

TAAVI VAASMA

Enrichment, atmospheric dispersion
and deposition of naturally occurring
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power plants



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Department of Bio and Environmental Physics, Institute of Physics, Faculty of Science and Technology, University of Tartu, Estonia.

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LIST OF PUBLICATIONS INCLUDED IN THE THESIS

This thesis is based on the following publications, which are referred to in the text by their Roman numerals.

- I** **Vaasma, T.**, Kiisk, M., Meriste, T., Tkaczyk, A.H., 2014a. The enrichment of natural radionuclides in oil shale-fired power plants in Estonia – The impact of new circulating fluidized bed technology. *J. Environ. Radioact.* 129, 133–139. doi:10.1016/j.jenvrad.2014.01.002
- II** **Vaasma, T.**, Kiisk, M., Meriste, T., Tkaczyk, A.H., 2014b. The enrichment behavior of natural radionuclides in pulverized oil shale-fired power plants. *J. Environ. Radioact.* 138, 427–433. doi:10.1016/j.jenvrad.2014.02.027
- III** **Vaasma, T.**, Bityukova, L., Kiisk, M., Özden, B., Tkaczyk, A.H., 2016. Behaviour mechanisms and correlation between lead (Pb) and its isotope ²¹⁰Pb in industrial residue as an indicator for waste characterization. *Environ. Technol.* 37, 3208–3218. doi:10.1080/09593330.2016.1181673
- IV** Ozden, B., **Vaasma, T.**, Kiisk, M., Tkaczyk, A.H., 2017. A modified method for the sequential determination of ²¹⁰Po and ²¹⁰Pb in Ca-rich material using liquid scintillation counting. *J. Radioanal. Nucl. Chem.* 311, 365–373. doi:10.1007/s10967-016-4984-1
- V** **Vaasma, T.**, Karu, H., Kiisk, M., Pensa, M., Isakar, K., Realo, E., Alliksaar, T., Tkaczyk, A.H., 2017a. Pb-210 and fly ash particles in ombrotrophic peat bogs as indicators of industrial emissions. *J. Environ. Radioact.* 174, 78–86. doi:10.1016/j.jenvrad.2016.07.027
- VI** **Vaasma, T.**, Loosaar, J., Gyakwaa, F., Kiisk, M., Özden, B., Tkaczyk, A.H., 2017b. Pb-210 and Po-210 atmospheric releases via fly ash from oil shale-fired power plants. *Environ. Pollut.* 222, 210–218. doi:10.1016/j.envpol.2016.12.054
- VII** **Vaasma, T.**, Loosaar, J., Kiisk, M., Tkaczyk, A.H., 2017c. Radionuclide concentration variations in the fuel and residues of oil shale-fired power plants: Estimations of the radiological characteristics over a 2-year period. *J. Environ. Radioact.* 173, 25–33. doi:10.1016/j.jenvrad.2016.10.005
- VIII** **Vaasma, T.**, Kaasik, M., Loosaar, J., Kiisk, M., Tkaczyk, A.H., 2017. Long-term modelling of fly ash and radionuclide emissions as well as deposition fluxes due to the operation of large oil shale-fired power plants. *J. Environ. Radioact.* 178–179, 232–244. doi:10.1016/j.jenvrad.2017.08.017.

AUTHOR'S CONTRIBUTION

The publications included in this thesis are a result of a collective effort by all of the authors. The author of this thesis has contributed as follows:

X – The author of this thesis has contributed at least 50% of the work.

Activity	Publication I	Publication II	Publication III	Publication IV	Publication V	Publication VI	Publication VII	Publication VIII
Hypothesis formation	X	X	X	X	X	X	X	X
Data collection	X	X	X	X	X	X	X	X
Sample preparation and measurement	X	X	X	X	X	X	X	X
Data analysis	X	X	X		X	X	X	X
Manuscript writing	X	X	X		X	X	X	X
Publishing	X	X	X		X	X	X	X

ABBREVIATIONS

APH	– Air pre-heater
BPP	– Baltic Power Plant
CFB	– Circulating Fluidized Bed
CV	– Coefficient of Variation
ECO	– Economizer
EPP	– Estonian Power Plant
ESP	– Electrostatic Precipitator
EU BSS	– European Union Basic Safety Standard
EURATOM	– European Atomic Energy Community
IAEA	– International Atomic Energy Agency
LSC	– Liquid Scintillation Counting
MDA	– Minimum Detectable Activity
NID	– Novel Integrated Desulphurization
NORM	– Naturally Occurring Radioactive Material
PF	– Pulverized Fuel
PP	– Power Plant
SFAP	– Spherical fly ash particles
SH	– Super Heater
UNSCEAR	– United Nations Scientific Committee on the Effects of Atomic Radiation

1. INTRODUCTION

The oil shale industry has been one of the largest industrial sectors in Estonia for almost 100 years (Aaloe et al., 2006). The exploitation of oil shale has been dominantly related with shale oil, electricity and heat production. Two of the world's largest oil shale-fired power plants (PP) have been operating at full capacity since the 1970s. The use of oil shale for electricity production has varied through different time periods with the maximum during the 1980s with around 30 million of tonnes per year (Punning et al., 1997). Due to the high ash content of the used oil shale (approximately 50%), significant amount of residual ash has been created yearly, which is precipitated as bottom or various fly ash fractions within the boiler system. Depending on the employed technology and flue gas purification system, part of the formed fly ash is also emitted to the environment via flue gases. The amount of fly ash released to the atmosphere has been reduced many orders of magnitude during the last 20 years by implementing new boiler types and higher efficiency purifications systems (Kaasik et al., 2008, 1999; Karofeld, 1996a; Punning et al., 1997).

The amount of fly ash and other pollutants, such as SO_x , NO_x and heavy metals emitted from the PPs have been monitored over longer time periods. However, oil shale also contains naturally occurring radionuclides from the ^{238}U and ^{232}Th series as well as ^{40}K (Realo et al., 1996). Radionuclides and heavy metals become enriched in fly ash fractions and are preferentially attached to particles with smaller aerodynamic diameter and larger specific surface area (Realo et al., 1996; Realo and Realo, 1997; Reinik et al., 2013). Often the fly ash fraction escaping to the atmosphere is the most enriched fraction. There has been lack and outdated information available on the radiological parameters of the fly ash from oil shale combustion. Also the radionuclide emission load from these PPs to the surrounding environment has not been evaluated. Available studies on coal-fired PPs in various countries have shown high enrichment values of radionuclides in fly ash (Charro and Pena, 2013; Coles et al., 1978; Flues et al., 2007; Gür and Yaprak, 2010; Karangelos et al., 2004; Lu et al., 2011; Mishra, 2004; Nowina-Konopka, 1993; S. K. Sahu et al., 2014; Suhana and Rashid, 2016; Zeevaert et al., 2006; U.S. Environmental Protection Agency, 1995; Vreček and Benedik, 2003). In many instances, the emissions of fly ash enriched with radionuclides have caused significant radiological burden on the surrounding environment (Bem et al., 2002; Dinis et al., 2014; Flues et al., 2002; Hasani et al., 2014; Papastefanou, 2010; Papp et al., 2002; Parmaksiz et al., 2011; Sert et al., 2011; Ugur et al., 2004). Similarly to coal PPs, the magnitude of the radionuclide deposition load from the oil shale PPs needs to be determined. The oil shale-fired PPs have gone through significant changes during their operational period. Changes in oil shale consumption, power output, operational boiler types, and purifications systems have had significant effect on their environmental impact. The current thesis focuses on radiologically characterizing the by-products from oil shale combustion and estimating the magnitude of

radionuclide emissions from the oil shale PPs during their working period and provide systematic overview of the impact that the modernization of the PPs has entailed. The work also includes a brief outline of the legislative aspects that deal with industries that produce naturally occurring radioactive material (NORM) as by-products. The thesis provides a basis for assessments if and at what scale the oil shale PPs can be considered as part of the NORM-related industry. To achieve the aims, the current work involves three important subthemes:

- a) Characterization of the oil shale PPs from the radiological aspect. This includes samplings and measurements during multiple years of input fuel, bottom and fly ash fractions and mass balance calculations and estimations of atmospheric emission from the PPs;
- b) Atmospheric dispersion modelling of fly ash and radionuclides attached to them. This also includes determining the magnitude of the PPs' radiological burden on the environment and to the general public;
- c) Comparison of emission data with environmental monitoring and sampling data.

2. NATURALLY OCCURRING RADIONUCLIDES

Natural radiation sources surround us in various environments. This includes cosmic rays from space, terrestrial radionuclides in the Earth's crust, radionuclides in air-water and foodstuffs as well as building materials. In addition to natural sources, humans are exposed to man-made and/or enhanced sources (nuclear industry, medical field, fossil fuel industry and others). Radiation sources of natural origin constitute the majority of annual doses (UNSCEAR, 2010). The majority of this is due to inhalation of radon (^{222}Rn) and its progenies (UNSCEAR, 2010). External irradiation is mainly present due to gamma radiation originating from the primordial radionuclides in the ^{238}U and ^{232}Th series as well as from ^{40}K . The decay chains include several radionuclides with long half-lives (e.g. $4.5 \cdot 10^9$ years for ^{238}U), which cause extended periods of exposure to the ionizing radiation due to their existence. The main dose contribution to humans is due to the presence of these radionuclides in soil. The activity concentrations of these isotopes depend also on the soil properties (texture, porosity, permeability) and type. Higher radioactivity levels have been determined in igneous rocks and lower levels in sedimentary rocks. The reported worldwide median values in soil for ^{238}U , ^{232}Th and for ^{40}K have been 35, 30 and 400 Bq kg^{-1} , respectively (UNSCEAR, 2010). These values are subjected to variations, depending on the local geological conditions. Even the countrywide values in Estonia fluctuate significantly due to some anomalies in the North of Estonia. The mean activity concentration values in Estonia are 35, 27 and 520 Bq kg^{-1} for ^{238}U , ^{232}Th and ^{40}K (Realo and Realo, 2005). It has to be pointed out that the inhalation of ^{222}Rn , which originates from the soil, gives the highest dose to Estonian population – around 2.1 mSv per year, while the average yearly dose to Estonian population is around 3.2 mSv (Lust, 2012).

In soils, the parent and daughter radionuclides are considered to be in secular equilibrium. This means that the activity concentrations of each radionuclide in the decay series is equal to the parent radionuclide (^{238}U and ^{232}Th). However, when the soil or other material taken from the Earth's crust is processed, the secular equilibrium is often lost. This is due to the different physicochemical properties of the radionuclides, causing them to behave differently from one another. During high temperature processes, such as fossil fuel combustion, more volatile elements and radionuclides become vaporized in the furnace and attach to fly ash particles with different size. It is important to be aware of such processes and take these situations into account when collecting samples and conducting analysis.

3. OIL SHALE AND OIL SHALE-FIRED POWER PLANTS (PPs)

3.1 Overview of oil shale

Oil shale is usually classified as a carbonaceous sedimentary rock that contains solid organic matter. Estonian oil shale, which is named *kukersite*, contains organic matter (kerogen) usually between 15% and 55%, depending on the specific deposition layer and area (Aaloe et al., 2006). The noncombustible mineral part consists of calcareous and terrigenous matter. The Estonian oil shale was formed near the coastline in shallow seabed, where dead algae formed mats on the seabed. Mineral matter deposited together with the organic material, forming the oil shale that is mined today in Estonia. The productive oil shale layer, which is economically feasible to be mined, has a thickness of 2.5 to 3 meters. This includes oil shale with limestone sublayers (Aaloe et al., 2006).

The oil shale burned in the large PPs in Estonia has a lower heating value between 7.8 and 8.9 MJ kg⁻¹, with an average of 8.4 MJ kg⁻¹ (Plamus et al., 2011b). For comparison, the heating value of commonly burned coal usually remains between 9 and 27 MJ kg⁻¹. The oil shale burned in the PPs is a mixture of extracted fuel from underground mines and quarries, in order to achieve necessary calorific value. The majority of the oil shale ash produced by the PPs is deposited in the nearby ash fields. Due to the high content of mineral matter, mostly between 50% and 55%, large amounts of ash is created annually. In the recent years around 11 and 13 million tonnes of oil shale is being burned in the PPs, which has resulted up to 7 million tonnes of ash (Ministry of Finance, 2016). The majority of the ash is directed to the nearby ash fields via hydro transport. Only a small fraction of finer fly ash has had commercial value so far. Thus the oil shale industry has had a very strong impact on the environment, which includes the creation of atmospheric and terrestrial pollution, ground and mine water issues, leaching of hazardous elements and influences on the biota nearby. However, during the last decades, significant efforts have been made to reduce the environmental impact of the oil shale industry. This includes modernization of the PPs technological set-up; reducing fly ash emission by employing novel filter systems; improving oil shale mining and management of landfills (Loosaar et al., 2009; Pihu et al., 2012; Plamus et al., 2011b).

Oil shale contains also various amounts of trace elements and naturally occurring radionuclides, which have been incorporated to the oil shale during its formation processes. For coals, uranium is considered to be mainly associated with the organic fraction, while thorium is present in the inorganic phases (Papastefanou, 2010; Suhana and Rashid, 2016). The average radionuclide activity concentration in oil shale is similar to the values found in soils of Estonia (Realo et al., 1996; Realo and Realo, 2005). More precise description of the oil shale radionuclide concentration is provided in 7.1.

3.2 Historical overview of oil shale-fired PPs

Two of the world largest oil shale-fired PPs (Estonian and Baltic Power Plant) located in the north-east of Estonia have been operational for nearly half a century. The PPs had a combined initial installed power capacity around 3000 MW. The Baltic Power Plant (BPP) reached its full capacity in 1966, operating on 26 pulverized fuel type (PF) of boilers. The Estonian Power Plant (EPP) was built between 1969 and 1973. The PP consisted of 16 PF boilers, which in total provided a power capacity of 1600 MW. Initially these PPs produced over 90% of the yearly electric energy consumed in Estonia. This percentage has decreased over time and is around 80% nowadays. The PPs have gone through significant changes during their operational period. The first and most remarkable improvement of these PPs started in 1998 through the installation of new electrostatic precipitators (ESPs) with higher efficiency. As a result, the fly ash emissions were reduced from few g per m⁻³ down to ~100 mg m⁻³. In 2001, renovation works were started in the EPP to replace two PF boilers with new circulating fluidized bed (CFB) boilers. Within years, significant modifications were also conducted in BPP, where 17 older PF boilers were shut down and one PF energy unit was replaced with a CFB one. Improvements continued in the EPP from 2009 with the installation of novel integrated desulphurization (NID) and deNO_x systems with bag filters on PF boilers previously operating with ESPs. This again reduced the atmospheric emissions of various pollutants such as SO_x, NO_x, and total suspended particles (TSP). This reduced the fly ash emissions down to few mg per m³. From 2015/2016, majority of the PF boilers are operating on the NID system with bag filters or with modernized ESPs.

The PPs have been large emission sources of airborne pollutants with the maximum emission rates during the 1980s (Kaasik et al., 1999). The impact of fly ash from the PPs on the near-by peat bogs and wetlands has been well documented (Kaasik et al., 2000; Karofeld, 1996a; Pensa et al., 2004). Also the radionuclides found in oil shale are carried together with the fly ash into the surrounding environment. Radionuclide emission rates and behavior in the combustion system depends on the employed combustion technology (technological set-up, prevailing temperatures and installed purification systems); characteristics of the formed fly ash (chemical composition, aerodynamic diameter, specific surface area) as well as the coagulation and condensation processes taking place in the flue gas duct (Corbett, 1983; Nowina-Konopka, 1993; Smith et al., 1979). Up to this point there has been no available studies to estimate the magnitude and trends of such impacts.

3.3 The employed technology and fly ash characteristics at EPP and BPP

At the start of 2000's two PF boilers were replaced with novel CFB boilers in EPP as well as in BPP. The differences in the technological set-up have had a strong impact on the formed ash characteristics. The following chapter includes the description of important technological factors that impact the radiological characteristics of the formed ash fractions. Detailed technical information about the PPs can be found in (Ots, 2006).

a) Technological parameters and ash characteristics of PF boilers

Prior the PF combustion boiler (Figure 1), oil shale is ground into fine powder form where the median particle size is in the range of 35 to 60 μm (Ots, 2006).

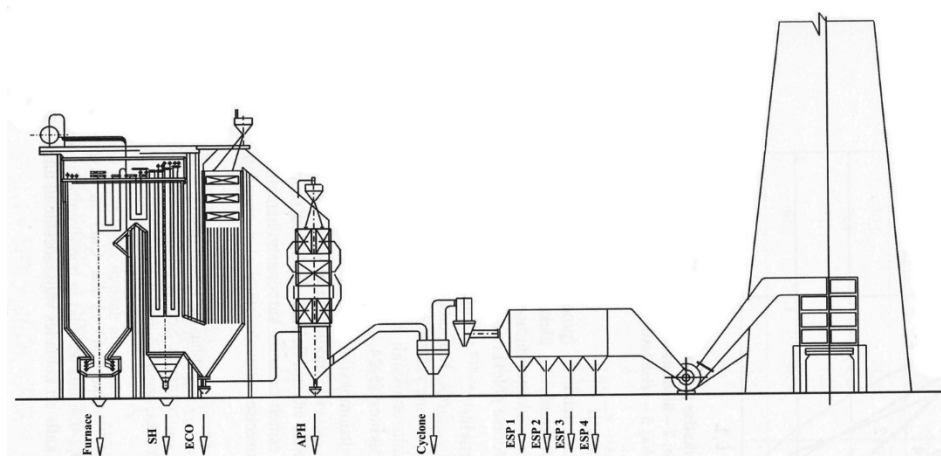


Figure 1. PF boiler with ESPs. SH – Super Heater; ECO – Economizer; APH – Air pre-heater; ESP1-ESP4 – Electrostatic Precipitators 1–4. Figure is a modified version from (Ots, 2006).

The size distribution and specific surface area of the ash particles varies in different parts of the flue gas duct in PF as well as in CFB boilers (Table 1) (Ots, 2006; Reinik et al., 2013). The median aerodynamic diameter of the particles decreases towards the back end of flue gas duct for both boiler types. The specific surface area of the particles varies between PF and CFB boilers (Table 1). This is due to the differences in the combustion properties of the boilers and the physicochemical characteristics of the formed ash fractions (Bitjukova et al., 2010). In case of the NID system and bag filters we can presume that over 90% the ash particles in the NID system remain under 0.045 mm, similarly as in ESPs (Kuusik et al., 2005). The PF boilers are identical, thus the formation of ash particles is well comparable prior different purification systems. Also the proportion of precipitated ash at various stages of PF and CFB boiler systems differ. Majority of the ash in PF boilers is precipitated as bottom and cyclone

ash, 39% and 32%, respectively (Ots, 2006). For CFB boilers, the bottom ash (37%) and ash from ESP's first field (46%) constitute the major ash fractions (Plamus et al., 2011a).

Table 1. Size distribution and specific surface area of fly ash particles in PF and CFB boilers. Data from (Ots, 2006; Plamus et al., 2011a; Reinik et al., 2013).

Parameter	Furnace	Super Heater	Econo- mizer	Pre- heater	Cyc- lone	ESP 1	ESP 2	ESP 3	ESP 4
Median size (PF boiler), μm	230–270	140–180	130–170		50–60	8–12	7–10	6–8	5–6
Median size (CFB boiler), μm	1133	21				11	8		
Specific surface area (PF boiler), m^2/g	2.0	0.5		0.7	0.3	0.5	0.8	1.4	
Specific surface area (CFB boiler), m^2/g	2.7					6.9	7.1	7.3	6.9

Temperatures in the PF boiler furnace reach as high as 1500 °C (Ots, 2006). The temperatures gradually decrease toward the back end of the flue gas duct. Flue gases emitted to the atmosphere are in the temperature range of 130–160 °C for boilers with ESPs and around 100 °C for NID system with bag filters. The NID technology and bag filters are more efficient in removing fly ash and SO₂ from flue gases compared to ESPs. The SO₂ is combined with carbonaceous oil shale ash, water and added lime in the NID reactor system, which results in reduced SO_x emissions from the combustion boiler. There are distinctive differences in the atmospherically emitted fly ash amounts between PF boilers with ESP and NID as well as with CFB boilers. These are described in the context of radionuclide concentrations in chapters 7.1–7.5.

The ash particles generated in the PF boilers are characterized by regular spherical shape with smooth surface, which is more notable toward finer ash particles. These spheroidal particles are created during high combustion temperatures by fusion of inorganic minerals such as aluminosilicates (T. Alliksaar, 2000) and are very specific to industrial activity. Another characteristic property is the increase of specific surface area of fly ash towards the finer fractions and larger specific surface area has a strong impact on the enrichment levels of radionuclides. Detailed chemical composition description of various PF boiler ashes can be found in (Bitjukova et al., 2010). The main components of ash according to weight percentage are lime (CaO), quartz (SiO₂), portlandite

(Ca(OH)₂), calcite (Ca(CO)₃) and anhydrite (CaSO₄). The distribution of these chemical compounds varies between the ash fractions. For example the content of lime decreases in the finest fly ashes opposite to the content of anhydrite, which increases. This is related to the chemical reaction between free lime and SO₂ in the back end of flue gas duct. There are various physicochemical processes taking place during the combustion process that in addition to the technological set-up influence the attachment of radionuclides onto ash particles.

b) Technological parameters and ash characteristics of CFB boilers

Two boilers in BPP and EPP were replaced with a novel CFB boilers at the start of 2000s. The installed CFB boilers have a higher fuel burning efficiency and lower emission rates of gaseous pollutants to the atmosphere to PF boilers (Ots, 2006). In CFB (Figure 2) boilers additional airflow is generated in the furnace from the bottom. This airflow lifts the bed material (often sand) and oil shale and keeps it in a suspension, where the combustion of the fuel takes place. The inserted fuel does not need to be pulverized prior feeding it to the furnace. The inserted fuel particle size remains between 1 and 10 mm. However, the intense mechanical friction between fuel particles in the circulating layer of the CFB boiler furnace significantly decreases the particle size (Kuusik et al., 2005; Ots, 2006). As a result, the fly ash particles are finer in some stages of CFB boiler (Table 1) compared to the ones in PF boilers, but ash fractions in the ESPs are comparable. Due to the boiler's rather stable operating regime and fuel burning process, it can be presumed that the ash particle granulometry does not vary extensively with time when employing the same technology. The furnace temperatures for CFB boilers range between 750 °C and 950 °C compared to 1400 °C and 1500 °C for PF boilers. Differences exist in the flue gas temperatures at different stages of the flue gas duct. The flue gas temperature after the ESPs of CFB boilers remains around 170 °C, compared to 200 °C and around 100 °C for PF boilers with ESPs and NID system, respectively.

There are also differences between the ash mass flow of CFB and PF boilers. The CFB boilers do not have a cyclone and the majority of fly ash that exits the furnace chamber is precipitated in the first field of ESP. Approximately 85–90% of the total particles remain under 0.045 mm in the ESP fields of CFB boilers (Kuusik et al., 2005), where 55%–65% (mass percentage) particles are with size up to 2.5 mm, 33%–43% remain between 2.5 and 10 mm and 2%–4% of the particles are larger than 10 mm (Parve et al., 2011). Although the chemical composition of CFB and PF boiler ashes is the same, there are variations in the proportions of different chemical compounds (Bityukova et al., 2010; Ots, 2006; Plamus et al., 2011b) and distinctive differences in the shape and structure of the ash (Bityukova et al., 2010; Blinova et al., 2012). The CFB boiler ashes have an irregular and porous structure (Blinova et al., 2012) with clearly increasing specific surface area towards the filter ashes (Reinik et al., 2013).

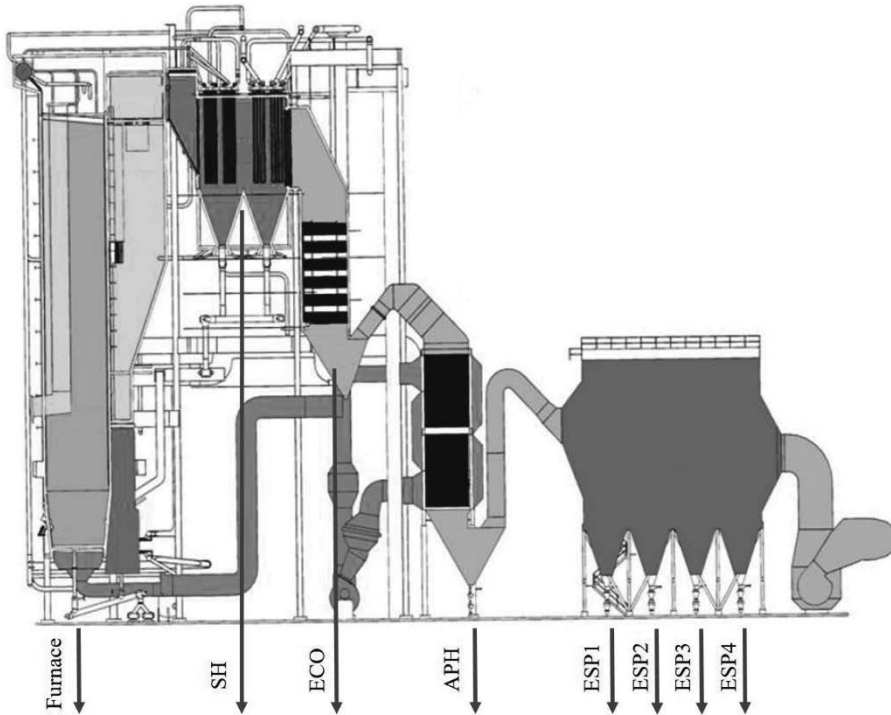


Figure 2. CFB boiler. SH – Super Heater; ECO – Economizer; APH – Air pre-heater; ESP1-ESP4 – Electrostatic Precipitators 1–4. Figure is a modified version from (Vaasma et al., 2014a).

Overall, the installment of CFB boilers with purification systems have increased the combustion efficiency and improved fly ash removal from flue gases compared to conventional PF boilers with ESPs. Fly ash concentrations emitted to the atmosphere by CFB boilers dominantly fluctuate between 25 and 30 mg m⁻³ compared to 200 mg m⁻³ from PF boilers with ESPs (Pihu et al., 2006).

4. RADIOLOGICAL ASPECTS OF NORM-RELATED INDUSTRIES

The Estonian practice to burn oil shale for electricity production is quite unique globally. Oil shale is found and mined in various parts of the world (Aaloe et al., 2006), but its quality and economic feasibility to produce energy is often rather low. Estonia's experience in using oil shale for shale oil production and also burning it in large combustion boilers has on the other hand been remarkable. This has however come with its own price in the form of negative environmental aspects, which over time have been significantly reduced. Oil shale mining, created waste streams and environmental pollution pathways have been regulated and monitored. Necessary licensing for these activities has been enabled through the Ministry of Environment and the Environmental Board.

The radiological aspects related to oil shale industry have long been left out of sufficient consideration from the regulatory body as well as by the operators. This has mostly derived from the lack of awareness of the radiological issues related with oil shale industry as well as insufficient available studies on these topics. Comparison studies are found for other types of fuels, such as coal, heavy oil and natural gas where the creation of NORM has been identified (Al-Masri et al., 2014; Al-Masri and Haddad, 2012; Nowina-Konopka, 1993; U.S. Environmental Protection Agency, 1995; Vreček and Benedik, 2003). Also the production of phosphate fertilizers, metallurgy, production of rare metals, cement and zircon etc. has often produced NORM as a by-product (Douay et al., 2006; Hofmann et al., 2000; Komárek et al., 2008; S.K. Sahu et al., 2014; Vanmarcke et al., 2008; G. Xhixha et al., 2013; Gerti Xhixha et al., 2013). Thus the exposure to radiation sources due to the creation of NORM residues can be extensive. There are recommendations and preliminary guidances concerning NORM topics in different national strategies, such as the National Action Plan for Radioactive Waste Management, National Development Plan for Radiation Safety, but their content is not fully up to date in regards to the findings on NORM-related topics during the past years. There is an inescapable need to identify the potential NORM-related industries, especially due the requirements stated in the new European Basic Safety Standard EURATOM 2013/59 (EU BSS) and the need to include the requirements from the EU BSS into the national legislation of the Member States. The EU BSS considers the natural radiation sources to be regulated under the same terms as artificial sources. The EU BSS has identified various NORM-related industrial activities where potential radiological hazards need to be assessed. Oil shale combustion will be considered as one of the potential NORM producing industries. This has further enhanced the need to collect and analyze radiological information on the oil shale PPs. During the current work, the PPs were systematically investigated and raw material and various ash fractions were collected to radiologically characterize the PPs. The obtained information also provides input during the transposition of the EU BSS into Estonian legislation.

5. SAMPLE COLLECTION

5.1 Oil shale and ash

Multiple oil shale and oil shale ash samplings during 5 years were conducted from the PPs. Partially, ash samples were obtained in cooperation with a research group from the Tallinn University of Technology. Regular and systematic collection and analysis of the gathered samples allowed to assess the variations of the radionuclide concentrations over a longer period of time. Due to the large ash amounts created annually, long term studies are necessary to assess the variations in these processes and to increase accuracy of the results. Samples were collected from PF and CFB boilers operating with ESPs as well as with NID system and bag filters (employed on PF technology only) and from various ash precipitation points as indicated in Figures 1 and 2. In addition, fly ash samples entering the NID system and samples after purification systems (ESP and NID) were obtained from partners at the Tallinn University of Technology. Oil shale samples were collected from Estonia mine and from Narva quarry.

The mass of the ash samples collected from various precipitation points remained usually between 0.5 and 2 kg from which a portion was taken for measurement. When samples were taken by the PP's personnel, then a coordination was carried out by our laboratory staff. Fly ash samples collected directly from the flue gas duct prior the NIDs were around 10–20 g and between 50–200 mg when obtained after the filter systems.

5.2 Peat samples

Environmental samples (peat cores) were collected approximately 40 kilometers from the PPs, which allowed to investigate the range of the fly ash and radionuclide distribution in the near-by areas. These samples were collected in collaboration with a research group from the Institute of Ecology and Earth Sciences at the University of Tartu. Due to the lack of resources (human and financial) no large scale sampling grid was organized to obtain samples also from close proximity of the PPs. Regardless of this, the results were put into context of available studies conducted at the same locations or near-by, which is more thoroughly discussed in (Vaasma et al., 2017c).

The sampling site (Selisoo mire) is located in the northeastern part of Estonia. It is mostly a *Sphagnum*-dominated peat bog with sparse pine cover (Figure 3) and many bog pools (Hiemaa et al., 2014). Its ombrotrophic nature and vicinity to the oil shale PPs has made the mire a suitable area for air pollution research. The mire also partially situates above oil shale resources and within the permitted mining area. The mire has been affected by human activities in many ways: oil shale mining, drainage and industrial pollution. The most influenced has been the eastern side due to draining, production of industrial peat and mining activities. Also pollutants from near-by PPs have

damaged the bog's natural ecosystem (Kaasik et al., 2008; Karu et al., 2014; Pensa et al., 2004).



Figure 3. Selisoo mire.

Two 30 cm long peat cores were collected from the mire. The core was cut out, packaged and frozen. The frozen cores were sliced with an industrial saw into 1 cm slices except for the surface moss layer, where 2–4 cm slices were used. Bulk densities (dry weight) were estimated for all subsamples. The collected samples were placed in the same type of cylindrical containers as used for ash samples and measured with gamma spectrometry. In addition to radionuclide measurements, concentrations of spherical fly ash particles (SFAP) were estimated in each sample. A known volume of peat sample was chemically treated to remove organic matter, after which spheroidal particles were counted under light microscope at 400x magnification (Punning and Alliksaar, 1997).

6. SAMPLE PREPARATION AND ANALYTICAL METHODS

6.1 Gamma-ray spectrometry

Solid samples (oil shale, oil shale ash and peat) were preprocessed by drying and compacting. Drying took place at 105 °C for 24 h for ash samples and 48 h at 70 °C for peat samples. Oil shale and bottom ash samples needed to be additionally ground to achieve larger homogeneity for analysis. The grinding was done using a hand mill to get a particle size of 0.5 mm or less. Ash samples consisted of fine and homogenous particles that did not require additional mechanical processing. In case of peat, the whole sublayers were compacted into the measured sample. The dried samples were compacted with a hydraulic press to cylindrically shaped metal containers with a volume of 55 cm³ or 57 cm³ (Figure 4) (depending on the availability of the containers) and taken to gamma spectrometric analysis. The final mass of ash samples ranged between 40 and 100 grams, depending on the particle size and porosity of the material. The mass of peat samples fluctuated roughly between 2 and 40 grams depending on the density of the samples. To avoid radon (²²²Rn) emanation, all samples were sealed hermetically. This was done using plasticine and insulating tape to seal the container and the lid together. Validation has confirmed the functionality of this method. To achieve secular equilibrium between radium (²²⁶Ra) and its progenies, ²²²Rn and its short lived daughters (²¹⁴Pb and ²¹⁴Bi), the sealed samples were stored for at least 23 to 27 days prior the measurements.

Fly ash samples collected after the purification systems were small in mass and the total activity of the samples was lower than the MDA value of the gamma detectors. These samples were prepared for alpha spectrometric measurement (²¹⁰Po) and Liquid Scintillation Counting (LSC) (²¹⁰Pb). The development and employment of the corresponding methods are more precisely described in 6.2 and 6.3.



Figure 4. Sample measurement containers.

Samples were measured with high-purity germanium detectors, planar BSI GPD-50400 (BSI, Latvia), coaxial RG Ortec GEM-35200 (EG&G ORTEC, USA) and BeGe BE 3830-P (Canberra, USA). Activity concentrations of the ^{238}U and ^{232}Th series radionuclides and ^{40}K were calculated according to the following gamma energies: ^{238}U (^{234}Th – 63.3 keV), ^{226}Ra (^{214}Pb – 242.0, 295.2 and 351.9 keV; ^{214}Bi – 1764.9 keV), ^{210}Pb (46.5 keV), ^{232}Th and ^{228}Th (^{212}Pb 238.6 keV), ^{228}Ra (^{228}Ac – 911.2, 964.8 and 969.0 keV) and ^{40}K (1460.8 keV).

The activity concentration of ^{238}U was determined through its daughter ^{234}Th (63.3 keV), presuming that all of the ^{234}Th in the samples originates from ^{238}U . Our previous laboratory and measurement experience has shown that the equilibrium between ^{238}U and ^{234}Th has remained in place in bottom and fly ash fractions. Re-measurements after six months have confirmed this.

^{232}Th is estimated based on the values of its daughter product – ^{228}Th . This is derived from the idea that isotopes of the same element and from the same origin behave similarly, as also suggested by (Ault et al., 1970). Our experiments have also shown a persistent equilibrium between ^{228}Ra and ^{228}Th and the unchanged activity concentration of these isotopes in re-measured samples after 2 years, which also confirms that the decay of ^{232}Th as the parent nuclide determines the activity concentration values in this decay chain.

The measurement's energy calibration was done using a RGU-1 source. RGU-1, RGTh-1 and RGK-1 sources were used in efficiency calculations. These sources (RGU-1, RGTh-1 and RGK-1) are IAEA certified reference materials used for gamma-ray spectrometer calibration for the determination of U, Th and K in geological materials (International Atomic Energy Agency, 1987). The reference materials RGU-1 and RGTh-1 were prepared by dilution of uranium ore BL-5 (7.09% U) and thorium ore OKA-2 (2.89% Th), respectively (where ^{238}U and ^{232}Th are in secular equilibrium with their daughter products), with floated silica powder of similar grain size distribution. The RGK-1 source contains high purity (99.8%) potassium sulfate. Due to partial absorption of emitted photons in the sample matrix, a self-absorption correction was applied in gamma spectrometric analysis when emitted gamma energies remained <100 keV. The correction was applied for ^{210}Pb and ^{234}Th . Additional measurements were done using uranium dioxide and lead sources with higher activities to determine the attenuated and unattenuated beam intensities. Self-absorption calculations were performed according to (Cutshall et al., 1983). GammaVision-32 (version 6.07, EG&G ORTEC) software was used to analyze the gamma ray spectra.

6.2 Alpha particle spectrometry

Along with the acquirement of an alpha particle measurement system, the laboratory started to establish a methodology for ^{210}Po measurements in environmental samples. In 2016, ^{210}Po measurement from mineral samples with an alpha particle detector was validated (during a student's master's programme)

and put in use. This has enabled our laboratory to conduct ^{210}Po measurements from emitted fly ash fractions from the PPs. Determination of ^{210}Po from solid samples also required to set up a suitable sample preparation method.

A separation method for ^{210}Po and ^{210}Pb , based on IAEA, (2014), Kim et al., (2008) and Vajda et al., (1997) was modified and applied to be fit for purpose for the specific sample characteristics (oil shale ash) and for the laboratory set-up. For this, a sample digestion procedure was designed for Ca-rich fly ash samples that contain considerable amount of siliceous material (up to 20% by weight) to be processed with a microwave digestion system (Anton Paar multiwave 3000). Samples were dissolved using a mixture of concentrated hydrofluoric (HF), nitric (HNO_3) and saturated boric (H_3BO_3) acids with two digestions runs. The precise sample digestion procedure can be found in Ozden et al., (2017). ^{209}Po was used as a tracer to evaluate the chemical yield and total efficiency of ^{210}Po during the sample preparation and measurement procedure. ^{209}Po standard solution was prepared from a stock solution (shipped in a 1M HNO_3 solution) acquired from Oak Ridge National Laboratory (USA) with an initial activity of 37000 Bq (1 μCi). A weighted amount of ^{209}Po tracer was added in each sample according to the expected ^{210}Po activity concentration within the sample.

^{210}Po and ^{210}Pb separation was based on IAEA procedure (IAEA, 2014) using Strontium (Sr) resin columns (Figure 5). The IAEA procedure was modified, tested and applied (Ozden et al., 2017). The digested samples were taken through the Sr column, processed and directed to measurement via alpha spectrometer and Liquid Scintillation Counting (LSC). LSC was used to measure ^{210}Pb . A detailed description of the established sample separation method can be found in Ozden et al., (2017).

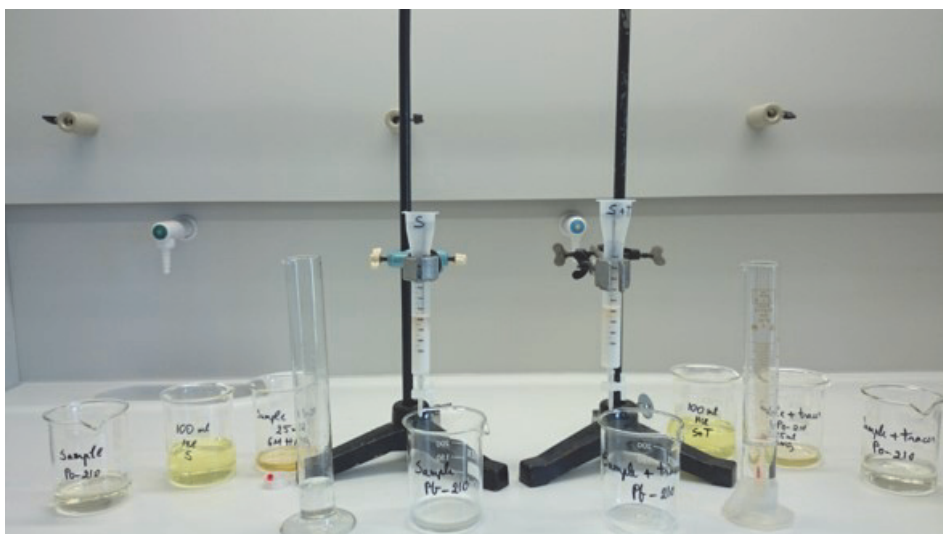


Figure 5. Separation columns for ^{210}Po and ^{210}Pb .

^{210}Po samples were deposited on copper discs (99.9% purity) obtained from Goodfellow Cambridge Limited (UK). Deposition was carried out at 85 °C for 4 h while agitating the solution. The active area of the sample had a diameter of 24 mm. Samples were counted from 1 to 3 days with a Canberra alpha-particle spectrometer (Model 7401), using an Ultra™ Alpha-particle detector with a 450 mm² active surface area. The spectrometer was calibrated using ^{241}Am and ^{239}Pu source obtained from the Czech Metrology Institute. Spectrum analysis was conducted using a Region of Interest (ROI) approach as the two peaks have a similar shape and are well distinguished in the spectrum.

6.3 Liquid Scintillation Counting (LSC)

The separated and further treated ^{210}Pb samples were taken for measurement with liquid scintillation counter Quantulus 1220 (PerkinElmer, USA). ^{210}Pb was measured via LSC when the total activity within the sample was below the MDA value of the gamma spectrometers. Samples were placed in 20 ml polyethylene vials and mixed with 1 ml of 6M HNO_3 and 15 ml Optiphase HiSafe III scintillation cocktail (PerkinElmer, USA). The measurement was conducted with low bias mode with the Pulse Shape Analysis (PSA) set as 10. The activity concentration of ^{210}Pb was determined according to Vajda et al., (1997). Stable lead ($\text{Pb}(\text{NO}_3)_2$) was used as a tracer to calculate the recovery of ^{210}Pb according to the IAEA procedure (IAEA, 2014).

7. RESULTS AND DISCUSSION

7.1 Radionuclides in oil shale and oil shale ash (Based on publications I and II)

The obtained and analyzed oil shale samples used in this work originated from Estonia mine, Narva and Aidu quarries over multiple years. The radionuclide activity concentration values in these samples remained similar (Table 2). Larger differences occurred with the ^{40}K values, but these remain comparable to expected values in soils (UNSCEAR, 2010). The oil shale radionuclide composition can be considered more or less homogenous within and between the mining locations.

Table 2. Radionuclide activity concentrations (Bq kg^{-1}) in oil shale with expanded uncertainty.

	Narva quarry	Aidu quarry	Estonia mine and Narva quarry fractions mixed
Radionuclide			
^{238}U	24.6 ± 6.8	21.6 ± 7.2	26.4 ± 6.4
^{226}Ra	23.8 ± 1.8	24.8 ± 2.0	28.7 ± 2.0
^{210}Pb	26.0 ± 8.0	23.4 ± 10.8	25.3 ± 7.6
^{228}Ra	12.1 ± 2.0	12.4 ± 2.2	14.4 ± 3.2
^{232}Th	12.0 ± 1.8	11.9 ± 1.8	15.2 ± 2.0
^{40}K	393.4 ± 14.8	360.0 ± 14.0	488.5 ± 24.1

Before the 1990s, the used oil shale was partially imported from a Leningrad deposit, which situated near the city of Slantsy in the Leningrad District of Russia. Previous studies (Realo et al., 1996; Realo and Realo, 1997; Vaasma et al., 2017d, 2014a) have shown that the activity concentrations of the ^{238}U and ^{232}Th series radionuclides and ^{40}K are well comparable to the values determined in the Estonian oil shale deposits and remain relatively constant during various time periods.

The mined oil shale is transported to the PPs and processed further to have the fuel particle size suitable for the employed technology. Similarly to coal, radionuclides from the uranium and thorium decay chain are associated with the fuel (oil shale) mineral and organic part. The radionuclides are largely released from the fuel matrix during fuel combustion processes and redistributed between bottom and fly ash fractions. This depends on the volatility of the specific element and its chemical form in the original material.

7.2 Radionuclide distribution in the ashes of PF boilers (Based on publications II and III)

There are different type of boilers with varying set-up employed in EPP and BPP as described more thoroughly in 3.3. In order to estimate the potential radionuclide emission loads from these combustion boilers, radionuclide behavior in these systems needed to be evaluated. Boilers operating on PF technology and with ESPs have shown an increasing trend in radionuclide activity concentrations from the furnace toward the purification system (Figure 6). This enrichment trend is most noticeable for ^{210}Pb and ^{40}K values.

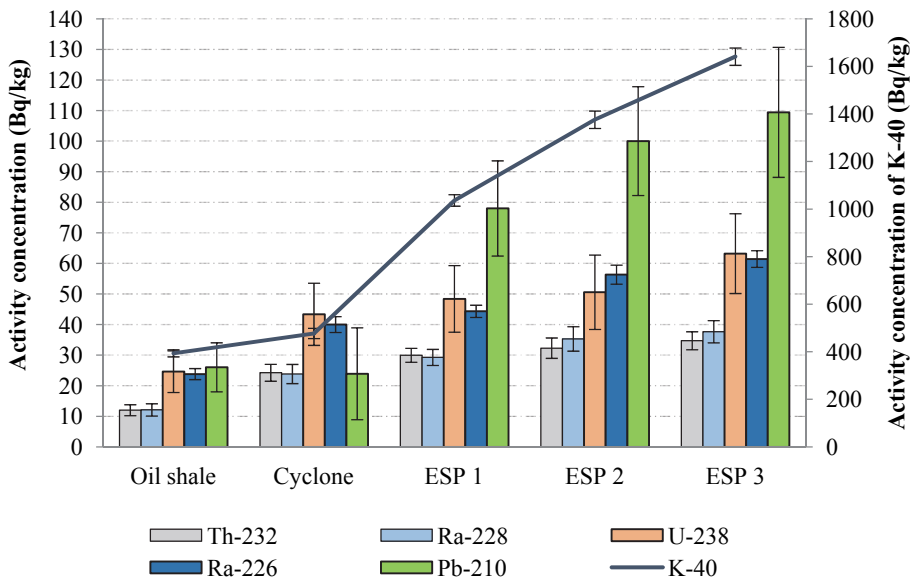


Figure 6. Radionuclide activity concentrations (Bq kg^{-1}) in different ash fractions of a PF boiler. Data from (Vaasma et al., 2014b).

More volatile radionuclides are vaporized at high furnace temperatures and transported towards the back end of the flue gas duct via fly ash and flue gases. As the flue gas temperature decreases, the volatilized elements start to condensate onto ash particles and other surfaces. As the median size of the ash particles decreases from the furnace toward the ESP fields (see Table 1), it favors additional attachment of radionuclides onto the finer fly ash.

Lead is often depleted in the bottom ash due to its volatile nature. On the contrary, ^{210}Pb concentrations are highest in the last filter fields, remaining usually over 100 Bq kg^{-1} . Values up to 140 Bq kg^{-1} have been determined in a previous study (Vaasma et al., 2016). Other radionuclides, such as radium, uranium and thorium isotopes follow a gradual increasing concentration trend toward finer ash fractions. Highest values for ^{238}U and ^{226}Ra remain around

60 Bq kg⁻¹, while ²³²Th and ²²⁸Ra values do not exceed 40 Bq kg⁻¹ in PF boilers with ESPs. ⁴⁰K activity concentration in the last fields can be up to 1650 Bq kg⁻¹ or higher. The radionuclide behavior characteristics are similar to the ones described by Realo et al. (1996) and Realo and Realo, (1997) in studies on oil shale PPs. This enrichment trend is also typical for coal-fired PPs (Papastefanou, 2010). Radionuclide activity concentrations in coals and coal fly ash are often higher due to the higher initial values in the fuel and lower ash content of the used coal.

It can be clearly seen that the radionuclides found in oil shale exhibit varying enrichment trends during the combustion processes (Figure 7).

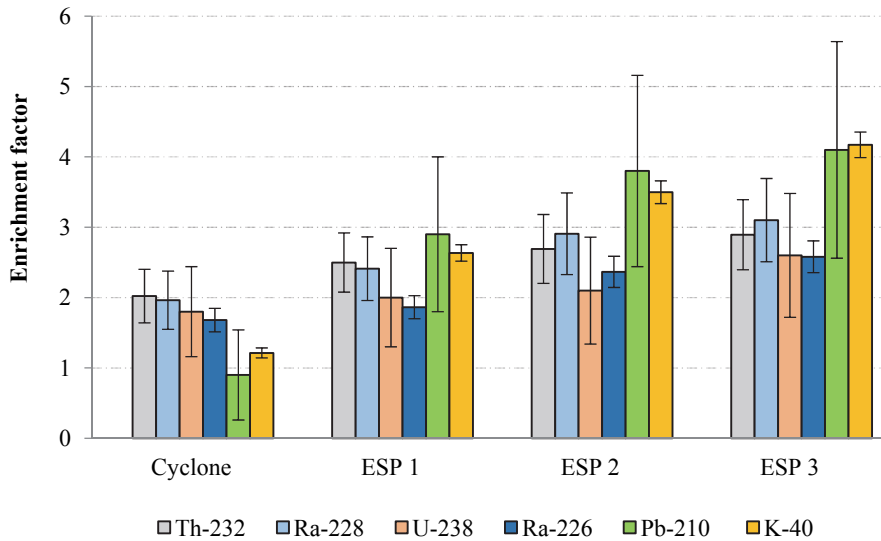


Figure 7. Radionuclide enrichment values in ash fractions of a PF boiler. Data from (Vaasma et al., 2014b).

Here we define the enrichment factor as a ratio of a radionuclide activity concentration in a given ash fraction to that measured in the dry oil shale. Burn out of organic material from oil shale is the primary cause for the elevated radionuclide activity concentrations in the ash fractions. Similarly to activity concentrations, the enrichment factors increase toward the finer ash fractions in the ESPs. More volatile radionuclides (²¹⁰Pb and ⁴⁰K) have higher enrichment values especially in the last fields of ESP (up to 4.2) compared to uranium, radium and thorium that demonstrate enrichment values up to 3. It is expected that ash fractions escaping the purification systems will be smaller in size and have even higher radionuclide enrichment values.

PF boilers with NID system and bag filters

Within the NID system, all the fly ash that is not separated by the cyclone is mixed together and precipitated. Additional lime and water is added and mixed

with fly ash and flue gases to remove sulphur dioxide from the combustion products. The flue gas temperatures are reduced to below 100 °C, compared to 170–200 °C in PF with ESPs.

Samplings from the NID system and bag filters were organized multiple times. The combined results are shown in Figure 8.

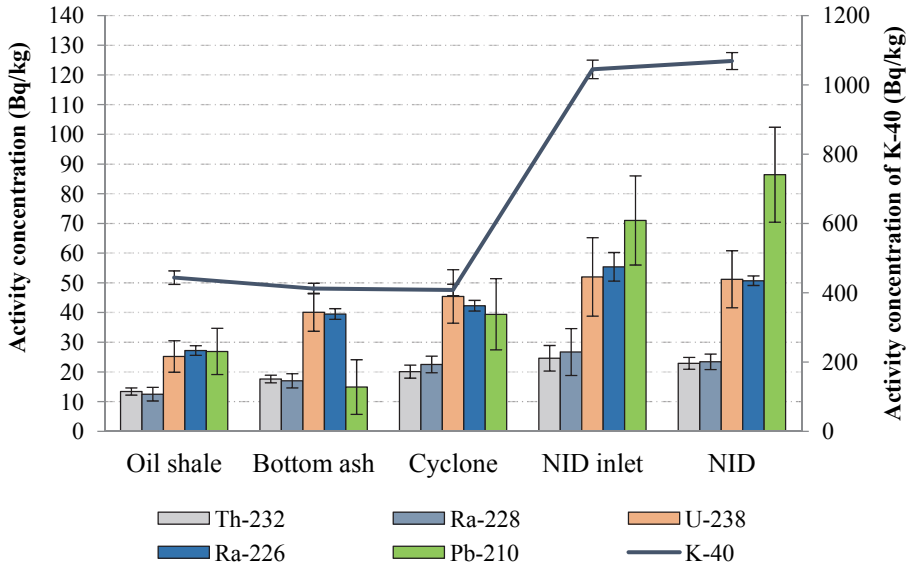


Figure 8. Radionuclide activity concentrations in the oil shale and ashes of PF boiler operating with NID technology and bag filters. Data from (Vaasma et al., 2017d, 2014b).

Similarly to ESPs, the radionuclides activity concentrations increase in finer ash fractions. There is a depletion of ^{210}Pb in bottom ash due to its volatilization in the combustion chamber. Highest ^{210}Pb values were determined in the NID ash, reaching $86 \pm 16 \text{ Bq kg}^{-1}$. These values are lower to the ones determined in the last fields of ESPs. This is due to the fact that the NID ash contains a large variety of ash particles with varying size, which homogenizes the overall activity values. ^{210}Pb and ^{40}K values are very similar between NID and first field of the ESP. The first field of the ESP captures the majority of fly ash (approximately 78%) entering the purification system, which makes this fraction the most suitable to compare with NID ashes. The values of ^{238}U , ^{232}Th and radium isotopes in NID fraction fall also closely together with the ones determined in the PF boiler's first ESP field. There are also no significant discrepancies between the NID inlet and NID values, indicating that the overall ash particle size distribution in these fractions is expected to be similar.

Radionuclide enrichment values (Figure 9) demonstrate modest increases in the NID ashes.

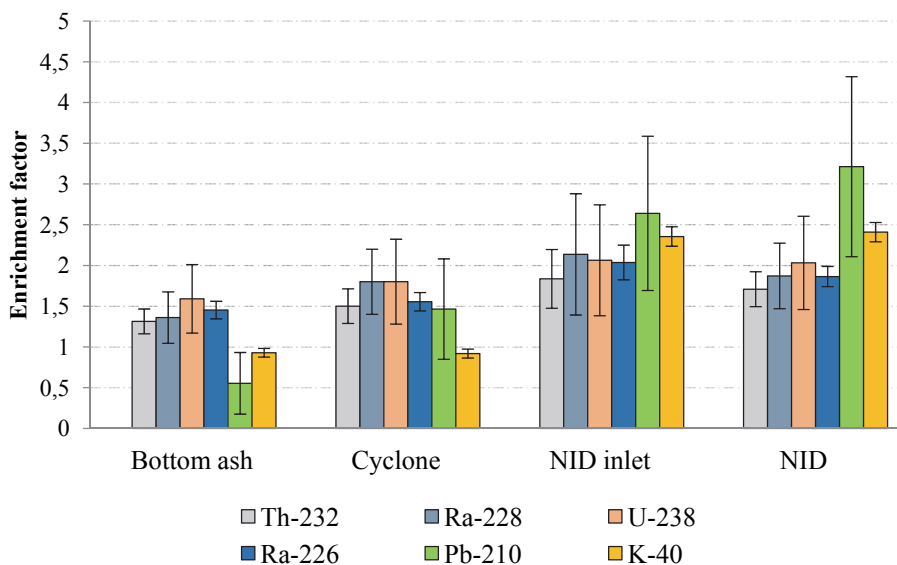


Figure 9. Radionuclide enrichment values in PF boilers with NID system and bag filters. Data from (Vaasma et al., 2017d, 2014b).

Less volatile radionuclides, such as uranium, thorium and radium isotopes are also enriched in bottom ash, opposite to ^{210}Pb , which is volatilized and carried away from the furnace. On the other hand, ^{210}Pb is enriched up to 3 times and ^{40}K has 2.5 times higher concentration in the NID ash compared to the values in original oil shale. Values for other radionuclides in the NID ash remain approximately two times higher to the ones in oil shale. Again, this compares well with the results obtained in the first field of ESP ash. An important point to emphasize is that the physicochemical properties of the used oil shale have also have an important impact on the radionuclide concentrations and enrichment levels in various fly ashes. The chemical form and abundance of radionuclides in oil shale influence its distribution in the formed ashes. Results from sampling over a longer time period helped to assess the variations in radionuclide concentrations and determine the causes for the variations. This will be discussed in more detailed in 7.4.

7.3 Radionuclide distribution in the ashes of CFB boiler (Based on publication I)

The CFB boilers have a higher electrical efficiency (34% compared to 29% in PF boilers), lower combustion temperatures and lower SO_x and fly ash emissions compared to PF boilers. There are no remarkable differences in the chemical composition of CFB and PF boiler ashes (Ots, 2006; Plamus et al., 2011b), but clear dissimilarities occur in the shape and structure of the ash

particles (Bityukova et al., 2010). Ash particles created in the CFB boiler have an irregular and porous structure, which differentiates from the spherical particles generated by PF boilers (Bityukova et al., 2010) (Figure 10).

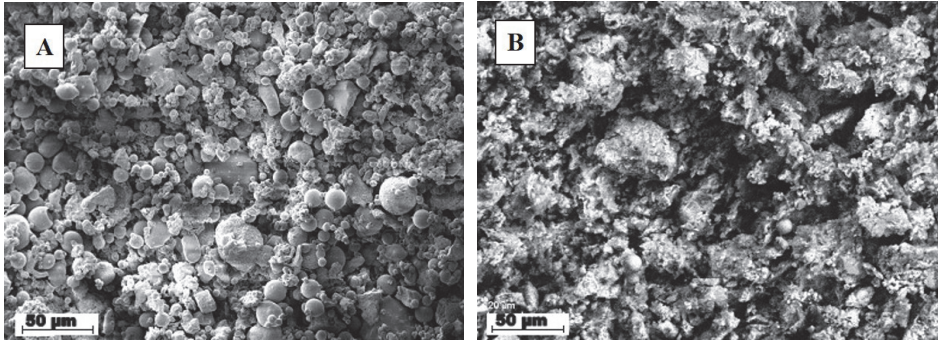


Figure 10. Ash particles from the PF (A) and CFB (B) boiler, first field of ESP. Modified images from (Bityukova et al., 2010).

The new technological set-up also affects the radionuclide distribution between bottom and fly ash fractions (Figure 11). The CFB boiler is working without a cyclone, thus majority of the generated ash (47%) is captured by the first field of ESP (Plamus et al., 2011a). This is 3.5 times more compared to the corresponding ESP field in PF boilers (Ots, 2006).

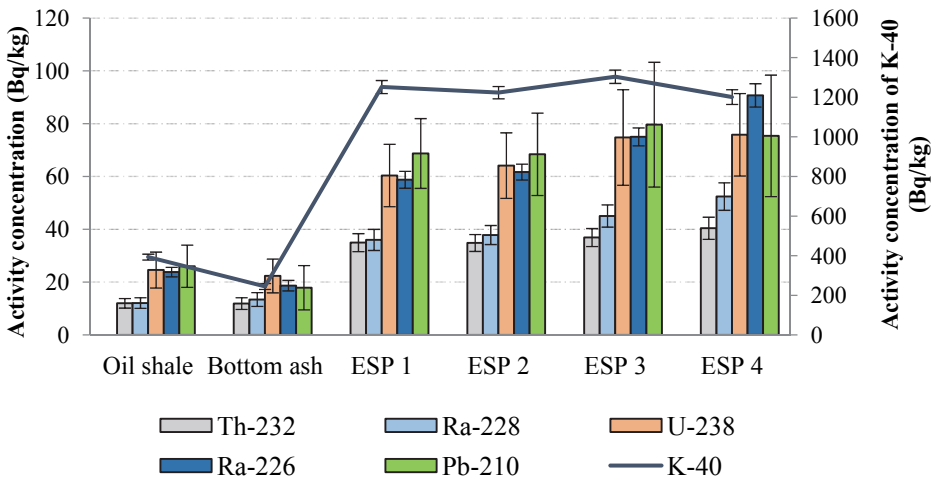


Figure 11. Radionuclide activity concentrations (Bq kg^{-1}) in different ash fractions of a CFB boiler. Data from (Vaasma et al., 2014a).

The radionuclide activity concentrations in the collected ashes follow a similar trend as seen in PF boilers. There is a slight accumulation or depletion of radionuclides in bottom ash, depending on the volatility of the radionuclide. Increased

concentrations can be seen in filter ashes, with the highest values in the third and fourth field. The radionuclide concentration differences between the ESP fields is however rather modest, as it exhibits a homogenous distribution between the ash fractions. Similar trend has also been observed in another study (Vaasma et al., 2016) that focused specifically on ^{210}Pb . ^{210}Pb values in the CBF boiler ashes are up to $80 \pm 24 \text{ Bq kg}^{-1}$. Maximum values for ^{238}U and ^{226}Ra reach $76 \pm 16 \text{ Bq kg}^{-1}$ and $91 \pm 4 \text{ Bq kg}^{-1}$, respectively. ^{232}Th and ^{228}Ra show concentrations up to 52 Bq kg^{-1} in the finest fractions. The radium isotopes exhibit a slightly elevated concentrations compared to their parent nuclides. These are most noticeable in the last filter field, compared to other fractions where the values coincide in the limits of uncertainty. This can be derived from the technological set-up of the boiler, as such observations differ from the ones made on PF boilers. ^{40}K and ^{210}Pb values remain approximately 30% lower in the filter ashes compared to PF boilers. On the contrary, ^{238}U , ^{232}Th , ^{226}Ra and ^{228}Ra concentrations are 15% to 30% higher in the CFB finest ash fraction compared to PF filter ash. The technological differences and combustion conditions can be considered the cause for these differences as the used oil shale had the same radionuclide concentration values.

Enrichment factors in the CFB boiler fly ashes (Figure 12) are quite homogeneously distributed. Values for radium isotopes exceed the ones obtained in PF boilers. Uranium and thorium are well comparable to PF boilers, but ^{210}Pb and ^{40}K exhibit up to 30% lower values in CFB last ESP fields.

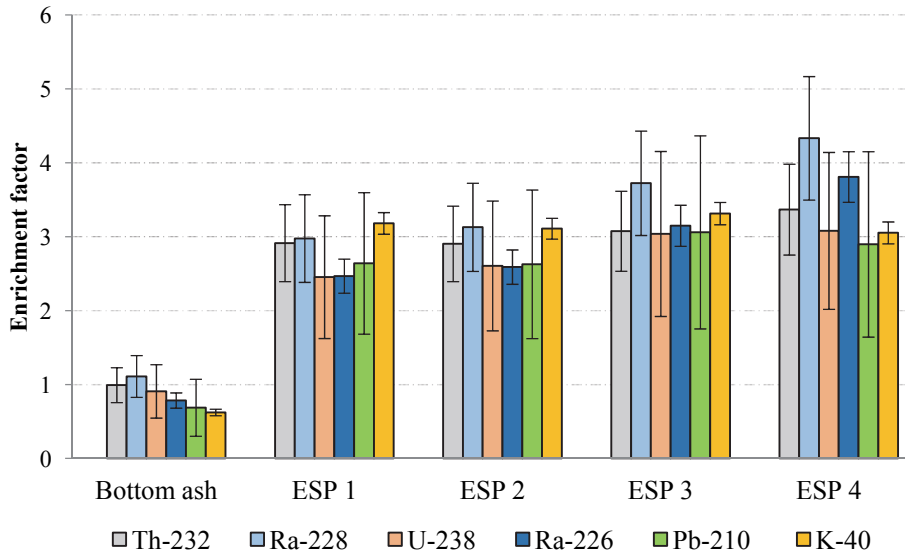


Figure 12. Radionuclide enrichment values in CFB boilers with ESPs. Data from (Vaasma et al., 2014a).

^{228}Ra has highest enrichment value (4.2) in the last ESP field. The enrichment for ^{228}Ra gradually increases from ESP 1 toward ESP 4. In general, the enrichment factors have similar values in the ESP fields for all the radionuclides. Compared to bottom ash, the values are 3 times higher. The values have distinct differences to the ones obtained in PF boilers with ESPs. This is due to the technological characteristics, combustion and flue gas temperatures, oil shale disintegration processes in the furnace as well as ash particle shape and size.

7.4 Radionuclide concentration variations in oil shale ashes (Based on publication VII)

Available research and the obtained data during the PhD work provides a reason to believe the fly ash and radionuclide emissions from the PPs can pose an additional radiological influence on the population and the surrounding environment. The previous studies (Realo et al., 1996; Realo and Realo, 1997; Vaasma et al., 2016, 2014a, 2014b) are however based on one time samplings, which somewhat reduce their representativeness when extrapolating the results over a longer time period. The boilers' combustion parameters can change in time, affecting also the radionuclide enrichment levels in the ashes. In order to determine the variability of the activity concentrations of the naturally occurring radionuclides, multiple extended samplings were conducted during a 2-year period while also registering boiler's combustion parameters, e.g. boiler load, steam production, temperatures in the flue gas duct and concentration of ash particles. By determining the variations in the activity concentrations of ^{238}U and ^{232}Th series radionuclides, more reliable estimations can be provided on the longer term radionuclide behavior and enrichments within the combustion system. A thorough characterization of the radionuclide enrichment trends provides a basis for better radiological estimations of the technological process and possibly eliminate need to conduct excessive and regular samplings and measurements in the future. The obtained data could also help to verify or elaborate the results obtained from earlier studies.

During the 2-year period multiple samplings of oil shale, bottom ash and fly ash samples were conducted continuously during 4 or 6 days:

- Total of 40 oil shale, bottom ash and fly ash samples were collected in 2013 during a 6-day continuous sampling period.
- 15 samples of oil shale and fly ash were obtained in 2014 during a 4-day sampling from the same PP and energy unit (PF boiler with NID and bag filters).
- 8 samples were collected from a PF boiler with an ESP in 2014 also during 4 days.

The sampling was done by personnel from the operator and Tallinn University of Technology from the same collection points during each day. As the PF

boilers have identical technological setup, samples from PF boilers with ESPs and NID system can be successfully compared as the sampling was conducted prior the purification systems.

Sampling results

The average bottom ash and NID inlet values are described in chapter 7.2. The results demonstrate a secular equilibrium in oil shale between radionuclides in the ^{238}U (between ^{238}U , ^{226}Ra and ^{210}Pb) and ^{232}Th series (between ^{228}Ra and ^{228}Th) during both years. In most cases, secular equilibrium was also preserved between ^{238}U and ^{226}Ra in the bottom and fly ashes. The secular equilibrium was preserved in all samples between long-lived radionuclides from the ^{232}Th series. ^{210}Pb has demonstrated higher concentrations in the collected ashes compared to its parent nuclides. In the samples collected in 2013, ^{210}Pb values reached $105\pm 20\text{ Bq kg}^{-1}$, while the corresponding values for ^{238}U and ^{226}Ra remained at $69\pm 7\text{ Bq kg}^{-1}$ and $74\pm 21\text{ Bq kg}^{-1}$, respectively. The volatile nature of ^{210}Pb and its affinity towards small fly ash particles with higher specific surface area has been determined in all the previous studies. All the sample batches collected during different years exhibited similar radionuclide enrichment trends as seen in earlier studies.

To estimate the variations, an ANOVA test was applied to compare the means and variations from the mean between different NID inlet ashes within a single sampling batch and between the samplings in different years.

Variations within a sampling year and between sampling years

No statistically significant differences (significance level 0.05) in the radionuclide activity concentrations were found between the NID samples collected within a single sampling during both years, with a few exceptions. This is indicative of a situation where the mean values of radionuclide activity concentrations are well comparable and the values do not fluctuate significantly between the collected fly ash fractions. To assess the sources of these differences, the coefficient of variation (CV) and the relative standard measurement uncertainties were estimated and compared (Table 3). The CV allows to present the standard deviation (SD) relative to the calculated mean and assess the range of the variations. This permits the determination of the percentage that the fluctuation (given as standard deviation) constitutes from the mean value. The measurement uncertainties are calculated as pooled values for the whole measurement period.

Table 3. The coefficient of variation (CV) and relative standard uncertainty values based on sampling in 2013. Data from (Vaasma et al., 2017d).

Sample	CV	Rela-	CV	Rela-	CV	Rela-	CV	Rela-	CV	Rela-	CV	Rela-
	(%)	tive	(%)	tive	(%)	tive	(%)	tive	(%)	tive	(%)	tive
		unc.		unc.		unc.		unc.		unc.		unc.
		(%)		(%)		(%)		(%)		(%)		(%)
	U-238		Ra-226		Pb-210		K-40		Ra-228		Th-232	
Oil shale	10.6	10.6	10.0	2.9	11.5	14.9	8.6	2.2	6.0	9.4	8.6	4.5
Bottom ash	12.6	8.3	12.4	2.5	26.8	30.5	9.4	1.9	11.5	7.5	12.7	3.8
NID*	18.5	12.9	13.4	4.3	19.2	10.8	13.6	2.6	9.4	15.0	14.2	8.7

* NID* represent the average value from different inlet points of the NID system. Each boiler has four inlet sampling points.

The majority of the values remain between 4 and 15%. Higher values in the bottom ash are due to the low radionuclide activity concentrations that increases the measurement uncertainty. In can be seen that the CV and relative standard uncertainties often remain in the same range, especially for ^{238}U , ^{232}Th and ^{228}Ra . This suggests that the majority of variations are introduced due to the measurement method and approach. In the case of ^{226}Ra , ^{210}Pb and ^{40}K , higher CV values compared to the relative uncertainties indicate that additional random or systematic components have an impact on the results. However, when deducting the measurement uncertainty value, the variations remain around 10 and 15%, which can be considered rather modest during the complex combustion processes. In general, the measured samples have small variations, suggesting that the distribution of radionuclide activity concentrations in the fuel and in various ash fractions within a single sampling patch is relatively homogeneous.

Statistically significant variations occur between some of the radionuclide concentration values when comparing the two years, 2013 and 2014 (Figures 13–14).

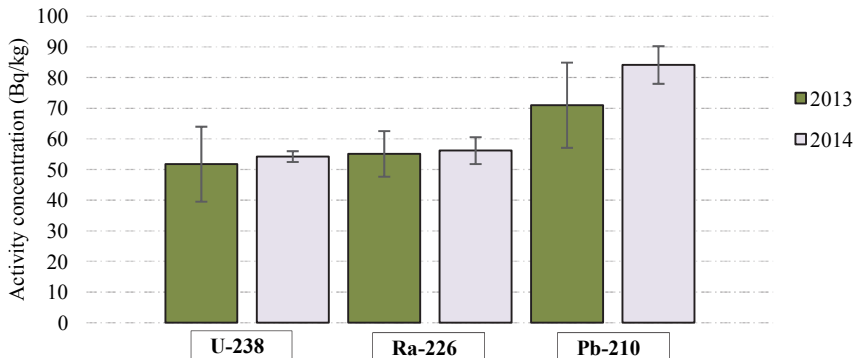


Figure 13. Mean activity concentrations with standard deviation for ^{238}U , ^{226}Ra and ^{210}Pb in different years. Data from (Vaasma et al., 2017d).

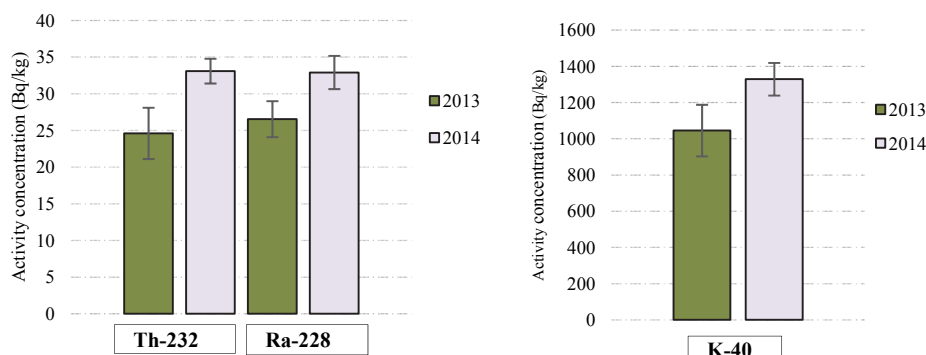


Figure 14. Mean activity concentrations with standard deviation for ^{232}Th , ^{228}Ra and ^{40}K in different years. Data from (Vaasma et al., 2017d).

The ^{238}U and ^{226}Ra values are well comparable between the years, while ^{210}Pb , ^{40}K , ^{232}Th and ^{228}Ra exhibit higher values in the samples collected during 2014. ^{210}Pb values have the highest measurement uncertainties, which should be taken into account when comparing the variations between the years. Within the limit of uncertainty, the values coincide well within and between sampling years. The systematic differences in between the ^{232}Th , ^{228}Ra and ^{40}K values in the 2013 and 2014 samples is related with the use of oil shale with varying radionuclide concentrations (Table 4).

Table 4. Radionuclide activity concentrations (Bq kg^{-1}) in oil shale samples collected in 2013 and 2014. Data from (Vaasma et al., 2017d).

	Pb-210 U(A)	Ra-226 U(A)	U-238 U(A)	K-40 U(A)	Ra-228 U(A)	Th-232 U(A)
Oil shale 2013 (Bq kg^{-1})	26.9	7.8	27.2	1.6	25.2	5.3
Oil shale 2014 (Bq kg^{-1})	23.7	7.3	30.2	2.3	27.5	7.4

Clear differences in the radionuclide activity concentrations can be observed between the sampling years (Figure 15).

Figure 15 indicates that ^{232}Th , ^{228}Ra and ^{40}K values were around 20% higher in the oil shale collected in 2014 and this is also represented in the higher values of the NID ashes collected in 2014. For ^{238}U and ^{226}Ra , these differences are over 2 times lower. The largest differences can be seen for ^{210}Pb . Although higher ^{210}Pb concentrations are found in the oil shale collected in 2013, the values in the NID ash are 16% lower in 2013. This indicates a greater concentration variability of ^{210}Pb in collected samples, most probably due its volatile nature, chemical form in the fuel, and redistribution processes within the combustion system.

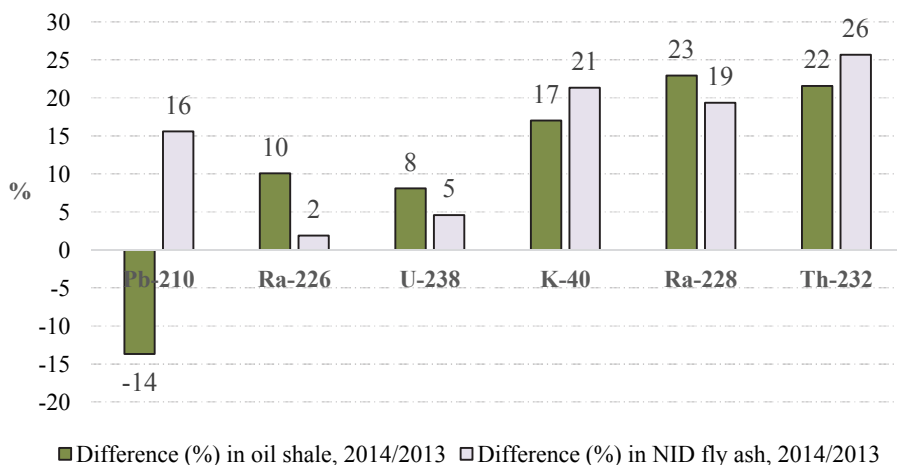


Figure 15. Radionuclide activity concentration differences (%) in oil shale and fly ash between 2014 and 2013 samples.

Results from the third sampling in 2014 from a PF boiler with ESPs showed that statistically significant differences were found between ^{210}Pb , ^{40}K and ^{232}Th values between the two samplings conducted in 2014. When the mean values were combined with the obtained standard deviations, all the results fell within the same range for all the radionuclides. The same oil shale was used during both samplings.

Based all the sampling results during the two years, it is possible to conclude that activity concentrations for all the measured radionuclides collected from identical deposition points remained in the same magnitude. No statistically significant differences between were found for ^{238}U and ^{226}Ra . Variations between ^{40}K , ^{228}Ra and ^{232}Th values are caused by the use of oil shale with somewhat varying radionuclide concentrations. The differences in ^{210}Pb values are most likely linked to its volatile nature and redistribution processes in the furnace. The obtained radionuclide activity concentrations coincide well with the values found in previous studies done on oil shale PPs. This provides additional confidence to the validity on previously published values.

Boiler's working parameters and radionuclide activity concentrations

The following boiler parameters (not exhaustive) were registered during sampling to assess the radionuclide concentration dependence on combustion parameters:

- Boiler steam capacity (t/h);
- Steam temperature ($^{\circ}\text{C}$);
- Flue gas temperature ($^{\circ}\text{C}$);
- Fly ash content in flue gas at 6% O_2 (g nm^{-3}).

The combustion boilers do not operate on a constant regime. The power output and working time fluctuate daily as well as seasonally. Variations in the boiler load influence the temperature distribution and the flue gas velocity within the boiler.

Regression analysis based on samples collected in 2013 showed weak or no correlation between the radionuclide activity concentrations and the boiler's combustion. Regardless of a few strong negative and positive correlations in single subsets, no constantly stable correlation trend was observed when including all the subsets. These few single strong correlations indicate to a random incident. None of the NID data showed statistically significance relationship between the described boiler parameters and radionuclide activity values at significance level $p < 0.05$. The findings provide clear evidence that the analyzed boiler parameters have no statistically significant ($p < 0.05$) effect on the radionuclide activity concentration values and suggest that the main influence will be the characteristics of the used fuel. However, it has to be stressed that the overall variations in flue gas temperatures were small (up to 20 °C). A stronger impact on radionuclide concentration levels due to larger differences in the temperature could be expected.

To conclude, non-volatile radionuclides, such as ^{238}U , ^{232}Th and Ra isotopes can be relatively well predicted in the fly ash according to their concentrations in the fuel and based on previous knowledge on the boiler type. More volatile elements, especially ^{210}Pb as well as ^{210}Po should be more frequently determined in the original fuel and in the fly ash fractions to obtain trustworthy radiological data. The results from the variation study also reassure that previously conducted samplings and results can be considered representative over a longer time period. This would be however valid only when the fuel with a similar composition is used and when the combustion boilers operate with a uniform setup (same boiler type and purification system). Any significant changes in the technological set up could introduce changes and larger variations also to the radionuclide enrichment levels in bottom and fly ashes.

Based on the analysis in paper VII and the work done by Lust and Realo, (2012), additional doses to habitats in dwellings arising from the use of the fly ash as building material would be below 1 mSv/a.

7.5 Volatile radionuclide emissions from oil shale-fired PPs (Based on publication VI)

Through the studies described in the previous paragraphs, we have characterized the radionuclide migration and mobility trends in various ashes and quantitatively estimated radionuclide activity concentration values in ash fractions from different type of combustion boilers. We have also demonstrated that the radionuclide concentration variations in the combustion system are mostly dependent on the input oil shale. Since similar types of oil shale have been used in the PPs, the radionuclide concentrations can be fairly well esti-

mated and predicted in the formed ashes. In addition to the ashes formed inside the combustion unit, it is important to estimate the magnitude of fly ash emissions from the PPs, which can pose a radiological hazard to the general public.

The enrichment factors in the ashes has been different between various radionuclides. According to (Coles et al., 1979; Klein et al., 1975), chemical elements (and radionuclides) have been categorized into three basic groups: volatile, semivolatile and none volatile elements. ^{210}Pb and ^{210}Po will be considered as volatile radionuclides, which has also been shown through the enrichment levels in measured oil shale ash fractions. These two radionuclides have also high dose coefficients, which means that inhaling or consuming water and food products contaminated with these radionuclides would increase the exposure to internal radiation, dominantly through their alpha and beta decay mechanisms. This increases the need to determine the magnitude of radionuclide emissions from the PPs in order to estimate the potential radiological impact to the public and the environment. ^{210}Pb and ^{210}Po have been shown to be the most abundant radionuclides emitted also from coal fired PPs (Coles et al., 1978; Corbett, 1983; Nowina-Konopka, 1993; S. K. Sahu et al., 2014; Vreček and Benedik, 2003). During the releases of radionuclides via fly ash and flue gases, radiological contamination has been detected near such PPs (Bem et al., 2002; Dinis et al., 2014; Flues et al., 2002; Hasani et al., 2014; Papp et al., 2002; Sert et al., 2011; Ugur et al., 2004). Due to the considerable half-lives of these isotopes, 22.2 years for ^{210}Pb and 138.4 days for ^{210}Po , their radiological burden on the environment can accumulate over a longer period.

Previous studies have shown that up to 30% of ^{210}Pb can be released via fly ashes and flue gases from the oil shale PPs (Realo and Realo, 1997; Vaasma et al., 2014a). Experimentally determined data on ^{210}Po emissions from oil shale PPs has been missing, largely due to the difficulties of establishing a suitable procedures for sampling and measurement. Thus the enrichment of ^{210}Po compared to ^{210}Pb in the fly ash fractions has not been previously precisely established.

^{210}Pb and ^{210}Po measurements from the escaping fly ash

In collaboration with researchers at the Tallinn University of Technology, fly ash sampling was conducted from Estonian and Baltic PPs. Samples were collected from the flue gas duct, prior the filters, from filters and after the purification systems (prior the stack) from a CFB boiler operating with ESPs and from a PF boiler operating with a NID system and bag filters. These are the main operating boiler set-ups nowadays, thus the obtained results would also be characteristic of future conditions. Majority of the particles emitted to the atmosphere remain under 2.5 μm for both boiler types. For PF boilers with NID system, particle size under 2.5 μm in the emitted fraction constitutes around 66%, compared to 54% for CFB boilers with ESPs.

Samples collected from the NID system demonstrated high activity concentration values for both ^{210}Pb and ^{210}Po (Figure 16).

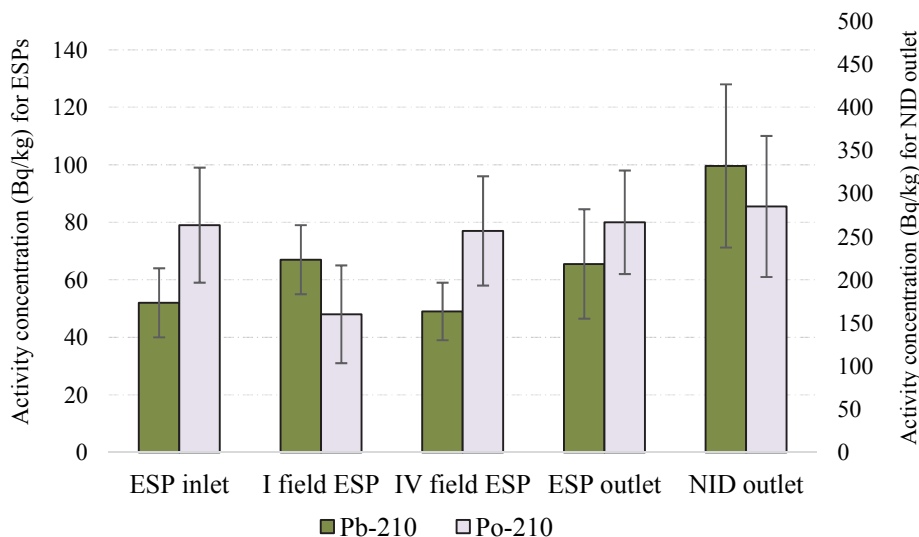


Figure 16. Pb-210 and ²¹⁰Po activity concentrations in various fly ash fractions of EPP and BPP. Data from (Vaasma et al., 2017c).

The results indicate that ²¹⁰Pb and ²¹⁰Po values in the CFB boiler ashes are well comparable in the limits of uncertainty. The ²¹⁰Pb activity concentration values range between $49 \pm 10 \text{ Bq kg}^{-1}$ (ESP field IV) and $67 \pm 12 \text{ Bq kg}^{-1}$ (ESP field I). These values are in rather close accordance to the ²¹⁰Pb values determined in a previous study (Vaasma et al., 2014a) on CFB boilers, where homogeneous activity distribution was determined in the fly ashes, ranging between 68 Bq kg^{-1} and 80 Bq kg^{-1} . ²¹⁰Po values are comparable to the ²¹⁰Pb ones, fluctuating between $48 \pm 17 \text{ Bq kg}^{-1}$ and $80 \pm 18 \text{ Bq kg}^{-1}$. These are however significantly lower to the values determined in the NID outlet, where an averaged ²¹⁰Pb values is $332 \pm 95 \text{ Bq kg}^{-1}$ and $285 \pm 82 \text{ Bq kg}^{-1}$ for ²¹⁰Po. The results shown in Figure 16 demonstrate average values of 2, 3 or 4 replicate samples depending on their available amount (2–3 for outlet sample, 3 for filter samples and 4 for inlet sample). The overall variations between the replicate samples are small. The calculated relative standard deviation values are around 3 times lower compared to the measurement's relative uncertainty values.

Differences in the radionuclide activity concentration values between the boiler types can be related to the technological set up of the purifications systems and flue gas temperatures after the filters. For the CFB boiler, temperature for emitted flue gases remains around $170 \text{ }^\circ\text{C}$, compared to $100 \text{ }^\circ\text{C}$ for the NID system. This affects the adsorption and condensation processes of ²¹⁰Pb onto particulate matter in the flue gases. It is suggested by Aunela-Tapola et al. (1998) that majority of the lead in the flue gases will be present as lead chlorides (mainly PbCl_2 , PbCl and PbCl_4). This is due to the formation process of Estonian oil shale – it was formed in a shallow sea bed near the coastline through the deposition of organic matter along with calcareous and clay

particles. The boiling point for lead chlorides remains under 1000 °C and as the temperature decrease, lead starts to condensate onto surfaces and fly ash particles. The chloride influence on lead volatilization has been also shown in coal-fired PPs (Linak, 1997).

The obtained results indicate that the ^{210}Pb and ^{210}Po concentrations are well comparable between one another in the same measured fly ash samples. The ration between ^{210}Pb and ^{210}Po in the escaping fly ash fractions is between 0.8 and 1.2. Similar ratio has been reported also in studies focusing on coal-fired PPs (Al-Masri et al., 2014; Corbett, 1983; Kaakinen et al., 1975). This ratio will be an important input in further atmospheric dispersion modelling calculations, when estimating ^{210}Pb and ^{210}Po fluxes over an extended period of time.

Considering the high purification efficiency (up to 99.9%) of NID filters on PF boilers and ESPs on CFB boilers to remove fly ash from flue gases, the amount of fly ashes emitted to the surrounding environment nowadays remains very low. Thus the radionuclide emissions have been reduced as well. Based on a previous study by Aunela-Tapola et al. (1998), it is expected that 97% of lead will be escaping attached particulate matter and up to 3% of lead will be in gaseous phase or attached to submicron particles. As the temperatures have further decreased due to the renovation of the purification systems, the proportion of gaseous phase may have been additionally reduced. The radionuclides attached to solid phase will be considered as the main carrier of radionuclides to the environment.

7.6 Modelling of radionuclide emissions from oil shale PPs (Based on publication VIII)

A validated Gaussian-plume model, AEROPOL (Kaasik, 2004, 2000; Kaasik and Kimmel, 2003) was used to conduct atmospheric dispersion modelling of fly ash and radionuclides emitted from the PPs in order to determine the quantity and a magnitude of fly ash and radionuclide deposition fluxes during different decades. 1975 was chosen as the starting year, during which both PPs were operating at full capacity.

Meteorological data for modelling was obtained from the Estonian Environment Agency, which is responsible for carrying out meteorological surveys under a continuous monitoring programme. Technological data concerning the PPs was obtained from the operator and collected from available literature (Eesti Energia AS, 1994a, 1994b; Paist, 2011).

7.6.1 Emissions through the years

There has been significant changes in amount of mined oil shale as well as quantities of emitted fly ash from the PPs between 1970 and nowadays (Figure 17).

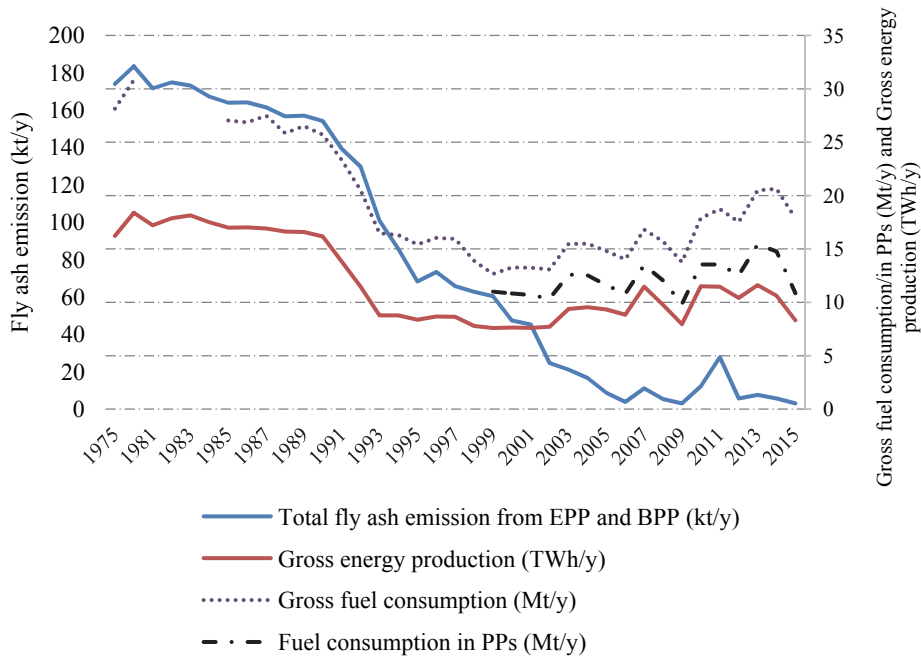


Figure 17. Total oil shale consumption in Estonia and the consumption in the PPs; fly ash emissions (values on the left vertical axis) and gross energy production by the PPs. Data from Environmental Agency, Statistics Estonia, Liblik and Maalma, (2005) and Punning et al. (1997) and Vaasma et al. (2017a).

The largest exploitation of oil shale has occurred in the 1970s and 1980s, with up to 30 millions of tonnes per year (Ministry of Finance, 2016). A significant decrease in the oil shale mining occurred in the 1990s, as seen in Figure 17, due to the collapse of the Soviet Union. Part of the produced electricity had been exported across the border and after this market shrank, the electricity production in the PPs decreased rapidly. The gross energy production of the (TWh y^{-1}) as well as the total fly ash emissions from the PPs follows the same pattern as fuel mining and consumption. This is due to the fact that majority of the mined oil is used for electricity production in the PPs. The rest is used by other smaller power plants as well as to produce shale oil and fine chemistry.

Multiple technological improvements have been carried out on the PPs at different time stages, which have significantly reduced the amount of emitted fly ash (described also in chapter 3.2). It is expected that the emission rates in the future will remain in the same range or will be reduced somewhat further, depending on the national strategy of oil shale exploitation.

7.6.2 Radionuclides concentrations in the emitted fly ash fractions

The radionuclide activity concentrations in the emitted fly ash has been regularly studied during the past 5–6 years (Vaasma et al., 2017c, 2017d, 2016, 2014a, 2014b). As described in Chapter 7.4, the main factors influencing the radionuclide variations in the formed fly ash fractions were the radionuclide content in the input fuel. Other selected boiler parameters did not demonstrate significant correlation with radionuclide concentrations in fly ash. Thus having the information on radionuclide content in oil shale, it is possible to provide more precise estimations on the radionuclide concentrations in the fly ash during various PPs operational periods. To put the values in a broader context, comparison with radionuclide activity concentrations determined in various studies on coal and coal fly ash are brought out in Table 5. It can be seen that the values vary significantly. This depends on the geology of the mining location, type of coal (lignite, subbituminous, bituminous and anthracite) and its physicochemical characteristics. Values in the fly ash are additionally affected by the employed combustion technology.

Radionuclide activity concentration values (Table 5) used to model radionuclide atmospheric dispersion were derived from available studies in oil shale PPs (Realo et al., 1996; Realo and Realo, 1997; Vaasma et al., 2017c, 2017d, 2014a, 2014b). During time periods where radionuclide enrichment levels in the emitted fly ash were not directly available, certain approximations were made. This included data derivation from studies done on microelement emissions (Aunela-Tapola et al., 1998; Häsänen et al., 1997; Pets et al., 1985; Reinik et al., 2013) on the same PPs and also using the radionuclide enrichment data found on studies done on coal-fired PPs (Coles et al., 1979; Kaakinen et al., 1975; Mann et al., 1978; Nowina-Konopka, 1993). A more detailed description and justification of the derived radionuclide concentration values in the emitted fly ash fraction can be found in (Vaasma et al., 2017a).

The values shown in Table 5 can be subjected to changes of some magnitude over the modelled time periods. However, the PPs have been operating mostly on PF type of boilers and similar type of oil shale which has been dominantly mined locally. Thus the radionuclide concentrations in the fuel have been well comparable (Novikova and Knizhnikov, 1985; Realo et al., 1996), helping to provide additional confidence in the validity of the obtained data and its representativeness over a longer time period.

Table 5. Radionuclide activity concentrations in oil shale, various coals and corresponding fly ashes. The table is an extended version from (Vaasma et al., 2017a).

Country	Material	Radionuclide activity concentrations (Bq/kg)							Reference
		U-238	Ra-226	Pb-210	Th-232	Ra-228	K-40		
Estonia	Oil shale	16	14	15	7		135	(Realo and Realo, 1997)	
	Oil shale fly ash	64	61	102	30		1103		
Estonia	Oil shale	22-28	24-30	23-27	12-17	12-16	360-535	(Vaasma et al., 2017d, 2014a, 2014b)	
	Oil shale fly ash	54-76	56-91	73-109	29-40	32-52	1100-1640		
United States	Coal	6-43	7-42	6-37		6-19		(Lauer et al., 2015)	
	Coal fly ash	85-341	93-325	70-483		53-139			
Brazil	Coal	18-807	27-698	41-1745		20-100	136-1230	(Flues et al., 2007)	
	Coal fly ash	64-1424	62-1284	150-3232		52-174	534-1668		
Spain	Coal	20-30	22-37		15-30		148-310	(Charro and Pena, 2013)	
	Coal fly ash	103	128		88		860		
Turkey	Coal		56-356		4-39		40-243	(Gür and Yaprak, 2010)	
	Coal fly ash		291-1260		12-118		121-658		
Greece	Coal	243 (117-399)	266 (44-236)	134 (59-205)		18 (9-14)	108 (59-227)	(Papastefanou, 2010)	
	Coal fly ash	356 (263-950)	366 (142-605)	275 (133-428)		50 (27-68)	297 (204-382)		
Poland	Coal	13-39	10-28	13-35	9-20		44-153	(Bem et al., 2002)	
	Coal fly ash	94-185	54-119	44-264	48-92		449-758		
Serbia	Coal	43 (18-71)	29 (14-52)		21 (11-32)		120 (45-243)	(Janković et al., 2011)	
	Coal fly ash	129 (21-246)	120 (45-270)		72 (29-121)		360 (174-489)		
India	Coal		24 (11-67)		39 (19-93)	39 (19-93)	83 (15-444)	(Mishra, 2004)	
	Coal fly ash		78 (41-152)		126 (96-178)	126 (96-178)	374 (148-840)		
China	Coal		21-61		21-73		60-187	(Lu et al., 2011)	
	Coal fly ash		46-148		59-165		123-343		
Australia	Coal	25 (9-47)	21 (19-24)	28 (20-33)	24 (17-29)	34 (11-69)	75 (23-140)	(Fardy et al., 1989)	

7.6.3 Deposition of emitted fly ash and radionuclides

The largest fly ash deposition rates ($\text{mg m}^{-2} \text{d}^{-1}$) in the surrounding area of the PPs have been during the 1970s and 1980s with maximum over $300 \text{ mg m}^{-2} \text{d}^{-1}$ nearby the PPs. The deposition flux depends on amount of burned oil shale, installed filter systems, combustion technology, and height of the stacks as well as meteorological conditions. Nowadays the fly ash deposition has been significantly reduced, remaining between 6 and $2 \text{ mg m}^{-2} \text{d}^{-1}$ in the vicinity of the PPs (Vaasma et al., 2017a). Majority of the radionuclides are carried to the environment via fly ash, only a small fraction of more volatile elements remain in the gaseous phase, thus the radionuclide deposition fluxes follow the same trend as fly ash.

Figures 18–23 show the deposition rates of ^{210}Pb in surrounding area. ^{210}Pb as well as ^{210}Po emissions from the PPs are higher compared to other radionuclides found in oil shale (Vaasma et al., 2017c) and have the highest radiological burden on the surrounding environment.

Selected figures are taken from (Vaasma et al., 2017a) where a more precise description on the deposition during various years is found. The grid area is $60 \times 70 \text{ km}$ (60 km from north to south), with one square kilometer resolution. The radionuclide deposition maps focus on the area that remains within the Estonian borders. PPs are marked as triangles on the maps.

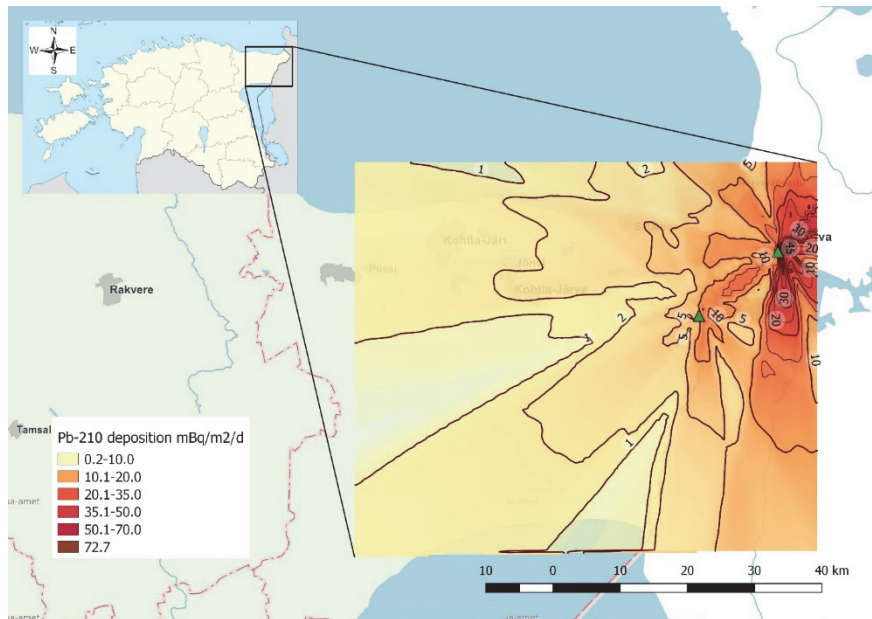


Figure 18. ^{210}Pb deposition ($\text{mBq m}^{-2} \text{d}^{-1}$) in 1975.

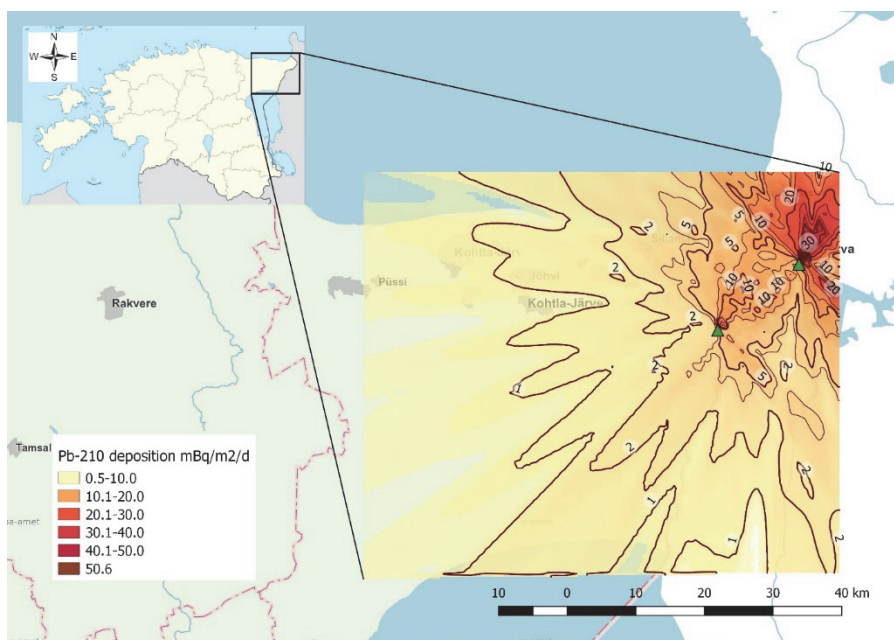


Figure 19. ^{210}Pb deposition ($\text{mBq m}^{-2} \text{d}^{-1}$) in 1980.

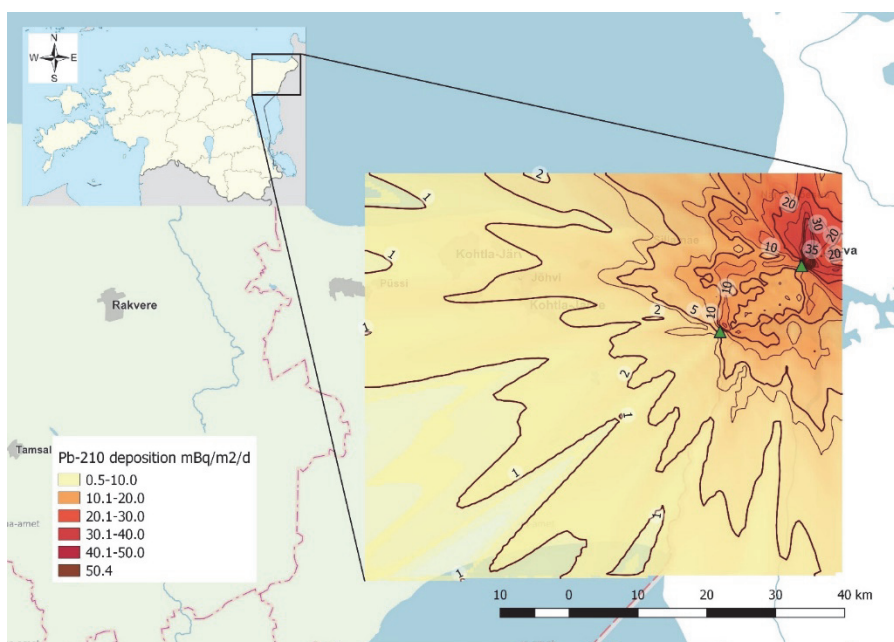


Figure 20. ^{210}Pb deposition ($\text{mBq m}^{-2} \text{d}^{-1}$) in 1990.

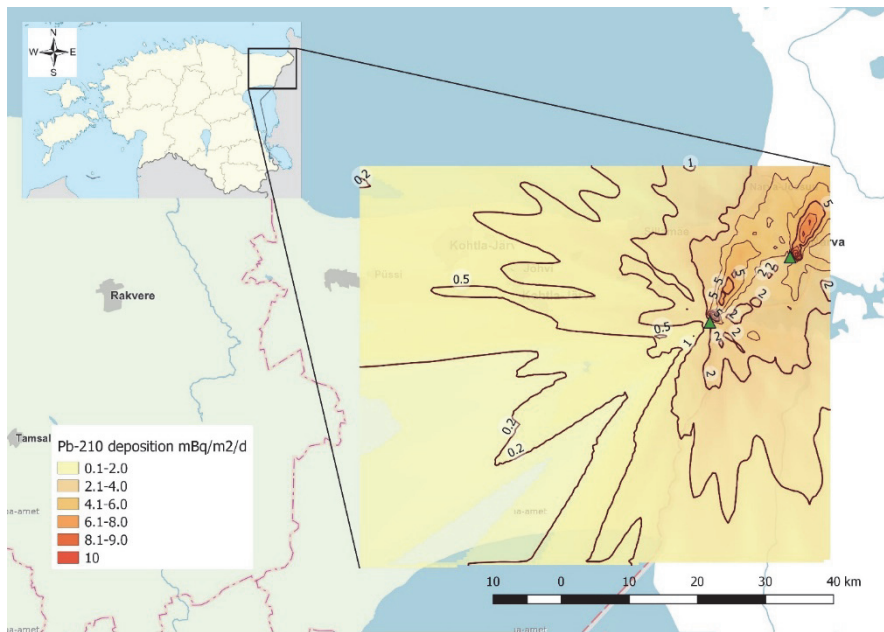


Figure 21. ^{210}Pb deposition (mBq m⁻² d⁻¹) in 2000.

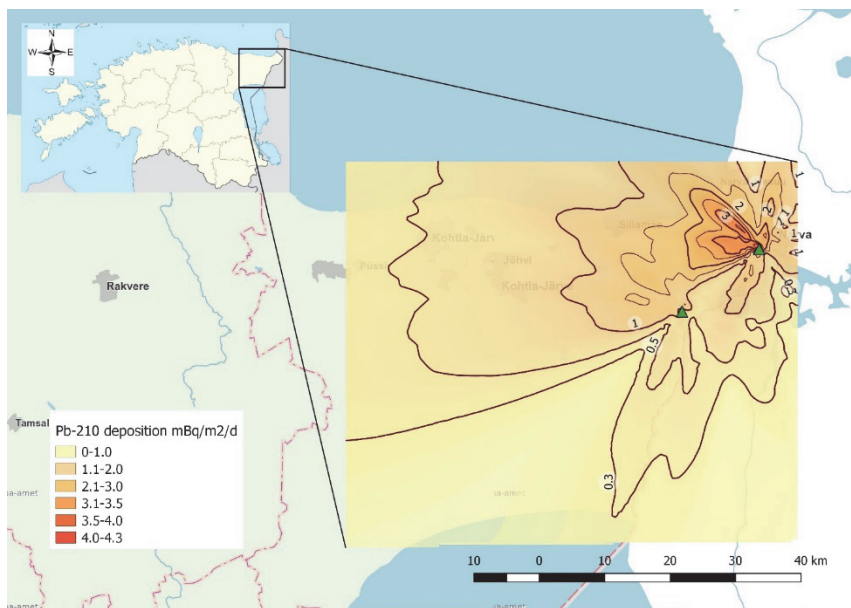


Figure 22. ^{210}Pb deposition (mBq m⁻² d⁻¹) in 2010.

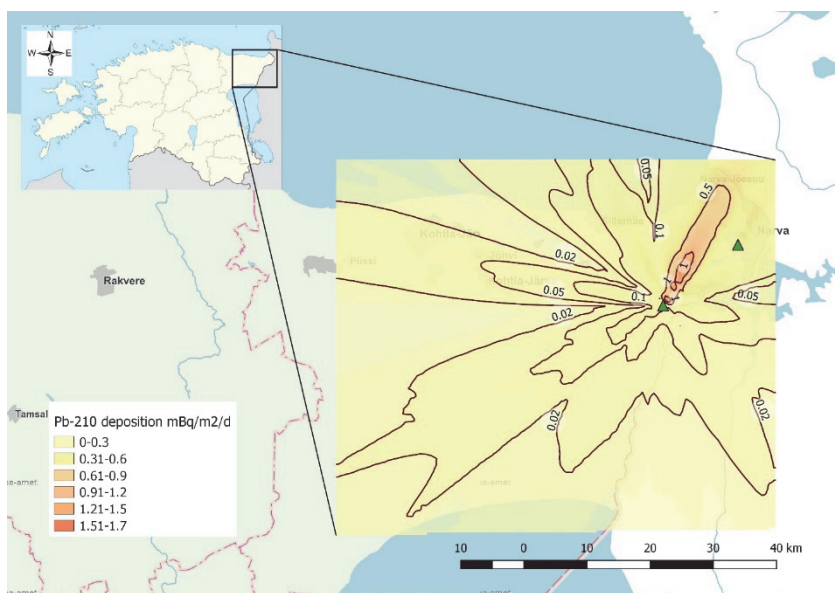


Figure 23. ^{210}Pb deposition ($\text{mBq m}^{-2} \text{d}^{-1}$) in 2015.

The deposition maps of 1975 and 1980 indicate that the majority of pollution is transported towards north east due to the prevailing winds. The amount of fly ash and radionuclides deposited within Estonian borders is thus reduced. The maximum values remain within couple of km from the PPs. The distance of maximum deposition has changed during time with the modifications of the number and height of the stacks. The demolition of shorter stacks has reduced the deposition peak nearby the PPs.

The maximum ^{210}Pb deposition values in 1975 reached up to $73 \text{ mBq m}^{-2} \text{d}^{-1}$ near the BPP. This however rapidly decreased down to $46 \text{ mBq m}^{-2} \text{d}^{-1}$ within the next kilometers. A similar trend is also observable for 1980, with a sharply decreasing deposition gradient away from the PPs. Maximum values remain around $50 \text{ mBq m}^{-2} \text{d}^{-1}$ in the 1980. About 30 km from the PPs towards inland, the deposition fluxes have dropped to $5 \text{ mg m}^{-2} \text{d}^{-1}$ and $1 \text{ mBq m}^{-2} \text{d}^{-1}$ for fly ash and ^{210}Pb , respectively.

In 1990, the ^{210}Pb deposition fluxes remained at a similar level as in the 1980s. Near the BPP, ^{210}Pb deposition remained between 20 and $40 \text{ mBq m}^{-2} \text{d}^{-1}$ compared to $5\text{--}15 \text{ mBq m}^{-2} \text{d}^{-1}$ nearby the EPP. During the 1990s there was a significant reduction in the amount of burned oil shale and production of electricity. Also, large renovation works started in 1998 to replace the existing filter systems with newer ones, which significantly reduced atmospherically emitted fly ash amount. This led to the reduction in fly ash and ^{210}Pb deposition around the PPs in 2000. The maximum ^{210}Pb deposition flux remained between 5 and $10 \text{ mBq m}^{-2} \text{d}^{-1}$ near the PPs and below $1 \text{ mBq m}^{-2} \text{d}^{-1}$ at distances of 20–30 km from the PPs (towards inland). It can be also seen that these transitions have more or less evened out the emission fluxes from the PPs.

From the 2000s, the emissions from the BPP have fluctuated significantly due to continuing renovations at the PP. Also the atmospheric emissions have been reduced even further, whereas ^{210}Pb deposition remained below $5 \text{ mBq m}^{-2} \text{ d}^{-1}$ nearby the PPs and below $1 \text{ mBq m}^{-2} \text{ d}^{-1}$ 10–20 km from the PPs. The meteorological conditions have clear impact on the orientation of the deposition plume. It is more toward the west in 2010 and toward the northeast in 2015. Thus there will be yearly differences on the amount of radionuclides deposited in the surrounding area.

Considering the exploitation of oil shale and the technological changes conducted at the PPs, it can be expected that the deposition fluxes of fly ash and radionuclides will remain similar to the situation determined in 2015, which is almost 60 times less compared to the pollution burden in the 1980s.

During the long PPs exploitation period, significant amounts of fly ash and radionuclides have been emitted to the surrounding environment, where they have accumulated. In terms of ^{210}Pb deposition, the PPs have constituted around 20–28% (near the PPs) of the deposition flux compared to natural background values during the high time of oil shale combustion. Nowadays this has been reduced to below 1%. For the other radionuclides (e.g. ^{210}Po), the PPs have in many instances been the major sources of additional radionuclide deposition load on the nearby environment. Previous study by Realo et al. (1998) has shown that a 30-year cumulative fly ash deposition in surrounding area has resulted in annual doses up to $200 \mu\text{Sv a}^{-1}$. This radiological burden from the PPs cannot be left neglected and up-to-date evaluations on the magnitude of additional doses posed on human population and non-human biota nearby the PPs should be conducted (in the light of new and accurate technological and emission data). Some parallels can be drawn with studies done on coal-fired PPs (Amin et al., 2013; Bem et al., 2002; Cevik et al., 2008; Dinis et al., 2015; Flues et al., 2002; Papp et al., 2002; Zeevaert et al., 2006). Similarly to the oil shale PPs, increased deposition rates of fly ash and radionuclides nearby coal-fired PPs were determined that lead to elevated radionuclide concentrations in soil samples collected nearby the PPs.

7.7 Environmental sampling from the north-east of Estonia (Based on publication V)

The potential radiological impact from the oil shale PPs on the surrounding environment was first brought under discussion in the 1990's. Fly ash deposition rate up to $0.25 \text{ kg m}^{-2} \text{ a}^{-1}$ has been reported around the area of the PPs (Realo et al., 1996). Due to the complex and diverse geological conditions in north-eastern Estonia, the range and magnitude of the PPs' radionuclide deposition load has not been easy to assess. Areas with significant ^{226}Ra and ^{210}Pb anomalies, partially related to locally found alum shale deposits, have made distinguishing between natural radionuclide non-equilibriums and fly ash induced increased levels challenging (Realo and Realo, 2005, 2001). One

possibility is to analyze sample cores from ombrotrophic peat deposits that have the potential to provide additional estimations on the range of fly ash and radionuclide deposition from the PPs.

7.7.1 Peat samples from an ombrotrophic peat bog

Ombrotrophic *Sphagnum*-dominated peat bogs are effective in adsorbing particulate matter and pollutants deposited from the atmosphere, which makes such peat bogs valuable indicators of atmospheric pollution (Gstoettner and Fisher, 1997; Komárek et al., 2008; Shotyk et al., 2002; Weiss et al., 1999; Vile et al., 2000). Approximately 22% of Estonia's territory is covered with peatlands. Many of such peatlands have been directly affected by industry such as mining and combustion of fossil fuels (Hiemaa et al., 2014; Punning et al., 1997). One of such is the Selisoo mire (Figure 24), located in the north-east of Estonia, approximately 40 km from the large oil shale PPs. Due to the large stack height (up to 250 m) and the significant emission loads from the stacks, several authors have shown that the fly ash particles from the PPs can be transported to considerable distances from the source (Tiiu Alliksaar, 2000; Kaasik et al., 2005; Karofeld, 1996b).

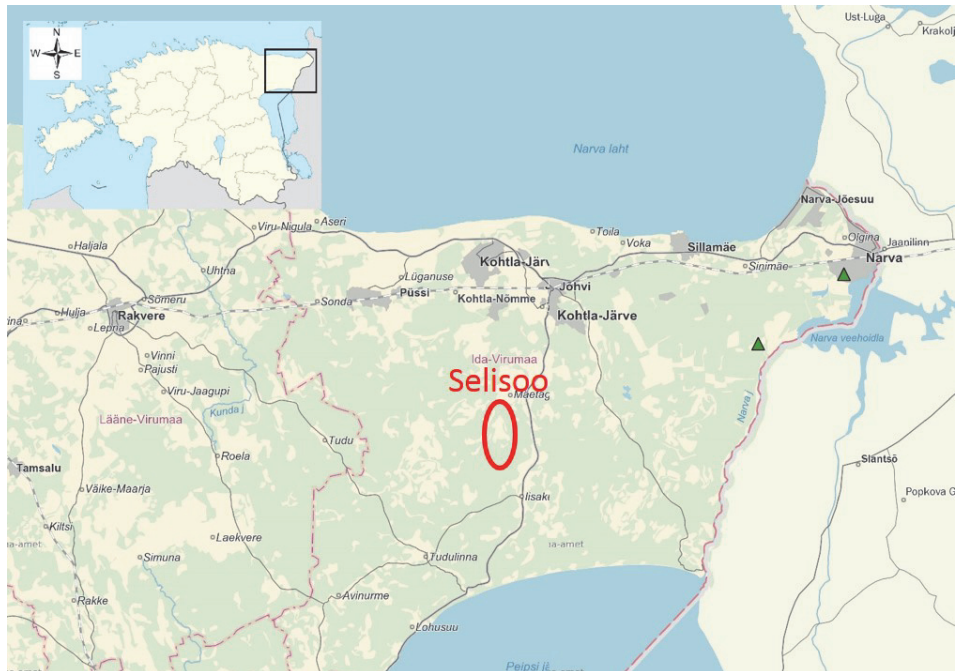


Figure 24. Selisoo mire and the distance from oil shale-fired PPs.

Two 30 cm long peat cores were taken from the Selisoo mire, sliced into 1 cm sublayers (2 cm at the top) and directed for gamma spectrometric and spherical fly ash particle (SFAP) measurements. SFAP are created during high combustion temperatures (up to 1400–1500 °C) and consist of aluminosilicates formed by fusion of inorganic minerals. These particles can be well distinguished from other solid material within the sample due to their dominating spherical shape (Figure 25) (Alliksaar et al., 1998; Tiiu Alliksaar, 2000). Methods described by Alliksaar et al., (1998) and Wik and Renberg, (1996) were the basis for such work.

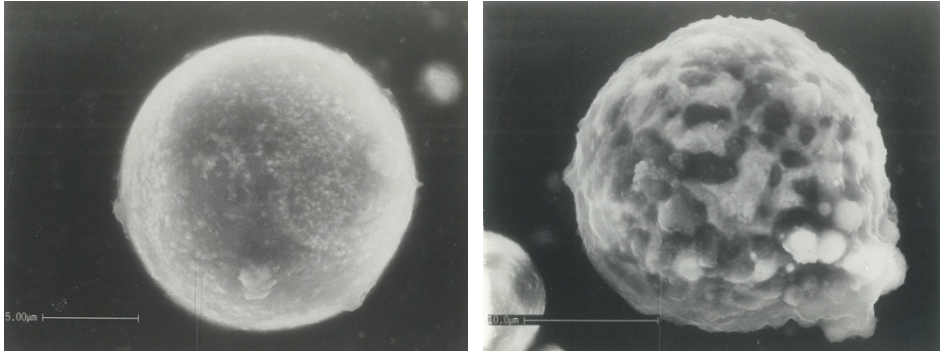


Figure 25. Images of SFAP. Data from (Vaasma et al., 2017b).

SFAP can be applied as tracer to determine the periods during which the industrial activities and atmospheric emissions have been greater. The particles are resilient to environmental conditions and only minimally migrate in peat cores as shown by (Punning and Alliksaar, 1997). These properties give SFAP the potential to be used as markers in determining the influx of fly ash particles and radionuclides from oil shale PPs. Similar particles from fossil fuel PPs have been successfully used for such purposes by other authors (Rose and Juggins, 1994; Wik and Renberg, 1996). The concentration of SFAP in fly ash, magnitude and distance of the SFAP dispersion from the PPs were based on the works of other authors (Tiiu Alliksaar, 2000; Kaasik et al., 2008, 2005, 1999).

Results from the peat core analysis

Initially, one of the aims prior collecting the peat cores was to determine if the additional influx of ^{210}Pb from the PPs in the Selisoo area can be detected. Secondly, there was an interest to assess, if SFAP in the peat cores can be quantified. Both the SFAP and ^{210}Pb exhibit a similar change in their concentration values along the depth of a collected peat core (Figure 26).

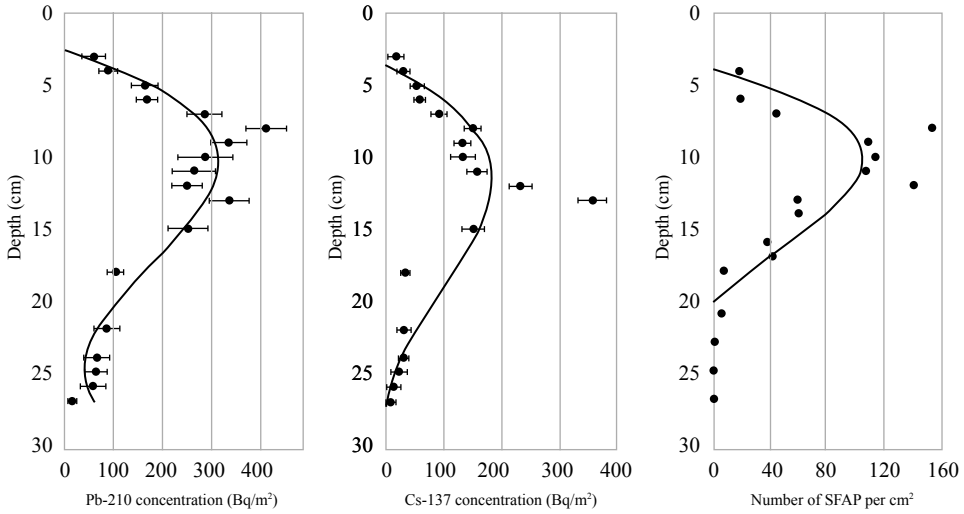


Figure 26. ^{210}Pb , ^{137}Cs (both Bq m^{-2}) and SFAP (number per cm^2) concentrations in the collected peat core. Data from (Vaasma et al., 2017b).

To smoothen the fluctuating data, a polynomial trendline was applied to convey the overall trend of the changes in concentrations in relation to depth. The maximum ^{210}Pb (413 Bq m^{-2}) and SFAP (154 per cm^2) concentration remain between 6 and 15 cm. From there on, the values decrease with increasing depth. At the depth of 26–27 cm, both values are close to 0. The ^{226}Ra and ^{238}U concentrations remained dominantly below the detection level, which indicates that the determined ^{210}Pb is considered as unsupported fraction and is derived from atmospheric deposition. Also, it is important to note that 1 cm of peat at different depths includes varying years of peat accumulation. The top layers consist of growing moss and are more voluminous. The lower layers are already more decomposed and compressed, containing also more years of accumulated peat compared to top layers. The bulk density (g cm^{-3}) analysis of the peat layers suggest that at the depth of 6–8 cm, there is a transitional layer from the growing part of the moss to a partially decomposed part. This explains the higher concentrations in these layers, as ^{210}Pb has not yet significantly decayed and also more years have been compacted to a single layer. Based on the yearly ^{210}Pb flux in the Selisoo area ($133 \text{ Bq m}^{-2} \text{ y}^{-1}$) and predicted fly ash influx via oil shale PPs ($5\text{--}50 \text{ mg m}^{-2} \text{ d}^{-1}$), it was shown that ^{210}Pb deposition load from the PPs ($0.2\text{--}2 \text{ Bq m}^{-2} \text{ y}^{-1}$) constitutes only a small fraction of the natural background. Thus at 40 km from the PPs, the radionuclide deposition load can be considered negligible. This knowledge leads the conclusion that the correlation between ^{210}Pb and SFAP seen in Figure 26 is random. ^{210}Pb values are influenced by the nature of the peat and its decomposition. Concentration of SFAP in the core depends additionally on the emission loads from the oil shale

PPs. These happen to coincide in way, which may lead to false conclusions – i.e. there is a significant influx of ^{210}Pb from the PPs.

SFAP are considered to have low mobility and high resilience to environmental conditions and the corresponding concentration change indicates to periods with higher emission loads (described in chapter 7.6). Due to the inert and stable characteristics of SFAP, they can act as potential tracers in chronological studies. When combining such data with radiometric measurements (^{210}Pb , ^{241}Am and ^{137}Cs) more reliable results could be obtained for dating purposes. Thus the SFAP can act as an indicator that helps to identify the age of the peat layers in areas that are industrially affected. The ^{137}Cs peak between 10 and 15 cm in Figure 26 (unpublished data) indicate to the Chernobyl fallout in 1986. As ^{137}Cs is partially taken up by plants and released again after the plants have died, the initially sharp peak has been smeared between various layers over time. However, the maximum concentration is still well distinguishable.

Also, a second peat core was obtained in close vicinity. The concentration curves for the second core were different from the first one. Exact values and longer description is available in Vaasma et al. (2016b). However, the concentration trends for ^{210}Pb and SFAP follow similar trend within the parallel core. Similarly to the first core, the differences in bulk density of the layers helps to explain these variations. The differences between these cores demonstrate the heterogeneity of peat, as samples taken from only 10 meters apart can exhibit clear dissimilarities. This is often due to small-scale variability in bog microtopography – hummocks are alternating with hollows and the conditions for peat accumulation differ (Ninemets et al., 2011). However, the peat cores clearly demonstrate that the fly ash from the oil shale PPs has reached the Selisoo area and indicate the differences in emission intensities at different time periods. At this point, it is not possible to provide exact fly ash deposition quantification based on the SFAP measurement, but it has been initiated as a results of these findings and similar research conducted previously (Tiiu Alliksaar, 2000; Kaasik et al., 2005). It has also given ground to try to use SFAP as additional markers in age dating models to identify the age of the peat layers. This in turn is relevant to determine yearly peat accumulation rates and possibly determine periods, when the peat growth has been influenced by human activities i.e. mining, draining and fuel combustion.

It is important to include as much available environmental sampling data as possible to provide higher representativeness of the modelling results. This can be done through radionuclide as well as SFAP measurements in the surrounding areas.

Other environmental samples

Measurements of naturally occurring radionuclides in environmental samples, such as soil and peat have been scarce and irregular. However, snow samples have been regularly collected by other authors during past three decades in the northern Estonia in order to determine the concentration of deposited fly ash in the surrounding area. These samples have been analyzed for their anion, cation

and elemental composition to connect this data with source origin – oil shale PPs. The results from these samplings, partially published by Kaasik et al. (2000), were also applied to validate the model output against the deposition fluxes obtained via snow samples.

Separately to total fly ash, SFAP has been determined in sediment, moss, ice and snow samples (Alliksaar et al., 1998; Tiiu Alliksaar, 2000; Alliksaar and Punning, 1998). Such studies provide a good platform to assess the areal magnitude of fly ash and SFAP deposition, which in turn can be used to validate modelling results.

8. CONCLUSIONS

The current thesis focuses on providing the input to radiologically characterize the oil shale-fired PPs in Estonia. The EPP and BPP have been operational for approximately 50 years, during which time significant emissions to the environment have occurred. Although the magnitude of various organic and inorganic pollutants emitted from the PPs have been repeatedly estimated and measured, before this work, little and outdated data has been available on radiological characteristics of the formed ash fractions. The work conducted within this study has shown:

1. The activity concentration of naturally occurring radionuclides in oil shale used by Estonian PPs remains at a similar level as in surrounding soil. During high temperature combustion processes in the PPs, these radionuclides become enriched in fly ash fractions. The highest enrichment occurs for more volatile radionuclides such as ^{210}Po and ^{210}Pb , where concentrations can be up to 10 times higher in the emitted fractions compared to the values in oil shale.
2. The behavior and enrichment of radionuclides in the ash fractions depends on multiple factors: the type of combustion technology (PF or CFB boilers); the purification technology (ESPs or NID with bag filters); prevailing temperatures in the furnace and flue gas duct; size and specific surface area of the formed ash particles as well as characteristics and chemical composition of the used oil shale. The radionuclide concentrations in ash fractions formed in PF and CFB boilers have noticeable differences. Higher enrichment values were determined for PF (with ESPs) fly ashes, while the radionuclide content in bottom ash showed some levels of depletion for volatile radionuclides. Boilers operating with NID system and bag filters are very efficient of removing fly ash from flue gases. However, the very fine fraction escaping the filters, dominantly below $2.5\ \mu\text{m}$, are highly enriched with ^{210}Po and ^{210}Pb .
3. Results from comprehensive multi-day samplings over a 2 year period demonstrate that the radionuclide activity concentration variations in fly ashes are dominantly caused by the differences in the input oil shale. The investigated boiler operational parameters have a small or untraceable effect in influencing radionuclide concentration changes. This gained knowledge provides higher reliability in assessing the radionuclide concentration processes in this type of boiler systems.
4. The obtained knowledge on radionuclide enrichment processes combined with fly ash and radionuclide emission studies provides the basis to estimate the radionuclide emission loads from the PPs. It can be concluded that the emissions per unit of produced energy ($\text{Bq Gwh}_{\text{el}}^{-1}$) from the PPs prior the renovation works that started at the end of 1990s is comparable with similar type of coal fired PPs. At present, this has been reduced 1 to 2 orders of magnitude. The reduction of burned oil shale, installation of CFB boilers and

multiple renovations done on the purification systems have significantly reduced the environmental impact of the PPs when comparing different time periods.

5. Analysis of collected peat and snow samples collected by other authors has aided to determine the size of the affected area and deposition fluxes of fly ash and radionuclides from the PPs. Results indicate that the emitted fly ash can be transported at distances over 50 km from the source, depending on the height of the stacks. However, the deposition fluxes at such long distances have been significantly reduced and do not possess considerable environmental hazards.
6. Modelling results conducted for various periods starting from 1975 and until 2015 have demonstrated a significant change in the radionuclide deposition fluxes. Over a long exploitation period of these PPs, the radionuclide deposition fluxes have been reduced around 60 times. The largest deposition rates have remained within couple of km from the PPs. During the high time of oil shale combustion, the additional radionuclide load from the PPs has been comparable or exceeded the deposition values otherwise expected from the natural background processes. Due to the prevailing wind direction towards the northeast, majority of the pollution plume has been transported across the Estonian border. On the other hand, yearly fluctuations in the meteorological conditions have also revealed years when the Estonian inland has received larger deposition fluxes.

The long operational period of the oil shale PPs has caused an accumulation of deposited radionuclides in the surrounding environment. Due to the long half-life of these radionuclides, they will remain present in or nearby the deposition location for extended periods. Thus, the potential radiological impact from the PPs cannot be left neglected. Available data has indicated that cumulative doses to the public and the environment during the PPs working period can be considerable, particularly near the sources. Quantitative studies on the doses received by most exposed members of the public (e.g local farmers) in the vicinity of the PPs through various pathways (inhalation, ingestion, immersion, cloudshine and groundshine) should be conducted, in the light of findings presented in this thesis. Considering the transition of oil shale exploitation, similar studies on shale oil production should be carried out as well.

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SUMMARY IN ESTONIAN

Looduslike radionukliidide kontsentreerumine põlevkivi põletamisel ning nende atmosfäärne levi ja sadenemine elektrijaamade ümbruses

Käesoleva doktoritöö eesmärk on kiirguskaitseks karakteriseerida Eesti põlevkivi elektrijaamad ning hinnata sealt atmosfääri emiteeritavate radionukliidide kontsentratsioonid ja nende leviala ulatus. Eesti ja Balti elektrijaamad on töötanud juba ca 50 aastat, mille jooksul on atmosfääri paisatud märkimisväärne kogus erinevaid saasteühendeid. Kuigi erinevate orgaaniliste ning anorgaaniliste saasteühendite heitkoguseid on korduvalt ja põhjalikult mõõdetud ning hinnatud, on puudu ajakohastest ning põhjalikest andmetest põlevkivituhas sisalduvate radionukliidide aktiivsuse kontsentratsioonidest. Seda puudujääki asuti täitma käesoleva tööga. Selle käigus on välja selgitatud:

1. Põlevkivis sisalduvate looduslike radionukliidide aktiivsuse kontsentratsioonid on samas suurusjärgus võrreldes ümbritsevas pinnases tuvastatuga. Põlevkivi põletuskateldes toimub aga nende kontsentreerumine lendtuha fraktsioonidesse. Enim on rikastunud atmosfääri emiteeritavad tuhaosakesed (paljuski tulenevalt suurest eripinnast) ning seda just lenduvate radionukliididega, nagu ^{210}Pb ja ^{210}Po .
2. Radionukliidide kontsentreerumine tuhkades sõltub paljudest teguritest: kasutatav tehnoloogia (tolmpõletus- või keevkihtkatlad); rakendatavad puhastussüsteemid (elektrifiltrid või väävlipuhastusseadmed); temperatuurid katlakäigus; tuhaosakeste aerodünaamiline diameeter ning eripind ning kasutatava põlevkivi füüsikalised-keemilised omadused. Tolmpõletuskatelde elektrifiltri lendtuhkades tuvastati kõrgemad radionukliidide kontsentratsioonid võrreldes keevkihtkateldes tuvastatuga. Sealjuures olid kolde-tuhad lenduvatest radionukliididest vaesestunud. Väävlipuhastusseadmetega töötavatest kateldest emiteeritavad lendtuha kogused on madalamad võrreldes elektrifiltritega töötavatest kateldest, kuid vastav lendtuhk on suuremal määral ^{210}Pb ja ^{210}Po ga rikastunud.
3. Andmed ulatuslikust proovivõtuseeriast 2 aasta jooksul demonstreerisid, et põhiline faktor, mis mõjutab radionukliidide aktiivsuse kontsentratsiooni varieeruvusi katlasüsteemis on põlevkivi omadused. Hinnatud katla tööparameetrid omasid väiksemat mõju radionukliidide kontsentratsioonide muutusele. Vastavate tulemuste alusel on võimalik suurema usaldusväärsusega hinnata radionukliidide kontsentreerumisprotsesse põletuskateldes.
4. Eesti ja Balti elektrijaamast enne filtersüsteemide renoveerimist 1990' date lõpus keskkonda emiteeritud radionukliidide summaarsed aktiivsused toodetud elektrienergia kohta ($\text{Bq Gwh}_{\text{el}}^{-1}$) jäid samasse suurusjärku sarnast tüüpi kivisöe elektrijaamadega. Tänapäevaks on see hulk vähenenud 1–2 suurusjärku tänu ulatuslikele renoveerimistödele nii filtersüsteemide kui ka katla-tüüpide osas. Samuti tulenevalt väiksemast põlevkivi põletamiskogustest.

5. Olemasoleva kirjanduse ning kogutud keskkonnaproovide analüüsi põhjal nähtus, et jaamadest emiteeritud põlevkivi lendtuhk võib kanduda üle 50 km sisemaale. Siiski on sellistel kaugustel lendtuha sadenemiskoormused märkimisväärselt vähenenud ning ei oma ohtu keskkonnaseisundile.
6. Lendtuha ning radionukliidide modelleerimistulemused perioodil 1975–2015 demonstreerisid suuri muutusi sadenemiskoormuste osas jaamade ümbruses, näidates ca 60-kordset vähenemist jaamade töötamise algusperioodist tänapäevaks. Suurimad sadenemiskoormused on jaamade lähistel, mõne kilomeetri raadiuses. Seal on ka mitmete lenduvamate radionukliidide sadenemishulgad ületanud looduslike protsesside tagajärjel esinevaid sadenemishulki. Tulenevalt domineerivatest tuultest kirde suunas, on suurem osa saasteemissioonidest kantud Eesti piirest eemale. Samas täheldati aastakäike, mil meteoroloogiliste olude tõttu domineeriv osa emiteeritud saastest Eesti sisemaale kanti.

Tulenevalt Eesti ja Balti elektrijaamade aastakümnete pikkusest tööajast on ümbritsevasse keskkonda paisatud ning seal akumulunud märkimisväärne hulk radionukliide. Tulenevalt paljude radionukliidide pikast poolestusajast, jäävad need sadenenud asukohtadesse või nende lähedusse pikkadeks ajaperioodideks. Sellest tulenevalt on möödapääsmatu hinnata vastavate põlevkivi elektrijaamade radioloogilist keskkonkakoormust. Edasised täiendavad kvantitatiivsed hinnangud emiteeritud ning sadenenud radionukliidide poolt põhjustatud kiirgusdooside osas on vajalikud. Seda nii töötajate, elanike kui ka keskkonna osas läbi erinevate doosiradade (sissehingamine, – söömine ja väline kiiritus). Tulenevalt põlevkivi kasutamise strateegiatest tulevikus, oleks vajalik samaväärseid uuringuid ning hinnanguid läbi viia ka põlevkivi õlitööstuste osas.

PUBLICATIONS

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Education

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2010–2012 University of Tartu, Faculty of Science and Technology, master's studies in Environmental Technology. Graduated *cum laude*
2006–2010 University of Tartu, Faculty of Science and Technology, bachelor's studies in Environmental Technology.

Professional employment

2015–2017 Junior scientist position under project: “Nationwide study to prepare for the implementation of the requirements from the Council Directive 2013/59/EURATOM to national legislation”.
2015 Specialist in developing and maintaining a functioning quality system in the gamma spectrometric measurement laboratory.

Field of research

Environmental radioactivity, naturally occurring radioactive material (NORM), radionuclide enrichment processes, radiochemistry, gamma-ray spectrometry, alpha-particle spectrometry.

Professional trainings

2017 “Assessing Risk to Humans and the Environment”, NMBU, Norway.
2016 “3rd Training School on reuse of NORM in building materials”, NTUA, Greece
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2015 “Exchange competence on nuclear measurements techniques for radionuclide determination in NORM”, Ege University, Turkey.
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Publications

1. **Vaasma, Taavi**; Kaasik, Marko; Loosaar, Jüri; Kiisk, Madis; Tkaczyk, Alan Henry (2017). Long-term modelling of fly ash and radionuclide emissions as well as deposition fluxes due to the operation of large oil shale-fired power plants. *Journal of Environmental Radioactivity*, 178–179, 232–244. doi:10.1016/j.jenvrad.2017.08.017.
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3. **Vaasma, Taavi**; Loosaar, Jüri; Kiisk, Madis; Tkaczyk, Alan Henry (2017). Radionuclide concentration variations in the fuel and residues of oil shale-fired power plants: Estimations of the radiological characteristics over a 2-year period. *Journal of Environmental Radioactivity*, 173, 25–33. doi:10.1016/j.jenvrad.2016.10.005.
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6. **Vaasma, Taavi**; Bitjukova, Liidia; Kiisk, Madis; Özden, Banu; Tkaczyk, Alan Henry (2016). Behaviour mechanisms and correlation between lead (Pb) and its isotope ²¹⁰Pb in industrial residue as an indicator for waste characterization. *Environmental Technology*, 37 (24), 3208–3218, doi:10.1080/09593330.2016.1181673.
7. **Vaasma, Taavi**; Kiisk, Madis; Realo, Enn; Loosaar, Jüri; Tkaczyk, Alan H. (2016). Radionuclide concentration variations in residues from potential NORM industries in Estonia: the example of oil shale-fired power plants. *Book of Abstracts: V. Terrestrial Radioisotopes in Environment International Conference on Environmental Protection, 17.05 –20.05.2016, Veszprem, Hungary*. Editors: Tibor Kovács, Edit Tóth-Bodrogi, Gergő Báto. Veszprem, Hungary: Social Organization for Radioecological Cleanliness, 30.
8. **Vaasma, Taavi**; Kiisk, Madis; Tkaczyk, Alan Henry (2016). The process and progress of implementing the requirements from the new BSS to the Estonian legislation: issues with NORM. *EANNORM: 8th Workshop: EANNORM: 8th Workshop “Three years into the new EU BSS: How far have we come with the transposition and what is the impact on NORM industrial activities?”*, 5–7 December 2016, Stockholm. Editors: Markos Koufakis; Astrid Schellenberger; Hartmut Schulz. *EANNORM*, 1.

9. **Vaasma, Taavi**; Karu, Helen; Kiisk, Madis; Pensa, Margus; Tkaczyk, Alan Henry (2015). Pb-210 and fly ash particles as indicators of industrial impact in peatlands. In: Proceedings of the 3rd International Conference on Po and Radioactive Pb Isotopes (65–71).
10. **Vaasma, Taavi**; Tkaczyk, Alan H.; Kiisk, Madis; Realo, Enn; Suursoo, Siiri; Isakar, Kadri; Jantsikene, Alar (2015). Overview of NORM-related research conducted at the University of Tartu, Estonia. Abstracts of the NordicNORM 2015 Workshop: Nordic NORM 2015 workshop, 15.09-16.09.2015, Helsinki, Finland. Editor: Liisa Sirkka. Helsinki, Finland: STUK (Radiation and Nuclear Safety Authority), 13.
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Haridus

2012–2017 Tartu Ülikool, Füüsika Instituut, doktoriõpe
keskkonnatehnoloogia erialal.
2010–2012 Tartu Ülikool, Füüsika Instituut, MSc (*cum laude*)
keskkonnatehnoloogia erialal.
2006–2010 Tartu Ülikool, Füüsika Instituut, BSc keskkonnatehnoloogia
erialal.

Teenistuskäik

2015–2017 Nooremteaduri positsioon projektis: “Uuring direktiivi
2013/59/EURATOM looduslike radioaktiivsete ainete (NORM)
nõuete ülevõtmise ettevalmistamiseks riigisisesele
õigusloomesse”.
2015 Spetsialist. Gammaspetsimeetria mõõtelabori
kvaliteedisüsteemi eest vastutamine.

Teadustöö põhisuunad

Looduslikud ioniseeriva kiirguse allikad, looduslikult esinev radioaktiivne
materjal (NORM), radionukliidide rikastusprotsessid, radiokeemia, gamma-
spektrometria, alfaspektrometria

Erialased koolitused

2017 “Assessing Risk to Humans and the Environment”, NMBU, Norra.
2016 “3rd Training School on reuse of NORM in building materials”, NTUA,
Kreeka
2016 “Training course on atmospheric dispersion modelling and risk assess-
ment”, SCK•CEN, Belgia
2015 “Training course on environmental risk assessment and the ERICA
tool”, TÜ, Eesti.
2015 “Exchange competence on nuclear measurements techniques for
radionuclide determination in NORM”, Ege University, Türgi.
2015 “Course on naturally occurring radioactive material (NORM) in the
environment”, GIG, Poola.
2013 “Training on Practical Gamma-ray Spectrometry”, TÜ, Eesti.
2010 “Radioactive Waste Management Technology and Infrastructure”, TU
Clausthal, Saksamaa.

Publikatsioonid

1. **Vaasma, Taavi**; Kaasik, Marko; Loosaar, Jüri; Kiisk, Madis; Tkaczyk, Alan Henry (2017). Long-term modelling of fly ash and radionuclide emissions as well as deposition fluxes due to the operation of large oil shale-fired power plants. *Journal of Environmental Radioactivity*, 178–179, 232–244. doi:10.1016/j.jenvrad.2017.08.017.
2. **Vaasma, Taavi**; Loosaar, Jüri; Gyakwaa, Francis; Kiisk, Madis; Özden, Banu; Tkaczyk, Alan Henry (2017). Pb-210 and Po-210 atmospheric releases via fly ash from oil shale-fired power plants. *Environmental Pollution*, 222, 210–218. doi:10.1016/j.envpol.2016.12.054.
3. **Vaasma, Taavi**; Loosaar, Jüri; Kiisk, Madis; Tkaczyk, Alan Henry (2017). Radionuclide concentration variations in the fuel and residues of oil shale-fired power plants: Estimations of the radiological characteristics over a 2-year period. *Journal of Environmental Radioactivity*, 173, 25–33. doi:10.1016/j.jenvrad.2016.10.005.
4. **Vaasma, Taavi**; Karu, Helen; Kiisk, Madis; Pensa, Margus; Isakar, Kadri; Realo, Enn; Alliksaar, Tiiu; Tkaczyk, Alan Henry (2017). Pb-210 and fly ash particles in ombrotrophic peat bogs as indicators of industrial emissions. *Journal of Environmental Radioactivity*, 174, 78–86. doi:10.1016/j.jenvrad.2016.07.027.
5. Ozden, Banu; **Vaasma, Taavi**; Kiisk, Madis; Tkaczyk, Alan Henry (2017). A modified method for the sequential determination of ²¹⁰Po and ²¹⁰Pb in Ca-rich material using liquid scintillation counting. *Journal of Radioanalytical and Nuclear Chemistry*, 311 (1), 365–373. doi:10.1007/s10967-016-4984-1.
6. **Vaasma, Taavi**; Bitjukova, Liidia; Kiisk, Madis; Özden, Banu; Tkaczyk, Alan Henry (2016). Behaviour mechanisms and correlation between lead (Pb) and its isotope ²¹⁰Pb in industrial residue as an indicator for waste characterization. *Environmental Technology*, 37 (24), 3208–3218, 10.1080/09593330.2016.1181673.
7. **Vaasma, Taavi**; Kiisk, Madis; Realo, Enn; Loosaar, Jüri; Tkaczyk, Alan H. (2016). Radionuclide concentration variations in residues from potential NORM industries in Estonia: the example of oil shale-fired power plants. *Book of Abstracts: V. Terrestrial Radioisotopes in Environment International Conference on Environmental Protection, 17.05–20.05.2016, Veszprem, Hungary*. Editors: Tibor Kovács, Edit Tóth-Bodrogi, Gergő Báto. Veszprem, Hungary: Social Organization for Radioecological Cleanliness, 30.
8. **Vaasma, Taavi**; Kiisk, Madis; Tkaczyk, Alan Henry (2016). The process and progress of implementing the requirements from the new BSS to the Estonian legislation: issues with NORM. *EANNORM: 8th Workshop: EANNORM: 8th Workshop “Three years into the new EU BSS: How far have we come with the transposition and what is the impact on NORM industrial activities?”*, 5–7 December 2016, Stockholm. Editors: Markos Koufakis; Astrid Schellenberger; Hartmut Schulz. *EANNORM*, 1.

9. **Vaasma, Taavi**; Karu, Helen; Kiisk, Madis; Pensa, Margus; Tkaczyk, Alan Henry (2015). Pb-210 and fly ash particles as indicators of industrial impact in peatlands. In: Proceedings of the 3rd International Conference on Po and Radioactive Pb Isotopes (65–71).
10. **Vaasma, Taavi**; Tkaczyk, Alan H.; Kiisk, Madis; Realo, Enn; Suursoo, Siiri; Isakar, Kadri; Jantsikene, Alar (2015). Overview of NORM-related research conducted at the University of Tartu, Estonia. Abstracts of the NordicNORM 2015 Workshop: Nordic NORM 2015 workshop, 15.09-16.09.2015, Helsinki, Finland. Editor: Liisa Sirkka. Helsinki, Finland: STUK (Radiation and Nuclear Safety Authority), 13.
11. **Vaasma, Taavi**; Kiisk, Madis; Meriste, Tõnis; Tkaczyk, Alan H. (2014). The enrichment behavior of natural radionuclides in pulverized oil shale-fired power plants. *Journal of Environmental Radioactivity*, 138, 427–433.10.1016/j.jenvrad.2014.02.027.
12. **Vaasma, Taavi**; Kiisk, Madis; Meriste, Tõnis; Tkaczyk, Alan H. (2014). The enrichment of natural radionuclides in oil shale-fired power plants in Estonia – The impact of new circulating fluidized bed technology. *Journal of Environmental Radioactivity*, 129, 133–139.10.1016/j.jenvrad.2014.01.002.
13. Kiisk, Madis; **Vaasma, Taavi**; Özden, Banu; Realo, Enn; Tkaczyk, Alan Henry (2014). Natural radionuclides in the combustion products of oil shale-fired power plants in Estonia. EU-NORM 2 Book of abstracts: EU-NORM 2 Symposium, Prague, Czech Republic, June 17–19, 2014. 44.
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