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Evaluation of environmental quality in
Northern Estonia by the analysis of leachate

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ORIGINAL PUBLICATIONS

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- IV. **Selberg, A.**, Viik, M., Pall, P., Tenno, T. 2009. Environmental impact of closing of oil shale mines on river quality on North-Eastern Estonia. *Oil Shale*, 26, 169–183.

Author's contribution

Publication I: The author is partially responsible for the sampling and analysis of water (about 50%), and for writing the manuscript (80%).

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Publication IV: The author is partly responsible for the sampling and analysis of water (40%), and for writing the manuscript (75%).

ABBREVIATIONS

BOD ₅	–	biological oxygen demand (5 days)
BOD ₇	–	biological oxygen demand (7 days)
COD	–	chemical oxygen demand
DS	–	dry solids
EC	–	electrical conductance
HEM	–	hexane extractable material
k_H	–	Henry's constant
MB	–	Methylene blue
MBAS	–	Methylene blue active substances
n_g	–	amount of gaseous compounds (mol)
NAPLs	–	non-aqueous phase liquids
ND	–	not determined
NH ₄ ⁺ –N	–	ammoniacal nitrogen
NO ₂ [–] –N	–	nitrite nitrogen
NO ₃ [–] –N	–	nitrate nitrogen
N _{tot}	–	total nitrogen
p_g	–	total pressure of the gas phase (Pa)
PO ₄ ^{3–} –P	–	phosphate phosphorus
P _{tot}	–	total phosphorus
R	–	general gas constant (8.314 J mol ^{–1} K ^{–1})
[S ^{2–}] _{tot}	–	concentration of total sulfide (including dissolved H ₂ S, HS [–] and S ^{2–} ions)
T	–	absolute temperature (K)
USEPA	–	United States Environmental Protection Agency
WWTP	–	wastewater treatment plant

ABSTRACT

Fluid percolated through a porous media (deposited waste or soil) forms a solution or a suspension called leachate. The generated leachate has a significant influence on the environment through different physical and chemical processes (attenuation, degradation).

In the current PhD dissertation we have assessed the influence of leachate on the quality of the environment through the chemical analysis of oil-polluted soil, surface water from the Pääsküla, Kunda and Pühajõgi Rivers and leachate from soil columns and Pääsküla landfill. Additionally, we determined the time required to reach the distribution equilibrium of H_2S and CO_2 between water and gas phases in a closed system and compared the emission of H_2S from wastewater to the emission from the solution of NaHS.

Pääsküla landfill was built as a temporary waste disposal site without a project into a used peat-cutting area. A surrounding ditch, which operates as an oxidation pond, has been dug around the landfill and leachate from the landfill flew through drainage ditches into the Pääsküla and Vääna Rivers. The landfill generated leachate with a high concentration of pollutants: COD $668 \text{ mg O}_2 \text{ L}^{-1}$, N_{tot} 62.6 mg L^{-1} , P_{tot} 6.9 mg L^{-1} and $[\text{S}^{2-}]_{\text{tot}}$ 6.0 mg L^{-1} in March 2004. In July 2003, the COD of the water from the Pääsküla River was 22% higher than in July 1971 (before the landfill was built), showing that landfill leachate raised the pollution load of the Pääsküla River and consequently the pollution load of the Vääna River as well. At the sampling point of Hüüru the calculated fluxes of N_{tot} , NH_4^+-N , and P_{tot} were quite similar in July 2003 and 2004, although the discharge of water was more than 3 times higher in July 2004, indicating the leaching of nitrogen from the soil or sediments.

Hydrophobic pollutants, including petroleum hydrocarbons, are not easily biodegraded due to their low availability to microorganisms and bioavailability is increased due to added surfactants. Nevertheless, the leaching of a mixture of surfactants and pollutants could be generated in case the biodegradation of pollutants is not fast enough.

The experiments in bioremediation were carried out in Plexiglas columns which contained 1.4 L (2.2 kg) of coarse-grained or fine sandy soil contaminated with different petroleum hydrocarbons. In the experiments the columns with soil were treated once with a diluted solution of bioremediation agent SR-100, containing nutrients and anionic surfactants. Analysis of the upper layer (0–5 cm) of soil columns showed that surfactants were washed out from the upper layer during the first 35 days regardless of the type of soil. The highest amount of anionic surfactants was determined in the leachate of unpolluted coarse-grained soil column (15.8% of added surfactants), while the amounts of leached anionic surfactants were below 5% in case of oil-polluted soil. Initial content of oxygen was $64 \pm 5\%$ of O_2 saturation but the content of O_2 was below 10% of the saturation in lower soil fractions (24–36 cm).

The equilibrium between aqueous hydrogen sulfide and hydrosulfide ion in water depends on the pH of the solution. The lowering of pH generates the emission of H_2S that exceeds the equilibrium value of solubility at given conditions in the solutions, being connected with the growth of pressure inside the closed flask. The average measured times required to reach constant pressure due to the emission of gaseous CO_2 or H_2S corresponding to the equilibrium state of distribution of carbonate or sulfide in water after the lowering of pH were 16.7 ± 1.5 min and 19.5 ± 5.5 min respectively. Experiments with wastewater showed that gaseous H_2S was emitted faster from the wastewater due to the decreased solubility and the average time required to achieve distribution equilibrium between gas and liquid phases for H_2S was 16.2 ± 3.6 min.

The water quality of the Pühajõgi River catchments was evaluated because the mining water from oil shale mines was discharged into the Pühajõgi, water samples from the Kunda catchment were analyzed for comparison.

High content of different forms of nitrogen and phosphorus could cause accelerated eutrophication of lakes or rivers. Ammonia and nitrite ions, however, are directly toxic to the aquatic biota and thus measuring the concentrations of ammonia and nitrite nitrogen can be used to examine the ecotoxicity of surface water. The highest concentration of nitrite nitrogen (up to 7.8 mmol m^{-3} in Kukruse) in the water samples of the Pühajõgi catchment were determined in 2000, whereas in 2005 the concentration of nitrite was 3.5 mmol m^{-3} . The highest concentration of $\text{NH}_4^+\text{-N}$ up to 520 mmol m^{-3} was determined in the water sampled from Toila crossroads in 1995, decreasing more than 95% in the next ten years. The calculated fluxes of nitrogen showed that 80% of the nitrogen had infiltrated into the Pühajõgi River between the sampling points of Kotinuka and Toila crossroads as $\text{NH}_4^+\text{-N}$ and water from the Rausvere River increased the flux of nitrogen in the Pühajõgi mainly with $\text{NO}_3^-\text{-N}$ (74% from the total nitrogen) and 17% of nitrogen occurred as organic nitrogen in 1995. In 2005, the fluxes of nitrogen had reduced 3–5 times in comparison with 1995, indicating the positive influence of the closing of mines and the fluxes of organic nitrogen were more than 50% of the fluxes of total nitrogen in the Pühajõgi.

The concentration of nitrite nitrogen was below 1.2 mmol m^{-3} in the water samples of the Kunda catchment over the whole sampling area and period (1995–2005). The calculated mean values of $\text{NO}_2^-\text{-N}$ concentration had decreased up to 50% during the ten years (1995–2005). The highest concentration of $\text{NH}_4^+\text{-N}$ up to 3.1 mmol m^{-3} was determined in the water sampled from the sampling point of Lammasmäe (the Kunda River) in 1995, but the mean value of concentration was 0.91 mmol m^{-3} . In 2005, the highest concentration of ammonia was up to 2.3 mmol m^{-3} (determined in the water samples from Kulina and Kohala), but the mean value of ammonia concentration was 1.1 mmol m^{-3} . The fluxes of inorganic nitrogen constituted more than 85% of the fluxes of total nitrogen in the water of the Kunda River in 1995 and 2005

while the fluxes of toxic NO_2^- -N and NH_4^+ -N formed less than 1% (1995) or 2% (2005) of inorganic nitrogen.

The comparison of phosphorus fluxes in the Pühajõgi River showed a significant (up to 50 times) decrease during ten years (1995–2005) and the fluxes of different forms of phosphorus increased further downstream of the Pühajõgi, indicating continuous infiltration of phosphorus into the Pühajõgi in 1995 and 2005. In the water of the Kunda River the calculated fluxes of different forms of phosphorus were quite similar in 1995 and 2005. The fluxes of PO_4^{3-} -P formed about 50% of the flux of total phosphorus in the water of the Kunda River and similar situation was observed in the Pühajõgi River in 2005. Therefore, the Pühajõgi could achieve natural conditions after the closing of oil shale mines. The comparison of the water quality from the Pühajõgi and Kunda catchments indicated significant discharge of phosphorus through the mining water into the Pühajõgi.

I. INTRODUCTION

Leaching and leachate are very often associated with landfills. Landfill Directive (Council Directive 1999/31/EC) has defined the term “**leachate**” as any liquid percolating through the deposited waste and emitted from or contained within a landfill [Council directive]. Encyclopedia of environmental analysis and remediation has defined **leachate** as a liquid that is produced when water or another liquid comes in contact with waste [Meyer, 1998]. In soil science, the term “leachate” is applied to a solution collected in laboratory analysis and in column or lysimeter investigations, when soil is washed with specific extractants or water [Canarache et al., 2006]. In general, **leachate** is a solution or a suspension formed when a fluid percolates through a porous media [Canarache et al., 2006].

The potential of a landfill to pollute the environment can be realized by considering the process of waste degradation. Waste products can be produced in the following three phases: (1) solid (basically degraded waste); (2) liquid (called leachate); and (3) gas (generally referred to as landfill gas) [Butt and Oduyemi, 2003]. Leachate is the longest lasting emission from landfills [Kylefors et al., 2003].

Landfill leachate may contain compounds originally present in the landfilled waste as well as compounds formed in waste degradation processes [Ding et al., 2001, Kjeldsen et al., 2002, Marttinen et al., 2003]. Leachate can cause serious problems due to its ability to transport contaminating materials that may cause the contamination of soil, groundwater as well as surface water, and long-term environmental impacts last for several decades [Huo et al., 2008, Kylefors et al., 2003]. The composition of landfill leachate is highly dependent upon the stage of degradation in the landfill, waste composition, operational procedures, and co-disposal of industrial waste [Christensen et al., 2001, El-Fadel et al., 1997, Kennedy and Everett, 2001, Warith 2003, Ziyang et al., 2009]. The toxicity of leachate is a consequence of numerous contaminants in leachate, their synergistic or antagonistic effects, and different physical–chemical properties [Marttinen et al., 2002], and it is mostly due to metals, apolar compounds, suspended solids and soluble basic compounds [Isidori et al., 2003].

A lot of organic pollutants are hydrophobic and thus readily adsorbed on wastewater (leachate) solids, but the adsorption of organic pollutants may occur on solid or dissolved humic substances and in debris [Marttinen et al., 2003]. Leachate treatment is very complicated, expensive, and it generally requires various process applications. Furthermore, the optimal technologies of treatment for landfill leachate could vary depending on the age of the landfill [Huo et al., 2008, Marttinen et al., 2002].

Natural attenuation in landfill leachate plumes has been investigated in a few cases and the interpretation of natural attenuation processes is complicated by the heterogeneity and the long lifetime of a landfill as a source for pollution [Baun et al., 2003, Thornton et al., 2000a, Thornton et al., 2000b]. Degradation,

sorption, dilution, volatilization, precipitation, and ion exchange are processes which attenuate pollution, but only degradation really removes the mass of organic contaminants [Thornton et al., 2000b, van Breukelen et al., 2003].

Abiotic processes that could contribute to the natural attenuation of pollutants could be grouped into (1) processes that transform contaminants into less harmful compounds and (2) processes that immobilize some contaminants within the matrix. Abiotic transformation processes include hydrolysis, oxidation-reduction reactions at mineral interfaces and elimination reactions with spontaneous rearrangements of molecules [Alvarez and Illman, 2006]. Reduction and oxidation (redox) reactions are typically irreversible and transform contaminants into different compounds by means of electron transfer and redox reactions are often mediated by microorganisms [Scherer et al., 2000, McCormick et al., 2002]. Sulfides, which are produced by sulfate-reducing bacteria are present as structural components of some minerals (such as pyrite) and can participate in nucleophilic substitution reactions with halogenated methanes [Roberts et al., 1992]. Some contaminants could be immobilized by sorption to the matrix (common mechanisms for organic compounds) or precipitation from the dissolved phase (typical for metals) [Scherer et al., 2000]. Indigenous microorganisms often exploit the biodegradation of many different types of organic compounds as a metabolic niche to obtain energy and building blocks for the synthesis of new cellular material [Alvarez and Illman, 2006].

The dilution of landfill leachate as an insufficient process for decreasing the pollution load was discussed in **publication I** [Selberg et al., 2005]. In some cases a dominant role of intrinsic bioremediation of polluted soil or groundwater has been suggested as a comparatively large amounts of solid Fe(III) compounds (>1000 mg/kg) and dissolved SO_4^{2-} (50 to ~1000 mg/l) can occur naturally in contrast to O_2 and NO_3^- , because the naturally occurring concentrations of O_2 and NO_3^- are usually small in groundwater [Kennedy and Everett, 2001].

Interactions of landfill leachate with the sediment have been observed in field studies and SO_4^{2-} reduction often occurs in the presence of substantially large amounts of mineral Fe(III) compounds producing hydrosulfide ions [Kennedy and Everett, 2001]:



Leachate generated in anaerobic conditions inside landfills or in the deeper layer of soil contains various reduced compounds including sulfides [Kjeldsen et al., 2002]. The higher concentration of sulfide could be generated into the leachate especially in case of sulfur rich biowaste or contaminants during bacterial sulfate reduction [Morse et al., 1987, White et al., 2004]. A similar situation occurs in the pipelines of wastewater with high concentration of sulfate due to the reduction of sulfate by sulfate reducing bacteria [Delgado et al., 1999; Kärmas, et al. 2004]. Equilibrium of different forms of sulfide in

water depends on the pH of the solution and it has been quite well studied [Broderius and Smith, 1977, Chen and Gupta, 1973, Hersey et al., 1998, Kamyshny et al., 2004, Morse et al., 1987, Rao and Hepler, 1976/1977].

At the same time, decomposition of organic compounds in aerobic conditions generates different carboxylic acids as intermediates which lower the pH of the leachate [Kjeldsen et al., 2002]. Acidic compounds could be dissolved from the soil or from the solid matrix of landfills. Mixing the leachates with different pH could lower the pH of the mixture generating the emission of gaseous H_2S [Burgess et al., 2001, Spedding and Vujcich, 1982]. The determination of time required to reach the distribution equilibrium of H_2S between water and gas phases in comparison with the analogous measurements for CO_2 was discussed in **publication III** [Selberg et al., 2007].

In addition to landfills, leachate is generated when the polluted soil is washed with specific extractants or water [Canarache et al., 2006]. It means that different pollutants can also be leached out from the polluted soil during *in situ* bioremediation, especially through the use of surfactants for the surfactant-enhanced remediation of soil contaminated with hydrophobic organic compounds [Al-Sabagh et al., 2004, Chu and Kwan, 2003, Rouse et al., 1994, Stelmack et al., 1999, Suchanek et al., 2000, Wang and Mulligan, 2004]. Suitable surfactants for environmental remediation must decrease the surface tension of water, have low volatility and efficiently solubilize or mobilize NAPLs. Anionic surfactants are usually chosen for soil flushing procedures because of their lower degree of adsorption on the soil than that by cationic and nonionic surfactants [Kühler and Shnaak, 1997, Lee et al., 2002]. At the same time, nonionic surfactants generally donate greater enhancement of biodegradation whereas ionic surfactants are more inhibitory [Wang and Mulligan, 2004], thus cationic surfactants are more toxic than anionic and non-ionic surfactants [Singh et al., 2002]. In the remediation of organic-polluted environment with high surfactant concentrations, soil and groundwater may be significantly contaminated by surfactants due to the leaching of surfactants or surfactants/pollutants mixtures [Wang and Mulligan, 2004, Zhu and Feng, 2003]. The principal criterion for the ecological behavior of surfactants is their biodegradability which must be performed naturally by water or soil microorganisms, leading to natural products such as CO_2 , H_2O , and salts [Dhouib et al., 2003, Gejlsbjerg et al., 2003]. The effectiveness of surfactants is attenuated in case these are adsorbed by the soil and its mobility through the medium to which it is applied is reduced. The adsorption of surfactants by soil components may lead to a significant reduction in their effectiveness to remove contaminants from soils [Rodríguez-Cruz et al., 2005] and thus leaching from the soil is decreased. The results of a study on the behavior of anionic surfactants in oil-polluted sandy soil are discussed in **publication II** [Selberg et al., 2007].

In addition to surfactants and different pollutants, inorganic compounds of nitrogen and phosphorus have a negative influence on the quality of the environment. The quality of surface water is evaluated and characterized by

different parameters and their combinations: chemometric techniques (cluster analysis, principal component analysis, discriminant analysis, and factor analysis [Brodnjak-Vončina et al., 2002, Felipe-Sotelo et al., 2007, Kowalkowski et al., 2006], chemical analysis of water [Neal et al., 2006, Simeonov et al., 2003], abundance of micro and macro organisms [Cotton et al., 2006, Cuffney et al., 2000], and dissolved oxygen modeling [Cox, 2003a, b]. Due to spatial and temporal variations in water chemistry, a representative and reliable estimation of the quality of surface waters is necessary. Therefore, Water Quality Index as a mathematical means of calculating a single value from multiple test results was developed [Pesce and Wunderlin, 2000, Sanchez et al., 2007, Štambuk-Gilanovic, 1999]. Anthropogenic influences (urban [Felipe-Sotelo et al., 2007, Pesca and Wunderlin, 2000, Robson, et al., 2006], industrial [Kahru and Põllumaa, 2006, Zagorc-Koncan and Gotvain, 2000;] and agricultural [Cuffney et al., 2000, Iital et al., 2010, Withers and Lord, 2002] activities, increasing consumption of water) as well as natural processes (precipitations, erosion, weathering) degrade surface water quality [Cotton, et al., 2006, Dakova et al., 2000, Jones, 2001, Neal et al., 2006, Simeonov et al., 2003]. Man's activities drive freshwater ecosystems by the anthropogenic inputs of inorganic and organic substances [Jones 2001]. As a result, the environment is exposed to global impact and thus endangered [Zagorc-Koncan and Gotvain, 2000]. Mining is one of the industries which deteriorate lithosphere as well as hydrosphere because the huge amount of water is discharged into the surface in the process of mining [Perens et al. 2006, Rätsep et al., 2002, Tiwary, 2001]. The discharged water often contains high load of dissolved solids and metals [Liblik and Punning, 1999, Nordstrom et al., 2000, Tiwary et al., 2001]. Whereas the discharged water from the mines of the metal ore is characterized by low pH due to the oxidation of pyrite [Nordstrom et al., 2000], oil shale mine water has a pH above 7 due to limestone as a sedimentary rock [Liblik and Punning, 1999]. In such a case, the input of ions to the river water due to the water/rock interactions is controlled by the dissolution of carbonate [Grasby and Hutcheon, 2000, Panigrany and Raymahanhay, 2005]. The impact of oil shale mining on water ecosystem has been studied quite well [Liblik and Punning, 1999 and 2005, Perens et al. 2006, Rätsep et al., 2002]. Because of the changes in the economical situation of Estonia in 1990, four oil shale mines were closed in 1999–2002 [Liblik and Punning, 2005]. Thus, an opportunity arose to study leaching from the closed mines. The state of technogenic water body in the central part of an oil shale deposit was studied by Reinsalu et al. [2006]. The Purtse River is located in the centre of a mining area and the water quality and hydrological conditions of the Purtse catchment have been studied quite well [Liblik and Punning, 1999 and 2005, Rätsep and Liblik, 2004]. The results of the chemical analysis of the water quality of the Pühajõgi catchment are discussed in **Publication IV** [Selberg et al., 2009] and the impact of oil shale mine water on hydrology and runoff of the Pühajõgi River has been studied by Vaht and Rätsep [2009].

I.1. Objectives

The main objective of the current PhD dissertation is to assess the influence of leachate on the quality of the environment in Northern Estonia through a chemical analysis of oil-polluted soil, surface water from the Pääsküla, Kunda and Pühajõgi Rivers and leachate from soil columns as well as Pääsküla landfill. The sub-objectives for achieving the main goal are the following:

To determine the changes in the quality of water of the Pääsküla and Vääna Rivers during the closing of Pääsküla landfill and examine the natural attenuation of landfill leachate (**publication I**).

To study leaching and biodegradation of anionic surfactants and their influence on the behavior of petroleum hydrocarbons in oil-polluted sandy soil (**publication II**).

To determine the time required to reach distribution equilibria of H_2S and CO_2 between water and gas phases in a closed system due to the lowering of pH and to compare the emission of H_2S from wastewater to emission from the solution of NaHS (**publication III**).

To examine the chemical characteristics of the Pühajõgi River during the closing of oil shale mines and in comparison the water quality of the Kunda River was evaluated (**publication IV**).

2. MATERIALS AND METHODS

2.1. Site descriptions

The current PhD dissertation analyses water from the Pääsküla River, Pühajõgi River and Kunda River. The Pääsküla River is located in the southern part of a suburb of Tallinn, the capital of Estonia. The leachate from Pääsküla landfill flows through an additional drainage ditch and through the Pääsküla River into the Vääna River, which flows into the Gulf of Finland (Figure 2.1.). Pääsküla landfill was built as a temporary waste disposal site in 1974 and was closed in 2005. The landfill was built without a project into a used peat-cutting area. The area is 30 hectares and its relative altitude is 30 m. The amount of deposited waste is about 4 million tons and there has been no leachate treatment in this landfill. A surrounding ditch, which operates as an oxidation pond, has been dug around the landfill. Willow thickets grow in the areas around the landfill, ditches, and the Pääsküla River, whereas the ditches and the river have become overgrown with cattail and reed. Samples of leachate and river water were taken from the ditch and the Pääsküla River in July 2003 and in spring 2004 when the closing of Pääsküla landfill was started.

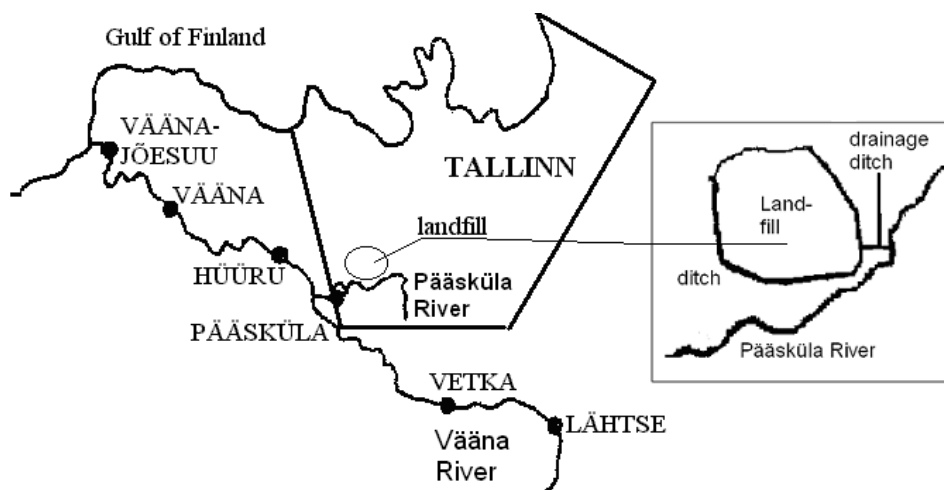


Figure 2.1. Location of Pääsküla landfill, the Pääsküla and Vääna Rivers with sampling points (●).

Water quality of the Pühajõgi and Kunda Rivers was examined during 1995–2005. Both rivers are located in similar geological conditions having limestone ground as sedimentary rock, and the influence of carbonate weathering on the water quality is equal. The Pühajõgi catchment is located in the central part of

East-Viru County between the oil shale mining area and the Gulf of Finland. The Kunda catchment is located in West-Viru County and it is not directly connected with oil shale mines (Figure 2.2.). Water was sampled in different points of the main rivers and streams in 1995, 2000 and 2005, and the sampling points were chosen to monitor the main river and the larger tributaries evenly. The distance between sampling points was ca 7 km and access to sampling points was open in any case. Sampling was made in July when the water level is usually at the lowest, water quality parameters are the most stable and well comparable.

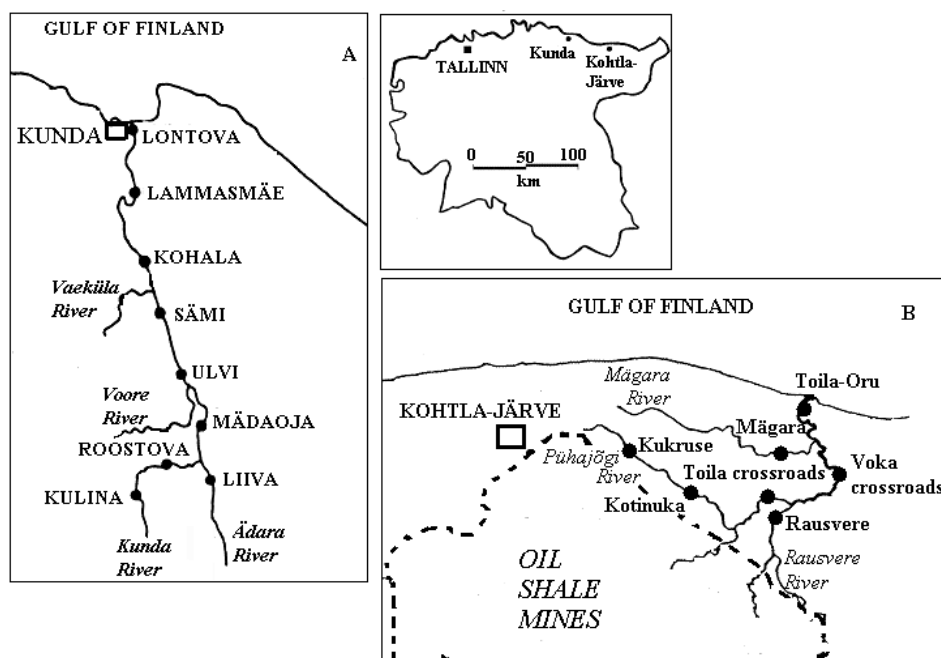


Figure 2.2. Location of sampling points (●) of the Kunda (A) and Pühajõgi (B) catchments and oil shale mines in Northern Estonia.

2.2. Column experiments with soil

The experiments in bioremediation were carried out in Plexiglas columns (length 50 cm, inner diameter 6 cm) (Figure 2.3.). The columns with holes on the side were used for the measurement of oxygen concentration in the soil air using oxygen meter Oxi340 (WTW, Germany). Each column contained 1.4 L (2.2 kg) of soil, which was added into the column by 200 mL and tightened by manual shaking. In the experiments the columns with soil were treated once with 80 cm³ of the diluted solution of bioremediation agent SR-100 (E-Tech,

USA). Every week, 30 cm³ of aerated distilled water was added to the column to moisten the soil and supply the soil with oxygen in order to model natural conditions (rain). After the experiments the content of the columns was divided into four equal fractions by volume (Figure 2.3).

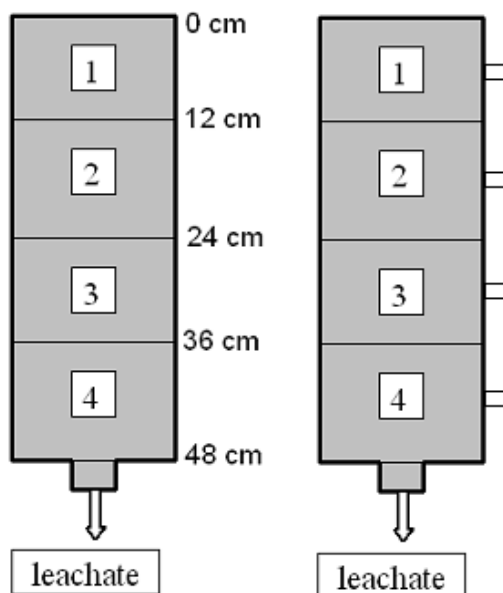


Figure 2.3. Scheme of column and the fractions of soil.

First series of the experiments were carried out with contaminated coarse-grained (diameter 2–8 mm) sandy soil from Ämari Airport (northwestern Estonia). The soil was contaminated with jet and diesel fuel as well as lubricating oil. To achieve a higher porosity in the test the polluted soil was mixed with unpolluted sand and the final concentration of the hydrocarbons was 500–600 mg HEM kg⁻¹.

Another series of experiments was carried out with fine (diameter 0.2–4 mm) natural sandy soil from Kloogaranna beach (northwest of Estonia). It was artificially contaminated with used diesel oil and the concentration of hydrocarbons was also about 500–600 mg HEM kg⁻¹ DS. The column with the unpolluted sand was used to compare the leaching of hydrocarbons and surfactants.

The leachate was collected and the concentrations of the leached surfactants and hydrocarbons were determined.

2.3. Experiments for gaseous emissions

For the study of gaseous emissions, NaHCO_3 and NaHS were selected to prepare initial solutions without pH regulations [$\text{pH}(\text{NaHS}) = 8.3$ and $\text{pH}(\text{NaHCO}_3) = 9.3$]. Wastewater from Kiviõli-Püssi pipeline of Kohtla-Järve WWTP was used for the study. Kohtla-Järve, with its surroundings, is a main industrial district of Estonia producing different chemicals (shale oil, fertilizers). All the wastewater entering Kohtla-Järve WWTP has caused problems for wastewater treatment and surroundings due to its high sulfate (average concentration 433 mg L^{-1}) and sulfide contents (average concentration 34 mg L^{-1}) [Kärmas et al., 2004]. The concentration of the examined sulfide solutions was determined by the results of wastewater analysis. All chemicals used in the study were analytical grade. The experiments were carried out in air-tight closed flasks with a volume of 1200 mL. The flasks with the solutions were kept and all measurements were carried out at a temperature of 20°C in the thermostat TS 606-G/4 (WTW, Germany). The manometric system OxiTop® (WTW, Germany) was used to measure the pressure inside the flasks (Figure 2.4.) and the pressure was recorded every 10 seconds. A magnetic stirrer was used to achieve equal agitation (150 rpm) of the solutions during the measurements.

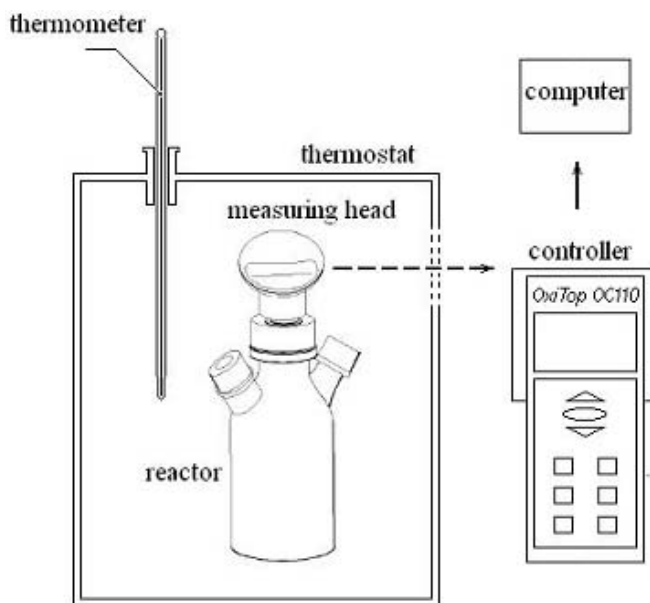


Figure 2.4. Scheme of the manometric OxiTop® system.

2.4. Chemical analysis

The pH of the leachate and water samples was measured by a pH-meter (SensION1, Hach, USA). Soil pH was determined by extracting the soil samples with 5 volumes of distilled water and measured with a glass electrode. The EC of water samples was measured by a conductivity meter and the values have been corrected to a constant temperature of 25°C [Standard Methods, 1985].

The concentration of anionic surfactants in the soil and leachate was determined by the spectrophotometric method using MB [Koga et al., 1999] and the concentration was calculated by the calibration curve as the MBAS.

The concentration of hydrocarbons in the soil and leachate was determined gravimetrically as HEM by the USEPA method 1664 [USEPA].

BOD₇ was determined by the seeded dilution method and COD was determined by the dichromate method. Water samples were digested with persulphate to determine N_{tot} and P_{tot} [Grasshoff, 1999]. The concentrations of N_{tot}, NO₂⁻-N and NO₃⁻-N were determined by the cadmium reduction method. The highly colored azo dye formed was measured by a spectrophotometer at 545 nm [Standard Methods, 1985]. The concentration of NH₄⁺-N was determined by the indophenol blue method, and the absorbance of the solution was measured by a spectrophotometer at 670 nm [Standard Methods, 1985]. The concentrations of P_{tot} and PO₄³⁻-P were determined by the ascorbic acid method, and the absorbance of the solution was measured at 880 nm [Grasshoff, 1999].

The concentration of sulfide was determined as a total sulfide [S²⁻]_{tot} (including dissolved H₂S, HS⁻ and S²⁻ ions) by the iodometric method at a certain pH [Pawlak and Pawlak, 1999, Standard Methods, 1985].

3. RESULTS AND DISCUSSION

3.1. Leaching from Pääsküla Landfill

Samples of leachate as well as water samples from the Pääsküla and Vääna Rivers were taken in July 2003 and in spring 2004. In comparison, the results of a comprehensive hydrobiological fieldwork in 1993 were used [Järvekülg, 2001]. Water results from the Pääsküla and Vääna Rivers before building Pääsküla landfill were presented by Roosalu [Roosalu, 1972]. The landfill generated leachate with high concentration of pollutants: COD = 668 mg O₂ L⁻¹, N_{tot} = 62.6 mg L⁻¹, P_{tot} = 6.9 mg L⁻¹ and [S²⁻]_{tot} = 6.0 mg L⁻¹ in March 2004 and the ratio of concentrations of NH₄⁺-N to NO₃⁻-N was 11.4. In April 2004, the leachate was diluted with snowmelt and the concentrations of pollutants had decreased: COD = 511 mg O₂ L⁻¹, N_{tot} = 55.0 mg L⁻¹ and P_{tot} = 1.1 mg L⁻¹ and [S²⁻]_{tot} = 4.0 mg L⁻¹, but the ratio of concentrations of NH₄⁺-N to NO₃⁻-N was 11.0. A summary of characteristic parameters of the leachate from the ditch surrounding Pääsküla landfill and the drainage ditch are presented in Table 3.1.

Table 3.1. Characteristic parameters of leachate from Pääsküla landfill.

Sampling time	pH	COD, mg O ₂ L ⁻¹	BOD ₇ , mg O ₂ L ⁻¹
Surrounding ditch			
July 2003	7.09	150	ND
March 2004	8.28	668	160
April 2004	7.01	511	237
May 2004	7.31	196	65
June 2004	7.29	218	53
July 2004	7.16	155	70
Drainage ditch			
June 1971	6.80	70	26*
July 1971	7.45	ND	3.2
July 2003	6.88	46	ND
March 2004	6.75	211	53
April 2004	6.54	54	17
May 2004	6.84	78	15
June 2004	7.54	178	32
July 2004	6.96	56	20

*BOD₅ was determined

In March 2004, the leachate was sampled under ice and the COD value (Table 3.1) was 4.5 times higher when compared with the results of July 2003. In April 2004, the value of COD of the leachate sample had lowered, which was connected with the dilution effect of snowmelt water. In May, June and July 2004, the values of COD were around $200 \text{ mg O}_2 \text{ L}^{-1}$ and the values of COD were equal in July 2003 and 2004, indicating similar composition of leachate during the closing procedure of the landfill. In April 2004, a higher value of BOD_7 showed higher concentration of biodegradable compounds that had leached from the soil and flowed with snowmelt into the surrounding ditch. In May, June and July 2004, the values of BOD_7 were quite similar and the biodegradable compounds had leached evenly.

The measured COD values of the water from the drainage ditch were 2–3 times lower than the COD of the leachate from the surrounding ditch, only in June the ratio of COD values was 1.2, indicating insufficient dilution or degradation of the leachate. Analyses of the water sampled from the drainage ditch showed that nitrogen occurred mainly as $\text{NH}_4^+\text{-N}$ and phosphorus in the form of phosphate. The ratios of concentrations of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ were above 10 both in July 1971 and in July 2003. However, in July 1993 the water was sampled 300 m downstream and the ratio of concentrations of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ was 1.4. That indicated that ammonia had oxidized to nitrate in the ditch.

Along the Vääna River, a high concentration of ammoniacal nitrogen (12 mg L^{-1} in 2003) was determined only at the sampling point of Pääsküla, thus resulting from the landfill leachate. In 2003, the highest $\text{NO}_3^-\text{-N}$ concentrations were determined in Hüüru (3.7 mg L^{-1}) and Vääna (3.6 mg L^{-1}), which are downstream from the Pääsküla River and could therefore be connected with the oxidation of ammonia in the Vääna River. A very low concentration of $\text{NH}_4^+\text{-N}$ in Hüüru (0.01 mg L^{-1}) showed an active nitrification process in the Vääna River (Figure 3.1.).

In 2003, the highest value of COD for the water sampled from the Vääna River was determined at Pääsküla sampling point ($46 \text{ mg O}_2 \text{ L}^{-1}$). Moreover, the values remained high as far as up to the mouth of the Vääna River at Vääna-Jõesuu ($41 \text{ mg O}_2 \text{ L}^{-1}$), testifying that landfill leachate had increased the pollution load on the Vääna River. The so-called natural attenuation of the pollutants was mainly connected with dilution and it was insufficient to reduce the pollution of the Vääna River.

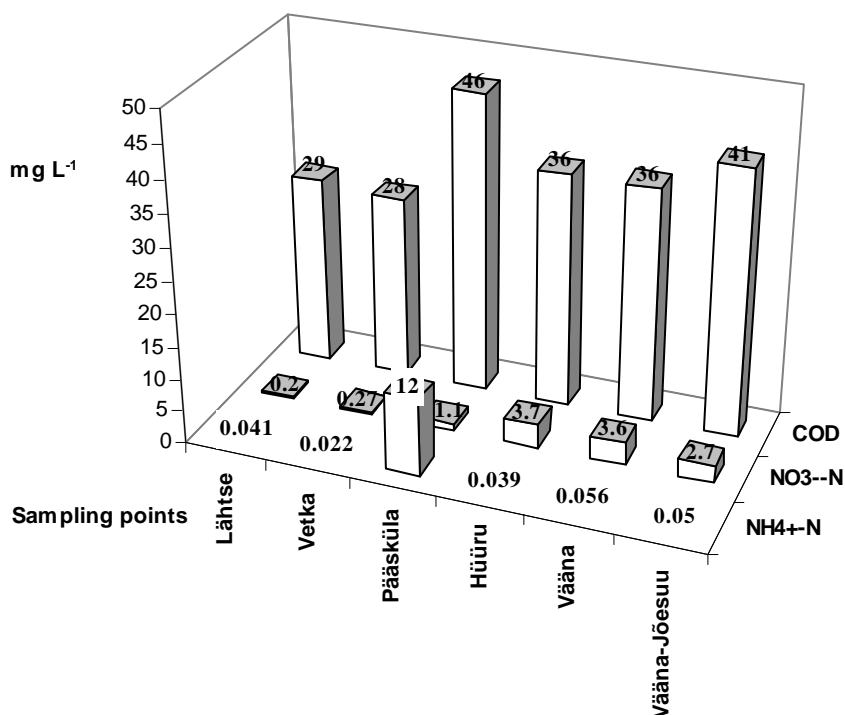


Figure 3.1. The profiles of $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$ and COD along the Vääna River in July 2003.

Discharge of the Vääna River was determined at the sampling point of Hüüru, which is next to the infiltration of the water from the Pääsküla River into the Vääna River. The calculated fluxes of N_{tot} , $\text{NH}_4^+\text{-N}$, and P_{tot} are presented in Table 3.2.

Table 3.2. Fluxes of dissolved nitrogen and phosphorus at the sampling point of Hüüru of the Vääna River.

Sampling time	Discharge, L s^{-1}	N_{tot} , mg s^{-1}	$\text{NH}_4^+\text{-N}$, mg s^{-1}	P_{tot} , mg s^{-1}
July, 2003	350	4340	2835	140
March, 2004	3800	3572	2356	76
April, 2004	2700	6480	1107	135
May, 2004	750	930	547.5	85.5
June, 2004	550	682	93.5	335.5
July, 2004	1300	4550	2730	195

The calculated fluxes of N_{tot} , $[\text{NH}_4^+-\text{N}]$, and P_{tot} were quite similar at the sampling point of H  uru in July 2003 and 2004, although the discharge of water was more than 3 times higher in July 2004 (Table 3.2). The higher discharge could be connected with the leaching of a lot of nitrogen from the soil or sediments through precipitations as discharges were quite low in May and June 2004. There was no clear relationship between fluxes of P_{tot} and the discharge of the V  ana River: the fluxes of P_{tot} differed about 10% in March and May 2004, but the discharge in March was 5 times higher in comparison with the discharge in May. The flux of P_{tot} was the highest in June 2004 when the discharge was quite low. The behavior of phosphorus could be connected with the rate of dissolution and precipitation of phosphorus in the natural water.

3.2. Leaching from oil-polluted soil

Concentrations of anionic surfactants were measured regularly in the upper layer (0–5 cm) of the soil in the columns. The columns with soil were treated once with the solution of SR-100 (the total amount of anionic surfactants was 816 ± 9 mg MBAS). First time the concentration of surfactants was detected the next day after the treatment when the solution of surfactants had immersed completely into the soil in the columns. The determined concentrations of anionic surfactants as MBAS in the experiments with polluted sandy soil are presented in Table 3.3.

Table 3.3. Concentration of anionic surfactants (mg MBAS g^{-1}) in the upper layer (0–5 cm) of the columns with soil.

Time, days	Unpolluted soil		Oil-polluted soil		Oil-polluted soil with CaCO_3	
	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil
0	172	292	172	260	351	312
8	121	176	91.4	142	261	149
15	95.7	108	85.4	97.5	212	101
29	51.7	46.6	48.5	2.1	69.3	54.7
49	8.9	2.3	8.4	1.1	24.8	10.5
60	8.1	1.5	8.1	0.93	23.7	1.7

Results of the analysis showed that the initial concentration of surfactants in unpolluted and oil-polluted coarse-grained soils (Table 3.3.) was two times smaller than the concentration of surfactants within the mixture of coarse soil and limestone powder. The columns with unpolluted or polluted coarse-grained soil had a negligible difference in the concentration of surfactants in the upper

soil layer (0–5 cm) during the experiment. The higher concentration of surfactants in the upper soil layer in case of a mixture of soil and CaCO_3 could be explained by the specific higher surface of limestone powder which adsorbed the anionic surfactants by the soaking of the solution of surfactants in the soil [Canbolat et al., 2004].

For fine soil, the initial concentration of surfactants and its reduction in the upper layer (Table 3.3.) was similar in all soil samples. The surfactants were washed out of the upper layer in the columns of unpolluted and polluted soil during the first 35 days. The concentration of anionic surfactants decreased linearly during the last 40 days of the experiment with the mixture of polluted soil and CaCO_3 , and the surfactants were washed out of the upper layer during the 60 days in the column.

The experiments continued for 60 days after which all four fractions of soil samples were analyzed and the calculated masses of anionic surfactants are presented in Table 3.4.

Table 3.4. The cumulative masses of surfactants (mg MBAS) in soil fractions and leachate of the columns after the experiments.

Fraction of the column	Unpolluted soil		Oil-polluted soil		Oil-polluted soil with CaCO_3	
	Coarse soil	Fine soil	Coarse soil	Fine soil	Coarse soil	Fine soil
1 (0–12 cm)	22.7	10.4	8.5	19.6	23.5	24.6
2 (12–24 cm)	52.6	17.1	75.9	75.5	35.3	32.9
3 (24–36 cm)	64.3	93.8	4.4	88.4	30.9	93.2
4 (36–48 cm)	271	617	4.1	351	14.1	573
leachate	125	40.4	20.2	50.4	36.8	26.4
total	535	779	113	584	141	750

The masses of surfactants in coarse soil fractions (Table 3.4) had no clear relationship with the type of soil. After the experiments, oil-polluted coarse soil contained generally the lowest amounts of surfactants but in the second fraction (12–24 cm) it was the highest in comparison with other soil columns. The lowest layer (36–48 cm) of unpolluted coarse soil contained much higher amount of surfactants in comparison with other columns.

The amounts of residual surfactants in the different fractions of the fine soil column (Table 3.4) had a clear trend: the lower fraction contained more surfactants. This trend indicated leaching of the surfactants from upper fractions into lower ones.

The highest amount of anionic surfactants was determined in the leachate of unpolluted soil column (15.8% of added surfactants) while the highest amount of anionic surfactants determined in the leachate of fine soil column was only

6.2% of the added surfactants in case of oil-polluted soil. That indicated significant leaching of surfactants from unpolluted soil which had low microbial activity. These results show the degradation of surfactants in oil-polluted soil, but the period of 60 days was not enough to degrade the surfactants in the soil completely. Therefore, leaching from coarse-grained soil was detected.

Calculation of mass balance of anionic surfactants showed that the biggest amount (86%) of anionic surfactants had degraded in the column of coarse-grained oil-polluted soil. The mass balance of anionic surfactants indicated lower degradation of surfactants in the columns with fine sandy soil. In the experiments with fine sandy soil the highest degradation of anionic surfactants (28% from the added surfactants) was determined in the column with oil-polluted soil. Due to the low porosity of fine soil the amount of oxygen that diffused into the soil was not enough to achieve the aerobic conditions needed for the surfactants degradation.

In the current experiments the concentrations of petroleum hydrocarbons (as HEM) in the soil fractions were also determined. The analysis of hydrocarbons showed that the concentration of residual hydrocarbons in coarse-grained soil was about 30–40% of the initial concentration. After the experiment the samples of fine sandy soil contained 50–60% of the initially added petroleum hydrocarbons. The lower concentrations of hydrocarbons in coarse-grained soil columns were connected with the better supply of oxygen into the soil due to the higher porosity of coarse-grained sandy soil. Dry residual of the leachate from the columns contained about 5% of hydrocarbons.

Faster biodegradation of surfactants and pollutants is carried out in aerobic conditions and the porosity of soil is an important factor for the diffusion of oxygen into the lower soil layer. The results of measured oxygen content in the gas phase of the soil fractions due to saturation are presented in Table 3.5.

Table 3.5. Saturation (%) in the gas phase of soil fractions with oxygen

Soil fraction	Coarse soil				Fine soil			
	Initial	Unpol- luted soil	Oilpol- luted soil	Soil with CaCO ₃	Initial	Unpol- luted soil	Oilpol- luted soil	Soil with CaCO ₃
1 (0–12 cm)	64	27	20	22	65	18	12	15
2 (12–24 cm)	67	20	16	19	63	14	12	13
3 (24–36 cm)	58	12	6	8	56	2	3	9
4 (36–48 cm)	72	39	34	37	67	28	33	25

Initial content of oxygen measured before adding the solution of SR-100 did not depend on the location of a soil fraction or the type of soil (mean content of O₂ 64 ± 5%), indicating that the porosity of sandy soils was good enough.

Measurements at the end of the experiment showed higher contents of oxygen in the upper and the lowest fractions of soil columns due to the better diffusion of O_2 . The content of O_2 was very low ($< 10\%$) in soil fractions 3 (24–36 cm) (Table 3.5), indicating the reduced porosity of the soil due to the leaching of the solution of surfactants and pollutants. Indigenous microorganisms can be also leached into the lower layer together with the solution generating higher oxygen consumption. Very low oxygen content in lower soil layers indicated that it would be necessary to guarantee enough aeration of soil during the biostimulation of oil-polluted soil, being more important during the time of heavy or long precipitation, and the soil washing occurs instead of biostimulation.

3.3. Gaseous emissions of H_2S and CO_2

Solubility of CO_2 in water and its transfer between air and water have been studied quite well. The state of equilibrium between dissolved CO_2 and bicarbonate ions HCO_3^- is characterized by the ionization constant K_1 and the mean value for pK_1 at $20^\circ C$ is 6.38 [Segal, 1989].

In the solution of sodium bicarbonate ($NaHCO_3$), by lowering the pH, the new equilibrium of the system is achieved, the emission of gaseous CO_2 occurs and the pressure inside the closed system starts to grow. The measured time required to reach the constant pressure corresponding to the distribution equilibrium is presented in Figure 3.2. The results indicate that the time required to reach the equilibrium state of distribution is not related to the initial concentration of $NaHCO_3$. The average time required to achieve the distribution equilibrium was 16.7 ± 1.5 min.

The chemistry of H_2S in water is similar to that of CO_2 as both of them are soluble in water and both acids (H_2S and H_2CO_3) have diprotic dissociation. The equilibrium between aqueous H_2S and HS^- in water is characterized by ionization constant K_1 and the mean value for pK_1 at $20^\circ C$ is 7.05 [Hersey et al., 1998]. After the injection of acid into sulfide-containing solution, the emission of H_2S that exceeds the equilibrium value of solubility at given conditions in the solutions generates the growth of pressure inside a closed flask. The measured time required to reach the constant pressure corresponding to the distribution equilibrium is presented in Figure 3.3.

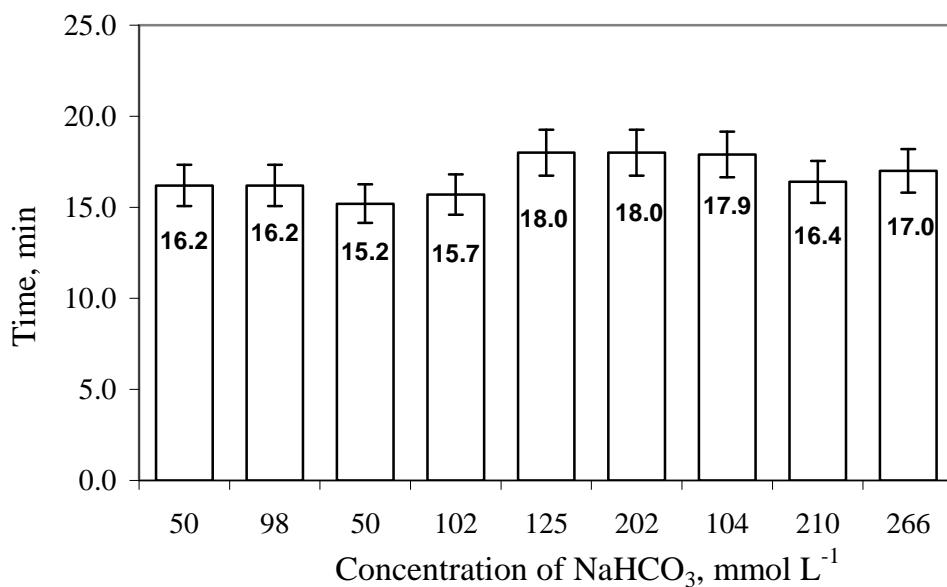


Figure 3.2. Time required to reach a constant pressure in a closed system corresponding to the distribution equilibrium between gas and liquid phases for CO₂ at 20°C.

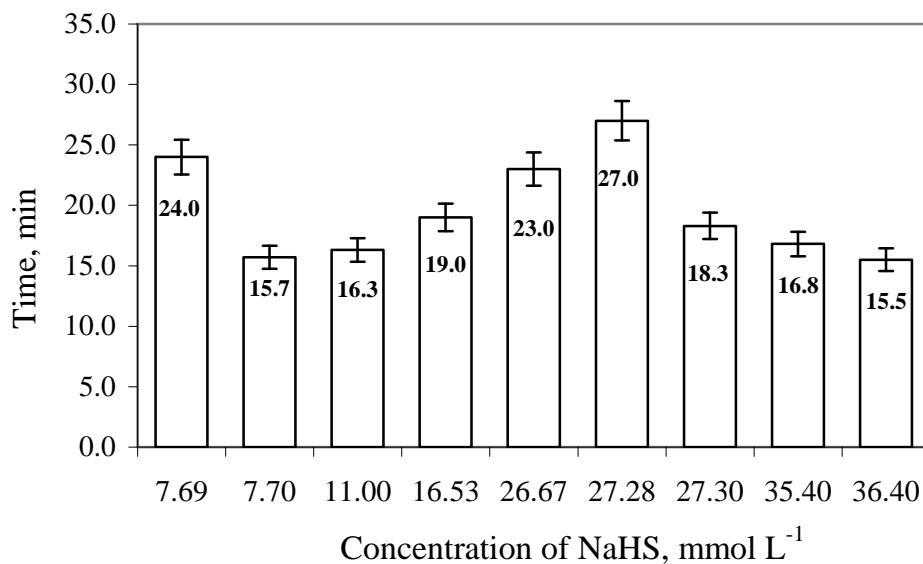


Figure 3.3. Time required to reach a constant pressure in a closed system corresponding to the distribution equilibrium between gas and liquid phases for H₂S at 20°C.

The results showed no clear correlation between the initial concentration of NaHS and the time required to reach the equilibrium state of distribution of the system. The average time required to achieve a constant pressure due to the emission of gaseous H₂S was 19.5 ± 5.5 min, which was ca. 16% longer in comparison with the system of carbonate. It could be explained by the different behavior of H₂S in the solution (Spedding and Vujcich, 1982), because polysulfides in the hydrogen sulfide solution can increase the time required to reach the equilibrium in the solution of sulfide (Chen and Gupta, 1973).

The total pressure p_g generated due to the emission of the amount of gaseous compound n_g can be calculated using the ideal gas law:

$$p_g = \frac{n_g}{V_g} \times RT$$

The values of Henry's constant were calculated for temperature 20°C (293.15 K) as follows: for CO₂ $k_H = 1.0632 \text{ mol L}^{-1} / (\text{mol L}^{-1})$ by the data of Weiss (1974) and for H₂S $k_H = 0.3601 \text{ mol L}^{-1} / (\text{mol L}^{-1})$ by the data of Morse et al. (1987).

The equations of linear regression between the values of measured or theoretical relative pressure and the concentration of dissolved salt are presented in Table 3.6.

Table 3.6. The equations of linear regression between the values of measured or theoretical relative pressure (p) and the concentration of dissolved salt (c).

Analyzed system	Measured pressure	Calculated pressure	Ratio of the measured and calculated pressure
CO ₂ – NaHCO ₃	$p = 18.027c$ ($r^2 = 0.9868$)	$p = 20.376c$ ($r^2 = 1.000$)	0.90±0.05
H ₂ S – NaHS	$p = 16.13c$ ($r^2 = 0.9527$)	$p = 17.798c$ ($r^2 = 0.9868$)	0.86±0.14

The ratios of measured and calculated pressures did not depend on the concentration of salts (NaHCO₃ or NaHS) in the initial solution and their values indicate the approximation used for the characterization of the system of dissolved CO₂ and H₂S. The average ratio of measured and calculated values of pressure was ca. 4.5% lower for H₂S in comparison with CO₂ and the equilibrium of NaHS solution is more complicated due to the containment of polysulfides in the sulfide system [Chen and Gupta, 1973].

Results of the measurements with wastewater showed that experimentally measured values of relative pressure through the emission of gaseous H_2S were twice lower than the calculated values, confirming that the used value of Henry's constant $k_{\text{H}} = 0.3601$ (Morse et al., 1987) was not correct in case of wastewater. Experiments with wastewater gave the average time required to achieve the distribution equilibrium between gas and liquid phases for H_2S as 16.2 ± 3.6 min, where the solutions with higher sulfide concentration needed longer time to achieve the equilibrium. Acceleration of the emission of gaseous H_2S from wastewater showed that the emission of H_2S from leachate can also be quite fast due to the lowering of pH.

3.4. Leaching from oil shale mines

The water qualities of the Pühajõgi and Kunda catchments were evaluated because the mining water from oil shale mines was discharged into the Pühajõgi River, but the Kunda catchment is not connected with oil shale mines.

Concentrations of different forms of nitrogen and phosphorus are determined to evaluate the quality of surface water and their higher concentrations cause accelerated eutrophication of lakes or rivers. At the same time, ammonia and nitrite ions are directly toxic to aquatic biota. Therefore, measurements of ammonia and nitrite nitrogen concentrations can be used to examine the ecotoxicity of surface water. Nitrite nitrogen is generated through the oxidation of ammonia (NH_4^+) and nitrite anion is toxic to the living organisms in water. In addition to nitrite, high concentration of ammonia (NH_3) is an indicator for the toxicity of river water. Ionization of ammonia ($\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$) depends mainly on the pH of water and it is significant in the water with pH below 7. Additionally, higher temperature decreases the ionization of ammonia, but its influence is lower than that of pH [Emerson et al., 1975]. Ammonia (NH_3) is toxic to living organisms [Camargo et al., 2006] and its fraction becomes increasingly important at pH above 7. In studied rivers the water was mainly weakly alkaline (pH 7.3–8.0). Considering the measured pH, water temperature, and equilibrium calculations of ammonia [Emerson et al., 1975] the fraction of ammonium (NH_3) was up to 10% (at pH 8) in the water samples of the rivers studied.

Concentrations of ammonia and nitrite ions are calculated in millimoles per m^3 of water (mmol m^{-3}) for a better comparison of the amounts of different ions in the water samples and results of water samples from the Pühajõgi and Kunda catchments are presented in Tables 3.7 and 3.8, respectively.

Table 3.7. Concentrations of nitrite $[\text{NO}_2^--\text{N}]$ and ammoniacal nitrogen $[\text{NH}_4^+-\text{N}]$ in the water samples from the sampling points of the Pühajõgi catchment in July.

Sampling point	1995		2000		2005	
	$[\text{NO}_2^--\text{N}]$, mmol m^{-3}	$[\text{NH}_4^+-\text{N}]$, mmol m^{-3}	$[\text{NO}_2^--\text{N}]$, mmol m^{-3}	$[\text{NH}_4^+-\text{N}]$, mmol m^{-3}	$[\text{NO}_2^--\text{N}]$, mmol m^{-3}	$[\text{NH}_4^+-\text{N}]$, mmol m^{-3}
Kukruse	0.43±0.03	340±30	7.8±0.5	22±2	3.5±0.3	94±7
Kotinuka	0.79±0.05	2.6±0.2	1.9±0.1	1.1±0.1	0.29±0.02	2.5±0.2
Toila crossroads	0.14±0.01	520±40	1.4±0.1	15±1	0.36±0.03	4.6±0.3
*Rausvere	2.1±0.2	14±1	6.8±0.6	59±4	0.79±0.04	5.2±0.3
Voka crossroads	2.5±0.2	98±7	6.8±0.5	21±2	0.79±0.05	9.4±0.5
*Mägara	0.14±0.01	1.1±0.1	0.060±0.003	0.36±0.02	0.14±0.01	1.8±0.2
Toila-Oru	1.2±0.1	18±2	2.6±0.2	4.1±0.3	1.8±0.1	9.3±0.6

* Sampling points of a tributary

Concentrations of nitrite were quite low in the water samples from the catchment of the Pühajõgi and higher concentrations of nitrite were determined at the sampling points of Rausvere and Voka crossroads in 1995 (above 2.1 mmol m^{-3}) and 2000 (above 6.8 mmol m^{-3}). The results were connected with the infiltration of mine water into the Rausvere River as the concentration of nitrite was 0.79 mmol m^{-3} at the sampling points of Rausvere and Voka crossroads in 2005 when the mines were closed. The highest concentration of nitrite nitrogen (up to 7.8 mmol m^{-3} in Kukruse) in the water samples of Pühajõgi catchment were determined in 2000, whereas in 2005, the concentration of nitrite was 3.5 mmol m^{-3} , indicating the positive effect of closing mines.

Variations of concentrations of ammoniacal nitrogen were significant in the Pühajõgi catchment and the highest concentration of NH_4^+-N up to 520 mmol m^{-3} was determined in the water sampled from Toila crossroads in 1995. The concentration decreased more than 95% during the next ten years. The water sampled from Rausvere and Voka crossroads contained relatively great amount of ammonia in 1995 and 2000, but the concentration of NH_4^+-N was below 10 mmol m^{-3} in 2005.

Table 3.8. Concentrations of nitrite [NO_2^- -N] and ammoniacal nitrogen [NH_4^+ -N] in the water samples from the Kunda catchment sampling points in July.

Sampling point	1995		2000		2005	
	[NO_2^- -N],	[NH_4^+ -N],	[NO_2^- -N],	[NH_4^+ -N],	[NO_2^- -N],	[NH_4^+ -N],
	mmol m ⁻³	mmol m ⁻³	mmol m ⁻³	mmol m ⁻³	mmol m ⁻³	mmol m ⁻³
Kulina	0.36±0.02	0.71±0.04	0.14±0.01	1.0±0.1	0.14±0.01	2.3±0.2
Roostova	0.29±0.02	0.79±0.04	0.21±0.02	0.71±0.04	0.21±0.02	0.71±0.04
*Liiva	0.50±0.03	0.36±0.02	0.43±0.08	1.3±0.1	0.36±0.02	1.1±0.1
Mädaoja	1.0±0.1	0.43±0.03	0.64±0.04	1.3±0.2	0.64±0.05	0.43±0.03
Ulvi	1.2±0.1	0.36±0.02	0.50±0.04	1.2±0.1	0.36±0.02	0.86±0.05
Sämi	0.44±0.03	0.43±0.03	0.57±0.04	1.2±0.1	0.29±0.02	0.29±0.02
Kohala	0.36±0.03	1.1±0.1	0.50±0.03	1.5±0.2	0.21±0.02	2.3±0.02
Lammasmäe	0.29±0.02	3.1±0.2	0.57±0.05	1.4±0.1	0.29±0.02	0.93±0.06
Lontova	0.29±0.02	0.93±0.06	0.71±0.05	1.7±0.2	0.14±0.01	1.0±0.1

* Sampling point of a tributary

The water samples of Kunda catchment had quite a steady concentration of nitrite (below 1.2 mmol m⁻³) over the whole sampling area and period (1995–2005) (Table 3.8). The calculated mean values of NO_2^- -N concentration decreased during the ten years (1995–2005) as the mean values were 0.53±0.34, 0.48±0.18 and 0.29±0.1 mmol m⁻³, respectively.

Concentrations of ammonia in the water sampled from the Kunda catchment were quite steady in comparison with the results from the water sampled from the Pühajõgi catchment (Table 3.8). The highest concentration of NH_4^+ -N up to 3.1 mmol m⁻³ was determined in the water sampled from Lammasmäe sampling point in 1995, but it was below 1 mmol m⁻³ at the other sampling points. In 2000, concentrations of ammonia were below 1.7 mmol m⁻³ while in 2005 the highest concentrations of ammonia up to 2.3 mmol m⁻³ were determined in the water sampled from the sampling points of Kulina and Kohala.

Although the quality of surface water is evaluated by the concentrations of biogens or pollutants, their fluxes are used to examine the accumulation or degradation of the compounds. The fluxes of different forms of nitrogen in the water of the Pühajõgi River are presented in Tables 3.9 and 3.10.

Calculated fluxes of nitrogen (Table 3.9) showed that 80% of nitrogen had infiltrated into the Pühajõgi River between the sampling points of Kotinuka and Toila crossroads as NH_4^+ -N in 1995. Water from the Rausvere River increased the flux of nitrogen in the Pühajõgi mainly with NO_3^- -N (74% from the total nitrogen) and 17% of nitrogen occurred in the form of organic nitrogen in 1995. The fluxes of NO_2^- -N and NH_4^+ -N were reduced in further downstream of the Pühajõgi due to oxidation as the fluxes of nitrate increased.

In 2005 (Table 3.10), the fluxes of nitrogen had reduced 3–5 times in comparison with 1995, indicating the positive influence of closing mines. The fluxes of organic nitrogen constituted more than 50% of the fluxes of total nitrogen in the Pühajõgi River and the flux of NO_3^- -N was the biggest (35% from the total nitrogen) of the water from the Rausvere River in 2005. The fluxes of inorganic and organic nitrogen increased further downstream of the Pühajõgi, but the fluxes of toxic nitrite and ammonia were quite steady. The highest fluxes of NO_2^- -N and NH_4^+ -N were calculated for the sampling point of Toila-Oru, indicating the influence of settlement of Toila-Oru in the water of the Pühajõgi in 2005.

Table 3.9. The fluxes of dissolved nitrogen at the sampling points of the Pühajõgi River in July, 1995.

Sampling point	Discharge, L s^{-1}	N_{tot} , mg s^{-1}	NO_3^- -N, mg s^{-1}	NO_2^- -N, mg s^{-1}	NH_4^+ -N, mg s^{-1}	N_{inorg} , mg s^{-1}	N_{org} , mg s^{-1}
Kukruse	8	39	0.4	0.05	38	39	0.1
Kotinuka	40	56	30	0.4	1	32	24
Toila crossroads	100	903	7	0.2	728	735	168
*Rausvere	500	1304	969	15	95	1078	226
Voka crossroads	870	3993	2186	31	1188	3404	589
*Mägara	30	13	0.9	0.06	0.5	1	12
Toila-Oru	900	4131	3177	15	225	3417	714

* Sampling points of a tributary

Table 3.10. The fluxes of dissolved nitrogen in the sampling points of the Pühajõgi River in July 2005.

Sampling point	Discharge, L s^{-1}	N_{tot} , mg s^{-1}	NO_3^- -N, mg s^{-1}	NO_2^- -N, mg s^{-1}	NH_4^+ -N, mg s^{-1}	N_{inorg} , mg s^{-1}	N_{org} , mg s^{-1}
Kukruse	20	48	3	1	26	30	18
Kotinuka	20	18	0.3	0.08	0.7	1	17
Toila crossroads	60	57	2	0.3	4	6	51
*Rausvere	400	431	152	4	29	186	245
Voka crossroads	450	630	153	5	59	218	412
*Mägara	60	48	13	0.1	2	14	34
Toila-Oru	1500	1460	390	39	195	624	836

* Sampling points of a tributary

The fluxes of nitrogen in the water of the Kunda River are presented in Tables 3.11 and 3.12. The fluxes of inorganic nitrogen formed more than 85% of the fluxes of total nitrogen in the water of the Kunda River in 1995 and the fluxes of toxic NO_2^- -N and NH_4^+ -N formed less than 1% of inorganic nitrogen.

In 2005, the fluxes of nitrogen were lower than in 1995, but the discharge of water was also lower in the upper reach of the Kunda River. Inorganic nitrogen formed more than 85% of the fluxes of the total nitrogen in the upper reach, but it was below 75% in the lower reach of the Kunda River in 2005. The fluxes of toxic NO_2^- -N and NH_4^+ -N formed less than 2% of inorganic nitrogen. The fluxes of different forms of nitrogen increased further downstream of the Kunda River, indicating continuous infiltration of nitrogen from untreated or purely treated wastewater of settlements and agricultural sources into the Kunda River in 1995 and 2005.

Table 3.11. The fluxes of dissolved nitrogen at the sampling points of the Kunda River in July 1995.

Sampling point	Discharge, L s^{-1}	N_{tot} , mg s^{-1}	NO_3^- -N, mg s^{-1}	NO_2^- -N, mg s^{-1}	NH_4^+ -N, mg s^{-1}	N_{inorg} , mg s^{-1}	N_{org} , mg s^{-1}
Kulina	ND	x	x	x	x	x	x
Roostova	650	1190	1099	3	7	1108	81
*Liiva	600	1458	1273	4	3	1280	178
Mädaoja	1200	2293	1956	17	7	1980	313
Ulvi	ND	x	x	x	x	x	x
Sämi	2000	4204	3874	12	12	3898	306
Kohala	2000	4112	3980	10	30	4020	92
Lammas-mäe	ND	x	x	x	x	x	x
Lontova	2900	5174	4481	12	38	4531	644

* Sampling point of a tributary

x – flux was not calculated

Table 3.12. The fluxes of dissolved nitrogen at the sampling points of the Kunda River in July 2005.

Sampling point	Discharge, L s ⁻¹	N _{tot} , mg s ⁻¹	NO ₃ ⁻ -N, mg s ⁻¹	NO ₂ ⁻ -N, mg s ⁻¹	NH ₄ ⁺ -N, mg s ⁻¹	N _{inorg} , mg s ⁻¹	N _{org} , mg s ⁻¹
Kulina	360	337	278	0.7	12	290	47
Roostova	540	797	747	2	5	754	43
*Liiva	700	990	799	4	11	813	177
Mädaoja	1400	2059	1856	13	8	1877	182
Ulvi	ND	x	x	x	x	x	x
Sämi	ND	x	x	x	x	x	x
Kohala	ND	x	x	x	x	x	x
Lammas-mäe	7000	11410	8288	28	91	8407	3003
Lontova	7000	13230	8757	14	98	8869	4361

* Sampling point of a tributary

x – flux was not calculated

The fluxes of P_{tot} and PO₄³⁻-P in water of the Pühajõgi and Kunda Rivers are presented in Tables 3.13 and 3.14, respectively.

The comparison of fluxes of phosphorus in the Pühajõgi River shows a significant (up to 50 times) decrease during ten years (1995–2005) (Table 3.13). In 1995, the fluxes of PO₄³⁻-P formed about 90% of the fluxes of total phosphorus and PO₄³⁻-P discharged into the Pühajõgi between the sampling points of Kotinuka and Toila crossroads and through the Rausvere River, indicating the influence of mine water on the Pühajõgi.

Table. 3.13. The fluxes of total phosphorus (P_{tot}) and phosphate phosphorus PO₄³⁻-P in the water of the Pühajõgi River in July.

Sampling point	1995			2005		
	P _{tot} , mg s ⁻¹	PO ₄ ³⁻ -P, mg s ⁻¹	P _{org} , mg s ⁻¹	P _{tot} , mg s ⁻¹	PO ₄ ³⁻ -P, mg s ⁻¹	P _{org} , mg s ⁻¹
Kukruse	12	11	1	6	5	1
Kotinuka	5	2	3	0.9	0.5	0.4
Toila crossroads	247	228	19	4	2	2
*Rausvere	240	210	30	14	8	6
Voka crossroads	720	635	85	14	5	9
*Mägara	2	0.9	1.1	2	0.6	1.4
Toila-Oru	846	693	153	108	81	27

* Sampling points of a tributary

Table. 3.14. The fluxes of total phosphorus (P_{tot}) and phosphate phosphorus $\text{PO}_4^{3-}\text{-P}$ in the water of the Kunda River in July.

Sampling point	1995			2005		
	$P_{\text{tot}}, \text{mg s}^{-1}$	$\text{PO}_4^{3-}\text{-P}, \text{mg s}^{-1}$	$P_{\text{org}}, \text{mg s}^{-1}$	$P_{\text{tot}}, \text{mg s}^{-1}$	$\text{PO}_4^{3-}\text{-P}, \text{mg s}^{-1}$	$P_{\text{org}}, \text{mg s}^{-1}$
Kulina	x	x	x	3	2	1
Roostova	18	4	14	2	1	1
*Liiva	22	8	14	13	5	8
Mädaoja	31	20	11	32	8	24
Ulvi	x	x	x	x	x	x
Sämi	56	42	14	x	x	x
Kohala	60	46	14	x	x	x
Lammas-mäe	x	x	x	161	56	105
Lontova	107	64	43	238	98	140

* Sampling point of a tributary

x – flux was not calculated

In 2005, the situation of the fluxes of phosphorus (Table 3.13) was much better and $\text{PO}_4^{3-}\text{-P}$ formed about 50% of the fluxes of total phosphorus as it was at the sampling point of Mägara (the tributary is not directly connected with oil shale mines) in 1995. The fluxes of phosphorus increased further downstream of the Pühajõgi River, indicating continuous infiltration of phosphorus into the Pühajõgi in 1995 and 2005.

The calculated fluxes of phosphorus were quite similar in the water of the Kunda River in 1995 and 2005 (Table 3.14). The fluxes of $\text{PO}_4^{3-}\text{-P}$ formed about 50% of the flux of total phosphorus in the water of the Kunda River and a similar situation was observed in the Pühajõgi River in 2005. Therefore, the Pühajõgi River could achieve natural conditions after closing oil shale mines.

4. CONCLUSIONS

The influence of leachate from soil and landfill to the quality of the environment through the chemical analysis of oil-polluted soil, surface water from the Pääsküla, Kunda and Pühajõgi Rivers and leachate was analyzed. The values of chemical parameters during the significant changes of the fluxes of pollutants, e.g. the closing of Pääsküla landfill and oil shale mines, adding a solution of surfactants to the soil contaminated with petroleum hydrocarbons, lowering the pH of solutions containing sulfide, were observed in detail. Based on the results the following conclusions could be made:

- Although the deposition of additional waste was stopped and preparations for the closing of Pääsküla landfill were started, continuous anaerobic degradation of biowaste in the landfill generated leachate with high concentration of pollutants. Comparison of concentrations of pollutants in the water of the Pääsküla and Vääna Rivers showed high concentration of ammoniacal nitrogen (12 mg L^{-1} in 2003) at the sampling point of Pääsküla while the highest NO_3^- -N concentrations were determined in Hüüru (3.7 mg L^{-1}) and Vääna (3.6 mg L^{-1}), which are downstream from the Pääsküla River and could be connected with the oxidation of ammonia in the Vääna River. At the sampling point of Hüüru the calculated fluxes of N_{tot} , NH_4^+ -N, and P_{tot} were quite similar in July 2003 and 2004, although the discharge of water was more than 3 times higher in July 2004, indicating the leaching of nitrogen from the soil or sediments due to precipitations.
- Surfactants are used to increase the bioavailability of hydrophobic pollutants (hydrocarbons), but the added anionic surfactants were washed out of the upper layer of soil columns during the first 35 days regardless of the type of soil. After the experiments (60 days), the analysis of different soil fractions showed that up to 86% of anionic surfactants had degraded in the column of coarse-grained polluted soil while up to 28% of the added surfactants had degraded in the column of fine sandy soil. Higher amount of anionic surfactants was determined in the leachate of columns of coarse-grained soil and the higher porosity of soil could increase the leaching of surfactants due to the lower surface area of coarse-grained soil. The mean value of initial saturation of oxygen in the gas phase of soil measured before adding solution SR-100 was $64 \pm 5\%$ regardless of the soil fraction and the type of soil confirmed that the porosity of sandy soils was good enough. At the end of the experiments, higher contents of oxygen (between 12–39%) were measured in the upper and the lowest fractions of soil columns while oxygen saturation was below 10% in the central fractions of soil columns.
- Due to the lowered pH in the solutions of NaHCO_3 and NaHS the equilibrium of carbonate or sulfide was achieved, followed by the emission of gaseous CO_2 or H_2S . The average measured times required to reach constant pressure in closed systems corresponding to the equilibrium state of distribution of carbonate or sulfide in water after the lowering of pH were

16.7 ± 1.5 min (for NaHCO_3) and 19.5 ± 5.5 min (for NaHS). Gaseous H_2S was emitted faster from the wastewater (the average time required to achieve the distribution equilibrium was 16.2 ± 3.6 min) due to decreased solubility. The experimentally measured values of pressure through the emitted H_2S from the wastewater were twice lower than the theoretical values, indicating that the catalyzed formation of polysulfides in the solution of sulfides containing different organic or inorganic compounds decreases the amount of the emitted H_2S but increases the rate of emission.

- Analysis of water samples of the Pühajõgi River showed that the concentrations of nitrite were quite low and the higher concentrations of nitrite were determined at the sampling points of Rausvere and Voka crossroads in 1995 (above 2.1 mmol m^{-3}) and 2000 (above 6.8 mmol m^{-3}). The higher concentrations were connected with the infiltration of mine water into the Rausvere River as the concentration of nitrite was 0.79 mmol m^{-3} at the sampling points of Rausvere and Voka crossroads in 2005 when the mines were closed. In 2005, the fluxes of nitrogen had reduced 3–5 times in comparison with 1995, and the fluxes of organic nitrogen constituted more than 50% of the fluxes of total nitrogen in the Pühajõgi River. The flux of $\text{NO}_3^- - \text{N}$ was the biggest (35% from the total nitrogen) in the water of the Rausvere River in 2005. The fluxes of inorganic and organic nitrogen increased further downstream of the Pühajõgi, but the fluxes of toxic nitrite and ammonia were quite steady. The concentration of total phosphorus had lowered by more than 90% during 1995–2005, indicating a significant discharge of phosphorus through the mining water into the Pühajõgi. In 2005, the $\text{PO}_4^{3-} - \text{P}$ formed about 50% of the fluxes of total phosphorus as it was at the sampling point of Mägara (the tributary is not directly connected with oil shale mines) in 1995. The fluxes of different forms of phosphorus increased further downstream of the Pühajõgi, indicating continuous infiltration of phosphorus into the Pühajõgi in 1995 and 2005.

The results of the study showed that analyzing leachate can give significant information about the processes inside the landfill, polluted soil or closed mines. Toxic gaseous H_2S gas can be emitted from leachate due to pH lowering through the mixing of leachate with acidic solutions. In natural ecosystems leachate is diluted, but natural attenuation of leachate does not decrease the pollution load to the surface or ground water sufficiently.

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SUMMARY IN ESTONIAN

Keskkonna kvaliteedi hindamine Põhja-Eestis nõrgvee analüüsi alusel

Vesi on universaalne lahusti, mis lahustab üsna erinevaid ühendeid, kuigi nende ühendite lahustuvus sõltub nii ühendite keemilisest koostisest kui ka temperatuurist. Oma osa mängib ka ühendite koosinemise mõju nende lahustuvusele. Keskkonna seisukohalt on erinevate ühendite lahustuvus oluline mitmesuguste tahkete materjalide kokkupuutes veega, mille tulemusena võib sel viisil tahketest materjalidest leostuda erineval hulgal erinevaid ühendeid. Enamasti seostub leostumine prügilatesse ladestatud jäätmetest erinevate ühendite väljaleostumisega, kuid leostumise tulemusena väheneb ka pinnases nii taimekasvuks vajalike toitainete kui ka ohtlike või vähemohhtlike reoainete kontsentratsioon. Leostumine ohustab nii pinnavee (jões, järved, mered) kui ka põhjavee kvaliteeti. Käesolevas doktoritöös analüüsiti Pääsküla prügilast väljaleostuva nõrgvee mõju Pääsküla ja Vääna jõe veele 2003. ja 2004. aastal, kui alustati prügila sulgemist ning põlevkivikaevanduste sulgemise järel nendest suletud kaevandustest väljuva nõrgvee mõju Pühajõe veekvaliteedile, mida võrreldi kaevandustest mõjutamata Kunda jõe vee vastavate parameetritega. Selle kõrval uuriti ka toksilise gaasilise divesiniksulfiidi lendumist nii naatrimvesiniksulfiidi lahusest kui ka sulfiidioone sisaldanud Kohtla-Järve biopuhastisse jõudnud reoveest nende vete pH alandamisel.

Jäätmete ladestamine Pääsküla prügilasse oli sisuliselt lõpetatud, kuid ladestatud biojäätmete anaeroobse lagunemise tulemusena jätkus kõrge reoainete kontsentratsiooniga nõrgvee väljavool prügilast ning nõrgvee koostist 2004. aasta märtsis tehtud analüüside järgi iseloomustasid järgmised parameetrid: $\text{COD} = 668 \text{ mg O}_2 \text{ L}^{-1}$, $\text{N}_{\text{tot}} 62,6 \text{ mg L}^{-1}$, $\text{P}_{\text{tot}} 6,9 \text{ mg L}^{-1}$ ja $[\text{S}^{2-}]_{\text{tot}} 6,0 \text{ mg L}^{-1}$; NH_4^+-N ja NO_3^--N kontsentratsioonide suhe oli 11,4. Sama aasta aprillis tehtud analüüsid näitasid nõrgvee koostises olevate reoainete sisalduse ($\text{COD} = 511 \text{ mg O}_2 \text{ L}^{-1}$, $\text{N}_{\text{tot}} = 55,0 \text{ mg L}^{-1}$, $\text{P}_{\text{tot}} = 1,1 \text{ mg L}^{-1}$ and $[\text{S}^{2-}]_{\text{tot}} = 4,0 \text{ mg L}^{-1}$) vähenemist, mida põhjustas nõrgvee lahjenemine lumesulamisveega. 2004. aasta mais, juunis ja juulis tehtud analüüsid näitasid COD väärtuseks ligikaudu $200 \text{ mg O}_2 \text{ L}^{-1}$, mis oli samasugune kui 2003. aasta juuliski, kui prügilasse veel jäätmeid ladestati. Biolagunevate reoainete sisaldust iseloomustav BOD_7 oli kõrgeim 2004. aasta aprillis analüüsitud proovides ning täiendavat biolagunevat orgaanilist ainet leostus pinnasest lumesulamisveega. Sama aasta mais, juunis ja juulis tehtud analüüsid näitasid üsna ühtlasi BOD_7 väärtusi ja seega reoaineid oluliselt juurde ei leostunud, kuid samas ei toimunud oluliselt ka nende lagunemist. Prügilat ümbritsevasse Pääsküla rappa kaevatud kuivenduskraavi veeproovid sisaldasid oluliselt vähem reoaineid, mis näitab nõrgvee olulist lahjenemist.

Prügilast väljuv nõrgvesi suubus Pääsküla jõkke ja sealt edasi Vääna jõe kaudu Soome lahte. Pääsküla jõest võetud veeproove on analüüsitud ka 1971. aasta juunis ja juulis, kui Pääsküla prügilat ei olnud veel rajatud. 1993. aasta juulis oli Pääsküla jõest võetud veeproovide COD väärtus 31% kõrgem kui 1971. aastal ning 2003. juulis oli COD väärtus 22% kõrgem kui enne prügila rajamist. Seega on prügila rajamine suurendanud reostuskoormust Pääsküla jõe (ja seega ka Vääna jõe) veele. Reoainete kontsentratsioonide võrdlemine näitas, et prügilast leostunud nõrgvee looduslik hajumine on toimunud peamiselt lahjenemise kaudu, kuid see ei olnud oluliselt vähendanud reostuskoormust Pääsküla jõe veele.

Lämmastiku ja fosfori arvatud vood olid nii juulis 2003 kui ka 2004 ligilähedased, kuigi 2004. aasta juulis oli Vääna jõe voolu kiirus Hüüru vaatluspunktis (see asetseb allavoolu Pääsküla sissevoolust Vääna jõkke) üle 3 korra kõrgem. See võib olla seotud lämmastiku leostumisest pinnasest või jõesetest, sest mais ja juunis 2004 oli voolukiirus Hüüru vaatluspunktis üsna madal. Kui lämmastikuvoog üldiselt vähenes voolukiiruse vähenemisel, siis fosforivoog ei omanud selget korrelatsiooni voolukiirusega. Prügi ladestamise lõpetamine on muutnud nõrgvees olevate reoainete kontsentratsiooni, kuid Pääsküla ja Vääna jõe vesi jääb mõjutatuks prügila nõrgveest.

Hüdrofoobsed reoained (nende seas on eriti olulised naftasaadused) on keskkonnas üldiselt raskesti biolagundatavad ja seega võivad need reoained püsida keskkonnas (eriti pinnases) üsna kaua. Selle põhjuseks on hüdrofoobsete reoainete madalast lahustumisest põhjustatud vähene kättesaadavus looduses esinevatele mikroorganismidele. Hüdrofoobsete reoainete (süsivesinike) lahustumise parandamiseks kasutatakse reostunud pinnase töötlemist mitmesuguste pindaktiivsete ainetega, millest enim kasutatakse anioonseid pindaktiivseid aineid. Samas loob hüdrofoobsete reoainete suurem lahustuvus vees võimaluse tekkinud emulsiooni leostumiseks pinnase sügavamatesse kihtidesse ning pinnavõi põhjavette. Sellise leostumise uurimiseks kasutati kolonnkatseid naftasaadustega reostunud jämedateralise (pärides Ämari lennuväljalt) ja peeneateralise (Kloogaranna rannast pärit liiv segati kasutatud diiselõliga) liivase pinnasega, kusjuures pinnasele lisati anioonseid pindaktiivseid aineid sisaldavat pinnase tervendamiseks kasutatavat preparaati (SR-100) ning kord nädalas lisati kolonnidele aereeritud vett, et simuleerida looduses esinevat vihma. Analüüsiti nii kolonnist väljunud nõrgvett kui ka kolonnis olnud pinnase erinevaid fraktsioone.

Pinnasekolonnide ülemise pinnakihi (sügavus 0–5 cm) analüüs näitas anioonsete pindaktiivsete ainete ühtlast vähenemist ajas ning need ained pesti kõikide kolonnide ülakihist 35 päeva jooksul välja. Katse lõppemisel (katse kestis 60 päeva) pinnase erinevate fraktsioonidega tehtud analüüsid näitasid, et kõige suurem osa (86% lisatud pindaktiivsest aineist) anioonseid pindaktiivseid aineid lagundati jämedateralise reostunud pinnase kolonnis. Jämedateralises reostumata pinnases lagundati sama ajaga vaid 34% lisatud pindaktiivsetest ainetest ning peenestatud lubjakivi (CaCO_3) lisandiga pinnases lagunes

pindaktiivsetest ainetest 83%. Peeneteralise pinnase kolonnides lagunes anioonset pindaktiivset ainet oluliselt vähem: reostunud pinnases 28%, CaCO_3 lisandiga kolonnis 8,1% ning reostumata pinnase kolonnis 4,6%. Need tulemused näitasid, et peeneteralise pinnase väikesest poorsusest tingituna ei difundeerunud sellisesse pinnasesse piisavalt hapnikku, et toimuks anioonsete pindaktiivsete ainete olulist aeroobset lagundamist.

Pinnasekolonnidest väljunud nõrgvee analüüs näitas kõrgeimat anioonsete pindaktiivsete ainete kontsentratsiooni jämedateralise reostumata pinnase kolonni nõrgvees (15,8% lisatud pindaktiivsest ainet), kuid CaCO_3 lisandiga reostunud pinnase korral oli see 4,5% ja reostumata pinnase korral 2,5%. Peeneteralise pinnase korral oli anioonsete pindaktiivsete ainete sisaldus nõrgvees palju ühtlasem: reostunud pinnase kolonni korral 6,2%, reostumata pinnase korral 5,0% ja CaCO_3 lisandi korral 3,3% pinnasele lisatud pindaktiivsetest ainetest.

Katseteks kasutatud aeg ei olnud piisav, et kogu reoaine jõuaks pinnases bioloogiliselt laguneda ning jämedateralise pinnase kolonnides lagunes 60 päevaga ligikaudu 60–70% süsivesinikest ning peeneteralise pinnase korral 40–50%. Kolonnidest väljunud nõrgvee kuivjääk sisaldas ligikaudu 5% süsivesinikke sõltumata pinnase tüübist. Bioloogilise tervendamise preparaadi SR-100 kasutamine näitas anioonsete pindaktiivsete ainete leostumise võimalust pinnasest, mis võib ohustada põhjavett. Samuti näitasid katsetulemused, et pinnase aereerimine on küllaltki oluline tegevus reoainete biolagundamise kiirendamiseks. Enne reostunud pinnase töötlemist oli pinnaseõhus üsna palju hapnikku (hapniku sisaldus ligikaudu 64% küllastusest) ja see ei sõltunud ei pinnase tüübist ega pinnasefraktsiooni asukohast kolonnis. Katse lõpus oli hapnikusisaldus kolonni ülemises ja alumises fraktsioonis ligi 20% küllastusest või üle selle, kuid kolonni keskel olevates fraktsioonides oli hapnikusisaldus alla 10% küllastusest.

Anaeroobsetes tingimustes tekitavad mitmed mikroorganismid oma elutegevuse käigus mitmesuguseid redutseeritud ühendeid, millest üheks ohtlikumaks on sulfiidid, mis esinevad vesilahuses neutraalse või nõrgalt leeliselise pH juures vesiniksulfiidioonina. Lahuste pH alanemisel, mis võib toimuda ka erinevate omadustega nõrgvete segunemisel, nihkub sulfiidide tasakaal H_2S kontsentratsiooni suurenemise suunas ja lahusest hakkab lenduva mürgist ja halvasti lõhnavat divesiniksulfiidi. Antud doktoritöö raames uuriti divesiniksulfiidi lendumist nii naatriumvesiniksulfiidi lahusest kui ka sulfiidirikkast reoveest (nimetatud reovesi tekitas mõni aeg tagasi Kohtla-Järve reoveepuhastis suuri probleeme) pH alandamise käigus. Lendumist uuriti manomeetrilise OxiTop® süsteemi abil kinnistes anumates ja võrdlusena viidid samad mõõtmised läbi ka NaHCO_3 lahustega, kust lendub pH alandamise järel CO_2 .

Mõõtmised näitasid, et kui NaHCO_3 lahusest eraldunud CO_2 korral saavutus suletud süsteemis püsiv rõhk $16,7 \pm 1,5$ min järel, siis NaHS lahusest eraldunud H_2S põhjustatud rõhu kasv saavutas püsiväärtuse $19,5 \pm 5,5$ min järel. Mõlemal juhul ei olnud seost ajavahemiku ja lahuse algkontsentratsiooni vahel. Erinevad

ajavahemikud näitasid, et CO_2 ja H_2S käitusid lahustes erinevalt, mille põhjuseks võib olla NaHS lahuses esinevad polüsulfiidioonid. Viimast väidet kinnitab ka püsivate rõhkude teoreetiliste arvutuste ja eksperimentaalsete mõõtmistulemuste vaheline halvem seos H_2S korral võrreldes CO_2 -ga. Reoveega tehtud mõõtmised andsid sulfiidi jaoks ajavahemiku $16,2 \pm 3,6$ min, mis oli oluliselt lühem kui NaHS lahuse korral saavutatu. Seega lendus reoveest divesiniksulfiid kiiremini ning seejuures oli kõrgema sulfiidi kontsentratsiooni korral püsiva rõhu saavutamiseks vajalik aeg pikem. Reovee korral olid eksperimentaalselt määratud püsiva rõhu väärtused 2 korda väiksemad kui teoreetiliselt arvutatud väärtused. Viimane tulemus näitas, et erinevaid orgaanilisi või anorgaanilisi ühendeid sisalduvates sulfiidilahustes toimub katalüütiline polüsulfiidide teke, mis vähendab lenduva H_2S hulka, kuid samas kiirendab lendumist

Lisaks prügilatele ja reostunud pinnasele leiab erinevate ainete leostumine aset ka suletud kaevandustes, kus vett enam välja ei pumbata, kuid hüdroloogilised tingimused on oluliselt muudetud. Suletud kaevandustest väljuva nõrgvee mõju uuriti Pühajõe baasil, mis voolab vahetult põlevkivikaevanduste kõrval ning sinna pumbati aastaid üsna suurtes kogustes kaevandusvett. Kaevandusvee mõju võrdlemiseks analüüsiti ka samas piirkonnas asuvat Kunda jõge, mis põlevkivikaevandustega ei ole otseselt seotud.

Pühajõe vees oli nitrit-lämmastiku sisaldused üsna madalad (kõrgeim sisaldus $2,5 \text{ mmol m}^{-3}$ 1995. aastal Voka teeristis) ja lämmastik esines peamiselt ammooniumlämmastikuna (kõrgeim sisaldus 520 mmol m^{-3} 1995. aastal Toila teeristis). Allavoolu liikudes vähenes Pühajões ammooniumlämmastiku sisaldus ja kasvas nitraatlämmastiku kontsentratsioon, mis näitab ammooniumiooni oksüdeerumist nitraatiooniks. Nitritlämmastiku kõrgeim sisaldus ($7,8 \text{ mmol m}^{-3}$ Kukrusel) määrati 2000. aastal, kuid 2005. aastal oli see 2 korda väiksem. Samuti oli vähenenud ammooniumlämmastiku sisaldus ning 2005. aastal jäi see alla 10 mmol m^{-3} .

Kunda jõe vees oli nitritlämmastiku sisaldus üsna ühtlane, jäädes alla $1,2 \text{ mmol m}^{-3}$, kuid keskmised sisaldused vähenesid $0,53 \text{ mmol m}^{-3}$ (1995) kuni $0,29 \text{ mmol m}^{-3}$ (2005). Ka ammooniumlämmastiku sisaldused olid Kunda jõe vees ühtlased ning kõrgeim sisaldus $3,1 \text{ mmol m}^{-3}$ määrati Lammasmäe vaatluspunktis 1995. aastal. 2005. aastal määrati kõrgeimad ammooniumlämmastiku sisaldused ($2,3 \text{ mmol m}^{-3}$) Kulina ja Kohala vaatluspunktides, kuid keskmised ammooniumlämmastiku sisaldused olid väga lähedased 1995. aastal ($0,91 \text{ mmol m}^{-3}$) ja 2005. aastal ($1,09 \text{ mmol m}^{-3}$).

Lämmastikuvoogude arvutused näitasid, et 1995. aastal sisenes 80% lämmastikust Pühajõkke ammooniumlämmastikuna Kotinuka ja Toila teeristi vaatluspunktide vahel, kuid Rausvere jõest saabus Pühajõkke palju nitraatlämmastikku (74% lämmastikust). 2005. aastal olid lämmastikuvood vähenenud 3–5 korda, mis kinnitas kaevanduste sulgemise olulist mõju. Samas oli 2005. aastal suurimad nitrit- ja ammooniumlämmastiku vood Toila-Oru vaatluspunktis, mis osutas Toila-Oru asunduse mõjule Pühajõe kvaliteedile.

Aastatel 1995–2005 vähenes Pühajões fosforivoog kuni 50 korda ning samuti vähenes ortofosfaatne fosfori osakaal fosforivoos (1995. aastal 90% ja 50% 2005. aastal).

1995. aastal moodustas Kunda jões 85% lämmastikuvoost anorgaaniline lämmastik ning nitrit- ja amooniumlämmastiku voog moodustas alla 1%. 2005. aastal olid Kuna jões lämmastikuvood vähenenud, kuid nitrit- ja ammooniumlämmastiku osakaal oli tõusnud ligikaudu 2%-ni lämmastiku koguvoost. Mõlemal aastal vähenes lämmastikuvoog liikudes allavoolu, mis näitab lämmastiku sisenemist põllumajandusest ja asundustest. Arvutatud fosforivood olid Kuna jões 1995. ja 2005. aastal üsna lähedased ja fosforivoost moodustas 50% ortofosfaatne fosfor.

Uuringute tulemused näitasid, et nõrgvee analüüsimine võib anda olulist informatsiooni protsessidest prügilate, reostunud pinnase või suletud kaevanduste sisemuses. Sulfiidi sisalduvate nõrgvete pH alanemisel võib lenduda toksilist gaasi – H_2S , mis ohustab nii inimese tervist kui ka keskkonda. Looduslikus keskkonnas võib nõrgvesi lahjeneda, kuid nõrgvees esinevate ohtlike ühendite looduslik hajumine ei pruugi piisavalt vähendada reoainete voogu pinna- või põhjavette.

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