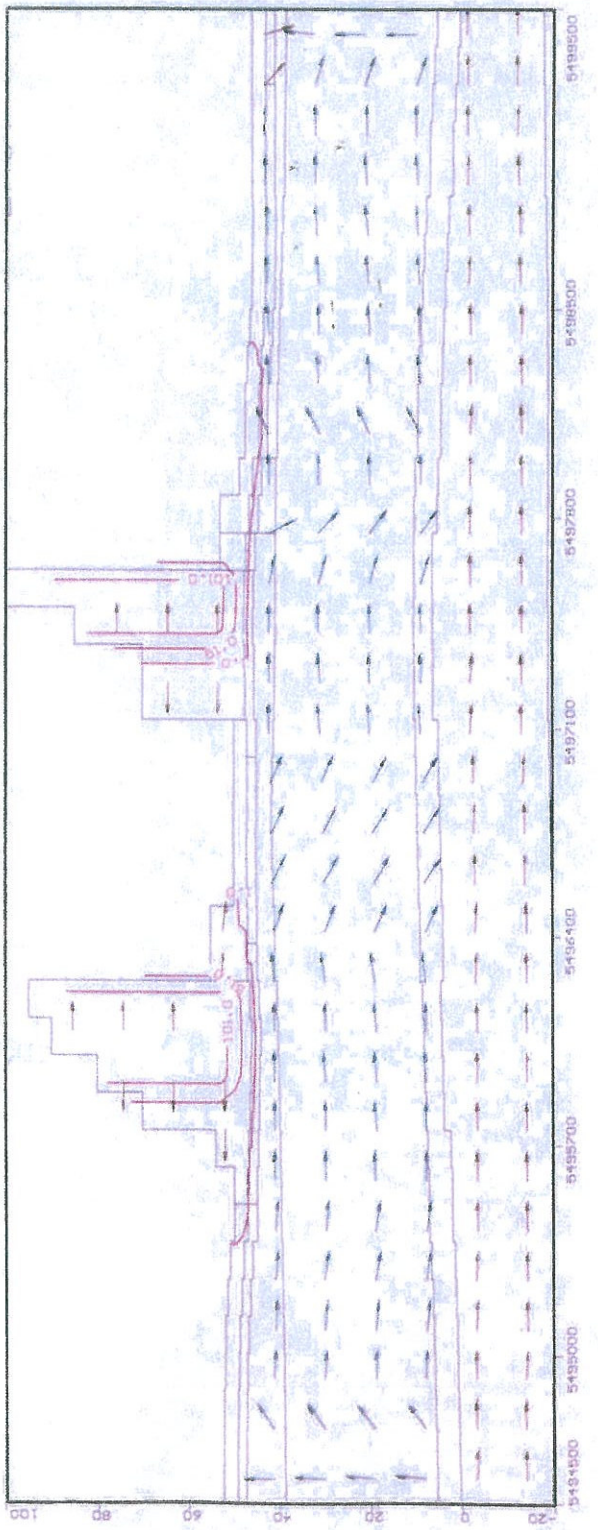


Fig. 13.1.1.2 Kiviõli profile E-F (west-east).
Extent of phenol plume

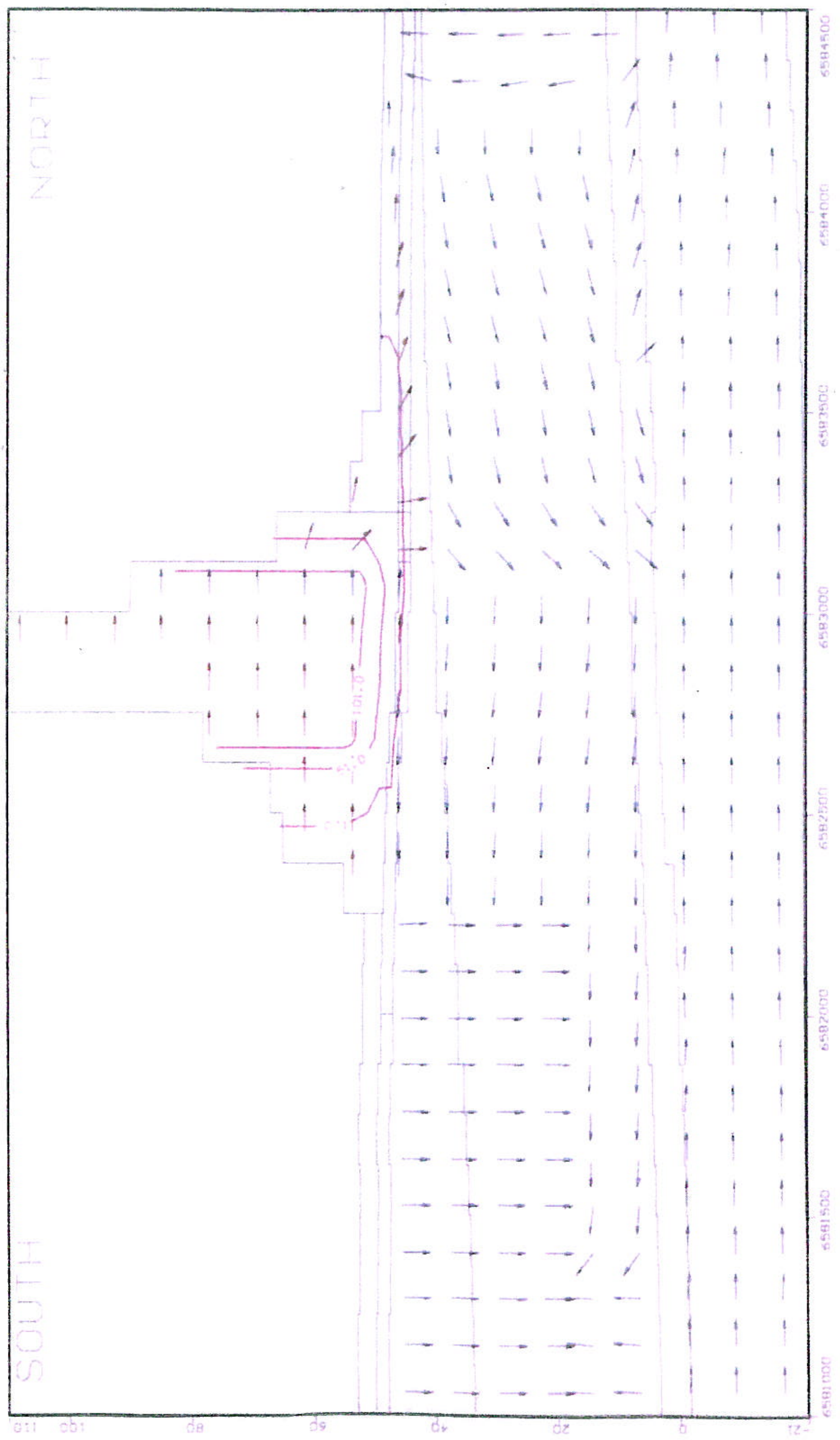


Fig. 13.1.1.3 Kiviõli, profile A-B (south-north)
Extent of phenol plume

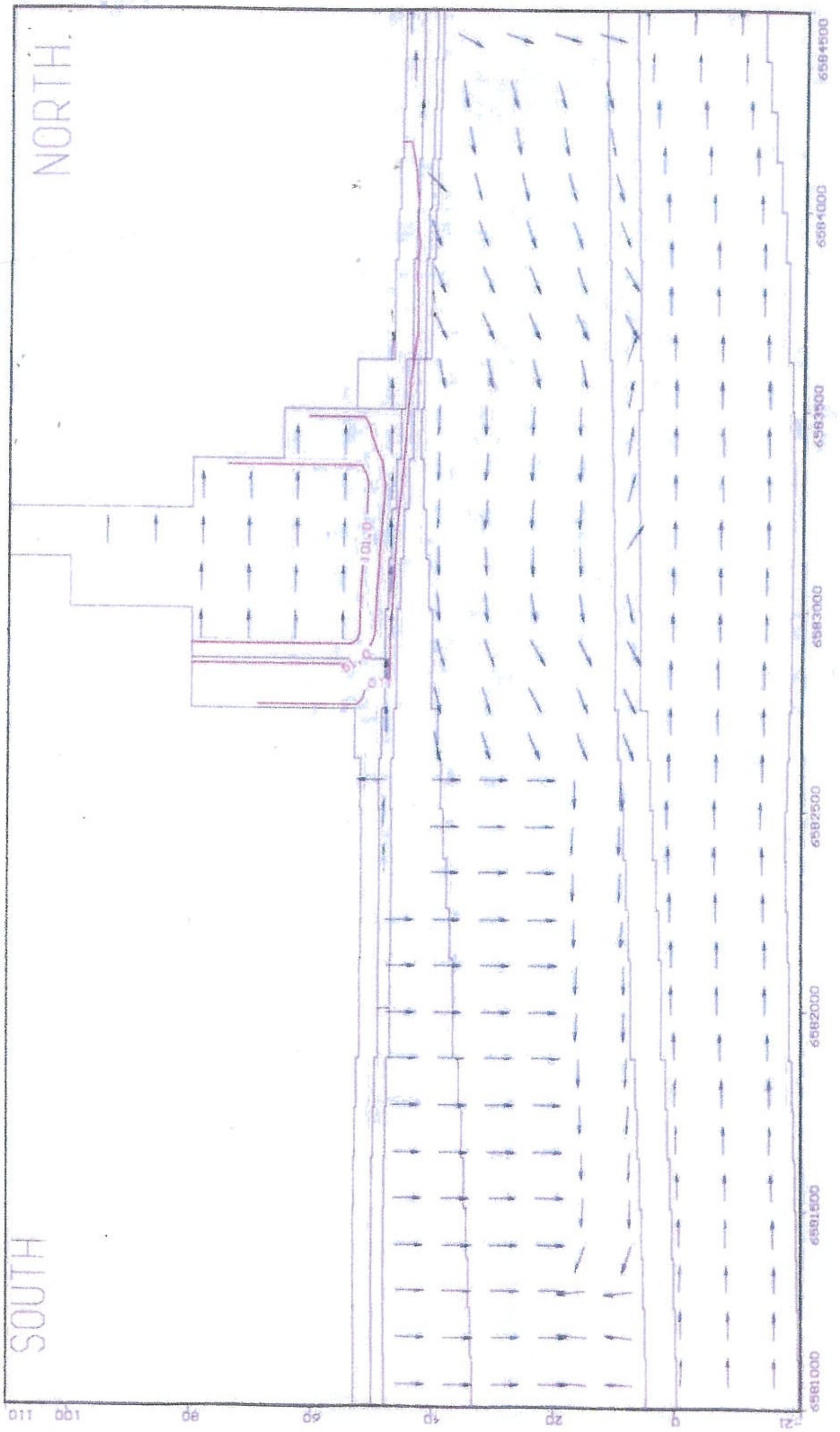


Fig. 13.1.1.4 Kiviõli, profile C-D (south-north)
Extent of phenol plume

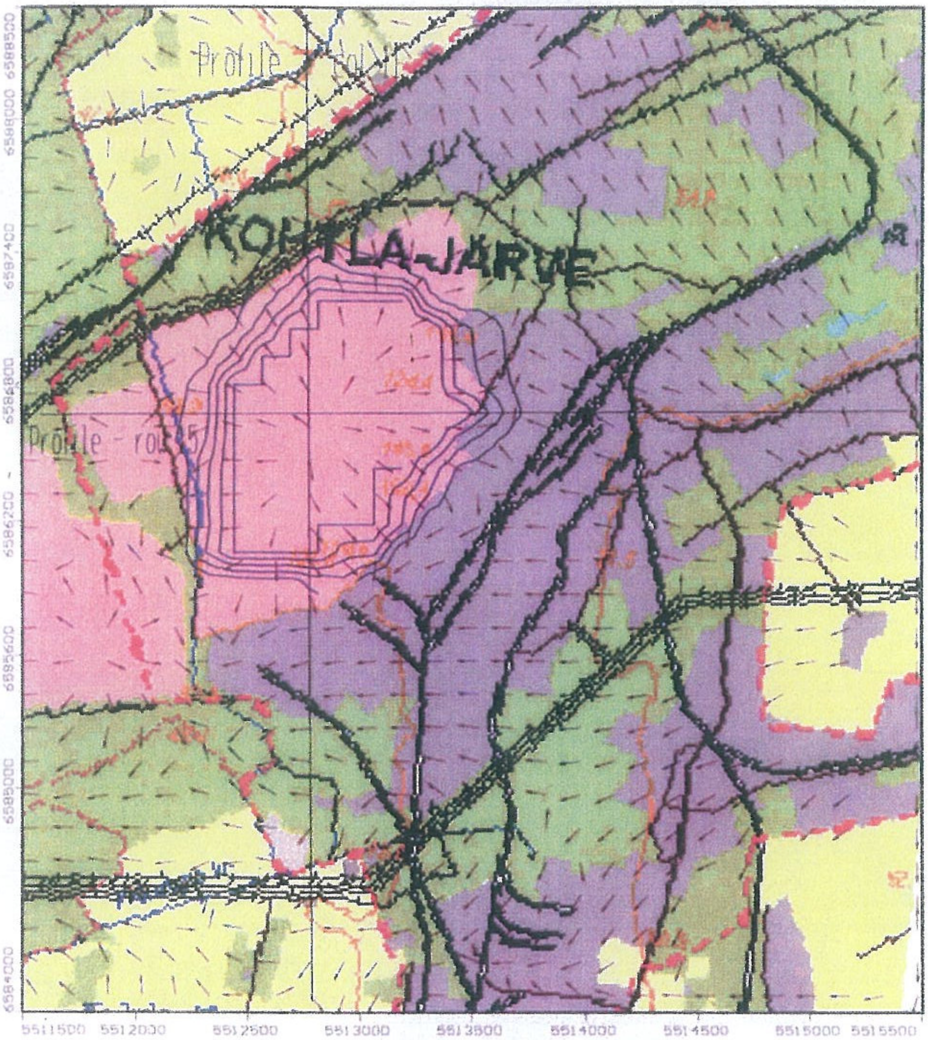


Fig. 13.1.2.1 Kohtla-Järve landfill. Extent of phenol plume in upper layer (lilac contour lines). Initial concentration 25 mg/l

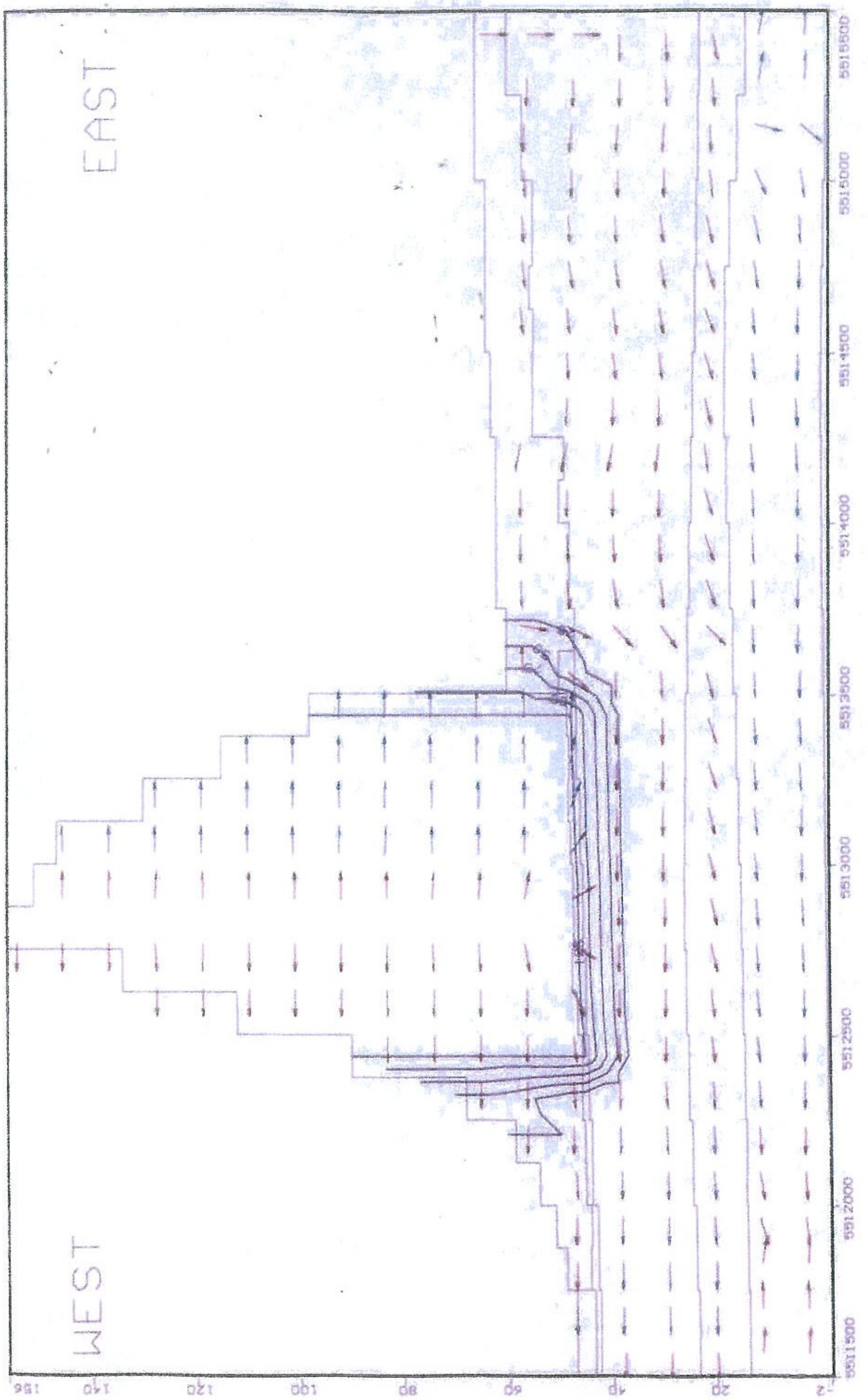


Fig. 13.1.2.2 Kohtla-Järve landfill, profile west-east
Extent of phenol plume

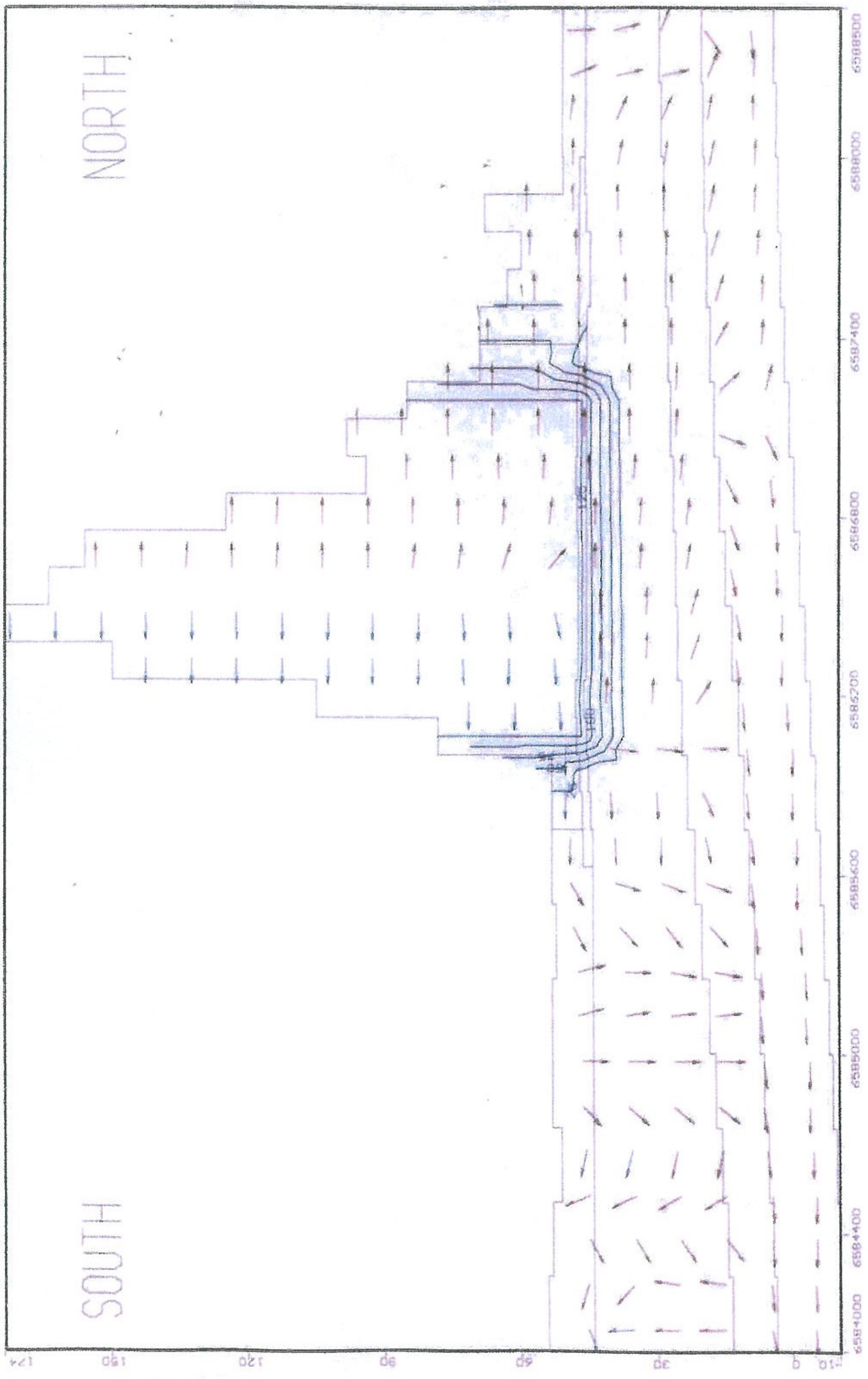
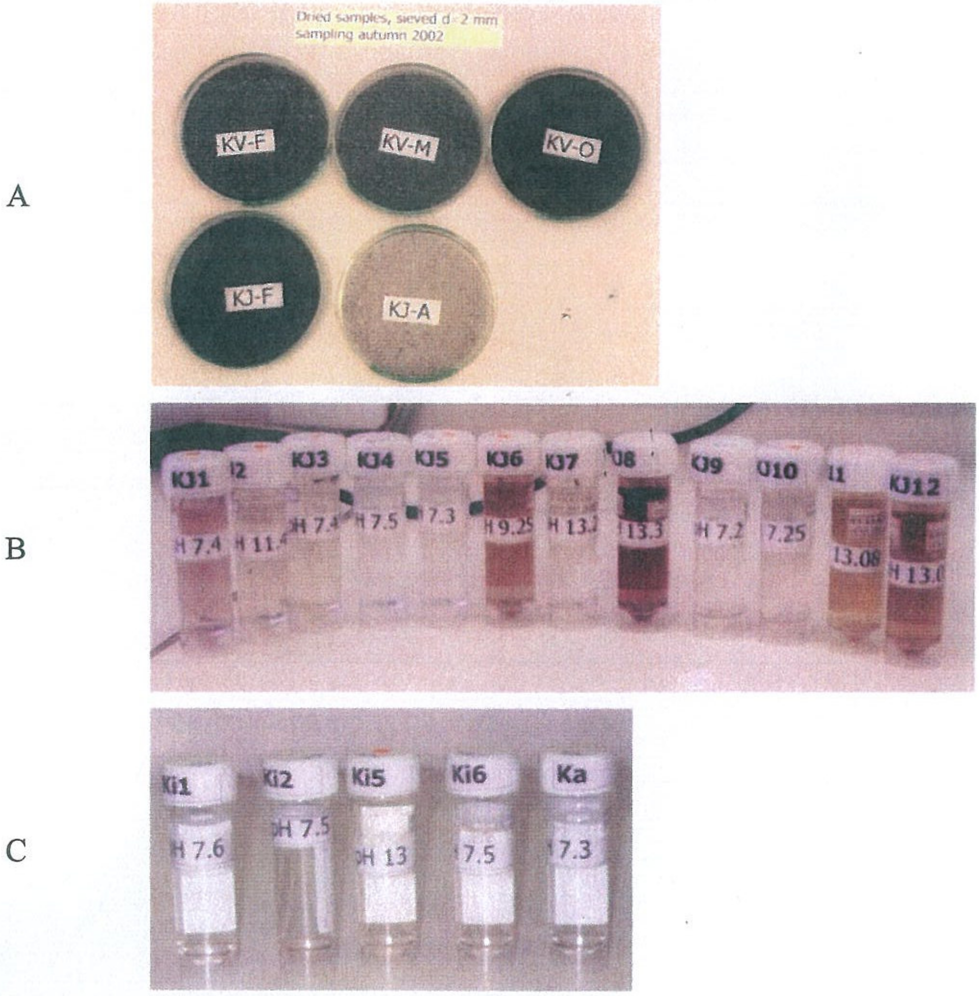


Fig. 13.1.2.3 Kohtla-Järve landfill, profile south-north.
Extent of phenol plume



Designations and description in more detail in Table 14.1.

Fig. 14.1 Samples of semi-cokes and ashes (A), waters from Kohtla-Järve (B) and Kiviõli (C)

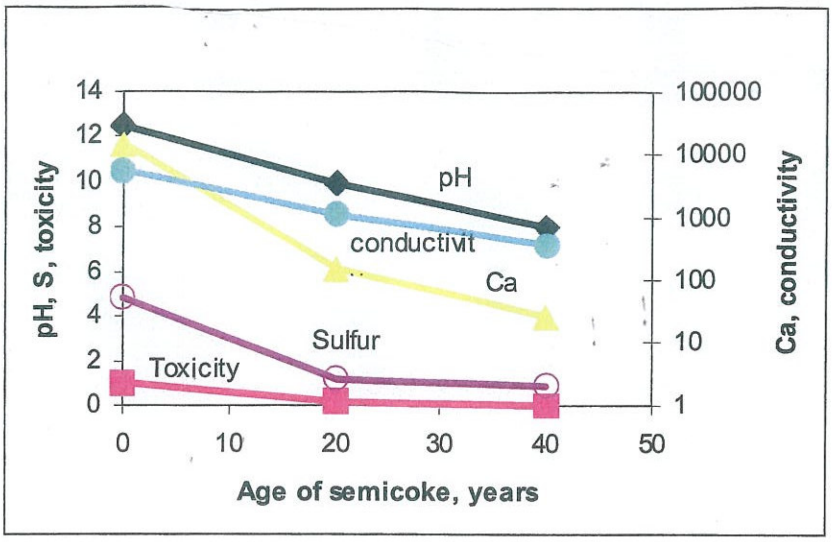


Fig. 14.2 The effect of aging of semi-coke on the water-extractable toxicity and chemical components

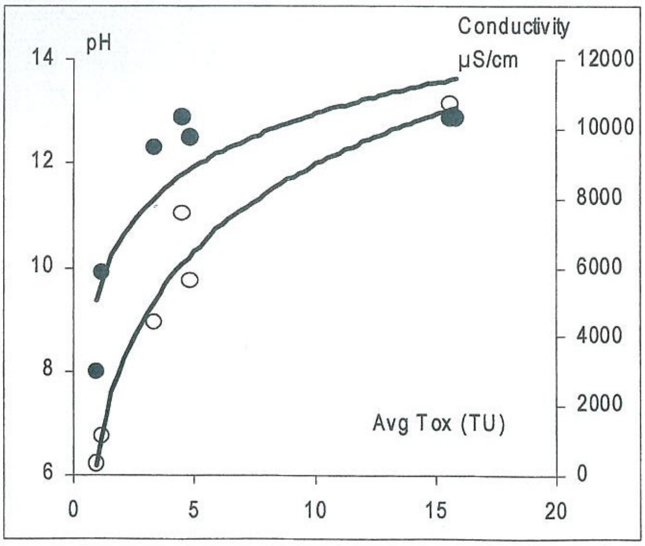


Figure 14.3 The effect of pH (filled symbols) and mineral salts content (open symbols) to toxicity of water eluates of oil shale solid wastes

List of Tables

Table 4 Location of main type of waste landfills in North-eastern Estonia

								Longtitude/latitude (WGS 84) Coordinates		L-EST	
Location	Local nr.	Mark	Age	Height, m	Area, ha	Volume *1000m^3	Type of waste	EO D/M/S	N D/M/S	EO meters	N meters
Kiviõli chemical factory	1-1	●	1949-1968	38	4.2	1 100	Rest after enrichment of oil shale (RAE)	$26^0$56'51.0"	$59^0$21'42.0"	667575.6	6584086.0
	1-2	●	1922-1975	96	35.0	10 000	Semi-coke	$26^0$57'36.0"	$59^0$21'79.0"	668235.3	6585261.2
	1-3	●	1951-now	116	47.0	11 300	Semi-coke	$26^0$55'92.0"	$59^0$21'62.0"	**667248.6**	6584691.2
Püssi TPS	2-1	●	1956-1982	38	7.84	410	Ash	$27^0$01'88.0"	$59^0$21'53.0"	672878.7	6584663.7
	2-2	●	1980-…	24	3.15	94	Ash	$27^0$01'98.6"	$59^0$21'58.4"	673038.3	6584838.2
Aidu quarry	3	●	1984-1999	14	0.87	1 400	RAE	$27^0$04'67.0"	$59^0$20'47.0"	675481.6	6582738.1
Kohtla-Nõmme mine	4-1	●	1952-1975	41	1.55	198	RAE	$27^0$10'06.5"	$59^0$21'12.9"	680172.1	6583759.3
	4-2	●	1956-1968	40	2.95	576	RAE	$27^0$10'.52.0"	$59^0$21'20.4"	680879.3	6584025.1
	4-3	●	1968-…	26	9.35	1431	RAE	$27^0$10'40.4"	$59^0$21'34.9"	680674.9	6584464.6
	4-4	●	1952-1980	28	5.16	765	Ash	$27^0$09'93.8"	$59^0$21'46.7"	680553.5	6584824.4
Kohtla-Järve chemical factory and TPS	5-1	●	1921-now	110	93.4	62 067	Semi-coke	$27^0$13'50.0"	$59^0$23'50.0"	683465.7	6588783.5
	5-2	●	1961-….	22	65.6	4373	Ash	$27^0$13'55.0"	$59^0$23'92.0"	683481.9	**6590085.5**
Sompa-4 mine	6-1	●	19….	39	7.12	1171	RAE, self-burned	$27^0$16'42.0"	$59^0$20'71.0"	686417.2	6584000.7
	6-2	●	19…. -….	40	4.58	990	RAE	$27^0$16'55.7"	$59^0$20'68.8"	686636.8	6583943.3
	6-3	●	19… -1974	17	1.18	67	RAE	$27^0$16'32.5"	$59^0$20'68.8"	686270.6	6583943.3
Sompa mine	7-1	●	1948-1964	42	4.27	344	RAE, self-burned	$27^0$16'21.0"	$59^0$19'47.0"	686212.5	6581388.3
	7-2	●	1949-1966	44	3.50	571	RAE, self-burned	$27^0$16'62.2"	$59^0$19'65.8"	686834.8	6582001.2
	7-3	●	1964-1967	31	1.60	188	RAE, self-burned	$27^0$16'51.7"	$59^0$19'69.0"	686664.1	6582091.9
	7-4	●	1964-1970	23	3.10	280	RAE	$27^0$16'33.7"	$59^0$19'39.5"	686424.5	6581166.3
	7-5	●	1968-1999	18	12.53	1 057	RAE	$27^0$16'75.0"	$59^0$19'36.8"	687080.9	6581114.8
Käva mine	8-1	●	1951-1959	61	5.22	982	RAE, self-burned	$27^0$17'44.0"	$59^0$22'75.0"	687207.3	6587881.3
	8-2	●	1960-1972	13	1.03	71	RAE, self-burned	$27^0$17'33.4"	$59^0$22'73.4"	687042.6	6587823.6
	8-3	●					RAE	$27^0$17'17.0"	$59^0$22'63.0"	686799.8	6587489.5
Kukruse mine	9-2	●	1945-1951	27	1.31	195	RAE	$27^0$18'64.0"	$59^0$23'75.0"	688376.8	6589798.0
	9-1	●	1951-1967	41	4.76	756	RAE, self-burned	$27^0$20'54.0"	$59^0$23'58.0"	690136.5	6589358.8

Table 4 Location of main type of waste mounds in North-eastern Estonia

Jõhvi. No 2 mine	10-1	●		25	3.0	458	RAE, self-burned	$27^0$23'33.9"	$59^0$21'59.8"	692841.5	6585832.4
	10-2	●		41	1.30	267	RAE, self-burned	$27^0$23'63.6"	$59^0$21'62.7"	693305.5	6585945.8
	10-3	●		38	2.40	619	RAE	$27^0$23'48.7"	$59^0$21'64.1"	693068.3	6585977.2
	10-4	●		28	3.20	617	RAE	$27^0$23'03.0"	$59^0$21'56.0"	692360,0	6585690.4
	10-5	●		26	1.40	134	RAE	$27^0$22'07.3"	$59^0$21'24.8"	691529.8	6584681.8
	10-6	●		32	2.20	336	RAE	$27^0$21'93.4"	$59^0$21'29.7"	691934.0	6584854.0
Tammiku mine	11-1	●	1951-1965	12	1.50	63	RAE	$27^0$23'37.9"	$59^0$20'37.4"	693033.6	6583289.0
	11-2	●	1975-1999	25	15.40	2 375	RAE	$27^0$23'53.7"	$59^0$20'56.2"	693253.6	6583882.7
	11-3	●	1970-…	40	18.0	4 444	RAE	$27^0$22'86.0"	$59^0$20'67.0"	692799.5	6584194.3
Viru mine	12-1	●	1965-1980	16	8.10	945	RAE	$27^0$21'40.5"	$59^0$17'79.5"	691394.1	6578933.7
	12-2	●	1967-1975	23	15.0	2 754	RAE	$27^0$21'67.0"	$59^0$17'58.0"	691846.3	6578290.3
	12-3	●	1974-….	35	27.90	12 230	RAE	$27^0$22'10.4"	$59^0$17'75.7"	691872.5	6578840,0
Estonia kaevandus	13-1	●	1973-now	47	105.80	37 610	RAE	$27^0$22'81.7"	$59^0$11'31.3"	693631.4	6566399.2
	13-2	●	1973-1978	19	13.50	1 964	RAE	$27^0$23'69.0"	$59^0$10'53.0"	694441.4	**6565253.6**
Ahtme mine and TPS	14-1	●	1946-…	55	5.55	1 320	RAE	$27^0$28'49.9"	$59^0$18'85.8"	698073.5	6581329.0
	14-2	●	1965-2002	44	44.03	16 690	RAE	$27^0$29'11.3"	$59^0$18'64.3"	698446.1	6580682.1
	14-3	●	1969-….	16	50.40	4 938	Ash	$27^0$28'33.0"	$59^0$19'46.0"	697774.2	6581939.4
Balti TPS	15-1	●	1959-now	31	360.0	29 945	Ash	$28^0$03'67.0"	$59^0$20'50.0"	731344.7	6585812.8
	15-2	●	1964-now	26	400.0	34 036	Ash	$28^0$06'50.0"	$59^0$20'50.0"	**733916.1**	6585969.9
Eesti TPS	16	●	19...	21	500.0	43 975	Ash	$27^0$56'50.0"	$59^0$17'50.0"	724778.1	6579840.0

Table 4.2 Oil shale mining in opencasts and underground mines from Estonian deposit. (Kattai, 2000)

Name	1919 -1930	1931-1940	1941-1950	1951-1960	1961-1970	1971-1980	1981-1990	1991-1998	Total
Vanamõisa	33	1							34
Pavandu	1035								1035
Ubja	106	488	306	547					1447
Kiviõli	654	4095	5818	9700	13840	11176	4560	-	46140
Aidu	-	-	-	-	-	14134	35391	18851	68376
Kohtla	-	235	1019	2989	9005	13683	9737	4263	40931
Sompa-4	-	-	-	4721	11768	5907	-	-	22396
Sompa	-	-	412	7264	12122	15064	7922	3393	46177
Käva	703	2401	4933	11180	14915	2153	-	-	36285
Kukruse	777	1727	5434	9937	6924	-	-	-	24799
Jõhvi	-	-	128	5644	13570	3690	-	-	23o32
Tammiku	-	-	-	4763	12484	16888	15583	6919	56637
Viru	-	-	-	-	5246	20572	19172	10561	55551
Estonia	-	-	-	-	-	36199	53077	25845	115121
Ahtme	-	-	581	10376	14930	20534	18645	8652	73718
Viivikonna	-	646	889	3283	11472	26619	24777	5851	73537
Sirgala	-	-	-	-	19833	48345	37443	15662	121283
Narva	-	-	-	-	170	27372	21553	12535	61630
Total	3308	9593	19520	70404	146279	262336	247860	112532	871832

Table 4.3.1 Oil shale output and use in 1930-2000 (Kattai, 2003)

Year	Output, Mln t/ya	From total output, Mln t/y		Output variation, Mln t/y
		For technological aims	For energy production	
1930	0.5	0.05	0.45	0
1935	0.6	0.25	0.35	+0.1
1940	1.9	1.0	0.9	+1.3
1945	0.8			-1.1
1950	3.5	1.4	2.1	+2.7
1955	7.0	2.6	4.4	+3.5
1960	9.2	3.4	5.8	+2.2
1965	15.9	4.4	11.5	+6.7
1970	18.9	4.2	14.7	+3.0
1975	28.5	4.0	24.1	+9.6
1980	31.3	3.7	27.6	+2.8
1985	26.4	2.8	23.6	-4.9
1990	22.5	2.5	20	-3.9
1995	13.1	2.5	10.6	-9.4
2000	11.7	2.1	9.6	-1.4

Table 4.3.2 Results of thermoprocessing of oil shale (Jefimov, 2000)

	Unit	Kohtla-Järve		Kiviõli	
		chamber ovens (KA)	vertical retorts (GGJ)	tunnel ovens (TA)	vertical retorts (GGJ)
Equipment productivity	t/day	17.5	927	388	155
Oil shale:					
Laboratory oil yield	%	23.7	24.3	23.5	24.3
Calorific value (by bomb method)	MJ/kg	13.52	13.82	13.36	13.82
	kcal/kg	32.30	3300	3190	3300
Shale oil:	%	4.9	16.4	20.8	16.5
Industrial oil yield	%	22.6	74.0	97.5	74.5
Gas:					
Output	m3/t	348	434	20	450
Energy value	MJ/m3	16.7	3.6	27.3	4.0
Semi-coke					
Output	Kg/t	630	580	648	580
Calorific value	MJ/kg	5.8	3.89	2.68	4.18
Content:					
Carbone oxide	%	10.6	12.0	25.5	17.5
Ash	%	738	76	65.3	70.3
Combustible matter	%	15.6	12.0	9.2	12.2
(amount of oil)	%	0	1.0-2.0	0.4-0.5	1.0-2.0

Table 4.4 Chemical composition of ash from ash plateau of Baltic PP

	Numbers of samples (from interval 1.5-2m)	Content, %		
		Min	Max	Average, in weight %
SiO_2	40	17.06	24.14	19.84
Al_2O_3	40	4.09	5.87	4.70
Fe_2O_3	40	3.28	5.42	4.30
FeO	40	0.22	0.81	0.38
TiO_2	40	0.24	0.35	0.29
CO_2	40	5.41	15.03	10.26
CaO	40	34.49	45.83	41.88
CaO free	40	1.77	15.04	6.87
MgO	40	312	4.94	3.85
S total	40	0.97	1.60	1.24
Na_2O	40	0.05	0.15	0.1
K_2O	40	0.72	2.30	1.34
LOI	40	15.52	23.43	18.69

Table 6.1.1.1 Element contents in different types of waste from Kiviõli and Kohtla-Järve

Region		Kiviõli						Kohtla-Järve			
Waste		Semicoke, fresh		Semicoke (<20yold)		Semicoke (> 40y old)		Semicoke, fresh		Ash from powerplant	
Sample		S-KV-F		S-KV-M		S-KV-O		S-KJ-F		S-KJ-A	
		total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia
Al	%	2.42	1.08	2.2	1.13	2.77	0.69	3.15	1.18	3.37	2.06
Ca	%	22.01	20.72	21.82	20.13	18.03	18.12	16.86	16.75	18.45	17.55
Fe	%	2.89	2.69	2.89	2.59	2.68	2.37	2.78	2.34	2.75	2.47
K	%	1.77	0.74	1.31	0.47	1.94	0.34	2.23	0.79	2.65	1.8
Mg	%	1.39	1.49	0.96	0.95	0.45	0.37	2.22	1.95	2.78	2.67
Na	%	0.078	0.048	0.053	0.027	0.057	0.017	0.069	0.039	0.129	0.064
P	%	0.04	0.04	0.039	0.038	0.047	0.045	0.05	0.056	0.055	0.051
S	%	1.96	1.41	2.16	1.59	0.11	0.04	1.83	1.48	1.02	0.72
Ti	%	0.146	0.04	0.134	0.033	0.163	0.007	0.188	0.026	0.214	0.104
Ag	ppb	90	26	58	28	68	22	123	31	90	32
As	ppm	4	5	8.4	4.1	9.5	5.1	11.4	5.4	14	7
Au	ppm	<0 .1	<0 .2	<0 .1	<0 .2	<0 .1	<0 .2	<0 .1	<0 .2	<0 .1	<0 .2
B	ppm		54		57		18		66		98
Ba	ppm	106	47.6	97	42.7	124	31.3	150	58	166	110.1
Be	ppm	1		< 1		1		1		1	
Bi	ppm	0.05	0.05	0.05	0.04	0.06	0.05	0.06	0.05	0.06	0.05
Cd	ppm	0.1	0.02	0.07	0.02	0.08	0.02	0.1	0.02	0.11	0.02
Ce	ppm	25.49	15.2	23.01	13.4	26.64	16	31.92	16.5	30.72	21.7
Co	ppm	3.8	2.7	2.9	2.6	3.4	2.9	4.9	3.9	5.1	4
Cr	ppm	36	19.8	34	16.5	56	17.3	43	20.4	44	29.5
Cs	ppm	2.4		2.1		2.7		3.5		4	
Cu	ppm	5.57	4.85	6.2	5.48	6.55	6.36	10.85	10.5	9.34	7.38
Dy	ppm	1.7	1.29	1.7	1.13	1.9	1.35	2.2	1.43	2.2	1.61
Er	ppm	0.9	0.66	0.9	0.63	0.9	0.65	1	0.76	1.1	0.84
Eu	ppm	0.5	0.34	0.4	0.31	0.5	0.37	0.6	0.39	0.5	0.41
Ga	ppm	5.61	3.9	5.78	3.7	6.97	2.9	7.92	4.3	8.64	6.8
Gd	ppm	1.9	1.62	2	1.46	2.5	1.61	2.6	1.79	2.3	1.94
Hf	ppm	1.17		1.12		1.38		1.5		1.85	
Hg	ppb		< 5		< 5		36		11		13
Ho	ppm	0.3	0.23	0.3	0.21	0.3	0.25	0.4	0.24	0.4	0.28
La	ppm	18	9.6	15	8.6	18	9.6	22	10.6	21	13.5
Li	ppm	20.4		20.6		23.9		27.3		30.5	
Mn	ppm	338	337	300	295	234	220	353	328	421	412
Lu	ppm	0.1	0.09	0.1	0.08	0.1	0.08	0.2	0.1	0.2	0.12
Mo	ppm	4.55	3.87	4.04	3.12	3.49	2.62	4.7	3.64	4.65	3.41
Nb	ppm	4.15		3.79		4.33		5.29		5.54	
Nd	ppm	13	7.61	10.9	6.7	13.1	7.96	15.4	8.42	14.2	9.82
Ni	ppm	21.7	15.8	21.1	14.3	22.3	20.9	22.8	17.8	20.9	18
Pb	ppm	38.49	32.41	41.52	32.39	44.14	37.53	42.16	37.61	36.82	29.96
Pr	ppm	3.3	2.14	3	1.85	3.4	2.24	4.1	2.33	3.9	2.78
Rb	ppm	44.1		35.2		48.3		61.7		71.1	
Sb	ppm	0.23	0.11	0.21	0.11	0.2	0.08	0.34	0.15	0.31	0.17
Sc	ppm	4	3.4	3.7	3.1	4.2	2.6	5	4	5.2	4.7
Se	ppm		0.3		0.5		0.3		0.4		0.5
Sm	ppm	2.4	1.69	2.4	1.47	2.8	1.82	3.3	1.74	3	2.09
Sn	ppm	0.8		0.8		1.1		1.3		1.2	
Sr	ppm	305	280.5	291	257.5	288	261.9	287	243.2	242	227.4
Ta	ppm	0.3		0.2		0.3		0.4		0.4	
Tb	ppm	0.4	0.24	0.4	0.21	0.4	0.26	0.4	0.27	0.4	0.3
Te	ppm		0.03		0.04		0.03		0.03		< 0.02
Th	ppm	5.7	3.4	5.2	2.9	6.6	4	7.1	4.1	7.3	4.3
Tl	ppm		0.04		0.04		< 0.02		0.06		0.41
Tm	ppm	0.1	0.1	0.1	0.09	0.1	0.09	0.2	0.11	0.2	0.13
U	ppm	3.4	2.3	3	2	4.1	2.6	3.6	2.2	3.4	2.4
V	ppm	26	22	27	20	34	13	34	21	36	38
W	ppm	1.5	0.6	0.6	0.2	1.7	0.2	1.1	0.2	1	0.3
Y	ppm	11.3	8.1	10.6	7.27	12.1	7.98	13.6	8.61	13	9.35
Yb	ppm	1	0.69	1	0.64	1.2	0.64	1.2	0.75	1.4	0.89
Zn	ppm	24.6	20.1	26.7	20.9	19.8	14.4	36.6	29.2	32.2	25.8
Zr	ppm	35.6		34.3		44.7		47.2		56.4	
Corg	%	7.34		7.84		10.88		11.16		1.2	
LOI			29.8		34.4		37.8		30.7		25.1

Table 6.1.1.2 Organic compounds in waste from Kiviõli landfills

	Region	Kiviõli		
	Waste	Semicoke		
	Age	fresh	<20y old	> 40y old
	Dry residue %	65.4	68.5	73.7
	Corg.,%	7.34	7.84	10.88
PAH, mg/kg DR	Naphthalin	0.5	<0.1	<0.1
	Acenaphthen	<0.01	0.1	<0.01
	Acenaphthylen	<0.1	<0.1	<0.1
	Fluoren	<0.01	0.06	0.15
	Phenanthren	<0.01	0.47	0.17
	Anthracen	<0.01	0.11	0.01
	Fluoranthen	0.01	1.1	0.07
	Pyren	<0.01	0.31	0.05
	Benzo[a]anthracen	<0.01	0.25	<0.01
	Chrysen	<0.01	0.08	0.01
	Benzo[b]fluoranthen	<0.01	0.24	<0.01
	Benzo[k]fluoranthen	<0.01	0.06	<0.01
	Benzo[a]pyren	<0.01	0.23	<0.01
	Indeno(123-cd)pyren	<0.01	0.11	<0.01
	Dibenz[ah]anthracen	<0.01	0.12	<0.01
	Benzo[ghi]perylen	<0.01	0.11	<0.01
	Sum PAH	0.01	3.9	0.46
BTX, mg/kg DR	Benzol	0.011	<0.01	<0.01
	Toluol	0.026	0.023	<0.01
	Ethylbenzol	<0.01	<0.01	<0.01
	m+p-Xylol	0.058	0.033	<0.01
	Styrol	<0.01	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01	<0.01
	1,3,5-Trimethylbenzo	<0.01	<0.01	<0.01
	Sum BTX	0.095	0.056	n.n.
Phenols, mg/kg DR	Phenol	<1	<1	<1
	Resorcin	<0.05	<0.05	<0.05
	5-Methylresorcin	<0.05	<0.05	<0.05
	2,5-Dimethylresorcin	<0.05	<0.05	<0.05
	4-Ethylresorcin	<0.05	<0.05	<0.05
	4-Methylphenol	0.33	<0.05	<0.05
	3,4-Dimethylphenol	0.052	<0.05	<0.05
	2,3-Dimethylphenol	0.25	<0.05	<0.05
	2,4-Dimethylphenol	0.22	0.14	<0.05
	Sum phenols	0.752	0.14	

Table 6.1.1.3 Organic compounds in different types of waste from Kohtla-Järve

	Region	Kohtla-Järve	
	Waste	Semicoke fresh	Ash from powerplant
	Dry residue %	69.4	58.3
	Corg..%	11.16	1.2
PAH. mg/kg DR	Naphthalin	<0.1	<0.1
	Acenaphthen	0.09	<0.01
	Acenaphthylen	<0.1	<0.1
	Fluoren	0.16	<0.01
	Phenanthren	0.51	0.01
	Anthracen	0.37	<0.01
	Fluoranthen	1	<0.01
	Pyren	0.86	<0.01
	Benzo[a]anthracen	0.46	<0.01
	Chrysen	0.04	<0.01
	Benzo[b]fluoranthen	0.34	<0.01
	Benzo[k]fluoranthen	0.16	<0.01
	Benzo[a]pyren	0.36	<0.01
	Indeno(123-cd)pyren	0.05	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01
	Benzo[ghi]perylen	0.07	<0.01
	Sum PAH	4.5	0.01
BTX. mg/kg DR	Benzol	0.058	<0.01
	Toluol	0.088	0.029
	Ethylbenzol	0.016	<0.01
	m+p-Xylol	0.087	0.054
	Styrol	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01
	1.3.5-Trimethylbenzol	<0.01	<0.01
	Sum BTX	0.25	0.083
Phenols. mg/kg DR	Phenol	<1	<1
	Resorcin	<0.05	<0.05
	5-Methylresorcin	<0.05	<0.05
	2.5-Dimethylresorcin	<0.05	<0.05
	4-Ethylresorcin	<0.05	<0.05
	4-Methylphenol	4.6	<0.05
	3.4-Dimethylphenol	0.31	<0.05
	2.3-Dimethylphenol	1.9	<0.05
	2.4-Dimethylphenol	2.6	<0.05
	Sum phenols	9.41	n.n

Table 6.1.2 Element contents in different types of ash from Narva

Region		Narva			
Waste		Ash from filter		Ash from cyclone	
Sample		**S-N-AF**		**S-N-AC**	
		total	aqua regia	total	aqua regia
TOC	%	<0.03		<0.03	
Al	%	4.57	2.8	3.36	2.33
Ca	%	23.45	19.19	30.31	26.29
Fe	%	3.09	2.61	3.11	2.77
K	%	4.06	2.9	1.87	1.56
Mg	%	2.09	1.92	2.17	2.21
Mn	%	0.0407	0.0367	0.0523	0.053
Na	%	0.114	0.07	0.105	0.048
P	%	0.083	0.069	0.069	0.06
S	%	3.78	1.99	1.75	0.9
Ti	%	0.284	0.135	0.253	0.147
Ag	*ppb*	123	55	82	35
As	ppm	40.4	23.4	11.7	9.2
Au	ppm	<0 .1	<0 .2	<0 .1	0.2
B	ppm		226		87
Ba	ppm	183	151.6	186	143.4
Be	ppm	1		1	
Bi	ppm	0.18	0.14	0.07	0.06
Cd	ppm	0.25	0.1	0.16	0.04
Ce	ppm	39.31	23.8	34.96	25.3
Co	ppm	7.2	4.7	4.8	4
Cr	ppm	70	59.8	38	30.9
Cs	ppm	9.8		3.2	
Cu	ppm	10.48	8.18	11.04	7.53
Dy	ppm	3	1.8	2.8	2
Er	ppm	1.4	1	1.4	1.12
Eu	ppm	0.7	0.43	0.7	0.5
Ga	ppm	15.56	11.2	8.41	6.9
Gd	ppm	3	2.26	3	2.44
Hf	ppm	2.61		2.19	
Hg	*ppb*		22		< 5
Ho	ppm	0.4	0.33	0.4	0.36
La	ppm	28	15.7	25	15.8
Li	ppm	32.9		24.3	
Lu	ppm	0.2	0.13	0.2	0.16
Mo	ppm	10.31	7.77	4.57	3.77
Nb	ppm	7.44		7.82	
Nd	ppm	18.6	11.28	17.3	11.94
Ni	ppm	30.5	22.9	22.6	19.4
Pb	ppm	96.8	63.37	43.0	33.94
Pr	ppm	5	3.16	4.4	3.23
Rb	ppm	129.6		47.7	
Sb	ppm	10.1	0.55	0.4	0.22
Sc	ppm	6.4	5.3	5.8	5.3
Se	ppm		0.8		0.4
Sm	ppm	3.8	2.38	3.7	2.33
Sn	ppm	3.1		1.1	
Sr	ppm	276	222	329	301.4
Ta	ppm	0.5		0.5	
Tb	ppm	0.6	0.34	0.5	0.36
Te	ppm		0.03		0.02
Th	ppm	8.9	4.9	7.8	5
Tl	ppm		1.95		0.42
Tm	ppm	0.2	0.14	0.2	0.18
U	ppm	5	3.3	3	2.8
V	ppm	61	53	34	40
W	ppm	1.9	0.7	1.2	0.4
Y	ppm	16.6	10.46	16.3	12.01
Yb	ppm	1.8	0.98	1.7	1.22
Zn	ppm	88.5	61.8	57.9	48.6
Zr	ppm	80.2		73.3	
LOI			6.4		6.4

Table 6.1.3.1 Description of the core from the well of Kukruse landfill

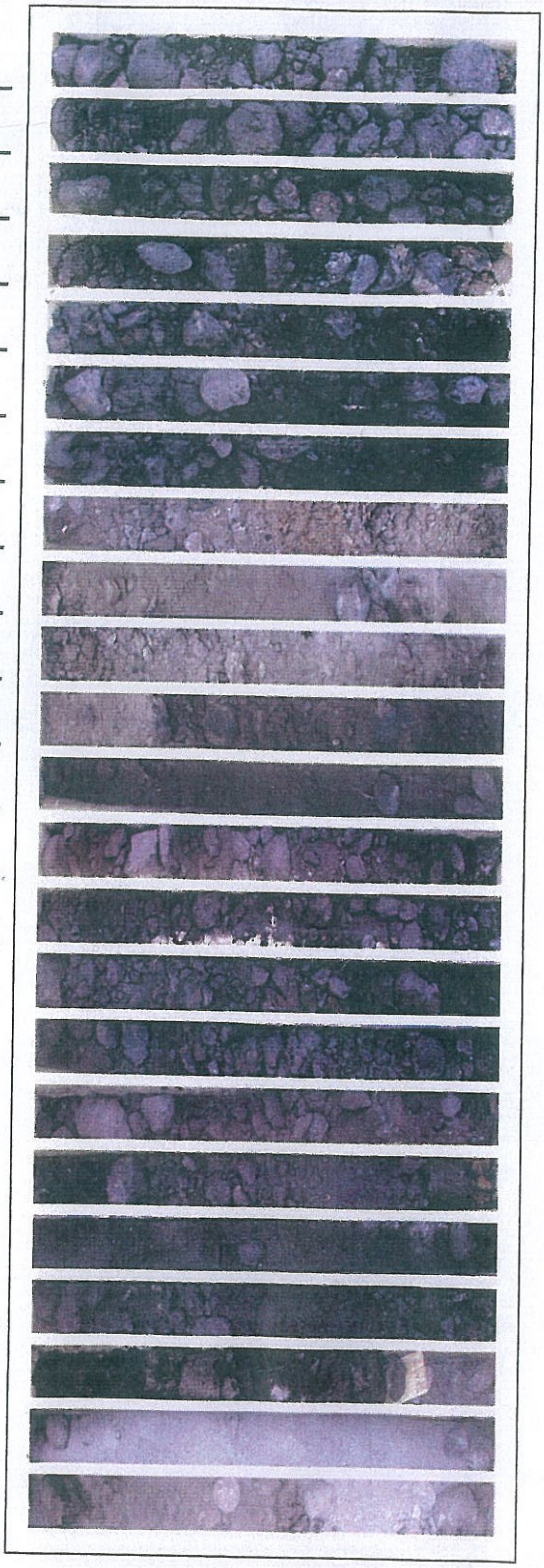
Depth,m	Core photo	XRFanalysis	XRD analysis	analyses of organic compounds	Description
0-1m		●	▲		Very dark grey up to black coke. The size of lumps from two up to 10cm. The warming is observed from surface. Temperature on the depth 1,5 m 63^{0}C
1-2m		●	▲		
2-3m		●	▲		
3-4m		●	▲		
4-5m		●	▲		
5-6m		●	▲		
6-7m		●	▲		
7-8m		●	▲		Warmed grey carbonate rocks with very small (up to sandy) size of lumps. Temperature 65^{0}C
8-9m		●	▲	◆	
9-10m		●	▲		
10-11m		●	▲		Black, somethere dark brown coke.Size of lumps ranges from several cm up ti very fine fraction. Temperature 73^{0}C
11-12m		●	▲	◆	
12-13m		●	▲		
13-14m		●	▲		Coke black, soft, some times oily. Temperature 84^{0}C
14-15m		●	▲		
15-16m		●	▲		Black coke, mainly powder with lumps having the size up to several cm. Temperature 92^{0}C
16-17m		●	▲		
17-18m		●	▲		
18-19m		●	▲	◆	
19-20m		●	▲		
20-21m		●	▲		Grey pieces of the limestone and powder fraction of the limestone. Temperature 96^{0}C
21-22m		●	▲		
22-23m		●	▲		

Table 6.1.3.2 Organic compounds in burned oil shale from Kukruse landfill

	Region	Kukruse 1		
	Sample	Kukruse 1	Kukruse 2	Kukruse 3
	Depth, m	8.4-8.6	11.6-11.8	19.0
	Dry residue %	95.8	96.5	100
PAH, mg/kg DR	Naphthalin	< 0.1	< 0.1	< 0.1
	Acenaphthen	< 0.01	< 0.01	< 0.01
	Acenaphthylen	< 0.1	< 0.1	< 0.1
	Fluoren	< 0.01	< 0.01	< 0.01
	Phenanthren	< 0.01	< 0.01	< 0.01
	Anthracen	< 0.01	< 0.01	< 0.01
	Fluoranthen	< 0.01	< 0.01	< 0.01
	Pyren	< 0.01	< 0.01	< 0.01
	Benzo[a]anthracen	< 0.01	< 0.01	< 0.01
	Chrysen	< 0.01	< 0.01	< 0.01
	Benzo[b]fluoranthen	< 0.01	< 0.01	< 0.01
	Benzo[k]fluoranthen	< 0.01	< 0.01	< 0.01
	Benzo[a]pyren	< 0.01	< 0.01	< 0.01
	Dibenz[ah]anthracen	< 0.01	< 0.01	< 0.01
	Benzo[ghi]perylen	< 0.01	< 0.01	< 0.01
	Indeno(123-cd)pyren	< 0.01	< 0.01	< 0.01
	Sum PAH	n.n.	n.n.	n.n.
	PAH (PLV for industrial area =200, living area =20)			
BTX, mg/kg DR	Benzol	0.018	0.016	<0.01
	Toluol	0.076	0.075	<0.01
	Ethylbenzol	0.014	0.012	<0.01
	m+p-Xylol	0.046	0.085	< 0.01
	Styrol	< 0.01	< 0.01	< 0.01
	iso-Propylbenzol	< 0.01	< 0.01	< 0.01
	1,3,5-Trimethylbenzol	< 0.01	< 0.01	< 0.01
	Sum BTX	0.15	0.19	n.n.
	BTX (PLV for industrial area =5000, living area =500)			
Phenols, mg/kg DR	Phenol	2.9	3.2	0.21
	Resorcin	< 0.05	< 0.05	< 0.05
	p-cresol	6.2	12	0.26
	2.5-Dimethylresorcin	< 0.05	0.16	< 0.05
	4-Ethylresorcin	< 0.05	< 0.05	< 0.05
	3.4-Dimethylphenol	0.3	1.4	< 0.05
	2.3-Dimethylphenol	7.2	17	0.26
	2.4-Dimethylphenol	10	16	0.12
	Sum Phenols	17	16	0.85
	Phenols (PLV for industrial area =100, living area=10)			

n.n. – no detectable

Table 6.2.1.1 pH, EC and temperature measurements in the waste leaches

Sample	pH	Electrical conductivity µS/cm	t° C
KV-F	12.54	10,4	20,2
KV-M	11,22	9.84	20,0
KV-O	8,47	1,39	20,2
KJ-A	12,38	8,54	19,9
KJ-A	12,44	7.52	20.4
N-AF	12.73	15,55	20,1
N-AC	*12,72*	*12,75*	*20,2*

Table 6.2.1.2 Elements concentration (c_1) in the leaches from different types of waste$^{x)}$

Region		Kiviõli			Kohtla-Järve		Narva		Inert	Non-hazardous	Hazardous
Sample		Semicoke fresh	<20y old	> 40y old	Semicoke fresh	Ash from powerplant	Ash from filter	Ash from cyclone		mg/kg	
Ratio		L/S=10	L/S=10	L/S=10	L/S=10	L/S=10	L/S=10	L/S=10			
Ag	ppb	3.2	<0.05	<0.05	0.08	<0.05	<0.05	<0.05			
Al	ppb	290	653	14	47	8664	14	21			
As	ppb	67	1.1	<0.5	4.5	0.7	9.6	6.1	0.5	2	25,00
Au	ppb	140.5	0.22	<0.05	2.14	<0.05	0.48	0.41			
B	ppb	9850	163	146	633	68	991	1287			
Ba	ppb	2912.6	16.25	9.49	308.51	79.18	547.62	345.46	20	100	300
Be	ppb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
Bi	ppb	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
Br	ppb	79750	1490	59	7594	1224	44065	13974			
Ca	ppb	14400000	144435	26036	1144784	63798	1833709	1704881			
Cd	ppb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.04	1,00	5,00
Ce	ppb	0.6	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Cl	*ppm*	2370	28	3	159	26	369	155	550	15000	25000
Co	ppb	<0.02	< 0.02	<0.02	<0.02	0.17	<0.02	<0.02			
Cr	ppb	21	1.6	0.9	3	5.1	384.9	70.7	0.5	10	70
Cs	ppb	6.5	0.38	< 0.01	0.37	29.15	27.67	8.29			
Cu	ppb	73	1.2	4.9	15.1	5.8	5.5	2.3	2	50	100
Fe	ppb	2940	35	< 10	359	< 10	< 10	101			
Ga	ppb	0.6	2.44	< 0.05	0.13	11.52	< 0.05	< 0.05			
Ge	ppb	1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
Hf	ppb	< 0.02	<0.02	< 0.02	0.04	< 0.02	< 0.02	< 0.02			
Hg	ppb	< 0.1	<0.1	<0.1	<0 .1	<0.1	5.9	5.4	0.01	0.2	2
In	ppb	0.1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Ir	ppb	0.5	<0.05	<0.05	<0.05	<0.05	0.4	0.15			
K	ppb	979660	37378	402	97124	869852	562386	116962			
La	ppb	0.1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Li	ppb	510	37.2	0.5	35.1	357.5	131.2	33.5			
Mg	ppb	370	290	979	< 50	< 50	< 50	< 50			
Mn	ppb	13.1	0.18	0.42	0.39	1.08	0.61	0.29			
Mo	ppb	305	5.1	2.1	42.6	31.6	245.8	48	0.5	10	30
Na	ppb	279570	9309	4873	12958	37680	13073	3544			
Nb	ppb	0.1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01			
Nd	ppb	0.04	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01			
Ni	ppb	<0.2	< 0.2	1	<0.2	0.7	<0.2	1.3	0.4	10	40
Os	ppb	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
P	ppb	70	< 20	< 20	83	< 20	128	95			
Pb	ppb	20	< 0.1	< 0.1	5.4	5.7	38.5	< 0.1	0.5	10	50
Pd	ppb	1	< 0.2	<0.2	<0.2	<0.2	<0.2	<0.2			
Pt	ppb	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01			
Rb	ppb	228.6	130.07	0.45	204.25	2665.61	1482.4	332.4			
Re	ppb	0.05	0.01	< 0.01	0.06	0.13	0.63	0.21			
Ru	ppb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
S	*ppm*	995	213	10	1439	18	706	526			
Sb	ppb	0.1	0.09	<0.05	0.1	0.08	4.13	0.77	0.06	0.7	5
Sc	ppb	0.3	2.55	0.56	0.79	0.79	0.6	0.78			
Se	ppb	20	2.9	0.8	24.3	2.9	81.6	17.8	0.1	0.5	7
Si	ppb	470	8195	1511	184	2300	152	419			
Sm	ppb	< 0.02	< .02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02			
Sn	ppb	0.1	< .05	<0.05	<0.05	<0.05	0.22	<0.05			
Sr	ppb	5184.3	921.06	43.25	3612.09	624.12	2361.02	3278.79			
Ta	ppb	< 0.02	<0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02			
Te	ppb	<0.05	<0.05	<0.05	0.16	0.07	<0.05	0.21			
Th	ppb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
Ti	ppb	< 10	< 10	< 10	< 10	< 10	< 10	< 10			
Tl	ppb	< 0.01	< 0.01	< 0.01	< 0.01	0.65	109.64	10.02			
U	ppb	< 0.02	<0.02	1.23	0.04	< 0.02	0.33	0.07			
V	ppb	< 0.02	10.7	< 0.2	< 0.2	4.8	2.5	< .2			
W	ppb	0.3	0.18	0.09	0.33	0.64	4.66	1.13			
Y	ppb	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01			
Yb	ppb	0.2	0.02	0.01	0.23	0.01	0.15	0.15			
Zn	ppb	29	13.5	14.6	42.3	18.5	8.8	4.8	4	50	200
Zr	ppb	0.02	<0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02			

$^{x)}$ c_1 (ug/L) × (1/100) = c_1 (mg/kg)

Table 6.2.1.3 Organic compounds (C_1) in leaches of different waste$^{x)}$

	Age	fresh	<20y old	> 40y old			
	Ratio	L/S=10	L/S=10	L/S=10	L/S=10	L/S=10	mg/kg
PAH, µg/l	DOC, mg/l	23	8	2,4	26	7,2	
	Naphthalin	<0,01	<0,01	<0,01	*0,2*	<0,01	
	Acenaphthen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Acenaphthylen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Fluoren	<0,01	<0,01	<0,01	<0,01	<0,01	
	Phenanthren	<0,01	<0,01	<0,01	<0,01	<0,01	
	Anthracen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Fluoranthen	*0,014*	<0,01	<0,01	<0,01	*0,027*	
	Pyren	<0,01	<0,01	<0,01	<0,01	*0,051*	
	Benzo[a]anthracen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Chrysen	<0,01	<0,01	<0,01	<0,01	*0,011*	
	Benzo[b]fluoranthen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Benzo[k]fluoranthen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Benzo[a]pyren	<0,01	<0,01	<0,01	<0,01	<0,01	
	Indeno(123-cd)pyren	<0,01	<0,01	<0,01	<0,01	<0,01	
	Dibenz[ah]anthracen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Benzo[ghi]perylen	<0,01	<0,01	<0,01	<0,01	<0,01	
	Sum PAH	***0,014***	n.n.	n.n.	0,2	***0,089***	?
BTX, µg/l	Benzol	<0,5	< 0,5	< 0,5	<0,5	< 0,5	
	Toluol	<0,5	<0,5	<0,5	*2,1*	< 0,5	
	Ethylbenzol	<0,5	<0,5	<0,5	<0,5	< 0,5	
	m+p-Xylol	<0,5	<0,5	<0,5	<0,5	< 0,5	
	Styrol	<0,5	<0,5	<0,5	<0,5	< 0,5	
	Chlorbenzol	<0,5	<0,5	<0,5	<0,5	<0,5	
	o-Xylol	<0,5	<0,5	<0,5	<0,5	<0,5	
	Cumol	<0,5	<0,5	<0,5	<0,5	<0,5	
	3+4-Ethyltoluol	<0,5	<0,5	<0,5	<0,5	<0,5	
	Mesitylen	<0,5	<0,5	<0,5	<0,5	<0,5	
	2-Ethyltoluol	<0,5	<0,5	<0,5	<0,5	<0,5	
	Sum BTX	n.n.	n.n.	n.n.	2,1	n.n.	6
Phenols, µg/l	Phenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	Resorcin	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	5-Methylresorcin	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	4-Methylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	3,4-Dimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,3-Dimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,4-Dimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2+3-Methylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,6-Dimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	3,5-Dimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,4,6-Trimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,3,6-Trimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	2,3,5-Trimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	3,4,5-Trimethylphenol	< 0,5	< 0,5	< 0,5	< 0,5	< 0,5	
	Sum phenols	n.n.	n.n.	n.n.	n.n.	n.n.	0.5

$^{x)}$ c_1 (ug/L) × (1/100) = c_2 (mg/kg)

Table 7.2 Element concentration in Dictyonema shale, phosphorite and oil shale in North-eastern Estonia (in ppm, S in %)

Element	Dictyonema shale		Phosphorite	Oil shale (kukersite)		Clark for clay [4]
	Toolse[1]	Sillamäe[2]	Toolse[1]	Aidu[1]	Commercial oil shale[3]	
S	5.07				0.88	0.24
As	38	123	<5		7.6	13
Cu	75	114	59	16	17	45
Sr	58	62	1370	205	151	300
Mo	406	920	10	2	3	2.6
Cd	1.3	4.6	<1	1.1	4	0.3
Ba	360	430	190	150	140	580
Ni	140	71	20	13	21	68
Pb	120	410	29	16	24	20
Se	4.3	4.7			<0.1	0.6
Th	14.5	13.7	<8	2.2	3.4	12
U	162	300	22	2	2.9	3.7
V	1040	995	58	20	28	130
Zn	170	231	45	<40	49	95

[1]Petersell et al., 1997; [2]Petersell, unpublished data; [3]Пец и др., 1985; [4]Turekijan, Wedepohl, 1961

Table 8.2 Main measured parameters of studied wells and water in North-eastern Estonia

Area	Well or channel	Longitude/ latitude (WGS84) EO	N	Water aquifer location	Altitude	Depth	Water table	pH	*EJ 20°C	NH_4	Alkalinity		O_2sat,%	O_2ppm	t°	O_2sat,%	O_2ppm
		D/M/S	D/M/S		m				µs/cm	mg/l	mg/l	mg-ekv	February, 2003			May, 20	
Narva	RA-N-1	59°20'68.3"	28°07'90.3"	lg Qm	38.2	4.7	0.1	7.8	318	<0.05	152.5	2.5	067	09.3	1.5	048	05.5
	RA-N-2	59°20'06.2"	28°07'44.4"	waste, pore water	49.4	10.3	9.12	12.8	31260	0.73	8311.3	136.25				093	0.92
	RA-N-3	59°20'03.8"	28°07'46.9"	waste, pore water	31.9	14.5	6.25	12.4	8630	1.43	2333.3	38.25				048	04.8
	N-2-1	59°20'51.0"	28°07'39.0"	O_2ls-O_2vl	26.0	9.0	3.88	6.7	2390	1.44	817.4	13.4	032	04.0	5.7		
	N-6-1	59°20'03.4"	28°07'58.0"	O_2ls-O_2vl	28.3	7.7	2.7	6.6	2350	3.99	1433.5	23.5				020	02.6
	N-7	59°19'36.2"	28°07'32.0"	lg Qm	23.9	8.1	1.3	6.3	780	8.61	430.1	7.05	027	03.6	7.0		
	N-8	59°19'36.0"	28°07'34.0"	O_1pk-Є$_1$ts	26.5	13.0	2.5	6.6	1150	7.16	546	8.95	028	03.7	5.5		
	N-45/2	59°20'07.0"	28°07'36.0"	O_2ls-O_2vl	27.4	14.7	2.5	6.7	2230	8.46	610	10	032	04.0	4.5		
	N-46/1	59°21'01.0"	28°07'40.0"	O_2ls-O_2vl	28.2	24.0	3.56	8.2	1250	2.17	600.9	9.85	027	03.7	5.6		
	N-46/2	59°20'08.0"	28°07'36.0"	O_2ls-O_2vl	27.7	26.0	2.54	6.8	2370	8.04	561.2	9.2	028	03.5	5.1		
	N-CH	59°20'50.5"	28°07'12.5"	channel water	39.5			13	34540	1.34	7609.8	124.75	072	10.2	0.6	079	07.3
Kohtla-Järve	RA-KJ-1	59°24'02.9"	27°13'30.9"	O_2ls-O_2kn	38.0	5.7	1.62	7	2700	0.44	433.1	7.1	042	05.7	3.5	024	02.9
	RA-KJ-2	59°23'33.8"	27°12'12.2"	O_2ls-O_2kn	43.0	8.4	3.25	9.8	1262	5.43	173.9	2.85	063	08.6	2.3	033	04.0
	RA-KJ-3	59°23'29.5"	27°11'56.2"	O_2ls-O_2kn	31.0	9.5	3.55	9.3	5010	24.84	671	11	028	03.6	5.3	034	04.0
	RA-KJ-4	59°24'10.3"	27°12'57.5"	O_2ls-O_2kn	52.0	5.7	2.85	7.2	1798	<0.05	445.3	7.3	055	07.3	4.0	029	03.5
	RA-KJ-5	59°23'69.7"	27°13'15.0"	waste, pore water	97.0	19.3	13.66	12.5	16320	288.22	4117.5	67.5				019	01.8
	RA-KJ-6	59°23'66.9"	27°12'91.1"	waste, pore water	62.9	21.9	6.10	11.9	14480	131.89	3364.2	55.15				083	09.0
	KJ-600	59°23'50.1"	27°12'59.4"	O_2ls-O_2kn	52.7	20.7	3.87	8.8	2140	4.18	228.8	3.75	030	03.8	3.7	013	01.4
	KJ-601	59°23'50.1"	27°12'59.4"	O_1pk-Є$_1$ts	52.7	39.5	9.66	11.9	7990	7.29	1677.5	27.5	035	04.5	5.0	021	02.3
	KJ-602	59°24'00.8"	27°13'03.3"	O_2ls-O_2kn	49.7	22.3	0.80	9.1	6140	12.42	750.3	12.3	026	03.4	2.5	022	02.7
	KJ-603	59°24'00.8"	27°13'03.3"	O_1pk-Є$_1$ts	49.7	37.1	6.78	7.5	800	0.41	390.4	6.4	029	03.8	3.8	032	03.8
	KJ-608	59°24'06.3"	27°13'52.3"	O_2ls-O_2kn	53.4	26.5	1.06	7	1780	2.14	527.7	8.65	050	06.7	2.8	056	06.8
	KJ-609	59°24'06.4"	27°13'53.6"	O_1pk-Є$_1$ts	53.6	45.9	9.40	8	930	0.24	411.8	6.75	050	06.5	3.5	060	07.3
	KJ-610	59°24'00.6"	27°14'04.0"	O_2ls-O_2kn	54.0	29.8	2.20	7	1920	1.52	536.8	8.8	048	06.2	4.7	033	03.8
	KJ-611	59°24'00.6"	27°14'04.0"	O_1pk-Є$_1$ts	54.0	39.4	9.51	7.5	1050	0.44	417.9	6.85	040	05.0	5.0	032	03.7
	KJ-616	59°22'43.5"	27°12'13.9"	O_2ls-O_2kn	48.6	36.5	1.76	9.5	327	<0.05	48.8	0.8	093	12.4	3.3	091	10.5
	KJ-620	59°22'05.5"	27°11'10.1"	O_2ls-O_2kn	47.0	35.9	0.52	7.3	961	0.11	402.6	6.6	076	9.9	4.3	090	10.1
	KJ-622	59°23'36.6"	27°12'20.6"	O_2ls-O_2kn	50.6	30.7	3.75	11	6780	25.66	1372.5	22.5	009	01.4	2.6	008	0.09
	KJ-623	59°23'36.6"	27°12'20.6"	O_1pk-Є$_1$ts	50.9	52.6	8.17	8.2	690	0.23	344.1	5.65	040	05.4	2.9	019	02.3
	KJ-CH1	59°24'12.1"	27°13'83.9"	channel water	53.0			12.5	12490	4.19	2220.4	36.4				075	06.9
	KJ-CH2	59°23'44.2"	27°12'19.2"	channel water	47.3			11.8	7670	39.46	1070.6	17.55				011	0.08

Table 8.2 Main measured parameters of studies wells and water in North-eastern Estonia

Area	Well or channel	Longitude/ latitude (WGS84)		Water aquifer location	Altitude	Depth	Water table	pH	*EJ 20°C	NH$_4$	Alkalinity		O$_2$sat,%	O$_2$ppm	t°	O$_2$sat,%	O$_2$ppm	t°
		EO	N															
		D/M/S	D/M/S		m				µs/cm	mg/l	mg/l	mg-ekv	February, 2003			May, 2003		
Kiviõli	RA-KV-1	59°21'55.1"	26° 56'25.4"	O_3kl-O_3kk	55.7	7.3	2.47	12.8	15130	4.07	3513.6	57.6				026	03.2	7.9
	RA-KV-2	59°21'81.4"	26°56'86.4"	O_3kl-O_3kk	46.2	5.2	3.30	8.2	2625	3.38	152.5	2.5	042	05.5	6.5	045	05.2	9.2
	RA-KV-3	59°21'43.5"	26°57'27.6"	O_3kl-O_3kk	48.3	4.0	2.3	7.2	2295	0.31	512.4	8.4	073	07.7	6.4	041	04.7	9.8
	RA-KV-4	59°21'56.6"	26°55'21.9"	O_3kl-O_3kk	45.7	3.0	1.60	7.6	2815	0.82	549,0	9	057	07.7	4.9	035	04.3	6.9
	RA-KV-5	59°21'77.4"	26°55'70.0"	waste, pore water	64.8	17.1	15.95	12.5	10540	13.74	1845.3	30.25				016	01.8	14.6
	RA-KV-6	59°21'84.7"	26°55'73.2"	waste, pore water	50.1	7.1	2.79	10.2	8730	1.57	472.8	7.75				018	02.2	9.2
	KV-6	59°21'36.6"	26°56'26.3"	O_1pk-$Є_1$ts	53.0			7.8	820	0.37	311.1	5.1	051	06.3	8.0			
	KV-9	59°21'63.0"	26°56'61.9"	O_1pk-$Є_1$ts	51.2			7.6	2000	0.44	231.8	3.8	059	07.6	6.5			
	KV-2309	59°21'15.1"	26°57'01'9"	O_1pk-$Є_1$ts	91.0			7.8	930	0.61	323.3	5.3	035	04.2	9.6			
	KV-CH1	59°21'89.0"	26°55'66.2"	channel water				7.2	9500	5.24	73.2	1.2						
	KV-CH2	59°21'73.5"	26°55'21.4"	channel water				6.3	6330	1.83	115.9	1.9						
	CH	59°20'45.5"	27°00'55.4"	mine water	49.0			7.5	1004	<0.05	341.6	5.6	050	06.7	5.0	048	05.7	8.9
Kukruse	KK-1/1	59°23'39.7"	27°20'32.0"	O_3kl-O_3kk	57.0	6.0	1.1	10.3	577	0.99	103.7	1.7				0.43	04.7	12.6
	KK-1/2	59°23'34.3"	27°20'20.9"	O_3kl-O_3kk	57.0	4.0	3.9	8.0								043	04.4	13.1
	KK-2	59°23'47.9"	27°18'31.6"	O_3kl-O_3kk	68.0	6.0	5.4	8.0	713	<0.05	231.8	3.8				095	11.7	6.2

Table 9.2.1 Main statistical parameters of chemical elements distribution in topsoil in Kiviõli

		Kiviõli							
		total				aqua regia			
		min	max	average	median	min	max	average	median
Al	%	1.64	6.08	4.10	4.22	0.29	1.79	1.17	1.22
Ca	%	1.19	19.73	7.32	4.36	0.96	18.78	6.93	4.55
Fe	%	1.78	3.81	2.82	2.77	1.45	3.72	2.46	2.43
K	%	0.87	3.07	2.16	2.29	0.11	1.01	0.36	0.34
Mg	%	0.16	3.03	0.63	0.53	0.11	2.98	0.46	0.36
Na	%	0.074	0.854	0.360	0.327	0.007	0.029	0.015	0.013
P	%	0.041	0.58	0.142	0.136	0.034	0.638	0.131	0.116
S	%	0.02	0.52	0.18	0.13	0.04	0.52	0.17	0.12
Ti	%	0.066	0.293	0.192	0.196	0.004	0.042	0.016	0.013
Ag	ppb	45	4029	316	93	23	3624	229	71
As	ppm	2.5	15.8	9.7	9.9	3.1	13.1	7.4	7.6
Au	ppm	<0.1	<0.1	<0.1	<0.1	0.1	2.2	0.6	0.5
B	ppm					3	33	18	18
Ba	ppm	154	456	294	309	32.5	242	80.1	74.3
Be	ppm	1	2	1	1				
Bi	ppm	0.02	0.21	0.11	0.11	0.03	0.23	0.14	0.15
Cd	ppm	0.09	0.51	0.23	0.24	0.02	0.5	0.17	0.18
Ce	ppm	23.24	74.36	47.93	48.14	11.7	54.3	34.25	36.05
Co	ppm	1.6	9.6	5.5	5.4	2.3	7.8	4.9	4.8
Cr	ppm	29	76	55	58	15.5	51.5	33.7	35.9
Cs	ppm	1.4	5.5	3.4	3.3				
Cu	ppm	9.7	20.54	14.45	13.89	7.28	18.74	12.62	12.39
Dy	ppm	1.5	5	3.3	3.4	0.88	4.25	2.38	2.44
Er	ppm	0.7	2.6	1.8	1.8	0.45	2.05	1.19	1.17
Eu	ppm	0.3	1.3	0.9	0.9	0.23	1.29	0.71	0.71
Ga	ppm	4.47	16.41	10.16	10.17	1.3	6.6	4.2	4.4
Gd	ppm	1.6	5.5	3.5	3.6	1.1	6.07	3.44	3.6
Hf	ppm	1.08	4.73	2.70	2.7				
Hg	ppb					6	278	80	57
Ho	ppm	0.2	0.9	0.6	0.6	0.17	0.8	0.46	0.46
La	ppm	12	41	28	29	6	30.3	19.0	18.9
Li	ppm	7.8	28.5	19.6	20.8				
Lu	ppm	0.1	0.3	0.2	0.2	0.05	0.23	0.13	0.14
Mn	ppm	294	1827	598	503	261	2077	583	490
Mo	ppm	2.77	9.76	4.25	3.69	2.07	8.83	3.81	3.49
Nb	ppm	2.35	9.47	5.80	5.97				
Nd	ppm	10.7	34.1	23.3	24.4	6.51	33.89	19.74	20.19
Ni	ppm	10.6	29.3	19.9	20.4	10.2	32.1	18.0	18.3
Pb	ppm	17.4	138.1	37.4	29.7	9.79	127.01	31.18	26.44
Pr	ppm	3	9.7	6.4	6.6	1.62	8.24	4.84	4.97
Rb	ppm	38.8	124.8	84.7	86				
Sb	ppm	0.2	0.5	0.3	0.3	0.12	0.41	0.21	0.19
Sc	ppm	1.7	11	6.5	6.3	1	5.4	3.0	3
Se	ppm					0.2	1.9	0.6	0.6
Sm	ppm	2.3	7.5	5.0	5.2	1.27	6.6	3.90	4.03
Sn	ppm	1	2	2	2				
Sr	ppm	81	403	156.3	127	19.2	345.9	98.9	56.7
Ta	ppm	0.2	0.6	0.4	0.4				
Tb	ppm	0.3	1	0.7	0.7	0.18	0.95	0.54	0.57
Te	ppm					0.01	0.08	0.04	0.03
Th	ppm	4.8	11.6	8.3	8.6	0.9	5.2	2.9	2.9
Tl	ppm					0.04	0.39	0.21	0.21
Tm	ppm	0.1	0.4	0.2	0.2	0.07	0.28	0.17	0.17
U	ppm	1	7	3	3	0.7	5.4	1.8	1.6
V	ppm	9	73	44.7	45	6	36	23	24
W	ppm	2.7	15.2	6.5	5.9	1	14.5	4.0	3
Y	ppm	7.4	28.4	18.8	19.4	4.61	23.01	13.30	13.29
Yb	ppm	0.9	2.6	1.8	2.0	0.35	1.76	1.03	1.08
Zn	ppm	22.5	189.7	63.8	53.7	16.2	154.1	56.15	49
Zr	ppm	31.7	141.8	80.3	75.7				
LOI						5.8	66.6	26.7	23.1

Table 9.2.2.1 Chemical composition of subsoil in Kiviõli

Region						Kiviõli					
Sample		**SR-KV-1**		**SR-KV-2**		**SR-KV-3**		**SR-KV-4-1**		**SR-KV-4-2**	
Rocks type		grey sandy siltstone		grey siltstone		dark brown, brown siltsone		grey-brown clayey siltstone		grey-brown siltstone (moraine)	
Depth, m		4.5-5.5		0.5-2.5		0.5-1.3		0-1.0		1.0-1.5	
		total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia
TOC	%	6.39		1.66		0.98		20.79		1.82	
Al	%	2.21	0.67	6.11	1.54	3.49	0.69	4.67	1.92	4.26	0.96
Ca	%	23.76	20.68	2.03	1.68	1.13	0.71	4.23	3.92	17.02	16
Fe	%	1.88	1.51	4.04	2.43	2.21	1.63	2.47	1.74	2.43	1.66
K	%	1.51	0.51	3.38	0.63	1.91	0.19	1.29	0.17	2.19	0.38
Mg	%	0.37	0.35	0.83	0.46	0.21	0.13	0.46	0.27	0.72	0.49
Na	%	0.162	0.022	0.417	0.021	0.825	0.04	0.257	0.01	0.233	0.016
P	%	0.07	0.061	0.058	0.047	0.056	0.046	0.123	0.113	0.048	0.043
S	%	0.36	0.22	0.1	0.04	0.08	0.02	0.2	0.15	0.07	0.1
Ti	%	0.111	0.018	0.32	0.021	0.118	0.021	0.192	0.01	0.234	0.009
Ag	ppb	59	16	89	42	59	27	125	88	82	25
As	ppm	6.2	4.8	5.8	3	5.1	3.8	5.2	3.6	7.1	3.7
Au	ppm	<0.1	0.2	<0.1	1.1	<0.1	0.7	<0.1	0.3	<0.1	0.3
Ba	ppm	129	32.1	449	74.2	376	47.8	230	100	251	47.6
Bi	ppm	0.04	0.03	0.22	0.19	0.1	0.09	0.25	0.22	0.12	0.1
Cd	ppm	0.09	0.04	0.16	0.09	0.14	0.03	0.76	0.64	0.14	0.06
Ce	ppm	28.87	16	76.53	45	50.09	34.3	87.17	56.3	48.77	27.6
Co	ppm	3	2.4	12.4	10.4	4	3.5	6.3	5.5	7.3	5.7
Cr	ppm	34	20.7	60	31.2	64	61	53	31.1	51	21.2
Cu	ppm	15.56	14.21	57.39	67.08	10.1	7.38	48.82	47.58	10.69	9.04
Dy	ppm	1.9	1.45	4.3	2.18	3	1.83	5.9	4.52	3	1.76
Er	ppm	1	0.78	2.3	0.96	1.3	0.79	2.8	2.12	1.6	0.8
Eu	ppm	0.5	0.37	1.2	0.76	0.8	0.4	1.7	1.07	0.9	0.5
Ga	ppm	5.2	2.3	18.65	5.8	8.78	2.6	11.92	5.6	11.23	3.8
Gd	ppm	2.3	1.83	5.6	3.87	3.5	2.72	7.9	6.2	3.6	2.47
Ho	ppm	0.3	0.25	0.7	0.35	0.5	0.28	1	0.78	0.7	0.28
La	ppm	19	9.2	43	22.2	30	18.4	58	33.4	32	14.3
Lu	ppm	0.1	0.08	0.3	0.11	0.2	0.08	0.4	0.26	0.2	0.1
Mn	ppm	345	297	305	222	653	544	212	172	319	264
Mo	ppm	5.16	4.36	3.28	2.33	12.85	11.69	1.97	1.65	2.28	1.62
Nd	ppm	13.8	8.38	33.6	20.46	21.8	14.46	44.8	28.2	22.2	13.38
Ni	ppm	14.4	11.1	26.6	21.8	11.8	9.8	17.2	15.8	15.6	12.4
Pb	ppm	22.4	18.01	15.37	7.22	15.93	6.74	15.83	11.6	12.13	7.55
Pr	ppm	3.5	2.18	8.6	5.55	5.9	4.19	11.9	7.71	5.9	3.49
Sb	ppm	0.15	0.08	0.29	0.1	0.17	0.1	0.26	0.16	0.21	0.07
Sc	ppm	3,1	2,2	9	4	3,1	1,8	8,6	4,3	6,4	3,2
Sm	ppm	2.9	1.81	6.7	4.24	4.4	3.14	9.2	6.21	4.5	2.83
Sr	ppm	211	170.3	118	42.7	117	25.2	81	41.9	180	129.2
Tb	ppm	0.4	0.24	0.9	0.48	0.6	0.37	1.4	0.89	0.6	0.36
Th	ppm	5.2	2.6	13.3	8.8	9.5	5.8	11.9	4.1	9.2	5.1
Tm	ppm	0.1	0.1	0.3	0.13	0.2	0.11	0.4	0.3	0.2	0.11
U	ppm	2.2	1.4	2.4	0.9	1.9	1	12.4	11.2	2.1	1
V	ppm	20	11	77	26	17	13	60	39	50	19
W	ppm	7	4.2	3.8	0.4	29.5	19.2	2.3	1.1	3.9	0.7
Y	ppm	12.4	8.17	21.9	11.12	15.3	8.65	37.5	27.47	17.6	9.16
Yb	ppm	1	0.66	2.5	0.85	1.5	0.71	3.2	1.98	1.8	0.71
Zn	ppm	25.8	19.3	84.1	70.1	23.5	16.8	57.1	42	37.1	24.9
LOI	%	34.5	0	8.6		3.3		50.3		24.9	

Table 9.2.2.2 Organic compounds in subsoil from wells near Kiviõli waste landfills

	Region	**Kiviõli**				
	Sample	**SR-KV-1**	**SR-KV-2**	**SR-KV-3**	**SR-KV-4-1**	**SR-KV-4-2**
	Rocks type	grey sandy siltstone	grey siltstone	dark brown, brown siltstone	grey-brown clayey siltstone	grey-brown siltstone (moraine)
	Depth, m	4.5-5.5	0.5-2.5	0.5-1.3	0.5-1.0	1.0-1.5
	Dry residue %	70.3	81.3	81.8	43.4	82.4
	Corg.,%	6.39	1.66	0.98	20.79	1.82
PAH, mg/kg DR	Naphthalin	<0.1	<0.1	<0.1	<0.1	<0.1
	Acenaphthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Acenaphthylen	<0.1	<0.1	<0.1	<0.1	<0.1
	Fluoren	<0.01	<0.01	<0.01	<0.01	<0.01
	Phenanthren	<0.01	<0.01	0.02	0.02	<0.01
	Anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Pyren	<0.01	0.01	<0.01	<0.01	<0.01
	Benzo[a]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Chrysen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[b]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[k]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[a]pyren	<0.01	<0.01	<0.01	<0.01	<0.01
	Indeno(123-cd)pyren	<0.01	<0.01	<0.01	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum PAH	n.n.	0.01	0.02	0.02	n.n.
BTX, mg/kg DR	Benzol	<0.01	<0.01	<0.01	<0.01	<0.01
	Toluol	<0.01	<0.01	<0.01	<0.01	<0.01
	Ethylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	m+p-Xylol	<0.01	0.02	0.012	<0.01	0.05
	Styrol	<0.01	<0.01	<0.01	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	1,3,5-Trimethylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum BTX	n.n.	0.02	0.012	n.n.	0.05
Phenols, mg/kg DR	Phenol	<1	<1	<1	<1	<1
	Resorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	5-Methylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	2,5-Dimethylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	4-Ethylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	4-Methylphenol	<0.05	<0.05	<0.05	<0.05	0.083
	3,4-Dimethylphenol	<0.05	<0.05	<0.05	<0.05	<0.05
	2,3-Dimethylphenol	<0.05	<0.05	<0.05	<0.05	<0.05
	2,4-Dimethylphenol	<0.05	<0.05	<0.05	<0.05	<0.05
	Sum phenols	n.n.	n.n.	n.n.	n.n.	0.083

Table 9.2.3.1 Chemical composition of water in Kiviõli area

Wells or channel		RA-KV-1	RA-KV-2	RA-KV-3	RA-KV-4	RA-KV-5	RA-KV-6	KV-6	KV-9	KV-2309	KV-CH1	KV-CH2
Water aquifer		O_3kl- O_3kk	O_3kl- O_3kk	O_3kl- O_3kk	O_3kl- O_3kk	waste, pore water	waste, pore water	O1pk- Є1ts	O1pk- Є1ts	O1pk- Є1ts	channel water	channel water
Al	ppb	962	22	25	3	261	3813	4	10	3	366	69
As	ppb	2.4	4.5	1.7	1.6	4,8	21,9	0.7	1.7	0.6	9.3	5.8
B	ppb	10	225	472	221	< 20	155	524	512	635	114	639
Ba	ppb	494	55	33	24	243	39	327	719	137	88	78
Br	ppb	5028	2702	2658	5072	31156	37712	1324	26971	2550	72269	36963
Ca	ppb	396064	566161	326245	237523	181442	56459	41312	111344	41205	261821	813157
Cd	ppb	<0.05	<0.05	<0.05	<0.05	0,58	<0,05	<0.05	<0.05	<0.05	0.85	0.71
Ce	ppb	<0.01	0.05	0.02	<0.01	0,06	5,19	<0.01	<0.01	<0.01	0.24	0.99
Cl	ppm	120	33	176	190	868	1189	105	739	97	1867	1105
Co	ppb	0.28	0.81	1.16	1.17	0,08	3,61	0.05	<0.02	<0.02	4.09	13.73
Cr	ppb	6.4	1.6	0.5	0.7	5,2	17,5	<0.5	<0.5	0.5	1.7	2.4
Cs	ppb	1.00	0.01	0.01	0.01	4,21	1,07	<0.01	0.12	0.01	11.43	0.14
Cu	ppb	4	23,9	45,.6	28.6	8	20	26.4	1.6	1.1	12.8	63.6
Fe	ppb	12	5	5	5	142	5820	360	1014	245	2515	4034
Ga	ppb	6.37	0.21	<0.05	<0.05	1,39	4,44	<0.05	<0.05	<0.05	0.21	0.09
Gd	ppb	0.03	<0.01	<0.01	<0.01	0,24	1,05	0.01	0.03	0.01	0.27	0.15
Ge	ppb	<0.05	0.58	0.07	<0.05	0,2	0,67	0.14	0.27	0.12	0.22	0.16
Hg	ppb	0.1	<0.1	<0.1	<0.1	<0,1	<0,1	<0.1	<0.1	<0.1	2.8	<0.1
K	ppb	2078943	67131	58565	26163	1811574	1469475	9911	43267	10781	2587651	803000
La	ppb	<0.01	0.02	<0.01	<0.01	0,02	2,68	<0.01	<0.01	<0.01	0.15	0.83
Li	ppb	45.0	32.3	36.0	38.3	146,1	154,7	21.2	31.8	25.3	263.9	5.0
Mg	ppb	< 50	19880	53560	17400	< 50	1055	29128	54894	31046	3897	48476
Mn	ppb	6	147	269	277	4	42	42	112	41	1700	4710
Mo	ppb	73.5	57.5	1.8	14.6	148,9	76,4	2.1	65.0	35.4	207.8	7.4
Na	ppb	61961	20922	63730	325428	622469	110610	80047	104232	86680	327528	73689
Nb	ppb	<0.01	0.03	0.01	0.01	0,01	0,55	<0.01	<0.01	<0.01	0.02	0.01
Nd	ppb	<0.01	0.05	0.01	<0.01	0,08	3,65	<0.01	<0.01	<0.01	0.15	0.25
Ni	ppb	4.7	<0.2	3.9	<0.2	0,2	21,1	<0.2	<0.2	<0.2	0.3	<0.2
P	ppb	57	40	<20	<20	149	238	<20	<20	<20	54	31
Pb	ppb	1.1	9.9	1.6	<0.1	<0,1	3	<0.1	0.1	<0.1	3.9	<0.1
Rb	ppb	2717.12	21.52	20.40	13.06	3203,66	2261,29	4.09	22.87	4.55	4589.53	133.35
Re	ppb	0.06	0.03	0.01	0.01	0,13	0,1	<0.01	<0.01	<0.01	0.16	0.12
S	*ppm*	67	522	206	253	466	972	13	7	18	763	674
Sb	ppb	1.80	0.43	0.14	0.19	<0,05	0,66	<0.05	<0.05	<0.05	0.30	0.11
Sc	ppb	0.94	1.37	1.42	1.90	1	5	0.81	0.86	0.86	1.71	0.77
Se	ppb	<0.5	1.9	0.9	1.6	58,5	64	<0.5	<0.5	<0.5	5.9	4.5
Si	ppb	10	6893	6438	8197	1285	12949	3463	3139	3536	8669	4128
Sn	ppb	0.09	<0.05	<0.05	<0.05	0,09	0,35	<0.05	0.06	<0.05	0.19	5.33
Sr	ppb	2250	3282	1876	414	3320	872	657	1882	660	3912	3230
Ti	ppb	<10	<10	<10	<10	< 10	172	<10	<10	<10	<10	<10
U	ppb	<0.02	2.29	3.25	0.66	0,02	2,97	0.17	0.10	0.06	0.04	0.77
V	ppb	0.4	1.0	1.1	1.4	8,4	54,9	0.2	0.7	0.3	7.0	1.7
W	ppb	4.15	4.82	0.18	0.36	56,18	14,11	0.02	0.03	0.07	0.12	0.13
Y	ppb	<0.01	0.09	0.02	<0.01	0,05	6,32	0.01	0.02	0.02	0.21	0.55
Zn	ppb	16.5	26.3	31.9	34.5	20,7	42,5	84.0	76.0	88.9	87.1	126.8
Zr	ppb	0.05	1.28	0.37	0.35	0,08	15,53	0.02	0.04	0.07	0.29	0.28

Content of Ag, Bi, Os, Ru is < 0.05 in all samples
Content of 'Dy, Er, Eu , Ho, In, Lu , Pr, Pt , Rh, Tl, Tm, Yb is <0.01 in all samples
Trace content (>0.01) of Dy, Er, Eu , Ho, In, Lu, Pr, Pt, Rh, Tb, Tl, Tm, Yb is in porous water
Trace content (>0.02) of Hf, Sm and Ta and Au, Be, Ir, 'Te, Th (>0.05) is in porous water

Table 9.2.3.2 Organic compounds in water from Kiviõli area

	Wells or channel	RA-KV-1	RA-KV-2	RA-KV-3	RA-KV-4	RA-KV-5	RA-KV-6	KV-6	KV-9	KV-2309	KV-CH1	KV-CH2	Mine water
	Water aquifer	O$_3$kl-O$_3$kk	O$_3$kl-O$_3$kk	O$_3$kl-O$_3$kk	O$_3$kl-O$_3$kk	waste, pore water	waste, pore water	O$_1$pk-Є$_1$ts	O$_1$pk-Є$_1$ts	O$_1$pk-Є$_1$ts	channel water	channel water	
	DOC, mg/l		35	7,6	5,9	49	11	3,3	1,9	0,5			7,7
PAH, µg/l	Naphthalin	<0.01	<0.01	<0.01	<0.01	0.91	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	1-Methylnaphthalin	<0.01	<0.01	<0.01	<0.01	0.19	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	2-Methylnaphthalin	<0.01	<0.01	<0.01	<0.01	0.12	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Acenaphthylen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Acenaphthen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Fluoren	<0.01	<0.01	<0.01	0.023	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.018
	Phenanthren	<0.01	0.144	0.561	0.065	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.026
	Anthracen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Fluoranthen	0.014	0.011	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Pyren	0.013	<0.01	<0.01	0.019	<0.01	<0.01	<0.01	<0.01	<0.01	0.013	<0.01	<0.01
	Benzo[a]anthracen	0.018	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Chrysen	0.027	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[b]fluoranthen	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[k]fluoranthen	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[a]pyren	0.019	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Indeno[123cd]pyren	0.041	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum PAH, PLV=10	0.152	0.155	0.561	0.117	1.22	n.n.	n.n.	n.n.	n.n.	0.013	n.n.	0.044
BTX, µg/l	Benzol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Toluol	3.7	3.3	3.6	3	< 0.5	< 0.5	<0.5	<0.5	4	<0.5	<0.5	<0.5
	Chlorbenzol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Ethylbenzol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	m+p-Xylol	2.5	2.6	3.1	2.7	< 0.5	< 0.5	<0.5	<0.5	12.9	<0.5	<0.5	<0.5
	o-Xylol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Styrol	<0.5	<0.5	<0.5	<0.5	< 0.5	1.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Cumol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	3+4-Ethyltoluol	<0.5	3.6	2.3	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Mesitylen	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	2-Ethyltoluol	<0.5	<0.5	<0.5	<0.5	< 0.5	< 0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Sum BTX, PLV= 600	6.2	9.5	9	5.7	n.n.	1.8	n.n.	n.n.	16.9	n.n.	n.n.	n.n.
Phenols, µg/l	Phenol	2032	2.88	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Resorcin	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	5-Methylresorcin	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2+3-Methylphenol	2313	4.86	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	4-Methylphenol	183	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,6-Dimethylphenol	< 0.5	3.11	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	3,4-Dimethylphenol	< 0.5	2.86	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,3-Dimethylphenol	< 0.5	1.41	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,4+2,5-Dimethylphenol	235	3.92	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	3,5-Dimethylphenol	< 0.5	1.25	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,4,6-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,3,6-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	2,3,5-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	3,4,5-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Sum phenols, PLV=200	4763	20.4	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.	n.n.

Table 9.3.1 *Main statistical parameters of chemical elements distribution in topsoil in Kohtla-Järve*

		Kohtla-Järve							
		total				aqua regia			
		min	max	average	median	min	max	average	median
Al	%	0.74	5.54	3.02	3.12	0.15	2.51	0.97	0.87
Ca	%	0.3	21.05	6.32	3.68	0.11	21.27	6.44	4.01
Fe	%	0.81	3.3	1.83	1.83	0.7	3.31	1.69	1.67
K	%	0.26	2.44	1.46	1.65	0.05	1.86	0.34	0.24
Mg	%	0.06	1.82	0.53	0.33	0.04	2	0.48	0.24
Na	%	0.035	0.916	0.392	0.388	0.006	0.068	0.018	0.015
P	%	0.016	0.242	0.091	0.083	0.013	0.258	0.089	0.077
S	%	0.02	0.99	0.23	0.16	0.01	0.96	0.24	0.16
Ti	%	0.035	0.234	0.134	0.151	0.007	0.106	0.025	0.016
Ag	ppb	48	580	111	93	19	540	81	66
As	ppm	3.1	91.4	11.1	9.3	2	81.4	11.2	8
Au	ppm	<0.1	<0.1	<0.1	<0.1	0.1	9	1.0	0.6
B	ppm					1	47	16	13
Ba	ppm	84	525	281	282	25.1	233.1	82.7	75.1
Be	ppm	<1	2	1	1				
Bi	ppm	0.05	0.21	0.11	0.10	0.04	0.25	0.12	0.12
Cd	ppm	0.1	0.82	0.29	0.24	0.05	0.85	0.22	0.15
Ce	ppm	6.97	69.61	36.46	38.46	6.8	49.4	25.4	23.7
Co	ppm	0.7	9.6	3.4	3.4	1.3	8.5	3.6	3.2
Cr	ppm	11	209	42	36	6.7	182.3	30.7	23.9
Cs	ppm	0.5	5.4	2.5	2.3				
Cu	ppm	6.4	110.35	19.72	14.13	6.75	167.72	20.78	14.67
Dy	ppm	0.5	5.3	2.5	2.5	0.6	4.44	1.75	1.51
Er	ppm	0.3	2.9	1.3	1.3	0.32	2.06	0.86	0.75
Eu	ppm	0.1	1.3	0.7	0.7	0.13	1.26	0.45	0.38
Ga	ppm	1.82	14.25	7.50	8.2	0.7	7.5	3.4	3
Gd	ppm	0.6	7.2	2.8	2.7	0.75	6.05	2.44	2.13
Hf	ppm	0.37	7.76	2.94	2.65				
Hg	ppb					3	369	91	50
Ho	ppm	0.1	0.9	0.4	0.4	0.1	0.78	0.32	0.29
La	ppm	4	40	21	22	4	29.3	14.2	13.3
Li	ppm	2.7	27.4	14.2	13.9				
Lu	ppm	0.1	0.4	0.2	0.2	0.03	0.21	0.10	0.09
Mn	ppm	192	957	432	395	102	1229	445	384
Mo	ppm	0.62	5.46	1.69	1.36	0.41	5.45	1.62	1.34
Nb	ppm	1.2	8.75	5.10	5.51				
Nd	ppm	3.7	37.4	18.2	18.1	3.71	29.26	13.35	12.35
Ni	ppm	3.8	54.4	12.2	10.8	4	43.4	11.4	10.6
Pb	ppm	12.0	95.5	27.6	22.8	4.84	94.39	24.81	20.26
Pr	ppm	1	10	4.8	5.1	0.93	7.34	3.48	3.23
Rb	ppm	12.1	109.5	66.2	74.7				
Sb	ppm	0.1	0.8	0.3	0.3	0.1	4.16	0.45	0.19
Sc	ppm	1	7.6	4.1	3.8	0.5	4.3	1.9	1.6
Se	ppm					0.1	1.7	0.6	0.5
Sm	ppm	0.7	7.7	3.6	3.7	0.75	6.39	2.78	2.46
Sn	ppm	1	4	1	1				
Sr	ppm	61	600	170.1	139	5.2	577.1	120.6	71.1
Ta	ppm	0.1	0.6	0.3	0.3				
Tb	ppm	0.1	1.1	0.5	0.5	0.12	0.95	0.35	0.31
Te	ppm					0.01	0.15	0.04	0.04
Th	ppm	1.4	9.2	5.5	5.6	0.1	5.7	2.2	2.4
Tl	ppm					0.04	2.31	0.33	0.24
Tm	ppm	0.1	0.4	0.2	0.2	0.04	0.27	0.12	0.11
U	ppm	1	7	3	3	0.5	8.5	2.3	1.9
V	ppm	6	76	27.3	25	4	52	19	18
W	ppm	0.3	11	2.3	1.5	0.2	9.1	1.6	0.8
Y	ppm	3.4	29.4	14.7	13.9	2.94	26.3	9.48	8.2
Yb	ppm	0.3	2.8	1.4	1.4	0.25	1.64	0.75	0.66
Zn	ppm	8.3	160.9	34.6	30.3	8.2	150.3	30.1	25
Zr	ppm	12.2	238.2	90.5	88.1				
LOI						2.2	83.3	35.2	27.9

Table 9.3.2.1 Chemical composition of subsoil in Kohtla-Järve

Region		Kohtla-Järve									
Sample		SR-KJ-1		SR-KJ-2		SR-KJ-3-1		SR-KJ-3-2		SR-KJ-4	
Rocks type		grey-brown, red-brown clay (moraine)		green-grey clay, clayey siltstone (moraine)		green-grey clay, clayey siltstone (moraine)		green clay, clayey siltstone (moraine)		dark-yellow, brown siltstone (moraine)	
Depth, m		0.2-2.0		1.0-5.0		0-1.1		1.1-4.2		0.3-2.4	
		total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia
TOC	%	0.97		0.61		2.24		0.29		1.13	
Al	%	5.12	1.11	5.26	1.11	2.99	0.77	6.64	1.45	4.70	1.16
Ca	%	6.38	5.61	1.77	1.13	6.62	6.12	1.25	0.74	7	6.54
Fe	%	3.05	2.31	2.5	1.78	1.48	1.25	3.44	2.54	2.84	2.26
K	%	2.36	0.3	2.8	0.4	1.45	0.22	3.07	0.5	2.19	0.35
Mg	%	1.65	1.42	0.44	0.3	0.47	0.44	0.79	0.51	2.22	1.95
Na	%	0.661	0.022	1.16	0.059	0.589	0.026	1.063	0.037	0.631	0.033
P	%	0.116	0.102	0.05	0.043	0.041	0.039	0.066	0.049	0.126	0.12
S	%	0.1	0.03	0.1	0.11	0.23	0.16	0.07	0.05	0.02	0.02
Ti	%	0.24	0.026	0.262	0.052	0.113	0.031	0.351	0.065	0.221	0.024
Ag	ppb	98	43	114	51	71	28	100	53	132	42
As	ppm	19.5	13	4.7	3	3.5	3	4.5	3.2	8.8	5.6
Au	ppm	<0.1	0.7	<0.1	0.3	<0.1	0.4	<0.1	0.1	<0.1	0.4
Ba	ppm	440	57.3	584	81.8	350	72.9	585	93.9	398	60.8
Bi	ppm	0.19	0.15	0.16	0.13	0.07	0.06	0.22	0.18	0.14	0.14
Cd	ppm	0.24	0.12	0.27	0.05	0.17	0.04	0.21	0.05	0.22	0.13
Ce	ppm	74.91	44.5	77.02	57.7	36.39	1.4	78.19	52.6	68.66	45.3
Co	ppm	0.4	0.3	0.5	0.6	0.6	2	2.3	0.3	7	7.8
Cr	ppm	47	24.9	36	31.8	35	31.4	55	47.2	55	25.2
Cu	ppm	41.3	46.07	20.04	21.78	7.67	7.77	17.79	17.47	26.29	27.8
Dy	ppm	4	2.81	4.5	2.75	1.8	1.19	4.1	2.74	4	2.91
Er	ppm	2.1	1.36	2.4	1.35	1	0.61	2.3	1.36	2	1.42
Eu	ppm	1.2	0.79	1.1	0.54	0.6	0.28	1.2	0.67	1.2	0.76
Ga	ppm	13.09	4.4	13.91	4.3	6.94	2.6	19.45	6.4	11.41	4.5
Gd	ppm	5.3	4.16	6.2	4.12	2.4	1.43	5.9	4.12	5.6	4.12
Ho	ppm	0.8	0.45	0.8	0.44	0.3	0.19	0.8	0.41	0.7	0.46
La	ppm	45	23.1	43	28.9	22	11.8	42	26.7	43	25
Lu	ppm	0.3	0.15	0.4	0.16	0.2	0.06	0.3	0.16	0.3	0.15
Mn	ppm	820	725	348	217	249	197	533	407	778	729
Mo	ppm	2.91	2.52	4.53	4.03	6.05	5.91	4.35	6.1	2.78	2.52
Nd	ppm	32.5	20.86	34.9	24.43	14.6	9.34	34.2	22.84	31.5	21.52
Ni	ppm	19.2	17.2	18.4	15.6	7.2	6.8	25.1	19.9	14.8	16.4
Pb	ppm	17.6	10.22	21.0	8.11	15.7	8.74	19.6	7.67	16.2	9.79
Pr	ppm	8	5.53	8.5	6.73	3.8	2.62	8.6	6.3	7.4	5.51
Sb	ppm	0.4	0.19	0.3	0.14	0.1	0.09	0.2	0.09	0.3	0.15
Sc	ppm	6.3	3.3	6.2	3.1	2.3	1.8	8.2	3.8	6	3.4
Sm	ppm	6	4.44	6.3	5.02	2.8	1.93	6.6	4.83	6.2	4.59
Sr	ppm	139	40.5	164	33.8	298	227.5	152	29.5	121	42.8
Tb	ppm	0.8	0.54	0.9	0.54	0.4	0.22	0.9	0.52	0.9	0.54
Th	ppm	11.4	6.4	14.6	9.4	6.3	2.6	12.2	9.4	12.1	6.8
Tm	ppm	0.3	0.17	0.4	0.18	0.2	0.07	0.4	0.18	0.3	0.18
U	ppm	3	1.9	3	1.6	2	1.1	3	1.4	3	2
V	ppm	45	24	37	21	15	13	70	32	40	26
W	ppm	13.8	6.3	5.6	2.1	14.2	11.9	7.3	2.1	23.3	5.7
Y	ppm	24	14.14	25.7	13.14	11.8	6.34	23.4	14.14	23.7	16.15
Yb	ppm	2.6	1.2	3	1.34	1.3	0.56	3	1.24	2.3	1.31
Zn	ppm	63.5	52.1	39.2	27.3	14.9	12.3	65.4	49.5	50.6	45.1
LOI	%	13.0		4.3		13.3		4.8		14.8	

Table 9.3.2.2 Organic compounds in subsoil from wells near Kohtla -Järve waste landfills

	Region	**Kohtla-Järve**				
	Sample	**SR-KJ-1**	**SR-KJ-2**	**SR-KJ-3-1**	**SR-KJ-3-2**	**SR-KJ-4**
	Rocks type	grey-brown, red-brown clay (moraine)	green-grey clay, clayey siltstone (moraine)	green-grey, clay, clayey siltstone (moraine)	green clay, clayey siltstone (moraine)	dark-yellow, brown siltstone (moraine)
	Depth, m	0.2-2.0	1.0-5.0	0. 2-1.1	1.1-4.2	0.3-2.4
	Dry residue %	70.3	76.2	66.5	81.7	86.8
	Corg.,%	0.97	0.61	2.24	0.29	1.13
PAH, mg/kg DR	Naphthalin	<0,1	<0,1	<0,1	<0,1	<0,1
	Acenaphthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Acenaphthylen	<0.1	<0.1	<0.1	<0.1	<0.1
	Fluoren	<0.01	<0.01	<0.01	<0.01	<0.01
	Phenanthren	0.02	<0.01	0.02	<0.01	0.04
	Anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Fluoranthen	<0.01	<0.01	<0.01	<0.01	0.02
	Pyren	<0.01	<0.01	0.02	<0.01	0.02
	Benzo[a]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Chrysen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[b]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[k]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[a]pyren	<0.01	<0.01	<0.01	<0.01	<0.01
	Indeno(123-cd)pyren	<0.01	<0.01	<0.01	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum PAH	0.02	n.n.	0.02	n.n.	0.08
BTX, mg/kg DR	Benzol	<0.01	<0.01	<0.01	<0.01	<0.01
	Toluol	0.017	<0.01	0.019	<0.01	<0.01
	Ethylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	m+p-Xylol	0.019	<0.01	0.014	0.023	0.011
	Styrol	<0.01	<0.01	<0.01	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	1,3,5-Trimethylbenzol	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum BTX	0.036	n.n.	0.033	0.023	0.011
Phenols, mg/kg DR	Phenol	<1	<1	<1	<1	<1
	Resorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	5-Methylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	2,5-Dimethylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	4-Ethylresorcin	<0.05	<0.05	<0.05	<0.05	<0.05
	4-Methylphenol	<0.05 **	<0.05	<0.05	<0.05	<0.05
	3,4-Dimethylphenol	<0.05	<0.05	<0.05	<0.05	<0.05
	2,3-Dimethylphenol	<0.05	<0.05	<0.05 **	<0.05	<0.05
	2,4-Dimethylphenol	<0.05	<0.05	0.066	<0.05	<0.05

** = Traces

Table 9.3.3.1 Chemical composition of water from Kohtla-Järve

Well or channel		RA-KJ-1	RA-KJ-2	RA-KJ-3	RA-KJ-4	KJ-600	KJ-602	KJ-608	KJ-610	KJ-616	KJ-620	KJ-622	RA-KJ-5	RA-KJ-6	KJ-601	KJ-603	KJ-609	KJ-611	KJ-623	KJ-CH1	KJ-CH2
Water aquifer		O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	waste, pore water	waste, pore water	O_1pk-Є$_1$ts	O_1pk-Є$_1$ts	O_1pk-Є$_1$ts	O_1pk-Є$_1$ts	O_1pk-Є$_1$ts	channel water	channel water
Al	ppb	2	11	8	2	7	31	10	4	15	8	23	218	166	35	5	4	3	2	3926	2
As	ppb	2.7	9.5	19.9	0.6	5.7	11.9	1.1	1.2	<0.5	0.5	19.4	47	31	10.1	<0.5	<0.5	<0.5	<0.5	12.3	25.7
Au	ppb	<0.05	<0.05	0.46	<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	<0.05	<0.05	0.54	0.38
B	ppb	120	36	91	96	79	55	198	160	172	56	46	< 20	< 20	56	412	539	389	552	60	162
Ba	ppb	43.26	235.35	304.87	26.29	344.42	19.27	41.01	37.90	103.54	82.70	88.41	1578	1741	57.92	292.05	123.28	208.33	281.32	62.82	172.86
Be	ppb	<0.05	<0.05	0.64	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.95	<0,05	<0,05	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	0.50
Br	ppb	24852	14186	33541	946	36207	45394	5069	3972	732	273	60792	54628	62286	38972	2259	849	779	389	54855	60417
Ca	ppb	358497	33509	4615	281565	41986	37407	212045	240349	8973	152441	3416	1259577	1213096	2708	67499	67119	93582	21564	64788	294100
Ce	ppb	<0.01	0.14	0.07	<0.01	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	0.23	0,13	0,12	0.15	<0.01	<0.01	<0.01	<0.01	0.07	<0.01
Cl	ppm	518	346	836	39	651	902	168	148	31	42	1254	1423	1457	709	49	37	39	27	986	1394
Co	ppb	2.00	0.35	0.26	0.17	0.08	0.26	0.08	<0.02	0.06	0.08	0.35	<0,02	<0,02	0.14	0.02	0.08	<0.02	0.03	3.57	0.61
Cr	ppb	<0.5	0.7	2.4	0.5	0.6	1.2	<0.5	<0.5	<0.5	<0.5	2.1	9,8	12,9	1.5	<0.5	<0.5	2.8	<0.5	3.4	5.0
Cs	ppb	<0.01	0.12	0.10	<0.01	0.34	0.40	0.01	0.01	0.01	<0.01	0.18	11,61	12,14	5.67	0.01	0.02	0.02	0.01	36.67	6.20
Cu	ppb	3.2	3.7	4.8	23.9	1.0	3.2	8.4	2.5	15.0	5.6	2.1	3,2	3,4	3.2	5.5	7.2	2.5	3.5	80.3	2.4
Fe	ppb	7057	43	124	5	94	5	2034	1779	5	249	5	253	178	5	182	177	251	116	5	90
Ga	ppb	<0.05	<0.05	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05	<0.05	<0.05	0,49	0,75	0.22	<0.05	<0.05	<0.05	<0.05	2.53	<0.05
Gd	ppb	<0.01	0.04	0.12	<0.01	0.01	0.11	0.01	<0.01	0.02	0.01	0.09	0,13	0.2	0.03	0.01	<0.01	<0.01	0.01	0.11	0.03
Ge	ppb	<0.05	0.14	0.46	<0.05	0.41	0.19	0.13	0.09	<0.05	<0.05	0.29	0,35	0,33	0.35	0.22	0.13	0.27	0.14	0.10	0.14
Hg	ppb	<0.1	<0.1	3.4	<0.1	0.1	2.5	<0.1	<0.1	<0.1	<0.1	1.7	<0,1	<0,1	1.8	<0.1	<0.1	<0.1	<0.1	0.6	<0.1
In	ppb	<0.01	<0.01	0.04	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	0.03	0,09	0,03	0.02	<0.01	<0.01	<0.01	<0.01	0.05	0.04
K	ppb	11587	259678	1167527	7208	357529	1469106	7493	9245	15435	3047	2031986	2302405	2036788	1840365	12916	9377	11829	8263	2583023	1777621
Li	ppb	13.5	25.3	35.2	17.9	44.8	111.9	9.5	7.5	22.7	6.3	45.3	414,3	435,7	143.3	15.4	19.8	11.3	20.2	510.5	203.8
Mg	ppb	53896	4392	12842	62162	27890	16933	56265	54846	6162	22680	664	142	146	66	32245	37032	38496	14398	73	938
Mn	ppb	713	19.69	24.55	58.06	3.25	2.67	126.12	250.07	0.27	273.62	1.46	7	5	1.14	34.74	10.21	35.10	25.37	16.49	1.32
Mo	ppb	2.6	17.0	6.7	0.3	11.6	8.1	0.2	0.2	1.2	0.3	6.5	9	10,6	21.0	0.2	0.3	0.5	0.8	77.2	90.9
Na	ppb	46285	42007	159227	40693	86208	146028	68517	63687	24195	12803	156643	109135	125167	142256	27929	52829	12491	109231	181741	156450
Ni	ppb	16.3	3.5	16.0	0.6	2.1	12.8	<0.2	<0.2	1.9	0.1	39.7	0,2	0,2	22.3	<0.2	<0.2	<0.2	<0.2	178.7	6.5
P	ppb	<20	101	129	<20	<20	71	<20	<20	<20	<20	147	40	69	42	<20	<20	<20	<20	61	85
Pb	ppb	0.1	4.6	4.4	1.3	<0.1	<0.1	0.1	0.7	0.1	<0.1	0.5	0,8	<0,1	2.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Pd	ppb	<0.2	<0.2	0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0,2	<0,2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Rb	ppb	5.53	150.87	685.00	4.19	251.66	1199.03	4.78	5.68	15.63	2.02	1383.19	4256,25	4485,61	2309.10	4.73	5.71	10.74	4.58	4632.75	2538.19
Re	ppb	0.02	0.05	0.14	0.01	0.07	0.17	<0.01	<0.01	<0.01	<0.01	0.15	0,07	0,07	0.25	<0.01	<0.01	<0.01	<0.01	0.62	0.10
S	ppm	167	23	61	213	15	176	106	110	19	48	51	120	172	70	7	20	12	7	192	288
Sb	ppb	0.07	0.52	0.17	0.11	0.12	0.13	<0.05	<0.05	0.17	<0.05	0.30	0,09	0,07	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	0.16
Sc	ppb	1.53	1.73	7.99	0.64	5.54	1.25	1.12	1.13	0.12	1.66	25.41	1	1	42.82	0.79	0.92	1.05	0.63	2.40	<0.05
Se	ppb	0.7	3.1	<0.5	<0.5	0.7	1.3	0.7	<0.5	<0.5	1.4	<0.5	121	114	<0.5	<0.5	0.5	0.5	0.8	<0.5	4.1
Si	ppb	5605	7346	48672	3087	31638	3045	5570	5228	692	6229	122181	483	551	232527	4134	4286	5189	3096	14205	2290
Sr	ppb	448	239	153	411	352	107	447	368	123	238	44	16574,01	16114,13	147	576	720	723	315	725	4379
Te	ppb	<0.05	<0.05	0.24	<0.05	<0.05	0.23	<0.05	<0.05	<0.05	<0.05	<0.05	2,26	0,84	0.08	<0.05	<0.05	<0.05	<0.05	0.09	<0.05
Ti	ppb	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	16	< 10	< 10	27	<10	<10	<10	<10	<10	<10
U	ppb	0.90	0.50	0.09	4.51	0.11	0.23	0.08	0.26	0.02	0.31	0.08	0,02	0,02	<0.02	0.28	0.32	0.38	0.18	<0.02	0.16
V	ppb	0.8	5.5	25.9	<0.2	3.9	37.1	0.6	0.5	0.5	<0.2	45.0	6,5	8,4	18.0	0.5	0.2	<0.2	<0.2	15.8	54.3
W	ppb	0.12	2.98	1.14	0.77	0.43	1.08	0.07	0.03	1.88	0.19	0.74	0,16	0,49	0.54	0.08	0.07	0.05	0.11	0.51	0.26
Y	ppb	0.01	0.06	0.17	0.02	0.01	<0.01	0.03	0.01	<0.01	0.04	0.74	0,13	0,13	0.15	<0.01	<0.01	<0.01	0.02	0.11	<0.01
Zn	ppb	60.3	13.0	144.8	82.2	3.9	10.9	66.7	57.7	15.1	33.3	1.6	36,9	22	14.3	28.6	67.3	81.3	68.4	14.8	16.4
Zr	ppb	0.13	0.21	3.66	0.18	0.17	1.82	0.25	0.28	0.02	0.32	2.30	0,12	0,13	0.57	0.09	0.11	0.11	0.13	0.35	0.20

Content of 'As, Bi, Ir , Os is <0.05 in all samples
Content of 'Dy, Er, Eu, Ho, Lu , Tm, Tl, Yb, Tb, Rh <0.01 in all samples
Trace content of (>0.01) In, La, Nb, Nd, Pr, Pt in porous water
Trace content (<0.05) of 'Cd, Th, Ru , Sn in porous water
Content of 'Hf, Sm , Ta is <0.02 in all samples

Table 9.3.3.2 Organic compounds in the water from Kohtla-Järve area

	Wells or channel	RA-KJ-1	RA-KJ-2	RA-KJ-3	RA-KJ-4	RA-KJ-5	RA-KJ-6	KJ-600	KJ-601	KJ-602	KJ-603	KJ-608	KJ-610	KJ-616	KJ-620	KJ-622	KJ-CH1	KJ-CH2
	Water aquifer	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	waste, pore water	waste, pore water	O_2ls-O_2kn	O_1pk-$Є_1ts$	O_2ls-O_2kn	O_1pk-$Є_1ts$	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	O_2ls-O_2kn	channel water	channel water
	DOC, mg/l	12	14	100	2.2	473	19	77	55	14	3.6	7.8	6.8	1.5	10	214	50	530
PAH, µg/l	Naphthalin	<0.01	<0.01	<0.01	0.277	517	400.3	6.8	<0.01	24.3	<0.01	<0.01	0.12	<0.01	4.75	4.19	0.31	19
	1-Methylnaphthalin	<0.01	<0.01	<0.01	<0.01	38.8	29.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	2-Methylnaphthalin	<0.01	<0.01	<0.01	<0.01	31.2	25.9	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	<0.01
	Acenaphthylen	<0.01	<0.01	<0.01	<0.01	15.7	0.21	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Acenaphthen	<0.01	<0.01	<0.01	<0.01	6.3	2.7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01
	Fluoren	<0.01	<0.01	<0.01	<0.01	7.9	1.7	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	1.33	<0.01	<0.01	<0.01
	Phenanthren	<0.01	<0.01	<0.01	0.031	10.2	1.2	<0.01	<0.01	<0.01	<0.01	0.01	0.02	<0.01	2.74	<0.01	<0.01	<0.01
	Anthracen	<0.01	<0.01	<0.01	<0.01	0.8	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.79	<0.01	<0.01	<0.01
	Fluoranthen	<0.01	<0.01	<0.01	<0.01	0.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.45	<0.01	<0.01	<0.01
	Pyren	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.46	<0.01	<0.01	<0.01
	Benzo[a]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Chrysen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	<0.01
	Benzo[b]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[k]fluoranthen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[a]pyren	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Indeno[123cd]pyren	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Sum PAH, PLV=10	n.n.	n.n.	n.n.	0.308	628.4	461.4	6.8	n.n.	24.3	n.n.	0.01	0.14	n.n.	10.55	4.19	0.322	19
BTX, µg/l	Benzol	<0.5	69.3	310	<0.5	8570	431	80.3	31.3	60.5	<0.5	123	193	<0.5	<0.5	127	<0.5	1040
	Toluol	1.8	8.7	28.1	1.7	6580	316	14.1	4.6	14.7	3.3	4.7	4.1	3.3	4.3	17.5	4.2	641
	Chlorbenzol	<0.5	<0.5	<0.5	<0.5	24	32.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
	Ethylbenzol	<0.5	<0.5	<0.5	<0.5	1200	28.7	10	<0.5	10.9	<0.5	<0.5	9.9	<0.5	11.6	<0.5	<0.5	86.6
	m+p-Xylol	<0.5	3.6	1.8	<0.5	1080	83.7	13.2	12.3	14.4	<0.5	12.8	13	17.7	13.5	12.9	12.4	141
	o-Xylol	<0.5	2.5	2.5	<0.5	600	< 0.5	9.9	<0.5	10.5	<0.5	<0.5	<0.5	<0.5	<0.5	9.4	9.3	104
	Styrol	<0.5	<0.5	<0.5	<0.5	830	77.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	24.6
	Cumol	<0.5	3.3	3.5	<0.5	142	26.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	32.4
	3+4-Ethyltoluol	<0.5	3.8	3.9	<0.5	201	31	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	29.7
	Mesitylen	<0.5	<0.5	<0.5	<0.5	87.8	120	7.4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	65.9
	2-Ethyltoluol	<0.5	<0.5	<0.5	<0.5	228	65.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	63.5
	Sum BTX, PLV=600	1.8	91.2	349.8	1.7	19543	1213	134.9	48.2	111	3.3	140.5	220	21	29.4	166.8	25.9	2228.7
Phenols, µg/l	Phenol	< 0.5	12.3	22193	< 0.5	28450	31070	559	226.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	7880.3	< 0.5	22530
	Resorcin	< 0.5	0.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	5-Methyl-resorcin	< 0.5	6.1	5288	< 0.5	34500	< 0.5	63.9	218.5	0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	211	< 0.5	< 0.5
	2+3-Methylphenol	< 0.5	26.4	23195	< 0.5	10500	19460	522.8	97.7	126.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	5270.5	128.8	18436
	4-Methyl-phenol	< 0.5	13.4	5158	< 0.5	< 0.5	9840	363.4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1664.8	< 0.5	7014.1
	2,6-Dimethylphenol	< 0.5	5.3	4470	< 0.5	< 0.5	< 0.5	101.8	216.1	60.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	533.0	36.9	1311.9
	3,4-Dimethylphenol	< 0.5	18.6	5140	< 0.5	11470	7580	155.6	248.8	118.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	837.5	116.9	5000
	2,3-Dimethylphenol	< 0.5	20.7	6940	< 0.5	< 0.5	19480	237.5	147.6	215.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1069	173.3	3773.9
	2,4+2,5-Dimethylphenol	< 0.5	20.1	2693	< 0.5	< 0.5	< 0.5	129.7	291.9	93.0	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	899.3	91.6	4167.7
	3,5-Dimethylphenol	< 0.5	< 0.5	4207	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	22.2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	800.8	< 0.5	< 0.5
	2,4,6-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	8475	< 0.5	< 0.5	46.4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	482.1	< 0.5	1535.9
	2,3,6-Trimethylphenol	< 0.5	20.9	2949	< 0.5	< 0.5	< 0.5	97.7	254.2	93.4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	91.4	2586.2
	2,3,5-Trimethylphenol	< 0.5	17.6	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	279.5	184.2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	159.3	2113.3
	3,4,5-Trimethylphenol	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	Sum phenols, PLV=200	n.n.	162.2	82235	n.n.	93395	87430	2231	2027	914.1	n.n.	n.n.	n.n.	n.n.	n.n.	19648	798.2	68469

Table 9.3.3.3 Total content of organic compounds in the groundwater from the wells in Kohtla-Järve

	Water aquifer	Depth, m	pH	DOC	Sum PAH	Sum BTX	Phenols	Sum PAH*	Sum BTX*	Phenols*
				mg/l			µg/l			
RA-KJ-1	O_2ls-O_2kn	5.4	7	12	<0.01	1.8	<0.5			
RA-KJ-2	O_2ls-O_2kn	8.4	9.8	14	<0.01	91.2	162.2			
RA-KJ-3	O_2ls-O_2kn	9.5	9.3	100	<0.01	349.8	82235			
RA-KJ-4	O_2ls-O_2kn	5.7	7.2	2.2	0.308	1.7	<0.5			
KJ-600	O_2ls-O_2kn	20.7	8.8	77	6.8	134.9	2231	<0.2		6948
KJ-601	O_1pk-Є$_1$ts	39.5	11.9	55	<0.01	48.2	2027			
KJ-602	O_2ls-O_2kn	22.3	9.1	14	24.3	111	<0.5	5.3		5088
KJ-603	O_1pk-Є$_1$ts	37.1	7.5	3.6	<0.01	3.3	<0.5			
KJ-608	O_2ls-O_2kn	26.5	7	7.8	0.01	140.5	<0.5			
KJ-610	O_2ls-O_2kn	29.8	7	6.8	0.14	220	<0.5			
KJ-616	O_2ls-O_2kn	36.5	9.5	1.5	<0.01	21	<0.5		<10	31
KJ-620	O_2ls-O_2kn	35.9	7.3	10	10.5	29.4	<0.5			
KJ-622	O_2ls-O_2kn	30.07	11	214	4.19	166.8	19648	5.3		24037
KJ-CH1			12.5	50	0.322	25.9	<0.5			
KJ-CH2			11.8	530	19	2228.7	68469			
Leaches					0.2	2.1	<0.5			
PLV					*10*	*600*	*200*	*10*	*600*	*200*

Table 9.4.1.1 Chemical composition of water in Kukruse area

Well		KK-1/1	KK-1-2	KK-2
Water aquifer		O_3kl-O_3kk	O_3kl-O_3kk	O_3kl-O_3kk
Al	ppb	126	55	20
As	ppb	2.4	2.4	0.6
B	ppb	240	34	22
Ba	ppb	127	302	31
Br	ppb	2716	60	183
Ca	ppb	10190	61743	148389
Cd	ppb	0.07	<0.05	<0.05
Ce	ppb	0.05	0.09	0.04
Cl	ppm	79	3	7
Co	ppb	3.56	0.13	0.67
Cr	ppb	2.2	1.2	1.1
Cs	ppb	0.02	0.01	<0.01
Cu	ppb	158.4	9.5	8.9
Fe	ppb	12	< 10	< 10
Ga	ppb	1.52	0.07	<0.05
Gd	ppb	0.02	0.03	0.02
Hg	ppb	<0.1	<0.1	<0.1
Ho	ppb	<0.01	<0.01	<0.01
K	ppb	152851	25017	8915
La	ppb	0.02	0.06	0.04
Li	ppb	16.2	4.5	4.3
Mg	ppb	2499	6519	22703
Mn	ppb	1.75	2.55	77.53
Mo	ppb	56.4	6.8	0.7
Na	ppb	12467	2074	2301
Nd	ppb	0.04	0.07	0.04
Ni	ppb	41.6	0.2	2.4
P	ppb	35	237	< 20
Pb	ppb	3.5	0.7	<0.1
Pd	ppb	<0.2	<0.2	<0.2
Rb	ppb	62.88	17.17	3.43
Re	ppb	0.16	<0.01	0.02
S	ppm	19	12	96
Sb	ppb	0.95	0.46	0.24
Sc	ppb	1.38	2	1
Se	ppb	2.5	<0.5	0.9
Si	ppb	6297	6644	2365
Sn	ppb	0.16	<0.05	<0.05
Sr	ppb	107	126	149
Ti	ppb	<10	< 10	< 10
Tl	ppb	0.07	0.25	0.03
U	ppb	0.35	1.23	4.95
V	ppb	7.3	1.1	0.3
W	ppb	2.15	0.36	0.05
Y	ppb	0.03	0.05	0.09
Zn	ppb	12.4	35.7	32.7
Zr	ppb	0.21	0.18	0.13

Content of Ag, Au, Be, Bi, Ge, IR, Os, Ru, Sn, Tl, Th is <0.05 in all samples
Content of Dy, Er, Eu,Ho, In, Lu, Nb, Pr, Pt, Ph, Tb, Yb, Tm is <0.01 in all samples
Content of Hf, Sm and Ta <0.02 in all samples

Table 9.4.1.2 Organic compounds in water from wells near Kukruse waste mounds

	Well	KK-1/1	KK-2
	Aquafer	O_3kl-O_3kk	O_3kl-O_3kk
	DOC, mg/l	29	4,1
PAH, µg/l	Naphthalin	0,387	<0,01
	1-Methylnaphthalin	0,095	<0,01
	2-Methylnaphthalin	<0,01	<0,01
	Acenaphthylen	<0,01	<0,01
	Acenaphthen	<0,01	<0,01
	Fluoren	0,096	<0,01
	Phenanthren	0,075	<0,01
	Anthracen	<0,01	<0,01
	Fluoranthen	0,011	<0,01
	Pyren	<0,01	<0,01
	Benzo[a]anthracen	<0,01	<0,01
	Chrysen	<0,01	<0,01
	Benzo[b]fluoranthen	<0,01	<0,01
	Benzo[k]fluoranthen	<0,01	<0,01
	Benzo[a]pyren	<0,01	<0,01
	Indeno[123cd]pyren	<0,01	<0,01
	Dibenz[ah]anthracen	<0,01	<0,01
	Benzo[ghi]perylen	<0,01	<0,01
	Sum PAH, PLV=10	0,664	
BTX, µg/l	Benzol	<0,5	< 0,5
	Toluol	6,7	< 0,5
	Chlorbenzol	<0,5	< 0,5
	Ethylbenzol	9,9	< 0,5
	m+p-Xylol	15,1	< 0,5
	o-Xylol	9,9	< 0,5
	Styrol	<0,5	< 0,5
	Cumol	<0,5	< 0,5
	3+4-Ethyltoluol	<0,5	< 0,5
	Mesitylen	<0,5	< 0,5
	2-Ethyltoluol	<0,5	< 0,5
	Sum BTX, PLV=600	41,6	
Phenols, µg/l	Phenol	< 0,5	< 0,5
	Resorcin	< 0,5	< 0,5
	5-Methylresorcin	< 0,5	< 0,5
	2+3-Methylphenol	< 0,5	< 0,5
	4-Methylphenol	< 0,5	< 0,5
	2,6-Dimethylphenol	< 0,5	< 0,5
	3,4-Dimethylphenol	< 0,5	< 0,5
	2,3-Dimethylphenol	< 0,5	< 0,5
	2,4+2,5-Dimethylphenol	< 0,5	< 0,5
	3,5-Dimethylphenol	< 0,5	< 0,5
	2,4,6-Trimethylphenol	< 0,5	< 0,5
	2,3,6-Trimethylphenol	< 0,5	< 0,5
	2,3,5-Trimethylphenol	< 0,5	< 0,5
	3,4,5-Trimethylphenol	< 0,5	< 0,5
	Sum, PLV=50	n.n.	n.n

Table 9.4.2.1 Chemical composition of subsoil in Kukruse

Region		Kukruse							
Sample		SR-KK-1-1-1		SR-KK-1-1-2		SR-KK-1-2		SR-KK-2	
Rock type		grey siltstone (moraine)		green-grey siltstone (moraine)		grey clay (moraine)		brown-grey clay (moraine)	
Depth, m		0.15-0.5		0.5-2.5		0.2-4.0		1.5-2.6	
		total	aqua regia	total	aqua regia	total	aqua regia	total	aqua regia
TOC	%	2.93		1.88		2.84		0.71	
Al	%	4.06	0.89	1.64	0.41	1.37	0.40	5.46	1.31
Ca	%	10.36	9.42	28.88	25.13	24.76	24.02	3.42	2.84
Fe	%	2.62	1.94	1.22	1.02	1.02	1.42	3.33	2.40
K	%	2.18	0.37	1.28	0.23	0.94	0.19	2.08	0.42
Mg	%	0.65	0.48	0.63	0.64	0.54	0.60	0.62	0.40
Na	%	0.533	0.021	0.08	0.016	0.05	0.013	0.823	0.033
P	%	0.096	0.089	0.096	0.093	0.09	0.098	0.077	0.072
S	%	0.11	0.06	0.06	0.01	0.06	0.02	0.02	0.01
Ti	%	0.212	0.011	0.102	0.002	0.088	0.001	0.259	0.026
Ag	ppb	138	44	65	18	72	23	136	61
As	ppm	11.8	8.1	15.8	7.3	17.9	17.4	14.2	9.2
Au	ppm	<0.1	0.3	<0.1	0.2	<0.1	0.1	<0.1	0.3
Ba	ppm	317	53.9	86	18.9	73	19.0	471	56.5
Bi	ppm	0.12	0.10	0.04	0.04	0.05	0.04	0.2	0.19
Cd	ppm	0.33	0.13	0.08	0.04	0.16	0.07	0.23	0.06
Ce	ppm	62.51	35.0	23.91	15.1	19.51	14.2	81.4	53.7
Co	ppm	6.1	4.4	2.2	1.8	2.5	2.2	10.2	10.2
Cr	ppm	65	31.2	32	10.2	30	19.2	61	31.1
Cu	ppm	10.22	9.71	7.63	6.64	8.39	7.89	21.49	19.99
Dy	ppm	3.7	2.29	1.9	1.39	1.6	1.25	5.6	3.08
Er	ppm	2	1.1	0.8	0.71	0.8	0.61	2.4	1.44
Eu	ppm	1	0.57	0.5	0.37	0.4	0.34	1.5	0.8
Ga	ppm	10.34	3.4	4.24	1.7	3.44	1.7	15.75	5.2
Gd	ppm	4.5	3.11	2.3	1.93	1.8	1.69	6.9	4.49
Ho	ppm	0.6	0.38	0.3	0.24	0.3	0.22	0.8	0.51
La	ppm	39	19.9	15	8.7	13	8.7	47	27.7
Lu	ppm	0.3	0.13	0.1	0.07	0.1	0.07	0.4	0.18
Mn	ppm	656	564	330	327	294	300	535	428
Mo	ppm	5.93	4.80	2.71	2.33	5.58	5.64	5.63	4.73
Nd	ppm	28.8	16.42	12.4	8.43	10.5	7.98	38.9	23.73
Ni	ppm	13.3	12.8	10.1	7.1	13.4	13.0	21.1	20.3
Pb	ppm	45.0	35.10	14.2	12.20	17.3	15.38	20.0	11.37
Pr	ppm	7.6	4.71	3.2	2.21	3.2	2.11	10	7
Sb	ppm	0.4	0.19	0.2	0.09	0.2	0.18	0.4	0.17
Sc	ppm	5.4	2.4	2.6	1.7	2.3	1.6	7.7	3.9
Sm	ppm	6	3.42	2.7	1.89	2.2	1.76	8	5.28
Sr	ppm	180	113.4	198	172.3	145	142.1	141	25.4
Tb	ppm	0.8	0.48	0.4	0.26	0.3	0.28	1.1	0.68
Th	ppm	11.1	3.0	4.5	2.4	4.1	2.30	12.7	7.24
Tm	ppm	0.3	0.15	0.1	0.09	0.1	0.08	0.4	0.2
U	ppm	2.7	1.2	2.2	1.4	3.2	2.5	3.4	2.1
V	ppm	37	18	18	8	17	9.	64	30
W	ppm	8.8	4.6	1.2	0.4	6.1	3.9	3.7	0.9
Y	ppm	23.1	12.22	12.1	8.35	10	7.4	28.2	17.20
Yb	ppm	2.3	0.92	1	0.55	0.8	0.53	2.9	1.36
Zn	ppm	72.8	56.8	31.6	24.6	39.5	35.2	56.6	41.3
LOI	%	18.9		36		34.4		7.7	

Table 9.4.2.2 Organic compounds in subsoil near to waste heap Kukruse I

Region		**Kukruse**			
Sample		**SR-KK-1-1/1**	**SR-KK-1-1/2**	**SR-KK-1-2**	**SR-KK-2**
Rock type		grey siltstone (moraine)	green-grey siltstone (moraine)	grey clay (moraine)	brown-grey clay (moraine)
Depth, m		0.15-0.5	0.5-2.5	0.2-4.0	1.5-2.6
	Dry residue %	82.6	84.9	86.8	86
	Corg.,%	2.93	1.88	2.84	0.73
PAH, mg/kg DR	Naphthalin	<0.1	<0.1	<0.1	<0.1
	Acenaphthen	<0.01	<0.01	<0.01	<0.01
	Acenaphthylen	<0.1	<0.1	<0.1	<0.1
	Fluoren	<0.01	<0.01	<0.01	<0.01
	Phenanthren	0.05	<0.01	<0.01	<0.01
	Anthracen	<0.01	<0.01	<0.01	<0.01
	Fluoranthen	0.02	<0.01	<0.01	<0.01
	Pyren	0.02	<0.01	<0.01	<0.01
	Benzo[a]anthracen	<0.01	<0.01	<0.01	<0.01
	Chrysen	0.02	<0.01	<0.01	<0.01
	Benzo[b]fluoranthen	0.01	<0.01	<0.01	<0.01
	Benzo[k]fluoranthen	<0.01	<0.01	<0.01	<0.01
	Benzo[a]pyren	<0.01	<0.01	<0.01	<0.01
	Indeno(123-cd)pyren	<0.01	<0.01	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01	<0.01	<0.01
	Sum PAH	0.12	n.n.	n.n.	n.n.
BTX, mg/kg DR	Benzol	<0.01	<0.01	<0.01	<0.01
	Toluol	0.016	<0.01	<0.01	0.036
	Ethylbenzol	<0.01	<0.01	<0.01	0.012
	m+p-Xylol	0.033	0.016	<0.01	0.088
	Styrol	<0.01	<0.01	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01	<0.01	<0.01
	1,3,5-Trimethylbenzol	<0.01	<0.01	<0.01	<0.01
	Sum BTX	0.049	0.016	n.n.	0.14
Phenols, mg/kg DR	Phenol	<1	<1	<1	<1
	Resorcin	<0.05	<0.05	<0.05	<0.5
	5-Methylresorcin	<0.05	<0.05	<0.05	<0.5
	2,5-Dimethylresorcin	<0.05	<0.05	<0.05	<0.5
	4-Ethylresorcin	<0.05	<0.05	<0.05	<0.5
	4-Methylphenol	<0.05	<0.05	<0.05	<0.5
	3,4-Dimethylphenol	<0.05	<0.1	<0.05	<0.2
	2,3-Dimethylphenol	<0.05	<0.1	<0.05	<0.2
	2,4-Dimethylphenol	<0.05	<0.1	<0.05	<0.2

Table 9.5.1.1 Main statistical parameters of chemical element distribution in topsoil in Narva

		Narva							
		total				aqua regia			
		min	max	average	median	min	max	average	median
Al	%	0.4	5.99	3.67	3.94	0.12	1.78	0.92	0.95
Ca	%	0.42	16.15	3.67	2.31	0.32	15.59	3.32	2.09
Fe	%	0.83	40.91	3.15	2.49	0.68	42.31	2.75	2.04
K	%	0.17	3.63	2.02	2.23	0.04	1.05	0.27	0.23
Mg	%	0.04	5.58	0.94	0.52	0.02	5.05	0.83	0.43
Na	%	0.018	1.057	0.500	0.455	0.003	0.038	0.013	0.013
P	%	0.039	0.9	0.222	0.146	0.038	0.812	0.210	0.143
S	%	0.02	0.66	0.140	0.11	0.005	0.62	0.105	0.08
Ti	%	0.019	0.346	0.174	0.178	0.003	0.053	0.014	0.012
Ag	ppb	40	723	162	135	15	579	109	86
As	ppm	1.5	499.6	12.7	6.35	1.8	595.6	12.6	4.7
Au	ppm	<0.1	<0.1	<0.1	<0.1	0.1	39.3	1.89	1.1
B	ppm					<1	54	13	11
Ba	ppm	115	911	389	411	20.9	926	141.3	104.9
Be	ppm	<1	3	1	1				
Bi	ppm	0.04	2.9	0.21	0.15	0.01	7.53	0.25	0.16
Cd	ppm	0.09	0.79	0.29	0.27	0.03	0.86	0.21	0.17
Ce	ppm	4.18	88.77	51.25	51.23	3.3	73.6	40.6	41.6
Co	ppm	0.8	12.5	4.8	4.5	0.9	10.5	5.0	4.6
Cr	ppm	6	306	56	53	4.7	302.8	42.6	38.7
Cs	ppm	0.4	6.5	2.7	2.6				
Cu	ppm	5.06	71.74	11.61	10.63	4.61	74.03	11.04	9.64
Dy	ppm	0.4	8.3	4.1	3.8	0.3	7.8	3.3	2.9
Er	ppm	0.2	4.4	2.2	2.2	0.19	3.73	1.62	1.37
Eu	ppm	0.1	2.3	1.1	1	0.08	2.03	0.82	0.7
Ga	ppm	0.97	16.08	9.15	9.91	0.5	7.2	3.5	3.4
Gd	ppm	0.4	9.5	4.6	4.3	0.45	9.89	4.39	4.02
Hf	ppm	0.23	6.04	3.04	3.01				
Hg	ppb					9	383	66	53
Ho	ppm	0.1	1.6	0.8	0.7	0.07	1.36	0.62	0.53
La	ppm	2	56	30	31	2	46.7	25.3	26.2
Li	ppm	1.8	9.6	11.5	11.5				
Lu	ppm	0.1	0.6	0.3	0.3	0.02	0.41	0.19	0.16
Mn	ppm	169	5273	1405	973	126	5665	1375	904
Mo	ppm	1.37	11.88	4.29	3.81	1.45	13.13	4.34	3.77
Nb	ppm	0.56	11.9	6.19	6.17				
Nd	ppm	2.2	54.6	26.4	25.6	1.73	40.22	21.85	21.67
Ni	ppm	5.6	25.4	13.1	13.5	3.7	31.6	12.7	12.9
Pb	ppm	10.3	275.2	29.2	23.6	6.17	227.97	24.14	17.67
Pr	ppm	0.5	12.5	6.8	6.7	0.39	10.13	5.34	5.45
Rb	ppm	7.1	125.6	79.7	86.9				
Sb	ppm	0.1	2.4	0.4	0.3	0.1	2.45	0.29	0.22
Sc	ppm	0.7	15.4	6.2	5.7	0.2	8.2	2.9	2.5
Se	ppm					<0.1	12.5	0.6	0.4
Sm	ppm	0.5	11.2	5.6	5.3	0.42	9.33	4.81	4.55
Sn	ppm	<0.1	9.7	1.8	1.6				
Sr	ppm	37	145	99.2	105	7.8	113.2	43.9	34.7
Ta	ppm	0.1	0.8	0.4	0.4				
Tb	ppm	0.1	1.7	0.9	0.8	0.07	1.48	0.64	0.57
Te	ppm					<0.02	0.31	0.06	0.04
Th	ppm	0.7	6.9	8.4	8.4	0.1	7.5	2.8	2.5
Tl	ppm					<0.02	1.12	0.20	0.16
Tm	ppm	<0.1	0.6	0.3	0.3	0.02	0.6	0.23	0.20
U	ppm	0.8	67.1	5.0	3.5	0.6	77.6	4.0	2.3
V	ppm	4	143	42	39	3	91	27	25
W	ppm	<1	18	8	8	0.4	20	5.6	4.8
Y	ppm	2.3	50.1	24.3	22	1.8	42.43	17.44	15.15
Yb	ppm	0.2	4.3	2.2	2.2	0.2	3.17	1.43	1.26
Zn	ppm	10.3	250.9	54.0	51.5	5.4	254	46.6	45.6
Zr	ppm	8.5	202.8	100.9	103.2				
LOI						4.4	83.4	22.0	17.8

Table 9.5.1.2 Element concentration in oil shale, oil shale ash and topsoil in Narva (in ppm, K_2O and P_2O_5 in %)

Element	Oil shale					Air-borne solid matter**	Narva topsoil	Humus horisont, Estonia
	Commercial oil shale[3]	Semi-coke	Ash from cyclone	Ash from filter (II)	Chimney ash			
K_2O	1.68	2.21	2.74	5.41	6.84		2.46	2.08
P_2O_5	0.07	0.11	0.13	0.13			0.49	0.12
As	7.6	9.16	7.43	28.8	45.1		7.5	5.1**
Cu	17	24.5	23	19	33	206	11.7	10.6
Hg	0.03	<0.02		0.039	0.082		0.066’	0.029
Sr	151	334	344	291	259		100	107
Mo	3	5.5	6.2	10.3	12.3		4.2	1.3
Cd	4		2			15.1	0.29	
Ba	140	153	205	235	256		383	383
Ni	21	29	28	38	53	258	13.1	21.9
Pb	24	13	56	98	163	182	29.3	16.4
Sb	0.47	0.41	0.48	1.31	1.63		0.37	
Rb	39	43	57	120	168		80.5	69.4
U	2.9	5.5	5.1	7.5	5.8		5.0	1.87
V	28	34	60	59	39		43	43.6
Zn	49	81	61	116	184	1733	54	37.3

[1]Petersell et al., 1997; [2]Petersell, unpublished data; [3]Пец и др., 1985; [4]Turekijan, Wedepohl, 1961

Table 9.5.2 Chemical composition of subsoil in Narva

Region		Narva			
Sample		SR-N-1		SR-N-2	
Rocks type		'dark-yellow sandy soil		green-grey clay, siltstone	
Depth, m		0-1.1		1.1-4.5	
		total	aqua regia	total	aqua regia
TOC	%	1.57		0.35	
Al	%	3.36	0.40	6.83	1.98
Ca	%	0.78	0.40	0.95	0.48
Fe	%	1.26	1.11	3.77	2.90
K	%	2.15	0.11	2.97	0.53
Mg	%	0.15	0.11	0.93	0.68
Na	%	1.084	0.065	1.119	0.045
P	%	0.037	0.028	0.075	0.063
S	%	0.07	0.04	0.04	0.02
Ti	%	0.061	0.015	0.395	0.083
Ag	ppb	69	28	124	61
As	ppm	4	2.8	5.4	3.7
Au	ppm	<0.1	0.5	<0.1	1
Ba	ppm	462	37	648	162
Bi	ppm	0.06	0.05	0.26	0.22
Cd	ppm	0.12	0.02	0.25	0.07
Ce	ppm	29.42	19.7	100.35	83.3
Co	ppm	1.7	1.50	15.1	12.2
Cr	ppm	33	30	61	40.3
Cu	ppm	14.31	13.74	20.64	23.74
Dy	ppm	1.4	0.97	5	3.85
Er	ppm	0.8	0.48	2.8	1.99
Eu	ppm	0.7	0.23	1.4	0.95
Ga	ppm	10.2	1.93	20.4	8.57
Gd	ppm	2.	1.36	6.7	6.1
Ho	ppm	0.3	0.16	0.9	0.64
La	ppm	18	11.2	56	41.4
Lu	ppm	0.1	0.05	0.4	0.24
Mn	ppm	147	107	440	330
Mo	ppm	7.41	6.89	1.81	1.48
Nd	ppm	11.1	8.10	44.2	34.92
Ni	ppm	10.1	8.5	30.8	24.9
Pb	ppm	17.31	5.02	20.81	10.61
Pr	ppm	3	2.28	10.6	9.86
Sb	ppm	0.2	0.14	0.3	0.09
Sc	ppm	1.4	0.7	9.8	6.1
Sm	ppm	2.1	1.55	8.1	7.05
Sr	ppm	111	11.1	137	23.3
Tb	ppm	0.3	0.18	1,1	0.76
Th	ppm	4.5	1.2	13.6	12
Tm	ppm	0.1	0.06	0.4	0.25
U	ppm	1.2	0.7	3.9	2.6
V	ppm	3	4	83	45
W	ppm	5.7	4.1	4.8	0.9
Y	ppm	8.4	5	27.9	20.4
Yb	ppm	0.9	0.43	3.3	1.85
Zn	ppm	13	7.9	77	63.9
LOI	%	3.4		5.1	

Table 9.5.3 Chemical composition of water from Narva area

Well or channel		N-7	RA-N-1	RA-N-2	RA-N-3	N-2/1	N-6/1	N-45/2	N-46/1	N-46/2	N-8	N-CH
Water aquifer		lg Qm	lg Qm	waste, pore water	waste, pore water	O_2ls-O_2vl	O_2ls-O_2vl	O_2ls-O_2vl	O_2ls-O_2vl	O_2ls-O_2vl	O_1pk-$Є_1$ts	channel water
Al	ppb	45	40	743	509	7	22	16	29	9	4	3608
As	ppb	0.8	1.4	1.5	2.7	1.6	8.9	2.6	0.9	1.8	2.6	8.0
B	ppb	10	57	< 20	< 20	36	45	53	188	60	21	10
Ba	ppb	877	332	935	519	1808	259	6109	4382	6389	889	261
Br	ppb	1115	107	7923	24125	37814	4338	48779	6554	35608	128	64688
Ca	ppb	78064	40380	213683	128991	225158	361224	294296	52242	257589	134035	34775
Ce	ppb	0.33	0.24	0.04	0.19	0.01	0.20	0.07	0.15	0.15	0.01	0.24
Cl	ppm	18	12	103	324	482	63	539	84	397	5	779
Co	ppb	1.16	1.07	0.32	0.53	0.19	10.71	0.15	0.08	0.13	0.77	0.36
Cr	ppb	2.1	1.4	7.4	3.5	<0.5	1.7	1.1	<0.5	<0.5	0.7	1.8
Cs	ppb	0.01	<0.01	14.7	121.11	0.01	<0.01	0.02	0.02	0.03	0.01	128.2
Cu	ppb	0.3	44.2	12.6	12.3	2.7	0.6	1.0	0.9	0.5	0.1	2.5
Fe	ppb	27581	23	525	1332	10668	74544	12093	255	13273	29403	5
Ga	ppb	<0.05	<0.05	3.04	4.4	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	5.29
Gd	ppb	0.08	<0.01	0.09	0.26	0.01	0.05	0.03	0.02	0.03	0.02	<0.01
Ge	ppb	<0.05	<0.05	<0.05	<0.05	0.28	0.07	0.33	0.50	0.44	0.15	0.06
Hg	ppb	<0.1	0.1	<0.1	<0.1	0.2	<0.1	0.1	<0.1	<0.1	<0.1	2.0
K	ppb	14774	5216	1230395	5891791	56307	8672	12991	144040	21045	1901	6418920
La	ppb	0.17	0.11	<0.01	0.02	<0.01	0.09	0.08	0.05	0.10	<0.01	0.06
Li	ppb	8.9	24.7	267.8	1565.6	44.3	12.6	12.6	11.5	8.4	11.2	1716.6
Mg	ppb	36517	9968	167	97	84588	79665	34597	41833	25412	25987	123
Mn	ppb	2120	1317	13.41	12.92	583	6771	169	32	278	751	14
Mo	ppb	0.3	3.0	42.5	73.3	0.6	2.0	0.2	6.2	0.2	0.3	69.7
Na	ppb	8664	15691	69319	166652	65672	31630	27163	51651	19113	7896	159290
Nd	ppb	0.23	0.15	0.01	<0.01	<0.01	0.14	0.02	0.05	0.09	<0.01	0.08
Ni	ppb	1.0	2.2	1	4.2	<0.2	7.6	7.8	1.1	0.2	<0.2	25.2
P	ppb	78	<20	36	39	31	22	66	32	63	156	92
Pb	ppb	0.2	6.3	20.8	84.4	0.1	<0.1	0.1	0.1	<0.1	<0.1	1.3
Rb	ppb	17.81	2.55	2451.49	11497.71	17.28	3.23	7.31	36.60	6.10	3.22	12423.00
Re	ppb	<0.01	0.01	0.28	0.68	0.03	<0.01	0.03	0.02	0.02	<0.01	0.69
S	ppm	1	3	25	30	6	35	<1.0	<1.0	<1.0	<1.0	74
Sb	ppb	<0.05	0.77	0.08	<0.05	<0.05	0.07	<0.05	<0.05	<0.05	<0.05	0.07
Sc	ppb	5.75	1.88	< 1	< 1	2.75	4.14	3.02	1.02	3.00	6.58	1.48
Se	ppb	<0.5	<0.5	13.4	43.4	<0.5	<0.5	<0.5	<0.5	0.7	0.6	7.1
Si	ppb	21889	8060	1229	907	15933	15286	16746	5267	15517	24937	6750
Sm	ppb	0.05	0.03	<0.02	<0.02	<0.02	0.04	0.02	0.03	0.04	<0.02	<0.02
Sr	ppb	122.90	144.52	1715.98	3012.71	466.82	707.96	511.39	341.92	436.49	190.90	2423.54
Tl	ppb	<0.01	0.02	0.03	0.32	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.03
U	ppb	0.04	2.02	0.05	0.02	0.03	10.92	<0.02	0.43	<0.02	<0.02	0.09
V	ppb	<0.2	0.8	2.8	2.5	1.1	1.0	1.1	2.0	1.1	<0.2	10.8
W	ppb	0.11	1.03	9.12	5.11	0.17	0.13	0.05	0.64	0.02	0.06	0.51
Y	ppb	0.46	0.16	0.04	0.03	0.04	0.39	0.12	0.16	0.21	0.06	0.07
Yb	ppb	0.04	0.01	<0.01	<0.01	0.01	0.03	0.09	0.02	0.06	<0.01	<0.01
Zn	ppb	132.4	87.6	83.7	40.4	80.0	76.3	71.5	19.9	59.4	105.0	25.4
Zr	ppb	0.93	0.33	0.07	0.12	0.49	6.44	0.20	0.26	0.17	0.33	0.15

Content of Dy, Er, Eu, Ho, In, Lu, Nb, Pr, Pt, Rh, Tb, Tm is <0.01 in all samples
Content of Hf, Ta is <0.02, Pd < 0.2 and Ti <10 in all samples
Content of Be, Bi , Cd, Ir, Os, Ru, Te, Th is <0.05 in all samples
Trace content (>0.05) of Ag, Au, Sn in porous waste water

Table 10.1 Chemical composition of stream sediments

Region		Erra River				Narva stream	
Sample		SS-ER-1		SS-ER-2		SS-Narva	
Stream		black fine silt		black fine silt		dark brown silt	
Depth, m		0.5		1		0.5	
		total	aqua regia	total	aqua regia	total	aqua regia
Al	%	2.55	0.64	1.51	0.38	4.34	0.88
Ca	%	5.22	5.88	11.05	12.68	2.25	1.92
Fe	%	4.82	4.56	8.32	8.51	2.43	1.98
K	%	0.98	0.18	0.55	0.11	2.06	0.24
Mg	%	0.35	0.26	0.22	0.2	0.47	0.39
Na	%	0.125	0.038	0.108	0.053	0.723	0.016
P	%	0.179	0.171	0.152	0.151	0.127	0.1
S	%	2.94	3.32	2.28	2.83	0.61	0.68
Ti	%	0.098	0.011	0.058	0.008	0.182	0.029
Ag	ppb	108	105	68	66	1476	450
As	ppm	10	9.1	8	8.2	4	3.5
Au	ppm	<0.1	9.9	<0.1	0.1	<0.1	2.5
Ba	ppm	41	70.1	50	85.7	321	163
Bi	ppm	0.16	0.12	0.07	0.06	0.18	0.21
Cd	ppm	0.85	0.66	0.33	0.3	0.56	0.38
Ce	ppm	30.61	16.4	20.23	12.2	50.32	31.4
Co	ppm	8.5	8.3	3.4	4.7	5.8	5.2
Cr	ppm	23	13.8	12	6.7	43	34.8
Cu	ppm	45.88	35.47	10.18	10.56	55.65	53.98
Dy	ppm	2.2	1.47	1.8	1.06	3.3	1.86
Er	ppm	1.2	0.74	0.8	0.55	1.8	0.87
Eu	ppm	0.6	0.38	0.4	0.26	0.9	0.43
Ga	ppm	5.9	2.2	3.54	1.3	12.43	3.6
Gd	ppm	2.2	1.66	1.5	1.39	3.3	2.64
Ho	ppm	0.4	0.31	0.3	0.22	0.5	0.35
La	ppm	17	9.0	11	6.9	29	16.9
Lu	ppm	0.2	0.1	0.1	0.08	0.2	0.12
Mn	ppm	1171	1315	1356	1621	299	249
Mo	ppm	1.89	1.76	0.79	0.84	2.17	2.22
Nd	ppm	15.3	9.36	10	6.67	24.4	16.19
Ni	ppm	15.4	17.9	5	6	23.9	20.9
Pb	ppm	126.6	122.74	8.4	8.08	41.1	46.7
Pr	ppm	4.2	2.34	2.8	1.69	7.2	4.31
Sb	ppm	0.5	0.23	0.1	0.17	1.0	0.91
Sc	ppm	4.4	1.5	2.5	1	6	2.2
Sm	ppm	3.1	1.99	2.1	1.46	5.1	3.27
Sr	ppm	89	65.6	127	108.5	109	34.8
Tb	ppm	0.5	0.22	0.3	0.17	0.7	0.32
Th	ppm	3.8	1.5	2.4	1.1	6.6	2.4
Tm	ppm	0.3	0.1	0.1	0.08	0.2	0.13
U	ppm	2.4	1.8	0.9	0.6	3.6	2.9
V	ppm	30	19	24	18	35	19
W	ppm	0.8	0.4	0.4	0.1	2	1.2
Y	ppm	13	7.85	9.7	6.29	17.5	9.01
Yb	ppm	1.2	0.68	0.9	0.51	1.8	0.81
Zn	ppm	291.8	359.2	39.5	35.3	202.2	214.8
LOI	%	51.5		40		21.2	

Table 10.2 Organic compounds in stream sediments of the River Erra (Kiviõli)

	Region	**Erra River**	
	Sample	**SS-ER-1**	**SS-ER-2**
	Rocks type	black fine silt	black fine silt
	Depth, m	0.5	1
	Dry residue %	51.5	40
	Corg.,%		21,.5
PAH, mg/kg DR	Naphthalin	<0.1	<0.1
	Acenaphthen	<0.01	0.01
	Acenaphthylen	<0.1	0.02
	Fluoren	<0.01	0.14
	Phenanthren	<0.01	0.03
	Anthracen	<0.01	0.04
	Fluoranthen	<0.01	0.02
	Pyren	<0.01	0.01
	Benzo[a]anthracen	<0.01	<0.01
	Chrysen	<0.01	<0.01
	Benzo[b]fluoranthen	<0.01	<0.01
	Benzo[k]fluoranthen	<0.01	<0.01
	Benzo[a]pyren	<0.01	<0.01
	Indeno(123-cd)pyren	<0.01	<0.01
	Dibenz[ah]anthracen	<0.01	<0.01
	Benzo[ghi]perylen	<0.01	<0.01
	Sum PAH	n.n.	0.27
BTX, mg/kg DR	Benzol	<0.01	<0.01
	Toluol	<0.01	<0.01
	Ethylbenzol	<0.01	<0.01
	m+p-Xylol	0.024	0.022
	Styrol	<0.01	<0.01
	iso-Propylbenzol	<0.01	<0.01
	1,3,5-Trimethylbenzol	<0.01	<0.01
	Sum BTX	0.024	0.022
Phenols, mg/kg DR	Phenol	<1	<1
	Resorcin	<0.1	<0.1
	5-Methylresorcin	<0.1	<0.1
	2,5-Dimethylresorcin	<0.1	<0.1
	4-Ethylresorcin	<0.1	<0.1
	4-Methylphenol	<0.1	<0.1
	3,4-Dimethylphenol	<0.1	<0.1
	2,3-Dimethylphenol	<0.1	<0.1
	2,4-Dimethylphenol	<0.1	<0.1
	Sum phenols	n.n.	n.n.

Table 11 Elements concentration in the vegetation from different regions

Region		Kiviõli			Kohtla-Järve			Narva		
Number of samples		n=5			n=5			n=5		
		min	max	aver	min	max	aver	min	max	aver
Al	%	0.01	0.05	0.03	0.01	0.03	0.02	0.01	0.04	0.02
Ca	%	1.19	1.5	1.36	0.81	1.33	1.04	0.98	1.67	1.38
Fe	%	0.029	0.137	0.059	0.013	0.086	0.046	0.018	0.054	0.029
K	%	0.76	1.66	1.06	1.08	1.62	1.32	0.83	1.27	1.06
Mg	%	0.529	0.585	0.562	0.53	0.635	0.584	0.553	0.7	0.601
Na	%	0.002	0.058	0.014	0.002	0.014	0.007	0.003	0.011	0.006
P	%	0.184	0.245	0.214	0.144	0.253	0.196	0.163	0.23	0.200
S	%	0.16	0.23	0.20	0.19	0.31	0.24	0.15	0.22	0.18
Ti	ppm	13	18	15.4	11	17	13	10	22	13.8
Ag	*ppb*	2	13	6.2	7	20	10.6	4	10	6
As	ppm	0.2	0.6	0.3	0.1	0.4	0.2	0.2	0.4	0.3
Au	*ppb*	0.1	0.1	0.1	0.1	0.4	0.3	0.1	0.2	0.1
B	ppm	33	44	39	36	38	37	39	46	43
Ba	ppm	11.7	22.0	16.4	18.7	47.8	36.5	18.5	88.8	48.0
Bi	ppm	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	ppm	0.01	0.43	0.10	0.06	0.48	0.26	0.05	0.16	0.11
Co	ppm	0.09	0.69	0.26	0.13	0.54	0.30	0.1	0.25	0.14
Cr	ppm	1.67	2.55	2.068	1.63	4.04	2.24	1.55	2.64	1.94
Cu	ppm	12.24	26.63	18.98	19.83	40.96	30.85	19.47	31.85	24.49
Ga	ppm	0.1	0.2	0.12	0.1	0.1	0.1	0.1	0.2	0.12
Hg	*ppb*	1	12	5	5	9	6	2	6	4
La	ppm	0.21	1.43	0.63	0.1	0.57	0.34	0.21	0.85	0.39
Mn	ppm	9	89	42	39	153	82	25	101	65
Mo	ppm	0.62	4.05	1.93	0.34	1.86	0.97	0.35	1.59	0.95
Ni	ppm	0.7	2.8	1.6	0.5	1.4	1.1	0.5	1.1	0.8
Pb	ppm	0.61	1.21	0.83	0.3	1.27	0.69	0.33	1.5	0.67
Sb	ppm	0.03	0.06	0.04	0.01	0.03	0.02	0.02	0.06	0.03
Sc	ppm	0.1	0.4	0.24	0.1	0.3	0.18	0.1	0.3	0.2
Se	ppm	<0.1	0.2	0.12	<0.1	0.2	0.1	<0.1	0.1	0.07
Sr	ppm	27.2	91.0	53.0	26.9	46.5	38.0	21.8	29.3	25.7
Te	ppm	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Th	ppm	0.03	0.15	0.09	0.02	0.07	0.05	0.02	0.09	0.05
Tl	ppm	0.02	0.05	0.03	0.03	0.42	0.16	0.05	0.19	0.11
U	ppm	0.12	0.45	0.23	0.02	0.53	0.25	0.04	0.66	0.23
V	ppm	1	3	2	1	3	1.6	2	4	2.6
W	ppm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	ppm	34.7	62.8	46.0	27.1	56.9	39.1	49.8	70.4	56.3

Table 13 Species parameters used for the MT3D transport model

Species	Concentration (mg/l)	$t_{1/2}$	R	K_d (1/mg/L)	K_mob (1/day)	K_sorb (1/day)
napthalene	1	258	13	3.1	0.003	0
BTEX	18	300	6	1.26	0.002	0
phenol	125	7	2	0.25	0.099	0

Table 14.1 Characterization of the samples analyzed for the toxicity

Sample code	Characterisation of the samples (depth of the well/water table)	Organics measured: DOC-dissolved organic carbon; F - phenols	Sampling for the toxicity testing
NARVA			
N-AF	Waste leachate (eluate) (eluate), ashes from filter 1+10	DOC*	Autumn 2002
N-AC	Waste leachate (eluate), ashes from collector, 1+10	DOC*	Autumn 2002
KOHTLA JÄRVE			
KJ-F	Waste leachate (eluate), fresh semi-coke from KJ (sampled from the truck), 1+10	DOC*,F*, BTX*,PAH*	Autumn 2002
KJ-A	Waste leachate (eluate), ashes from the powerplant in KJ, 1+10	DOC*,F*,PAH*	Autumn 2002
KJ-600	Groundwater, existing mon. well - 20.7 m / 3.87 m, KJ mound on the limit of semi-coke and powerplant ashes. Close to 601. Shallow	DOC*, F, BTX*, PAH*	Spring 2003
KJ-601	Groundwater, existing mon. well - 39.5 m / 9.66 m, KJ mound on the limit of semi-coke and powerplant ashes, close to 600. Deep	DOC*, F, BTX*, PAH*	Spring 2003
KJ-602	Groundwater, existing monitoring well - 22.3 m / 0.8 m, on the limit of the KJ mound. Shallow	DOC*, F, BTX*, PAH*	Spring 2003
KJ-608	Groundwater, existing monitoring well near KJ mound - 26.5 m / 1.06 m, Half-deep	DOC*, F*, BTX*, PAH*	Spring 2003
KJ-610	Groundwater, existing monitoring well near KJ mound- 29.8 m / 2.20 m. Deep	DOC*, F*, BTX*, PAH*	Spring 2003
KJ-622	Groundwater, existing monitoring well - 30.7 m / 3.75 m, on the limit of the KJ mound. Deep	DOC*, F, BTX*, PAH*	Spring 2003
KJ-CH1	Channel water, channel in KJ, powerplant ashes side	DOC, F, BTX*, PAH*	Spring 2003
KJ-CH2	Channel water, channel in KJ, semicoke side	DOC, F, BTX*, PAH*	Spring 2003
RA-KJ-2	Groundwater, risk assessment well near KJ mound, 8.4 m/3.25 m. Shallow	DOC*, F*, BTX*, PAH*	Spring 2003
RA-KJ-3	Groundwater, risk assessment well near KJ mound, 9.5m / 3.55 m, ca 30 m from the mound. Shallow	DOC*,F, BTX*, PAH*	Spring 2003
RA-KJ-5	Waste pore water from KJ mound, upper borehole near fuss-lake	DOC, F, BTX, PAH	Spring 2003
RA-KJ-6	Waste pore water from KJ mound, lower borehole	DOC, F, BTX, PAH	Spring 2003
KIVIÕLI			
KV-F	Waste leachate (eluate), fresh semi-coke from Kiviõli (sampled from the truck), 1+10	DOC*, F*, BTX*, PAH*	Autumn 2002
KV-M	Waste leachate (eluate), medium (ca 20 years) age semi-coke from Kiviõli new mound, 1+10	DOC*, F*, BTX*, PAH*	Autumn 2002
KV-O	Waste leachate (eluate), old (ca 40 years) semi-coke from Kiviõli old mound, 1+10	DOC*, F*, BTX*, PAH*	Autumn 2002
KV-6	Groundwater, existing monitoring well, very deep, ca 90 m (layer where also drinking water for Kiviõli is taken)	DOC*, F*, BTX*, PAH*	Spring 2003
KV-9	Groundwater, existing monitoring well, very deep, ca 90 m (layer where also drinking water for Kiviõli is taken)	DOC*, F*, BTX*, PAH*	Spring 2003
RA-KV-1	Groundwater, risk assessment well, 7.3m/2.47 m, on the limit of new Kiviõli mound, on top of semicoke used for filling of the ground below the road. Shallow	DOC, F, BTX*, PAH*	Spring 2003
RA-KV-2	Groundwater, risk assessment well, 5.2 m/3.3 m, ca 20 m from the limit of old Kiviõli mound. Shallow	DOC*, F*, BTX*, PAH*	Spring 2003
RA-KV-5	Waste pore water water from Kiviõli new mound, upper borehole	DOC, F, BTX, PAH	Spring 2003
RA-KV-6	Waste pore water from Kiviõli new mound, lower borehole	DOC, F, BTX, PAH	Spring 2003
SH	Groundwater from the mine near Kiviõli	DOC*, F*, BTX*, PAH*	Spring 2003
KUKRUSE			
KK-1/1	Groundwater, risk assessment well (6 m) (Kukruse), mound that have burned sevsral times	DOC*, F*, BTX*, PAH*	Autumn 2003

*Phenols, BTX and PAHs were measured from samples taken in autumn 2002, DOC was measured from samples taken in January 2003. For the parameters not marked by asterisk the chemical and toxicological analysis was made from the same sample.

Table 14.2 Characterization of the tests used in current study

	Test	**Test organism**	**Toxicity endpoint/ exposure time/test type**
1	Algal test	Green microalgae *Selenastrum capricornutum*	Growth inhibition, 72 h, a chronic test
2	Daphtoxkit F™ magna	Crustaceans *Daphnia magna*	Mortality, 48 h, an acute test
4	Thamnotoxkit F™	Crustaceans *Thamnocephalus platyurus*	Mortality, 24 h, an acute test
3	Protoxkit F™	Protozoa *Tetrahymena thermophila*	Growth inhibition, 24 h, a chronic test
5	*Vibrio fischeri* luminescence inhibition test (Microtox™ test)	Bacteria *Vibrio fischeri*	Inhibition of bioluminescence, 15 min, an acute test
6	Flash Assay	Bacteria *Vibrio fischeri*	Inhibition of bioluminescence, 30 sec, an acute test
7	ToxScreen™ test	Bacteria *Photobacterium leiognathi*	Inhibition of bioluminescence, 30 min, an acute test

Table 14.3 *Toxicological characterization of samples*

Designation			pH	Thamno, TU	Algae, TU	Protox, TU	Mtox, pH=7, TU	Mtox, orig.pH, TU	Tox. red. after neutr. (Mtox)	ToxScr (OP, neutr), TU	Avg Tox, TU		Max Tox, TU	
NARVA														
N-AF		ASH	**12,9**	50	11	0,7	1,6	253	160	3,5	**15,8**	☠☠	**50,0**	☠☠
N-AC		ASH	**12,9**	50	9	1,0	1,9	234	123	0,5	**15,6**	☠☠	**50,0**	☠☠
KOHTLA JÄRVE														
KJ-F		SC	**12,3**	5,3	3,2	0,7	4,0	78	20	16,9	**3,3**	☠	**5,3**	☠
KJ-A		ASH	**12,9**	5,0	9,4	1,1	2,5	158	63	0,5	**4,5**	☠	**9,4**	☠
KJ-600	Lasnamäe-Kunda	GW-MW	7,4	5,5	3,3	9,6	23,8	24		100	**10,6**	☠☠	**23,8**	☠☠
KJ-601	Ordovician-Cambrian	GW-MW	**11,5**	4,9	2,7	0,7	1,3	21	17	13	**2,4**	☠	**4,9**	☠
KJ-602	Lasnamäe-Kunda	GW-MW	7,5	0	0	1,0	0	0		0,2	**0,2**	☺	**1,0**	☠
KJ-608	Lasnamäe-Kunda	GW-MW	7,5	0	0	0,9	0	0		0	**0,2**	☺	**0,9**	☺
KJ-610	Lasnamäe-Kunda	GW-MW	7,3	0	0,3	1,0	0	0		0	**0,3**	☺	**1,0**	☠
KJ-622	Lasnamäe-Kunda	GW-MW	**9,3**	4,2	1,8	2,6	31,3	29	1	133	**10,0**	☠	**31,3**	☠☠
KJ-CH1		CH	**13,2**	20	16,5	0,5	0,9	159	174	20	**9,5**	☠	**20,0**	☠☠
KJ-CH2		CH	**13,3**	48	22	1,1	345	265	0,8	250	**104**	☠☠☠	**344,8**	☠☠☠
RA-KJ-2	Lasnamäe-Kunda	GW-RAW	7,6	0	0	1,2	0	0		2,2	**0,3**	☺	**1,2**	☠
RA-KJ-3	Lasnamäe-Kunda	GW-RAW	7,5	0	0	0,9	0	0		7,7	**0,2**	☺	**0,9**	☺
RA-KJ-5		WPW	**13,1**	27	63	50,0	304	436	1,4	175	**111**	☠☠☠	**303,7**	☠☠☠
RA-KJ-6		WPW	**13,1**	100,0	1,1	#N/A	449	412	0,9	250	**184**	☠☠☠	**449,0**	☠☠☠
KIVIÕLI														
KV-F		SC	**12,5**	10,0	5,2	0,8	3,3	417	126	3,2	**4,8**	☠	**10,0**	☠☠
KV-M		SC	**9,9**	1	0,4	0,5	3,0	2,5	0,8	1,9	**1,2**	☠	**3,0**	☠

KV-O		SC	8,0	0	0,0	1,0	2,5	2,5		0,4	**0,9**	☺	**2,5**	☠
KV-6	Ordovician-Cambrian	GW-MW	7,2	0	1,0	0,3	0	0		0	**0,3**	☺	**1,0**	☠
KV-9	Ordovician-Cambrian	GW-MW	7,3	0	0,4	0	0	0		0	**0,1**	☺	**0,4**	☺
RA-KV-1	Keila-Kukruse	GW-RAW	**13,0**	32	18	4,2	1,4	169	124	25	**13,9**	☠	**31,8**	☠☠
RA-KV-2	Keila-Kukruse	GW-RAW	7,5	1,0	0,0	1,0	0,0	0,0		0	**0,5**	☺	**1,0**	☠
RA-KV-5		WPW	**13,2**	27	12	1,8	5,0	103	21	111	**11,3**	☠☠	**26,7**	☠☠
RA-KV-6		WPW	**10,5**	2,7	1,4	#N/A	4,4	3,7	1	7,7	**2,8**	☠	**4,4**	☠
SH		GW	7,3	0	0,28	2,2	0,0	0		0	**0,6**	☺	**2,2**	☠
KUKRUSE														
KK-1/1	Keila-Kukruse	GW-RAW	7,7	0	0	#N/A	0,0	0		6,3	**0**	☺	**0,0**	☺

Average and highest TU values of tests 1-4 were used for ranking of the sample (Average and Maximal toxicity)
SC oil-shale semicoke, ASH oil-shale burning ash, CH channel water, GW ground water, MW monitoring well, RAW risk assassment well, WPW waste pore water, #N/A - not analyzed

Table 14.4 *Chemical and toxicological characterization of oil shale combustion ashes and their aquatic leachates (eluates) from Narva investigation area and one groundwater samples from Kukruse area*

		NARVA		KUKRUSE
		N-AF	N-AC	
		Ashes, filter	*Ashes, collector*	
		Waste (solid sample)		
Organics	PLV (Estonia), living area			
C org, %		0,02	0,02	
Total phenols, mg/kg	20	not tested	not tested	
Total PAHs, mg/kg	20	not tested	not tested	
Total BTX, mg/kg	20	not tested	not tested	
LOI - LOSS ON IGNITION, %		6.4	6.4	
Heavy metals				
As, ppm	30	40,4	11,7	
Cd, ppm	5	0,25	0,16	
Cr, ppm	300	70	38	
Cu, ppm	150	10,5	11	
Hg, ppm	2	0,022	<0.005	
Pb, ppm	300	97	43	
Zn, ppm	500	89	58	
Other inorganics				
S, %		3,78	1,75	
P, %		0,083	0,069	
K, %		4,06	1,87	
Ca, %		23	30	
				KK-1/1
				RAW, shallow
Waste leachate (eluate), 1 part of waste + 10 parts of water				
Organics	PLV (Estonia), groundwater (piirarv)			
DOC, mg/L	100*	not tested	not tested	29
Phenols, ppb	200	not tested	not tested	0
BTX, ppb	100	not tested	not tested	42
PAH, ppb	10	not tested	not tested	0,664
Heavy metals				
As, ppb	100	9,6	6,1	2.4
Cd, ppb	10	< .05	< .05	.07
Cr, ppb	200	**385**	70,7	2.2
Cu, ppb	73	2,3	68	158.4
Hg, ppb	2	**5,9**	**5,4**	< .1
Pb, ppb	200	38,5	< .1	3.5
Zn, ppb	5000	8,8	4,8	12.4
Other inorganics etc				
S, ppm		0.706	0.526	19
P, ppm		0.128	0.095	0.035
K, ppm		562	117	153
Ca, ppm		1834	1705	10
Conductivity, µS/cm	2500**	**10330**	**10720**	838
pH	6...9	**12,9**	**12,9**	7,7
Water-leached Ca, % from total		7,8	5,6	

Toxicity			
Average toxicity (TU), tests 1-4 from Table ??	15,8	15,6	0,0
Max TU (test)	50 (Thamno)	50 (Thamno)	0,0
Tox. red. after neutr. (Microtox)	160	123	
Classification	Very toxic	Very toxic	Not toxic
	☠☠	☠☠	☺
% of toxicity of neutralized sample explained by phenols (Mtox) - not tested			#N/A
Organoleptic and microbiological description			
Oilshale smell	not tested	not tested	+/-
Growth on LB	not tested	not tested	+++
Growth on M9+phenol	not tested	not tested	++
Classification (by Avg TU)	Very toxic	Very toxic	Not toxic
Classification (by Avg TU)	☠☠	☠☠	☺

Table 14.5 *Chemical, microbiological and toxicological characterization of leachates of semi-coke and oil shale combustion ash, channel water, waste pore water and groundwater from Kohtla-Järve investigation area*

		KJ-F	KJ-A
		Semi-coke (fresh)	*Ashes*
		Waste (solid sample)	
Oganics	PLV (Estonia), living area		
C org, %		12	1,2
Total phenols, mg/kg	20	9,41	0
Total PAHs, mg/kg	20	0,25	0,083
Total BTX, mg/kg	20	4,5	0,01
LOI - LOSS ON IGNITION, %		31	25
Heavy metals			
As, ppm	30	11,4	14
Cd, ppm	5	0,1	0,11
Cr, ppm	300	43	44
Cu, ppm	150	10,9	9,3
Hg, ppm	2	0,011	0,013
Pb, ppm	300	42	37
Zn, ppm	500	37	32
Other inorganics			
S, %		1,83	1,02
P, %		0,05	0,055
K, %		2,23	2,65
Ca, %		17	18

				KJ-600	KJ-601	KJ-602	KJ-608	KJ-610	KJ-622	RA-KJ-2	RA-KJ-3	KJ-CH1	KJ-CH2	RA-KJ-5	RA-KJ-6
Organics	PLV (Estonia), groundwater (piirarv)														
DOC, mg/L	100*	26	7,2	77	55	14	7,8	6,8	214	14	100	50	530	473	19
Phenols, ppb	200	0	0	16925	0	0	0	0	13830	162	914	2588	96000	93395	87430
BTX, ppb	100	2,1	#N/A	135	48	111	141	220	167	91	350	26	2229	19543	1213
PAH, ppb	10	0,2	0,089	6,8	n.n.	24	0,01	0,14	4,19	n.n.	n.n.	0,322	19	628	461

Heavy metals															
As, ppb	100	4,5	0,7	5.7	10.1	11.9	1.1	1.2	19.4	9.5	19.9	12.3	25.7	47	31
Cd, ppb	10	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	< .05	<0.05	<0.05
Cr, ppb	200	3	5,1	.6	1.5	1.2	< .5	< .5	2.1	.7	2.4	3.4	5.0	9,8	13
Cu, ppb	73	5,8	5,5	1.0	3.2	3.2	8.4	2.5	2.1	3.7	4.8	80.3	2.4	3,2	3,4
Hg, ppb	2	< .1	< .1	.1	1.8	2.5	< .1	< .1	1.7	< .1	3.4	0.6	< 0.1	<0.1	<0.1
Pb, ppb	200	5,4	5,7	< .1	2.1	< .1	.1	.7	.5	4.6	4.4	< .1	< .1	0,8	<0.1
Zn, ppb	5000	42	18,5	3.9	14.3	10.9	66.7	57.7	1.6	13.0	144.8	14.8	16.4	37	22
Other inorganics etc															
S, ppm		1,439	0,018	15	70	176	106	110	51	23	61	192	288	120	172
P, ppm		0,083	<0.02	< 0.02	0.042	0.071	< 0.02	< 0.02	0.147	0.101	0.129	0.061	0.085	0,04	0,069
K, ppm		97	870	358	1840	1469	7	9	2032	260	1168	2583	1778	2302	2037
Ca, ppm		1145	64	42	2,7	37	212	240	3,4	34	4,6	65	294	1260	1213
Conductivity, µS/cm	2500**	**4440**	**7600**	**2950**	1424	867	1120	1184	**4560**	597	1904	**11240**	**14160**	**18000**	**15090**
pH	6...9	**12,3**	**12,9**	7,4	**11,5**	7,5	7,5	7,3	**9,3**	7,6	7,5	**13,2**	**13,3**	**13,1**	**13,1**
Water-leached Ca, % from total		6,8	0,35												
Toxicity															
Average toxicity (TU), tests 1-4 from Table ??		3,3	4,5	10,6	2,4	0,2	0,2	0,3	10,0	0,3	0,2	9,5	104	111	184
Max TU (test)		5.3 (Thamno)	9.4 (Algae)	24 (Mtox)	4.9 (Thamno)	1.0 (Protox)	0.9 (Protox)	1.0 (Protox)	31 (Mtox)	1.2 (Protox)	0.9 (Protox)	20 (Thamno)	345 (Mtox)	304 (Mtox)	449 (Mtox)
Tox. red. after neutr. (Microtox)		20	63	1	17				1			174	0,8	1,4	0,9
Classification		Toxic	Toxic	Very toxic	Toxic	Toxic	Not toxic	Toxic	Very toxic	Toxic	Not toxic	Very toxic	Extremely toxic	Extremely toxic	Extremely toxic
		☠	☠	☠☠	☠	☠	☺	☠	☠☠	☠	☺	☠☠	☠☠☠	☠☠☠	☠☠☠
% of toxicity of neutralized sample explained by phenols (Mtox) - not tested				37	0	0	#N/A	#N/A	11	#N/A	0	18	9	11	8
Organoleptic and microbiological description															
Oilshale smell		not tested	not tested	++++	++	+	-	-	+++++	+++	+++	+	+++	+++	+++
Growth on LB		not tested	not tested	++++	+++	+++	+	++	++	+++	+++	-	-	+	-
Growth on M9+phenol		not tested	not tested	++	+++	++	-	+++	-	+	++	-	-	-	-
Classification (by Avg TU)		Toxic	Toxic	Very toxic	Toxic	Not toxic	Not toxic	Not toxic	Toxic	Not toxic	Not toxic	Toxic	Extremely toxic	Extremely toxic	Extremely toxic
Classification (by Avg TU)		☠	☠	☠☠	☠	☺	☺	☺	☠	☺	☺	☠	☠☠☠	☠☠☠	☠☠☠

Table 14.6 *Chemical, microbiological and toxicological characterization of leachates of semi-coke, channel water, waste pore water and groundwater from Kiviõli investigation area*

		Waste (solid sample)									
		KV-F	**KV-M**	**KV-O**	KV-6	KV-9	RA-KV-1	RA-KV-2	RA-KV-5	RA-KV-6	SH
		Semi-coke (fresh)	*Semi-coke (20 y)*	*Semi-coke (40 y)*							
Oganics	PLV (Estonia), living area										
C org, %		7,3	7,8	11							
Total phenols, mg/kg	20	0,852	0,14	0							
Total PAHs, mg/kg	20	0,095	0,056	n.n.							
Total BTX, mg/kg	20	0,01	3,9	0,46							
LOI - LOSS ON IGNITION, %		30	34	38							
Heavy metals											
As, ppm	30	4	8,4	9,5							
Cd, ppm	5	0,1	0,07	0,08							
Cr, ppm	300	36	34	56							
Cu, ppm	150	5,6	6,2	6,6							
Hg, ppm	2	<0.005	<0.005	0,036							
Pb, ppm	300	38	42	44							
Zn, ppm	500	25	27	20							
Other inorganics											
S, %		1,96	2,16	0,11							
P, %		0,04	0,039	0,047							
K, %		1,77	1,31	1,94							
Ca, %		22	22	18							
Waste leachate (eluate), 1 part of waste + 10 parts of water											
Organics	PLV (Estonia), groundwater (piirarv)										
DOC, mg/L	100*	23	8	2,4	3,3	1,9	100	35	49	11	7,7
Phenols, ppb	200	0	0	0	0	0	2452	20	0	0	0
BTX, ppb	100	n.n.	n.n.	n.n.	n.n.	n.n.	6,2	10	0	1,8	n.n.
PAH, ppb	10	0,014	n.n.	n.n.	n.n.	n.n.	0,152	0,155	1,2	0	0,044

Heavy metals											
As, ppb	100	67	1,1	< .5	.7	1.7	2.4	4.5	4,8	21,9	.5
Cd, ppb	10	< .05	< .05	< .05	< .05	< .05	< .05	< .05	0,6	<0,05	< .05
Cr, ppb	200	21	1.6	0.9	< .5	< .5	6.4	1.6	5,2	17,5	.6
Cu, ppb	73	1.2	4.9	15	26.4	1.6	4.2	23.9	8,3	20,3	4.6
Hg, ppb	2	< .1	< .1	< .1	< .1	< .1	.1	< .1	<0.1	<0.1	< .1
Pb, ppb	200	20	< .1	< .1	< .1	.1	1.1	9.9	<0.1	3,0	.2
Zn, ppb	5000	29	14	15	84.0	76.0	16.5	26.3	21	43	51.4
Other inorganics etc											
S, ppm		0,995	0,213	0,01	13	7	67	522	466	972	80
P, ppm		0,07	<0.02	<0.02	< 0.02	< 0.02	0.057	0.04	0,1	0,2	< 0.02
K, ppm		980	37	0	10	43	2079	67	1812	1469	22
Ca, ppm		14441	144	26	41	111	396	566	181	56	149
Conductivity, µS/cm	2500**	**5600**	1123	357	700	968	**10000**	2450	**12150**	**9950**	854
pH	6...9	**12,5**	**9,9**	8	7,2	7,3	**13,0**	7,5	**13,2**	**10,5**	7,3
Water-leached Ca, % from total		66	0,66	0,14							
Toxicity											
Average toxicity (TU), tests 1-4		4,8	1,2	0,9	0,3	0,1	13,9	0,5	11,3	2,8	0,6
Max TU (test)		10 (Thamno)	3 (Mtox)	2.5 (Mtox)	1 (Algae)	0.4 (Algae)	32 (Thamno)	1.0 (Thamno)	27 (Thamno)	4.4 (Mtox)	2.2 (Protox)
Tox. red. after neutr. (Microtox)		126	0,8	1			124		20,7	0,8	
Classification		Very toxic ☠☠	Toxic ☠	Toxic ☠	Toxic ☠	Not toxic ☺	Very toxic ☠☠	Toxic ☠	Very toxic ☠☠	Toxic ☠	Toxic ☠
% of toxicity of neutralized sample explained by phenols (Mtox)					#N/A	#N/A	11	#N/A	0	0	#N/A
Organoleptic and microbiological description											
Oilshale smell		not tested	not tested	not tested	-	-	+	+	++	+++	-
Growth on LB		not tested	not tested	not tested	+	+	-	+	-	-	+
Growth on M9+phenol		not tested	not tested	not tested	+	+	-	+	-	-	-
Classification (by Avg TU)		Toxic	Toxic	Toxic	Not toxic	Not toxic	Not toxic	Very toxic	Not toxic	Toxic	Not toxic
Classification (by Avg TU)		☠	☠	☠	☺	☺	☺	☠☠	☺	☠	☺

Table 14.7 Toxicity of phenolic compounds, some PAHs, BTXs and Hg towards Microtox test

Compound	**Key hazardous pollutant group**	**Toxicity to Microtox, EC50**		**Reference**
		mg/L	**µg/L**	
Phenol	Monobasic phenolic compounds	19	19000	Kahru et al., 2000
p-cresol		1	1000	Kahru et al., 2000
o-cresol		16,3	16300	Kahru et al., 1996
m-cresol		5,5	5500	Kahru et al., 1996
2,4-dimethylphenol		3,7	3700	Kahru et al., 2000
2,3-dimethylphenol		5,3	5300	Kahru et al., 2000
3,4-dimethylphenol		0,39	390	Kahru et al., 2000
2,6-dimethylphenol		10,6	10600	Kahru et al., 1996
2,3,5-trimethylphenol		7,5	7500	Kahru et al., 1996
5-methylresorcinol	Dibasic phenolic compounds	129	129000	Kahru et al., 2000
2,5-dimethylresorcinol		95	95000	Kahru et al., 2000
benzene	BTX	531	531000	Kahru, 1993
toluene		33	33000	Kahru, 1993
xylene		97	97000	Kahru, 1993
naphthalene	PAHs	1,9	1900	Loibner et al., 2004
phenanthrene		0,48	480	Loibner et al., 2004
Hg^{2+}	Heavy metals	0,036	36	Ribo et al., 1989

Table 14.8 Distribution of samples (all 27) by two different toxicity evaluation indices

Toxicity evaluation index	*non toxic* samples	*toxic* samples	*very toxic* samples	*extremely toxic* samples
Average toxicity (AvgTox)	11	7	6	3
Maximal toxicity (MaxTox)	4	12	8	3

Table 14.9 Summary of the ecotoxicological risk assessment results obtained during this project

Characterization of samples by sampling regions	Nr of samples where priority pollutants exceeded the PLV*	Conductivity (µS/cm), pH and average toxicity (TU) Average, minimum and maximum values			% of not toxic samples **	Possible causes of the toxicity***
		µS/cm	pH	TU		
Groundwater: 14 samples						
8 existing and 5 risk assessment wells & 1 mine water. (8 samples from Kohtla-Järve area, 5 from Kiviõli and 1 from Kukruse)	Phenols: 4 BTX: 6 PAHs: 1 Total: 7	2173 (600-10000)	8.3 (7.2-13)	**2.8** (0-13.9)	10/14 **(71%)**	High alkalinity (2 samples) Phenols (3 samples)
Laboratory leachates (aquatic eluates of solid waste (1 part of waste +10 parts of water): 7 samples						
2 oils hale combustion ashes from Narva (filter and collector ashes), Fresh semi-coke and oil-shale combustion ash from Kohtla-Järve 3 semi-cokes from Kiviõli (fresh, 20-years and 40-years old)	heavy metals: 2	5738 (357-10720)	11.6 (8-12.9)	6.6 (0.9-15.8)	1/7 **(14%)**	High concentration of mineral salts, high alkalinity (5 samples)
Natural leachates from semi-coke mountains: 2 samples						
Channel water samples from the ditch surrounding the semi-coke mountain in Kohtla-Järve (2 samples from different sides of the mountain)	Phenols: 2, BTX: 1, PAHs: 1	12700 (11240-14160)	13.3 (13.2-13.3)	57 9.5-104	0/2 **(0%)**	High concentration of mineral salts, high alkalinity phenols (till 18%)
Risk assessment borehole porewaters: 4 samples						
2 boreholes from Kohtla-Järve semi-coke heap & 2 boreholes from Kiviõli more recent heap	Phenols: 2, BTX: 2, PAHs: 2	13797 (9950-18000)	12.5 (10.5-13.2)	77 (2.8-184)	0/4 **(0%)**	High concentration of mineral salts, high alkalinity phenols (till 11%)

* Estonian PLV for groundwater was applied

** by average toxicity

***as a rule, explain only part of the toxicity of the sample analyzed

Kontroll- og referanseside/
Review and reference page

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