

# The potential use of chelating agents to remove heavy metals from biostabilised waste

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## Introduction

This research explored the potential of the use of ethylenediaminetetraacetic acid (EDTA) for the removal of heavy metals from refuse derived compost (RDC) through a lab based simulation of a RDC washing process.

Mechanical Biological Treatment (MBT) was introduced in Scotland recently to help meet diversion targets outlined in the Landfill Directive (Directive 1999/31/EC). Typically, the input material (mixed solid waste, MSW) undergoes a mechanical screening process featuring a trommel screen, over band magnet and a controlled composting process, effectively isolating much of the organic fraction. The material may then undergo a secondary screening and milling process. The end product has similar characteristics as green waste compost, and producers would like to extract value from this by using it as a low grade compost substitute or soil additive, for example in the restoration of landfills or land reclamation. However, this refuse derived compost (RDC) is typically contaminated with heavy metals (HM) and other potentially toxic elements (PTE), and subsequent utilisation of the product is hindered, in practice, mainly due to its high content of lead and copper, which is typically outwith the limits set by relevant quality standards (SEPA, 2004; Table 1).

Table 1: HM content of RDC, normalised to 40% OM content, compared to SEPA quality standard

	Average [mg/kg]	Std. Dev.[%]	Average [Mols/ kg]	SEPA standard[mg/kg]
Lead	442.3	14.04	0.0021332	<200
Nickel	38.7	14.85	0.0006780	<100
Zinc	582.7	14.50	0.0854930	<1000
Cadmium	1.9	97.05	0.0000172	<3
Chromium	20.9	17.22	0.0004192	<400
Copper	202.5	25.96	0.0032913	<200
Mercury	1.1	28.51	0.0000057	<1

Results are based on 25 representative point samples.

The complex heterogeneous nature of the MSW matrix makes it unlikely that significant reductions in the heavy metal content of the end product could be achieved through further mechanical screening (Veeken and Hamelers, 2002). Further improvement of the input material requires longer term (public education) strategies and in the meantime it is desirable to investigate extracting heavy metals from the material through other means. Washing with chelating agents such as ethylenediaminetetraacetic acid (EDTA) has been demonstrated as a method of removing heavy metals from contaminated soils (Kim et al., 2003) (Pitchel and Anderson, 1997) (Mulligan et al., 2001) and this research investigated the suitability of this method for the removal of heavy metals from RDC.

During the MBT process organic matter (OM) is metabolised to carbon dioxide and water, typically the OM is reduced from 60% to 30%. Further reduction to 20% OM is possible during longer composting or maturation (open windrow stockpiling) stages.

The humic substances in organic matter chelate with available metals reducing their solubility. It is hypothesised that reduction in the organic matter content of the material through re-composting will allow more effective extraction of metals with EDTA.

To test this extraction experiments were undertaken on normal MBT material (around 40% OM) and recomposted material (around 30%OM).

## Materials and methods

The RDC for this study was obtained from Dalinlongart landfill, Dunoon, Argyll, Scotland, which operates a Cambridge batch system consisting of 8 composting bunkers. MSW material is processed mechanically via a 50mm trommel screen and ferrous metal separator (over band magnet). The fines are moistened, macerated and transferred to the first bunker, which is filled in around ten days. The material is then transferred in bulk to the second bunker, where biodegradation continues. Temperature measurements are taken throughout the material mass to ensure compliance with the Animal By-Product Regulations (DEFRA, 2002). Once the material exceeds its target temperature for the specified time it is moved to the subsequent bunkers. During this transfer, the material is mixed, broken up and aerated. As the material passes from bunker 1 to bunker 8 the moisture content drops, as no further moisture is added to the process, and this improves screening of the final product (after bunker 8) through a 30mm screen; the fines are then hammer-milled, screened again and the resulting fraction <3mm is classed as the final product. Overall, the biodegradation process in the clamps requires between 10 and 14 weeks.

EDTA extraction was conducted following MAFF (method 10, MAFF, 1986) whereby soil samples are extracted by a (0.05 M pH8) EDTA solution using a 1:5 RDC:EDTA volumetric ratio, where 100 ml of the dry material were found to equal 50g weight.

When mixed with EDTA, metals are separated from a matrix such as contaminated soil as a 1:1 metal-ligand coordination compound. This is held in solution and readily washed out. The process is analogous to a chemical claw. EDTA is a non-specific chelating agent and will bond with a variety of metals in a matrix. The stoichiometric ratios between EDTA and the metals thus should be taken into consideration. The iron content of the RDC is typically much higher, on a molar basis, than that of lead (factor ~100) and copper (factor ~70), so that occlusion of the EDTA as iron compounds may be expected. Kim & Ong (1999) illustrated the conditional stability for various metal-EDTA complexes at different pH's and showed that most EDTA complexes, including lead and copper, are stable between pH 7 and 9. Iron, however, is less stable in this range and is the only metal complex stable at pH lower than 6. Maintaining a pH of around 8 should thus minimise the effect of occlusion by iron, and EDTA was adjusted to pH 8 through the addition of NaOH solution as described by Kim et al. (2003). This was mixed with the RDC and shaken for 1 hour at 210 rpm with a Heidolph Rotamax 120 orbital shaker. After shaking the pH of the mixture was recorded to ensure that there was no significant drift. The mixture was then centrifuged at 5000rpm (with a Beckman CPKR) for 30 minutes, the supernatant decanted, filtered with Whatman No. 540 paper (80µm) and retained. The solid fraction was dried at 105°C for 24 hours. Three replicates of analysis were performed.

*Aqua regia* extraction was based on BS EN 13650:2001. 3g of each sample was placed in a spherical glass reaction vessel; to this the following was added: 0.5 ml of deionised water, 21 ml of hydrochloric acid and 7 ml of nitric acid. The samples were allowed to stand for approximately 16 hours, after which they were then refluxed for 2 hours according to the BSI method. Once cool they were made up to 100ml with deionised water in volumetric flasks, before being filtered with Whatman No. 540 paper (80µm).

Figure 1: lead copper and iron content of RDC before and after re-composting, data normalised to 40% OM.

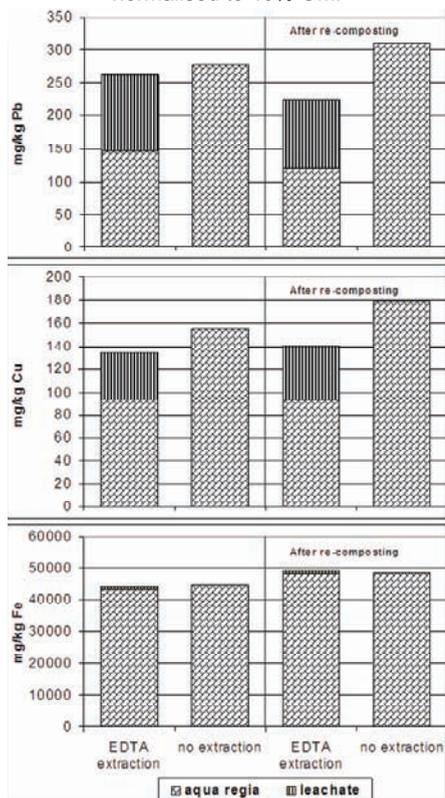
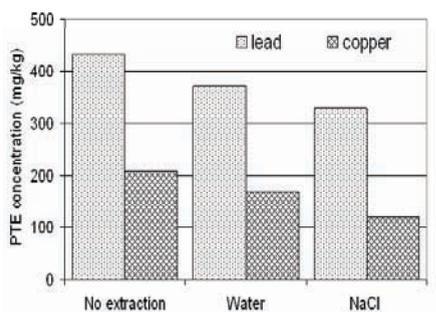


Figure 2: lead and copper content of RDC after extraction with H<sub>2</sub>O and NaOH, data normalised to 40% OM



Iron, copper and lead in the samples was analysed using a Perkin Elmer 1100B Atomic Absorption Spectrometer (AAS). The standard additions method (Harris, 2003) was used to establish the extent of any interference (matrix) effect from the digest solutions.

For the re-composting experiments, two representative sub sample of the material were taken, one was desiccated and set aside for further analysis. The other, around 7kg, was re-composted under controlled conditions in the laboratory by placing the material in a 20 litre plastic bucket, remoistening it to 35% and incubating it at 30°C. Aeration and moisture were maintained by shaking the bucket daily and the occasional addition of water. The material was incubated for 4 weeks, and then desiccated for storage and further analysis.

The biodegradability of both sub samples was calculated by undertaking a dynamic respiration index (DRI) analysis (Godley et al., 2004). Additional control mixtures were included in the procedure as (1) compost seed only, so that the results could be corrected for biodegradable material in the seed, (2) for comparison, a positive control containing cellulose and (3) an empty (blank) incubation.

A separate batch of RDC from Dalinlongart was analysed to establish the extractability of metals through washing with both water and sodium chloride. 1:5 v/v mixtures for both water and 0.05M sodium chlorides (NaCl) were shaken, *aqua regia* extracted and analysed by AAS. The analysis was performed in triplicate.

## Results and discussion

The results (Figure 1) showed that the washing of RDC with EDTA leads to a significant reduction in heavy metal content in the RDC; the lead and copper content of the EDTA extracted samples was reduced by roughly 44% and 31%, respectively. Relatively little of the iron content was removed only 2%, which indicates that buffering at pH 8 may have prevented occlusion by iron, even though non-buffered controls were not conducted. At these reduction rates, the process would be suitable to reduce to within the regulatory limits the concentration of the critical heavy metals lead and copper. Further experiments may be needed to investigate the efficacy of the EDTA washing process for other heavy metals; the effect of pH on iron occlusion also warrants further investigation.

The data (Table 2) also showed that re-composting of the RDC resulted in significant reduction in OM content and maturity as indicated by DR4 (dynamic respiration index over 4 days). However, this further biodegradation did not lead to further improvements in the heavy metal removal capacity of the EDTA washing process. It can be speculated that all heavy metals were sufficiently disaggregated from organic material after original biodegradation. Further research on the overall effect of biodegradation on the efficiency of EDTA washing may be required in order to fine tune a commercial application of this process.

Table 2: Changes in RDC maturity after re-composting

	Organic Matter [% w/w]	DR4 [mgO/kgDM]	DR4 [mgO/kgLOI]
Original RDC	25.5	33,200	68,000
Re-composted	19.7	14,900	34,900

However, the empirical observations made during this research put in question the overall suitability of the process for commercial application: significant mechanical agitation of the MBT/EDTA slurry was required for heavy metal leaching. In large scale, commercial applications, this is unlikely to be achievable, and further research on the effect of agitation on HM removal efficiency is required. More importantly, this work has shown that the EDTA process is, in principle, suitable for HM removal from RDCs. A rough estimation of EDTA input into the process shows, though, that the financial cost of this process may be too high for commercial application. Based on a wholesale price of £11.75/ kg for EDTA and using the extraction parameters investigated by this research (0.05M EDTA at 1:5 v/v ratio), the treatment would cost around £1716 per tonne DM of RDC; assuming 80% recovery of the EDTA can be achieved this may be reduced to £628/ tonne. Further cost reduction may be achieved by reducing the amount of EDTA so that the washing process is terminated when the regulatory threshold of HM is reached. Other leaching agents such as deionised water or sodium chloride (NaCl) have been shown in this research to be only partly effective at reducing the content of lead and copper (Figure 2). It may be advantageous to carry out an initial water or sodium chloride washing stage, followed by a polishing phase using EDTA.

Still, the initial results obtained during this research indicate that much further work is required before the method can be considered on a commercial basis. Thus, it loses its attraction as a possible interim measure to achieve RDC regulatory compliance until improved MSW collection and segregation practices will lead to intrinsically cleaner RDC.

## Conclusions

- The EDTA chelating technique previously described for soil washing can be applied in the cleaning of refused derived compost in order to reduce heavy metal content to within regulatory limits.

- The maturity of RDC does not significantly effect the extraction of metals with EDTA.
- The cost of EDTA extraction as a treatment method for RDC may be prohibitively expensive.
- Overall, it appears that the removal of heavy metals from the compost product is not well suited, even as an interim measure, and that further emphasis should be placed on source segregation of organic wastes.

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