Clopyralid Problems in Mulch and Compost

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The composting process is expected to degrade chemical compounds produced by living organisms, such as complex carbohydrates, and also to degrade pesticides. In compost piles, high temperatures, microbial activity, and chemical processes such as hydrolysis cause breakdown of large organic molecules into simpler molecules.

Nevertheless, the herbicide clopyralid has been reported in compost in Washington state (Rynk 2002), the Pennsylvania State University (Houck and Burkhart 2001) and in compost made in San Diego County (Green 2001). Advances in analytical chemistry may allow detection of concentrations of a herbicide below those affecting plants. However, the concentrations of clopyralid reported from Washington (see Table), of 10-75 ppb at Penn State (Houck and Burkhart 2001) and 50-1500 ppb in San Diego (Green 2001) are sufficient to have herbicidal activity against sensitive plants. The herbicide was first detected in Washington because vegetable plants showed phytoxicity symptoms in gardens where city compost was used.

Clopyralid was introduced in 1975 as a selective postemergence herbicide for broadleaf weed control in grains and some broadleaved crops (Cremlyn 1991). It was first introduced for agricultural production, and is an effective material (Transline^{TM}) against the invasive exotic weed yellowstar thistle. It is also used for other broadleaf and thistle control (e.g. Canada thistle) in crops such as grass hay (Uhlar-Hefner 2002). Clopyralid has also been introduced into the lawn care market (Confront^{TM}, Millennium^{TM}) and from there apparently made its way into municpal compost.

Clopyralid is a pyridine derivative, with a six-membered aromatic ring of five carbon atoms and one nitrogen atom characteristic of pyridine-based compounds. A chemically similar compound is include picloram (Figure 1), one of the more persistent herbicides (Cremlyn 1991). The structure of clopyralid (Figure 2) is also similar to that of 2,4-D (Figure 3) and indeed clopyralid has the same mode-of-action, acting as an analog of the naturally occurring plant hormone indole-3-acetic acid (Figure 4). Clopyralid stimulates RNA synthesis and protein formation at low concentrations while inhibiting oxidative phosphorylation at high concentrations (Cremlyn 1991). The herbicide is quite water soluble, 1000 mg kg^{-1} (Farm Chemicals Handbook 1995) and is therefore mobile in soil It is active at the low rates of 50-400 g active ingredient per hectare (Cremlyn 1991), approximately equivalent to 3/4-5 oz per acre. Clopyralid shows activity against tomatoes and peppers at concentrations as low as 10 ppb (Rynk 2002). Most plants are not as sensitive to clopyralid as are these crops.

In general, pesticides currently marketed have short half-lives and do not persist in the environment as did many chemical compounds sold in the 1950's and 1960's, but clearly a range of persistence is still to be found. Because of the structure of clopyralid, specifically with regard to its aromatic ring subtended by two chlorine atoms, it is perhaps not surprising that this compound has been detected in compost. Because of its potency at low doses, again perhaps it is not surprising that clopyralid could be found to be injurious even at low levels after the composting process. However, the discovery of clopyralid residues in compost in several

locations now negates the earlier generalization that pesticides are degraded to below-active levels through the composting process.

Table. Examples of clopyralid concentrations found in compost in Washington state (from Rynk 2002).

Compost material	Clopyralid concentration (ppb)
Mixed yard trimmings	25
Commercial yard waste	24
Mixed yard waste, immature compost	86
Mixed yard waste, mature compost	124
Leaves and grass	23

The discovery of clopyralid activity from compost is particularly significant in California because of the emphasis on greenwaste diversion from landfills to composting facilities. To conserve landfill space, the California legislature mandated diversion of at least 50% of the waste stream away from landfills by municpalities, and in Los Angeles about 2000 tons per day of leaves, brush and grass clippings are collected at curbside for composting (Green 2001). At Penn State, damage to plants occurred after about four weeks, suggesting short-term bioassays may not be adequate to assess herbicide presence (Houck and Burkhart 2001).

On April 11, 2002, Dow Agrosciences (Dow 2002) announced it was proceeding to discontinue registration of clopyralid for residential turf in California, and on June 26, 2002 extended this label change to the entire U.S. Professional applicators would have to notify property owners not to compost clippings from grass treated with the compound. Clopyralid would remain available for farm and ranch use.

Figure 1. Structure of picloram.

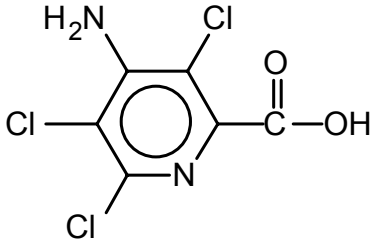


Figure 2. Structure of clopyralid.

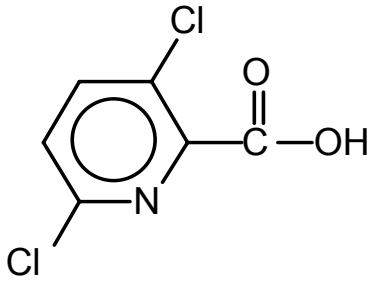


Figure 3. Structure of 2,4-D.

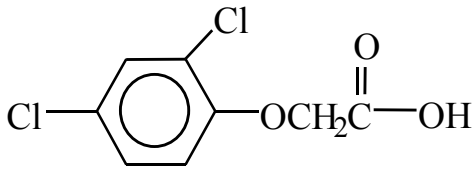
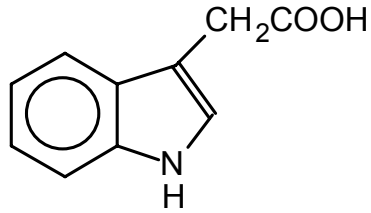


Figure 4. Structure of indole-3-acetic acid (IAA), a naturally occurring auxin.



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