Sorption behaviour of maneb in the agriculture soils and its correlation with soil properties

Bhawna Vyas[1], Anil Kumar Singh[2], Swaranjit Singh Cameotra[3]

[1,2,3]Institute of Microbial Technology, Sector 39 A, Chandigarh 160036, India

Abstract— *Maneb is a broad spectrum fungicide, often reported as a carcinogenic, teratogenic and neurodegenerative agent. Thus, the occurrence of maneb at non-targeted sites is a cause of concern. The present study investigates adsorption–desorption behaviour of maneb in the agricultural soils to know its fate, mobility and availability in the soil. The sorption study was carried out by batch equilibration procedure. Maneb adsorption followed Langmuir isotherm and was accompanied by increase in manganese content of the soil. Maximum adsorption was observed in soil having the highest clay content. High maneb retention was observed in presence of soils modified with organic matter. The results of this study indicate that the clay and organic matter content of soil have significant influence on sorption behaviour of maneb. Amending soil with organic matter can reduce maneb pollution at non-targeted sites.*

Keywords— Fungicide, Parkinson disease, Manganese, Organic matter

I. INTRODUCTION

Maneb is a polymeric complex of manganese (Mn) with the ethylene bis (dithiocarbamate). Maneb, is a broad spectrum fungicide that is extensively applied against a wide range of fungal pathogens affecting ornamental plants, food and feed crops **(Garcinuno et al., 2004).** For instance, in the early years of this century in the USA approximately 2.5 million pounds of maneb are used annually targeting fungal diseases of almonds, apple, banana, bean, lettuce, walnut and peppers **(US EPA,2005)**. In India maneb is abundantly used in states like Punjab, Haryana, Uttar Pradesh, Himachal Pradesh, Jammu and Kashmir, Tamil Nadu, Madhya Pradesh, Bihar and Andhra Pradesh for protecting food/feed crops **(Bhushan et al., 2013)**. The problem related the difficulty in applying them to the targets and limiting their distribution in the non-targeted environmental sites. The extensive use of maneb has been shown to cause soil and water pollution in a banana production region of tropical Mexico **(Geissen et al., 2010).**

Maneb and its degradation intermediates have been reported to act as carcinogenic, neurodegenerative agent and teratogenic agents **(Sharma et al., 2005; Baltazar et al., 2014). Baltazar et al., (2014)** highlighted maneb as one of the potential etiological factor for neurodegenerative diseases like Parkinson disease, Alzhmeir's disease and amyotrophic lateral sclerosis. Consequently**,** maneb was among the highest ranked hazardous pesticide for overall chronic health risk, while ranking the agriculture pesticides used in Yuma County, Arizona, USA **(Sugeng et al., 2013). Sugeng et al., (2013)** highlighted maneb as an endocrine disrupting carcinogenic fungicide.

Extensive uses at higher doses and hazardous nature of maneb have made it a global concern for policymakers and environmentalists **(Bhushan et al., 2013)**. Its ecotoxicological impact, environmental mobility and rate of degradation in environment is influenced by its soil sorption behavior and physico-chemical properties of soil. Fungicide sorption and desorption in soil generally occurs at mineral, organo-mineral and organic particle surfaces. Since, soil has a complex composition and architecture, the overall sorption of a chemical is a composite of many surface interactions occurring in parallel **(Wu and Gshwend, 1986)**. Better understanding of sorption and factors affecting it make it possible to regulate a pesticide's uses and thus manage its environmental impacts.

The aim of the present study was to determine the adsorption-desorption behavior of maneb in the agricultural soils collected from Punjab and Himachal Pradesh, India. Kinetics and isotherm adsorption experiments were carried out to have a better insight into the sorption process of maneb in relation to the soil properties. Farmers tend to add organic matter (OM) to soil for increasing the yield. Hence, the influence of externally added OM on adsorption-desorption behavior of maneb was also studied.

II.   MATERIAL AND METHODS

2.1 Chemicals

All the chemicals and reagents used in the present study are of the highest purity grade available. The chemicals were purchased from Central Drug House Pvt. Limited, New Delhi, India and Sigma-Aldrich Co,St. Louis, Mo, USA. Maneb used in the present study was ~ 91 % purified and purchased from Sigma, USA. Water used in the study was de-ionized in Milli-Q equipment (Millipore, Bedford, MA) and had a resistivity of 18 MΩ.

2.2 Chemical and physical characterisation of soils

The soils used in the present study were collected from 4 different agricultural sites located in Himachal Pradesh and Punjab. The soil samples were collected from the surface layer (0-20 cm depth), air dried and sieved to pass through 2.0 mm mesh. Physical and chemical characterisation of the soils was performed following earlier described methods **(Nelson and Sommers, 1996; Singh and Cameotra, 2013).**Background Mn concentration in the soils were determined after acid digestion. The samples were analysed by Atomic Absorption Spectrophotometer (AA6800, Shimadzu, Japan) at recommended wavelength of 279.5 nm.

2.3 Maneb adsorption to the soil

Batch equilibration experiments were set up to monitor the adsorption properties of the fungicide. The fungicide was dissolved in $CaCl_2$ solution (5mM) to obtain a final concentration of 5, 10, 25, 50 and 70 mg/l. Sodium azide (0.1% w/v) was also added to the solution to inhibit bacterial growth. For equilibration experiments 1g of soil was added to 9 ml of the fungicide solution. The suspension was then shaken on a horizontal shaker at 150 rpm and 25.0 ±1.0°C for 12 hours. Aliquots of 500µl were withdrawn from supernatant at different time intervals. The samples were centrifuged at 1180 x g for 5 min and the supernatant so obtained was subjected to High Performance Liquid Chromatography (HPLC) analysis for quantifying maneb.

2.4 Organic matter (OM)

Soil samples collected for the study have low organic content. Hence, 5% (w/w) OM in the form of plant composite manure was added to all the soil samples. Soil amended with OM was then used for studying adsorption- desorption using the afore mentioned batch experimental process.

2.5 Maneb desorption from the soil

Desorption experiments were carried out immediately after adsorption experimentations. The supernatant was decanted and the residual fungicide present on the soil was determined by HPLC. To the soil with fungicide, equal volume of fresh 5mM $CaCl_2$ solution was added. The resulting soil slurries were then shaken on a horizontal shaker at 150 rpm at 25.0 ±1.0°C for 8 hours. Aliquots of 500µl were withdrawn from supernatant at different time intervals. The samples were centrifuged and amount of maneb present in the supernatant was quantified by HPLC.

2.6 Maneb quantification

Quantification of maneb was done using HPLC analysis performed with a Prominence HPLC system (Shimadzu, Japan) connected with a PDA detector (SPD-M20A, Shimadzu, Japan). The column used was Phenomax-C18 (5µ, 250mm   x 4.5mm) while mobile phase was acetonitrile / water (10/90, v/v) at a flow rate of 1 ml/min. The samples were injected through auto-sampler at a volume of 5µl and detected at 232 nm absorbance wavelength. The compound was identified and quantified by comparing the retention peaks of samples with authentic standards. External calibration curves with standard solutions between 5 and 215 mg/l were used for the calculations.

2.7 Data Analysis

Adsorption-desorption data were fitted on the Langmuir model (Eq.1) and Freundlich model (Eq.2)

$$S=q_{max}bC_e/ (1+ bC_e) \tag{1}$$

$$S=K_fC_e^{1/n} \tag{2}$$

where S is the amount of pesticide sorbed per mass of soil (mg/kg soil), C_e is the concentration of the fungicide in the liquid phase (mg/l), q_{max} is the maximum adsorption capacity of the adsorbent, b is the Langmuir constant, K_f is the Freundlich sorption coefficient (l/kg), and 1/n is a dimensionless parameter called the adsorption constant.

III. RESULTS AND DISCUSSION

3.1 Chemical and physical characterisation of soils

The agricultural soil properties **(Table 1)** used in the present study have different physicochemical properties. For instance, soil organic content is in the range of 0.08-0.30%. The zeta potential of soil samples was found to be in the range of -18.8 and -27.2 mV. Negative potential of soil is in accordance with previous reports **(Kaya and Yukselen, 2005; Moayedi et al., 2011).** No maneb was detected in the collected soil samples.

Maneb has manganese in combination to ethylene bis(dithiocarbamate) anionic ligand **(Fig 1)**. Hence, the background manganese content of the soil was quantified and was found to vary in the range of 139.0 mg/kg to 422.0 mg/kg. Presence of manganese in the soil is indispensable, as it is one of nine essential micronutrients required for vigorous plant growth. However, excess manganese is known to harm health of living organisms. In soil, manganese occurs as exchangeable manganese salts, manganese oxide, organic manganese and a component of ferro-mangesian silicate minerals **(Schulte and Kelling 1992).**

TABLE 1
PHYSICAL AND CHEMICAL CHARACTERISTICS OF AGRICULTURE SOIL USED IN THE PRESENT STUDY

Soil Characteristics	M1	M2	M3	M4
Sampling site	Manikaran,HP	Kasol,HP	Bhuntar, HP	IMTECH,PB
Texture	Silt loam clay	Clay	Silt loam	Silt clay
Clay(%)	35	65	25	40
Silt(%)	50	23	65	40
Sand(%)	15	12	10	20
Moisture(%)	9.71±0.23	19.39±0.71	15.53±.09	29.08±0.53
pH	8.0±0.1	8.1±0.1	7.26±0.15	6.7±0.2
ConductivityµS/cm)	64.4±0.92	20.4±1.1	68.4±1.1	46.3±1.1
Sp.gravity	2.4	2.7	2.2	2.3
Zeta potential(mV)	-25.6±1.7	-27.2±10	-18.8±1.5	-20.6±5
Total Dissolved solid (ppm)	33.4±2.9	10.1±3.7	34.6±2.0	24.2±2.5
Organic Matter(%)	0.08	0.27	0.30	0.22
Manganese(ppm)	347.0	422.0	372.0	139.0
CEC(cmol$_c$/kg)	131.63	202.74	365.96	227.11

HP-Himachal Pradesh, PB-Punjab

FIGURE 1: CHEMICAL STRUCTURE OF MANEB (MANGANESE ETHYLENE-1, 2-BISDITHIOCARBAMATE)

3.2 Maneb adsorption kinetics

Batch equilibration experiments were performed to determine the contact time required for attaining adsorption equilibrium. The adsorption kinetics of maneb exhibited two distinct stages of adsorption on all the soil samples used in the study **(Fig. 2)**. A very rapid initial adsorption followed by a further slower adsorption. This observation may be attributed to the fact that in initial stage a large number of vacant surface sites were available for maneb adsorption, but once most of the vacant surfaces were occupied, the repulsive forces between the solute molecules of the solid and bulk phases came into play, thus delaying the adsorption process.
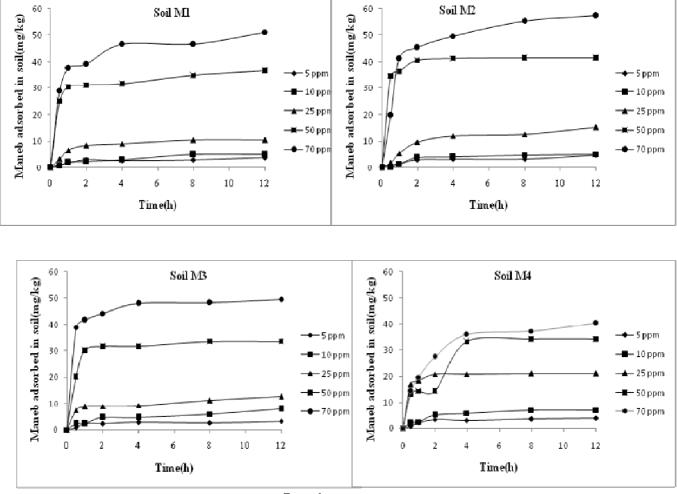

Figure 2

FIGURE 2: ADSORPTION KINETICS OF MANEB ON AGRICULTURAL SOILS. THE VALUES REPRESENT AN AVERAGE VALUE OF THREE INDEPENDENT EXPERIMENTS.

Soil has a number of functional groups contributing towards adsorption of maneb. Each functional group interacts with different binding force and consequently, exhibits different affinity for maneb. Certain functional groups have higher affinity towards maneb and/or Mn and the presence of such groups increases the adsorption rate in the initial stages. Once such functional groups are completely occupied, the rate of adsorption reduces. Thereafter, the adsorption occurs due to other functional groups which have less affinity towards maneb. Similar observation has been reported for several other pesticides **(Kumar and Philip, 2006; Gondar et al., 2013; Singh and Cameotra, 2013; Nam et al., 2014).** Maneb reached adsorption equilibrium within 2h of incubation in all the soil samples used in the present study. Interestingly, at lower concentrations (i.e 10 mg/kg and 5mg/kg) maneb exhibited almost similar adsorption behavior irrespective of physicochemical properties of soil. This may be due to greater availability of vacant sites for adsorption of maneb molecules. However, at higher maneb concentrations (50 ppm and 70ppm) adsorption to the soil surface varied depending upon the soil physicochemical properties. The maximum maneb adsorption was observed in the soil M2 at *ambient* conditions. The minimum adsorption was observed in soil M4.

Soil OM and clay content act as important sorbents for the adsorption of pesticides in the soil **(Kumar and Philip, 2006; Durovic et al., 2009; Flores et al., 2009). Farenhorst (2006)** reported soil OM as the most important factor influencing sorption of compounds in the soil. Soil OM acts as a non-polar phase or surface, and is available as the main sorbent for pesticides with non-polar characteristics **(Kumar and Philip, 2006)**. Contrary hydrophilic or lesser hydrophobic pesticides tend to adsorb more readily to the clay fraction of soil **(Kumar and Philip, 2006)**. Maneb adsorption pattern observed in the present study may be related to the clay content of the soil. In present condition, soil organic matter was not considered to display any significant influence on maneb adsorption since organic matter content of soil was very low. Soil M2 with significantly high clay content of 65% exhibited maximum maneb adsorption. **Durovic et al., (2009)** reported that apart from organic content of the soil, clay fraction may also influence adsorption of pesticides like atrazine, oxyfluorfen, pendimethalin and acetochlor. Organic matter of soil can block sorption sites of clay thereby decreasing adsorption of pesticides **(Kumar and Philip, 2006)**. This may be the reason for the maneb adsorption trend observed in soil M4.

Exposure to high concentration of Mn is known to cause toxicity **(Jaoual and Cox, 1998; Carmona et al., 2014)** have highlighted that maneb cytotoxicity is not only due to dithiocarbamate residues but also due to the manganese ions released from the maneb. Adsorption of maneb to the soil was also accompanied by the increase in Mn concentration of the soil (Supplementary Figure1). Minimum adsorption of manganese was observed in soil M3while for other soil samples amount of manganese adsorbed was nearly similar. Literature suggests that the amount and type of clay minerals and organic matter have significant influence on heavy metal ion adsorption behavior **(Schmitt et al., 2002; Bradl, 2004; Al-Qunaibit et al., 2005)**. The amount of Mn that got adsorbed to the soil was relatively more than the amount of maneb adsorbed perhaps due to the net negative residual charge present on the soil.

3.3 Maneb adsorption isotherms

For determining isotherms, adsorption study was performed at 25°C and decrease in the fungicide concentration during adsorption studies was considered to be due to adsorption of maneb to soil. Both the **Langmuir (1918) and Freundlich (1926)** equilibrium models were applied to understand the adsorption behavior of maneb to the soil. These soil adsorption experiment showed that maneb followed the Langmuir adsorption isotherm better than Freundlich adsorption isotherm **(Table 2). Kumar and Philip (2006)** reported Langmuir adsorption isotherm better for endosulfan adsorption. They hypothesized that lower concentration of adsorbate in the solution, such that there was no competition for the abundantly available adsorption sites in the soil may have contributed to the observation **(Kumar and Philip, 2006)**.Contrary, several other research groups have elucidated pesticide adsorption isotherms with help of Freundlich adsorption isotherms **(Gondar et al., 2013; Singh and Cameotra, 2013; Nam et al., 2014).**

TABLE 2
ADSORPTION ISOTHERM VALUES OF MANEB AS DETERMINED BY LANGMUIR AND FREUNDLICH ISOTHERMS MODEL. THE VALUES REPRESENT AN AVERAGE VALUE OF THREE INDEPENDENT EXPERIMENTS

Soil	Langmuir isotherm			Freudlich isotherm		
	Q_{max}	b	R^2	K_f(mg/kg)	1/n	R^2
M1	112.35	.005	0.984	-0.651	1.0695	0.9823
M2	1428.57	.0004	0.994	-0.657	1.0832	0.9729
M3	400.00	.001	0.994	-0.732	1.167	0.9715
M4	238.09	.0026	0.980	-0.450	0.9669	0.9728

3.4 Desorption behavior of maneb on soils

Looking into the desorption process of pesticides is vital since it determines the release rate and the potential mobility of pesticides in the soil as well as the treatment strategy for the contaminated soils **(Kumar and Philip, 2006; Singh and Cameotra; 2013)**. The pesticides with a lower desorption rate may possess higher risk to the successive crops, while pesticides with higher desorption rate have higher risk of contaminating the immediate vicinity. Thus, desorption kinetic

studies were conducted to assess the desorption potential of adsorbed maneb and the results are shown in **Table 3.** Desorption was found to be influenced by concentration load of maneb on the soil. Soil having less amount of maneb on the surface exhibited slower desorption than the soil with higher load. Desorption involves release of maneb from the soil surface. Force of interaction between soil surface functional groups and maneb decides ease with which it can get desorbed. In present study, functional groups present on the soil components seem to have more affinity for maneb, as rate of desorption was very slow as compared to the rate of adsorption. The OM of soil are known to play important role in the desorption process of non-ionic pesticides **(Gondar et al., 2013).** However, this do not hold good in the present work as maneb is ionic fungicide and also amount of organic carbon is very low in the soil samples.

TABLE 3
DESORPTION ISOTHERM VALUES OF MANEB IN THE AGRICULTURAL SOILS. THE VALUES REPRESENT AN AVERAGE VALUE OF THREE INDEPENDENT EXPERIMENTS.

Soil	Q_{max}(mg/kg)	b	R^2
M1	48.07	0.014	0.995
M2	71.94	0.012	0.996
M3	212.76	.003	0.978
M4	35.33	.022	0.971

Retention of fungicide after adsorption-desorption reaction in the soils suggests that adsorption of fungicide occurs with a limited degree of reversibility. The amount of fungicide retained with in the soil depends upon both the physico–chemical properties of the molecules and the soils involved in the process **(Siripattanakul et al., 2009).** Soil retaining fungicide decreases the chance of environment pollution by limiting the mobility **(Siripattanakul et al., 2009; Singh and Cameotra, 2013).** The entrapping of pesticides molecules within the condensed soil organic matter makes a significant contribution to fungicide retention **(Gondar et al., 2013; Singh and Cameotra, 2013) .** However, in the present study influence of OM content on fungicide retention was not observed as all the soil samples have low organic matter content. The amount of maneb retained in the soil during the study, suggest that the adverse effect of maneb on the succession crop will be noticed, especially when maneb is applied on soils with high clay and low organic content.

3.5 Influence of organic matter on adsorption-desorption hysteresis

Soil organic matter is the most important component of soil. It significantly influences the physical, biological and chemical properties of soil which in turn determines the soil productivity **(Wauchope et al., 2002)**. Farmer tends to add organic matter to soil for increasing the yield. Hence, in the present study the amount of OM was low, so, organic matter was added.

In OM amended soil, maneb adsorption pattern was similar to the collected soil samples having low OM content. There was initial rapid increase in adsorption followed by a slow maneb adsorption. However, the total amount of maneb that was adsorbed to the soil increased significantly. In OM amended soil, amount of maneb that adsorbed to the soil was in the range of 51.6 mg/kg to 60.99 mg/kg as compared to 40.36 mg/kg to 55.33 mg/kg in native soil. Similarly, amount of manganese that got adsorbed to the soil increased in OM amended soil. Amount of manganese that adsorbed increased in the OM amended soil compared to the non-amended soils (120- 440 mg/kg compared to 62.50- 113.0 mg/kg).

 The present observation suggests that plant composite manure used in the present study have several sites to allow more maneb adsorption. In the present study, addition of OM in form of plant composite manure provided additional sites for maneb adsorption, thus increasing the total amount of maneb that got adsorbed to the soil. With the increase in maneb adsorption, there was an increase in the amount of Mn that got adsorbed to OM amended soil.

During desorption study in the presence of OM the amount of maneb that got desorbed from soil was comparatively less. In the presence of OM, less maneb was desorbed from the soil. For instance, in soils M1 and M4 there was nearly 10 fold increase in maximum adsorption capacity suggesting that the OM induced retention of maneb to the soil. The entrapping of pesticides molecules within the condensed soil OM makes a significant contribution to retention of pesticide to the soil **(Gevao et al., 2000; Wauchope et al., 2002).**   Contrary in soil M3, OM induced retention of maneb was not observed

during desorption study **(Table 4).** This may be due to high silt content of the soil. Silt can mask the functional groups involved in retention of maneb.

TABLE 4: ADSORPTION AND DESORPTION PARAMETERS OF MANEB IN THE AGRICULTURAL SOILS AMENDED WITH 5%ORGANIC MATTER. THE VALUES REPRESENT AN AVERAGE VALUE OF THREE INDEPENDENT EXPERIMENTS.

	Adsorption			Desorption		
Soil	Qmax(mg/kg)	b	R^2	Qmax(mg/kg)	b	R^2
M1	169.49	0.004	0.968	1666.66	0.0004	0.998
M2	77.51	0.008	0.951	357.14	0.002	0.985
M3	151.51	0.004	0.974	133.33	0.007	0.989
M4	85.47	0.008	0.982	909.09	.0008	0.999

IV. CONCLUSION

This study contributes to the understanding of maneb sorption process in the agricultural soil. Clay content of the soil has significant influence on the adsorption of maneb only when organic content is low. Addition of OM to soil increased retention of maneb. The study suggests that use of organic matter in the agricultural fields restricts the mobility of maneb and prevents its pollution to non target sites. The results from the present study would help in designing of effective maneb management strategies in agricultural fields.

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