

## Distribution of the herbicides clomazone and pendimethalin in soils, and implications for activity and persistence

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**Summary** The major soil factors influencing herbicide persistence were examined for two commonly used pre-emergent herbicides. Clomazone and pendimethalin sorption kinetics were examined on the separated fractions of four Tasmanian soils. In all soils the K<sub>d</sub> of clomazone and pendimethalin sorption increased in the order; sand < silt < clay < particulate organic matter. The degree of sorption of both herbicides increased with increasing humification of organic matter associated with soil fractions. Pendimethalin exhibited greater sorption on all soil fractions compared with clomazone, which may explain accumulation of pendimethalin soil residues.

**Key words** Clomazone, pendimethalin, herbicide, sorption kinetics, adsorption.

### INTRODUCTION

The Tasmanian vegetable and broad acre cropping industries rely on the use of residual herbicides for effective weed control. Clomazone and pendimethalin are two products gaining wide use, but both have also been associated with carry-over problems. Clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone) applied post-emergence to opium poppies (*Papaver somniferum*) has caused damage in a subsequent crop of malting barley (*Hordeum vulgare*). Pendimethalin (*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzamine) provides residual weed control in pyrethrum daisies (*Tanacetum cinerariaefolium* L.) but with potential for subsequent carry-over effects upon opium poppy crops. As a result, accurate herbicide application rate is required to avoid carry-over effects and maintain crop-rotation choice in the Tasmanian production system. Generation of application rate recommendations has been restricted by significant variation between soils in herbicide persistence. Preliminary studies have been undertaken in Tasmania to identify the dominant soil properties influencing herbicide behaviour in cropping soils. Initial soil sorption measurements indicated that herbicide persistence was linked to adsorption to soil colloids. Furthermore, this initial study indicated that the varied nature of individual soil constituents may have a large bearing upon sorption. The objective of this research was to evaluate the kinetics and degree

of sorption to various soil fractions in four important agricultural soils in Tasmania.

### METHODS AND MATERIALS

**Soils** The kinetics of clomazone and pendimethalin sorption were studied in soil fractions of four soils; clay loam ferrosol with >5% free iron oxides (ferrosol), acidic silty loam (sodosol), smectitic black cracking clay (vertosol), and a hydrophobic loamy sand with large amounts of particulate organic matter (kurosol). All soils were classified according to the Australian soil classification system (Isbell 1996).

Soils were fractionated into sand (>20 µm), silt (2–20 µm) and clay (2 µm) by sedimentation according to the method of Kunze and Dixon (1986). Disruption of aggregates being achieved by mechanical agitation and sonification. Particulate organic matter (POM) was separated using an aqueous solution of sodium polytungstate (Na<sub>6</sub>(H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>).H<sub>2</sub>O) of density 1.6 mg m<sup>-3</sup> (Golchin *et al.* 1994). Clay-fraction separation of whole clay (<2 µm) and fine clay (<0.02 µm) fractions was achieved by sedimentation and centrifugation (Laird *et al.* 1991). A sample of the clay fractions extracted from the ferrosol and vertosol was also treated with 30% H<sub>2</sub>O<sub>2</sub> for removal of organic matter (Kunze and Dixon, 1986). This oxidised ferrosol sample was also treated with sodium dithionite and sodium citrate in a system buffered with sodium bicarbonate (DCB treatment) for removal of free Fe compounds (Kunze and Dixon 1986).

The chemistry of the clay fractions was investigated by X-ray diffraction (XRD), selected fractions also being examined by scanning electron microscopy (SEM). Total carbon was determined by dry combustion in a LECO furnace, and total N by Kjeldahl digestion.

**Sorption kinetics of herbicides onto the soils** The kinetics of clomazone and pendimethalin adsorption by the soil fractions were determined using the batch equilibration method. Each soil fraction (1.0 g or 0.5 g for POM, in triplicate) was equilibrated with 0.01M CaCl<sub>2</sub> (5 mL) containing clomazone (1 mg L<sup>-1</sup>) or pendimethalin (0.4 mg L<sup>-1</sup>). Incubation times were 0.5, 1, 2, 4, 8 and 24 hours, after which samples were

centrifuged for 5 min at 10,000 rpm, filtered to 0.45 µm and extracted with dichloromethane.

**Field dissipation of herbicides** Rates of dissipation of clomazone and pendimethalin in the field were assessed in ferresol, sodosol, vertosol and kurosol soils. The soils were located at three sites, with the vertosol and kurosol soils at the same location. Herbicides were applied at recommended rates and soil samples collected at regular intervals over a 12 month period. Herbicide residues were extracted as described above.

**Chemicals and analysis** Analytical grade (99.1%) clomazone and pendimethalin were obtained from the Australian Standards Laboratory. All quantification was performed using a Varian Saturn GC-MS/MS operated at 28°C. Samples (2 µL) were injected into

the column at 40°C using a carrier gas of helium at a flow rate of 2 mL min<sup>-1</sup>. This column temperature was maintained for 1 minute, increased to 190°C at 30°C min<sup>-1</sup>, and finally increased at 10°C min<sup>-1</sup> to 280°C and held there for 6 minutes.

## RESULTS

The key chemical components of each soil fraction are presented in Table 1. The organic matter associated with each soil fraction was qualitatively assessed according to palynological classification (Tyson, 1995) to determine the most dominant type of organic matter present. The POM fractions in all soils contained large amounts of relatively undegraded plant debris or phytoclast (PH) material. In addition, the POM fraction of the vertosol, and to a lesser extent of the kurosol, contained appreciable amounts of charcoal.

**Table 1.** Characteristics of soil fractions and organic matter.

| Soil fraction                 | Mass (%) <sup>a</sup> | Total carbon (%) | C:N ratio | Organic matter type <sup>b</sup> | Clay matrix <sup>c</sup> |
|-------------------------------|-----------------------|------------------|-----------|----------------------------------|--------------------------|
| <b>Kurosol</b>                | 100                   | 2.1              | 21        | PH/AOM/CH                        | SM/IL                    |
| POM                           | 1.2                   | 27               | 29        | PH/CH                            | –                        |
| Sand                          | 90                    | 1.35             | 22        | AOM <sup>c</sup>                 | –                        |
| Silt and clay                 | 9                     | 9.29             | 13        | CM                               | –                        |
| Sand-OM                       | –                     | –                | –         | –                                | –                        |
| <b>Sodosol</b>                | 100                   | 2.4              | 19        | AOM/PH/CM                        | Kaolin                   |
| POM                           | 1                     | 28               | 25        | PH                               | –                        |
| Sand                          | 85                    | –                | 23        | AOM                              | –                        |
| Silt and clay                 | 12                    | –                | 15        | CM/AOM                           | Kaolin                   |
| Silt and clay-OM <sup>d</sup> | –                     | –                | –         | –                                | –                        |
| <b>Ferrosol</b>               | 100                   | 5.3              | 12        | CM/PH/OAM                        | Kaolin                   |
| POM                           | 2.1                   | 25               | 24        | PH                               | –                        |
| Sand and silt                 | 12                    | 6.28             | 21        | OAM                              | –                        |
| Clay                          | 82                    | 5.22             | 10        | CM                               | Kaolin                   |
| Clay-OM and Fe <sup>e</sup>   | –                     | –                | –         | –                                | –                        |
| <b>Vertosol</b>               | 100                   | 3.4              | 14        | CM/OAM/PH                        | Smectite                 |
| POM                           | 0.8                   | 26               | 29        | PH/CH                            | –                        |
| Sand and silt                 | 46                    | 1.72             | 34        | OAM                              | –                        |
| Clay                          | 33                    | 4.33             | 10        | CM                               | Smectite                 |
| Fine clay                     | 18                    | 1.84             | 7         | CM                               | SM/IL                    |
| Fine clay-OM                  | –                     | –                | –         | –                                | SM/IL                    |

<sup>a</sup> Percentage of the total soil mass.

<sup>b</sup> Dominant organic matter present in order of content in each fraction; PH- phytoclast material, AOM- amorphous organic matter, CH- charcoal, CM- clay/humic association.

<sup>c</sup> Clay mineralogy as determined by XRD; a single entry represents greater than 90% of a dominant mineral present, SM/IL indicates mixed smectite/illmenite.

<sup>d</sup> Treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter.

<sup>e</sup> Treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter and DCB to remove free iron compounds.

As has been reported previously (Karapanagioti *et al.* 2000) the presence of charcoal may explain the comparatively high  $K_d$  value (Table 2) for clomazone on the vertosol POM fraction. In contrast, the presence of amorphous organic coatings (AOM) in the sand fraction of the kurosol provides an important sorptive site for rapid uptake of clomazone. The silt/clay fraction, with clay/humic association (CM), of the sodosol would be expected to result in an intermediate uptake rate of clomazone.

Clomazone sorption kinetics increased in the order of slowest to fastest; clay<sand<POM. The relative contribution of each soil fraction to the sorption of clomazone by the whole soil is affected by the type and distribution of organic matter. Soil clay fractions with a lower C:N ratio (Table 1), and hence more humified organic matter exhibit a greater affinity for clomazone (Table 2). Whilst the readily accessible POM which constitutes less than 2% of soil mass in all soils,

contributes over 5% to clomazone sorption by each soil (Table 2). Clomazone also exhibits an apparent affinity for pure clay fractions, in particular the smectite clay fraction of the vertosol (Table 2).

The hydrophobic pendimethalin molecule has a very strong affinity for organic surfaces. POM fractions exhibit large  $K_d$  values for pendimethalin, and contribute significantly to whole soil sorption (Table 2). Pendimethalin also shows greater adsorption to clay than sand fractions, which is most likely linked to the degree of humification of OM in the clay fractions. Importantly, clay fractions treated to remove organic matter also exhibit a strong affinity for pendimethalin (Table 2).

Rates of dissipation in the field were consistent with the sorptive characteristics of the four soils. Dissipation of clomazone was fastest in the ferresol (37% of applied concentration 14 days after application), intermediate in the kurosol (59%) and sodosol (59%)

**Table 2.** Sorption of clomazone and pendimethalin by the soil fractions.

| Soil fraction                 | % soil mass <sup>a</sup> | Clomazone $K_d$<br>(mL g <sup>-1</sup> ) | % contribution<br>to soil $K_d$ <sup>b</sup> | Pendimethalin $K_d$<br>(mL g <sup>-1</sup> ) | % contribution<br>to soil $K_d$ <sup>c</sup> |
|-------------------------------|--------------------------|--|--|--|--|
| <b>Kurosol</b>                | 100                      | 1.8                                      | –  | 157  | –  |
| POM                           | 1.2                      | 7.6                                      | 5  | 1806   | 14   |
| Sand                          | 90                       | 1.5                                      | 85   | 111  | 79   |
| Silt and clay                 | 9                        | 3.5                                      | 10   | 202  | 8  |
| Sand-OM                       | –                        | 0.1                                      | –  | 26   | –  |
| <b>Sodosol</b>                | 100                      | 1.7                                      | –  | 170  | –  |
| POM                           | 1                        | 6.6                                      | 5  | 1962   | 13   |
| Sand                          | 85                       | 1.2                                      | 68   | 115  | 63   |
| Silt and clay                 | 12                       | 2.7                                      | 27   | 247  | 24   |
| Silt and clay-OM <sup>d</sup> | –                        | 0.8                                      | –  | 88   | –  |
| <b>Ferresol</b>               | 100                      | 3.6                                      | –  | 194  | –  |
| POM                           | 2.1                      | 7.2                                      | 5  | 1693   | 19   |
| Sand and silt                 | 12                       | 3.7                                      | 55   | 108  | 28   |
| Clay                          | 82                       | 2.5                                      | 46   | 176  | 53   |
| Clay-OM and Fe <sup>e</sup>   | –                        | 1.2                                      | –  | 112  | –  |
| <b>Vertosol</b>               | 100                      | 2.4                                      | –  | 191  | –  |
| POM                           | 0.8                      | 13                                       | 6  | 1994   | 11   |
| Sand and silt                 | 46                       | 1.1                                      | 21   | 80   | 17   |
| Clay                          | 33                       | 2.6                                      | 51   | 218  | 48   |
| Fine clay                     | 18                       | 2.1                                      | 22   | 203  | 24   |
| Fine clay-OM                  | –                        | 1.8                                      | –  | 164  | –  |

<sup>a</sup> Percentage of the total soil mass.

<sup>b</sup> Percentage contribution of soil fraction to whole soil clomazone sorption.

<sup>c</sup> Percentage contribution of soil fraction to whole soil pendimethalin sorption.

<sup>d</sup> Treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter.

<sup>e</sup> Treated with H<sub>2</sub>O<sub>2</sub> to remove organic matter and DCB to remove free iron compounds.

and slowest in the vertosol (82%). The trend continued with time, and after 365 days the clomazone concentrations as a percentage of applied concentration were 3.1%, 4.1%, 4.1% and 15% for the ferrosol, kurosol, sodosol and vertosol respectively. Field dissipation of pendimethalin was more rapid than for clomazone. Extractable pendimethalin concentrations 7 days after application were 41%, 52%, 46% and 40% for ferrosol, kurosol, sodosol and vertosol respectively. After 365 days, concentrations as a percentage of applied concentration had declined to 4%, 3%, 2% and 10% for ferrosol, kurosol, sodosol and vertosol respectively.

#### CONCLUSION

Clomazone and pendimethalin exhibit a strong affinity for clay/humic associations (CM) which may result in accumulation of residues in the clay rich ferrosol and vertosol. In addition, exposed organic surfaces such as POM provide a site for rapid strong binding of herbicide. It is likely that exposed POM surfaces and AOM coatings in sand fractions represent a labile pool of bound herbicide in each soil. Such of a pool of herbicide would be readily subject to desorption given mechanical disruption and/or increased soil moisture.

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