Bull. Environm. Contam. Toxicol. 22,475-478 (1979)

Residues of Mancozeb and Ethylenethiourea in Grain Samples[1]

Christina Rosenberg and Hilkka Siltanen
State Institute of Agricultural Chemistry, P. O. Box 282, SF-00171 Helsinki 17, Finland

The increasing use of pesticides brings about an actual risk of inaccurate spraying and subsequent contamination of nearby-lying areas.

The present investigation was initiated by such a local accident. A grain field was sprayed by mistake on the air-spraying of a potato field with Dithane M-45 against potato blight. In Finland Dithane M-45, a product containing 80 % mancozeb, is also used for controlling spot diseases and as dressing of seed potato.

Ethylenebisdithiocarbamate (EBDC) fungicides (maneb, zineb, mancozeb) are a widely used group of organic fungicides. One of the decomposition products of EBDC is ethylenethiourea (ETU, 2-imidazolidenethione). ETU may be present in formulations (BONTOYAN et al. 1972) or may be formed under conditions of aeration (HYLIN 1973) or by cooking (NEWSOME 1976, ONLEY et al. 1977).

ETU has been found to be carcinogenic (GRAHAM et al. 1973), goitrogenic (GRAHAM 1972) and teratogenic (KHERA 1973). Residues of EBDC and ETU have been analyzed in potatoes, spinach, applesauce and milk (ONLEY 1977), in pears (RIPLEY and SIMPSON 1977), in apples and tomatoes (NEWSOME 1972, 1976) as well as in Canadian foodstuffs (PECKA et al. 1975).

The present investigation reports the residues of mancozeb, expressed as maneb, and ETU in barley, oats and wheat from the contaminated grain field. The grain was also heat-treated to determine elevated ETU residues.

---

[1] Presented (in part) at the IVth International Congress of Pesticide Chemistry (IUPAC), Zürich 1978.

0007-4861/79/0022-0475 $01.00

MATERIALS AND METHODS

The contaminated area was 0.9 ha. The potato field was air-sprayed with a helicopter at the recommended rates (2 kg/ha a.i.). Nineteen samples were collected. Of the samples, which comprised the grain plus 5-10 cm of the straw, 5 were barley, 9 oats and 5 wheat samples. The samples were taken 3 weeks after spraying at the distances of 1, 5, 10, 25 and 50 meters from the potato field. The mancozeb residues were determined 2 to 11 days after sampling, while the ETU residues were analyzed 3 to 6 months later. The samples were ground in a laboratory mill and stored in a freezer (-24 °C) before analysis.

Analysis of mancozeb. Mancozeb is a complex of maneb and zinc and since its molecular weight was not avaiable, the results were expressed as maneb (ONLEY et al. 1977). Maneb was determined using the carbon disulphide evolution method described by KEPPEL (1971).

Analysis of ethylenethiourea.ETU residues were analyzed by gas-liquid chromatography of the trifluoroacetylated S-benzyl derivative. The analytical procedure was a modification of the method described by PECKA et al.(1975). The modifications made were the following: 1) throughout the method methylene chloride and toluene may be substituted for the more toxic solvents chloroform and benzene, 2) after the benzylation the addition of aqueous potassium hydroxide is changed to 10 ml 1.5 N instead of 5 ml 1 N according to the work by NASH (1974), 3) when the S-benzyl derivative has been extracted into methylene chloride the analysis can stay overnight, if necessary, and be continued the next day, 4) the trifluoroacetylated S-benzyl derivative is stable for several hours, nevertheless the derivative should be chromatographed immediately.

The gas-liquid chromatography was performed on Varian Aerograph gas chromatographs equipped with an electron capture detector (^{63}Ni and ^{3}H). The columns used were the following: SE-30 (glass capillary, 25 m x 0.3 mm, split 1:20, t_c = 190°C) and 2 % butanediolsuccinate on Varaport 30 100/120 mesh (glass 1.4 m x 3 mm, t_c = 210°C).

Recovery tests were made by adding ETU at the levels of 0.025 ppm to 0.1 ppm. The average recovery was 93 %.

Heat treatment. The sample (5 g) was placed in a 250 ml beaker and 20 ml of distilled water was added. The beaker was covered with a watch glass and heated to boiling. After boiling for 30 minutes the suspension was cooled and extracted with absolute ethanol and analyzed according to the method mentioned above. The pH of the suspension after boiling was 6.2.

According to MARSHALL (1977) the conversion to ETU depends on the pH of the solution. If the pH is above 6, the conversion rate from EBDC to ETU is high, while below pH 6 the conversion is low. The average recovery for cooked samples, when ETU was added at the levels of 0.1 to 1.0 ppm, was of the same order as in the case of uncooked samples.

RESULTS AND DISCUSSION

Table 1 summarizes results of the analyses. Of the 19 samples 3 samples did not contain detectable levels of maneb, 9 samples contained less than 2 ppm, whereas

TABLE 1

Residues of mancozeb, expressed as maneb, and ETU in barley, oats and wheat, and ETU residues formed by cooking.

Sample N:o	Distance from the potato field, m	Maneb (ppm)	ETU (ppm)	ETU(ppm) formed by cooking
barley				
1	1	21	0.08	5.9
2	1	3.8	0.03	1.1
3	5	3.9	0.03	1.1
4	10	0.7	0.01	0.3
5	25	1.0	0.02	0.4
oats				
6	1	5.5	0.01	1.2
7	5	1.0	<0.01	0.2
8	10	0.2	<0.01	0.1
9	25	0.7	<0.01	0.2
10	1	0.5	<0.01	0.2
11	5	0.2	<0.01	0.1
12	10	0.3	<0.01	0.1
13	25	<0.1	<0.01	<0.01
14	50	<0.1	<0.01	<0.01
wheat				
15	1	15	0.09	2.6
16	5	6.5	0.02	1.0
17	10	3.2	0.01	0.6
18	25	0.6	<0.01	0.2
19	50	<0.1	<0.01	<0.01

7 samples contained more than 2 ppm. 2 ppm is the proposed tolerance limit for EBDC fungicides in Finland. The highest residue were found in samples collected 1 m from the potato field. The values were 21 ppm for barley, 5.5 ppm for oats and 15 ppm for wheat. Of the 9 oats samples nos. 10 to 14 show significantly low residue values. Said samples were taken south of the potato field, while all the other samples were taken north of the field.

No ETU residues were found in 10 samples. Of the remaining 9 samples 7 contained less than 0.05 ppm and 2 samples over 0.05 ppm. The two highest values were 0.09 and 0.08 ppm in one wheat and one barley sample containing 15 and 21 ppm of maneb, respectively.

The ETU residues found in raw grain samples represent the ETU originally present in the formulation and/or the ETU formed by decomposition. In addition, ETU may be formed during the benzylation derivatization up to 1 to 2 % of the amount of the EBDC (PEASE and HOLT 1977). In their paper PEASE and HOLT consider reported ETU residues below the 0.05 ppm level questionable on account of the possibility of ETU being formed during the analysis. According to PEASE and HOLT only 2 samples of the 19 samples analyzed would exceed the 0.05 ppm level. On the other hand, Sweden has established a tolerance limit of 0.01 ppm for ETU (SLV FS 1977:7). In view of this, 9 samples would be above the Swedish tolerance limit.

The effect of cooking is also presented in Table 1. Elevated levels of ETU were found in all samples containing residues of maneb. The amount of ETU formed by cooking was 30 % on an average. As can be seen, low residues of maneb, even below the proposed tolerance limit, form high residues of ETU after cooking.

In conclusion, it is to be said that spraying of crop land with EBDC fungicides can result in the production of ETU and subsequent health hazards to the consumer.

REFERENCES

BONTOYAN, W.R., J.P. LOOKER, T.E. KAISER, P. GIANG and B.M. OLIVE: J. Assoc. Offic. Anal. Chem. 55, 923 (1972)

GRAHAM, S.L. and W.H. HANSEN: Bull. Environ. Contam. Toxicol. 7, 19 (1972)

GRAHAM, S.L., W.H. HANSEN, K.J. DAVIS and C.H. PERRY: J. Agr. Food Chem. 21, 324 (1973)

HYLIN, J.W.: Bull. Environ. Contam. Toxicol. 10, 227 (1973)

KEPPEL, G.E.: J. Assoc. Offic. Anal. Chem. 54, 528 (1971)
KHERA, K.S.: Teratology 7, 243 (1973)
MARSHALL, W.D.: J. Agr. Food Chem. 25, 357 (1977)
NASH, R.G.: J. Assoc. Offic. Anal. Chem. 57, 1015 (1974)
NEWSOME, W.H.: J. Agr. Food Chem. 20, 968 (1972)
NEWSOME, W.H.: J. Agr. Food Chem. 24, 99 (1976)
ONLEY, J.H. and G. YIP: J. Assoc. Offic. Anal. Chem. 54, 165 (1971)
ONLEY, J.H., L. GIUFFRIDA, N.F. IVES and R.R. WATTS: J. Assoc. Offic. Anal. Chem. 60, 1105 (1977)
ONLEY, J.H.: J. Assoc. Offic. Anal. Chem. 60, 1111 (1977)
PEASE, H.L. and R.F. HOLT: J. Agr. Food Chem. 25, 561 (1977)
PECKA, Z., P. BAULU and H. NEWSOME: Pestic. Monit. J. 8, 232 (1975)
RIPLEY, B.D. and C.M. SIMPSON: Pestic. Sci. 8, 487 (1977)
SLV FS 1977:7, Statens Livsmedelsverks författningssamling, 1977:7, Sweden, ISSN 0346-119X