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Effects of the Toxicity of Mineral Oil and Solvent Emulsifier upon Sea Fishes

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The solvent emulsifier does not solely exist in the sea water but in a state necessarily mixed with spilt oil. In the present experiment, therefore, we are going to discuse the effects of toxicity, respectively with fish and with mineral oil, through the observations of the fishes bred in the sea water containing mineral oils and solvent emulsifier.

Keywords ; oil pollution, solvent emulsifier

With the development of the marine transportation of petroleum and with the wider exploitation of submarine oil fields, troubles of oil spilling have lately been multiplied. As a natural consequence of it, water pollution by oil occurs more and more frequently, and its inevitable effects on the marine life has become one of the serious social problems today. The reports on those effects have also run to a considerable number.

We have, however, so few reports of the results from the experiments about the effects of the toxicity of mineral oils upon fishes, and most of them, if any, are nothing more of those of the toxicity of such individual components as Phenol, Cresol, Naphthalene, Xylene, Benzene, Hydrogen sulfide and all, upon freshwater fishes and their spawn.

In recent years, the toxicity of the solvent emulsifier spread over the sea water in case of the oil spilling accidents has raised issues, where it is often admonished that the solvent emulsifier has further multiplied the damages in those troubles. Let us first outline, therefore, the original aims of the dispersal of solvent emulsifier and about its effects. The solvent emulsifier is one of the chemicals, which, however, neither decomposes nor detoxicates mineral oils by its chemical reaction, but its virtue is only of a physical function(OHKUBO, 1976). In other words, the solvent emulsifies mineral oils into corpuscles to be suspended in the sea water. The corpuscular oil is aimed to be decomposed and extinguished by marine bacteria and through the reaction with sea water.

Materials and Methods

The sea fishes used in the present experiment are these 6 species : marine catfish (*Plotosus anguillaris*), common mullet (*Mugil cephalus*), chicken grunt (*Parapristipoma trilineatum*), gluttonous goby (*Chasmichthys gulosus*), black rockfish (*Sebastes inermis*), and stone flounder (*Kareius bicoloratus*).

The oils used in the experiment are of the following kind; crude oil (Arabian right crude oil), heavy oil A, heavy oil B, and solvent emulsifier, whose trade name is NEOS AB 3000 and whose principal ingredient is the diethanol amid of nonionic detergent. The rate of mineral oil and the added solvent emulsifier was made up 3 to 1, to follow with suit the concentration of the solvent which will be spread over in cases of actual oil spill. For the adjustment of the breeding water which contains those mineral oils, ultrasonication had been operated for 5 minutes to raise the suspension to the full (TOKUDA, 1976).

The fishes used in the experiment had been bred in water tanks, with capacity of 20 liters, the breeding water fully kept aerated during the experiment, and no food had been given to the experimental fishes.

We have a couple of reports in which they discuss upon the poisoning power of the mineral oils effecting fishes, figured by the mortality in a given time, of the fishes in the breeding water of a given concentration. In the present paper, however, to make clearer the comparison in the experimental results, we have first figured out the values of TLm (median tolerance limit) under which the toxicity of mineral oils will be discussed. For the estimation of TLm values, DOUDOROFF'S method (1951) was adopted.

Results

Table 1 shows the mineral oils and test fishes used in the present experiment.

Table 1. Toxicity test for fishes in sea water containing oils and solvent emulsifier.

Substances / Fishes	C.O.	C.O. + S.E.	H.A.	H.A. + S.E.	H.B.	H.B. + S.E.	S.E.
Marine catfish (young)		○		○		○	○
(adult)		○					
Common mullet	○	○					○
Chicken grunt		○		○		○	○
Gluttonous goby		○		○		○	○
Black rockfish		○					
Stone flounder	○	○	○	○	○	○	○

○, tested fish; C.O., crude oil; H.A., heavy oil A; H.B., heavy oil B; S.E., solvent emulsifier

1. Effects on marine catfish

As test fish were taken marine catfish of different size: one is with young fish (mean body length 21.75 mm, mean body weight 0.09 g) of some 50 days old after hatching, and the other is with adult fish (mean body length 162.60 mm, mean body weight 36.78g). The experiment bad been carried out with 5 fishes in each experiments of water temperature 23±2°C. The values of the dissolved oxygen and pH in the breeding water had been kept within the normal condition limits for the breeding.

1) The kind and concentration of the mineral oils used in the experiment on the young fish, the cumulative mortality, and the quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 2. The TLm values of the mineral oils on the test fish are in Table 3.

Table 2. Effects of mineral oil and solvent emulsifier upon young marine catfish ; time course of cumulative mortality (%), dissolved oxygen and pH.

Substances		C.O.+S.E.		H.A.+S.E.			H.B.+S.E.			S.E.		control
Conc.(cc/l) / Time		0.1	1	0.1	1	10	0.1	1	10	0.3	3.3	
2 (hr.)					40	100			40			
4					80			40	100			
6			20		100			80			20	
12			100					100		20	100	
24		20		20						20		
36		20		60				60		20		
48		40		60				60		20		20
72		60(%)		80				80		20		20
D.O. (ppm)	1(hr.)	6.6	6.6	6.6	6.3	6.1	6.6	6.2	6.2	6.2	6.7	6.3
	12	7.0	7.0	7.0	6.9		7.0	6.6	6.7	6.7	6.7	7.0
	48	6.8		6.9			6.9			6.9	6.4	6.9
pH	1(hr.)	8.1	8.1	8.1	8.2	8.1	8.1	8.1	8.1	8.0	8.0	8.1
	12	8.1	8.1	8.1	8.0		8.1	8.0		8.0	7.9	8.1
	48	8.1		8.1			8.1			8.0		8.0

Table 3. TLm of mineral oil and solvent emulsifier upon young marine catfish.

TLm(cc/l) / Substances	6(hr.)	12	24	48	72
C.O. + S.E.	>1.0	0.3	0.2	0.1	<0.1
H.A. + S.E.	0.3	0.3	0.2	<0.1	<0.1
H.B. + S.E.	0.4	0.3	0.3	<0.1	<0.1
S.E.	>3.3	0.9	0.9	0.9	0.9

From those Tables, strength of the toxicity of the mineral oils on the young fish is in the following order ; heavy oil A+solvent emulsifier ≧ heavy oil B + solvent emulsifier ≧ crude oil+solvent emulsifier > solvent emulsifier. Excepting the case of the solvent emulsifier alone, however, no significant differences in the toxicity were found between the kinds of mineral oil. Each of them did show a strong toxicity.

2) The test oil for the experiment on the adult fish was only crude oil+solvent emulsifier examined, but the concentration of the mineral oils, the cumulative mortality, the quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 4. The TLm values of the mineral oils on the test fish are in Table 5.

Table 4. Effects of mineral oil and solvent emulsifier upon adult marine catfish ; time course of cumulative mortality (%), dissolved oxygen and pH.

Substances		C. O. + S. E.			control
Time \ Conc. (cc/l)		1	10	100	
1 (hr.)			80	100	
12			80		
24			100		
48		0(%)			0
D. O. (ppm)	1 (hr.)	5.7	5.7	5.7	5.7
	24	5.7	6.3		6.4
pH	1 (hr.)	8.1	8.1	8.1	8.1
	24	7.5	7.8		7.7

Table 5. TLm of mineral oil and solvent emulsifier upon adult marine catfish.

Substance \ TLm(cc/l)	6(hr.)	12	24	48
C. O. + S. E.	4.3	4.3	3.2	3.2

Those Tables affirmed us that the adult marine catfish have more than ten times as high tolerance against the toxicity of mineral oils as the young fish.

2. Effects of common mullet

The experiment was made, breeding 5 young common mullet (mean body length 69.47 mm, mean body weight 6.47g). In each of the experiments the water temperature was 20±2°C. The kind and concentration of the mineral oils used in the experiment, the cumulative mortality, and the quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 6, and TLm values of the mineral oils on the test fish are in Table 7.

Table 6. Effects of mineral oil and solvent emulsifier upon common mullet; time course of cumulative mortality (%), dissolved oxygen and pH.

Substances		C. O.			C. O. + S. E.			S. E.			control
Conc. (cc/l) / Time		1	10	100	1	10	100	0.3	3.3	33.3	
2 (hr.)				80			100				
6				100		100				60	
12					20			20	20	100	
24					20			40	40		
48					100			40	100		
72		0(%)	40					40			40
D. O. (ppm)	48(hr.)	5.1	6.2	7.2	5.5	6.2	5.8	4.8	6.2	6.0	7.3
pH	24(hr.)	7.8	7.8	8.1	7.4	7.4	7.4	7.4	7.3	7.2	7.9
	48	7.6	7.8		7.4			7.5	7.3		8.1

Table 7. TLm of mineral oil and solvent emulsifier upon common mullet.

TLm(cc/l) / Substances	6 (hr.)	12	24	48
C. O.	32	32	32	32
C. O. + S. E.	3.2	2.4	2.4	< 1
S. E.	22.5	7.8	4.8	0.5

As those Tables show, once the solvent emulsifier mixed with crude oil, its toxicity on the fish becomes over ten times as strong, and that the solvent emulsifier is stronger in its toxicity than crude oil.

3. Effects on chicken grunt

The experiment was made with 10 fishes (mean body length 96.59mm, mean body weight 19.95g). In each of the experiments the water temperature was 23±2°C. The kind and concentration of the mineral oils used in the experiment, the cumulative mortality and the quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 8, and the TLm vales of the mineral oils on the test fish are in Table 9.

From those Tables, the strength of the toxicity of the mineral oils is in the following order: heavy oil A+solvent emulsifier>heavy oil B+solvent emulsifier≒crude oil+solvent emulsifier> solvent emulsifier.

4. Effects on gluttonous goby

The experiment was made with 5 fishes (mean body length 34.78mm, mean body weight 0.98g). In each of the experiment the water temperature was 23±2°C. The kind and concentration of the mineral oils used in the experiment, the cumulative mortality

Table 8. Effects of mineral oil and solvent emulsifier upon chicken grunt ; time course of cumulative mortality (%), dissolved oxygen and pH.

Substances		C.O. + S.E.		H.A. + S.E.		H.B. + S.E.		S.E.		control
Conc. (cc/l) / Time		0.1	1	0.1	1	0.1	1	0.3	3.3	
6 (hr.)		20	20	10	80		30			
12		40	50	40	90	10	60			
24		60	100	60	100	40	90			
36		80		80		60	100			
48		80(%)		100		70		0	40	0
D.O. (ppm)	1(hr.)	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7	5.7
	24	5.2	4.0	6.2	6.2	5.6	5.6	4.5	4.6	6.6
	48	6.3		6.4		6.4		5.4	6.5	6.7
pH	1(hr.)	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1	8.1
	24	7.5	7.3	7.7	7.8	7.6	7.6	7.4	7.4	7.8
	48	7.8		7.9		7.9		7.9	7.9	8.0

Table 9. TLm of mineral oil and solvent emulsifier upon chicken grunt.

TLm(cc/l) / Substances	6 (hr.)	12	24	48
C.O. + S.E.	>1	1	<0.1	<0.1
H.A. + S.E.	0.4	0.2	<0.1	<0.1
H.B. + S.E.	>1	0.6	0.2	<0.1
S.E.	>3.3	>3.3	>3.3	>3.3

Table 10. Effects of mineral oil and solvent emulsifier upon gluttonous goby; time course of cumulative mortality (%), dissolved oxygen and pH.

Substances		C.O. + S.E.		H.A. + S.E.		H.B. + S.E.		S.E.			control
Conc. (cc/l) / Time		1	10	1	10	1	10	0.3	3.3	33.3	
6 (hr.)					20						
12					80	60					
24			40	20	100	100					
36			80	20							
48		0(%)	100	20		20		0	0	0	0
D.O. (ppm)	1(hr.)	6.6	6.6	6.3	6.1	6.2	6.2	6.2	6.7	6.6	6.3
	24	7.0	7.0	6.9	6.8	6.6	6.7	6.7	6.7	6.9	7.0
	48	6.9	6.9	6.8		6.8		6.9	6.4	6.8	6.9
pH	1(hr.)	8.1	8.1	8.2	8.1	8.1	8.1	8.0	8.0	8.1	8.1
	24	8.1	8.0	8.0	8.1	8.0	8.1	8.0	7.9	8.0	8.1
	48	8.0	8.0	8.0		8.0		8.0	7.9	7.9	8.0

Tabie 11. TLm of mineral oil and solvent emulsifier upon gluttonous goby.

TLm(cc/l) / Substances	6 (hr.)	12	24	48
C. O. + S. E.	>10	>10	>10	3.2
H. A. + S. E.	>10	4.2	2.4	2.4
H. B. + S. E.	>10	6.8	3.2	2.4
S. E.	>10	10	10	10

and the quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 10, and the TLm values of the mineral oils on the test fish are in Table 11.

From those Tables, the strength of the toxicity is in the following order:heavy oil A+solvent emulsifier> heavy oil B+solvent emulsifier> crude oil+solvent emulsifier > solvent emulsifier.

5. Effects on black rockfish

The experiment was made with 5 fishes (mean body length 113.93mm, mean body

Table 12. Effects of mineral oil and solvent emulsifier upon black rockfish; time course of cumulative mortality (%), dissolved oxygen and pH.

Substance		C. O. + S. E.		control
Time \ Conc. (cc/l)		0.1	1	
6 (hr.)			20	
12			40	
24			100	
36		40		
48		80(%)		0
D. O. (ppm)	1(hr.)	5.7	5.7	5.7
	12	5.5	5.2	5.7
	24	5.2	4.0	6.4
	48	6.3		6.3
pH	1(hr.)	8.1	8.1	8.1
	12	7.6	7.4	7.8
	24	7.5	7.3	7.7
	48	7.9		7.8

Table 13. TLm of mineral oil and solvent emulsifier upon black rockfish.

TLm(cc/l) / Substance	6 (hr.)	12	24	48
C. O. + S. E.	>1	>1	0.3	<0.1

weight 49.57g). In each of the experiment the water temperature was 23±2°C. The experiment was in only one instance of the mixed oil, with solvent emulsifier added to mix in crude oil. The concentration, the cumulative mortality and the quantity of dissolved oxygen and pH values in the breeding water are shown in Table 12, and the TLm values on the test fish are in Table 13.

As those Tables show, orude oil+solvent emulsifier has a strong toxicant effect upon black rockfish.

6. Efeects on stone flounder

The experiment was made with 5 fishes (mean body length 118.77mm, mean body weight 36.95g). In each of the experiments the water temperature was 10 ±2°C. The kind and concentration of the mineral oils used in the experiment, the cumulative mortality and quantity of dissolved oxygen and pH values in the breeding water are as shown in Table 14, and the TLm values of the mineral oils on the test fish are in Table 15.

Table 15. TLm of mineral oil and solvent emulsifier upon stone flounder.

TLm(cc/l) / Substances	6 (hr.)	12	24	48	72
C. O.	>100	>100	>100	>100	>100
C. O. + S. E.	6.8	4.3	3.2	3.2	2.4
H. A.	>100	>100	23.5	23.5	14.7
H. A. + S. E.	4.3	3.2	0.7	0.3	0.3
H. B.	>100	>100	>100	>100	>100
H. B. + S. E.	>100	6.8	1.5	0.5	0.4
S. E.	> 33.3	> 33.3	> 33.3	7.9	1.1

As those Tables show, the strength of the toxicity of mineral oils, when solvent emulsifier mixed with it, becomes more than 10 times as strong. Here, as shown in Table 14, the toxicity of mineral oils, when used independently, is in order of strength ; heavy oil A > crude oil ≧ heavy oil B. On the other hand, in the case solvent emulsifier added to the mix, the toxicity of mineral oils in the TLm values for 24 and 48 hours, is shown in the following order; heavy oil A+solvent emulsifier > heavy oil B+solvent emulsifier ≧ crude oil +solvent emulsifier.

Discussion

The TLm values, for 24 and 48 hours, of the mineral oils, solvent emulsifier (NEOS AB 3000) and of their mixed oils, which had effects on those fishes used in the present experiment, are collectively shown in Table 16.

As is evident from the results of the experiments on common mullet and stone

Table 14. Effects of mineral oil and solvent emulsifier upon stone flounder; time course of cumulative mortality(%), dissolved oxygen and pH.

Substances		C. O.			C. O. + S. E.			H. A.			H. A. + S. E.				H. B.			C. O. + S. E.				S. E.			control
Conc. (cc/l) / Time		1	10	100	1	10	100	1	10	100	0.1	1	10	100	1	10	100	0.1	1	10	100	0.3	3.3	33.3	
2 (hr.)							100																		
6						60				20			80	100											
12				40		80				40			100							60	100				
24				40		100			20	100		60							40	100					
48				40					20			100							80				20	100	
72		0(%)	0	40	20			0			0				0	0	20	0	80			0	100		0
D. O. (ppm)	1(hr.)	7.6	7.8	7.7	7.2	7.2	7.2	7.9	7.8	7.7	7.9	7.3	6.9	7.0	7.7	7.8	7.8	8.0	5.9	6.5	7.0	7.3	7.0	7.0	7.5
	24	7.8	7.9	8.1	7.8	8.4	8.4	8.0	7.9	8.1	8.2	7.9	8.2	8.2	8.1	7.6	7.8	8.3	7.8	8.2	8.2	7.9	7.2	7.9	8.2
	48	8.3	8.3	8.3	6.9			8.2	8.2		8.1	7.3			8.2	7.2	8.3	8.3	7.3			7.2	5.6	6.8	8.0
	72	8.2	6.2	8.2	7.6			8.0	7.7		8.4				8.1	7.7	8.0	8.4	7.7			7.7	4.3		8.2
pH	1(hr.)	7.9	8.0	7.9	8.0	7.9	7.8	8.0	8.0	8.0	8.1	8.0	8.0	7.7	8.0	8.0	8.0	8.0	7.9	7.9	7.8	8.1	8.0	7.8	7.9
	24	7.8	8.0	7.9	7.8	8.0	8.0	7.9	7.9	8.0	7.9	7.8	8.0	8.0	7.7	7.7	7.8	7.9	7.7	7.9	7.9	7.7	7.6	7.7	7.8
	48	8.1	8.1	8.1	7.9			8.0	8.1		7.3	8.0			8.0	7.9	8.1	7.3	8.0			7.3	7.3	7.4	7.7
	72	8.1	7.9	8.0	7.8			8.0	8.0		7.4				8.0	7.7	8.0	7.4	8.0			7.8	7.3		7.7

Table 16. TLm for 24 and 48 hours of mineral oil and solvent emulsifier upon sea fishes.

Fshes	Marine catfish				Common mullet		Chicken grunt		Gluttonous goby		Black rockfish		Stone flounder	
	Young		Adult											
TLm(cc/l) / Substances	24(hr.)	48	24	48	24	48	24	48	24	48	24	48	24	48
C. O.					32	32							100	100
C. O. + S. E.	0.2	0.1	3.2	3.2	2.4	<1	<0.1	<0.1	>10	3.2	0.3	<0.1	3.2	3.2
H. A.													23.5	23.5
H. A. + S. E.	0.2	<0.1					<0.1	<0.1	2.4	2.4			0.7	0.3
H. B.													>100	>100
H. B. + S. E.	0.3	<0.1					0.2	<0.1	3.2	2.4			1.5	0.4
S. E.	0.9	0.9			4.8	0.48	>3.3	>3.3	>10	>10			>33.3	7.90

C. O., crude oil; H. A., heavy oil A; H. B., heavy oil B ; S. E., solvent emulcifier (NEOS AB 3000)

flounder, the toxicity of mineral oils become more stronger when solvent emulsifier is mixed in them. The conceivable reasons are that mineral oils, essentially soluble in water and of low toxicity becuase of its incomplete dispersion in water, are emulsified when the solvent is added, and their diffusion into water is so much accelerated that the occasions of their contact with fishes becomes more frequent, and as the result the toxicity also produces a strong effect.

Next, the tolerance against mineral oils, compared among fishes, is stronger in marine catfish (adult), gluttonous goby and stone flounder, and weak in common mullet, chicken grunt and black rockfish. In the case of the former fishes, the scales over their bodies are feeble, and mucous glands have developed to cover them, while in the latter case, the contrary it true. In the case of the same species of fish, as is shown in the instance of marine catfish, the tolerance of adult fish is markedly higher than that of the young.

Here, take the example of the stone flounder of which we have fortunately many experimental instances, and the strength of the toxicity of mineral oils effecting upon sea fishes is the strongest in heavy oil A, and about the same between heavy oil B and crude oil. In this case, when the solvent emulsifier is added to the mix, the toxicity is the strongest in heavy oil A+solvent emulsifier, then followed by heavy oil B+solvent emlusifier. In either case, heavy oil A shows the strongest toxicity.

Generally, the mineral oil in the sea water, especially its emulsifier, comes to stick on the surface of the gills of fish to disturb their normal respiration. Still more, in the case of the sea fish, contrary to that of freshwater fish, as they gulp down sea water to regulate the osmotic pressure, they seem to take in the toxicant ingredients of oil not only through the gills but also through the oral cavity. As was observed in the present experiment, in the low concentration of the mineral oil, the oil adhering to the body and gills had been washed away by their normal mucus secretion, and the fish were protected from the toxicity of the oil, while in the experiments with a high concentration, the fish were found to have perished, not only with their bodies covered all over with the over-secreted mucus but also with the oil stuck to the mucus, and even with their gills hyperemic and swollen.

The present experiment was carried out in the breeding water under full aeration, but once it had been stopped in the middle, the dissolution of the oxygen of the air into the water would have been slackened, and besides, by the oxidation of the oil and the respiration of the fish, the quantity of dissolved oxygen in the water would have been rapidly diminished, finally causing the test fishes to be suffocated to death.

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