

ENVIRONMENTAL FATE OF MANCOZEB

Sue Xu

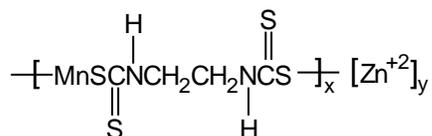
Environmental Monitoring & Pest Management
Department of Pesticide Regulation
Sacramento, CA 95814-3510

Mancozeb is one member of ethylenebisdithiocarbamate (EBDC) fungicides. This compound has a negligible vapor pressure, therefore it has a low potential to volatilize into the air. In water, mancozeb can be quickly hydrolyzed with a half-life of less than 2 days. The identified hydrolysis degradates are ethylenethiourea (ETU), ethyleneurea (EU) and ethylene bisisothiocyanate sulfide (EBIS). Mancozeb is of low soil persistence with half-lives of less than 2 and 8 days in aerobic and anaerobic soils, respectively. The major metabolites are ETU and EU. Under aerobic conditions, the metabolites breakdown further to produce CO₂. Mancozeb and its degradates moderately bind to soils with adsorption coefficient values (K_d) varied from 7 to 12 cm³/g. The compound has moderate mobile potential in soils, but due to the relatively high rate of chemical and microbial degradation mancozeb is not likely to leach into subsurface flow.

A. PHYSICAL AND CHEMICAL PROPERTIES

1. Common Name: Mancozeb
2. Chemical Name: [[1,2-ethanediylbis-[carbamodithioato]](2-)] manganese, mixture with [[1,2-ethanediylbis-[carbamodithioato]]-(2-)]zinc
3. Trade Names: Aazimag®, Fore®, Dithane M-45®, Manzate 200®
4. CAS Registry No.: 8018-01-7

5. Structural Formula:



$$x : y \approx 10 : 1$$

6. Empirical Formula: $(C_4H_6MnN_2S_4)_x (Zn)_y$
7. Molecular Weight: $(265.3) + (65.4)$
8. Melting Point: $192 - 194^{\circ}C$
9. Solubility: Water:
 6 mg/L at $25^{\circ}C$
 (Heller and Herner, 1990; Kidd and James, 1991)
 16 mg/L at $25^{\circ}C$ (R&H Company, 1987a)
 6-20 mg/L at $25^{\circ}C$ (IAO, 1997)
- Organic Solvents at $25^{\circ}C$ (R&H Company, 1987a)
 Ethanol: < 5 mg/L
 o-Dichloro-benzene: < 5 mg/L
 Dimethylformamide: < 5 mg/L
10. Vapor pressure: $< 10^{-5}$ mm Hg (Royal Society of Chemistry, 1987)
 $< 10^{-7}$ mm Hg (R&H Company, 1987a)
11. Octanol/water partition coefficient: < 22 at $25^{\circ}C$ ($\log P_{ow} \leq 1.34$)
12. Henry's law constant: $< 2.23 \times 10^3 \text{ atm m}^3(\text{g.mol})^{-1}$ @ $25^{\circ}C$
 (R&H Company, 1987a)

B. ENVIRONMENTAL FATE

Hydrolysis

Mancozeb hydrolyzes rapidly over a range of pHs; hydrolysis half-lives of ^{14}C -Dithane at pH 5, 7 and 9 ranged from 1-1.5 days at $25^{\circ}C$ under sterile and dark conditions (R&H Company, 1987b). In another study, the half-lives for mancozeb in water at pH 5-9 were reported as less than 1 day (Lyman and Lacoste 1975). The degradates and their relative amounts are pH-dependent. The identified hydrolysis products include ethylene bisisothiocyanate sulfide (EBIS), ethylenethiourea (ETU) and ethyleneurea (EU). Hydantoin is found as additional degradate at pH 9. One possible degradation route to form EBIS is via the oxidation of ethylene bisdithiocarbamate

(EBDC) dianion to ethylenethiuram disulfide (ETD), which was subsequently decomposed into EBIS (Engrst and Schnaak, 1970; Aldridge and Magos, 1978).

Photolysis

Aqueous photolysis studies on mancozeb were performed at concentrations of 6 ppm and 20 ppm over 24 hours and 72 hours, respectively (R&H Company, 1987c). In both cases, the photolysis half-lives were less than 3 hours with complete disappearance of mancozeb. Identified decomposition products were EBIS, ETU, ethylenediamine (EDA) and EU. A possible mechanism for degradation of mancozeb in the presence of water is the conversion of ethylene bisdithiocarbamate dianion to ethylenethiuram disulfide (ETD) and subsequent degradation to EBIS. EBIS may ultimately degrade to ETU or EDA. ETU is a suspected human carcinogen but it may be quickly photo-oxidized to EU and subsequently to glycine in water with a half-life of less than 3 days (Houeto *et al.*, 1995; Ross and Crosby, 1973; Cruickshank and Janrow, 1973).

The soil photolysis of mancozeb was studied in silt loam from Newtown, Pennsylvania, using continuous exposure (24 hrs/day) to artificial sunlight for a total of 30 days (R&H company, 1987d). There was no measurable decrease in concentration over 30 days in dry soil; the results were similar to a dark control. In wet soil, mancozeb degrades quickly due to its rapid hydrolysis as opposed to photolytic degradation

Soil Metabolism

Mancozeb is easily degraded in soil. It decreased to nondetectable levels in nonsterile soils in three months (Doneche *et al.*, 1983). The metabolism of 20 ppm and 10 ppm ¹⁴C-mancozeb was investigated on silt loam soil (nonsterile and sterile) under aerobic and sequential aerobic/anaerobic conditions at an average temperature of 23⁰ ± 0.6⁰C (R&H Company, 1987d and 1987e). Both sterilized and unsterilized soils yielded EU via intermediates EBIS and ETU. A small amount of EU was further degraded to 2-imidazoline and other unknown compounds under anaerobic conditions. Both biological and chemical mechanisms lead to the formation of EU (Kaars *et al.*, 1974; Vonk *et al.*, 1976). The approximate half-lives of mancozeb in nonsterile aerobic and anaerobic soils

were less than 2 days and 8 days, respectively (ARS, 1995). ETU had a half-life of less than two days in nonsterile soil.

The mineralization of mancozeb degradates to carbon dioxide only occurred in nonsterilized soils; no detectable carbon dioxide was released from sterile soils, indicating that mineralization was mainly conducted by microorganisms. The estimated half-lives of mineralization for 20 and 10 ppm Dithane M-45 were 50 and 90 days, respectively (Lyman and Lacoste 1975).

Soil Adsorption

A batch soil adsorption/desorption study on ^{14}C -Dithane M-45 was conducted on four soils: a Georgia sand, a Georgia sandy loam, a Pennsylvania silt loam and a Mississippi clay loam (R&H Company, 1987e). The 48-hour K_d values were experimentally obtained via ^{14}C measurements. Because mancozeb exists as an anion, the soil adsorption is probably much lower than that the experimental K_d value indicated.

The soil adsorption coefficient values (K_d) were 11.67, 9.89, 7.26, 10.13 cm^3/g for sand, sandy loam, silt loam and clay loam, respectively (R&H Company, 1987e). The soil desorption coefficients for 8 hours were 77.88, 35.93, 50.25 and 53.58 cm^3/g , respectively. These results indicated that mancozeb and its degradates moderately bind to soils. ETU and its degradates were weakly adsorbed by soils; their soil adsorption coefficient values (K_d) were 0.71, 0.67, 1.13 and 0.51 for sand, sandy loam, silt loam and clay loam, respectively.

Mobility

Generally speaking, mancozeb is more mobile in wet and sandy soil than in dry and organic rich soil (World Health Organization, 1988). Mancozeb has moderate leaching potential if one considers its solubility, environmental persistence and adsorption properties (Univ. of Maine, 1997). Its major degradate, ETU, has greater tendency to be mobile due to its high water solubility and weak adsorption in soil (Rajagopal *et al.* 1984).

The soil leaching of ^{14}C -mancozeb was examined using soil columns in five different soil types: a clay loam, a silty clay loam, a silt loam, a cecil clay and a sandy loam (Lyman and Lacoste 1975). The organic contents of the soils were 15.1%, 5.3%, 3.42%, 0.4% and 0.4%; clay contents 32%, 18%, 28%, 54% and 6%; the pH of the soils were 7.4, 6.0, 6.4, 4.7 and 4.9, respectively. Aqueous slurries of ^{14}C -mancozeb (15 mg) were applied to the top of every soil column (10 inches high and 5 ¼ inches diameter) with a concentration equivalent to 10 pounds per acre. One inch (2.5 cm) of water was added to the top of each column once a week for 9 weeks. The water was collected and no radioactivity leached through four of the five soils. About 1.8 to 5% of radioactivity was detected in the runoff water of the clay column. The majority of the recovered radioactivity, including mancozeb and its degradation products, remained in the top one-inch segment in the soil columns. Significant loss of radioactivity was reported, possibly resulting from volatilization and mineralization to carbon dioxide. The leaching of mancozeb was also studied through silty clay loam (OM 2.73%; clay 39.1%; pH 6.87) by other researchers (Calumpang *et al.*, 1993). Dithane M-45 (0.00393 g) was mixed with 5-mL water and then applied to the top of the column. The total rainfall was 31.1 mm during the investigation period. Mancozeb residues were found only in the top one-inch segment of the column and ETU was found in the top 3.2 inches after 21 days.

Plant Metabolism

The research on the metabolism of mancozeb has been undertaken on and in several plants including eggplants, sugar beets, lettuces, turnips, tomatoes and potatoes (Kumar and Agarwal 1992; Lyman 1971; Newsome 1979). ^3H , ^{14}C and ^{35}S labeled Dithane M-45 were applied to leafy plants (sugar beets, lettuces or turnips) to investigate its metabolism in plants (Lyman 1971). The following metabolites were detected after two weeks: Elemental sulfur, EBIS, ETU, EU, ethylenediamine, 3-(2-imidazolin-2-yl)-2-imidazolidinethione (Jaffe's base) and sulfate ion. On potatoes, low concentrations of ETU (0.0022 ppm) and EU (0.0056 ppm) were found. A significant portion of radioactivity was present as glycine and ethylenediamine in starch. Lyman (1971)

suggested that Dithane M-45 was converted into ethylenediamine via unidentified intermediate steps then subsequently oxidized to glycine.

An investigation on eggplants revealed the following metabolites after 28 days: ethylenethiuram disulfide (ETD), ETU, EU, and small amount of other unknown compounds. EU was detected as the predominant metabolite since the majority of ETU was degraded to EU (Kumar and Agarwal, 1992). The half-life of mancozeb on the whole plant was 10.6 days.

Groundwater Monitoring

Mancozeb has low solubility in water and moderate adsorption capacity in soil. It can be hydrolyzed within one day and has a field half day of 1 to 7 days (Wauchope *et al.* 1992). Therefore mancozeb is of low soil persistence. However, its metabolite, ETU, has high water solubility and a greater potential to be mobile in soils (U.S.EPA., 1987). Of 80 wells sampled for ETU in California, only one sample was detected at 0.725 ppb (Cal. EPA, 1999). However, follow-up sampling of this and proximate wells yielded no detections at a minimum detection level of 0.578 ppb (Spurlock, 2000).

Air Monitoring

Mancozeb has a negligible vapor pressure and a low potential to volatilize into the environment (U.S.EPA. 1984; Ligocki and Pankow, 1989; Linde, 1994). However, it might be found associated with air-borne particulates or as spray drift. In May 1993, air monitoring was conducted in potato fields before, during and after 72 hours application of mancozeb in Kern County, California. Of 32 analyzed samples, approximately 54 percent had detectable residues, ranging from $0.29 \mu\text{g}/\text{m}^3$ (0.02 ppb) to $1.81 \mu\text{g}/\text{m}^3$ (0.13 ppb) (Kollman, 1995).

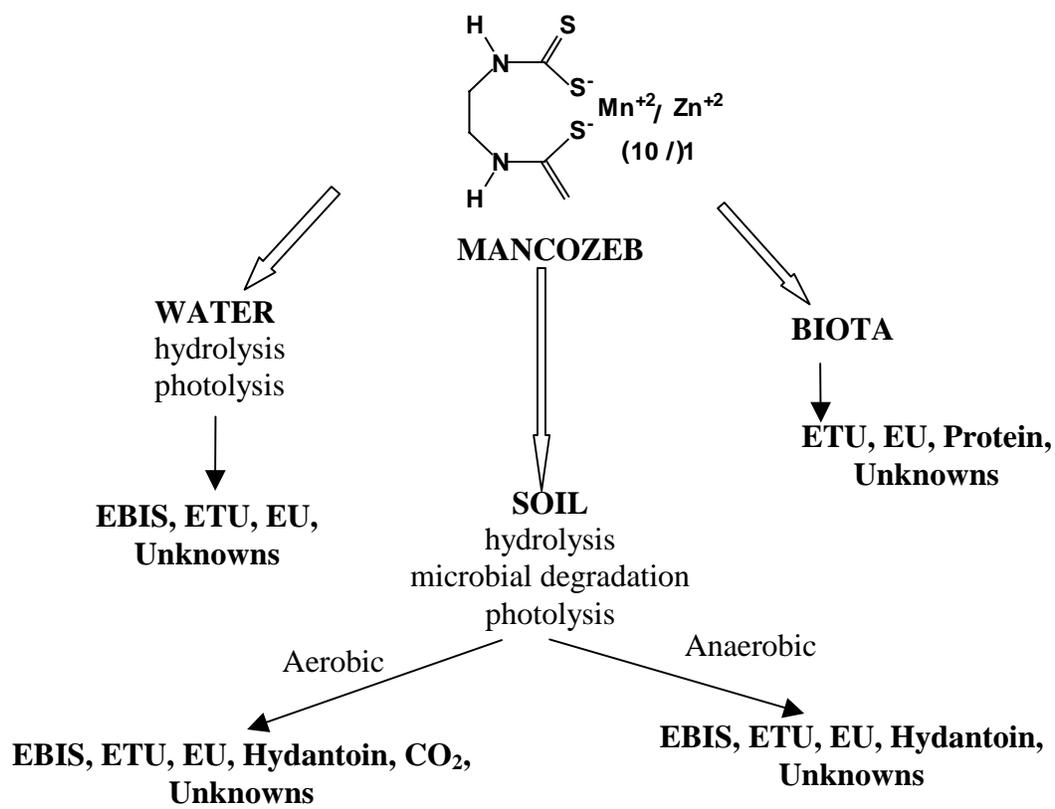
References

- Aldridge, W.N. and L. Magos (1978) "Carbamates, thiocarbamates, dithiocarbamates", Luxembourg, Commission of the European Communities, Report No. V/F/1/78/75 EN.
- ARS (1995) ARS pesticide properties. Available:
<http://wizard.arsusda.gov/rsml/textfiles/MANCOZEB>
- California EPA. (1999) "Well inventory database", Department of Pesticide Regulation, Sacramento, CA.
- Calumpang, S.M.F., M.J.B. Medina, N.P. Roxas and E.D. Magallona (1993) "Movement and degradation of mancozeb fungicide and its metabolites, ethylenethiourea and ethyleneurea in silty clay loam soil", *Intern. J. of Pest Management*, 39(2), 161-166.
- Cruickshank, P.A and H.C. Jarrow (1973) "Ethylenethiourea degradation", *J. Agric. food Chem.*, 21(3), 333-335.
- Doneche, B., G. Seguin and P. Ribereau-Gayon (1983) "Mancozeb effect on soil microorganisms and its degradation in soils", *Soil. Sci.* 135,361.
- Engst, R. and W. Schnaak (1970) "Studies on the metabolism of the ethylenebisdithiocarbamate fungicides maneb and zineb." *Z. Lebensm. Unters. Forsch.*, 143 (2), 81-85.
- Heller, S.R. and A.E. Herner (1990) "ARS pesticide properties database.", USDA-ARS Systems Research Laboratory, Beltsville, MD.
- Houeto, P., G. Bindoula and J.R.Hoffman (1995) "Ethylenebisdithiocarbamates and ethylenethiourea: possible human hazards", *Environ. Health Perspec.*, 103, 568-573.
- IAO (1997) "Data on pesticides in current use in Denmark", available:
<http://inet.uni-c.dk/~iaotb/pestdb.htm>
- Kaars, S. A. and J.W. Vonk (1974) "Decomposition of bisdithiocarbamates and metabolism by plants and microorganism", Abstr. 033, 3rd, *Internat. Congress pest. chem.*.
- Kidd, H., and D.R. James (1991) *The Agrochemicals handbook*, Royal Society of Chemistry Information Services, Cambridge, UK.
- Kollman, W. S. (1995) "Summary of assembly bill 1807/3219, pesticide air monitoring results", Department of Pesticide Regulation, Sacramento, CA.

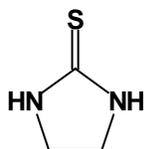
- Kumar, U., and H. C. Agarwal (1992) "Fate of [14C]mancozeb in egg plants (*Solanum melongena* L.) during summer under sub-tropical conditions", *Pestic. Sci.*, 36, 121-125.
- Ligocki, M.P. and J.F. Pankow (1989) "Measurements of the gas/particle distribution of atmospheric organic compounds", *Environ Sci. Technol.*, 23, 75-83
- Linde, C.D. (1994) *Physico-Chemical Properties and Environmental Fate of Pesticides*, Department of Pesticide Regulation, Sacramento, CA.
- Lyman, W. R.(1971) "The metabolic fate of Dithane M-45(coordination product of zinc and manganous ethylene bisdithiocarbamate)", *International Symposium on Pesticide Terminal Residues*,, Israel, London, Butterworth.
- Lyman, W. R., and R. J. Lacoste (1975) "New developments in the chemistry and fate of ethylenebis(dithiocarbamate) fungicides", *Environ. Qual. Saf., suppl* 3, 67-74.
- Newsome, W. H. (1979) "Residues of mancozeb, 2-Imidazoline, and ethyleneurea in tomato and potato crops after field treatment with mancozeb", *J. Agric. Food Chem.*, 27(6), 1188-1190.
- Rajagopal, B.S., G.P.Brahmaprakash, B.R. Reddy, U.D. Singh and N. Sethunathan (1984) "Effect and persistence of selected carbamate pesticides in soil", *Res. Reviews*, 93, 1-199.
- R&H Company. (1987a) "Bulk density, water solubility, solvent solubility, vapor pressure, octanol/water, Henry's law, photolysis in water", DPR Vol. 176-039, Department of Pesticide Regulation, Sacramento, CA
- R&H Company. (1987b) "The hydrolytic decomposition of Dithane M-45 at room temperature", DPR Vol. 176-040 #53693, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987c) "Water photolysis study of mancozeb", DPR Vol. 176-039 #53690, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987d) "Soil Photolysis Study of Mancozeb", DPR Vol. 176-040 #53692, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987e) "Aerobic and anaerobic soil metabolism of mancozeb", DPR Vol. 176-041 #53694&53695, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987f) "Batch soil adsorption/desorption of mancozeb", DPR Vol.176-042 #53696, Department of Pesticide Regulation, Sacramento, CA..

- Ross, R.D. and D.G. Crosby (1973) "Photolysis of ethylenethiourea", *J. Agric. Food Chem.*, 21(3), 335-337.
- Royal Society of Chemistry. (1987) *The agrochemicals handbook*, Royal Society of Chemistry, Nottingham, England.
- Spurlock, F. (2000) Personal Communication, Department of Pesticide Regulation, Sacramento, CA.
- University of Maine, Cooperative Extension, (1997) "Protecting groundwater from nutrients and pesticides - best management practice for Maine agricultural procedures", Available:
http://hermes.ecn.purdue.edu/gopher_dir/The%20Purdue%20Cooperative%20Extension%20Gopher%20Information%20Server/Wais/wais-index/wq_pub/BEST%20MANAGEMENT%20PRACTICES%20FOR%20MAINE%20AGRICULTURAL%20PRODUCERS
- U.S. EPA. (1984). "Health and environmental effects profile for mancozeb.", Report No.: EPA/600/X-84/129.
- U.S. EPA.(1987) "Pesticide fact sheet number 125: Mancozeb", Washington, DC.
- Vonk, J. W. and A.S. Kaars (1976) "Formation of ethylenethiourea from 5,6-dihydro-3H-imidazo-[2,1-c]-1,2,4-dithiazole-3-thione by microorganisms and reducing agents", *J. Environ. Sci. Health*, 11, 33.
- Wauchope, R. D., T. M. Buttler, A.G., H., P. W. M. Augustjin-Beckers, and J. P. Burt. (1992) "SCS/ARS/CES pesticide properties database for environmental decision making." *Rev. Environ. Contam. Toxicol.*, 123, 1-155.
- World Health Organization (1988) *Dithiocarbamate pesticides, ethylenethiourea, and proplenthiourea: a general introduction*, United Nations Environment program, the International Labor Organization, and the World Health Organization, Geneva.

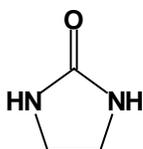
DEGRADATION PATHWAY OF MANCOZEB



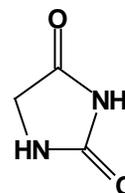
Chemical Structures



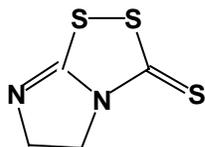
Ethylenethiourea (ETU)



Ethyleneurea (EU)



Hydantoin



Ethylene bisisothiocyanate sulfide (EBIS)