Compositional changes of heavy oil and aliphatic hydrocarbon from the spilled NAKHODKA-Oil washed asore at Fukui, Ishikawa and Niigata Prefectures, Japan

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ABSTRACT

Heavy oil and aliphatic hydrocarbon from the spilled NAKHODKA-oil washed ashore at Fukui, Ishikawa and Niigata Prefectures were investigated on compositional changes using elemental and GC&GC/MS analyses. During the first month after the oil spill, primary change in the heavy oil (brown mousse) was due to chemical/physical processes by water washing with strong waves in winter. The diagram of H/C versus O/C suggests that seawater absorption by heavy oil firstly occurred and some hydrocarbons successively escaped from the heavy oil during floating in the sea. After floating and reaching the shore, the heavy oil were dried and oxidized to be dark-brown or black solid. Increasing O/C ratio of the heavy oil on the shore suggests that evaporation and oxidation were predominant during the successive process. On the other hand, *n*-alkane distribution indicates a little degradation by

bacterial activity. Based on a specific distribution pattern of the *n*-alkanes with survived low molecular *n*-alkanes, bacterial degradations of hydrocarbon under anaerobic inner-condition of heavy oil seem to be rather low through the first year after the oil spill. But for oxidation of outer-part of heavy oil, aerobic bacteria may fairly work near surface of heavy oil. After about 6 years, remained heavy oil finely dispersed in beach sand had hydrocarbons with a lot of biodegradation. Oxidation condition may support to increase the bacterial activity.

INTRODUCTION

The oil tanker NAKHODKA has sunk in the western East Sea (western Japan Sea) on January 2, 1997, and the spilled oil from the tanker has polluted shore along the southern East Sea. The heavy C oil from the tanker NAKHODKA, which was heavy and sticky, is composed of a complicated organic compound, hardly flowing under the normal temperature. The heavy C oil NAKHODKA is a residue after distilling petroleum and is the most viscous high ingredient among heavy oils, which are made adding light oil to it.

The spilled heavy oil from the tanker NAKHODKA was washed with seawater to break down by winds, waves and currents, and become heavier than water. The heavy C oil, then, had an influence on the ecosystem and the human being's life of shoreline in the Prefectures Ishikawa, Fukui and Niigata. For environmental restoration, it is necessary to clarify how heavy oil composition has changed and decomposed.

In the present study, we focus on a process of compositional changes in heavy oil within one year after the oil spill, and we discuss a main process to change or decompose the heavy oil, i.e. chemical/physical process and biodegradation. We performed elemental analyses for hydrogen (H), nitrogen (N), carbon (C) and sulfur (S), and gas-chromatography (GC) / mass spectrometry (MS) analyses on the heavy C oil NAKHODKA and heavy oils derived from the tanker NAKHODKA collected at 12 seashore sites of Fukui, Ishikawa and Niigata Prefectures. Mousse-like heavy oils taken within one month could represent the primary change during floating process in the sea, while heavy oils taken after one to 12 months show the successive change after reaching the shore and being exposed to air and sunlight.

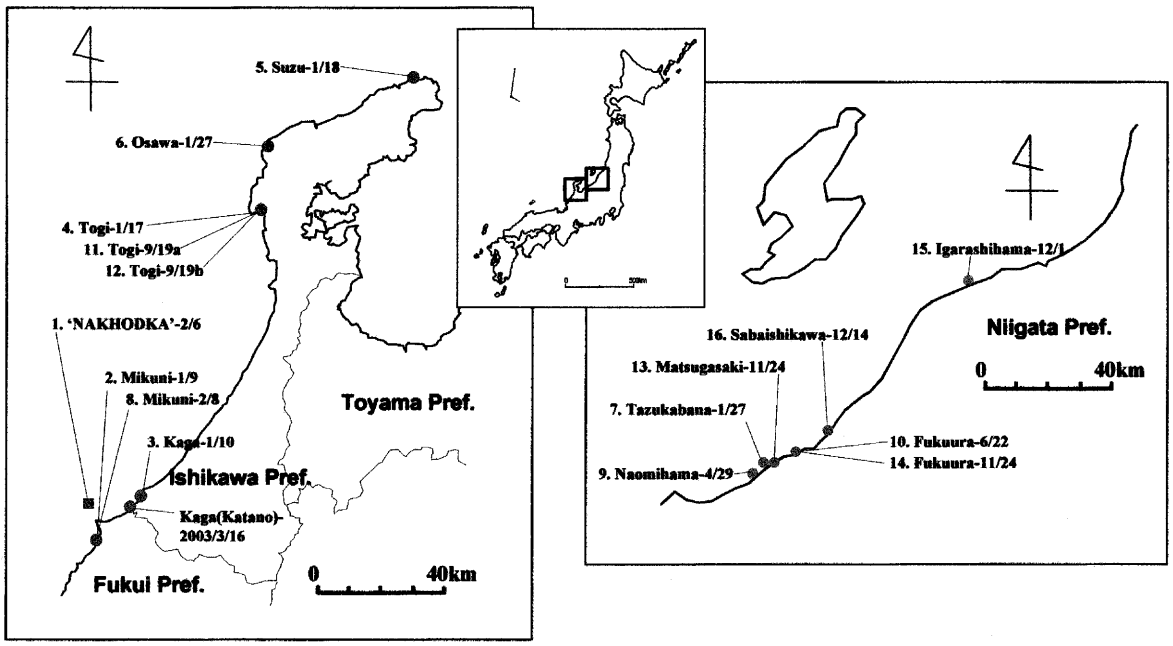

Figure 1 Map showing the sampling sites with date in 1997.

Samples

The heavy oils derived from the tanker NAKHODKA were collected in 1997 by the Professor Tazaki Group, Kanazawa University and the Professor Yoshimura Group, Niigata University. Six mousse-like heavy oils were from Ishikawa prefecture, 2 mousse-like heavy oils were from Fukui prefecture, and seven heavy oils were from Niigata prefecture (Fig.1). An original heavy C oil NAKHODKA was taken by direct from a stem part of the oil tanker NAKHODKA that has floated to the offshore Fukui Prefecture. Figure 2a shows the spilled heavy C oil NAKHODKA with stickiness and dark brown.

Four heavy oil samples in Fukui, Ishikawa and Niigata prefectures were again collected at three sites (Mikuni, Togi and Fukuura) after about one to eight months (TABLE I). Additional one heavy oil, which has rarely remained in coarse sand (Fig.2b), was collected at Katano beach near Kaga city (Fig.1) in 2003 by the Associate Professor Sawano Group, Seiryo Women's Junior College.

Within one month after the oil spill, mousse-like heavy oil have covered the shoreline of Ishikawa, Fukui and Niigata prefectures, and then deposited in the sea and on the shore surface. During the first month, all mousse-like heavy oil samples generally showed yellowish - brown color, while after the first month heavy oil showed

brown or black color.

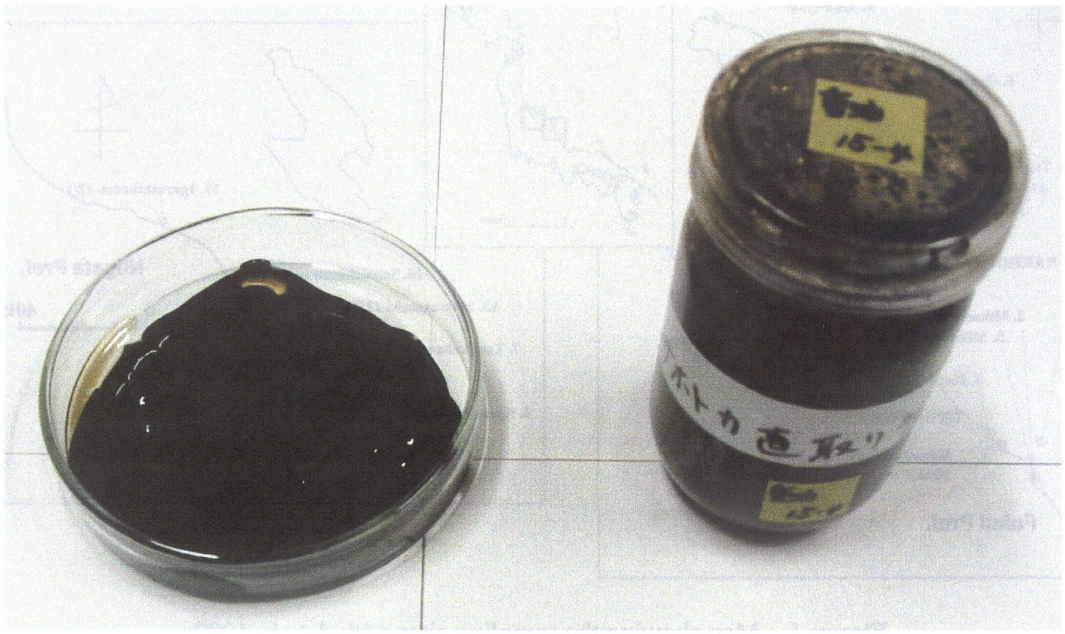

Figure 2a The heavy C oil NAKHODKA-1997/2/6 taken directly from a stem part of the oil tanker sunk near Mikuni.

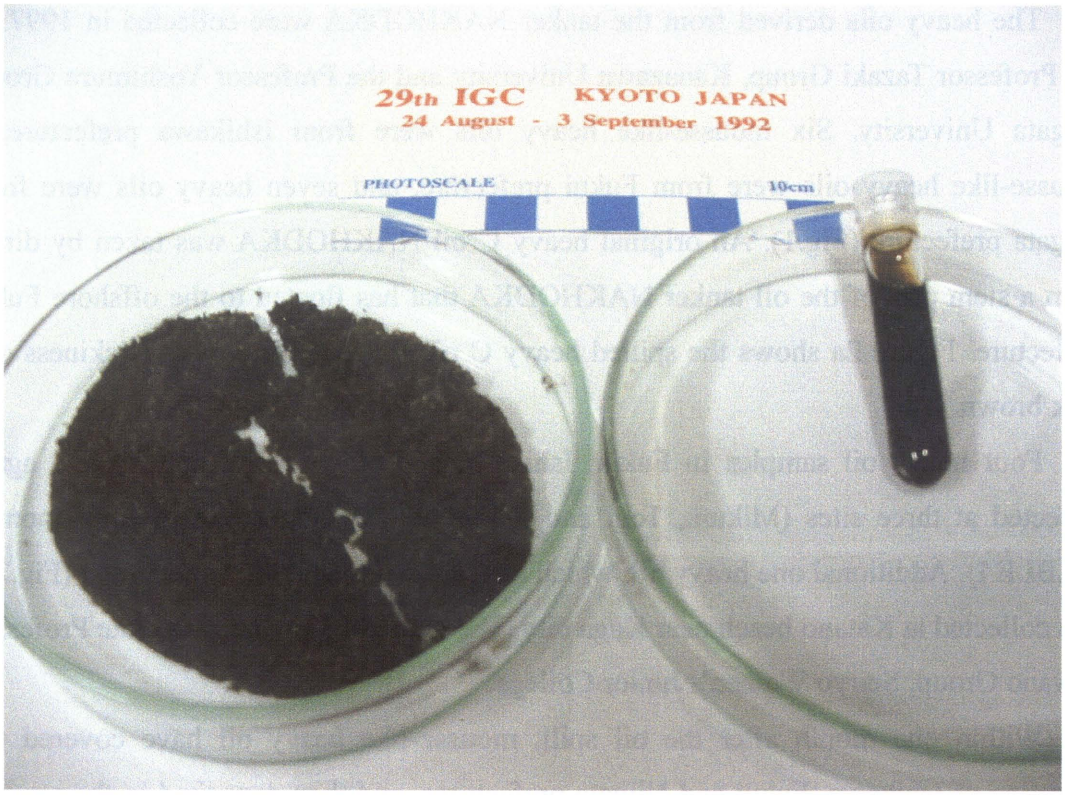

Figure 2b The dispersed heavy oil with the sea sand from Katano beach near Kaga city. In the right micro-tube, extracted oil from the dispersed heavy oil by benzene + methanol (9+1) solution is stored.

Experimental

A. Carbon, nitrogen, hydrogen and sulfur elemental analyses

About 5 g of sample was put in the 50 cc beaker and dried at 50°C for 48 hours. Then, about 3 mg was taken into a tin (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. BBOT (2,5 – bis - (5 – tert – butyl – benzoxazol – 2 - yl) - thiophen) was used for standard and the 5 points liner fit method was employed for calibration.

B. GC and GC/MS

About 5 g of dried sample was extracted with benzene and methanol mixing solution (9:1 volume ratio) at 60°C by soxhlet apparatus for 48 hours. The extracts were divided using TLC (Thin Layer Chromatography) 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; QP5050A only for Kaga-2003/3/16). Outer-standard *n*-alkane C_{32} was used for quantitative and qualitative analyses.

Table 1 Elemental composition of heavy oils from the tanker NAKHODKA

	Sample name	Sampling date	Prefecture	N (%)	C (%)	H (%)	S (%)	O (%)	H/C (atomic)	O/C (atomic)	N/C (atomic)	S/C (atomic)
1	NAKHODKA-2/6	1997/2/6	Ishikawa	0.246	62.2	10.1	<0.1	27.4	1.95	0.33	0.003	<0.001
2	Mikuni-1/9	1997/1/9	Fukui	0.196	41.2	10.1	0.29	48.2	2.94	0.88	0.004	0.003
3	Kaga-1/10	1997/1/10	Ishikawa	0.114	8.41	1.2	0.15	90.2	1.64	8.04	0.012	0.007
4	Togi-1/17	1997/1/17	Ishikawa	0.341	65.7	9.9	0.89	23.2	1.81	0.26	0.004	0.005
5	Suzu-1/18	1997/1/18	Ishikawa	0.190	38.8	10.4	0.07	50.5	3.22	0.98	0.004	0.001
6	Osawa-1/27	1997/1/27	Ishikawa	0.214	35.8	10.1	0.14	53.7	3.39	1.13	0.005	0.001
7	Tazukabana-1/27	1997/1/27	Niigata	0.938	45.8	11	0.43	41.8	2.88	0.68	0.018	0.004
8	Mikuni-2/8	1997/2/8	Fukui	0.321	42.4	8.2	0.43	48.7	2.31	0.86	0.006	0.004
9	Naomihama-4/29	1997/4/29	Niigata	1.020	44.3	5.3	0.28	49.1	1.44	0.83	0.020	0.002
10	Fukuura-6/22	1997/6/22	Niigata	1.155	42.9	8.3	0.30	47.3	2.32	0.83	0.023	0.003
11	Togi-9/19a	1997/9/19	Ishikawa	1.152	38.0	6.8	0.32	53.7	2.15	1.06	0.026	0.003
12	Togi-9/19b	1997/9/19	Ishikawa	1.183	27.6	2.7	<0.1	68.5	1.17	1.86	0.037	<0.001
13	Matsugasaki-11/24	1997/11/24	Niigata	0.623	29.1	5.2	<0.1	65.1	2.14	1.68	0.018	<0.001
14	Fukuura-11/24	1997/11/24	Niigata	0.177	27.1	8.0	1.60	63.1	3.54	1.75	0.006	0.022
15	Igarashihama-12/1	1997/12/1	Niigata	2.302	59.8	8.9	<0.1	29.0	1.79	0.36	0.033	<0.001
16	Sabaishikawa-12/14	1997/12/14	Niigata	0.923	32.9	6.0	1.03	59.1	2.19	1.35	0.024	0.012

RESULTS

A. Carbon, nitrogen, hydrogen and sulfur contents

TABLE I shows the result of TN, TOC, TH and TS elemental analyses. For determination of O %, TN, TOC, TH and TS % were deducted from 100 %.

TOC contents of the original heavy C oil NAKHODKA and heavy oils from Togi-1/17 and Igarashihama-12/1 are higher about 60 % (59.8-65.7%). The heavy oils within 9 months after the oil spill from Mikuni-1/9, Suzu-1/18, Osawa-1/27, Tazukabana-1/27, Mikuni-2/8, Naomihama-4/29, Fukuura-6/22 and Togi-9/19a show around 40 % (35.8-45.8%) of TOC content. The heavy oils after 9 to 12 months from Togi-9/19b, Matsugasaki-11/24, Fukuura-11/24 and Sabaishikawa-12/14 show around 30% (27.1-32.9%). Only Kaga-1/10 shows less than 10 % of TOC content.

TH contents of the heavy oils within one month (up to January 27) show higher values about 10 % (9.9-11 %), excluding Kaga-1/10 of 1.2 %. After February 8, TH contents decrease under 8.9 % (2.7-8.9 %).

TN contents of the heavy oils are, on the contrary, low within one month (up to January 27) about 0.3% on average ranging from 0.11 to 0.94 %, and high after April 29 about 1 % on average ranging from 0.18 to 2.3 %.

TS contents were generally low less than 1 %, except for Fukuura-11/24 with 1.6% and Sbaishikawa-12/14 with 1.0 %.

Table 2 Extractable organic matter of heavy oils from the tanker NAKHODKA

	Sample name	Sampling date	Prefecture	Sample (g)	Bitumen (g)	Bitumen/Sample (%)	Total *n*-alkane (mg)	Total *n*-alkane/Sample (mg/g)	C_{16-23}/C_{16-36} ratio
1	NAKHODKA-2/6	1997/2/6	Ishikawa	5.21	2.54	48.7	33.62	6.45	0.39
2	Mikuni-1/9	1997/1/9	Fukui	5.63	1.85	32.9	-*	-	-
3	Kaga-1/10	1997/1/10	Ishikawa	6.55	0.58	8.9	5.21	0.80	0.42
4	Togi-1/17	1997/1/17	Ishikawa	5.80	1.41	24.3	5.79	1.00	0.33
5	Suzu-1/18	1997/1/18	Ishikawa	6.63	1.48	22.4	10.37	1.56	0.39
6	Osawa-1/27	1997/1/27	Ishikawa	5.87	1.71	29.2	9.94	1.69	0.41
7	Tazukabana-1/27	1997/1/27	Niigata	3.27	1.05	32.1	109.90	33.61	0.42
8	Mikuni-2/8	1997/2/8	Fukui	8.97	3.71	41.4	4.90	0.55	0.36
9	Naomihama-4/29	1997/4/29	Niigata	3.64	0.99	27.2	85.80	23.57	0.43
10	Fukuura-6/22	1997/6/22	Niigata	3.27	1.26	38.5	34.70	10.61	0.57
11	Togi-9/19a	1997/9/19	Ishikawa	3.14	1.08	34.4	11.70	3.73	0.42
12	Togi-9/19b	1997/9/19	Ishikawa	2.11	0.20	9.5	1.50	0.71	0.47
13	Matsugasaki-11/24	1997/11/24	Niigata	3.00	0.93	31.0	112.30	37.43	0.47
14	Fukuura-11/24	1997/11/24	Niigata	2.81	0.83	29.5	112.00	39.86	0.49
15	Igarashihama-12/1	1997/12/1	Niigata	3.15	1.93	61.3	221.00	70.16	0.38
16	Sabaishikawa-12/14	1997/12/14	Niigata	2.41	0.81	33.6	77.40	32.12	0.51

* - : not measurable

B. GC and GC/MS

The amount of bitumen (extractable organic matter in organic solution) and total *n*-alkane are shown in TABLE II. Total bitumen content is about 50 % in the original heavy C oil NAKHODKA and 22.4 to 41.4 % in the derived heavy oils, except for 8.9 % of Kaga-1/10 and 61.3 % of Igarashihama-12/1.

Total *n*-alkane content is 6.45mg/g in the heavy C oil NAKHODKA. Total *n*-alkanes of the mousse-like heavy oils within one month are about 1mg/g, which are from Kaga-1/10, Togi-1/17, Suzu-1/18 and Osawa-1/27 in the order of low to high content. While those of heavy oils after one to 12 months show wide range from 0.55mg/g of Mikuni-2/8 to 70.16 mg/g of Igarashihama-12/1.

Abundance of low molecular weight *n*-alkanes to high molecular ones is an indicator for bacterial degradation [1]. A typical gas-chromatogram (Fig.5 and 6) shows a peak by *n*-C_{23} or *n*-C_{24} alkane. Therefore, the abundance ratio of *n*-$C_{16\text{-}23}$ alkanes (total amounts of *n*-alkanes with carbon number from 16 to 23) to *n*-$C_{16\text{-}36}$ alkanes (total amounts of *n*-alkanes with carbon number from 16 to 36) is to be an indicator for bacterial degradation in the present case study. The ratio of *n*-$C_{16\text{-}23}$/*n*-$C_{16\text{-}36}$ alkanes of the heavy C oil NAKHODKA is 0.39, and those within one month from Togi-1/17, Suzu-1/18, Osawa-1/27 and Kaga-1/10 are 0.33, 0.39, 0.41 and 0.42, respectively, which are similar to the ratio of the heavy C oil NAKHODKA. The ratios of *n*-$C_{16\text{-}23}$/*n*-$C_{16\text{-}36}$ alkanes after one to 12 months show a little higher value of about 0.5 ranging 0.36 of Mikuni-2/8 to 0.57 of Fukuura-6/22.

Additionally, such biomarkers as sterane (m/z=217) and hopane (m/z=191) were not detected in all samples. The reason is considered an originally absence in the heavy C oil NAKHODKA or loss/decomposition during the industrial rectification process. High maturity level was indicated by methylphenanthrene isomer ratio (MPI3 = [2MP+3MP] / [1MP+4MP+9MP]) [2] with the value of 2.0 corresponding to %Ro = 1.3 based on the equation [%Ro = 0.79•MPI3 - 0.30] [3] showing an over matured zone of oil generation for the heavy C oil NAKHODKA.

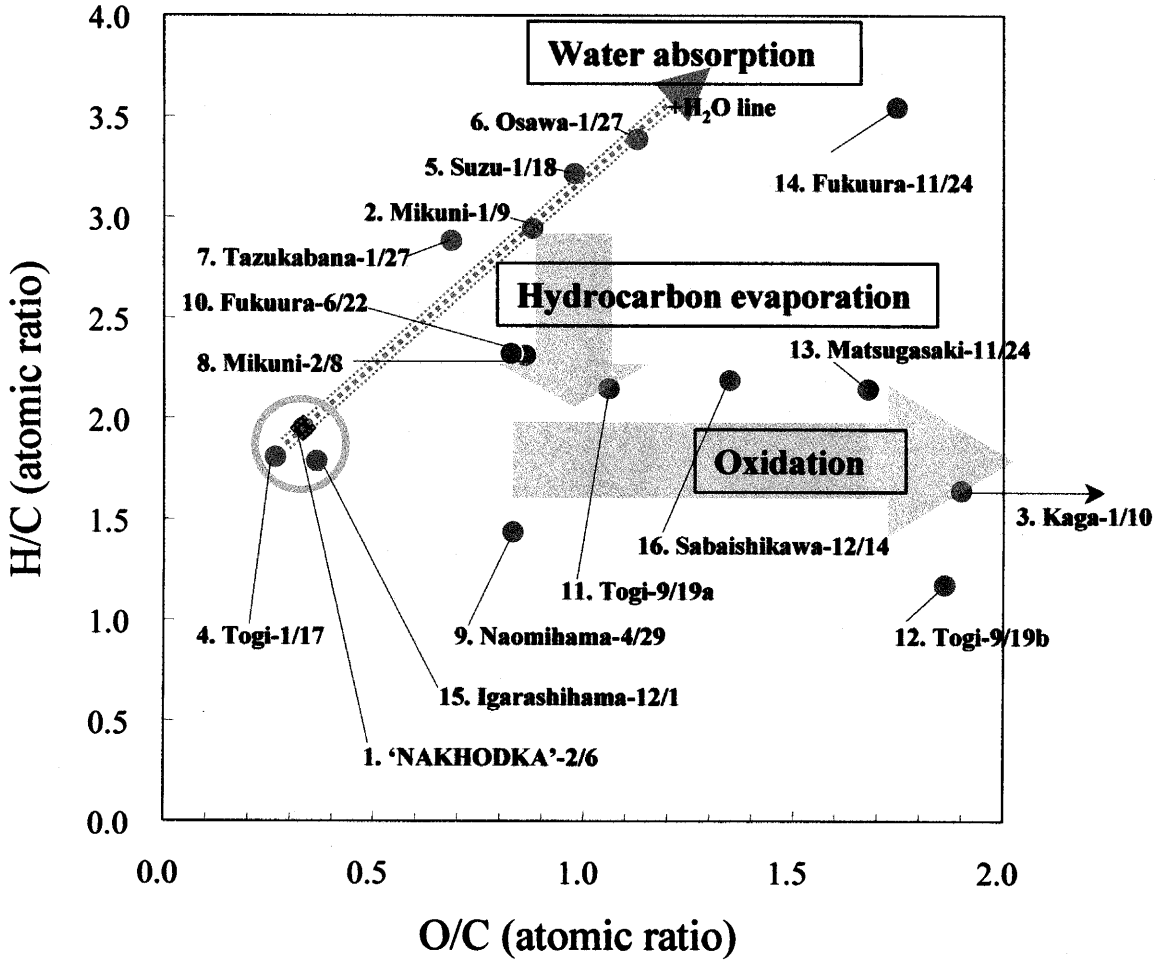

Figure 3 Atomic H/C – O/C plots. Three arrows indicate the process of water absorption, hydrocarbon evaporation and oxidation, respectively.

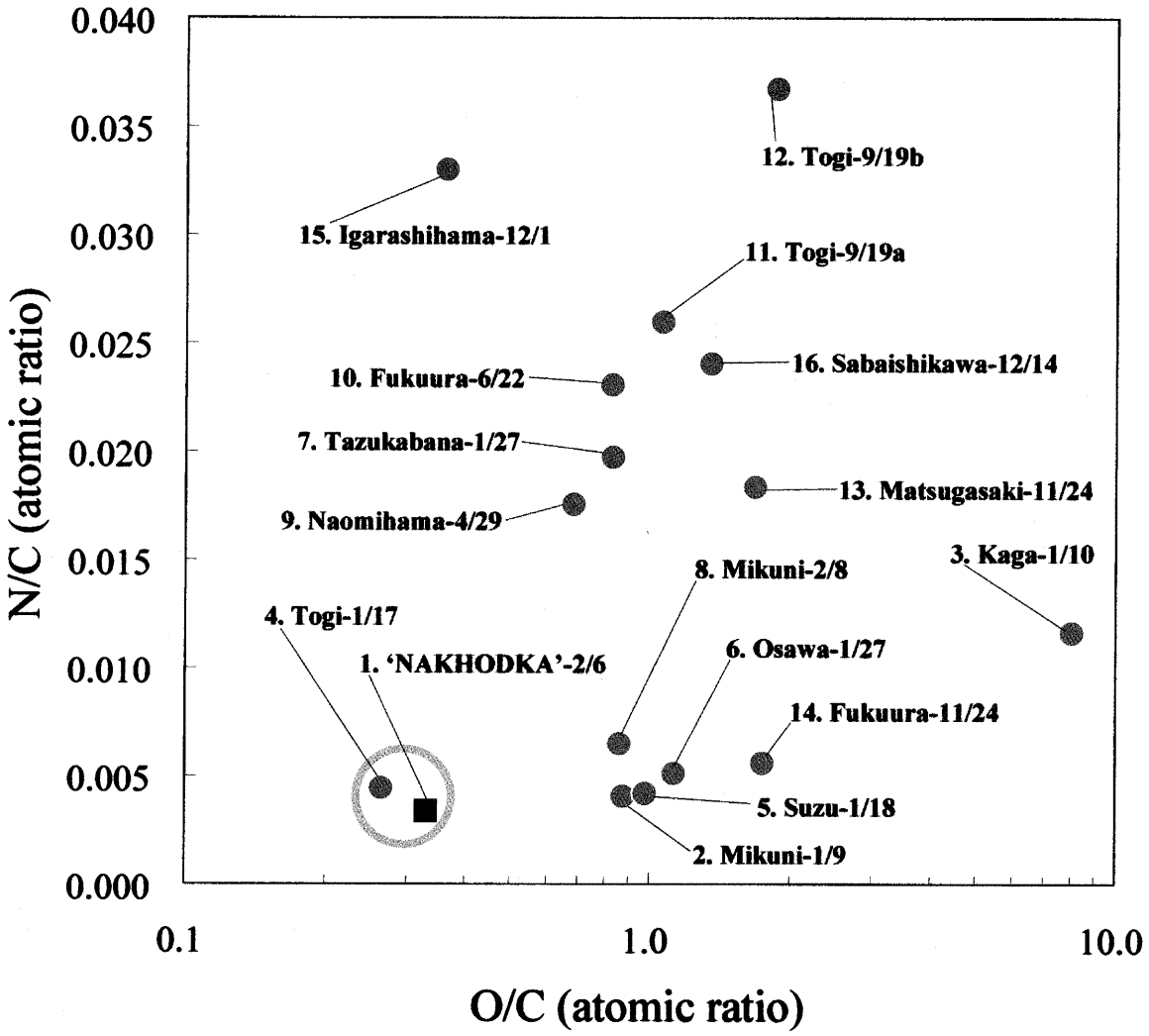

Figure 4 Atomic N/C – O/C plots.

DISCUSSION

A. Elemental changes of heavy oil

[The first month]

As shown in Fig.3, elemental changes of heavy oil can be evaluated on atomic H/C - O/C diagram (van Krevelen diagram) [4]. The original heavy C oil NAKHODKA is plotted on the left-below portion of the sample area on the diagram. Only Togi-1/17 and Igarashihama-12/1 are plotted on the non-progressed area near the heavy C oil NAKHODKA.

The line [+H_2O] in Fig.3 indicates an ideal compositional change with increasing in water absorption (or water inclusion). Within one month after the oil spill, mousse-like heavy oils of Mikuni-1/9, Suzu-1/18 and Osawa-1/27 are on this line and

shift to the higher position in this order, suggesting an increasing in water absorption. Especially for Osawa-1/27, the water absorption could be up to 1.7 times heavier than the heavy C oil NAKHODKA. The Osawa-1/27 was most strongly affected by wave actions and seawater current due to winter hard-climate in the East Sea. These results suggest that the first compositional change with increasing in H/C and O/C ratios is a function of seawater dynamics and floating time (Fig. 9).

After reaching the shore, mousse-like heavy oils decreased H/C ratio and increased O/C ratio. The decreased H/C ratio could reflect a release of hydrocarbon and drying process, and the increased O/C ratio could reflect an oxidation of heavy oil (Fig. 10). The H/C ratio of Mikuni-2/8 decreased more than that of Mikuni-1/9 (Fig. 3), suggesting an evaporation of volatile component in drying process of heavy oils. This is one of the supplying processes of toxic hydrocarbon to environments (Fig. 9 and 10).

On the other hand, the plot of Kaga-1/10 (Fig. 3) is abnormally shifted from this line to the right direction. This reason may be due to a hard oxidation or a contamination of significant sand particles. Considering the short period after the oil spill and the cold climate, such a hard oxidation would not be possible. Therefore, we exclude Kaga-1/10 for discussion.

Figure 4 shows atomic N/C - O/C plots. N/C ratios of the heavy oils after the winter are rather higher than those in the winter except for Fukuura-11/24. These higher N/C ratios may be due to the activated aerobic bacteria. The Togi-9/19b, which was a hardly dried heavy oil on the beach, has the highest N/C value of 0.037. While, the ratio of the heavy C oil NAKHODKA shows the lowest value of 0.003.

[The 2-12 months]

The heavy oils taken after 2-12 months are plotted on an oxidized area in Fig.3. According to plotted position of each sample in Fig.3, oxidation process of heavy oils seems to progress with increasing time. Temperature effect on aerobic bacteria [5] after the winter may take place for the effective oxidation of heavy oil. The most oxidized heavy oil was Togi-9/19b. The Togi-9/19b, which was a hardly dried black heavy oil, shows a rather higher O/C ratio of 1.86 than 1.06 of the Togi-9/19a, which looked a soft brown-black heavy oil. Although these two samples were taken at the same beach, the degree of oxidation is quite different. Drying process seems to progress an oxidation of

heavy oil. Additionally, Togi-9/19b is also characterized by low H/C ratio (Fig.3). This could depend on a hydrocarbon evaporation, considering a quite low value of total *n*-alkanes to sample of the Togi-9/19b (0.71mg/g) to the other samples (0.55-70.16 mg/g: TABLE 2). These processes of oxidation and hydrocarbon evaporation seem to closely relate with a drying process.

On the other hand, heavy oil of Fukuura-11/24 was plotted near the line [$+H_2O$] with high H/C (3.54), even though this heavy oil was exposed to air on the shore about 10 months. This is because the heavy oil of Fukuura-11/24 was deposited with seawater between the gravels on the beach.

B. Estimation of bacterial activity based on *n*-alkane distribution

In general, *n*-alkanes are more easily eaten by bacteria than iso-alkanes, biomarkers and aromatics. Further, light *n*-alkanes are more sensitive for biodegradation than heavy *n*-alkanes [1, 6, 7]. Therefore, as stated above the relative abundance of light *n*-alkanes to heavy ones is considered to be a good indicator for bacterial activity.

Through the first year after the oil spill, the ratio of $n\text{-}C_{16\text{-}23}/n\text{-}C_{16\text{-}36}$ alkanes from all samples about 0.4-0.5 is similar to that of the heavy C oil NAKHODKA. In addition, samples with rather low values of total *n*-alkane/sample from Kaga-1/10, Mikuni-2/8 and Togi-9/19b are not different from the other samples in *n*-alkane distribution (TABLE 2 and Fig.5-7). Therefore, the reason why the three samples have rather low values of total *n*-alkane/sample could not be due to biodegradation, but should be due to hydrocarbon evaporation. Although we fear an underestimation of aerobic bacterial activity for oxidation at the outer part of heavy oil, anaerobic bacteria could be lowly activated at the inner part of heavy oil.

After about 6 years, however, Kaga(Katano)-2003/3/16 shows a different pattern in *n*-alkane distribution from the other samples (Fig. 8). Abundance of the *n*-alkanes is quite small in the heavy oil, suggesting that biodegradation has significantly occurred. This is due to a long time after the oil spill and dispersed sample condition. For Kaga(Katano)-2003/3/16, heavy oil was completely and finely dispersed in coarse sand. Oxic condition of the dispersed heavy oils could increase activity of bacteria. Because, aerobic bacteria is commonly a major worker to decompose oils rather than anaerobic bacteria which decompose oils more slowly than aerobes [1, 8].

Based on above results, simplified process for compositional changes on the heavy oils from the tanker NAKHODKA can be proposed as shown in Fig. 11.

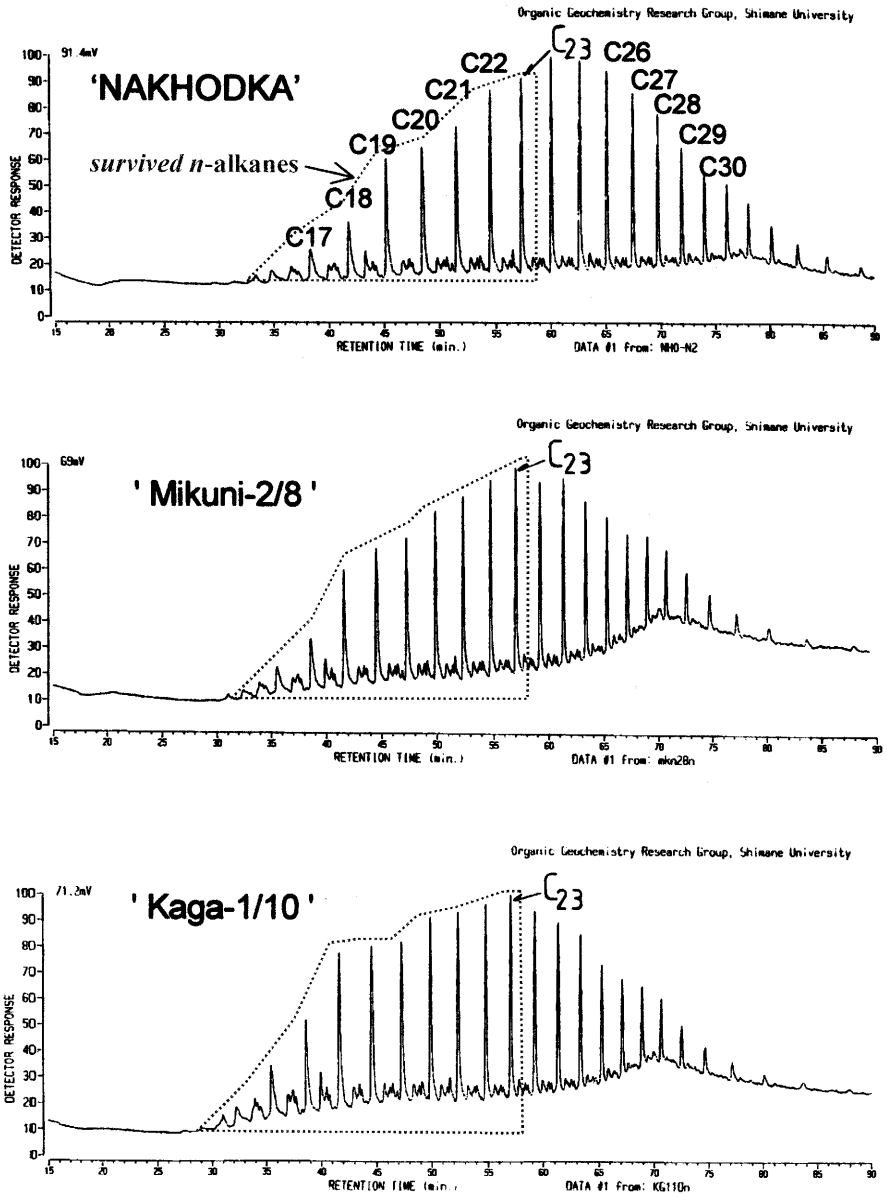

Figure 5 Gas-chromatograms of *n*-alkane fraction from NAKHODKA, Mikuni-2/8 and Kaga-1/10.

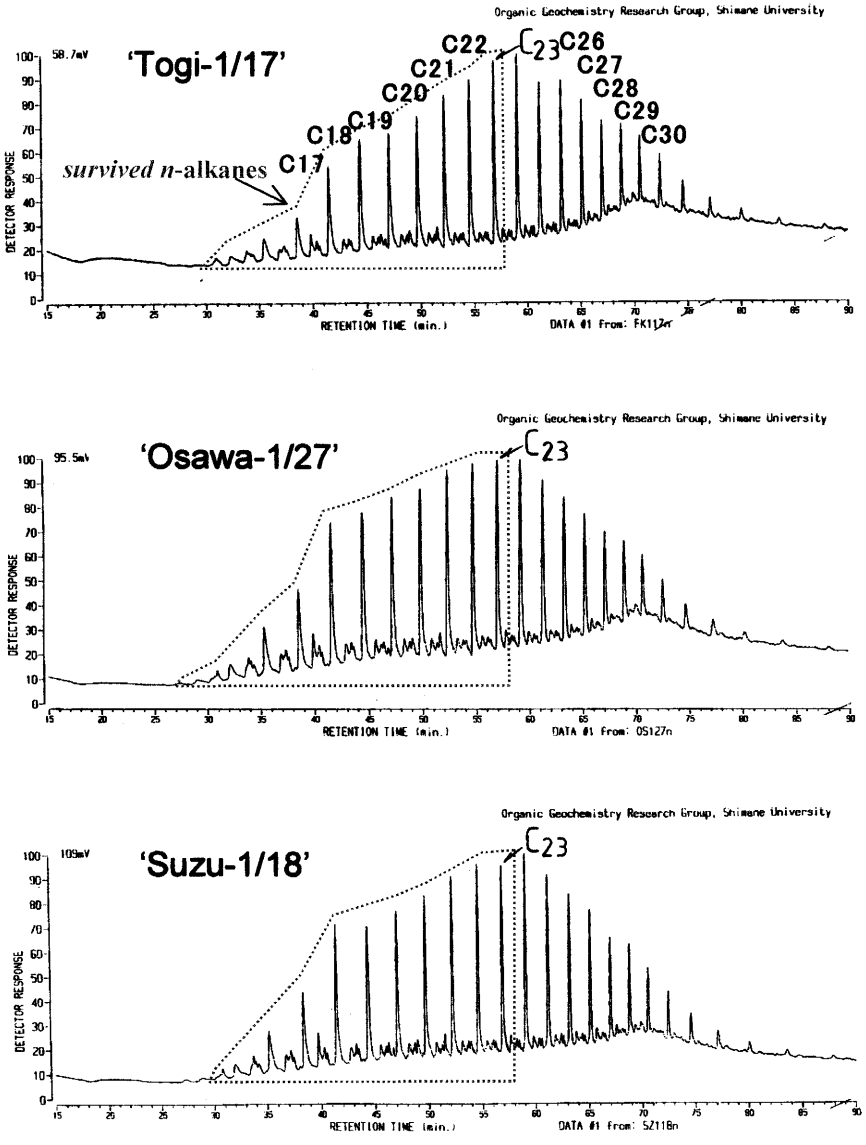

Figure 6 Gas-chromatograms of *n*-alkane fraction from Togi-1/17, Osawa-1/27 and Suzu-1/18.

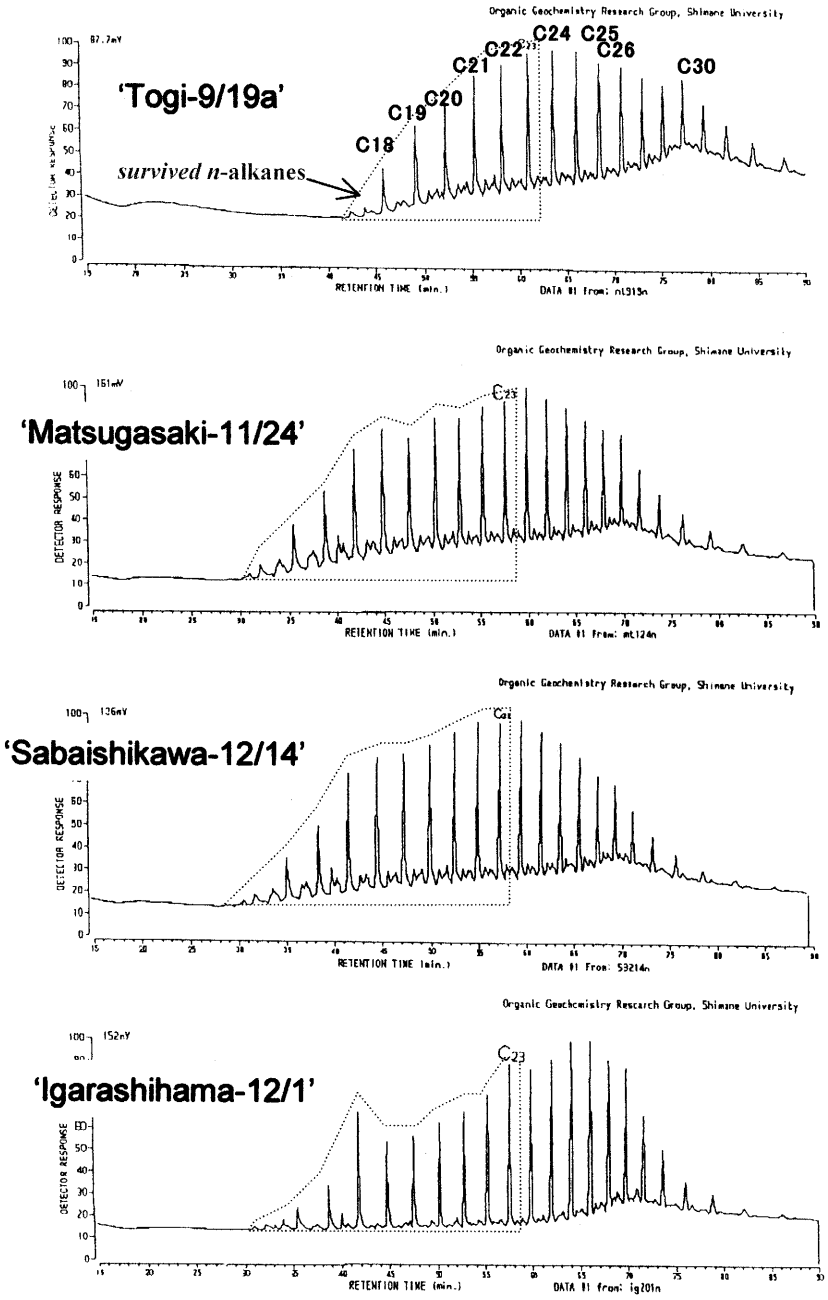

Figure 7 Gas-chromatograms of *n*-alkane fraction from Togi-9/19a, Matsugasaki-11/24, Sabaishikawa-12/14 and Igarashihama-12/1.

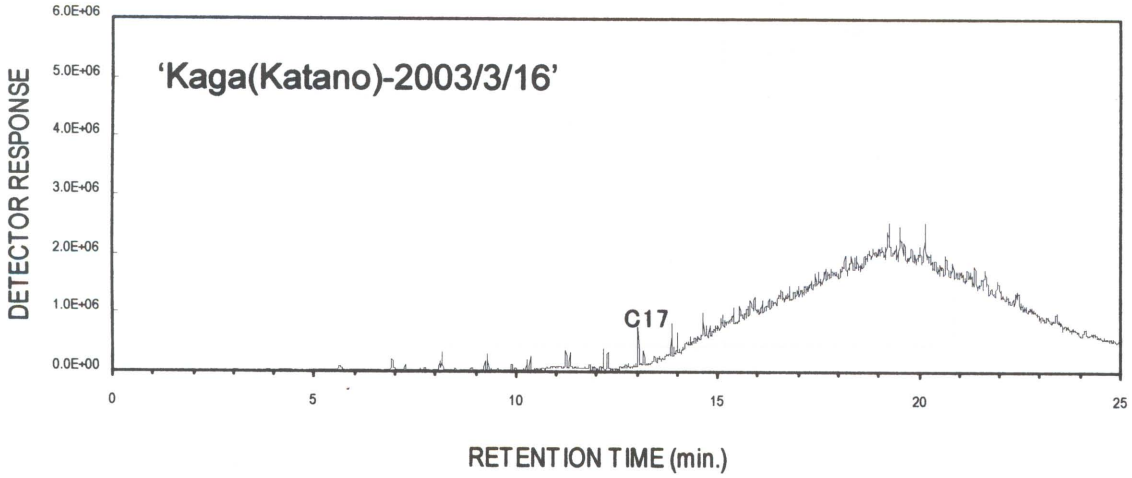

Figure 8 Gas-chromatogram of *n*-alkanes (m/z=57) from Kaga (Kagano)-2003/3/16.

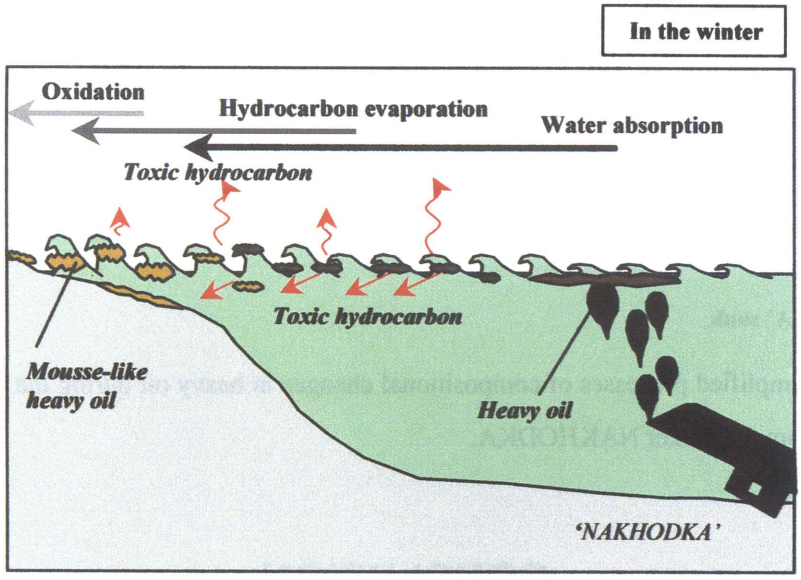

Figure 9 Schematic diagram of compositional changes in heavy oil during floating in the winter sea. Water absorption is predominant in this process.

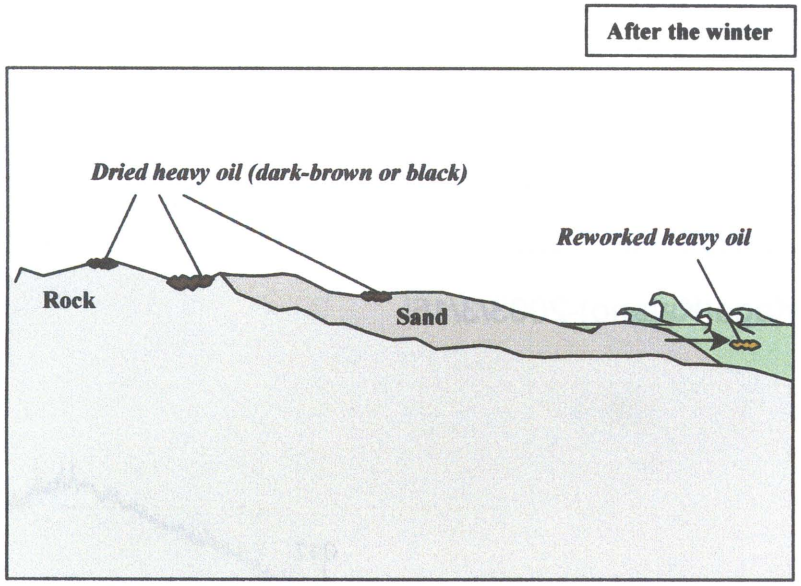

Figure 10 Schematic diagram of heavy oil on the land after the winter.

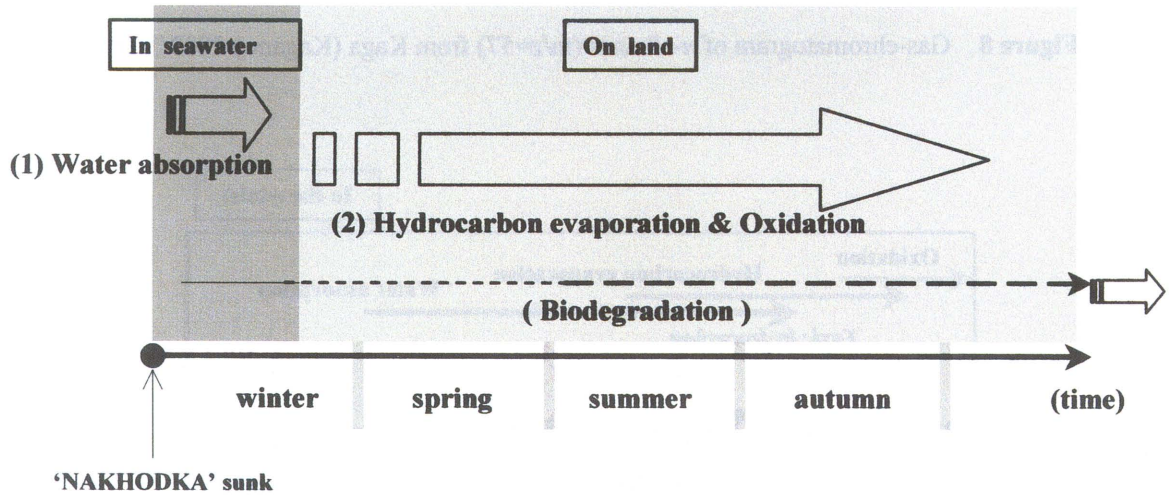

Figure 11 Simplified processes of compositional changes in heavy oil during the first year after the oil spill from the tanker NAKHODKA.

CONCLUSION

Compositional changes of heavy oils through one year after the oil spill from the tanker NAKHODKA were investigated based on the elemental and *n*-alkane analyses. The results show that chemical/physical process mostly influenced the decomposition of heavy oils, and the rate of biodegradation was low.

During floating in the East Sea under winter hard-climate, water washing has

entirely influenced the heavy oil, i.e. water absorption up to 1.7 times heavier than the original heavy C oil has occurred. After reaching the shore, the heavy oil were dried and oxidized. According to decreasing H/C and increasing O/C ratios of the heavy oil on the land, evaporation of hydrocarbon and oxidation of heavy oil were predominant as second processes.

n-Alkane distribution indicated a slow biodegradation under anoxic inner part of heavy oil through the first year after the oil spill, based on a lot of survived low molecular *n*-alkanes. But for outer part of the heavy oil, aerobic bacteria may fairly work to oxidize and break down the heavy oil. After about 6 years, remained heavy oils finely dispersed in beach sand had hydrocarbons with a lot of biodegradation. Namely, abundance of *n*-alkanes was quite small in the heavy oil. Oxic condition may support to increase the bacterial activity. This result suggests that fine dispersion of heavy oil on land is the most effective factor for high-rate biodegradation.

ACKNOWLEDGEMENT

We are grateful to staffs of Tazaki, Yoshimura and Sawano Groups for collecting the heavy C oil NAKHODKA and the derived heavy oils. We thank Teikoku Oil Company, chief researcher A. Hirai for offering information and literature on the general oil spill. Our gratitude is also to Miss Y. Kurakado, Miss A. Shimizu and Mr M. Hosaka of Shimane University for help of the GC analyses.

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