Various styles and long-term chemical changes of the heavy oil spilled from "Nakhodka"

VARIOUS STYLES AND LONG-TERM CHEMICAL CHANGES OF THE HEAVY OIL SPILLED FROM "*NAKHODKA*"

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ABSTRACT

Field observations and chemical analyses of the weathered heavy oils spilled from the Russian tanker *Nakhodka* were performed in the summer of 2003 to understand the elimination process of the spilled oils. Heavy oils buried in Shioya-Katano sandy beaches remain only small amount at the front of the green belt, agglutinating sand grains. Large amounts of residual heavy oils were found in Noto peninsula, particularly on the seashores where wave energy is low. The surface of the residual heavy oil is covered with crumbly crust consisted mainly of high molecular weight hydrocarbons. Under the crust, emulsions so called "Chocolate moose" are preserved with high water contents up to 70 weight percents. Chemical composition of heavy oil shows sequential concentration of higher molecular weight hydrocarbons with serious weathering. Distribution pattern of polycyclic aromatic hydrocarbons (PAH) with 4-ring structures and PAHs containing sulfur in the *Nakhodka* heavy oil are distinctive and well preserved in the weathered oils.

INTRODUCTION

In January 1997, C-heavy oil spilled from the Russian tanker *Nakhodka* seriously polluted large coastal area of Ishikawa and Fukui prefectures. For a few years since the accident, a number of studies on the oil pollution and fate of the spilled oils had been conducted by scientists and the government agencies (e.g., Tazaki et al. 1997; Itagaki and Ishida 1999; Shibata et al., 1997; Sekiyu Renmei 1997; Kizu et al., 1998; Environment and Security Department of Ishikawa Prefecture, 1998). To keep monitoring of the long-term change of remained heavy oil is essential for assessment of their dispersion in the environment and cleanup process. However there are a few reports concerning with situations of the *Nakhodka* spilled oils in resent several years. It is known that spilled heavy oil will be removed from the environment by various processes: evaporation, solution in water, degradation through chemical reactions and microbial activities. Lessons of a lot of oil spill accidents happened in the world have lead to great advances on the investigation of the recovery process from petroleum contamination (e.g. Wells et al., 1995; American petroleum institute,1997). However many factors which would influence the oil reduction rate and process: composition of spilled oil, weather, temperature, water chemistry and so on, are variable with individual case. Therefore it is desirable to conduct a thoroughgoing survey on the fate of the *Nakhodka* heavy oils continuously for well understanding of the impact and recovery process of oil pollution on the coast of the Hokuriku district.

In the summer of 2003, we conducted field survey and chemical analyses on the *Nakhodka* heavy oils remained in the shore of Ishikawa prefecture in order to understand the condition of residual oils after 7 years weathering. In this paper, we report the stile, nature and chemical compositions of heavy oils remained in various conditions, and on the basis of these analyses, weathering process of heavy oils spilled from *Nakhodka* are discussed.

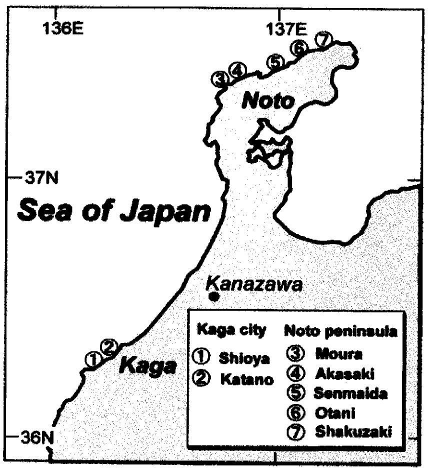

Figure 1 Localities of field survey and sampling sites

FIELD OBSERVATIONS

Field observations were performed at the sand beaches in Kaga city and rocky shores and gravel beaches in Noto peninsula where large volumes of spilled heavy oils had drifted on after the accident (Fig. 1). At Shioya and Katano beaches in Kaga city, oils were buried in the sand in approximately 20-30m away from shoreline during the cleanup activity just after the accident. The sand in sandy beach is unstable at the effects of wave and wind, and liable to move in large-scale at storm (e.g. Sawano, 2003). Heavy oils buried in Shioya-Katano beach have been almost removed by the spring of 2003. Residues are found in small amounts at the front of the zone of vegetation. Heavy oil exposed on the surface agglutinates sand grains forming a sandy block, which is almost dry, dark brown in color and non-smell (Fig. 2a). Heavy oils covered with sand also fills pore spaces among sand grains, but are still wet and viscous with strong petroleum smell (Fig. 2b).

Heavy oils remained in the rocky shores and gravel beaches were observed at five localities: Shakuzaki, Otani, Senmaida, Akasaki and Moura in Noto peninsula (Fig. 1). In the seashore directly exposed to the sea, heavy oils are only remained at the higher positions than those influenced by tidal waves. In the sheltered shores where wave energy is low, abundant heavy oil is found, particularly on the shore side of a rock. One typical style of weathered oil is patchy form (Fig. 2c,d). This residue is black-reddish brown, non-smell, and crumbly with strong viscosity. Heavy oil is often found as a large volume mass in the pore space, among gravels and boulders on the shore. The surface of the mass is covered by crumbly crust with 1-4mm thickness. Under the crust, light brown emulsion which is extremely sticky and has intense petroleum smell, so called “chocolate moose” is preserved, which was generated by mixing seawater and suspended particles with heavy oil (Fig. 2e, f).

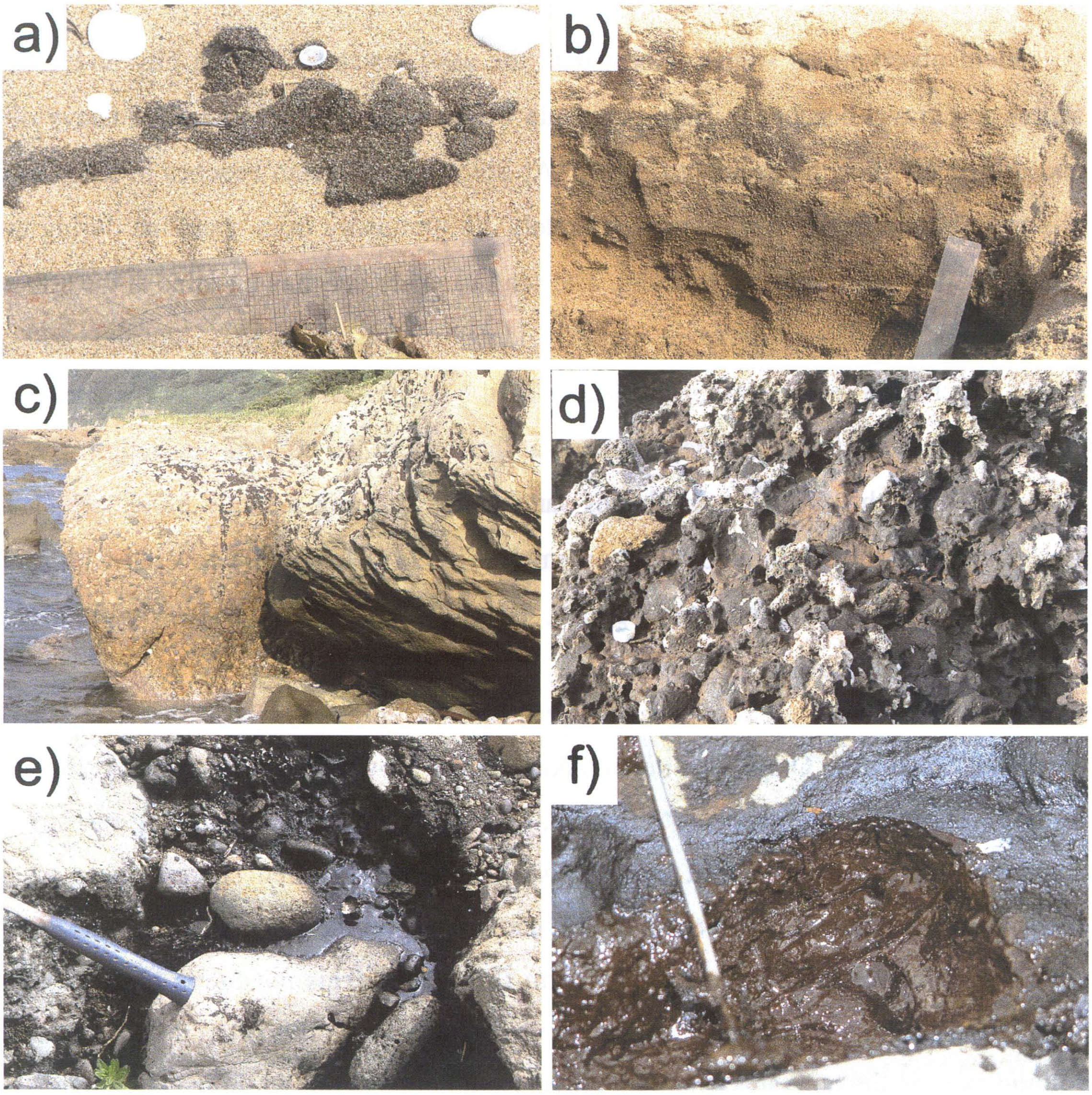

Figure 2 a) Heavy oil exposed on the surface of Katano sandy beach. b) Heavy oil layers buried in the Katano sandy beach. c) Heavy oil patches attached on the boulder on shoreline of Akasaki. d) Heavy oil mass remained on the boulder on the shoreline of Akasaki. e) Heavy oil remained in the gravel beach of Moura. f) Crust and emulsion of heavy oil remained in a large pore space among boulders in Akasaki seashore. Diameter of the bar is 2 mm.

CHEMICAL ANALYSES

Methods

Weathered heavy oils with varieties of styles and natures were collected from 7 localities for chemical analyses (Table 1). For the comparison, heavy oil collected from the ship-head of the *Nakhodka* and spilled oils collected in several weeks after accident (Akashima and Sodeura in Table 1), which are sealed and preserved under -10℃ in the refrigerator, also analyzed. Element analysis was performed with ED-XRF. Composition of hydrocarbon was analyzed by gas chromatography (GC) equipped with flame ionization detector (FID) + flame photometric detector (FPD), and GC with mass spectrometry (GC/MS). Heavy oil samples were separated into components soluble and insoluble in hexane using centrifugal separator. The former was separated into aliphatic and aromatic compounds by silicagel column chromatography, and used for GC/MS analysis, respectively. The latter is mainly consisted of water and high molecular weight hydrocarbons. High molecular hydrocarbons and water contents were estimated by comparing the weights between before and after dehydration treatment, kept at 110 ℃ for 6 hours in the oven.

Table 1 Relative concentrations of compounds of heavy oils spilled from the *Nakhodka*

	n-Alkan		PAH			
Samples	**C12/C30**	**C18/C30**	**NPT/p2**	**PNT/p2**	**p1/p2**	**p3/p2**
Nakhodka	0.8	3.39	1.41	2.97	0.72	0.52
Akashima	0.16	2.53	ND	0.43	0.68	0.41
Sodeura	0.02	2.33	0.07	0.41	0.6	0.45
Shakuzaki Emulsion	ND	1.2	ND	0.06	0.48	0.37
Otani Emulsion	ND	0.57	ND	0.1	0.81	0.57
Senmaida Emulsion	0.08	1.37	0.02	0.24	0.47	0.49
Akasaki Emulsion	0.07	1.97	0.05	0.56	1.06	0.6
Moura Emulsion	0.18	1.38	ND	0.15	0.34	0.3
Shakuzaki Weathered	ND	0.09	ND	0.06	0.46	0.48
Akasaki Weathered	0.09	1.63	ND	ND	0.5	0.42
Moura Weathered	ND	0.18	ND	ND	0.8	0.42
Akasaki Crust	ND	1.19	ND	0.29	0.9	0.43
Moura Crust	ND	ND	ND	ND	0.88	0.45
Moura Crust in the sea	ND	ND	ND	ND	ND	0.02

Note: NPT: Naphthalene, PNT: Phenanthrene.
p1,p2,p3 refer to peaks of the 4-ring PAHs shown in Fig. 5, respectively.

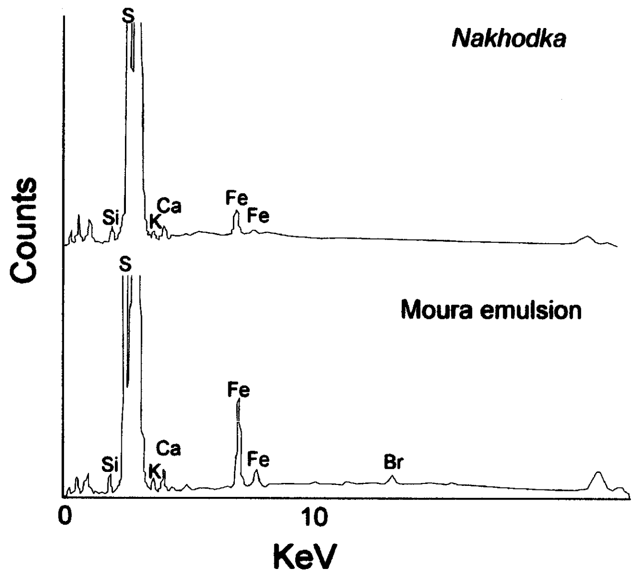

Figure 3 ED-XRF analyses of heavy oil spilled from Nakhodka.

Results

Since hardly exposed in the air nor mixed with seawater, the composition of C-heavy oil collected from the head of *Nakhodka* could be a composition as much as that of original oil. The *Nakhodka* heavy oil contains sulfur, calcium, silica and iron as major non-hydrocarbon components (Fig. 3). n-alkans with carbon number larger than 10 (C_{10}) are detected, and those ranging from C_{15} to C_{30} are abundantly contained in the *Nakhodka* oil (Fig. 4). Naphthalenes, phenantholenes and polycyclic aromatic hydrocarbons (PAHs) with 4-ring structure are also abundant (Fig. 5). The GC peaks of the component containing sulfur shows high intensities particularly at dibenzothiophenes (Fig. 6). The contents of high molecular weight hydrocarbons, which are defined as insoluble in hexane, are estimated about 5 weight percent of the total amount in the *Nakhodka* oil (Fig. 7).

Water contents of weathered heavy oils significantly change depending on their styles (Fig. 7). The emulsions contain large amounts of water ranging from 50 to 75 weight percents, on the other hand, crusts of the heavy oil are extremely dry. XRF analysis shows that the emulsions contain bromine (Fig. 3), which is a common element found in seawater and not detected in the heavy oil collected from the *Nakhodka.* Heavier compounds tend to be concentrated in the heavy oil with seriously weathered.

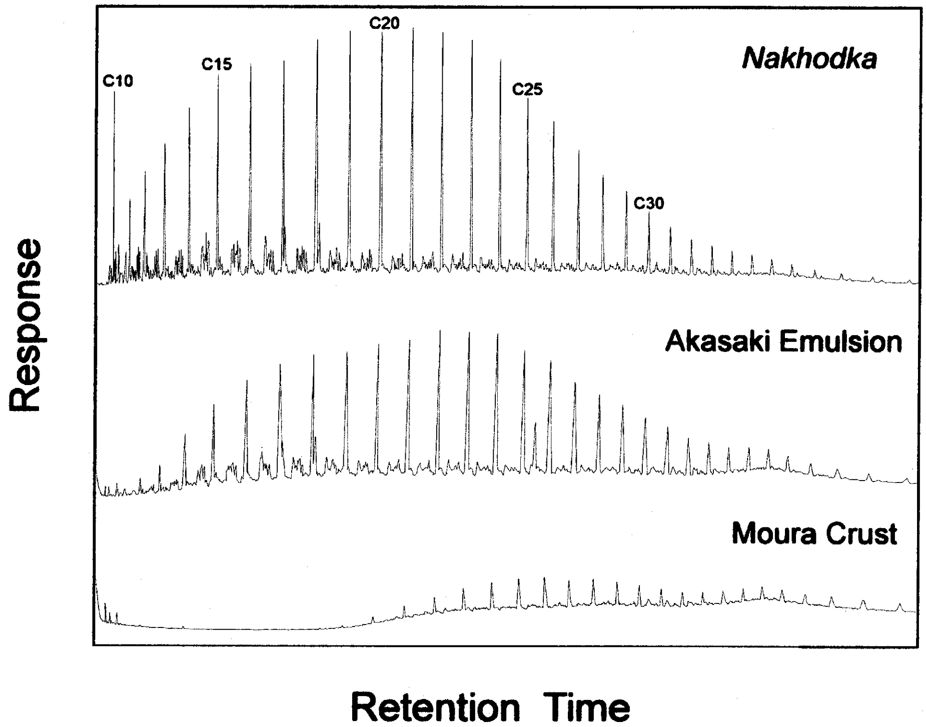

Figure 4 Three representative gas chromatograms of aliphatic compounds for differently weathered heavy oil.

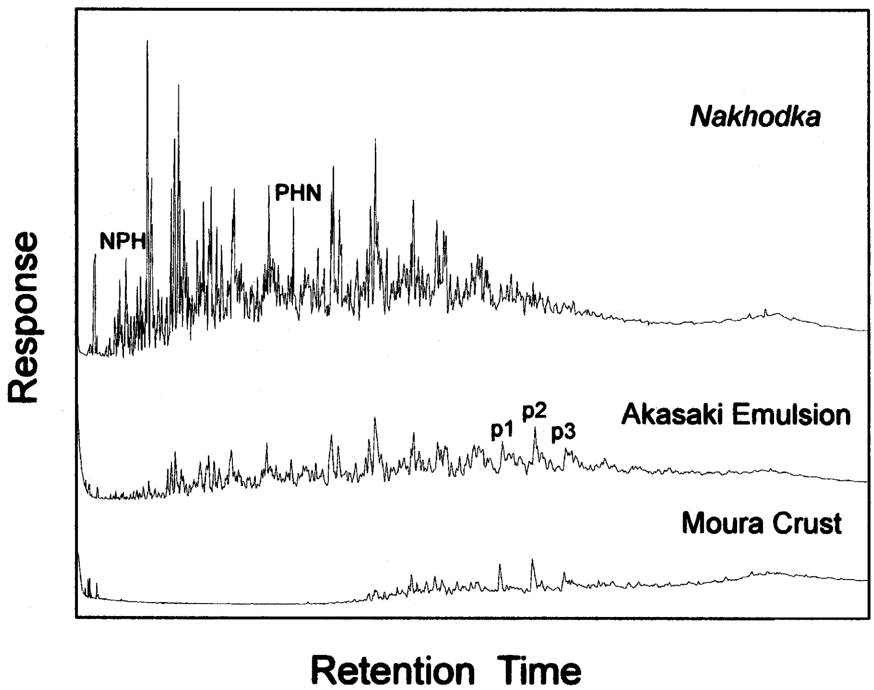

Figure 5 Three representative gas chromatograms of aromatic compounds for differently weathered heavy oil. FID was used. NPH: Naphthalene, PHN: Phenantholene. p1,p2,p3 are 4ring PAHs with prominent GC peaks.

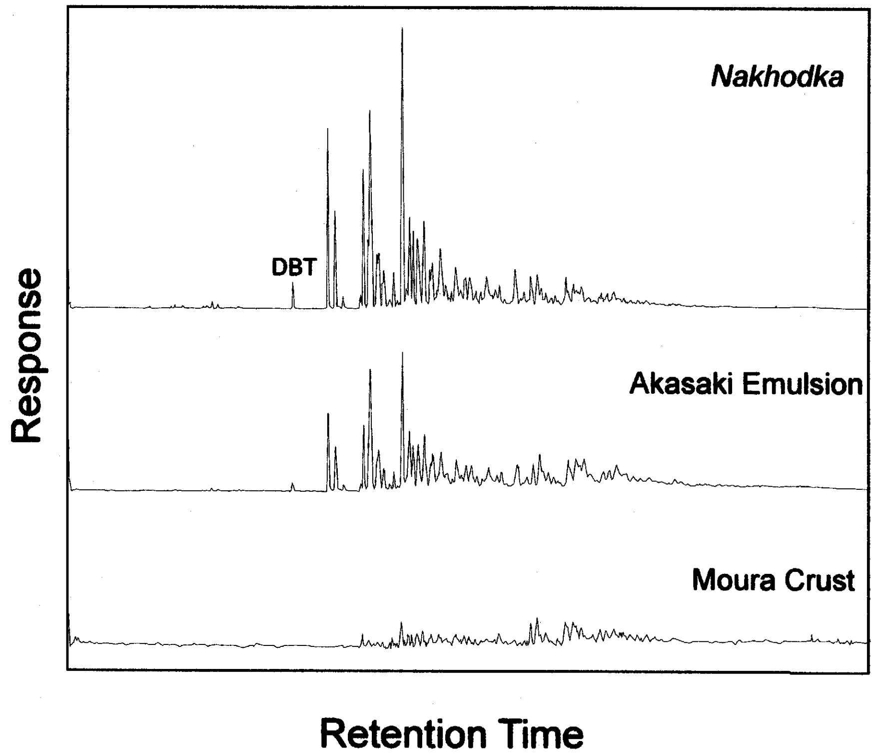

Figure 6 Three representative gas chromatograms of aromatic compounds for differently weathered heavy oil. FPD was used. DBT:dibenzothiophene

Emulsions show subtle changes in the ratio of heavy molecular compounds comparing with the *Nakhodka* oil, while very high concentration up to 60 percent in the dry crusts (Fig. 7). n-alkan smaller than C_{13} are almost disappeared in the emulsions, while undetected those smaller than C_{20}-C_{25} in the crusts (Fig. 4). Naphthalenes and phenanthrenes are significantly decreased in weathered oils. However 4-ring PAHs such as benzo[a]anthracenes, chrysenes and triphenylenes are well remained. Particularly compounds indicated as p1, p2 and p3 in Fig. 5 show prominent peaks even in seriously weathered samples. Distinctive distribution pattern of the PAHs containing sulfur is well maintained in the weathered oils (Fig. 6).

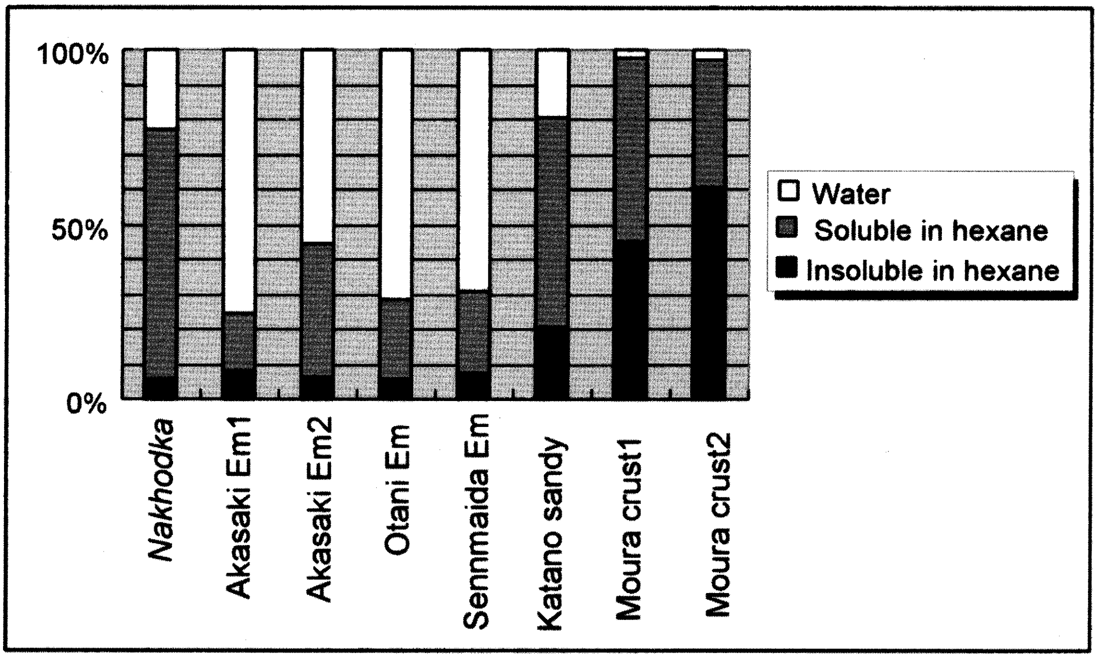

Figure 7 Compositions of weathered heavy oils. Em: emulsion,

DISCUSSIONS and CONCLUSIONS

Evaporation, photooxidation and biodegradation are representative cleanup mechanisms of spilled oils. Effective operation of either of these process or combination of them could enhance the rapid removal of the spilled oil from the environment. However our results of field observations and chemical analyses revealed that large amount of spilled oils are still remained on the seashore of Ishikawa prefecture with various styles and conditions depending on the coastal environments. It is worthy mentioning that oil emulsions are preserved abundantly in the large pore spaces on the gravel beaches and rocky shores. These chemical compositions have been little changed in 7 years except for some volatile compounds.

It is reasonable to consider that heavy oil masses left behind in the pit and pore spaces on the seashore are no longer of subjects of bioremediation by microbes. Moreover, with light compound's evaporating and photooxidating at the surface of mass, thin crust consisting of only high molecular weight hydrocarbons would be formed covering the whole oil mass. This suppresses the operation of all possible mechanisms of oil removal, and resulting in preservation of heavy oils over a long period. Accordingly rate of disappearance of heavy oil from the environment could be controlled only by physical erosion of the crust consisting of high molecular weight hydrocarbons. Therefore, when the oil spill accident happens, recovering oil drifts in offshore and preventing them from shoreline are primarily important for oil pollution defense.

To characterize oils and to identify their sources are necessary for long-term monitoring of spilled oils. As mentioned in previous works (e.g. Shibata and Morita, 1998), hydrocarbons associated with sulfur such as dibenzothiophenes in the *Nakhodka* C-heavy oil show a distinctive distribution pattern. This feature is maintained in most of the residues of the *Nakhodka* spilled oil analyzed in present study. Therefore these hydrocarbons are useful for identification of the *Nakhodka* spilled oil as an effective fingerprint.

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