DOCTORAL THESIS

Hazardous Properties of Ash Generated in Estonia and Possibilities to Reduce the Hazardousness

Mari-Liis Ummik

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

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signature

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Contents

List of Publications

The list of author's publications, on the basis of which the thesis has been prepared:

I **Ummik, M.-L.**, Järvik, O., Reinik, J., Konist, A. Ecotoxicity assessment of ashes from calcium-rich fuel combustion: contrasting results and regulatory implications. Environmental Science and Pollution Research, 2024, 31, 48523−48533. https://doi.org/10.1007/s11356-024-34387-3

II **Ummik, M.-L.**, Järvik, O., Konist, A. Dioxin concentrations and congener distribution in biomass ash from small to large scale biomass combustion plants. Environmental Science and Pollution Research, 2024, 31, 58946−58956. https://doi.org/10.1007/s11356-024-35141-5

III **Ummik, M.-L.**, Tamm, K., Järvik, O., Nešumajev, D., Roosalu, K., Pihu, T., Konist, A. Quantification of oil shale industry ash flows – their chemical and mineralogical composition. Oil Shale, 2025, 42(2), 129−166. https://doi.org/10.3176/oil.2025.2.01

IV **Ummik, M.-L.**, Järvik, O., Konist, A. Environmental advantages of oil shale ash as a secondary raw material: a focus on dioxin levels. Oil Shale, 2026, 43(1), 1–30. https://doi.org/10.3176/oil.2026.1.01

Author's Contribution to the Publications

Contribution to the papers in this thesis are as follows:

I Participated in the conceptualisation of the study in collaboration with all co-authors. Contributed to the development of the methodology and the validation of results. Responsible for drafting the original manuscript.

II Contributed to the study's conceptual design in cooperation with all co-authors. Assisted in methodology development and result validation. Took the lead in writing the original manuscript.

III Involved in conceptualising the study and developing the methodology alongside co-authors. Partially conducted the experimental and analytical work. Contributed to result validation and took part in drafting and revising the manuscript.

IV Took the lead in conceptualising the study and designing the methodology. Oversaw the validation of results. Responsible for drafting and revising the manuscript in close collaboration with co-authors.

Introduction

Over the past five decades, the global population has surged, surpassing 8.2 billion in 2025 and significantly increasing the demand for natural resources [1]. Given the planet's finite resources, the traditional linear business model – produce, use, dispose – has become unsustainable. In response, the European Commission introduced the Circular Economy Action Plan (CEAP) [2], promoting sustainable production and consumption. The CEAP focuses on minimising waste and maximising resource use, ensuring materials are retained in the economy for as long as possible. Any unavoidable waste is recycled, reducing reliance on virgin materials.

One area where these principles are increasingly relevant is the energy sector. Globally, the combustion of fossil fuels, biomass, and waste generates large volumes of ash and gas-cleaning residues. Biomass, in particular, has become a key source of renewable energy. In 2022, global use of energy from solid biofuels reached approximately 60 EJ, with continued growth projected [3]. This expansion contributes to the annual production of roughly 80 million tonnes [4] of biomass ash, a figure that is expected to continue rising.

Estonia offers a focused example of these challenges and opportunities at the national level. Estonia's primary solid fuel for producing electricity and heat is oil shale. Oil shale is used in power plants to produce electricity and heat, as well as in the shale oil industry. In Estonia, power production and shale oil production generate approximately 5 million tonnes of ash each year [5].

Until 2020, oil shale ash was classified as hazardous waste, which significantly limited its reuse potential. In contrast, biomass ash has not been considered hazardous, and its recovery is well established. As a result, while biomass ash is almost entirely recovered, oil shale ash continues to be largely landfilled despite its growing recognition as a potential secondary raw material [5].

In 2023, about 33 000 TJ of solid biofuels were used in Estonia for heat and electricity generation in dedicated combustion facilities, with 16 000 TJ consumed in combined heat and power plants [6]. This process produced 14 460 tonnes of fly ash and 24 513 tonnes of bottom ash (excluding household sources). Notably, approximately 99% of this biomass ash was successfully recovered [5].

Following thorough research by Tallinn University of Technology and University of Tartu [7], the legislation was amended, and oil shale ash was reclassified as non-hazardous waste. However, some uncertainty remains regarding the future classification of oil shale ash and other types of ash. In particular, there is no widely accepted methodology for assessing the ecotoxicity of ashes, leaving the issue unresolved and creating uncertainty for their future utilisation.

Another growing concern in the use of secondary raw materials – especially ashes – is the potential presence of hazardous substances such as dioxins. These persistent organic pollutants (POPs) are known for their long-term toxicity and environmental persistence [8].

In the EU, the management of POPs is regulated by the POPs Regulation, which was updated in 2022 to expand the list of recognised toxic substances and tighten the limit values for dioxins in recoverable waste [9, 10]. Stricter thresholds also apply when ashes are used in fertilisers, as defined by the Fertilising Products Regulation [11]. These increasingly stringent standards reflect growing awareness of the potential environmental and health risks associated with secondary raw materials.

The circular economy plays a crucial role in promoting sustainability, with the use of secondary materials being a key component. However, the safe use of these materials must be ensured. Pollution – one of the three pillars of the global triple planetary crisis – remains a critical challenge. As such, the circular economy must not only be resource-efficient but also uphold high standards for environmental protection and human health. At the same time, it is important to avoid excessive regulation and to consider the full life cycle of materials, ensuring that already generated resources are not unnecessarily landfilled but instead effectively reintegrated into the economy.

Research Objectives and Novelty

Estonia's energy independence relies heavily on oil shale resources, which have supported the country's energy system for decades. Unlike many European nations that depend on imported fuels, Estonia generates most of its electricity from domestically mined oil shale. This ensures a stable and secure energy supply. The importance of this approach has been underscored by the war in Ukraine, which highlighted the risks of relying on energy imports from Russia and reinforced the necessity of domestic energy security.

The oil shale sector generates a significant amount of ash, which has traditionally been disposed of and not fully recognised as a valuable by-product of the energy sector. In 2015, the EU revised its waste classification legislation, prompting Estonia to address the classification of oil shale ash. While biomass ash and coal ash were classified as non-hazardous waste, oil shale ash was left in an unfair position regarding its recovery potential. With the changes in EU legislation, oil shale ash was re-evaluated and compared to coal ash, leading to its reclassification.

However, not all hazardous properties of oil shale and biomass ashes have been thoroughly investigated. This research aims to systematically explore the hazardous substances present in the ashes produced in Estonia. Special attention is given to ecotoxicity, concentrations of heavy metal(loid)s, and POPs such as dioxins, which may pose significant risks to human health and the environment. The study evaluates whether the presence and behaviour of these substances could impede the potential recovery and reuse of ash. In addition, different ash fractions collected from several combustion facilities – each employing somewhat different technologies and process configurations – are examined separately. For each facility, ash was sampled from multiple collection points throughout the combustion and flue-gas cleaning systems to determine whether specific ash fractions, process stages, or facility technologies are associated with more hazardous characteristics than others. Factors such as toxicity and leaching potential are critically assessed in relation to current environmental regulations and the feasibility of recovery.

The first objective of this research is to characterise and describe the physical and chemical properties of oil shale and biomass ashes produced in Estonia, including differences between ash fractions and combustion technologies. For oil shale ash, this is addressed in **Paper III**; for biomass ash, in a Master's thesis [12] supervised by the author.

The second objective is to investigate the hazardous properties of ash and its different fractions, including:

- Ecotoxicological effects using biological assays **(Paper I)**,
- Concentrations of hazardous substances such as heavy metal(loid)s and dioxins **(Papers II, III, and IV)**,
- Leaching behaviour of potentially toxic elements (for oil shale ash, **Paper III**; for biomass ash, Master's thesis [12] supervised by the author).

The third objective is to compare the content of hazardous substances with regulatory thresholds, including those under EU waste, POPs, and fertilising product regulations, and to assess their implications for ash classification and recovery potential **(Papers II, III, and IV)**.

The fourth objective is to analyse how combustion technologies and operational conditions influence the hazardousness of ash, and to explore whether certain practices can reduce environmental risks and improve the potential for safe reuse **(Papers I, II, III, and IV)**.

The novelty of this research lies foremost in presenting the first-ever comprehensive analysis of dioxin concentrations in both oil shale ash and biomass ash generated in Estonia, thereby filling a significant national and scientific knowledge gap. To date, very limited data are available on the presence or levels of dioxins in Estonian ashes, despite their potential regulatory and environmental relevance.

Beyond this, the study offers a comprehensive, multi-parameter hazard characterisation of ash types, integrating chemical composition, leaching behaviour, and ecotoxicological testing across multiple ash fractions. The research applies a systematic approach to oil shale ashes, examining ashes from different oil shale processing facilities that are currently in active use in Estonia. By sampling and analysing ash from multiple process stages and technologies within these facilities, the study provides a structured and comparative assessment of their ash characteristics.

Furthermore, the research brings new insights into the regulatory ambiguity surrounding the classification of ashes, particularly regarding ecotoxicity (HP14) and POP content. By critically evaluating current EU and national regulatory thresholds, this work contributes to ongoing discussions on how hazardous properties may affect material recovery pathways – an essential but often overlooked dimension of circular economy implementation.

Research Contribution and Dissemination

The findings of this research offer substantial contributions to both scientific knowledge and practical decision-making in the field of waste management, environmental safety, and circular economy implementation.

For regulators and policymakers, the research provides a scientific evidence base to support the development and refinement of environmental regulations, particularly in relation to hazard classification, ecotoxicity (HP14) assessment, and dioxin content thresholds. By systematically analysing the chemical, ecotoxicological, and leaching behaviour of oil shale and biomass ash, the study helps clarify whether these materials meet existing safety standards for recovery, reuse, or landfilling. It also contributes to the interpretation and potential revision of regulatory frameworks, such as the EU POPs Regulation, the Waste Framework Directive, and the Fertilising Products Regulation. In particular, the research informs discussions on the feasibility and scientific justification for establishing or adjusting limit values for dioxins and other hazardous substances in secondary materials.

For industry stakeholders, including power plant and oil shale industry operators, construction or material recovery companies, and farmers, the study provides critical insights into the composition, hazardousness, and environmental behaviour of the ash they generate or seek to utilise. This knowledge can support risk assessments, product development, and compliance strategies, particularly for companies aiming to valorise ash as a raw material in applications such as construction, soil amendment, or CO_2

mineralisation. The findings can also inform fuel quality management – especially for biomass plants – by identifying the implications of feedstock composition (e.g. the presence of treated wood) for ash hazardousness.

The dissemination of this research through peer-reviewed publications and engagement with regulatory agencies ensures that the findings contribute to both academic discourse and real-world implementation. By bridging data gaps and proposing scientifically grounded recommendations, the study supports the transition towards a safer, more transparent, and circular use of industrial by-products in Estonia and potentially in other regions facing similar energy and material challenges.

Abbreviations

APH	Air preheater
BA	Bottom ash
CCA	Chromated copper arsenate
CLP	Classification, labelling and packaging
CY	Cyclone
CFBC	Circulating fluidised bed combustion
EC	Electrical conductivity
ECO	Economiser
ESP	Electrostatic precipitator
EU	European Union
FA	Fly ash
FF	Fabric filter
HE	Heat exchanger
HP	Hazardous property
LOI	Loss on ignition
LOQ	Limit of quantification
MCA	Micronised copper azole
NID	Novel integrated desulphurisation
PC	Pulverised combustion
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
POP	Persistent organic pollutant
PP	Power plant
SH	Super heater
SHC	Solid heat carrier
TDS	Total dissolved solids
TEQ	Toxic equivalent
TIC	Total inorganic carbon

1 Literature Review

1.1 Overview of Oil Shale and Biomass Ash Generation and their Classification

In Estonia, approximately 5 million tonnes of oil shale ash is generated annually. With the country's total waste generation at approximately 20 million tonnes per year, oil shale ash accounts for 25% of that total [5]. Until 2020, oil shale ash was classified as hazardous waste, which made Estonia the number one hazardous waste generator per capita in the EU, producing almost thirty times more per person than EU average. Based on a study by Tallinn University of Technology and University of Tartu [7], the ash was reclassified. After the reclassification in 2020, Estonia remained a significant hazardous waste producer, but only four times above the EU average (Figure 1) [13].

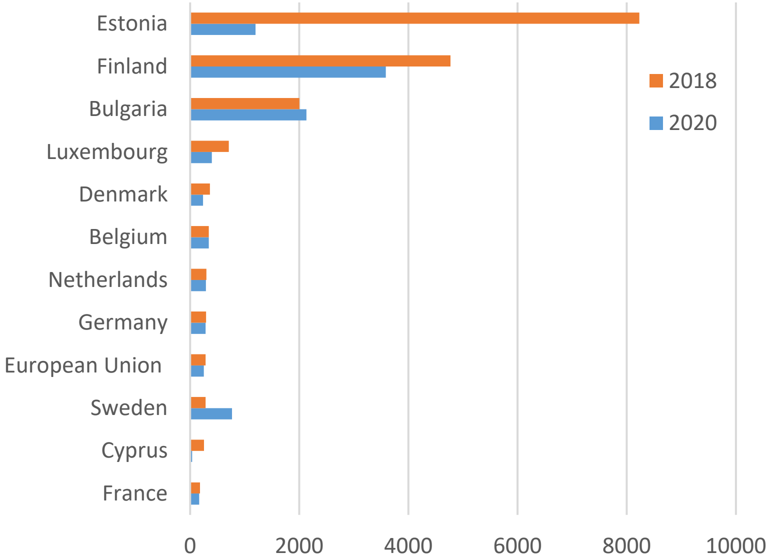

Figure 1. Hazardous waste generation by EU countries and the EU average in 2018 and 2020 [13].

Biomass ash generation in Estonia has been in the range of 40 000 to 50 000 tonnes annually [5]. The amount of biomass ash does not appear as significant as oil shale ash, but it is still essential. Most district heating plants use biomass as a fuel, and the subsequent biomass ash and its treatment are of utmost importance.

The generation and treatment of ashes have been almost at the same level for the past years (Figure 2). Most oil shale ash is landfilled, with only a very marginal part recovered. Biomass ash shows an opposite trend: most of it is recovered, and only a very small part is landfilled.

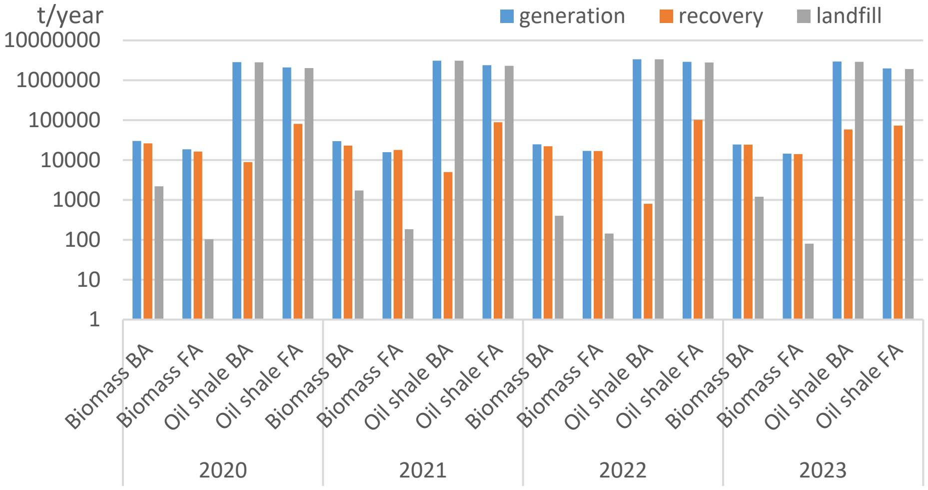

Figure 2. Biomass and oil shale ash generated, recovered, and landfilled in 2020–2023 [5].

Ash is classified in the waste statistics as bottom ash (BA) and fly ash (FA). However, in practice, ashes are more diverse, and waste statistics do not reflect this in much detail. Oil shale ash is generated in oil shale-fired power plants and in the shale oil industry. Ashes from the shale oil industry differ substantially from combustion ashes. For power production, two technologies are employed: pulverised combustion (PC) and circulating fluidised bed combustion (CFBC); the properties and composition of the resulting ashes also differ [7].

1.2 The Current Use of the Ashes

1.2.1 Oil Shale Ash

The classification of oil shale ash as hazardous waste has significantly limited the use of its full potential. As a result, most oil shale ash continues to be landfilled. In contrast, coal ash in the United States is not classified as hazardous, enabling far greater use: in 2023, the U.S. recovered 69% of the 66.7 million tonnes of coal combustion residues generated that year [14].

Even though oil shale ash is currently disposed of, its potential as a valuable secondary raw material has been extensively studied [15–21]. One of its key characteristics is its pozzolanic and latent hydraulic activity, which makes it a promising substitute for conventional cementitious materials [22]. Research has shown that oil shale ash-based concrete is suitable for low-strength concrete applications and for backfilling in mining operations [23]. In particular, concrete incorporating circulating fluidised bed (CFB) ash has demonstrated improved water resistance and reduced expansion, owing to its higher content of reactive silica [22].

Beyond construction, oil shale ash is highly suitable for CO_2 mineralisation processes aimed at capturing and storing CO_2 [24]. The carbonation reactions that form stable calcium carbonate not only sequester CO_2 but also render the waste material chemically stable, reducing the leachability of heavy metals and other contaminants. Studies highlight that pre-treatment steps such as hydration significantly enhance the CO_2 binding efficiency of oil shale ash, making the process more energy-efficient [25].

Oil shale ash has also shown effectiveness in road construction and soil stabilisation. Field studies on road sections built with oil shale ash have reported enhanced soil strength and reduced settlement, especially in peat-rich areas [26]. Its alkaline properties have also been leveraged as a soil amendment in acidic peatlands, where it increases soil pH and enhances nutrient availability for plants. Furthermore, granulated oil shale ash has been evaluated for environmental safety, showing minimal leaching of heavy metals such as cadmium (Cd), mercury (Hg), and lead (Pb) under controlled conditions [27]. In addition to its alkalinity, the nutrient content of oil shale ash has also been explored for its potential use as a fertiliser [28–30].

1.2.2 Biomass Ash

Biomass ash contains essential nutrients such as calcium (Ca), potassium (K), magnesium (Mg), and phosphorus (P), making it a potential soil amendment and fertiliser. It also has liming properties due to its alkalinity, which can help neutralise acidic soils. Applications have shown benefits in forest and agricultural soils, although contaminant levels must be monitored to ensure safety [31, 32]. Wood ash has also been tested as a stabilising material in forest road construction [33].

Scandinavian countries, with their extensive use of wood for bioenergy, have been at the forefront of efforts to transform wood ash into a valuable resource. In Finland, the use of wood ash as a soil amendment began as early as 1935, while Sweden has conducted research on returning wood ash to forest soils since the 1970s. Although there is strong interest in recycling nutrients back into forest ecosystems, legal restrictions limit the direct application of wood ash as a fertiliser or liming agent to only high-quality ash, typically at low application rates of just a few tonnes per hectare [33, 34].

Some biomass ashes, particularly those derived from waste biomass, have pozzolanic properties and are being explored as substitutes for cement in concrete or as additives in synthetic aggregates and fillers. Their application depends on ash composition and the levels of contaminants present [32]. Additionally, there is a growing interest in alkali-activated binders made from ash. For example, Pereira et al. [34] found that wood fly ash can be successfully used as the sole binder component in concrete production, particularly when materials with suitable particle size fractions are used. This opens up new opportunities for the use of wood ash in the construction sector, where its potential has so far been underutilised.

1.3 Hazardous Classification Systems and their Relevance to Ash

Ashes originating from combustion processes are usually considered waste. Waste is classified as hazardous or non-hazardous based on its hazardous properties, including ecotoxicity. There are diverse ways to determine hazardous waste. The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal is a global agreement that defines hazardous waste [35]. The Basel Convention has 191 Parties, which means that all participating countries need to respect the definition of hazardous waste set out in the Convention. While biomass and oil shale ash are not explicitly listed as hazardous, they may contain trace amounts of metals such as chromium (Cr), copper (Cu), zinc (Zn), arsenic (As), Cd, and Hg. The presence of such constituents can make ash subject to hazardous waste assessment. One of the key criteria is ecotoxicity (H12), defined as the potential of a substance or waste to cause immediate or delayed adverse impacts on the environment. However, the guidelines for assessing ecotoxicity under the Basel Convention [36] remain interim and have not been updated since 2003, meaning that no universally agreed approach currently exists.

In the EU, waste is classified according to Waste Framework Directive (WFD) [37] and Commission Decision 2000/532/EC [38]. Under these regulations, some waste is always hazardous, while some is always non-hazardous. For wastes for which either hazardous or non-hazardous waste codes may be assigned, the assessment of hazardous properties (HP) is mandatory (Figure 3). Waste is classified as hazardous if it contains hazardous substances that cause it to display one or more properties from HP1 to HP15, as defined in Annex III of the WFD. HPs can be assessed based on substance concentrations listed in Annex III of the WFD or through testing under Regulation (EC) No 440/2008 [39] or other internationally recognised methods. It is generally agreed that experimental ecotoxicity (HP14) testing results should prevail over the calculation method [40]; however, the exact experimental approaches and test batteries have yet to be determined.

Waste containing dioxins listed in the EU POPs Regulation that exceed the concentration limits indicated in Annex IV to that Regulation, shall also be classified as hazardous.

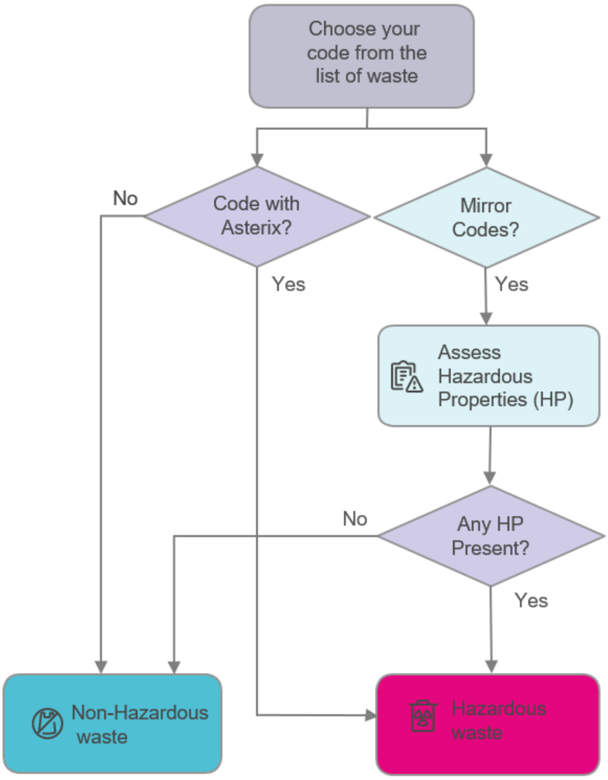

Figure 3. Waste classification according to EU legislation (created by the author).

According to Commission Decision 2000/532/EC [38], bottom ash and fly ash originating from the combustion of coal, peat, and untreated wood are always considered non-hazardous waste. However, ash arising from the co-combustion of waste and other fuels may potentially be deemed hazardous, given its alignment with mirror codes in the waste list. Oil shale ash is not explicitly outlined in the EU waste list, and Estonian regulators have therefore assigned national codes to oil shale ashes [41].

1.4 Regulative Background

1.4.1 Ecotoxicity (HP14) Regulation

Regulation (EU) 2017/997 [40] explicitly addresses hazardous property HP14: “Ecotoxic”. In practice, this means that waste containing substances hazardous to the aquatic environment must be carefully assessed. Waste streams are often complex mixtures of multiple substances; therefore, the assessment does not focus only on individual components but on their cumulative impact.

A waste is considered ecotoxic if it contains one or more substances that are classified as aquatic acute toxicity (H400) or aquatic chronic toxicity categories 1, 2, or 3, corresponding to hazard statement codes H410, H411, H412, or H413, in accordance with the Classification, Labelling and Packaging (CLP) Regulation [42]. The determination involves calculating the sum of the concentrations of these hazardous substances within the waste and comparing it with the threshold values set out in the regulation. If the aggregated concentration surpasses the specified threshold (>25%), the waste is deemed hazardous due to its ecotoxic potential.

Importantly, Regulation (EU) 2017/997 introduces multiplication factors for certain substances to account for their disproportionately higher toxicity. For instance, substances classified as aquatic chronic category 1 (H410) are multiplied by a factor of 100, whereas those in aquatic chronic category 2 (H411) are multiplied by a factor of 10. This weighting mechanism ensures that the most hazardous substances exert a greater influence on the overall classification, thereby preventing an underestimation of risk when highly toxic components are present even at relatively low concentrations.

1.4.2 EU POPs Regulation

In the EU, the production, marketing, use, and handling of POPs are regulated by the EU POPs Regulation [9]. The regulation also governs the management of waste containing POPs. Generally, disposal or recycling practices that could lead to the reuse, recycling, recovery, or re-entry of POPs into the market are prohibited. Waste containing POPs must be destroyed or irreversibly transformed to ensure that these substances do not pose future risks. This aligns with the EU’s precautionary principle and the goal of a toxic-free circular economy.

Annex IV of the EU POPs Regulation sets limit values for the content of POPs in waste. Waste containing POPs above these thresholds is classified as hazardous. Unlike other hazardous wastes, which may still be eligible for recovery or recycling, POPs-contaminated hazardous waste must be disposed of in a manner that ensures the destruction of the POPs. In 2022, the regulation [10] was amended, and 12 dioxin-like polychlorinated biphenyls (PCBs), alongside existing polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), were listed as POPs. The amendment also reduced the limit value for total dioxin content in waste suitable for recovery to 5 µg TEQ/kg (previously 15 µg TEQ/kg). Furthermore, the regulation requires that the Commission shall review this content limit and, where appropriate, submit a legislative proposal to lower that limit, if feasible according to advances in science and technology, by 30 December 2027.

1.4.3 Fertilisers Regulations

When ash is used as a fertiliser, it is subject to fertiliser regulations. In Estonia, fertilisers must comply with the criteria set out in the Fertilisers Act [43] and related national regulations – particularly the regulation concerning the requirements for fertiliser composition by type [44]. Under this regulation, oil shale ash and biomass ash are classified as lime fertilisers, and limit values for certain trace elements are specified in Table 1.

Table 1. Limit values for trace elements in lime fertilisers, mg/kg.

Element	Limit value
Cd	3
Hg	2
Pb	100
Ni	100
As	50
Cu	600
Zn	1500
Cr	50

Additionally, the fertilisers may be subject to the EU Fertilising Products Regulation [11] that includes provisions on product criteria for EU fertilising products. These criteria outline requirements for the categories of end products and component materials. In 2021, through a delegated regulation [45], thermal oxidation materials were added as a component material category in the annex of the Fertilising Products Regulation. Ash, which falls under the thermal oxidation materials category, must meet the requirements set for this category, including a limit value for PCDD/PCDF of 20 ng TEQ/kg.

1.4.4 Soil and Water Regulations

The use of ash as a secondary raw material is affected by environmental regulations designed to protect soil and water resources. In Estonia, the soil regulation [46] establishes both limit values and target values for hazardous substances in soil. Target values denote concentrations at which soil is considered to be in good environmental condition and pose minimal risk to human health or ecosystems. If ash materials contain trace elements or other contaminants below these thresholds, their use in applications involving direct soil contact – such as road base construction or land reclamation – is generally unrestricted. However, if concentrations exceed the legal limit values, the ash is classified as potentially hazardous to the environment and must be disposed of in a different manner.

Similarly, the water regulation [47] addresses the risk of leaching from ash deposits into nearby water bodies. It sets environmental quality standards for a wide array of priority and priority hazardous substances, such as heavy metals and persistent organic pollutants. These standards must be met to avoid degradation of surface water and groundwater quality. For ash to be used near or within hydrologically sensitive areas, leaching tests must confirm that soluble contaminant concentrations remain well below the stipulated thresholds. Exceeding these standards may not only restrict the use of ash materials but also require remediation or containment measures to mitigate potential water pollution.

1.4.5 Landfill Directive

The EU Landfill Directive 1999/31/EC [48] addresses the environmental hazards associated with landfilling and promotes more sustainable waste management practices. Complementing the directive is Council Decision 2003/33/EC [49], which sets out detailed criteria and procedures for the acceptance of waste at landfills.

The EU Landfill Directive provides a comprehensive strategy to minimise the negative effects of landfill use on the environment, particularly with regard to groundwater, surface water, soil, and air. Its primary goals are to reduce the amount of waste sent to landfill, improve the environmental performance of landfill sites, and encourage waste treatment and recovery. The directive categorises landfills into three types based on the nature of the waste they accept: hazardous waste, non-hazardous waste, and inert waste. Each category is subject to specific operational and technical requirements. One of the core provisions of the directive is the mandatory pre-treatment of waste before landfilling, which typically involves physical, chemical, or biological processes to reduce the environmental impact of the waste.

Council Decision 2003/33/EC provides the technical and procedural framework for the acceptance of waste at different classes of landfill. One of the most critical aspects of the acceptance criteria is leachability. Leachability refers to the potential of pollutants within the waste to dissolve and migrate into the surrounding environment, particularly into groundwater, through the action of water percolating through the landfill. Essentially, it measures how easily contaminants can leach out of the waste material when exposed to water.

The leaching limit values (Table 2) for heavy metals and anions vary depending on the class of landfill the waste is destined for:

- Inert landfills – accept only very stable materials with extremely low leachability. These wastes must not pose any significant risk to the environment or human health, even in the long term.
- Non-hazardous landfills – allow for more variation in waste composition but must still comply with leachate limits to prevent pollution.
- Hazardous landfills – may accept wastes with higher leachability, but these facilities are required to have stricter containment systems and monitoring.

Table 2. Leaching limit values for waste acceptance at landfills (L/S = 10/1), mg/kg [49].

	Inert	Non-hazardous	Hazardous
As	0.5	2	25
Ba	20	100	300
Cd	0.04	1	5
Cr_{total}	0.5	10	70
Cu	2	50	100
Hg	0.01	0.2	2
Mo	0.5	10	30
Ni	0.4	10	40
Pb	0.5	10	50
Sb	0.06	0.7	5
Se	0.1	0.5	7
Zn	4	50	200
Cl^-	800	15000	25000
SO_4^{2-}	1000	20000	50000
TDS	2500	60000	100000

These criteria are fundamental because leachate poses one of the most significant risks associated with landfilling. If not properly controlled, it can contaminate soil and groundwater, leading to serious environmental and health consequences. By setting binding leachability thresholds, the Council Decision ensures that waste likely to generate harmful leachate is pre-treated and stabilised prior to landfilling.

1.5 Dioxin Generation and Heavy Metal(loid)s Distribution in Combustion Processes

Dioxins are formed as by-products during combustion processes where carbon, chlorine, and oxygen are present. The formation of these toxic compounds can occur through two primary mechanisms at lower post-combustion temperatures: *de novo* synthesis and precursor pathways. *De novo* synthesis, generally regarded as the dominant route between 200–400 °C, occurs when unburnt carbonaceous material, such as soot or fly ash, undergoes oxidation and chlorination on particle surfaces in the presence of oxygen, chlorine, and metal catalysts. This heterogeneous process is strongly influenced by temperature, fuel composition, and the availability of chlorine species.

The precursor pathway, by contrast, involves the transformation of structurally related compounds such as chlorophenols and chlorobenzenes. These substances can condense and subsequently react either in the gas phase or on particle surfaces, ultimately producing PCDD/PCDFs. Both *de novo* and precursor routes may act simultaneously and independently in different regions of the system.

In addition to these two low-temperature pathways, a third mechanism can occur at higher combustion temperatures (≈500–800 °C): homogeneous gas-phase reactions. Under these conditions, dioxins may form directly from smaller chlorinated hydrocarbons, but the elevated temperatures also favour rapid thermal destruction. As a result, overall dioxin yields are typically much lower compared with those in the cooler post-combustion zone, where *de novo* synthesis is most strongly favoured [50–52].

These temperature windows are particularly critical in combustion processes with flue gas cleaning systems. For instance, fly ash – collected from cyclones (CY) and electrostatic precipitators (ESP) – often shows higher dioxin concentrations compared to bottom ash [53]. This is attributed to the fact that fly ash particles linger within the optimal temperature range for dioxin formation as they cool while passing through the flue gas cleaning system.

Another critical environmental and resource recovery consideration in the utilisation of oil shale and biomass ash is the presence and distribution of heavy metals and metalloids. The concentration of heavy metals and metalloids in ash depends on their content in the fuel itself [54, 55]. During combustion, both organic and inorganic components undergo thermal decomposition, and volatilisation, causing elements to redistribute between solid and gas phases. Depending on their volatility and chemical behaviour, these elements may remain in the solid phase or volatilise into the gas phase, subsequently condensing onto finer ash particles as the flue gases cool. Elements classified as more volatile (e.g. Hg, Sb, Cd, Pb, Zn) tend to redistribute towards finer fractions, whereas low-volatility elements (e.g. Cr, Th, V, Mo) remain largely in bottom ash [55, 56].

The distribution of trace elements is closely linked to the combustion technology employed and the ash collection system in place. PC boilers operate at higher temperatures (1400–1500 °C), leading to stronger volatilisation of easily volatile elements (e.g. Hg, Sb, Cd, Pb, Zn), which subsequently concentrate in the later stages of the ESP. In contrast, CFBC operates at significantly lower temperatures (below 850 °C), resulting in reduced volatilisation and generally lower concentrations of these volatile trace elements in CFBC fly ash compared to PC fly ash [54, 56].

2 Experimental Methods

This thesis is based on four individual studies. While each paper provides detailed information on the samples, analysis methods, and methodologies, this section presents a general overview of the materials and analysis methods used throughout the study.

In addition to the published studies, biomass ash was analysed for its chemical composition and heavy metal(loid) content. A leaching test was conducted, and the resulting leachates were examined for heavy metals, chloride, sulphate, and electrical conductivity (EC). These analyses were carried out as part of a Master's thesis [12] supervised by the author.

2.1 Materials and Methods

2.1.1 Ash Samples

Oil shale ash samples were collected from a variety of industrial facilities in Estonia using different combustion technologies, including PC, CFBC, and solid heat carrier (SHC) systems used in shale oil production. The collected samples represent a range of operational conditions, equipment configurations, and ash collection points, providing a comprehensive view of ash characteristics. The ash samples originated from:

- CFBC boilers at Auvere Power Plant (Auvere PP) and Eesti Power Plant (Eesti PP)
- PC boilers at Eesti PP equipped with novel integrated desulphurisation (NID) unit
- Shale oil production facilities, specifically Enefit280 (CFBC-based), Enefit140, and Petroter I–III

Each facility yields multiple ash fractions, commonly classified as BA, collected from the base of combustion chambers, and FA, collected from flue gas cleaning systems such as superheaters (SH), economisers (ECO), heat exchangers (HE), air preheaters (APH), CYs, ESPs, and fabric filters (FF) (Table 3).

Table 3. Characteristics of oil shale plants and ash sample collection areas.

Facility	Sample collection area	Technology	Annual oil shale input, Mt/year*	Fuel used in the power plant
Auvere PP	BA, SH, ECO, APH, ESP1–5, FF	Power plant, CFBC	2.5	Oil shale, biomass, retort gas
Eesti PP PC	BA, SH, ECO, CY, NID, FF	Power plant, PC	2.0	Oil shale, retort gas
Eesti PP CFBC	BA, SH, ECO, APH, ESP1–4	Power plant, CFBC	1.9	Oil shale, retort gas
Enefit280	BA, WHB, CY, ESP	Shale oil plant SHC + CFBC	2.2	Oil shale
Enefit140	Bunker of total ash, ESP	Shale oil plant, SHC + lift-pipe combustor	1.2	Oil shale
Petroter	CY, ESP	Shale oil plant, SHC + lift-pipe combustor	1.2	Oil shale

* Based on operation at nominal gross capacity for 8760 h/a under steady-state conditions, with 100% oil shale [7].

Biomass ash was collected from nine biomass combustion plants located across different regions of Estonia. The primary fuel used at all sites was wood chips – the most common form of biomass fuel in Estonia. These wood chips consisted mainly of forest biomass residues but may also have included portions of waste wood. The plants selected for sampling had distinct technical characteristics (as detailed in Table 4). Of these, eight facilities operated with grate boilers, while one used a CFB boiler. Ash sampling took place between August and November 2022, with both bottom ash and fly ash collected. Fly ash was obtained from CY or ESP. In one instance, only mixed ash was available due to limitations in the ash handling system, which prevented the separation of ash fractions. At one facility, samples were collected from two different boilers and two separate ESP units.

Table 4. Technical parameters and sample numbers of the biomass combustion plants investigated in this study ***[adapted from Paper II]****.*

ID	Capacity, MW_{th}	Boiler type	Fuel	Cleaning system	Sample No.
1	23	Grate	Wood chips	CY + ESP	1 BA; 1 CY; 1 ESP
2a	22	Grate	Wood chips	ESP	2a BA; 2a ESP
2b	22	Grate	Wood chips	ESP	2b BA; 2b ESP
3	8	Grate	Waste wood	CY + ESP	3 BA; 3 CY; 3 ESP
4	1	Grate	Wood chips	CY	4 BA; 4 CY
5	1	Grate	Wood chips	CY	5 BA; 5 CY
6	3	Grate	Wood chips	CY	6 BA; 6 CY
7	3.5	Grate	Wood chips	CY	7 mixed
8	3.5	Grate	Wood chips	ESP	8 BA; 8 ESP
9	>50	CFB	Wood chips	ESP	9 BA; 9 ESP

2.1.2 Analysis

The leaching test was performed in accordance with standard EN 12457-4 [57], maintaining a liquid-to-solid ratio of 10:1.

Ecotoxicological analysis using two test organisms, *Daphnia magna* (acute toxicity test; SN EN ISO 6341 [58]; STN 83 8303) and *Aliivibrio fischeri* (Microtox test; CSN EN ISO 11348–2 [59]), was conducted in the accredited ALS laboratory in the Czech Republic.

Chemical composition was determined in the laboratory of the Department of Energy Technology at Tallinn University of Technology using a Rigaku ZSX Primus II 4 kW wavelength dispersive X-ray fluorescence spectroscope.

Mineralogical composition was analysed in the laboratory of the Department of Geology at the University of Tartu using powder X-ray diffraction on a Bruker D8 diffractometer equipped with SolX and super-speed LynxEye detectors.

The determination of free CaO was conducted by first grinding and sieving the sample through a 100 µm mesh sieve, except for fly ash, which did not require grinding. The prepared sample was then slaked with boiling water to initiate the hydration process. To enhance the solubility of calcium hydroxide, a sugar solution was added. The resulting solution was subsequently titrated with standardised 0.1 M hydrochloric acid, utilising phenolphthalein as an indicator to determine the endpoint. The volume of acid consumed during titration was used to quantify the free CaO content in the sample.

The mineral CO_2 content of the sample was determined by measuring the total inorganic carbon (TIC) using a Vario MACRO elemental analyser. The TIC value was then used to calculate the carbonate-derived CO_2 content.

Quantification of trace elements in both ash and eluates was conducted using inductively coupled plasma mass spectrometry (ICP-MS) with a Thermo iCAP Qc, following the standard test method ASTM D6357-21a.

The content of sulphates (SO_4^{2-}) and chloride (Cl^-) ions was determined using liquid ion chromatography with a Dionex ICS-1000, in accordance with the EVS-EN ISO 10304-1:2009 standard [60].

Dioxin concentrations were analysed in the accredited ALS laboratory in the Czech Republic. The following methods and standards were used: quantification of tetra- to octa-chlorinated dioxins and furans was performed using the isotope dilution technique with high-resolution gas chromatography–high-resolution mass spectrometry (HRGC-HRMS), following US EPA 1613B and CSN EN 16190 standards. Similarly, the quantification of PCBs was carried out employing HRGC-HRMS and adhering to the CSN EN 1948–4 + A1 and US EPA TO-4A standards.

3 Results and Discussion

3.1 Material Characterisation

3.1.1 Oil Shale Ash

The type of combustion technology used in oil shale processing directly shapes the chemical, mineralogical, and physical properties of the resulting ash. In addition, distinct ash fractions generated by different technologies each have unique properties.

PC boilers burn finely ground oil shale (<0.01 mm) at temperatures of approximately 1400–1500 °C. These extreme conditions drive the near-complete decomposition of carbonate and clay minerals, leading to ash that is rich in free CaO and reactive silicate phases such as C_2S (dicalcium silicate) and C_4AF (calcium alumino-ferrite) (Table 5). These compounds give PC ash a high binding capacity, making it particularly attractive for use in construction materials. Across various collection points, the composition remains relatively consistent, although bottom ash shows a higher free CaO content. Fabric filter ash from the NID unit contains elevated sulphate (SO_3) levels due to in-situ desulphurisation.

Table 5. Mineralogical composition of the ashes from Eesti Power Plant PC unit with NID, wt% ***[from Paper III]****.*

	BA	SH	ECO	CY	NID FF
Quartz (SiO_2)	3.5	6.7	6.9	6.8	10.5
Adularia ($KAlSi_3O_8$)	4.6	5.4	6.0	4.3	2.5
Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$)	1.8	n.d*	n.d	n.d	1.2
Calcite ($CaCO_3$)	5.3	9.3	9.6	4.2	11.5
Dolomite ($CaMg(CO_3)_2$)	n.d	n.d	n.d	n.d	n.d
Lime (CaO)	24.6	19.8	21.1	24.6	8.8
Portlandite ($Ca(OH)_2$)	8.1	12.8	11.8	8.9	8.3
Periclase (MgO)	4.7	3.9	4.3	8.0	4.1
Anhydrite ($CaSO_4$)	3.8	8.0	6.2	9.5	11.8
C_2S/C_4AF ($Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$)	20.9	14.4	15.6	16.5	18.8
Merwinite ($Ca_3Mg(SiO_4)_2$)	6.1	5.3	4.9	6.7	4.8
Akermanite ($Ca_2MgSi_2O_7$)	14.6	9.2	8.9	5.6	4.0
Sylvite (KCl)	n.d	n.d	n.d	n.d	1.2
Hematite (Fe_2O_3)	1.3	2.8	2.5	2.2	1.1
CaO_{free}	19.8	17.1	14.7	17.3	11.8
CO_2	1.86	0.84	3.87	1.4	4.12
TIC	0.51	0.23	1.06	0.38	1.12

* n.d – not detected.

CFBC boilers operate at moderate temperatures (~800–850 °C) and accept oil shale particles up to 25 mm in size. These conditions preserve more of the original mineral structure, resulting in ash with moderate to low free CaO but high anhydrite ($CaSO_4$) content due to efficient sulphur capture. The ash fractions in CFBC systems – BA, SH, ECO, APH, and multiple ESP stages – differ significantly in composition (Table 6).

Bottom ash in CFBC units contains higher calcite and lower silica and alumina contents, while ESP fly ash fractions are finer and richer in secondary silicates such as C_2S/C_4AF. The fine fractions from ESP fields, particularly those from later stages, show lower free CaO but higher contents of reactive silicate phases.

Table 6. Mineralogical composition of the ashes from Auvere Power Plant, wt% ***[from Paper III]***.

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
Quartz (SiO_2)	3.6	14.3	12.5	12.7	10.8	10.6	6.6	5.3	3.1
Adularia ($KAlSi_3O_8$)	2.2	18.3	13.3	17.3	15.9	15.7	11.9	10.9	8.6
Muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$)	2.1	4.6	3.3	5.2	5.1	3.7	3.1	3.9	2.4
Calcite ($CaCO_3$)	35.0	15.4	12.5	10.0	10.8	17.7	18.1	9.5	9.6
Dolomite ($CaMg(CO_3)_2$)	5.1	n.d*	0.5	n.d	n.d	n.d	n.d	n.d	n.d
Lime (CaO)	18.4	16.0	19.2	19.4	20.3	9.8	10.1	9.1	<LOQ**
Portlandite ($Ca(OH)_2$)	2.0	0.9	1.3	1.0	1.0	4.8	6.3	17.8	14.6
Periclase (MgO)	7.0	5.3	6.8	5.6	5.4	5.3	5.3	4.9	7.7
Anhydrite ($CaSO_4$)	10.1	6.3	10.0	6.9	6.7	7.0	8.2	7.6	7.3
C_2S/C_4AF ($Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$)	7.1	9.5	10.2	10.9	13.0	14.7	18.7	19.0	9.3
Merwinite ($Ca_3Mg(SiO_4)_2$)	3.1	5.3	5.2	5.9	6.4	6.6	7.8	8.0	5.3
Akermanite ($Ca_2MgSi_2O_7$)	3.6	2.3	3.9	3.2	3.1	2.1	2.2	2.1	8.8
Arcanite (K_2SO_4)	n.d	n.d	n.d	0.4	0.3	n.d	n.d	n.d	3.4
Sylvite (KCl)	0.3	n.d	n.d	n.d	0.3	0.3	0.4	0.9	0.6
Hematite (Fe_2O_3)	0.6	1.5	1.1	1.3	1.0	1.2	1.0	0.7	<LOQ
CaO_{free}	16.7	16.1	18.2	19.0	19.3	14.2	14.4	16.2	12.8
CO_2	22.3	7.2	6.8	5.4	5.2	6.1	6.4	5.7	9.6
TIC	6.1	4.7	2.0	1.5	1.4	1.7	1.7	1.6	2.6

* n.d – not detected, ** – LOQ limit of quantification.

In SHC systems such as Enefit280 and Petroter, the combustion of semi-coke – a by-product of shale oil production – occurs at temperatures below 800 °C. The objective is to conserve energy and avoid the breakdown of carbonates, which is reflected in the characteristics of the resulting ash. The free CaO content is minimal, and carbonate minerals such as calcite and dolomite remain largely intact. Consequently, SHC ashes lack the reactive binding phases (C_2S/C_4AF) observed in PC and CFBC ashes (Table 7).

SHC installations generate ash fractions such as BA, CY ash, and ESP ash, depending on the plant layout. Bottom ash in Enefit280, for example, contains the highest calcite levels, while ESP fractions contain slightly more silicates and aluminosilicates. In Petroter, a large proportion of the ash is captured in the CY, and only a small amount reaches the ESP. Interestingly, Petroter ESP ash has a notably high muscovite content, and its dolomite content across fractions is higher than in any other combustion technology examined. These ashes also show higher loss on ignition (LOI), indicating greater amounts of unburnt carbon or volatile matter – especially in bottom and coarse ash fractions. This limits their suitability for applications that require high purity or chemical stability.

*Table 7. Mineralogical composition of the ashes from Enefit280 and Petroter, wt% **[from Paper III]**.*

	Enefit280				Petroter	
	BA	WHB	CY	ESP	CY	ESP
Quartz SiO_2	3.4	16.8	16.0	14.9	10.5	11.3
Adularia $KAlSi_3O_8$	3.3	22.1	17.6	29.9	4.6	16.5
Muscovite $KAl2(AlSi_3O_{10})(F,OH)_2$	0.9	6.0	9.4	10.9	5.4	38.7
Calcite $CaCO_3$	57.6	29.3	32.4	20.4	50.2	20.0
Dolomite $CaMg(CO_3)_2$	14.6	6.6	3.4	5.0	14.3	1.0
Hematite Fe_2O_3	1.1	2.5	2.3	n.d*	n.d	0.5
Lime CaO	n.d	n.d	n.d	0.7	n.d	0.5
Portlandite $Ca(OH)_2$	0.5	n.d	n.d	0.6	0.6	0.8
Periclase MgO	3.1	2.8	2.1	1.0	1.7	<0.5
Anhydrite $CaSO_4$	10.7	9.3	8.9	5.0	2.9	1.2
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	3.8	1.8	5.0	3.5	3.7	0.5
Merwinite $Ca_3Mg(SiO_4)_2$	1.3	0.8	1.4	0.6	2.1	2.1
Akermanite $Ca_2MgSi_2O_7$	0.7	1.9	1.3	2.2	1.4	1.7
Sylvite KCl	n.d	n.d	n.d	1.3	n.d	n.d
CaO_{free}	1.1	n.a	1.8	1.04	1.48	0.37
LOI	33.5	17.7	n.a	31.7	26.7	16.6

* n.d – not detected.

3.1.2 Biomass Ash

The chemical composition of biomass ashes varies significantly depending on the combustion facility and the particulate removal method used. Table 8 provides a comparative analysis of ash compositions from different biomass combustion facilities employing either CY or ESP systems.

LOI values, indicating the amount of unburnt carbon and volatile matter, range broadly from 11% to 29%. Cyclone ashes tend to show higher LOI values, suggesting less complete combustion compared with ESP ash. This trend reflects the mechanical limitations of cyclones in capturing finer particles, possibly allowing more unburnt material to remain in the ash.

Calcium (presented as CaO) is a major component across all samples, with especially high values in ESP ash – reaching up to 39%. High Ca levels are typical of wood-based biomass [61]. Silica (presented as SiO_2) concentrations vary markedly. For example, sample 1 CY shows an exceptionally high SiO_2 content of 34.9%, while sample 3 ESP shows no detectable amount. This suggests significant variation in fuel type or contamination with soil or sand. A notable exception is sample 9 ESP, which shows a high SiO_2 level of 32%. This is explained by the use of CFB technology in that system, where sand is used as a SHC, contributing directly to the elevated silica content in the ash.

Potassium (presented as K_2O), another prominent compound, peaks at 22.9% in sample 8 CY and 18.7% in sample 3 ESP, while remaining around 5–6% in most ashes. Sulphur (presented as SO_3) content is highest in sample 8 CY (24.8%), indicating possible sulphur-rich biomass or contamination. Cyclones again tend to retain more sulphur (S) than ESP systems. The rest of the substances occur at relatively moderate levels but vary depending on the system and input material.

Table 8. Chemical composition of biomass ashes, wt% [12].

	1 ESP	1 CY	2b ESP	3 ESP	4 CY	6 CY	8 ESP	9 ESP
LOI	17.3	15.2	16.8	17.4	29.2	23.5	11.5	17.9
Na_2O	0.99	0.53	0.30	3.29	0.22	0.33	1.57	0.59
MgO	4.02	3.01	3.65	2.34	3.44	3.26	2.0	2.95
Al_2O_3	1.14	2.27	1.56	0.01	1.01	2.58	0.5	3.34
SiO_2	4.75	34.9	10.8	n/d	5.77	15.8	0.92	32.0
P_2O_5	4.72	3.13	3.75	1.59	4.34	4.13	3.28	2.69
SO_3	15.0	1.39	3.89	12.9	4.52	3.73	24.8	2.31
K_2O	12.4	6.02	4.86	18.7	6.48	5.59	22.9	5.19
CaO	27.2	26.2	39.7	16.6	32.4	31.8	13.1	28.9
TiO_2	0.12	0.17	0.14	0.07	0.10	0.19	0.09	0.20
Cr_2O_3	0.01	<0.01	<0.01	0.03	0.01	0.01	0.01	<0.01
Fe_2O_3	0.95	0.98	0.98	0.52	1.42	2.36	0.77	1.35
ZnO	1.56	0.19	0.30	3.60	0.26	0.30	1.74	0.18
SrO	0.07	0.07	0.06	0.03	0.06	0.06	0.03	0.05
MnO_2	1.49	1.60	0.27	0.42	0.28	0.26	0.12	0.42

3.2 Heavy Metal(loid)s Content in Ash

3.2.1 Oil Shale Ash

Oil shale ash produced in Estonia, regardless of combustion technology, consistently exhibits low heavy metal(loid)s contents, with the exception of manganese (Mn), strontium (Sr), and titanium (Ti) (Table 9) **[Paper III]**. Across all the ashes surveyed in the study, the majority of heavy metal(loid)s, including environmentally critical elements such as Pb, As, and Cd, were present in similarly low quantities. Heavy metal(oid)s in oil shale ash typically reflect their abundance in the oil shale itself. Estonian kukersite oil shale contains low concentrations of heavy metal(loid)s; consequently, the resulting ash also generally exhibits low trace element contents. The elevated levels of Mn, Sr, and Ti observed in the ash are attributed to their naturally higher abundances in kukersite oil shale [54].

Combustion temperature and process conditions influence the mineralogy and speciation of ash components, particularly with regard to calcium-bearing phases. However, the technology utilised does not alter the total concentrations of trace elements. For example, ashes from both PC and CFBC units showed broadly similar levels of vanadium (V), Cr, Zn, and nickel (Ni). Even in the SHC-based Enefit280 and Petroter plants, which operate under reducing conditions and at lower temperatures, trace element levels remained within the same general range as those observed in CFBC and PC ashes.

More pronounced than the differences between combustion technologies are the variations between ash fractions, particularly between bottom ash and fly ash. Finer fly ash, especially that collected in ESPs or FFs, tends to concentrate trace elements more than coarser bottom ash. This pattern is consistent across all technologies and is attributed to the volatilisation–condensation mechanism, which favours the enrichment of semi-volatile elements in finer particles. For instance, at Auvere PP (CFBC), elements such as As and Pb were found in higher concentrations in ESP ash compared to bottom ash. A similar distribution was observed in PC ash from Eesti PP and in fly ash from SHC units such as Petroter and Enefit280.

Table 9. Heavy metal(loid)s contents in bottom ash and fly ash from different oil shale plants, mg/kg ***[based on Paper III]****.*

	Auvere PP BA	Auvere PP FA	Eesti PP CFBC BA	Eesti PP CFBC FA	Eesti PP PC BA	Eesti PP PC FA	Enefit280 BA	Enefit 280 FA	Petroter
Li	6.6	25.7	1.8	37.6	22.7	24.5	6.2	21.2	13.4
Be	0.4	0.5	<LOQ	<LOQ	1.1	<LOQ	0.3	0.5	0.75
Ti	702	2930	885	4128	2306	2713	572	2873	1502
V	29.2	82	17	74.5	42.5	53.3	13.1	51.9	32.6
Cr	17.8	49.6	16.7	72.6	36.5	52.2	10.3	51.7	34.5
Mn	771	591	821	584	744	571	525	373	463
Co	4	7	2.5	7.6	5.4	5.8	2.8	6.7	4.3
Ni	18.9	33	13.5	37.8	23.2	25.9	11.9	31.1	18.7
Cu	3.9	9.8	5.1	11.9	9.0	15.4	3.0	8.2	8.9
Zn	235	167	22.9	34	31.7	43.1	159	88.9	39
As	53.4	27	8.1	15.2	7.4	16.5	19.6	28.8	7.6
Se	0.3	0.8	n.d	1.3	0.7	1	0.6	0.5	1.5
Sr	360	380	296	427	397	338	352	326	253
Mo	7.3	8.3	0.8	4.6	1.3	2.7	4.2	14	1.48
Cd	0.3	0.8	<LOQ*	<LOQ	n.d**	n.d	0.3	0.4	1
Sb	0.2	0.3	<LOQ	<LOQ	<LOQ	<LOQ	n.d	n.d	n.d
Tl	1.3	1.6	0.4	1.6	0.5	1.5	0.8	1.1	0.7
Pb	27.8	101	17.1	61.2	13.5	49.7	18.5	73.4	34.8

* LOQ – limit of quantification, ** n.d – not detected.

3.2.2 Biomass Ash

Heavy metals and metalloids are naturally present in biomass and persist in the ash or flue gas following combustion. Their fate is largely determined by the efficiency of the flue gas cleaning systems. Advanced flue gas treatment systems tend to capture a greater proportion of these elements, resulting in higher concentrations in the collected fly ash. Similar to observations in oil shale combustion, biomass fly ash typically exhibits elevated levels of heavy metals and metalloids compared to bottom ash.

Table 10. Heavy metal(loid)s contents in biomass ash, mg/kg [partially from [12]].

	1 BA	1 ESP	2a ESP	3BA	3 ESP	4 CY	4 ESP	6 CY	8 BA	8 ESP	9 BA	9 ESP
Li	10	88.7	16.5	18.1	67.8	10.4	6.9	15.0	3.8	6.3	2.4	5.4
Be	0.2	0.3	0.2	0.2	0.1	0.2	0.2	0.3	0.3	0.1	0.2	0.3
Sc	0.8	0.8	1.7	2.0	0.2	2.0	1.3	2.3	2.2	0.6	2.2	2.4
V	5.9	8.3	12.1	<LOQ	<LOQ	9.7	4.8	11.5	11.7	5.5	5.2	14.1
Cr	7.1	26.2	26.5	368	271	41.5	77.6	77.8	39.1	59.0	6.8	25.9
Co	4.4	7.0	5.7	8.5	7.5	4.1	4.8	6.2	3.0	2.4	1.8	4.8
Ni	9.3	18.1	10.3	17.0	7.0	8.2	12.0	17.1	8.6	7.4	3.6	13.0
Cu	38.8	135	133	73.0	427	88.5	162	147	70.6	347	10.5	79.0
Zn	341	9499*	1837	384	21654	289	1796	1642	231	11090	198	1202
As	0.56	9.4	2.8	0.8	5.2	<LOQ	19.3	4.4	0.74	37.6	<LOQ	2.2
Se	0.3	4.7	1.9	0.9	11.0	0.8	2.1	1.7	1.1	3.8	0.5	1.3
Sr	330	510	454	387	246	298	512	414	284	252	106	375
Cd	1.9	34.1	10.7	1.2	18.2	6.1	46.7	48.8	2.1	23.3	3.3	4.2
Pb	3.5	38.5	27.5	30.8	72.4	9.0	27.0	28.0	9.3	318	1.1	15.3

* Values marked in red are outside the calibration range.

As shown in Table 10, specific biomass ash samples exhibit elevated concentrations of Cr, Cu, Zn, and Pb. In combustion plants, such increases may occur when the fuel feedstock is insufficiently screened and inadvertently includes treated wood mixed with natural biomass. In Estonia, regulatory thresholds for specific pollutants in wood waste have been established [62] to ensure the safe incineration of such materials in biomass-fired plants. These thresholds are based on research conducted by the Department of Chemistry and Biotechnology at Tallinn University of Technology [63]. Table 11 presents the maximum concentrations found in hardwood logs and bark, along with the corresponding calculated concentrations in the resulting ash.

Table 11. Heavy metal(loid) maximum concentrations in natural hardwood and in the resulting ash (calculated assuming an ash content of 2%), mg/kg.

	Hardwood log	Ash	Hardwood bark	Ash
Cr	0.15	7.5	0.69	34.5
Ni	0.1	5	2.6	130
Cu	3.5	175	16	800
Zn	23	1150	180	9000
As	0.04	2	0.11	5.5
Cd	0.2	10	0.48	24
Pb	0.32	16	1.79	90

The elevated concentrations of Cu and Zn in ash sample 3ESP are expected, since the combustion plant also incinerates waste wood (see Table 4). However, elevated levels of certain elements, exceeding those theoretically derived from natural wood, were also observed in ash samples from combustion plants 1, 4, and 8. This suggests the possible presence of treated wood in the fuel mix, even in plants primarily designated for natural biomass.

Wood treated with preservative substances may contain metals such as Cu, As, Pb, Cr, and Zn. One of the most historically widespread preservatives, chromated copper arsenate (CCA), is a compound consisting of Cr, Cu, and As, in varying proportions. Although CCA has been extensively used since the 1930s under various trade names, it has raised significant health concerns due to its As content – a known carcinogen. As a result, the production and use of CCA-treated wood for residential and consumer applications have been restricted [64]. In the EU, the use and marketing of arsenic-based preservatives, including CCA, and the use of CCA-treated wood in residential buildings were prohibited following the enforcement of Directive 2003/2/EC in 2004 [65].

More recently, a newer preservative known as micronised copper azole (MCA) has gained popularity as an alternative to CCA. MCA formulations primarily contain copper and are free from As and Cr [66], which may explain why certain ash samples show elevated copper levels without corresponding increases in As or Cr. Zn, also commonly used in several wood preservatives [67, 68], could likewise account for the elevated Zn concentrations detected in some of the biomass ash samples. These findings highlight the importance of thorough fuel quality control in biomass combustion plants to prevent the unintended co-incineration of chemically treated wood.

3.3 Leaching Characteristics of the Ashes

3.3.1 Oil Shale Ash

The overall concentrations of trace elements in oil shale ash leachates were low (Table 12), reflecting their generally low concentration in the ash. Elements of particular interest, such as As, molybdenum (Mo), Pb, Cr, Cd, and Zn, were detected in low concentrations across all ash types.

In general, fly ash fractions showed higher concentrations of leached trace elements compared with bottom ash, consistent with their finer particle size, which enhances dissolution potential. However, the differences between combustion technologies were relatively modest.

Chloride (Cl^-) and sulphate (SO_4^{2-}) were among the most soluble components detected in the leachates, often appearing in elevated concentrations, particularly in fly ash samples. Chloride is highly mobile and not typically bound in stable mineral phases, making it a good indicator of short-term environmental mobility. Sulphate, originating primarily from the oxidation of S in oil shale and from the formation of anhydrite ($CaSO_4$) in CFBC systems, was consistently observed in moderate to high concentrations in leachates. In particular, ashes from CFBC plants such as Auvere and Eesti PP showed higher sulphate leachability due to their process design, which promotes sulphur capture as sulphate minerals.

The EC of ash leachates was high across all installations, reflecting a high total dissolved solids (TDS) content dominated by ions such as Cl^-, SO_4^{2-}, Na^+, and K^+ (although Na and K were not quantified in leaching in this study). The elevated EC values support the conclusion that oil shale ash, particularly fly ash, has a substantial capacity to release soluble salts. High conductivity is not inherently hazardous but serves as an important proxy for salinity-related risks to soil and water systems, especially if ash is stored under unconfined conditions.

Table 12. Release of components from ash samples at pH_{mat} (L/S = 10/1), mg/kg ***[from Paper III]****.*

	Auvere PP BA	Auvere PP ESP1	Auvere PP FA	Eesti PP CFBC BA	Eesti PP CFBC ESP1	Eesti PP CFBC FA	Eesti PP PC BA	Eesti PP PC NID	Eesti PP PC FA	Enefit280 BA	Enefit280 CY	Enefit280 FA	Petroter CY	Petroter ESP
Li	0.248	0.611	0.684	0.174	0.329	0.289	0.334	0.279	0.247	0.103	0.117	0.113	0.189	0.122
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ti	0.004	0.003	0.003	0.006	0.004	0.005	0.004	0.017	0.006	0.004	0.008	0.004	0.004	0.019
V	0.001	0.004	0.004	0.001	0.003	0.003	<LOQ	0.004	0.002	0.102	0.161	0.171	0.024	0.460
Cr	0.001	0.999	0.965	<LOQ	1.173	1.100	0.001	0.422	0.350	0.210	1.507	1.397	0.001	0.075
Mn	0.001	0.002	0.001	0.006	0.001	0.001	0.002	0.003	0.002	0.001	0.006	0.002	0.001	0.015
Co	0.003	0.002	0.002	0.002	0.003	0.003	0.002	0.003	0.003	0.002	0.002	0.002	0.002	0.002
Ni	0.010	0.007	0.006	0.008	0.008	0.008	0.006	0.009	0.008	0.004	0.006	0.004	0.004	0.005
Cu	0.003	0.006	0.015	0.003	0.010	0.005	0.011	0.013	0.004	0.003	0.016	0.005	0.020	0.018
Zn	0.060	0.026	0.023	0.009	0.015	0.013	0.016	0.012	0.010	0.002	0.018	0.006	0.024	0.036
As	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.003	0.002	0.010	0.008	0.012	0.005	0.024
Se	0.004	0.034	0.036	0.009	0.034	0.032	0.002	0.004	0.004	0.007	0.052	0.046	0.001	0.026
Sr	39.08	54.38	57.24	26.50	35.08	38.22	51.81	16.643	20.81	8.95	19.07	16.41	11.77	10.58
Mo	0.501	0.742	0.736	0.153	0.514	0.522	0.143	0.460	0.376	0.780	2.919	2.578	0.407	0.882
Cd	0.002	0.003	0.003	0.002	0.002	0.002	0.001	0.002	0.002	0.006	0.008	0.007	0.002	0.003
Sb	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.004	0.005	0.001	0.001	0.002	0.007
Tl	<LOQ	0.048	0.046	<LOQ	0.037	0.030	<LOQ	0.047	0.041	0.000	0.004	0.007	<LOQ	0.077
Pb	0.000	0.110	0.103	<LOQ	0.041	0.053	0.003	0.034	0.028	<LOQ	0.001	<LOQ	0.000	0.014
Cl^-	420	2550	2030	330	1980	2260	210	2880	2640	780	1790	3700	930	900
SO_4^{2-}	15406	8648	6651	14042	13770	14317	3622	11730	13479	17708	11940	13975	5998	7230
Conductivity, µS/cm	10500	11840	10990	11200	9780	11000	9500	11350	11650	3472	3240	3357	3321	1980
pH	13.01	13.14	13.12	13.11	12.82	13.13	13.07	12.9	13.11	12.35	12.06	12.1	12.67	10.42

3.3.2 Biomass Ash

The leachability of trace elements from biomass ash varied significantly between samples (Table 13). In certain samples, notably from combustion plants 1, 3, and 8, leached concentrations of Cu and Zn exceeded the expected levels based on natural wood content, suggesting the possible co-incineration of treated wood. This is further supported by elevated levels of Cr and Pb in some ash eluates. Wood treated with preservatives such as CCA, historically used for outdoor and structural timber, is known to release these elements upon combustion. Although the use of CCA is now restricted in the EU, its legacy presence in waste wood remains a concern.

Cl^- and SO_4^{2-} were consistently among the most mobile components in biomass ash leachates. Their concentrations were often high and are attributed to their inherent solubility and lack of stable binding in ash mineral phases. Cl^- is generally associated with fuel impurities or specific biomass types (e.g. straw), while sulphate may derive from both fuel-bound sulphur and process additives.

The EC of leachates was high in many cases, indicating a substantial content of dissolved salts. High EC values are not in themselves toxic, but they reflect the ionic strength of the ash, which may affect water quality and plant growth if the ash is applied to land.

Table 13. Release of components from biomass ash samples at pH_{mat} (L/S = 10/1), mg/kg [12].

	1 CY	1 ESP	2a ESP	3 ESP	4 CY	6 CY	8 ESP	9 ESP
Li	0.079	1.272	0.504	8.77	0.094	0.163	2.94	0.482
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
V	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cr	0.925	8.493	4.443	132.2	8.80	6.34	22.13	6.83
Mn	0.032	0.158	0.077	0.254	0.137	0.103	0.23	0.084
Co	0.019	0.0123	0.021	0.007	0.096	0.054	0.005	0.0224
Ni	<LOQ	0.022	0.107	<LOQ	0.025	0.042	<LOQ	<LOQ
Cu	0.333	11.37	17.22	18.61	20.57	5.19	2.78	0.625
Zn	0.782	30.40	20.58	56.68	3.920	20.32	37.36	0.829
As	0.016	0.112	0.036	0.10	0.039	0.026	0.363	0.030
Se	0.113	0.872	0.373	0.839	0.320	0.208	1.44	0.367
Sr	23.80	17.69	19.40	10.75	11.11	14.86	4.61	17.05
Cd	<LOQ	0.002	<LOQ	<LOQ	0.002	0.002	0.001	<LOQ
Tl	<LOQ	0.019	0.002	0.283	0.001	0.001	0.311	<LOQ
Pb	0.051	1.712	1.128	4.60	0.157	0.203	6.33	0.163
Cl^-	2.52	24.03	4.99	67.17	3.92	2.57	34.08	4.32
SO_4^{2-}	12.37	115.72	31.96	166	52.23	34.60	239	27.16
Conductivity, µS/cm	13940	46600	22330	86670	22450	18300	59800	20080
pH	12.42	12.69	12.54	12.93	12.38	12.40	12.46	12.54

3.4 Ecotoxicity Assessment

3.4.1 Ecotoxicity Tests

The classification of industrial waste under the EU's hazardous property HP14 (ecotoxicity) is critical for environmental protection and regulatory compliance. The EU allows two methods for assessing HP14: computational models based on chemical composition and experimental bioassays using indicator organisms [40]. While EU regulation prefers experimental results when available, it does not standardise the organisms or conditions used for such tests, leading to considerable variability among Member States. In the case of oil shale ash, experimental testing was conducted using two widely accepted aquatic organisms: *Daphnia magna*, a freshwater microcrustacean, and *Aliivibrio fischeri*, a bioluminescent marine bacterium.

The experimental results revealed a stark contrast between the two test organisms. The *Daphnia magna* acute immobilisation test indicated ecotoxicity for most ash samples, with EC50 values falling within the range considered acutely toxic (Table 14 and Table 15). In contrast, the *Aliivibrio fischeri* Microtox test detected no measurable toxicity in any sample, as the EC50 threshold was not reached. These divergent results suggest that *Daphnia magna* is significantly more sensitive to the characteristics of oil shale ash leachate than *Aliivibrio fischeri*.

Table 14. Hazard classification system for wastes discharged into the aquatic environment [69].

TU		Toxicity
<0.4	Class I	No acute toxicity
0.4 < TU < 1	Class II	Slight acute toxicity
1 < TU < 10	Class III	Acute toxicity
10 < TU < 100	Class IV	High acute toxicity
TU > 100	Class V	Very high acute toxicity

Table 15. Results of ecotoxicity assessment of different ashes from the oil shale industry ***[from Paper I]****.*

	Daphnia magna		*Aliivibrio fischeri*	
Sample	EC50 48 h, ml/l	TU	EC50 15 min, ml/l	TU
Auvere PP BA	23.2	4.3	N/A	N/A
Auvere PP ESP1	44.2	2.3	N/A	N/A
Auvere PP FA	27.9	3.6	N/A	N/A
Eesti PP CFBC FA	19.3	5.2	N/A	N/A
Eesti PP CFBC BA	20.1	5.0	N/A	N/A
Eesti PP CFBC ESP1	28.5	3.5	N/A	N/A
Eesti PP PC FA	20.5	4.9	N/A	N/A
Eesti PP PC NID FF	23.2	4.3	N/A	N/A
Eesti PP PC BA	21.6	4.6	N/A	N/A
Enefit280 BA	278	0.4	N/A	N/A
Enefit280 CY	362	0.3	N/A	N/A
Enefit280 ESP	178	0.56	N/A	N/A
Petroter CY	108	0.92	N/A	N/A
Petroter ESP	N/A*	N/A	N/A	N/A

*N/A – it was not possible to determine ecotoxicity because the inhibition value was not reached; i.e. the sample was not toxic enough to determine the dilution value.

One reason for this discrepancy lies in the physiological differences between the two organisms. *Daphnia magna* is highly sensitive to elevated pH and ionic strength, conditions commonly associated with oil shale ash leachate, which often has a pH above 12.5. Conversely, *Aliivibrio fischeri*, being a marine organism, is naturally adapted to higher salinity environments and appears unaffected by the same leachate conditions. **[Paper I]**

In contrast, computational assessments based on EU formulas for HP14 showed a uniform result across all samples: none of the ash samples exceeded threshold concentrations of hazardous elements. These assessments incorporated concentrations of trace metals such as Cr, As, Se, and Pb, each weighted by toxicity multipliers. Even under a worst-case scenario – where all elements were assumed to be in their most harmful valence states – none of the samples approached the 25% toxicity limit required for HP14 classification. The highest value recorded was only 3.918%, far below the hazard threshold [70, 71].

Pearson's bivariate correlation analysis of trace element concentrations in oil shale ash leachates, alongside pH and conductivity **[Paper I]**, further supports the conclusion that trace metals are not responsible for the observed ecotoxicity. *Daphnia magna* toxicity showed either weak or negative correlations with metal concentrations, reinforcing the computational finding that these elements are unlikely to be the key toxic drivers. In contrast, strong positive correlations were observed between *Daphnia magna* responses, pH, and conductivity, suggesting that these physicochemical parameters – rather than metal content – may play a dominant role in the observed toxic effects.

3.4.2 Ecotoxicity Calculation

In the application of the computational method outlined in Regulation (EU) 2017/997 [40] for the evaluation of hazardous property HP14 (ecotoxicity), particular attention must be given to substances bearing the hazard statement H410. This method incorporates multiplication factors to account for the relative environmental toxicity of specific substances, with H410-classified substances requiring a weighting factor of 100. The HP14 threshold is met when the following condition is satisfied:

$$100 \times \Sigma c\,(\mathrm{H410}) + 10 \times \Sigma c\,(\mathrm{H411}) + \Sigma c\,(\mathrm{H412}) \geq 25\%. \qquad (1)$$

Importantly, the regulation stipulates that individual substances should be excluded from the calculation if their concentrations fall below 0.1% for H410, and below 1% for H411 and H412, respectively. Previous work by Lees et al. [70, 71] has confirmed that, in oil shale ash, the concentrations of individual heavy metal(loid)s typically remain below these thresholds.

However, when considering biomass ash samples, Zn emerges as a critical element due to its relatively high concentration. Based on the data presented in Table 8, the content of ZnO in all biomass ash samples exceeds the 0.1% threshold. While the specific chemical speciation of Zn in the ash is not definitively known, it is reasonable to assume, given the oxidative combustion environment, that a significant proportion exists as ZnO. Under the CLP Regulation [42], ZnO carries the H410 hazard statement and is therefore subject to the multiplication factor of 100.

Table 16 illustrates the outcomes of HP14 calculations for several biomass ash samples under the conservative assumption that all Zn is present in the form of ZnO. The computed values far exceed the 25% threshold for samples from the ESP ash streams of combustion plants 1, 3, and 8, with results reaching as high as 360%. This suggests that even if only a fraction of Zn is present as ZnO, the HP14 threshold would still be surpassed.

Table 16. Ecotoxicity HP14 calculation results for biomass ashes, %.

	1 CY	1 ESP	2b ESP	3 ESP	4 CY	6 CY	8 ESP	9 ESP
ZnO	19	156	30	360	26	30	174	18

These findings underscore the critical importance of accurate speciation data for Zn in biomass ash. Without definitive knowledge of the Zn compounds present, the application of computational methods may yield overly conservative or misleading results. Hence, to reliably assess the HP14 classification of biomass ash, particularly in borderline cases, it is essential to supplement concentration data with detailed mineralogical or chemical speciation analyses [12].

3.5 Dioxin Content in Ash

3.5.1 Oil Shale Ash

The dioxin content in oil shale ash had not been extensively studied. To address this knowledge gap, ash from a pilot-scale unit was first analysed. The operating conditions of the pilot unit closely replicated those of the full-scale Enefit280 facility, particularly with respect to temperature distribution and oxygen concentration. This comparability enhances the reliability of extrapolating the pilot-scale findings to industrial-scale operations. The temperatures within the pilot unit ranged from 579 to 797 °C, a range conducive to the formation of dioxins. Nevertheless, all measured dioxin congeners in both the ash samples and the flue gas were found to be below the detection limit. **[Paper IV]**

To further evaluate the influence of combustion temperature and technology on dioxin formation under actual operating conditions, ash samples were collected and analysed from several oil shale power plants and shale oil plants. Consistent with the pilot-scale results, dioxin congeners in all full-scale samples were also below detection limits **[Paper IV].**

This study systematically examined whether varying operational conditions across different power plants influenced dioxin formation in ash. Ash samples were obtained from facilities operating at different capacities. Although operation at partial capacity has been shown to affect mineral decomposition, particle size distribution, and bulk density of ash [17], such variations did not appear to impact dioxin content. In Estonian oil shale plants, oil shale is typically co-combusted with biomass and/or retort gas. Additionally, wastewater generated during shale oil production is utilised in oil shale combustion through direct injection into the furnace, thereby achieving thermal degradation. As shown in Table 17, dioxin concentrations remained consistently below detection limits, regardless of the capacity, fuel type, or wastewater utilisation.

In this study, the total dioxin content was estimated using the upper-bound approach, whereby concentrations below the limit of quantification (LOQ) were assumed to be equal to the LOQ. Even under this conservative, worst-case scenario, the total dioxin concentration expressed as toxic equivalents (TEQs) was approximately 5 ng TEQ/kg. **[Paper IV]**

Table 17. Dioxin content in ash samples (upper-bound approach) in relation to plant capacity, fuel type, and wastewater addition ***[from Paper IV]****.*

Sample	Rated capacity (gross), MW_e	Capacity during sampling, MW_e	Fuel mix based on heat input	Wastewater, t/h	∑dioxins, TEQng/kg DW
Auvere PP BA			Oil shale 60%	0	5.75
Auvere PP ESP	305	233	Biomass 10%		5.6
Auvere PP FF			Retort gas 30%		5.81
Eesti PP PC BA	185–195	165	Oil shale 20% Retort gas 80%	0	5.46
				16	5.69
Eesti PP PC FF				0	5.44
				8	5.12
				16	5.44
Eesti PP CFBC BA	215	215	Oil shale 50% Retort gas 50%	0	5.49
				8	5.69
				16	5.74
Eesti PP CFBC FF	215	215		0	5.41
				8	5.31
				16	5.71
Enefit280 CY			Oil shale	0	7.97
Enefit280 ESP					5.42
Enefit140 total			Oil shale	0	5.48
Enefit140 ESP					5.26
Petroter CY			Oil shale	0	4.93
Petroter ESP					5.23

3.5.2 Biomass Ash

The dioxin content in most biomass ash samples was below the LOQ. However, a subset of three fly ashes stood out due to their elevated dioxin content. Among these, the highest concentration was observed in ESP ash. The actual maximum content measured was 279 ng TEQ/kg. Dioxin generation is a complex process, with Cl being an essential component in it. However, the tests revealed that at Cl contents ranging from 0.007% to 0.016%, Cl alone is not the sole determinant of the observed variations in dioxin content (Figure 4). Instead, an intricate interplay of contributing factors beyond Cl content warrants further investigation.

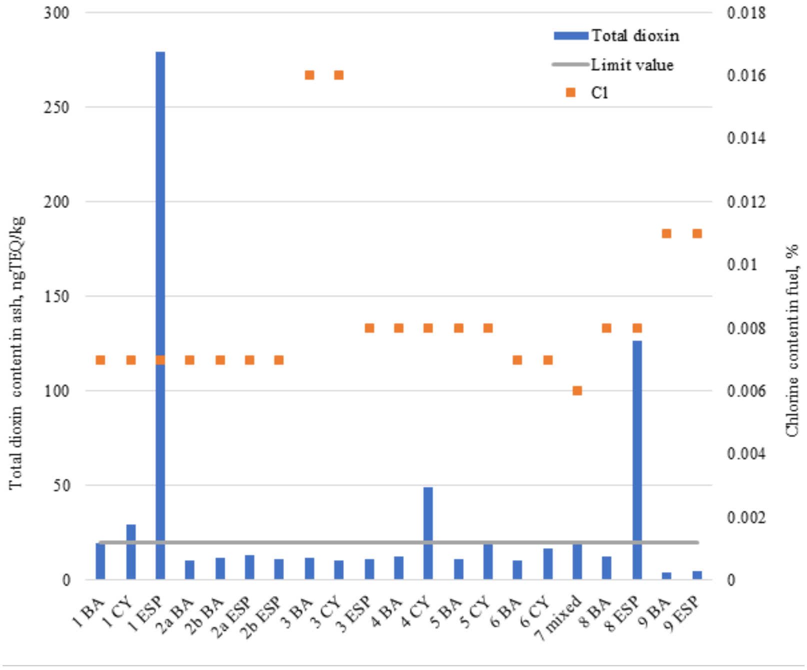

Figure 4. Correlation between total dioxin concentration in ashes and Cl content in fuels, with the indicated dioxin limit value of 20 ng TEQ/kg according to the Fertilising Products Regulation. ***[from Paper II]***

The preeminent contributor to the cumulative dioxin TEQ content in most cases are PCDDs, while PCBs are of marginal significance, exerting a negligible influence on the overarching dioxin TEQ content (Figure 5).

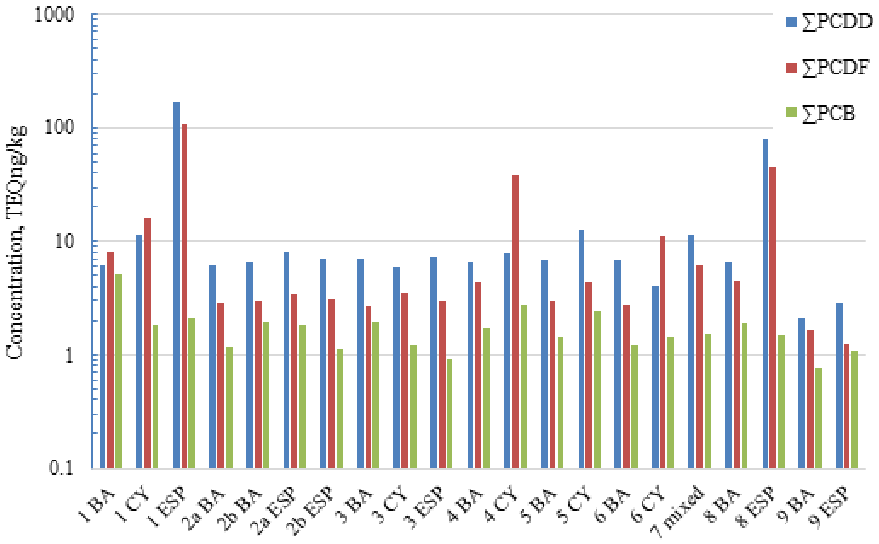

Figure 5. Total PCDD, PCDF, and PCB TEQ concentrations in biomass ashes. ***[from Paper II]***

3.6 Regulatory Assessment and Reuse Potential

3.6.1 The EU POPs Regulation Thresholds

One of the critical considerations in evaluating the potential for the recovery and reuse of waste materials, including combustion ashes, is compliance with the EU POPs Regulation [9].

Specifically, the regulation outlines strict conditions under which waste containing POPs may be recovered or must be disposed of. Annex IV of the regulation establishes concentration limits for various POPs, beyond which waste is considered non-recoverable and must be destroyed or irreversibly transformed, typically via landfilling. Among the substances listed, PCDD/PCDFs – commonly referred to as dioxins – are of particular concern due to their extreme toxicity, even at very low concentrations.

The regulatory threshold for dioxins, as expressed in TEQ, is set at 5 µg TEQ/kg of dry matter in waste. Any material exceeding this threshold cannot be subjected to recovery operations and is instead mandated for disposal through controlled and environmentally safe means. This presents a potential barrier to the valorisation of combustion residues, especially from sources known to produce trace amounts of POPs, such as waste incineration or uncontrolled combustion.

However, in the case of the biomass and oil shale ash samples under consideration, the measured concentrations of dioxins fall significantly below the regulatory threshold. In all analysed cases, the dioxin content was well below 5 µg TEQ/kg, often by orders of magnitude. **[Papers II and IV]**

Even more notably, oil shale ashes were found to contain dioxin levels lower than those observed in biomass ashes. This finding is significant, particularly given the historical classification of oil shale ash as hazardous waste under other criteria. The exceptionally low dioxin concentrations in oil shale ashes reinforce their regulatory acceptability and enhance their profile as a candidate for reuse, especially in the context of promoting circular economy practices. **[Paper IV]**

The implication of these findings is clear: neither the biomass nor the oil shale ashes examined fall under the restrictive provisions of the EU POPs Regulation with respect to PCDD/PCDF content. This regulatory clearance effectively removes one of the major barriers to their recovery and valorisation.

3.6.2 Fertilisers Regulations

When using ashes as fertilisers, it is essential to ensure compliance with the threshold limits established under the EU Fertilising Products Regulation [11]. Annex I of this regulation establishes a stringent threshold for dioxins: waste-derived materials used as components in fertilising products must not exceed a concentration of 20 ng TEQ/kg. This low threshold reflects the high toxicity and environmental persistence of dioxins, even at trace levels, and is designed to prevent long-term accumulation in agricultural soils and the food chain.

Analysis of dioxin concentrations in biomass ash samples reveals that, while many fall below the regulatory threshold, certain samples – particularly those derived from more variable or poorly controlled combustion processes – exceed the 20 ng TEQ/kg limit. This raises concerns regarding their suitability for use in fertilising products and necessitates further scrutiny in the classification and treatment of these materials.

In contrast, oil shale ashes consistently demonstrate dioxin concentrations significantly below the threshold. Even under conservative assumptions and worst-case analytical scenarios, dioxin levels in oil shale ash remain around 5 ng TEQ/kg. This margin of safety suggests that oil shale ash, provided other agronomic and ecotoxicological criteria are met, may represent a viable component in fertiliser formulations, especially in applications requiring high-calcium or sorbent-rich materials.

However, a methodological challenge arises when assessing trace dioxin concentrations that approach or fall below the analytical LOQ. At such low concentrations, the treatment of non-detects – i.e. congener concentrations below the LOQ – can substantially influence the reported total TEQ value. To address this, three different approaches are commonly used in regulatory toxicology:

- Upper bound: non-detects are assumed to be present at the LOQ (most conservative)
- Medium bound: non-detects are assigned half the LOQ
- Lower bound: non-detects are treated as zero (least conservative).

Each approach can yield different cumulative TEQ values, and the choice among them becomes particularly consequential when total concentrations approach regulatory thresholds such as the 20 TEQ ng/kg limit. For example, in a sample where most congeners fall below the LOQ, the upper-bound approach may produce a value just above the threshold, whereas the medium- or lower-bound approach might indicate compliance. **[Paper II]**

Currently, the EU Fertilising Products Regulation does not specify which bound approach should be adopted for compliance determination. This absence of guidance introduces ambiguity and the potential for inconsistent application across laboratories, Member States, and product assessments. Such variability undermines the harmonisation objectives of the regulation and complicates the decision-making process for material recyclers, producers, and regulators alike.

To ensure consistency and reliability in dioxin assessments, it is essential that the European Commission or relevant competent authorities issue clarifying guidance. This should define a harmonised approach for treating non-detects in ultra-trace dioxin analysis, ideally aligned with existing methodologies under other EU frameworks (e.g. food and feed safety or environmental monitoring). Until such harmonisation is achieved, stakeholders must remain cautious and transparent in their analytical methods, explicitly stating the bound approach used when reporting dioxin concentrations.

In addition to POPs such as dioxins, the regulatory framework for fertilising products places strict limits on the concentrations of heavy metal(loid)s in waste-derived materials used as fertiliser components. This is to prevent the long-term accumulation of potentially toxic elements in agricultural soils, which may pose risks to plant health, soil microbiota, and ultimately to human health through bioaccumulation in the food chain.

When comparing ashes derived from different fuel types, a clear distinction emerges between biomass ash and oil shale ash in terms of heavy metal(loid) content. Oil shale ash typically exhibits lower concentrations of regulated heavy metals such as Zn, Cu, Pb, and Cr **[Paper III]**, making them inherently more suitable for potential fertiliser applications under existing Estonian regulation [44].

By contrast, biomass ash – especially from mixed or poorly controlled sources – more frequently exceeds the threshold values for several regulated elements. Among these, Zn and Cu are the most commonly elevated, with Cr and Pb also occasionally surpassing permissible levels. These exceedances are often linked to two primary factors: the intrinsic composition of the feedstock and the quality control practices in biomass sourcing and combustion.

Natural wood inherently contains trace amounts of metals such as Zn and Cu, which are essential micronutrients in small quantities but become problematic when concentrated in ash. However, significantly elevated levels of these metals, particularly when accompanied by higher dioxin concentrations, may indicate contamination of the biomass fuel. This can result from the inclusion of treated wood, contaminated construction or demolition waste, or other non-virgin materials in the feedstock – sources that are not permissible under strict bioenergy or circular economy frameworks. Such patterns strongly suggest that fuel quality, rather than combustion technology alone, plays a pivotal role in determining the environmental acceptability of the resulting ash.

The observed correlation between elevated heavy metal concentrations and increased dioxin levels in some biomass ash samples further reinforces these concerns. This co-occurrence implies that substandard or contaminated biomass inputs may not only breach regulatory limits for individual pollutants but also contribute to a broader degradation in ash quality, making it unsuitable for fertiliser use without significant pre-treatment or exclusion. Given these findings, oil shale ash emerges as a more stable and predictable material in terms of compliance with heavy metal thresholds.

In conclusion, heavy metal(loid) concentrations represent a critical determinant in the feasibility of ash valorisation for fertiliser use. Oil shale ash demonstrates consistent compliance with relevant thresholds, whereas biomass ash poses more variable and context-dependent risks, primarily associated with inconsistent fuel quality and poor source control. Addressing these issues will require harmonised fuel standards, stricter feedstock quality assurance, and more robust traceability systems – especially for biomass-derived residues intended for agricultural reuse.

3.6.3 Landfill Acceptance Criteria

This classification has important implications for waste management. Ashes exceeding waste landfill thresholds for leachable metals must undergo pre-treatment or stabilisation prior to disposal. Such treatments aim to reduce the mobility of pollutants and ensure compliance with leaching criteria, thereby preventing environmental contamination through landfill leachate. These additional steps incur both environmental and economic costs, and complicate the logistics of biomass ash management.

The mobility of trace elements in oil shale ash, when compared with the limit values set for waste acceptance at landfills, demonstrates significantly lower levels than those established for inert waste, with the exception of Mo (Table 18). While the metals are in compliance with the thresholds for inert waste landfills, the levels of Cl ions in the fly ash eluates, along with sulphates, fall below the thresholds for non-hazardous waste. This means that oil shale ash follows the thresholds set for non-hazardous waste landfills. **[Paper III]**

*Table 18. Release of components from ash samples at pH_{mat} (L/S = 10/1), mg/kg **[adapted from Paper III]**.*

	Auvere PP FA	Eesti PP CFBC FA	Eesti PP PC FA	Enefit280 FA	Petroter ESP	Limit value inert waste	Limit value non-hazardous waste
Cr	0.965	1.100	0.350	1.397	0.075	0.5	10
Ni	0.006	0.008	0.008	0.004	0.005	0.4	10
Cu	0.015	0.005	0.004	0.005	0.018	2	50
Zn	0.023	0.013	0.010	0.006	0.036	4	50
As	<LOQ	<LOQ	0.002	0.012	0.024	0.5	2
Se	0.036	0.032	0.004	0.046	0.026	0.1	0.5
Mo	**0.736**	**0.522**	0.376	**2.578**	**0.882**	0.5	10
Cd	0.003	0.002	0.002	0.007	0.003	0.04	1
Sb	0.001	0.001	0.004	0.001	0.007	0.06	0.7
Pb	0.103	0.053	0.028	<LOQ	0.014	0.5	10
Cl^-	**2030**	**2260**	**2640**	**3700**	**900**	800	15000
SO_4^{2-}	**6651**	**14317**	**13479**	**13975**	**7230**	1000	20000
EC	**10990**	**11000**	**11650**	**3357**	1980	2000*	30000*

* Conductivity is estimated as half of the total dissolved solids value.

In contrast to the relatively consistent and compliant profile of oil shale ash, biomass ashes demonstrate a more complex and variable performance, particularly in relation to heavy metal content and leachability. In several instances, concentrations of Zn – and in one case Cr – in biomass ash have not only exceeded the thresholds set for use in fertilising products, but have also surpassed the regulatory limits established for acceptance at hazardous waste landfills (Table 19).

Table 19. Release of components from biomass ash samples at pH_{mat} (L/S = 10/1), mg/kg [12].

	1CY	1ESP	2b ESP	3 ESP	4 CY	6 CY	8 ESP	9 ESP	Non-hazardous	Hazardous
Cr	0.91	8.39	4.36	**131**	8.72	6.32	22	6.77	10	70
Ni	0.01	0.02	0.11	0.02	0.02	0.04	<LOQ	<LOQ	10	10
Cu	0.33	3.77	16.9	18.5	20.4	5.17	2.75	0.62	50	100
Zn	7.8	**304**	**206**	**567**	39	**203**	**374**	8.3	50	200
As	0.02	0.11	0.04	0.1	0.04	0.03	0.36	0.03	2	25
Se	0.11	0.86	0.37	0.83	0.32	0.21	1.43	0.36	0.5	7
Cd	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1	5
Pb	0.05	1.69	1.11	4.56	0.16	0.2	6.28	0.16	10	50
Cl^-	25.5	243	50.8	677	39.5	25.8	344	43.6	15000	25000
SO_4^{2-}	125	1170	326	1673	527	347	2409	274	20000	50000
EC	13940	46600	22330	**86670**	22450	18300	**59800**	20080	30000*	50000*

* Conductivity is estimated as half of the total dissolved solids value.

A noticeable correlation is observed between elevated concentrations of metals such as Zn and Cr and high EC values in the ash. High EC typically reflects the presence of soluble ionic species, including metal salts, and may serve as a useful indirect indicator of potential pollution risk. This relationship suggests that EC could be employed as a rapid, cost-effective screening tool for identifying biomass ash streams that require further analysis or treatment.

3.7 Influence of Combustion Technologies on Ash Hazardousness and Potential for Risk Reduction

The hazardous properties of ash – such as heavy metal content, leachability, ecotoxicity, and the presence of dioxins – are primarily influenced by the type of fuel combusted and the resulting ash fraction, rather than by the combustion technology itself. While different technologies were represented in the dataset, variation in hazardousness was more strongly linked to fuel characteristics (e.g. contamination with treated wood) and fraction-specific properties (fly ash vs bottom ash).

Ash samples studied in this work originated from a range of combustion setups, including PC, CFBC, SHC systems, and various biomass boilers, some of which co-fired treated wood. The results showed that ash characteristics differed significantly depending on the fuel mix and ash fraction.

Across both oil shale and biomass systems, fly ash typically exhibited higher concentrations of hazardous substances compared with bottom ash. This was especially evident for heavy metals (such as Zn and Pb), soluble salts (Cl, SO_4), and dioxins. For ecotoxicity, especially in *Daphnia magna* tests, toxicity was strongly EC- and pH-dependent, with ashes of lower EC and pH showing reduced toxic effects. **[Paper I]**

Fuel quality had a marked impact on dioxin concentrations. **[Paper II]** Biomass plants co-firing treated wood or using poorly sorted waste-derived fuels produced fly ash with elevated levels of PCDD/PCDFs, in some cases approaching or exceeding regulatory limits for fertiliser use. In contrast, when clean fuels were used, dioxin levels remained comparatively low.

The findings suggest that certain practices can reduce the hazardousness of ash. These include:

- Careful selection and monitoring of fuel inputs, particularly in biomass combustion, to prevent contamination with treated or painted wood.
- Fraction-specific testing and treatment, such as isolating fly ash for controlled disposal or pre-treatment.

While this thesis did not experimentally evaluate mitigation technologies, the results provide a strong basis for identifying where risk originates – chiefly in fuel composition and ash fraction – and where targeted management interventions can support safer reuse of ash. This aligns with broader circular economy goals by not only emphasising material recovery but also ensuring environmental safety.

4 Conclusions and Recommendations

Oil shale and biomass play an important role in Estonia's energy and heat production. However, they are also major contributors to waste generation in the sector. Within the framework of the circular economy, it is essential to ensure that all materials produced are utilised efficiently while protecting human health and the environment. Therefore, to maintain the sustainable use of oil shale and biomass in the future, it is crucial to focus on the recovery and valorisation of ashes.

This research provides a comprehensive assessment of the hazardous properties of oil shale and biomass ash generated in Estonia, focusing on their chemical composition, ecotoxicity, leaching behaviour, and dioxin content. Understanding these hazardous characteristics is crucial for determining the safe and sustainable future use of the ashes and ensuring that their utilisation aligns with environmental protection and circular economy principles.

The study presents an integrated hazard characterisation of Estonian oil shale and biomass ash using multiple assessment parameters. Although the oil shale ash fractions – particularly the fly ashes – exhibited some variation in their properties depending on combustion technology and collection point, the differences in hazardous characteristics among the various fly ash fractions were relatively modest. While the finest fractions contained higher concentrations of heavy metals, these differences did not affect their overall hazard classification. Biomass ashes, on the other hand, did not demonstrate the same consistency as oil shale ash. Their properties varied significantly depending on fuel composition. Some biomass ashes also contained elevated levels of heavy metals (Zn, Cu, Cr), which in turn influenced their overall toxicity.

This work delivers the first-ever comprehensive data on dioxin concentrations in Estonian oil shale and biomass ash. All oil shale ash samples had dioxin contents below the LOQ. Differences in plant capacity, technology used, collection point, and additional fuels had no effect on dioxin concentrations. In contrast, some fly ash samples from biomass combustion were above the LOQ and near or exceeded critical dioxin limits for fertilisers. The use of biomass ash may be hindered not only by dioxin content but also by Zn, Cu, and Cr concentrations that may exceed the permitted fertiliser limit values. Together with the elevated heavy metals content in those samples, the reason for higher dioxin levels is most likely fuel quality rather than combustion technology or operating conditions.

Ecotoxicological testing revealed that while *Daphnia magna* tests classified many oil shale ash fractions as hazardous, the computational method and *Aliivibrio fischeri* test proved otherwise. Although no ecotoxicity tests were conducted on biomass ashes, the computational method showed that, due to high Zn content, many of these ashes should be considered ecotoxic.

Leaching tests demonstrated that oil shale ash, in most cases, complies with the thresholds set for inert waste landfills, while in some cases (Cl^-, SO_4^{2-}, EC) it follows the thresholds for non-hazardous waste landfills. Biomass ash showed a different pattern; some ashes did not comply even with the criteria set for hazardous waste landfills, mostly due to Zn release.

In comparison with all the hazardous aspects analysed in this study, oil shale ash demonstrates a lower level of hazardousness than biomass ash. It exhibits lower concentrations of dioxins and heavy metals, reduced leachability, and lower ecotoxicity associated with Zn content. Despite these characteristics, oil shale ash has long been classified and managed as hazardous waste, while biomass ash has been recovered as non-hazardous. This regulatory disparity has resulted in a recovery rate of nearly 100% for biomass ash but only 2–3% for oil shale ash, illustrating how existing regulations have hindered the utilisation of a potentially valuable secondary material. These findings highlight the importance of aligning waste classification and management practices with current scientific evidence to support sustainable resource use and circular economy objectives.

Furthermore, the research underscores regulatory uncertainty, especially in the interpretation of ecotoxicity and the handling of results below the LOQ. A more transparent framework is needed to ensure both environmental protection and fair assessment of materials within circular economy initiatives. Regulatory bodies should provide clear guidance on how to interpret values below the LOQ, especially for substances such as dioxins, where thresholds are extremely low. Ambiguity in this area can hinder risk assessment and decision-making.

Further development of standardised and harmonised test protocols for ecotoxicity (HP14) is needed across the EU. Careful justification of test organisms and bioassay design is essential to avoid over-sensitivity and to reduce the risk of false-positive outcomes in HP14 assessment.

In conclusion, oil shale ash shows comparatively low hazardousness, with low heavy metal(oid) and dioxin levels. Biomass ash, however, presents greater concern due to elevated Zn and occasional dioxin levels, which may hinder safe reuse. Combustion technologies themselves did not significantly alter hazard characteristics, suggesting limited mitigation through process changes. For biomass, the main reduction measure lies in stricter fuel screening, particularly avoiding treated or contaminated wood.

Ash reuse should be encouraged, provided that material properties meet defined safety criteria. Pre-treatment methods to stabilise or reduce contaminants should be explored and implemented where necessary.

To support circular economy goals, future research should include comparative life cycle analyses of ash-derived products and their virgin material alternatives (e.g. ash vs lime fertilisers or cement). This would provide a broader sustainability perspective beyond hazard-based evaluation.

Especially in biomass combustion, fuel screening practices should be improved to avoid the inclusion of treated or contaminated wood. Ash handling practices should also ensure the separation of fractions for appropriate testing and reuse.

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Abstract

Hazardous Properties of Ash Generated in Estonia and Possibilities to Reduce the Hazardousness

The combustion of solid fuels inevitably generates large amounts of ash, which, depending on its composition and hazardous properties, can either represent a resource for secondary use or a risk to the environment and human health. Estonia, with its long tradition of oil shale utilisation and growing reliance on biomass for energy, produces approximately 5 million tonnes of oil shale ash and 40 000–50 000 tonnes of biomass ash annually. While biomass ash is largely recovered and used in soil improvement and other applications, oil shale ash is predominantly landfilled. However, the potential to valorise both types of ash within a circular economy framework is increasingly recognised. Despite this, a lack of comprehensive information on hazardous constituents – particularly persistent organic pollutants such as dioxins, heavy metals, and regulatory classification of ecotoxic properties – creates uncertainty for safe reuse.

This research provides the first integrated hazard characterisation of oil shale and biomass ashes produced in Estonia. Ashes from multiple combustion technologies and industrial processes were collected and systematically analysed. The research combined mineralogical and chemical analyses, leaching studies, and ecotoxicological assays (*Daphnia magna* and *Aliivibrio fischeri*), alongside targeted determination of heavy metals, metalloids, and dioxins.

The results demonstrate differences in hazardousness between oil shale and biomass ashes, as well as between bottom ash and finer fly ash fractions. Oil shale ash was found to contain generally low concentrations of heavy metals, with fly ash showing higher concentrations compared to bottom ash. Its leachates showed high EC due to soluble salts, but trace metal concentrations remained well below regulatory thresholds. In contrast, several biomass fly ash samples exhibited elevated levels of Zn, Cu, and Pb, in some cases exceeding landfill acceptance criteria and raising concerns regarding its further use.

A key novelty of this study lies in the first-ever quantification of dioxin concentrations in Estonian ashes. The dioxin content in oil shale ash was below the limit of quantification in all samples, with negligible effect from combustion technologies and conditions. On the other hand, some biomass fly ash samples revealed dioxin levels approaching or surpassing EU thresholds for fertilising products.

Ecotoxicity testing further highlighted ambiguities: results varied depending on the organism used, with *Daphnia magna* indicating higher sensitivity than *Aliivibro fischeri*. While the computational method and the test conducted with *Aliivibrio fischeri* indicate that oil shale ash is not hazardous, the *Daphnia magna* test suggests otherwise. This discrepancy demonstrates the limitations of current EU ecotoxicty (HP14) guidance and complicates waste classification when bioassays and calculation methods yield conflicting outcomes.

Overall, the study shows that oil shale ash complies with regulative acceptance criteria and may be safely valorised in various applications. While different combustion technologies, additional fuels, and different collection points in the process cause somewhat different properties in the ash's chemical and mineralogical composition, they do not alter the hazardous properties. However, biomass ash shows different hazard levels between bottom ash and fly ash, with fly ash showing elevated concentrations of

hazardous substances in certain ashes. As no clear evidence indicated a technological impact, fuel quality was most likely the main factor contributing to hazardousness. Therefore, biomass combustion requires stricter fuel quality control to prevent the formation of hazardous substances in the resulting ash.

The research contributes novel data to international discussions on ash hazardousness and fills an important national knowledge gap for Estonia. Its findings support regulators in refining classification methods, particularly regarding ecotoxicity and dioxin content, and assist industry stakeholders in designing risk-aware recovery pathways. Ultimately, this work demonstrates that while ashes hold significant potential as secondary raw materials, their safe utilisation requires careful characterisation and alignment with evolving environmental standards. By bridging scientific knowledge and regulatory practice, the research advances the implementation of a circular economy while ensuring protection of the environment and human health.

Lühikokkuvõte

Eestis tekkivate tuhkade ohtlikkus ja võimalused selle vähendamiseks

Tahkekütuste põletamisel tekib vältimatult suur kogus tuhka, mis oma koostise ja ohtlike omaduste tõttu võib olla kas väärtuslik teisene tooraine või risk keskkonnale ja inimtervisele. Eestis, kus põlevkivi kasutamisel on pikk traditsioon ning kus järjest enam kasutatakse energia tootmiseks ka biomassi, tekib igal aastal ligikaudu 5 miljonit tonni põlevkivituhka ja 40 000–50 000 tonni biomassi tuhka. Kui biomassi tuhk valdavalt taaskasutatakse, näiteks mullaparanduses ja muudel kasutusaladel, siis põlevkivituhk ladestatakse peamiselt prügilatesse. Samas nähakse nii põlevkivi kui ka biomassi tuhas üha suuremat potentsiaali ringmajanduses. Vaatamata tuhkade potentsiaalile võib vähene teadmine nende omadustest, nagu püsivate orgaaniliste saasteainete ja raskmetallide sisaldused ning ökotoksiliste omaduste õiguslik käsitlus, takistada tuhkade kasutamist.

Käesolev doktoritöö käsitleb esmakordselt Eestis tekkivate põlevkivi- ja biomassi tuhkade ohtlikkuse iseloomustust. Erinevatest põletustehnoloogiatest ja tööstusprotsessidest koguti tuhaproovid, milles määrati mineraalne ja keemiline koostis ning viidi läbi leostuvus- ja ökotoksilisuse katsed (*Daphnia magna* ja *Aliivibrio fischeri*). Lisaks määrati raskmetallide, metalloidide ja dioksiinide sisaldus.

Tulemused näitasid erinevusi põlevkivi ja biomassi tuhkade vahel ning samuti põhja- ja lendtuhkade vahel. Põlevkivituhk sisaldas üldjuhul vähe raskmetalle. Lendtuhas oli eelduslikult raskmetallide sisaldus suurem kui põhjatuhas. Leostuskatsed näitasid, et lahustunud soolad annavad küll kõrge elektrijuhtivuse, kuid raskmetallide sisaldused jäävad alla regulatiivsete piirväärtuste. Biomassi tuhkade puhul esines aga mitmes lendtuhaproovis suur Zn-, Cu- ja Pb-sisaldus, mis ületas kohati isegi ohtlike jäätmete prügilakriteeriume, seades kahtluse alla nende kasutamise.

Oluliseks uudsuseks on dioksiinide esmakordne määramine Eesti tuhkades. Dioksiinisisaldus põlevkivituhkades jäi kõikides proovides alla määramispiiri. Tähelepanuväärne on, et põlemistehnoloogiad ja -režiimid ei avaldanud märgatavat mõju dioksiinide sisaldusele. Samas läheneb mõne biomassi lendtuha dioksiinisisaldus Euroopa Liidu väetisetoodete piirväärtustele või ületab neid.

Ökotoksilisuse katsed tõid esile regulatiivsed ebaselgused: erinevad testorganismid andsid erinevaid tulemusi, kusjuures *Daphnia magna* osutus tundlikumaks kui *Aliivibrio fischeri*. Kui arvutusmeetodil põhinev keskkonnaohtlikkuse hindamine ja *Aliivibrio fischeri*'ga läbi viidud katse põhjal on põlevkivituhad mitteohtlikud, siis *Daphnia magna* katse põhjal on enamik põlevkivituhaksid ohtlikud. See lahknevus näitab, et praegused Euroopa Liidu keskkonnaohtlikkuse (HP14) juhised on ebapiisavad ja raskendavad jäätmete klassifitseerimist olukorras, kus katsed ja arvutusmeetodid annavad vastukäivaid tulemusi.

Üldjoontes võib järeldada, et põlevkivituhk vastab seadusega ette nähtud kriteeriumitele ning seda saab ohutult kasutada erinevatel kasutusaladel. Kuigi erinevad põletustehnoloogiad, lisakütused ja kogumiskohad protsessis mõjutavad tuha keemilist ja mineraloogilist koostist, ei muuda need oluliselt ohtlikke omadusi. Biomassi tuha ohtlikkus on aga erinev põhjatuha ja lendtuha puhul, kusjuures lendtuhas on ohtlike ainete kontsentratsioon märgatavalt suurem. Kuna tehnoloogilise mõju kohta ei ole selgeid tõendeid, on kütuse kvaliteet tõenäoliselt peamine ohtlikkust mõjutav tegur.

Seetõttu vajab biomassi põletamine põhjalikumat kütuse kvaliteedikontrolli, et vältida ohtlike ainete sattumist tuhasse.

Uurimistöö täidab olulise teadmislünga Eesti jaoks ning annab uue panuse rahvusvahelistesse aruteludesse tuhkade ohtlikkuse teemal. Saadud tulemused aitavad reguleerijatel täiustada liigitamismeetodeid, eriti keskkonnaohtlikkuse ja püsivate orgaaniliste saasteainete sisalduse osas, ning annavad tööstusettevõtetele vajalikke teadmisi riskipõhiste taaskasutusvõimaluste kavandamiseks. Kokkuvõttes näitab töö, et kuigi tuhkadel on märkimisväärne potentsiaal teisese toorainena, eeldab nende ohutu kasutamine põhjalikku iseloomustust ja vastavust üha rangematele keskkonnastandarditele. Ühendades teaduslikud teadmised ja regulatiivsed nõuded, toetab töö ringmajanduse edendamist, tagades samal ajal keskkonna ja inimeste tervise kaitse.

Appendix (Publications)

Publication I

Ummik, M.-L., Järvik, O., Reinik, J., Konist, A. Ecotoxicity assessment of ashes from calcium-rich fuel combustion: contrasting results and regulatory implications. Environmental Science and Pollution Research, 2024, 31, 48523−48533. https://doi.org/10.1007/s11356-024-34387-3

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RESEARCH ARTICLE

Ecotoxicity assessment of ashes from calcium-rich fuel combustion: contrasting results and regulatory implications

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Abstract

The European Union's (EU) regulation for the waste classification based on their ecotoxicological hazard (hazardous property HP14) came into force on 5 July 2018. The regulation advocates the utilisation of computational formulae for the hazard classification of waste associated with hazardous property HP14. Concurrently, ecotoxicological testing remains an alternative. To date, the absence of a consensus regarding test organisms and methodologies has vested EU member states with autonomy in determining the approach for conducting ecotoxicity assessments. The discussions on waste classification are also ongoing globally, namely the discussions under the Basel Convention. This paper endeavours to elucidate whether the widely employed test organisms, *Daphnia magna* and *Aliivibrio fischeri*, may serve as suitable indicators for the evaluation of the ecotoxicity of waste. The research is grounded in the examination of ashes derived from a combustion process of calcium-rich fuel. Ecotoxicity testing was conducted on 14 ash samples with a liquid-to-solid ratio of 10:1. The results of the *Aliivibrio fischeri* testing indicated that all 14 ash samples were non-hazardous in terms of their ecotoxicity. However, the results of the *Daphnia magna* testing showed the opposite, suggesting that the ash samples may have the potential to be ecotoxic. This study offers valuable insights into ecotoxicity assessment and waste classification, emphasising the need for scientific rigour and comprehensive understanding before making regulatory decisions. It also situates its findings within the broader global context of waste management discussions, particularly those related to international agreements like the Basel Convention.

Keywords Waste classification · HP14 · Ecotoxicity · *Daphnia magna* · *Aliivibrio fischeri* · Ash

Introduction

Ecotoxicity refers to the harmful effects of substances on the environment, including living organisms such as plants and animals. Ecotoxicity is one of the characteristics that classify waste as hazardous (EU 2008).

Ashes originating from a combustion process are usually considered waste. Waste can be classified as hazardous or non-hazardous based on its hazardous properties, including ecotoxicity. However, there are diverse ways to determine hazardous waste. Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal is a legally binding global agreement that defines hazardous waste (Basel Convention 1989). The Basel Convention has 190 Parties, which means that all countries need to respect the definition of hazardous waste set in the Convention. Hazardous wastes for the Basel Convention are the wastes that are listed in Annex I of the Convention, provided they exhibit any of the hazardous properties listed in Annex III of the Convention.

Ash originating from combustion does not appear in Annex I of the Basel Convention, meaning that the ash should not be considered hazardous waste. Despite the current exclusion of ash from the present delineation in Annex I, the ongoing revisions to the Basel Convention's annexes, initiated during the twelfth meeting of the Conference of the Parties to the Basel Convention in 2015, imply a potential future incorporation of combustion-derived ash into the list. Consequently, ash may become subject to assessment for hazardous properties. In Annex III of the Basel Convention, HP Ecotoxic has a code H12, defined as substances or

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wastes which, if released, present or may present immediate or delayed adverse impacts to the environment through bioaccumulation or toxic effects upon biotic systems. The ecotoxicity assessment is clarified in “Interim guidelines on the hazardous characteristics of H12 – Ecotoxic” (Secretariat of the Basel Convention 2003). The interim guidelines were adopted in 2003 and still need to be updated, so there is no agreed approach to assessing ecotoxicity.

In the European Union (EU), waste is classified according to Directive 2008/98/EC (EU 2008) and Commission Decision 2000/532/EC (EU 2000). According to the latter, some waste is always hazardous, and some is always non-hazardous. For those wastes for which either hazardous or non-hazardous waste codes could be assigned, the hazardous properties (HP) assessment is mandatory. Ecotoxicity (HP14) can be predicted by applying calculation formulas based on the chemical composition of wastes and experimental testing. It is agreed that experimental ecotoxicity testing results should prevail over the calculation method (EU 2017); however, the exact experimental approaches and test batteries are yet to be determined. The evaluation of suitable organisms and conditions influencing the testing of HP14 has been and will likely remain a subject of further discussion because of the complexity of the problem (Bandarra et al. 2020; Höss and Römbke 2019; Huguier et al. 2015; Moser et al. 2010; Pandard et al. 2006; Pandard and Römbke 2013; Römbke et al. 2009; Stiernström et al. 2016, 2014, 2011; Tsiridis et al. 2012, 2006).

According to the Commission Decision 2000/532/EC (EU 2000), bottom and fly ash originating from the combustion of coal, peat, and untreated wood is always considered non-hazardous waste. However, ash arising from the co-combustion of waste and other fuels may potentially be deemed hazardous, given its alignment with mirror codes in the waste list. Oil shale ash is not explicitly outlined in the EU waste list, leaving the responsibility for determining its classification to the national authorities.

According to EU regulations, Lees et al. 2020 calculated the toxicity values of oil shale ashes and concluded that oil shale ash should not be considered hazardous waste based on ecotoxicity. To further investigate this conclusion, the present study focuses on the experimental assessment of the ecotoxicity of oil shale ash. The methodology employed involves the use of two aquatic organisms, *Daphnia magna* and *Aliivibrio fischeri*. Both *Daphnia magna* and *Aliivibrio ficheri* are frequently used to test the ecotoxicity of the leachates, including leachates from ashes (Abbas et al. 2018; Choi et al. 2013; Ikeda et al. 2016; Millemann and Parkhurst 1980; Peng et al. 2022; Reinik et al. 2015).

The accurate characterisation of ecotoxicity, an HP with implications for both the environment and human health, is of paramount importance. Striking a balance between thorough characterisation and avoiding over-regulation is crucial.

The objective of this article is to investigate the ecotoxicological hazard classification of waste, specifically focusing on HP14 as outlined in EU regulations. It aims to assess the effectiveness of ecotoxicological testing using *Daphnia magna* and *Aliivibrio fischeri* as test organisms, specifically when testing ashes. The study aims to compare and contrast the results obtained from these testing methods by analysing ashes derived from a combustion process of calcium-rich fuel. Additionally, the article emphasised the importance of scientific rigour and informed decision-making in waste classification processes, contributing valuable insights to the broader discourse on global waste management.

Materials and methods

In Estonia, oil shale is used to produce energy and shale oil. Estonian oil shale consists of organic matter, primarily kerogen, which makes up 30–40% of its composition. Kerogen is a high-molecular, polyfunctional organic matter with a high hydrogen and oxygen content, low nitrogen content, and significant amounts of organic sulphur and chlorine. The mineral matter is categorised into sandy-clay or terrigenous parts and carbonate matter, with calcite (calcium carbonate) being the predominant mineral component in the carbonate fraction. The sandy-clay part of oil shale contains mainly Si, Al, and K bound in different minerals (Lille 2003; Ots 2007; Paat 2002; Veiderma 2003).

Oil shale ash is generated from energy production using pulverised combustion (PC), circulating fluidised bed combustion (CFBC) boilers, and shale oil production. In Estonia, approximately 8 million tonnes of oil shale ash are produced yearly. The ash samples were taken from two different CFBC energy production facilities (CFBC Auvere, CFBC EEJ), one PC facility equipped with a novel integrated desulphurisation equipment (PC-NID), and two shale oil production facilities (Enefit 280, Petroter). The samples were divided into bottom ash (BA) and fly ash (FA). Fly ash was collected from different appliances like economiser (ECO), air preheater (APH), electrostatic precipitators (ESP), fabric filter (FF) for CFBC facilities, and superheater (SH), economiser, cyclone (CY) for PC-NID, and for Petroter ash samples were collected from heat exchanger (HE) and electrostatic precipitators (ESP). The descriptions of the technologies can be found in other articles (Konist et al. 2013; Plamus et al. 2011) and are not discussed here. In total, 14 ash samples (Table 1) were analysed. The distribution and quantities of the ashes by technology type can be found in the supplementary material.

Oil shale ash has a large CaO (lime) content ranging from 13 to 65%. Table 2 shows the chemical composition

Table 1 Sample abbreviations

Abbreviation	Sample description
CFBC Auvere BA	Auvere Power Plant, CFBC boiler, bottom ash
CFBC Auvere ESP1	Auvere Power Plant, CFBC boiler, ash from the first ESP field
CFBC Auvere FA	Auvere Power Plant, CFBC boiler, FA
CFBC EEJ FA	Estonian Power Plant, CFBC boiler, FA
CFBC EEJ BA	Estonian Power Plant, CFBC boiler, BA
CFBC EEJ ESP1	Estonian Power Plant, CFBC boiler, ash from the first ESP field
PC-NID FA	Estonian Power Plant, PC facility equipped with NID equipment, FA
PC-NID NID	Estonian Power Plant, PC facility equipped with NID equipment, ash from the NID
PC-NID BA	Estonian Power Plant, PC facility equipped with a NID equipment, BA
Enefit 280 BA	Shale oil production facility Enefit280, ash from BA
Enefit 280 CY	Shale oil production facility Enefit280, ash from CY
Enefit 280 ESP	Shale oil production facility Enefit280, ash from ESP
Petroter HE	Shale oil production facility Petroter, ash from the HE
Petroter ESP	Shale oil production facility Petroter, ash from the ESP

of some ash samples. The composition was determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) according to standard ISO 29581–2:2010.

Quantifying trace elements in both ash eluates and solid ash samples involved a series of steps. Ash samples, having been dried and reduced to analytical size, underwent dissolution in a microwave oven using concentrated nitric acid ($HNO_3 > 65\%$) for trace element content determination. Ash eluates were prepared in accordance with standard EN 12457–4, maintaining a liquid-to-solid ratio of 10:1. Quantification of trace elements in both ash and eluates was conducted through inductively coupled plasma mass spectrometry (ICP-MS) utilising Thermo iCAP Qc Quadrupole Inductively according to standard test method ASTM D6357-21a. Notably, the average relative standard deviation for all measurements remained below 3%.

The ecotoxicological analysis with two test organisms, *Daphnia magna* (Acute toxicity test; SN EN ISO 6341; STN 83 8303 and *Aliivibrio fischeri* (Microtox test; CSN EN ISO 11348–2), was conducted in the accredited laboratory ALS in the Czech Republic. The acute toxicity test with *Daphnia magna* was performed at a constant temperature of 22.1–23.3 °C, over a 48-h period, using neonates less than 24 h old. The test conditions excluded aeration and feeding. The pH of the solution was measured at the beginning and end of each test, ranging from 10.6 to 9.2 initially and decreasing to 9.2 to 7.6 by the end of the test. Dissolved oxygen levels were also recorded after 48 h, ranging from 8.1 to 7.5 mg/L. The *Daphnia magna* acute toxicity test works by determining the initial or dilute concentration that can immobilise 50% of exposed Daphnia magna neonates within 48 h (ISO 2012). This specific concentration is referred to as the 48-h effective initial inhibitory concentration (EC50 48 h). For the Microtox test, the intensity changes of the luminescence of the *Aliivibrio fischeri* cultures were measured after a contact time of 15 min. The inhibitory effect of the water sample is determined as EC50, where the EC is the effective concentration (ISO 2007).

Results and discussion

Ecotoxicity of ashes

In accordance with the calculation methodology outlined in the EU Regulation, it has been determined that the oil shale ash, when assessed for ecotoxicity, does not meet the criteria for classification as hazardous waste (Lees et al. 2022, 2020). Lees et al. 2020 also found that the main components affecting the end result are the concentrations of trace elements. Nevertheless, determining waste ecotoxicity through experimental ecotoxicity testing is also feasible, even without unanimous agreement on the methodologies employed. The literature reflects diverse evaluations of ecotoxicity across various ash types. Blinova et al. 2012 have analysed oil shale ash from the last fields of CFBC and PC boiler electrostatic precipitators (ESPs), which account for 0.2 to 1% of the total boiler ash. The ash from the ESP is known to have an increased concentration of trace elements. Their results showed that leachate (liquid-to-solid ratio of 10:1) is toxic (mainly PC ash) to various aquatic organisms (*Daphnia magna*, *Pseudokirchneriella subcapitata*, and *Aliivibrio fischeri*) mainly due to its' alkaline pH ($pH > 9$) and probably also because of the salinity, while exposure to soil significantly reduces leachate toxicity. Neutralised CFBC ash leachate was toxic only to *Daphnia magna* due to salinity. Kahru and Põllumaa 2006 studied the toxicity of the oil shale ash from the ESP and cyclone of the PC boiler, and

Table 2 Chemical composition of the ash samples, w %

	CFBC Auvere BA	CFBC Auvere ESP1	CFBC EEJ BA	CFBC EEJ ESP1	PC-NID BA	PC-NID NID	Enefit 280 BA	Enefit 280 CY	Enefit 280 ESP	Petroter HE	Petroter ESP
MgO	7.97	6.41	6.57	5.86	8.65	3.91	3.19	3.25	1.71	4.02	2.60
Al_2O_3	1.77	6.49	3.48	9.57	5.62	6.62	1.26	6.66	7.45	4.37	13.75
SiO_2	12.26	30.18	10.72	29.92	20.91	30.20	9.25	30.82	27.01	19.08	40.34
SO_3	19.90	10.72	2.15	7.13	0.8	17.63	9.60	9.74	3.04	4.02	0.95
K_2O	0.60	3.33	1.08	3.6	2.07	3.41	0.46	3.14	3.09	1.48	5.17
CaO	52.33	37.70	65.34	35.72	53.53	33.88	45.61	29.50	20.99	35.18	13.54
Fe_2O_3	2.62	3.33	3.40	4.92	4.01	2.89	1.58	0.36	2.67	2.73	3.89

Table 3 Hazard classification system for wastes discharged into the aquatic environment (Persoone et al. 2003)

TU		Toxicity
< 0.4	Class I	No acute toxicity
$0.4 < TU < 1$	Class II	Slight acute toxicity
$1 < TU < 10$	Class III	Acute toxicity
$10 < TU < 100$	Class IV	High acute toxicity
$TU > 100$	Class V	Very high acute toxicity

Table 4 Results of ecotoxicity assessment of different ashes from the oil shale industry*

	D. magna		*Aliivibrio fischeri*	
Sample	EC50 48 h, ml/l	TU	EC50 15 min, ml/l	TU
CFBC Auvere BA	23.2	4.3	N/A	N/A
CFBC Auvere ESP1	44.2	2.3	N/A	N/A
CFBC Auvere FA	27.9	3.6	N/A	N/A
CFBC EEJ FA	19.3	5.2	N/A	N/A
CFBC EEJ BA	20.1	5.0	N/A	N/A
CFBC EEJ ESP1	28.5	3.5	N/A	N/A
PC-NID FA	20.5	4.9	N/A	N/A
PC-NID NID	23.2	4.3	N/A	N/A
PC-NID BA	21.6	4.6	N/A	N/A
Enefit 280 BA	278	0.4	N/A	N/A
Enefit 280 CY	362	0.3	N/A	N/A
Enefit 280 ESP	178	0.56	N/A	N/A
Petroter HE	108	0.92	N/A	N/A
Petroter ESP	N/A	N/A	N/A	N/A

*N/A – it was not possible to determine ecotoxicity because the inhibition value was not reached; i.e., the sample is not toxic enough to determine the dilution value

they concluded that the toxicity of the ash leachate is mainly due to the alkalinity. Kahru and Põllumaa 2006 also showed that in the Microtox test, toxicity to *Aliivibrio fischeri* after leachate neutralisation reduced 63 to 130-fold, depending on the ash. The ecotoxicity testing of alkali leachate from concrete and concrete-based construction waste shows similar behaviour (Choi et al. 2013; Mocová et al. 2019).

Insufficient information was obtained regarding the experimental ecotoxicity of oil shale ash due to the exclusion of certain types of ash from testing. In order to evaluate the suitability of the *Daphnia magna* acute toxicity test and *Aliivibrio fischeri* Microtox test as ecotoxicity testing methods for oil shale ash, 14 ash samples were tested. The results obtained in both ecotoxicity tests were also calculated as toxic units (TU) using the formula: $TU = [1/EC50] \times 100$. The hazard classification based on TU is shown in Table 3, and the results of the ecotoxicity tests are shown in Table 4.

Based on the results of the *Daphnia magna* acute toxicity test, almost all types of oil shale ash should be considered hazardous waste. Only ashes originating from Enefit 280 and Petroter's ESPs can be considered non-hazardous. In contrast, the *Aliivibrio fischeri* acute toxicity test indicates that all the ashes are non-hazardous.

The test organisms displayed diverse responses to oil shale ashes, prompting questions about the methodologies used to classify analogous materials such as coal ashes and evaluate their ecotoxicity.

The composition of coal ashes varies considerably because of the differences in the mineral composition of coal (Baba and Kaya 2004; European Commission, Joint Research Centre et al. 2017; Tsiridis et al. 2012) and depending on combustion technology. Several studies have assessed the ecotoxicity of coal ash. Due to the significant variability of the composition of coal, the estimates of the toxicity of coal ash, mainly through leachate testing, also differ—it varies from very toxic to non-toxic (Baba and Kaya 2004; Bandarra et al. 2020; Millemann and Parkhurst 1980; Neufeld and Wallach 1984; Palumbo et al. 2007; Tsiridis et al. 2012). There are also indications of the genotoxicity of coal ash (Chakraborty and Mukherjee 2009) and overall adverse effects on human health (Kravchenko and Lyerly 2018). The consensus is that fly ash is more toxic than bottom ash (Gallardo et al. 2015a; Skodras et al. 2009). The ecotoxicity assessment depends on the specific coal ash (Schwartz et al. 2018) and the test organism used. Generally, the widely used test organism *Daphnia magna* is more sensitive to coal ash leachate than *Aliivibrio fischeri* (Darakas et al. 2013; Tsiridis et al. 2012, 2006).

As the exact cause of the coal ash ecotoxicity is not evident, it has been concluded that it is either caused by the pH value of the leachate (Bandarra et al. 2020; Griffin et al. 1980; Ikeda et al. 2016; Palumbo et al. 2007), high ionic strength of the analysed solution (expressed by solute content or electrical conductivity) (Griffin et al. 1980); or high content of leachable heavy metals (Karuppiah and Gupta 1997; Sherrard et al. 2015).

Based on several ecotoxicity research on coal ash (Baba and Kaya 2004; Bushumov et al. 2018; Chakraborty and Mukherjee 2009; Gallardo et al. 2015b; Griffin et al. 1980; Kravchenko and Lyerly 2018; Millemann and Parkhurst 1980; Neufeld and Wallach 1984; Palumbo et al. 2007; Skodras et al. 2009; Tsiridis et al. 2012), it can be concluded that the ecotoxicity of coal ash is similar to oil shale ash.

Probable causes of ecotoxicity

One possible cause of ashes' ecotoxicity is the concentration of trace elements, including heavy metals, in the leachates. The concentration of trace elements increases from bottom ash towards finer fractions of fly ash, reaching the highest concentration in the last fields of the electrostatic precipitators. Even with the highest concentrations, the majority of the trace elements in oil shale ash are below 100 ppm (Lees et al. 2022).

The trace elements were also analysed in the leachates of the 14 oil shale ash samples. Since the content of trace elements in the oil shale is incredibly low, it is clear that the concentration in the leachate of oil shale ashes is even lower (Table 5). Furthermore, it is imperative to highlight that the variance in trace element concentrations between the specimens exhibiting the utmost (CFBC EEJ FA) and the lowest (Enefit 280 CY) TU is deemed negligible. This observation fails to demonstrate a discernible correlation between trace element levels and the manifestation of ecotoxicity of oil shale ash.

The composition of coal fly ashes, and the concentrations of trace elements vary widely and are documented in several articles (Moreno et al. 2005; Papadakis 2000; Uliasz-Bochenczyk and Mokrzycki 2006; Vassilev and Vassileva 2007). The concentrations of trace elements in these ashes highlight their diverse nature, with levels typically below 1000 ppm. However, one of the leading causes of the ecotoxicity of ashes is estimated to be leached trace elements.

A comparison between coal-fired power plant boiler fly ash and oil-shale-fired power plant boiler fly ash is presented in Table 6. The content of trace elements in coal and oil shale ashes is at the same level or lower in oil shale ashes. In general, the content of trace elements for both ashes varies on a large scale. However, the variation is notably more significant for coal ashes, primarily because the composition of coal displays substantial fluctuations (Ahamed et al. 2019). In contrast, the oil shale used for energy and oil production in Estonia is a kukersite known for its relatively stable content (Väli et al. 2008).

Organic substances like PAHs have been detected in the oil shale ash (Kirso et al. 2005, 1994; Kirso and Irha 1999; Paalme et al. 1990); however, the content of these substances is so marginal that it is of interest only from a scientific point of view. In the CFBC ashes, PAHs are up to 50 μg/kg, and 110 μg/kg in the PC ashes. The research conducted by Irha et al. 2015, revealed that the concentration of total content of PAHs in leachates from oil shale ash was determined to be notably low, ranging from 0.025 to 0.059 μg/L. This finding is particularly noteworthy when contrasted with the regulatory standards established by the EU Directive on the quality of water intended for human consumption (EU 2020), which prescribes a limit value of 0.1 μg/L for the sum of concentrations of the following specified compounds: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, and indeno(1,2,3-cd)pyrene. The results suggest that the levels of PAHs in the examined oil shale ash leachates fall well below the specified regulatory threshold, emphasising the relative insignificance of their presence in comparison

Table 5 pH, conductivity, and leachable contents of trace elements from oil shale ashes (μg/L) (L/S = 10)

	CFBC Auvere BA	CFBC Auvere ESP1	CFBC Auvere FA	CFBC EEJ BA	CFBC EEJ ESP1	CFBC EEJ FA	PC-NID BA	PC-NID NID	PC-NID FA	Enefit 280 BA	Enefit 280 CY	Enefit 280 ESP	Petroter HE	Petroter ESP
Li	24.82	61.12	68.42	17.35	32.87	28.9	33.38	27.86	24.65	10.26	11.68	11.30	18.87	12.17
Be	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Ti	0.44	0.31	0.28	0.59	0.39	0.48	0.4	1.72	0.56	0.37	0.77	0.38	0.38	1.92
V	0.1	0.40	0.36	0.09	0.25	0.26	< LOQ	0.38	0.21	10.16	16.05	17.13	2.40	46.02
Cr	0.05	99.88	96.45	< LOQ	117.34	109.96	0.09	42.16	34.96	21.01	150.71	139.67	0.05	7.51
Mn	0.13	0.18	0.12	0.56	0.14	0.12	0.21	0.27	0.16	0.11	0.57	0.17	0.13	1.49
Co	0.25	0.22	0.21	0.24	0.27	0.26	0.21	0.28	0.25	0.17	0.18	0.17	0.17	0.21
Ni	0.97	0.69	0.60	0.79	0.78	0.78	0.64	0.91	0.77	0.38	0.6	0.38	0.39	0.54
Cu	0.34	0.62	1.49	0.25	1.03	0.5	1.14	1.28	0.41	0.32	1.63	0.54	1.98	1.82
Zn	6.03	2.61	2.32	0.87	1.5	1.31	1.63	1.24	1.04	0.22	1.82	0.57	2.35	3.57
As	0.02	0.01	< LOQ	0.01	0.01	0.0	< LOQ	0.27	0.17	1.02	0.76	1.18	0.45	2.39
Se	0.43	3.35	3.62	0.91	3.4	3.22	0.19	0.36	0.37	0.65	5.18	4.63	0.07	2.64
Sr	3908.1	5438.19	5724.14	2650.32	3508.3	3821.98	5180.78	1664.26	2080.76	894.67	1906.88	1640.83	1176.75	1058.31
Mo	50.09	74.16	73.56	15.3	51.38	52.19	14.26	46.03	37.61	77.97	291.88	257.8	40.68	88.16
Cd	0.23	0.28	0.31	0.15	0.22	0.23	0.14	0.21	0.19	0.55	0.81	0.72	0.2	0.3
Sb	0.17	0.11	0.14	0.1	0.12	0.08	0.07	0.1	0.37	0.48	0.1	0.08	0.21	0.67
Tl	< LOQ	4.77	4.6	< LOQ	3.65	3.03	< LOQ	4.71	4.09	0.04	0.43	0.07	< LOQ	7.72
Pb	0.01	11.0	10.33	< LOQ	4.14	5.31	0.28	3.37	2.81	< LOQ	0.13	< LOQ	0.02	1.44
pH	13.01	13.14	13.12	13.11	12.82	13.13	13.07	12.9	13.11	12.35	12.06	12.1	12.67	10.42
Conductivity, μS/cm	10,500	11,840	10,990	11,200	9780	11,100	9500	11,350	11,650	3472	3240	3357	3321	1980

LOQ limit of quantitation

Table 6 Examples of trace element concentrations (mg/kg) in coal-fired power plant boiler fly ash and oil-shale-fired power plant boiler fly ash

Element	Coal				Oil shale				
	PC * (Silva et al. 2010)			PC** (Llorens et al. 2001)	CFBC Auvere FA	CFBC EEJ FA	PC-NID FA	Enefit 280 CY	Petroter HE
Li	85.3	90.3	104.6	235	27.9	31.0	24.8	21.8	14
Be	10.3	10.1	12.6	11	0.5	0	0.2	0.7	0.82
V	199.5	234.7	351.3	208	83.7	54.5	49.6	48.9	29
Cr	106.4	122.8	161.1	134.2	46.2	52.3	48.1	48.4	22
Mn	554.2	348.5	326.5	324.6	589.1	474.8	556.3	340.5	325
Co	19.3	16.9	17.7	29.2	5.2	5.8	5.3	6.8	3.2
Ni	44.3	38.8	43.6	87.9	26.8	31.1	27.2	33.5	17
Cu	47.1	41.1	54.8	71.8	10.7	10.2	9.9	8.0	9.2
Zn	203.4	287.4	913.0	221	201.3	44.8	67.5	79.2	39
As	2.1	15.0	139.0	60.0	25.3	11.9	15.7	27.5	7.8
Se	7.6	7.0	18.6	1.6	4.3	4.0	4.0	0.3	< 2
Sr	113.4	136.8	200.3	720	336.9	360.7	330.6	332.3	220
Mo	5.8	6.2	19.6	14.6	9.7	5.8	5.7	12.5	3.1
Cd	< 1	1.1	3.4	1.3	1.1	0.3	0.3	0	< 0.1
Sb	2.5	2.3	7.1	3.8	0	0	0	0	< 1.0
Pb	34.4	51.9	161.0	52	129.3	64.4	60.3	52.5	30

*Medium-sulphur coal (< 2% total S) with ~ 40% ash

**Homogenised mixture of 95% low-quality sub-bituminous coal and 5% bituminous coal

to established water quality guidelines. PAH content within coal ashes has been documented to exhibit relatively higher concentrations than ashes derived from oil shale. This disparity in PAH content spans a range encompassing values from 0.3 to 1698 µg/kg (Apostolova et al. 2021; Liu et al. 2018; Verma et al. 2015).

The toxic effect of physiologically unacceptable pH levels on aquatic organisms is evidenced by the viability of *Daphnia magna*, a water flea species. The pH range for the survival of *Daphnia magna* is observed to be within the values of 4.55 and 10.13 (El-Deeb Ghazy et al. 2011). In addition to the limitations of pH tolerance, it should be considered that the test organism *Daphnia magna* inhabits fresh to brackish water bodies. Based on the results by Schuytema et al. 1997, it can be inferred that *Daphnia magna* can thrive and procreate satisfactorily in water with salinities below 4 g/l. Consequently, this organism is not the most appropriate choice for assessing the ecotoxicological status of environments characterised by high mineral content due to their elevated salinity levels.

In such contexts, alternative test organisms like *Aliivibrio fischeri* may offer greater applicability. Commonly found in subtropical and temperate marine environments, *Aliivibrio fischeri* inherently possesses adaptations that favour saline conditions. Various studies have evaluated the toxicity of different trace elements using Microtox assays, with results revealing diverse toxicity profiles (Abbas et al. 2018). For example, beryllium was identified as the most toxic metal, while thallium showed minimal toxicity (Hsieh et al. 2004). Similarly, studies by Fulladosa et al. 2005 and Ishaque et al. 2006 reported varying toxicity levels among trace elements, with mercury, lead, cadmium, and arsenic exhibiting significant toxicity. In addition, *Aliivibrio fischeri* was found to be less sensitive than other test organisms, such as *Daphnia magna*, suggesting its suitability for assessing specific types of toxicity, possibly influenced by the presence of chromium (Tsiridis et al. 2006).

Bayo et al. (2009) evaluated the ecotoxicity of biologically treated water from a municipal wastewater treatment plant using *Aliivibrio fischeri*. Their results showed significant correlations between toxicity levels and parameters such as total carbon, total inorganic carbon, total nitrogen, chlorine, and pH. Factors like total organic carbon, chemical oxygen demand, electrical conductivity, and turbidity did not affect toxicity.

Pearson's bivariate correlation analysis involving the concentrations of trace elements in leachates of oil shale ashes, pH, and conductivity suggests that while pH may be a potential factor, conductivity is even more likely to be the primary driver of ecotoxicity in the ashes.

Since the *Aliivibrio fischeri* showed no toxicity to the ash eluates, only the toxicity results to *Daphnia magna* were used in Pearson's correlation. The correlation between the *Daphnia magna* results and the trace elements is weak or strongly negative (Table 7). The strongest positive

Table 7 Pearson's bivariate correlation between selected parameters and toxicity (*D. magna*) in water extracts of 14 oil shale ash samples (L/S = 10) (bold at significance level $p < 0.01$)

	Li	*Be*	*Ti*	*V*	*Cr*	*Mn*	*Co*	*Ni*	*Cu*	*Zn*	*As*	*Se*	*Sr*	*Mo*	*Cd*	*Sb*	*Pb*	*pH*	*Conductivity*	*D. Magna*
Li	1.000																			
Be	−0.491	1.000																		
Ti	−0.526	**0.983**	1.000																	
V	−0.447	**0.769**	**0.759**	1.000																
Cr	0.292	−0.191	−0.192	−0.044	1.000															
Mn	−0.595	**0.914**	**0.919**	**0.744**	−0.139	1.000														
Co	−0.477	**0.995**	**0.985**	**0.750**	−0.191	**0.897**	1.000													
Ni	−0.305	0.644	**0.690**	0.385	−0.241	0.591	**0.703**	1.000												
Cu	0.169	0.163	0.224	0.200	0.452	0.244	0.154	−0.006	1.000											
Zn	−0.377	**0.931**	**0.904**	**0.700**	−0.206	**0.818**	**0.933**	**0.739**	0.140	1.000										
As	−0.501	**0.773**	**0.770**	**0.984**	−0.059	**0.729**	**0.752**	0.353	0.155	**0.683**	1.000									
Se	0.470	−0.474	−0.500	−0.278	**0.844**	−0.353	−0.488	−0.469	0.367	−0.439	−0.349	1.000								
Sr	**0.872**	−0.558	−0.625	−0.509	0.236	−0.620	−0.550	−0.296	0.059	−0.386	−0.577	0.450	1.000							
Mo	−0.374	0.478	0.481	0.561	0.492	0.546	0.450	0.167	0.360	0.452	0.613	0.100	−0.332	1.000						
Cd	−0.283	−0.009	−0.003	0.228	0.450	0.145	−0.073	−0.454	0.361	−0.043	0.239	0.482	−0.334	0.492	1.000					
Sb	−0.554	**0.949**	**0.923**	**0.753**	−0.264	**0.819**	**0.935**	0.499	0.022	**0.857**	**0.790**	−0.552	**−0.668**	0.446	0.070	1.000				
Pb	**0.896**	−0.280	−0.307	−0.297	0.494	−0.412	−0.262	−0.202	0.160	−0.236	−0.332	0.534	0.653	−0.181	−0.172	−0.332	1.000			
pH	0.647	**−0.888**	**−0.887**	**−0.851**	0.028	**−0.879**	**−0.860**	−0.397	−0.295	−0.796	**−0.866**	0.290	**0.715**	−0.636	−0.402	**−0.886**	0.437	1.000		
Conductivity	**0.672**	**−0.759**	**−0.738**	**−0.729**	0.024	**−0.765**	**−0.709**	−0.138	−0.254	**−0.653**	**−0.757**	0.210	**0.701**	−0.599	−0.579	**−0.807**	0.491	**0.949**	1.000	
D. magna	0.419	−0.631	−0.609	**−0.700**	−0.157	−0.634	−0.576	0.004	−0.309	−0.557	**−0.725**	0.001	0.549	−0.617	**−0.686**	**−0.687**	0.213	**0.864**	**0.918**	1.000

Bold at significance level $p < 0.01$

correlations are found between *Daphnia magna*, pH, and conductivity.

Conclusions

The computational method for assessing the ecotoxicity of waste is agreed upon in the EU. However, tests are still possible. This paper analysed the two frequently used aquatic organisms, *Daphnia magna* and *Aliivibrio fischeri*, for ecotoxicity testing of oil shale ash. The content of trace elements in the ashes and leachates and their effect on the test organisms were also discussed. The results of oil shale ash's ecotoxicity were compared with coal ashes.

The test results of *Daphnia magna* and *Aliivibrio ficheri* were contradicting. In total, 14 samples of industrial oil shale ashes were analysed. According to *Daphnia magna*, most of the ashes should be classified as ecotoxic, while *Aliivibrio ficheri* shows that none are ecotoxic. Similarly, a literature review on coal ash presents conflicting findings.

The results suggest that the pH and conductivity have the most considerable influence on the *Daphnia magna,* giving a positive response to ecotoxicity. *Daphnia magna*, as a freshwater organism, is not optimally suited to assess ecotoxicological conditions in highly mineralised environments. Consequently, the reliability of results derived from the marine bacteria *Aliivibrio fischeri* is greatly enhanced under such circumstances.

Determining hazardous properties such as HP14 Ecotoxic (or H12 for the Basel Convention) for particular wastes is a multifaceted and contentious process, often posing significant challenges. At the same time, it is a critical feature for many potentially recyclable waste streams. The final decisions on ecotoxicity require a thorough analysis of short- and long-term consequences, especially regarding the circular economy.

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RESEARCH ARTICLE

Dioxin concentrations and congener distribution in biomass ash from small to large scale biomass combustion plants

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Abstract
Biomass plays a pivotal role in global energy production, with a significant share allocated for industrial heat and power generation. The combustion of biomass generates biomass ash, which is widely utilized as a fertiliser. However, concerns arise regarding the presence of dioxins in biomass ash, which may limit its continued use. Dioxins are toxic compounds listed under the Stockholm Convention due to their persistence and detrimental effects on human health and the environment. This study investigates the dioxin content in biomass ashes produced in various combustion plants with a capacity of 1–50MWth in Estonia, where biomass is widely used for heating and power production. The research encompassed samples from nine biomass combustion plants with varying technical parameters considering both bottom and fly ash. Dioxin concentrations were determined for 7 polychlorinated dibenzo-p-dioxins (PCDDs), 10 polychlorinated dibenzofurans (PCDFs), and 12 dioxin-like PCBs (PCBs). The results indicate that dioxin TEQ content in all samples was well below the European Union's (EU) POP Regulation limit of 5 μg TEQ/kg, with most values being at least tenfold lower. However, some samples failed to meet the EU Fertilising Products Regulation's threshold of 20 ng TEQ/kg. Notably, fly ash exhibited higher dioxin concentrations than bottom ash. While PCBs were in significant concentrations, PCDDs dominated the overall dioxin TEQ content. This study provides essential insights into the dioxin content in biomass ash and its correlation with current EU regulatory limits. It also highlights the complex distribution of dioxin congeners, particularly PCBs, within biomass ash, emphasizing the continued research's importance.

Keywords Biomass ash · Dioxins · PCDDs · PCDFs · PCBs · POP Regulation · Fertilising Products Regulation

Introduction

Biomass is widely used to generate energy. In 2022, approximately 60 EJ of solid bioenergy were utilized globally. The inefficient, traditional deployment of biomass for cooking and heating accounted for roughly 24 EJ. This distribution was predominantly witnessed in Africa and Asia. Around 35 EJ of modern solid bioenergy were harnessed in 2022, catering mainly to power generation and industry, with a smaller yet significant portion utilized in the buildings sector. According to various scenarios the bioenergy supply is expected to grow, offering dispatchable renewable power, a cost-competitive source of clean heat for industry, and an alternative to traditional solid biomass use in emerging markets and developing economies (International Energy Agency 2023).

The by-product of biomass combustion is biomass ash. Currently, there is a lack of regular publication of biomass ash production data. Consequently, directly gauging the global production of ash from sustainable fuels becomes challenging. Biomass combustion yields approximately 1–2% ash (for woody feedstocks) to 5–9% ash by weight (for herbaceous feedstocks) (Zhai et al. 2021).

Biomass ash is widely used as a fertiliser (IEA Bioenergy 2019). However, there might be limitations in continuing usage of the ash as a fertiliser due to the content of hazardous substances like dioxins. The term "dioxins" is often used as a general term to describe 75 polychlorinated dibenzo-p-dioxins (PCDDs), 135 polychlorinated dibenzofurans (PCDFs), and sometimes also 209 polychlorinated biphenyls (PCBs) (Zhang et al. 2016). So far 10 PCDFs,

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7 PCDDs, and 12 PCB-s out of the 419 dioxin congeners have been recognized as having toxic effects on humans by WHO (Van Den Berg et al. 2006).

The majority of the toxic and biological effects stemming from dioxins are mediated via the aryl hydrocarbon receptor, a cytosolic receptor protein found in most vertebrate tissues. This receptor exhibits a strong affinity for 2,3,7,8-substituted PCDDs and PCDFs, as well as certain PCBs (Safe 1998, 1986). Since not all the dioxin congeners are equally toxic, the concept of toxic equivalency emerged in the mid-1980s. This concept employs relative effect potency values attributed to individual PCDD, PCDF, and PCB compounds in relation to a reference compound, 2,3,7,8-TCDD, to quantify their toxic or biological effects. The comprehensive Toxic Equivalent (TEQ) is practically determined through the summation of products obtained by multiplying the concentration of each compound by its corresponding toxic equivalency factor (TEF) value. This value serves as an estimation of the overall 2,3,7,8-TCDD-like activity within the mixture (Barnes 1991; Van Den Berg et al. 2006).

PCDDs, PCDFs, and PCBs are classified as persistent organic pollutants (POPs) by the Stockholm Convention (2001). This international treaty serves as a worldwide mechanism for safeguarding human health and the environment against the adverse effects of POPs. POPs exhibit the distinctive quality of enduring unchanged in the environment over extended periods. They have the tendency to disperse extensively across geographical regions, accumulating within the fatty tissues of humans and wildlife, thereby causing detrimental consequences for both human health and the ecosystem (UNEP n.d.).

Dioxins are formed in all types of combustion processes when carbon, chlorine, and oxygen are present. Favourable temperatures for dioxin formation range between 500 and 800 °C, where a homogeneous pyrogenic reaction occurs in the gas phase, and between 200 and 400 °C, where a heterogeneous catalytic reaction takes place between gas and solid substances (Abad et al. 2002; Stanmore 2004; Tame et al. 2007; Zhang et al. 2016).

The incineration of municipal solid waste (MSW) is considered one of the primary sources of dioxins (Abad et al. 2002). Therefore, the formation of dioxins in MSW incinerators is very well investigated (Abad et al. 2002; Chang and Huang 1996; Gullett et al. 1998; McKay 2002; Olie et al. 1977; Pan et al. 2013; Peng et al. 2020; Tuppurainen et al. 1998; Weidemann et al. 2016; Zhao et al. 2022a, b; F. Zhao et al. 2022a, b). While biomass combustion is not as significant contributor to dioxin generation as MSW incineration, it still plays a role. The process of dioxin formation during biomass combustion is also well studied (Åmand and Kassman 2013; Khan et al. 2009; Zhang et al. 2022, 2016), though less attention is given to dioxins present in biomass ash (Lopes and Proença 2020; Wyrzykowska et al. 2009; Zhai et al. 2022).

In the European Union (EU), the production, marketing, use, and handling of POPs are regulated by Regulation (EU) No 2019/1021 of the European Parliament and of the Council (EU 2019a), also known as the POP Regulation. The POP Regulation also governs the management of waste containing POPs. Generally, disposal or recycling practices that could lead to the reuse, recycling, recovery, or re-entry of POPs into the market are prohibited. In 2022, the European Parliament and the EU Council signed a regulation amending Annexes IV and V of the POP Regulation. This amendment recognizes 12 dioxin-like PCBs (PCBs) alongside existing PCDDs and PCDFs as POPs. The amendment also lowered the limit value of total dioxin content in waste suitable for recovery to 5 µg TEQ/kg (previously 15 µg TEQ/kg). Furthermore, the regulation states that “the Commission shall review this content limit and, where appropriate, submit a legislative proposal to lower that limit, if feasible according to advances in science and technology, by 30 December 2027” (EU 2022).

The limit of 5 µg TEQ/kg total dioxin content in waste does not impose constraints on the utilization of biomass ash, as the dioxin levels, as indicated by available data, are anticipated to remain below this specified limit (Lopes and Proença 2020; Wyrzykowska et al. 2009; Zhai et al. 2022). Nonetheless, the information concerning dioxins in biomass ash, particularly the recently included PCBs, is constrained, potentially posing an issue when the limit values are reassessed.

Biomass ash is often used as a fertiliser and is subject to fertiliser regulations. The Fertilising Products Regulation (EU 2019b) includes provisions on product criteria for EU fertilising products. These criteria outline requirements for the categories of end-products and component materials. In 2021, with a delegated regulation (EU 2021), thermal oxidation materials were added as a component material category in the annex of the Fertilising Products Regulation. Biomass ash, which falls under the thermal oxidation materials category, must meet the requirements set to this category, including a limit value for PCDD/PCDF of 20 ng TEQ/kg.

Estonia, encompassing an area of 45,226 km^2, is a compact state in the northern part of Europe, positioned approximately 80 km to the south of Finland. The prevailing climate is northern continental, characterized by extended winters and brief summers, with an average annual temperature of 6–7 °C (Estonian Environment Agency 2023a), which is why the utilization of biomass for energy generation, particularly heating, is widespread in Estonia. In 2022, a total of 29,208 TJ of solid biofuels was employed for the generation of heat and electricity in dedicated combustion facilities. Notably, 17,035 TJ was allocated for utilization in combined heat and power plants (Statistics Estonia 2023).

In Estonia, 16,907 tonnes of fly ash stemming from biomass (sometimes biomass and peat) combustion were generated in 2022, and 24,705 tonnes of bottom ash not accounting for household sources. Most of the produced ash (94%) was effectively recovered (Estonian Environment Agency 2023b).

The regulatory amendments leading to the reduction of dioxin limit values hold the potential to impact the management of biomass ashes in Estonia. Consequently, a screening process was undertaken to evaluate the dioxin content inherent in a spectrum of ashes originating from diverse biomass combustion facilities. This study seeks to scrutinize the dioxin content prevalent in varied biomass ashes in Estonia and, by extension, its compliance with the stipulated regulatory limit values. Furthermore, an in-depth investigation of the differentiation among distinct dioxin congeners is included, enriching the comprehensive analysis of these hazardous compounds. In this study, PCDDs, PCDFs, and PCBs refer to those congeners listed in the POP Regulation, and the term “dioxin” is used as a general term to describe those PCDDs, PCDFs, and PCBs.

Table 1 Technical parameters and sample numbers of the combustion plants investigated in this study

ID	Capacity, MW_{th}	Boiler type	Cleaning system	Sample no
1	23	Grate	CY + ESP	1 BA; 1 CY; 1 ESP
2a	22	Grate	ESP	2a BA; 2a ESP
2b	22	Grate	ESP	2b BA; 2a ESP
3	8	Grate	CY + ESP	3 BA; 3 CY; 3 ESP
4	1	Grate	CY	4 BA; 4 CY
5	1	Grate	CY	5 BA; 5 CY
6	3	Grate	CY	6 BA; 6 CY
7	3.5	Grate	CY	7 mixed
8	3.5	Grate	ESP	8 BA; 8 ESP
9	> 50	CFB	ESP	9 BA; 9 ESP

Methodology

Nine biomass combustion plants were selected in different regions in Estonia, featuring varying technical parameters (as outlined in Table 1). Among these, 8 plants utilize grate boilers, while 1 employs a circulating fluidized bed boiler (CFB). Both bottom ash (BA) and fly ash were collected at these facilities between August 2022 and November 2022. Fly ash was collected from cyclones (CY) or electrostatic precipitators (ESP). On one occasion, only mixed ash could be collected due to limitations in the ash removal system, preventing distinct separation. From one combustion plant, the ash samples were gathered from two distinct boilers and two separate ESPs.

These plants primarily used woodchips as their main fuel source, the prevalent biomass fuel in Estonia. These woodchips predominantly comprise forest biomass residues while potentially encompassing untreated waste wood. During the collection of ash samples, concurrent fuel samples were also obtained. These fuel samples underwent analysis to determine their moisture content, ash content, calorific value, and chlorine (Cl) content. Since industrial combustion processes are continuous, fuel is continuously fed into the system. As a result, it is challenging to precisely determine the composition of the ash derived from the fuel that was subjected to analysis. Despite the inherent heterogeneity in the composition of solid biofuels, the orders of magnitude for the elemental composition remain consistent. Detailed information regarding the fuel parameters is found in Table 2.

The analysis of the fuel and ash samples involved standardized testing procedures to ensure accurate and reliable results. The determination of the ash content of the fuel followed standard EVS-EN ISO 18122:2015. Moisture

Table 2 Characteristics of fuel samples

ID	Moisture, %	Ash content in dry mass, %	Calorific value			Cl content in dry mass, %
			Dry mass, net calorific value, MJ/kg	Dry mass, gross calorific value, MJ/kg	As received, net calorific value, MJ/kg	
1	33.4	2.18	20.24	18.89	11.76	0.007
2	33.0	2.17	20.46	19.09	11.98	0.007
3	37.7	1.1	21.57	22.9	12.57	0.016
4	34.3	1.8	18.35	19.67	11.22	0.008
5	20.1	1.9	18.32	19.65	14.15	0.008
6	34.3	2.0	18.39	19.71	11.24	0.007
7	34.1	1.8	17.86	19.21	10.94	0.006
8	25.3	1.9	17.61	18.96	12.54	0.008
9	49.7	1.9	18.75	20.01	8.22	0.011

content was assessed in accordance with the specifications outlined in EVS-EN ISO 18134–2:2017 and calorific value as outlined in EVS-EN ISO 18125:2017. The Cl content, a parameter with environmental and operational significance, was determined using the ion chromatography method in compliance with EVS-EN ISO 16994:2016 and EVS-EN ISO 10304–1:2009 standards.

The concentrations of 7 PCDD, 10 PCDF, and 12 PCBs listed in the POP Regulation (EU 2019a) were analysed in the accredited laboratory ALS in Czech Republic. The following methods and standards were used: the quantification of tetra- to octa-chlorinated dioxins and furans was executed using the isotope dilution technique HRGC-HRMS, following US EPA 1613B and CSN EN 16190 standards. Similarly, the quantification of PCBs was carried out employing HRGC-HRMS and adhering to the standards CSN EN 1948–4 + A1 and US EPA TO-4A.

Before extraction, analogues of target analytes were added to the samples. The extraction procedure was carried out using nonpolar organic solvents in a Soxhlet extractor for 24 h, followed by raw extract clean-up procedures using multilayer silica gel columns. The final extract was concentrated by evaporation, and standard injection was spiked. The final extract in vials was analysed by an HRGC/HRMS system. Target analytes were quantified relative to their labelled analogues, compensating for extraction and clean-up efficiencies in their calculated concentrations.

The limit of detection is defined as the amount of analyte producing a signal with S/N ≥ 3. Measurement uncertainty is expressed as a double ($k = 2$) relative standard deviation (RSD%) corresponding to a 95% confidence interval. The uncertainty estimation of each 2,3,7,8-PCDD/F congener and each PCB congener is 30%, while for PCB6/PCB7 is 20%.

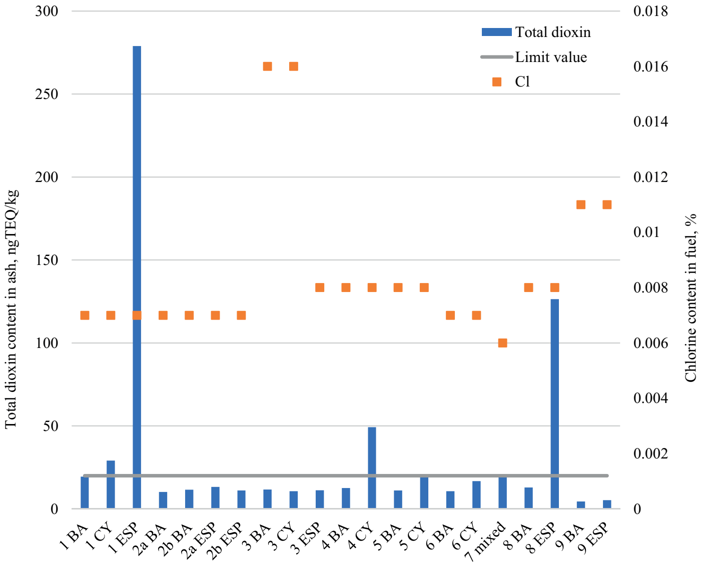
The dioxin concentrations in this study are ng/kg and ng TEQ/kg, based on dry weight. The dioxin concentrations in ng TEQ/kg have all been calculated in accordance with the POP Regulation, employing the TEFs outlined therein. The majority of dioxin congener concentrations fell below the detection limit. Addressing values below the detection limit can be addressed using upper-, medium-, or lower-bound approaches (EU 2017). This study utilized the upper-bound method, which involves treating concentrations below the detection limit as equal to the detection limit itself.

Results and discussion

Dioxin content analysis

The dioxin TEQ content in all the samples was at least tenfold lower than the threshold in POP Regulation, where the limit value is 5 µg TEQ/kg. The actual maximum content measured was 279 ng TEQ/kg (Fig. 1). The majority of the dioxin content within the samples exhibits concentrations below 20 ng TEQ/kg, which is the maximum allowed content according to the Fertilising Products Regulation. However, a subset of four fly ashes stands out due to their elevated dioxin content. Among these, the highest concentration is observed in ESP's ashes, while the remaining two correspond to CY's ashes. Concurrently, several fly ashes

Fig. 1 Correlation between total dioxin concentration in ashes and Cl content in fuels with indicated dioxin limit value 20 ng TEQ/kg according to Fertilising Products Regulation



from ESP demonstrate markedly low dioxin content, with fluidized bed ashes registering the lowest concentrations.

As many authors have indicated (Oehme and Müller 1995; Pohlandt and Marutzky 1994; Stanmore 2004; Zhai et al. 2022), the concentrations are notably higher in the fly ashes than in the bottom ashes. The rationale behind this is that the peak of dioxin formation is commonly observed within temperatures between 300 and 400 °C. Additionally, the duration of particle residence within the optimal temperature range plays a significant role (Everaert and Baeyens 2002). This pivotal point in the process significantly aligns with the stage when fly ash is undergoing a cooling phase, transitioning from the combustion chamber to the emission control systems. This transitional stage, marked by the movement of particles, provides a critical window for the generation of dioxins. Intriguingly, the dioxin concentrations exhibit their peak levels in ESPs, typically serving as the final emission control filter. In conjunction with this, particle size assumes a vital role, whereby finer particles display the highest concentrations (Stanmore 2004).

In light of this comparative analysis, it becomes evident that despite the consistent use of similar fuels among the combustion plants, with Cl contents ranging from 0.007 to 0.016%, Cl alone is not the sole determinant of the observed variations in dioxin content (Fig. 1). Instead, an intricate interplay of contributing factors extending beyond Cl content warrants further investigation.

The ashes from six biomass-firing combustion plants meet the Fertilising Products Regulation threshold of 20 ng TEQ/kg, but the fly ashes from three combustion plants exceed this limit. The 20 ng TEQ/kg threshold was suggested in a report by EU Commission's Joint Research Centre in Seville (JRC—Seville) (Huygens et al. 2019). However, the threshold applies to all thermal oxidation materials, and there is limited information on biomass fly ashes in the report. In terms of the dioxin content of bottom ash, the levels were usually reported to be below 20 ng TEQ/kg.

When many of the dioxin congeners are below the detection limit, it becomes crucial to identify how these values are addressed. The EU Commission Regulation (EU 2017) outlines three approaches to tackle the non-detected congeners: the upper-bound approach uses the limit of quantification of the non-detected congener as the concentration, the lower-bound uses zero, and the medium-bound requires using half of the limit of quantification of each non-quantified congener. In a study by Lopes and Proença 2020 dioxin content in ashes from biomass combustion was investigated. The results for blended ashes using an upper-bound approach were 9 to 27.2 ng TEQ/kg. They also presented the medium- and lower-bound results, which showed the importance of the approach chosen. With the medium-bound approach, the results were 13.5 to 13.8 ng TEQ/kg, and with the lower-bound only 0.009 to 0.43 ng TEQ/kg. The current study indicates that the selected approach has a significant impact on the reported dioxin concentrations, particularly when the concentrations are low (Fig. 2). Low concentrations indicate that most of the congeners are below the limit of detection (Table 3).

The preeminent contributor to the cumulative dioxin TEQ content in most cases is PCDDs, while the PCBs are of marginal significance, exerting a negligible influence on the overarching dioxin TEQ content (Fig. 3).

Dioxin congener analysis and variability

The TEQ concentration of dioxin congeners in the bottom ash resides below 10 ng TEQ/kg, a level that exerts marginal influence on the cumulative concentration. In contrast, the fly ash exhibits a notably higher dioxin concentration. Within the fly ash, the concentrations of PCDD and PCDF congeners consistently maintain levels well below 25 ng

Fig. 2 Total PCDD, PCDF, and PCB TEQ concentrations in biomass ashes with total dioxin content > 20 ng TEQ/kg: comparison of upper (UB)-, medium (MB)-, and lower-bound (LB) approaches

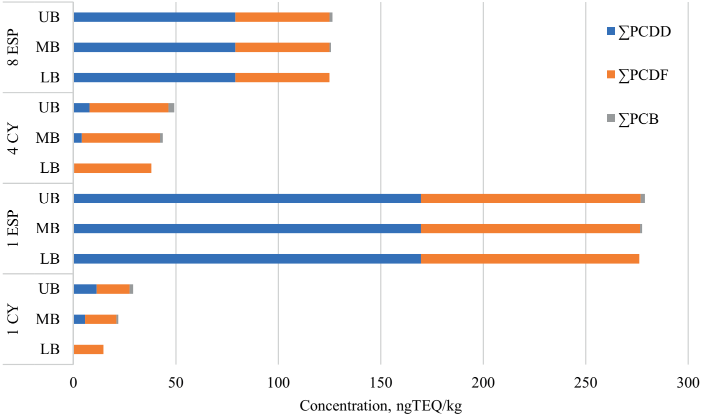


Table 3 PCDD, PCDF, and PCB concentrations in biomass ash (*BA* bottom ash, *CY* cyclone's ash, *ESP* electrostatic precipitator's ash)

ng/kg	1 BA	1 CY	1 ESP	2a BA	2b BA	2a ESP	2b ESP	3 BA	3 CY	3 ESP	4 BA	4 CY	5 BA	5CY	6BA	6 CY	7 mixed	8 BA	8 ESP	9 BA	9 ESP
1,234,678-HpCDD	< 9.0*	< 63	**200**	< 7.1	< 6.3	< 7.0	< 7.7	< 6.8	< 21	< 83	< 9.4	**31**	< 5.2	< 39	< 10	< 10	< 13	< 6.6	**630**	< 2.8	< 1.5
1,234,678-HpCDF	< 12	< 7.8	< 6.3	< 4.4	< 22	< 6.1	< 5.8	< 6.6	< 12	< 10	< 25	**69**	< 9.4	< 16	< 4.0	< 23	< 10	< 11	**61**	< 17	< 1.3
123,478-HxCDD	< 7.7	< 5.9	**93**	< 6.8	< 6.3	< 8.3	< 6.7	< 6.1	< 6.1	< 5.9	< 5.1	< 13	< 9.3	< 9.9	< 6.6	< 4.2	< 8.9	< 9.0	**56**	< 2.6	< 2.0
123,478-HxCDF	< 5.1	< 3.7	**22**	< 3.5	< 4.0	< 3.3	< 3.2	< 3.2	< 2.8	< 3.8	< 4.5	**27**	< 3.1	< 5.2	< 3.3	< 9.1	< 6.9	< 3.7	**45**	< 1.9	< 1.3
1,234,789-HpCDF	< 45	< 10	< 9.8	< 6.2	< 14	< 8.3	< 9.7	< 8.1	< 11	< 5.9	< 35	< 10	< 19	< 20	< 6.8	< 13	< 17	< 64	**18**	< 7.2	< 1.7
123,678-HxCDD	< 8.1	< 2.3	**94**	< 5.0	< 4.7	< 5.6	< 5.3	< 5.7	< 5.3	< 5.0	< 4.9	< 10	< 6.7	< 8.1	< 5.3	< 3.7	< 6.2	< 6.5	**190**	< 1.6	< 1.4
123,678-HxCDF	< 6.3	< 3.3	**29**	< 2.8	< 3.2	< 3.7	< 2.5	< 2.6	< 3.0	< 4.1	< 4.3	**29**	< 2.7	< 5.1	< 3.0	< 8.7	< 6.1	< 3.5	**55**	< 1.6	< 1.1
12,378-PeCDD	< 2.2	< 7	**90**	< 2.7	< 2.9	< 3.5	< 3.3	< 3.1	< 2.4	< 3.1	< 3.0	< 2.8	< 2.6	< 6.6	< 2.7	< 1.9	< 4.7	< 2.6	**26**	< 0.87	< 1.3
12,378-PeCDF	< 4.5	**15**	**130**	< 3.2	< 3.4	< 3.1	< 2.6	< 2.1	< 2.1	< 2.3	< 2.0	**25**	< 2.2	< 5.0	< 2.7	< 15	< 5.0	< 3.4	**46**	< 1.7	< 1.2
123,789-HxCDD	< 7.7	< 2.2	**39**	< 4.8	< 4.5	< 5.3	< 5.1	< 5.5	< 5.1	< 4.8	< 4.7	< 5.0	< 6.4	< 7.8	< 5.1	< 3.5	< 6.0	< 6.3	**120**	< 1.5	< 1.3
123,789-HxCDF	< 20	< 2.5	< 5.2	< 3.7	< 3.5	< 7.0	< 6.2	< 4.8	< 5.9	< 5.6	< 9.4	< 7.4	< 6.2	< 6.6	< 4.2	< 6.0	< 15	< 14	**15**	< 2.2	< 2.1
234,678-HxCDF	< 7.1	< 2.1	**25**	< 3.8	< 3.3	< 5.0	< 4.9	< 3.3	< 3.3	< 4.3	< 5.6	**48**	< 3.9	< 5.4	< 4.2	< 10	< 9.4	< 4.5	**70**	< 1.7	< 1.2
23,478-PeCDF	< 6.1	**20**	**110**	< 3.6	< 3.1	< 3.3	< 3.1	< 3.1	< 5.1	< 2.5	< 3.0	**67**	< 2.8	< 4.4	< 3.0	< 18	< 5.7	< 2.4	**41**	< 1.7	< 1.6
2378-TCDD	< 1.5	< 2.7	**55**	< 1.8	< 2.1	< 2.6	< 1.9	< 2.1	< 1.7	< 1.9	< 2.0	< 1.9	< 1.8	< 3.1	< 2.2	< 0.97	< 4.6	< 1.7	**10**	< 0.65	< 1.1
2378-TCDF	< 18	**82**	**620**	< 2.0	< 2.1	< 2.2	< 1.9	< 1.5	< 1.6	< 1.9	< 3.3	**58**	< 1.7	< 2.6	< 2.2	< 16	< 3.6	< 3.3	**130**	< 1.1	< 1.2
OCDD	< 22	< 31	**110**	< 8.9	< 10	< 15	< 9.7	< 12	< 10	< 29	< 19	**25**	< 12	< 44	< 10	< 6.4	< 24	< 13	**290**	< 12	< 2.1
OCDF	< 17	< 9.1	< 13	< 6.9	< 7.7	< 12	< 7.5	< 9.0	< 13	< 7.4	< 15	< 9.3	< 19	< 10	< 7.8	< 16	< 19	< 10	< 25	< 9.3	< 2.4
UB ∑PCDD	58.2	114.1	681	37.1	36.8	47.3	39.7	41.3	51.6	132.7	48.1	88.7	44	118.5	41.9	30.67	67.4	45.7	1322	22.02	10.7
UB ∑PCDF	141.1	155.5	970.3	40.1	66.3	54	47.4	44.3	59.8	47.8	107.1	349.7	70	80.3	41.2	134.8	97.7	119.8	506	45.4	15.1
PCB 105	< 210	< 210	< 440	< 460	< 520	< 530	< 530	< 460	< 410	< 510	< 120	< 240	< 450	< 660	< 430	< 580	< 220	< 180	< 530	< 130	< 120
PCB 114	< 46	< 13	< 31	< 14	< 21	< 23	< 10	< 5.9	< 17	< 23	< 9.5	< 14	< 27	< 41	< 26	< 28	< 8.1	< 10	< 14	< 3.9	< 6
PCB 118	< 1100	< 950	< 1600	< 2000	< 2000	< 1800	< 2000	< 1500	< 1200	< 1400	< 950	< 1100	< 1200	< 2000	< 1300	< 2100	< 910	< 950	< 1700	< 830	< 640
PCB 123	< 46	< 13	< 31	< 16	< 21	< 11	< 11	< 6.1	< 16	< 22	< 8.6	< 13	< 22	< 27	< 9.9	< 25	< 7.9	< 8.1	< 13	< 3.9	< 5.8
PCB 126	< 36	< 12	< 13	< 7.6	< 13	< 13	< 7.5	< 14	< 8.8	< 6.1	< 12	< 16	< 13	< 17	< 8.3	< 9	< 10	< 12	< 12	< 6.3	< 7.9
PCB 156	< 160	< 170	< 320	< 220	< 240	< 250	< 200	< 190	< 150	< 270	< 210	< 190	< 170	< 260	< 210	< 220	< 110	< 110	< 250	< 110	< 62
PCB 157	< 58	< 15	< 42	< 17	< 110	< 26	< 14	< 7.2	< 20	< 23	< 12	< 25	< 33	< 50	< 45	< 28	< 30	< 11	< 13	< 13	< 6.7
PCB 167	< 75	< 71	< 160	< 150	< 120	< 110	< 160	< 61	< 91	< 130	< 73	< 47	< 92	< 86	< 70	< 99	< 52	< 58	< 110	< 45	< 45
PCB 169	< 45	< 18	< 22	< 10	< 19	< 14	< 8.7	< 15	< 8.7	< 7.2	< 16	< 38	< 1.3	< 21	< 10	< 12	< 15	< 21	< 5.8	< 2.9	< 9.1
PCB 189	< 93	< 15	< 55	< 22	< 9.7	< 23	< 20	< 9.7	< 26	< 21	< 12	< 29	< 48	< 18	< 15	< 7.8	< 12	< 15	< 41	< 5.5	< 8.3

Table 3 (continued)

PCB 77	<120	<98	<300	<97	<150	<89	<98	<47	<78	<140	<24	<20	<44	<120	<79	<160	<79	<20	<130	<48	<51
PCB 81	<300	<15	<42	<20	<52	<51	<75	<83	<26	<23	<9.4	<18	<74	<24	<29	<170	<69	<34	<27	<3.3	<6.4
UB ∑PCB	2289	1600	3056	3033.6	3275.7	2940	3134.2	2398.9	2051.5	2575.3	1456.5	1750	2174.3	3324	2232.2	3438.8	1523	1429.1	2845.8	1201.8	968.2
ng TEQ/kg	1 BA	1 CY	1 ESP	2a BA	2b BA	2a ESP	2b ESP	3 BA	3 CY	3 ESP	4 BA	4 CY	5 BA	5CY	6BA	6 CY	7 mixed	8 ESP	8 BA	9 BA	9 ESP
∑PCDD	**6.15**	**11.38**	**169.63**	**6.23**	**6.62**	**8.09**	**6.99**	**7.00**	**5.96**	**7.41**	**6.57**	**7.82**	**6.70**	**12.68**	**6.70**	**4.11**	**11.55**	**6.55**	**78.99**	**2.12**	**2.89**
∑PCDF	**8.19**	**15.99**	**107.18**	**2.86**	**3.00**	**3.35**	**3.04**	**2.68**	**3.49**	**2.95**	**4.27**	**38.58**	**2.96**	**4.32**	**2.78**	**11.19**	**6.24**	**4.48**	**45.98**	**1.66**	**1.24**
∑PCB	**5.11**	**1.80**	**2.08**	**1.16**	**1.99**	**1.83**	**1.13**	**1.95**	**1.21**	**0.92**	**1.73**	**2.80**	**1.43**	**2.44**	**1.21**	**1.42**	**1.52**	**1.88**	**1.48**	**0.76**	**1.10**

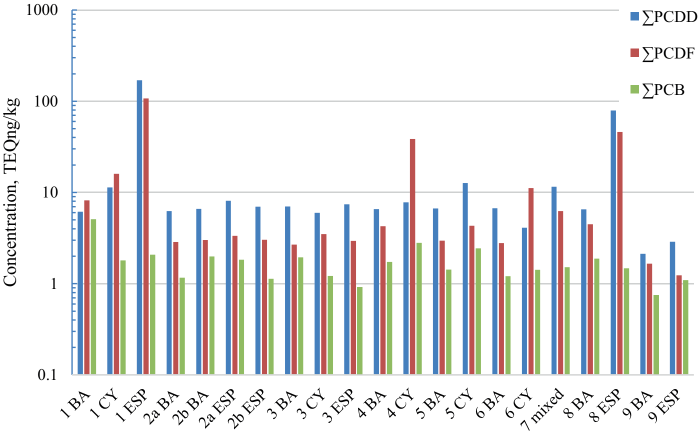
*Results marked" <" are lower than the limit of detection

TEQ/kg, with some instances of peak concentrations surpassing this threshold (Fig. 4). The bars in Figs. 4 and 5 illustrate the concentration distributions of the congeners, where on each box, the central mark indicates the median and the bottom and top edges of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "•" symbol.

The distribution of PCDD and PCDF congeners exhibits a scattered pattern, indicating that the dominance of any single congener is relatively modest. Nonetheless, it is noteworthy that among these congeners, 23,478-PeCDF, 2378-TCDF, and 12,378-PeCDD stand out as the most influential in terms of their impact on the overall dioxin TEQ content. Additionally, the actual content is notably high for 1,234,678-HpCDD and OCDD (Fig. 4). These findings align with those of Pham et al. who conducted a comparative study across various thermal industrial facilities, encompassing steelmaking, tin production, aluminium recycling, waste incinerators, coal-fired power plants, brickmaking, and industrial boilers. Pham et al. observed similarly heightened concentrations of 1,234,678-HpCDD and OCDD, with TEQ concentrations peaking for 23,478-PeCDF and 12,378-PeCDD (Pham et al. 2019) Likewise, congruent observations were made in the co-processing of hazardous waste within cement kilns (Ye et al. 2022) and wood combustion (Wunderli et al. 2000), where 23,478-PeCDF emerged as the predominant homologous compound in the TEQ distribution. Concurrently, 1,234,678-HpCDD and OCDD exhibited the highest actual concentrations, thereby substantiating the present study's findings. Regardless of the specific fuel employed or the nature of the combustion processes, a discernible pattern emerges, indicating the prominence of certain congeners over others in contributing to dioxin profiles.

The distribution of PCB congeners is relatively uniform, with only a few exceptions evident (Fig. 5). PCB-118 emerges as the most prevalent PCB congener in the samples. However, its significance is limited due to its low TEF, indicating a relatively lower level of toxicity despite potentially high concentrations. Most PCB congeners exhibit deficient TEQ concentrations, suggesting minimal toxicity levels. However, two specific PCB congeners, namely PCB-169 and PCB-126, stand out due to their notably elevated TEQ values, surpassing a threshold of 1 ng TEQ/kg (Fig. 5). While the individual TEQ concentrations of PCB-169 and PCB-126 may appear modest, their prominence raises pertinent questions requiring further investigation. This finding aligns with a study in China, where investigations into 18 coal-fired power plant fly ashes revealed PCB-169 and PCB-126 as the top PCBs, with higher TEQ concentrations (Li et al. 2016). Similarly, research conducted in Taiwan on woodchip boiler facilities yielded noteworthy results. The major congeners among PCBs in one plant were PCB-77, PCB-126,

Fig. 3 Total PCDD, PCDF, and PCB TEQ concentrations in biomass ashes



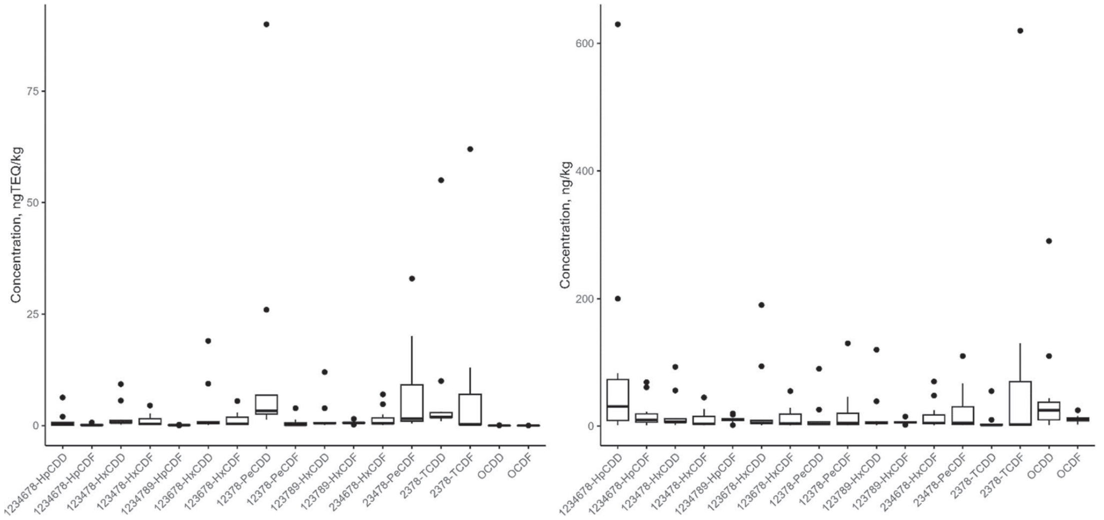


Fig. 4 Distribution of PCDD and PCDF congeners in the fly ash

and PCB-169, whereas in the other plant PCB-77, PCB-126, and PCB-189 emerged as major congeners (Bai et al. 2017). These comparative findings underscore the nuanced variability in PCB congener prevalence across diverse combustion sources, emphasizing the need for a comprehensive understanding of individual congeners' profiles in specific contexts.

Conclusions

The principal aim of this study was to analyse the total dioxin content present within biomass ash, with a concurrent exploration into the potential implications of the threshold values outlined in EU regulations, particularly concerning the utilization of biomass ash. The investigation has unveiled a significant contrast between the existing dioxin content and the established threshold values in POP Regulation, signifying a substantial margin of safety. However, meeting the threshold value in the Fertilising Products Regulation presents challenges.

Nonetheless, it is worth noting that certain samples exhibited markedly elevated dioxin concentrations that could not be adequately accounted for by variations in chlorine content. This observed discrepancy calls for a more comprehensive investigation and analysis to elucidate the factors contributing to the substantial differences in dioxin levels among the samples.

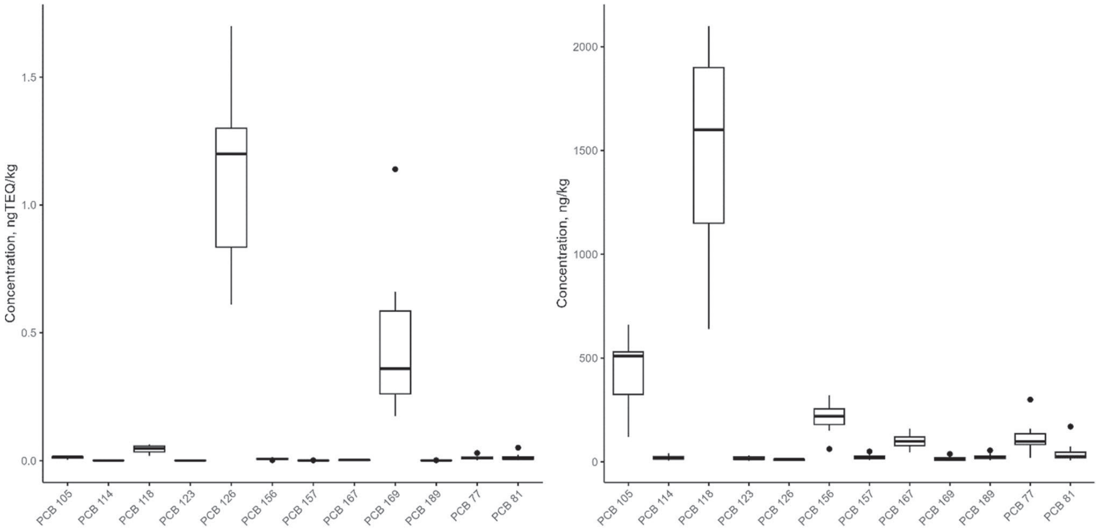


Fig. 5 Distribution of PCB congeners in the fly ash

Furthermore, intricate scrutiny was directed toward the distribution of various congeners of PCDDs, PCDFs, and PCBs. The observed prevalence of congeners 23,478-PeCDF and 12,378-PeCDD in TEQ distribution concurs with existing literature, reinforcing their significance in the dioxin landscape. However, although the impact of PCBs on the overall dioxin content appears to be relatively insignificant, the distribution of the different congeners is of interest. The distributions of PCB congeners provide grounds for further studies, in particular with regard to the mechanisms underlying the formation of these PCB analogues. Future research aimed at elucidating these mechanisms may provide valuable insight into the complex dynamics of dioxin formation and distribution.

Author contribution Mari-Liis Ummik: conceptualization, methodology, writing original draft.

Oliver Järvik: writing—review and editing, supervision.

Alar Konist: conceptualization, methodology, resources, writing—review and editing, supervision, project administration.

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Data availability The authors declare that the data supporting the findings of this study are available within the paper. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

The data supporting the findings of this study are available from the corresponding author upon reasonable request. The datasets generated and/or analysed during the current study are not publicly available due to efforts to minimize digital waste and ensure data privacy. However, they can be accessed from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable.

Consent to participate Yes.

Consent for publication Yes.

Competing interests The authors declare no competing interests.

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Quantification of oil shale industry ash flows – their chemical and mineralogical composition

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Abstract. *The global demand for resources is escalating in today's rapidly evolving world. As traditional raw materials become scarcer and more expensive, alternative sources have to be found. One such emerging resource is oil shale ash. This article provides a comprehensive overview of the various fractions of oil shale ash generated in the oil shale industry in Estonia. The ash results from the direct combustion of oil shale with pulverised combustion (PC) and circulating fluidised bed combustion (CFBC) technologies, as well as from shale oil production processes. It offers detailed information about the proportions of ash derived from different technological processes and a thorough analysis of their mineralogical and chemical compositions, trace element content, and leaching characteristics. By examining these diverse characteristics, the study enhances understanding of the ash's potential implications and applications.*

Keywords: *oil shale ash, ash characterisation, material recovery, leaching.*

1. Introduction

The United Nations Environment Programme's Global Resources Outlook reported that in 2019, the global economy consumed a total of 105.7 billion tonnes of materials [1]. Of this, roughly 91% was sourced through direct harvesting and extraction, while only 9% came from recycled and recovered resources. Global demand for natural resources is steadily rising, with projections indicating a 60% increase in resource consumption by 2060 compared to 2020 levels. This rise follows a more than threefold growth in material use over the past 50 years.

The world energy sector has a substantial demand for global resources, consuming around 500 EJ of fossil fuels annually from coal, oil, and natural

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gas, with biomass contributing an additional 60 EJ, primarily for heat and power [2]. While these fuels require large resource inputs, their combustion produces significant amounts of ash that can be repurposed. This ash, which comes from a range of sources, including biomass, municipal waste, coal, lignite, and oil shale, is increasingly recognised as a valuable secondary raw material. It can be used in construction materials or as a source for extracting valuable elements, reducing the need for virgin materials [3–13]. This approach helps mitigate waste and promotes a circular economy by transforming by-products into sustainable resources.

Oil shale is a type of sedimentary rock that contains a mixture of organic and inorganic matter. The organic matter of Estonian oil shale, known as kukersite, has a high hydrogen and oxygen content, low nitrogen content, and significant amounts of organic sulphur and chlorine [14, 15]. Estonia possesses substantial oil shale resources, estimated at 6.3 billion tonnes, which includes 2 billion tonnes deemed economically viable for mining. This positions Estonia among the top ten countries with the largest oil shale reserve [16]. Oil shale is used to produce energy and shale oil. Historically, Estonia was the only country operating oil shale fired power plants to supply most of its electricity, with excess power exported to neighbouring countries. However, the share of oil shale in electricity production has decreased in recent years [14]. In 2016, oil shale accounted for 80% of Estonia's electricity production; by 2023, this share had decreased to 35%, generating 7.1 TJ, as the country increased its reliance on renewable energy sources [17].

Estonia's oil shale industry (power plants and shale oil production plants) generates around 5 million tonnes of oil shale ash annually, classified in waste statistics [18] as fly ash and bottom ash. However, this classification simplifies a more complex reality. The ash can be divided into distinct fractions depending on the technology used and the specific collection points, with each fraction exhibiting unique characteristics.

In Estonia, oil shale fired power plants employ two combustion technologies: pulverised combustion (PC) and circulating fluidised bed combustion (CFBC). PC technology is used at Eesti Power Plant (Eesti PP), where the TP-101 high-pressure boilers are equipped with sulphur-capturing units. CFBC technology is employed in unit 8 of Eesti PP, unit 11 of Balti Power Plant (Balti PP), and Auvere Power Plant (Auvere PP).

In addition to power plants, Estonia also has oil shale thermal processing plants for shale oil production. There are two methods for shale oil production: gaseous heat carrier (GHC) and solid heat carrier (SHC). Utilising the SHC method, the semi-coke is combusted in a lift pipe combustor (also known as an aero-fountain combustor) or a CFB furnace, producing oil shale ash. In contrast, with the GHC method, the semi-coke is deposited in landfills [19]. Conventional SHC oil shale retorting technologies use lift pipe combustors (Enefit140 and Petroter), while Enefit280 employs CFBC technology.

Over the past two decades, there have been notable changes in the oil shale industry. Significant developments include the restructuring of power generation facilities, which involved the partial decommissioning of older PC units and the retrofitting some with new CFB boilers (at Balti PP and Eesti PP units 11 and 8, respectively, in 2004–2005). A new 305 MW_{el} power unit at Auvere PP was commissioned in 2016. Some older PC units (units 3, 4, 5, and 6 at Eesti PP) were upgraded with desulphurisation (deSOx) and denitrification (deNOx) technologies between 2010 and 2012 to comply with emissions regulations [20]. Additionally, there has been a shift from using oil shale for power generation to producing shale oil, with new shale oil production plants constructed between 2009 and 2015. Furthermore, one plant is currently under construction and is planned to be operational in 2025. A summary of the current state of oil shale utilisation in power generation and shale oil production is provided in Table 1.

Table 1. Overview of the primary oil shale utilising plants (adapted from [20])

Plant	Type	Fuel	Rated capacity (gross), MW_{el}	Commissioning
Power plants				
Balti PP unit 11	2 CFB boilers per single turbine	Oil shale, up to 50% biomass	215 MW_{el}	Turbine 1970s, boilers 2005
Eesti PP unit 8	2 CFB boilers per single turbine	Oil shale, up to 50% retort gas (in one boiler)	215 MW_{el}	Turbine 1970s, boilers 2005
Auvere PP	1 CFB – 1 turbine	Oil shale, retort gas, up to 50% biomass	305 MW_{el}	2016–2018
Eesti PP units 3, 4, 5, 6	2 PC boilers per 1 turbine	Oil shale, retort gas	185–195 MW_{el}	1970s, deSOx 2010–2012, deNOx
Eesti PP units 1, 2, 7	2 PC boilers per 1 turbine	Oil shale	185–195 MW_{el}	Decommissioned 2020
Shale oil production plants				
Enefit140	SHC	Oil shale		1980
Enefit280	SHC + CFBC	Oil shale		2012
Petroter I	SHC	Oil shale		2009
Petroter II	SHC	Oil shale		2014
Petroter III	SHC	Oil shale		2015

The oil shale is pre-treated to ensure that its particle size remains within the specifications required by the combustion technology. PC technology needs pulverised oil shale with an average grain size of less than 0.01 mm. CFBC boilers use oil shale with an average grain size of up to 25 mm, although for Auvere PP, the corresponding value is approximately 10 mm, and for the Enefit280 oil plant, less than 6 mm [21].

PC technology operates at high temperatures of 1350–1450 °C (up to 1500 °C), facilitating extensive decomposition of carbonate minerals and melting of clay minerals, which leads to the formation of secondary Ca-silicate and Ca-Al-silicate phases. Conversely, CFBC technology, with its optimum furnace temperature of about 800 °C, results in only partial decomposition of calcite ($CaCO_3$) and preservation of clay mineral phases, with the loss of physically and chemically bound water. As a result, the formation of new mineral phases is less likely compared to processes operating at higher temperatures. Consequently, PC ashes are enriched in free CaO and secondary Ca-silicate phases. It should be noted that the distinction between total CaO and free CaO in different ashes is affected by the presence of indissoluble minerals, as well as variations in carbonate content. In contrast, CFBC ashes contain a higher proportion of residual mineral phases and are characterised by higher sulphur concentrations, primarily in the form of anhydrite ($CaSO_4$). This sulphur concentration is due to the nearly complete desulphurisation of flue gas, facilitated by the prolonged contact between ash particles containing $CaO/CaCO_3$ and SO_2 in flue gas, the lower temperature in the combustion chamber, and the CFBC technology process system [22, 23]

Arro et al. [24] noted significant morphological differences between CFBC and PC ashes based on surface observations. The ash particles from CFB boilers have irregular shapes, with an insignificant presence of melted spherical particles. In contrast, PC ash predominantly consists of spherical, melted particles. This difference indicates that mineral decomposition and the formation of new minerals occur at a considerably higher rate in PC boilers, where furnace temperatures exceed 1400 °C, compared to CFB boilers, which operate at around 800 °C. Additionally, the specific surface area of CFBC ashes is up to ten times greater than that of PC ashes.

Ash can be collected from the boiler unit assemblies and flue gas cleaning equipment (Fig. 1). Ash that accumulates at the bottom of the furnace is referred to as bottom ash, while the ash transported by the gas flow from the boiler is known as fly ash. Fly ash consists of particles that gravitationally settle out of the gas stream.

Depending on the technology, the ash collection points are different. For example, in a PC unit, the ash discharge points include the bottom of the furnace, external heat exchanger, superheater, economiser, air preheater, cyclone, and fabric filter. In a CFBC unit, the fly ash is precipitated in the superheater, economiser, air preheater, and electrostatic precipitators (ESP). In addition to the ESPs, Auvere PP has an extra cleaning stage using fabric filters to achieve particulate matter concentrations below 10 mg/m^3.

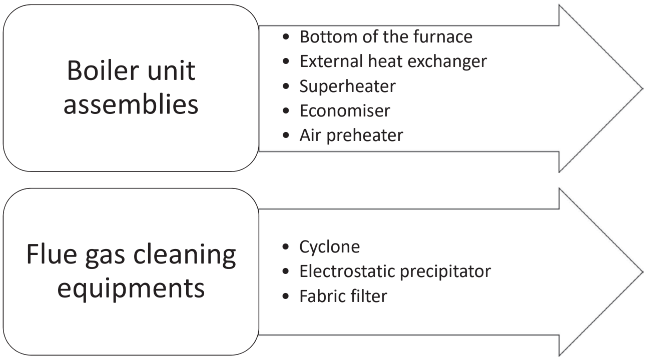

Fig. 1. Simplified scheme for possible ash collection points.

Over the years, the properties and characteristics of oil shale ash have been extensively investigated and documented [11–13, 22, 23, 25–29]. However, a comprehensive understanding of all oil shale ash fractions generated through different technologies is still lacking. As resource demand rises, maximising the efficiency of already excavated and processed materials becomes critical. Oil shale ash has considerable potential as a construction material or as a source for extracting various substances and elements. A detailed characterisation of each ash fraction is essential to fully harness this potential, enabling optimised utilisation of the material and minimising waste. Therefore, this article aims to provide a detailed overview of the properties of different types of ash from the Estonian oil shale industry, which are crucial for their effective utilisation and valorisation.

2. Materials and methods

Ash samples were collected from the operating power plants (Eesti PP, Auvere PP) and shale oil production installations (Enefit280 and Petroter). The samples were gathered over an extended period, allowing to account for potential variations in fuel composition and operational conditions. The values presented in this study represent the average composition of the fractions, providing a more representative assessment of the ash characteristics. The specific locations of ash collection are detailed in the following sections of the article.

The mineralogical composition was analysed in the Department of Geology at the University of Tartu laboratory using powder X-ray diffraction (XRD) on a Bruker D8 diffractometer equipped with SolX and super-speed LynxEye detectors. The chemical composition was determined in the laboratory of the Department of Energy Technology at Tallinn University of Technology using a Rigaku ZSX Primus II 4 kW wavelength dispersive X-ray fluorescence spectroscope (WD-XRF).

The determination of free CaO was conducted by first grinding and sieving the sample through a 100 µm mesh sieve, except in the case of fly ash, which did not require grinding. The prepared sample was then slaked with boiling water to initiate the hydration process. To enhance the solubility of calcium hydroxide, a sugar solution was introduced. The resulting solution was subsequently titrated with standardised 0.1 M hydrochloric acid, utilising phenolphthalein as an indicator to determine the endpoint. The volume of acid consumed during titration was used to quantify the free CaO content in the sample.

The mineral CO_2 content in a sample was determined by measuring the total inorganic carbon (TIC) using a Vario MACRO elemental analyser. The TIC value was then used to calculate the carbonate-derived CO_2 content.

A composite fly ash sample was employed in the leaching tests rather than utilising individual ash fractions. This composite sample was created by mixing the various ash fractions obtained from each installation. The proportions used in this mixing process were determined based on each installation's specific ash balance. This approach ensured that the composite fly ash sample accurately represented the overall ash characteristics for each installation, facilitating a more comprehensive analysis of leaching behaviour.

Leaching tests were conducted in accordance with standard EVS-EN 12457-4 [30], maintaining a liquid-to-solid ratio of 10:1. Quantification of trace elements in both ash and eluates was conducted using inductively coupled plasma mass spectrometry (ICP-MS) with a Thermo iCAP Qc, following the standard test method ASTM D6357-21a [31]. The content of sulphates (SO_4^{2-} ions) and chloride (Cl^- ions) was determined using liquid ion chromatography (IC) with a Dionex ICS-1000, in accordance with the EVS-EN ISO 10304-1:2009 standard [32].

3. Results and discussion

3.1. Auvere Power Plant

Auvere PP, completed in 2015 with acceptance tests finalised in 2018, stands as the most modern oil shale power plant in Estonia. It has a gross capacity of 305 MW_{el} and operates as a monobloc system, where a single boiler supplies steam to the turbine [33, 34]. The primary fuel is oil shale with a calorific value of 7–11 MJ/kg and a grain size of up to 10 mm. Per Auvere PP's environmental permit [35], biomass and retort gas are also co-combusted with oil shale.

Acceptance tests indicate that the net efficiency of the unit at nominal capacity and under steady-state conditions, with oil shale at a calorific value of 8.3 MJ/kg, exceeds 40%, while the boiler's efficiency surpasses 90%. The boiler operates at a temperature of around 850 °C, which significantly

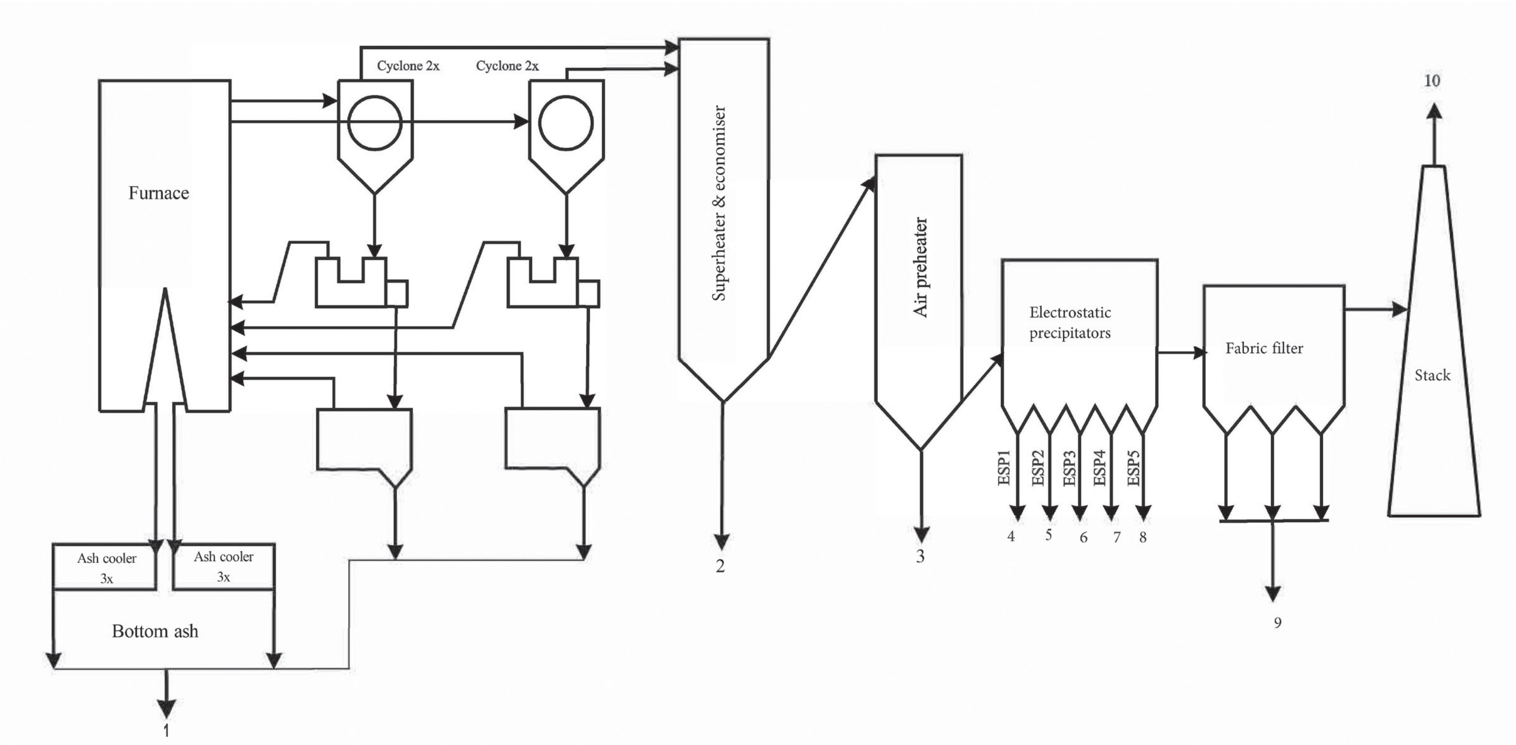

Fig. 2. Layout of Auvere Power Plant and the ash collection points (adapted from [34]): bottom ash (1), superheater and economiser ash (2), air preheater (3), electrostatic precipitators – ESP1 (4), ESP2 (5), ESP3 (6), ESP4 (7), ESP5 (8), fabric filter (9), ash in flue gas (10).

influences the decomposition behaviour of the carbonate minerals in the oil shale's mineral part. The plant layout and the main ash generation points are illustrated in Figure 2.

The annual amount of ash generated depends on the plant's capacity, plant availability, and the fuels used, and is a direct result of consumption and the open electricity market. The estimated average ash flow is 1.4 to 1.5 million tonnes per year, of which approximately 30% is estimated to be bottom ash and 70% fly ash. The ash balance of Auvere PP has not been determined experimentally. Thus, the amount of bottom ash was determined by the thermal mass balance of the bottom ash coolers. The rest of the relative ash balance of Auvere PP (Fig. 3) is based on Balti PP CFBC unit that was determined experimentally [36]. The largest share of fly ash (collection points 2 to 10) is separated from the first field of the ESP (about 50% of the total ash flow). The remaining part of the total ash flow is less than 20%, and it is estimated that most of it comes from the superheater-economiser cyclone ash (approx. 9%) and the second field of the ESP (approx. 7%). The ash fraction in flue gas (ash particles leaving the stack) is very low, and the maximum concentration allowed under the current industrial emissions legislation [37] is 10 mg/Nm^3.

The chemical composition of the ash precipitated at different points along the boiler's gas passage varies significantly. Samples from Auvere PP reveal distinct differences among ash fractions: bottom ash shows notably higher Ca and lower Si content compared to other fractions (Table 2). These observations align with findings from Ots [21] regarding CFBC ashes. However, while Ots noted that free CaO content is typically highest in the bottom ash and lowest in

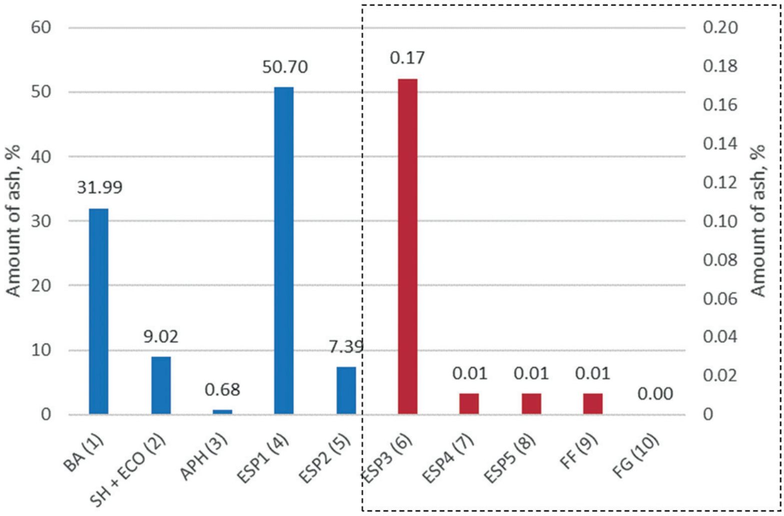

Fig. 3. Ash balance of Auvere Power Plant. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash, FG – ash in flue gas.

the finest fractions, Auvere PP's ash exhibits a slightly different pattern. Due to the finer fuel (<10 mm), combustion is more complete and uniform, leading to finer fly ash particles, which could result in the higher free CaO content in the ash collected from the final stages of the flue gas cleaning system.

Table 2. Chemical composition of the ashes from Auvere Power Plant, wt%

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
SiO_2	8.9	31.1	26.6	30.4	28.8	28.6	24.6	21.2	11.0
Fe_2O_3	2.4	3.6	3.3	3.7	3.6	3.7	3.4	2.9	8.4
Al_2O_3	1.4	6.9	5.7	6.5	6.5	6.9	6.1	5.1	2.1
CaO	52.2	36.8	39.7	37.0	39.6	37.6	41.9	46.0	47.1
MgO	5.6	5.3	5.7	4.7	5.0	4.7	4.5	4.3	2.1
Na_2O	0.05	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3
K_2O	0.6	3.5	2.7	3.6	3.4	3.5	2.8	2.3	0.7
$SO_{3(total)}$	8.0	5.9	9.6	6.5	6.4	6.5	7.6	7.0	1.9
Cl	0.2	0.5	0.5	0.6	0.5	0.5	0.7	0.7	0.4
CaO_{free}	16.7	16.1	18.2	19.0	19.3	14.2	14.4	16.2	12.8
CO_2	22.3	7.2	6.8	5.4	5.2	6.1	6.4	5.7	9.6
TIC	6.1	4.7	2.0	1.5	1.4	1.7	1.7	1.6	2.6

Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

The mineral composition supports the findings of different authors on CFBC ashes [21–23, 36], showing that calcite makes up more than 35% of the bottom ash, while in other fractions, it ranges from 9% up to 15% (Table 3). As reported by other authors [23, 24], the anhydrite content is generally high in all fractions, but slightly elevated in the bottom ash and APH ash. Longer residence time in the boiler and higher SO_2 concentrations allow better SO_2-CaO interaction, leading to higher anhydrite content compared to finer fly ash fractions. The compounds C_2S (Ca_2SiO_4) and C_4AF ($Ca_2(Al,Fe^{3+})_2O_5$), both standard components of Portland cement [38], are present in significant amounts, particularly in the ESP ash. In finer fly ash fractions, due to higher cooling rates and lower SO_2 contact, free CaO instead reacts with SiO_2, Al_2O_3, and Fe_2O_3, leading to C_2S and C_4AF formation rather than anhydrite. Along with the free CaO content, these compounds impart binding properties to the ash, as demonstrated in studies by Uibu et al. [13] and Arro et al. [24]. The portlandite ($Ca(OH)_2$) content is the highest in the ash fractions from the last collection points (collection points 8 and 9, Fig. 2), likely due to the lower temperatures and higher humidity in these sections.

Table 3. Mineralogical composition of the ashes from Auvere Power Plant, wt% [39]

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
Quartz SiO_2	3.6	14.3	12.5	12.7	10.8	10.6	6.6	5.3	3.1
Adularia $KAlSi_3O_8$	2.2	18.3	13.3	17.3	15.9	15.7	11.9	10.9	8.6
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	2.1	4.6	3.3	5.2	5.1	3.7	3.1	3.9	2.4
Calcite $CaCO_3$	35.0	15.4	12.5	10.0	10.8	17.7	18.1	9.5	9.6
Dolomite $CaMg(CO_3)_2$	5.1	n.d*	0.5	n.d	n.d	n.d	n.d	n.d	n.d
Lime CaO	18.4	16.0	19.2	19.4	20.3	9.8	10.1	9.1	<LOQ**
Portlandite $Ca(OH)_2$	2.0	0.9	1.3	1.0	1.0	4.8	6.3	17.8	14.6
Periclase MgO	7.0	5.3	6.8	5.6	5.4	5.3	5.3	4.9	7.7
Anhydrite $CaSO_4$	10.1	6.3	10.0	6.9	6.7	7.0	8.2	7.6	7.3
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	7.1	9.5	10.2	10.9	13.0	14.7	18.7	19.0	9.3
Merwinite $Ca_3Mg(SiO_4)_2$	3.1	5.3	5.2	5.9	6.4	6.6	7.8	8.0	5.3
Akermanite $Ca_2MgSi_2O_7$	3.6	2.3	3.9	3.2	3.1	2.1	2.2	2.1	8.8
Arcanite K_2SO_4	n.d	n.d	n.d	0.4	0.3	n.d	n.d	n.d	3.4
Sylvite KCl	0.3	n.d	n.d	n.d	0.3	0.3	0.4	0.9	0.6
Hematite Fe_2O_3	0.6	1.5	1.1	1.3	1.0	1.2	1.0	0.7	<LOQ

* n.d – not detected, ** LOQ – limit of quantification. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

The concentration of trace elements in the ash reflects their presence in the oil shale [21], which itself contains low levels of trace elements. As a result, trace element concentrations in the oil sale ash are also low, typically below 100 mg/kg, with some exceptions such as manganese (Mn), zinc (Zn), strontium (Sr), and titanium (Ti). As described by other authors [21, 40], trace element concentrations tend to be higher in finer ash fractions. However, some anomalies are observed – arsenic (As), Mn, and Zn have slightly higher concentrations in the bottom ash (Table 4). Lees et al. [41] conducted a similar analysis of trace element content across various oil shale ash fractions, including samples from Auvere PP, and obtained comparable results. Their findings confirmed that trace element concentrations remained low and did not exceed the regulatory limits set for soil [42].

Table 4. Content of trace elements in the ashes from Auvere Power Plant, mg/kg [39]

	BA	SH + ECO	APH	ESP1	ESP2	ESP3	ESP4	ESP5	FF
Li	6.6	23.4	18.3	26.2	24.5	25.4	19.7	16.8	11.2
Be	0.4	0.3	0.4	0.6	0.5	1.1	0.9	0.9	0.2
Ti	702	2843	2171	2947	2986	2959	2836	2692	2022
V	29.2	72.9	59.7	83.3	86.4	86.5	88.0	80.6	60.3
Cr	17.8	50.5	39.0	49.5	50.0	50.2	48.5	47.2	41.5
Mn	771	527	688	602	586	518	522	496	501
Co	4.0	6.8	5.8	7.1	6.9	7.5	7.1	6.6	5.7
Ni	18.9	32.0	27.5	33.4	32.0	35.6	32.5	30.5	27.1
Cu	3.9	9.2	7.6	9.9	9.7	10.1	9.7	9.1	10.1
Zn	235	151	171	173	145	158	126	117	116
As	53.4	22.2	39.9	27.5	28.2	31.2	37.0	35.8	43.8
Se	0.3	0.8	0.7	0.8	0.9	1.0	1.0	1.0	1.0
Sr	360	351	342	383	401	404	430	432	428
Mo	7.3	7.8	8.4	8.3	8.7	11.7	13.1	11.9	16.6
Cd	0.3	0.6	0.6	0.8	0.8	0.9	0.6	0.6	0.3
Sb	0.2	0.1	0.2	0.2	1.4	0.3	0.3	0.3	0.2
Tl	1.3	0.7	0.9	1.3	4.6	1.6	1.8	1.6	1.2
Pb	27.8	94.1	70.3	103	98.1	96.9	92.4	88.5	48.0

Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FF – fabric filter ash.

As Auvere PP is the most recently built, its ash has received less attention than that of other power plants. However, Uibu et al. [13] conducted a study that contained a composition of oil shale ash from Auvere PP's ESP fields 1–5 and the overall ash from the main silo. Their findings indicate a higher calcite concentration in the total ash than in the ESP ash, supporting the hypothesis of a higher calcite concentration in the bottom ash. Furthermore, their report indicates an amorphous phase of 30% for Auvere PP's ESP ash and 12% for the total ash, rendering direct comparisons challenging. It also shows that the quality and characteristics of ashes are variable. However, some similarities and tendencies can be observed.

3.2. Eesti Power Plant CFBC unit

The 215 MW_{el} double-unit at Eesti PP was commissioned in 2004. The power unit was built at Eesti PP to replace a PC unit and consists of a predecessor modernised steam turbine and two circulating steam turbines with CFBC technology. The switch from PC to CFBC technology was primarily driven by environmental objectives, as CFBC technology achieves significantly better results in flue gas management, notably with substantially lower sulphur dioxide (SO_2) emissions. The characteristics and properties of Eesti PP CFBC unit are discussed extensively by Hotta et al. [43]. The primary fuel for the CFBC boiler is oil shale with a particle fraction of up to 20 mm. The average calorific value of the oil shale used is 8.4 MJ/kg. However, oil shale can be used in both forms: with lower calorific values, starting from 7 MJ/kg, and higher calorific values between 11.5–12 MJ/kg. It is also possible to co-combust retort gas from shale oil production. Figure 4 illustrate the layout of the plant and the primary locations where ash is collected. In case the unit operates at nominal load and uses 100% oil shale with a calorific value of 8.3 MJ/kg as fuel, the estimated ash flow is around 1 million tonnes per year.

The boiler's ash balance shows the distribution of combustion ash streams between all ash removal points and the stack (Fig. 5). The ash balance for Eesti PP CFBC unit has not been experimentally determined. However, since the boiler at Eesti PP CFBC unit is identical to that of Balti PP, for which an experimental ash balance has been established [36], the relative ash balance

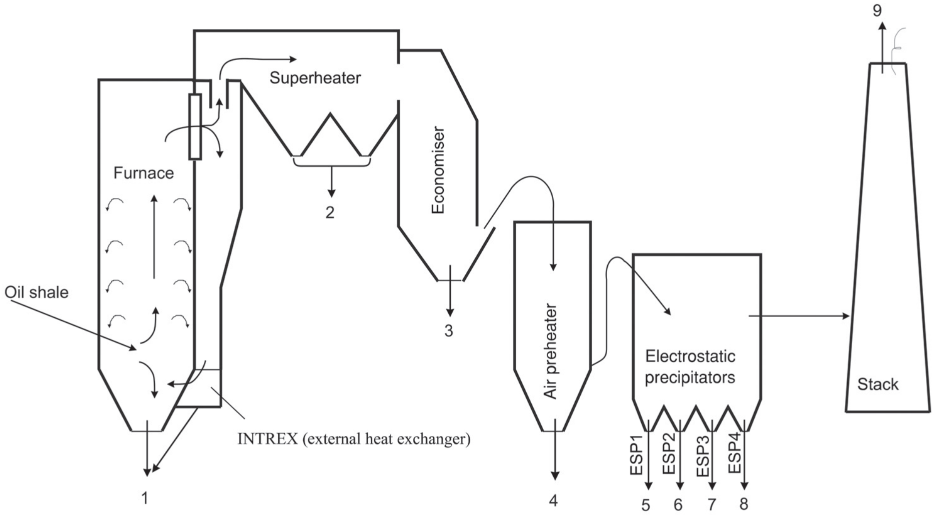

Fig. 4. Layout of Eesti Power Plant CFBC unit and ash collection points (adapted from [44]): bottom ash + INTREX (circulating ash) (1), superheater (2), economiser (3), air preheater (4), electrostatic precipitators – ESP1 (5), ESP2 (6), ESP3 (7), ESP4 (8), ash in flue gas (9).

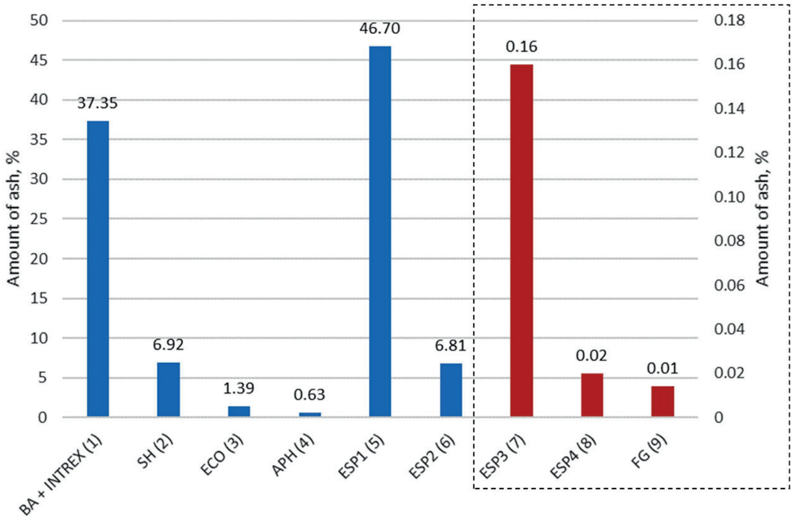

Fig. 5. Ash balance of Eesti Power Plant CFBC unit. Abbreviations: BA – bottom ash, INTREX – circulating ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

for Eesti PP CFBC unit is derived from Balti PP's data. The bottom ash from the boiler (which also contains circulating ash, the so-called INTREX ash) makes up about 37% of the total ash generated during combustion. Most of the fly ash is removed from the boiler by the ESP. The main part of the combustion ash is removed from the furnace. The share of the first field of the ESP in the ash fraction increases up to 49%. The amounts of fly ash leaving the stack are approximately 0.014% of the total combustion ash, which corresponds to a particle content in dry flue gases of about 20 mg/Nm^3 at 6% O_2.

The ash from Eesti PP CFBC unit has a chemical composition similar to that of Auvere PP's ash. Bottom ash contains the highest Ca concentration, exceeding 54%, while other fractions show Ca levels between 31% and 37% (Table 5). Similar to Auvere PP, Si concentration is lowest in the bottom ash. In contrast to Auvere PP, the free CaO content is generally lower, ranging between 14% to 19%, with the lowest levels found in the ash from the final stage of the flue gas cleaning system. This distribution aligns closely with the findings of Ots [21].

The mineral composition of the different fractions of Eesti PP CFBC ash also varies significantly (Table 6), with the most notable differences being the content of calcite, quartz (SiO_2), and adularia ($KAlSi_3O_8$). The bottom ash and ash in flue gas contain almost 40% of calcite, while it ranges between 10% and 17% in the other fractions. The bottom ash also contains modest amounts of quartz and adularia, whereas the other fractions exhibit significantly higher

Table 5. Chemical composition of the ashes from Eesti Power Plant CFBC unit, wt% [39]

	BA	SH	ECO	APH	ESP1	ESP2	ESP3	ESP4	FG
SiO_2	6.2	31.9	31.9	26.6	32.4	32.9	29.9	25.6	27.4
Fe_2O_3	2.7	4.1	4.1	3.8	4.3	4.3	4.6	4.6	4.7
Al_2O_3	2.1	9.6	9.9	8.3	10.3	10.6	10.3	9.4	9.1
CaO	54.5	31.5	32.3	37.3	32.5	32.0	32.7	34.4	34.2
MgO	4.4	5.7	6.0	7.1	5.6	5.8	6.4	6.7	7.1
Na_2O	0.03	0.1	0.1	0.1	0.2	0.2	0.1	0.7	0.1
K_2O	0.5	3.8	3.8	2.9	3.9	4.0	3.5	2.5	2.8
$SO_{3(total)}$	4.1	7.4	6.3	10.7	6.1	6.9	7.3	9.2	9.8
Cl	0.05	0.3	0.4	0.3	0.2	0.3	0.4	0.7	0.6
CaO_{free}	18.1	14.2	15.6	19.0	16.3	15.3	11.5	8.2	n.a*
CO_2	23.7	3.6	3.0	2.0	2.8	2.7	3.3	3.9	2.8
TIC	6.5	1.0	0.8	0.6	0.8	0.8	0.8	0.9	1.1

* n.a – not analysed. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

concentrations of these minerals. The content of C_2S/C_4AF is slightly lower than in Auvere ash but remains notable, particularly with higher concentrations observed in the ESP ash. Similar to Auvere PP's ash, anhydrite preferably forms in the bottom ash, while C_2S/C_4AF are more prevalent in the finer fractions. The content of dolomite ($CaMg(CO_3)_2$) and sylvite (KCl) is similar to that of Auvere PP's ash, while there are no traces of arcanite (K_2SO_4). Though in modest concentrations, hematite (Fe_2O_3), which is not found in Auvere ash, is present in almost all fractions.

Table 6. Mineralogical composition of the ashes from Eesti Power Plant CFBC unit, wt%

	BA	ECO	APH	ESP1	ESP2	ESP3	ESP4	FG
Quartz SiO_2	5.9	17.0	15.1	15.5	18.8	16.5	12.8	8.5
Adularia $KAlSi_3O_8$	4.3	17.1	11.8	15.1	16.6	16.9	15.4	6.4
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	<LOQ*	1.5	5.9	5.7	6.5	6.1	6.1	4.1
Calcite $CaCO_3$	35.9	11.7	10.3	12.7	12.4	11.7	11.5	38.8
Dolomite $CaMg(CO_3)_2$	3.1	n.d**	n.d	n.d	n.d	n.d	n.d	n.d
Lime CaO	8.2	5.8	10.5	11.6	6.2	4.0	1.9	5.0
Portlandite $Ca(OH)_2$	7.7	8.9	8.5	1.7	4.5	3.4	2.7	4.4
Periclase MgO	4.7	4.9	5.4	3.2	3.4	3.3	3.7	3.7
Anhydrite $CaSO_4$	15.7	11.6	14.0	11.2	9.7	10.9	13.3	9.9
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	6.5	8.9	8.6	13.8	9.3	12.1	15.8	5.8
Merwinite $Ca_3Mg(SiO_4)_2$	2.2	1.7	2.1	2.2	2.3	2.9	3.4	1.9
Akermanite $Ca_2MgSi_2O_7$	7.8	8.5	8.1	8.7	6.4	7.3	8.5	8.4
Sylvite KCl	<LOQ	0.5	0.6	n.d	n.d	n.d	n.d	n.d
Hematite Fe_2O_3	1.7	2.0	2.8	4.3	3.9	4.8	5.3	3.0

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

The trace element content is generally similar between the ashes from Auvere PP and Eesti PP CFBC unit, with the exception of As, lead (Pb), and Zn, which are significantly lower in the ash from Eesti PP (Table 7). At Auvere PP, the concentrations of As, Mn, and Zn are higher in the bottom ash, whereas in Eesti PP CFBC unit, only Mn shows an elevated concentration in the bottom ash. Reinik et al. [40] investigated trace elements in Balti PP CFBC ash, finding a trace element composition similar to that in the current study, with notably higher Mn concentrations in the bottom ash.

Bityukova et al. [23] examined the composition of various ash fractions from the CFBC units of Balti PP and Eesti PP, and their findings largely align with the results of the current study. Notably, while dolomite was not identified in the bottom ash from Eesti PP CFBC unit, it was detected in the bottom ash

Table 7. Trace elements content of the ashes from Eesti Power Plant CFBC unit, mg/kg [39]

	BA	ECO	APH	ESP1	ESP2	ESP3	ESP4
Li	1.8	40.3	30.2	38.8	29.7	37.7	29.4
Be	<LOQ*	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ti	885	4206	3190	4280	3167	3675	3237
V	17.0	72.7	56.2	75.1	72.0	80.2	76.3
Cr	16.7	70.4	55.1	73.9	66.0	74.4	73.9
Mn	821	757	797	590	492	479	447
Co	2.5	7.6	6.1	7.8	6.6	7.2	7.6
Ni	13.5	39.3	29.8	38.3	35.0	36.5	39.3
Cu	5.1	15.0	9.7	12.0	10.7	12.0	14.4
Zn	22.9	40.9	35.7	34.6	28.7	29.7	30.0
As	8.1	15.9	19.5	15.0	15.6	23.1	29.8
Se	n.d**	1.4	1.1	1.3	1.2	1.3	1.1
Sr	296	458	415	437	357	422	424
Mo	0.8	5.3	4.1	4.7	3.4	6.5	5.7
Cd	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Sb	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	0.4	1.1	0.8	1.6	1.6	1.9	1.9
Pb	17.1	57.9	37.9	62.9	51.8	69.1	60.8

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, ECO – economiser ash, APH – air preheater ash, ESP – electrostatic precipitator ash.

from Balti PP. Similarly, although wollastonite (CaO·SiO2) was absent in the ash fractions from Eesti PP, it was present in those from Balti PP. Since the CFBC technology is similar, and identical in both Balti PP and Eesti PP, these observations suggest that the differences in the mineralogical composition of the ashes are more significantly influenced by the quality and composition of the fuel used rather than by the combustion technology itself.

3.3. Eesti Power Plant PC unit with NID

Eesti PP's PC energy unit consists of a turbogenerator and two TP-101 type dust incinerators. The main steam parameters of boiler TP-101 are a steam production of 320 t/h, with main and intermediate superheated steam pressures downstream of the boiler at 13.2/2.2 MPa, and steam temperatures of 520/525 °C, respectively. The nominal gross power of the unit is 185 MW_{el}, and the unit efficiency is less than 30%. The boiler's efficiency at nominal capacity at steady state is between 86% and 88% [28]. The median particle size of the pulverised oil shale fed into the boiler through the burners is in the ranges from 45 to 55 μm, and the combustion of the fuel particles takes place at a boiler temperature of approximately 1400 °C. When operating at nominal load using 100% oil shale with a calorific value of 8.1 MJ/kg as fuel, the estimated annual ash production is approximately 0.9 million tonnes. However, the actual amount of ash generated can vary significantly depending on the unit's operating hours and the mix of fuels used. Notably, the unit can utilise shale oil retort gas for up to 80% of its heat input, which, combined with variations in plant availability, contributes to considerably lower ash outputs under different conditions.

Measurements of the ash balance carried out on this type of boiler [28] showed that the bottom ash represents approximately 42% of the total ash generated. The fly ash leaving the combustion chamber is divided between the other ash removal points as follows: 3.7% from the bottom of the superheater heating surfaces in the flue gas passage, 4.7% from the economiser (rising gas pass), 14.5% from the cyclone, 35% from the NID unit, and 0.02% from the stack.

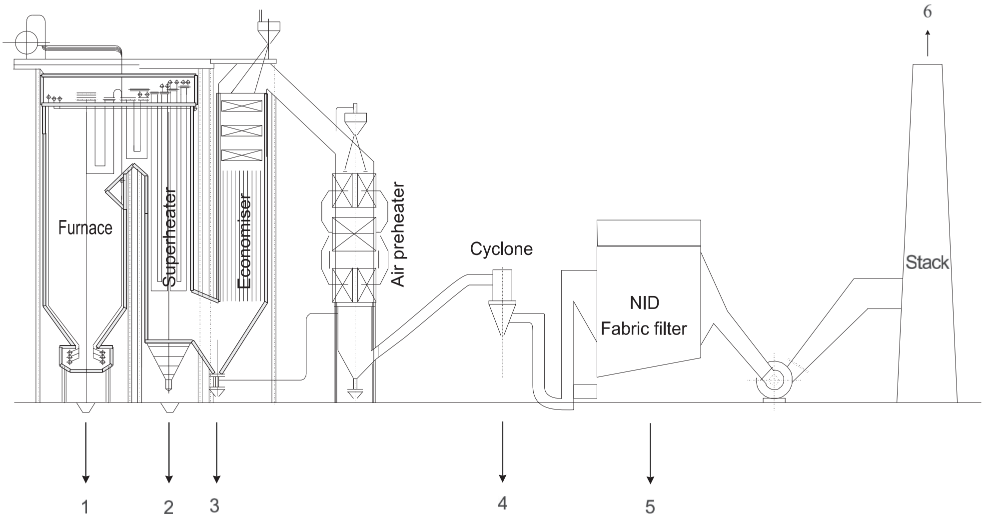

Fig. 6. Layout of Eesti Power Plant PC unit with novel integrated desulphurisation (NID) unit and ash collection points (adapted from [28]): bottom ash (1), superheater (2), economiser (3), cyclone (4), NID fabric filter (5) ash in flue gas (6).

The NID device incorporates a fabric filter for fly ash capture, which has a higher particle capture efficiency than an electrostatic precipitator. The measurement results show that fly ash in the flue gas leaving the stack from the NID unit is less than 20 mg/Nm^3, which allows for the calculation of the ash fraction coming from the NID unit.

The chemical composition of Eesti PP PC's ash (Table 8) differs from that of Auvere and Eesti PP CFBC ash. While Auvere PP's and Eesti PP CFBC's ash had lower Si content in the bottom ash, the PC ash had Si content rather unified ranging from 21% in the bottom ash to 26% in the fabric filter ash. Additionally, the free CaO content is the highest in the PC bottom ash, significantly exceeding the levels observed in CFBC ashes. A study by Konist et al. [28] reported a similar chemical composition for PC ash; however, this analysis was conducted prior to the installation of the NID device. The primary function of the NID is to reduce SO_2 levels in the flue gas. In the NID unit, free CaO binds with sulphur, which notably increases the sulphate content in the NID fabric filter ash.

The higher combustion temperature and finer particle size of oil shale in PC unit lead to an almost immediate decomposition of carbonates upon furnace entry. This rapid decomposition results in the formation of free CaO, which then reacts to form new minerals. [21] The mineralogical composition of ash fractions from Eesti PP PC is relatively unified, except quartz, anhydrite, and calcite in slightly higher concentrations in the NID fabric filter (Table 9). The mineralogical content of PC NID ash differs from CFBC ash mainly due to Ca containing minerals; the calcite content is significantly lower in PC NID ash while lime (CaO) and portlandite content are higher. In PC ash, the content of C_2S/C_4AF is significantly higher than in other ashes, which correlates with the findings of other authors [13, 24, 45] that PC ash has the best binding properties.

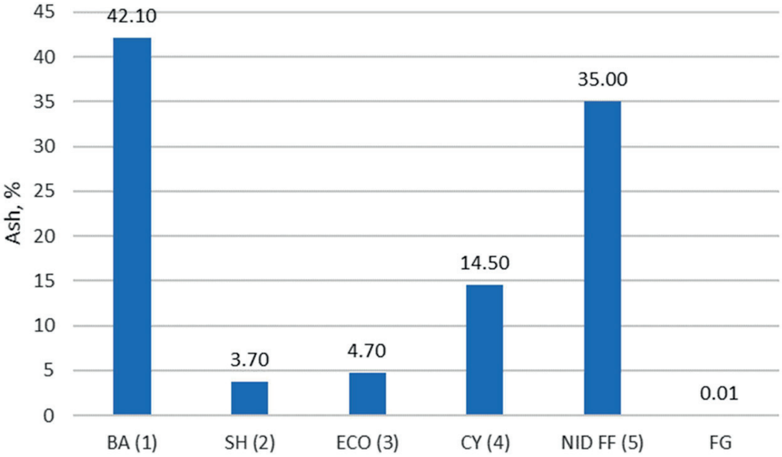

Fig. 7. Ash balance of Eesti Power Plant PC unit with NID. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash, FG – ash in flue gas.

Table 8. Chemical composition of the ashes from Eesti Power Plant PC unit with NID, wt%

	BA	SH	ECO	CY	NID FF
SiO_2	23.6	24.6	23.5	24.8	28.4
Fe_2O_3	3.7	3.8	3.7	3.8	3.1
Al_2O_3	5.3	6.4	6.2	6.7	7.4
CaO	52.1	45.1	45.8	48.8	33.7
MgO	7.6	7.2	5.8	6.1	38
Na_2O	0.2	0.06	0.08	0.08	0.2
K_2O	2.0	2.5	2.5	2.3	4.1
$SO_{3(total)}$	3.4	8.2	7.4	4.8	15.1
Cl	0.03	0.04	0.1	0.1	0.6
CaO_{free}	19.8	17.1	14.7	17.3	11.8
CO_2	1.86	0.84	3.87	1.40	4.12
TIC	0.51	0.23	1.06	0.38	1.12

* LOQ – limit of quantification. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

Table 9. Mineralogical composition of the ashes from Eesti Power Plant PC unit with NID, wt%

	BA	SH	ECO	CY	NID FF
Quartz SiO_2	3.5	6.7	6.9	6.8	10.5
Adularia $KAlSi_3O_8$	4.6	5.4	6.0	4.3	2.5
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	1.8	n.d*	n.d	n.d	1.2
Calcite $CaCO_3$	5.3	9.3	9.6	4.2	11.5
Dolomite $CaMg(CO_3)_2$	n.d	n.d	n.d	n.d	n.d
Lime CaO	24.6	19.8	21.1	24.6	8.8
Portlandite $Ca(OH)_2$	8.1	12.8	11.8	8.9	8.3
Periclase MgO	4.7	3.9	4.3	8.0	4.1
Anhydrite $CaSO_4$	3.8	8.0	6.2	9.5	11.8
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	20.9	14.4	15.6	16.5	18.8
Merwinite $Ca_3Mg(SiO_4)_2$	6.1	5.3	4.9	6.7	4.8
Akermanite $Ca_2MgSi_2O_7$	14.6	9.2	8.9	5.6	4.0
Sylvite KCl	n.d	n.d	n.d	n.d	1.2
Hematite Fe_2O_3	1.3	2.8	2.5	2.2	1.1

* n.d – not detected. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

The trace element content is relatively modest, with cadmium (Cd) and antimony (Sb) falling below the limit of quantification (Table 10). The concentrations of trace elements are fairly consistent across different fractions, resulting in somewhat higher concentrations along the gas passage. The levels of As and Pb in the samples were notably lower than those observed in the CFBC ashes discussed earlier. This difference can be attributed to the types of gas cleaning equipment used; CFBC plants utilised an ESP, while the current case employed a fabric filter. Previous research [21, 40] has also shown elevated concentrations of these elements in the ESP of PC power plants that lacked an NID system.

Table 10. Trace element content of the ashes from Eesti Power Plant PC unit with NID, mg/kg [39]

	BA	SH	ECO	CY	NID FF
Li	22.7	22.0	20.2	24.9	25.2
Be	1.1	<LOQ*	<LOQ	<LOQ	0.3
Ti	2306	2335	2406	2582	2848
V	42.5	46.2	48.1	51.7	55.4
Cr	36.5	39.4	41.5	46.2	57.4
Mn	744	667	706	783.2	454
Co	5.4	4.5	4.9	5.0	6.4
Ni	23.2	20.5	23.3	22.5	28.2
Cu	9.0	10.3	9.8	37.6	7.5
Zn	31.7	29.6	23.9	19.6	56.9
As	7.4	8.0	10.7	8.2	21.6
Se	0.7	0.9	1.0	1.0	1.0
Sr	397	352	387	418	297
Mo	1.3	n.d**	0.9	n.d	4.4
Cd	n.d	n.d	n.d	n.d	n.d
Sb	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Tl	0.5	0.5	0.5	0.8	2.1
Pb	13.5	30.0	28.2	25.9	64.5

* LOQ – limit of quantification, ** n.d – not detected. Abbreviations: BA – bottom ash, SH – superheater ash, ECO – economiser ash, CY – cyclone ash, NID FF – NID fabric filter ash.

Bityukova et al. [23] analysed PC ashes from Balti PP and Eesti PP, which were not equipped with a NID system at the time of their study. They observed significant differences in the mineralogical composition of ashes from the two similar power plants, particularly in the composition of secondary calcium-bearing phases. The findings of the current study also indicate differences in the mineralogical composition of ash samples when compared to those reported by Bityukova et al.; specifically, the akermanite ($Ca_2MgSi_2O_7$) content was found to be notably higher, and melilite ($(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$) was not detected in the current samples.

3.4. Enefit280

Construction of a shale oil production plant based on Enefit280 technology started in 2012. Enefit280 is based on SHC technology, with a design capacity of 280 t/h for oil shale with a particle size of up to 6 mm. The main distinguishing feature of the Enefit280 technology, compared to other SHC-based technologies used in Estonia, is that the semi-coke produced during the pyrolysis process is combusted in an adiabatic CFB combustor [46]. When operating at nominal load, the estimated ash amount generated is 1.2 million tonnes per year. The layout of the plant and the primary locations where ash is collected are shown in Figure 8.

The combustion of the semi-coke in the combusting chamber takes place under adiabatic conditions in an oxidising atmosphere, the temperature in the furnace being kept below 800 °C with the basic objective of reducing the decomposition of carbonate minerals. The heat released from the semi-coke combustion in the boiler is primarily used to heat the retort solid material (solid heat carrier). Another part of the heat is used for drying the oil shale. The remaining heat, including the heat from cooling of the bottom ash and the gases leaving the furnace, is used to generate electricity through a steam cycle based on the Rankine cycle. However, the steam parameters are relatively modest compared to those used in the adjacent power plants. This results in the Enefit280 oil plant's relatively low electricity generation efficiency of around 26% [47].

The ash balance for Enefit280, presented in Figure 9, was indirectly obtained based on the technological parameters and the chemical analysis of ash gained at different points of the plant. At the same time, no direct measurement of ash discharge fluxes at different plant points has been carried out, and the actual ratios may slightly deviate from the presented values. The majority of the ash discharged from the boiler is bottom ash, comprising over 60% of the total ash produced. The next largest source of ash is collected from the utilisation boiler cyclone. The remaining ash is captured by the ESP, with only a very small fraction escaping as particulate matter in the flue gas.

The chemical composition of Enefit280 ash (Table 11) is similar to power plants' CFBC ashes, with a low Si content in the bottom ash and a significantly higher content in other fractions. However, unlike the ash from power

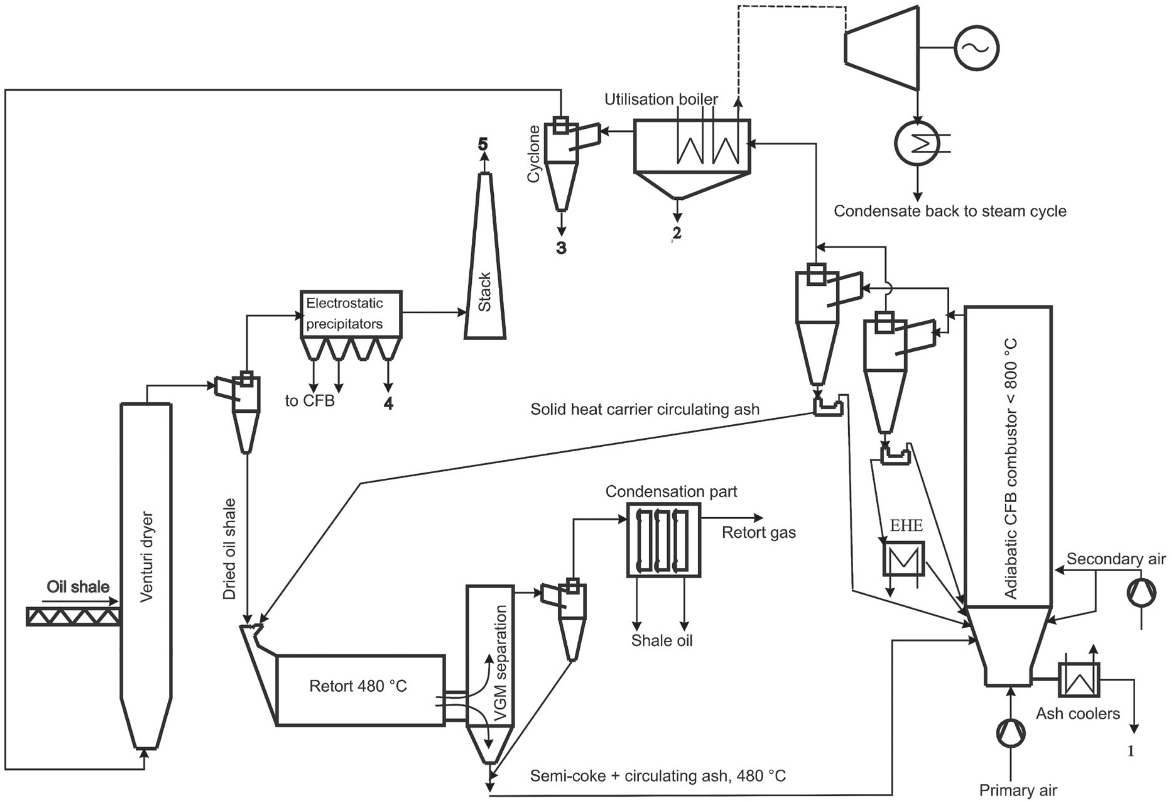

Fig. 8. Layout of Enefit280 technology and ash collecting points (adapted from [46]): bottom ash (1), utilisation boiler (2), cyclone (3), electrostatic precipitator (4), ash in the flue gas (5). Abbreviations: CFB – circulating fluidised bed, VGM – vapor-gas mixture, EHE – external heat exchanger.

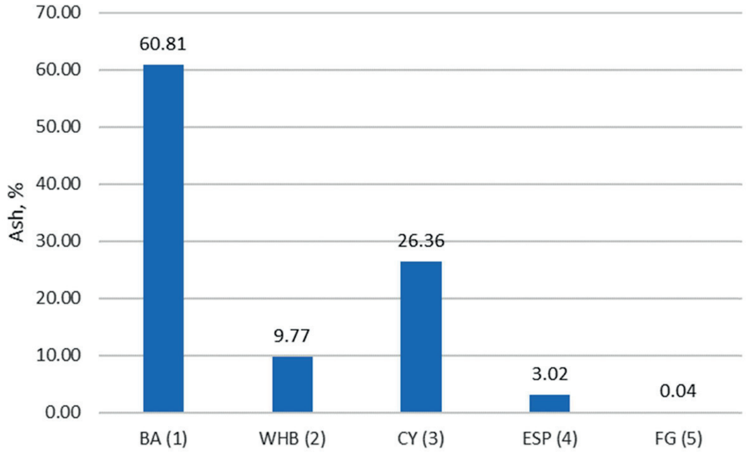

Fig. 9. The ash balance of Enefit280. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash, FG – ash in flue gas.

plants, the free CaO content in Enefit280 ash is modest, around 1%. The limited amount of free CaO confirms that the low combustion temperature substantially reduces the decomposition of carbonate minerals. As a result, the mineralogical composition of Enefit280 ash is markedly different from that of power plant ashes. Specifically, Enefit280 ash contains higher concentrations of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), while exhibiting significantly lower ratios of C_2S/C_4AF ($Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$). Additionally, it contains almost no lime or portlandite, as shown in Table 12.

Table 11. Chemical composition of the ashes from Enefit280, wt%

	BA	WHB	CY	ESP
LOI	33.5	17.7	n.a	31.77
SiO_2	9.3	36.9	30.8	27.0
Fe_2O_3	1.6	4.5	3.3	2.8
Al_2O_3	1.3	11.1	6.7	7.5
CaO	45.6	23.0	29.5	22.2
MgO	3.2	2.5	3.2	1.7
Na_2O	0.04	0.2	0.2	0.1
K_2O	0.5	4.4	3.1	3.1
$SO_{3(total)}$	9.6	5.6	5.5	1.9
Cl	0.06	n.a*	0.08	n.a
CaO_{free}	1.1	n.a	1.8	1.04

* n.a – not analysed. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Table 12. Mineralogical composition of the ashes from Enefit280, wt% [39]

	BA	WHB	CY	ESP
Quartz SiO_2	3.4	16.8	16.0	14.9
Adularia $KAlSi_3O_8$	3.3	22.1	17.6	29.9
Muscovite $KAl2(AlSi_3O_{10})(F,OH)_2$	0.9	6.0	9.4	10.9
Calcite $CaCO_3$	57.6	29.3	32.4	20.4
Dolomite $CaMg(CO_3)_2$	14.6	6.6	3.4	5.0
Hematite Fe_2O_3	1.1	2.5	2.3	n.d*
Lime CaO	n.d	n.d	n.d	0.7
Portlandite $Ca(OH)_2$	0.5	n.d	n.d	0.6
Periclase MgO	3.1	2.8	2.1	1.0
Anhydrite $CaSO_4$	10.7	9.3	8.9	5.0
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	3.8	1.8	5.0	3.5
Merwinite $Ca_3Mg(SiO_4)_2$	1.3	0.8	1.4	0.6
Akermanite $Ca_2MgSi_2O_7$	0.7	1.9	1.3	2.2
Sylvite KCl	n.d	n.d	n.d	1.3
Chlorite	n.d	n.d	n.d	4.1

* n.d – not detected. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

The concentrations of trace elements in Enefit280 ash, as with ash from power plants, are relatively modest (Table 13). Consistent with CFBC ash patterns, trace element concentrations are generally lower in the bottom ash compared to other fractions, with the exceptions of Mn and Zn, which exhibit higher levels in the bottom ash.

Table 13. Trace elements content of the ashes from Enefit280, mg/kg [39]

	BA	WHB	CY	ESP
Li	6.2	19.1	21.8	22.3
Be	0.3	n.d*	0.7	n.d
Ti	572	2876	2817	3362
V	13.1	54.2	48.9	70.1
Cr	10.3	57.2	48.4	63.0
Mn	525	484	341	291
Co	2.8	5.9	6.8	8.3
Ni	11.9	25.1	33.5	30.1
Cu	3.0	8.3	8.0	9.7

Table 13. (continued)

	BA	WHB	CY	ESP
Zn	159	113	79.2	95.4
As	19.6	30.6	27.5	33.9
Se	0.6	0.9	0.3	0.9
Sr	352	346	332	215
Mo	4.2	15.5	12.5	22.5
Cd	0.3	1.2	n.d	1.4
Sb	n.d	n.d	n.d	n.d
Tl	0.8	1.6	n.d	9.6
Pb	18.5	121	52.5	102.2

* n.d – not detected. Abbreviations: BA – bottom ash, WHB – utilisation boiler ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Uibu et al. [13] analysed the chemical composition, mineralogical profile, and trace element content of bottom ash, cyclone ash, and total ash from Enefit280. Their findings are consistent with those of the present study, providing additional support and validation for its conclusions.

3.5. Petroter

The Petroter technology uses the SHC method to produce shale oil. Petroter has a capacity of 140 tonnes of crude oil shale (up to 25 mm) per hour (approx. 3000 t/day). The first Petroter unit was commissioned in 2009, followed by Petroter II in 2014 and Petroter III in 2015 [48]. The schematic diagram of the unit is shown in Figure 10.

Semi-coke combustion occurs in a reducing atmosphere (in the absence of oxygen) at a temperature of about 760–810 °C. The low combustion temperature, lack of oxygen, and relatively short residence time of the particles in the combustor determine the properties of the resulting ash. After combustion, the hot ash and gas mixture is split into two streams. One stream is directed to the heat transfer cyclones, where the ash is separated from the gas and retorted as a solid heat carrier. The second stream is directed to a three-stage ash cyclone, where ash separation takes place to clean the gas stream of solid material. A utilisation boiler is placed downstream of the ash cyclone (on the gas side), where the unburned organic components (H_2S, CO, VOCs, etc.) are combusted. The residual heat in the gas is utilised to dry the oil shale (Fig. 10) [47, 48].

The annual ash generated by the Petroter technology (all three units) ranges from 1.6 to 1.8 million tonnes [48]. The ash is removed from the process at two main separation points (Fig. 11): about 95% in the ash cyclones and about 5% in the ESP. A small fraction of the ash generated is emitted into the atmosphere.

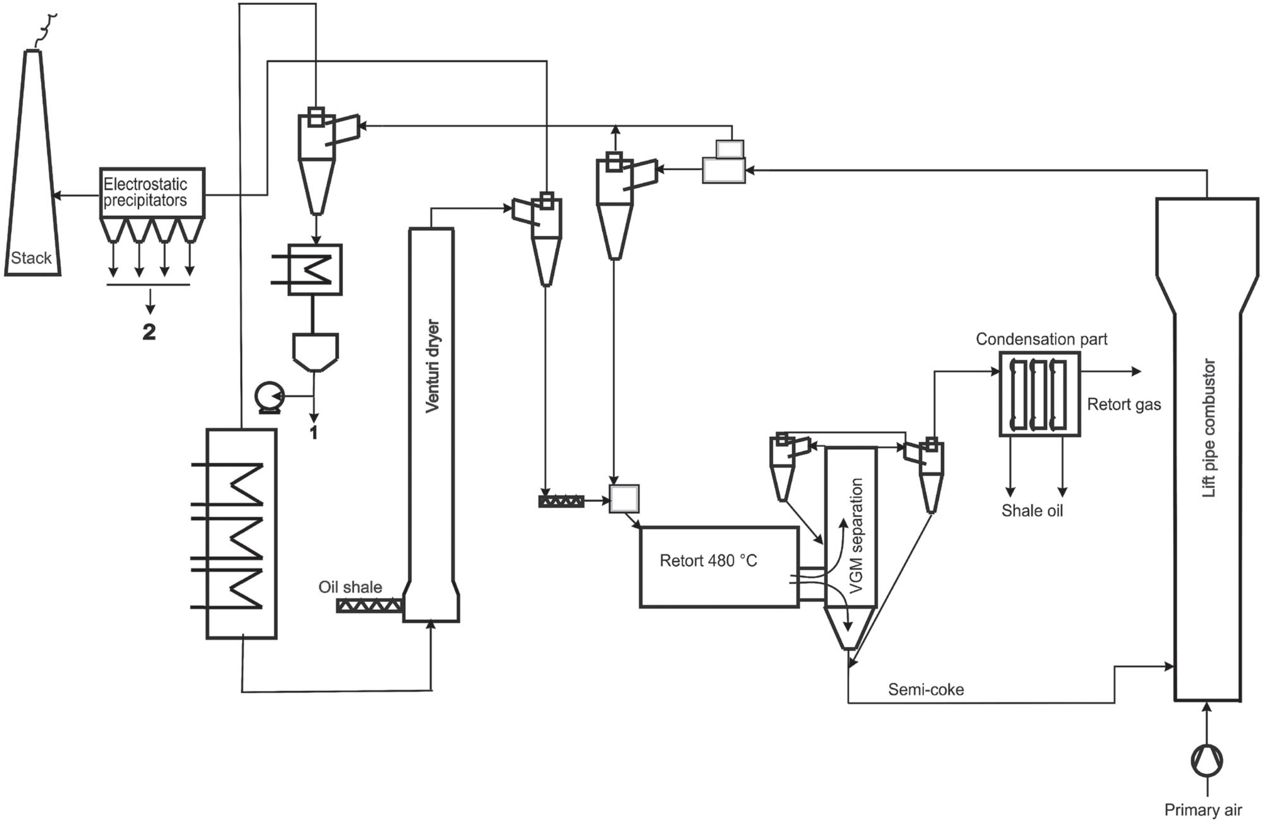

Fig. 10. Layout of the Petroter technology (adapted from [46]) and ash collecting points: cyclone (1), electrostatic precipitators (2), ash in the flue gas (3). Abbreviation: VGM – vapor-gas mixture.

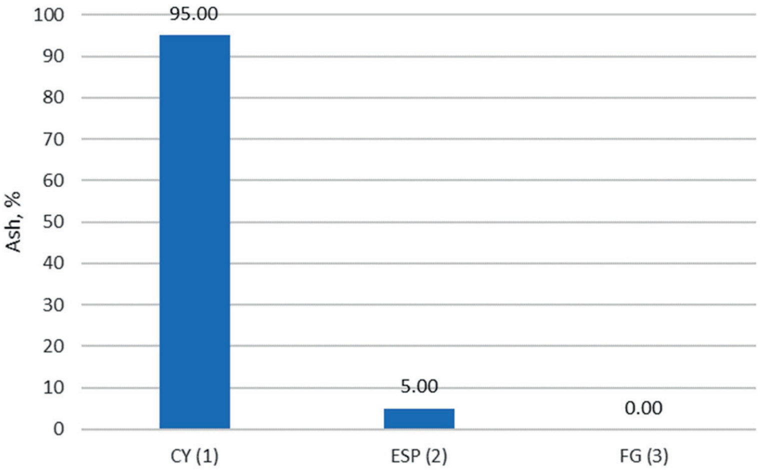

Fig. 11. Ash balance of Petroter ashes. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash, FG – ash in the flue gas.

The chemical composition of Petroter's ash varies significantly between the fractions from the cyclone and the ESP. Since the majority of ash is collected before reaching the ESP, the overall chemical composition of the total ash closely resembles that of the cyclone ash (Table 14). The low combustion temperature, lack of oxygen, and relatively short residence time of the particles in the combustor reduce the decomposition of carbonates, resulting in ash with minimal free CaO content. This limited free CaO content leads to a particularly distinctive mineralogical composition (Table 15). The concentration of dolomite ($CaMg(CO_3)_2$) is significantly higher than in any other ash fraction from other installations, while the content of muscovite ($KAl_2(AlSi_3O_{10})(F,OH)_2$) is also notably high, especially in the finest fraction in the ESP (>38%).

Table 14. Chemical composition of Petroter ashes, wt%

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
LOI	26.7	16.6	23.5	24.4	24.5
SiO_2	19.1	40.3	21.8	20.3	26.0
Fe_2O_3	2.7	3.9	3.1	2.9	3.8
Al_2O_3	2.6	13.7	5.0	4.8	6.1
CaO	35.2	13.5	33.8	35.0	47.6
MgO	4.0	2.6	4.4	4.4	5.2
Na_2O	0.1	0.1	0.08	0.13	0.04
K_2O	1.4	5.2	1.8	1.7	2.4

Table 14. (continued)

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
$SO_{3(total)}$	5.2	4.2	4.3	4.0	4.2
Cl	0.1	0.02	n.a*	n.a	n.a
CaO_{free}	1.48	0.37	2.62	3.01	2.6

* n.a – not analysed. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

Table 15. Mineralogical composition of Petroter ashes, wt% [39]

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
Quartz SiO_2	10.5	11.3	14.1	9.9	11.6
Adularia $KAlSi_3O_8$	4.6	16.5	9.3	7.2	9.2
Muscovite $KAl_2(AlSi_3O_{10})(F,OH)_2$	5.4	38.7	9.1	6.9	6.9
Calcite $CaCO_3$	50.2	20.0	43.0	44.7	48.4
Dolomite $CaMg(CO_3)_2$	14.3	1.0	10.8	19.7	10.3
Hematite Fe_2O_3	n.d*	0.5	n.d	n.d	n.d
Lime CaO	n.d	0.5	n.d	n.d	n.d
Portlandite $Ca(OH)_2$	0.6	0.8	n.d	n.d	n.d
Periclase MgO	1.7	<0.5	2.0	2.1	2.0
Anhydrite $CaSO_4$	2.9	1.2	2.3	1.4	2.5
C_2S/C_4AF $Ca_2SiO_4/Ca_2(Al,Fe^{3+})_2O_5$	3.7	0.5	0.7	0.9	0.8
Merwinite $Ca_3Mg(SiO_4)_2$	2.1	2.1	2.0	1.4	1.8
Akermanite $Ca_2MgSi_2O_7$	1.4	1.7	n.d	n.d	n.d
Oldhamite CaS	n.d	n.d	3.1	2.3	2.5
Magnetite Fe_3O_4	n.d	n.d	1.6	1.2	1.4
Apatite $Ca_5(PO_4)_3(F,OH,Cl)$	n.d	n.d	2.0	1.7	2.6

* n.d – not detected. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

The variation in the trace element content between the two ash fractions is considerable, with markedly higher concentrations observed in the ash from the ESP. As with the ashes from other installations described earlier, some discrepancies are evident; for instance, the concentrations of cuprum (Cu) and Mn are significantly higher in the ash from the cyclone.

Table 16. Trace elements content of Petroter ashes, mg/kg

	CY	ESP	Petroter I total	Petroter II total	Petroter III total
Li	11.5	56.8	13.7	13.1	13.1
Be	0.4	2.4	0.9	0.8	0.8
Ti	1285	5640	n.a*	n.a	n.a
V	23.0	105.5	37.1	33.9	32.2
Cr	21.5	85.4	40.1	37.2	35.9
Mn	530	271	458	452	426
Co	4.0	11.9	4.5	4.3	4.1
Ni	15.3	41.4	20.4	19.0	18.6
Cu	78.7	9.0	9.7	7.1	6.2
Zn	37.3	35.2	47.2	35.4	36.4
As	6.4	8.7	8.7	7.8	7.2
Se	<0.2	0.5	1.2	1.1	1.2
Sr	264	245	256	245	259
Mo	1.4	3.0	n.a	n.a	n.a
Cd	n.d**	n.d	1.6	0.7	0.6
Sb	n.d	n.d	n.a	n.a	n.a
Tl	n.d	n.d	0.6	1.2	0.3
Pb	25.1	135	38.5	37.8	32.8

* n.a – not analysed, ** n.d – not detected. Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash.

3.6. Leaching characteristics of ashes

The system pH of the ash eluates is significantly higher for ashes derived from power plants, with values around 13, compared to those from shale oil production facilities (Table 17). Notably, the eluate from the ash collected from the Petroter ESP exhibits the lowest system pH, measuring only 10.42. A clear correlation exists between the pH and conductivity, with higher conductivity observed in eluates with higher pH values. As CFBC ashes contain higher sulphur concentrations, sulphate (SO_4^{2-} ions) concentrations are highest in the eluates of CFBC ashes, as well as in those from the Enefit280 process, which also employs CFBC technology, and in the eluates of PC NID and fly ash. In contrast, leachates of ashes from PC furnaces and Petroter processes display significantly lower concentrations of SO_4^{2-} ions. Chloride concentrations (Cl^- ions) are lower in bottom ash eluates compared to finer fractions, with slightly higher levels in Enefit280 ashes and slightly lower levels in Petroter ashes.

The concentration of trace elements in oil shale ash from Estonian oil shale is relatively low, attributed to the depositional environment of kukersite oil shale, primarily composed of regular marine carbonate rocks rich in hydroxides and calcium. In this setting, trace elements did not accumulate significantly [49]. Therefore, the leaching of trace elements from the ash samples is minimal, with concentrations often falling below the limit of quantification. Even elements present in higher concentrations within the ash, such as Mn, Ti, and Zn, exhibit minimal leaching. While the majority of elements demonstrate leaching rates of less than 1 mg/kg, the mobility of Sr is notably higher, ranging from 8.94 to 57.24 mg/kg. It is particularly elevated in ash from power plants compared to that from shale oil production. Additionally, chromium (Cr) exhibits slightly increased mobility in Enefit280 ash and CFBC fly ash. Molybdenum (Mo) also shows marginally higher mobility in Enefit280 ash (Table 17). Similar findings regarding the mobility of Cr and Mo were also reported by Uibu et al. [13]

The mobility of trace elements in oil shale ash, when compared to the limit values set for waste acceptance at landfills in EU Commission Decision 2003/33 [50], demonstrates significantly lower levels than those established for inert waste, with the exception of Mo. Notably, while the chlorine ion content is lower in the eluates from bottom ash, the levels of chlorine ions in the eluates from fly ash, along with the sulphates found in all types of eluates, are below the thresholds for non-hazardous waste (Table 17).

Some trace elements, even at low levels, can pose significant risks to aquatic ecosystems. To protect the aquatic environment, the EU has established environmental quality standards (EQS) [51] for priority substances and certain other pollutants to protect water bodies. Among the trace elements analysed, Cd and Pb are classified as priority substances under current EU legislation, primarily due to their toxic effects on aquatic life, bioaccumulation potential, and persistence in the environment. Cd and Pb compounds are present in ash samples at marginal concentrations, with mobility less than 0.1 mg/kg for Pb and even lower for Cd. In contrast, Sr, Cr, and Mo, which exhibit higher mobility in ashes, are not currently listed as priority substances under EU legislation. The EU Commission has recently proposed a revision [52] to amend the list of priority substances, reflecting the evolving understanding of the environmental impacts of various chemicals. However, the revision does not include Sr, Cr, and Mo as priority substances.

Table 17. Release of components from ash samples at pH_{mat} (L/S = 10/1), mg/kg

	Auvere PP BA	Auvere PP ESP1	Auvere PP FA	Eesti PP CFBC	Eesti PP CFBC ESP1	Eesti PP CFBC FA	Eesti PP PC NID BA
Li	0.248	0.611	0.684	0.174	0.329	0.289	0.334
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ti	0.004	0.003	0.003	0.006	0.004	0.005	0.004
V	0.001	0.004	0.004	0.001	0.003	0.003	<LOQ
Cr	0.001	0.999	0.965	<LOQ	1.173	1.100	0.001
Mn	0.001	0.002	0.001	0.006	0.001	0.001	0.002
Co	0.003	0.002	0.002	0.002	0.003	0.003	0.002
Ni	0.010	0.007	0.006	0.008	0.008	0.008	0.006
Cu	0.003	0.006	0.015	0.003	0.010	0.005	0.011
Zn	0.060	0.026	0.023	0.009	0.015	0.013	0.016
As	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Se	0.004	0.034	0.036	0.009	0.034	0.032	0.002
Sr	39.08	54.38	57.24	26.50	35.08	38.22	51.81
Mo	**0.501**	**0.742**	**0.736**	**0.153**	**0.514**	**0.522**	0.143
Cd	0.002	0.003	0.003	0.002	0.002	0.002	0.001
Sb	0.002	0.001	0.001	0.001	0.001	0.001	0.001
Tl	<LOQ	0.048	0.046	<LOQ	0.037	0.030	<LOQ
Pb	0.000	0.110	0.103	<LOQ	0.041	0.053	0.003
Cl^-	420	**2550**	**2030**	330	**1980**	**2260**	210
SO_4^{2-}	**15406**	**8648**	**6651**	**14042**	**13770**	**14317**	**3622**
Conductivity, µS/cm	**10500**	**11840**	**10990**	**11200**	**9780**	**11000**	**9500**
pH	13.01	13.14	13.12	13.11	12.82	13.13	13.07

Table 17. (continued)

	Eesti PP PC NID FF	Eesti PP PC NID FA	Enefit 280 BA	Enefit 280 CY	Enefit 280 FA	Petroter CY	Petroter ESP	Limit value inert waste	Limit value non-hazardous waste
Li	0.279	0.247	0.103	0.117	0.113	0.189	0.122		
Be	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ		
Ti	0.017	0.006	0.004	0.008	0.004	0.004	0.019		
V	0.004	0.002	0.102	0.161	0.171	0.024	0.460		
Cr	0.422	0.350	0.210	1.507	1.397	0.001	0.075	0.5	10
Mn	0.003	0.002	0.001	0.006	0.002	0.001	0.015		
Co	0.003	0.003	0.002	0.002	0.002	0.002	0.002		
Ni	0.009	0.008	0.004	0.006	0.004	0.004	0.005	0.4	10
Cu	0.013	0.004	0.003	0.016	0.005	0.020	0.018	2	50
Zn	0.012	0.010	0.002	0.018	0.006	0.024	0.036	4	50
As	0.003	0.002	0.010	0.008	0.012	0.005	0.024	0.5	2
Se	0.004	0.004	0.007	0.052	0.046	0.001	0.026	0.1	0.5
Sr	16.643	20.81	8.95	19.07	16.41	11.77	10.58		
Mo	0.460	0.376	**0.780**	**2.919**	**2.578**	0.407	**0.882**	0.5	10
Cd	0.002	0.002	0.006	0.008	0.007	0.002	0.003	0.04	1
Sb	0.001	0.004	0.005	0.001	0.001	0.002	0.007	0.06	0.7
Tl	0.047	0.041	0.000	0.004	0.007	<LOQ	0.077		
Pb	0.034	0.028	<LOQ	0.001	<LOQ	0.000	0.014	0.5	10
Cl^-	**2880**	**2640**	780	**1790**	**3700**	**930**	**900**	800	15000
SO_4^{2-}	**11730**	**13479**	**17708**	**11940**	**13975**	**5998**	**7230**	1000	20000
Conductivity, µS/cm	**11350**	**11650**	**3472**	**3240**	**3357**	**3321**	1980	2000*	30000*
pH	12.9	13.11	12.35	12.06	12.1	12.67	10.42		

* Conductivity is estimated as half of the total dissolved solids (TDS) value. Abbreviations: PP – power plant, BA – bottom ash, ESP – electrostatic precipitator ash, FA – fly ash, CFBC – circulating fluidised bed combustion, NID – novel integrated desulphurisation unit, FF – fabric filter ash, CY – cyclone ash, ESP – electrostatic precipitator ash.

Conclusions

The main aim of this study was to present detailed information about the different oil shale ash fractions generated in Estonia and to demonstrate significant variability in ash characteristics, depending on the technology and collection point in the process. Understanding these differences is essential for optimising the utilisation and valorisation of these ashes in various applications.

The distribution of ash fractions in circulating fluidised bed combustion (CFBC) power plants is notable, with approximately 30% consisting of bottom ash and 70% of fly ash. The first field of the electrostatic precipitator plays a pivotal role in this distribution, capturing about 50% of the total ash flow. In shale oil production, the distribution of ash fractions varies significantly between technologies. Enefit280 technology generates more than 60% bottom ash, leveraging its CFBC combustion process. In contrast, the Petroter technology produces exclusively fly ash, with most of it collected through cyclones.

Distinct differences between bottom ash and other fractions are observed, with notable variations in mineralogical composition and free CaO content. Pulverised combustion (PC) ashes exhibit a more uniform mineral composition across fractions, whereas CFBC ashes are more diverse in their chemical and mineralogical content. Differences in the mineralogical composition of ashes from similar technologies indicate that variations are influenced not only by the combustion technology used but also by the mineralogical content of the oil shale itself.

Ashes from power plants have a significantly higher free CaO content, reaching up to 31%, compared to ashes from shale oil production, which have a maximum of 3%. The presence of free CaO and compounds such as C_2S (Ca_2SiO_4) significantly enhances the binding properties of ashes from power plants. Free CaO, upon hydration, reacts with water to form $Ca(OH)_2$, which contributes to the pozzolanic and cementitious reactions by interacting with siliceous and aluminous components. Meanwhile, C_2S is a key hydraulic phase that undergoes slow hydration, forming calcium silicate hydrate (C-S-H) gel, which provides long-term strength development. These reactions are particularly pronounced in ashes from PC technology, where higher free CaO content leads to increased reactivity, as well as in finer fractions from CFBC plants. Consequently, these ashes hold potential for use in construction materials, such as binders or supplementary cementitious materials, thus improving their valorisation prospects.

Ashes from the shale oil industry have a fundamentally different mineral composition compared to combustion plant's ashes due to lower processing temperatures, which prevent the decomposition of carbonates. As a result, these ashes do not contain free CaO and lack significant binding properties. However, they remain a valuable resource for the extraction of calcium and other compounds, offering potential for various industrial applications.

The concentration of trace elements in oil shale ash mirrors their presence in the oil shale itself, which generally contains low levels of those elements. Consequently, trace element concentrations in the oil sale ash are also low, typically below 100 mg/kg. However, there are some exceptions, such as Mn, Zn, Sr, and Ti. As expected, trace element concentrations tend to be higher in the finer ash fractions.

The leachability test reveals that Cl^- ions leach significantly less from bottom ash compared to fly ash; however, this trend does not apply to SO_4^{2-} ions. For trace elements, the leachability is notable for certain elements such as Sr, Cr, and Mo. Despite their leaching potential, these elements are not classified as priority hazardous substances for the aquatic environment.

This variability in ash composition is influenced by factors such as fuel quality, combustion or processing technology, and the specific stage at which the ash is collected. These findings suggest that ash utilisation strategies could be tailored according to the specific properties of the ash fractions generated by each technology and process stage.

Data availability statement

Data are available on request from the authors.

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Publication IV

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Environmental advantages of oil shale ash as a secondary raw material: a focus on dioxin levels

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Abstract. *Secondary raw materials, such as ashes from the combustion of various fuels, are frequently used as alternatives to virgin raw materials. Among these, oil shale ash, a residue from oil shale power production and the shale oil industry, presents significant potential for use in sectors such as construction and agriculture. However, these materials might contain hazardous substances, such as dioxins, which are by-products of thermal treatment and other industrial processes. To date, the dioxin content in oil shale ash has been insufficiently examined. This article provides a comprehensive analysis of the dioxin content in oil shale ash from both a pilot unit and full-scale facilities. Additionally, the study compares the dioxin concentrations in oil shale ash with those in other types of ash and evaluates compliance with regulatory limits. The results showed that dioxin concentrations in the ash were below the limit of detection, regardless of the combustion technology, plant capacity, use of supplementary fuels, or utilisation of wastewater. The findings contribute new knowledge by highlighting the environmental advantages of oil shale ash as a secondary raw material, particularly due to its comparatively lower dioxin content relative to other types of ash.*

Keywords: *oil shale ash, secondary raw material, dioxins, PCDD, PCDF, PCB.*

1. Introduction

The world population has increased rapidly in the last five decades, reaching over 8.2 billion in 2025 and causing massive demand for natural resources [1]. With limited resources and a growing population, the linear business model (produce, use, dispose) is not sustainable. In 2020, the European Commission adopted the new Circular Economy Action Plan (CEAP) [2]. The main principles of the circular economy are sustainable production and consumption. The CEAP ensures that waste is prevented and that resources are used fully

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and for as long as possible. Finally, waste that cannot be prevented is recycled and used instead of virgin materials.

In the energy sector, combustion processes – whether from fossil fuels, biomass, or waste incineration – produce significant quantities of ash and gas-cleaning residues. These by-products have traditionally been treated as waste, but growing research has focused on how they can be recovered and repurposed [3–10]. Combustion residues can be used as construction materials [11], as sources for extracting valuable elements [4], as soil amendment components [12], or as fertilisers [13]. By converting these residues into useful products, the demand for virgin raw materials can be reduced, supporting a more circular economy. In 2023, the American Coal Ash Association [14] reported that the United States generated 66.7 million tonnes of coal combustion residues, with 69% of that beneficially recovered – a sign of progress toward more sustainable waste management.

While waste recovery offers clear environmental benefits, it also raises concerns, as several toxic compounds are produced in combustion processes. Pollution is one of the triple planetary crises, along with climate change and biodiversity loss, so it is crucial to achieve a circular economy without generating hazardous pollutants.

Dioxins represent a category of persistent organic pollutants (POPs) [15] of particular concern in the context of waste management, especially regarding the residues generated from waste incineration. Even at lower concentrations than those found in waste incineration residues, dioxins can also form during the combustion of traditional fuels such as biomass, coal, and oil shale.

The formation of dioxins in combustion systems occurs primarily through two mechanisms: *de novo* and precursor pathways. *De novo* formation is regarded as the dominant route at post-combustion temperatures between 200–400 °C. In this process, dioxins are generated from unburned carbonaceous material such as soot or fly ash through oxidation and chlorination on particle surfaces in the presence of oxygen, chlorine, and metal catalysts. This heterogeneous mechanism is highly sensitive to temperature, fuel composition, and the availability of chlorine species [16, 17].

In contrast, the precursor pathway involves the transformation of chemically related compounds such as chlorophenols and chlorobenzenes. These compounds undergo condensation and subsequent reactions either in the gas phase or on particle surfaces, leading to the formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs). Both mechanisms can occur simultaneously and independently in different regions of the combustion system. At higher temperatures (500–800 °C), homogeneous gas-phase reactions dominate, but overall dioxin formation is greatly reduced compared with the cooler post-combustion zone, where conditions strongly favour *de novo* synthesis [17].

The term ‘dioxins’ is a general term used to describe 75 polychlorinated PCDDs, 135 PCDFs, and sometimes also 209 polychlorinated biphenyls

(PCBs) [18]. Not all dioxin congeners are considered toxic; so far, 10 PCDFs, 7 PCDDs, and 12 PCBs out of the 419 dioxin congeners have been recognised by the World Health Organisation (WHO) as having toxic effects on humans [19]. The congeners of dioxins exhibit varying toxic effects.

The International Toxic Equivalency Factor (I-TEF) system, established in the late 1980s, was an early method to assess the toxicity of dioxins and furans by assigning toxic equivalency factors (TEFs) to various congeners relative to 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), the most toxic dioxin. Within this system, the overall toxic equivalent (TEQ) is calculated by multiplying the concentration of each congener by its assigned TEF and summing the results across all congeners. In 1998, and again in 2005, the WHO updated this approach, resulting in the WHO (2005) TEQ system (see Table 1). This revision incorporated new scientific data, leading to adjustments in TEFs for certain congeners and the inclusion of dioxin-like PCBs. Consequently, the WHO (2005) TEQ provides a more comprehensive assessment of toxicity by considering a broader range of compounds and reflecting updated toxicological understanding [19, 20]

Studies have shown that TEQ values calculated using the WHO (2005) TEFs can be approximately 20% lower than those calculated with the older I-TEQ system, due to the revised TEFs and the inclusion of additional compounds [21]. In 2022, the WHO reviewed and updated the TEF values, further refining the toxicity assessment framework [22].

Table 1. Summary of toxic equivalency factors (TEFs) [22–24]

Compound	I-TEF	1998 WHO-TEF	2005 WHO-TEF	2022 WHO-TEF
Dioxins				
2,3,7,8-TCDD	1	1	1	1
1,2,3,7,8-PeCDD	0.5	1	1	0.4
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.09
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.07
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.05
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.05
OCDD	0.001	0.0001	0.0003	0.001
Furans				
TCDF	0.1	0.1	0.1	0.07
1,2,3,7,8-PeCDF	0.05	0.05	0.03	0.01
2,3,4,7,8-PeCDF	0.5	0.5	0.3	0.1

Continued on the next page

Table 1. *Continued*

Compound	I-TEF	1998 WHO-TEF	2005 WHO-TEF	2022 WHO-TEF
1,2,3,4,7,8 HxCDF	0.1	0.1	0.1	0.3
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.09
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.2
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.02
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.1
OCDF	0.001	0.0001	0.0003	0.002
Non-ortho-substituted PCBs				
3,3’,4,4’-tetraCB (PCB77)		0.0001	0.0001	0.0003
3,4,4’,5-tetraCB (PCB81)		0.0001	0.0003	0.006
3,3’,4,4’,5-pentaCB (PCB126)		0.1	0.1	0.05
3,3’,4,4’,5,5’-hexaCB (PCB169)		0.01	0.03	0.005
Mono-ortho-substituted PCBs				
2,3,3’,4,4’-pentaCB (PCB105)		0.0001	0.00003	0.00003
2,3,4,4’,5-pentaCB (PCB114)		0.0005	0.00003	0.00003
2,3’,4,4’,5-pentaCB (PCB118)		0.0001	0.00003	0.00003
2’,3,4,4’,5-pentaCB (PCB123)		0.0001	0.00003	0.00003
2,3,3’,4,4’,5-hexaCB (PCB156)		0.0005	0.00003	0.00003
2,3,3’,4,4’,5’-hexaCB (PCB157)		0.0005	0.00003	0.00003
2,3’,4,4’,5,5’-hexaCB (PCB167)		0.00001	0.00003	0.00003
2,3,3’,4,4’,5,5’-heptaCB (PCB189)		0.0001	0.00003	0.00003

Oil shale is a sedimentary rock, with over 600 known deposits worldwide. However, only 33 countries have deposits that are considered to have potential economic value. The estimation of oil shale resources is typically expressed in terms of barrels of oil, indicating how much oil can be extracted from the rock. Estimates suggest that there are between 5 and 6 trillion barrels (760–960 billion cubic metres) of shale oil, of which approximately 1.0 to 1.6 trillion barrels (160–300 billion cubic metres) may be technically recoverable. The largest oil shale resources are concentrated in a few key countries. The United States holds the most significant reserves, estimated at around 6 trillion barrels, followed by China with 330 billion barrels, Russia with 270 billion barrels, and Israel with 250 billion barrels. Jordan and the Democratic Republic of the Congo each possess approximately 100 billion barrels, while Estonia has an estimated 16 billion barrels [25–27].

Oil shales can be classified using various methods. Hutton [27] categorises them into three groups based on their depositional environment: terrestrial, lacustrine, and marine. Marine oil shales are further classified by location into marinite, tasmanite, and kukersite. Alternatively, Tissot and Welte [28] classify oil shales based on their organic matter, specifically kerogen, using its hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios. The Van Krevelen diagram is introduced to distinguish between type I, type II, and type III kerogens. The oil shale found in Estonia is sometimes also referred to as type II, close to type I, and it is called kukersite. Kukersite has a high content of hydrogen and oxygen, a low nitrogen content, and significant amounts of organic sulphur and chlorine [29, 30].

In Estonia, oil shale is used in power plants to produce electricity and heat, and in the shale oil industry, where the rock is pyrolysed (i.e. thermally treated at around 500 °C in the absence of oxygen) to produce oil. During shale oil production, retort gas is also produced, which serves as a fuel in power plants. Retort gas primarily consists of light hydrocarbons, hydrogen, carbon monoxide, and carbon dioxide [31]. In Estonia, power production and shale oil production generate about 5 million tonnes of ash per year [32], although in the past it has been twice as much.

The oil shale ash generated in Estonia has been very well studied [11, 33–39] and it has great potential as a raw material. One of the main characteristics of oil shale ash is its pozzolanic and latent hydraulic properties, which make it a suitable substitute for conventional cementitious materials [40]. Studies have shown that oil shale ash-based concrete can achieve compressive strengths of up to 25 MPa within 28 days, making it a viable material for low-strength concrete applications and backfilling in mining operations [41, 42]. Furthermore, oil shale ash-based concrete has exhibited enhanced water resistance and reduced expansion, particularly when circulating fluidised bed (CFB) ash with a higher active silica content is incorporated [40].

In addition to its use in concrete, oil shale ash has been proven to be an effective material for road construction and soil stabilisation. Studies of road sections constructed with oil shale ash have shown improved soil strength and reduced settlement, particularly in peat-rich environments [43]. In addition, oil shale ash has been tested as a soil amendment for acidic peatlands, where its alkaline properties help to raise soil pH, improving nutrient availability for plants [44]. The granulated form of oil shale ash has also been investigated to control the mobility of potentially hazardous elements, with results indicating minimal leaching of heavy metals such as cadmium (Cd), mercury (Hg), and lead (Pb) under controlled conditions [45]

Dioxin content can be a limiting factor when it exceeds regulatory limits, rendering the ash material unsuitable for recovery or further use. Dioxins are classified as unintentional POPs under the Stockholm Convention [15]. The Stockholm Convention requires the destruction of POPs wastes and bans the recycling of wastes contaminated with POPs. Low POPs content levels define whether certain wastes should be categorised as POPs waste or not. In the general technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants [46] the low POPs content levels are set. The current low POPs content for PCDD/PCDFs is up to 15 µg TEQ/kg, while the discussion is still ongoing, with several stakeholders requesting the value to be 5 µg TEQ/kg or even 1 µg TEQ/kg [47].

The EU has established stringent regulations to control the presence of dioxins and other POPs in materials such as waste and ash, particularly under the EU POPs Regulation [48] and the EU Fertilisers Regulation [49]. These regulations set specific concentration limits for dioxins to ensure the protection of human health and the environment. Any waste, including ash, that exceeds 5 µg TEQ/kg total dioxin content cannot be recovered and must be disposed of in a controlled manner. The dioxin threshold for fertilising materials is even stricter. Specifically, for Component Material Category (CMC) 15, which includes ashes, the regulation stipulates the concentration limit for PCDDs/PCDFs at 20 ng TEQ/kg dry matter.

The generation of dioxins in the oil shale industry was investigated 20 years ago [50, 51]. The results showed that most of the dioxin congeners in oil shale fly ash were below the detection limit, indicating that the dioxins were not a cause for concern. However, the oil shale industry has changed significantly over the past 20 years. New technologies have been introduced, and the focus has shifted from power production to shale oil production. Oil shale is often co-combusted with biomass or with the retort gas from the shale oil industry. A thorough research study was conducted to evaluate the dioxin content across different fractions of oil shale ash and to assess the potential influence of the technologies utilised in its production. In this study, PCDDs, PCDFs, and PCBs refer to those congeners listed in the EU POPs Regulation. The term 'dioxin' is used here as a general term to describe these PCDDs, PCDFs, and PCBs.

2. Methods and materials

2.1. Samples from pilot unit

Dioxin content in oil shale ash, as well as in the flue gas, was investigated in a 60 kW_{th} CFB pilot unit. A detailed description of the pilot unit is given by Baqain et al. [52]. Figure 1 shows a schematic of the pilot unit, including ash sampling points.

The combustion process was carried out under conditions comparable to those of the Enefit280 shale oil plant, where semi-coke is incinerated in a circulating fluidised bed combustion (CFBC) boiler. Since semi-coke alone was unable to sustain stable combustion due to its relatively low calorific value, co-firing with oil shale was employed to enhance the overall energy

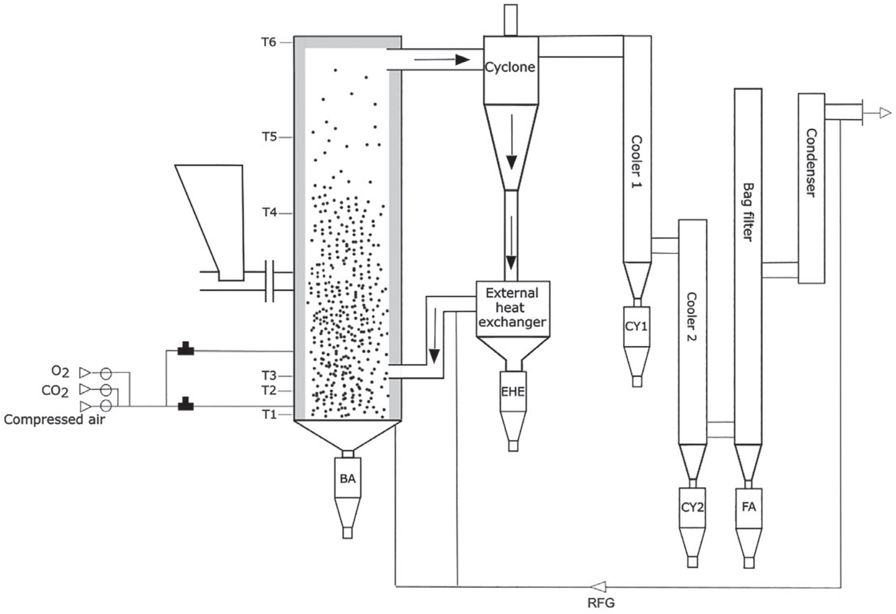

Fig. 1. Schematic of the 60 kW_{th} circulating fluidised bed pilot unit, including temperature measurement points (T1–T6) and ash sampling points: bottom ash (BA), ash from the external heat exchanger (EHE), cyclone ash (CY1 and CY2), and ash from the bag filter (FA) (adapted from [52]). RFG – recycled flue gas.

input. The fuel blend, consisting of semi-coke and oil shale in a mass ratio of 4:1, was combusted for five hours. The elemental composition of the fuel is shown in Table 2. Ash samples were collected from different collection points, as shown in Figure 1. Samples were taken several times during the process to obtain an average sample for each collection point. The combustion chamber operating temperatures, which are critical for evaluating co-firing performance and ash behaviour, are summarised in Table 3.

Table 2. Elemental composition of the oil shale fuel mixture (oil shale + semi-coke) used in the incineration test, wt%

C	H	S	Inorganic C	Organic C
8.22	0.62	0.82	3.01	6.13

Table 3. Measured temperatures (°C) at different heights in the combustion chamber

T1 0.11 m	T2 0.9 m	T3 1.17 m	T4 2.145 m	T5 3.22 m	T6 4.37 m	T (EHE)
658–663	653–656	661	699–674	699–763	753–797	579–581

Dioxin samples from the flue gas were collected isokinetically by experts from the Estonian Environmental Research Centre. The dioxins were captured using a heated sampling probe. Solid particles were separated from the sample using a glass fibre plane filter located at the outlet of the heated sampling probe. After passing through the filter, the gas flowed through a spiral cooler and the XAD2 adsorbent column, which captured contaminants in the gas phase. After passing through the XAD2, the gas was dried and then routed to a gas clock to determine its volume.

The sample was collected on the pre-filter, the XAD2 adsorbent, and in the washing solution. To obtain the washing solution, the gas path passing through the equipment was cleaned afterwards. The total amount of compounds per sample was obtained as a result of the analysis. When calculating the concentration, the mass obtained was divided by the gas volume measured using the gas clock.

2.2. Samples from full-scale facilities

Oil shale ash was collected from the installations of the main oil shale users. The covered plants were Auvere Power Plant (Auvere PP), the pulverised combustion (PC) unit and the CFB unit of Eesti Power Plant (Eesti PP), and the shale oil production installations Enefit280, Enefit140, and Petroter. At least two different ash samples were collected from each installation. In total, twenty ash samples were analysed for dioxin content (see Table 4). A detailed description of the technologies and ashes produced in the Estonian oil shale industry can be found in an article by Ummik et al. [53].

In shale oil plants, oil shale ash is produced when a mixture of semi-coke and recirculated ash (solid heat carrier) from the retort is combusted in either a lift-pipe combustor (used in the Enefit140 and Petroter technologies) or CFB combustor (used in the Enefit280 technology). This means that the ash originates from oil shale. In oil shale power plants, retort gas from shale oil production or biomass is co-combusted with oil shale. Pyrolytic wastewater originating from shale oil production (Enefit140 and Enefit280) is also sometimes incinerated in power plant boilers [54]. To better understand whether these additional fuels or pyrolytic wastewater might affect dioxin formation, ashes generated under different conditions were investigated.

Ash from the Auvere PP CFB boiler was collected during the co-combustion of oil shale, retort gas, and biomass (wood chips). The boiler has a gross electrical capacity of 305 MW_e and was operating at 233 MW_e during sampling. The fuel mix was based on heat input as follows: 60% oil shale, 30% retort gas, and 10% biomass. Ash samples were collected from three locations: the bottom of the boiler (bottom ash, BA), the first field of the electrostatic precipitator (ESP), and the fabric filter (FF).

In the Eesti PP CFB unit, oil shale and retort gas were co-combusted at a heat input ratio of 50% oil shale and 50% retort gas. The boiler operated at

Table 4. Characteristics of plants and ash samples used in the study

Sample	**Sample collection area**	**Technology**	**Rated capacity (gross), MW$_e$**	**Capacity during sampling, MW$_e$**	**Fuel mix (based on heat input)**	**Waste-water, t/h**
Auvere PP BA	Bottom of the boiler	Power plant, CFBC	305	233	Oil shale 60%, biomass 10%, retort gas 30%	0
Auvere PP ESP	Electrostatic precipitator (ESP)					
Auvere PP FF	Fabric filter (FF)					
Eesti PP PC BA	Bottom of the boiler	Power plant, PC	185–195	165	Oil shale 20%, retort gas 80%	0, 8, 16
Eesti PP PC FF	FF		185–195	165		
Eesti PP CFBC BA	Bottom of the boiler	Power plant, CFBC	215	215	Oil shale 50%, retort gas 50%	0, 8, 16
Eesti PP CFBC FF	FF		215	215		
Enefit280 CY	Cyclone (CY)	Shale oil plant, SHC + CFBC			Oil shale 100%	0
Enefit280 ESP	ESP					
Enefit140 total	Bunker of total ash	Shale oil plant, SHC + lift-pipe combustor			Oil shale 100%	0
Enefit140 ESP	ESP					
Petroter CY	CY	Shale oil plant, SHC + lift-pipe combustor			Oil shale 100%	0
Petroter ESP	ESP					

Abbreviations: PP – power plant, BA – bottom ash, CFBC – circulating fluidised bed combustion, PC – pulverised combustion, SHC – solid heat carrier, FF – fabric filter ash, ESP – electrostatic precipitator ash, CY – cyclone ash.

full capacity, i.e. 215 MW$_e$. Ash samples were collected from the bottom of the boiler (BA) and the first field of the ESP. Additionally, ash samples were collected when pyrolytic wastewater was added to the boiler at mass flow rates of 8 t/h and 16 t/h. The composition and characteristics of the pyrolytic wastewater are described in detail by Konist et al. [54].

In the Eesti PP PC unit, oil shale and retort gas were co-combusted, with oil shale accounting for 20% of the heat input and retort gas accounting for 80%. The boiler operated at a capacity of 165 MW_e, slightly below its full capacity of 185–195 MW_e. Ash samples were collected from the bottom of the boiler (BA) and from the novel integrated desulphurisation (NID) fabric filter (FF). Additionally, ash samples were collected when pyrolytic wastewater was added to the boiler at mass flow rates of 8 t/h and 16 t/h.

Ashes from the Enefit280 and Petroter shale oil production units were collected from the cyclone (CY) and the ESP. As with the Enefit140 unit, ash was collected from the total ash bunker and the ESP.

2.3. Dioxin analysis

The concentrations of seven PCDDs, ten PCDFs, and twelve PCBs listed in the EU POPs Regulation were analysed at the accredited ALS Laboratory in the Czech Republic. The quantification of tetra- to octa-chlorinated dioxins and furans was carried out using the isotope dilution technique HRGC-HRMS (high-resolution gas chromatography/high-resolution mass spectrometry), in accordance with the US EPA 1613B and ČSN EN 16190 standards. Similarly, PCBs were quantified using HRGC-HRMS in accordance with the ČSN EN 1948-4+A1 and US EPA TO-4A standards. A detailed description of the analysis can be found in Ummik et al. [55].

For PCDDs/PCDFs, the limit of detection (LOD) was defined as the concentration corresponding to a signal-to-noise ratio (S/N) ≥ 3, while the limit of quantification (LOQ) was set at twice the detection limit. In contrast, for PCBs, the LOQ was established on the basis of the blank level, and the LOD was similarly defined using an S/N ≥ 3 criterion. In most cases, concentrations were reported as the LOQ; however, for certain PCB congeners, results were only available at the LOD level. Measurement uncertainty was estimated at approximately 30% for individual congeners, with values validated through the analysis of certified reference materials under reproducibility-controlled conditions.

The dioxin concentrations presented in this study are based on dry weight and expressed in ng/kg and ng TEQ/kg. All dioxin concentrations expressed in ng TEQ/kg were calculated in accordance with the POPs Regulation [48], using the TEFs outlined therein. The TEF values in the EU POPs Regulation are identical to the 2005 WHO-TEFs [19]. To provide a conservative estimate of the potential maximum concentrations, the upper-bound approach [56] was applied, whereby all results below the LOQ are assumed to be equal to the LOQ value.

3. Results and discussion

3.1. Dioxins from oil shale pilot unit

There is a noticeable lack of information regarding the dioxin content of Estonian oil shale ashes. The only exception is a study by Roots [50], which focused on analyses conducted in 1998 of fly ash from the PC unit of Balti Power Plant. On average, oil shale organic matter contains 0.75% chlorine [29], an essential component for dioxin formation. Dioxins can form during any type of combustion process when carbon, chlorine, and oxygen are present. They form most readily within two temperature ranges: 500–800 °C and 200–400 °C [16, 17]. The temperature in a PC boiler can reach 1400 °C [36], meaning that dioxins form only when the ash cools. However, the temperature in a CFB boiler is approximately 800 °C [57], and the fly ash leaving the boiler is cooling along the gas passage, creating favourable conditions for dioxin formation.

The incineration conditions in the pilot unit closely mirrored those of the full-scale Enefit280 facility, particularly in terms of temperature distribution and oxygen concentration. This alignment supports the validity of extrapolating the results to full-scale operations. The temperature in the pilot unit was in the range of 579–797 °C, which is suitable for the formation of dioxins. However, all the measured dioxin congeners in both the ash samples and the flue gas were below the LOQ.

Although all measured dioxin congeners in the ash and flue gas samples were below the LOQ, this outcome does not confirm their complete absence. Even with state-of-the-art HRGC methods [58, 59], which can detect at the parts-per-trillion range [60], trace concentrations below quantifiable levels may still be present. This highlights an inherent limitation in dioxin analysis: analytical methods cannot guarantee absolute absence but can only establish that concentrations fall below a defined threshold of quantification. The use of the upper-bound approach offers a worst-case estimate of possible dioxin content in the samples. However, it should be noted that no official guidance currently supports this approach for waste or for secondary uses such as fertilisers.

Table 5 presents the concentrations of dioxin congeners in the oil shale ash from the pilot unit using the upper-bound approach. While this ensures a worst-case estimate, it also means that apparent variations between samples, or between the present results and previously published datasets, cannot be interpreted as true differences in dioxin content. Such discrepancies arise primarily from differences in LOQ values, which are influenced by matrix effects, background noise, and blank levels during analysis, rather than reflecting real changes in concentration.

Table 5. Dioxin content of the oil shale ash from the pilot unit calculated using the upper-bound approach, ng/kg DW

Ash sampling point	BA	EHE	CY1	CY2	FA1	FA2
PCB 105	180	160	220	93	120	150
PCB 114	7.5	13	3	2.1	8.1	16
PCB 118	770	650	950	760	750	510
PCB 123*	7.2	11	3.1	2.1	7	16
PCB 126	7.3	7	5.3	7.4	6.6	3.9
PCB 156	160	140	110	130	100	120
PCB 157*	12	16	26	9.7	7.7	20
PCB 167	71	59	74	24	62	52
PCB 169	8.8	11	11	8.6	7.8	2.2
PCB 170	150	170	330	150	220	250
PCB 180	460	430	560	350	490	420
PCB 189*	9.4	24	8.5	5.5	16	22
PCB 77	35	53	21	37	57	61
PCB 81	23	19	6.6	15	11	5.1
∑ PCB	1291	1163	1438	1094	1153	978
∑ TEQ PCB	**1.04**	**1.07**	**0.9**	**1.04**	**0.93**	**0.49**
1234678-HpCDD	2.7	3.7	2	2.3	2.3	1.8
1234678-HpCDF	2.4	4	4.4	2	2.6	5.6
123478-HxCDD	2.8	2.7	2.6	2.6	2.7	2.4
123478-HxCDF	1.8	1.9	1.5	1.6	1.4	1.2
1234789-HpCDF	5.5	18	2.9	2.8	16	6.5
123678-HxCDD	2	2	1.7	2.1	2.2	2
123678-HxCDF	1.9	1.8	1.4	1.5	1.2	1.2
12378-PeCDD	0.96	1.2	1.7	1.7	0.71	1.4
12378-PeCDF	1.4	1	1.5	1.5	1	1.1
123789-HxCDD	1.9	1.9	1.6	2	2.1	1.9
123789-HxCDF	3.7	3.2	1.6	2.3	6.6	2.5
234678-HxCDF	2.6	2.2	1.2	1.5	1.7	1.4
23478-PeCDF	1.8	1.4	1.3	1.5	1.8	1.4
2378-TCDD	0.58	0.64	1	0.72	0.58	0.84
2378-TCDF	1.3	0.79	0.89	0.86	1	2.2

Continued on the next page

Table 5. *Continued*

Ash sampling point	BA	EHE	CY1	CY2	FA1	FA2
OCDD	7.4	15	23	4.9	7.1	2.7
OCDF	5.7	11	1.8	3.8	5.5	6.4
∑PCDD	10.9	12.1	10.6	11.4	10.6	10.3
∑PCDF	28.1	45.29	18.49	19.36	38.8	29.5
∑ TEQ PCDD	**2.23**	**2.53**	**3.31**	**3.11**	**2.01**	**2.90**
∑ TEQ PCDF	**1.79**	**1.66**	**1.16**	**1.32**	**1.94**	**1.43**
∑ TEQ dioxins	**5.07**	**5.27**	**5.38**	**5.47**	**4.90**	**4.80**

* Limit of detection was used instead of limit of quantification.
Abbreviations: BA – bottom ash, EHE – external heat exchanger ash, CY – cyclone ash, FA – bag filter ash, TEQ – toxic equivalent.

As EU air emission regulations such as the Industrial Emissions Directive [61] and the Best Available Technique for Large Combustion Plants [62] only cover PCDDs and PCDFs, PCBs were not measured. The dioxin concentrations in the flue gas were below the detection limit (see Table 6), indicating that dioxins are not forming during oil shale combustion.

Table 6. Dioxin content in the flue gas, pg/Nm^3

Compound	Concentration
2378-TCDD	< 1.92
12378-PeCDD	< 2.35
123478-HxCDD	< 4.32
123678-HxCDD	< 4.32
123789-HxCDD	< 4.32
1234678-HpCDD	< 4.32
OCDD	< 10.32
2378-TCDF	< 9.38
12378-PeCDF	< 3.89
23478-PeCDF	< 3.89
123478-HxCDF	< 4.64
123678-HxCDF	< 4.64
123789-HxCDF	< 4.64
234678-HxCDF	< 4.64
1234678-HpCDF	< 6.10
1234789-HpCDF	< 6.10
OCDF	< 7.51

3.2. Total dioxin content analysis from full-scale facilities

While the incineration conditions in the pilot unit were similar to those of the full-scale Enefit280 facility, the resulting pollutant concentrations may not be entirely representative. This discrepancy primarily arises from physical differences, particularly in the size of the combustion chambers and the gas flow pathways. In the full-scale facility, the larger gas passage results in a longer residence time for the flue gases, facilitating a slower cooling rate of the ash. This extended cooling period may promote the formation of dioxins, potentially resulting in higher concentrations than those observed under pilot-scale conditions.

To evaluate the influence of combustion temperature and technology on dioxin formation under real conditions, ash samples were collected from various operating oil shale plants and subsequently analysed. The concentrations of dioxin congeners in all samples were found to be below the analytical detection limits (Appendices 1 and 2). This correlates with the pilot tests but differs from the findings reported by Roots [50]. According to Roots' study, the total concentrations of PCDDs, PCDFs, and PCBs in one fly ash sample were 32 ng/kg, 26 ng/kg, and 2400 ng/kg, respectively. A second sample from the same study showed lower concentrations. However, it was not specified which dioxin congeners were included in the total concentrations. Of the dioxin congeners considered toxic, only four were above the detection limit in Roots' study: OCDD, 1,2,3,4,6,7,8-HpCDD, 2,3,4,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF. Even though they were present in very low concentrations and the congeners had low TEF values, their presence indicates that oil shale fly ash contained trace levels of toxic dioxins in 1998.

The absence of detectable dioxin congeners in the current study may be due to technological advancements. In 1998, PC technology was used, and fly ash was collected from electrostatic precipitators (ESPs). Today, PC units are equipped with NID units, and the fly ash is collected from fabric filters. As Roots' study [50] did not provide detailed information on ash formation conditions or collection methods, it is not possible to make a direct comparison of the conditions influencing dioxin formation in the two studies.

The current study thoroughly investigated ash samples to determine whether different conditions could affect dioxin formation. Ash was collected from power plants operating at varying capacities. While partial capacities compared to nominal have been shown to influence the mineral decomposition, the particle-size distribution, and bulk density of ash [36], this variation did not affect the dioxin content.

In Estonian oil shale power plants, oil shale is co-combusted with biomass and/or retort gas. According to Ummik et al. [55], the chlorine content in biomass ranges from 0.006% to 0.016%, which is generally lower than that of oil shale. Retort gas from oil shale pyrolysis contains no measurable chlorine [31]. Given the low chlorine content of these supplementary fuels, their influence on dioxin formation is unlikely – a conclusion supported by our results (Table 5).

In oil shale power plants, wastewater generated during shale oil production is utilised by injecting it into the combustion chamber, facilitating its elimination through thermal degradation. Although water does not directly form or eliminate dioxins, it can affect their formation. Li et al. [63] observed that at higher temperatures, the presence of moisture can promote dioxin formation. In this study, the addition of water to the oil shale combustion process increased the flue gas moisture content by approximately 0.7–2.8%, a relatively modest rise. Under these conditions, our findings showed that the increased moisture had no observable effect on dioxin formation. As presented in Table 7, the dioxin concentrations remained relatively consistent regardless of whether wastewater was added.

Table 7. Dioxin content in ash samples (upper-bound approach) in relation to plant capacity, fuel type, and wastewater addition

Sample	**Type**	**Rated capacity (gross), MW_e**	**Capacity during sampling, MW_e**	**Fuel**	**Wastewater, t/h**	**∑ dioxins, TEQ ng/kg DW**
Auvere PP BA	CFBC	305	233	Oil shale, biomass, retort gas	0	5.75
Auvere PP ESP						5.6
Auvere PP FF						5.81
Eesti PP PC BA	PC	185–195	165	Oil shale, retort gas	0	5.46
					16	5.69
Eesti PP BC FF	PC	185–195	165		0	5.44
					8	5.12
					16	5.44
Eesti PP CFBC BA	CFBC	215	215	Oil shale, retort gas	0	5.49
					8	5.69
					16	5.74
Eesti PP CFBC FF	CFBC	215	215		0	5.41
					8	5.31
					16	5.71
Enefit280 CY	SHC + CFBC			Oil shale	0	7.97
Enefit280 ESP						5.42
Enefit140 total	SHC			Oil shale	0	5.48
Enefit140 ESP						5.26
Petroter CY	SHC			Oil shale	0	4.93
Petroter ESP						5.23

Abbreviations: PP – power plant, BA – bottom ash, CFBC – circulating fluidised bed combustion, PC – pulverised combustion, SHC – solid heat carrier, FF – fabric filter ash, ESP – electrostatic precipitator ash, CY – cyclone ash, TEQ – toxic equivalent, DW – dry weight.

The results reveal that, even in the worst-case scenario, the total TEQ concentration of dioxins is around 5 ng TEQ/kg. The limit value for dioxins in the EU POPs Regulation is 5 µg TEQ/kg, which is 1000 times higher. The limit value in the EU Fertilisers Regulation is 20 ng TEQ/kg, which is also four times higher.

Oil shale ash contains significantly lower concentrations of dioxins than other combustion residues (see Table 8). Ash from municipal solid waste incineration (MSWI) has been found to contain high levels of dioxins, which vary widely depending on the incineration technology used, the pollution control devices employed, the chlorine content, and the operational conditions. TEQ levels for fly ash from MSWIs are high, reaching up to 2500 ng WHO (2005) TEQ/kg [64, 65]. Bottom ash typically contains lower concentrations of PCDDs/PCDFs than fly ash [65]. Biomass ashes, particularly fly ash, also exhibit higher dioxin TEQ values than oil shale ash, reaching up to 1139 ng TEQ/kg [66]. Ummik et al. [55] investigated biomass ashes from different biomass combustion plants using wood chips as fuel. While the dioxin content was generally below the detection limit, some fly ashes still had dioxin concentrations that exceeded the limit set for fertilisers in the EU [49]. PCDD/PCDF levels in fly ash from coal-fired power plants are reported to be significantly lower than in MSWI ash. Fly ash from a coal-fired power plant contained PCDD/PCDF levels ranging from 0.1 to 78 ng TEQ/kg [67]. Fly ash samples from coal and sewage sludge co-combustion contained dioxin levels between 1.32 and 5.78 ng TEQ/kg [68].

While chlorine is an essential component for dioxin formation, variations in fuel chlorine content alone cannot fully account for the observed patterns in dioxin concentrations. Oil shale typically contains around 0.75 wt% chlorine [29], yet its ashes show very low dioxin concentrations, suggesting that its mineral matrix and combustion conditions suppress dioxin formation. Wood, in contrast, has very low chlorine contents (0.001–0.006 wt% [55]), but its fly ashes may still contain elevated dioxin levels. Municipal solid waste is especially complex: its chlorine content is highly variable, depending on the waste origin [69], which partly explains the wide range of dioxin concentrations observed in MSWI residues. Coal occupies an intermediate position, with chlorine contents ranging from 0.01 wt% in low-rank coals up to 0.5 wt% or more in some bituminous coals, and occasionally above 1 wt% [70, 71]. Nevertheless, coal fly ash typically contains only 0.1–78 ng TEQ/kg, much lower than MSWI ashes.

Table 8. PCDD, PCDF, PCB, and total dioxin concentrations in different types of ashes

Fuel	Sample ID	ng/kg					I-TEQ, ng/kg			TEQ (WHO 2005), ng/kg				
		PCDD	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**
Oil shale	Range current stay	22–275	21–103	43–378	269–2603	312–2981				2.37–3.97	0.65–1.72	3.02–5.69	0.63–1.18	3.65–6.87
MSW [64]	Chuzhou						35.9	95.8	131.7					
	Jilin						11.0	24.3	35.3					
	Zhengzhou						82.3	298.9	381.2					
	Zibo						109.4	453	562.4					
MSW [65]	BA			262	114				7.36			7.8	0.83	8.578
	SH			205	37.7				13.3			14.7	0.63	15.326
	HE			62851	1554				1210			1297	33.5	1330.5
	SDA			4306	154				99.4			107	3.09	110.09
	BF			27463	3097				981			1069	64.5	1133.5
	FAP			27185	1544				781			836	30.9	866.9

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Table 8. *Continued*

Fuel	Sample ID	ng/kg					I-TEQ, ng/kg			TEQ (WHO 2005), ng/kg				
		PCDD	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**
MSW [72]	FA1	51000	79000	130000	2300	132300								1800
	FA2	1100	1600	2700	95	2795								34
	FA3	59000	34000	93000	2900	95900								1000
	FA4	38000	24000	62000	1400	63400								710
	FA5	10000	31000	41000	500	41500								550
	FA6	28000	35000	63000	1700	64700								1000
	FA7	100000	73000	173000	9300	182300								2500
	FA8	39000	16000	55000	370	55370								560
	FA9	5600	4200	9800	210	10010								110
	FA10	20000	18000	38000	1900	39900								580
	FA11	26000	24000	50000	1500	51500								640
	FA12	10000	17000	27000	360	27360								440
Coal + 10% SS [68]	Coal FA	195.21	56.72	251.93			0.72	2.71	3.43					
	Coal BA	4.76	0.34	5.1			0.025	0.039	0.064					
Coal [67]	Coal FA	1.57	0.46	2.03						0.038	0.043	0.081		
	Coal boiler FA	334	439	773						32.1	46.3	78.4		
	Coal + wood BA	6.58	158	164						0.002	11.7	11.7		

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Table 8. *Continued*

Fuel	Sample ID	ng/kg					I-TEQ, ng/kg			TEQ (WHO 2005), ng/kg				
		PCDD	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCDD**	**PCDF**	**∑PCCD/F**	**PCB**	**∑dioxin**
Biomass [73]	Agric. residue FA											63	0.04	63.04
	Agric. residue BA/total											5.5	0.18	5.68
	Wood FA											121	25	146
	Wood BA/total											2.3	0.14	2.44
	Waste wood FA											3133		
	Waste wood BA/total											22	3	25
Biomass (woodchips) [55]	1 BA									6.15	8.19	14.34	5.11	19.45
	1 CY									11.38	15.99	27.37	1.8	29.17
	1 ESP									169.63	107.18	276.81	2.08	278.89
	4 BA									6.57	4.27	10.84	1.73	12.57
	4 CY									7.82	38.58	46.4	2.8	49.2
	5 BA									6.7	2.96	9.66	1.43	11.09
	5CY									12.68	4.32	17	2.44	19.44
	6BA									6.7	2.78	9.48	1.21	10.69
	6 CY									4.11	11.19	15.3	1.42	16.72
	8 BA									6.55	4.48	11.03	1.88	12.91
	8 ESP									78.99	45.98	124.97	1.48	126.45
Biomass (forest biomass residues) [66]	BFB1 BA	626.8	129	755.8					18.4			19.7		
	BFB1 FA	668	63	731					35.9			34.6		
	BFB4 BA	0	0	0					11.9			13.5		
	BFB4 FA	1504	1639	3143					224			207		
	GF BA	141	0	141					12.2			13.8		
	GF FA	19336	4716	24052					1144			1139		

Abbreviations: MSW – municipal solid waste, SS – sewage sludge, agric. – agricultural.

Conclusion

This article provides a comprehensive overview of the dioxin content in oil shale ash from various facilities and combustion conditions. Despite concerns about dioxins as hazardous by-products of combustion processes, this analysis found that dioxin concentrations in oil shale ash were below the detection limit and remained significantly lower than regulatory thresholds, even in a worst-case scenario using the upper-bound approach.

The study showed that for oil shale, the combustion technology and production scale – whether pilot-scale, partial load, or nominal capacity – had no discernible effect on dioxin formation in the resulting ashes. Likewise, the utilisation of pyrolytic wastewater and supplementary fuels such as biomass and retort gas did not influence dioxin concentrations.

Compared to other combustion residues such as municipal solid waste, biomass, and coal ash, oil shale ash demonstrates substantially lower levels of dioxins. In this study, the dioxin concentrations in oil shale ash were consistently below the limit of quantification, corresponding to around 5 ng TEQ/kg in a worst-case upper-bound estimate. For comparison, municipal solid waste fly ash can reach values up to 2500 ng TEQ/kg, biomass fly ash up to 1100 ng TEQ/kg, and coal fly ash typically ranges between 0.1 and 78 ng TEQ/kg. Given its low dioxin content, oil shale ash has significant potential for utilisation in the construction, agriculture, and resource recovery sectors without presenting any dioxin-related risks.

Data availability statement

Data are available from the authors upon request.

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Appendix 1. Dioxin congeners and total concentrations in the ashes from shale oil production plants and Auvere Power Plant, ng/kg

	Enefit280 CY	**Enefit280 ESP**	**Enefit140 total**	**Enefit140 ESP**	**Petroter CY**	**Petroter ESP**	**Auvere BA**	**Auvere ESP**	**Auvere FF**
PCB 105	<200	<300	<220	<790	<480	<360	<87	<66	<120
PCB 114	<14	<14	<11	<46	<24	<12	<4.8	<5.5	<6
PCB 118	<260	<340	<300	<1000	<550	<380	<100	<84	<150
PCB 123	<4.7	<12	<3.9	<27	<17	<15	<5	<5.5	<6
PCB 126	<7.8	<6.9	<7.7	<3.9	<5.6	<7.2	<8.4	<8.5	<8.2
PCB 156	<31	<67	<49	<140	<160	<63	<19	<18	<34
PCB 157	<8.3	<15	<9	<23	<14	<6.5	<12	<17	<14
PCB 167	<5.9	<19	<15	<40	<47	<21	<6.9	<8.2	<8.5
PCB 169	<7.7	<6.4	<7	<4.2	<7.2	<7.8	<11	<10	<9.8
PCB 189	<7.5	<25	<9.5	<43	<43	<16	<91	<12	<35
PCB 77	<140	<190	<150	<470	<220	<170	<52	<30	<69
PCB 81	<v5	<9.4	<8	<16	<17	<16	<4	<4.3	<4.4
∑ UB PCB	691.9	1004.7	790.1	2603.1	1584.8	1074.5	401.1	269	464.9
∑ TEQ PCB	**1.04**	**0.93**	**1.02**	**0.63**	**0.84**	**1.0**	**1.18**	**1.16**	**1.13**
1,2,3,4,6,7,8-HpCDD	<3.8	<4.2	<3.3	<83	<29	<6.1	<6.4	<5.9	<5.9
1,2,3,4,6,7,8-HpCDF	<2.4	<6.6	<4.9	<10	<28	<4.6	<5.6	<4.6	<10
1,2,3,4,7,8-HxCDD	<2.1	<2.1	<2.1	<1.9	<1.9	<2.8	<3	<2.6	<2
1,2,3,4,7,8-HxCDF	<1.9	<1.5	<1.3	<1.3	<1.1	<1.4	<1.4	<1.7	<2

Appendix 1. (continued)

	Enefit280 CY	Enefit280 ESP	Enefit140 total	Enefit140 ESP	Petroter CY	Petroter ESP	Auvere BA	Auvere ESP	Auvere FF
1,2,3,4,7,8,9-HpCDF	<5.2	<5.1	<3.3	<3.3	<31	<4.8	<5.7	<7	<3.1
1,2,3,6,7,8-HxCDD	<2.1	<2.1	<2.1	<4.1	<1.7	<2.5	<2.9	<2.8	<2.1
1,2,3,6,7,8-HxCDF	<1.8	<1.8	<1.6	<0.6	<0.98	<1.6	<1.4	<1.7	<2.1
1,2,3,7,8-PeCDD	<1.6	<1.5	<1.2	<1.6	<0.8	<1.2	<1.7	<1.3	<1.8
1,2,3,7,8-PeCDF	<0.91	<0.91	<0.95	<0.62	<0.34	<1.2	<0.95	<0.84	<0.7
1,2,3,7,8,9-HxCDD	<2.3	<2.3	<2.3	<4.4	<1.9	<2.7	<3.2	<3.1	<2.3
1,2,3,7,8,9-HxCDF	<2.4	<2.2	<2	<0.7	<4.9	<1.7	<2	<2.5	<1.3
2,3,4,6,7,8-HxCDF	<2.1	<1.6	<1.9	<0.66	<1.7	<2.2	<1.7	<2.1	<1.1
2,3,4,7,8-PeCDF	<0.9	<0.96	<0.97	<0.4	<0.65	<1.6	<1.1	<0.97	<0.91
2,3,7,8-TCDD	<1	<1	<1.4	<0.45	<0.7	<0.79	<0.7	<0.92	<1
2,3,7,8-TCDF	<0.82	<1.5	<0.96	<0.5	<0.49	<0.73	<0.56	<0.68	<0.89
OCDD	<11	<19	<9.6	<180	<110	<20	<18	<11	<43
OCDF	<3.6	<6.1	<3.1	<14	<34	<6.4	<12	<7.1	<14
∑ UB PCDD	23.9	32.2	22	275.45	146	36.09	35.9	27.62	58.1
∑ UB PCDF	22.03	28.27	20.98	32.08	103.16	26.23	32.41	29.19	36.1
∑ TEQ PCDD	**3.29**	**3.20**	**3.28**	**3.97**	**2.37**	**2.86**	**3.38**	**3.13**	**3.51**
∑ TEQ PCDF	**1.28**	**1.29**	**1.18**	**0.65**	**1.72**	**1.37**	**1.18**	**1.30**	**1.17**
∑ TEQ dioxins	**7.97**	**5.42**	**5.48**	**5.26**	**4.93**	**5.23**	**5.75**	**5.60**	**5.81**

Abbreviations: CY – cyclone ash, ESP – electrostatic precipitator ash, BA – bottom ash, FF – fabric filter ash, UB – upper-bound approach, TEQ – toxic equivalent.

Appendix 2. Dioxin congeners and total concentrations in the ashes from Eesti Power Plant, ng/kg

	Eesti PC FF	**Eesti PC BA**	**Eesti PC FF**	**Eesti PC BA**	**Eesti PC FF**	**Eesti CFBC ESP**	**Eesti CFBC BA**	**Eesti CFBC ESP**	**Eesti CFBC BA**	**Eesti CFBC ESP**	**Eesti CFBC BA**
Wastewater, t/h	0	0	16	16	8	0	0	16	16	8	8
PCB 105	<290	<230	<160	<210	<140	<140	<120	<200	<98	<170	<150
PCB 114	<13	<11	<11	<9.4	<7.7	<4.9	<6	<13	<4.2	<11	<12
PCB 118	<300	<280	<180	<210	<160	<180	<160	<230	<130	<210	<180
PCB 123	<5.4	<4.9	<5.8	<5.8	<5.7	<5.9	<3.1	<5.8	<3.9	<6.5	<4.6
PCB 126	<7.2	<7.8	<7.9	<8.2	<8.3	<8.5	<8.2	<8	<9.1	<8.5	<7.9
PCB 156	<67	<39	<33	<59	<62	<35	<23	<58	<21	<44	<30
PCB 157	<7	<9.2	<4.9	<7.6	<17	<5.9	<1.6	<8	<11	<8.7	<7.2
PCB 167	<20	<15	<12	<18	<17	<7.8	<7.4	<18	<4.7	<12	<12
PCB 169	<9.2	<6.1	<9	<6.3	<6.5	<4.7	<10	<6.3	<5.3	<5.7	<10
PCB 189	<43	<17	<9.9	<33	<32	<15	<8.1	<17	<11	<15	<18
PCB 77	<160	<140	<100	<120	<82	<75	<110	<140	<60	<100	<110
PCB 81	<15	<4.9	<24	<5.9	<7.1	<7.5	<13	<5.1	<4	<5.9	<4.2
∑ UB PCB	936.8	764.9	557.5	693.2	545.3	490.2	470.4	709.2	362.2	597.3	545.9
∑ TEQ PCB	**1.04**	**1.0**	**1.09**	**1.04**	**1.05**	**1.01**	**1.14**	**1.02**	**1.08**	**1.05**	**1.11**
1,2,3,4,6,7,8-HpCDD	<4.8	<3.6	<3.7	<5.3	<4.4	<4.7	<10	<4.2	<17	<20	<5.4
1,2,3,4,6,7,8-HpCDF	<6	<7.3	<5.8	<26	<5.4	<6.2	<13	<5.4	<27	<28	<4
1,2,3,4,7,8-HxCDD	<2.6	<1.4	<1.6	<0.75	<1.9	<1.9	<2.5	<2.4	<3.3	<1.3	<2.5
1,2,3,4,7,8-HxCDF	<1.7	<0.77	<1.7	<2.7	<1.4	<1.4	<1.6	<2	<1.3	<1	<1.8

Appendix 2. (continued)

	Eesti PC FF	Eesti PC BA	Eesti PC FF	Eesti PC BA	Eesti PC FF	Eesti CFBC ESP	Eesti CFBC BA	Eesti CFBC ESP	Eesti CFBC BA	Eesti CFBC ESP	Eesti CFBC BA
1,2,3,4,7,8,9-HpCDF	<4.5	<2.6	<2.8	<3.2	<4.1	<3.3	<4.2	<3.2	<2.1	<2.1	<6.1
1,2,3,6,7,8-HxCDD	<2.5	<1.2	<2	<0.8	<1.7	<1.8	<2	<2.6	<1.5	<1.6	<2.2
1,2,3,6,7,8-HxCDF	<1.8	<0.85	<2	<1.1	<1.3	<1.8	<1.5	<2.1	<1.1	<1.1	<1.7
1,2,3,7,8-PeCDD	<1.4	<1.8	<1.2	<2.1	<1.5	<1.3	<1.3	<1.9	<1.8	<1.4	<1.7
1,2,3,7,8-PeCDF	<0.96	<0.89	<1.3	<1.1	<0.97	<0.8	<1.1	<0.97	<0.86	<1	<1.2
1,2,3,7,8,9-HxCDD	<2.7	<1.3	<2.2	<0.87	<1.9	<2	<2.1	<2.8	<1.6	<1.7	<2.4
1,2,3,7,8,9-HxCDF	<2.3	<1	<2.4	<1.4	<2	<1.7	<2.1	<2.1	<2.2	<1.9	<2.5
2,3,4,6,7,8-HxCDF	<1.8	<1.2	<1.5	<1.2	<1.5	<1.8	<2.1	<2.1	<1.7	<1.4	<2.6
2,3,4,7,8-PeCDF	<1.3	<2.1	<1.5	<1.5	<1.2	<1	<1.2	<1.1	<0.97	<1.1	<1.1
2,3,7,8-TCDD	<0.8	<1	<1.1	<0.73	<0.8	<1.3	<0.91	<0.65	<0.73	<0.86	<0.71
2,3,7,8-TCDF	<0.81	<0.88	<0.89	<0.97	<0.68	<0.73	<0.73	<0.33	<0.68	<0.82	<0.65
OCDD	<19	<27	<28	<44	<11	<28	<14	<23	<35	<200	<24
OCDF	<6.3	<6	<6.2	<18	<7.2	<18	<9.4	<3.1	<11	<16	<15
∑ PCDD	33.8	37.3	39.8	54.55	23.2	41	32.81	37.55	60.93	226.86	38.91
∑ PCDF	27.47	23.59	26.09	57.17	25.75	36.73	36.93	22.4	48.91	54.42	36.65
∑ TEQ PCDD	**3.03**	**3.23**	**2.92**	**3.13**	**2.90**	**3.22**	**3.0**	**3.38**	**3.35**	**2.98**	**3.18**
∑ TEQ PCDF	**1.37**	**1.23**	**1.42**	**1.51**	**1.17**	**1.17**	**1.31**	**1.31**	**1.31**	**1.29**	**1.40**
∑ TEQ dioxins	**5.44**	**5.46**	**5.44**	**5.69**	**5.12**	**5.41**	**5.49**	**5.71**	**5.74**	**5.31**	**5.69**

Abbreviations: PC – pulverised combustion, FF – fabric filter ash, BA – bottom ash, CFBC – circulating fluidised bed combustion, ESP – electrostatic precipitator ash, UB – upper-bound approach, TEQ – toxic equivalent.

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