Assessment of Hazard Classification of UK IBA

Report for the January-December 2011 IBA dataset

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This project was conducted under the remit of a collaborative agreement between the Environmental Services Association and Defra's Waste and Resources Evidence Programme to deliver a programme of Research and Development, seeking to present the scientific evidence required to inform the regulatory framework governing the management of incinerator bottom ash (IBA).

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Contents

Appendices

List of Tables

List of Figures

Glossary

Acid/alkali reserve	Acid/alkali reserve determined by titration and expressed as g NaOH equivalent per 100 g substance required to adjust the pH to the appropriate value. For alkali reserve, the prepared sample is titrated with HCl to pH 10.
95th percentile	The value below which 95% of all observations fall.
Aqua regia	Hydrochloric/nitric acid, used hot to digest solid samples for determination of mineral acid soluble ‘total’ concentration.
BS EN 12457	European standard leaching tests – compliance leaching test for granular wastes (Parts 1-3 are a series of batch tests for material at <4 mm particle size, at L/S2; L/S10; or L/S2 and L/S8, cumulative L/S10).
CEN	Comité Europeén de Normalisation (European Standards Organisation
CEN TC292	CEN Technical Committee 292 (Characterisation of Waste).
CLP Regulation	CLP Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures.
Eluate	Solution obtained after leaching a solid material with a leachant during a standardised laboratory-leaching test.
ESA	Environmental Services Association.
IBA	Incineration bottom ash.
Note 1	Reference to Note 1 of CLP Table 3.2 “The concentration stated or, in the absence of such concentrations, the generic concentrations of this Regulation (Table 3.1) or the generic concentrations of Directive 1999/45/EC (Table 3.2), are the percentages by weight of the metallic element calculated with reference to the total weight of the mixture.”
LOW	List of wastes.
PAHs	Poly-aromatic hydrocarbons.
PCBs	Polychlorinated biphenyls.
PCDD/DF	Polychlorinated dibenzodioxins/dibenzofurans (‘dioxins/furans’).
TC	Total carbon content.
TDS	Total dissolved solids.
TOC	Total organic carbon.
WM2	Environment Agency (2011) Hazardous waste - Interpretation of the definition and classification of hazardous waste Technical Guidance WM2.

Summary

i Background

Operators of municipal energy from waste (EfW) facilities have been collecting incinerator bottom ash (IBA) according to ESA's sampling and testing protocol[1] for the assessment of hazard status of incinerator bottom ash (ESA, 2010), since January 2011. This report collates chemical composition data for 419 samples of UK IBA collected under the ESA protocol between January and December 2011 and presents the results of a full hazard assessment using this extensive IBA dataset.

Characterisation and geochemical modelling of two fresh IBA samples has been undertaken in conjunction with Hans van der Sloot to strengthen the evidence with respect to speciation of key metals in IBA. The outcomes have been used to support the hazard assessment.

ii Conclusions

On the basis of the first 12 months' data, no single participating facility recorded more than six exceedances. The IBA from the participating facilities would therefore be characterized as 'non hazardous' according to the approach laid out in the ESA protocol (2010).

The outcome of the geochemical modelling was used to inform the hazard assessment. This concluded that the mineralogy controlling the release of zinc, copper and nickel in fresh IBA was dominated by zinc silicate, copper bound by particulate organic matter (POM) and iron (III) hydroxide, copper hydroxide and nickel hydroxide. This approach makes no allowances for the presence of copper, nickel or zinc metal or alloys in the sample. Where risk phrases exist for these metals or alloys, they have less stringent hazard thresholds than the compounds used in this assessment. This is seen as a precautionary approach.

A tiered hazard assessment was taken, in line with the Environment Agency's approach to environmental risk assessments and following their guidance on assessment of hazardous wastes (WM2, Environment Agency, 2011). This incorporated a high level assessment of the properties that are relevant to IBA based on knowledge of its gross characteristics and composition (Tier 1), followed by further investigation of selected hazard properties using a worst case assessment approach (Tier 2). Detailed investigation of any compounds that remained, informed by technical knowledge of the waste inputs and combustion process, or

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[1] A sampling and testing protocol for the assessment of hazard status of incinerator bottom ash. Environmental Services Association (2010).

specific testing was undertaken in Tier 3. Compounds with relevant risk phrases identified from data sources other than the CLP were considered in Tier 4 for key metals.

The Tier 1 hazard assessment showed that hazard properties H1, H2, H3, H9, H12 and H15 did not need to be assessed further for the UK 12 month IBA dataset.

The Tier 2 assessment showed that on the basis of a worst case assessment none of the samples exceeded the thresholds for hazard for H5/H6, H8, H10, H11 and H13. Within the UK IBA data set two samples out of 419 were shown to exceed the H4 hazard threshold, 12 were classed as exceedances for H4 and H8 due to insufficient datasets and five samples exceeded the H7 hazard threshold. Potential ecotoxicity (H14) was investigated extensively as part of the Tier 3 and Tier 4 assessments.

Using the conclusions about the speciation of the key metals in IBA derived from the geochemical modelling and methods laid out in WM2, 25 samples of the 419 IBA samples collected in 2011 exceeded hazard thresholds for one or more hazard property.

Specifically:

- H4/H8: two samples within the dataset exceeded the threshold for H4 (irritancy) only, 12 samples had insufficient data to complete the assessment and were therefore classed as exceedances by H4 (irritancy) and H8 (corrosivity).

- H7: on the assumption that all the nickel in each sample was present as nickel (II) hydroxide, with no allowance for nickel alloys, five of 411 samples exceeded the hazard threshold for H7. These were all samples that had been tested with a maximum of three analytical replicates, rather than the 11 metal replicates recommended by the ESA protocol.

- H14: following an extensive assessment of potential compounds and sources of risk phrases, the assessment of ecotoxicity considered the concentrations of nickel hydroxide, lead and 20% of copper concentrations as copper hydroxide. Using the equation for ecotoxity provided in WM2, seven of the 419 samples taken exceeded the H14 (ecotoxic) threshold for hazard.

Taking a worst-case position, 25 of the 419 samples collected under the ESA protocol in 2011 exceeded thresholds for hazard in one or more hazard property.

These conclusions are supported by detailed evidence in Appendix A.

Iii Recommendations

Testing

Alkali reserve (reported as mg NaOH/100 g^{-1}) should always be undertaken to support the assessment, with pH, of H4 irritancy. Additional testing to confirm the alkali reserve result is likely to be required by the next version of WM2.

Chromium (VI) should be tested in addition to total chromium to confirm the absence of chromates in all IBA samples.

The ESA protocol recommends the determination of metals on 11 replicate *aqua regia* digests. As a minimum this should be undertaken for copper, lead, zinc and nickel. This will provide a more robust measure of the metals concentrations in the sample, which are highly variable at the analytical (0.5 g) scale.

Hazard assessment

Where the assessment indicates an exceedance of a hazard threshold, reasons for the exceedance must be investigated and addressed.

We recommend that full characterisation and assessment of 15 hazard properties is undertaken annually. However, for IBA from facilities that have participated in this assessment process, on-going monthly assessments of IBA t can be limited to hazard properties H4/8 (irritancy/corrosivity). H7 (carcinogenicity) and H14 (ecotoxicity).

The assessment of ecotoxicity can be restricted to copper hydroxide, lead (as Pb) and nickel (II) hydroxide following the equation provided in the Environment Agency guidance (WM2).

These recommendations should be revisited if any of the compounds are reclassified in CLP Table 3.2, or further data become available, specifically:

- geochemical modelling information that is specific to the facility generating the IBA;
- data to quantify proportions of copper or nickel metal that contribute to the total *aqua regia* digest concentrations.

iv Résumé of Contents

Section 1 and 2 provide background to the project and key principles of the ESA sampling protocol for the hazard assessment of IBA (ESA 2010). Section 3 presents summary compositional data for the UK IBA dataset. The full hazard assessment is presented in Appendix A and the approach and results are summarised in Section 4. Conclusions are provided in Section 5. Appendix B provides concentration data for key determinands for each energy from waste facility, with a summary of exceedances of hazard thresholds during 2011.

This assessment is based on samples collected in January-December 2011 under the 2010 version of the ESA protocol. A revised protocol is due to be published and will come into effect in in January 2013.

1. Setting the Scene

The List of Wastes (LoW) Regulations 2005 requires all wastes to be assigned a code on the basis of the origin of the waste. The LoW classifies IBA as non-hazardous (19 01 12) or hazardous (19 01 11*) dependent on whether it contains 'dangerous substances'. As such the waste must undergo an assessment against all 15 hazard properties following the protocols set out in the technical guidance document WM2 (Environment Agency, 2011).

To support the discussions about the classification of IBA, WRc has worked with ESA to undertake the following:

- development of a new sampling and testing protocol for IBA (ESA, 2010) to ensure that sampling and testing was conducted in a consistent and robust manner. The protocol adopts the principles of the European Centre for Normalisation Technical Committee 292 (Waste Characterisation) Working Group 1 (Sampling) which has produced a Framework Standard (BS EN 14899) and supporting technical reports to guide the waste industry on sampling and testing issues. The basis of the chosen sampling approach specified in the ESA protocol was agreed with the Environment Agency. ESA Member EfW facilities in England adopted the protocol for monthly sampling of IBA in January 2011;

- characterisation of IBA from two UK moving-grate facilities collected according to the ESA protocol and geochemical modelling of zinc species in the IBA samples by Hans van der Sloot (formerly of ECN, Energy research Centre of the Netherlands) (WRc, 2011 and 2012b); and

- an assessment of the data for IBA collected by 18 facilities in 2011. This has been assessed in two stages. The assessment of data from January to June 2011 was reported in WRc (2012c).

The aim of this latest phase of work was to update the first six month hazard assessment in line with the new data from the second half of 2011. Chemical composition data for UK IBA collected under the ESA protocol during January to December 2011 and undertake a full hazard assessment using the IBA dataset. ESA arranged for data from 18 EfW facilities to be submitted to WRc for collation. WRc collated the data as described in Section 3. A four tiered hazard assessment of the UK IBA compositional dataset has been undertaken and is reported here[2]. This report will support the evidence base for the assessment of hazard of IBA in the UK.

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[2] A tiered approach, commencing with a screening step to exclude parameters or properties from detailed assessment, is consistent with the Environment Agency's approaches to environmental risk assessment.

2. Key Aspects of ESA Protocol

The full procedures for sampling IBA are presented in ESA (2010) and background is providing in an ‘explanatory note’ (WRc, 2012a). Key principles of the ESA protocol for the sampling of IBA are as follows.

- Unprocessed IBA: the sampling and testing protocol generates samples that represent ash in the condition in which it would be consigned for reprocessing, recycling or disposal.

- Monthly sampling: two samples are collected on the same day (morning and afternoon). The number of samples to be tested is a key issue and in this case is based on a level of precision and confidence that was accepted by the Environment Agency.

- Scale of sampling: each sample is equivalent to a load of IBA as it is consigned for reprocessing or disposal.

- Number of incremental samples: 20 incremental samples are collected over the period of time taken to discharge sufficient IBA to fill one load. A composite of these 20 samples (approximately 200 kg in total) is representatively sub-sampled on site to generate a >40 kg sample for despatch to the laboratory.

- After drying, at least 20 kg is prepared for analysis and representatively sub-sampled (each sample).

- 11 replicates: from the representative analytical sample, 11 separate *aqua regia* digests are prepared for subsequent determination of key metals copper, lead and zinc (each sample).[3]

- Analysis: EfW operators are required to test for a sufficiently comprehensive suite of parameters to assess the material for all hazard properties, unless evidence is available to restrict the testing suite.

- ‘As received ‘reporting: the evaluation of hazard should be undertaken on the material as it would leave the site of production. However, IBA analysis is undertaken on a dried sample and the data reported on a dry weight basis. The analytical data must be adjusted to represent the sample ‘as received’, taking into account moisture and the

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[3] At nine of the 18 sites up to 30 metal determinands were measured on 11 replicates. It should be noted that at the remaining sites the additional metals were analysed on between one and three replicates.

weight of any inert, non-grindable components removed during sample preparation. Inert components may include stones and ceramics etc., but not metal or clinker.

- Hazard threshold exceedances: provided the facility has recorded six or fewer exceedances during the first year of monitoring, the IBA should be classed as non-hazardous and a reduction in the sample frequency to two samples in two months is permitted (a total of 12 samples per year instead of 24 samples per year).

- The ESA protocol uses a face value approach for the exceedance test, combined with a 90th percentile compliance assessment test with confidence limits set by the benefit of doubt approach. This approach was discussed and agreed with the relevant UK ‘involved party’, the Environment Agency. The protocol ensures that the risk of compliant IBA being mistakenly classified as hazardous waste is limited to 5% probability. This approach, and in particular a 12 month assessment period is used extensively in the wastewater sector (e.g. effluent discharge consents) and other waste sectors to control processes within prescribed limits, whilst making allowance for occasional exceedances due to inherent sample heterogeneity or process variability. This regime is recognised by the Environment Agency as providing appropriate environmental protection.

- The Agency has accepted the statistical approach set out in the protocol such that IBA is not classed as hazardous until seven exceedances have been recorded in any 12 month period. To minimize the period where the IBA is classified as hazardous, the sampling frequency may be changed to two samples on at least six occasions within a period of not less than one month and not greater than six months. This change would only be justified if the facility has undertaken quantifiable measures that aim to improve ash quality. If five or more of these extra samples are hazardous, the IBA will continue to be classed as hazardous and increased sampling must continue. Individual facility performance is summarised in Appendix B.

- The paragraphs above summarise the rationale from the 2010 version of the ESA protocol, which was used to collect the samples discussed in this report. A revised version of the ESA protocol is due to take effect from January 2013.

3. UK IBA Dataset - 2011

Compositional IBA analyses provided by 18 ESA member energy from waste (EfW) facilities have been collated into a substantial UK IBA dataset. Each facility has supplied compositional data for two samples per month for January to December 2011, i.e. up to 419 samples. Up to 51 determinands have been reported for each sample. Table 3.1 presents basic statistical analysis of the whole dataset.

Table 3.1 Compositional analysis of unprocessed IBA collected under the ESA protocol (2010)

Determinand	Average	95th percentile[1]	Maximum[2]	RSD%[3]	Count[4]
Concentration in mg kg^{-1} as received unless stated					
pH (-)	11.7	12.6	12.9	8%	418*
Alkali Reserve (mg NaOH 100g^{-1})	0.78	3.84	5.40	149%	399
Moisture Content @ 30°C (%)	16.3	25.6	34.0	39%	383
Residual moisture @ 105°C (%)	1.85	4.90	10.2	97%	186
Total carbon (%)	2.03	3.58	5.35	49%	134
Total organic carbon (%)	1.13	2.23	4.80	53%	248
Nitrogen as N	1618	2525	40783	270%	105
Aluminium	21625	39364	74775	45%	325
Antimony	67.5	135	289	55%	419
Arsenic	8.44	28.2	160	154%	410
Barium	324	594	2270	61%	325
Beryllium	1.36	2.35	5.00	48%	224
Boron	74.2	125	977	115%	323
Cadmium	11.2	30.1	72.4	91%	419
Calcium	91677	151075	164064	36%	222
Chromium	246	990	1358	124%	419
Cobalt	26.9	51.8	362	82%	419
Copper	1900	3679	17871	65%	419
Iron	25722	47953	80420	48%	228
Lead	820	1608	2296	53%	419
Lithium	17.0	47.6	51.6	61%	228
Magnesium	6980	10251	12300	31%	325
Manganese	823	1217	4597	45%	419
Mercury	2.21	11.4	65.0	223%	384
Molybdenum	8.74	21.8	104	116%	316
Nickel	135	420	1050	95%	417

Determinand	Average	95th percentile[1]	Maximum[2]	RSD%[3]	Count[4]
Phosphorus	4838	7551	8660	40%	228
Potassium	3564	5228	17297	41%	228
Selenium	5.34	14.9	390	488%	230
Silver	14.8	79.4	96.5	133%	227
Sodium	8564	19033	38044	57%	228
Strontium	189	273	319	31%	216
Thallium	3.59	9.02	25.8	134%	382
Tin	164	400	844	74%	324
Titanium	1936	4873	32933	110%	325
Vanadium	29.5	59.6	732	151%	419
Zinc	2107	3292	9389	36%	418*
Chromium hexavalent	0.53	1.00	1.70	56%	98
Silicone	171753	251074	255332	20%	18
Free Cyanide	0.88	1.00	1.35	19%	32
Total Cyanide	0.66	1.00	1.00	59%	46
Fluoride	88.3	219	281	90%	44
Bromide	13.5	29.5	35.0	71%	44
Sulphate	527	2155	2503	142%	44
Ammoniacal Nitrogen	2.67	6.13	9.26	81%	44
Total polycyclic aromatic hydrocarbons (PAH)	3.60	5.00	7.57	57%	49
Total polychlorinated biphenyls (PCB)	1.38	4.72	6.97	113%	120
Total petroleum hydrocarbons (TPH) C10-C40	144	310	324	58%	55
Sulphide	0.64	1.11	1.16	50%	12
Total Dioxins/furans (ITEQ) (ng kg^{-1})	0.001	0.004	0.006	137%	53

Notes

[1] The concentration below which 95 percent of values will fall. This is a commonly used assessment approach used in environmental risk assessments that provides a statistically-based, unbiased metric that is insensitive to the number of samples.

[2] This is the highest concentration reported for the 12 month dataset.

[3] Relative standard deviation indicates the level of variability within the 12 month's dataset for each determinand.

[4] The number of determinations within the 12 month dataset. ESA (2010) focuses on metal determinations but datasets for all available determinands were requested. This number of determinations is greatest for those required by EfW facility Environmental Permits. Operators are advised to review their routine testing schedules. For example TPH is used as a screening parameter to exclude organic compounds from the hazard assessment and chromium (VI) is used to demonstrate that ecotoxic chromium compounds do not exceed the appropriate threshold.

*Facility 9 had a missing pH value and Facility 17 had a missing zinc value.

In addition to providing average, 95th percentile and maximum values for the whole data set, the report also examines facility specific performance. This is summarised in Appendix B.

3.1 Variability assessment and implications for IBA monitoring

The IBA monitoring data taken according to the ESA protocol during 2011 from 18 energy from waste facilities in the UK has been assessed to identify patterns of contaminant variability and differences in facility performance. Three metals, lead, nickel and zinc were selected to examine the variability of reported test data. These three elements were selected because:

- they have been identified as key metals of concern for the hazard assessment of IBA;
- they have been measured in all of the samples analysed during 2011; and
- they have differing concentration ranges in the dataset to capture different dataset distribution patterns.

The data was examined at facility level on a single day i.e. two samples in the morning and afternoon of the same day over the 12 month monitoring period (January to December 2011). The dataset for analysis consisted of 200 paired morning and afternoon samples. Statistical analysis was conducted using ‘R’, an advanced statistical software package.

This analysis has revealed differences among energy from waste facilities in concentrations of key parameters. The differences observed were most pronounced for nickel and least pronounced for zinc. The presence of differences in facility performance indicates that it would be inappropriate to undertake a combined national hazard assessment using data collected from different facilities. As required by the existing monitoring protocol, compliance should be assessed on a facility by facility basis to identify any that are not meeting the required limit values. However, the geochemical modelling work completed on both UK and world-wide IBA has provided no evidence to suggest that the underlying mineralogy of IBA produced at these facilities is different. Future assessment of data currently being generated according to the ESA protocol should therefore still adopt the approach provided in the 12 month IBA hazard assessment for 2011. This demonstrates that comparisons of reported concentrations with hazard thresholds should only be applied to the proportion of the underlying mineralogy which attracts appropriate risk phrases

Zinc and lead, and to a lesser degree nickel, showed appreciable variability in mean concentration from month to month. This indicates that the composition of IBA varies during the year and means that samples taken from different loads on the same day will be positively correlated and will not provide truly independent measures of IBA quality. This result supports the approach of the existing monitoring protocol to treat morning and afternoon samples taken on the same day as non-independent as is allowed for in the current 90th percentile benefit of doubt approach. It also suggests that better information about IBA quality would be obtained by sampling one load per day twice a month rather than two loads per day once a month as at present.

The current 24 samples are treated in the compliance programme as representing only 12 independent pieces of information (because paired samples are correlated), which provides an allowance of six exceedances in a 12 month period. Moving to 24 independent samples means that the power of the scheme is improved but at the same time the proportion of samples allowed to exceed *decreases*. Thus, as we have more information available to us, the amount of uncertainty reduces, and so there is less doubt in the 'benefit-of-doubt' approach i.e. it shrinks and the number of allowed exceedances would reduce accordingly to five. This greater number of independent samples means that we can be more confident that a non-compliant plant will be identified and that the risk decreases that a non-compliant facility will 'slip through the net'.

4. IBA Hazard Property Assessment

4.1 Approach

The recent update to WM2 (Environment Agency, 2011) states that all wastes should be considered under each of the hazard codes in the Waste Framework Directive (EC, 2010). It also lists a number of data sources for identifying appropriate risk phrases for each compound that may potentially be present in a waste. This list now includes Table 3.2 of the Classification, Packaging and Labelling Regulation (CLP), (EC, 2008). This table has been selected for the hazard assessment of IBA as it is a harmonised, European list that provides a reasonable, transparent basis for the assessment. Additional sources of risk phrase information have been used in the Tier 4 assessment.

WRc has created a spreadsheet tool covering hazard properties and risk phrases that are appropriate for specific wastes. For a largely inorganic waste such as IBA, different high level approaches are taken for organic and inorganic compounds.

- *Organic compounds:* As a product of combustion, the level of organic matter in IBA is generally very low (UK IBA dataset average, 95th percentile and maximum TOC concentrations are 1.13% and 2.23% and 4.80% w/w (Table 3.1)). Those organic molecules that are present are of high molecular weight and these are generally considered to be non-toxic. The determination of total petroleum hydrocarbons (TPH) can be used as a screen for low molecular weight toxic compounds. The 95th percentile concentration of TPH for the UK IBA dataset (Table 3.1) is 324 mg kg^{-1}, i.e. the concentration of low molecular weight organic compounds is very low, indicating that most of the (small amount) of organic carbon is present as large biologically benign compounds of high molecular weight. Organic compounds in general can therefore be excluded from further assessment. However, specific organic compounds (dioxins, furans and dioxin-like PCBs) have been included as they are particular contaminants of concern.

- *Inorganic compounds:* inorganic determinands are normally reported as the elemental concentration. The spreadsheet tool is used to identify potential worst-case compounds by risk phrase and hazard property and to convert the elemental concentration to the concentration of selected compounds. These can then be compared with the appropriate hazard threshold.

- *Compounds of zinc, copper and nickel.* Geochemical modelling of characterization data for fresh IBA collected under the ESA protocol (2010) has been undertaken by Hans van der Sloot using leachXS/ORCHESTRA (van der Sloot *et al*, 2008) and placed in context with 10 other samples from around the world, including UK aged IBA. This research (WRc, 2012) and has confirmed the relevant species considered to dominate the mineralogy of zinc, copper and nickel and specifically excluded some compounds from the assessment. In these cases the worst-case compounds have been replaced by known mineral phases, namely copper bound by particulate organic matter (POM) and iron (III) hydroxide, copper hydroxide, nickel (II) hydroxide and zinc silicate.

WRc recommends a four tiered approach to the hazard assessment of IBA. This incorporates a high level assessment of the properties that are relevant to IBA based on knowledge of its gross characteristics and composition (Tier 1), followed by further investigation of selected hazard properties using a worst case assessment approach (Tier 2) and finally, detailed investigation of any compounds that remain, informed by technical knowledge of the waste inputs and combustion process, or specific testing and geochemical modelling (Tiers 3 and 4).

4.2 Results

The results of the four-tiered assessment for IBA are reported in full in Appendix A.

4.2.1 Tier 1

The Tier 1 screening exercise discounted H1 (explosive), H2 (oxidising), H3A/B (flammable), H9 (infectious), H12 (release of toxic gases) and H15 (waste capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics above) from the Tier 2 assessment.

4.2.2 Tier 2

Using worst case examples of compounds that could be present in <u>any</u> waste, the Tier 2 assessment determined that IBA of average quality and at 95th percentile concentrations did not exceed thresholds for hazard properties H8 (corrosive), H5 (harmful), H6 (toxic), H7 (carcinogenic), H10 (toxic for reproduction) and H11 (mutagenic).

Table 4.1 summarises the results of the first two tiers of the assessment.

Table 4.1 Results of Tiers 1 and 2 of hazard assessment

Hazard property code and label		Pass achieved	
		1	2
H1	Explosive: substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.	√	
H2	Oxidizing: substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances.	√	
H3-A	Highly flammable: • liquid substances and preparations having a flash point below 21°C (including extremely flammable liquids), or • substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any application of energy, or	√	

Hazard property code and label		Pass achieved	
		1	2
	• solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or be consumed after removal of the source of ignition, or • gaseous substances and preparations which are flammable in air at normal pressure, or • substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.		
H3-B	Flammable: liquid substances and preparations having a flash point equal to or greater than 21°C and less than or equal to 55°C.	√	
H4	Irritant: non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.		√
H5	Harmful: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.		√
H6	Toxic: substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.		√
H7	Carcinogenic: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.		
H8	Corrosive: substances and preparations which may destroy living tissue on contact.		√
H9	Infectious: substances and preparations containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.	√	
H10	Toxic for reproduction: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.		√
H11	Mutagenic: substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.		√
H12	Waste which releases toxic or very toxic gases in contact with water, air or an acid.		√
H13(*)	Sensitizing: substances and preparations which, if they are inhaled or if they penetrate the skin, are capable of eliciting a reaction of hypersensitisation such that on further exposure to the substance or preparation, characteristic adverse effects are produced. (*) *As far as testing methods are available.		√
H14	Ecotoxic: waste which presents or may present immediate or delayed risks for one or more sectors of the environment.		
H15	Production of hazardous substance after disposal: Waste capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics above.	√	

**The Waste (England and Wales) Regulations 2011 amends Annex III of the Hazardous Waste (England and Wales) Regulations 2005 to bring it in line with the Revised Waste Framework Directive (2006/12/EC).

Tier 2 identified H4 (irritancy), H7 (carcinogenicity) and H14 (ecotoxicity) as hazard properties that required further assessment.

- H4: WM2 allows the results of the alkali reserve to be used to assess the buffering capacity of wastes with pH>11.5 to determine whether the waste is irritant according to the calculation: pH + (1/6 alkali reserve) ≥ 13.0.

  This calculation has been applied as follows:

  - a pH value of <11.5 was reported for 163 samples out of 419 samples. These were discounted from further assessment;
  - of the remaining 256 samples, 251 had corresponding alkali reserve results and were subjected to the calculation above; two of these were found to exceed the H4 (irritancy) threshold for hazard, none exceeded the threshold for H8 (corrosivity); and
  - 12 samples out of 419 could not be assessed for irritancy (H4) or corrosivity (H8) as they had incomplete data or the wrong test had been performed.

  Out of the 419 samples in the ESA dataset that could be assessed for H4, 405 samples were below the hazard thresholds for irritancy (H4) or corrosivity (H8). Two samples exceeded the thresholds for H4 (irritancy) but not H8 (corrosivity). 12 samples could not be assessed for irritancy (H4) or corrosivity (H8) due to incomplete or incorrect analytical data. Therefore taking the precautionary approach these samples are assumed to have exceeded hazard thresholds. These properties need to be checked on a case-by-case basis and reasons for high pH or alkali reserve must be investigated.[4]

- H7: The average and 95th percentile concentrations for the 12 month UK IBA dataset were below the hazard thresholds for H7. On the assumption that all the nickel in each sample is present as nickel (II) hydroxide, with no allowance for nickel metal (no relevant risk phrase) or nickel alloys (risk phrase R40 with much higher hazard threshold than nickel hydroxide), five out of 419 samples exceeded the hazard threshold for H7. Occasional high levels of nickel in IBA will therefore need to be assessed on a case-by-case basis. As the samples with high concentrations were reported on single, duplicate or triplicate analytical data, the determination of nickel on 11 replicates as carried out for some other metals is recommended to improve confidence in the nickel dataset

- H14: worst case conditions were applied to increase the likelihood of a compound exceeding the lowest trace impurity threshold of 1000 mg kg^{-1}, below which a compound[5] can be discounted from further assessment of H14. On the basis of worst-case assessment principles, Tier 2 excluded all compounds carrying relevant risk phrases with the exception of compounds of aluminium, barium, chromium, copper, manganese, magnesium, nickel, phosphorus, zinc and lead.

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[4] Note: the next version of WM2 is likely to require additional in vitro testing to confirm alkali reserve testing results.

[5] Elemental concentrations are converted to worst case compound concentrations for assessment unless the worst case compound is designated ‘Note 1’ of Table 3.2 of CLP. Note 1 specifies that elemental concentrations rather than the compound concentrations specific compound are considered. The waste impurity threshold of 1000 mg kg^{-1} has therefore been applied to relevant concentration of compound or element according to the CLP regulations.

4.2.3 Tier 3 - H14 (ecotoxic)

The Tier 3 assessment used technical knowledge about the leachability and speciation of key compounds listed in CLP Table 3.2 to assess whether IBA samples exceeded hazard thresholds with respect to H14 (ecotoxicity). The details of the Tier 3 assessment are presented in Appendix A3.3; the key points are summarized below. Tier 4 considered compounds that were identified in data sources other than CLP Table 3.2, as requested by the Environment Agency.

Technical considerations based on knowledge of the input streams, combustion process, and relevant characteristics of the identified elements (e.g. boiling point and solubility) were used to discount aluminium, chromium, manganese, magnesium and phosphorus from the assessment.

WM2 allows metals that are determined below the relevant ‘trace impurity threshold’ to be excluded from further assessment. Only key metal species of copper, nickel, zinc and lead remained as metals that have been determined in IBA above this concentration and therefore require assessment. The assessments for these three metals are detailed in Appendix A3.3.2 and summarized here.

Copper

Copper concentrations for the IBA dataset were above WM2’s ‘trace impurity thresholds’ for ecotoxicity and therefore need to be assessed. Different species of copper bear different risk phrases. None of the 25 compounds listed on CLP Table 3.2 and carrying risk phrase R50-53 relevant to the H14 assessment were considered to be present in IBA. This was confirmed by the results of the geochemical modelling (WRc, 2012c) which indicated that the dominant copper phases were copper bound to POM and iron (III) hydroxide and copper hydroxide, none of which were listed on CLP. The 25 copper compounds listed on CLP were therefore discounted from the hazard assessment. The compounds identified from the geochemical modelling and the non-CLP listed compounds are considered in Tier 4.

Zinc

The summary statistics for *aqua regia* zinc concentrations are shown in Table 4.2. The distribution of concentration data is presented as a histogram in Figure 4.1.

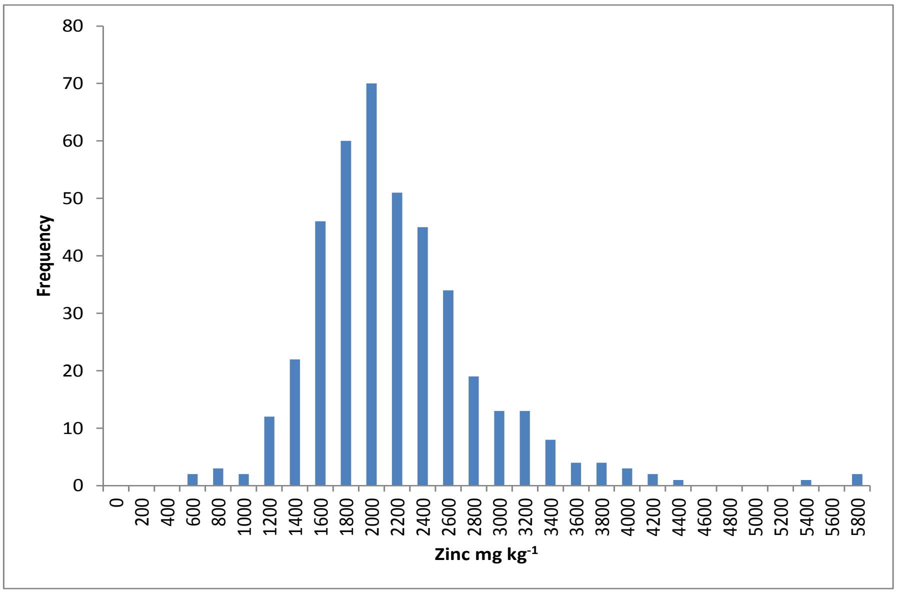
Zinc concentrations for the IBA dataset are above WM2’s ‘trace impurity threshold’ for compounds bearing risk phrase R50-53 of 1000 mg kg^{-1} and therefore could not be discounted from the assessment. However, not all zinc species are ecotoxic; for example zinc oxide, zinc phosphide and zinc chromate are relevant to ecotoxic assessments of waste but zinc silicates are not, as can be determined by reference to MSDSs from chemical suppliers and Table 3.2 of CLP. The species of zinc present cannot be determined by chemical analysis as routine techniques are not sensitive enough to quantify zinc compounds at <0.5%.

Table 4.2 Summary statistics for IBA zinc concentrations

Parameter	Value
Minimum	506 mg kg^{-1}
Average	2107 mg kg^{-1}
95th percentile	3292 mg kg^{-1}
Maximum[1]	9389 mg kg^{-1}
RSD	36%
Count	418

[1] Highest reported concentration

Figure 4.1 Histogram of frequency of zinc concentrations for IBA sampled in January – December 2011



To assess the potential ecotoxicity of zinc species, testing of the composition and leaching behaviour of IBA (undertaken by ECN) supported by the geochemical modelling of zinc species in IBA (by Hans van der Sloot) was undertaken (WRc, 2012c). This was based on compositional and leaching behaviour data from IBA collected from two of the EfW facilities participating in this monitoring exercise and hazard assessment. The data and modelling of the two moving grate IBA samples (termed IBA1 and IBA2) were fully reported in WRc (2012c) and are summarised in Appendix A, Text Box 1.

In summary, the geochemical modelling showed that the zinc mineralogy of the two UK fresh IBA samples was dominated by the silicate ($ZnSiO_3$) within the normal pH range for fresh IBA. This is a non-ecotoxic species[6] and not listed in CLP.

Zinc compounds listed on CLP can therefore be discounted from the hazard assessment. Non-CLP listed compounds are considered in Tier 4.

Nickel

Many nickel compounds carry the R50-53 risk phrases. Nickel alloys do not carry ecotoxic risk phrases. Of the non-nickel alloy fraction, the geochemical modelling has demonstrated that the dominant nickel mineral phase is nickel (II) hydroxide ($Ni(OH)_2$). This assessment assumes that all the nickel in the sample is present as nickel (II) hydroxide whereas it is known that the *aqua regia* used to digest the IBA sample will also dissolve at least a portion of the nickel that is present as nickel alloys which do not carry relevant risk phrases.

The summary statistics for nickel are presented in Table 4.3.

Table 4.3 Summary statistics for IBA nickel concentrations

Parameter	Value
Minimum	0.64 mg kg^{-1}
Average	135 mg kg^{-1}
95th percentile	420 mg kg^{-1}
Maximum[1]	1050 mg kg^{-1}
RSD	95%
Count	417

[1] Highest reported concentration

The distribution of nickel (II) hydroxide concentrations is presented in Figure 4.2.

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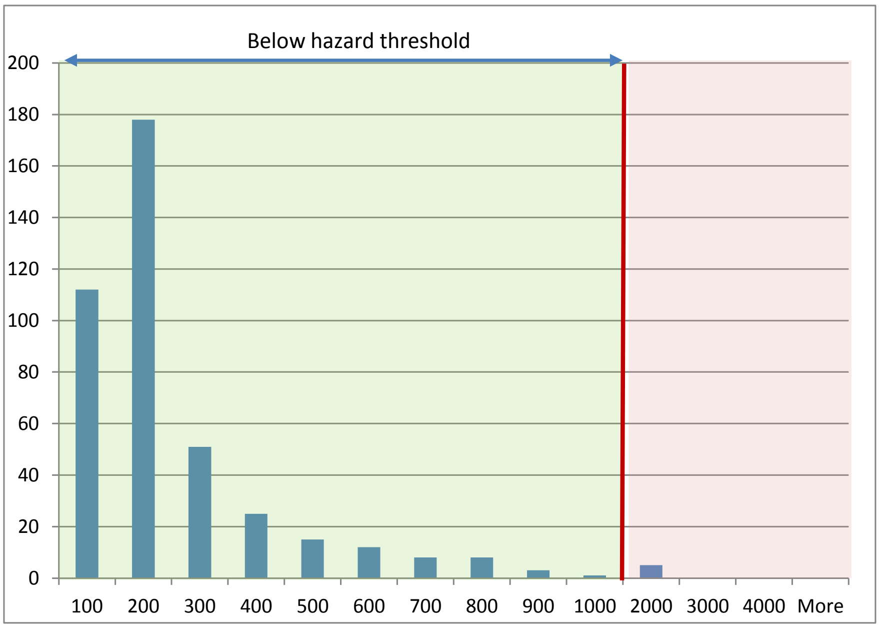
[6] These compounds are not listed on Table 3.2 of CLP or other sources of risk phrases cited in WM2.

Figure 4.2 Histogram of potential nickel (II) hydroxide concentrations for IBA samples collected in 2011



As shown by the histogram only five of the 419 samples contained nickel (II) hydroxide equivalent concentrations above the trace impurity threshold. These require further assessment.

Lead

The only element remaining that could potentially be present at concentrations above the 0.25% hazard threshold for H14 (acute aquatic toxicity) is lead.

The summary statistics for lead are shown in Table 4.4.

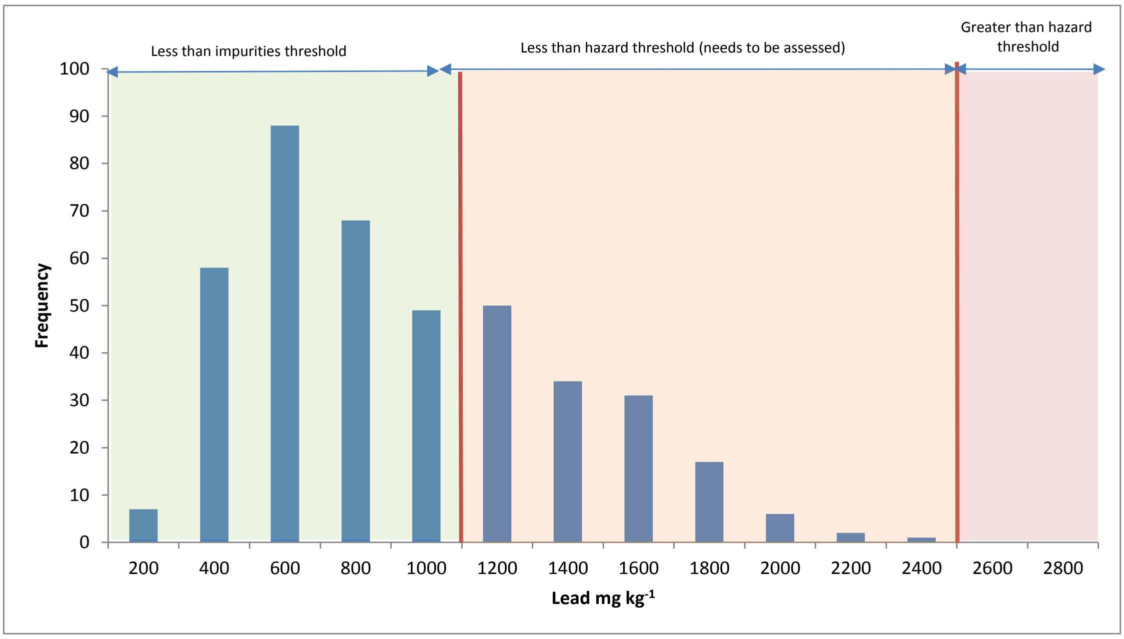
Table 4.4 Summary statistics for IBA lead concentrations

Parameter	Value
Minimum	124 mg kg^{-1}
Average	820 mg kg^{-1}
95th percentile	1608 mg kg^{-1}
Maximum[1]	2296 mg kg^{-1}
RSD	53%
Count	419

[1] Highest reported concentration

The frequency of lead concentrations is provided as a histogram in Figure 4.2.

Figure 4.3 Histogram of IBA lead concentrations for IBA samples collected January to December 2011



The results show that all the samples contained lead concentrations below the 2500 mg Pb kg^{-1}, the hazard threshold, and 65 % of the samples would not require any assessment, being below the trace impurity threshold of 1000 mg kg^{-1}. Higher concentrations would need to be considered with the results of the Tier 4 assessment.

4.2.4 Tier 4 – H14 (ecotoxicity)

The CLP presents harmonised classifications for thousands of compounds. To increase the rigour of the assessment further a wider data search of a large number of relevant databases for nickel, copper and zinc compounds was undertaken. These included the HSE pesticide and biocide databases, the EU pesticide and biocide databases, the UK veterinary products database and the European veterinary products databases for copper and zinc compounds that that have been approved for use, changed or banned. All REACH registered copper and zinc compounds were also included in this wider data search. Details of the Tier 4 assessment are provided in Annex A4.

A systematic assessment of relevant properties of an extensive list of compounds was carried out. All the zinc compounds and most of the additional copper compounds located in the wider search were discounted from assessment of ecotoxicity in IBA with the exception of copper bound by POM and iron (III) hydroxide and copper hydroxide which were demonstrated by the geochemical modelling exercise to dominate copper mineralogy in fresh IBA samples.

Copper bound by POM and iron (III) hydroxide and copper hydroxide remained and were identified as key phases from the geochemical modelling.

The modelling exercise (WRc, 2012c) indicated that, excluding copper metal, 10-20% of copper in the fresh IBA samples is controlled by copper hydroxide and the remaining 80-90% is by copper bound by POM and iron (III) hydroxide, neither of which are listed in CLP.

- ***Copper hydroxide:*** Copper hydroxide does not have a harmonized classification as it is not listed in the CLP. It has not been registered under the Registration, Evaluation, Authorization and restriction of Chemicals (REACH, 2006) and therefore no REACH dossier is currently available.[7]

  It does have a number of non-harmonised classifications, some of which indicate that it is acutely and/or chronically toxic to aquatic organisms. There are 16 non-harmonised classifications which have been submitted by a number of manufacturers for which we have no details or have access to any of the data or methodology used to classify the substance. However, the majority of the registrants have classified copper hydroxide as acutely and chronically toxic to aquatic organisms (H400-H410)[8]. Using a weight of evidence approach it has been decided that copper hydroxide should be classified as being acutely and chronically toxic to aquatic organisms and be assigned the risk phrase R50-53.

- ***Copper bound by POM and iron (III) hydroxide***: there is no data available on the classification of copper bound to particulate organic matter and no similar compounds by which information could be drawn. However, it is unlikely to be ecotoxic. Iron (III) hydroxide ($Fe(OH)_3$) does not have a harmonized classification as it is not listed in the CLP. None of the non-harmonised classifications for $Fe(OH)_3$ classify it as ecotoxic and it is unlikely to have this property as it is used in aquariums and water treatment as a natural absorber of heavy metals and phosphate. As a cautious assessment of copper compounds in fresh IBA, it has been assumed that 20% of the total copper concentration is found as copper hydroxide.

All the additional copper and zinc compounds located in the wider search can be discounted from assessment of ecotoxicity. Where concentrations of copper, nickel and lead approach the threshold for trace impurities for compounds with risk phrase of R50-53 (1000 mg kg^{-1}) the following approach is recommended on a case-by-case basis.

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[7] REACH (2006) regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

[8] ECHA (2012) C&L inventory database - http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database - Last accessed 22/10/12

The outcome of the analysis of species likely to be present in IBA shows that the assessment should focus on the nickel (as nickel hydroxide), lead (as elemental lead) and 20% of the copper concentration (as copper hydroxide).

Using equation 1 from WM2, for the 2011 IBA dataset, the procedure for undertaking the H14 assessment was as follows, on a sample by sample basis:

(a) Identify which samples exceed the trace impurity threshold and need to go forward into the assessment (trace impurities threshold = 1000 mg kg^{-1} for R50-53, R51-53 and R50 compounds, and 10 000 mg kg^{-1} for R52-53, R52, R53 compounds).

  (i) Multiply the nickel concentration by 1.58 to convert to nickel (II) hydroxide and compare it to the 1000 mg kg^{-1} threshold;

  (ii) Compare the elemental lead concentration directly with the 1000 mg kg^{-1} trace impurity threshold;

  (iii) Calculate 20% of the total copper concentration then multiply this by 1.54 to convert it to $Cu(OH)_2$ and compare this to the 1000 mg kg^{-1} trace impurity threshold.

(b) Use concentrations that exceed the threshold for trace impurities in Equation 1 (from WM2) as follows:

Equation 1

$$((\Sigma.R50\text{-}53 / 2500)+(\Sigma.R51\text{-}53 / 25\,000)+(\Sigma.R52\text{-}53 / 250\,000)) \geq 1$$

Where
Σ.R50-53 = sum concentration of compounds classified as R50-53
Σ.R51-53 = sum concentration of compounds classified as R51-53
Σ.R52-53 = sum concentration of compounds classified as R52-53

As there are no compounds to be assessed which bear risk phrases R51-R53 and R52-53 the result from point b) can be compared with the threshold for compounds with R50-53 risk phrases.

Using this proposed approach, seven of the 419 samples analysed under the ESA protocol in 2011 were found to be exceed the hazard threshold for H14 (ecotoxic).

This assessment is provided in the absence of either geochemical modelling information that is specific to the facility generating the IBA, or quantification of the proportion of copper or nickel metal that contribute to the total *aqua regia* digest concentration. Either will allow the proportions of the mineral phases to be altered, and in the case of the metal contribution, reduced. The assessment may need to be revisited if any of the compounds are reclassified in CLP Table 3.2.

4.3 Outcome of the hazard assessment

The assessment showed that none of the samples in the 2011 dataset exceeded threshold concentrations for hazard properties H5/H6, H8, H10, H11, H13 and that H1, H2, H3A/B, H9, H12 and H15 were not relevant to IBA. There were a few exceedances for hazard properties H4, H8, H7 and H14.

Using the conclusions about the speciation of the key metals in IBA derived from the geochemical modelling and methods laid out in WM2 it was found that 25 samples out of the 419 samples taken from EfW facilities in 2011 exceeded thresholds for hazard for one or more hazard property. Specifically:

- H4 and H8: two samples out of 419 were found to exceed the H4 limit value only; an additional 12 samples were also classified as exceedances by H4 and H8 because they had insufficient datasets and could not be fully assessed.

  This property (pH and a proportion of the alkali reserve) needs to be checked on a case-by-case basis and reasons for high pH or alkali reserve must be investigated.

- H7: On the assumption that all the nickel in each sample was present as nickel (II) hydroxide, with no allowance for nickel metal, five of 418 samples exceeded the hazard threshold for H7. Therefore occasional high levels of nickel in IBA (>1000 mg kg^{-1} $Ni(OH)_2$, >633 mg kg^{-1} Ni) will need to be assessed on a case-by-case basis and retests ordered , specifying 11 replicates.

- H14: looking at all the available data and, taking a speciation position based on the geochemical modelling results, it is proposed that the key compounds for assessment of IBA for H14 (ecotoxicity) are:

  - 20% of the total copper concentration as copper (II) hydroxide (R50-53);
  - lead concentration (as Pb) (R50-53); and
  - nickel (II) hydroxide (R50-53).

  The concentrations that exceed the relevant trace impurities threshold (1000 mg kg^{-1} for R50-53 compounds) should be included in the “Equation 1” as set out in the WM2 to assess whether the concentrations exceed the threshold for hazard.

Using the proposed approach, seven of the 419 samples analysed under the ESA protocol in 2011 were found to exceed the hazard threshold for H14 (ecotoxic).

Overall, 25 samples out of the 419 analysed under the ESA protocol in 2011 were found to exceed hazard thresholds for either H4/H8, H7, H14, or a combination of one or more of these hazard properties. No individual facility recorded more than six exceedances.

These recommendations should be revisited if any of the compounds are reclassified in CLP Table 3.2, or further data become available, specifically:

- geochemical modelling information that is specific to the facility generating the IBA;
- quantification of proportions of copper or nickel metal that contribute to the total *aqua regia* digest concentration.

5. Conclusions and Recommendations

Compositional IBA data provided by 18 ESA Member energy from waste facilities has been collated into a substantial UK IBA dataset. ESA Member facilities have supplied compositional data for 411 samples taken between January and December 2011. Up to 50 determinands have been reported for each sample.

Geochemical modelling of characterization data for fresh IBA collected under the ESA protocol (2010) has been undertaken by Hans van der Sloot using leachXS/ORCHESTRA (van der Sloot *et al*, 2008) and placed in context with 10 other samples from around the world, including UK aged IBA. This research (WRc, 2012) has confirmed the relevant species considered to dominate the mineralogy of zinc, copper and nickel namely copper bound by particulate organic matter (POM) and iron (III) hydroxide, copper hydroxide, nickel (II) hydroxide and zinc hydroxide. In the case of zinc, the modelling has excluded specific ecotoxic and non-ecotoxic compounds from the assessment.

The Tier 1 high level assessment of the characteristics of IBA discounted the following hazard properties from further assessment: H1 (explosive), H2 (oxidising), H3A/B (flammable), H9 (infectious), H12 (release of toxic gases) and H15 (waste capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics above). On the basis of a high level assessment of IBA properties and composition, IBA is non-hazardous with respect to these properties.

Under the Tier 2 assessment, worst case examples of compounds with appropriate risk phrases were compared with the hazard thresholds set out in WM2. On the basis of a worst case assessment none of the samples exceeded the thresholds for hazard for: H5/H6 (harmful/toxic), H8 (corrosivity), H10 (toxic for reproduction), H11 (mutagenic) and H13 (sensitising).

A small number of extremely high concentrations exceeded threshold values for H4 (irritancy), H8 (corrosivity), H7 (carcinogenicity) and H14 (ecotoxicity).

- H4/H8: two samples within the dataset exceeded the threshold for H4 (irritancy) only and 12 samples had insufficient data to complete the assessment. These samples were therefore classed as exceedances by H4 (irritancy) and H8 (corrosivity), bringing the total number of H4/H8 exceedances to 14**.** This property (pH and a proportion of the alkali reserve) needs to be checked on a case-by-case basis and reasons for high pH or alkali reserve must be investigated.

- H7: on the assumption that all the nickel in each sample was present as nickel (II) hydroxide, with no allowance for nickel alloys, **five of 411 samples exceeded the hazard threshold for H7**. These were all samples that had been tested with a maximum of three analytical replicates, rather than the 11 metal replicates recommended by the ESA protocol.

- H14: following an extensive assessment of potential compounds and sources of risk phrases, the assessment of ecotoxicity considered the concentrations of nickel hydroxide, copper hydroxide and lead following the calculation provided in WM2. Using this equation and the metals species mentioned above, **seven of the 419 samples exceeded the H14 (ecotoxicity) hazard threshold**.

Overall 25 of the 419 samples taken under the ESA protocol in 2011 exceeded thresholds for hazard in one or more hazard property.

No individual plant recorded more than six exceedances. IBA from the participating plants would therefore be characterized as 'non hazardous' according to the approach laid out in the ESA protocol (2010).

These conclusions should be revisited if any of the compounds are reclassified in CLP Table 3.2. In addition a less conservative assessment would be appropriate in the light of geochemical modelling information that is specific to the facility generating the IBA or if the proportions of copper or nickel metal that contribute to the total *aqua regia* digest concentration were quantified.

It should be noted that Adaptations to Technical Progress (ATPs) to the CLP Regulation are expected to be produced on an approximately annual basis. These may amend chemical risk phrases and increase the number of compounds that need to be assessed as part of a waste hazard assessment, including risk phrases relevant to zinc compounds. A watching brief needs to be held on these developments, as well as changes to the CLP, as it is not possible to predict their changes or impacts.

The authors also recommend that alkali reserve and Cr(VI) are always included in the routine testing suite for IBA hazard assessment and that nickel, preferably all metals, are determined on 11 replicate *aqua regia* digests, as specified in the ESA protocol (2010). It should also be noted that the Environment Agency is likely to require *in vitro* test confirmation of irritancy results based on combined pH and alkali reserve testing in the next version of WM2.

References

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Appendix A Assessment of Hazard Properties

A1 Approach

UK guidance for hazard assessment of wastes (WM2, Environment Agency, 2011) lists a number of potential data sources for risk phrase information for compounds that may potentially be present in a waste. This list includes Table 3.2 of the Classification, Packaging and Labelling Regulation (CLP)[9]. This table is a harmonised European list. As IBA is a residue from treatment of mixed, largely non-hazardous household-derived wastes, rather than a specific production process, Table 3.2 of CLP has been selected as the source of risk phrases for potential compounds in IBA. This is a reasonable and transparent approach to identify the principle contaminants of concern which have then been assessed further using information from other data sources in Tier 4. Table 3.2 of CLP presents a list of thousands of compounds, most with a variety of risk phrases covering more than one hazard property. The full list of risk phrases that must be considered is presented in Table 4.1[10]. WRc has identified the inorganic compounds listed in CLP Table 3.2 that carry each relevant risk phase (Table A.1) (Organic compounds are not included here).

Table A.1 List of risk phrases showing hazard properties and number of inorganic compounds bearing each risk phrase

Risk phrase	Description	Hazard property
R1	Explosive when dry	H15 by H1
R10	Flammable	H3B
R11	Highly flammable	H3A
R11-15		H3A
R12	Extremely flammable	H3A
R14	Reacts violently with water	-
R14/15	Reacts violently with water, liberating extremely flammable gases	H3A
R15	Contact with water liberates extremely flammable gases	H3A
R15/29	Contact with water liberates toxic, extremely flammable gases	H12
R15-17		H3A
R16	Explosive when mixed with oxidising substances	H15 by H1
R17	Spontaneously flammable in air	H3A
R18	In use, may form flammable/explosive vapour-air mixture	H15 by H1
R19	May form explosive peroxides	H15 by H1
R2	Risk of explosion by shock, friction, fire or other sources of ignition	H1
R20	Harmful by inhalation	H5
R20/21	Harmful by inhalation and in contact with skin	H5
R20/21/22	Harmful by inhalation, in contact with skin and if swallowed	H5
R20/22	Harmful by inhalation and if swallowed	H5
R20-48/22		H5

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[9] CLP Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulations)

[10] Where hazard property is blank, the risk phrase need not be considered in assessment of hazard

Risk phrase	Description	Hazard property
R21	Harmful in contact with skin	H5
R21/22	Harmful in contact with skin and if swallowed	H1
R22	Harmful if swallowed	H5
R22-48/20		H6 (H5)
R22-48/20/21/22		H6 (H5)
R22-48/22		H6 (H5)
R23	Toxic by inhalation	H6 (H5)
R23/24	Toxic by inhalation and in contact with skin	H6 (H5)
R23/24/25	Toxic by inhalation, in contact with skin and if swallowed	H6 (H5)
R23/25	Toxic by inhalation and if swallowed	H6 (H5)
R23/25-48/23		H6 (H5)
R23-48/23		H6 (H5)
R24	Toxic in contact with skin	H6 (H5)
R24/25	Toxic in contact with skin and if swallowed	H6 (H5)
R24/25-48/23		H6 (H5)
R25	Toxic if swallowed	H6 (H5)
R25-48/23		H6 (H5)
R26	Very toxic by inhalation	H6 (H5)
R26/27	Very toxic by inhalation and in contact with skin	H6 (H5)
R26/27/28	Very toxic by inhalation, in contact with skin and if swallowed	H6 (H5)
R26/28	Very toxic by inhalation and if swallowed	H6 (H5)
R27	Very toxic in contact with skin	H6 (H5)
R27/28	Very toxic in contact with skin and if swallowed	H6 (H5)
R28	Very toxic if swallowed	H6 (H5)
R29	Contact with water liberates toxic gas.	H12
R3	Extreme risk of explosion by shock, friction, fire or other sources of ignition	H1
R30	Can become highly flammable in use	-
R31	Contact with acids liberates toxic gas	H12
R32	Contact with acids liberates very toxic gas	H12
R33	Danger of cumulative effects	-
R34	Causes burns	H8 (H4)
R35	Causes severe burns	H8 (H4)
R36	Irritating to eyes	H4
R36/37	Irritating to eyes and respiratory system	H4
R36/37/38	Irritating to eyes, respiratory system and skin	H4
R36/38	Irritating to eyes and skin	H4
R37	Irritating to respiratory system	H4
R37/38	Irritating to respiratory system and skin	H4
R37-41		H4
R38	Irritating to skin	H4
R38-41		H4
R39	Danger of very serious irreversible effects	H6 (H5)
R39/23	Toxic: danger of very serious irreversible effects through inhalation	H6 (H5)
R39/23/24	Toxic danger of very serious irreversible effects through inhalation and in contact with skin	H6 (H5)
R39/23/24/25	Toxic danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed	H6 (H5)
R39/23/25	Toxic danger of very serious irreversible effects through inhalation and if swallowed	H6 (H5)
R39/24	Toxic danger of very serious irreversible effects in contact with skin	H6 (H5)
R39/24/25	Toxic danger of very serious irreversible effects in contact with skin and if swallowed	H6 (H5)

Risk phrase	Description	Hazard property
R39/25	Toxic danger of very serious irreversible effects if swallowed	H6 (H5)
R39/26	Very Toxic: danger of very serious irreversible effects through inhalation	H6 (H5)
R39/26/27	Very Toxic: danger of very serious irreversible effects through inhalation and in contact with skin	H6 (H5)
R39/26/27/28	Very Toxic: danger of very serious irreversible effects through inhalation, in contact with skin and if swallowed	H6 (H5)
R39/26/28	Very Toxic: danger of very serious irreversible effects through inhalation and if swallowed	H6 (H5)
R39/27	Very Toxic: danger of very serious irreversible effects in contact with skin	H6 (H5)
R39/27/28	Very Toxic: danger of very serious irreversible effects in contact with skin and if swallowed	H6 (H5)
R39/28	Very Toxic: danger of very serious irreversible effects if swallowed	H6 (H5)
R4	Forms very sensitive explosive metallic compounds	H15 by H1
R40	Limited evidence of a carcinogenic effect	H7
R41	Risk of serious damage to eyes	H4
R42	May cause sensitisation by inhalation	H13
R42/43	May cause sensitization by inhalation and skin contact	H13
R43	May cause sensitisation by skin contact	H13
R44	Risk of explosion if heated under confinement	H15 by H1
R45	May cause cancer	H7
R46	May cause heritable genetic damage	H11
R48	Danger of serious damage to health by prolonged exposure	H6 (H5)
R48/20	Harmful: danger of serious damage to health by prolonged exposure through inhalation	H6 (H5)
R48/20/21	Harmful: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin	H6 (H5)
R48/20/21/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed	H6 (H5)
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed	H6 (H5)
R48/21	Harmful: danger of serious damage to health by prolonged exposure in contact with skin	H6 (H5)
R48/21/22	Harmful: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed	H6 (H5)
R48/22	Harmful: danger of serious damage to health by prolonged exposure if swallowed	H6 (H5)
R48/23	Toxic: danger of serious damage to health by prolonged exposure through inhalation	H6 (H5)
R48/23/24	Toxic: danger of serious damage to health by prolonged exposure through inhalation and in contact with skin	H6 (H5)
R48/23/24/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed	H6 (H5)
R48/23/25	Toxic: danger of serious damage to health by prolonged exposure through inhalation and if swallowed	H6 (H5)
R48/24	Toxic: danger of serious damage to health by prolonged exposure in contact with skin	H6 (H5)
R48/24/25	Toxic: danger of serious damage to health by prolonged exposure in contact with skin and if swallowed	H6 (H5)
R48/25	Toxic: danger of serious damage to health by prolonged exposure if swallowed	H6 (H5)
R49	May cause cancer by inhalation	H7
R5	Heating may cause an explosion	H15 by H1
R50	Very toxic to aquatic organisms	H14
R50-53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	H14
R51	Toxic to aquatic organisms	H14

Risk phrase	Description	Hazard property
R51-53	Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment	H14
R52	Harmful to aquatic organisms	H14
R52-53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment	H14
R53	May cause long-term adverse effects in the aquatic environment	H14
R54	Toxic to flora	H14
R55	Toxic to fauna	H14
R56	Toxic to soil organisms	H14
R57	Toxic to bees	H14
R58	May cause long-term adverse effects in the environment	H14
R59	Dangerous for the ozone layer	H14
R6	Explosive with or without contact with air	H15 by H1
R60	May impair fertility	H10
R60-61		H10
R61	May cause harm to the unborn child	H10
R62	Possible risk of impaired fertility	H10
R62-63		H10
R63	Possible risk of harm to the unborn child	H10
R64	May cause harm to breast-fed babies	-
R65	Harmful may cause lung damage if swallowed	H5
R66	Repeated exposure may cause skin dryness or cracking	-
R67	Vapours may cause drowsiness and dizziness	-
R68	Possible risk of irreversible effects	H11 (H5)
R7	May cause fire	H2
R8	Contact with combustible material may cause fire	H2
R9	Explosive when mixed with combustible material	H2

WRc has created a spreadsheet tool covering hazard properties and risk phrases that are appropriate for specific wastes. For a largely inorganic waste such as IBA, different high level approaches are taken for organic and inorganic compounds.

- *Organic compounds:* As a product of combustion, the level of organic matter in IBA is generally very low (UK IBA dataset average and 95th percentile TOC concentrations are 1.13% w/w and 2.23% (Table 3.1)). Those organic molecules that *are* present are of high molecular weight and these are generally considered to be non-toxic[11]. The determination of total petroleum hydrocarbons (TPH) accounts for chain lengths containing less than 44 carbon atoms and can be used as a screen for low molecular weight non-toxic compounds. The levels of TPH in IBA tend to be very low. The average and 95th percentile concentration of TPH for the UK IBA dataset (Table 3.1)

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[11] It is generally considered that organic molecules of high molecular weight are non-toxic as 'large' molecules cannot pass through membranes (unless there is an active transport membrane) and will not have biological activity (e.g. Brooke, D.N., Dobbs, A.J. and Williams, N. (1986) Octanol-water partition coefficients (P) measured, estimated and interpreted: particular for chemicals with P > 105. Ecotoxicology and Environmental Safety, 11, 251; Van Gestel, C. A. M., K Otermann, K. and Canton, J.H. (1985) Relation between water solubility, octanol/water partition coefficients, and bioconcentration of organic chemicals in fish: A review. Regulatory Toxicology and Pharmacology, 5, 422-431. Zitko, V. (1980) Metabolism and distribution by aquatic animals In: Handbook of Environmental Chemistry, Volume 2, Part A. (Ed: 0. Hutzinger) Springer-Verlag, Berlin. pp. 221-229).

are 149 mg kg^{-1} and 310 mg kg^{-1}, i.e. the concentration of low molecular weight organic compounds is extremely low, indicating that most of the (small amount) of organic carbon is present as large biologically benign compounds of high molecular weight.

There are some potential hazards related to organic compounds do not therefore need to be considered further in the hazard assessment of the UK IBA dataset, as concentrations of the screening parameter, TPH, and therefore individual compounds are well below relevant hazard thresholds.

- *Inorganic compounds:* inorganic determinands are normally reported as the elemental concentration (e.g. total cadmium compounds) in analytical reports, as current routine analytical techniques measure concentrations in this way. Taking cadmium as an example, cadmium concentrations are reported as ‘total’ cadmium (in the case of IBA, the average concentration for the UK IBA dataset is 11.2 mg kg^{-1}). However, cadmium compounds that carry risk phrases are cadmium (non-pyrophoric), cadmium oxide (non-pyrophoric), cadmium cyanide, cadmium fluoride, cadmium chloride, cadmium sulphate, cadmium (pyrophoric). Each of these compounds carries specific risk phrases and hazard thresholds. A different compound may therefore be selected for different hazard properties and concentration of the specific compound calculated from the elemental concentration in order to compare its concentration with the appropriate hazard property threshold. Some of the compounds listed in Table 3.2 have been designated ‘Note 1’ which means that the elemental concentration of the main constituent is used for assessment rather than the calculated concentration of the entire compound. Where these ‘Note 1’ compounds are considered relevant for assessment, the elemental concentration of the main constituent is used. This has been highlighted in each instance.

- *Compounds of zinc, copper and nickel.* Geochemical modelling of characterization data for fresh IBA collected under the ESA protocol (2010) has been undertaken by Hans van der Sloot using leachXS/ORCHESTRA (van der Sloot *et al*, 2008) and placed in context with 10 other samples from around the world, including UK aged IBA. This research (WRc, 2012) and has confirmed the relevant species considered to dominate the mineralogy of zinc, copper and nickel and specifically excluded some compounds from the assessment. In these cases the worst-case compounds have been replaced by known mineral phases.

Given the number of compounds that must be considered, WRc recommends a four tiered hazard assessment of IBA. This incorporates a high level assessment of the properties that are relevant to IBA based on knowledge of its gross characteristics and composition (Tier 1), followed by further investigation of selected hazard properties using a worst case assessment approach (Tier 2) and finally, detailed investigation of any compounds that remain, informed by technical knowledge of the waste inputs and combustion process, or specific testing (Tier 3 and 4). As most metals are present in low concentrations in IBA (i.e. well below the hazard threshold), the worst case compound for each hazard property is selected for Tier 1 and

Tier 2 of the hazard assessment. Where the worst case compound is known not to be present in IBA, a more realistic compound may be selected as undertaken in Tier 3 of the hazard assessment.

The use of a tiered approach is consistent with approaches to environmental risk assessment required by the Environment Agency for example for contaminated land, landfill and cemetery development.

The four tiered risk assessment is more robust than the approach strictly required by WM2 where compounds likely to be present in IBA would be identified first and then their concentrations compared with relevant hazard thresholds. In this report we specifically list all inorganic compounds with appropriate risk phrases and then systematically assess their physical-chemical properties to justify the presence or absence of each compound in the detailed assessment. This is to make available to ESA the technical justification for the exclusion of specific compounds which might be of interest to future readers of the report.

A2 Tier 1 of the hazard property assessment

The recently updated WM2[5] states that all wastes should be considered for hazardous properties under all of the hazard codes in Revised Waste Framework Directive (2006/12/EC). It can be shown that some hazard properties can be discounted from the assessment based on knowledge of the process without need for further investigation. Under Tier 1 of the IBA hazard assessment, WRc has considered the properties and characteristics of IBA with respect to the 15 hazard properties. Table A.2 provides the justification for exclusion of specific hazard properties from the Tier 2 hazard assessment of IBA.

On the basis of the Tier 1 hazard assessment (screening), further assessment of IBA composition data with respect to H1, H2, H3, H3A, H9, H12 and H15 is not necessary.

Table A.2 Results of Tier 1 hazard assessment (screening)

Hazard property	Justification for no further assessment
H1	No compounds with appropriate risk phrases listed in CLP are considered to be relevant to IBA. Wastes with relevant risk phrases (R1, R2, R3) are very unlikely to be present in the input stream to municipal waste incinerators. Where they are present, they would be destroyed during the incineration process. There are no known reported cases of raw IBA showing explosive properties, although there is some evidence of causing explosive atmospheres when mixed in foamed concrete.
H2	H2 covers risk phrases R7-R9. No compounds with appropriate risk phrases listed in CLP are considered to be relevant to IBA. Any oxidising compounds would be destroyed in the incineration process, and are also very unlikely to be in the input stream.

Hazard property	Justification for no further assessment
H3-A	No compounds with appropriate risk phrases listed in CLP are considered to be relevant to IBA. IBA has been through an incineration process and therefore compounds present in the ash are not flammable.
H3-B	IBA is not a liquid, therefore H3-B is not applicable (solid residues are covered by H3-A).
H9	No compounds with appropriate risk phrases listed in CLP are considered to be relevant to IBA. Any pathogens present would be destroyed during the incineration process. In addition IBA is an alkaline solid (pH>10) which is unlikely to support microorganisms that are significant to human or animal health.
H12	No toxic gases (e.g. HF, H_2S) are produced from IBA in contact with water or air. IBA will produce CO_2 liberated from carbonates in contact with acid, but CO_2 is not a toxic gas.
H15	WM2 appears to indicate that H15 is not relevant for IBA. WM2 states that only H1-H14 apply to products of waste combustion. WM2 is ambiguous as to whether H15 applies to waste that is recovered (e.g. reprocessed IBA) rather than when disposed to landfill. WM2 lists relevant risk phrases as R1, R4, R5, R6, R16, R18, R19 and R44. Compounds bearing these risk phrase are highly unlikely to be present in IBA. IBA is unlikely to generate a hazardous landfill leachate as the leachability of most metals is low. All parameters leach at levels below the German criteria for H13 (now renumbered H15) as listed in Guidelines on the Application of the Waste Catalogue Ordnance. 10 December 2001.

The following hazard properties remain for further assessment in Tier 2 hazard assessment: H4/H8 – Irritant/corrosive, H5 – harmful, H6 – toxic; H7 – carcinogenic, H10 – toxic for reproduction, H11 – mutagenic, H13 – sensitising, H14 – ecotoxic and H15 production of a hazardous substance after disposal.

A3 Tier 2 of the hazard property assessment

A3.1 Hazard properties, risk phrases and relevant compounds

Table A.3 summarises the hazard thresholds relevant for the Tier 2 assessment of IBA. The table also shows whether the threshold is applied to individual compounds or cumulative concentration of compounds bearing the relevant threshold. In the latter case, this property is termed ‘additive’.

Table A.3 Hazard property thresholds (from WM2, EA 2011)

Hazard code	Risk phrases	Hazard threshold	Single compound or additive threshold
H4, H8	R34, R35, R41 R36/37/38,	Cumulative concentration of all compounds compound bearing the R35 risk phrase ≥1%. Cumulative concentration of all compounds compound bearing the R34 risk phrase ≥5%. Cumulative concentration of all compounds bearing R36/37/38 ≥ 20% Cumulative concentration of all compounds bearing R41 ≥ 10% H4 and H8 hazard can also be calculated from the materials pH and acid/alkali reserve using thresholds stated in the WM2 guidance.	Additive
H5	R26,R27, R28	Cumulative concentration of all compounds bearing R26,R27,R28 risk phrases ≥0.1%	Additive
H6	R26,R27, R28	Cumulative concentration of all compounds bearing R26,R27,R28 risk phrases ≥ 7%	Additive
H7	R45, R49	Single compound bearing the R45 or R49 risk phrases ≥ 0.1%.	Single compound
H10	R60, R61	Single compound bearing the R60 or R61 risk phrases ≥ 0.5%.	Single compound
H11	R46	Single compound bearing the R46 risk phrase ≥0.1%.	Single compound
H13	R42, R43	Single compound bearing the risk phrase R42, R43 or R42/43 that is equal or greater than either threshold stated in CLP or CHIP.	Single compound
H14	R50-53	Cumulative concentration of all compounds bearing R50-53 risk phrases ≥ 0.25%. Cumulative concentration of all compounds bearing R51-53 risk phrases ≥ 2.5%. Cumulative concentration of all compounds bearing R50 or R52 or R53 or R52-53 risk phrases ≥ 25%. Only compounds bearing any of these risk phrases that are equal or greater than the relevant trace impurity threshold (0.1% or 1% as relevant) needs to be considered in this assessment.	Additive

A summary of the compounds that need to be assessed under each hazard property is provided in Table A.4. For example (different) selenium compounds need to be considered in the assessment of properties H13 and H14. Specific compounds with relevant risk phrases are excluded from routine IBA monitoring and therefore from the hazard assessment, either because they are gases (nitrogen dioxide), or unlikely to be present in the IBA (asbestos, erionite, uranium).

Table A.4 Compounds assessed under each hazard property[12]

Determinand/ Hazard code	H4, H8	H5, H6	H7	H10	H11	H13	H14
pH	🟥						
Acid/alkali reserve	🟥						
Mercury		🟥					🟥
Chromium		🟥	🟥	🟥	🟥	🟥	🟥
Lead		🟥		🟥			🟥
Aluminium							🟥
Barium							🟥
Arsenic		🟥	🟥				🟥
Tin		🟥					🟥
Beryllium		🟥	🟥			🟥	
Calcium							🟥
Cadmium		🟥	🟥	🟥	🟥		🟥
Cobalt			🟥			🟥	🟥
Boron		🟥					
Zinc							🟥
Copper							🟥
Cyanide		🟥					🟥
Manganese							🟥
Magnesium							🟥
Phosphorus							🟥
Nickel		🟥	🟥	🟥		🟥	🟥
Fluorine		🟥					
Thallium		🟥					
Phosphorus compounds		🟥					🟥
Selenium						🟥	🟥
Bromine		🟥					
Di-n-octylaluminium iodide							🟥
Hydrogen sulphide		🟥					
Potassium bromate			🟥				
Potassium					🟥		🟥
Refractory ceramic fibres*			🟥				
Silver nitrate							🟥
Molybdenum							🟥

Notes: * = not determined

A3.2 Hazard property assessment

For a description of each hazard property, refer to Table 4.1.

A3.2.1 Irritant (H4) and corrosive (H8) hazard assessment

It is feasible to compare concentrations of known compounds with relevant risk phrases against the hazard thresholds for certain products and wastes. However, for a heterogenous

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[12] Summarised from Table 3.2 of Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulations).

material like IBA, where concentrations of relevant compounds are not known, the use of an indicator test such as acid and alkali reserve as permitted by WM2 is a pragmatic solution.[13]

The ESA dataset contains pH measurements for 199 samples. The mean, 95th percentile and maximum pH values recorded were pH 11.7, 12.6 and 12.9. WM2 allows acid/alkali reserve to be used to assess the buffering capacity of wastes with pH>11.5 or < 2.5 to determine whether the waste is irritant or corrosive. If the pH plus 1/12 the alkali reserve is greater than or equal to 14.5, the sample is classed as corrosive, whilst if the pH plus 1/6 the alkali reserve is greater than or equal to 13, the sample is classed as irritant, i.e. a waste is:

- corrosive (H8) if pH + (1/12 alkali reserve) ≥ 14.5;
- irritant (H4) if pH + (1/6 alkali reserve) ≥ 13.0.

This calculation has been applied as follows:

- a total of 163 samples out of 419 samples had a pH of <11.5 and could therefore be discounted from further assessment;
- of the remaining 256 samples, 251 had corresponding alkali reserve results and were subjected to the calculation above; two of these were found to exceed the H4 (irritancy) threshold for hazard, none exceeded the threshold for H8 (corrosivity); and
- 12 samples out of 419 could not be assessed for irritancy (H4) or corrosivity (H8) as they had incomplete data or the wrong test had been performed.

Of the 419 samples, two samples exceeded the thresholds for H4 (irritancy) only, 12 samples were classed exceedances by H4 and H8 because they could not be assessed due to incomplete or incorrect analytical data.

Although IBA of average quality does not exceed the H4 (irritancy) threshold some extreme examples do. Therefore this property needs to be checked on a case-by-case basis and reasons for high pH or alkali reserve must be investigated.[14]

A3.2.2 Harmful (H5) and toxic (H6) hazard assessment

Limits for assigning hazard to properties H5 and H6 (harmful/toxic) are shown in A.5.

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[13] Changes in European legislation are likely to require in vitro testing for irritancy/corrosivity to confirm the results of the alkali/acid reserve test. A watching brief should be maintained as the testing may need to be adapted accordingly.

[14] Note: the next version of WM2 will require additional *in vitro* testing to confirm alkali reserve testing results.

Table A.5 Limits for assigning hazards to harmful and toxic[15]

Classification	Risk phrases	Thresholds for classification as hazardous waste	Limits for assigning hazard	
			H5:Harmful	H6: Toxic
Very Toxic	R26, R27, R28 and combined risk phrases with or without R39	≥ 0.1%	0.1% ≥ total conc. <7%	≥ 7%
Toxic	R23, R24, R25 and combined risk phrases with or without R39 or R48	≥ 3%	3% ≥ total conc. <25%	≥ 25%
Harmful	R20, R21, R22, R65, Xn R68 and combined risk phrases with or without R48	≥ 25%	≥ 25%	n/a

Due to the low concentrations of metals in IBA, the most sensitive assessment is against the 0.1% (1000 mg kg^{-1}) threshold for compounds with risk phrases "R26, R27, R28 and combined risk phrases with or without R39". Likely concentrations of relevant compounds for the other risk phrases listed in Table A.5 are orders of magnitude lower than the relevant thresholds.

Inorganic compounds with risk phrases R26, R27 and R28 and combined risk phrases with or without R39 are compounds of arsenic, beryllium, cadmium, chromium (VI), cobalt, cyanide, mercury and thallium. Lead alkyl, tin and boron compounds also bear relevant risk phrases but are excluded on the basis that they are thermally unstable organometallic compounds or gaseous at room temperature.

The worst-case examples of the range of compounds carrying these risk phrases, are presented in Table A.6. Concentrations of these compounds based on the average, 95th percentile and maximum elemental concentrations reported in Table 3.1 are also presented.

Taking the average and 95th percentile concentrations of the UK IBA dataset, the sum of the potentially harmful compounds is 32.3 and 87.2 mg kg^{-1}, approximately thirty and 10 times lower than the threshold of 1000 mg kg^{-1}.

None of the samples in the 12 month UK IBA dataset exceeded the hazard thresholds for H5 and H6 for the extensive suite of parameters determined and compounds assessed.

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[15] Table C5.1, Environment Agency (2011) Hazardous waste - Interpretation of the definition and classification of hazardous waste. Technical Guidance WM2. V2.3.

Table A.6 Potential concentrations of compounds for assessment of hazard properties H5 and H6

H5, H6	***Potential concentrations of compound in mg kg^{-1}***		
	Average	***95th percentile***	***Maximum***
Arsenic trioxide	11.1	37.3	211
Beryllium oxide	3.79	6.52	13.9
Cadmium sulphate	20.6	55.7	134
Chromium (VI) trioxide	1.03	1.92	3.26
Mercury compounds as Hg*	2.21	11.4	65.0
Thallium thiocyanate	4.67	11.7	33.5
Total	32.3	87.2	250

Note: these are estimated concentrations assuming 100% of the main element present is present only as the most hazardous compound, i.e. this is a worst-case assessment; actual concentrations of these compounds in the IBA are likely to be lower than those reported.

The only cobalt compound bearing the relevant risk phrase is cobalt lithium nickel oxide. This has not been included as geochemical modelling has shown that nickel species will be dominated by nickel (II) hydroxide and therefore sufficient nickel would not be available to form this compound.

*Relevant compounds are 'note 1' elements on CLP Table 3,2 and therefore elemental rather than compound concentrations are assessed.

A3.2.3 Carcinogenicity (H7) hazard assessment

A waste is hazardous by H7 when individual category 1 or 2 carcinogens (compounds carrying the risk phrases R45 and R49) are present at concentrations of >0.1% (1000 mg kg^{1}) or category 3 compounds carrying the risk phrase R40 are present at <1%. The worst-case examples of the range of inorganic compounds, i.e. those with the lowest hazard threshold and that carry the risk phrases R45 and 49 are presented in Table A.7. Concentrations of these compounds based on the average, 95th percentile and maximum elemental concentrations reported in Table 3.1 are also presented.

This data shows that the average and 95th percentile concentrations are below the threshold for hazard. However when it is assumed that all the nickel in the sample is present as nickel (II) hydroxide, the maximum value for nickel (II) hydroxide exceeded the hazard threshold as shown in the distribution for nickel (II) hydroxide plotted in Figure A.1.

Table A.7 Potential concentrations of compounds for assessment of hazard property H7

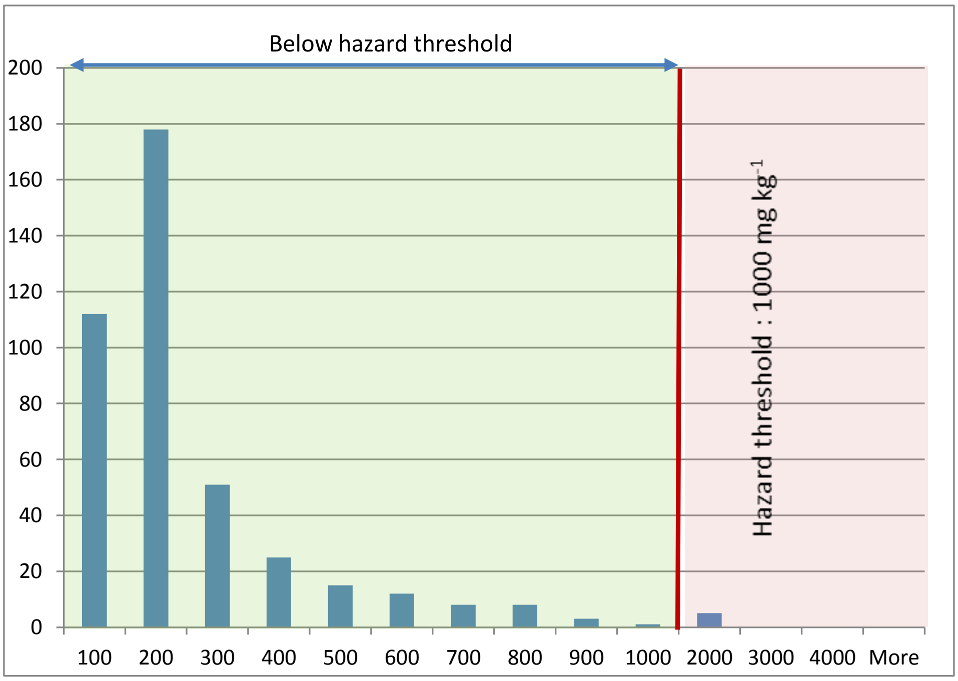
H7	*Potential concentrations of compound in mg kg^{-1}*		
	Average	*95th percentile*	*Maximum*
Beryllium oxide	3.79	6.52	13.9
Chromium[1]	0.53	1.00	1.70
Arsenic trioxide	11.1	37.3	211
Cobalt carbonate	48.5	93	651
Cadmium sulphate	20.6	55.7	134
Nickel (II) hydroxide *	213	663	1655
Total dioxins/furans (ITEQ)**	0.0009	0.004	0.006

Note: these are estimated concentrations assuming 100% of the main element present is present only as the most hazardous compound; actual concentrations in the IBA are likely to be lower than those reported. [1] All the chromium compounds listed in the CLP are Cr(VI) compounds, therefore the assessment is carried out against the total concentration of hexavalent chromium.

*Geochemical modelling has shown that the most likely dominant species is either nickel (II) hydroxide which has therefore been taken as the worst case compound.

**Organic compounds have largely been excluded from assessment (See Section A1) however dioxins and furans have been included as particular contaminants of concern.

Figure A.1 Distribution of nickel (II) hydroxide in 12 month IBA dataset



The distribution demonstrates graphically the statistical information provided in Table A.7. The average concentration is approximately one-fifth the hazard threshold and the 95th percentile is approximately half the hazard threshold. Five samples out of 411 contained nickel (II) hydroxide equivalent concentrations above the threshold for hazard (1010, 1139, 1063, 1659, 1176 mg kg^{-1} $Ni(OH)_2$. Concentrations between 800 and 1000 mg kg^{-1} (which is approaching the hazard limit) were reported for 11 samples.

This assessment assumes that all the nickel in the sample is present as nickel hydroxide whereas it is known that the *aqua regia* used to digest the IBA sample will also dissolve at least a portion of the nickel that is present as nickel metal and nickel alloys. Nickel metal carries the risk phrase R40 which has a less stringent threshold for hazard than nickel (II) hydroxide (1% or 10 000 mg kg^{-1}). Therefore, assuming that 100% of the nickel found in IBA is nickel (II) hydroxide is a very precautionary approach.

It should also be noted that unlike lead, copper and zinc, which are determined on 11 analytical replicates (separate *aqua regia* digests), this is not the case for nickel at many facilities. All the samples with high nickel concentrations were reported on single, duplicate or triplicate analytical data. It is therefore recommended that nickel is also tested in replicates of 11.

The average and 95th percentile concentrations for the 12 month UK IBA dataset are below the hazard thresholds for H7.

On the assumption that all the nickel in each sample is present as nickel (II) hydroxide, with no allowance for nickel metals or nickel alloys, five of 411 samples exceeded the hazard threshold for H7. Occasional high levels of nickel in IBA will therefore need to be assessed on a case-by-case basis and retests ordered , specifying 11 replicate *aqua regia* digests if this has not already been undertaken.

A3.2.4 Toxic for reproduction (H10)

A waste is hazardous by H10 when individual compounds which carry the R60 and R61 risk phrases are present in the material at concentrations of $\geq$0.5% (5000 mg kg^{-1}) or compounds carrying the R62 and R63 risk phrases are >5% (50 000 mg kg^{-1}). The most sensitive assessment is therefore against the 1% hazard threshold. The worst-case examples of the range of inorganic compounds, i.e. those with the lowest hazard threshold and that carry the risk phrases R60 and R61 are presented in Table A.8. Concentrations of these compounds based on the average, 95th percentile and maximum elemental concentrations reported in Table 3.1 are also presented.

Table A.8 Potential concentrations of compounds for assessment of hazard property H10

H10	*Potential concentrations of compound in mg kg^{-1}*		
	Average	*95th percentile*	*Maximum*
Lead compounds as Pb*	820	1608	2296
Cadmium sulphate	15.0	40.3	97
Mercury compounds as Hg*	2.21	11.4	65.0
Nickel (II) hydroxide *	213	663	1655

*Relevant compounds are 'note 1' elements on CLP Table 3,2 and therefore elemental rather than compound concentrations are assessed. *Geochemical modelling has shown that the most likely dominant species is either nickel (II) hydroxide which has therefore been taken as the worst case compound.

None of the samples in the 12 month UK IBA dataset exceeded the 5000 mg kg^{-1} threshold for hazard.

Taking the 95th percentile IBA concentrations for lead compounds and mercury compounds and assuming the worst case position, that all the cadmium occurs as the sulphate, the highest concentration is 2296 mg kg^{-1} lead, significantly lower than the hazard threshold of 5000 mg kg^{-1}.

None of the samples in the 12 month UK IBA dataset exceeded hazard thresholds with respect to H10 for the extensive suite of parameters determined and compounds assessed.

A3.2.5 Mutagenicity (H11) hazard assessment

A waste is hazardous by H11 when individual compounds with the R46 risk phrase exceed >0.1% (1000 mg kg^{-1}) or compounds carrying risk phrase R68 exceed 1% (10 000 mg kg^{-1}). The most sensitive assessment is against the 0.1% threshold.

The worst-case examples of the range of inorganic compounds, i.e. those with the lowest hazard threshold and that carry the risk phrases R46 are presented in Table A.9. Concentrations of these compounds based on the average, 95th percentile and maximum elemental concentrations reported in Table 3.1 are also presented.

Table A.9 Potential concentrations of compounds for assessment of hazard property H11

H11	***Potential concentrations of compound in mg kg^{-1}***		
	Average	***95th percentile***	***Maximum***
Potassium chromate*	1.66	3.10	5.27
Cadmium sulphate	20.6	55.7	134

Note: these are estimated concentrations assuming 100% of the main element present is present only as the most hazardous compound; actual concentrations in the IBA are likely to be lower than those reported.
* On the basis of Cr(VI) concentration.

**Cadmium sulphate does not carry note 1 in CLP Table 3.2

Using the 95th percentile UK IBA dataset concentrations and assuming that 100% of the Cr(VI) and cadmium occurs in the worst case compounds potassium chromate and cadmium sulphate, the highest concentration of either compound would be 134 mg kg^{-1}, approximately 6 times below the hazard threshold.

Nickel (II) hydroxide which has been identified as a key compound for assessment in the geochemical modelling has an R68 risk phrase and so would be assessed against the 1% (10 000 mg kg^{-1}) threshold for hazard.

None of the samples in the 12 month UK IBA dataset exceeded hazard thresholds with respect to H11 for the extensive suite of parameters determined and compounds assessed.

A3.2.6 Sensitising (H13) hazard assessment

Sensitising (H13) was added to hazard properties to be assessed in April 2011. Over 200 new compounds were added which must be assessed, and it includes some of the lowest limit thresholds for any of the hazard properties.

Where individual compounds which carry the risk phrases R42, R43 or R42/43 risk phrase are present in the waste, they must be assessed against relevant thresholds. The assessment for sensitising (H13) is not additive, so each compound is assessed against the threshold individually.

Taking the reasonable, transparent approach of using the CLP as the source of risk phrase information for compounds in the IBA[16], threshold concentrations against which each compound have been identified. Some compounds have specific thresholds stated in CLP[17]

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[16] Further compounds that have not been listed in CLP are considered in Tier 4 of the assessment.

[17] CLP Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulations).

whilst others without a specific threshold have a nominal threshold of 1% (10 000 mg kg^{-1}) taken from the CHIP[18].

Table A.11 lists the compounds that are relevant to IBA and are considered to be the worst case compounds for assessment. All the compounds listed in Table A.10 have the higher hazardous threshold of 1% (10 000 mg kg^{-1}).

Table A.10 Concentrations of potential worst-case compounds for assessment of hazard property H13

	Average	*95th percentile*	*Maximum*
Beryllium oxide	3.79	6.52	13.9
Chromium[1]	0.53	1.00	1.70
Cobalt carbonate	48.5	93.2	651
Nickel (II) hydroxide *	213	663	1655
Total dioxins/furans (ITEQ)*	0.004	0.006	145%

Note: these are estimated concentrations assuming 100% of the main element present is present only as the most hazardous compound; actual concentrations in the IBA are likely to be lower than those reported. [1] All the chromium compounds listed in the CLP are Cr(VI) compounds, therefore the assessment is carried out against the total concentration of hexavalent chromium.

*Geochemical modelling has shown that the most likely dominant species is nickel (II) hydroxide which has been selected as the worst case compound.

The beryllium, chromium, cobalt and nickel compounds listed in Table A.10 are present at concentrations significantly below the 1% (10 000 mg kg^{-1}) threshold.

None of the samples in the 12 month UK IBA dataset exceeded the hazard thresholds with respect to H13 for the extensive suite of parameters determined and compounds assessed.

A3.2.7 Ecotoxicity (H14) hazard assessment

There are standard biotests that can be used to assess the impact of chemicals on aquatic and terrestrial organisms. However WM2 emphasises the use of compositional data to assess ecotoxicity (as used for the assessment of other hazardous properties) and discourages direct ecotoxicity testing on organisms wherever possible. If direct ecotoxicity is to be undertaken, fish testing is also required to ensure that impact on three trophic levels (e.g. algae, crustaceans and fish) is assessed as specified in the CLP. There is no allowance to undertake the battery of tests recommended by CEN TC292/WG7 based on exposure of organisms to eluates from water based leaching tests.

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[18] The Chemicals (Hazard Information and Packaging for Supply) Regulations 2002, Statutory instrument, Health and Safety 2002, No. 1689.

Using the compositional approach, ecotoxicity is an additive property, but there are a number of risk phrase combinations to be taken into account.

If the sum of those compounds which carry the following combinations of risk phrases, is equal or greater than the relevant hazard threshold, then the waste is classed as being hazardous by H14 (ecotoxicity).

- The sum of compounds bearing the R50-53 risk phrase has an ecotoxic threshold of 0.25% (2500 mg kg^{-1}).
- The sum of compounds bearing the R51-53 risk phrase has an ecotoxic threshold of 2.5% (25,000 mg kg^{-1}).
- The sum of compounds bearing the R50 or R51 or R53 or R52-53 risk phrase has an ecotoxic threshold of 25% (250,000 mg kg^{-1}).
- Individual impurity thresholds to be taken into consideration are 1000 mg kg^{-1} for compounds with risk phrases R50-53, R51-53 and R50 and 10,000 mg kg^{-1} for compounds with risk phrases R52-53, R52 and R53. Below these concentrations relevant compounds can be discounted from the assessment. However, this needs to be considered on a sample specific basis.
- The concentrations of the compounds that exceed the relevant thresholds for hazard must then be included in a series of four equations/mathematical tests as set out in WM2 to determine whether the H14 threshold is exceeded.

Criteria for the ecotoxic risk phrases related to terrestrial flora and fauna (R54 to R58) have not yet been developed by the Commission and are not included in the CLP. These risk phrases have therefore been excluded from the hazard assessment, as recommended by WM2 guidance document.

Table A.11 presents compounds listed in the Table 3.2 CLP[19] that bear risk phrases relevant to the assessment of ecotoxicity.

Many can be excluded from further consideration as they are organic compounds which are unlikely to be of relevance to IBA (Section A1.1).

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[19] This table has been selected for the hazard assessment of IBA as it is a harmonized, European list that provides a reasonable, transparent basis for the assessment of a residue from treatment of mixed, largely non-hazardous, household-type waste.

Table A.11 List of compounds carrying ecotoxic risk phrases

Risk Phrase	Hazard threshold	Trace impurity threshold	Compound listed in CLP Table 3.2[12]
R50	25%	0.1%	aluminium phosphide; barium polysulphides; barium sulphide; Bromine; calcium hypochlorite; calcium phosphide; tricalcium diphosphide; calcium polysulphides; calcium sulphide; Chlorine; chlorine dioxide; chlorine dioxide ... %; disulphur dichloride; sulfur monochloride; hydrogen sulphide; Iodine; magnesium phosphide; trimagnesium diphosphide; ammonia ....%; ammonia, anhydrous; ammonium polysulphides; hydroxylammonium nitrate; sodium nitrite; white phosphorus; sulphur dichloride; sulphur tetrachloride; sulphuryl difluoride; Diamminediisocyanatozinc; diphosphorus pentasulphide; phosphorus pentasulphide; dipotassium sulphide; potassium sulphide; disodium sulfide; sodium sulphide; Phosphine; potassium nitrite; potassium polysulphides; sodium hypochlorite, solution ... % Cl active; sodium polysulphides; tetraphosphorus trisulphide; phosphorus sesquisulphid
R50-53	0.25%	0.1%	silver nitrate; silver sodium zirconium hydrogenphosphate; Arsenic; arsenic acid and its salts with the exception of those specified elsewhere in this Annex; arsenic compounds, with the exception of those specified elsewhere in this Annex; diarsenic pentaoxide; arsenic pentoxide; arsenic oxide; diarsenic trioxide; arsenic trioxide; Arsine; calcium chromate; calcium cyanide; cadmium (non-pyrophoric); [1] cadmium oxide (non-pyrophoric) [2]; cadmium (pyrophoric); cadmium chloride; cadmium compounds, with the exception of cadmium sulphoselenide (xCdS.yCdSe), reaction mass of cadmium sulphide with zinc sulphide (xCdS.yZnS), reaction mass of cadmium sulphide with mercury sulphide (xCdS.yHgS), and those specified elsewhere in this Annex; cadmium cyanide; cadmium diformate; cadmiumformate; cadmium fluoride; cadmium iodide; cadmium sulphate; cadmiumhexafluorosilicate(2-); cadmium fluorosilica; metal salts of thiocyanic acid, with the exception of those specified elsewhere in this Annex; cobalt acetate; cobalt carbonate; cobalt dichloride; cobalt lithium nickel oxide; cobalt nitrate; cobalt oxide; cobalt sulphate; cobalt sulphide; Chromium (VI) compounds, with the exception of barium chromate and of compounds specified elsewhere in this Annex; chromium (VI) trioxide; dichromium tris(chromate); chromium III chromate; chromic chromate; ammonium dichromate; chromyl dichloride; chromic oxychloride; potassium chromate; potassium dichromate; sodium chromate; sodium dichromate; copper chloride; copper (I) chloride; cuprous chloride; copper sulphate; dicopper oxide; copper (I) oxide; slimes and sludges, copper electrolyte refining, decopperised; hydrogen cyanide ...%; hydrocyanic acid ...%; hydrogen cyanide; hydrocyanic acid; dimercury dichloride; mercurous chloride; calomel; Mercury; mercury dichloride; mercuric chloride; inorganic compounds of mercury with the exception of mercuric sulphide and those specified elsewhere in this Annex; di-n-octylaluminium iodide; diammonium nickel hexacyanoferrate; dinickel hexacyanoferrate; nickel (II) sulfide; [1] nickel sulfide; [2] millerite [3]; nickel bis(sulfamidate); nickel sulfamate; nickel bis(tetrafluoroborate); nickel boride (NiB); [1] dinickel boride; [2] trinickel boride; [3] nickel boride; [4] dinickel silicide; [5] nickel disilicide; [6] dinickel phosphide; [7] nickel boron phosphide [8]; nickel carbonate; basic nickel carbonate; carbonic acid, nickel (2+) salt; [1] carbonic acid, nickel salt; [2] [μ-[carbonato(2-)-O:O']] dihydroxy trinickel; [3] [carbonato(2-)] tetrahydroxytrinickel [4]; nickel chromate; nickel diarsenide; [1] nickel arsenide [2]; nickel dichlorate; [1] nickel dibromate;

Risk Phrase	Hazard threshold	Trace impurity threshold	Compound listed in CLP Table 3.2[12]
			[2] ethyl hydrogen sulfate, nickel(II) salt [3]; nickel dichloride; nickel dichromate; nickel dicyanide; nickel difluoride; [1] nickel dibromide; [2] nickel diiodide; [3] nickel potassium fluoride [4]; nickel dihydroxide; [1] nickel (II) hydroxide [2]; nickel dinitrate; [1] nitric acid, nickel salt [2]; nickel diperchlorate; perchloric acid, nickel(II) salt; nickel dipotassium bis(sulfate); [1] diammonium nickel bis(sulfate) [2]; nickel dithiocyanate; nickel hexafluorosilicate; nickel hydrogen phosphate; [1] nickel bis(dihydrogen phosphate); [2] trinickel bis(orthophosphate); [3] dinickel diphosphate; [4] nickel bis(phosphinate); [5] nickel phosphinate; [6] phosphoric acid, calcium nickel salt; [7] diphosphoric acid, nickel(II) salt [8]; nickel matte; nickel oxalate; [1] oxalic acid, nickel salt [2]; nickel selenite; nickel selenide; nickel sulphate; nickel telluride; nickel(II) selenite; nickel(II) silicate; [1] dinickel orthosilicate; [2] nickel silicate (3:4); [3] silicic acid, nickel salt; [4] trihydrogen hydroxybis[orthosilicato(4-)]trinickelate(3-) [5]; nickel(II) sulfite; [1] nickel tellurium trioxide; [2] nickel tellurium tetraoxide; [3] molybdenum nickel (II) hydroxide oxide phosphate [4]; nickel(II) trifluoroacetate; [1] nickel(II) propionate; [2] nickel bis(benzenesulfonate); [3] nickel(II) hydrogen citrate; [4] citric acid, ammonium nickel salt; [5] citric acid, nickel salt; [6] nickel bis(2-ethylhexanoate); [7] 2-ethylhexanoic acid, nickel salt; [8] dimethylhexanoic acid nickel salt; [9] nickel(II) isooctanoate; [10] nickel isooctanoate; [11] nickel bis(isononanoate); [12] nickel(II) neononanoate; [13] nickel(II) isodecanoate; [14] nickel(II) neodecanoate; [15] neodecanoic acid, nickel salt; [16] nickel(II) neoundecanoate; [17] bis(d-gluconato-O1,O2)nickel; [18] nickel 3,5-bis(tert-butyl)-4-hydroxybenzoate (1:2); [19] nickel(II) palmitate; [20] (2-ethylhexanoato-O)(isononanoato-O)nickel; [21] (isononanoato-O)(isooctanoato-O)nickel; [22] (isooctanoato-O)(neodecanoato-O)nickel; [23] (2-ethylhexanoato-O)(isodecanoato-O)nickel; [24] (2-ethylhexanoato-O)(neodecanoato-O)nickel; [25] (isodecanoato-O)(isooctanoato-O)nickel; [26] (isodecanoato-O)(isononanoato-O)nickel; [27] (isononanoato-O)(neodecanoato-O)nickel; [28] fatty acids, C6-19-branched, nickel salts; [29] fatty acids, C8-18 and C18-unsaturated, nickel salts; [30] 2,7-naphthalenedisulfonic acid, nickel(II) salt; [31]; tetracarbonylnickel; nickel tetracarbonyl; trinickel bis(arsenate); nickel(II) arsenate; trinickel bis(arsenite); trinickel disulfide; nickel subsulfide; [1] heazlewoodite [2]; trinickel tetrasulfide; slimes and sludges, copper electrolytic refining, decopperised, nickel sulphate; triphenyl phosphite; lead acetate, basic; lead alkyls; lead chromate; lead chromate molybdate sulfate red; C.I. Pigment Red 104; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77605.]; lead compounds with the exception of those specified elsewhere in this Annex; lead di(acetate); lead diazide; lead azide; lead hexafluorosilicate; lead hydrogen arsenate; lead sulfochromate yellow; C.I. Pigment Yellow 34; [This substance is identified in the Colour Index by Colour Index Constitution Number, C.I. 77603.]; trilead bis(orthophosphate); tetraammine palladium (II) hydrogen carbonate; aluminium-magnesium-carbonate-hydroxide-perchlorate-hydrate; platinum(IV) nitrate/nitric acid solution; selenium compounds with the exception of cadmium sulphoselenide and those specified elsewhere in this Annex; strontium chromate; trizinc bis(orthophosphate); trizinc diphosphide; zinc phosphide; zinc chloride; zinc chromates including zinc potassium chromate; zinc oxide; zinc powder - zinc dust (pyrophoric); zinc powder - zinc dust (stabilised); zinc sulphate (hydrous) (mono-, hexa- and hepta

Risk Phrase	Hazard threshold	Trace impurity threshold	Compound listed in CLP Table 3.2[12]
			hydrate); [1] zinc sulphate (anhydrous) [2]; hydrazine; polyphosphoric acid, copper, sodium, magnesium, calcium, silver and zinc salt; potassium permanganate; Reaction products of tungsten hexachloride with 2-methylpropan-2-ol, nonylphenol and pentane-2,4-dione; salts of hydrogen cyanide with the exception of complex cyanides such as ferrocyanides, ferricyanides and mercuric oxycyanide and those specified elsewhere in this Annex; silicic acid, lead nickel salt; sodium azide
R51-53	2.5%	0.1%	tricresyl phosphate (m-m-m-, m-m-p-, m-p-p-, p-p-p-); tritolyl phosphate (m-m-m-, m-m-p-, m-p-p-, p-p-p-); tricresyl phosphate (o-o-o-, o-o-m-, o-o-p-, o-m-m-, o-m-p-, o-p-p-); tritolyl phosphate (o-o-o-, o-o-m-, o-o-p-, o-m-m-, o-m-p-, o-p-p-); barium calcium cesium lead samarium strontium bromide chloride fluoride iodide europium doped; barium chlorate; beryllium compounds with the exception of aluminium beryllium silicates, and with those specified elsewhere in this Annex; potassium chlorate; sodium chlorate; trisodium hexafluoroaluminate; cryolite; gadolinium(III)sulfite trihydrate; manganese sulphate; antimony compounds, with the exception of the tetroxide (Sb_2O_4), pentoxide (Sb_2O_5), trisulphide (Sb_2S_3), pentasulphide (Sb2S5) and those specified elsewhere in this Annex; antimony pentachloride; antimony trichloride; antimony trifluoride; sodium selenite; dithallium sulphate; thallic sulphate; thallium compounds, with the exception of those specified elsewhere in this Annex; thallium thiocyanate; uranium compounds with the exception of those specified elsewhere in this Annex; divanadium pentaoxide; vanadium pentoxide; vanadium(IV) oxide hydrogen phosphate hemihydrate, lithium, zinc, molybdenum, iron and chlorine-doped; divanadyl pyrophosphate; zinc hexacyanocobaltate(III), tertiary butyl alcohol/polypropylene glycol complex
R52-53	25%	1.0%	alkali salts and alkali earth salts of thiocyanic acid, with the exception of those specified elsewhere in this Annex; sodium cyanate; nickel powder; [particle diameter < 1 mm]; hydroxydisulfito platinum(II) acid; tetraammine platinum (II) hydrogen carbonate; tin tetrachloride; stannic chloride; hexasodium tungstate hydrate; aluminium-magnesium-zinc-carbonate-hydroxide; red phosphorus; sulphamidic acid; sulphamic acid; sulfamic acid; vianadyl pyrophosphate
R53	25%	1%	cadmium sulphide; cobalt; dinickel trioxide; nickel dioxide; nickel monoxide; [1] nickel oxide; [2] bunsenite [3]; selenium; thallium; uranium

Note: see CLP Table 3.2 for detailed notes on specific compounds

The inorganic compounds or species which carry the risk phrases between R50 and R53 that are considered by WRc to need detailed consideration are summarised in Table A.12. As before, worst case compounds have been selected. This means that where a number of compounds for a particular element are available, a compound is listed as 'worst-case' because:

1. it is the compound with the largest molecular weight so that the element to compound conversion factor is greatest (this increases the likelihood of the compound exceeding the 1000 mg kg^{-1} trace impurity threshold and therefore going forward to Tier 3); and/or

2. it has the most stringent hazard threshold, of the compounds listed in CLP (and therefore has the greatest chance of going forward to Tier 3).

All compounds of the elements identified are considered in Tier 3, when consideration is given to whether or not a listed compound can be present in IBA.

Compounds with maximum concentrations that approach or exceed the trace impurity threshold, and/or that have average concentrations below half the trace impurity threshold (500 mg kg^{-1}) have been excluded: silver sodium zirconium hydrogenphosphate, diarsenic pentaoxide; beryllium compounds, bromine, cadmium iodide, cobalt sulphate, trisodium hexafluoroaluminate;, gadolinium(III)sulfite trihydrate, hydrogen cyanide%; mercury dichloride;, sodium hypochlorite, di-n-octylaluminium iodide, hydrazine, sodium azide, diammonium nickel hexacyanoferrate, tetraammine palladium (II) hydrogen carbonate, aluminium-magnesium-carbonate-hydroxide-perchlorate-hydrate, sulphur tetrachloride, antimony pentachloride, strontium chromate, thallium thiocyanate, uranium compounds, and divanadium pentaoxide.

Of particular note: polyaromatic hydrocarbon (PAHs) (worst case example phenanthrene), and polychrinated biphenyls (PCBs) had very low concentrations (PAH maximum concentration = 5.37 mg kg^{-1}; PCB maximum concentration = 5.72 mg kg^{-1}).

All other compounds are listed in Table A.12. Those compounds that are close to or above the trace impurity threshold of 1000 mg kg^{-1} (0.1%) or 10 000 mg kg^{-1} (1%) are shown in bold. Those below these thresholds can be excluded from further assessment.

Table A.12 Concentrations of potential worst-case compounds for assessment of hazard property H14

H14 *Element*	***'Worst case' compound***	***Risk phrase***	**Potential concentrations of worst case compound in mg kg^{-1}**		
			Average	***95th percentile***	***Maximum***
Al	aluminium phosphide	R50	**46454**	**84559**	**160629**
Ba	barium chlorate	R51-53	521	**957**	**3653**
Ca	calcium chromate calcium chromate**	R50-53	**320871** 1.44	**528761** 2.70	**574226** 4.59
Cu	copper chloride; copper (I) chloride; cuprous chloride	R50-53	**2938**	**5690**	**27645**
Co	cobalt sulphate	R50-53	70.8	136	**951**
Cr Cr(VI)	potassium dichromate potassium dichromate**	R50-53	**1131** 2.46	**4552** 4.60	**6242** 7.82
Ni	nickel (II) hydroxide	R50-53	213	663	**1655**

H14 ***Element***	***'Worst case' compound***	***Risk phrase***	**Potential concentrations of worst case compound in mg kg^{-1}**		
			Average	***95th percentile***	***Maximum***
Mg	magnesium phosphide; trimagnesium diphosphide	R50	**15995**	**23492**	**28188**
Mn	manganese sulphate	R51-53	**2259**	**3340**	**12620**
P	white phosphorus	R50	**4838**	**7551**	**8660**
Pb	lead compounds*	R50-53	**820**	**1608**	**2296**
Sb	antimony pentachloride	R51-53	145	290	621
Se	sodium selenite	R51-53	6.89	19.0	**503**
Sr	strontium chromate	R50-53	403	582	681
Sr	strontium chromate**		1.92	3.60	6.12
Zn	zinc chromates including zinc potassium chromate zinc chromates including zinc potassium chromate**	R50-53	**5349** 1.71	**8357** 3.20	**23835** 5.44

Note: this worst-case assessment does not provide a judgment of whether a listed compound can be present in IBA. Compounds exceeding the H14 trace impurity threshold of 1000 mg kg^{-1} are highlighted.

*Relevant compounds are 'note 1' elements on CLP Table 3,2 and therefore elemental rather than compound concentrations are assessed.

*based on chromium (VI) concentration

The only compounds in the IBA that bear the relevant risk phrases and are present at a concentration that is equal or greater than the trace impurities threshold of 0.1% (1000 mg kg^{-1}) are aluminium (see Table 3.1), barium, cobalt, copper, manganese, magnesium, nickel, phosphorus, lead and zinc. Compounds of these 12 elements require further consideration under Tier 3.

A3.3 Tier 3 of the hazard property assessment

As most metals are present in low concentrations in IBA (i.e. well below the hazard thresholds), the worst case compound for hazard property H14 were selected for Tier 1 and Tier 2 of the hazard assessment. Where the worst case compound is known not to be present in IBA, a more realistic compound may be selected as undertaken in Tier 3 of the hazard assessment.

Table A.13 presents the total (*aqua regia*) and leachable (BS EN 12457-3) of nickel.

Table A.13 Total and leachable nickel concentration in IBA

Parameter	Nickel concentration in mg kg^{-1}	
	Average	**95th percentile**
Total (*aqua regia*) Ni	135	420
Leachable Ni at L/S10 (BS EN 12457-3)	0.12	0.34

Note: leachability data supplied by 11EfW facilities as not all 18 facilities routinely monitor leachability

Collated leachability data (BS EN 12457-3) for IBA from 11 facilities show that the average and 95th percentile concentrations of leachable nickel are 0.12 and 0.34 mg Ni kg^{-1}. These levels are similar to 34 samples in the historical data set held by WRc.

The leachable (soluble) concentrations reported in Table A.13 (i.e. <1 mg Ni kg^{-1}) represent less than 0.1% of the total nickel concentrations (average of 135 mg Ni kg^{-1}). Nickel must therefore be present in IBA as non-soluble forms such as nickel alloys and nickel (II) hydroxide (as shown by the geochemical modelling exercise) rather than the soluble phases that carry risk phrases relevant to H13.

Using leaching test data as evidence of the poor solubility of nickel compounds present in IBA, nickel can be excluded from potential list of compounds that exceed relevant hazard thresholds for H13 as the water-soluble proportion is almost three orders of magnitude below the hazard threshold of 100 mg kg^{-1}. Average and 95th percentile concentrations of all other worst case compounds were shown to be below relevant hazard thresholds in the Tier 2 assessment.

A3.3.1 Ecotoxicity (H14) hazard assessment

On the basis of worst-case assessment principles, Tier 2 of the hazard assessment excluded all compounds carrying relevant risk phrases with the exception of compounds of aluminium, barium, chromium, copper, manganese, magnesium, nickel, phosphorus, zinc and lead. These require further consideration under Tier 3 as reported below.

Aluminium

Aluminium will be predominantly present as alloys (for example beverage cans) in waste inputs to EfW facilities. Alloys of aluminium do not carry ecotoxic risk phrases. The only compound listed in the CLP for aluminium with the risk phrase R50-53 is aluminium-magnesium-carbonate-hydroxide-perchlorate-hydrate. This is a product from a specific industrial process (no CAS number) and therefore unlikely to be present in IBA. As aluminium can be present at high concentrations in IBA (95th percentile for UK dataset is 74775 mg kg^{-1}), compounds with risk phrase R51-53 should also be considered, with a limit of 2.5% to be considered hazardous by H14. The only aluminium compound listed with the R51-53 risk phrase is trisodium hexafluoroaluminate, the presence of which would be precluded by low fluoride concentrations found in IBA (95th percentile 219 mg kg^{-1}).

Monomeric aluminium can be formed upon the hydrolysis of aluminium salts (aluminium chloride, aluminium nitrate and aluminium sulphate) under low pH conditions of typically <pH 6.5. These substances have a low decomposition temperature and a high solubility which precludes their presence in IBA[20].

Barium

Barium will be present in input streams to EfW facilities from a range of sources. The barium compound selected as the worst case compound in Table A.14 and which carries the R50-53 risk phrase, is from a specific industrial process and is highly unlikely to be in the waste input stream for EfW facilities.

All barium compounds listed in CLP with ecotoxic risk phrases are soluble. 11 facilities were able to supply barium leachability data (BS EN 12457-3) for IBA. The average and 95th percentile leachable concentration of barium was 11 and 40 mg Ba kg^{-1} showing that <6% of the total barium in IBA is in leachable, i.e. in soluble form. This evidence of relatively low leachability is supported by the 34 samples in the historical data set held by WRc (average and 95th percentile concentrations of 6.3 and 19.2 mg Ba kg^{-1}).

Table A.14 Total and leachable barium concentration in IBA

Parameter	**Barium concentration (mg kg^{-1})**	
	Average	**95th percentile**
Total (*aqua regia*) Ba	324	594
Leachable Ba (L/S10 BS EN 12457-3)	11.0	40.4

Note: leachability data supplied by 11 EfW facilities as not all 18 facilities routinely monitor leachability

The small proportion of barium that is soluble and therefore present as ecotoxic species is well below the threshold value for the material to be considered hazardous. This concentration is also well below the trace impurity threshold of 1000 mg kg^{-1}. Barium can be discounted from the H14 assessment.

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[20] Environment Canada (2008) priority substances list assessment report follow-up to the state of science report, 2000 for aluminium chloride, aluminium nitrate, aluminium sulphate. http://www.ec.gc.ca/lcpe-cepa/documents/substances/sa-as/assessment_rpt-eng.pdf

Calcium

Table 3.2 of the CLP states that the following calcium compounds bear risk phrase R50-53, i.e. are toxic to the aquatic environment at concentrations above the relevant hazard threshold: calcium chromate, calcium cyanide, calcium phosphide and calcium polysulphides.

Calcium chromate is a chromium (VI) compound. Due to the low concentration of chromium (VI) in IBA (1 mg kg^{-1}) the concentration of calcium chromate can be considered below the relevant hazard threshold. For the same reason calcium cyanide concentration is below the relevant hazard threshold due to the low concentration of cyanides (1 mg kg^{-1}) in IBA. Calcium hypochlorite and calcium phosphide degrade at temperatures significantly lower than those found in an incineration process (>800 ºC) therefore their presence in IBA can be discarded; similarly the presence of calcium polysulphides can be discarded, being liquid with a boiling point below 200 ºC. As these ecotoxic compounds will not be present in IBA, calcium can be discounted from the hazard assessment.

Cobalt

Table 3.2 of the CLP states that the following cobalt compounds bear risk phrase R50-53, i.e. are toxic to the aquatic environment, at concentrations above the relevant hazard threshold: cobalt acetate, cobalt carbonate, cobalt dichloride, cobalt lithium nickel oxide, cobalt nitrate, cobalt oxide, cobalt sulphate, cobalt sulfide.

Cobalt sulphate and cobalt dichloride both readily dissolve in water and as the leachable fraction of cobalt is very small (Table A.15) these substances will be present well below the trace impurities threshold.

Table A.15 Total and leachable barium concentration in IBA

Parameter	Cobalt concentration (mg kg^{-1})	
	Average	**95th percentile**
Total (*aqua regia*) Co	26.9	51.8
Leachable Co (L/S10 BS EN 12457-3)	0.03	0.06

Note: leachability data supplied by 8 EfW facilities as not all 18 facilities routinely monitor leachability

Cobalt nitrate, cobalt carbonate and cobalt acetate all degrade at temperatures between 100°C and 140°C which mean that if they were present in the MSW they would decompose during the incineration process. Cobalt sulphide will be oxidised to cobalt sulphate in the highly oxidising incineration conditions.

The presence of cobalt nickel lithium oxide is precluded by the geochemical modelling exercise which has shown that nickel mineralogy is dominated by the hydroxide. This compound could not be present at concentrations that require assessment.

As these ecotoxic compounds will not be present in IBA, cobalt can be discounted from the hazard assessment.

Chromium

The 95th percentile concentration of chromium, taken in worst-case form, potassium dichromate (Table A.12), is 5451 mg kg^{-1}. However, all chromium compounds that carry risk phrases related to H14 are compounds of chromium (VI). As chromium (VI) is unstable, chromium is more likely to be present in IBA as chromium (III) which does not carry H14 risk phrases. As chromium (VI) is not routinely determined in IBA, only 86 determinations were supplied as part of the UK IBA dataset (Table 3.1). The 95th percentile concentration of potassium dichromate based on Cr(VI) rather than total Cr (Table A.12) is 11.4 mg kg^{-1}, orders of magnitude below both the trace impurity threshold of 1000 mg kg^{-1}, and the relevant hazard threshold (2500 mg kg^{-1}).

Chromium can therefore be discounted from the H14 assessment.

It is recommended that all facilities include Cr(VI) as well as Cr (total) in their routine testing to confirm the prevalence of non-ecotoxic Cr(III) compounds.

Copper

The toxicity of copper is dependent on the chemical form (species) in which copper is present. Much of the copper in municipal waste would be expected to be present as copper metal (e.g. electrical wire and plumbing fittings) and alloys with zinc, tin or other trace metals. Copper metal and alloys are not ecotoxic and are largely unaffected by the incineration process with the exception of a thin oxide layer on copper metal products. These compounds are however dissolved into solution by the ‘total’ *aqua regia* dissolution method. Any assessment based on the analytical data is therefore worst case as a considerable quantity of the concentration of copper measured in this determination will be non-ecotoxic copper metal.

Anecdotal evidence from ash reprocessors that recover and sell ferrous and non-ferrous metals indicates that, of the baseload of 2000 mg kg^{-1} Cu in IBA (average concentration for the ESA dataset, Table 3.1), up to 1000 mg kg^{-1} is likely to represent metallic copper. Similarly, excursions above this value (e.g. values of 3000, 5000 or 10000 mg kg^{-1}) almost certainly represent copper metal fragments, such as e.g. copper wire (van der Sloot, *pers. comm.)* or alloys such as brass. However, these non-hazardous forms are indistinguishable from other copper phases dissolved in the *aqua regia* digest.

Any assessment of the contribution to copper to an ecotoxicity assessment based on *aqua regia* digest concentrations is therefore highly conservative as it makes no allowance for the presence on non-ecotoxic metallic copper in IBA.

The Classification, Labelling and Packaging Regulation (CLP, 2008) lists 25 ecotoxic copper compounds. Most of these are organic compounds that would not survive the combustion process. The three inorganic compounds listed are copper sulphate, copper (I) oxide and copper (I) chloride. The listed sulphate and oxide would not be expected to be found in IBA as, under the high temperature, highly oxidising incineration conditions, the copper sulphate would decompose at 650ºC[21] and much of the copper (I) oxide would be oxidised to copper (II) oxide which the CLP lists as carrying an R50 risk phrase (with a hazard limit of 25%) [20].

However, geochemical modelling has indicated that key copper phases are copper bound by iron (III) hydroxide, organic matter and copper hydroxide, none of which are listed in CLP.

The majority of copper species in the bottom ash would be expected to be copper metal and alloys largely unaffected by combustion and other species not listed in CLP. Copper compounds listed in CLP Table 3.2 can therefore be discounted from the assessment.

However to ensure a robust assessment, non-CLP listed compounds are considered in Tier 4.

Manganese

The toxicity of manganese is dependent on the chemical form (species) in which manganese is present. Only manganese sulphate has been identified as bearing risk phrase N50-53 i.e. ‘is toxic to the aquatic environment at concentrations above the relevant hazard threshold’. The primary source of manganese in the waste input stream will be stainless steel. The IBA leachability dataset shows that <0.1% of total manganese in IBA is available for leaching (Table A.16).The low leachable concentrations are similar to the 34 samples in WRc’s in house dataset[22].

As manganese sulphate is extremely soluble (solubility of 393 g l^{-1} in water)[15], manganese cannot exist in this form in IBA. Manganese would predominantly be present as alloys which are not ecotoxic and can therefore be discounted from further assessment for H14.

Table A.16 Total and leachable manganese in IBA

Parameter	Manganese concentration (mg kg^{-1})	
	Average	**95th percentile**
Total (*aqua regia*) Mn	823	1217
Leachable Mn (L/S10 BS EN 12457-3)	0.14	0.52

Note: leachability data supplied by 11 EfW facilities

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[21] The Merck Index. An encyclopedia of chemicals, drugs and biological. Eleventh edition. Merck and co Inc, (1989).

[22] WRc in-house data set: average <0.34 mg Mn kg-1, 95th percentile 1.3 Mn mg kg^{-1} at L/S10.

Magnesium

Magnesium compounds listed in the CLP with the R50-53 risk phrase are all compounds with some other element responsible for toxicity, as magnesium itself is relatively non-toxic. The compounds which carry the R50-53 that contain magnesium are “aluminium-magnesium-carbonate-hydroxide-perchlorate-hydrates” and “polyphosphoric acid, copper, sodium, magnesium, calcium, silver and zinc salt”. Both are mixtures of compounds (they have no CAS numbers) from specific industrial processes which are unlikely to be present in EfW input. Magnesium can be discounted from further assessment for H14.

Nickel

Many nickel compounds carry the R50-53 risk phrases. However, nickel alloys do not carry ecotoxic risk phrases.

The average and 95th percentile concentrations were below the trace impurity threshold and therefore in the large majority of cases, nickel can be discounted from further assessment.

However, five of the 419 samples contained nickel (II) hydroxide equivalent concentrations were above the trace impurity threshold and do require assessment.

This assessment assumes that all the nickel in the sample is present as nickel hydroxide whereas it is known that the *aqua regia* used to digest the IBA sample will also dissolve at least a portion of the nickel that is present as nickel metal and nickel alloys. Nickel metal carries the risk phrase R40 which has a less stringent threshold for hazard than nickel (II) hydroxide (1% or 10 000 mg kg^{-1}). Therefore assuming that 100% of the nickel found in IBA is nickel (II) hydroxide, this is a very precautionary approach.

Due to the exceedance of the five samples above the trace impurity threshold, the nickel compounds listed on CLP have been considered.

Of the compounds that are listed in CLP, the worst case nickel compound carrying the risk phrases R50-R53 and listed in Table A.12 is nickel dipotassium bis(sulphate). This compound is a specialist chemical product that is unlikely to be present in the municipal waste stream, not least because it is not registered under REACH and therefore only produced at <10 tonnes/year. Other compounds of nickel carrying the R50-R53 risk phrases that could exceed the 0.1% trace impurity threshold assuming they contain 100% of the nickel present in the IBA are: dinickel hexacyanoferrate, nickel bis(tetrafluoroborate), nickel dichromate and nickel selenite. The cyanide, chromium (VI) and selenium compounds can be discounted from being present in the IBA due to the low concentration of cyanide, chromium (VI) and selenium (see Table 3.1).

Nickel bis(tetrafluoroborate) is an acidic salt which is soluble in water. However, nickel has low leachability of nickel in water (Table A.13) Table A.17 presents the total (*aqua regia*) and leachable (BS EN 12457-3) of nickel.

Table A.17 Total and leachable nickel

Parameter	**Nickel concentration in mg kg^{-1}**	
	Average	**95th percentile**
Total (*aqua regia*) Ni	135	420
Leachable Ni at L/S10 (BS EN 12457-3)	0.12	0.34

Note: leachability data supplied by11 EfW facilities as not all 18 facilities routinely monitor leachability

Collated leachability data (BS EN 12457-3) for IBA from 11 facilities show that the average and 95th percentile concentrations of leachable nickel are 0.12 and 0.34 mg Ni kg^{-1}. These levels are similar to 34 samples in the historical data set held by WRc. The leachable nickel concentration of <1 mg kg^{-1} represents less than 0.1% of the total nickel concentrations (average of 135 mg Ni kg^{-1}). Nickel is therefore present in IBA as non-soluble forms such as alloys and nickel hydroxide, rather than leachable forms such as nickel bis(tetrafluoroborate).

Using the average and 95th percentile concentrations for 12 month dataset, all other nickel compounds carrying the risk phrases relevant to H14 hazard are below the 0.1% trace impurity threshold.

The geochemical modelling has demonstrated that the dominant phase for nickel is nickel (II) hydroxide which requires further assessment at concentrations greater than the trace impurity threshold (>1000 mg kg^{-1} $Ni(OH)_2$). This is assessed further in Tier 4 of the assessment and Section B5.

Phosphorus

Phosphorus was identified during the Tier 2 worst case assessment on the basis of phosphoric acid and white phosphorus. These two compounds can be specifically excluded as they cannot be present in IBA. The presence of phosphoric acid is precluded by the high pH of IBA (pH 10-11). White phosphorus is an explosive compound that would be broken down in the in the combustion process. The third phosphorus compound with H14 risk phrases is phosgene, which is a gas. Phosphorus can therefore be discounted from further assessment of H14.

Potassium

Potassium compounds listed in the CLP with the R50-53 risk phrase are all compounds with some other element responsible for toxicity, as potassium itself is relatively non-toxic. The compounds which carry the R50-53 that contain potassium are potassium chromate, potassium dichromate, potassium nickel fluoride, nickel dipotassium bis(sulphite), zinc potassium chromate, potassium permanganate. Amongst these, the chromium compounds (all containing chromium hexavalent), the two nickel compounds and potassium permanganate can be discounted from the assessment of H14 due to the low concentration of chromium, nickel and manganese in the IBA (246, 135 and 823 mg kg^{-1} respectively).

Sodium

Sodium compounds listed in the CLP with the R50-53 risk phrase are all compounds with some other element responsible for toxicity, as sodium itself is relatively non-toxic. The compounds which carry the R50-53 that contain sodium are silver sodium zirconium hydrogen phosphate, sodium chromate, sodium dichromate, “polyphosphoric acid, copper, sodium, magnesium, calcium, silver and zinc salt” and sodium azide. Amongst these, the chromium compounds (all containing hexavalent chromium), and silver sodium zirconium hydrogen phosphate can be discounted from the assessment of H14 due to the low concentration of hexavalent chromium and silver in the IBA (1 and 14.9 mg kg^{-1} respectively). Polyphosphoric acid, copper, sodium, magnesium, calcium, silver and zinc salt is a mixture (has no CAS numbers) from specific industrial processes which is unlikely to be present in ERF input. Sodium azide has a melting point of 275 ºC, therefore would degrade under the high temperatures in an incinerator and its presence in IBA can be discounted.

Zinc

The toxicity of zinc is dependent on the chemical form (species) in which zinc is present. Table 3.2 of the CLP and reference to relevant MSDSs shows that only the following zinc compounds bear risk phrase N50-53 (i.e. are toxic to the aquatic environment at concentrations above the relevant hazard threshold): zinc oxide, zinc chloride, zinc phosphide, zinc chromate, zinc powder.

Zinc is used as rolled strip (10%) and zinc coatings for iron and steel (35% production) but mainly in alloys with copper (brass) with or without aluminium, magnesium, tin and other trace metals[23]. Alloys present in household items will be largely unaffected by the incineration process and therefore most of the zinc present in IBA is considered to be present in a benign form. However, evidence, in the form of zinc speciation data is difficult to obtain. It cannot be inferred from the analytical data, as there are currently no routine techniques sensitive enough to quantify zinc species at <0.5%.

Modelling of IBA from a number of European energy from waste facilities, has shown that the zinc mineralogy is dominated by a zinc silicate, a non-ecotoxic form of zinc (van der Sloot *et al* (2008, 2009)). The geochemical work has been replicated by van der Sloot for ESA

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[23] Comprehensive inorganic chemistry Volume 3. Bailar J C, Emeleus, H.J, Nyholm, R and Trotman-Dickenson, A.F (Eds) Pergamon, 1973.

(WRc, 2012)[24] The geochemical modelling showed that dominant zinc phases in fresh and aged IBA were silicates ($ZnSiO_3$ or $ZnSiO_4$) or $Ca_4Zn(PO_4)_3OH$, although zinc silicates alone were dominant at the pH of fresh ash. (see Text Box 1). No ecotoxic risk phrases were identified for these phases in Table 3.2 of CLP and other data sources listed in WM2[25].

Therefore zinc compounds listed in CLP Table 3.2 can be discounted from further assessment for H14 in the 12 month dataset. However, non-CLP listed compounds are considered further in Tier 4.

Lead

Table 3.2 of the Classification, Labelling and Packaging Regulation states that ‘all lead compounds with the exception of those specified in this Annex’ bear the risk phrase N50-53, i.e. are toxic to the aquatic environment at concentrations above the relevant hazard threshold.

The average concentrations were all well below the hazard threshold of 2500 mg kg^{-1}.The 95th percentile and maximum (highest reported) concentrations of lead in the IBA dataset are 1608 and 2296 mg Pb kg^{-1} in comparison with the threshold of 2500 mg kg^{-1}. Examination of the highest concentration reported also showed that two of the 411 samples in the UK IBA dataset exceeded hazard thresholds for lead with respect to H14.

These are considered further in Tier 4 of the hazard assessment and Section B5.

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[24] An Assessment of the Mineralogy of UK MSW Incinerator Bottom Ash. WRc plc, September 2012. UC 8564.9 In prep.

[25] Data sources for risk phrases included Agency for Toxic Substances and Disease Registry, CHEMID plus (US National Library of Medicine), European Inventory of Existing Commercial chemical Substances, Hazardous Substance Databank, International program on Chemical Safety, Integrated Risk Information System and International Uniform Chemical Information Database.

Text Box 1 - Synopsis of geochemical modelling undertaken for ESA: zinc

IBA samples from two UK moving-grate EfW facilities were collected according to the ESA protocol in December 2010. Testing was undertaken to determine composition and a wide range of leachable contaminants under low to high pH conditions and liquid to solid ratios to determine the major ions that will dominate the mineralogical phases. In addition, reactive Al/Fe oxides and organic carbon fractionation were also determined in order to obtain the chemical speciation fingerprint for zinc, and to model the leaching behaviour of the ash. The primary tests undertaken include *aqua regia* composition, the pH-dependence leaching test (CEN/TS 14429:2005) and the upflow percolation test (CEN/TS 14405:2005).The compositional data showed the samples to be representative of UK IBA and used to undertake geochemical modelling of the zinc, copper and nickel species in IBA by Hans van der Sloot (formerly of ECN, Energy research Centre of the Netherlands).

The modelling approach took into account partitioning between the dissolved and solid phases of the material to determine the major mineral phases present for each element that controlled observed leaching characteristics. Mineral phases were selected on the basis of saturation indices at various pH conditions.

For zinc, the modelling work identified a (‘best fit’) for silicates ($ZnSiO_3$ or $ZnSiO_4$) or $Ca_4Zn(PO_4)_3OH$ at the normal pH of IBA for samples from around the world, aged IBA from the UK and the two December 2010 fresh IBA samples. Specifically for fresh IBA, **zinc silicate** would be dominant at the higher pH encountered in fresh, rather than aged, IBA.

Repeat modelling runs showed a poor fit for ZnO, CaZincate (calcium zinc oxide), $Zn(OH)_2$, willemite ($ZnSiO_4$), $ZnCl_2$ and bianchite ($Zn_{0.75}Fe_2+0.25(SO_4)•6(H_2O)$), (of these compounds zinc oxide, hydroxide and chloride are ecotoxic). This implies that the latter phases are not the phases controlling leaching over the pH range of relevance to IBA in normal exposure conditions, or in fresh ash as it leaves the facility. In addition any soluble zinc phases (e.g. $ZnCl_2$) would be expected to dissolve and more or less immediately re-precipitate as the less soluble silicates and phosphates – as would happen when the ash is quenched as it comes out the boiler.

Similar modelling was undertaken for copper and nickel (Text box 2).

An Assessment of the Mineralogy of UK MSW Incinerator Bottom Ash. WRc plc, October 2012 UC 8564.9

A4 Tier 4 of the waste hazard property assessment

A4.1.1 Ecotoxicity (H14) hazard assessment

Further data sources were searched to ensure that all the potentially ecotoxic copper and zinc compounds that could be present in IBA are investigated and assessed. These included the HSE pesticide and biocide databases, the EU pesticide and biocide databases, the UK veterinary products database and the European veterinary products databases for copper and zinc compounds that that have been approved for use, changed or banned. All REACH registered copper and zinc compounds were also included in this wider data search.

All the assessed copper and zinc compounds in these wider searches are included in the tables below. These include substances that have been given a harmonised hazard classification under the GHS and those that do not have a harmonised classification. These GHS hazard codes have been translated into R phrases as these classifications are used in the WM2 guidance.

Tier 4 has also been informed by the results of the geochemical modelling.

Table A.18 Additional copper compounds located in extended data search

Risk Phrase	Hazard threshold	Trace impurity threshold	Classification	Compounds located in additional data sources.
R50 (GHS – H400)	25%	0.1%	Harmonised	Copper dinitrate Copper oxide Residues, copper speiss acid leaching Residues, copper-iron-lead-nickel matte, sulfuric acid-insol.
			Non-harmonised	Copper carbonate hydroxide Copper pyrithione Oxine-copper
R53 (GHS – H410, H411, H12 and H413)	25%	1%	Harmonised	Reaction mass of cobalt and copper and iron Black copper, copper smelting Copper cyanide Copper hydroxide nitrate Copper Lead Resorcylate Salicylate Complex Cupro, copper processing Electrolytes, copper-manufg., spent Lead, dross, copper-rich Nitric acid, barium salt, reaction products with ammonia, chromic acid ($H2CrO_4$) diammonium salt and copper(2^+) dinitrate, calcined Scale (coating), copper Slags, copper refining Slimes and Sludges, copper electrolytic
			Non-harmonised	Copper Gluconate

Risk Phrase	Hazard threshold	Trace impurity threshold	Classifica-tion	Compounds located in additional data sources.
R50/53 (GHS – H400 and H410 H411, H412 or H413)	0.25%	0.1%	Harmonised	Cement copper copper sulphate copper(II) carbonate--copper(II) hydroxide (1:1) Speiss, copper tricopper arsenide
			Non-harmonised	Bis-n-(cyclohexyldiazeniumdioxy)-copper Copper (II) hydroxide Copper chloride oxide hydrate or copper chloride hydroxide Copper (II) acetate Copper (II) chloride Copper oxychloride Cuprous thiocyanate
-	-	-	No classification	[1,3,8,16,18,24-hexabromo-2,4,9,10,11,15,17,22,23,25-decachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper [2,9,16,23-tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper [tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper 29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32 copper Anode, copper Bordeaux mixture Chlorophyllin copper Copper ammonium carbonate Copper chlorophthalocyanine Copper complex: 8-hydroxyquinolin with salicylic acid Copper silicate Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, brominated chlorinated Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, chlorinated Mancopper Matte, copper Polychloro copper phthalocyanine Slags, copper smelting Tribasic copper sulphate

Table A.19 Additional zinc compounds located in extended data search

Risk Phrase	Hazard threshold	Trace impurity threshold	Classification status	Compounds located in additional data sources.
R50 (GHS – H400)	25%	0.1%	Harmonised	Hexaboron dizinc undecaoxide Zinc bis(dihydrogen phosphate) Diammonium tetrachlorozincate(2-) Zinc hydroxide Carbonic acid, zinc salt, basic Trizinc dicitrate Slimes and sludges, zinc sulfate electrolytic
			Non-harmonised	Zinc Stearate
R53 (GHS – H410, H411, H12 and H413)	25%	1%	Harmonised	Zinc bis[bis(dodecylphenyl)] bis(dithiophosphate) Flue dust, zinc-refining Calcines, lead-zinc ore conc. Calcines, zinc ore-conc. Potassium hydroxyoctaoxodizincatedichromate(1-) Di[carbonato(2-)]hexahydroxypentazinc Zinc bis(dibenzyldithiocarbamate) Zinc di(benzothiazol-2-yl) disulphide Zinc bis[o,o-bis(2-ethylhexyl)] bis(dithiophosphate) Pentazinc chromate octahydroxide Ammonium zinc chloride Phosphorodithioic acid, mixed o,o-bis(iso-bu and pentyl) esters, zinc salts Phosphorodithioic acid, mixed o,o-bis(sec-bu and 1,3-dimethylbutyl) esters, zinc salts Phosphorodithioic acid, mixed o,o-bis(2-ethylhexyl and iso-pr) esters, zinc salts Leach residues, zinc ore, lead-contg. Zinc, desilverizing skims Zinc nitrate Phosphorodithioic acid, mixed o,o-bis(1,3-dimethylbutyl and iso-pr) esters, zinc salts Phosphorodithioic acid, mixed o,o-bis(2-ethylhexyl and iso-bu and iso-pr) esters, zinc salts Zinc bromide Zinc bis[o-(6-methylheptyl)] bis[o-(sec-butyl)] bis(dithiophosphate) Zinc selenite
R50/53 (GHS – H400 and H410 H411, H412 or H413)	0.25%	0.1%	Harmonised	Ziram Leach residues, zinc ore-calcine, zinc cobalt Bis(3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoato-o1,o2)zinc Reaction products of zinc oxide and glycerol Residues, zinc smelting
			Non-harmonised	Zinc borate Zinc pyrithione Zinc sulphide

Risk Phrase	Hazard threshold	Trace impurity threshold	Classification status	Compounds located in additional data sources.
-	-	-	No classification	Acypetacs zinc Dadz (zinc-dimethylditiocarbamate) Zinc insulin Fatty acids, tall oil, oligomeric reaction products with maleic anhydride and rosin, calcium magnesium zinc salts, consisting of mainly calcium, magnesium, zinc salts of maleated rosin, fatty acids and rosin. Fatty acids, c14-18 and c16-18-unsatd., zinc salts Cobalt zinc aluminate blue spinel Zinc ferrite brown spinel Resin acids and rosin acids, calcium zinc salts Zinc, dross Fatty acids, c16-18, zinc salts Slags, lead-zinc smelting Reaction mass of disodium [2,2'-(imino-κn)dibutanedioato-κ2o1,o4(4-)]zincate(2-) and sodium nitrate

Of the compounds listed, any which carry the risk phrase R50 or R53 can be excluded from further assessment as the trace impurities threshold and threshold for hazard are 1% and 25%. However, these phases have not been identified in the geochemical modelling.

All the substances that have been classified as R50/53 or have not been classified require further assessment. However after assessing relevant physical and chemical characteristics (e.g. boiling point and solubility in water) for each of these compounds most can be discounted from further assessment as summarised in Table A.21 and Table A.22 for the following reasons:

- they have a low boiling point (for compounds with organic or volatile/semi-volatile components only) or decompose at high temperatures and therefore would not be present in IBA;
- they are very soluble and cannot therefore be present in high concentrations given the proportion of copper and zinc which is leachable in IBA (q.v.) (see Table A.20);

Table A.20 Total and leachable copper and zinc

Parameter	Copper	Zinc
Total metal (mg kg^{-1})	1957	2181
Leachable metal (L/S10 BS EN 12457-3 mg kg^{-1})	4.67	1.16

- the low concentration of the corresponding anion or key element (e.g. borate, bromide, selenium, arsenic, sulphide and cyanide compounds of copper or zinc) would preclude its presence at concentrations which exceeded hazard thresholds;

- an assessment as to the likelihood of the substances to be present in the input streams was also made. Compounds that are specifically from industrial processes as wastes or intermediates that are highly unlikely to be disposed of at municipal waste incinerators. For example residues and slags from zinc or copper refining are unlikely to be found in the input waste stream and can therefore be excluded from assessment.

Table A.21 Justification for excluding copper compounds from further assessment of IBA for ecotoxicity (H14)

Copper compounds	Reason for exclusion from further assessment			
	Low melting point	High water solubility	Low concen-tration of anion	Unlikely to be present in the input waste stream
[1,3,8,16,18,24-hexabromo-2,4,9,10,11,15,17,22,23,25-decachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper	✓		✓	
[2,9,16,23-tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper			✓	
[tetrachloro-29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]copper			✓	
29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32 copper	✓		✓	
Anode, copper		✓		✓
Bordeaux mixture		✓		
Chlorophyllin copper	✓			
Copper ammonium carbonate	✓			
Copper chlorophthalocyanine	✓		✓	
Copper complex: 8-hydroxyquinolin with salicylic acid	✓			
Copper silicate	✓			
Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, brominated chlorinated	✓		✓	
Copper, [29H,31H-phthalocyaninato(2-)-N29,N30,N31,N32]-, chlorinated			✓	
Mancopper	✓			
Matte, copper				✓
Polychloro copper phthalocyanine			✓	
Slags, copper smelting				✓
Tribasic copper sulphate	✓			
Bis-n-(cyclohexyldiazeniumdioxy)-copper	✓			
Copper (II) hydroxide				
Copper chloride oxide hydrate or copper chloride hydroxide				
Copper II acetate	✓	✓		

Copper compounds	Reason for exclusion from further assessment			
	Low melting point	High water solubility	Low concen-tration of anion	Unlikely to be present in the input waste stream
Copper II chloride		✓		
Cement copper				
Copper sulphate		✓		
Copper oxychloride	✓			
Copper(II) carbonate--copper(II) hydroxide (1:1)				
Speiss, copper	✓			
Tricopper arsenide			✓	
Cuprous thiocyanate	✓			

Table A.22 Justification for excluding zinc compounds from further assessment of IBA for ecotoxicity (H14)

Zinc compounds	Reason for exclusion from further assessment			
	Low melting point	High water solubility	Low concen-tration of anion	Unlikely to be present in the input waste stream
Acypetacs zinc	✓			
DADZ (zinc-dimethylditiocarbamate)	✓			
Zinc insulin	✓			
Fatty acids, tall oil, oligomeric reaction products with maleic anhydride and rosin, calcium magnesium zinc salts, consisting of mainly calcium, magnesium, zinc salts of maleated rosin, fatty acids and rosin.	✓			
Fatty acids, C14-18 and C16-18-unsatd., zinc salts	✓			
Cobalt zinc aluminate blue spinel			✓	
Cinc ferrite brown spinel				✓
Resin acids and Rosin acids, calcium zinc salts	✓			
Zinc, dross				✓
Fatty acids, C16-18, zinc salts	✓			
Slags, lead-zinc smelting				✓
Reaction mass of disodium [2,2'-(imino-κN)dibutanedioato-κ2O1,O4(4-)]zincate(2-) and sodium nitrate	✓	✓		
Zinc borate				✓
Zinc pyrithione	✓			
Ziram	✓			
Leach residues, zinc ore-calcine, zinc cobalt	✓			
Bis(3,5-bis(1,1-dimethylethyl)-2-hydroxybenzoato-O1,O2)zinc		✓		
Reaction products of zinc oxide and glycerol	✓			
Residues, zinc smelting				✓

The additional copper and zinc compounds not listed in the CLP have been assessed. A number were discounted from the ecotoxic assessment due to:

- absence of an ecotoxic risk phrase; or
- the risk phrase assigned has a trace impurities threshold of 1% (10 0000 mg kg^{-1}) and a limit for hazard of 25% (250 000 mg kg^{-1}), both of which are much higher concentrations than is possible for the concentrations of elemental copper and zinc in the ESA IBA dataset;
- their physicochemical properties e.g. they would be destroyed during the incineration process or would be shown to leach from the IBA during leaching tests;
- the low concentration of other elements or anions in the compound are too low to enable that concentration to exist at concentrations that exceed the trace impurities threshold;
- they are specific industrial compounds from activities such as copper smelting or processing, or are intermediate products in industrial processes, that would not be part of inputs to a municipal waste EfW facility.

All the zinc compounds and most of the additional copper compounds located in the wider search can be discounted from assessment of ecotoxicity.

Three copper compounds remain including copper hydroxide and copper hydroxide complexed with other phases. Copper hydroxide has been identified as a key phase from the geochemical modelling of IBA for the control of copper release as have copper bound with particulate organic matter and iron (III) hydroxide as described in Text Box 2.

These compounds are considered in detail below.

Copper hydroxide

Copper hydroxide does not have a harmonized classification as it is not listed in the CLP. It has not been registered under the Registration, Evaluation, Authorization and restriction of Chemicals (REACH, 2006) and therefore no REACH dossier is currently available.[26]

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[26] REACH (2006) regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).

Text Box 2 - Synopsis of geochemical modelling undertaken for ESA: copper and nickel

IBA samples from two UK moving-grate EfW facilities were collected according to the ESA protocol in December 2010 and testing and geochemical modeling undertaken as described in Section A3.3.1 Text Box 1. Similar modeling was undertaken for copper and nickel.

Nickel

A consistent outcome was obtained for nickel in both fresh and aged samples (i.e. in the condition as they would leave the EfW facility and after several weeks of ageing at the ash reprocessors). This showed that dominant phase controlling the release of nickel was **nickel hydroxide**.

Copper

The phases controlling copper release in fresh ashes were ***iron (III) hydroxide and particulate organic matter, and in aged ashes copper hydroxide and/or phosphate hydroxides.*** Sulphate hydroxides were identified as minor phases in some samples but outside the normal pH domain of IBA.

The modelling exercise has highlighted that the ash ageing process represents a continuum until full carbonation of the IBA at pH 7-8 over decades. It is understood that in the early stages of this process, when the ash is still at high pH (>11) and at the same time that organic matter is gradually removed, copper hydroxide is repeatedly precipitated as a coating on inorganic particles. This secondary mineralisation increases the dominance of copper hydroxide with time, followed by the conversion to other inorganic phases, depending on the availability of other ions, e.g. phosphate hydroxides or sulphate hydroxides, and over many decades, carbonates.

However, in very fresh IBA samples, i.e. the samples as they would leave the EfW facility for disposal or treatment, the organic matter in the ash would have little time for microbial degradation or wash out, hence key phases for copper release were identified as iron (III) hydroxide or copper bound with particulate organic matter.

It should be noted that the modeling cannot account for the non-hazardous metal items which are also dissolved in *aqua regia* with potentially hazardous phases and therefore presents a conservative position.

An Assessment of the Mineralogy of UK MSW Incinerator Bottom Ash. WRc plc, October 2012 UC 8564.9

Copper hydroxide does have a number of non-harmonised classifications, some of which indicate that it is acutely and/or chronically toxic to aquatic organisms. There are sixteen non-harmonised classifications which have been submitted by a number of manufacturers for which we have no details or have access to any of the data or methodology used to classify the substance. However, the majority of the registrants have classified copper hydroxide as acutely and chronically toxic to aquatic organisms (H400-H410)[27]. Using a weight of evidence approach it has been decided that copper hydroxide should be classified as being acutely and chronically toxic to aquatic organisms and be assigned the risk phrase R50-53.

This classification is supported by the risk assessments performed for copper (II) hydroxide as an active substance in pesticides and biocides. Of note, there is a European Commission assessment report for the inclusion of copper (II) hydroxide into Annex I or Annex IA of Directive 98/8/EC, biocidal products on the market (EC, 2011)[28]. This report includes a thorough human health and environmental risk assessment of copper (II) hydroxide as used in wood preservatives. As part of this assessment the EC have provided a proposed risk classification under the CLP regulations (Directive 67/548/EEC) of R50-53 (Very toxic to aquatic organisms, may cause long term health effects in the aquatic environment).

A European Food Safety Authority report (EFSA, 2008) also classified the copper species (including copper (II) hydroxide) used in plant protection products as R50-53. This assessment has been based on the lowest aquatic toxicities found for the group of copper substances including copper (II) hydroxide. These authoritative risk assessments both propose R50-53 classifications for copper (II) hydroxide and give strong indication that copper (II) hydroxide could be a substance of concern for the classification of IBA under hazard property H14 (ecotoxicity).

It is therefore proposed that copper (II) hydroxide should be assigned the risk phrase R50-53 for the purposes of the assessment of ecotoxicity in IBA.

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[27] ECHA (2012) C&L inventory database - http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database - Last accessed 22/10/12

[28] European Commission (EC) (2011) Directive 98/8/EC concerning the placing of biocidal products on the market. Inclusion of active substances in Annex I or IA to Directive 98/8/EC. Assessment Report, Copper (II) Hydroxide, Product type-8 (Wood preservatives). September 2011.

Calcium copper phosphate hydroxide ($Ca_4Cu(PO_4)OH$)

This phase may be a minor phase controlling copper release in some aged samples, and like copper hydroxide would be a transient phase.

Risk phrase information on the compound is limited[29]. Non harmonized classifications are listed in the CLP inventory for H412 or aquatic chronic 3 and would carry risk phrase R53 with a hazard threshold of 25%. This information may be relevant to the modelling of other IBA samples. However, it is unlikely to be relevant to the geochemistry of fresh and copper concentrations rarely exceed the trace impurity threshold relevant for R53 compounds (1% or 10 000 mg kg^{-1}).

Iron (III) hydroxide ($Fe(OH)_3$)

Iron (III) hydroxide ($Fe(OH)_3$) does not have a harmonized classification as it is not listed in the CLP. There are non-harmonised classifications for $Fe(OH)_3$ none of which classify it as ecotoxic. It should be noted that this form of iron (III) hydroxide is used in aquariums and water treatment as a natural absorber of heavy metals and phosphate therefore it is very unlikely that this compound has any ecotoxic properties.

Particulate organic matter

There is no data available on the classification of copper bound to particulate organic matter and no similar compounds by which information could be drawn.

Position on copper speciation

Neither iron (III) hydroxide nor particulate organic matter are ecotoxic but secondary mineralisation of copper hydroxide (an ecotoxic transient phase) would commence during the ash ageing process. As the exact timing of copper hydroxide precipitation is unknown, a worst-case position has been taken for copper speciation in very fresh IBA.

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[29] No data could be located on calcium copper phosphate hydroxide ($Ca_4Cu(PO_4)OH$) specifically. As such a similar compound was sought for information on the likely risk phrases that may be appropriate for this compound. A similar compound, copper phosphate hydroxide ($Cu_2(PO_4)OH$, CAS 12158-74-6), was found but this does not have a harmonised classification or registration under REACH. It has a number of non-harmonised classifications under CLP which identify it as H412 or aquatic chronic 3 and therefore would carry risk phrase R53. It has also been approved for use in packaging in contact with food by EFSA (2012).

Intermediary compounds to calcium copper phosphate hydroxide that could be considered are copper orthophosphate and copper phosphate. Neither copper phosphate nor copper orthophosphate are listed in the Table 3.2 of the CLP and they do not have harmonised classifications. They have not been registered under the Registration, Evaluation, Authorization and restriction of Chemicals (REACH, 2006) and therefore no REACH dossier is currently available. Non harmonized classifications were listed in the CLP inventory for H412 or aquatic chronic 3 and therefore would carry risk phrase R53.

As such with the limited data available a classification of calcium copper phosphate hydroxide is not possible. Data on similar and intermediary compounds indicate that it may be chronically toxic to aquatic organisms and may carry the risk phrase R53 with a hazard threshold of 25% (250 000 mg kg^{-1}).

The assumption has been made that the underlying copper mineralogy that is controlling the release of copper is based on 20% copper hydroxide and 80% iron (III) hydroxide and particulate organic matter.

Table A.23 presents the concentrations of for copper in fresh IBA in the ESA dataset as copper metal and 20% copper hydroxide. These values make no allowance for copper metal in the sample.

Table A.23 Assessment of copper for ecotoxicity (R50-53)

Proportion compound in IBA (excluding Cu metal)	Conversion factor (Cu to compound)	Concentrations in IBA from ESA dataset mg kg^{-1}			
		Minimum	Average	95th percentile	Maximum
Copper hydroxide (20%) in IBA					
Total copper mg kg^{-1} (as Cu)		71.3	1900	3679	17871
20% total copper as copper hydroxide mg kg^{-1}	1.54	22.0	585	1133	5504

A4.1.2 Procedure for assessment of ESA dataset for H14 (ecotoxicity)

The outcome of the analysis of species likely to be present in IBA shows that the assessment should focus on the nickel (as nickel hydroxide), lead (as elemental lead) and 20% of the copper concentration (as copper hydroxide).

Using equation 1 from WM2, the procedure for undertaking the H14 assessment is as follows, on a sample by sample basis:

(a) Identify which samples exceed the trace impurity threshold and need to go forward into the assessment (trace impurities threshold = 1000 mg kg^{-1} for R50-53, R51-53 and R50 compounds, and 10 000 mg kg^{-1} for R52-53, R52, R53 compounds).

   (i) Multiply the nickel concentration by 1.58 to convert to nickel (II) hydroxide and compare it to the 1000 mg kg^{-1} threshold;

   (ii) Compare the elemental lead concentration directly with the 1000 mg kg^{-1} trace impurity threshold;

   (iii) Calculate 20% of the total copper concentration then multiply this by 1.54 to convert it to $Cu(OH)_2$ and compare this to the 1000 mg kg^{-1} trace impurity threshold.

(b) Use concentrations that exceed the threshold for trace impurities in equation 1 (from WM2) as follows:

Equation 1

$$((\Sigma.\text{R50-53} / 2500)+(\Sigma.\text{R51-53} / 25\,000)+(\Sigma.\text{R52-53} / 250\,000)) \geq 1$$

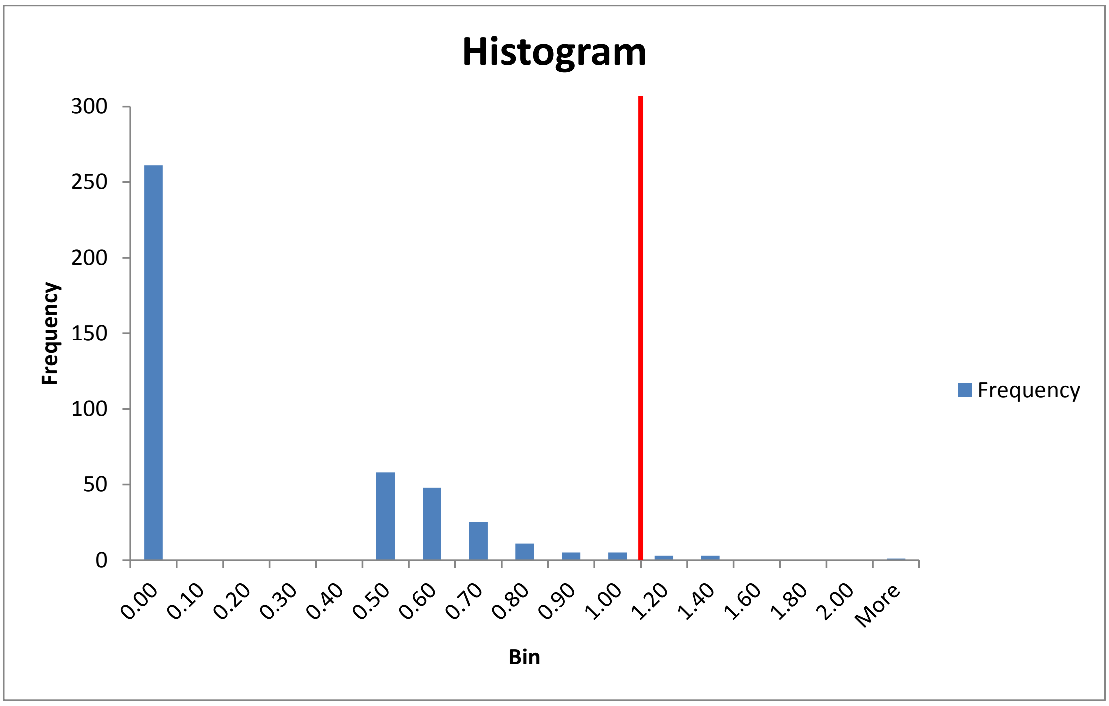
Where
Σ.R50-53 = sum concentration of compounds classified as R50-53
Σ.R51-53 = sum concentration of compounds classified as R51-53
Σ.R52-53 = sum concentration of compounds classified as R52-53

Note: R53 phrases such as those associated with calcium copper phosphate hydroxide would need to be assessed using Equation 4 in the WM2, but only if they exceed the trace impurities threshold of 1% (10 000 mg kg^{-1}).

As there are no compounds to be assessed which bear risk phrases R51-R53 and R52-53 the result from point b) can be compared with the threshold for compounds with R50-53 risk phrases.

The distribution of the results of the ecotoxicity assessment are shown in Figure A.1. The threshold of 1.00 is the threshold for Equation 1 presented above. Over half of the 419 samples recorded a value of below 0.1. Seven samples reported a value which exceeded the threshold value of 1.00, the highest value recorded was 2.65.

Figure A.1 Distribution of results from ecotoxicity assessment (H14)



Using the proposed approach, seven of the 419 samples analysed under the ESA protocol in 2011 were found to exceed the H14 (ecotoxic) hazard threshold. These were generated by five facilities in 2011.

However, it should be noted that copper metal is easily brought into solution by *aqua regia* digestion and therefore a significant but unquantifiable component of the IBA is likely to be present as non-ecotoxic copper metal fragments (e.g. copper wire) and brass. The assessment above is therefore highly conservative as it makes no allowance for the metallic copper in IBA.

A5 Conclusions for hazard assessment of IBA collected in 2011

The average and 95th percentile concentrations for the IBA dataset were below hazard thresholds for H8, H5/6, H10, H11 and H13. Maximum concentrations exceeded hazard thresholds for H4, H8, H7 and H14.

- H4/H8: two samples out of 419 were found to exceed the H4 limit value only; an additional 12 samples were also classified as exceedances by H4 and H8 because they had incomplete datasets and could not be fully assessed.

  This property (pH and a proportion of the alkali reserve) needs to be checked on a case-by-case basis and reasons for high pH or alkali reserve must be investigated.

- H7: On the assumption that all the nickel in each sample is present as nickel (II) hydroxide, with no allowance for nickel metal, five of 418 samples exceeded the hazard threshold for H7. Occasional high levels of nickel in IBA (>1000 mg kg^{-1} $Ni(OH)_2$, >633 mg kg^{-1} Ni) will therefore need to be assessed on a case-by-case basis and retests ordered , specifying 11 replicates.

- H14: looking at all the available data and taking a speciation position based on the geochemical modelling results it is proposed that the key compounds for assessment of IBA for H14 (ecotoxicity) are:

    - 20% of the total copper concentration as copper (II) hydroxide (R50-53);

    - lead concentration (as Pb) (R50-53); and

    - nickel (II) hydroxide (R50-53).

  The concentrations that exceed the relevant trace impurities threshold (1000 mg kg^{-1} for R50-53 compounds) should be included in the "Equation 1" as set out in the WM2 to assess whether the concentrations exceed the threshold for hazard.

  Using the proposed approach, seven of the 419 samples analysed under the ESA protocol in 2011 were found to be exceed the hazard threshold for H14 (ecotoxic). These were generated by five facilities in 2011.

These recommendations should be revisited if any of the compounds are reclassified in CLP Table 3.2, or further data become available, specifically:

- geochemical modelling information that is specific to the facility generating the IBA

- quantification of proportions of copper or nickel metal that contribute to the total *aqua regia* digest concentration.

Overall, 25 samples out of the 419 analysed under the ESA protocol in 2011 were found to exceed hazard thresholds for either H4, H8, H7, H14 or a combination of one or more of these hazard properties. Ten of the facilities had one or more exceedances in 2011, but on the basis of the first 12 months' data, no single participating facility recorded more than six exceedances. The IBA from the participating facilities would therefore be characterized as 'non hazardous' according to the approach laid out in the ESA protocol (2010).

Databases searched for Tier 4 assessment

HSE (2012a). Pesticides Register of UK Authorised Products, https://secure.pesticides.gov.uk/pestreg/, Last accessed May-2012.

HSE (2012b). Pesticide Products with UK Authorisation for use in the Garden, https://secure.pesticides.gov.uk/garden/prodsearch.asp, Last accessed May-2012

HSE (2012c). Non-agricultural pesticides approved under: The Control of Pesticides Regulations 1986 (as amended), http://www.hse.gov.uk/biocides/copr/approved.htm, Last accessed May-2012

HSE (2012d). HSE BPR/BPR NI Certificate of Exemptions Database http://webcommunities.hse.gov.uk/connect.ti/pesticides/view?objectId=6052, Last accessed May-2012

HSE (2012e). HSE BPR/BPR NI Authorised/Registered Products, http://webcommunities.hse.gov.uk/connect.ti/pesticides/view?objectId=6020, Last accessed May-2012

EU (2012a) Pesticide residue MRLS database, http://ec.europa.eu/sanco_pesticides/public/index.cfm?event=activesubstance.selection, Last accessed May-2012

EU (2012b) Biocides: Substances included in Annex I or IA to Directive 98/8/EC http://ec.europa.eu/environment/biocides/annexi_and_ia.htm, Last accessed May-2012

Veterinary medicines directorate (2012) Product Information Database, http://www.vmd.defra.gov.uk/ProductInformationDatabase/, Last accessed May-2012

European Medicines Agency (2012) Veterinary medicines database, http://www.ema.europa.eu/ema/, Last accessed May-2012

ECHA (2012) REACH Registered substances database, http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances, Last accessed June 2012

Property data gathered from:

EFSA (2012). Publications database http://www.efsa.europa.eu/en/publications.htm, Last Accessed May-2012

TOXNET (2012) Toxicology data network, http://toxnet.nlm.nih.gov/, Last Accessed May 2012

ChemID (2012). Chemical database, http://chem.sis.nlm.nih.gov/chemidplus/, Last Accessed May 2012.

ECHA (2012). ESIS: European chemical Substances Information System, http://esis.jrc.ec.europa.eu/, Last Accessed May 2012.

Pesticides Properties Database (2012). http://sitem.herts.ac.uk/aeru/footprint/en/, Last accessed May 2012.

Sigma-aldrich (2012) Databases and MSDS documents http://www.sigmaaldrich.com/united-kingdom.html, Last accessed May 2012

Appendix B Data by Participating Facility

Table B.1 Key test data by participating facility

		Number of exceedances	pH	Alkali Reserve	Al	Ba	Cd	Cr	Cu	Pb	Mg	Mn	Ni	P	K	Zn	TPH
				g 100g^{-1}	mg kg^{-1}												
All plants	Average	25	11.7	0.78	21625	324	11.2	246	1900	820	6980	823	135	4838	3564	2107	144
	95th Percentile		12.6	3.84	39364	594	30.1	990	3679	1608	10251	1217	420	7551	5228	3292	310
	Maximum		12.9	5.40	74775	2270	72.4	1358	17871	2296	12300	4597	1050	8660	17297	9389	324
1	Average	0	12.0	0.21	22194	274	7.0	73	1844	550	7195	648	60	5247	3616	1929	
	95th Percentile		12.4	0.44	27119	415	12.8	99	2870	1007	9914	853	94	7209	5105	2469	
	Maximum		12.5	0.50	42130	423	14.8	141	7315	1050	10206	962	105	7420	5201	3566	
2	Average	0	11.8	1.14	15528	261	2.8	148	2067	383	4344	971	114	1952	2620	1736	156
	95th Percentile		12.4	4.20	31430	489	7.6	277	5188	680	7712	1355	203	4976	5529	3581	251
	Maximum		12.6	4.23	38709	508	8.5	280	5649	1159	8066	4562	257	5363	5899	4291	262
3	Average	1	11.6	0.28	24062	264	6.8	71	1960	585	7568	643	72	5757	3881	1879	29
	95th Percentile		12.5	0.81	37303	429	14.4	114	2568	1199	9681	943	120	7550	5042	2430	29
	Maximum		12.7	1.04	46539	516	17.3	124	6399	1294	9903	968	209	8220	6266	2463	29
4	Average	0	11.6	0.25	28300	278	10.5	85	2368	684	9254	717	75	5591	4590	2440	43
	95th Percentile		12.5	0.94	40507	513	18.0	107	4592	1048	12217	904	114	8207	5630	3869	43
	Maximum		12.6	1.80	46580	558	72.4	109	5787	1380	12300	909	163	8660	17297	4166	43
5	Average	2	11.9	0.15	31461	299	10.6	87	2901	585	7027	986	77	5577	3763	3044	
	95th Percentile		12.6	0.31	52501	480	18.4	112	6369	1079	9409	1663	131	7228	5030	5345	
	Maximum		12.6	0.38	62875	500	19.0	126	17871	1121	10428	4597	254	7639	5240	9389	0
6	Average	0	11.6	0.16	13225	215	11.2	331	1738	1389	4597	742	184	1164	1269	1839	158
	95th Percentile		12.5	0.27	28741	408	26.6	758	2042	1912	7382	1342	440	1455	2007	2264	305
	Maximum		12.6	0.32	44900	444	28.0	906	2243	2167	9240	1971	565	1474	2214	2573	310
7	Average	1	10.5	1.74			20.3	777	1686	1160		991	293			1799	
	95th Percentile		11.1	3.83			39.4	1216	2289	1556		1248	555			2487	
	Maximum		11.2	3.96			44.2	1315	2383	1641		1591	673			2571	
8	Average	0	10.7	2.23			26.1	812	1789	1456		795	296			1861	
	95th Percentile		11.7	3.99			51.1	1211	2303	1986		1122	472			2289	
	Maximum		11.7	4.02			64.8	1240	2414	2296		1127	581			2590	
9	Average	1	11.0	1.89			19.5	670	1681	1200		969	185			1932	
	95th Percentile		11.8	4.22			43.3	1206	2078	1755		1220	379			2304	
	Maximum		12.1	4.33			68.4	1358	2140	2109		1589	433			2357	
10	Average	1	12.0	0.33	23788	286	9.0	78	1840	693	8638	692	77	5785	3989	2179	
	95th Percentile		12.5	0.88	36066	489	15.5	100	2401	1046	10901	839	118	7340	5179	2806	
	Maximum		12.6	1.08	44492	496	16.9	102	3968	1529	11920	914	120	8001	6182	3367	
11	Average	0	12.2	0.23	22100	266	6.2	66	1467	565	6126	590	54	5539	3173	1935	29
	95th Percentile		12.6	0.50	32360	427	10.5	80	2695	817	8115	1021	91	7714	4139	3658	29
	Maximum		12.7	0.51	39475	478	11.5	91	2927	919	8147	1087	100	8146	4315	5279	29

		Number of exceedances	pH	Alkali Reserve	Al	Ba	Cd	Cr	Cu	Pb	Mg	Mn	Ni	P	K	Zn	TPH
				g $100g^{-1}$	mg kg^{-1}												
12	Average	2	11.6	0.19	28845	356	7.0	137	2348	905	8146	880	129	4441	3858	2336	40
	95th Percentile		12.4	0.47	45356	771	12.6	254	4622	1614	10601	1179	279	5677	5233	3600	40
	Maximum		12.5	0.51	74775	811	16.5	586	4857	1648	11684	1190	300	6318	5310	5739	40
13	Average	5	12.3	0.84	17264	495	8.4	73	1765	754	8664	884	142			2417	9
	95th Percentile		12.9	1.39	27576	645	17.9	101	2163	1153	10143	1134	421			2845	9
	Maximum		12.9	1.53	29300	716	21.6	105	2232	1446	11067	1134	1050			2897	9
14	Average	6	12.2	1.11	18660	614	7.6	67	1926	589	8211	812	109			2363	9
	95th Percentile		12.9	4.64	25160	682	15.0	91	2882	930	9136	999	220			3083	9
	Maximum		12.9	5.40	26007	2270	29.8	100	3178	1501	10237	1107	745			3236	9
15	Average	0	12.2	0.27	25541	228	10.0	109	1904	481	7462	875	88	5251	3679	2691	49
	95th Percentile		12.6	0.48	35722	552	16.8	153	4523	837	8971	1202	157	7110	4765	3807	49
	Maximum		12.7	0.64	43019	581	34.8	171	5761	857	9577	1330	220	7359	5022	4056	49
16	Average	2	11.4	1.93	13773	311	9.5	409	1415	1140	5010	1017	241			1766	170
	95th Percentile		12.4	4.13	27134	470	16.0	675	2184	1567	6451	1546	634			2147	311
	Maximum		12.5	4.27	38201	816	19.5	900	2231	1689	9082	2480	721			2473	324
17	Average	4	12.5	1.02	14578	439	18.3	85	1840	693	5672	880	112			2257	
	95th Percentile		12.7	2.08	22168	633	40.6	122	2901	1363	8651	1237	172			3278	
	Maximum		12.7	2.20	23100	679	64.2	131	3034	1540	9350	1394	185			3465	
18	Average	0	10.9	0.59	29195	391	8.10	291	1579	917	7569	768	129	4862	3249	1590	
	95th Percentile		11.5	1.24	30517	402	15.0	720	3016	1362	7849	1172	288	5516	3399	2303	
	Maximum		12.4	1.72	30664	403	20.2	1147	7956	1379	7880	1200	451	5588	3415	2380	