The Environmental Bonafides for CCP Use in Australian Agricultural and Horticultural Systems

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KEYWORDS: coal combustion products, ash, legislation, regulatory, research, Australia, agricultural, utilisation

ABSTRACT

The Ash Development Association of Australia undertook an environmental investigation programme into coal combustion products (CCP’s). The aim of this investigation was to collate and interpret the analytical knowledge on its members’ CCP’s through a coordinated sampling, analysis and reporting programme.

The programme investigated the chemical characteristics of CCP’s from several producers and marketers, which will assist the Association in identifying alternative uses to which CCP’s can be used as a secondary resource.

The methodology consisted of collecting fine, medium, coarse fly ash and furnace bottom ash samples from ADAA members throughout Australia. The samples were analysed for a range of metals (total and leachate), dioxins and furans. Fifty four (54) samples were tested for leachate and thirteen (13) were selected for total metals analysis. Three (3) were analysed for dioxins and furans.

In summary the four major findings were; (1) Total metal results for Cadmium (Cd), Lead (Pb) and Mercury (Hg) were within the proposed guidelines (Fertiliser Act 1985) nominated by Department of Environment and Conservation; (2) All leachate results, under the worse case scenario, were either below or just above the laboratory detection limit for each analyte and so were well within the maximum acceptance criteria; (3) Leachate results from the previous investigations (1993 – 2001) were also low; either below or slightly above the detection limit, for the same range of analytes; (4) All three samples tested for dioxins and furans met the 100 pg/g criterion.

These investigations were seen as an important step towards demonstrating the responsible and environmentally sustainable use of CCP for applications, but not limited to, civil engineering fills, raw materials for the cement and concrete industries and for agricultural and horticultural purposes.

These results coupled with the agreed investigation methods of the regulatory authority provided the scientific evidence to pave the way for approval for CCP re-use in agricultural applications. These findings, process and criteria will be discussed.
INTRODUCTION

The use of coal combustion products (CCP’s) in particular fly ash to amend sandy soils has been an ongoing area of investigation since the mid 1990’s, with one major study of four (4) years with the University of Western Australia concluding in 2002 various environmental and crop production benefits from CCP use [1].

The study assessed, amongst other things, the potential water saving [physical] and nutrient properties [chemical] of CCP’s on local sandy soils of Western Australia [2]. The findings of this study were very encouraging, in particular, demonstrated improved crop yields, increased turn around time for turf farming harvests, improved growth colour and general health, improved water take up and reduced watering requirements. The study also reported no adverse effects of fly ash use to the environment (e.g. potential release of heavy metals) and plants used in study.

Given these reassuring findings the Association has undertaken recommendations for extension work from the study. The overall aim of the new project is to capture to more data on the use of CCP’s in agriculture systems, and publish information that demonstrates the cost/benefits of various applications of ash amendments in horticultural and agricultural systems.

The tasks included investigating the potential for particle migration and surface erosion (i.e., possible off-site movements), trace element loadings to soils and long term fates of these elements, long-term evaluation of the persistence of beneficial changes in soil properties in the field, data on properties of a wider number of sources of coal ashes available in Australia, performance of other agricultural crops grown on amended soils and optimisation of fertiliser agronomy for crop production on amended soils [2].

Coincident with the development of our new research project for the next 4 years, a series of articles were published in the Sydney Morning Herald during May 2002 regarding contaminants in a wide variety of industrial residues [3-10]. These articles claimed that a range of industrial wastes were being used as fertilizer [7]. Following the initial elevated levels of enquiry by bureaucrats, flowing onto regulators and government agencies – many of these claims have proven incorrect, however the reports do highlight the need for greater public transparency and accountability on the issue of mechanisms to regulate industrial residues and use in agricultural systems.

In the mid 1990s State jurisdictions had repealed their fertiliser registration requirements, which was believed to have removed one of the safeguards against the disposal of industrial waste as fertilizer. Reliance was thus placed on environmental legislation to manage any risks associated with the application of waste materials to land [11]. In part an issue unaddressed here is the absence of appropriate legislation and assessment criteria to allow for appropriate reclassification of industrial by-products, with beneficial properties, to be used in agricultural systems.

Within the broader context of public [media], regulatory and jurisdictional concerns raised above, our Associations goals are focused on the development of sustainable, environmentally sound, recycling and reuse legislation which would allow for CCP’s
use in agricultural systems where appropriate. The continued absence of well considered national policy for reuse options of CCP’s will ultimately hamper our industry research & development investment to further investigate the environmental bonafides of CCP’s.

Previous legislation has generally been aimed at the manufacture and sale of fertilizers, intended to improve the nutrient status or the condition of the soil. The legislation generally has not been framed to control the inappropriate disposal of industrial by-products, thus leaving industry with an unclear pathway or framework to demonstrate CCP’s credentials for use in agricultural systems [12].

In the absence of legislation and regulatory framework, industry has typically demonstrated great reluctance in making significant investments within an uncertain legal framework, which exposes them to potential contingent liabilities.

AIMS OF REPORT

The Ash Development Association of Australia (ADAA) has undertaken an extensive analysis investigation into the metal concentration and leachability of those metal species from coal combustion products (CCPs) using the USEPA TCLP and total metals methods\(^1\) against an agreed criteria.


The aim of this investigation was to collate and interpret the analytical knowledge of its member’s CCP’s through a co-ordinated sampling, analysis and reporting programme, building on information collected in previous years.

The findings will be used to produce important benchmarks to underpin the Associations case for selected CCP reuse in applications where significant environmental interactions may occur, e.g. agriculture systems.

All data has been treated with strict confidentiality and no published results identify individual participants. Participating members were provided with a unique identifier (client code) to assist with distinguishing their respective material/s for internal assessment purposes and for comparison against other CCP sources from throughout Australia. Table 1 lists the participants in this sampling programme.

\(^1\) Method: USEPA method 200.2 (modified) for determination of total metals and TCLP method 1311 for leachate
Site identification and characteristics have been maintained for confidentiality purposes. Each site was allocated a unique client code known to only them, our researchers and the ADAA CEO. This system allows each site to view their results and compare these to the complete data set.

The code consisted of a two-digit number for each participant and then a sub-classification code with fly ash samples coded according to fine (FAF), medium (FAM), coarse (FAC). Bottom ash is simply (BA). In some cases individual producers used terms more meaningful to their site, or where the classification was unclear were tagged ‘X’.

The programme consisted of collecting fly ash of fine, medium, coarse grades and bottom ash samples from members listed in Table 1 [14]. These samples were then analysed for a range of leachable metals.

Coincident with the programme, and media reports discussed previously, the Department of Environment and Conservation - New South Wales (DEC) engaged in discussion with the ADAA on our future research and development activities for the use of CCP’s in agricultural systems. Following these discussions additional nominated total metals, dioxins and furans were included into our methodology and assessment criteria.

Stemming from these discussions, total metal analyses for a further three (3) samples of bottom ash were analysed for the total metals, and seven (7) samples were analysed for fineness by mass passing 45 µm sieve to investigate whether metals (particularly Hg) had a tendency to move to bottom ash; and whether size fractions of fly ash influenced metal concentration.

\[^2\] AS 3582.1—1998 has a table on page 8 describing ash grades.
All of these new results were compiled with leachate data previously gathered by the Association and assessed against current criteria.

ASSESSMENT CRITERIA

In consultation with the DEC and Agriculture NSW, the ADAA used the following guidelines for nominated metals (total) and dioxins and furans. The proposed criteria are referenced and listed below:

(a) Fertilisers Act 1985 (Order No 2001/02 or 2001/07) Total metals
(b) Chlorinated dioxin and furan TEQ limit of 100 ng/kg as referenced for land application of biosolids in Europe.

<table>
<thead>
<tr>
<th>Cadmium</th>
<th>Phosphatic Fertiliser</th>
<th>300 mg/kg of phosphorus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-phosphatic Fertiliser</td>
<td>10 mg/kg of non-phosphatic fertiliser</td>
</tr>
<tr>
<td></td>
<td>Liming Material</td>
<td>10 mg/kg of liming material</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lead</th>
<th>Fertiliser</th>
<th>100 mg/kg of fertiliser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liming Material</td>
<td>100 mg/kg of liming material</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mercury</th>
<th>Fertiliser</th>
<th>5 mg/kg of fertiliser</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liming Material</td>
<td>5 mg/kg of liming material</td>
</tr>
</tbody>
</table>

Table 2 - Criteria for Total Metals (a)

ANALYTICAL RESULTS

Total Metals (Cd, Pb, Hg) are summarised in the following table for thirteen (13) randomly selected ash samples from the total of fifty four (54) samples collected.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>05-FAF</th>
<th>05-ROS</th>
<th>05-FAC</th>
<th>06-FAF</th>
<th>06-FAM</th>
<th>06-FAC</th>
<th>06-BA</th>
<th>10-CS</th>
<th>10-FM</th>
<th>11-FAX</th>
<th>01-BA</th>
<th>12-BA</th>
<th>13-BA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Max mg/kg)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd (10)</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Pb (100)</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>6</td>
<td>8</td>
<td>7</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>Hg (5)</td>
<td>0.2</td>
<td>0.4</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.4</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

Table 3 - Total Metals Results
Leachate (TCLP) results total of fifty four (54) samples were analysed for TCLP for the following analytes.

- Silver
- Cadmium
- Lead
- Zinc
- Arsenic
- Chromium
- Antimony
- Selenium
- Barium
- Copper
- Thallium
- Mercury
- Beryllium
- Nickel

In addition to these 2003 results, historical data has also been incorporated on the above analytes conducted between 1993 and 2001 by AWT. The following table reports the minimum, maximum and mean results for each analytes for the current study and data reported for the period 1993 to 2003.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Max Conc (mg/L)</th>
<th>2003 Test Results (54 samples)</th>
<th>1993-2001 Test Results (36 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>Silver</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Arsenic</td>
<td>&lt;50</td>
<td>&lt;0.1</td>
<td>0.7</td>
</tr>
<tr>
<td>Barium</td>
<td>&lt;1500</td>
<td>&lt;1</td>
<td>2</td>
</tr>
<tr>
<td>Beryllium</td>
<td>&lt;15</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;0.5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Chromium</td>
<td>&lt;100</td>
<td>&lt;0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Copper</td>
<td>&lt;250</td>
<td>&lt;0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt;100</td>
<td>&lt;0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;150</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Antimony</td>
<td>&lt;15</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Thallium</td>
<td>&lt;5</td>
<td>&lt;0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Zinc</td>
<td>&lt;500</td>
<td>&lt;0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;5</td>
<td>&lt;0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Mercury</td>
<td>&lt;0.5</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Table 4 - Leachate (TCLP) results

Dioxin and furans analysis were conducted on three (3) randomly selected samples. The following table summarises the dioxin and furan analyses for each sample.
DISCUSSION OF RESULTS

TOTAL METALS

Samples were analysed for nominated total metals from separate process locations and consisted of fine, medium, coarse and bottom ash, coarse sand and filter material.

If the ash material was considered a liming agent in terms of agricultural application, the levels of cadmium, lead and mercury reported in these samples are well below the proposed criteria, as referenced in the *Fertiliser Act 1985*. The analytical results are below all proposed criteria in this Act.

The bottom ash sample (06-BA) initially produced an abnormal result when compared with the historical data for mercury at (2.1 mg/kg). It was unclear from this one sample whether mercury had a propensity to move to bottom ash, so the sample was re-analysed. The four new analyses showed mercury ranged from not detected (<0.1 mg/kg) to 0.5 mg/kg. These results are lower than the original level of 2.1 mg/kg, which may indicate the sample was not completely homogenous.

All other results are below the proposed mercury criterion and therefore not considered an issue. The samples 05-ROS and 11-FAX were both finer grades and do indicate slightly higher Mercury at 0.4mg/kg than the furnace bottom ash samples.

Lead (Pb) results are all low. Cadmium (Cd) was not detected in any samples.

LEACHATE RESULTS

The majority of the analytical results are below the detection limit for each analyte, with the remaining results just over the detection limit. There are no standout results that significantly exceed the detection limit. Since many results were reported as the limit of detection, no statistical analysis would be useful and accordingly was not conducted.

The historical leachate data (1993 – 2001) shows a similar trend. The majority of analytical results are very low, being below or just above the detection limit. There are no results that show a high degree of variation.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>4) ES 43607 (06-FAF)</th>
<th>5) ES 43607 (06-FAM)</th>
<th>10) ES 43607 (11-FAX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-TEQ (100)</td>
<td>1.65</td>
<td>2.73</td>
<td>2.25</td>
</tr>
<tr>
<td>(Maximum Criterion ng/kg)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
DIOXIN AND FURANS

In recent correspondence from the DEC, the chlorinated dioxin and furan TEQ limit of 100 ng/kg (100 pg/g) was referenced as proposed criterion for land application of biosolids in Europe.

Three (3) ash samples were analysed for dioxins and furans and produced results that equate to “not detected.” The low values in table 5 above are conservative values representing the detection limit for each sample.

The results from this analysis programme are again well below this proposed criterion.

CONCLUSIONS

This investigation examined nominated analytes of CCPs against an agreed criteria established by the DEC – NSW for the purposes of establishing CCP’s environmental bonafides for use in agricultural systems.

The four major findings were; (1) Total metal results for Cadmium (Cd), Lead (Pb) and Mercury (Hg) were well below the proposed guidelines (Fertiliser Act 1985) nominated by Department of Environment and Conservation; (2) All leachate results, under the worse case scenario, were either below or just above the laboratory detection limit for each analyte and so were well within the maximum acceptance criteria; (3) Leachate results from the previous investigations (1993 – 2001) were also low; either below or slightly above detection limit, for the same range of analytes; (4) All three samples tested for dioxins and furans met the 100 pg/g criterion.

Other studies (notably in Western Australia) focusing on the horticultural systems have described the beneficial effects of using CCPs to enhance agricultural land performance. That is, the studies documented improved crop yields, increased turn around time for turf farming harvests, improved growth colour and general health, improved water take up and reduced watering requirements. The study furthermore reported similar conclusions as addressed in this paper that CCP’s produced from Australian coals demonstrate very low levels of leachability for the nominated analytes, in particular concluding there was no detectable presence in the soil or uptake of metals by the plants in the study [1].

The findings of this study will be used to compliment current research into investigating the expected benefits of the application of ash amendments in horticultural and agricultural systems.
COMPLIANCE WITH ACCEPTANCE CRITERIA

The analytical results presented here indicate that there may be a feasible opportunity to use CCPs as a secondary resource in agricultural systems. Given the following results of the investigation programme found;

- Not one nominated acceptance criterion has been exceeded, and
- No results of this investigation approach the maximum acceptable criteria levels.

SUSTAINABLE DEVELOPMENT

Where agricultural circumstances support the application of CCPs, either chemical [nutrient] or physical [structural] benefits can be derived by users of CCP’s, the environmental benefits of re-use as opposed to landfill containment could be significant.

Much of the literature for the beneficial use of CCPs in agricultural applications describes application rates with soils in ratios of 5% to 20%[15]. Application rates are modified according to soil type and the characteristic being modified (e.g. pH modification, drainage etc).

RECOMMENDATIONS

These investigations demonstrate the potential for responsible and environmentally sustainable use of CCPs in the areas such as, civil engineering fills, raw materials for the cement and concrete production and for agricultural and horticultural purposes.

Importantly these results should be coupled with an appropriate ongoing monitoring program to assist regulatory authorities and the ADAA to build on sound scientific evidence required for ongoing appropriate use of CCPs as a secondary resource.

Resulting from the study the Association has implemented a number of recommendations arising from the original report.

In particular, ADAA has sort additional guidance and agreement with National and State authorities on the elements or species of concern, and their criteria for reclassification of CCP’s for use in agricultural systems.

Encouraged National and State Environment authorities, in conjunction with relevant Agriculture departments to develop a national frame, with all parties to countersigned to clarify

- national standards or guidelines for analytes levels in fertilisers;
- criteria for reclassification of CCPs as products for use in agricultural systems
- product application scenario when and how to use CCPs, and an agreed chemical/physical specification
REFERENCES


