LANDFILL CODISPOSAL OF PENTACHLOROPHENOL (PCP)-TREATED WASTE WOOD WITH MUNICIPAL SOLID WASTE

F. G. Pohland*, F. Karadagli*, J. C. Kim* and F. P. Battaglia**

* Department of Civil and Environmental Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA
** SMITH Environmental Technologies Corporation, 777 Penn Center Boulevard, Suite 200, Pittsburgh, PA 15235, USA

ABSTRACT

Pentachlorophenol (PCP) has been used as a biocide and preservative for wood power poles and crossarms. If disposed in landfills, the natural capacity of landfills to transform hazardous constituents to less hazardous or inert substances may also apply to such PCP-treated materials. The principal reaction of interest in the anaerobic environment of a landfill is reductive dechlorination.

The fate and transformation of PCP-treated wood was investigated in simulated landfill bioreactors operated under single pass leaching and leachate recirculation. The wood samples consisted of 2% of the total mass by weight loaded into the bioreactors. The PCP leaching potential was examined at varying pH conditions with TCLP and Soxhlet extractions. Adsorption of PCP to the synthetic solid waste was used to determine its role in immobilizing leachate PCP. Routine indicator parameters were used to describe the acidogenic and methanogenic phases of landfill stabilization. Leached PCP was transformed without inhibitory effects on landfill stabilization, thereby affirming the acceptability of such a codisposal practice. © 1998 Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Landfill codisposal; power poles and crossarms; municipal solid waste; leachate recycle; PCP transformation; reductive dechlorination.

INTRODUCTION

(Delirinated organics constitute the largest single group of compounds on the list of priority pollutants compiled by the U.S. Environmental Protection Agency (EPA), and has created a challenge with regard to disposal requirements of wood power poles and crossarms treated with PCP. Therefore, the objective of this research was to determine the potential for transformation of PCP when codisposed with municipal solid waste during landfill stabilization.)
Numerous landfill investigations have suggested that stabilization proceeds through five sequential phases. The rate and characteristics of leachate and biogas generated vary from phase to phase. The initial adjustment phase (phase I) is associated with initial placement of solid waste and accumulation of moisture. In the transition phase (phase II), field capacity is often exceeded with leachate production and transformation from an aerobic to an anaerobic environment. In the acid formation phase (phase III), microbial waste conversion results in the production of hydrogen and intermediate volatile organic acids (VOAs) and a low pH. During the methane fermentation phase (phase IV), VOAs are consumed by methane-forming consortia with the production of methane and carbon dioxide, ammonia nitrogen and an elevated pH. During the maturation phase (phase V), nutrients and available substrate become limiting, and biological activity becomes relatively dormant with dramatic reductions in gas production and leachate strength and humic-like substances are released. In conventional landfill practice, leachate is periodically removed from the landfill and externally treated. This washout causes an eventual reduction of nutrients required for continued in situ microbial degradation of the waste mass. By recycling the leachate, nutrients and other substrates are returned to the landfill to promote in situ conversion. Hence, leachate recycling decreases both the total volume and strength of leachate requiring treatment prior to or after landfill closure.

Previous studies have indicated the potential for reductive dechlorination of hazardous compounds during the acid formation and methane fermentation phases in landfills (Reinhart and Pohland, 1991). Substrates such as acetate, glucose and methanol may be needed as primary carbon sources, and acetate is an abundant decomposition product in landfill leachates. Bouwer and McCarty (1983) indicated transformation of a wide variety of chlorinated compounds by a methanogenic mixed culture with acetate as a primary substrate.

Ferguson et al. (1994) observed degradation of PCP and its metabolites in laboratory-scale batch anaerobic digesters operated at a solids retention time of 25 days. PCP was converted to 3-monochlorophenol (3-MCP) and 2,5-dichlorophenol (2,5-DCP). A large proportion of the chlorophenols partitioned to the solid phase. Degradation kinetics were studied utilizing serum bottles filled with sludge from the digesters which were separately spiked with each chlorophenol. Conversion of PCP and tetrachlorophenols (2,3,4,5-TeCP and 2,3,5,6-TeCP) followed first-order kinetics, the trichlorophenols (3,4,5-TCP, 2,3,5-TCP) and 3,5-DCP followed zero-order kinetics, and 3-MCP and 2,5-DCP were not dechlorinated. PCP degradation was rate-limiting. Such slow degradation of PCP followed by more rapid degradation of daughter products may result in concentrations of daughter products that fall below detection limits, unless the degradation pathway is discontinued and the daughter product begins to accumulate.

Mikesell and Boyd (1986) achieved complete mineralization of PCP by first acclimating anaerobic sludge to monochlorophenol (MCP). The initial dehalogenation at either the ortho, meta or para positions was controlled by acclimation to either 2-CP, 3-CP or 4-CP, respectively. When sludge acclimated to all three isomers of MCP was combined, the mixture was capable of degrading 40 mM spikes of PCP within 3 to 6 days. A sequence of five spikes of PCP (over an 18-day period) produced accumulations of 3,4,5-TCP, 3,5-DCP and 3-CP (40-60 mM). These were subsequently degraded completely within 40 days. Spikes of $^{14}$C-PCP showed stoichiometric recovery of total mineralized carbon of 95.3%, with 22.9% appearing as CO$_2$ and 32% as CH$_4$. Subsequent degradation of phenol was shown once the chlorinated moieties were completely dehalogenated.

Adsorption of PCP has been shown to occur on soil, clay, aerobic and anaerobic sludges, and leaves. Kinetic, equilibrium, and transport experiments with soil columns by Lafrance et al. (1994) indicated that natural dissolved organic matter (NDOM) affected adsorption of PCP. For low concentrations, the effect of NDOM on PCP adsorption was negligible at pH 5.2, 5.4, and 6.1, but at high concentrations, NDOM increased adsorption of PCP at pH 5.4 and 6.1. Based on these investigations, PCP adsorption to organic material within a landfill may play an important role. Solid phase partitioning may actually lower leachate concentrations to levels which may have otherwise been inhibitory to methanogenesis. Therefore, because both dehalogenation and adsorption have been shown to occur during methanogenesis, laboratory simulations were used to reveal dehalogenation patterns throughout the phases of landfill stabilization.
MATERIALS AND METHODS

The two cylindrical test reactors were of equal size, one was a single pass test reactor, or SPTR, operated to simulate conventional landfill practice with single pass leaching, and the other was a leachate recycle test reactor, or RTR, operated with leachate recirculation as used in bioreactor landfill practice. The dimensions were 38.1 cm (inside diameter) x 81.3 cm (height). A third reactor served as a control recycle reactor, or CRR, operated with leachate recirculation. It was smaller in size and contained just over half the volume of the other two reactors, with dimensions of 33 cm (inside diameter) x 61 cm (height). Operation of the CRR provided comparative data to those of the test reactors.

All reactors were equipped with gas and leachate sampling ports, and gas collection and pressure equalization systems. The recycle reactors were also provided with systems to recirculate leachate from the bottom to distribution systems at the top. Figure 1 presents a schematic diagram of the recycle landfill bioreactor; the single pass reactor was similar but without leachate recycle.

![Schematic diagram of the recycle landfill bioreactor](image)

Figure 1. Landfill bioreactor with leachate recycle.

To simulate landfill conditions, a representative waste material was formulated based on constituent values reported by Tchobanoglous et al. (1988), with nondegradable materials such as glass, plastic, rubber and textiles omitted. The ingredients chosen to represent the food waste component duplicated those used in a similar study (Rachdawong, 1994), and percentages of each constituent resulted in a mixture comparable to that reported by a number of sources summarized by Reinhart (1989), or 11.7, 49.8, 8.9, 24.2, 2.5 and 2.9% for waste food, paper, cardboard, yard waste, wood and soil, respectively. Uniformity was achieved by manually shredding and mixing a large batch of 100 kg, and a representative fraction was separated for each of three reactors. The two test reactors received 16.8 kg of waste which was mixed with 2% by weight (336 grams) of wood from PCP-contaminated wood waste that had been size-reduced in 0.623 x 0.623 x 2.54-cm segments and separated by various pole/crossarm sections for analysis according to similar studies (EPRI, 1990). Samples from each section were mixed in proportion to the power pole dimensions in order to achieve an overall sample that represented the entire pole. Because the fraction of municipal solid waste consisting of waste wood in a typical landfill varies between 1-4% by weight (Tchobanoglous et al., 1988), and not all waste wood disposed in landfills undergoes initial PCP treatment, a 2% by weight loading of PCP-treated wood was considered a liberal condition of codisposal which probably exceeded that expected in practice. The control reactor was loaded with 8.9 kg of the synthetic waste without the wood.

To determine PCP loading to the test reactors, Soxhlet extractions were performed in triplicate on wood pole and crossarm sections. Sample sizes ranging from 5 to 15 grams of wood, and the extracts were concentrated to 1 ml and analyzed by GC-MS. Results were converted to total mass of PCP per reactor (based on 336 grams of wood per test reactor). In addition, Toxicity Characteristic Leaching Procedure (TCLP) extractions were performed in triplicate on all wood pole and crossarm sections, with sample sizes of approximately 25
grams. Extracts underwent liquid/liquid extraction, concentration to 1 ml, and analysis by GC-MS. Results were converted to leachable mass per reactor.

After the three reactors were loaded and sealed, 2 l/day of moisture were added to the test reactors (half to the control reactor) to attain field capacity. When the volume added was equal to the volume collected as leachate each day, further moisture additions simulated rainfall percolation at 2.5 cm/month or about 1 l/week. Retained moisture within the SPTR and RTR was about 25-30 liters, and leachate recirculation was provided weekly.

EPA Methods (1986) or Standard Methods (1995) were employed for leachate and gas quality analysis (Battaglia, 1995; Karadagli, 1996). In addition, leachate PCP and transformation products were determined with solid phase extraction (SPE) and subsequent GC-MS analysis (Infante and Perez, 1991). Leachate, Soxhlet and TCLP extracts were also analyzed by gas chromatography (GC) according to EPA Method 8270, SW-846 (USEPA, 1986).

Jar tests were used to determine the extent of PCP adsorption to the solid waste matrix at varying pH. The synthetic waste mass was size-reduced to <1.0 mm and varying amounts were added to isotherm jars and allowed to equilibrate with a solution of PCP of known concentration. The amount of time allowed for equilibration was based on previous studies (Battaglia, 1995), and after equilibrium was achieved, samples were filtered through 0.45-μm pore size nylon filters and 100 ml of filtrate was extracted by solid-phase extraction and analyzed by GC-MS.

Table 1. Soxlet, TCLP, and pH leaching of PCP from waste wood samples*

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH 4.7</th>
<th>pH 6.5</th>
<th>TCLP (acidic)</th>
<th>Soxlet</th>
</tr>
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<tr>
<td>PCP</td>
<td>4.057</td>
<td>39.671</td>
<td>3.16</td>
<td>97.775</td>
</tr>
<tr>
<td>2,3,5,6-TeCP</td>
<td>0.417</td>
<td>3.637</td>
<td>0.332</td>
<td>3.485</td>
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<tr>
<td>2,3,4,5-TeCP</td>
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<td>0.043</td>
<td>0.414</td>
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<tr>
<td>2,3,4,6-TeCP</td>
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<td>BDL</td>
<td>BDL</td>
<td>5.163</td>
</tr>
<tr>
<td>2,3,4-TCP</td>
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<td>BDL</td>
<td>BDL</td>
<td>0.086</td>
</tr>
<tr>
<td>2,3,6-TCP</td>
<td>BDL</td>
<td>BDL</td>
<td>0.002</td>
<td>1.439</td>
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<tr>
<td>2,4,5-TCP</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.785</td>
</tr>
<tr>
<td>2,4,6-TCP</td>
<td>BDL</td>
<td>0.014</td>
<td>BDL</td>
<td>0.275</td>
</tr>
<tr>
<td>2,3,5-TCP</td>
<td>0.006</td>
<td>0.015</td>
<td>0.005</td>
<td>0.597</td>
</tr>
<tr>
<td>3,4-DCP</td>
<td>0.242</td>
<td>0.188</td>
<td>BDL</td>
<td>0.615</td>
</tr>
<tr>
<td>3,5-DCP</td>
<td>0.562</td>
<td>0.533</td>
<td>BDL</td>
<td>0.224</td>
</tr>
<tr>
<td>2,6-DCP</td>
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<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
</tr>
<tr>
<td>2,3-DCP</td>
<td>BDL</td>
<td>BDL</td>
<td>0.003</td>
<td>0.024</td>
</tr>
<tr>
<td>2,4 &amp; 2.5-DCP</td>
<td>BDL</td>
<td>BDL</td>
<td>0.002</td>
<td>0.297</td>
</tr>
<tr>
<td>3 &amp; 4-CP</td>
<td>BDL</td>
<td>BDL</td>
<td>0.005</td>
<td>0.061</td>
</tr>
<tr>
<td>2-CP</td>
<td>BDL</td>
<td>BDL</td>
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<td>0.202</td>
</tr>
<tr>
<td>Phenol</td>
<td>BDL</td>
<td>BDL</td>
<td>0.014</td>
<td>0.029</td>
</tr>
</tbody>
</table>

*Expressed as loading to each test reactor, 336 g of wood and 16.8 kg waste.
**BDL = Below Detection Limit

RESULTS AND DISCUSSION

Extraction and leachability results

Soxhlet extraction results for each pole section, coupled with wood pole proportions and reactor wood loading (2% by weight, 336 grams of wood), yielded a PCP loading of approximately 98 mg of PCP per test reactor. Similarly, TCLP extractions for "leachable" PCP indicated less than 4 mg of PCP leached from the wood. However, because landfills undergo both acidic and near neutral pH conditions during acidogenesis and methanogenesis, additional tests were performed near neutral pH. PCP concentrations were nearly ten...
times higher than with TCLP extraction (Table 1). These results suggested variable PCP and daughter product availability for potential transformation throughout the sequential phases of landfill stabilization.

**Acidogenic phase transformation**

During the acidogenic phase (through about Day 650), some PCP transformation probably occurred because PCP is amenable to dehalogenation under such anaerobic conditions, particularly in the presence of hydrogen, a common product during acidogenesis. However, accumulation of volatile organic acids (VOA) and COD concentrations (Fig. 2) both interfered with the PCP analysis and led to a reduction in pH (Fig. 3) and PCP solubility. Therefore, PCP availability for microbially-mediated transformation was also reduced during this phase, as suggested by the TCLP results.

![Figure 2. Leachate COD concentrations for landfill bioreactors.](image)

![Figure 3. Leachate pH for landfill bioreactors.](image)

**Methanogenic phase transformation**

Transformation of PCP to its daughter products was more clearly observed during the methanogenic phase of landfill stabilization (after about Day 650). Chlorophenol was the first product detected in some of the initial leachate samples from the recycle test reactor as conditions became more conducive for methanogenesis with increased pH and gas production (Fig. 4), ORP (Fig. 5) and COD reduction. Later leachate samples indicated sequential transformation of including tri-, di- and monochlorophenols and phenol (Figs 6 and 7), with more rapid and complete conversion in the RTR. Although past studies on PCP degradation indicated that transformation products such as di- and monochlorophenol tend to accumulate within anaerobic systems, as landfill methanogenesis proceeded, these compounds were transformed further to below detection levels (~ 0.05 mg/l). Results of a companion adsorption study indicated that adsorption to the solid waste matrix occurred and was important in reducing the concentration of PCP in the leachate. However, these tests also indicated that PCP availability for transformation was enhanced at near neutral pH during methanogenesis.
Figure 4. Cumulative gas production for landfill bioreactors.

Figure 5. Leachate ORP for landfill bioreactors.

Figure 6. Patterns of PCP transformation in SPTR.

Figure 7. Patterns of PCP transformation in RTR.
SUMMARY AND CONCLUSION

The overall purpose of this research was to determine the efficacy of codisposal of PCP-treated wood power poles and crossarms with municipal solid waste in landfills. The results indicated that during initial start-up and the acidogenic phases of landfill stabilization, leachate PCP concentrations were low and below levels reported to be inhibitory to the onset of methanogenesis. The release and disappearance of PCP with the appearance of daughter products in the leachate during methanogenesis suggested that anaerobic transformation of PCP, probably through reductive dechlorination, was achieved. Degradation pathways were similar to those of previous studies, and leachate recirculation enhanced overall stabilization and attenuation within the landfill reactors. The codisposal of PCP-treated wood power poles and crossarms did not adversely affect landfill stabilization or concentrate PCP or its daughter products to unacceptable levels in the liquid or gas phases at loadings of or below the 2% by weight used. Hence, the codisposal of PCP-treated power poles with typical municipal solid waste in municipal landfills is considered a feasible and acceptable solid waste management strategy.

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REFERENCES


