Residue Analyses in the Water System of East-Java (River Brantas, Ponds, Sea-Water) after Continued Large-Scale Application of THIODAN® in Rice

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INTRODUCTION

In the course of a national program of the Indonesian Government, the so-called BIMAS PROJECT intended to achieve an increase of rice production, 450 t.Thiodan(R) were used for control of the rice stem borer during the dry season 1969 (ca.100,000 ha.) and ca.800 t. during the wet season 1969/70. The Thiodan used was formulated as an emulsifiable concentrate and applied (1.4 l./700 l.water/ha.) partly by helicopter and partly by ground motor sprayers. Ca. 400 t. of the total quantity used in 1969/70 were applied in an area of 133,000 ha. in the delta region of the Brantas river which stretches over a distance of about 200 km. (24% of the total quantity mentioned above were applied in January, 33% in February, 24% in March, 9.5% in April). This large scale use presented a good opportunity to investigate the residue situation of Thiodan in the above water system, particularly right after application of the main quantity, i.e. in March. Thus, we thought, it should be possible to obtain a general picture of the residue situation.

The water of the entire Brantas river system is used for irrigation of the rice fields and according to the season can be re-used several times. Water flowing from the slopes of the mountains is diverted from the brooks into canals. From there it flows through the rice fields and - if there is enough water available - it is diverted from there into drainage canals which later become irrigation canals again. Even the water of large streams is biologically highly active since it is continuously contaminated by feces with only limited contamination by biocides.

In the Brantas delta, which is formed by the main rivers Porong and Kali Surabaja/Mas, there are ca. 40,000 fish ponds with an annual yield of ca. 10,000 t. fish. The whole delta is traversed by many small rivers and canals used for irrigation of the fish ponds. The water flowing away from the delta reaches the Strait of Madura. In this shallow part of the sea, which for geographical reasons is cut off from the large currents of the ocean, a brackish water zone stretching over a width of sometimes several kilometers is built up alongside the coast

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with an average depth of only 2 meters. In the rhythm of the tide this zone moves back and forth in the river deltas but also in a north-south direction along the coast. There is a considerable difference in the meteorogical data between the dry season and the rainy season, however, they remain relatively constant during either of these two seasons. The tests were made during the rainy season and the average amount of precipitation per day was 20-40 mm, mostly falling in the afternoon in short heavy showers. The temperatures at an altitude of 0-300 m above sea level range between 28° and 35° centigrade in the shade and the relative humidity was 90-100%. The water temperatures ranged from 27° to 31° centigrade in the flowing waters and were about 27° to 38° centigrade in stagnant shallow waters (rice fields). The average total hardness of the water was 4-5 d H° and the pH value was 6.5-7.0.

The analytical residue tests were made along the whole Brantas river and in the canals and fish ponds within the delta region. Moreover, water samples were also taken from the Madura Sea and in the mouth of larger canals and were analysed for Thiodan residues.

MATERIAL AND METHODS

The samples were taken by means of a one liter flask attached to a 1.5 kg. weight. This was done in several depths and aliquots of each sampling were combined to a one liter sample. In the laboratory each water sample was reduced to 850 ml and extracted in the same bottle with 30 ml hexane.

After phase separation, the organic phase was moved into the bottleneck by adding distilled water and 25 ml of the hexane were drawn off by a syringe. After drying, by means of sodium sulphate, the hexane was reduced to 0.5 ml by evaporation and transferred to a 1 ml graduated flask adding hexane to increase the volume up to 1 ml. Samples were analysed using a gas - chromatograph (Varian-Aerograph Mod. 1400) fitted with an electron capture detector. (1.5 m steel column

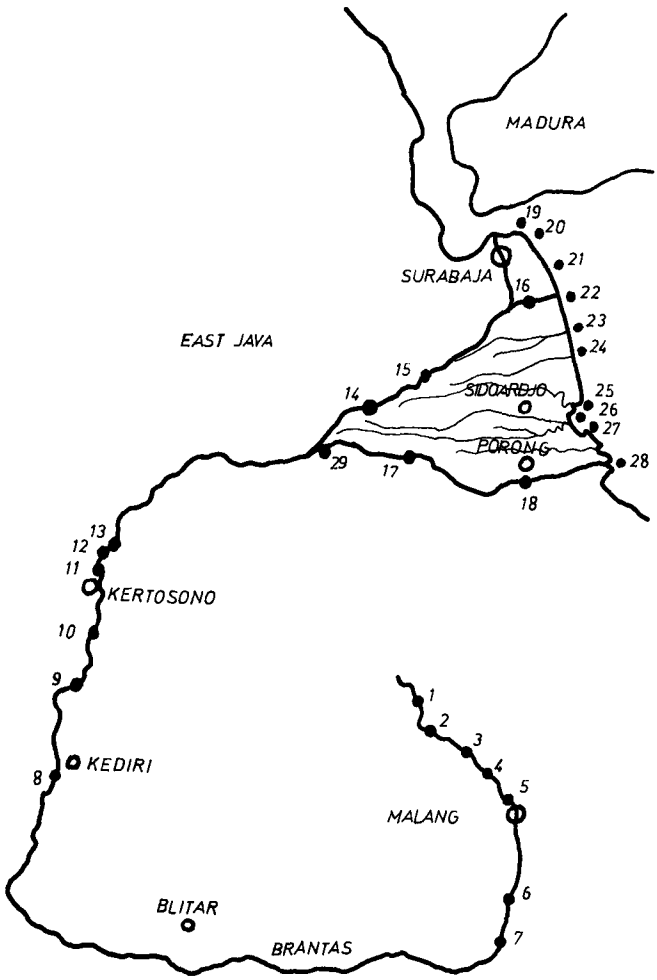

Figure 1 Sample-Stations in the River Brantas, Porong and in the Costal Area.

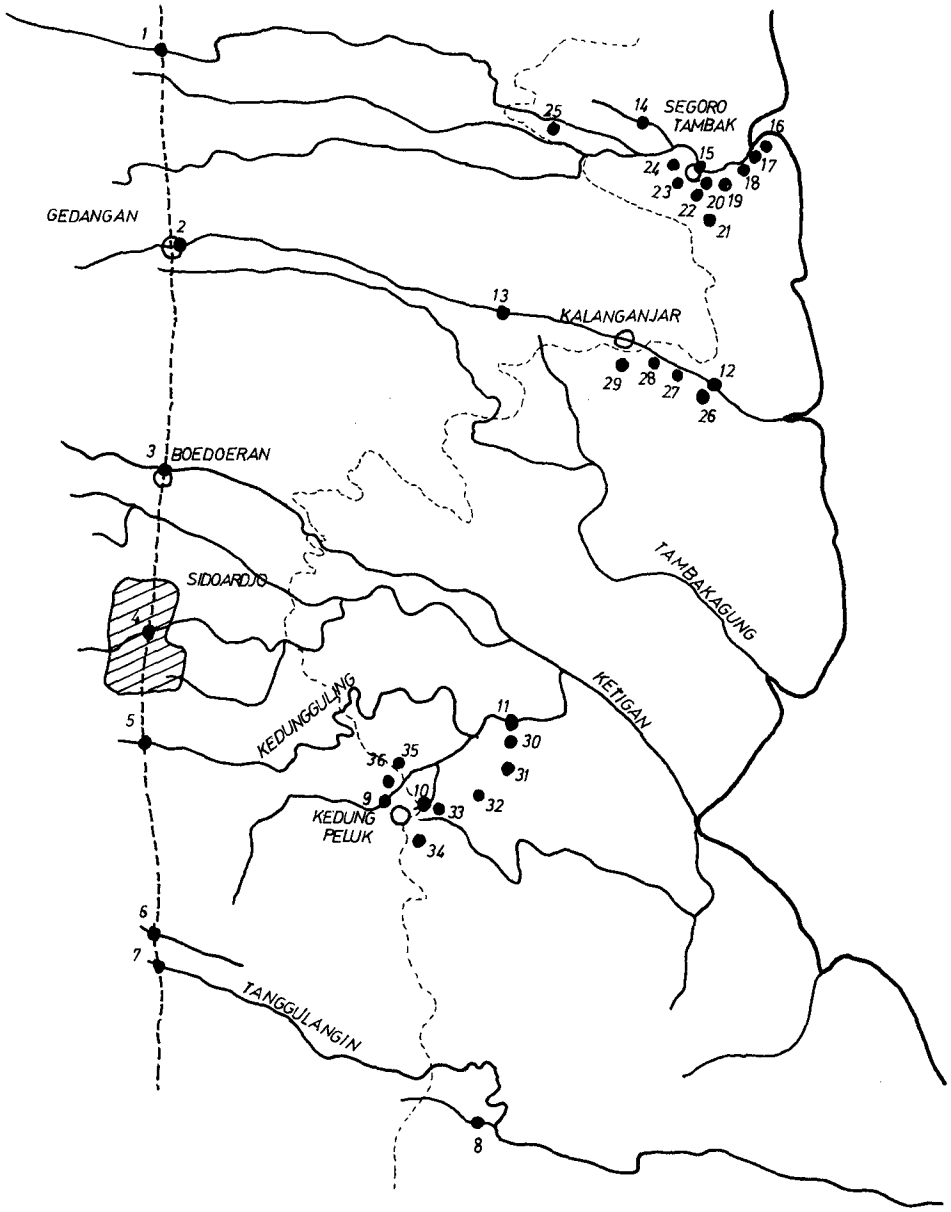

Figure 2 Sample-Stations in Fishponds and Canals in the River-Delta of the Brantas.

Table 1. Residues Found in Canals and Fish Ponds (see Figure 2)

No.	Date	α (ppb)	β (ppb)	S+* (ppb)	Total (ppb)
Canals					
1	12.3.70	0.03	0.04	0.06	0.13
2	12.3.70	<0.01	<0.01	<0.01	<0.03
3	12.3.70	0.3	0.32	0.18	0.8
4	12.3.70	0.25	0.23	0.08	0.56
5	12.3.70	0.07	0.08	0.15	0.3
6	10.3.70	0.32	0.27	0.42	1.0
	12.3.70	0.3	0.38	0.39	1.1
7	10.3.70	5.8	2.4	0.4	8.6
	12.3.70	0.23	0.24	0.55	1.0
8	18.3.70	<0.01	<0.01	<0.01	<0.03
9	18.3.70	<0.01	<0.01	<0.01	<0.03
10	12.3.70	0.16	0.06	<0.01	0.22
11	12.3.70	0.1	0.08	0.25	0.43
12	18.3.70	0.04	0.02	0.03	0.09
13	20.3.70	0.02	<0.01	0.05	0.07
14	18.3.70	0.15	0.06	0.37	0.58
15	18.3.70	0.15	0.06	0.33	0.54
Fish Ponds					
16	18.3.70	<0.01	<0.01	<0.01	<0.03
17	18.3.70	<0.01	<0.01	<0.01	<0.03
18	18.3.70	<0.01	<0.01	<0.01	<0.03
19	18.3.70	<0.01	<0.01	<0.01	<0.03
20	18.3.70	0.07	0.07	0.23	0.37
21	18.3.70	<0.01	<0.01	<0.01	<0.03
22	18.3.70	<0.01	<0.01	<0.01	<0.03
23	18.3.70	<0.01	<0.01	<0.01	<0.03
24	23.3.70	<0.01	<0.01	<0.01	<0.03
25	19.3.70	0.15	0.06	0.33	0.54
26	18.3.70	<0.01	<0.01	<0.01	<0.03
27	18.3.70	<0.01	<0.01	<0.01	<0.03
28	18.3.70	<0.01	<0.01	<0.01	<0.03
29	18.3.70	<0.01	<0.01	<0.01	<0.03
30	12.3.70	<0.01	<0.01	<0.01	<0.03
31	12.3.70	<0.01	<0.01	<0.01	<0.03
32	12.3.70	<0.01	<0.01	<0.01	<0.03
33	12.3.70	0.25	0.08	0.44	0.77
34	18.3.70	<0.01	<0.01	<0.01	<0.03
35	18.3.70	<0.01	<0.01	0.16	0.16
36	18.3.70	<0.01	<0.01	<0.01	<0.03

*S+ = Thiodan Sulfate

Table 2. Residues Found in the River System and in the Water of the Madura Sea (see Figure 1)

No.	Date	α (ppb)	β (ppb)	S+* (ppb)	Total (ppb)	
River System						
1	16.3.70	<0.01	<0.01	<0.01	<0.03	
2	16.3.70	0.07	0.016	0.08	0.31	
3	16.3.70	0.08	0.05	0.1	0.23	
4	16.3.70	0.6	1.2	0.4	2.2	
	21.3.70	0.02	0.01	0.04	0.07	
5	16.3.70	5.0	2.0	-	7.0	
	21.3.70	0.05	0.02	0.12	0.19	
6	16.3.70	0.35	0.35	0.05	0.75	
	21.3.70	0.03	0.02	0.1	0.15	
7	16.3.70	0.33	0.25	0.03	0.61	
8	19.3.70	0.05	0.06	0.45	0.56	
9	19.3.70	0.04	0.04	0.38	0.46	
10	19.3.70	0.02	0.03	0.38	0.43	
11	19.3.70	<0.01	<0.01	0.18	0.18	
12	19.3.70	0.15	0.18	0.4	0.73	
13	19.3.70	<0.01	0.03	0.37	0.4	
14	19.3.70	<0.01	0.03	0.24	0.27	
15	19.3.70	<0.01	0.03	0.22	0.25	
16	12.3.70	0.06	0.04	0.13	0.23	
17	19.3.70	0.02	0.02	0.22	0.26	
18	10.3.70	0.24	0.14	0.22	0.60	(right)
	10.3.70	0.03	0.07	0.22	0.32	(left)
	10.3.70	0.12	0.02	0.21	0.35	(middle)
	12.3.70	0.01	0.02	0.13	0.16	(")
29	19.3.70	0.01	0.03	0.28	0.31	
Madura Sea						
19	13.3.70	<0.01	<0.01	<0.01	<0.03	(1m)
20	13.3.70	<0.01	<0.01	<0.01	<0.03	(1m)
	23.3.70	<0.01	<0.01	<0.01	<0.03	(1m)
21	24.3.70	<0.01	<0.01	0.03	0.03	(10m)
	24.3.70	<0.01	<0.01	<0.01	<0.03	(surface)
22	13.3.70	<0.01	0.02	0.19	0.21	(")
	13.3.70	<0.01	<0.01	<0.01	<0.03	(1m)
	13.3.70	<0.01	<0.01	<0.01	<0.03	(3m)
23	24.3.70	<0.01	<0.01	<0.01	<0.03	(surface)
	24.3.70	<0.01	<0.01	<0.01	<0.03	(2.5m)
24	13.3.70	<0.01	<0.01	<0.01	<0.03	(1m)
25	13.3.70	0.07	0.07	0.3	0.44	(surface)
26	13.3.70	0.09	0.05	0.11	0.25	(")
	24.3.70	<0.01	<0.01	0.03	0.03	(2.7m)
	24.3.70	<0.01	<0.01	0.14	0.14	(surface)
27	13.3.70	0.09	0.05	0.28	0.42	(")
28	13.3.70	<0.01	<0.01	0.17	0.17	(")

*S+ = Thiodan Sulfate

packed with 3% SE 30 on Chromosorb W, N_2, 190°C column temperature). Calculations were made on the basis of measuring the peak height using a calculation factor which included the sample volume (850 ml of 1000 ml), the recovered quantity (80%) and the extraction volume (25 ml of 30 ml). Results are expressed in mg/l (ppm.), respectively µg/l (ppb.).

RESULTS

Rivers and Canals (Fig. 1 and 2, Table 1 and 2)

The residue concentrations (total of α-,β-Thiodan and Thiodan sulfate) amounted to an average of 0.00046 ppm.. This brings the residue concentration to only about 1/3 of the amount necessary to reach the LC 100 of *Puntius javanicus*, the most sensitive fish known up to now in the waters of Java (LC 100=0.00125 ppm) and only about 1/20 of the concentration necessary to reach the LC 100=0.01 ppm at which river fish normally react. Therefore, on the average, a biological safety factor of 10 was indicated.

The highest values found were 0.0086 and 0.007 ppm.. Both were below the LC 100 for normal river fish. Since the portion of Thiodan sulfate in the total residues is insignificant, it is believed that these two high values are so-called fresh residues i.g. the Thiodan must have gotten into the river shortly before sampling either by careless handling (rinsing of implements) or coming from brooks, travelling over a short distance only, after having collected water from newly treated rice fields with open dams.

However, these residues decrease very fast within a short period of time (see Table 2). This decrease may have been brought about either by dilution with non-contaminated river water or by natural decomposition. The latter is proven by a rising level of Thiodan sulfate. Insignificant composite residues (total of all degradation products) always contain high proportions of sulfate, a fact which also points to degradation of Thiodan in water.

Fish Ponds (Fig. 2, Table 1)

The samples taken from fish ponds in the Brantas delta situated near the irrigation canals, in 84% of the cases did not show any residues at all, though the water used for filling the ponds (which is done several times a year) originates from the main canals. As to the remaining 14%, only one sample showed residues of 0.0008 ppm. This pond was located alongside the Soko river (0.00022 ppm). It is likely that Thiodan was applied nearby and that residues had reached the pond accidentally. However, living fish showing no symptoms of poisoning were found in this pond as well.

Madura Sea (Fig. 1, Table 2)

No residues at all (<0.00003 ppm) were found in the water of the Madura Sea away from the river deltas. As expected, the residues found near the river deltas showed values equal to those found in the rivers and canals, but in the top layers of the water only. By density measurements and chloride analyses of the water samples it was possible to prove that the inflowing fresh water had formed a layer on top of the sea water. The bulk of water underlaying the fresh water did not contain any Thiodan (<0.00003 ppm). A high proportion of the metabolite "Thiodan sulfate" in the residues of the fresh water layer showed that vigorous degradation had taken place.

SUMMARY

In the so-called BIMAS PROJECT area of East Java investigations concerning Thiodan residues were made in the waters of the main waterway Brantas. The samples were taken from the water system towards the end of the main campaign of treatment with the insecticide Thiodan. Rivers, canals, fish ponds in the coastal area and sea water were analysed. It was found that on the average a low Thiodan content resulting from quick degradation of Thiodan existed in the flowing water system. In the fish ponds filled with water from the canal system, the residue values were almost below the detection limit (0.00003 ppm). The water of the Madura Sea contained insignificant residues in the top layer of fresh water near the river deltas. The sea water was free from Thiodan.