

Environmental Fate of Maneb

Elizabeth Downing
Environmental Monitoring and Pest Management
Department of Pesticide Regulation
830 K Street
Sacramento, CA 95814-3510

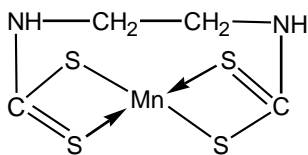
Summary

The fungicide maneb is moderately soluble in water and undergoes hydrolysis. Its main products for hydrolysis and photolysis are EU, ETU, EBIS, and glycine. Microbial degradation of maneb represents a minor breakdown route. Aquatic metabolism yields the main products EBIS, ETU, and EU. A field dissipation study showed that maneb persisted in soil for one week when applied at 100 ppm. Maneb is adsorbed strongly to most soils and is only slightly mobile. There is negligible mobility of maneb in the air since its vapor pressure is very low. Maneb is translocated primarily in the xylem of plants yielding the major metabolite ETU. There has been no evidence of maneb entering groundwater. Maneb is not seen as a likely contaminant of surface water and has not been monitored.

Physical and Chemical Properties

1. Common Name: Maneb
2. Chemical name: manganous ethylenebis[dithiocarbamate] (Merck, 1996)
3. Trade Names: Dithane M-22, Manzate, Chem Nab, Chlorable M, Kypman 80, Maneb 80, Maneba, Manam, Manebgan, Manesan, Polyram M, Rhodianebe, Sopranebe, Sup 'R Flo, Tremangol, Tubothane, Vancide (EPA, 1984)
4. CAS Registry No: 12427-38-2 (EPA, 1984)

5. Structural Formula (EPA, 1984):



6. Empirical Formula: C₄H₆MnN₂S₄ (EPA, 1984)

7. Molecular Weight: 265.3 (EPA, 1984)

8. Density: 1.92 (BCPC, 1977)

9. Solubility: water: 216 – 230 ppm (Rohm & Haas, 1983)

methanol: 0.133 g/L (Bio Dynamics, 1985)

dichloromethane: 0.0137 g/L (Bio Dynamics, 1985)

hexane: 0.0033 g/L (Bio Dynamics, 1985)

toluene: <0.0010 g/L (Bio Dynamics, 1985)

10. Vapor Pressure: < 1 x 10⁻⁷ torr (Bio Dynamics, 1985)

11. Octanol/Water Partition: 1.8 +/- 0.1 (Rohm & Haas, 1982)

12. Henry's Law Constant: < 156 atm·m³(g·mol)⁻¹ (Rohm & Haas, 1986)

13. Dissociation Constant, K: 2.71 x 10⁻⁷ at 25°C (Elf Atochem, 1995)

14. pH: 8.90 at 20°C (Elf Atochem, 1995).

Environmental Fate

Hydrolysis

Maneb undergoes hydrolysis to yield ethyleneurea (EU) as its main decomposition product. Ethylenethiourea (ETU) is also observed as a degradation product at pH levels of 5, 7, and 9. Ethylenebis(isothiocyanate) sulfide (EBIS) is detected in solution at pH 3, 5, and 7. At pH 9, EBIS is degraded within 3 days of hydrolysis. At pH 3, glycine and two unidentified fractions are also formed (Fraunhofer 1987a).

Photolysis

Soil:

The photolysis of maneb in soil was tested using loamy sand with the water content at 37.78% of maximum water capacity. Ethyleneurea (EU), ethylenethiourea (ETU), ethylenbis(isothiocyanate)sulfide (EBIS), carbimid, and six unidentified fractions were detected in the methanolic and aqueous fractions. There were both ultraviolet irradiated and non-irradiated samples. There were no significant differences between these samples with respect to degradation products, product pattern, or kinetics of their formation and degradation (Fraunhofer 1987b).

Water:

To determine the photolysis of maneb in water, both ultraviolet irradiated and non-irradiated samples were tested. EU, ETU, EBIS, and glycine were formed in both types of samples. EU is the main decomposition product of photolysis. The time when approximately half of the undissolved starting material is dissolved is 10.5 hours for the irradiated sample and 23.5 hours for the non-irradiated sample (Fraunhofer 1987c).

Soil Metabolism

It was found that after 32 days of aerobic incubation in loamy sand, 15.9% of applied radioactivity is mineralized and detected as $^{14}\text{CO}_2$. For a sandy loam soil with a 30-day incubation, 22.82% of radioactive $^{14}\text{CO}_2$ was recovered. The biodegradation of maneb in soil yields EU, ETU, carbimid, EBIS, and six unidentified fractions as its products (Fraunhofer 1987d).

The anaerobic biodegradation of maneb in soil was tested with loamy sand. After 31 days of incubation, 5.5% of applied radioactivity was mineralized and detected as $^{14}\text{CO}_2$. The degradation products of maneb are EU, ETU, carbimid, EBIS, and four unidentified fractions. The times of the first doubling in quantity of the products were determined. The unidentified fraction named as

“Number 2” was doubled in 1.25 days, while ETU was doubled in 2.5 days. The other products did not show significant change in quantity during the experiment (Fraunhofer 1987e).

Hylin (1973) studied the oxidative degradation of maneb in soil by mixing 20 mg of maneb with 100 g of soil at pH 7. Moist air was passed through the mixture and the amount of carbon disulfide (CS₂) was measured. 5 μmoles of CS₂ evolved after 10 hours. In an aqueous suspension, 25 μmoles of gas evolved after 7 hours at the same pH. The oxidation of maneb in soil is slower than in aqueous suspensions, but still represents a route of degradation of maneb in soil.

Microbial degradation is thought to represent a minor route in the breakdown of maneb. This is because maneb is hydrolytically decomposed by moisture present in soils (Sanborn et al., 1977). It has been shown that the denitrifying activity in soil was inhibited by maneb. At a concentration of maneb at 25 ppm, approximately 80% of the nitrate was recovered as nitrite (Bollag and Henninger, 1976).

Aquatic Metabolism

Anaerobic aquatic incubation leads to the rapid degradation of maneb. The maneb was fortified at 10 ppm. The major products formed were EBIS, ETU, and EU. EBIS disappears rapidly with a half-life of less than one day. ETU has a half-life of 149 days, while concentration of EU remained fairly constant. A minor unidentified product was also observed. Approximately 2.2% of the total dose applied were degraded to volatile organic compounds and/or CO₂. Mean recoveries of maneb metabolites in the water were 95.1% at Day 0 and 109.2% at Day 275. Sediment-bound residues increased slowly, 34.3% at Day 0 and 69.4% at Day 275 (Hazelton 1986).

Field Dissipation

The dissipation of maneb has been studied in several experiments with varying results. Nash and Beall (1980) applied maneb to tomato plants growing

on Galestown sandy loam (pH 6.7, organic matter content 5.2%). This took place in microagroecosystem chambers. The half-life of maneb was 36 days.

A field study was done with ^{14}C -maneb on Keyport silty loam. The chemical was applied at a rate of 2 lb/acre to 4-inch diameter soil sections. The half-life was 4 to 8 weeks. The total rainfall during this time was 1 to 11 inches (Rhodes 1977).

Chinn (1973) measured the persistence of maneb in soil using several species of fungi as bioassay. Maneb was applied at 100 ppm (based on dry weight of the soil) and it was found that fungicidal activity persisted for 1 week. When maneb was applied at 1000 ppm, fungicidal activity persisted for 11 weeks.

Soil Adsorption

Maneb is adsorbed readily from aqueous solutions onto Crosby silt loam, Stonelick sandy loam, Pullman clay loam, and moderately onto Knott loamy sand. Desorption of maneb is limited after it is adsorbed. Maneb's adsorptive and desorptive properties are consistent with its highly polar nature. There was no significant trend in partition coefficient versus soil pH (Batelle 1990).

Helling et al. (1974) measured maneb's soil adsorptive properties using thin layer chromatography (TLC) plates. One μg of maneb was applied to TLC plates with various soil types. This experiment showed that the higher the organic content the lower the R_f value for maneb. The R_f values for the five soil types are given below with the organic matter content given in the parentheses: 0.42 on Norfolk sandy loam (0.14%); 0 on Lakeland sandy loam (0.90%); 0.22 on Hagerstown silty clay loam (2.5%); 0.14 on Barnes clay loam (6.9%) and 0 on Celeryville muck (90.4%). This study indicates that maneb is adsorbed strongly to most soils (Helling et al., 1974).

Mobility

Soil:

Nash and Beall (1980) studied the mobility of maneb in soil in a micro-agroecosystem chamber. Maneb was applied to tomato plants growing in Galestown sandy loam. The pH was 6.7 with organic matter content of 5.2%. The maneb (detected as ethylenediamine) did not penetrate below 1 cm of depth. The concentration found in the leachate water was only 1.2 µg/L.

Rhodes (1977) conducted a field study with ¹⁴C-maneb to determine its soil mobility. The ¹⁴C-maneb was applied at a rate of 2 lb/acre to 4-inch diameter soil sections. Keyport silty loam was the soil type used. Residues of the fungicide leached to about a 5-inch soil depth after 52 weeks. The total rainfall for this time period was 51 inches; 26.5% of the radioactivity was still present in the top 1 inch of soil.

Helling et al. (1974) conducted a study on maneb's mobility on TLC plates with several different types of soils. The results indicated that maneb is adsorbed strongly to the soil (Helling et al., 1974).

These studies suggest that maneb and/or its degradation products are slightly mobile in the soil.

Water:

Maneb is moderately soluble in water. Hydrolysis, oxygen and light readily degrade the chemical. Because of these processes, microbial degradation in the aquatic environment is hard to measure. Maneb is not likely to volatilize from water since its vapor pressure is so low (EPA 1984).

Air:

Maneb has a negligible vapor pressure; therefore, it is not likely to volatilize into the air in any significant amounts. A likely way of entry into the atmosphere will be by spray drift during application. Also, maneb could be sorbed onto soil particles that could be carried in the wind. The degradation of maneb in the air depends on moisture content, temperature, photodegradation,

and oxidation. The half-life of maneb in air is 7 to 14 days (Nash and Beall, 1980).

Plant Metabolism

The major metabolite of maneb in plants is ethylenethiourea (ETU). Hoagland and Frear (1976) study the fate of ETU in plants, young seedlings and excised leaves of corn, lettuce, pepper, and tomato were pulse-treated with [4,5-¹⁴C]ETU. The labeled ETU was readily absorbed and was translocated primarily via the xylem. After 20 days, only 1 to 2 % of the initial dose remained as [¹⁴C]ETU, but several degradation and/or metabolic products were found. Methanol-soluble and insoluble degradation products were determined in the various tissue sections for a period of 20 days after treatment. Only minor amounts of ¹⁴CO₂ were found in treated plants of excised leaves. A major degradation product was obtained from pepper plants and was identified as ethylene urea (EU), which is the oxygen analog of ETU. This study concluded that these plants could readily degrade ETU once it is absorbed and translocated in the plant.

Groundwater Monitoring

According to the Department of Pesticide Regulation's Well Inventory Database (WIDB) (DPR 1998) there has not been any evidence of maneb in the groundwater. Maneb has been sampled for in 369 wells; there was no detection of maneb residues in any of these samples. The WIDB includes data from other state and federal agencies.

Surface Water Monitoring

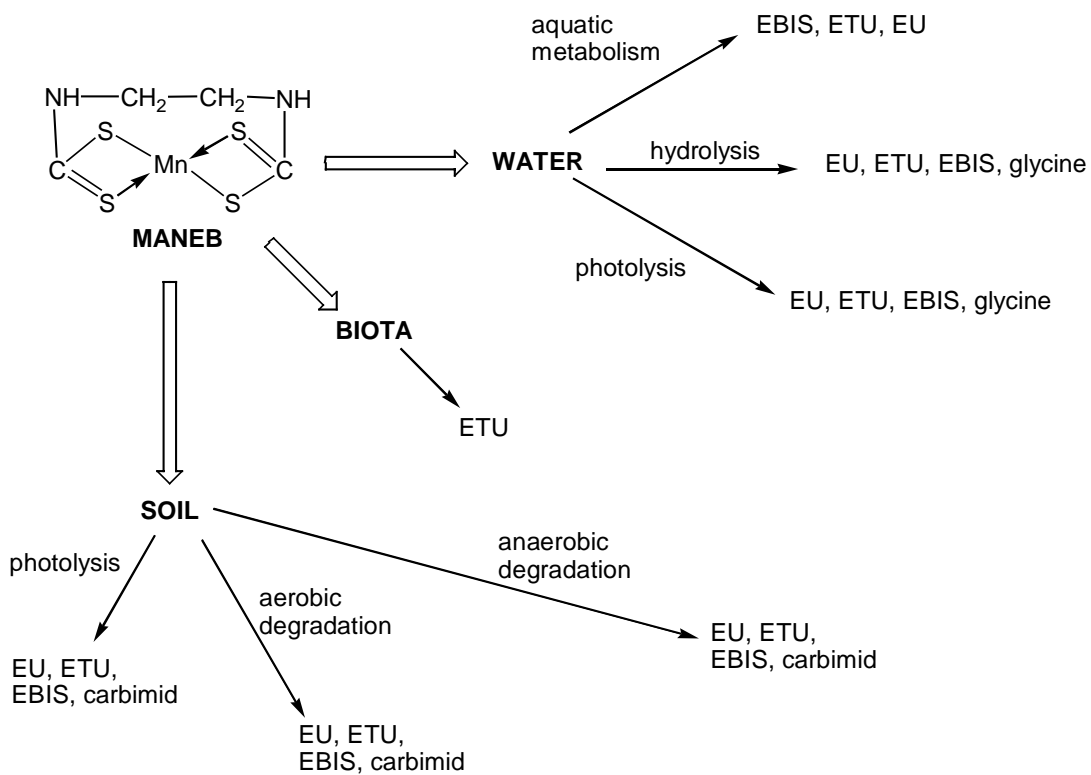
The Department of Pesticide Regulation also has a surface water database similar to the WIDB. Maneb has not been sampled for in surface water. Since maneb adsorbs to organic matter and break down relatively fast, it is not seen as a likely contaminant in surface water (DPR 1998).

References

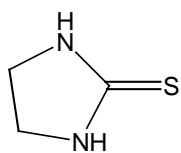
- Batelle Laboratories 1990. Adsorption/Desorption Of Manganese 14C-(1,2) Ethylene Bisdithiocarbamate On Soils By The Batch Equilibrium Method. *CDPR Volume Number: 110-050. #91054*
- BCPC (British Crop Protection Council) 1977. Pesticide Manual, 5th ed., Martin, H. and C.R. Worthing, Ed. p. 329.
- Bio Dynamics Inc. 1985. Solubility Of Maneb In Polar and Non-Polar Solvents. *CDPR Volume Number: 110-037. #54807*
- Bollag, J.M. and N.M. Henninger 1976. Influence of Pesticides on Denitrification in Soil and with an Isolated Bacterium. *J. Environ. Qual.* Vol. 5, no. 1, pp. 15-18.
- Chinn, S.H. 1973. Effect of eight fungicides on microbial activities in soil as measured by a bioassay method. *Can. J. of Microbiology.* Vol. 19, pp. 771-777.
- DPR 1998. Sampling for Pesticide Residues in California Well Water. Report No. EH98-04.
- Elf Atochem North America, Inc. 1995. Maneb 75DF-Physical and Chemical Characteristics. *CDPR Volume Number: 110-102. #139615*
- EPA (U.S. Environmental Protection Agency) 1984. Health and Environmental Effects Profile for Maneb. *NTIS #PB88-118930.* pp. 1-7.
- Fraunhofer Institut Schmallingenberg 1987a. Hydrolysis Of The EBDC-Fungicide Maneb. *CDPR Volume Number: 110-039. #63342*
- Fraunhofer Institut Schmallingenberg 1987b. Soil Photolysis Of The EBDC-Fungicide Maneb. *CDPR Volume Number: 110-039. #63343*
- Fraunhofer Institut Schmallingenberg 1987c. Water Photolysis Of The EBDC-Fungicide Maneb. *CDPR Volume Number: 110-039. #63344*
- Fraunhofer Institut Schmallingenberg 1987d. Aerobic Biodegradation In Soil Of The EBDC-Fungicide Maneb. *CDPR Volume Number: 110-039. #63345*
- Fraunhofer Institut Schmallingenberg 1987e. Anaerobic Biodegradation Of The EBDC-Fungicide Maneb. *CDPR Volume Number: 110-039. #63346.*

- Hazleton Laboratories America Inc 1986. Anaerobic Aquatic Metabolism of Maneb. *CDPR Volume Number: 110-049. #90216.*
- Helling, C.S., D.D. Gayle, D.D. Kaufman 1974. Fungicide movement in soils. *Phytopathology*. Vol. 64 (8), pp. 1091-1100.
- Hoagland, R.E. and D.S. Frear 1976. Behavior and Fate of Ethylenethiourea in Plants. *J. Agric. Food Chem.* 1976. Vol. 24, No. 1, pp. 129-133. *CDPR Volume Number: 110-022. #20210*
- Hyllin, J.W. 1973. Oxidative decomposition of ethylene-bis-dithiocarbamates. *Bulletin Environ. Contam. Toxicol.* Vol. 10(4), pp. 227-233.
- Merck Index: An Encyclopedia of Chemicals, Drugs, Biologicals. 1996. 12th Edition. Budavari, Ed. Merck & Co., Inc..pg. 976.
- Nash R.G. and M.L. Beall Jr. 1980. Fate of maneb and zineb fungicides in microagroecosystem chambers. *J. Agric. Food Chem.* Vol. 28 (2), pp. 322-330.
- Rhodes, R.C. 1977. Studies with manganese (14C)ethylenebis(dithiocarbamate) ([14C]maneb) fungicide and (14C)ethylenethiourea ([14C]ETU) in plants, soil, and water. *J. Agric. Food Chem.* Vol. 25 (3), pp. 528-533.
- Rohm and Haas Co. 1983. Water Solubility Of Maneb As Measured By UV Absorption. *CDPR Volume Number: 110-037. #54199*
- Rohm and Haas Co. 1982. Octanol/Water Partition Coefficients Of Dithane M-45, M-22, Z-78 and Ethylenethiourea. *CDPR Volume Number: 110-037. #54808.*
- Rohm and Haas Co. 1986. Maneb: Estimation of Henry's Law Constant for California. *CDPR Volume Number: 110-037. #54855.*
- Sanborn, J.R., Francis, B.M., and Metcalf, R.L. 1977. The degradation of selected pesticides in soil. *EPA 600/9-77-022.* pp. 573-582.

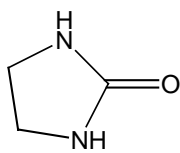
Degradation Pathway of Maneb



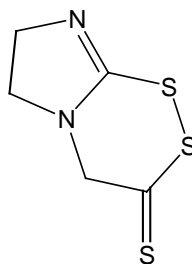
Chemical Structures:



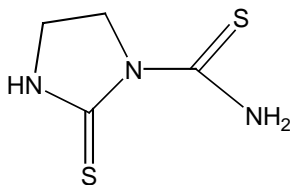
ethylenethiourea (ETU)



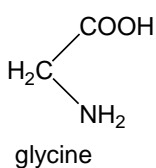
ethyleneurea (EU)



ethylenebis(isothiocyanate)sulfide (EBIS)

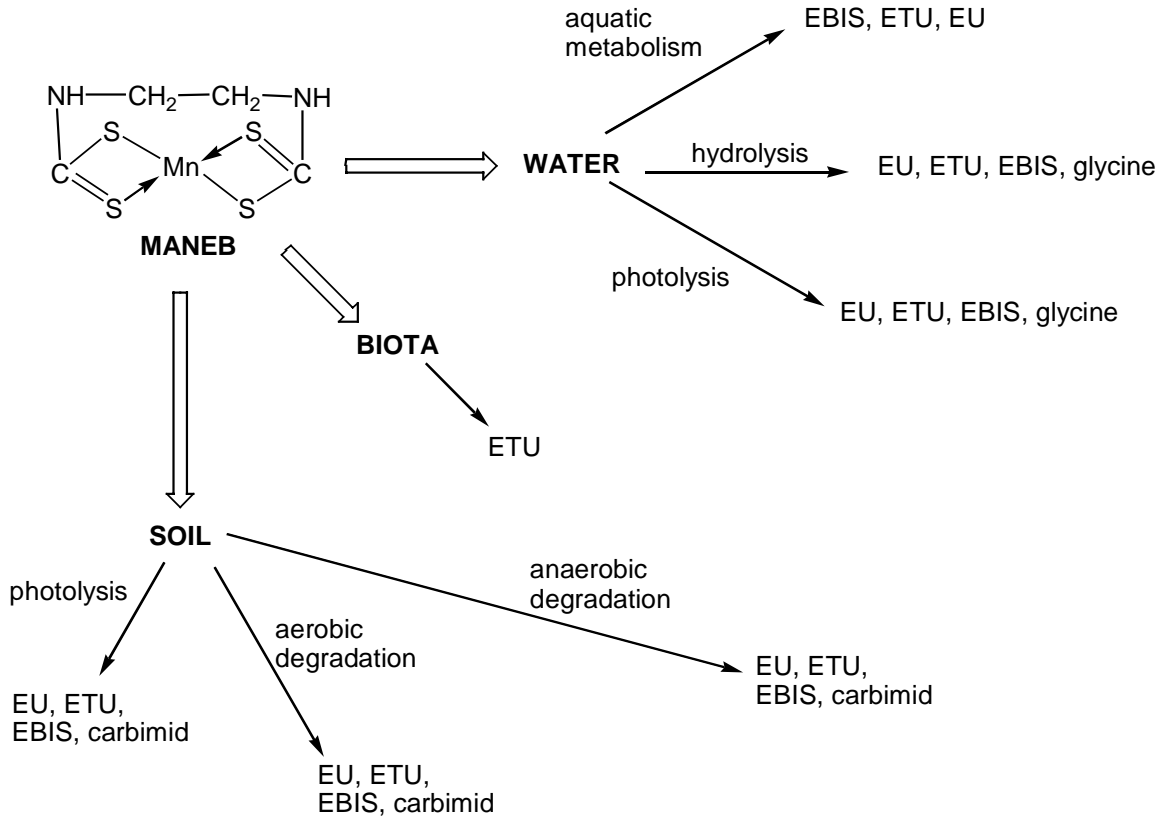


carbimid

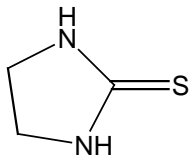


glycine

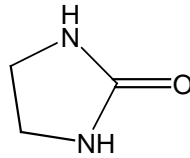
Degradation Pathway of Maneb



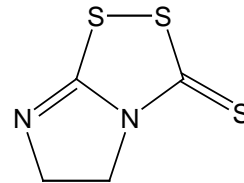
Chemical Structures:



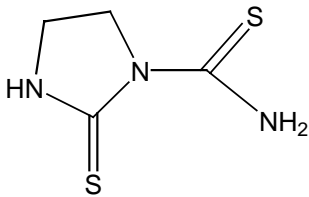
ethylenethiourea (ETU)



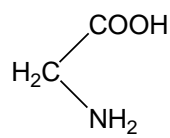
ehyleneurea (EU)



ethylenebis(isothiocyanate)sulfide (EBIS)



carbimid



glycine