

Memorandum

To : Ronald J. Oshima
Branch Chief
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Date : May 15, 1990

Place : Sacramento

From : Department of Food and Agriculture Kean Goh, Sr. Environ. Hazards Scientist
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Subject: Literature Review of the Environmental Fate of Ethoprop (Mocap)

This review was based on (1) data from the CDFA pesticide registration packages cited here as Rhone-Poulenc; (2) a report by the Environmental Hazards Assessment Program (Weaver et al. 1988); (3) open literatures searched through Analytical Abstracts (1980-90), AGRICOLA (79-90), CAB Abstracts (72-83), Chemical Abstracts (67-90), and BIOSIS (69-90). These open literature entries are cited by authors.

Air Concentration

Air concentration of 2.46 ug/m³ of ethoprop was detected at a fixed site downwind at the edge of field during a worker exposure study (Rhone-Poulenc, 1984a). The study was conducted by Rhone-Poulenc in 1981 by preplant broadcast of Mocap 6EC at 6 lb ai in 60 gals of water per acre to a 15 acre field in Salinas, CA. Personal air samplers consisted of open-face 37-mm cellulose-ester membrane filters in field-monitor cassettes backed by a 100-mg charcoal tube. Air was sampled at a rate of 1.5 Lpm. Concentrations (ug/m³) of ethoprop in air for various workers were 2.43 (loader), 1.31 (applicator), 7.2-48 (cultivators), and <0.07-8.0 (irrigators). The high levels experienced by the cultivators were associated with the high dust levels during the cultivation process when the surface applied ethoprop is incorporated into the subsurface soil. The dust produced by this operation contained 360-450 ppm of ethoprop. This is much larger than concentrations in the 1-cm deep soil samples of about 10 ppm (Rhone-Poulenc, 1984).

Volatilization was estimated to be 0.7 to 1.8% of the dosage applied by computer simulation (Leistra 1979). Simulation was based on ethoprophos (=ethoprop) applied at 10 kg ai/ha of Mocap 20G and homogenously incorporated into a top layer of 0.10 m in a sandy loam soil in the Netherlands. In general, loss of ethoprop from volatilization is considered too low because of its low vapor pressure (4.6 x10⁻² Pa at 26^o C). Vapor pressures of some common nematicides and insecticides are 1,3-D (3.7x10³ Pa/25^o C); chloropicrin (3.2x10³ Pa/20^o C); fenamiphos (1.3x10⁻⁴ Pa/30^o C); mevinphos (1.7x10⁻² Pa/20^o C); and parathion (5.0 x10⁻³ Pa/20^o C). In tests with 10G Mocap, very little volatilized from dry granules, but large

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amounts of degradates such as mercaptans and sulfides were produced (Huvor 1969 cited in Rohde et al. 1979).

Soil Metabolism and Transport

In field studies conducted in two California commercial daffodil fields, Weaver et al. (1988) reported that "ethoprop may pose a threat to shallow ground water due to leaching under conditions of high rainfall in Humboldt and Del Norte counties." Ethoprop was applied as a liquid (Mocap 70% liquid at 2 quarts/acre, Humboldt) or granule (Mocap 10G, 30 gm/22 ft over 10-in band, Del Norte). Ethoprop persisted for 8 months in soil and leached to 48-54 inches (the maximum sampling depths) following rainfall totalling 37 and 50 inches for Humboldt and Del Norte counties, respectively. However, ethoprop concentrations were low at 0.01-0.07 ppm at below 18" of soil at Humboldt and at 0.01-0.04 ppm in samples deeper than 30" at Del Norte. "Leaching occurred in spite of relatively high (2.5-6.6%) organic matter contents in the top foot of soil" (Weaver et al. 1988).

In field experiment in Tifton, GA, Rohde et al. (1979) showed that the formulation of Mocap influenced the persistence in soil and amount of runoff in surface water. Mocap 6L and 10G were applied at 9 kg ai/ha at 15 cm depth. Concentration and persistence of ethoprop in the top 10 cm of soil were higher for the 10G application: 1,207 ng/g and 110 days for >90% dissipation. The 6L application gave concentration of 710 ng/g and 30 days for >90% dissipation. Conversely, higher concentration of ethoprop was found in the runoff water for the liquid formulation (283 ug/L) than the granular formulation (45 ug/L) at 2-3 days after application.

In the Netherlands, the half-lives of ethoprop measured under field conditions in aluminium columns (40 cm long) were 87 days in humic sand (pH 4.5) and peaty sand (pH 4.6), and ranged between 14-28 days for sandy loam (pH 7.2) and loam soils (pH 7.3) (Smelt et al., 1977).

Microbial process was important in the transformation of ethoprop, and previous repeated application of ethoprop can accelerate the degradation of ethoprop through microbial adaptation. This was evident in the half-life of 408 days in autoclaved soil compared to 5 days in unautoclaved soil both from plots previously treated with ethoprop (Smelt et al. 1987).

In small field-plot tests in various states, the soil half-lives ranged 4-25 days and a secondary lag half-lives of 30-90 days for certain soils as shown in the following table (Rhone-Poulenc, 1986a). Ethoprop was applied as Mocap 6EC preplant at 12 lb ai/a to bare

ground and incorporated into the soil up to a depth of 3 inches.

Soil (location)	Half-life (1st/2nd phase) days
Clay (MO)	4/56
Silt Loam (IL)	7/30
Silty Clay Loam (IL)	25/90
Silt Loam (NB)	6
Sand (NJ)	12

Laboratory aerobic metabolism of ethoprop (11.9 ppm) in loamy sand soil (moisture 6.1%, organic matter 1.7%, pH 5.3, incubated in the dark at 25°C) showed that the major degradation product was CO₂ which accounted for 53.88% of the applied ethoprop after 252 days (Rhone-Poulenc, 1986b). Soil microorganisms were probably responsible for the metabolism. Volatilization was concluded to be not the major mechanism of loss from soil. O-ethyl-S-propylphosphorothioic acid was the soil major residual metabolite; O-ethyl-O-methyl-S-propylphosphorothioate and O-ethyl-S-methyl-S-propylphosphorodithioate was the minor metabolites (Rhone-Poulenc, 1986b).

Under anaerobic conditions, the half-life of ethoprop was 130 days and the accumulation of metabolites was much less than under aerobic conditions. Ethoprop was the major compound recovered from flooded soils (Rhone-Poulenc, 1986b).

Photodegradation

Photolysis of ethoprop was conducted for aqueous medium only. In unbuffered aqueous solutions containing 5 ppm ethoprop irradiated for 40 days with simulated sunlight, the half-lives were 24 days for photosensitizer (2% acetone) added solution and 75 days for nonsensitized solution (Rhone-Poulenc 1983). Under buffered condition at pH 7 and exposed to half the intensity of sunlight, ethoprop (22.4 ppm) was found to be photolytically stable hence a half-life could not be obtained.

Hydrolysis

There were three hydrolysis studies conducted in the laboratory by Rhone-Poulenc:

- 1) Half-lives of ethoprop (200 ppm) in aqueous solutions (27°C) at pH 4, 6, and 8 were 23.1, 60.2, and 14.9 weeks, respectively (Rhone-Poulenc, 1984b);
- 2) Ethoprop (10 ppm) incubated in the dark at 25°C was stable at pH 5 and 7 and degraded with a half-life of 83 days at pH 9. Major degradates formed were ethyl alcohol and S, S-dipropyl phosphorodithioate (Rhone-Poulenc, 1989b);
- 3) Ethoprop (2-200 ppm) was subjected to aqueous hydrolysis at pH 3, 6, and 9 and at 20°C and 35°C during a 42-day period. Hydrolysis was shown to increase with time, temperature, and pH; concentration had little effect. The average half-lives ranged from 39 weeks (200 ppm, pH 6, 20°C) to 1.5 weeks (2 ppm, pH 9, 35°C). Hydrolysis was most rapid at pH 9. The degradate was shown to be O-ethyl, S-propyl phosphorothioic acid (Rhone-Poulenc, 1984b).

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