Classification of waste to enable utilization in an environmental safe way

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Abstract

The Dept. of Applied Environmental Science (ITM), Stockholm University, and the Swedish Geotechnical Institute (SGI) have worked in projects with the main aim to improve the understanding of governing mechanisms for ecotoxicity of ash materials. With the ambition to provide recommendations on classification of waste according to H-14, we have characterised bottom and fly ash materials based on total levels in solid materials and eluates. In addition, the eluates have been characterized with a battery of ecotoxicity tests.

The most important findings from the projects are: (1) considering harmonization of waste and chemical legislations (i.e. CLP), the classification of waste according to H-14 will involve drastic changes as opposed to more traditionally waste characterization methods, both related to choice of leaching conditions (e.g. L/S ratios (>1000), pH) and ecotoxicity tests (test species, endpoints) (2) classification based on total content of substances over-estimates the ecotoxicological hazard potential as compared with ecotoxicity testing of eluates; (3) when leaching is performed at L/S ≤10 L/kg, components not classified as hazardous, in particular potassium, significantly influence the toxicity of the eluates, which is problematic from a hazard classification perspective, but likely negligible from a long-term environmental risk perspective.

Keywords: Ash; H-14; classification; risk assessment; ecotoxicity tests

1 Background

In recent years, the promotion of energy production from waste and biomass in the European Union has led to a strong increase in the amount of combustion residues, i.e. ash materials. Finding ways to utilize these ash materials in an environmental and economically efficient manner is an important goal throughout Europe. However, utilization must be done without danger for the human health and the environment in accordance with the current legislation.

According to the Waste Framework Directive (WFD; 2008/98/EC) waste and hazardous waste should be classified in accordance with the List of waste (European Commission, 2000), in which so-called mirror entries concern waste types with the potential to be either hazardous or non-hazardous depending on their composition and concentrations of hazardous substances. Bottom ash from municipal and industrial waste incineration has such mirror entry, and for which hazard classification is thus mandatory. The WFD further states that “classification of waste as hazardous waste should be based, inter alia, on the Community legislation on chemicals, in particular concerning the classification of preparations as hazardous...”. In this context, Regulation No 1272/2008 (CLP; European Regulation on Classification, Labeling and Packaging of chemical substances and mixtures) implements globally harmonized criteria for the classification of substances and mixtures according to their physical, health and environmental hazards (GHS; Globally Harmonized System of Classification and Labelling of Chemicals, Rev 4 United Nations 2011). Although no formal decision has been taken whether chemical and waste legislations should be harmonized in terms of hazardous properties and
test procedures, the enforcement of the CLP for mixtures by 2015, in our view, makes it highly relevant that this will be the case. Fifteen properties (i.e. H-criteria) of waste that may render it hazardous are listed in the WFD and, of these, criterion H-14 concerns the inherent ecotoxicological properties of waste. Currently, there are no harmonized quantitative criteria for H-14 classification, but several European countries have identified the need of biological test systems.

Over the last 4-year period the Dept. of Applied Environmental Science (ITM), Stockholm University, and the Swedish Geotechnical Institute (SGI), financed by Värme forsk (Thermal Engineering Research Association), Avfall Sverige (Swedish Waste Management) and the Swedish EPA, have worked in projects with the central aim to improve the understanding of governing mechanisms for ecotoxicity of ash eluates. The ambition has also been to provide recommendations on how these findings can be utilised within a formal classification framework of waste with respect to H-14.

2 Methods and Results

We have conducted four projects involving characterization of 10 Swedish bottom and fly ash materials based on total levels in solid materials and levels in eluates generated using different leaching methods. Eluates have also been characterised using a range of ecotoxicity tests. These projects are briefly summarized below.

2.1 PROJECT 1 – An ecotoxicological approach for hazard identification of energy ash (Stiernström et al., 2011).

With the main aim to increase the general understanding on how to classify energy ash materials with regards to criteria H-14, the objectives of this project were to evaluate if a) clear concentration-response relationships could be achieved for the selected toxicity tests (bacteria, algae, crustacean and fish), b) some test(s) were more sensitive than others and c) the toxic responses were consistent with the chemical analyses. The test battery used was selected to represent a wide range of biological variation and routes of exposure to trace an array of toxicity mechanisms. As model energy ash materials, bottom and fly ash from industrial, biofuel and municipal waste incineration were studied. Extracted water eluates were prepared either with the batch method described in EN 14735:2005 (L/S 10) or with a modified version of a recirculation column method, the ER-H method, developed by Gamst et al. (2007). Chemical analyses were made on both the solid matrices and on the eluates.

Overall, if considering both hazardous and non-hazardous substances in the eluates, the observed toxic responses were relatively consistent with the chemical analyses. However, classifications based on total content of substances in solid matrices drastically over-estimate the toxic responses. Our results further show that, in general, the selected test organisms responded with distinct concentration-responses and that the (sub)chronic tests were much more sensitive than the acute tests. Since no single test or test organism proved most sensitive to all ash eluates, characterising ash eluates should be based on a battery of test organisms representing a wide range of biological variation and different routes of exposure.

2.2 PROJECT 2 – Improved understanding of key elements governing the toxicity of ash eluates (Stiernström et al., Manuscript in preparation).

In the above mentioned project, an attempt was made to identify which elements were potentially responsible for the ecotoxicity of the eight ash eluates evaluated. Based on measured concentrations of elements in the eluates together with literature acute toxicity data on the crustacean N. spinipes we identified six elements (i.e. Zn, Cu, Pb, Al, K and Ca) potentially responsible for the observed ecotoxicity. However, comparing the used test methods with N. spinipes, the acute test was relatively insensitive to the eluates, whereas the (sub)chronic test was very sensitive. The overall aim of this follow-up study was to verify if the pinpointed elements could be responsible for the observed (sub)chronic toxicity of the eluates. Individual effect levels (i.e. NOEC values) for these six elements were therefore generated using the (sub)chronic test.
The findings clearly confirm our previous indications that the hazardous potential of eluates generated from ash materials from a range of Swedish incineration plants to a large extent is associated with elements not classified as hazardous. For six of the eight eluates the observed ecotoxicity can be explained by elements traditionally not classified as hazardous (i.e. Al, K and Ca). These elements will likely have significant implications for classification of ash according to H-14 and future strategies using ecotoxicological test methods for this purpose need to consider such artifacts, otherwise there is a risk for misclassification. At the same time, Cu, Pb and Zn were not identified as responsible for any of the observed effects of the eluates investigated in this study based on (sub)chronic data.

2.3 PROJECT 3 – Influence of leaching conditions (pH, L/S and particle size) for ecotoxicological classification (H-14) of ash (Breitholtz et al., 2012).

Harmonization of waste and chemicals legislations could involve rather drastic changes related to choice of both leaching and ecotoxicity test methods to be used for H-14 classification. To meet the CLP regulation, the primary aim of the present study was therefore to evaluate the influence of leaching parameters, i.e. pH (natural: ~10, and 7), L/S ratio (10 and 1000) and particle size (< 4 mm, < 1 mm, and < 0.125 mm), for subsequent chemical analysis and ecotoxicity testing in relation to classification of municipal waste incineration bottom ash (MSWIBA). Extracted water eluates were prepared either with the batch method described in CEN 14735 or a modified pH static method (SS-CENTS 14997). The impact of these parameters were mainly evaluated based on calculations of the Toxic Index (TI) for Ca, K, Zn, Cu, Al and Pb, elements which had been identified as responsible for the observed toxicity of a range of ash materials in project 1 and 2. For validation of the calculated TI values, two of the generated eluates were also tested with acute and (sub)chronic ecotoxicological test methods with the crustacean *N. spinipes*.

The findings from the present project clearly show that all three investigated parameters significantly influence the toxic potential of ash eluates and hence classification of ash. Calculated TIs were overall significantly higher at low particle size (<0.125 mm) as compared to particle fractions < 4 mm and < 1 mm, at natural pH of the ash material as compared to pH 7 and at L/S 10 as compared to L/S 1000.

2.4 PROJECT 4 – Use of MSWIBA in constructions – Long term ecotoxicological risks to the environment (Wik et al., 2011).

This study focuses on the environmental long-term risks of ash utilized for filling or for construction purposes. Previous studies by the project group have shown that aging of MSWIBA may drastically reduce the toxic potential. We therefore selected a 5-year old MSWIBA. The ash contained relatively high amounts of heavy metals and low amounts organic compounds, and was sufficiently aged for producing eluates with pH-values around 8, i.e. acceptable range for ecotoxicological testing. In the present project, we leached at the lowest possible L/S value while still generating a leachant volume sufficient for toxicological testing using a sequential batch leaching approach from L/S 1 to L/S 3. With the main aim to identify toxic elements, which may cause long-term environmental risks in the aquatic environment, generated eluates were i) tested at 0.5%, 1.5%, 4.5%, 13.5% and 40.5% with the (sub)chronic ecotoxicity test with *N. spinipes*, ii) analyzed for dissolved metals (filtered 0.45 µm), and iii) analyzed with DGT- filters to obtain available fractions of selected elements. The rationale for using a range of L/S ratios was to observe changes in leaching behavior for specific components in the eluates and compare these changes to the toxic effects observed. To validate the outcome of these investigations, our final ambition was to spike the highest tested concentration of the eluate generated at L/S 3 (40.5%) with concentration series of the components identified as problematic (which in this study was K and Cu). These spiked eluates were tested with the (sub)chronic test with *N. spinipes* and the used test media were both analyzed for both total content of elements and available fractions using DGT-filters.

The data provided indicate that K was mainly responsible for the toxicity observed at lower L/S ratios, but also reveals that the effect of the element was more pronounced when other elements were present.
at levels close to those were adverse effects are expected to occur. Also other elements (Al and Ca) were present at levels where toxicity could be expected but the use of DGT-filters revealed that the bioavailable fractions of these elements were so low that their contribution to the overall toxicity can be neglected, possibly due to carbonation processes and the formation of sulphates. Although the presence of Cu was slightly below levels where toxicity are expected we cannot exclude the possibility that this element may be problematic in aged bottom ash materials with higher leaching of Cu.

3 Conclusions

- Classification based on total content of substances in ash drastically over-estimates the ecotoxicological hazard potential as compared to ecotoxicity testing of eluates.
- In order to harmonize with the classification according to the CLP, eluates for ecotoxicity testing should be prepared using much higher L/S ratios than prescribed in CEN 14735. This makes the classification less conservative but more in consistence with the chemical legislation and thus in coherence with the WFD.
- When testing ash eluates prepared at low L/S ratios components not classified as hazardous, in particular potassium (K), significantly influence the toxicity of the eluates, which is problematic from a hazard classification perspective (risk of misclassification), but likely negligible from a long-term environmental risk perspective.

References


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