

Persistent Organic Pollutants Destruction Efficiency in UK Energy from Waste

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Persistent Organic Pollutants Destruction Efficiency in UK Energy from Waste

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Glossary

ABS	Acrylonitrile butadiene styrene
APCr	Air pollution control residues
BA	Boiler ash
BAT	Best Available Techniques
BDE-153	2,2',4,4',5,5'-Hexabromodiphenyl ether
BEHTBP	Bis(2-ethylhexyl) tetrabromophthalate
BFRs	Brominated flame retardants
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
BS	British Standard
CEN	European Committee for Standardisation
CFC	Chlorofluorocarbon
C&I	Commercial and Industrial waste
CNIM	Constructions Industrielles de la Mediterranee
CRT	Cathode ray tubes
CV	Calorific value
DBDPE	Decabromodiphenyl ethane
DCS	Distributed Control System
DE	Destruction efficiency
Deca-BDE	Decabromodiphenyl ether
Defra	Department for Environment Food and Rural Affairs
DEHP	Di (2-ethylhexyl) phthalate
DiNP	Diisononyl phthalate
DiOP	Diisooctyl phthalate
DPTE	2,3-dibromopropyl-2,4,6-tribromophenyl ether
DRE	Destruction Removal Efficiency
EfW	Energy from Waste
EN	Euronorm standard
EURL	European Union Reference Laboratories
ESA	Environmental Services Association
FPD	Flat panel display
GC-MS	Gas chromatography mass spectrometry

HBB	Hexabromobiphenyl
HBCDD	Hexabromocyclododecane
HDPE	High-density polyethylene
Hexa-BDE	Hexabromodiphenyl ether
HxBB	Polybrominated biphenyls
HZI	Hitachi Zosen Innova
IBA	Incinerator bottom ash
INERIS	Institut national de l'environnement industriel et des risques
I-TEQ	International Toxic Equivalent
LC-MS/MS	liquid chromatography tandem mass spectrometry
LoD	Limit of detection
LoQ	Limit of quantification
MCERTS	Monitoring Certification Scheme
MID	Method Implementation Document
MCCPs	Medium chain chlorinated paraffins
MCR	Maximum continuous rating
MS	Mass spectrometry
MSW	Municipal solid waste
MWIs	Municipal waste incinerators
NIPH	Norwegian Institute of Public Health
PAC	Powdered activated carbon
PBBz	Polybrominated benzenes
PBDE	Polybrominated diphenyl ethers
PBDD/F	Polybrominated dibenzo-p-dioxins and dibenzofurans
PCB	Polychlorinated biphenyl
PCDD/F	Polychlorinated dibenzo-p-dioxins and dibenzofurans
PE	Polyethylene
Penta-BDE	Pentabromodiphenyl ether
PFAS	Perfluoroalkyl and polyfluoroalkyl substances
PFHxS	Perfluorohexanesulphonic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
POP	Persistent organic pollutant
PP	Polypropylene

PVC	Polyvinyl chloride
RDF	Refuse derived fuel
SCCPs	Short chain chlorinated paraffins
TBBPA	Tetrabromobisphenol A
Tetra-BDE	Tetrabromodiphenyl ether
TS	Technical Standard
TTBP-TAZ	2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine
XRF	X-ray fluorescence spectroscopy
UV328	2-(2H-benzotriazol-2-yl)-4,6-di-tert-pentylphenol
UKAS	United Kingdon Accreditation Service
UNEP	United Nations Environment Programme
VOC	Volatile organic chemical
WEEE	Waste electrical and electronic equipment
WUDS	Waste upholstered domestic seating

Summary

Regulatory Framework

The UK is a signatory to the United Nations Stockholm Convention for Persistent Organic Pollutants (POPs) which controls and restricts the use of POPs and requires destruction of waste containing POPs above specified thresholds. In recent years multiple studies commissioned by UK industry and regulators have identified POPs in a variety of waste materials. Based on the Basel Convention technical guidelines, Defra currently consider that energy from waste (EfW) facilities are an appropriate disposal route for waste containing brominated flame retardants (BFRs) and there is currently no evidence to the contrary. A Defra Evidence Statement highlighted the need for more data on the emissions of POPs from thermal destruction processes and this research project was developed to establish the destruction efficiency of POPs in UK EfWs.

The POPs investigated originate predominantly from brominated, chlorinated and phosphate flame retardants legitimately added at the point of manufacture, but which are now listed and restricted as POPs. The list of POPs continues to expand and now, for example, includes three substances which are known as perfluoroalkyl and polyfluoroalkyl substances (PFAS). Different POPs are destroyed at different combustion temperatures. UK EfW facilities are required to operate at 850˚C or above. To meet UK obligations to the Stockholm Convention the POP content in stockpiles of POPs, POPs waste and waste containing POPs (above the low POP content limit) must be destroyed or irreversibly transformed.

Aims

This programme of work focussed on assessing the effectiveness of EfW facilities which may accept POPs waste, such as waste upholstered domestic seating (WUDS) or the 'enhanced-POPs' containing plastic fraction produced from treatment of waste electrical and electronic equipment (WEEE) to effectively destroy it. The programme was structured to determine the concentrations of key POPs compounds in both solid residues and air emission samples to establish the POPs destruction efficiency (DE) of EfW facilities processing POPs waste.

Approach

POPs combustion trials were completed at three separate UK EfWs. The plants were selected to provide reasonable representation of the UK EfW fleet. The methodology adopted was designed to ensure the installations were operated and sampled under normal process conditions and after introduction of an enhanced POPs feedstock (WEEE plastic). WEEE plastic additions were chosen over WUDS to maximise the presence of BFRs and were calculated to avoid significant alteration of the overall calorific value (CV) of the fuel (which could have rendered the results unrepresentative of normal operations) whilst ensuring sufficient POPs for the determination of DE.

Samples were collected from the solid combustion residues (incinerator bottom ash (IBA), air pollution control residues (APCr) and, where separately collected, boiler ash) and emissions from the stack. Residues were monitored for target primary POPs and examined for post combustion chemical formation including polychlorinated and polybrominated dibenzo p-dioxins and dibenzofurans (PCDD/F & PBDD/F). Stack emissions were also monitored for PCDD/F, PBDD/F and a range of fluorinated organics including chlorofluorocarbons. This data was used to estimate the DE range for POP BFRs for each of the three EfWs during processing of POPs waste. Due to the high flue gas temperatures (>850 ^{0}C) there was no realistic possibility of unreacted BFRs being present in the post-treatment flue gas as they are known to thermally degrade at temperatures around 450^{0}C and their chemical properties mean that they will be preferentially captured by the activated carbon present in the flue gas treatment system and APCr. Therefore, the focus was on identifying partial products of combustion, PCDD/F and PBDD/F, in the flue gases.

Calculation of Destruction Efficiency

An extended approach to the calculation of DE of two BFRs, decabromodiphenyl ether (decaBDE) and tetrabromobisphenol A (TBBPA), was undertaken using data collected from the field trials at the three operational EfWs. These BFRs were selected as they were identified in significant proportions in bromine-rich WEEE plastic waste streams. The three trial sites were observed to be operating normally on both days and were fully compliant with the continuous emissions limits in their permits. No BFRs or other POPs (Dechlorane Plus and UV-328) were detected in any of the IBA, APCr and boiler ash residues collected during either the baseline study or during the addition of POPs-rich WEEE plastic trials. All residues analysed comply with the definition for low POP content under the Stockholm Convention as enacted by UK legislation. Measurements of partial products of combustion in residues were also undertaken and included in the destruction efficiency calculation. Minimum extended DE values ranging from 99.927% – 99.952% for decaBDE and 99.896% – 99.936% (to 5 sig. fig) for TBBPA were determined. The corresponding maximum extended DE ranges were 99.996% to 100.000% for decaBDE and 99.998% to 100.000% for TBBPA.

Flue gas PCDD/F concentrations were compliant with periodic monitoring requirements and therefore met the provisional definition for levels of destruction and irreversible transformation, based upon absolute levels (i.e., waste output streams of treatment processes) in flue gases in UNEP (2023). There appears to be no consistent trend in PCDD/F flue gas emissions between the baseline day and the day in which enhanced-POPs WEEE plastic was added. PBDD/F flue gas concentrations were also low and appeared to demonstrate no consistent trend between the baseline day and the day in which enhanced-POPs WEEE plastic was added. Quantifying PBDD/Fs as partial products of combustion in the DE calculation for all solid and gaseous products of combustion had a minor impact on the overall outcome of the assessment as they were only found at very low concentrations.

The use of an enhanced WEEE plastic as a source of BFRs allowed destruction efficiency ranges (including the contribution from partial products of combustion) of between 99.896%

and 100.000% to be demonstrated in the field. The main limitation on BFR input was ensuring the combustion process was still representative of normal operations despite the addition of large quantities of high-CV material (enhanced-POPs WEEE plastic) with the benefits of increased BFR loading on destruction efficiency calculations. In practice, the quantities added resulted in CV perturbations of around 0.3 MJ/kg over a 30 minute period. Each of the sites operated well within the normal CV range encountered for the site.

The primary factor impacting on the determination of the minimum DE is the limit of quantification (LoQ) of BFRs in IBA as the largest residue by mass. An LoQ of the order of 0.005 mg/kg or less for BFRs in the solid residues would be required to demonstrate a minimum 99.999% destruction efficiency. In this test programme the typical range was between 0.07 to 0.10 mg/kg for decaBDE and 0.14 to 0.20 mg/kg for TBBPA. The analytical laboratory was a highly capable test facility and to have substantially improved the minimum DE threshold would have required the addition of 10-fold more POPs-enhanced WEEE plastic which would have moved the feedstock CV above normal operational ranges or significant incremental improvements in both LoQ and quantities of POPs-enhanced WEEE plastic.

The DE ranges determined in this trial range from 99.896% – 100.000% (to 3 decimal places) and include the contribution from unintentionally produced brominated POPs. Sub-sections a) to k) of UNEP (2023) indicate that Best Available Techniques (BAT) is to achieve a minimum DE of 99.999% destruction or irreversible transformation, with 99.9999% destruction removal efficiency (DRE) as a supplementary requirement where applicable to provide a practical benchmark for assessing disposal technology performance. Higher demonstrated DEs may be preferred on a case-by-case basis. As neither DE nor DRE consider the potential transformation of the original POP to an unintentionally produced POP, potential releases of unintentionally produced POPs should be considered when choosing a particular operation. It is recognised that the lower bounds obtained are below the BAT thresholds in UNEP (2023) they are constrained by the laboratory LoQ for BFRs in solid residues. The upper bound is broadly consistent with the environmentally sound disposal requirements of UNEP (2023) and associated UK guidance. UNEP (2023) recognises R1: Use as a fuel (other than in direct incineration) or other means to generate energy as an appropriate destruction and irreversible method for removal of POPs.

Other Findings

All six of the IBA and APCr samples analysed for short chain chlorinated paraffins were found to be below the limit of detection. Two of the IBA samples had detectable and very low levels of medium chain chlorinated paraffins (MCCPs) present (< 200 mg/kg). The remaining IBA sample and all three APCr samples analysed for MCCPs were found to be below the limit of detection.

No fluorinated organics, chlorofluorocarbons or chlorocarbons were detected during the screening carried out on flue gas. The relatively high limit of detection (typically 20 mg/m^3) for the screening method means that should there be concerns relating to the presence of poly-fluorinated compounds or their partial products of combustion then a more focused high-sensitivity assessment will be required. This analysis was undertaken as a screening exercise and was a secondary objective to the main testing programme.

Conclusions

Within the uncertainties inherent in any practical study, the results indicate a very high level of destruction efficiency has been achieved within the context of a reasonable real-world worst-case operational scenario. The dosing of brominated POPs material to an EfW was significantly higher than what would be realistic based on current and likely future UK EfW feedstocks. Therefore, the findings suggest that EfW facilities provide an effective means for the destruction of brominated POPs within the feedstock in a real-world operational context. A high volume, high concentration POPs feedstock resulting a calorific value outside of the normal operational ranges may require specialist treatment, although further field trials using significantly more bromine-rich feedstock would be required to assess such a scenario. Finally, it was not possible to draw any robust conclusions regarding the destruction of PFAS-containing materials based on this study although it is possible to conclude that a specific PFAS-rich feedstock trial would be required to evaluate the PFAS destruction efficiency.

1. Introduction

1.1 Project Rationale

The UK is a signatory of the United Nations Stockholm Convention for persistent organic pollutants (POPs) which controls and restricts the use of POPs and requires destruction of waste containing POPs above specified thresholds. In recent years multiple studies commissioned by UK industry and regulators have identified POPs in a variety of waste materials. Waste electronic and electrical equipment (WEEE) and waste upholstered domestic seating (WUDS) have both been identified as containing POPs classified brominated flame retardants. Additionally, more recent UK led investigations have identified that POPs compounds are present in other waste materials such as non-WEEE waste cables, carpets/flooring, polymer from battery cases, and residues from shredding of mixed waste including end-of-life vehicles. As a result, identification of POPs contaminated items is highly challenging and may result in broad classification of whole waste streams that require destruction. This will lead to an increased volume of waste requiring destruction i.e. thermal treatment.

In this study the most commonly identified POPs classified compound was decabromodiphenyl ether (BDE-209 / decaBDE). However, hexabromocyclododecane (HBCDD) and short-chain chlorinated paraffins (SCCPs) have also been identified in textiles and polymer materials. It is also plausible that household textiles act as a ‘sink’ for the POPs classified perfluoroalkyl and polyfluoroalkyl substances (PFAS) perfluorooctanoic acid (PFOA) which is commonly used in cleaning products. PFAS are known to be resistant to thermal degradation, unless under conditions of high temperature incineration, but due to their wide usage over the years they are likely to be present in wastes treated by Energy from Waste (EfW). Two PFAS (PFOS and PFOA), and perfluorohexanesulphonic acid (PFHxS) have been listed recently and are due to be enforced by the Convention in late 2023.

As a result, in the UK there are an increasing number of wastes that exceed concentration thresholds for POPs compounds. In addition to those wastes now being classified as POPs waste, other compounds are also under investigation for their persistent and accumulative characteristics. For instance, medium-chain chlorinated paraffins (MCCPs), dechlorane plus and UV-328 are chemicals proposed for listing under the Stockholm Convention. Further, tetrabromobisphenol A (TBBPA) has ‘*persistent, bioaccumulative and toxic*’ properties of concern according to the European Chemicals Agency. Specifically, TBBPA has been widely used in polymers as a replacement for other restricted/banned flame retardants. Should any of those chemicals be listed under the Stockholm Convention as POPs compounds, it is likely the number of different wastes classified as POPs waste will increase as would the volume. At present, high temperature thermal treatment is considered the best available technique to destroy POPs compounds present in POPs waste. Relevant legislation require that the operating temperature of thermal treatment facilities (for municipal waste) must exceed 850 °C for a gas residence minimum period of two seconds, which is significantly in excess of the temperature at which some POPs compounds decompose. For instance, 99% of deca-BDE decomposes at 300 °C. Different POPs are destroyed at different incineration temperatures. Some PFAS are likely more resilient to thermal degradation and decompose at significantly higher temperatures. In addition, some brominated flame retardants (BFRs) act as potent precursors for the secondary formation of polybrominated dibenzo-p-dioxins and furans (PBDD/Fs). Similarly, the carbon-fluorine bond of PFAS poses a challenge for compound destruction due to its high stability. Incineration of PFAS containing waste may result in the formation of ozone depleting chlorofluorocarbons (CFCs) as well as fluorinated greenhouse gases (tetrafluoromethane and hexafluoroethane), fluoro-dioxins, fluoro-benzofurans, fluorinated aromatic compounds and perfluorinated carboxylic acids. Process combustion control and grate loading may also play a key part in determining destruction efficiencies.

1.2 Aims

This programme of work focussed on assessing the effectiveness of EfW facilities which may accept POPs waste (such as WUDS or the ‘enhanced-POPs’ containing plastic fraction produced from treatment of WEEE) to effectively destroy it. The programme was structured to determine the concentrations of key POPs compounds in both solid residues and air emission samples to establish the POPs destruction efficiency of EfW facilities processing POPs waste.

The specific objectives of the project were to:

1. Monitor the emissions to air of PCDD/F and PBDD/F from three EfWs which are actively taking either WUDS or WEEE plastics from density separation plants.

2. Collect representative samples of the solid residues from the three EfWs and complete analysis for concentrations of PCDD/F, PBDD/F, total bromine, residual BFRs (including but not restricted to POPs previously identified in WUDS and WEEE) and PFAS including PFOS, PFOA and PFHxS. Existing information from the operator relating to these chemicals in IBA, APCr and emissions to atmosphere were also evaluated, where available.

3. Estimate the total quantities of PCDD/F, PBDD/F, total bromine, residual BFRs and PFAS within the solid residues. Estimate total quantities of PCDD/F, PBDD/F and volatile compounds including CFCs in the stack emissions.

4. Estimate the Destruction Efficiency for POP BFRs for each of the three EfWs.

5. Analyse and report the results and state conclusions in respect of the suitability and environmental impact of this disposal route, including comparison to results reported in relevant academic literature and relevant reports.

1.3 Supporting Studies

In 2021, WRc carried out an assessment of POPs-classified BFRs in waste domestic seating on behalf of the Environment Agency (WRc, 2021). A large number (282) samples of WUDs including separate textile components were taken. POPs-classified components were found predominately in the covers of textile and leatherette domestic seating. Based on the results from this study, it was found that POPs-classified brominated flame retardants comprised 0.36 – 0.48% by mass of waste domestic seating. The low incidence of brominated material as a proportion of the overall waste domestic seating stream means that it was not an ideal source of brominated flame retardants for EfW dosing studies.

A previous study completed the Institute for Electronics Recycling (WRc/ICER, 2020) identified deca-BDE as the most common POP in UK WEEE. A similar 2022 study by WRc into POPs in separated WEEE plastics has also been carried out (WRc, 2022). The flame retardants Deca-BDE, decabromodiphenyl ethane (DBDPE) and TBBPA were commonly identified in separated WEEE. 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE) was also identified in a small number of enhanced-POPs fraction samples. For most WEEE streams analysed, around 80-95% of BDEs were found in the enhanced-POPs fraction. The variability in the concentration of brominated flame retardants between samples taken from the same facility and between operators was low. X-ray fluorescence spectroscopy (XRF) showed cathode ray tube televisions (CRT) and flat panel display (FPD) fractions were more likely to contain elevated concentrations of bromine. Analytical data for deca-BDE, DBDPE and TBBPA in the enhanced-POPs fractions contained up to 27,000 mg/kg deca-BDE and 46,000 TBBPA respectively. Therefore, it was considered that the enhanced-POPs WEEE fraction, particularly WEEE from CRT and flat panel display was particularly suitable for use in the planned EfW dosing study.

There have been a limited number of trials to assess the destruction of BFRs reported in the literature and the results of this study generally accord with previous findings. TemaNord (2005) carried out field trials measuring emissions from the incineration of waste containing bromine in the form of decaBDE and TBBPA at the two-line, 10 t/h per line Oslo plant. They estimated a destruction efficiency of >99.999% based on measurement of residual emissions to air, measurement of the BFR content of residues and estimating the amount of BFR present in the waste feedstock. IBA was found to contain 91 – 97% of the residual BFR. They concluded that an increase in the amount of BFRs in the waste feedstock had no measurable impact on emissions of PBDD/F and PCDD/F.

Mark *et al*. (2015) co-incinerated a HBCDD rich polystyrene foam at an operational EfW plant in Europe. They observed that emissions to air and the residual HBCDD content of residues were unrelated to the HBCDD input rate. A destruction efficiency >99.999% was reported for HBCDD. Kajiwara *et al*. (2021) combusted plastic television waste rich in decaBDE alongside municipal waste at two commercial EfW facilities at temperatures of 1000 – 1100 ˚C. Destruction efficiencies >99.9999% were reported and PBDD/F discharge was found to be negligible. More than 70% of the residual decaBDE was found in the incinerator bottom ash (IBA) whilst >90% of the bromine was found in the APCr.

Bell (2021) reviewed the need for POPs waste destruction, the disadvantages of combustion technologies available to destroy POPs and the advantages of non-combustion approaches. The main concern they identified with the use of the default UNEP definition of destruction efficiency as a metric for POPs removal was that it did not account for the partial products of combustion, PCDD/Fs and PBDD/Fs, generated in the process of destroying the target POPs in the waste.

1.4 Report Structure

Section 1 provides an overview of the background to the work programme. Section 2 details the overarching methodology and analytical approach whilst Section 3 details the site-specific approach taken at each of the three sites. The findings in this report are provided in two sections. Section 4 provides the data obtained from site operations and laboratory testing. Section 5 describes the determination of the destruction efficiency range for two BFRs at each of the three EfWs. Section 6 provides the conclusions of the report. A supplementary report containing all the detailed analytical results accompanies this report (POPs destruction efficiency at EfW facilities - Supplementary dataset - UC17779.1).

2. Methodology

The approach to the testing programme was divided into the following key activities:

1. Site selection and evaluation
2. Infeed addition approach
3. Sampling times and data collection:
4. Stack emissions, IBA, APCr and boiler ash sample analysis.
5. Supporting data requirements for POPs destruction efficiency calculation.

To achieve the aims of this project, appropriate sites were selected to take part in the testing programme. A suitable sampling and testing regime was designed, complex data relating to facility input feed and operating conditions gathered and analysed, representative samples of air emissions and solid residues taken, and a broad suite of analysis completed on prepared analytical test samples.

2.1 Site Selection and Evaluation

The project was based on six measurement days. Two alternative approaches were considered in selecting the number of sites required for the trials:

i. Sample once at six different sites (three operating under baseline conditions and three with enhanced POPs); and
ii. Sample twice at three different sites (one baseline day and one enhanced POPs fuel feed-in day).

Following extensive discussions with Defra, the Environment Agency and industry it was agreed to pursue Option ii. The advantage of this approach was that it reduced the number of variables in the data interpretation when comparing the data between baseline conditions and POPs addition conditions. For instance, were elevated PBDD/Fs to be identified in a one-off POPs addition trial there would be no way of directly relating the observation to either the “baseline” performance of the plant or the additional POPs material.

Three sites were considered sufficient to provide representative coverage of the different operating technology types and facility ages in the UK fleet is dominated by moving grate technologies provided by two equipment manufacturers, Constructions Industrielles de la Méditerranée (CNIM) and Hitachi Zosen Innova (HZI). The moving grate approach is also the globally dominant applied technology for municipal residual waste.

The following key criteria were considered as part of selection:

- Technology / supplier type: The UK EfW facility fleet is dominated by the main equipment suppliers CNIM and HZI and as such both were a high priority for representation in the three sites selected. Other suppliers include Vyncke, Procedair, Babcock Wilcox Volund, Keppel Seghers and Steinmuller, although these represented a smaller number of facilities when compared to CNIM and HZI plants.
- Operator participation: There are many complexities associated with the input of specific POPs waste during a trial and the collection of matched IBA, APCr and stack emissions samples. Positive engagement with the facility operator was therefore essential. This was particularly pertinent given that a controlled input of post-density separation enhanced-POPs WEEE was to be used as the 'POPs enriched' trial condition.
- Control over feedstock: The selected facility and operator were able and willing to control the feedstock during the trial period.
- Outages: The selected facilities were operating under standard conditions for a reasonable period ahead of the trial.
- APCr, boiler ash and IBA sampling: The selected facility and operator were able and willing to support the collection of specific IBA APCr and boiler ash samples during the trial period. Due to the complexity associated with the collection of matched APCr and boiler ash samples, the facility ideally had an access point prior to discharge into the silo (or a similar solution to allow for direct sampling of material generated during the trial).
- Facility age: The age of selected facilities needed to be broadly representative of the majority of EfW facilities as the UK has a relatively modern fleet. However, it was considered important that facilities that were in commissioning were excluded as combustion conditions may not have been stable. Similarly, significantly older facilities were also excluded from selection as they may not have been representative of the wider EfW fleet.
- Operating capacity: The selected facilities were representative of the wider EfW fleet, specifically very small or large throughput facilities were excluded from selection.
- Number of operating lines: Due to the potential complexity involved with the collection of matched IBA, APCr and boiler ash samples on some multi-line facilities, priority was given to single-line facilities or facilities where feedstock addition and output residues could be monitored on a single line.

Following conversations with several UK EfW operators, three sites were identified that predominately met the above selection criteria. None of the sites normally accept a specific POPs-rich feedstock of enhanced-POPs WEEE plastic, although this material is likely to be present in some of the accepted general waste streams. Details of these facilities are provided in Table 2.1.

Table 2.1 Characteristics of trial sites

Parameter	Site 1	Site 2	Site 3
Technology	Mass burn, moving grate	Mass burn, moving grate	Mass burn, moving grate
Use of heat	Steam boiler feeding turbine generator	Steam boiler feeding turbine generator	Steam boiler feeding turbine generator
Flue gas treatment system	Bag filter with lime and PAC addition	Bag filter with lime and PAC addition	Bag filter with lime and PAC addition
Technology provider	HZI	CNIM	Other
Age	<10 years	<10 years	<10 years
Waste accepted	Mostly local authority with some C&I.	Mostly local authority with some C&I.	Mostly local authority with some C&I.
Size of line under test	150,000 – 300,000 t/y	150,000 – 300,000 t/y	<150,000 t/y
R1 status	Yes	Yes	Yes

2.2 Trial Approach and Feedstock Selection

It is likely that most, if not all, EfW facilities in England and Wales already some POPs-containing material in their feedstock through the general waste supply, whether as refuse derived fuel (RDF), in residual municipal solid waste (MSW) or as specific bulky wastes. Operator feedback has indicated that their sites are not specifically accepting separated enhanced-POPs WEEE plastics as a specific waste stream. None of the sites that participated in the trial accept enhanced-POPS WEEE plastics as a dedicated waste stream. Instead, the sites in the UK that currently accept this material will likely be receiving it pre-mixed in controlled amounts into RDF. Discussions with WEEE density separation operators indicates that the majority of the enhanced-POPs WEEE fraction is currently sent to a small number of sites (including cement kilns) or exported from the UK.

The agreed approach was to sample at three sites under two separate conditions on sequential days:

- Day 1. A ‘baseline’ condition, which was to be reflective of typical normal operating conditions with the regular municipal waste input (This waste would still likely contain a small and unknown proportion of items containing POPs) and
- Day 2. A specific ‘enhanced-POPs addition’ condition in which the normal feedstock was supplemented by the addition of controlled amounts of POPs-rich material containing known quantities of POPs.

The use of different feedstocks at the three facilities was actively considered for the enhanced POPs addition trial. Options considered included whether one selected facility should receive the POPs containing fraction from density separated WEEE only, one facility should include waste upholstered domestic seating (WUDS) only and one facility should include a mixed addition.

The use of an enhanced enhanced-POPs WEEE plastics for the POPs addition condition was identified as significantly more favourable than using WUDS for several reasons:

1. **Concentration of POPs present.** Two previous studies investigating separated WEEE plastics and soft furnishings completed by WRc provide evidence on the likely concentrations of POPs in each waste stream. WUDs were found to be a complex waste stream made up of a wide variety of material types. Some units contained highly elevated concentrations of deca-BDE, whereas many units did not contain any POPs. Overall, the study estimated between 364 and 476 tonnes of POPs-classified BFRs were present per 100,000 tonnes of waste.

   In contrast, analysis of enhanced-POPs WEEE plastics has indicated that the concentration of POPs and BFRs were related to the origin of the polymer. Polymer from CRT monitors and FPD televisions were found to contain significantly higher concentrations of bromine when compared to polymer from small mixed WEEE and fridges. In addition, any given sample CRT and FPD polymer was more likely to contain elevated concentrations of bromine when compared to small mixed WEEE and fridge polymer. The median bromine concentration of enhanced-POPs WEEE plastics from CRT and FPD waste was found to be 67,000 – 122,000 mg/kg.

   When comparing enhanced-POPs WEEE from CRTs/FPDs and WUDs, enhanced-POPs WEEE plastic represented both a larger and more consistent source of POPs. Both factors were important for the purpose of the POPs addition trial as much larger amounts of WUDs would be required to provide a similar amount of POPs addition. This would pose a challenge in terms of practical delivery of the material into the combustion process, and the potential to result in operating conditions that would be significantly more perturbed due to the quantities of WUDs required.

2. **Sampling of the infeed.** Sampling of enhanced-POPs WEEE plastic sourced from a density separation process operator has been shown to be feasible in precious studies by WRc. As the enhanced-POPs WEEE plastic was produced in a granulated form, representative sampling was completed. Representative sampling and analysis of the WUDs stream was particularly challenging due to the bulky nature of the waste, meaning an extremely large sub-sample would be required to produce a composite sample. Alternatively, analysis of many individual items was considered in calculating a likely bulk composition. However, these approaches were not considered practical within the context of this investigation.

3. **Complexity and variability of the soft furnishings / bulky waste stream.** WUDs include a range of items and at many facilities arrives as a mixed 'bulky waste' stream. As such, the POPs containing components (such as textile covers and foams) are mixed with wooden frames and other materials that do not contain POPs. In a scenario where 200 kg of WUDs was added to the process as a POPs addition, it would be uncertain as to the exact volume of POPs containing material. Any given 'grab' sample of WUDs by a feed crane is likely have a different composition to the next. This situation will be exacerbated by the fact that the bulk POPs composition of the WUDs input is likely to be low.

4. **Impact on the combustion process.** A key feature of the project was the need to be representative of normal EfW operations. The high concentration of BFRs present in in enhanced-POPs WEEE plastic meant that only relatively small quantities (~200 kg per site) were required to determine a suitably high destruction efficiency based on theoretically achievable analytical limits of detection in residues and estimates of the abundance of BFRs in enhanced-POPs WEEE plastics based on the results of previous studies ahead of full laboratory characterisation. Despite the high calorific value (~40 MJ/kg) of enhanced-POPs WEEE plastics, the impact of adding relatively small quantities in multiple additions meant that the impact on operational net CV of the fuel was intended to be small (~0.35 MJ/kg) and well within typical operational ranges (~8 – 12 MJ/kg, depending on the plant). The trial approach therefore avoided significantly affecting the overall CV of the plant, such that the DRE conclusions may be considered under "normal" operating conditions. Evidence of normal operations was a lack of deviation from certain process parameters, and air emissions data.

5. **Sourcing trial feedstock.** Enhanced-POPs WEEE plastic from processes treating CRT / FPDs (and therefore likely to be rich in key BFRs) is not a ubiquitous or high-volume waste stream. There are relatively few established processors in the UK for sourcing this material. Approximately half a tonne of high-quality enhanced-POPs WEEE plastic material was needed to facilitate the trial and sourcing large quantities of this material at short notice in the timeframe available proved to be constraint.

The input POPs mass needed to be high enough to ensure a POPs destruction efficiency could be calculated to a high confidence level without deviating from normal operations. In addition, a well characterised input POPs speciation provides confidence in the outcome of the POPs destruction efficiency calculation. Considering these factors, the use of a known amount of characterised enhanced-POPs WEEE for the POPs addition trials was the best option.

A density separation process operator who was involved in the Environment Agency funded investigation into POPs in separated WEEE provided the FPD / CRT enhanced-POPs WEEE. This enhanced-POPs WEEE material was sampled at WRc to produce three composite samples for analysis prior to being sent to the three facilities in the trial. The composite samples were cryogenically milled to produce a fine particle size test sample which were analysed to determine concentrations of BFRs present, including decaBDE and TBBPA.

2.3 POPs Feedstock Addition

A site reconnaissance visit and meeting involving SLR Consulting, as air emissions specialists, and the operational management at each of the facilities indicated that the method of addition of the enhanced-POPs WEEE plastics would differ between the sites for operational and logistical reasons. A site-specific plan was drafted in order to identify and collect all relevant samples at time intervals correlating to the POPs material transit times along the combustion line under test. The total mass of enhanced-POPs WEEE plastics added to each process was similar although the method of introduction varied.

At Site 1, there was an access point at hopper-level which provided straightforward (and risk free) direct access to the hopper. Therefore, the POPs-rich enhanced-POPs WEEE feedstock was pre-packaged into individual sacks and manually placed directly into the hopper at regular 15 minutes intervals. By using a regular discharge into the system, the likelihood of detecting the POPs signal in the sampled outputs was increased.

At Sites 2 and 3 there was no suitable manual access to the hopper due to practical limitations and health and safety considerations. Therefore, the POPs material was added into the process on three occasions by the grab crane. At Site 2, the large bags of enhanced-POPs WEEE plastics were placed in the waste bunker and lifted by the crane into the hopper. At Site 3, the enhanced-POPs WEEE plastic was placed in a redundant separate bay and lifted by the crane into the hopper. The quantities of enhanced-POPs WEEE plastic added to the process on the enhanced POPs addition trial trials are shown in Table 2.2.

Table 2.2 Enhanced-POPs WEEE plastic additions used during POPs trials

Input	Site 1	Site 2	Site 3
WEEE Bag 1	24 individual bags each averaging 7.4 kg each	50.5 kg	45.5 kg
WEEE Bag 2		39.5 kg	40.0 kg
WEEE Bag 3		35.5 kg	38.5 kg
Total input	178.5 kg	125.5 kg	124.0 kg

2.4 Monitoring and Sampling Considerations

The objective of routine sampling of IBA, APCr and boiler ash residues was to produce a sample representative of the wider waste stream produced at that facility. The specific objectives of this project meant that the sampling approach for collection of IBA, APCr and boiler ash (where separately collected) were undertaken in accordance with principles of the accepted protocols e.g. ESA (2018) although the approach was adapted to best meet project objectives in specific ways as detailed in Section 3.

Point source emissions sampling is normally undertaken to provide an assessment of the normal operational performance of the plant for a standard suite of determinands following relevant Environment Agency guidance (Environment Agency, 2022). In this project, the approach followed established protocols for stack emissions sampling under the EA's Monitoring Certification Scheme, MCERTS.

In the case of the baseline trial, the waste input was the typical waste feedstock, therefore specific sampling adjustments were not specifically required. Stack emissions sampling was carried out over a 6-hour period in the day. Residues sampling was based on collection of incremental samples across approximately two-hour periods which were mixed and sub-sampled to produce three IBA, three APCr samples (and where separately collected, three boiler ash samples). The actual number of residue samples collected differed during trials to maximise the potential for achieving the project outcomes whilst reflecting operational constraints.

Upon discharge of the POPs feedstock onto the furnace grate via the waste hopper and associated feeding system, thermal degradation will occur at a rate based on a set of, interacting factors. As the POPs containing enhanced-POPs WEEE plastic has a significantly elevated calorific value when compared to typical municipal solid waste feedstock (or RDF), and a relatively small particle size and low moisture content, it was anticipated that degradation or volatilisation of POPs could occur at a relatively rapid rate when compared with total burn out time for the general. As the thermal degradation time is difficult to define, sampling began ahead of the time when the first signal in the outputs was considered possible to be observed.

In the case of the stack, APCr and boiler ash, that latency period is likely of the order of minutes once thermal degradation commences as the flue gas moves through the combustion and boiler system before entering the gas treatment system and forming APCr. Similarly, the cleaned flue gas is discharged to atmosphere shortly after exiting the flue gas treatment system. Therefore, sampling of the stack and APCr was commenced shortly before the material was expected to discharge into the furnace to ensure that any signal was captured.

IBA has a significantly longer latency period than the flue gases due to the combined residence times of the entire grate and ash discharge systems. Similarly to the approach suggested for the stack and APCr samples, IBA sampling was commenced at a time that a first signal was considered reasonably possible.

Table 2.3 shows the operator's assessment of the typical likely process retention times for the various stages of the waste feed, combustion process and residue discharge for each of the trial facilities. The actual retention time will vary slightly depending on the operating characteristics of each process such as hopper level, waste calorific value, plant load and IBA discharger capacity.

Table 2.3 Indicative process times for trial sites

Site	Hopper	Grate	IBA discharge
Site 1	Around 45 minutes	Around 45 minutes	Around 15 minutes
Site 2	15 to 30 minutes	40 – 70 minutes	Around 10 minutes
Site 3	Up to 30 minutes	Up to 2 hours	Around 2 hours

The IBA discharge system differed across the three sites. At Site 1 it was not possible to collect incremental samples directly from a discharge point, as the ash is discharged into a quench pit which does not allow access. Therefore, sampling had to be completed from a grab crane which collected a roughly 1 to 2 tonne sample for mixing and sub-sampling. At Sites 2 and 3 incremental sampling of the IBA was possible as the trial IBA was discharged onto the floor of the IBA hall.

2.5 Sampling Approach

2.5.1 Stack emission sampling

PCDD/F and PBDD/F

Stack sampling was undertaken by an MCERTS-accredited test house for dioxins and brominated dioxins in line with BS EN 1948 – “Stationary source emissions. Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs” and the recently updated Environment Agency (2022) Method Implementation Document (MID), v6 August 2022, the relevant section of which is shown below:

A sample stream of gas is extracted from the main gas stream at representative measurement points for a measured time period. The sample gas passes through a sample probe and particulate filter then through a condenser, and then through a solid absorber which capture the PCDD/F, PBDD/F and PCB compounds. The mass of these compounds is determined analytically and along with the measured sample volume is used to calculate the mass volume concentration ng/m^3 *of each compound. These mass volume concentrations can then be normalised to a single reference result in ng/m*^{3} *I-TEQ, by multiplying the individual concentrations by the associated toxic equivalent factors listed in MID 1948.*

An out of stack filtration arrangement was used, where the sampling filter was located externally, downstream of the sampling probe, and was also heated to a temperature which prevented condensation of the gas stream.

The standard method, EN 1948, applies to sampling of samples for chlorinated dioxins, however the method was also applied to brominated dioxins as detailed in MID 1948. Analysis methods for PBDD/F remain developmental and therefore not currently fully accredited. The contracted specialist analytical laboratory used the current standard analytical approach for PBDD/F in accordance with the Environment Agency’s implementation guidance, MID 1948, to achieve the project outcomes. The method used was identical to that used for meeting PBDD/F monitoring requirements within current energy from waste environmental permits.

At each facility, one stack sample was taken under the baseline on Day 1 and another during the POPs addition trial on Day 2. The stack sampling duration was around six hours to achieve the desired limits of detection.

Chlorofluorocarbons and related halogenated organic compounds

One set of samples were collected at each site during the enhanced-POPs WEEE plastic addition. The samples were screened for CFCs and related volatile organic compounds (VOCs) which may be produced as partial degradation products of chlorinated and fluorinated organic compounds in the waste. At Sites 2 and 3, baseline operational VOC samples were also collected. Monitoring was undertaken using charcoal sorbent tubes following the MCERTS approved method CEN TS 13649 – “Determination of the mass concentration of individual gaseous organic compounds - Sorptive sampling method followed by solvent extraction or thermal desorption.”

2.5.2 IBA sampling

IBA sampling was undertaken during both the baseline testing (Day 1) and the POPs addition trial (Day 2). Three IBA samples were taken during an approximate six-hour window according to the stack testing and offset by a site-specific time period to account for the longer process retention time for IBA relative to flue gases and APCr.

Particular attention was given to the overall retention time of IBA on each site on Day 1, the baseline day on each site, so that IBA collection was optimised during the POPs addition trials on Day 2. The first sample collection period for IBA began around the time the POPs addition to the hopper is expected to have completed its journey through the system.

Sampling was undertaken in accordance with the core principles of the existing ESA IBA protocol and varied slightly across the three sites for operational reasons. Each IBA sample was produced in two stages:

- incrementally sampling the IBA over a 90 to 120 minutes period to generate a composite sample of approximately 200 kg.
- coning and quartering of the combined incremental samples to produce a ~40 kg sample which was sent to the WRc laboratory for further preparation ahead of analysis.

Where IBA was discharged into a bunker or produced at a multi-line facility (Site 1) the sampling approach was adapted to best meet project objectives whilst considering on site practicalities as well as health and safety requirements for sample collection. The details of each site-specific approach are described in Section 3.

Following sampling, all samples were placed in 10 litre buckets and sent to the WRc laboratory for further preparation in line with the core principles of the ESA (2018) IBA protocol. Sub-sampling was undertaken on the ~40 kg sample to produce a 20 kg sample for drying at 30ºC. Upon completion of sample drying, several sorting and particle size reduction steps were carried out to produce test samples for analysis.

2.5.3 APCr sampling

APCr sampling and analysis followed a similar general philosophy to the IBA sampling. There were additional considerations for sampling APCr:

- APCr is generally transported from the abatement system to a large silo for temporary storage ahead of removal from site by tanker. Sites may have one or more silos which service all operational lines. APCr silos are filled from the top and emptied from the bottom and are therefore stratified to some degree and obtaining a representative sample of APCr over the circa six-hour duration of a POPs addition trial particularly challenging. For that reason, silo sampling was avoided where possible, with the exception of Day 1 at Site 3 where a temporary mechanical failure prevented use of the bypass valve. This was resolved for the enhanced POPs addition on Day 2.

- APCr is hazardous and access to appropriate sampling locations required more manual and non-routine intervention than IBA sampling. Most sites have an APCr silo “bypass discharge” for use in non-routine operational circumstances which was the preferred location for APCr sampling as it allowed direct access to the APCr being generated prior to the silo.

The details of APCr sampling on each site are provided in Section 3.

2.5.4 Boiler ash Sampling

At two of the trial facilities (Sites 2 and 3) boiler ash was collected along with the IBA. In terms of sampling that means that the boiler ash was captured in the IBA as the waste streams are mixed together ahead of final discharge (where sampling was completed). In contrast, at Site 1, boiler ash was separated and subsequently discharged into the APCr silo. As sampling was completed at a point prior to discharge into the silo, it was necessary to sample the boiler ash in order the complete the mass balance for destruction efficiency determination. Boiler ash was collected in parallel with APCr as process transit times were believed to be similar.

2.5.5 Enhanced POPs WEEE plastic infeed

Enhanced-POPs WEEE plastic from a reputable processor who participated in previous POPs in the EA mixed WEEE study (WRc 2022) was delivered to WRc. The material was the BFR rich fraction which originated from FPD / CRT WEEE.

This material was divided into three batches, one for each site, based on the volume of material calculated to be used in each POPs trial. From those three batches, composite samples were taken for analysis. Therefore, the samples analysed include material taken form the specific WEEE plastic used in each of the three trials. Three composite samples were produced from each of the batches (a total of nine samples) which were analysed by XRF to determine total bromine. The samples were then cryogenically milled to produce a fine particle size test sample for laboratory analysis to determine concentrations of brominated flame retardants, including polybrominated diphenyl ethers (PBDEs) and TBBPA.

2.6 Analytical Suites

Figure 2.1 provides a summary of the testing approach for stack and solid residue samples taken during the baseline and POPs trials. All samples were analysed for key parameters including dioxins and furans (both chlorinated and brominated). All solid residue samples were analysed to determine concentrations of brominated flame retardants.

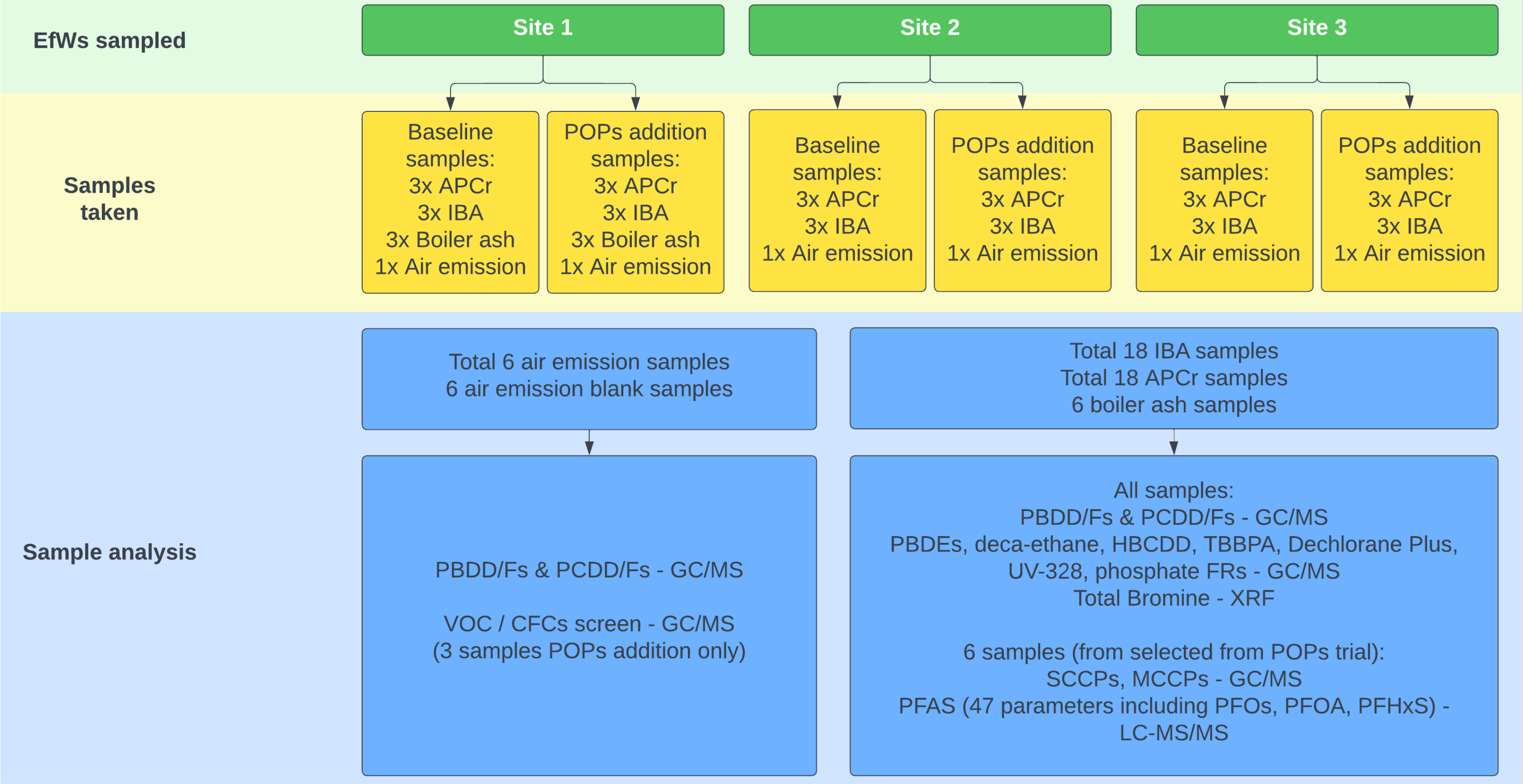
Due to the high temperatures and long retention times for flue gases in an EfW furnace (>850 ^{0}C for >2 seconds) there was no realistic possibility of unreacted BFRs being present in the post-treatment flue gas, as they are known to thermally degrade at temperatures around 450^{0}C. Therefore, the focus was on identifying partial products of combustion such as PCDD/F and PBDD/F in flue gases. Any unreacted BFRs would be expected to be present in the APCr.

IBA, APCr and boiler ash residues were analysed for a range of BFRs including PBDEs, HBCDD and TBBPA, which were expected to be present in the enhanced-POPs WEEE feedstock and therefore to subsequently form the basis of destruction efficiency calculations. Dechlorane Plus, UV328 and phosphate flame retardants were also included in the solid residue analytical suite. The full list of analytes is shown in the supporting addendum report.

One ‘set’ of IBA and APCr were analysed for concentrations of SCCPs, MCCPs and PFAS during the enhanced-POPs WEEE addition trial on Day 2 at each site. It was considered unlikely that these parameters would be found at concentrations above the limit of detection, as indicated based on previous analysis of thermal treatment residues by WRc during 2022 – 2023. As it was not possible to create a POPs addition scenario for SCCPs, MCCPs and PFAS in the same way it is possible for BFRs, the focus for those parameters was on identifying concentrations in the process outputs, rather than the calculation of a destruction efficiency.

XRF scanning was also undertaken by WRc on each solid residue sample to determine the indicative bromine concentration present in the solid residues. The external analytical laboratory also undertook XRF scanning of the sample residues prior to undertaking full sample preparation and detailed chemical analysis.

Figure 2.1 Monitoring approach summary



Sample preparation

1. Preparation of mixed plastic samples delivered to the WRc laboratory was completed using the following steps:
2. A series of incremental samples were collected from each “dumpy” bag. The incremental samples were then mixed into a composite and sub-sampled to produce a 1 kg laboratory sample.
3. Three individual sub-samples were taken from the 1 kg laboratory sample and these were analysed using a handheld XRF scanner.
4. Each sample was milled using cyclone-assisted cryogenic milling to produce a test sample of <1mm. The cyclone reduces the temperature generated during shredding by circulating air rapidly through the system while the samples were frozen cryogenically prior to the shredding. Milling using this method reduces the risk of degradation to the samples by heat that could be generated during the milling process. This sample was sub-sampled and sent to the test facility where further milling was undertaken to produce a sub-micron sample.
5. Following sample preparation each milled composite sample was analysed by XRF to determine the elemental concentrations prior to quantitative gas chromatography – mass spectrometry (GC-MS) analysis for PBDEs, and other brominated flame retardants.

XRF analysis

XRF scanning was undertaken using a Bruker S1 Titan analyser to determine the concentration of bromine. A mode specifically calibrated for mixed ash materials (geo-exploration) does not include analysis of bromine. Therefore ‘restricted materials’ mode was used to provide a bromine determination, although this mode is typically more suited for analysis of polymer materials. All solid residue samples were analysed three times using a scan period of 30 seconds to provide a suitable level of confidence in the determined concentration. XRF analysis of all samples was also completed by the laboratory completing the quantification of brominated flame retardants to provide confidence in the results.

2.6.2 Dioxins and furans

Testing was undertaken by Marchwood Scientific Services (MSS) who hold ISO 17,025 accreditation for dioxin and furan analysis of air and point source emissions samples. The accreditation was issued by the United Kingdom Accreditation Service (UKAS), Laboratory Number 1668, and refers to thermal residues and stack emission testing by high resolution GC-MS. The upkeep of accreditation is based on continually entering PT schemes such as EURL, NIPH, BIPEA, InterCIND, LGC and INERIS. Further details are provided in the supporting addendum report.

2.6.3 Brominated flame retardants

Fraunhofer IVV have been testing POP chemicals since 1999. Fraunhofer adopt a flexible approach to test for these chemicals and adapt the method according to the analytical needs and matrix using techniques which include gas chromatography (GC)-quadrupole mass spectrometry (MS), gas chromatography – high resolution mass spectrometry (GC-HRMS), liquid chromatography – mass spectrometry (LC-MS/MS) and where appropriate they use X-ray fluorescence (XRF) to check bromine extraction efficiences. Fraunhofer IVV is recognised as a world leader in PBDE analysis. It has been involved in pan-European interlaboratory assessments for PBDE analysis to ensure quality. Further details are provided in the supporting addendum report.

2.6.4 Per and polyfluorinated alkyl substances

Per and polyfluorinated alkyl substances (PFAS) analysis on the solid residues was undertaken by MSS using LC-MS/MS. The method quantities 34 selected PFAS, from 7 different groups, using LC-MS/MS. This method has been developed by MSS and is based on the US EPA method 537.1 v2.0 and draft method 1633. Further details are provided in the supporting addendum report.

2.6.5 Supporting data requirements

To assess the representativeness of each site's operational characteristics on the days of the trial, operational data from the distributed control system (DCS) and continuous emissions monitoring systems was acquired.

The information collected from existing automatic systems as well as from site management during the sampling period comprised:

- Actual stack flow rate.
- Flue gas temperature.
- Flue gas pressure.
- Flue gas water vapour content.
- Flue gas static pressure.
- Flue gas oxygen concentration (including whether wet or dry measurement).
- Relevant continuously monitored emissions parameters to demonstrate the plant is operating normally
- Input POPs mass data, feed rate (mass) and dosing times.
- Quantity of lime consumed and quantity of APCr generated during the trial period. APCr recirculation rate and steam injection rates (if available).
- Quantity of waste processed and quantity of IBA generated during the sampling period.
- Details of any relevant deviations from normal operating conditions immediately before or during sampling.

3. Site-Specific Approach

This section provides a basic general description of each of the three UK EfW facilities that participated in the trial and details the specific technical monitoring and sampling approach taken at each site.

3.1 Site 1 Trial

3.1.1 General description

Site 1 is a modern, R1-compliant, mass-burn, moving grate EfW based on technology provided by Hitachi Zosen Innova (HZI), a well-established participant in the UK and EU EfW market. The site burns predominantly household / Local Authority-collected waste along with very minor contribution from commercial and industrial wastes and a very small quantity of clinical waste.

In 2023, the line under test reported an operational availability of 98.1% with an average waste throughput of 18.1 t/h at a net CV of 9.0 MJ/kg, giving an average MCR of 98.4%. The site's annual average IBA production rate was 24.5% of the waste combusted and the annual average APCr production rate was 3.3% of the waste combusted. The APCr production rate includes the separately collected boiler ash as they are consigned together for disposal/recovery.

Stack sampling was carried out at the dedicated indoor sampling location used for routine compliance monitoring. The sampling location was compliant with the requirements of Environment Agency (2022), Guidance Monitoring stack emissions: measurement locations, December 2022 and had been previously assessed as meeting the homogeneity requirements of BS EN 15259: 2009.

3.1.2 Operating conditions

The plant was reported to be operating normally on both days of the trial. The site was fully compliant with the continuous monitoring permit requirements on both days. Continuous emissions monitoring data for the days of the trial along with 2023 averages are shown in the supporting addendum report.

Waste throughput, the net calorific value (CV) of the waste fuel being burned, the plant load and APCr production rates were consistent over the 2 days of the trial and representative of normal operational ranges (Table 3.1). The IBA production was provided by site operations for trial days. The maximum 30-minute impact of the enhanced-POPs WEEE addition on the CV of the process was 0.19 MJ/kg (2.1%). Quantities of APCr and boiler ash are determined form the long-term average production rate (3.3%), partitioned between APCr and boiler ash in the ratio 2:1, based on the average APCr production rates of the 2 other sites in the trial which do not collect boiler ash separately and have average APCr production rates of 2.2% of waste throughput.

Table 3.1 Plant operational profiles during test (Site 1)

Date	Waste processed (t/h)	Net CV (MJ/kg)	MCR (%)	Daily APCr produced (t)	Daily IBA Produced (t)	Daily BA Produced (t)
28/11/2023	19.0	9.2	105	10.0	80 t	5.0
29/11/2023	19.7	9.0	107	10.4	85 t	5.2

3.1.3 Day 1 baseline

The baseline trial period was aligned with the stack sampling period of six hours. Incremental samples of each of the three residues were taken over a two-hour period to produce three samples covering the whole six-hour stack monitoring period. The residue sampling was completed as follows:

IBA: At Site 1 IBA was discharged into a quench pit which was cleared frequently by a grab crane and discharged into a truck for removal from the site (Photograph A.3 in the supporting addendum report). During the two-hour sampling period, the grab crane did not clear the quench pit and IBA accumulated throughout. Over each two-hour period several tonnes of IBA accumulated in the quench pit. At the end of each two-hour period, the grab crab was used to mix the accumulated IBA by picking up and discharging the IBA a number of times. Then, the grab crane took a single several tonne grab of IBA which was then transferred to the discharge area to be used for sampling. From the grab crane, several hundred kilos of material were discharged (Photograph A4). That material was then coned and quartered by the on-site team to produce the sample covering the two-hour sampling period.

APCr: A small port was fitted to the flue gas treatment system below the baghouse filters (Photograph A5) which allowed for sampling to be completed frequently without associated health and safety concerns related to exposure to APCr. A tool was inserted into the sampling port which could collect a small sample of APCr, around 20 – 50 g. Due to the small sample volume, APCr sampling was completed every 15 minutes throughout the trial. Every 15 minutes the sampling tool was inserted into the sampling port until full and this was repeated at least three times. As such, the volume of APCr taken throughout the two-hour period was lower but due to the high number of increments taken frequently, the particles within the sample were representative of the entire sampling period. This process was repeated to produce three samples matching the six-hour stack sampling period.

Boiler ash: Boiler ash at Site 1 could be manually diverted by a valve into a ‘dumpy bag’. The discharge rate of the boiler ash was relatively consistent although some variations were observed throughout the sampling period. Therefore, the on-site sampling team worked closely with site personnel to manually divert the boiler ash into the bag for a period of roughly 1-2 minutes, depending on the discharge rate which was monitored throughout. Using this approach, the diversion was engaged every 30 minutes to produce an increment of several kilograms. At the end of the two-hour sampling period, the increments in the bag were thoroughly mixed and then a sub-sample taken. It was not possible to include higher frequency increments as the diversion required communication with control room as well as the sampling team in multiple different areas. Those factors made it impractical for the sampling team to manage high frequency APCr sampling alongside IBA sampling and manual control of the boiler ash diversion.

3.1.4 Day 2 enhanced-POPs WEEE addition trial

Sampling during the Day 2 enhanced POPs WEEE addition trial followed the same approach as during the Baseline trial, with some important distinctions. The enhanced POPs WEEE plastic was delivered to Site 1 in 24 small bags of around 7.5kg each. At Site 1 it was not considered practical to add the enhanced POPs WEEE plastic into the hopper by the grab cranes. An access area was available which meant that the site personnel could manually add the material directly to hopper. This was advantageous as it meant that more frequent POPs additions could be made throughout the trial meaning that the chance of capturing matched IBA, APCr and boiler ash samples was increased. Therefore, every 30 minutes, 15 kg of enhanced POPs containing WEEE plastic was added into the hopper. The POPs trial began immediately following the first addition.

Key latency times were identified as the time between the material added to the hopper prior to discharge to the furnace, the furnace transit time, the flue gas transit time and the IBA transit time. These latency times were discussed with site personnel to identify when stack, APCr, boiler ash and IBA sampling should commence.

Stack, APCr and boiler ash sampling all commenced 30 minutes after the first POPs addition to the furnace. The sampling was completed according to the same method outlined for the baseline trial. Due to a relatively long discharge period, IBA sampling (i.e. the time IBA was left to accumulate in the quench pit) began 90 minutes after the first POPs addition. After six hours, all POPs material had been added to the process, but the stack monitoring as well as solid residue sampling periods continued to complete the full six-hour period, accounting for the latency times.

3.1.5 Stack emission monitoring

Details of the emissions testing for both days of the trial together with the relevant applicable standards, as reported by the test house are presented in the addendum report. Stack gas temperatures, moisture, oxygen and velocities were recorded and found to be within the normal anticipated ranges. No deviations from the specified sampling methods were identified by the test house during the emissions sampling campaign.

Periodically measured PCDD/F concentrations in 2022 and 2023 (reported as I-TEQ) averaged 0.0021 ng/m^3 and 0.00078 ng/m^3 respectively. No routine PBDD/F measurements were reported in 2022 or 2023.

3.2 Site 2 Trial

3.2.1 General description

Site 2 is a modern, R1-compliant, mass-burn, moving grate EfW based on technology provided by CNIM, a major established participant in the UK and EU EfW market. The site burns almost exclusively household / Local Authority-collected waste along with a very small contribution from commercial and industrial wastes.

In 2023, the line under test reported an operational availability of 89.2% with an average waste throughput of 22.6 t/h at a net CV of 8.5 MJ/kg, giving an average MCR of 101%. The site's annual average IBA production rate was 21.0% of the waste combusted and the annual average APCr production rate was 2.4% of the waste combusted.

Stack sampling was carried out at the dedicated indoor sampling location used for routine compliance monitoring. The sampling location is compliant with the requirements of Environment Agency (2022) and had been previously assessed as meeting the homogeneity requirements of BS EN 15259: 2009.

3.2.2 Operating conditions

The plant was reported to be operating normally on both days of the trial. The site was fully compliant with the continuous monitoring permit requirements on both days. Monitored SO_2 concentrations were observed to be relatively high on both days of the trial when compared with long-term averages. However, it is not expected that the relatively high SO_2 concentrations will impact on test data as the key continuously monitored determinands carbon monoxide (CO), total volatile organic compounds (VOC), oxygen (O_2) and plant temperatures indicate that combustion conditions were normal. Continuous emissions monitoring data for the days of the trial along with 2023 averages are presented in the addendum report.

Waste throughput, the net calorific value of the waste fuel being burned, the plant load and APCr production rates were consistent over the 2 days of the trial and representative of normal operational ranges (Table 3.2). APCr production rates on both days seemed to be lower than the long-term averages derived from annual waste returns. IBA production was not specifically measured at the site. Although the weighbridge records quantities of IBA leaving site, it does not account for daily variations in the quantity temporarily stored on site therefore the IBA production rate has been estimated from the long-term weighbridge records as a proportion of waste combusted. The maximum 30-minute impact of the enhanced-POPs WEEE addition on the CV of the process was 0.29 MJ/kg (3.4%).

Table 3.2 Plant operational profiles during test (Site 2)

Date	Waste processed (t/h)	Net CV (MJ/kg)	MCR (%)	Daily APCr produced (t)	Estimated Daily IBA Produced (t)
22/11/2023 (Day 1)	22.3	8.10	101	13.03	21.4% x 22.3 x 24 = 114.0
23/11/2023 (Day 2)	22.3	8.16	102	13.03	21.4% x 22.3 x 24 = 114.0

3.2.3 Day 1 baseline

APCr sampling on Day 1 of the trial was carried out using the non-routine bag filter outlet diverter system connected to a “dumpy” bag. When samples were required, the diverter valve was operated and the used APCr diverted from the silo into the dumpy bag. The “dumpy” bag was manually sampled with a shovel and placed in 10 l buckets of approximately 2 – 3 kg each. Limited control of the APCr flow rate into the “dumpy” bag was possible during manual diversion therefore the samples were collected as a series of extended spot samples. Three samples were collected at 10:30, 16:00 and 16:30, corresponding to samples numbers W15609, W15610 and W15611.

IBA sampling was carried out in the IBA hall. The IBA hall floor below the conveyor was mechanically cleared and the IBA pile allowed to accumulate for ~2 hours. Each pile was then moved by machine and sub-sampled in accordance with the core principles of the existing ESA IBA protocol to generate an intermediate composite sample of approximately 200 kg before coning and quartering of the combined incremental samples to produce three ~40 kg baseline samples (coded by WRc as W15606, W15607 and W15608).

3.2.4 Day 2 enhanced-POPs WEEE addition trial

The enhanced-POPS WEEE plastic addition was undertaken by placing the large bags containing the enhanced-POPs WEEE plastic into the waste bunker and lifting them into the feed hopper with the crane. Three additions were carried out at 09:28, 12:01 and 13:35 on Day 2. Photographs of the addition are presented in the addendum report.

APCr sampling on Day 2 of the trial was carried out using the same method as Day 1. Three sets of samples were collected at 10:30, 16:00 and 16:30, corresponding to samples numbers W15615, W15616 and W15617. Three composite IBA samples were collected in the same manner as Day 1. IBA was accumulated between 11:15 – 13:15, 13:15 – 15:15 and 15:15 – 17:15, before being placed to the side by machine and manually sub-sampled, to give composite samples W15612, W15613 and W15614.

3.2.5 Stack emission monitoring

Details of the emissions testing for both days of the trial together with the relevant applicable standards as reported by the test house are presented in the addendum report. Stack gas temperatures, moisture, oxygen and velocities were recorded and found to be within the normal anticipated ranges. No deviations from the specified sampling methods were identified by the test house during the emissions sampling campaign.

Periodically measured PCDD/F concentrations in 2022 and 2023 (reported as I-TEQ) averaged 0.0045 ng/m^3 and 0.011 ng/m^3 respectively. No routine PBDD/F measurements were reported in 2022 or 2023.

3.3 Site 3 Trial

3.3.1 General description

Site 3 is a modern, R1-compliant, mass-burn, moving grate EfW based on technology provided by an established participant in the global EfW market with a minor presence in the UK. The site burns predominantly household / local authority-collected waste along with a smaller contribution from commercial and industrial wastes and some offensive waste from healthcare.

In 2023, the line under test reported an operational availability of 88.5% with an average waste throughput of 11.0 t/h at a net CV of 8.89 MJ/kg, giving an average MCR of 98%. The site’s annual average IBA production rate was 21.0% of the waste combusted and the annual average APCr production rate was 2.0% of the waste combusted.

Stack sampling was carried out at the dedicated indoor sampling location used for routine compliance monitoring. The sampling location was compliant with the requirements of Environment Agency (2022) and had been previously assessed as meeting the requirements of BS EN 15259: 2009. No significant deviations to the specified sampling approaches were undertaken during either day of the trial due to the sampling location.

3.3.2 Operating conditions

Site 3 was reported to be operating normally on both days of the trial. The site was fully compliant with the continuous emissions monitoring permit requirements on both days. Periodically elevated SO_2 emissions were observed on Day 2 and these have been attributed to a specific waste stream unrelated to the trial. Continuous emissions monitoring data for the days of the trial along with 2023 averages are presented in the supplementary addendum report.

Waste throughput, the net calorific value of the waste fuel being burned, the plant load and APCr production rates (Table 3.3) showed some variation over the 2 days of the trial. The variation in CV of the input fuel seemed to be the main factor behind the observed changes, varying by ±8% from the long-term average of 8.89 MJ/kg over the 2 days.

IBA production was not specifically measured at the site. Although the weighbridge does record quantities of IBA leaving site, it does not account for daily variations in the quantity temporarily stored on site therefore the IBA production rate has been estimated from the long-term weighbridge records as a proportion of waste combusted. APCr production was higher on Day 2 of the trial due to increased lime dosing for operational SO_2 management. The maximum 30-minute impact of the enhanced-POPs WEEE addition on the CV of the process was 0.24 MJ/kg (2.7%).

Table 3.3 Plant operational profiles during test (Site 3)

Date	Waste processed (t/h)	Net CV (MJ/kg)	MCR (%)	Daily APCr produced (t)	Estimated Daily IBA Produced (t)
20/11/2023 (Day 1)	11.0	9.68	106.8	5.09	21.0% x 11.0 x 24 = 55.5
21/11/2023 (Day 2)	12.1	8.35	100.8	7.51	21.0% x 12.1 x 24 = 61.0

3.3.3 Day 1 baseline sampling

On Day 1, baseline samples of APCr were collected from the APCr silo outlet by the APCr tanker driver as the APCr diverter valve was non-operational. Three samples were collected between 17:00 and 18:00, corresponding to samples numbers W15594, W15595 and W15596.

IBA sampling was carried out in the IBA hall. The accumulating pile was moved by machine and manually sub-sampled 3 times between 16:30 and 20:00 in accordance with the core principles of the existing ESA IBA protocol to generate an intermediate composite sample of approximately 200 kg before coning and quartering of the combined incremental samples to produce three ~40 kg baseline samples, W15591, W15592 and W15593.

3.3.4 Day 2 Enhanced-POPS WEEE addition trial

The enhanced-POPS WEEE plastic addition was undertaken by lifting the enhanced-POPs WEEE plastic bags directly from the crane maintenance bay into the feed hopper with the crane. Three additions were carried out at 11:25, 12:15 and 12:57 on Day 2 (and shown in the addendum report).

APCr sampling on Day 2 of the trial was carried out using the non-routine bag filter outlet diverter system connected to a “dumpy” bag. When samples were required, the diverter valve was operated and the used APCr diverted from the silo into the dumpy bag. The “dumpy” bag was manually sampled with a shovel and placed in 10 l buckets of approximately 2 – 3 kg each. No significant control of the APCr flow rate into the “dumpy” bag was possible during manual diversion therefore the samples were collected as a series of spot samples. Three composite samples were collected between 12:15 - 12:30, 13:00 - 13:12 and 14:02 – 14:11, corresponding to samples numbers W15600, W15601 and W15602.

The IBA hall floor below the conveyor was cleared at the identified time and the IBA pile allowed to accumulate for ~90 minutes. Each pile was then moved by machine and sub-sampled to generate a composite sample of approximately 200 kg before coning and quartering of the combined incremental samples to produce a ~40 kg sample. Three composite IBA samples were collected from 15:00 – 16:30, 16:30 – 18:00 and 18:00 – 19:30, corresponding to samples numbers W15597, W15598 and W15599.

Due to the relatively long anticipated retention time of IBA in the ash discharger at the site, a modified alloy wheel was placed in each bag of plastic feed for use as a marker of the transit of IBA through the process. The addendum report shows a photograph 2 of the alloy wheels in the oversize bin at the end of the ash discharger on Day 2, indicating that the IBA sampling was reasonably well aligned with the waste retention time through the entire hopper, grate and ash discharge systems. A third wheel was observed in the IBA hall during sample collection.

3.3.5 Stack emission monitoring

Details of the emissions testing for both days of the trial together with the relevant applicable standards as reported by the test house are presented in the addendum report. Stack gas temperatures, moisture, oxygen and velocities were recorded and found to be within the normal anticipated ranges. No deviations from the specified sampling methods were identified by the test house during the emissions sampling campaign. Periodically measured PCDD/F concentrations in 2022 and 2023 (reported as I-TEQ) for the site averaged 0.0018 ng/m^3 and 0.0015 ng/m^3 respectively. No routine PBDD/F measurements were reported in 2022 or 2023.

3.4 Approach Limitations

The available project timeframe presented a significant limitation to the approach which could be adopted for the analytical programme. Use of bromine rich WEEE plastic over WUDS was agreed between WRc and the Enviironment Agency / Defra following an initial methodology review as well as discussions between WRc and several EfW operators. As highlighted in Section 2, WUDS was not considered an appropriate material for a POPs trial due to the extremely large quantities that would be required to ensure input of a sufficient and measurable concentration of BFRs into the process. Previous analysis of WEEE plastic, particularly from CRT and FPD material, indicated that post-separation polymer would provide a more consistent source of BFRs than WUDS where many units may contain no BFRs. However, post-separation bromine rich WEEE specifically derived from CRT is no longer a high-volume waste stream and typically is produced only periodically by operators managing WEEE separation processes. Around 800 kg of bromine rich CRT/FPD WEEE was sourced in a period of three weeks to meet the deadline of the start of the three trials at the EfWs. Sourcing a significantly larger volume of bromine rich WEEE would have likely required a much longer timescale as the material is collected batch-wise as it is received. To add 10 or 20 times more bromine rich WEEE plastic to significantly increase the input signal of BFRs we would have needed a period of months to source the input plastic. It was not possible to get the analysis on the BFR rich plastic back ahead of use in the trial and it was assumed that it would be similar to testing undertaken for the EA in 2021. In reality, the concentration of BFRs were lower in the batch of material received.

Laboratory analysis to determine the concentrations of POPs in each of the 48 solid residue samples was completed between January and February 2024. That time scale included initial instrument calibration and validation to ensure methods were appropriate for the matrix and that determined concentrations of POPs were valid. Detection limits (and therefore quantification limits) could be targeted for high sensitivity analysis for samples where the concentration is known to be extremely low. Significantly lower limits of detection (and quantification) by a factor of 200 - 500 could be achieved through use of high-resolution GC-MS, specifically Sector Field Mass Spectrometry. However, use of this technique comes with additional issues relating to the much smaller linear range and robustness as well as requirements for a more sophisticated clean-up method. The time limitations around the analysis, coupled with the fact that the initial concentrations of BFRs in the ash samples were unknown, meant that it was not possible to employ more sensitive analytical methods. However, WRc are in discussions with the analytical laboratory and it may be possible for further analysis to significantly improve upon the limits of detection / quantification for several samples (which would require further analysis). A significant improvement in the limits of detection / quantification would allow for calculation of the POPs destruction efficiency to a greater resolution.

4. Monitoring Results

This section summarises the results of analysis of solid residues and flue gases undertaken in this project. The detailed analytical results are presented in the supporting addendum report.

4.1 Site 1

XRF scanning of the Site 1 composite residues following sample preparation was undertaken by WRc and again by Fraunhofer before detailed chemical analysis was carried out. There is very good agreement between the scans. IBA was found to contain low levels of bromine on both days of the trial. There were significant concentrations of bromine present in APCr on both days of the trial but no significant difference between the baseline and POPs addition days. Boiler ash showed intermediate levels of bromine, and indicatively higher concentrations during the addition of enhanced-POPs WEEE plastic on Day 2 (Table 4.1).

Table 4.1 Summary of Br content by XRF for Site 1 solid residues

Br by XRF (mg/kg)	IBA		APCr		BA	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
WRc	ND	ND	3209	3412	305	483
Fraunhofer	11	11	2916	3089	388	537

Table 4.2 summarises the key PCDD/F and PBDD/F results from stack emissions testing on both days of the trial. Similar very low levels of PCDD/F and PBDD/F were present on both test days. The total mass of both PCDD/F and PBDD/F was observed to be slightly lower on Day 2 of the trial. For comparison, the PCDD/F (as I-TEQ) monitoring results obtained during the trial (as presented in the addendum report) were well below the permitted limits at 0.0011 ng/m^3 (Day 1) and 0.00076 ng/m^3 (Day 2). No routine PBDD/F measurements were reported in 2022 or 2023.

Table 4.2 Key stack emission monitoring results (Site 1)

Parameter	Unit	Result	Uncertainty	Date	Times	Standard
PCDD/F	ng/m^3	0.0199	0.00017	28/11/2023	10:30-16:30	EN1948:2006
PCDD/F	ng/m^3	0.0113	0.00012	29/11/2023	09:44-15:44	EN1948:2006
PBDD/F	ng/m^3	0.0244	0.00013	28/11/2023	10:30-16:30	EN1948:2006
PBDD/F	ng/m^3	0.00902	0.000096	29/11/2023	09:44-15:44	EN1948:2006

The detailed analytical results can be found in the supporting addendum report. Measurements of chlorofluorocarbons, chlorocarbons and fluorocarbons by the sorbent-tube method, TS13649 made on Day 2, the enhanced-POPs WEEE plastic addition day, of the trial showed none were present above the limits of detection (29.1 mg/m^3).

No BFRs, Dechlorane Plus, UV-328 or phosphate flame retardants were identified in any of the APCr, IBA or boiler ash samples collected on either day of the trial (as detailed in the supporting addendum report).

Analysis of PCDD/Fs and PBDD/Fs in baseline APCr samples on Day 1 gave concentrations of 1,551 ng/kg and <309 ng/kg respectively. The corresponding analyses on samples collected on Day 2 were 1,390 ng/kg and 234 ng/kg.

Analysis of PCDD/Fs and PBDD/Fs in baseline IBA samples on Day 1 gave concentrations of 112 ng/kg and 1,085 ng/kg respectively. Analysis of Day 2 IBA sampling gave concentrations of 94.6 ng/kg and 1,055 ng/kg.

Analysis of PCDD/Fs and PBDD/Fs in baseline boiler ash samples on Day 1 gave concentrations of 812 ng/kg and 150 ng/kg respectively and 918 ng/kg and 68.8 ng/kg on Day 2.

Measured concentrations of PCDD/F and PBDD/F in all analysed residues were relatively consistent between the Day 1 baseline and Day 2 enhanced-POPs WEEE addition trials.

A single sample of APCr (W15661) and a single sample of IBA (W15658) from Day2 was analysed for SCCPs and MCCPs. Concentrations of both SCCPs and MCCPs were found to be below the limits of detection for both samples.

4.2 Site 2

XRF scanning of the Site 2 composite residues following sample preparation was undertaken by WRc and again by Fraunhofer before detailed chemical analysis was carried out. As with Site 1, there is very good agreement between the scans. IBA contained low levels of bromine on both days of the trial. Significant concentrations of bromine present in APCr on both days of the trial and there were indicatively higher concentrations during the addition of enhanced-POPs WEEE plastic on Day 2 (Table 4.3).

Table 4.3 Summary of Br content by XRF for Site 2 solid residues

Br by XRF (mg/kg)	IBA		APCr	
	Day 1	Day 2	Day 1	Day 2
WRc	23	21	3269	3879
FR	35	54	3315	3749

Table 4.4 summarises the key PCDD/F and PBDD/F results from stack emission testing on both days of the trial. Relatively low levels of PCDD/F and PBDD/F were present on both test days. The total mass of both PCDD/F and PBDD/F were observed to be higher on Day 2 of the trial when enhanced-POPs WEEE plastic was being added with the most highly halogenated furan congeners tended to dominate the observed mass. For comparison, the PCDD/F (as I-TEQ) monitoring results obtained during the trial (as presented in the addendum report) were well below the permitted limits at 0.00595 ng/m^3 (Day 1) and 0.0105 ng/m^3 (Day 2). No routine PBDD/F measurements were reported in 2022 or 2023.

Table 4.4 Key stack emission monitoring results (Site 2)

Parameter	Unit	Result	Uncertainty	Date	Times	Standard
PCDD/F	ng/m^3	0.0668	0.00093	22/11/2023	12:08-18:08	EN1948:2006
PCDD/F	ng/m^3	0.171	0.0017	23/11/2023	09:45-15:45	EN1948:2006
PBDD/F	ng/m^3	0.0258	0.00036	22/11/2023	12:08-18:08	EN1948:2006
PBDD/F	ng/m^3	0.0353	0.00015	23/11/2023	09:45-15:45	EN1948:2006

The detailed analytical results can be found in the supporting addendum report. Measurements of chlorofluorocarbons, chlorocarbons and fluorocarbons by the sorbent-tube method on Day 2, of the trial showed none were present above the limits of detection (17 – 34.9 mg/m^3).

No BFRs, Dechlorane Plus, UV-328 or phosphate flame retardants were identified in any of the APCr, IBA or boiler ash samples collected on either day of the trial (as detailed in the supporting addendum report).

Analysis of PCDD/Fs and PBDD/Fs in baseline APCr samples on Day 1 gave concentrations of 4,257 ng/kg and 223 ng/kg respectively. The corresponding analytical results on samples collected during enhanced-POPs WEEE addition on Day 2 were 1,446 ng/kg and 389 ng/kg.

Analysis of PCDD/Fs and PBDD/Fs in baseline IBA samples on Day 1 gave concentrations of 57.6 ng/kg and 953 ng/kg respectively. Analysis of Day 2 IBA sampling during enhanced-POPs WEEE addition gave concentrations of 61.0 ng/kg and 1446 ng/kg.

Measured concentrations of PCDD/F showed no consistent pattern between the Day 1 baseline and Day 2 enhanced-POPs WEEE addition trials. PBDD/F concentrations were higher in samples collected during enhanced-POPs WEEE addition on Day 2.

A single sample of APCr (W15616) and a single sample of IBA (W15613) from Day 2 were analysed for SCCPs and MCCPs. Concentrations of SCCPs were found to be below the limits of detection for both samples. MCCPs were detected at a concentration of 260 ng/g in the IBA sample whereas none were detected in the APCr sample.

4.3 Site 3

The results of XRF scanning of the Site 3 IBA and APCr undertaken by WRc and Fraunhofer are shown in Table 4.5. There is consistent agreement between the scans. As with Sites 1 and 2, IBA contained low levels of bromine on both days of the trial. APCr contained significant concentrations of bromine and significantly higher concentrations of bromine were observed on the baseline day, Day 1, when no specific addition of enhanced-POPs WEEE plastic was undertaken.

Table 4.5 Summary of Br content by XRF for Site 3 solid residues

Br by XRF (mg/kg)	IBA		APCr	
	Day 1	Day 2	Day 1	Day 2
WRc	ND	29	6468	2267
FR	35	65	5971	2160

Table 4.6 summarises the key PCDD/F and PBDD/F results from stack emissions testing on both days of the trial. Low levels of PCDD/F and PBDD/F were present on both test days. The total mass of both PCDD/F and PBDD/F were observed to be lower on Day 2 of the trial when enhanced-POPs WEEE plastic was being added. For comparison, the PCDD/F (as I-TEQ) monitoring results obtained during the trial (as presented in the addendum report) were well below the permitted limits at 0.00443 ng/m^3 (Day 1) and 0.00273 ng/m^3 (Day 2). No routine PBDD/F measurements were reported in 2022 or 2023.

The detailed analytical results can be found in the addendum report. Measurements of chlorofluorocarbons, chlorocarbons and fluorocarbons by the sorbent-tube method on Day 2, of the trial showed none were present above the limits of detection (19.7 – 20.6 mg/m^3).

Table 4.6. Key stack emission monitoring results (Site 3)

Parameter	Unit	Result	Uncertainty	Date	Times	Standard
PCDD/F	ng/m³	0.0466	0.00067	20/11/2023 (Day 1)	16:32-22:32	EN1948:2006
PCDD/F	ng/m³	0.0341	0.00042	21/11/2023 (Day 2)	11:18-17:18	EN1948:2006
PBDD/F	ng/m³	0.0711	0.00056	20/11/2023 (Day 1)	16:32-22:32	EN1948:2006
PBDD/F	ng/m³	0.0208	0.00022	21/11/2023 (Day 2)	11:18-17:18	EN1948:2006

No BFRs, Dechlorane Plus, UV-328 or phosphate flame retardants were identified in any of the APCr, IBA or boiler ash samples collected on either day of the trial (as detailed in the supporting addendum report).

Analysis of PCDD/Fs and PBDD/Fs in baseline APCr samples on Day 1 gave concentrations of 952 ng/kg and 158 ng/kg respectively. The corresponding analytical results on samples collected during enhanced-POPs WEEE addition on Day 2 were 447 ng/kg and 531 ng/kg.

Analysis of PCDD/Fs and PBDD/Fs in baseline IBA samples on Day 1 gave concentrations of 78.9 ng/kg and 398 ng/kg respectively. Analysis of Day 2 IBA sampling during enhanced-POPs WEEE addition gave concentrations of 234 ng/kg and 266 ng/kg.

Measured concentrations of PCDD/F showed no consistent pattern between the Day 1 baseline and Day 2 enhanced-POPs WEEE addition trials. PBDD/F concentrations were higher in APCr samples collected during enhanced-POPs WEEE addition on Day 2 and lower in IBA.

A single sample of APCr (W15601) and a single sample of IBA (W15598) from Day 2 were analysed for SCCPs and MCCPs. Concentrations of SCCPs were found to be below the limits of detection for both samples. MCCPs were detected at a concentration of 100 ng/g in the IBA sample whereas none were detected in the APCr sample.

5. Destruction Efficiency Determination

Quantifying the levels of destruction and irreversible transformation is essential in demonstrating compliance with the Stockholm and Basel Conventions. UNEP (2023) recognises that determining the levels of destruction and irreversible transformation for available treatment technologies is an issue due to the technical challenges involved.

The most frequently used measurement of POPs destruction is Destruction Efficiency (DE). DE is '*the percentage of originating POPs destroyed or irreversibly transformed by a particular method or technology*', UNEP (2023).

$$DE = \frac{M_{waste} - (M_{gas} + M_{liquid} + M_{solid})}{M_{waste}}$$

Where:

M_{waste} = mass of POPs substance in input waste

M_{gas} = mass of POPs substance in output gas emissions (flue gas)

M_{liquid} = mass of POPs substance in output liquid waste

M_{solid} = mass of POPs substance in output solid wastes (IBA, APCr and boiler ash)

Destruction Removal Efficiency (DRE) is another frequently used metric for POPs destruction and considers only emissions to air (UNEP, 2019). DRE is calculated by subtracting the remaining POP content in the gaseous residue /stack emissions from the mass of the POP content within the waste.

$$DRE = \frac{M_{waste} - M_{gas}}{M_{waste}}$$

UNEP (2023) reports that DREs >99.9% and even >99.999% have been reported for treatment of wastes consisting of, containing or contaminated with POPs.

Neither the DE nor the DRE as described in UNEP (2023) considers the partial products of combustion in stack or residues. This assessment includes the PBDD/F concentration of flue gases and solid residues in the assessment of DE and DRE by assuming that 1 BFR forms 1 PBDD/F congener. Due to the temperatures and retention times of the combustion process (T>850 °C for a minimum of two seconds) and the use of lime-activated carbon-based bag filtration systems, it was considered that there was no likelihood of detecting any unreacted BFRs in the treated flue gases above achievable limits of detection. The absence of detectable BFRs in all the IBA, APCr and boiler ash residue samples indicates that this assumption was robust.

For these trials, M_{waste} was assumed to be the measured concentration of specific BFRs present in the controlled quantity of enhanced-POPs WEEE plastic material added on Day 2 of the trials. A representative characterisation of the background BFR material within the normal waste stream (c 100 - 150 tonnes of residual waste) is technically challenging and beyond the scope of the study. The quantities of enhanced-POPs WEEE plastics added have been determined to not significantly change the normal operating ranges of calorific values of the waste combusted whilst containing sufficient target POPs to determine a destruction efficiency of ~99.9% based on current limits of detection of these materials in solid residues. The exact chemical composition of the enhanced-POPs WEEE plastic was initially estimated for planning the site trials and subsequently confirmed following laboratory analysis.

Therefore, the key variables in the DRE and DE calculations become:

M_{waste} = mass of POP substance in input enhanced-POPs WEEE plastic waste
M_{gas} = mass of PBDD/F in flue gas, corrected to mass of POP
M_{liquid} = 0 (as no liquid wastes are routinely produced)
M_{solid} = mass of POP substance + mass PBDD/F (as POP) in IBA, APCr and boiler ash

DE calculations are performed on two brominated flame retardants identified as being present in significant concentrations in the input enhanced-POPs WEEE plastics used during the POPs addition trial day on each facility - decaBDE and TBBPA.

Concentrations of brominated flame retardants were all below the limit of quantification (LoQ) in all samples. On advice from the testing laboratory the LoQ is 3 x LoD, therefore a concentration of 33.3% of the reported LoQ has been assumed for brominated flame retardants in all solid residues.

5.1 Calculation Variables

Input enhanced-POPs WEEE plastic: Samples of the WEEE plastic material were collected prior to the controlled feed into the incineration process to gather data on POP concentrations and characteristics. The samples have been analysed to determine the input concentrations (C_{waste}) of POPs. The mass of POPs input (M_{waste}) was therefore determined from the input concentrations and the mass of WEEE plastic added for each facility and 2 representative brominated flame retardants, decaBDE and TBBPA (Table 5.1).

$$M_{waste} = C_{waste} \times mass\ of\ WEEE\ plastic\ added$$

Output IBA: Samples of IBA were collected at appropriate time intervals based on the waste destruction times and IBA retention times at each site to determine the residual POP concentrations (C_{IBA}). The mass of POPs present in the IBA (M_{solid_IBA}) was calculated as the product of the mass of IBA produced in the sampling window and the residual POPs concentration. The calculation is shown in Table 5.2.

$$M_{solid\_IBA} = C_{IBA} \times M_{IBA}$$

Table 5.1 Mass of POPs input (M_{waste})

POP	Units	Site 1	Site 2	Site 3
C_{waste} DecaBDE	mg/kg	6,757	9,767	7,700
C_{waste} TBBPA	mg/kg	10,713	13,333	11,700
Mass of WEEE	kg	178.5	125.5	124.0
M_{waste} DecaBDE	**mg**	**1,206,065**	**1,225,717**	**954,800**
M_{waste} TBBPA	**mg**	**1,912,330**	**1,673,333**	**1,450,800**

Table 5.2 Mass of POPs in IBA (M_{solid_IBA})

IBA	Units	Site 1	Site 2	Site 3
Concentration of DecaBDE	mg/kg	0.027	0.026	0.026
Concentration of TBBPA	mg/kg	0.054	0.052	0.052
IBA produced	kg	21,250	28,500	1,5250
M_{solid_IBA} DecaBDE	**mg**	**567**	**728**	**390**
M_{solid_IBA} TBBPA	**mg**	**1,157**	**1,488**	**796**

Concentrations of PCDD/F and PBDD/F were generally very low across all site IBA samples. There was no discernible trend across the sites. PBDD/F concentrations in the IBA were approximately 10x higher than their chlorinated analogues at Site 1, ~200x higher at Site 2 and marginally lower at Site 3. The mass of each PBDD/F congener measured in IBA on Day 2 of the trial has been converted to an equivalent mass of each BFR assuming 1 PBDD/F congener is equivalent to 1 BFR. The "realistic maximum" concentration assumed has been based on assuming that all non-detected congeners are present at 50% of the LoD in all subsequent calculations of DE (Table 5.3).

Table 5.3 Mass of PBDD/F as POPs in IBA (M_{solid_IBA})

IBA	Units	Site 1	Site 2	Site 3
PCDD/F	ng/kg	94.69	60.99	234
PBDD/F	ng/kg	1,055	1,446	266
IBA produced	kg	21,250	28,500	15,250
PCDD/F	mg	2.01	1.74	3.57
PBDD/F	mg	22.43	41.20	4.06
<LOD = LOD/2				
M_{solid_IBA} PBDD/F as decaBDE	**mg**	**26.629**	**51.922**	**3.180**
M_{solid_IBA} PBDD/F as TBBPA	**mg**	**15.099**	**29.442**	**1.803**

Output APCr: Samples of APCr were collected at appropriate time intervals based on the waste destruction times and APCr retention times at each site to determine the residual POP concentrations (C_{APCr}). The mass of POPs present in the APCr (M_{solid_APCr}) was calculated as the product of the mass of APCr produced in the sampling window and the residual POPs concentration. Concentrations of brominated flame retardants were all below LoD therefore a concentration of 50% of the LoD has been assumed in subsequent DE calculations. Table 5.4 shows the POPs in APCr calculation.

$$M_{solid\_APCr} = C_{APCr} \times M_{APCr}$$

Table 5.4 Mass of POPs in APCr (M_{solid_APCr})

APCr	Units	Site 1	Site 2	Site 3
Concentration of DecaBDE	mg/kg	0.03	0.03	0.03
Concentration of TBBPA	mg/kg	0.07	0.07	0.07
APCr produced	kg	2,600	3258	1,878
M_{solid_APCr} DecaBDE	mg	**86.68**	**109**	**62.58**
M_{solid_APCr} TBBPA	mg	**173**	**217**	**125**

Concentrations of PCDD/F and PBDD/F were generally low across all site APCr samples. PBDD/F concentrations in the APCr were significantly lower than their chlorinated analogues at Sites 1 and 2 marginally lower at Site 3. The mass of each PBDD/F congener measured in APCr on Day 2 of the trial has been converted to an equivalent mass of each brominated flame retardant following a similar approach to IBA (Table 5.5).

Table 5.5 Mass of PBDD/F as POPs in APCr (M_{solid_APCr})

APCr	Units	Site 1	Site 2	Site 3
PCDD/F	ng/kg	1,390	6,126	467
PBDD/F	ng/kg	234	389	531
APCr produced	kg	2,600	3,258	1,878
PCDD/F	mg	3.61	19.96	0.88
PBDD/F	mg	0.61	1.27	1.00
LOD = LOD/2				
M_{solid_APCr} PBDD/F as decaBDE	**mg**	**0.452**	**1.307**	**0.749**
M_{solid_APCr} PBDD/F as TBBPA	**mg**	**0.257**	**0.741**	**0.425**

Output Boiler ash (Site 1 only): For operational reasons, samples of boiler ash were separately collected alongside APCr. The POPs concentrations (C_{BA}) were measured separately in boiler ash. The mass of POPs present in the boiler ash (M_{solid_BA}) was calculated as the product of the estimated mass of boiler produced in the sampling window and the residual POPs concentration.

$$M_{solid\_BA} = C_{BA} \times M_{BA}$$

On sites 2 and 3, the bulk of boiler ash was co-collected with IBA in accordance with normal operational practices. A portion of the lighter boiler ash fraction from the final passes and economiser are likely to end up in the APCr so any contribution from boiler ash is captured in the mass balance and destruction efficiency determination. No brominated flame retardants were detected in the boiler ash. Table 5.6 shows the calculations for boiler ash at Site 1.

Table 5.6 Mass of POPs in Boiler Ash (M_{solid_BA})

Boiler ash	Units	Site 1	Site 2	Site 3
Concentration of DecaBDE	mg/kg	0.03		
Concentration of TBBPA	mg/kg	0.07		
BA produced	kg	1,300		
M_{solid_BA} DecaBDE	mg	43.34		
M_{solid_BA} TBBPA	mg	86.68		

Concentrations of PCDD/F and PBDD/F were generally very low in the boiler ash samples. PBDD/F concentrations were significantly lower than their chlorinated analogues. The mass of each PBDD/F congener measured in boiler ash on Day 2 of the trial has been converted to an equivalent mass of each BFR for DE calculation as previously described for IBA and APCr (Table 5.7).

Table 5.7 Mass of PBDD/F as POPs in Boiler Ash (M_{solid_BA})

Boiler ash	Units	Site 1	Site 2	Site 3
PCDD/F	ng/kg	918		
PBDD/F	ng/kg	168		
BA produced	kg	1,300		
PCDD/F	mg	1.19		
PBDD/F	mg	0.22		
LOD = LOD/2				
M_{solid_BA} PBDD/F as decaBDE	**mg**	**0.144**		
M_{solid_BA} PBDD/F as TBBPA	**mg**	**0.082**		

Outputs flue gas: Flue gases were continuously sampled for an appropriate interval based on the waste destruction times, flue gas transit times and detection limit requirements:

$$Air\ Emissions\ POPs\ (Mgas) = Flowrate\ (ref)\ X\ emissions\ concetration\ (ref)\ X\ sampling\ duration$$

Concentrations of PCDD/F and PBDD/F measured in the flue gas were low on all sites. The contribution of PBDD/F in flue gas to the overall determination of a destruction efficiency is very small (< 0.0000025%). It is notable that at two of the three sites sampled, PBDD/F were observed to be higher on the “baseline” day when no specific bromine-rich feedstock was being added, which implies that the additional material has had no measurable adverse impact on the combustion process and factors other than the additional bromine loading were responsible for variations in the observed PBDD/F emitted. Table 5.8 summarises the calculations for M_{gas}.

Table 5.8 Mass of PBDD/F as POPs in stack gas (M_{gas})

Stack gas	Units	Site 1	Site 2	Site 3
Day 2 trial: Total PBDD/F	nmol/m^3	9.300E-06	4.701E-05	2.923E-05
Day 1 baseline: Total PBDD/F	nmol/m^3	2.791E-05	3.779E-05	9.908E-05
Stack flow	m^3	706,800	673,200	370,200
Day 2 trial: Total PBDD/F	nmol	6.57	31.65	10.82
Day 1 baseline: Total PBDD/F	nmol	19.73	25.44	36.68
Day 2 Enhanced-POPs				
M_{gas} PBDD/F as decaBDE	ng	6,305	30,358	10,379
M_{gas} PBDD/F as TBBPA	ng	3,575	17,214	5,885
Day 1 Baseline				
M_{gas} PBDD/F as decaBDE	ng	18,923	24,402	35,181
M_{gas} PBDD/F as TBBPA	ng	10,730	13,837	19,949

5.2 DE Calculations

Destruction efficiency has been separately determined for decaBDE and TBBPA at each site following the methodology and input data detailed in this section.

The quantity of IBA produced (~20% of waste input) means that the overall determination of DE was particularly sensitive to the quantities of residual BFRs detected in IBA and the limit of detection/quantification of the method for determining them in IBA. The quantities of PBDD/F present in flue gases were relatively insignificant.

The DE values ranged from 99.927% to 99.952% across the 3 sites for decaBDE (Table 5.9). These are effectively a lower bound estimate of DE as it was not possible to quantify the amount of decaBDE present in the routine waste feedstock. Therefore, M_{waste} was conservative and the true destruction efficiency of decaBDE has likely been understated.

Table 5.9 DE calculations for decaBDE

decaBDE	Units	Site 1	Site 2	Site 3
M_{waste}	mg	1,206,065	1,225,717	954,800
M_{solid_IBA}	mg	567	728	390
M_{solid_APCr}	mg	86.68	109	62.58
M_{solid_BA}	mg	43.34	-	-
M_{gas}	mg	0	0	0
M_{solid_IBA} (PBDD/F)	mg	26.63	51.92	3.18
M_{solid_APCr} (PBDD/F)	mg	0.45	1.31	0.75
M_{solid_BA} (PBDD/F)	mg	0.14	-	-
M_{gas} (PBDD/F)	mg	0.0063	0.0304	0.0104
DE	**%**	**99.940%**	**99.927%**	**99.952%**

Table 5.10 DE calculations for TBBPA

TBBPA	Unit	Site 1	Site 2	Site 3
M_{waste}	**mg**	1,912,330	1,673,333	1,450,800
M_{solid_IBA}	**mg**	1,157	1,488	796
M_{solid_APCr}	**mg**	173	217	125
M_{solid_BA}	**mg**	86.68	-	-
M_{gas}	**mg**	0	0	0
M_{solid_IBA} (PBDD/F)	**mg**	15.10	29.44	1.80
M_{solid_APCr} (PBDD/F)	**mg**	0.26	0.74	0.42
M_{solid_BA} (PBDD/F)	**mg**	0.08	-	-
M_{gas} (PBDD/F)	**mg**	0.0036	0.0172	0.0059
DE	**%**	**99.925%**	**99.896%**	**99.936%**

The DE values determined for TBBPA ranged from 99.896% to 99.936% respectively across the 3 sites (Table 5.10). The results follow similar trend to decaBDE and were conservative estimates of the true DE for TBBPA.

5.3 Calculations Assuming Non-Detected Substances Not Present

The DE values reported in Tables 5.11 and 5.12 assume that individual substances present below the LoQ (decaBDE and TBBPA) or LoD (individual PBDD/F congeners) are present at 33% and 50% of their respective thresholds. In this section, the DE calculation has been repeated using an assumption that any unquantified or undetected substance is not present following the approach used for reporting lower bound emissions of PCDD/F in laboratory reporting. The values presented in these tables therefore represent an upper boundary to the determination of a DE from these trials which also includes partial products of combustion.

Table 5.11 DE calculations for decaBDE assuming <LoD/LoQ = 0

decaBDE	Units	Site 1	Site 2	Site 3
M_{waste}	mg	1,206,065	1,225,717	954,800
M_{solid_IBA}	mg	0.00	0.00	0.00
M_{solid_APCr}	mg	0.00	0.00	0.00
M_{solid_BA}	mg	0.00	-	-
M_{gas}	mg	0.00	0.00	0.00
M_{solid_IBA} (PBDD/F)	mg	24.76	48.07	1.31
M_{solid_APCr} (PBDD/F)	mg	0.06	0.82	0.12
M_{solid_BA} (PBDD/F)	mg	0.01	-	-
M_{gas} (PBDD/F)	mg	0.0000	0.0001	0.0000
DE	**%**	99.998%	99.996%	100.000%

Table 5.12 DE calculations for TBBPA assuming <LoD/LoQ = 0

TBBPA	Unit	Site 1	Site 2	Site 3
M_{waste}	**mg**	1,912,330	1,673,333	1,450,800
M_{solid_IBA}	**mg**	0.00	0.00	0.00
M_{solid_APCr}	**mg**	0.00	0.00	0.00
M_{solid_BA}	**mg**	0.00	-	-
M_{gas}	**mg**	0	0	0
M_{solid_IBA} (PBDD/F)	**mg**	14.04	27.26	0.74
M_{solid_APCr} (PBDD/F)	**mg**	0.03	0.47	0.07
M_{solid_BA} (PBDD/F)	**mg**	0.01	-	-
M_{gas} (PBDD/F)	**mg**	0.0000	0.0000	0.0000
DE	**%**	99.999%	99.998%	100.000%

Using this approach, the calculated DE ranged from 99.996% to 100.000% (to 3 d.p.) for decaBDE and 99.998% to 100.000% (to 3 d.p.) for TBBPA. DE determination throughout this study has been based on using the broader definition of DE which includes partial products of combustion (specifically PBDD/F). The DE determined by this <LoD/LoQ = 0 approach is controlled primarily by the detectable PBDD/F congeners in IBA.

There was no definitive trend in the quantities of PBDD/F detected in IBA across the 3 sites between the baseline monitoring when no specific bromine-containing compounds were added to the general waste feedstock and the enhanced POPs WEEE addition trial. Therefore, attributing a proportion of the PBDD/F to the background waste is not possible and therefore no baseline subtraction to differentiate the contribution of the enhanced POPs containing WEEE from the organic bromine present in background waste has been carried out,

5.4 Simple Monte Carlo Simulation

To ascertain the sensitivity of the result to uncertainties in measurement determinands and process variables, a simple Monte Carlo simulation has been carried out on the impact of the potential range of key calculation variables based on decaBDE and Site 2. A Monte Carlo simulation picks a value at random from a distribution of potential values for variables in a calculation to evaluate the probabilities of specific outcomes. The key variables considered and their realistic ranges were:

- Waste throughput (20 – 25 t/h)
- Mass of enhanced-POPs WEEE plastic (110 – 140 kg)
- POPs content of enhanced-POPs WEEE plastic (1.000 – 10,000 mg/kg)
- IBA produced (19 – 23% of waste input)
- POPs LoD in IBA and APCr (0.001 to 0.08 mg/kg)
- Mass of APCr produced (6 – 8 t)
- Concentration of PBDD/F in IBA (0.1 – 34 nmol/kg)
- Concentration of PBDD/F in APCr (0.1 – 1.1 nmol/kg)
- Flue gas volumes (100,000 – 120,000 Nm3/h)
- PBDD/F LoD in flue gas (0.001 – 0.01 ng/m^3)

The results of the Monte Carlo simulation showed that the range of possible destruction efficiencies obtainable was 98.0206% to 99.9996%. Figure 5.1 is a histogram of the 100 simulations undertaken based upon the use of a realistic range of input data. 96% of simulated DEs are in the range 99.9 – 99.99% with the greatest sensitivity due to the LoD for decaBDE in IBA due the relatively large quantity of IBA produced as a proportion of overall residues.

Figure 5.1 Histogram of results of Monte Carlo simulation

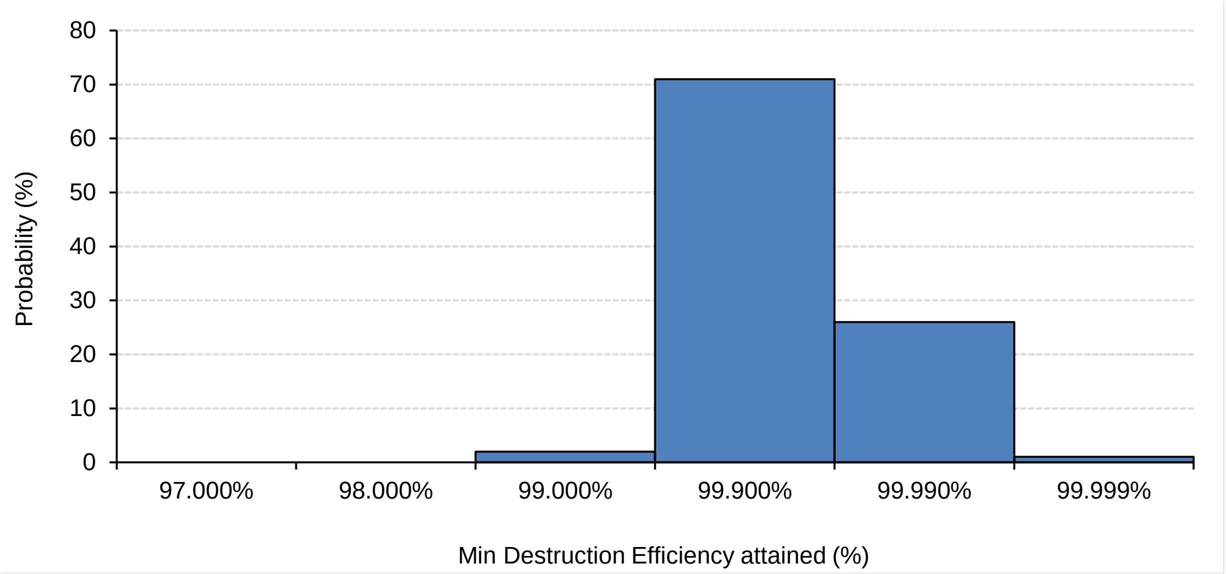


Figure 5.2 Schematic of the impact of solid residue LoD on destruction efficiency determination

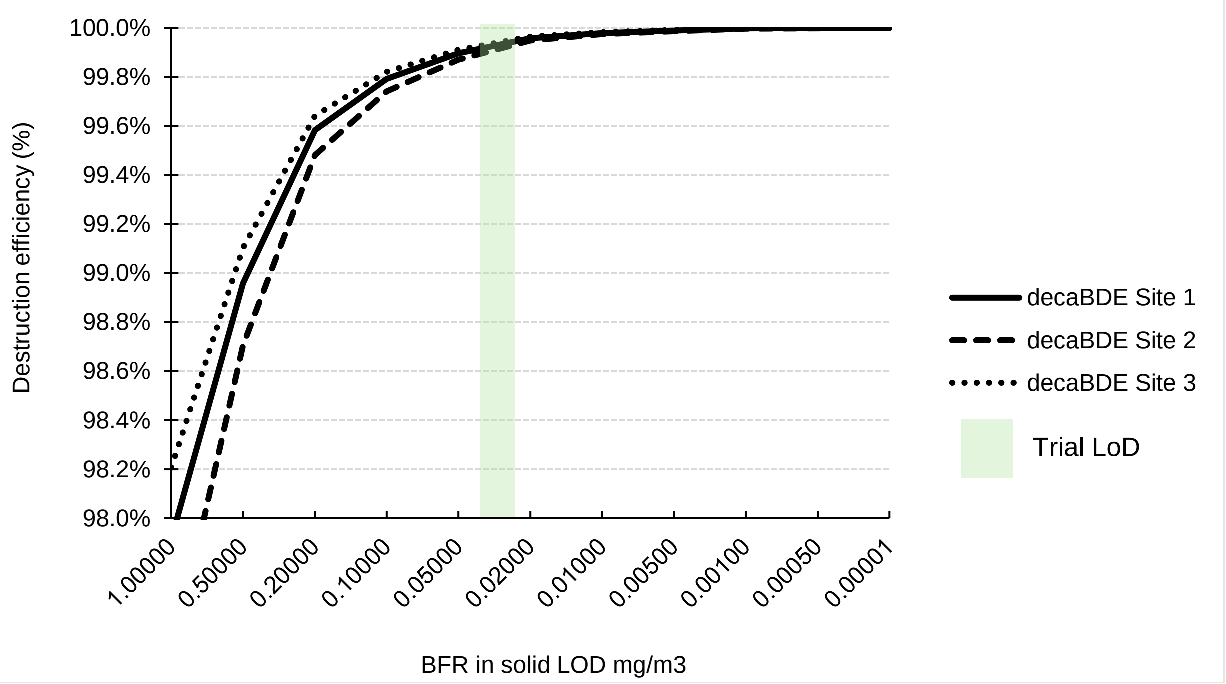


Figure 5.2 shows the theoretical impact of the LoD for decaBDE in solid residues on the determination of destruction efficiency using the real site data for each of the 3 trial sites. It reinforces the exponential impact of LoD on determining the demonstrable destruction efficiency.

Both figures show that to reliably demonstrate a destruction efficiency >99.999%, very low LoDs are required for POPs in solid residues (<0.005 mg/kg). Alternatively substantially more BFRs would need to be added to the process to minimise the impact of residues LoDs. Other parameters have a much less significant impact on the destruction efficiency determination based on the simulation of realistic variabilities.

Figure 5.3 Schematic of the impact of quantity of decaBDE added to the process on the minimum destruction efficiency threshold

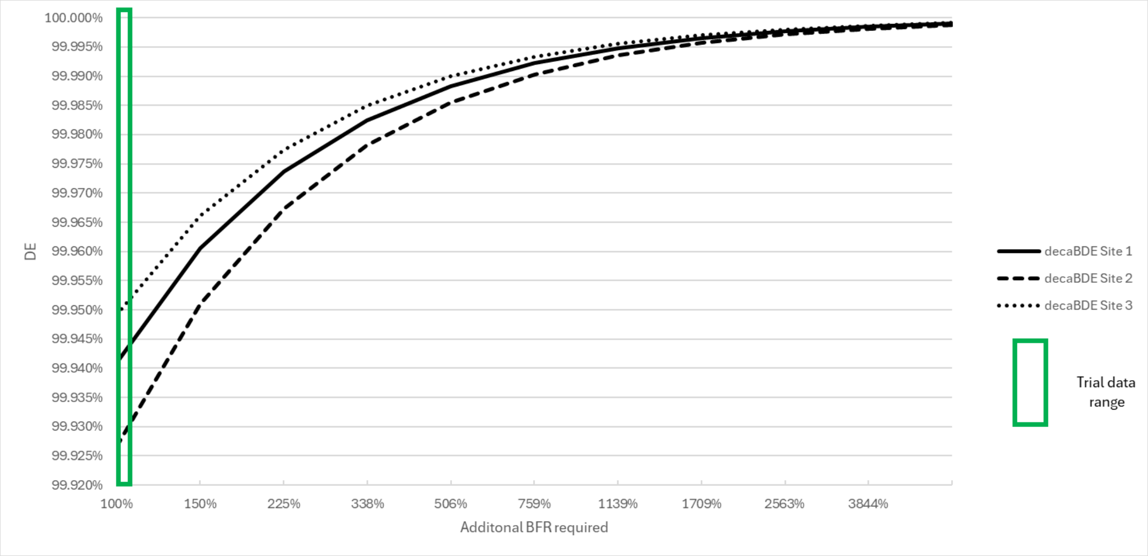


Figure 5.3 shows the theoretical impact of increasing the quantity of decaBDE added to the process on the determination of the minimum destruction efficiency based on the actual reported limits of quantification for decaBDE in solid residues for each of the 3 trial sites. In order to achieve minimum destruction efficiencies >99.999% more than 2000% additional decaBDE would have been required. This would translate into each trial requiring 20 – 35 tonnes of additional POPs enhanced WEEE plastic over the ~6 hour trial period. Such quantities of energy-dense material would substantially perturb the CV of the fuel beyond the bounds of the firing diagram on each site and would not be representative of normal EfW operations.

5.5 Discussion of Results

All three sites were considered to have been operating within their normal envelope of operations on both days of the field-based measurements. No significant adverse emissions were recorded, and the sites were compliant with the continuous emissions monitoring requirements of their respective environmental permits. The addition of the enhanced-POPs WEEE plastic on Day 2 at each site did not perturb the CV of the fuel by more than 0.35 MJ/kg over a half-hour period.

Where levels of SO_2 were observed to be higher than long-term averages during the trials, the key indicators of combustion (CO, VOC, O_2 and temperature) remained well-controlled so this observation was not expected to have had an impact on the POPs DE levels.

Laboratory analyses of the average concentrations of the enhanced-POPs WEEE fraction demonstrated that it was particularly rich in decaBDE and TBBPA, with average concentrations ranging from 6,757 to 13,333 mg/kg, concentrations aligned with previous studies of separated WEEE plastics (WRc, 2022). Therefore, the enhanced-POPs WEEE plastic feedstock was able to provide sufficient bromine-containing compounds to make the determination of a minimum DE ≥99.9% feasible.

The XRF scanning results showed there is a significant amount of bromine present in the general EfW feedstock at all three sites. The majority of the bromine is present in the APCr and residual concentrations in the IBA were low. Boiler ash showed intermediate levels of bromine. These results are consistent with the presence of bromine in a volatile form (probably mostly HBr) following combustion and its capture in the alkaline environment of the flue gas treatment system. The addition of the bromine-rich enhanced-POPS WEEE plastic did not lead to a substantial change in the amounts of bromine recorded in residues and it is not known why the baseline APCr samples at Site 3 exhibited significantly higher bromine that the samples collected during the enhanced-POPs WEEE addition, although operational constraints meant that the sample collection method differed across the two days.

All the IBA, APCr and boiler ash residues tested meet the low POP content threshold of 15 µg TEQ/kg for PCDD/F, 1,000 mg/kg for the sum of POPs-classified PBDEs: tetra-, penta-, hexa, hepta- and deca- bromodiphenylether and a concentration threshold of 1,000 mg/kg for HBCDD (UNEP, 2017 and 2023, UK Parliament 2019 and 2020).

Concentrations of PCDD/F and PBDD/F measured in the flue gas were low on all sites. At 2 of the 3 sites (Sites 1 and 3), both PCDD/F and PBDD/F were observed to be higher on the day of the baseline run without the specific addition of POPs-containing material. This observation is consistent with both the TemaNord (2005) field trials and Mark et al. (2015) and implies that the factors that control the quality of combustion are not directly impacted by the quantities of BFR-containing enhanced-POPs WEEE plastic material added to the normal waste feedstock in these trials.

Using the extended approach to calculating DE which includes measured partial products of combustion as identified by Bell (2021), DE values determined during the 3 site trials ranged from 99.927% to 99.952% for decaBDE and 99.836% to 99.925% for TBBPA assuming non-detected substances were present at 33% of the LoQ and 50% of the LoD respectively. If non-detected substances were assumed to be absent, the equivalent range of DE becomes 99.996% to 10.000% for decaBDE and 99.998% to 100.000% for TBBPA. The inclusion of PBDD/F as partial products of combustion in the DE calculation for all solid and gaseous products of combustion has no significant impact as they were found to be present in very low concentrations in flue gas and generally low concentrations in residues.

The key limiting factors on the quantification of DE are the detection limit BFRs in solid residues and the quantity of BFRs added to the process so as not to perturb normal operations. The uncertainty surrounding the quantity of BFRs in the general waste feed also contributes to the uncertainty in the estimate of DE. The Monte Carlo simulation shows that for the normal range of operational variables, LoDs of the order of 0.005 mg/kg for BFRs in solid residues would be required to reliably demonstrate a 99.999% destruction efficiency unless significantly more BFR-rich material is added to the process.

These determinations of DE will likely underestimate the true DE as the amount of decaBDE and TBBPA in the process residues has been assumed to be 50% of the LoD in each sample analysed. Also, the amount of each BFR present in the input does not include the unquantifiable BFRs present in the general waste feedstock, the quantity actually destroyed will be conservative.

Three IBA and three APCr samples, on per site collected on the day enhanced-POPs WEEE addition trial, were analysed for SCCPs and MCCPs. No SCCPs were detected in any of the samples analysed. All three APCr samples and one IBA sample analysed for MCCPs were found to be below the limit of detection. Two of the IBA samples had detectable and very low levels of MCCPs present (< 200 mg/kg).

No fluorinated organics, chlorofluorocarbons or chlorocarbons above the limit of detection were observed in flue gases during the VOC screening carried out.

6. Conclusions

Calculation of Destruction Efficiency

An extended approach to the calculation of destruction efficiency of two BFRs, decaBDE and TBBPA, was undertaken using data collected from the field trials at the three operational EfWs. These BFRs were selected as they were identified in significant proportions in bromine-rich WEEE plastic waste streams. The three trial sites were observed to be operating normally on both days and were fully compliant with the continuous emissions limits in their permits. No BFRs or other POPs (Dechlorane Plus and UV-328) were detected in any of the IBA, APCr and boiler ash residues collected during either the baseline study or during the addition of POPs-rich WEEE plastic trials. All residues analysed comply with the definition for low POP content under the Stockholm Convention as enacted by UK legislation. Measurements of partial products of combustion in residues were also undertaken and included in the DE calculation. Minimum extended DE values ranging from 99.927% – 99.952% for decaBDE and 99.896% – 99.936% (to 5 sig. fig) for TBBPA were determined. The corresponding maximum extended destruction efficiency ranges were 99.996% to 100.000% for decaBDE and 99.998% to 100.000% for TBBPA.

Flue gas PCDD/F concentrations were compliant with periodic monitoring requirements and therefore met the provisional definition for levels of destruction and irreversible transformation, based upon absolute levels (i.e., waste output streams of treatment processes) in flue gases in UNEP (2023). There appears to be no consistent trend in PCDD/F flue gas emissions between the baseline day and the day in which enhanced-POPs WEEE plastic was added. PBDD/F flue gas concentrations were also low and appeared to demonstrate no consistent trend between the baseline day and the day in which enhanced-POPs WEEE plastic was added. Quantifying PBDD/Fs as partial products of combustion in the DE calculation for all solid and gaseous products of combustion had a minor impact on the overall outcome of the assessment as they were only found at very low concentrations.

The use of an enhanced POPs WEEE plastic as a source of BFRs allowed destruction efficiency ranges (including the contribution from partial products of combustion) of between 99.896% and 100.000% to be demonstrated in the field. The main limitation on BFR input was ensuring the combustion process was still representative of normal operations despite the addition of large quantities of high-CV material (enhanced-POPs WEEE plastic) with the benefits of increased BFR loading on destruction efficiency calculations. In practice, the quantities added resulted in CV perturbations of around 0.3 MJ/kg over a 30 minute period. Each of the sites operated well within the normal CV range encountered for the site.

The full chemical analysis of the enhanced POPs WEEE plastic was not available at the time of the site trials therefore the quantity of material to add to the process was inferred based on the initial XRF screening and previous experience of characterising WEEE plastics. Additional quantities of enhanced POPs WEEE plastic could have been added during the trial to increase the known mass of BFRs had they been available although the quantities required to achieve a lower bound of the destruction efficiency determination to >99.999% would be substantial and would be unrepresentative of normal operations.

The primary factor impacting on the determination of the minimum destruction efficiency is the limit of quantification (LoQ) of BFRs in IBA as the largest residue by mass. An LoQ of the order of 0.005 mg/kg or less for BFRs in the solid residues would be required to demonstrate a minimum 99.999% destruction efficiency. In this test programme the typical range was between 0.07 to 0.10 mg/kg for decaBDE and 0.14 to 0.20 mg/kg for TBBPA. The analytical laboratory was a highly capable test facility and to have substantially improved the minimum DE threshold would have required the addition of 10-fold more POPs-enhanced WEEE plastic which would have moved the feedstock CV above normal operational ranges or significant incremental improvements in both LoQ and quantities of POPs-enhanced WEEE plastic.

The DE ranges determined in this trial range from 99.896% – 100.000% (to 3 decimal places) and include the contribution from unintentionally produced brominated POPs. Sub-sections a) to k) of UNEP (2023) indicate that Best Available Techniques (BAT) is to achieve a minimum DE of 99.999% destruction or irreversible transformation, with 99.9999% destruction removal efficiency as a supplementary requirement where applicable to provide a practical benchmark for assessing disposal technology performance. Higher demonstrated DEs may be preferred on a case-by-case basis. As neither DE nor DRE consider the potential transformation of the original POP to an unintentionally produced POP, potential releases of unintentionally produced POPs should be considered when choosing a particular operation. It is recognised that the lower bounds obtained are below the BAT thresholds in UNEP (2023) they are constrained by the laboratory LoQ for BFRs in solid residues. The upper bound is broadly consistent with the environmentally sound disposal requirements of UNEP (2023) and associated UK guidance. UNEP (2023) recognises R1: Use as a fuel (other than in direct incineration) or other means to generate energy as an appropriate destruction and irreversible method for removal of POPs. Section G of UNEP (2023) also recognises that moving grate energy from waste plants designed to treat MSW and commercial / industrial wastes at temperatures >850 ˚C with residence times of more than two seconds which are also fitted with state-of-the-art pollution-control methods are appropriate for treating POPs-containing wastes.

Other Findings

All six of the IBA and APCr samples analysed for SCCPs were found to be below the limit of detection. Two of the IBA samples had detectable and very low levels of MCCPs present (< 200 mg/kg). The remaining IBA sample and all three APCr samples analysed for MCCPs were found to be below the limit of detection.

No fluorinated organics, chlorofluorocarbons or chlorocarbons were detected during the screening carried out on flue gas. The relatively high limit of detection (typically 20 mg/m^3) for the screening method means that it is therefore only possible to state that there were no substantial emissions of fluorinated VOCs from the three EfWs monitored. Should there be concerns relating to the presence of poly-fluorinated compounds or their partial products of combustion then a more focused high-sensitivity assessment will be required. Depending on the nature of the compounds of interest and the level of detection required, a degree of method development may be required for flue gas measurements of fluorine-containing organic compounds. This analysis was undertaken as a screening exercise and was a secondary objective to the main testing programme.

Conclusions

Within the uncertainties inherent in any practical study, the results indicate a very high level of destruction efficiency has been achieved within the context of a reasonable real-world worst-case operational scenario. The dosing of brominated POPs material to an EfW was significantly higher than what would be realistic based on current and likely future UK EfW feedstocks. Therefore, the findings suggest that EfW facilities provide an effective means for the destruction of brominated POPs within the feedstock in a real-world operational context. A high volume, high concentration POPs feedstock resulting a calorific value outside of the normal operational ranges may require specialist treatment, although further field trials using significantly more bromine-rich feedstock would be required to assess such a scenario. Finally, it was not possible to draw any robust conclusions regarding the destruction of PFAS-containing materials based on this study although it is possible to conclude that a specific PFAS-rich feedstock trial would be required to evaluate the PFAS destruction efficiency.

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