DEPARTMENT OF AGRICULTURE, SOUTH AUSTRALIA

# Agronomy Branch Report

## PHYTOTOXICITY OF MANCOZEB

(A literature review compiled before investigations
into the poor emergence of mancozeb-treated
cereals)

J. Johnsson,
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Report No. 64

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# 1. DECOMPOSITION OF THE ETHYLENE BISDITHIOCARBAMATE FUNGICIDES

## 1.1 Nabam decomposition (sodium ethylene bisdithiocarbamate)

Owens in Torgeson's treatise (1969)[1] on fungicides presented the following scheme of the known and hypothetical reactions that might occur upon decomposition of nabam, the disodium salt of ethylene bisdithiocarbamic acid, in solution.



ETDS -ethylene thiuram disulfide

ETMS - ethylene thiuram monosulfide
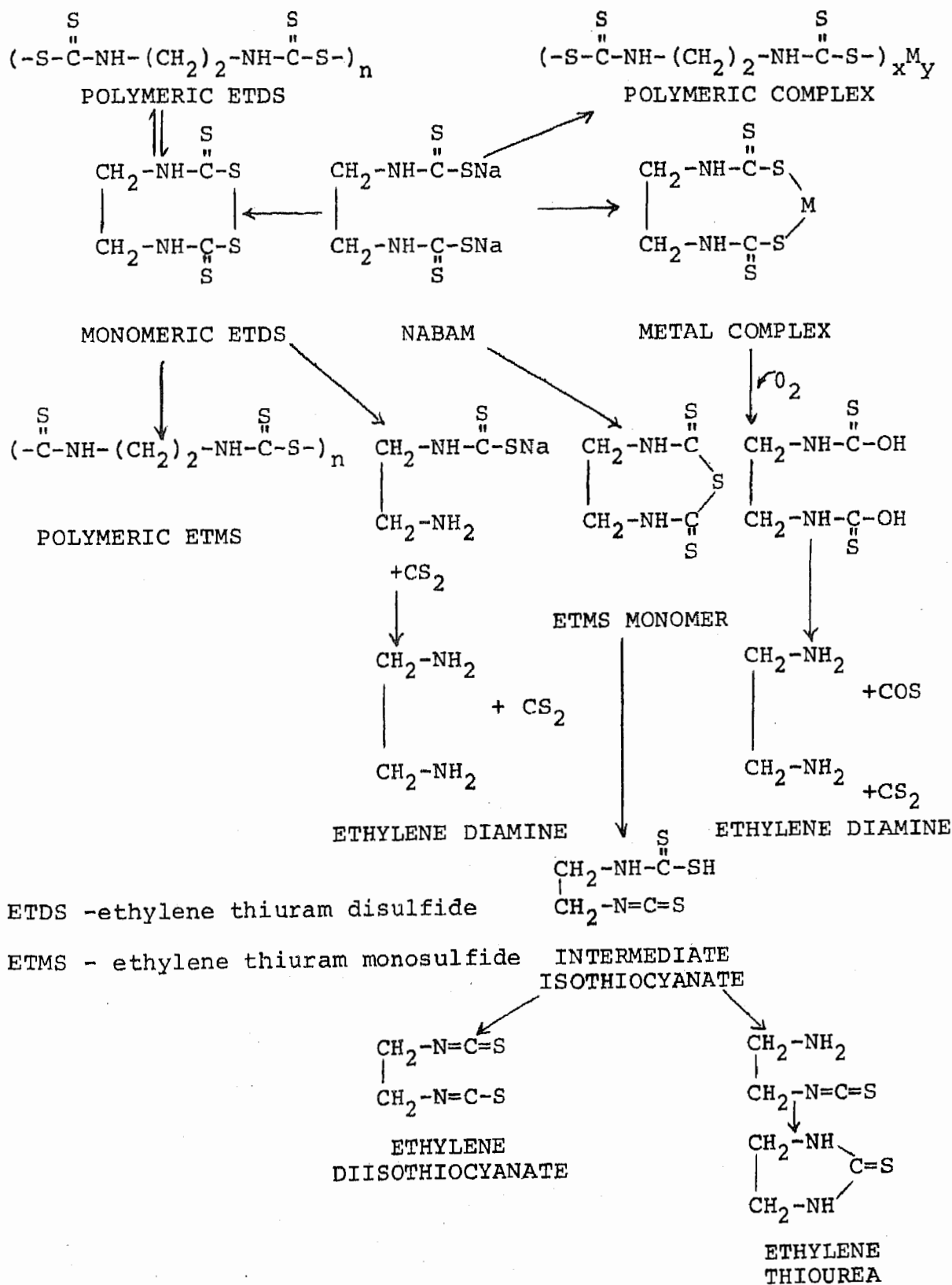
In view of the number of reactions and products formed, it is doubtful that a single mode of toxic action exists. Instead, a number of modes can be cited with evidence to support each.

Nabam is highly water soluble but on exposure to air, it forms an insoluble precipitate of ethylene thiourea (ETU), ethylene thiuram monosulfide (ETM) and polymers, with the concommitant evolution of carbon disulfide and hydrogen sulfide.[2,3]

Solutions of nabam are nearly neutral but become alkaline on exposure to air due to the oxidative decomposition occurring. They may reach pH 11[4].

Under acid conditions, nabam is hydrolysed to ethylene diamine (ED) and carbon disulfide[4]. Rich[5] obtained a residue of ETU while ED and $CS_2$ are volatile. The half life of nabam at pH 4, 5 and 6 is 2 hours, 30 hours and greater than four days respectively when kept at room temperature under nitrogen. A shift in pH from 5-6 to 5-4 altered the reactions from the oxidative decomposition type to the acid decomposition type and this shift brings about a change from fungicidal activity to inactivity. This pH shift is over the range that can be regulated naturally by $CO_2$ in water[4].

There are biological consequences of this[4]. Tomato plants sprayed with 2,000 ppm nabam solution sustained bad damage when plants were held in a darkened chamber while relatively little damage was caused to plants kept in an illuminated chamber. The damage was thought to be due to $CS_2$ formed on the breakdown of the nabam under more acid conditions prevailing in the absence of photosynthesis. There is a five-fold increase in $CS_2$ production on increasing the acidity from pH 6.3 to 5.7. Under alkaline conditions, extremely high yields of ETU may be obtained.

In aerated soil, nabam forms ETU and ETM or ED and $CS_2$ which are both volatile. ETU appears to be the only decomposition product that persists in the soil[6].

Munnecke[7] assayed nabam-treated soil using a continuously replenished supply of air and found the effluent vapours were not toxic to bioassay fungi and only copious quantities of $CS_2$ were detected. Rate curves were plotted of the breakdown of nabam as measured by the release of $CS_2$ and they indicated that undetected intermediary compounds were formed.

Other workers[8] found that nabam-treated soil (1,000 ppm) at 0 and four days after treating retarded the growth of Rhizoctonia solani in the vapour phase to 44% and 14% respectively. The activity increased with the soil acidity.

Cox[9] accounted for the high fungitoxicity of the vapour to fungus spores suspended in water above nabam solutions by assuming that the amine and $CS_2$ recombined to form the dithiocarbamate which was oxidatively degraded.

With a very acid soil treated with nabam, carbonyl sulfide (COS) and hydrogen sulfide were formed with COS as a fungitoxic agent[10]. The problem is far from being solved. Nabam produces a number of gaseous products, several of which, COS, EDI (ethylene di-isothiocyanate) and probably ED and $CS_2$ combined are apt to be fungitoxic.

### 1.2  Breakdown Products of Nabam

### 1.2.1  Ethylene thiuram monosulfide ETM[4].

This is an active fungicide with an $ED_{50}$ for spores of Monolinia fructicola being 1.5 ppm (monomer) 8-10 ppm (polymer). It exhibits the same antifungal spectrum as nabam and the di-isothiocyanates and is antagonised by the same thiol compounds. It could arise from the isothiocyanate by internal addition, but it could equally arise directly from ethylene bisdithiocarbamic acid with the loss of $H_2S$ or from ethylene thiuram disulfide with the loss of $S^4$.



isothiocyanate          ETM
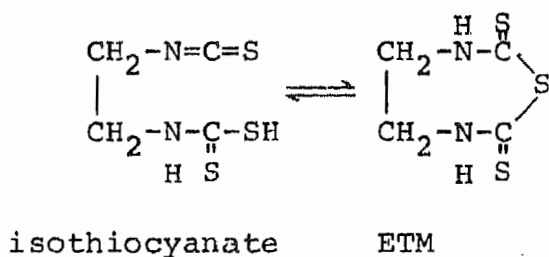
A dilute nabam solution gives rise to ETM monomers while a more concentrated solution yields the polymer.  The ETM in stored nabam solutions disappears in time[11].

There is an increased fungicidal activity of ETM in the presence of metal salts.

### 1.2.2  Ethylene thiuram disulfide ETD

It appears that ethylene bisdithiocarbamic acid and its disulfide exist in reversible equilibrium.  Ludwig and Thorn[4] presented the following schematic representation:-
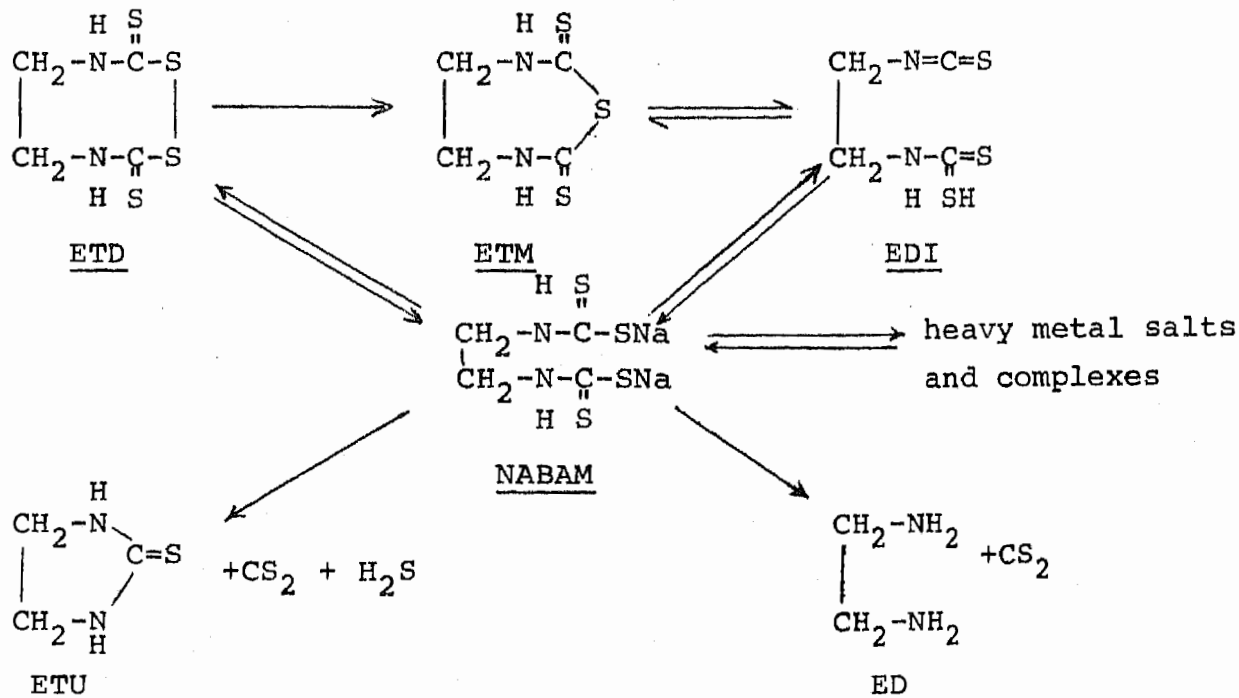
ETD is formed as a monomer and polymer mixture and under some circumstances it can be as active as the nabam decomposition products. Morehart and Grossan[12] found similarities in the metabolic effects of nabam and ETD and concluded that it was the probable ultimate toxic agent.

### 1.2.3  Ethylene thiourea ETU

This is a breakdown product formed both in acid decomposition and in vigorously aerated nabam solutions up to pH 10.5. It is a soluble compound, non-phytotoxic to germinating wheat and barley seeds or to tomato seedlings[13]. When nabam was sprayed onto plants, ETU was taken up by the roots and leaves of cucumber seedlings and by the roots of wheat seedlings and converted into a 2-imidazoline compound[14]. In aqueous suspension ETM is to some extent converted to ETU. In stored nabam solutions, ETU increases with time[15]. ETU appears to be the only decomposition product of bisdithiocarbamate fungicides that persists in soil[6].

### 1.2.4  Ethylene di-isothiocyanate EDI

Klopping in 1951[16] first presented the view that the fungistatic action of bisdithiocarbamates was primarily connected with their conversion in situ to di-isothiocyanates. Kaars Sijpesteyn and van der Kerk[17] thought the observed formation of ETM served as a direct indication for at least the intermediate appearance of isothiocyanate groups. These compounds have a high chemical reactivity so it is not surprising that their presence in solution has not been demonstrated. However, it is only those bisdithiocarbamates, or their derivatives, that bear in their molecular structure the potential possibility for an easy transformation into isothiocyanates, that are highly active fungicides. Another argument for the formation of isothiocyanates was the observation that the antifungal action of disodium ethylene bisdithio-carbamates and ETM could be antagonised by thiol compounds such as thioglycolic acid and cystein. Isothiocyanates were fungi-toxic because they inactivated essential -SH systems within the living cell. Traces of di-isothiocyanate have been found in aerated nabam solutions[4] and an isothiocyanate has been formed from ETM in a non aqueous medium[18].

However Kaars Sijpesteyn and van der Kerk[17] found that nabam and the di-isothiocyanate were equally toxic to Rhizopus nigricans since equivalent amounts (10 ppm) were required to inhibit growth. Thus nabam would have to be quantitatively converted to the di-isothiocyanate if the latter were the toxic agent. Weed[19] showed that the detoxification of nabam and a di-isothiocyanate by various absorbers was not the same.

Melnikov[20] assumes that the action of the ethylene bis-dithiocarbamates is associated with the formation of the corresponding isothiocyanates but the question is still open and currently being studied.

## 1.3  Metal Salts of Ethylene bisdithiocarbamic acid - Maneb and Zineb

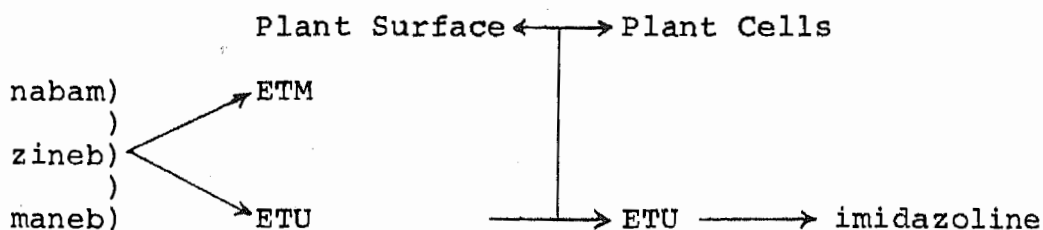The zinc salt, zineb, is unstable in the presence of

moisture and light. The moist compound (> 4% moisture) under unfavourable storage conditions may decompose to the extent of more than 50% in a year. Zineb also breaks down relatively rapidly (10-15 days) on plants with the final formation of volatile products. In warmer and clearer weather the breakdown of the compound takes place considerably faster. The final product of this decomposition is zinc sulfite which may play the role of a zinc micronutrient[20].

The manganese salt, maneb, is capable of spontaneous decomposition with charring when stored in bulk. This property is less marked when the compound is diluted with an inert diluent. Preparations with a low content of active ingredient decompose very readily at an elevated temperature in the presence of moisture[20].

Heuberger[21] found that zinc sulfate improved the fungicidal properties of nabam while Ludwig[22] reported that trace amounts of manganese catalysed the oxidation of nabam to ETM almost to the completion of the reaction. Ludwig[18] experimented to see whether the findings of nabam were applicable to its metal salts. The manganese salt of nabam is relatively water soluble in contrast to the almost complete insolubility of the zinc salt (.001 gm/l) and it gives a "nabam" spectrum. It is readily converted to ETM and ETM can be demonstrated in a commercial sample stored under laboratory conditions. The filtrate from water suspensions of the zinc salt gave no characteristic UV absorption peaks nor was it fungicidally active. The filtrate from alkali suspensions, however, gave a nabam-type spectrum and was fungicidally active. Further ETM was readily produced by aeration of pure zineb when suspended in alkali but not when suspended in water. The solubilising effect of alkali results from the production of dithiocarbamate ions which are then available for oxidation to the fungicide. It can be concluded therefore that manganese and zinc salts behave in the same manner as the parent nabam on aeration giving a fungicidal ETM.

Vonk and Kaars Sijpesteyn[14] concluded that suspensions of zineb and maneb were unstable in aqueous suspensions or in a moist atmosphere and decomposed to ETU, ETM, S and ETD which did not differ essentially from the breakdown of nabam. Czegledi-Janko[23] stored various formulations of zineb and maneb in the dark at 10°C (RH 0 and 80%) and 30°C RH (0, 25 and 80%). Zineb gave ETU, ETD and small amounts of ETM and S. Maneb gave ETU, ETD, EDA, ETM and S. The maneb decomposed more readily than zineb and increased decomposition resulted in a greater variety of degradation products.

This effect was tested in the field by Engst[24] who treated tomatoes with maneb and zineb. On the fifth day after application, ETM, ETU and S reached maximum values while after ten days they could be traced only in small amounts. As compared with zineb, a higher fungitoxic effect was found for maneb which is in conformity with the increased occurrence of ETM as a decomposition product on the plant. The following scheme was presented:-

```
              Plant Surface ←——→ Plant Cells
nabam)         ↗ ETM                │
      )                             │
zineb) ←                            │
      )                             │
maneb)         ↘ ETU    ────────────┴──→ ETU ────────→ imidazoline
```

The vapour phase activity of maneb and zineb in the soil at 1,000 ppm was tested[8]. The degree of growth retardation of Rhizoctonia solani at 0 and 4 days was maneb 61% and 35% and zineb 23% and 21% respectively. The activity of maneb increased with the soil acidity but the activity of zineb did not change with pH.

The complexes of heavy metals and ethylene bisdithiocarbamic acid are probably not simple salts but co-ordination complexes and complicated basic salts[4]. They can be highly polymeric depending on the method of preparation. Alkali has a solubilising effect and permits oxidation of even the highly polymeric form to ETM. The salts of the heavy metals affect the reactions of the ethylene bisdithiocarbamates in several ways:

1.  Heavy metal complexes are more stable than the sodium salt under mildly acid conditions.

2.  Manganese catalyses the oxidative decomposition of nabam.

3.  Heavy metals play a part in the conversion of the ethylene bisdithiocarbamates to isothiocyanates.

4.  The fungicidal activity of ETM is potentiated 4-8 times by the addition of a small amount of zinc hydroxide (10 ppm).

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2. PHYTOTOXICITY OF ETHYLENE BISDITHIOCARBAMATE FUNGICIDES

2.1 Non-phytotoxicity of the ethylene bisdithiocarbamate fungicides

There are many reported cases of the use of mancozeb, maneb and zineb on many different plants to control disease where no signs of phytotoxicity has occurred. We are interested in the use of mancozeb as a seed treatment, so included below are some cases where the fungicides have been used as a seed treatment or soil drench.

(a) Spraying sorghum seeds with maneb before harvest did not decrease germination.[1]

(b) Zineb and maneb did not adversely affect the milling and baking quality or seed viability of sprayed wheat.[2]

(c) Maneb, zineb and mancozeb used as drenches at 12,000 ppm proved non-phytotoxic to Chamaecyparis.

(d) Barley and oat seed treated with maneb and zinc plus maneb showed no indications of phytotoxic effects. However, the seed was planted soon after treatment.[4,5,6]

(e) Efficacy data from chemical companies and other workers include reports of mancozeb used as a seed dust on wheat, oats and barley with no effect on establishment. Seed was planted within two months of treatment.

2.2 Reports of Phytotoxicity of compounds related to mancozeb

2.2.1 Zineb (zinc ethylene bisdithiocarbamate)

There are very few reports of phytotoxicity of zineb except on Crataegus (hawthorn)[7], leaves and young fruits of some varieties of pear[8] and slight injury on cantaloupes[9].

2.2.2 Maneb (manganous ethylene bisdithiocarbamate)

Nabam + $MnSO_4$ and maneb cause severe injury to cantaloupes[9], leaf burning on watermelons[10] and yield reduction in cucumbers[11]. Oil-maneb sprays resulted in severe injury to grapefruit[12].

Experiments with oats treated with maneb (at Primal Chemicals) showed decreased germination in the laboratory. Trials in Victoria with four varieties of wheat treated with maneb and mancozeb showed reduced establishment with maneb but not mancozeb[13]. Barley treated with manebunt 75% (also Primal Chemicals) at 1500 ppm a.i. showed 59% establishment, at 1200 ppm a.i. 64% and 900 ppm a.i. 73%.

Workers[14] have studied the effects on two-year old red pine seedlings of manganous oxides formed under different levels of oxygenation when maneb and $MnSO_4$ were used in irrigated cultures. As long as the difference between soil porosity and the volume of water did not exceed 15%, weekly applications of 27 kg/ha maneb produced no adverse changes. However, when the

air content of the soil was below 7% by volume, the test plants
deteriorated.  The use of maneb fungicide or other Mn containing
compounds requires careful control of artificial irrigation
especially that established on fine-textured soils with a field
moisture capacity exceeding 20% by volume.

Maneb-treated wheat stored approximately two months
showed no phytotoxic effects on plant establishment.  The same
seed stored for approximately 13 months and 15 months showed
marked decreases in plant establishment ranging from 49%-94%
of untreated seed and 48%-78% of control respectively with
differences in different varieties[15].

### 2.2.3  Mancozeb (manganese-zinc ethylene bisdithiocarbamate)

This chemical used as a seed treatment on barley reduced
total head counts in one year but not the next year in field
tests (at Primal Chemicals).  Mancozeb caused injury when used
as a seed dust treatment resulting in poor seedling emergence
of tomatoes.  However when used as a soil treatment at the rate
of 168 kg/ha five days before sowing the seed, it had no effect[16].

Tomato growers[17] reported serious losses when tomato
seedlings in greenhouses were sprayed with manzate*.  It was
applied once at 1 1/2 gms/litre water.  The epidermal and
cortical tissues of the hypocotyl just above the soil line
collapsed and died.  Field spraying of tomato crops in Ontario
with maneb at rates of 3-4 gms/l was observed to be nonphytotoxic.
Both pepper and tomato seedlings younger than seven weeks exhibited
this sort of damage when sprayed.  No injury occurred on older
plants.  Results failed to indicate that ageing of manzate
increased its phytotoxicity.  However, it is not known whether
the conditions of fungicidal storage might alter the phytotoxic
properties of the material.  Only dithiocarbamate fungicides
containing manganese have been found to cause the described
injury.

The formation of a heavy metal salt of nabam increases
the amount of spray deposit, stabilises it on the foliage thus
permitting a longer oxidation period and reduces losses through
acid breakdown.  Manganese has a catalytic effect on the
oxidation process of nabam.  High incidence of injury occurred
in the close proximity to the soil and appeared to be associated
with slow evaporation of spray droplets.  These conditions may
favour the acid decomposition of manzate[17] to phytotoxic
compounds.

Manganese is absorbed and translocated from manzate sprays
on tomatoes but zinc is not absorbed from zerlate sprays[18].

### 2.2.4  Manganese

There are many reports in the literature of a wide range
of plants exhibiting symptoms of manganese toxicity.  These
cases are usually established plants that accumulate manganese
from the soil into their growing parts.

\* manzate is a trade name of mancozeb.

### 2.2.4.1  Manganese toxicity in seedlings

In a study[19] on the phytotoxicity of some inorganic salts, tomato seedlings watered for five days with 20 mls $McCl_2$ solution (10 m moles/1) and wheat seedlings watered for 7 days with the same solution exhibited signs of toxicity. The $ED_{50}$ (concentration in m moles/1 required to reduce growth of wheat seedling roots by 50%) of $McCl_2$ is 15.00, of $KMnO_4$ is 11.00. Comparative $ED_{50}$'s are NaCl - 97.00; KCl - 170.00; $CaCl_2$ - 82.00; $CuSO_4$ - 0.12.

### 2.2.4.2  Factors affecting manganese toxicity

Experiments[20] show a close correlation between soil acidity and manganese toxicity in potato. Other conditions being equal, this plant was affected more by an excess of manganese if the soil was sandy or gravelly than if it was finer textured. One large application of an appropriate fertiliser caused a more serious manganese toxicity of the foliage than a reduced application. Sodium and calcium decreased the damage while phosphorus and potassium accentuated it.

Regardless of pH, flooding increased the content of exchangeable manganese and the manganese content of alfalfa grown in a loamy sand[21]. In the absence of a source of easily decomposable organic matter, manganese mobilisation by flooding was considerably slower at pH 4.7 than pH 7.3. Where alfalfa was grown in the soil or finely milled oat straw was added, flooding mobilised more manganese in the acid than in the neutral soils. The favourable effect of organic matter on manganese toxicity was due to the retention of manganese in the exchangeable or complexed form[22]. Liming promoted the immobilisation of manganese on the resumption of normal soil moisture relations after flooding. Seventy-two hours of flooding increased the manganese content of the alfalfa on the unlimed soil from 426-6,000 ppm. Excess manganese tended to accumulate in the leaves and growing points of the plants.

In complete nutrient solution,[23] two annual medic species developed severe manganese toxicity symptoms at low manganese concentration (0.3 μM), when the pH was neutral and the Calcium concentration low (250 μM). Either increasing the Calcium content to 2500 μM or decreasing the solution pH to 5.4 eliminated these symptoms, decreased manganese concentration in the tops and increased growth. Increasing calcium concentration in solution alleviated manganese toxicity by decreasing sorption, whereas decreasing pH decreased both manganese sorption and transport of manganese from roots to tops. Two cultivars of Trifolium subterraneum developed no manganese toxicity symptoms. Sensitivity to manganese may be a factor contributing to the poor growth of medic species relative to subterranean clover on acid and waterlogged soils.

Peanuts in autoclaved soil showed manganese toxicity signs due to the direct release of manganese complexed with the

* zerlate is a trade name of zineb.

organic fraction of the soil and the killing of micro-organisms that normally transform available manganese into higher oxides[24].

### 2.2.4.3 Physiology of Manganese toxicity

Resistance to manganese toxicity is associated with low cation-exchange capacity. Leguminosae have twice the cation-exchange capacity of Gramineae. Plants of low fertility requirement have a lower cation-exchange capacity. In accordance with the Donnan theory, low cation-exchange capacity favours monovalent to divalent cation uptake. Thus the lower cation-exchange capacity of toxicity resistant selections may possibly be effective in increasing the uptake of monovalent cations at the expense of polyvalent cations[25] ($Mn^{++}$).

An investigation[26] was made into the effect of substrate manganese on tissue manganese levels and the activity of the IAA-oxidase system of cotton. For long-term and short-term exposure to manganese (126 days and 14 days) –

1.  there was a direct relationship between substrate and tissue manganese;

2.  at only 81 mg/l manganese, plants exhibited severe manganese toxicity symptoms;

3.  at the toxic level of manganese, an increased IAA oxidase and a decreased IAA-oxidase inhibitor was observed. There was a direct relationship between degree of enzyme response and severity of visible symptoms;

4.  crude extracts of plants grown with 81 mg manganese per litre solution destroyed IAA without the addition of $McCl_2$ to the assay medium.

From these results, the following hypothesis was advanced:- above a threshold concentration, tissue manganese allows or causes an increase in the activity of the IAA oxidase system which reduces the supply of auxin. The auxin deficiency produces abnormal growth as reflected by shortened internodes, restricted leaf expansion, abscission of leaves, proliferation of tissues, loss of apical dominance and death of apical buds. The hypothesis would suggest no significant modification of auxin destruction below a threshold concentration of manganese and would allow other effects and interactions of the element at toxic concentrations. The most apparent explanation for these results is that the high level of tissue manganese catalysed destruction of IAA oxidase inhibitors thus allowing the enzyme present to function more actively.

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