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Influence of phorate and carbofuran insecticides on nitrogen availability and their residues in soil and rice

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Abstract
An experiment was conducted in with two insecticides, phorate and carbofuran at rates of 10.0 and 16.5 kg ha^{-1} respectively, to investigate its effect on the availability of nitrogen in rhizosphere soils of rice (*Oryza sativa* L., variety IR-50). Application of the insecticides stimulated the availability of nitrogen in the rhizosphere soils, and the stimulation was more pronounced with phorate as compared to carbofuran. The residue of Carbofuron and phorate was detected below maximum residue limit of 0.1 mg kg^{-1} in grain after harvest.

Keywords: carbofuran insecticides, nitrogen availability, soil and rice

Introduction

Agricultural production has recorded remarkable growth over the past few decades. Though the high yielding varieties and hybrids have contributed significantly towards improving production, these varieties and hybrids are more demanding in terms of water requirement, insecticides and fertilizers. The major problem associated with the growth of agriculture sector is the use of fertilizers and insecticides throughout India. Although, the use of agricultural chemical has produced significant benefits in increasing crop yields, it has also resulted in various 'non target' impacts such as appearance of some fertilizers and insecticides in surface and groundwater toxicity to animals, shift in weed flora and appearance of resistant weed varieties. It is interesting to note that insecticides frequently applied in modern agriculture mostly belong to the organophosphate and Carbamate groups, but their comparative residual effects on nutrients availability under a particular soil conditions have rarely been reported (Das and Mukherjee, 1994) [6]. Insecticidal residues are generally degraded and degradation products are assimilated by soil microorganisms (El-Shahaat *et al*., 1987; Rache and Coats, 1988) [11, 20] resulting in increased population sizes and activities of microorganisms which in turn influences the transformations of plant nutrient elements in soil (Jana *et al*., 1998; Das and Mukherjee, 2000) [14, 10]. On the other hand, there are some insecticides which are not utilizable by soil microorganisms and these types of insecticides are degraded in soil by microorganisms through cometabolism (Bollag and Liu, 1990) [4]. Therefore, no definite conclusion can be made on the effect of insecticides on microorganisms and their associated transformations of nutrients in soil. It is interesting to note that insecticides frequently applied in modern agriculture mostly belong to the organophosphate and carbamate groups, but their comparative residual effects on microorganisms under a particular soil conditions have rarely been reported (El-Shahaat *et al*., 1987; Singh and Prasad, 1991) [11, 23]. phorate (an organophosphate) and carbofuran (a carbamate), the two systemic granular insecticides, are frequently used to combat the insects in rice cultivation, it becomes imperative to evaluate their effects on soil microorganisms in rice fields.

Soil plays an important role in water and chemical movement through it. The soil type has a great important influence on nutrient and pesticides leaching losses as the movement of these nutrients and pesticides in water is affected by the soil characteristics which define their retention. The factors known to influence the fate and behavior of insecticides in soil systems. These are chemical decomposition, photochemical decomposition, microbial decomposition, volatilization, movement, persistence, plant or organism uptake and adsorption. Moreover factors such as composition of soil, physical nature of chemical fertilizers and insecticides, soil reaction, nature of the saturating cations on the soil exchange sites and nature of the formulation directly influence the mobility of these compounds/chemicals in the soil system. The total amount of rainfall or irrigation water received, the intensity (water flux) and frequency of received water, all appear to effect movement of these chemicals in soils. Fertilizers and insecticides can move from their initial distribution by a number of processes. Transport of these may be the result of processes such as, the formation of soluble complexes with soil solution components such as dissolved organic matter and metals or the incomplete interaction of these compounds with the solid state organic or inorganic matter in the soil.

The first zone includes the laterite and lateritic soils which occupy whole Ratnagiri district and southern portion of Raigad district. The soils are developed from basalt by process of laterization. The soils are acidic in reaction due to leaching of bases. In general, poor in fertility and have high P-fixing capacity. The second zone comprises whole of Thane and remaining northern part of Raigad district. The soils of these zones are Medium black and neutral to slightly alkaline in reaction. They contain free calcium carbonate and are poor in phosphorous content, medium to high in nitrogen and potassium contents. The soils along the west coast of the Konkan (Panvel) is known as Coastal saline soil and it covers an area of about 65,465 ha (Report of the *Khar* Land Development committee, 1982). The alluvium is mostly derived from trap and the soils are impregnated with salts to a varying degree according to their location in respect to sea. The soils in immediate vicinity of sea are highly saline inspite of rainfall. The texture of Coastal saline soils ranges from clay loam to clay.

2. Materials and methods

An experiment was conducted to investigate the effect of Phorate (O, O-diethyl-S-ethylthiomethyl dithiophosphate) and Carbofuran (2, 3-dihydro-2, 2-dimethyl benzofuran-7-yl-N-methylcarbamate) at their recommended field application rates, on the nutrient availability as well as the persistence of the insecticides in the rhizosphere soils of rice. In order to represent these three distinct zones of Konkan, three representative soil field samples, one each from Lateritic, Medium black and Coastal saline soil were collected from different tahsils of Konkan namely Dapoli, Karjat and Panvel. All the locations are the Agricultural Research centers of Dr. Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli. At each location one rice growing soil field was selected. From each of the mentioned locations, one sample collected by following standard procedure of soil sample collection. To know the initial soil fertility status the collected soil samples were processed for analysis. (Table 1) The processed surface soil was used for conducting a pot culture experiment. Pot culture experiment was conducted in plastic pots of 10 kg capacity having 30 cm diameter and 45 cm height. Small quantities of pebbles were put at the bottom of the pots and ten kg of soil was filled in each pot. The hybrid rice variety Sahyadri-4, released by Dr. Balasaheb Sawant Konkan Krishi Vidyapeeth, Dapoli in 2008 was taken as a test crop during *Kharif* 2012 and 2013. There were nine treatment combinations in three replication. T_1 (Lateritic soil +RDF), T_2 (Lateritic soil +RDF+ P1), T_3 (Lateritic soil +RDF+ P2), T_4 (Medium Black soil +RDF), T_5 (Medium Black soil +RDF+ P1), T_6 (Medium Black soil +RDF+ P2), T_7 (Coastal saline soil +RDF), T_8 (Coastal saline soil +RDF+ P1), T_9 (Coastal saline soil +RDF+ P2). Treatment wise fertilizers were added and mixed thoroughly. RDF - Recommended dose of fertilizer i.e. NPK @ 150:50:50 through SSP - Single Super Phosphate, MOP - Muriate of Potash P_1: Carbamates insecticide: Cabofuron3G@recommended dose (16.5kgha^{-1}), P_2: Organophosphates insecticide: Phorate10G @ (10.0 kg ha^{-1}). Nitrogen @ 150 kg ha^{-1} was applied in three splits *viz.*, first dose of 40 per cent N at the time of transplanting, second dose of 40 percent 30 days after transplanting and third dose of 20 percent 60 days of transplanting. Phosphorus @ 50 kg ha^{-1} and potassium @ 50 kg ha^{-1} were applied in a single dose at the time of transplanting as per the treatments. Pesticides PI (Carbofuron3G) @ recommended doze of 16.5 kg ha^{-1} and pesticide PII (Phorate10G) @ recommended doze of 10.0kg ha^{-1} was applied as basal doze at the time of transplanting to each pot calculated on the basis of 10 kg soil per pot. The experiment were laid out separately in CRD design with nine treatments and replicated three times for each set of experiments. After puddling and mixing of basal dose of fertilizer in soil, twenty one days old rice seedlings (Variety Sahyandri-4) were transplanted. The soil was kept submerged (under 2.5 cm water) throughout the crop growth period. The various cultural operations were undertaken as and when required, In order to know the effect of various treatments on soil properties periodical soil samples (0-22 cm) were collected from each treatment pot at 30, 60, 90 days after transplanting and at harvest. After processing, the samples were stored in properly labeled corrugated boxes and used for determination of nutrient (N,) and pesticides (PI and PII) residues availability in the laboratory by following the standard analytical methods. The porosity was calculated by using the following relationship as described by Black (1965) [3]. It was determined by using Double ring infilterometer method as described by (Jaiswal, 2004) [13]. The pH of soil was determined using pH meter having glass and calomel electrode using 1**:**2.5 soil**:** water suspension ratio (Jackson, 1973) [12]. Electrical conductivity of soil was determined with the help of Systronic Conductivity Meter-306 using 1**:**2.5 soils**:** water suspension ratio (Jackson, 1973) [12]. It was determined by following Walkley and Black wet oxidation method (Black, 1965) [3]. Available nitrogen was determined by alkaline permanganate (0.32% $KMnO_4$) method (Subbiah and Asija, 1956) [24]. Available phosphorus was determined by extracting the soil P with 0.5 M $NaHCO_3$ at pH 8.5. Phosphorus in the extract was determined calorimetrically by using Spectrophotometer as per soil type as outlined by Olsen *et al*., (1954) [18] and Brays-I method (1945) [5]. Available K was estimated on Systronics Flame Photometer-128 using neutral-normal-ammonium acetate (NH_4OAc, pH 7.0) as per procedure given by Jackson (1973) [12]. Cation exchange capacity of soil was determined by leaching the soil with 1N ammonium acetate and excess of ammonium acetate was removed from the soil with absolute ethanol. The exchanged ammonium ions corresponding to CEC of soil was then extracted with 1N KCL solution and determined by kjeldahl distillation. Jackson (1973) [12]. Pesticide residues analysis was estimated by QUECHERS methods as described below given by Sharma (2005) [22]. The data were statistically analyzed by using the standard procedure given by Panse and Sukhatme (1967) [19].

3. Result and discussion

The soil samples were collected from Dapoli, Karjat and Panvel representing Lateritic, Medium Black and Coastal saline soil types respectively. Various initial physical properties of this soil properties have been determined. The results obtained are presented below in Table 1.

Table 1: physical and chemical properties of the soil.

Soil	Mechanical Composition (%)			Textural class	Porosity %	pH	EC dS m^{-1}	Org. C. %	CEC Cmole(P^+) kg^{-1}	Av.N kg ha^{-1}	Av. P_2O_5 kg ha^{-1}	Av. K_2O Kg ha^{-1}	IR cm hr^{-1}
	Sand	Silt	Clay										
Lateritic soil - Location Dapoli													
0-30	59.52	14.72	25.76	Sandy clay loam	38.10	5.8	0.08	1.8	28.40	298.8	9.1	229.8	2.1
Medium black soil - Location Karjat													
0-30	39.88	24.36	35.76	Clay loam	28.65	7.0	0.14	1.29	40.86	258.3	18.4	270	1.4
Coastal saline soil - Location Panvel													
0-30	33.04	20.48	46.48	Clay	20.60	7.3	3.8	0.78	46.6	312.4	23.4	972.8	0.9

3.1 Effect of treatments on changes in available nitrogen in soil at different growth stages

3.1.1 Available Nitrogen (kg ha^{-1})

It was observed that there was an increase in available nitrogen content in the pesticides (Carbofuron and Phorate) treated treatments along with 100 per cent RDF as compared to pesticide untreated soil i.e 100 per cent RDF alone irrespective of soil type. Madhuri and Rangaswamy (2000) [17] [10], Das and Mukherjee (1994) [6] and Das and Mukherjee (2000b) [8] reported the similar results. Das and Mukherjee, (1994) [6] also reported the increase in N availability and higher mineralization of N with the incorporation of insecticides Das *et al*., (2003) [9] reported that application if insecticides (Phorate, Carbofuron) at their recommended dose stimulated the population of bacteria, actinomycetes and fungi in the rice rhizosphere soils. The phorate was more effective than compared to carbofuron in contributing to the higher value of available N content. They also showed that the increase in nitrogen availability was more in case of Phorate as compared to Carbofuron may be due to stimulation was more pronounced with Phorate as compared to Carbofuran resulting in increased population size and activity of microorganisms which in turn influences the transformation of plant nutrient element in soil and increasing its availability of nitrogen. The reason for maximum N content at 60 DAT irrespective of the soil type in all the treatments is attributed to the decomposition of organic matter and split application of N. On the other hand maximum available N content in pesticides treated soil at 60 DAT was observed than pesticides untreated treatment. (Table 2).

Table 2: Effect of pesticides treatment on available Nitrogen at different growth stages of rice.

Treatment	Ava. Nitrogen kg ha^{-1}			
	30DAT	60DAT	90DAT	AH
T_1 Lateritic soil +RDF	333.4	354.4	296.9	301.1
T_2 Lateritic soil +RDF + P_1	353.6	376.8	306.5	307.2
T_3Lateritic soil + RDF + P_2	358.5	383.4	310.1	309.6
T_4 Med. Black soil + RDF	308.6	340.9	298.5	284.8
T_5 Med. Black soil + RDF + P_1	336.1	370.1	316.7	292.8
T_6 Med. Black soil + RDF + P_2	345.6	380.2	319.9	295.4
T_7 Coastal saline soil +RDF	344.1	356.1	334.7	338.1
T_8Coastal saline soil +RDF + P_1	359.4	372.2	340.2	341.5
T_9 Coastal saline soil +RDF + P_2	363.0	375.1	341.9	342.4
SEm$\pm$	4.75	2.79	2.75	2.23
CD@ 1%	13.6	11.3	11.1	9.11

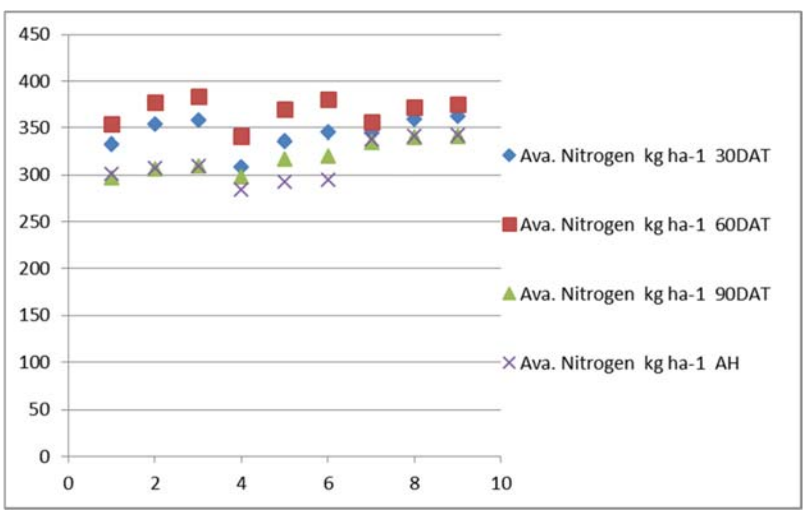

Fig 1: Effect of different treatment on available Nitrogen at different growth stages of rice.

Maximum available nitrogen content was recorded at 60 DAT stage in all the treatments. (Fig. 1) The reason for maximum available N content at 60DAT irrespective of soil type in all the treatment may be partly due to the decomposition of organic matter and submerged conditions. Das *et al*., (2003) [9] reported that, available nitrogen attains a highest peak at 60 DAT due to application of insecticides (Phorate, Carbofuron at their recommended dose at the time of transplanting of rice) over the pesticides untreated treatments. The available N content of soil in all treatments declined at 90 DAT. This may be due to the fact that soils are percolative in nature and leaching losses of nitrogen and denitrification under submerged conditions. The nitrogen uptake by the plants can be another reason for decline. Similar results were quoted by Das and Mukherjee (1994) [6].

3.2 Effect of treatments on residues of pesticides in soil (µg kg^{-1})

The data pertaining to the changes in pesticides residues in soil at different growth stages viz. 30, 60, 90 DAT (day after transplanting) and at harvest of rice as influenced by different treatments are presented in Table 3.

It can be revealed from the observations that during all four stages (30, 60, 90 and at harvest stage) of sampling, the pesticide residue content was influenced due to the various treatments. The pesticide residue content was recorded highest at 30 DAT and afterwards it showed decreasing trend in subsequent observations and it was recorded minimum in the last observation (at harvest) in experiment irrespective of soil type. The decrease from 30 DAT to at harvest stage of rice and it may be because either due to the utilization of pesticides by crop or may be due processes like adsorption, degradation. The results in the present investigation are in agreement with Das and Mukherjee (1998b) [7] and Das *et al*., (2003) [9].

Table 3: Effect of different treatment on pesticides residues in soil at different growth stages of rice.

DAT	Residues in soil µg kg^{-1}							
	Lateritic		Medium black		Coastal saline		SEm$\pm$	C.D. @ 1%
	PI	PII	PI	PII	PI	PII		
30	1104.7	634	1326.4	764.6	920.3	499.5	25.09	54.6
60	440.1	166.3	581.8	260.7	380.3	122.4	15.5	33.9
90	147.7	49.1	258.8	112.6	103.2	40.6	9.73	21.2
AH	58	35.1	88.3	53.4	44.9	23.9	5.36	11.6

Among all the soil types, the trend of pesticide residue content in soil was found viz. Medium black soil > Lateritic soil > Coastal saline soil. Among the various soil type under present study, the highest pesticides residues (PI and PII) content in soil was found significantly higher in Medium black soil over the other two soil types at all the stages (30, 60, 90 and at harvest stage). On the other hand the residues of both (PI and PII) pesticides in soil was found low in Coastal saline soil at all the stages (30, 60, 90 and at harvest stage). The higher pesticides residues content in smectitic rich soil was also recorded by Yaron (1978) [26]. He further concluded that residues content of pesticides increased with increasing swelling capacity of clay because of swelling type clay. Pesticides residues get absorbed and fixed in Smectite type of clay structure in higher amount whereas the pesticides residues get adsorbed on the Kaolinite type in lower amount. Keiger and Yaron (1975) [15] also concluded that soils which contain Smectite clay retain Pesticides much more strongly than kaolinitic clays. The pesticides residues content in Lateritic soil (Kaolinitic rich) treatment was found low as compared to Medium black soil treatment in the present study. Similar results were quoted by Keiger and Yaron (1975) [15]. This may be due to higher leaching losses of applied pesticides (PI and PII) from Lateritic soil due to high infiltration rate, low CEC of soil as compared to other two soil types under study. Higher leaching losses of pesticides reduce the residues content in soil (Lateritic soil).

The residues of both (PI and PII) pesticides in soil was found low in Coastal saline soil treatment over the other two soil types under study might be because of saline nature of soil which results in to faster degradation of both the pesticides. The faster degradation of pesticides in saline condition than compared to non-saline condition was also reported by Bhattala *et al*., (2012) [1].

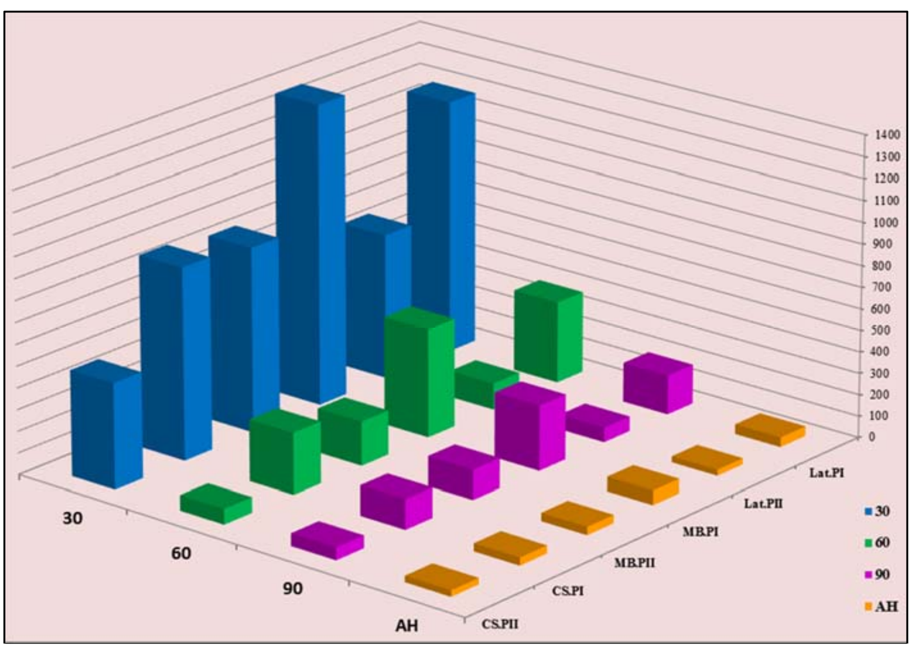

Fig 2: Effect of different treatment on pesticides residues in soil at different growth stages of rice.

Among the two pesticides (PI and PII) treatment in the present study, the Carbofuron (PI) pesticide residue content was found higher as compared to Phorate (PII) content irrespective of soil at all the stages of rice growth. This may be due to faster degradation rate and low solubility (22 mg l^{-1}) of Phorate as compared to Carbofuron (350 mg l^{-1}). According to Bhuvaneswari *et al.*, (2011) [2], Phorate residues degraded at faster rate as compared to Carbofuran in various treatments. Carbofuron moderately high affinity for adsorption to soil due to low degradation rate as compared to Phorate.

3.3 Pesticides content in grain and straw of rice crop in different soil types and pesticides

The pesticides content in grain and straw of rice recorded during study indicated there were significant differences with the various treatments. The data regarding to the pesticides content in grain and straw of rice (Sahyadri-4) as influenced by various treatments is given in Table 4 for experiment.

3.3.1 Pesticides content in grain

Among the various soil types, the studies of pesticides content in grain was found to be maximum in Medium black soil followed by Lateritic soil and was minimum in Coastal saline soil. The grain content of pesticides in the present study is found below maximum residue limit fixed by WHO and USEPA. Valliappan (1987) [25] reported the similar results. Kumar *et al.*, (2006) [16] the residue of Carbofuron and phorate was detected below maximum residue limit of 0.1 mg kg^{-1} in grain after harvest.

Table 4: Effect of different treatments on pesticides content in grain and straw of rice.

Pesticides content	µg kg⁻¹							
	Lateritic		Medium black		Coastal saline		SEm±	C.D.
	PI	PII	PI	PII	PI	PII		
Grain	20.56	17.40	29.13	23.56	16.76	14.80	0.66	2.05
Straw	12.53	10.50	16.53	13.76	9.73	7.86	0.35	1.10

PI: Carbofuron, PII: Phorate

3.3.2 Pesticides content in straw

Among the various soil types, the pesticides content in straw was found to be maximum in Medium black followed by Lateritic soil and was observed to be minimum in Coastal saline soil. The pesticides content in straw of rice in the present study is found below maximum residue limit fixed by WHO and USEPA. Seiber *et al.,* (1978) also showed that the residues of pesticides in rice plants did not exceed the 0.2 mg kg^{-1}.

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