

ENVIRONMENTAL FATE OF ETHYLENETHIOUREA

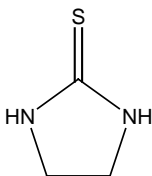
Sue Xu
Environmental Monitoring & Pest Management
Department of Pesticide Regulation
830 K Street
Sacramento, CA 95814-3510

Ethylenethiourea (ETU) is a major degradation product of widely used ethylenebisdithiocarbamate (EBDC) fungicides. In water, ETU is relatively stable to hydrolysis but can be rapidly photolyzed in the presence of photosensitizers, which are present in many natural waters. The photolysis half-lives of ETU in natural water are reported as 1 to 4 days. The identified degradates are glycine sulfate, Jaffe's base, ethyleneurea (EU) and hydantoin. In soil, ETU is chemically and biologically degraded to EU with half-lives of 1 to 7 days under field conditions. Under aerobic conditions, ETU and EU can be further mineralized to CO₂. ETU is fairly mobile in general wet soil due to its weak soil adsorption and high solubility. The field dissipation half-life of ETU is less than 1 week due to the rapid microbial degradation. If released to air, ETU can easily be removed by rain or through reacting with hydroxyl radicals. The half-lives of ETU in air are 8-9 days.

A. PHYSICAL AND CHEMICAL PROPERTIES

1. Common Name: Ethylenethiourea
2. Chemical Name: 2-Imidazolidinethione
Imidazoline-2-thiol
3. Trade Names: NA-22[®], NA-22-D[®], Pennac CRA[®], Robac-22[®],
Rodanin S- 62[®], Sancellor-22[®], Soxinol-22[®], Occeler-22[®]
4. CAS Registry No.: 96-45-7

5. Structural Formula:



6. Empirical Formula: $C_3H_6N_2S$
7. Molecular Weight: 102.2
8. Melting Point: $203-204^{\circ}C$
9. Solubility: Water (Merck Index, 1996)
 20,000 ppm at $30^{\circ}C$
 90,000 ppm at $60^{\circ}C$
 440, 000 ppm at $90^{\circ}C$
Organic Solvents at $18^{\circ}C$ (H&S, 1999)
 DMSO: $\geq 100,000$ ppm
 95% Ethanol: 1,000 – 5,000 ppm
 Dimethylformamide: 5,000 – 10,000 ppm
10. Vapor pressure: < 1 mm Hg at $20^{\circ}C$ (H&S, 1999)
11. Octanol/water partition coefficient: $\log P_{ow} = -0.66$ (Vershueren, 1996)

B. ENVIRONMENTAL FATE

Hydrolysis

Ethylenethiourea (ETU) is very stable to hydrolytic reactions (IUPAC, 1977). The concentration of 1 ppm ETU solution remained constant after 48 hours (Lyman and Lacoste, 1974). Crucickshank and Jarrow (1973) also reported that ETU was persistent to hydrolysis over the pH ranges of 5-9 at room temperature or at $90^{\circ}C$ for 90 days, as evidenced that the concentration of initial 1% ETU solution did not change during the study period.

Photolysis

Aqueous photolysis is considered a major degradation pathway for ETU (IUPAC, 1977; USEPA, 1988). Ross and Crosby (1973) reported that 0.64 ppm ETU degraded extremely slowly in deionized water in the absence of photosensitizers. However, after mixing with a photosensitizer (acetone), 95% of the initial dose (0.64 ppm) was degraded after 4 days under a laboratory photoreactor. ETU, with concentrations ranging from 10 to 25 ppm, was also exposed to sunlight with a photosensitizer (riboflavin); less than 5% of initial ETU was detected after 4 days. Ethyleneurea (EU) and glycine sulfate were identified as decomposition products.

In another experiment, 100 ppm ^{14}C -ETU was exposed to UV light (Rhode, 1977). Over 90% of ETU was decomposed after 6 hours and 3 hours in distilled and acetonesensitized water, respectively. ETU was probably oxidized to ethyleneurea by photochemically produced hydroxyl radicals. The identified degradates were glycine sulfate, 3-(2-imidazolin-2-yl)-2-imidazolidinethione (Jaffe's base), ethyleneurea and hydantoin.

ETU, adsorbed on silica gel at 100 ug/cm^2 , was also exposed to UV light ($300 \text{ }\mu\text{W/cm}^2$) with and without the photosensitizers (Crucickshank and Jarrow, 1973). The loss of ETU was approximately 40% after 96 hours in the absence of a sensitizer, and over 65% after 8 hours in the presence of a photosensitizer. At 1 ug/cm^2 , 97% of photosensitized ETU was decomposed after 20 hours when a more powerful sunlamp (3300 uW/cm^2) was used.

Photosensitizers are presumed to be present in natural water as evidenced by the quick disappearance of ETU in agricultural water (Ross and Cosby, 1973; Crucickshank and Jarrow, 1973). In an investigation, ETU was applied to water in field ditches, only 50% of initial dose was left after 1 day, 25% left after 7 days, and none was detected after 21 days (Blazquez, 1973).

Soil Metabolism

ETU is readily degraded in soil (Sittig, 1985). According to some researchers, ETU can be chemically and biologically decomposed to EU with half-lives of 1 to 7 days

under field conditions (Kaufman and Fletcher, 1973; Miles and Doerge, 1991; Nash and Beall, 1980; Rhodes, 1977; R&H company, 1987a&b). According to Kaufman and Fletcher (1973), 2, 20, and 200 ppm ETU were totally degraded and mainly converted to EU within 2, 2 and 8 days in silty clay loam, respectively.

ETU and EU can be microbiologically mineralized to CO₂ in nonsterile soils (Johannesen *et al.*, 1996; Miles and Doerge, 1991; Jacobsen and Bossi, 1997). The half-life of mineralization for 10-ppm ETU was around 22 days (Lyman and Lacoste, 1974). The metabolites of ETU in soils were EU, hydantoin, Jaffe's base, ethylenediamine (EDA), CO₂ and other unknown compounds.

Soil Adsorption

A batch soil adsorption/desorption study on ¹⁴C-ETU was conducted on four soils: a Georgia sand (OM 0.9%, pH 5.7), a Georgia sandy loam (OM 2.8%, pH 5.9), a Pennsylvania silt loam (OM 3.5%, pH 6.4) and a Mississippi clay loam (OM 2.5%, pH 7.4) (R&H Company, 1987c). Slight conversion of ETU to EU was reported during the study period. The 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. Their organic adsorption coefficient values (K_{oc}) were 142, 112, 57 and 34, accordingly.

The adsorption of ETU was also examined on three additional soil types: a Jaucus soil (OM <1%, pH 6.2), a Wahiawa soil (OM 1.5%, pH 6.2) and a Kaiwiki soil (OM 6.2%, pH 6.0) (Miles and Doerge, 1991). The sorption coefficient values (K_d) were 0.03, 0.09 and 0.12 for Jaucus, Wahiawa and Kaiwiki soils, respectively. The adsorption coefficient data for ETU indicated that ETU was weakly adsorbed to soils.

Soil Mobility and Dissipation

ETU is fairly leachable in wet soil due to its weak soil adsorption and high solubility in water (Lyman *et al.*, 1982; Ney, 1982), but is immobilized by dry soil (Nash and Beall, 1980; Helling, 1971; Helling and Thompson, 1974). The soil leaching of ETU was examined on five soils and a soil thin-layer chromatographic technique was utilized to obtain R_f values of soils (Helling and Thompson, 1974). The R_f values were 0.96 for a

Norfolk sandy loam (OM 0.14%, Moisture capacity 6.5%), 1.00 for a Lakeland sandy loam (OM 0.90%, Moisture capacity 8.5%), 0.96 for a silty clay loam (OM 2.5%, Moisture capacity 25.8%), 0.83 for a clay loam (OM 6.9%, Moisture capacity 28.5%) and 0.61 for a Celeryville muck (OM 90.4%, Moisture capacity 113%). R_f values showed that ETU is fairly leachable in general wet soil unless the soil contained high organic matter such as Celeryville muck (Helling and Thompson, 1974; Ney, 1995).

The dissipation of ^{14}C -ETU was examined on a silt loam soil from Delaware (Rhodes, 1977). Soils in five cylinders (12 inch tall and 4 inch diameter) were applied with 1 mL of ^{14}C -ETU at 1.82 mg/L. The soils were checked for ^{14}C in soil layers of 0-1", 1-3", 3-5", 5-8" and 8-12" at 0, 1, 4, 12 and 52 weeks. The total rainfalls were 0, 0.54, 3.34, 14.26 and 53.76 inches for 0, 1, 4, 12 and 52 weeks, respectively. Results showed that predominant recovered radioactivity (> 85%) was contained in the first top inch. After 52 weeks, 16% of originally applied radioactivity was detected in the top 1 inch, 4% in 1-3 inches, 1% in 3-5 inches, 0.5% in 5-8 inches and 0.1% in the layer of 8-12 inches. The estimated half-life of ETU was reported as less than one week.

In another experiment, Calumpang et al. (1993) reported an application of 1.59-ppm ETU on a loam soil (OM 2.73%, pH 6.87). Total rainfall during the investigation was 31.1 mm. ETU was only found in the top 3.2 inches of soil after 21 days. This result was similar to the data provided by Newsome et al. (1975) that ETU, generated from maneb, leached to a maximum of 2.5 inches 15 days after the application.

Volatilization

Nash and Beall (1980) had utilized microagroecosystem chambers (150 x 115 x 50 cm³) to study the volatility of ETU in the atmosphere. The tomato plants in sandy loam (OM 5.2%, pH 6.7) were sprayed with maneb and zineb at 2 kg active ingredient/ha. ETU in the chambers was collected by polyurethane foam filter and then was evaluated. The concentration of ETU in the air was about 0.9 ng/m³ 1 day after the application but decreased to about 0.0025 ng/m³ after 60 days. ETU comprised approximately 10% of total volatile chemicals in the chambers. The half-lives of ETU in the air were 8-9 days.

EPA (1988) suggested that the volatility of ETU was of little concern since ETU could easily be removed from the air by rain or through reacting with hydroxyl radicals.

Plant Metabolism

There have been numerous investigations on the transformation and degradation of ETU on and in crops (Hoagland and Frear, 1976; Kumar and Agarwar, 1992&1993; Newsome, 1976; Pease *et al.*, 1977; Rhode, 1977; Smith, *et al.*, 1988; Leidy, *et al.*, 1989). In an experiment, ETU was directly sprayed on the leaves or applied to the roots of lettuces (Smith *et al.*, 1988). Results showed that ETU on leaves was rapidly decomposed with an estimated half-life of 10 hours. ETU applied to roots was rapidly translocated to the leaves within 4 days and its subsequent degradation in leaves was rapid with levels undetectable after 20 days. The rapid degradation of ETU was partially attributed to photolysis. Possible metabolites were EU, CO₂ and other unknowns.

Rhode (1977) investigated the behaviors of ETU in tomatoes and beans by applying ¹⁴C-maneb and ¹⁴C-ETU to their foliage and stems. The application concentration for maneb was 2 lb/100 gal water; ETU was 0.2 lb/100 gal water. The concentrations of radioactivity and ETU decreased rapidly. After 7 days, the concentration of ETU was 0.03 ppm in tomatoes and bean; after 35 days, ETU was less than 0.01 ppm. In another study on tomatoes, 2 lbs/100 gal of ETU was sprayed on tomato and its concentration decreased to an undetectable level after 6 days (Blazquez, 1973). Kumar and Agarwar (1992 and 1993) examined the metabolism of ETU on eggplants. EU was found to be the major metabolites. The half-life of ETU on eggplants was estimated as 20 days. In summary, the degradation half-lives of ETU on crops varied from 10 hours to 20 days, greatly depending on the types of plants and the locations of ETU application.

Groundwater Monitoring

Ethylenethiourea is a potential groundwater contaminant based on its high water solubility (>20,000ppm) and low soil adsorption coefficient ($K_{oc} < 200 \text{ cm}^3/\text{g}$) (Ney, 1995; Linda, 1994). Of 80 wells sampled for ETU in California, only one sample was

detected at 0.725 ppb (CalEPA, 1999). However, follow-up sampling of this and proximate wells yielded no detection at a minimum detection level of 0.578 ppb (Spurlock, 2000).

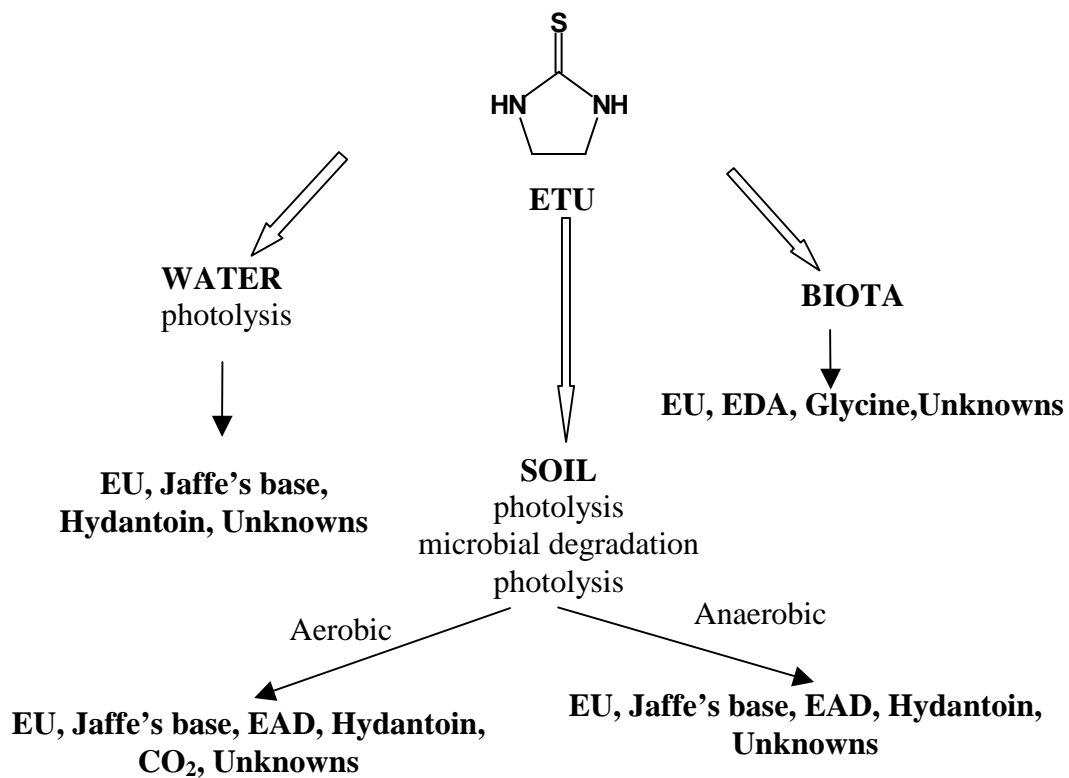
References

- Blazquez, C.H. (1973) "Residue determination of ethylenethiourea (2-Imidazolidinethione) from tomato foliage, soil and water", *J. Agric. Food Chem.*, 21(3), 330-332.
- California EPA. (1999) "Well inventory database", Department of Pesticide Regulation, Sacramento, CA. Available online.
- 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. Pest Management*, 39(2), 161-166.
- Cruickshank, P.A and H.C. Jarrow (1973) "Ethylenethiourea degradation", *J. Agric. Food Chem.*, 21(3), 333-335.
- Helling, C.S. (1971) "Pesticide mobility in soils III. influence of soil properties", *Soil. Sci. Soc. Amer. Proc.*, 35,734-748.
- Helling, C.S. and S.M. Thompson (1974) "Division S-3 - soil microbiology and biochemistry, azide and ethylenethiourea mobility in soils", *Soil. Sci. Soc. Amer. Proc.*, 38,80-85.
- Heller, S. R., and A. E. Herner (1990) "ARS pesticide properties database", USDA-ARS Systems Research Laboratory, Beltsville, MD.
- Hoagland, R.E and D.S. Frear (1974) "Behavior and fate of ethylenethiourea in plants", *J. Agric. Food Chem.*, 24, 129-133.
- H&S (Health and Safty Database) (1999) Ethylene Thiourea 96-45-7, available: http://ntp-server.niehs.nih.gov/cgi/iH_Indexes/Chem_H&S/iH_Chem_H&S_Frames.html
- IUPAC (International Union of Pure and Applied Chemistry) (1977) "Ethylenethiourea", *Pure & Appl. Chem.*, 49, 675-689.
- Jacobsen, O.S. and R.Bossi (1997) "Degradation of ethylenethiourea (ETU) in oxic and anoxic sandy aquifer", *FEMS Micro. Rev.*, 20, 539-544.

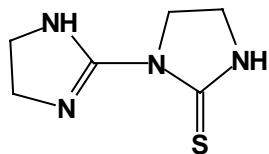
- Johannesen, H., A.B. Nielsen, A. Helweg and I.S. Fomsgaard (1996) "Degradation of [14C]ethylenethiourea in surface and subsurface soil", *The Science of the Total Environment*, 191, 271-276.
- Kaufman D.D. and C.L. Fletcher (1973) "Ethylenethiourea degradation in soil", in: Proceedings of the Second International Congress on Plant Pathology, Minneapolis, Minnesota, Abstract No. 1018.
- 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.
- Kumar, U. and H. C. Agarwal (1993) "Persistence, metabolism, and movement of ethylenethiourea in eggplants (*Solanum melongena* L.) under sub-tropical conditions." *Bull. Environ. Contam. Toxicol.*, 51, 46-53.
- Leidy, R.B., P.B. Shoemaker, T.J. Sheets and C.E. Main (1989) "EBDC and ETU residues in Burley tobacco treated with mancozeb", *Tobacco-International*, 191(11), 42-46.
- Lentza-Rizos, Ch. (1990) "Ethylenethiourea (ETU) in relation to use of ethylenebisdithiocarbamate (EBDC) fungicides", *Reviews of Environ. Contam. Toxi.*, 115,1-37.
- Linda, C.D. (1994) *Physico-Chemical Properties and Environmental Fate of Pesticides*. Department of Pesticide Regulation, Sacramento, CA.
- Lyman, W. R., and R. J. Lacoste (1974) "New developments in the chemistry and fate of ethylenebis(dithiocarbamate) fungicides." Proceedings of the 3rd International IUPAC Congress on Pesticide Chemistry, Helsinki, Stuttgart, George Thieme Publishers, 67-74.
- Lyman, W.J., W.F. Reehl and D.H. Rosenblatt (1982) *Handbook of Chemical Property Estimation Methods*, McGraw-Hill Book Company.
- Merck Index (1996) 12th ed., Whitehouse Station, New Jersey, Merck Co., Inc. 3839.
- Miles, C.J. and R. Doerge (1991) "Fate of ethylenethiourea in Hawaiian soil and water", *J. Agric. Food Chem.*, 39, 214-217.
- Nash, R.G. and M.L.Beall,Jr. (1980) Fate of maneb and zineb fungicides in microagroecosystem chambers", *J. Agric. Food Chem.*, 28, 332-330.
- Newsome W.H., J.B. Shields and D.C. Villeneuve (1975) "Residues of maneb ethylenethiourea monosulfide, ethylenethiourea and ethylenediamine on beans and tomatoes field treated with maneb", *J. Agric. Food Chem.*, 23(4), 756-758.

- Newsome, W.H. (1976) "Residues of four ethylenebis(dithiocarbamates) and their decomposition products on field-sprayed tomatoes", *J. Agric. Food Chem.*, 24(5), 999-1001.
- Ney, R.E., Jr. (1982) "Exposure assessment consideration and problems", Exposure Assessment Workshop, U.S. Environmental Protection Agency, Washington, D.C..
- Ney, R.E., Jr. (1995) *Fate and Transport of Organic Chemicals in the Environment, a practical guide*, 2nd ed., Government Institutes, Inc., Rochville, Maryland.
- Pease H.L. and R.F. Holt (1977) "Manganese ethylenebis(dithiocarbamate) (Maneb)/ethylenethiourea (ETU) residue studies on five crops treated with ethylenebis(dithiocarbamate) (EBDC) fungicides", *J. Agr. Food Chem.*, 25(3), 561-566.
- R&H Company. (1987a) "Soil Photolysis Study of Mancozeb", DPR Vol. 176-040 #53692, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987b) "Aerobic and anaerobic soil metabolism of mancozeb", DPR Vol. 176-042 #53694&53695, Department of Pesticide Regulation, Sacramento, CA.
- R&H Company. (1987c) "Batch soil adsorption/desorption of ethylenethiourea", DPR Vol.176-042 #53696, Department of Pesticide Regulation, Sacramento, CA.
- Rhodes, C.R. (1977) "Studies with manganese [¹⁴C]ethylenebis(dithiocarbamate) ([¹⁴C]mancozeb) fungicide and [¹⁴C]ethylenethiourea ([¹⁴C]ETU) in plants, soil and water", *J. Agric. Food Chem.*, 25(3), 528-533.
- Ross, R.D. and D.G. Crosby (1973) "Photolysis of ethylenethiourea", *J. Agric. Food Chem.*, 21(3), 335-337.
- Sittig., M.M. (1985) *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, 2nd ed., Park Ridge, NJ, Noyes Data Corporation.
- Smith, R.M., K.C. Madahar, W.G. Salt and N.A. Smart (1988) "Degradation of ethylenethiourea on lettuces", *Pestic. Sci.*, 23, 337-349.
- Spurlock, F. (2000) Personal Communication, Department of Pesticide Regulation, Sacramento, CA.
- U.S.EPA. (1988) *Health and environmental effects profile for ethylenethiourea*, Environmental Protection Agency, Cincinnati, OH, EPA/600/X-84/131.
- Vershueren, K. (1996) *Handbook of Environmental Data on Organic Chemicals*, 3rd ed., John Wiley and Sons, Inc.

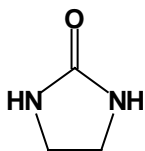
DEGRADATION PATHWAY OF ETHYLENETHIOUREA (ETU)



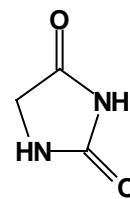
Chemical Structures



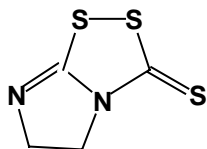
Jaffe's base



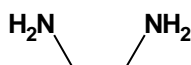
Ethyleneurea (EU)



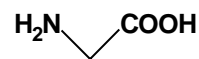
Hydantoin



Ethylene bisisothiocyanate sulfide (EBIS)



Ethylenediamine(EDA)



Glycine