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Compositional Changes of Heavy Oil and Hydrocarbon from Nahotoka Oil

- Primary Change in Spilled Oil during First Month in Seawater -

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Abstract - Class C oil and emulsion from the tanker NAHOTOKA were investigated by elemental and GC&GC/MS analyses. During first month in winter after the oil spill, major change in the heavy oil was due to seawater absorption and chemical/physical separation of hydrocarbon from non-hydrocarbon in the heavy oil. This information is important for evaluation of pollution after oil spill.

I. Introduction

On December 29th, 1996, the oil tanker NAHOTOKA sunk, and the spilled oil from the tanker has polluted shore along the Japan Sea. The class C oil from the tanker, which was heavy and sticky, was composed of a complicated organic compound, flowing hardly under the normal temperature. This class C oil was a residue after distilling petroleum and was the most viscous high ingredient among heavy oils which were made adding light oil to it.

The spilled heavy oil from 'NAHOTOKA' was mixed with seawater to break down by winds, waves and currents, and become heavier than water. Then, the class C oil had an influence on the ecosystem and the human being life of shoreline in the Prefectures Ishikawa and Fukui. Also, there were many harmful hydrocarbons in the volatile component. Therefore, it is necessary for environmental restoration to clarify how heavy oil composition has changed.

In this research, we did an elemental analysis and gas-chromatography/mass spectrometry analyses on the class C oils and emulsions from the tanker NAHOTOKA collected at 5 sites of Fukui and Ishikawa Prefectures seashore. As a result, we clarified the changes in the class C oil during the first month in winter season.

II. Samples

The class C oil and emulsions were collected by the Graduate School Tazaki Kazue Professor Group, Kanazawa University. Four emulsion samples were from Ishikawa Prefecture and 2 emulsion samples were from Fukui Prefecture (Fig.1). As for the class C oil, they got by direct from a stem part of the oil tanker NAHOTOKA, which has floated to the offshore Fukui Prefecture. Only one emulsion sample in Fukui Prefecture was again collected about one month later. Emulsions have covered the shoreline of Ishikawa and Fukui Prefectures. All emulsion samples showed brown - yellowish color.

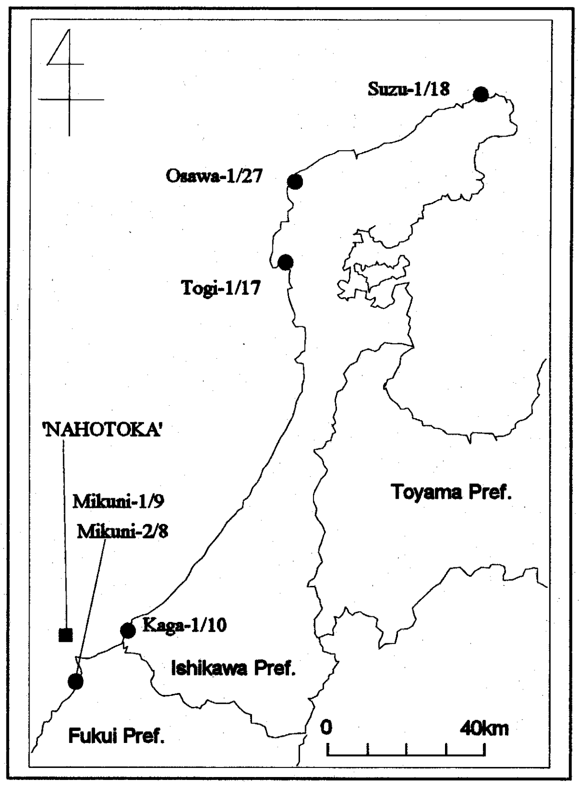

Fig. 1. Map showing the sampling site.

III. Experimental

Carbon, nitrogen, hydrogen and sulfur elemental analyses

At first, we put 5 g of sample in the 50 cc beaker and dried at 50℃ for 48 hours. Then, we took about 3 mg into the Sn foil cup. Total nitrogen (TN), total organic carbon (TOC), total hydrogen (TH) and total sulfur (TS) contents were determined using E.A.1108 (FISONS Inc.) elemental analyzer. We used BBOT (2,5 – bis - (5 – tert – butyl –

benzoxazol – 2 - yl) - thiophen) for standard and the 5 points liner fit method was employed for calibration.

GC and GC/MS

We extracted 5 g of dried samples at 60℃ by soxhlet apparatus for 48 hours with benzene and methanol mixing solution (9:1 volume ratio). We divided the extracts by TLC with hexane into *n*-alkane fraction, aromatic fraction and residual part. *n*-Alkane and aromatic fractions were analyzed using GC (Shimadzu GC14A) and GC/MS (Shimadzu QP2000A). Outer-standard *n*-alkane C_{32} was used for quantitative and qualitative analyses.

IV. Result

Carbon, nitrogen, hydrogen and sulfur contents

Table I shows the result of TN, TOC, TH and TS elemental analyses. We made the residual part deducted TN, TOC, TH and TS % to be O %. TOC contents of the emulsion from Mikuni-1/9 (site:Mikuni, date:January 9), Mikuni-2/8 and Suzu-1/18 and Osawa-1/27 show 30 - 40 %. TOC contents of the class C oil and emulsion from Togi-1/17 are higher about 60 %. Only Kaga-1/10 shows less than 10 % of TOC content.

TH contents of all emulsions show 8 - 10 %, excluding Kaga-1/10 with 1% level. TN and TS were a small amount less than 1 %.

TABLE I
Elemental composition of altered class C oil 'NAHOTOKA'

	Sample	N (%)	C (%)	H (%)	S (%)	O (%)	H/C (atomic)	O/C (atomic)
1	NAHOTOKA	0.246	62.2	10.1	<0.1	27.4	1.95	0.33
2	Mikuni-1/9	0.196	41.2	10.1	0.29	48.2	2.94	0.88
3	Mikuni-2/8	0.321	42.4	8.2	0.43	48.7	2.31	0.86
4	Kaga-1/10	0.114	8.41	1.2	0.15	90.2	1.64	8.04
5	Togi-1/17	0.341	65.7	9.9	0.89	23.2	1.81	0.26
6	Osawa-1/27	0.214	35.8	10.1	0.14	53.7	3.39	1.13
7	Suzu-1/18	0.190	38.8	10.4	0.07	50.5	3.22	0.98

GC and GC/MS

The amount of bitumen and total *n*-alkane are shown in Table II. Total bitumen is about 50 % in the class C oil and 20 - 40 % in the other emulsions. The bitumen from only Kaga-1/10 is less than 10 %. Total *n*-alkane is 6.45mg/g in the class C oil but shows a value below 2 mg/g in the other samples, which are from Mikuni-2/8, Kaga-1/10, Togi-1/17, Suzu-1/18 and Osawa-1/27 in the order of low to high content.

A typical gas-chromatogram (Fig.4) shows a peak position to be C_{23} or C_{24}. In Table II, L/(L+H) means the ratio of lower *n*-alkane ($<C_{20}$) to total *n*-alkane. L/(L+H) of the class C oil is 0.39, and those of Togi-1/17, Mikuni-2/8, Suzu-1/18, Osawa-1/27 and Kaga-1/10 are 0.33, 0.36, 0.39, 0.41 and 0.42, respectively. High value of L/(L+H) is meaning low a bacterial activity. The L/(L+H) of the class C oil is similar to those of the other emulsion.

Additionally, such biomarkers as sterane (m/z=217) and hopane (m/z=191) were not detected in all samples, and high maturity level indicated by methylphenanthrene isomer ratio (MPI3 = (2MP+3MP) / (1MP+4MP+9MP): Radke, 1987) corresponding to %Rm = 1.3 (based on Sampei et al., 1994) shows an over matured zone of oil generation for original class C oil.

TABLE II
Extractable organic matter from altered class C oil

	Smaple	Sample (g)	Bitumen (g)	Bitumen/Sample (%)	TOC (%)	TNA* (mg)	TNA/Sample (mg/g)	L/(L+H)** ratio
1	NAHOTOKA	5.21	2.54	48.7	48.4	33.62	6.45	0.39
2	Mikuni-1/9	5.63	1.85	32.9	25.3	-***	-	-
3	Mikuni-2/8	8.97	3.71	41.4	42.8	4.90	0.55	0.36
4	Kaga-1/10	6.55	0.58	8.9	9.8	5.21	0.80	0.42
5	Togi-1/17	5.80	1.41	24.3	22.4	5.79	1.00	0.33
6	Osawa-1/27	5.87	1.71	29.2	30.0	9.94	1.69	0.41
7	Suzu-1/18	6.63	1.48	22.4	24.1	10.37	1.56	0.39

* TNA:Total *n*-alkane *** - : not measurable
** L/(L+H): see text

V. Discussion

Compositional change of emulsion

Evolution of emulsion can be evaluated by moisture contents on atomic H/C - O/C diagram (van Krevelen diagram; Tissot and Welte, 1984) in Fig.2. The line (1) in Fig.2 indicates an ideal compositional change with increasing water inclusion. Mikuni-1/9, Suzu-1/18 and Osawa-1/27 are on this line and shift to the higher position in this order, suggesting that emulsion of Osawa-1/27 was most strongly affected by climate, seawater current and wave condition. This result suggests that the compositional change is a function of time and seawater dynamics. With progressing emulsion, water absorption could be estimated up to 1.7 times heavier than the class C oil. On the other hand, emulsion of Togi-1/17 is plotted on the non-progressed area near the class C oil. The plot of Kaga-1/10 is abnormally shifted from this line to the right direction. H/C ratio of Mikuni-2/8 decreased from the H/C ratio of Mikuni-1/9, suggesting a decrease in hydrocarbon contents.

Fig.3 shows atomic N/C - O/C plot. N/C ratio of Mikuni-2/8 and Kaga-1/10 are plotted differently from the other samples. This also may suggest an escape of hydrocarbon from the class C oil.

n-Alkane distribution and biodegradation

Generally, light *n*-alkanes are more easily eaten by bacteria than heavy *n*-alkanes (Alexander, 1983; Miles, 1994). However, L/(L+H) of the class C oil is similar to those of the other samples. In addition, total *n*-alkane/sample of Mikuni-2/8 and Kaga-1/10 were 0.55 and 0.80mg/g, respectively (Table II). The other samples are in the range of 1.0-1.96 mg/g. These levels are about ten times lower than in the class C oil (6.45mg/g). These results support the idea that the hydrocarbon decreased in the short period after the oil spill but bacterial activity was not so high.

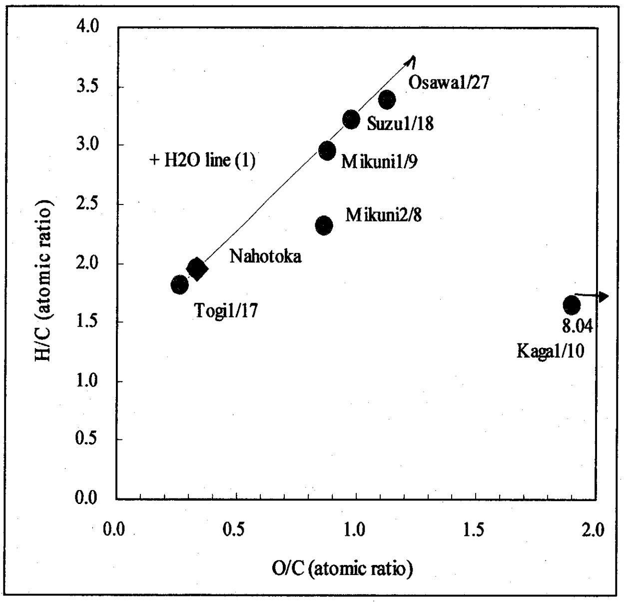

Fig. 2. Atomic H/C – O/C plots.

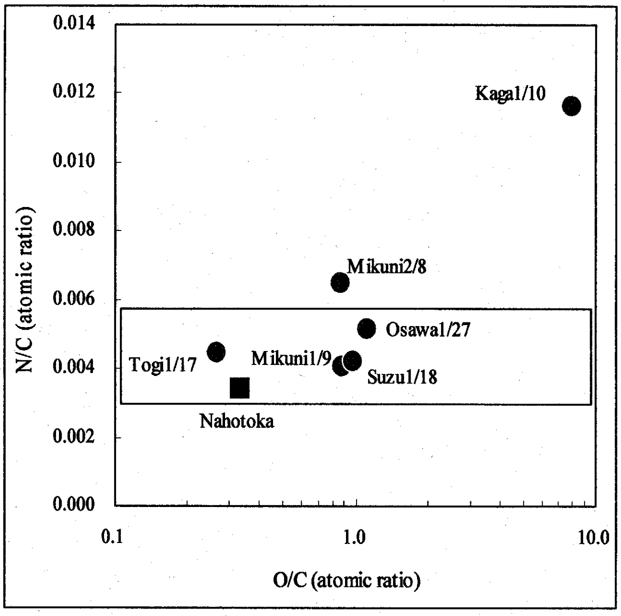

Fig. 3. Atomic N/C – O/C plots.

Based on these results, the decrease in total *n*-alkane/sample is considered not mainly due to biodegradation but to dispersal from the emulsion. Bacterial activity was low in the first month in winter season because the water temperature was low. In the successive warm season, bacterial activity could drastically increase, according to Shimizu (1989).

Biomarker and methylphenanthrene

Sterane and Hopane are not existed in all emulsion and the class C oil. The reason is considered an originally absence in the class C oil.

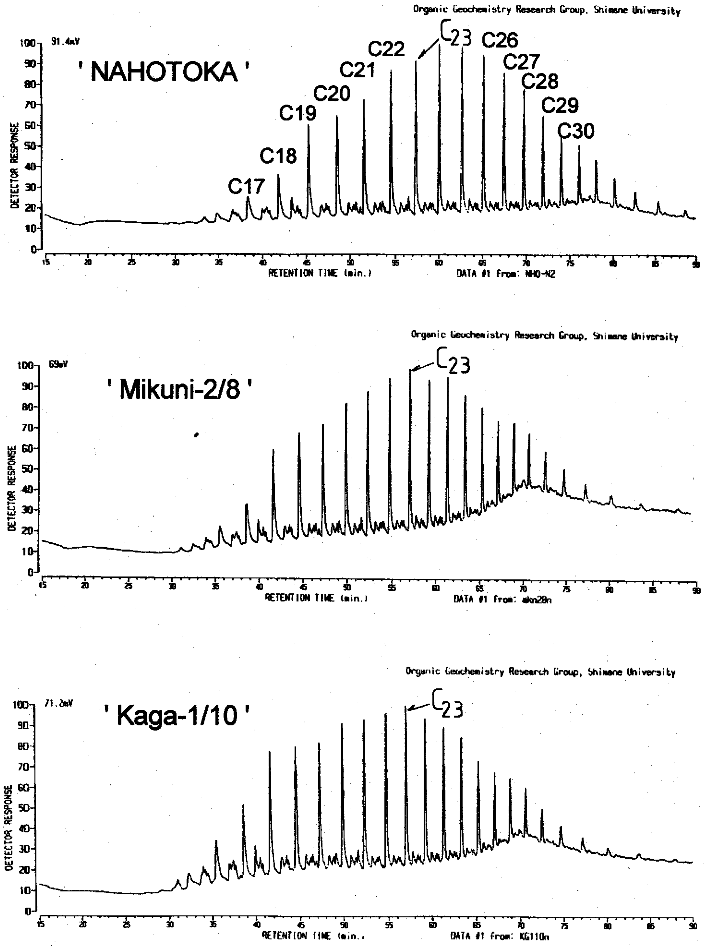

Fig. 4. Representative gas-chromatogram

VI. Summary and Conclusions

During first month after the oil spill from the tanker NAHOTOKA, emulsion has progressed as a function of time and seawater current condition. An increase in weight of emulsion by water absorption was estimated up to 1.7 times heavier than the class C oil. While, hydrocarbon content has decreased. *n*-Alkane decreased to be about 10% of the initial class C oil. This may be not due to bacterial activity but to dispersal in seawater and air. During first month after the oil spill in winter, chemical and physical process are important to decrease hydrocarbon in heavy oil. However, this is a supply process of toxic hydrocarbon to surroundings.

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