Co-composting of pharmaceutical wastes in soil

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Aims: Soils at a commercial facility had become contaminated with the pharmaceutical chemical residues, Probenecid and Methaqualone, and required remediation.
Methods and Results: Soil composting was investigated as an alternative to incineration for treatment. In laboratory trials, a factorial experimental design was used to evaluate organic matter amendment type and concentration, and incubation temperature. In pilot scale trials, Probenecid was reduced from 5100 mg kg\(^{-1}\) to < 10 mg kg\(^{-1}\) within 20 weeks in mesophilic treatments. An 8 tonne pilot scale treatment confirmed that thermophilic composting was effective under field conditions. In the full-scale treatment, 180 tonnes of soil were composted. Initial concentrations of the major contaminants in the full-scale compost treatment were 1160 mg kg\(^{-1}\) and 210 mg kg\(^{-1}\), for Probenecid and Methaqualone, respectively. Probenecid concentration reached the target level of 100 mg kg\(^{-1}\) in 6 weeks, and removal of Methaqualone to < 100 mg kg\(^{-1}\) was achieved after 14 weeks.
Conclusions: Co-composting was effective in reducing soil concentrations of Probenecid and Methaqualone residues to acceptable values.
Significance and Impact of the Study: Co-composting is a technology that has application in the remediation of pharmaceutical contaminants in soil.

INTRODUCTION

Composting has been used for many years for disposal of agricultural, municipal and domestic wastes. However, composting has only relatively recently been investigated for treatment of soils contaminated with polycyclic aromatic hydrocarbons (PAHs) (Guerin 2000; Semple et al. 2001), nitroaromatic explosives (Williams et al. 1992; Griest et al. 1993; Emery and Faessler 1997; Tuomi et al. 1997) and other hazardous wastes (Kannikar 1992; Betts 1993; Bennet and Barriuso 1997; Cook et al. 1997; Lewandowski and DeFilippi 1998; Semple et al. 2001). The type of organic amendments used and the ratio of contaminated soil to organic amendment are crucial parameters in making this technique cost-competitive with other disposal and treatment technologies.

The principles and concepts of bioremediation of contaminated soils are similar in many respects to composting. Both aim to maximize microbial activities through control of process conditions: matrix moisture content, pH, temperature, oxygen supply and elemental ratios. The major difference between the two processes is in the ratio of biodegradable materials to soil matter. In bioremediation of soil, the organics of concern occur typically in the range of 0.001 to 1.0% but in composting, organic matter concentrations would be more typically in the range 20 to 80% (Rhodes et al. 1994a,b). In some cases where the standard approaches to bioremediation are not effective, the higher rates of biodegradation activities and more diverse populations of micro-organisms found in compost (with therefore a much wider range of metabolic capabilities), in combination with physical and chemical effects, may be able to achieve degradation of the contaminants (Rhodes et al. 1994a,b). Examples of bioremediation processes, including composting, are given in Table 1.

Composting is an engineered process in which organic waste materials are degraded by micro-organisms, in the presence of air, to produce inorganic products (carbon dioxide, water, various salts) and stabilized organic matter, i.e. compost. Many different composting system designs have been used (Huang 1993). Mixed compost piles or windrows (long narrow piles) are mechanically turned to provide aeration. Static piles, on the other hand, may be
Table 1 Bioremediation technologies for contaminated soil and groundwater

<table>
<thead>
<tr>
<th>In situ techniques</th>
<th>Ex situ techniques</th>
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<tbody>
<tr>
<td>Bioventing</td>
<td>Landfarming (shallow mixed beds)</td>
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<tr>
<td>Biosparging</td>
<td>Static vented piles (biopiles)</td>
</tr>
<tr>
<td>Bioflushing</td>
<td>Composting in piles, or windrows</td>
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<tr>
<td>Lagoon treatments</td>
<td>Soil slurry reactors</td>
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<tr>
<td>(retention dams)</td>
<td>Water treatment units</td>
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<tr>
<td>Reinjection/reinfiltration</td>
<td></td>
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<tr>
<td>Natural or intrinsic remediation</td>
<td></td>
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<tr>
<td>Phytoremediation</td>
<td></td>
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<tr>
<td>Pump and treat*</td>
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</tbody>
</table>

*No longer recognized as an industry best practice.

The US Army has been evaluating composting treatments for soils contaminated with explosives such as TNT for some years. Bench and field studies showed the technical capability of the technique in reducing explosive concentrations to acceptable levels. They identified two process parameters crucial to making this approach cost-competitive with incineration as a disposal route. These were the type of organic amendments used, and the ratio of contaminated soil to organic amendment (Griest et al. 1993; Emery and Faessler 1997).

In the current study, soil contaminated with the pharmaceutical compounds Probenecid and Methaqualone was composted in an effort to treat these residues so that the soil could be re-used for landscaping purposes. The pharmaceutical residues were expected to be relatively non-toxic but are, by their nature, biologically-active compounds (Israili et al. 1972; Fernandez Gomez et al. 1984); they are described in Table 2. While the metabolism of these compounds is well understood, their fate in the environment has not been previously investigated.

The principal objective of the study was to apply composting technology to soil contaminated with pharmaceutical wastes to reduce its phytotoxicity and allow its re-use. The composting of pharmaceutical wastes is discussed, presenting the results of laboratory-, pilot- and field-scale composting.

MATERIALS AND METHODS
Site description

Expansion of facilities at a pharmaceutical manufacturing facility in south-eastern Australia required the excavation of an area previously used as landfill. Out of date, waste or ‘off-spec’ product was previously landfilled on the site. Other materials, including some laboratory wastes, were also placed in the landfill. A portion of the excavated soil was found to be contaminated with pharmaceutical process wastes and these residues included Probenecid (4-[(dipropylamino) sulphonyl] benzoic acid) and Methaqualone (2-methyl-3-(2-methylphenyl)-4(3H)-quinazolinone or Methaqualone hydrochloride (Fig. 1). A quantity of fillers and binders (e.g. lactose) was also present. Solvents such as xylene, aniline, dichlorobenzene, fatty acids and fatty acid esters, including volatile fatty acids, were also detected at low concentrations in some samples.

Description of contaminated soil

The contaminated soil was a silty clay. It contained a large amount of pharmaceutical contaminants present in forms ranging from extremely large lumps through small nodules.
of white chalky material to powder form. The soil also contained waste materials including bottles, glass and plastic, tablets, pipettes, rubber teats and bungs, and other assorted waste. All of these gross contaminants were removed prior to treatment. Physical properties of the soil suggested that some pre-processing operation would be required to break up large soil and residue aggregates, as well as to distribute the contaminants for effective composting. It was evident at the time of the soil excavation that an organic amendment would need to be selected to provide some bulking to the soil and to improve its structural properties.

Sample selection and preparation
The excavated material was extremely heterogeneous. Samples were collected for the laboratory study after the material was removed from the waste bins and placed in a single large pile in the warehouse building. These 21 samples were sieved to remove large ‘non-soil’ items such as broken glass, plastic etc., and thoroughly mixed to prepare a soil composite which was then split into portions for the experimental treatments. This initial composite was found to contain 8400 mg kg\(^{-1}\) Probenecid and 75 mg kg\(^{-1}\) Methaqualone, with lower concentrations of various organic acids.

Laboratory feasibility study
While the metabolism of these compounds is well understood in mammals (Israili et al. 1972; Fernandez Gomez et al. 1984), their fate in the environment has not been previously investigated. Hence, an appropriate treatment of the soil was seen to be desirable before disposal. A feasibility study was therefore undertaken to determine whether soil composting could degrade concentrations of the pharmaceutical residues. Treatments were carried out to simulate either a mesophilic process (incubation at 25°C) (Treatments 1, 2, 5 and 6) or a moderately thermophilic process (48°C). Soil was mixed with either horse manure (HM) or partially composted plant material (PM) at 30% by weight of the total final wet weight. In addition, two controls were run, one unamended soil and one poisoned with mercuric chloride (HgCl\(_2\)) to eliminate microbiological activity. The mercuric chloride was added to the soil mixture at a rate of 1 g to 100 g soil (1% w/w basis). These were incubated at 25°C and mixed weekly as per the treatments. Two controls included one unamended soil and one soil poisoned.
Pilot study

Following presentation of these preliminary results to the appropriate regulatory body, an interim criterion for a pilot scale treatment was established at 100 mg kg\(^{-1}\) for Probenecid. A pilot-scale treatment was carried out to enable assessment of the following design requirements for the full scale operation:

- the physical processing requirements of the contaminated soil prior to compost blending
- materials handling and compost mixing, volumes and space requirements
- the suitability of the available local raw materials for composting
- the effectiveness and rate of composting, i.e. the time required to reduce contaminant levels to target concentrations in a large-scale operation
- the heat generation characteristics of the compost, and requirements for temperature control, including effect of mixing rates and forced aeration
- odour and leachate control requirements.

The composting operations were conducted within a large warehouse, which had a concrete floor with a useable area of the floor slab, including those areas taken up by the stockpile warehouse, which had a concrete floor with a useable area of 400 m\(^2\). Approximately 8 tonnes of the floor slab, including those areas taken up by the stockpile warehouse, which had a concrete floor with a useable area of odour and leachate control requirements.

Full-scale treatment

This was commenced after reporting of the effectiveness of the pilot-scale trial only and were conducted using plate count methods. Specifically, total mesophilic, heterotrophic organisms were determined on Tryptone Soy Agar (TSA) (Oxoid) (Guerin 1999b) at 28°C. Mesophilic populations were incubated at 28°C and thermophilic populations by incubation of the same plates at 60°C. Fungi were enumerated using Rose Bengal Chloramphenical Agar. Presumptive coliforms were enumerated using MacConkey Agar for total coliforms. These were monitored because the proposed end-use would require site workers to handle the compost which included manure. Pseudomonads were enumerated on Pseudomonas Selective Media. The microbiological methods are described in Dindal (1991).

Temperature. All temperature measurements in the pilot- and full-scale processes were measured using field monitoring probes (Model DT 50 by DataTaker, Sydney, Australia). Temperature measurements in the laboratory-scale treatments were measured using a mercury thermometer.

RESULTS AND DISCUSSION

Laboratory study

Initial samples from the microcosms contained between 3500 mg kg\(^{-1}\) and 7700 mg kg\(^{-1}\) Probenecid on a dry soil basis (with a mean of 5100 mg kg\(^{-1}\)). Significant decreases in Probenecid concentration were noted after 19 weeks, with four treatments containing no detectable Probenecid.
Table 3. The most effective treatments were those maintained at 25°C. Probenecid removal in the thermophilic treatments ranged from 75 to 100%. Over the ranges tested, no significant effects were seen from either the type or the concentration of organic amendments. No decrease was observed in the poisoned control, but the unamended control also showed a substantial reduction in Probenecid concentration (78%). This probably reflected the biostimulation effect of mineral nutrients, moisture, mixing/aeration, and the presence of ‘compostable’ organics in the wastes added to the landfill, such as sugar-based binders and fillers, used in pharmaceutical formulations. Various organic acids, mainly fatty acids, sterols, hydrocarbons and cineole (a substituted aromatic compound found in eucalyptus oils), were also detected (data not shown). These were derived from the organic matter added to the soil, or from the biomass produced during the composting process. Over the course of the treatments the concentrations of these decreased. The most effective treatments were those maintained at 25°C.

Pilot study

A pilot-scale treatment was carried out to assess: soil processing requirements prior to compost blending; materials handling, bulking and space requirements; the suitability of the available local organic materials; the rate of contaminant removal in a large-scale operation; and the heat generation characteristics of the compost.

In the pilot study, initial concentrations of the major contaminant (Probenecid) in the compost, directly after blending operations, was measured at 1200 mg kg⁻¹. The temperature of the compost piles rose rapidly after mixing (with a 0.25 m³ bucket excavator) and peaked at 57°C after 30 h. The temperature then declined slowly as the biodegradable material was decomposed. The soil rapidly changed from a light grey–brown clay containing obvious white powdery residues, to a dark, organic appearance soon after the composting commenced.

Probenecid concentrations were reduced to below the target concentration (100 mg kg⁻¹) in a period of 2–3 weeks.

The initial compost microbial populations after amendment of the soil were 10⁹ g⁻¹ compost, i.e. about 10 times higher than for the contaminated soil. The microbial numbers increased over the first 3 weeks of treatment, then steadily declined as the compost ‘matured’. Characterization of significant sub-populations of organisms (pseudomonads, coliforms, yeasts and fungi, and thermophiles) showed that except for pseudomonads, these constituted 2% or less of the total mesophilic heterotrophic population (Table 4). The number of yeasts and fungi increased, and pseudomonads decreased slightly. A substantial decrease was measured in the number of coliforms (from more than 10⁷ to 10⁴ g⁻¹). These changes are a response to the changing conditions of substrate availability, temperature, pH and other parameters in the compost as it matures. There were no detectable thermophilic organisms in the soil compost mix. Addition of organic matter (OM) raised the numbers of each type, especially the thermophiles and coliforms. This most likely reflects the biologically-active state of the organic materials as delivered to the site. The manure in particular was warm and steaming as a result of its natural composting process, and the leaf mulch showed evidence of high temperatures in the centre of the stockpile. No significant effects were apparent on degradation rate or efficiency from the type or the concentration of organic amendment used, over the range tested. The rate of Probenecid degradation was significantly enhanced by the addition of organic matter.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Description</th>
<th>Initial* (mg/kg)</th>
<th>Final§ (mg/kg)</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean initial soil</td>
<td>–</td>
<td>6900</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Treatment 1</td>
<td>Low Temp; 30% PM†</td>
<td>4730</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Treatment 2</td>
<td>Low Temp; 60% PM</td>
<td>4580</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Treatment 3</td>
<td>High Temp; 30% PM</td>
<td>3500</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Treatment 4</td>
<td>High Temp; 60% PM</td>
<td>4680</td>
<td>1700</td>
<td>64</td>
</tr>
<tr>
<td>Treatment 5</td>
<td>Low Temp; 30% HM‡</td>
<td>4220</td>
<td>&lt; 10</td>
<td>100</td>
</tr>
<tr>
<td>Treatment 6</td>
<td>Low Temp; 60% HM</td>
<td>3830</td>
<td>3510</td>
<td>8</td>
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<tr>
<td>Treatment 7</td>
<td>High Temp; 30% HM</td>
<td>5320</td>
<td>1820</td>
<td>66</td>
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<tr>
<td>Treatment 8</td>
<td>High Temp; 60% HM</td>
<td>4700</td>
<td>610</td>
<td>87</td>
</tr>
<tr>
<td>Poisoned control</td>
<td>HgCl₂ (1%)</td>
<td>4560</td>
<td>4700</td>
<td>0</td>
</tr>
<tr>
<td>Unamended soil</td>
<td>–</td>
<td>7700</td>
<td>1700</td>
<td>78</td>
</tr>
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</table>

* Variation in the analyses ranged from 8 to 15%.
† PM = plant material (green tree waste).
‡ HM = horse manure.
§ Trial ended at 19 weeks.

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Presumptive coliforms in the soil-OM mixture were two orders of magnitude greater than those populations in the soil unamended with organic matter. These higher populations (2.3 x 10^7 colony-forming units (cfu) or cfu kg⁻¹ soil-OM mixture) decreased to numbers lower than those measured in the unamended soil (i.e. to 1.1 x 10^5 cfu kg⁻¹) after 4 days of composting. These results showed that any presumptive coliforms present in the compost soil mixture would be significantly reduced in the full-scale process.

The composting treatment resulted in changes to the physical appearance of the soil, so that no wastes or residues were visible. No objectionable odours were generated from the process, or were noticeable in the treated soil. Moisture additions were managed so that leachate was minimized.

All soil-processing and composting operations were conducted within a large warehouse building. Approximately 5 m³ (8 tonnes) of the contaminated soil were mixed with 16 m³ of organic material (commercially-available mulch consisting of chipped wood waste and leaf, horse manure and grass clippings).

The compost pile temperatures rose rapidly after mixing to peak at 57°C after 30 h. The temperatures then declined slowly as the biodegradable material was decomposed. The piles were regularly mixed to provide aeration using mobile earthmoving equipment.

The initial concentrations of Probencid and Methaqualone directly after the blending operations were 1200 mg kg⁻¹ and 60 mg kg⁻¹, respectively. Probencid concentrations were reduced to below the target level (100 mg kg⁻¹) in 2–3 weeks, and to < 10 mg kg⁻¹ after 5 weeks. Methaqualone concentrations declined at a slower rate, reaching < 10 mg kg⁻¹ at the completion of the pilot trial after 7 weeks.

After amendment of the soil with organic matter, the total microbial populations were 10⁹ g⁻¹ compost, i.e. approximately 10 times higher than for the contaminated soil. The microbial numbers increased over the first 3 weeks of treatment, then steadily declined as the compost matured. Characterization of significant sub-populations of organisms (thermophiles, yeasts and fungi, pseudomonads and coliforms) showed that addition of organic matter raised the numbers of each type, especially the thermophiles and coliforms (Table 4). This increase most likely reflects the origin and biologically-active state of the organic materials as delivered to the site. During soil composting, the thermophilic population declined slightly and was never more than 3% of the total mesophilic population. A substantial decrease was measured in the number of coliforms (from more than 10⁷ g⁻¹ to about 10⁵ g⁻¹) (Table 4).

The pilot-scale composting resulted in the soil changing from a light grey–brown clay, containing obvious white powdery residues, to a dark organic appearance soon after the composting commenced, so that no wastes or residues were visible. No objectionable odours were generated from the process or were noticeable in the treated soil. Moisture additions were managed so that leachate generation was minimized, and the final product was found to be suitable for re-use on site.

### Full-scale treatment

The entire remaining volume of contaminated soil was treated in a similar manner to the pilot-scale treatment. This was commenced after reporting of the effectiveness of the pilot-scale process.

Initial concentrations of the major contaminants (Probencid and Methaqualone) in the compost directly after blending operations were measured at 1160 ppm and 210 ppm, respectively. The target concentrations for the principal contaminant (Probencid) were achieved after 6 weeks of treatment. Extension of the composting treatment was required to reduce the concentrations of the
secondary contaminant (Methaqualone), found to be present in the compost, to regulatory requirements. Results of the analysis of replicate samples are presented in Fig. 2. Methaqualone had not previously been measured, while testing soil or compost, at concentrations above 65 ppm, and had not been considered to be a major contaminant prior to the start of the full-scale works. Removal of Methaqualone to below target concentrations (100 mg kg⁻¹) and final clean-up validation of the soil was achieved after 20 weeks. The compost was allowed to mature further, without processing, until 30 weeks, at which time the average Methaqualone concentration had fallen to 23 mg kg⁻¹. Temperatures reached 60°C in the full-scale treatment windrows.

As far as is known, no other studies conducting a similar composting process on these or related pharmaceuticals have been reported in the literature. Other co-composting studies reporting the composting of other organic contaminants have, however, shown similar heating profiles (Semple et al. 2001).

The project reported here provides an example of the successful application of soil composting as a bioremediation technique. The process has particular application where conventional land treatment processes are limited by the properties of the soil, or the complexity or behaviour of contaminants. Laboratory- and pilot-scale trials provided useful information on the suitability of quantities of organic amendments to apply to the full-scale treatment process. The composting process removed the contaminants to the agreed end-points. The compost has subsequently been used for landscaping purposes across the facility.

ACKNOWLEDGEMENTS

Stuart Rhodes (Rio Tinto Technical Services, Sydney, Australia) for technical support and project management, Philip Peck (formerly Minenco, Sydney) for technical support and project management, and John Leeder (Leeder Consulting, Melbourne) for analytical support. The work reported in this study are the opinions of the author and do not necessarily reflect those of Shell Engineering Pty Ltd.

REFERENCES


