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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

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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

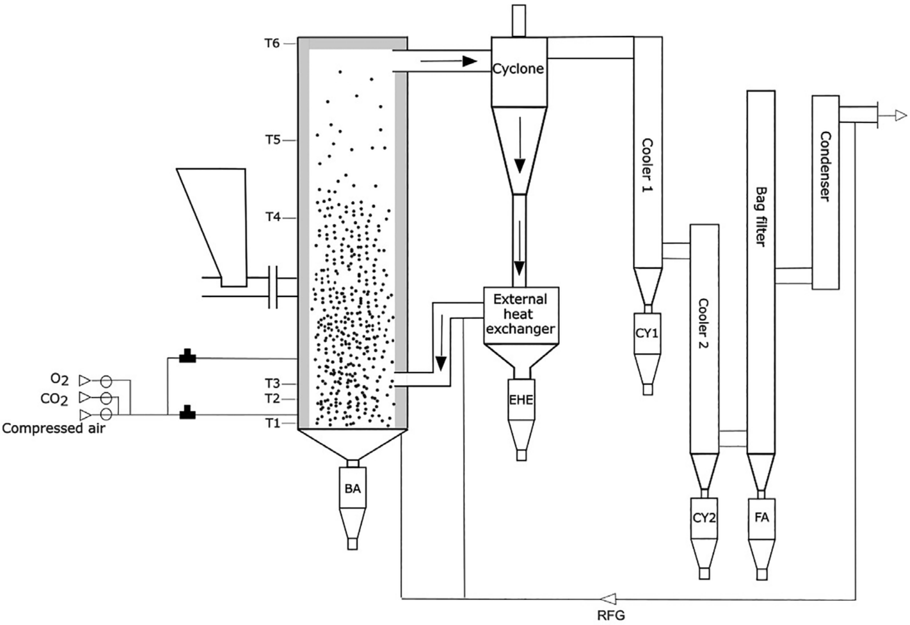

Fig. 1. Schematic of the 60 kW$_{th}$ circulating fluidised bed pilot unit, including temperature measurement points (T1–T6) and ash sampling points: bottom ash (BA), ash from the external heat exchanger (EHE), cyclone ash (CY1 and CY2), and ash from the bag filter (FA) (adapted from [52]). RFG – recycled 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 $(S/N) \geq 3$, 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 $S/N \geq 3$ 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

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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.