From: Sabrina Cantrell [KDHE]
Sent: Monday, July 02, 2018 11:37 AM
To: Tony Stahl [KDHE] <Tony.Stahl@ks.gov>
Subject: Udall Fishkill

Tony,
These are the metals results from the Udall North Point Lake Fishkill. Could you take a look at these and let me know if you see anything unusual? We are still waiting for the pesticide results. Erika Bauer sent Leila an email this morning to check on them. Last week, they discussed that they should be done and Leila was going to track them down.
Thank you,

Sabrina R. Cantrell
Kansas Department of Health and Environment
South Central District Office
RH Garvey Building
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Please note my new email address: sabrina.cantrell@ks.gov

E X T O X N E T

Extension Toxicology Network

A Pesticide Information Project of Cooperative Extension Offices of Cornell University, Michigan State University, Oregon State University, and University of California at Davis. Major support and funding was provided by the USDA/Extension Service/National Agricultural Pesticide Impact Assessment Program.

Pesticide
Information
Profile

Maneb

Publication Date: 9/93

TRADE OR OTHER NAMES

Some trade names include Dithane M-22, Manesan, Manex, Manzate, Nereb, Newspor. A chemical name for maneb is manganese ethylene bisdithiocarbamate (26).

REGULATORY STATUS

Maneb is registered as a general use pesticide by the U.S. Environmental Protection Agency (EPA). In July 1987, the Environmental Protection Agency announced the initiation of a special review of the ethylene bisdithiocarbamates (EBDCs), a class of chemicals to which maneb belongs. This Special Review was initiated because of concerns raised by laboratory tests on rats and mice. The EPA was concerned about

a. potential effects on the general population from dietary exposure to residues left on food crops and
b. potential occupational health risks to workers who handle and/or apply EBDC pesticides.

As part of the Special Review, EPA reviewed data from market basket surveys and concluded that actual levels of EBDC residues on produce purchased by consumers are too low to affect human health. The EPA concluded its Special Review in April, 1992 with new label requirements for protective clothing to be worn by industrial and agricultural workers, and with the establishment of a 24-hour reentry period for agricultural workers. Many homegarden uses of EBDCs have been canceled because the EPA has assumed that home users of these pesticides do not wear protective clothing during application (31). Toxicity data reviewed by the EPA as part of their Special Review of EBDCs are included in this document under "Toxicological Effects."

Containers of maneb must bear the signal word "CAUTION" (1).

INTRODUCTION

The EBDCs are fungicides used to prevent crop damage in the field and to protect harvested crops from deterioration in storage or transport (26). Maneb is used in the control of early and

late blights on potatoes and tomatoes and many other diseases of fruits, vegetables and field crops and ornamentals (25). Maneb controls a wider range of diseases than any other fungicide (8). It is available as granular, wettable powder, flowable concentrate, and ready-to-use formulations (26).

Maneb is one of the chemicals of a class called the ethylene- bisdithiocarbamates ('EBDCs') that are noted for their instability in the environment. The application of heat can break these chemicals down into a number of metabolites. In addition to natural environmental processes that break down EBDCs, cooking of vegetables that are contaminated with these fungicides can also change them into different metabolites. Ethylenethiourea, an EBDC metabolite that is considered to be cancer-producing, is formed when maneb-treated vegetables are cooked (11, 26).

TOXICOLOGICAL EFFECTS

ACUTE TOXICITY

Maneb is moderately toxic to humans (29). Occasional signs of local irritation or inflammation of the skin, eyes, or respiratory tract have been experienced upon contact with maneb. Acute inhalation of large amounts of maneb dust or spray may cause irritation of the mucous membranes, resulting in a scratchy throat, sneezing, cough, and inflammation of the linings of the nose and upper respiratory tract. Signs of poisoning from large amounts of maneb may include nausea, vomiting, diarrhea, loss of appetite, weight loss, headache, confusion, drowsiness, coma, slowed reflexes, respiratory paralysis and death (5). Maneb is a mild eye and skin irritant (24, 29).

Maneb is of moderately low toxicity to laboratory animals (6). Single toxic doses of maneb in rats induced hypotonia, slowed breathing and heart beat, functional abnormalities of the thyroid and liver, infiltrations in the lungs, bronchitis and tracheitis (29). The amount of a chemical that is lethal to one-half (50%) of experimental animals fed the material is referred to as its acute oral lethal dose fifty, or LD50. The oral LD50 for maneb in rats is 3,000 to 7,990 mg/kg, in mice is 2,600 mg/kg, and in guinea pigs is 7,500 mg/kg. The dermal LD50 for rats is greater than 5,000 mg/kg (1, 9, 12).

There is no evidence of 'neurotoxicity,' nerve tissue destruction or behavior change, from the EBDCs (30). However, EBDCs are partially chemically broken down, or metabolized, to carbon disulfide, a neurotoxin capable of damaging nerve tissue (7). EBDC residues in or on foods convert readily to ETU during commercial processing or home cooking (26).

CHRONIC TOXICITY

Prolonged exposure to large concentrations of maneb spray or dust may cause dermatitis (13, 29).

Feeding maneb to rats at 250 mg/kg for two years caused no injurious health effects (9). After several months of daily doses of 200 mg/kg, experimental dogs developed signs of toxicity such as tremors, weakness, lack of energy, gastrointestinal disturbances, and incoordination (5).

Rats were fed daily doses of 0, 1.25, 12.5, 62.5 or 125 mg/kg of maneb. After 97 days, those given the 62.5 mg/kg dose showed significant increases in thyroid weight (i.e. goiter) and reduced growth rate. After one year, rats at the 62.5 mg/kg dose also exhibited increased thyroid weight. The NOEL for this study was 12.5 mg/kg/day (26).

Rats which received 1500 mg/kg/day for 10 days showed weight loss, weakness of the hind legs and increased mortality. Rats given 0.25% maneb in the diet for 2 years developed thyroid abnormalities and goiter. Other effects observed in studies of lab animals exposed to chronic doses of maneb include depression of reflexes, paralysis, impaired kidney function, and benign lung tumors (29).

Ethylene bisdithiocarbamate pesticides (EBDCs), which include maneb, are generally considered to have low short-term mammalian toxicity. A major toxicological concern, however, is ethylenethiourea (ETU), an industrial contaminant and a breakdown product of maneb and other EBDC pesticides. In addition to having the potential to cause goiter, a condition in which the thyroid gland is enlarged, this metabolite has produced birth defects and cancer in experimental animals. ETU has been classified as a probable human carcinogen by the EPA (31). ETU can be produced when EBDCs are used on stored produce, and also when fruit or vegetables with residues of these fungicides are cooked (24).

Conversion of EBDCs into ETU can occur inside of spray tanks, during cooking of produce or processing of crops bearing EBDC residues, or as EBDCs are metabolized within the body. Residues of the EBDCs and of ETU can readily be removed from produce by washing or peeling (11, 26).

Disulfiram is an EBDC which is used in the treatment of alcoholics to produce an intolerance to alcohol. Ingestion of disulfiram and alcohol together causes symptoms of nausea, vomiting, headache, excessive sweating and chills. Other EBDC compounds may cause similar symptoms when combined with alcohol (24).

Reproductive Effects

Maneb had a negative effect on the course of gestation in female rats that were given 50 mg/kg body weight every other day during this period. There were increased numbers of embryo deaths, stillborn offspring, and newborns incapable of survival (16). Rats given a single dose of 770 mg/kg of maneb, the lowest dose tested, on the 11th day of gestation exhibited adverse effects on reproductive fertility and development. These effects included early fetal deaths and fetal abnormalities of the eye, ear, body wall, central nervous system, and musculoskeletal system (13, 29). The lowest oral toxic dose in mice which caused fetotoxicity when given under the same conditions as previously mentioned, was 1420 mg/kg (12).

Teratogenic Effects

Maneb is metabolized to ethylenethiourea, ETU, a known teratogen. Rats given an oral dose of 2,000 to 4,000 mg/kg of ETU on days 11 or 13 of gestation showed a high incidence of skeletal malformations and defects in the closing of the neural tube, an embryonic tube that eventually forms the brain and spinal cord (14). A single dose of ETU produced teratogenic effects in rats and mice (6, 13).

In pregnant rats fed ETU at 5.0 mg/kg/day, the lowest dose tested, developmental toxicity was observed in the form of delayed hardening if the bones of the skull in offspring. ETU has also been shown to be teratogenic in hamsters, but not in mice (31).

Mutagenic Effects

Several tests have shown that maneb is not mutagenic (26). Maneb is metabolized to ethylenethiourea, a suspected mutagen (7).

Carcinogenic Effects

All of the EBDC pesticides can be degraded or metabolized into ETU, which has been classified as a probable human carcinogen by the EPA (26, 31). Marked increases in the incidence of liver tumors were observed in mice fed 646 ppm of ETU daily for 80 weeks. Rats fed 175 or 350 ppm daily for 18 months developed malignant thyroid tumors. In rats fed ETU at doses of 0.1, 1.25, 6.25, 12.5, or 25 mg/kg for nearly 2 years, a dose related increase in thyroid tumors was observed at the 12.5 or 25 mg/kg doses. Female mice fed doses of 17 or 50 mg/kg ETU for up to 2 years exhibited a 58 or 96% incidence of malignant liver tumors, respectively. In this same study, there was also a significant increase in the incidence of thyroid tumors at the 59 mg/kg dose level (13, 31).

Chronic administration of cumulative oral doses of 62,980 mg/kg of ETU to rats, intermittently for 94 weeks, caused tumors of the gastrointestinal tract, skin, and appendages. Oral administration of ETU produced malignant thyroid tumors in rats and increased the incidence of liver cell tumors in two strains of mice (10, 26). In another study, maneb did not display significant carcinogenicity in laboratory tests with experimental animals (6, 17). Malignant tumors were observed in one study in which rats were given scrotal injections of 12.5 mg/kg body weight of 82.6% pure maneb (16).

Organ Toxicity

Poisoning from maneb may adversely affect the thyroid, kidneys and heart (13). Dogs that received oral doses of 200 mg/kg/day for three or more months showed damage to the spinal cord but not the thyroid gland (10). Rats given 0.25% maneb in food for two years showed abnormalities and/or excessive growth of thyroid cells (16).

Several studies of the effects of EBDCs on test animals have shown rapid reduction in the uptake of iodine and swelling of the thyroid (i.e. goiter). In one study, a marked reduction of iodine uptake was measured 24-hours after administration of a large dose of maneb. A 90- day study of

the effects of ETU, a common metabolite of the EBDCs on rat thyroids revealed a NOEL of 5 ppm (0.25 mg/kg/day) (24, 26, 30).

Fate in Humans and Animals

Research results vary on the fate of maneb in humans and animals. While nearly fifty-five percent of an oral dose of a radioactive form of maneb (14-C) in rats was excreted in the form of metabolites in the urine and feces within three days, after 24 hours, body organs contained 1.2% of the original dose as metabolites. On the 5th day, less than 0.18% remained (16). In another study with rats fed radio-labeled maneb, 20 to 30% of the administered dose was excreted in the urine and feces within two hours after dosage. The major metabolite of maneb was ethylenethiourea (ETU). By the seventh day after dosage, 70% had been excreted and the remaining radioactivity was concentrated in the thyroid, kidneys and liver (26). In other studies, maneb was not found in the tissues of rats that were fed as much as 2,500 parts per million (ppm) for two years. There was also no evidence of maneb in tissues of dogs which received 75 mg/kg/day for one year (10).

The EBDC pesticides break down in mammalian tissues into ETU, a metabolite which has caused goiter and cancer in laboratory animals (9, 31).

ECOLOGICAL EFFECTS

Harmful Effects on Birds

Maneb is practically non-toxic to birds (26). The 5-day LC50 for maneb in bobwhite quail and mallard ducklings is greater than 10,000 ppm (4).

Effects on Aquatic Organisms

Maneb is highly toxic to fish. The lethal concentration fifty, or LC50, is that concentration of a chemical in air or water that kills half of the experimental animals exposed to it for a set time period. The 96-hour LC50 for maneb is 1 ppm in bluegill sunfish. Its 48-hour LC50 is 1.9 ppm in rainbow trout. Its 58-hour LC50 is 1.8 ppm in carp (4, 9, 26). Water can be contaminated by the inappropriate storage, use, or disposal of maneb (1).

Effects on Other Animals (Nontarget species)

Maneb-treated crop foliage must not be fed to livestock (15). The fungicide is not thought to be toxic to bees (9). Its 72-hour LC50 is more than 40 ppm in crayfish. In tadpoles, the 48-hour LC50 is 40 ppm (4).

ENVIRONMENTAL FATE

The ethylenebisdithiocarbamates (EBDCs), including maneb, are noted for their instability in the environment (21). They are generally unstable in the presence of moisture, oxygen, and in

biological systems (26). The EBDCs rapidly degrade to ETU. This rapid degradation lowers the need for concern about the environmental fate of EBDCs and focuses such concern on ETU. The EPA has either called for or is currently reviewing data on the behavior of ETU in the environment (9, 21, 26).

Breakdown of Chemical in Soil and Groundwater

Maneb is nearly insoluble in water (0.5 ug/ml). It adsorbs strongly to soil particles. Thus, despite its lengthy soil half life (60 days), maneb is not expected to contaminate groundwater. It may enter surface waters if erosion of soil with adsorbed maneb occurs (32). Maneb breaks down under both aerobic and anaerobic soil conditions (26).

Maneb's half-life in soil, or the time that it takes for half of the amount of the fungicide in soil to be broken down by natural processes , was found to be four to eight weeks. Metabolites were found in soil 15 days after treatment of beans and tomatoes (11). Residues of a traceable form of maneb did not leach below the five-inch soil depth (2).

ETU, a metabolite of maneb, has been detected at 16 ppb in only one out of 1,295 drinking water wells tested (31).

Breakdown of Chemical in Water

Maneb degraded completely within one hour under anaerobic aquatic conditions (26).

Breakdown of Chemical in Vegetation

The main metabolite of maneb in plants is ethylenethiourea (ETU); this is then rapidly metabolized further (9). Maneb residues were higher on beans than on tomatoes when they were measured at intervals up to 15 days after treatment. The heating of maneb residues in vegetables can result in the formation of the metabolic carcinogen, ETU. Significant amounts of ETU were found in cooked vegetables that had been experimentally treated with maneb (11). Some varieties of apple, morello cherry and pumpkin can be negatively affected by maneb (9). Young greenhouse tomato and tobacco seedlings have also been injured (15).

PHYSICAL PROPERTIES AND GUIDELINES

Maneb is a yellow powder with a faint odor. Maneb is a flammable, combustible material which may decompose, heat up, or self-ignite if it is exposed to air or moisture. Fire may produce irritating or poisonous gases such as toxic oxides of nitrogen and sulfur. Runoff from fire control or dilution may cause pollution. Maneb should be kept away from flames and sparks (9, 18, 29).

Maneb must be stored in sealed original containers in well- ventilated places. The fungicide must not be allowed to become wet during storage (15). Its temperature should not exceed 25-30 degrees C. Water, feed, or food can be contaminated by inappropriate storage or disposal of maneb. Containers must be stacked in a way that permits free flow around piles (1). While

maneb is stable under normal storage conditions, it decomposes more or less rapidly when it is exposed to moisture or acidic conditions.

Long-term skin, eye, and respiratory tract exposure to small quantities of maneb should be avoided (9). Protective equipment should be worn by workers involved in the manufacture or agricultural application of maneb; those who spray crops should wear eye protection and respirators (16). Empty containers should not be reused; they should be buried in a safe place far from water supplies. Open dumping is prohibited (1).

Occupational Exposure Limits:

OSHA ceiling:	5 mg/m3
ACGIH TWA:	1 mg/m3: NIOSH recommended TWA
NIOSH recommended STEL:	3 mg/m3 (29)

Physical Properties:

CAS #:	12427-38-2
H20 solubility:	nearly insoluble in water: 0.5 ug/ml (29)
Solubility in other solvents:	soluble in chloroform and pyridine (13, 22, 29)
Melting point:	Decomposes before melting (pure compound) (23, 29)
Vapor pressure:	negligible, less than 10 to the minus 7 power mbar at 20 degrees C (9)
Chemical Class/Use:	carbamate; ethylenebisdithiocarbamate
ADI:	0-0.005 mg/kg body weight (16)

BASIC MANUFACTURER(S)

Atochem North America, Inc.
Three Parkway
Philadelphia, PA 19102

Review by Basic Manufacturer:

Comments solicited: January, 1992
Comments received:

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Chemical Class/Use:	carbamate; ethylenebisdithiocarbamate
ADI:	0-0.005 mg/kg body weight (16)

BASIC MANUFACTURER(S)

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