PRODUCTS OF PROPARGYL BROMIDE DEGRADATION IN SOIL

Sharon K. Papiernik, Jianying Gan, Robert Dungan* and Scott R. Yates
USDA-ARS, George E. Brown Jr. Salinity Laboratory, Riverside, CA

Propargyl bromide (C_3H_3Br; PrBr) is being investigated for its potential to partially replace methyl bromide (MeBr) as a soil fumigant. Information on its environmental fate, including mechanisms of degradation in soil, is required to evaluate PrBr's capacity for sustained usage. We have conducted a number of studies on the degradation on PrBr in soil, and monitored the formation of some of the products of PrBr degradation in soil and water.

Primary alkyl halides, including MeBr and PrBr react via nucleophilic substitution. This reaction mechanism imparts broad-spectrum toxicity through alkylation of nucleophilic groups in amino acids and peptides. All known mechanisms of PrBr and MeBr degradation in soil and water result in the formation of Br^-. Analysis of additional degradation products gives information on the mechanism of transformation.

Hydrolysis

Hydrolysis of PrBr occurs through S_N2 nucleophilic substitution to form propargyl alcohol (C_3H_3OH; PrOH) and Br^-:

$$C_3H_3Br + H_2O \rightarrow C_3H_3OH + Br^- + H^+$$

$$C_3H_3Br + OH^- \rightarrow C_3H_3OH + Br^-$$

This is analogous to the formation of methanol in MeBr hydrolysis. PrOH may be transformed to other products, including propiolic acid (C_3H_3OOH; PrOOH) and those in which the propargyl group is not intact.

PrBr and MeBr were spiked to water samples; vials were sealed with no headspace. Samples were incubated at 22°C. Triplicate vials were removed at various times and an aliquot of the water removed for analysis by GC-MS for PrBr and PrOH. An additional aliquot was removed for Br^- analysis by IC.

_Results indicated that hydrolysis of PrBr formed PrOH and Br– in equimolar amounts: for each mole of PrBr degraded, one mole of PrOH and one mole of Br– were formed (Figure 1). Similar results were observed for MeBr.

Degradation in Soil

It has been postulated that primary alkyl halides including MeBr and PrBr can undergo S_N2 nucleophilic substitution reactions with nuclephilic groups on soil organic matter, such as –SH, –NH, –NH_2, and –OH, to result in alkylation of soil organic matter (OM):

$$C_3H_3Br + OM–NH \rightarrow C_3H_3–N–OM + Br– + H^+$$

$$C_3H_3Br + OM–SH \rightarrow C_3H_3–S–OM + Br– + H^+$$

These reactions form bound residues: the carbon-containing portion of the molecule remains associated with the soil and is not extractable.

Soil samples (10 g dry weight) were spiked with PrBr, sealed in gas-tight vials, and incubated at 24°C. Samples were removed at various times and extracted with water (for PrOH and Br– analysis) or ethyl acetate (for PrBr analysis).

_The pattern of product formation indicated that degradation of PrBr in soil was not primarily due to hydrolysis. Degradation of one mole of PrBr formed one mole of Br–, but much less than one mole of PrOH (Figures 2 and 3). No other degradation products were identified. Similar results were observed for MeBr.

_The rate of PrBr and MeBr degradation increased with increasing soil organic matter content (Figures 2 and 3), consistent with an S_N2 nucleophilic substitution reaction mechanism.

_Degradation of ^{14}C-labeled MeBr in soil resulted in the formation of bound (unextractable) residues of the carbon-containing portion of the molecule, with concurrent release of Br–. Soil-bound ^{14}C residues increased as the extractable ^{14}C decreased and increased with time, suggesting that degradation of ^{14}C-MeBr was via alkylation of soil organic matter (Figure 4). A similar mechanism is proposed for PrBr degradation in soil.