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Accumulation and Dissipation of Organosulfur Compounds in Short-Necked Clam and Eel

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The transfer of organosulfur compounds to short-necked clam and eel (OGATA et al.1977), and their elimination from contaminated biota after being transferred and reared in clean sea water (OGATA & MIYAKE 1978) have been reported. Furthermore, the compounds transferred to fish or shellfish from crude oil suspension have been identified by a gas chromatograph-mass spectrometer (OGATA et al.1979a) and by a gas chromatograph-mass spectrometer attached with computer system (OGATA & MIYAKE 1979b). Thereafter, the organosulfur compounds found in marine biota have been presumed as indices of contamination by petroleum or crude oil (OGATA & MIYAKE 1979b).

In the present report, the experiment was designed to examine the tendencies of accumulation and elimination of several organosulfur compounds in marine biota kept in oil contaminated water or in clean sea water after the contamination. The obtained data were analyzed by curve fit method, the concentration ratio versus rearing time, concentration factor and half-life of each identified organosulfur compound was calculated.

MATERIALS AND METHODS

The petroleum used was a mixture of the Arabian Light Crude oil and the Zubea oil, the composition ratio of 4 to 1 by weight, with a specific gravity of 0.857. The fish tank was 45x60x37 cm in size. Control eels and short-necked clams were reared in clean water kept at 20°C with a constant air supply.

Short-necked clams (380) weighing about 15g each and 70 eels weighing 130 to 180g each were separately acclimated in tanks with clean sea water. Before the exposure experiment, a control group of short-necked clams or eels were sampled from acclimation tank. After 16 days of acclimation, short-necked clams were placed on the surface of the sea mud and reared in sea water containing 50 ppm of crude oil for 8 days as an exposure experiment. Eels were kept in 250 ppm oil suspension for 16 days. The suspension in the exposure tank was exchanged daily with new one. Short-necked clams (40) were sampled randomly 1,4,8 and 15 days after exposure and were frozen until analyzed.

Six eels were taken out 1,2,4,8 and 15 days after exposure and were frozen until analyzed. The rearing water was sampled daily and the levels of organosulfur compound were monitored.

After the exposure experiment, the remainder of the short-necked clams or eels were transferred to a tank with clean sea water as a disappearance experiment. Then the short-necked clams

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and the eels were taken out on the day, 2,3,5,8 and 15 and on the day 1,2,4,8 and 16 respectively. Eel flesh from one sample and the soft bodies from 10 short-necked clams were homogenized by a Waring blender in the cold room. Forty clams were divided into 4 groups, 10 clams were analyzed together; eels were analyzed individually. The analysis procedures and gas chromatographic determination for organosulfur compounds in biota and water were as described by OGATA & MIYAKE (1979b) with the flame photometric detector (FPD). The amount of organosulfur compound injected onto a gas chromatograph correlated to the square root of the peak height (FAIR & THRUSH 1968). Therefore the concentration ratio of organosulfur compounds in biota to those in the water were calculated with the square root of peak height ratio to the internal standard (the corrected peak height ratio). Initially we confirmed that the amount of authentic dibenzothiophene is proportional to square root of its peak height. Peaks of these organosulfur compounds in the biota were those which had been identified from the crude oil suspension by a gas chromatograph-mass spectrometer (OGATA et al. 1979a) and by a gas chromatograph-mass spectrometer attached with computer system (OGATA & MIYAKE 1979b).

RESULTS AND DISCUSSION

Gas chromatographic patterns of crude oil and extracts from clams and eels after exposure to the oil suspension, and their controls are shown in Fig. 1. Gas chromatographic studies revealed the transfer of identical peaks from crude oil to biota samples after the exposure. Mainly larger molecular weight compounds such as dibenzothiophenes transferred to the short-necked clams and the pattern looked like that of crude oil. On the other hand smaller molecular weight compound such as alkylbenzothiophenes transferred to eels. These discrepancies may be rationalized as follows; clams might have taken up these compounds not only via solution but also as particles from oil suspension in contrast to eels which might absorb them mostly through the gills via solution.

Table 1 and 2 show the accumulation and discharge process in clams (Table 1) and eels (Table 2). The accumulation ratios were calculated with the corrected peak height ratio, mentioned in methods,of biota sample to water sample, and the ratios in the discharge process were obtained from the comparison of the corrected peak height ratio of biota to that of water sample at the final exposure day. Overall, the ratios of both clams and eels increased as the exposure time increased and complete tissue saturation was not achieved within the present exposure periods used. Two characteristic tendencies were observed in the accumulation process. First, the isomers of each derivative compound, alkylbenzo- or dibenzothiophene, were accumulated proportionally similar to each other. Second, the clams had greater tendency to accumulate larger molecular weight compounds, and was not observed to accumulate monoalkylbenzothiophenes; the eels had the tendency to accumulate smaller molecular weight compounds and was not observed to accumulate trialkyldibenzothiophenes.

These two characteristics are well coincident with the gas chromatographic patterns shown in Fig. 1 and the tendencies of these

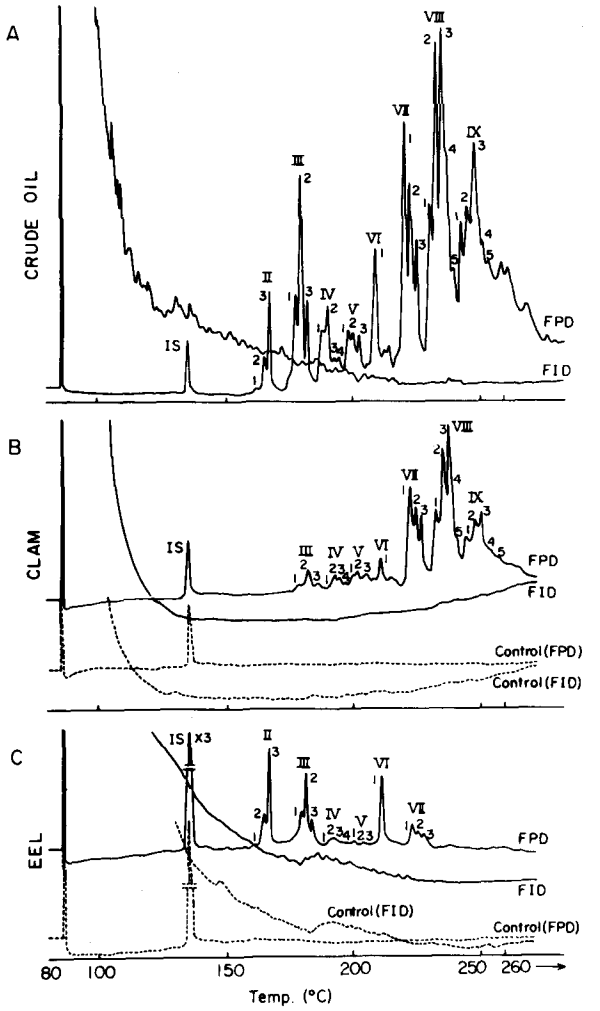

Figure 1. Gas chromatograms of organosulfur compounds. (A) Crude oil (7.5 μg). Upper curve is drawn by FPD and lower curve is drawn by the monitor of FID. (B) Straight line on chromatogram indicates short-necked clams reared in the suspension for 4 days taken on day; IS : internal standard. Dotted line does control short-necked clam. (C) Straight line on chromatogram indicates eels reared in the crude oil suspension for 2 days ; dotted line does control eel. Analytical sensitivity of FPD in (A) is 4 times as much as (B and C), injected volume; 1 μL.

TABLE 1

Changes in concentration ratios of organosulfur compound in short-necked clam (N=4)

Compound	Peak	No*	Sampling period after being reared in crude oil suspension (days)			Sampling period after being reared in clean sea water (days)					half life (days)
			1	4	8	1	3	5	8	15	
Di-a -bzth	II	1**	62±75	66±115	98±169	nd	nd	nd	nd	nd	NA
		2	77±54	77± 67	65±112	nd	nd	nd	nd	nd	NA
Tri-a -bzth	III	1	81±84	115± 28	91± 32	nd	nd	nd	nd	nd	NA
		2	143±80	155± 49	120± 21	31±27	nd	nd	nd	nd	0.5
		3	121±57	96± 23	102± 21	9±15	nd	nd	nd	nd	0.3
Tetra-a -bzth	IV	1	nd	129± 38	103± 4	35±30	nd	nd	nd	nd	0.6
		2	nd	164± 16	155± 3	72±14	14±24	nd	nd	nd	0.9
		3	nd	216±100	306± 24	163±62	nd	nd	nd	nd	1.1
		4	nd	217± 46	217± 25	25±43	nd	nd	nd	nd	0.3
Penta-a -bzth	V	1	nd	103± 31	163± 18	84±18	64±11	22±22	8±15	3± 5	2.6
		2	nd	139± 28	220± 34	102±24	77±17	26±27	20±35	2± 3	2.3
		3	nd	97± 31	162± 28	82±11	60±10	19±20	12±21	2± 3	2.4
Di-bzth	VI	1	40±11	90± 18	111± 6	59±22	28±11	32±15	29± 2	2± 1	2.9
Mono-a -dibzth	VII	1	46±99	150± 24	188± 18	71± 5	38±13	17± 6	13± 1	3± 1	2.8
		2	45±12	126± 19	154± 18	69±27	37±16	15± 6	4± 7	3± 1	2.6
		3	72±16	197± 40	214± 23	86±16	58±17	29±17	5± 9	5± 1	2.8
Di-a -dibzth	VIII	1	47±14	150± 27	189± 33	115±53	85±14	42±13	27± 7	6± 2	3.1
		2	38±13	158± 31	183± 31	136±27	66±16	37± 9	13± 4	4± 2	2.7
		3	37±22	139± 69	213± 38	135±49	71± 2	42±20	19± 6	5± 2	2.8
		4	65±28	202± 47	219± 34	168±62	62±16	41± 7	22± 2	5± 2	2.8
		5	55±18	171± 18	206± 31	129±16	71±29	56±13	23± 5	5± 2	2.9
Tri-a -dibzth	IX	1	29± 9	72± 8	216± 3	111± 8	67± 3	38±26	35± 7	24± 5	5.3
		2	34±23	110± 12	224± 47	173±41	115± 7	74±45	65±13	nd	4.3
		3	39±22	114± 14	198± 42	177± 5	104± 1	68±31	47±11	24±10	4.9
		4	34±15	76± 10	147± 1	114±12	74±10	56±22	36± 5	17± 8	4.9
		5	74±60	122± 27	158± 38	130±39	118±46	80±26	66±17	8± 4	3.6

* Peak groups and numbers were in Fig.1. ** Peak number of isomers. nd; not detected. NA; not available.

TABLE 2

Changes in concentration ratios of organosulfur compound in eels (N=6)

Compound	Peak	No*	Sampling period after being reared in crude oil suspension (days)					Sampling period after being reared in clean sea water (days)					half life (days)
			1	2	4	8	16	1	2	4	8	16	
Mono-a -bzth	I	1**	43±35	92±52	84± 53	99±100	315±103	276±160	349±180	nd	268± 56	nd	38.7
		2	35±19	58±33	108± 71	173±122	556±136	279±128	378±144	278±168	264± 54	93± 93	6.7
Di-a -bzth	II	1	47±15	60±31	114± 78	204±137	669±168	636±144	509±232	443±210	435± 92	220±121	13.0
		2	40±10	55±37	142± 97	260±169	732±160	727±158	535±216	538±220	470±102	266±150	14.9
		3	32±12	65±34	142±101	282±175	791±166	784±158	574±229	538±217	497±107	282±165	8.8
Tri-a -bzth	III	1	45±12	86±47	178±124	403±179	935±176	980±181	688±219	774±184	614±121	390±157	10.7
		2	43±11	96±51	193±138	463±191	1088±741	1093±199	794±241	900±197	696±133	462±172	11.6
		3	38± 7	77±41	138±102	342±133	681±121	661±106	431±139	412± 89	335± 66	181± 77	11.4
Tetra-a -bzth	IV	1	6±13	49±27	109± 75	258± 87	535± 89	467±210	395± 97	471± 91	344± 61	233± 72	14.5
		2	6±12	48±26	92± 66	226± 77	432± 76	478± 74	323± 91	362± 71	270± 51	166± 52	11.4
		3	nd	28±17	39± 24	75± 43	151± 35	138± 85	62± 48	145± 72	86± 19	39± 40	9.6
		4	nd	30±18	47± 30	106± 36	207± 38	195±119	96± 72	194± 71	495±434	562±562	8.1
Penta-a -bzth	V	1	nd	nd	29± 18	59± 16	114± 26	nd	91± 32	79± 55	46± 27	23± 24	6.9
		2	nd	nd	25± 22	61± 18	138± 28	67± 68	89± 23	84± 59	53± 30	45± 11	12.7
		3	nd	nd	16± 16	44± 18	71± 48	nd	32± 38	72± 57	39± 24	12± 21	7.0
Di-bzth	VI	1	31±19	69±29	177± 54	259±126	463± 57	466± 65	292± 48	249± 45	214± 30	113± 38	8.2
Mono-a -dibzth	VII	1	58± 5	87±24	144± 32	229± 71	260± 36	69±119	149± 29	23± 39	nd	nd	1.3
		2	52± 5	77±20	125± 25	289± 61	260± 39	71±123	151± 37	23± 39	nd	nd	1.3
		3	73± 6	105±27	181± 31	257± 80	356± 65	99±172	211± 58	34± 58	nd	nd	1.4
Di-a -dibzth	VIII	1	nd	7±14	4± 7	51± 68	nd	nd	nd	nd	nd	nd	NA
		2	nd	9±17	4± 7	50± 67	nd	nd	nd	nd	nd	nd	NA
		3	nd	11±22	19± 33	56± 74	nd	nd	nd	nd	nd	nd	NA
		4	nd	nd	16± 28	42± 55	nd	nd	nd	nd	nd	nd	NA
		5	nd	nd	15± 26	34± 42	nd	nd	nd	nd	nd	nd	NA

* Peak groups and numbers were in Fig.1. **Peak number of isomers. nd; not detected. NA; not available.

compound to each biota. The discharge process showed different patterns between clams and eels. Clams discharged contaminated organosulfur compounds quickly and eels showed a tendency to retain them relatively longer than the clams. The half-life of each compound in clams and eels were calculated from the data by curve fit method. As the population of the half-lives of these compounds in clams or eels looked like a normal distribution, the mean and the standard deviation calculated. These are 2.6 $\pm$ 1.4 days in clams and 10.4 $\pm$ 7.8 days in eels. The significance of the differency between them showed $p < 0.005$.

This discrepancy in half-lives might be reasoned by different lipid content. Comparing the half-lives in eels of organosulfur compounds with those of other aromatic hydrocarbons such as benzene and xylenes reported by (OGATA & MIYAKE 1978), the former were retained longer than the latter, the half-lives were 0.5 days for benzene to 2.6 days for p-xylene.

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