

Persistence & Fate of Some Organophosphorus Pesticides in Sea-Sediments along East Coast of India

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Stability and fate of pesticides, monocrotophos, phosphamidon and DDVP, were studied in sediment samples collected along the east coast of India. pH, salinity and exchangeable cations present in sediments exhibited profound influence on stability and fate of these pesticides. Rate of hydrolysis of these pesticides in freshwater, brackish water and sea-sediments followed the path of pseudo first order reaction. The rate constants (K_1) and the half life periods ($T_{1/2}$) of these pesticides were determined in freshwater, brackishwater and sea-sediments with and without the presence of all exchangeable cations and anions. The low stability of these pesticides in the sea-sediments indicates that the major elements, present in the sea-sediments as cations have reduced the toxic effects of these pesticides to the marine organisms.

Organophosphorus pesticides are increasingly used throughout the world in preference to organochlorine pesticides not only for their high insecticidal activity and less toxicity but also for their low persistence in the aquatic environment¹, resulting in relatively less residual effect to the aquatic life. The sea-sediments get contaminated due to discharge of drainage water from pesticide-treated lands, industrial effluents, aerial drift or accidental spills². Thus there is always a possibility of some residual effect of pesticides to the marine organisms. Most of the work in this field is concerned with the persistence of the organophosphorus pesticides in freshwater and lake sediments³⁻⁶. The present work deals with the stability and fate of some organophosphorus pesticides in the sea-sediments along the east coast of India.

Materials and Methods

Locations of stations where the sediments were collected, using Peterson grab during cruises 130 and 141 of *R V Gaveshani* (Jan. and Sept. 1984) in bay of Bengal are given in Table 1.

Technical grade reference samples of organophosphorus pesticides, viz. monocrotophos (o,o-dimethyl o-N-carbamoyl-1-methyl vinyl phosphate), DDVP (o,o-dimethyl 2,2-dichlorovinyl phosphate), phosphamidon [o,o-dimethyl o-(2-chloromethyl 2-N,N-dimethylcarbamoyl-1-methyl) vinyl phosphate] were used.

All the sediment samples were first dried and kept free from any possible contamination of pesticide by repeated washing with alkali solution (0.1 N). pH of the sediments was adjusted according to their original

values, after which a known concentration ($100 \mu\text{g.l}^{-1}$) of each of the above pesticides was separately mixed with the sediment samples, fresh-water and brackish water. All the sediment samples were further processed to make free from the exchangeable ions by repeated washing and dialysis in order to study the effect of mineral ions on the stability of the pesticides. The stability and fate of the organophosphorus pesticides were studied under 4 different conditions, viz., sediments with all exchangeable ions present, sediment without the presence of exchangeable ions, freshwater of different pH-values (8.2-9.2) and brackish water of similar pH-values.

Phosphate buffer solutions of pH 8.2-9.2 were prepared by mixing appropriate amounts of 0.1 M monobasic sodium phosphate and 0.1 M dibasic sodium phosphate and diluting to obtain 0.01 M working buffer solutions. pH of the solutions was adjusted to the required value with 0.01 N NaOH. Sodium chloride was finally added to give the salinity which represented brackish water. Extraction of the pesticides from the sediments was carried out using 15% methylene chloride in *n*-hexane. The combined extract was dehydrated with anhydrous sodium sulphate and concentrated to about 2 ml which was diluted to 10 ml with *n*-hexane and analysed spectrophotometrically using acetylcholinesterase method⁸⁻¹⁰. Acetylcholine bromide and bromothymol blue were used as substrate and indicator respectively. The absorbance of the solutions was measured spectrophotometrically at 620 nm at a regular interval of time (approximately 5 d). By plotting Log(% residue) versus time, a straight line was obtained indicating that the reaction is first order⁷. The half life period ($T_{1/2}$) was calculated according to the

Table 1— Physico-chemical Characteristics of Sediments along East Coast of India

St No.	Depth (m)	Lat. °N	Long. °E	pH	TOC (%)	Total conc. of elements on dry wt basis						
						Al (%)	Fe (%)	Ti (%)	Mn (ppm)	Zn (ppm)	Cu (ppm)	Ni (ppm)
3232	8	22°11.2'	88°9.8'	8.2	0.14	6.2	7.3	0.25	325	57	45	82
3233	12	22°0.4'	88°4.2'	8.45	0.25	7.3	8.2	0.35	425	67	35	92
3234	13	21°42.1'	88°1.0'	8.5	0.27	5.3	6.5	0.42	435	75	48	75
3235	50	20°13.8'	88°25.2'	8.5	0.28	7.1	4.9	0.52	521	85	60	87
3236	31	21°5.7'	88°58.5'	8.5	0.25	5.6	5.3	0.58	404	82	65	79
3237	43	20°18.1'	87°4.6'	8.6	0.31	4.8	4.5	0.56	306	98	57	80
3010	45	16°50.2'	82°43.8'	8.4	0.70	3.54	4.1	0.65	420	110	65	110
3012	40	16°26.0'	82°31.0'	8.7	0.85	2.05	4.5	0.71	425	115	72	98
3013	55	16°11.0'	81°47.5'	8.5	0.96	4.48	4.9	0.79	456	125	76	75
3014	50	15°56.5'	81°19.6'	8.8	0.35	3.05	5.2	0.81	520	134	82	120
3017	48	15°39.5'	81°00.0'	9.2	0.45	4.08	5.5	0.85	625	145	88	113
3018	52	15°22.8'	80°33.1'	8.7	0.57	4.3	5.9	0.89	680	150	95	85
3019	52	15°0.3'	80°16.7'	8.7	0.55	4.5	6.2	0.92	720	85	75	95
3024	49	12°00'	80°5.6'	9.2	0.98	3.5	6.6	0.98	750	180	45	110
3025	50	12°00.0'	80°4.2'	9.1	0.92	2.8	6.9	1.02	820	196	30	300
3026	52	11°00.0'	80°2.5'	9.1	0.85	3.2	7.2	1.05	910	210	45	125

equation, $(T_1) = \frac{0.693}{K_1}$ where K_1 is the first order

reaction constant. Total organic carbon of the sediment samples was determined by the hydrogen peroxide method¹¹. Total concentration of the elements; Al, Fe, Ti, Mn, Zn, Cu, Ni, etc. was determined by atomic absorption spectrophotometer (Perkin Elmer 5000), pH values of sediment samples and the water solutions were determined using a Phillips pH-meter, on board immediately after the collection of the samples.

Results and Discussion

Physico-chemical characteristics of all sediment samples are presented in Table 1. The values K_1 and (T_1) of pesticides in different sediments and aquatic solutions of different pH-values are reproduced in Table 2.

Relatively lower values of the half-lives of the pesticides in the sea-sediments indicate that the different exchangeable ions present within the sediments, influenced greatly the stability of the pesticides. The different metallic ions present (Table I) in the sediments catalysed the hydrolysis of the pesticides. The stability of pesticides decreased with the increase in concentration of the different metallic ions present. The half-life period of the pesticides are in the order: I < II < III < IV where, I—sediments containing the exchangeable cations; II—sediments without the presence of exchangeable cations; III—freshwater of different pH values; and IV—brackish water of different pH values.

The exchangeable ion retaining capacity of each of

Table 2— Values of Rate Constants (K_1) and Half-life Periods (T_1) of Organophosphorus Pesticides

St No.	I		II		III		IV	
	A	B	A	B	A	B	A	B
DDVP								
3232	36	1.92	40	1.73	60	1.15	70	0.99
3233	34	2.04	38	1.82	57	1.21	68	1.02
3234	33	2.10	38	1.82	57	1.21	67	1.03
3235	31	2.24	36	1.92	57	1.21	67	1.03
3236	30	2.31	37	1.87	58	1.19	68	1.02
3237	28	2.47	35	1.98	55	1.26	65	1.07
3010	26	2.67	38	1.82	59	1.17	68	1.02
3012	24	2.89	34	2.03	54	1.28	64	1.08
3013	22	3.15	35	1.98	56	1.23	66	1.05
3014	21	3.30	32	2.16	50	1.38	62	1.12
3017	20	3.46	25	2.77	40	1.73	50	1.38
3018	19	3.65	31	2.23	48	1.44	62	1.12
3019	18	3.85	30	2.31	45	1.54	60	1.16
3024	16	4.33	26	2.66	41	1.69	51	1.36
3025	14	4.95	27	2.56	42	1.65	52	1.33
3026	12	5.77	28	2.47	44	1.57	54	1.28
Monocrotophos								
3232	44	1.57	42	1.65	55	1.26	65	1.06
3233	40	1.73	41	1.69	53	1.30	63	1.10
3234	38	1.82	40	1.73	52	1.33	62	1.11
3235	36	1.92	40	1.73	52	1.33	61	1.13
3236	32	2.16	41	1.69	53	1.30	62	1.11
3237	30	2.31	42	1.65	51	1.35	63	1.10
3010	26	2.66	44	1.57	52	1.33	64	1.08
3012	24	2.88	40	1.73	50	1.38	61	1.13
3013	22	3.15	40	1.73	53	1.30	61	1.13
3014	20	3.46	35	1.98	45	1.54	57	1.21
3017	17	4.07	25	2.77	35	1.98	50	1.38
3018	15	4.62	35	1.98	44	1.57	57	1.21
3019	14	4.95	35	1.98	43	1.61	56	1.23

(Contd)

Table 2—Values of Rate Constants (K_1) and Half-life Periods ($T_{1/2}$) of Organophosphorus Pesticides—Contd

St No.	I		II		III		IV	
	A	B	A	B	A	B	A	B
	Monocrotophos							
3024	12	5.77	26	2.66	35	1.92	52	1.33
3025	10	6.93	27	2.56	37	1.87	53	1.30
3026	9	7.70	28	2.47	38	1.82	55	1.26
	Phosphamidon							
3232	28	2.48	36	1.92	45	1.54	50	1.38
3233	26	2.66	34	2.03	43	1.61	49	1.41
3234	24	2.89	33	2.10	42	1.65	48	1.44
3235	23	3.01	33	2.10	42	1.65	48	1.44
3236	22	3.15	35	1.98	43	1.61	49	1.41
3237	21	3.30	33	2.10	40	1.73	48	1.44
3010	20	3.46	34	2.03	42	1.65	50	1.38
3012	19	3.65	31	2.23	38	1.82	46	1.50
3013	18	3.64	33	2.10	42	1.65	48	1.44
3014	16	4.33	30	2.31	35	1.98	45	1.54
3017	14	4.95	22	3.15	30	2.31	35	1.98
3018	13	5.33	22	3.15	34	2.03	45	1.54
3019	13	5.33	30	2.31	32	2.16	36	1.92
3024	12	5.77	20	3.46	26	2.66	36	1.92
3025	11	6.30	22	3.15	27	2.56	38	1.82
3026	10	6.93	23	3.01	28	2.47	40	1.73

I = Sediments containing exchangeable ions; II = sediments without the presence of exchangeable ions; III = freshwater of different pH values; and IV = brackish water of similar pH values

$A = T_{1/2}(d)$ $B = K_1 (\times 10^2. d^{-1})$

the sediments is dependent on the variation of the cation exchange capacity and the total organic carbon content (Table 1). The infinite number of binding sites of the various organic compounds contained within the sediments, such as humic substances and the clay minerals, play an important role in retaining the exchangeable ions which are directly involved in the destabilization of the pesticides¹².

The pesticides were more stable in brackish water than in freshwater (Table 2) at the same pH-values indicating that with the increase in salinity of the water, the rate of hydrolysis of the pesticides decreased.

Sodium chloride does not seem to be involved in the hydrolysis of the pesticides¹³. However, as the ionic strength increases, the mobility (or activity co-efficient) of the hydroxide ion tends to decrease which may affect the rate of hydrolysis⁶. Thus, it is observed that the enolphosphates are more stable in water of high salinity as in seawater, but quite less stable in the sea-sediments containing the exchangeable ions. Under conditions of such high salinity, pesticides are more labile to exert toxic effects on the marine organisms but are less toxic to the marine benthic organisms.

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