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Radionuclide concentration variations in the fuel and residues of oil shale-fired power plants: Estimations of the radiological characteristics over a 2-year period

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ABSTRACT

Several multi-day samplings were conducted over a 2-year period from an oil shale-fired power plant operating with pulverized fuel type of boilers that were equipped with either novel integrated desulphurization system and bag filters or with electrostatic precipitators. Oil shale, bottom ash and fly ash samples were collected and radionuclides from the ^{238}U and ^{232}Th series as well as ^{40}K were determined. The work aimed at determining possible variations in the concentrations of naturally occurring radionuclides within the collected samples and detect the sources of these fluctuations. During the continuous multi-day samplings, various boiler parameters were recorded as well. With couple of exceptions, no statistically significant differences were detected (significance level 0.05) between the measured radionuclide mean values in various ash samples within the same sampling. When comparing the results between multiple years and samplings, no statistically significant variations were observed between ^{238}U and ^{226}Ra values. However, there were significant differences between the values in the fly ashes when comparing ^{210}Pb, ^{40}K, ^{228}Ra and ^{232}Th values between the various samplings. In all cases the radionuclide activity concentrations in the specific fly ash remained under 100 Bq kg^{-1}, posing no radiological concerns when using this material as an additive in construction or building materials. Correlation analysis between the registered boiler parameters and measured radionuclide activity concentrations showed weak or no correlation. The obtained results suggest that the main sources of variations are due to the characteristics of the used fuel. The changes in the radionuclide activity concentrations between multiple years were in general rather modest. The radionuclide activity concentrations varied dominantly between 4% and 15% from the measured mean within the same sampling. The relative standard deviation was however within the same range as the relative measurement uncertainty, suggesting that the main component of fluctuations is derived from the measurement method and approach.

The obtained results indicate that representativeness of the data over a longer time period is valid only when a fuel with a similar composition is used and when the combustion boilers operate with a uniform setup (same boiler type and purification system). The results and the accompanying statistical analysis clearly demonstrated that in order to obtain data with higher reliability, a repeated multi-day sampling should be organized and combined with the registered boiler technical and operational parameters.

1. Introduction

Estonian oil shale has been exploited almost for 90 years in oil as well as fine chemistry production, and as fossil fuel in oil shale-fired power plants (PPs).Burning oil shale has produced various atmospheric emissions including pollutants such as SO_x, NO_x, heavy metals, and total suspended particles (TSP) (Kaasik et al., 2008, 1999; Karofeld, 1996; Pensa et al., 2004). During the last decades, significant efforts have been made to reduce the environmental impact of the oil shale industry: (1) the reduction of fly ash and other pollutant emissions by installing higher efficiency purification systems and filters, (2) the installation of two advanced and efficient boilers at Narva power plants, (3) improved efficiency in oil shale mining, and (4) enhanced management of heaps and

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landfills of residue ash (Loosaar et al., 2009; Pihu et al., 2012; Plamus et al., 2011).

The activity concentrations of naturally occurring radionuclides in the ashes of the two large PPs have been studied during the 1990's and in 2013 (Realo et al., 1996; Realo and Realo, 1997; Vaasma et al., 2014a, 2014b). These studies have indicated that the natural radionuclides found in oil shale become significantly enriched in finer ash fractions (enrichment factor up to 8) depending on the used fuel, technology and boiler types. This gives reason to believe that due to the emissions of fly ash, the radionuclides carried to the surrounding environment can pose additional radiological burden. These studies are however based on one time samplings, which always leave a degree of uncertainty concerning the representativeness of the data. The operational parameters of the combustion boilers can change in time, which affect the radionuclide enrichment levels in the deposited ash fractions. Currently there is no data available on how various combustion parameters (boiler load, steam production, temperatures in the flue gas duct and concentration of ash particles) could impact the radionuclide concentration levels. It is important to create this knowledge in order to properly evaluate the radiological aspects that are related to oil shale combustion. This also includes evaluation of the situations when this fly ash is used in road construction, agriculture as well as in construction sector. In order to estimate the radiological influence from this material during different time periods, one has to be sure about the validity of the radiological parameters. There is partial data available (Lust, 2012) concerning the radiological features of various building materials where oil shale fly ash has been used. By providing an estimation of the radionuclide enrichment trends in the formed ash fractions, we can predict the radiological features of these construction products in a more long-term prospect. There is an extended interest of using waste materials and residues as a secondary material and in construction activities through such programmes as COST NORM4-Building and REDMUD (European Commission, 2014; European Cooperation in Science and Technology (COST), 2013). There is a high interest of providing thorough and extended overview about the radiological characteristics of these types of materials. Also the European Union member states are increasingly establishing additional surveillance and control on industries that are producers of material containing natural radionuclides (NORM). Especially, the new European Union Council Directive 2013/59/EURATOM (European Parliament, 2014) obliges the EU member states to determine the exposure to workers and to the public in industries producing and processing NORM, pushing countries to invest more into to research connected with NORM issues.

By determining the variations in the activity concentrations of ^{238}U and ^{232}Th series radionuclides, we could be able to make longer term estimations on the radionuclide behavior and enrichment trends within the combustion system. Characterizing the current situation can be the basis for future predictions on the radionuclide concentrations processes, eliminating the need to conduct excessive samplings and measurements. It can also verify or elaborate the results obtained from previous studies. The gathered knowledge can be used to estimate the historical impact of these PPs during periods of higher fuel consumption and atmospheric emission loads. This work aims to demonstrate how an extended sampling period combined with the determination of combustion boiler's working parameters helps to guarantee reliable results and provide the basis to critically assess previously collected data.

2. Study object

The two large oil shale-fired PPs are located in the North-East of Estonia. These are the world's largest oil shale PPs with the total installed power capacity of 2030 MW_{el}. These PPs have been operational since the 1960's, during which significant changes in the technological set up have been made. Over time higher efficiency filter systems such as electrostatic precipitators (ESP) and novel integrated desulphurization (NID) and $deNO_x$ systems with bag filters have been installed.

The main combustion technology applied is pulverized fuel (PF) type of boilers. In the 2000's two new circulating fluidized bed (CFB) boilers were installed – one in Eesti and one in Balti PP. The main PF boiler types are TP-67 and TP-101. Within the same type, the combustion systems have similar setup. This allows to extend the obtained results within the same type of combustion systems when same sort of fuel is used. Thorough overview of the technological parameters can be found in Ots (2006).

The amount of oil shale burned annually in these power plants remains nowadays between 9 and 13 million tonnes. Approximately half of it is left as ash after the combustion process. Depending on the used technology, the fraction of bottom and fly ash vary (Ots, 2006; Plamus et al., 2011).

The used oil shale originates from Estonia mine and from Narva quarry. This oil shale contains natural radionuclides from the ^{238}U and ^{232}Th series as well as ^{40}K. The enrichment processes of these radionuclides vary between bottom and fly ash fractions. As a general rule, the finer ash fractions are more enriched with these radionuclides (Realo and Realo, 1997; Vaasma et al., 2014a). But these trends depend also on the used combustion technology, as seen when comparing results from this study with the available ones (Realo et al., 1996; Realo and Realo, 1997; Vaasma et al., 2014a).

3. Materials and methods

3.1. Sample collection

Oil shale, bottom ash and fly ash samples were collected ($n = 40$) in 2013 during a 6-day continuous sampling period. During a 4-day sampling in 2014 oil shale and fly ash samples ($n = 15$) were obtained from the same energy block. Samples were collected from a PF boiler operating with NID system and bag filters. An additional 4-day sampling was conducted in 2014 during which fly ash samples ($n = 8$) were collected from a PF boiler with an ESP. The PF boilers have identical technological setup, which also allows to compare the obtained measurement results. The sampling was done from the same collection points during each day. The average amount of collected samples (analytical sample, averaged and divided) remained around 500 g for oil shale 1000 g for bottom ash and 10–20 g for fly ash samples. Oil shale was a combined 24 h sample collected periodically from the conveyer belt prior the fuel bunker of the boiler with stationary sampling machine. Bottom ash was gathered from a specific ash deposition point and fly ash samples were collected prior the different inlets of the NID units (4 on each boiler) and prior an ESP. The fly ash samples were collected isocinetically using Munktell quartz fibre cup shape filters type MK360.

Various boiler and combustion parameters were also registered during the sampling. These included (not conclusive):

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

These parameters were registered manually as well as automatically by the power plant operation and control system.