Chapter 16
Oil Spills and Polycyclic Aromatic Hydrocarbons

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Abstract Crude oil contains many kinds of polycyclic aromatic hydrocarbons, and its release into the marine environment causes serious damage. It is important to understand the behavior and biological effects of PAHs as components of oil. Over the last five decades, many large-scale oil spills, including the Gulf War oil spill in 1991 and the Gulf of Mexico oil spill in 2010, have occurred in the world. This chapter describes the long-term impact on marine and coastal environments by C-heavy (the last distilled fraction of heavy oil) oil spilled from the Nakhodka in the Japan Sea in 1997, where polycyclic aromatic hydrocarbons were monitored as pollution markers.

Keywords Nakhodka oil spill · Heavy oil · Polycyclic aromatic hydrocarbon · Japan Sea · Fish

16.1 Introduction

Crude oil contains many kinds of hydrocarbons such as polycyclic aromatic hydrocarbons (polynuclear aromatic hydrocarbons, PAHs), asphaltene, and resin. Oil spills from ships and oil wells cause serious damage to marine and coastal environments. It is important to understand the behavior and biological effects of PAHs as components of oil. The 1967 Torrey Canyon oil spill in the Dover Strait led to international rules to prevent oil contamination. Since then, 13 large-scale oil spills, over 100,000 tons, including the Gulf War oil spill in 1991 and the Gulf of Mexico oil spill in 2010, have occurred (Moss 2016; Smithsonian National Museum of Natural History 2016). In those oil spills, several long-term environmental impact assessments, such as the 1989 Exxon Valdez oil spill in Alaska, have been carried out

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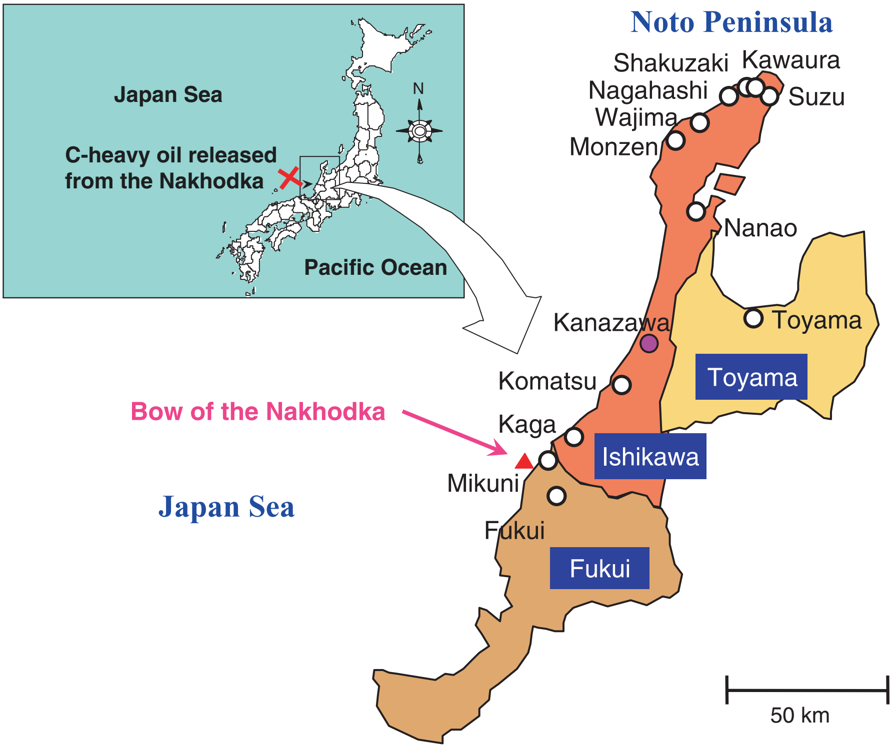


Fig. 16.1 Coastlines of Ishikawa and Fukui prefectures

(Maki 1991; Neff and Burns 1996; Davies and Toppong 1995; Wells et al. 1995). Most of these spills were crude oil spills.

A Russian tanker, the Nakhodka (13,157 gross tons), loaded with C-heavy oil, sank because of a strong northwest wind in the Japan Sea about 100 km offshore from Oki Islands, Japan, on January 2, 1997. Over 6000 kL of the loaded C-heavy oil leaked from the tanker, and a part of it was blown onto the Japanese coastlines from Shimane Prefecture to Akita Prefecture, Japan. The amount of beached C-heavy oil was significantly large on the coastlines of Fukui and Ishikawa Prefectures (Fig. 16.1). The Nakhodka oil spill was the third largest scale oil spill in the seas near Japan since 1970. After the spill, many people, including volunteers, attempted to clean up the spilled oil, and researchers from Japanese national and local governments and universities began environmental impact assessments.

Crude oil is distilled into gasoline, kerosene, light oil, heavy oil, and tar by increasing the temperature. C-heavy oil is the last distilled fraction of heavy oil. The concentrations of PAHs having four rings or more in C-heavy oil are much higher than in crude oil. This is the reason for the high viscosity and the longevity of C-heavy oil in the environment. It is well known that PAHs, such as benzo[*a*]pyrene, can act as carcinogens or mutagens. Because of this, PAHs in the blue mussel were investigated over a year after the Braer Corp crude oil spill in the Shetland Islands in 1993 (Webster et al. 1997). In addition, several metabolites of PAHs were found to show adverse effects to marine organisms. Several hydroxylated PAHs show agonistic and antagonistic activities in the estrogen receptor and disruption in bone metabolism in fish. Several PAH quinones cause the overproduction of reactive oxygen species (ROS) in cultivated cells (see Part VI). These results suggest both direct, indirect, long-, and short-term effects of spilled oil on marine and coastal ecosystems.

During the 2 years after the Nakhodka oil spill, the degree of oil contamination of coastlines in Ishikawa and Fukui Prefectures, Japan, was assessed. In addition, the recovery of the coastlines was monitored by examining PAHs in oiling lumps (oil ball and paste), sand, seawater, and fish.

16.2 Relationship Between Coastal Characteristics and Residual Tendency of C-Heavy Oil

Visual observations at coastlines contaminated with C-heavy oil from the Nakhodka were made on (1) March 21 and April 17–18, 1998 and (2) April 17–18 and May 15, 1999. The total length of the coastline investigated was 170 km, spanning from Suzu, Ishikawa Prefecture, to Mikuni, Fukui Prefecture (Fig. 16.1), with the exception of steep coasts which could not be reached by foot. The coastlines investigated were divided into 176 zones, and the amount of C-heavy oil was visually monitored. The substrates of the zones were classified into four types: bedrock (60 zones), boulder/cobble/pebble (particle size not less than 4 mm, 34 zones), gravel/sand (particle size <4 mm, 53 zones), and man-made material (concrete tetrapods, 29 zones). The shapes of the bedrock and boulder/cobble/pebble on the coasts were classified into three types: exposed (30 zones), pocketed (35 zones), and sheltered (32 zones).

After 1 year of observation (approximately 14.5 or 15.5 months after the spill), 47% of bedrock sites, 47% of boulder/cobble/pebble sites, and 50% of man-made material sites were classified as heavily oiled (level D) coasts, but only 6% of the gravel/sand coasts were classified as heavily oiled (Table 16.1). After 2 years of observation (approximately 27.5 or 28.5 months after the spill), the percentage of the heavily oiled coasts was remarkably lower. The coastlines of the Noto Peninsula are mainly covered with bedrock or boulder/cobble/pebble, while coastlines of the south part of Ishikawa Prefecture (Kaga area) are mainly covered with sand (Fig. 16.2a). The heavily oiled coasts were mainly observed in the Noto Peninsula 1 and 2 years after the spill (Fig. 16.2b). A strong correlation was observed between the heavily oiled sites and bedrock or boulder/cobble/pebble areas. Unlike the contamination in the bedrock or boulder/cobble/pebble areas, the contamination of coastal gravel/sand or man-made materials rapidly recovered. This difference suggests that the tidal strength was strong enough to wash the coastal gravel/sand and man-made materials. The coastal shape also tends to affect how long oil remains. After 1 year of observation, the high percentages of heavily oiled coasts were observed at sheltered sites for the bedrock coasts and sheltered sites for the boulder/cobble/pebble coasts (Picture 16.1).

Table 16.1 Relationship between oiling level and habitat of Ishikawa and Fukui coastlines

Habitat	n	After 1 year %				After 2 years %			
		A	B	C	D	A	B	C	D
Rock	60	29	9	15	47	13	62	17	8
Boulder/cobble/ Pebble/gravel	34	12	21	21	47	44	27	18	12
Sand	53	59	19	16	6	68	22	4	6
Man-made	29	31	7	12	50	38	37	25	0

Observations: (after 1 year) March 21, 22 and April 17, 18, 1998; (after 2 years) April 17, 18 and May 5

Oiling levels: A, none remaining; B, light; C, moderate; D, heavy

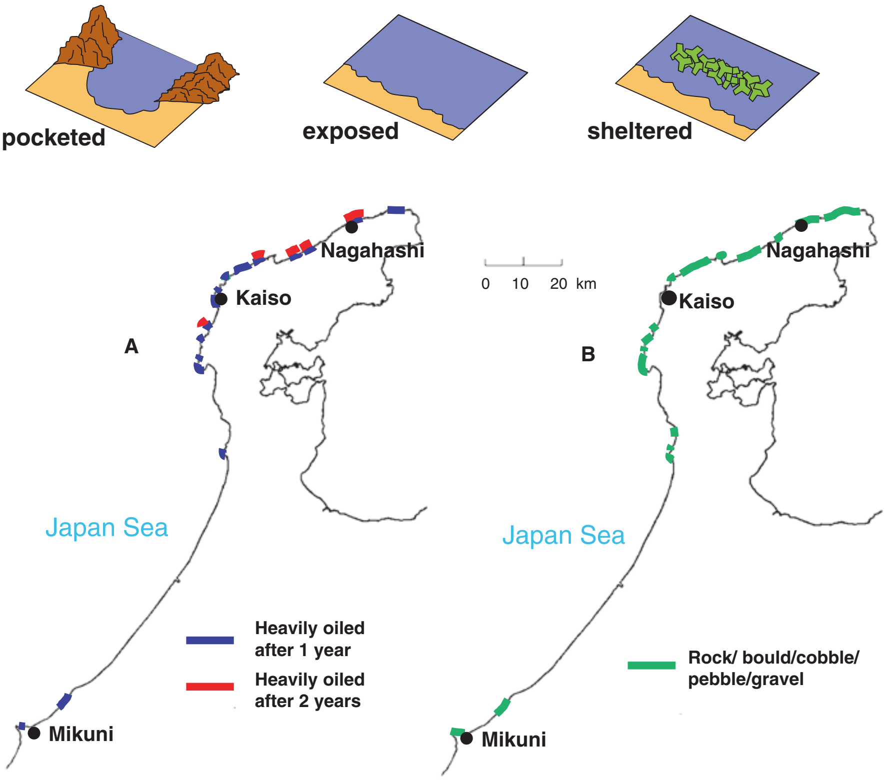
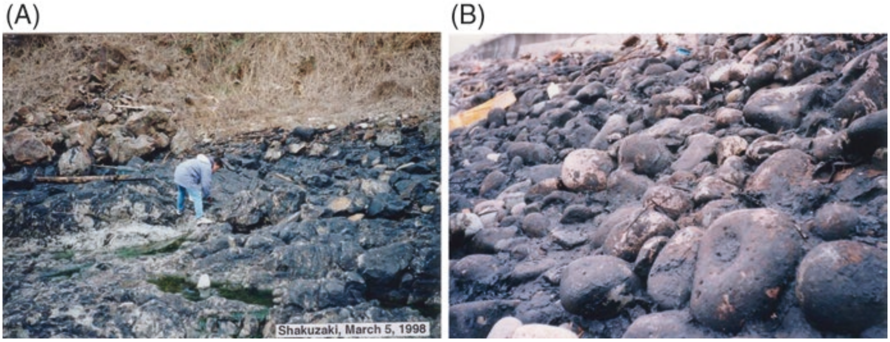


Fig. 16.2 Relationship between coastal characteristics and the longevity of C-heavy oil spilled from the Nakhodka. (**a**) Zones covered with bedrock or boulder/cobble/pebble, (**b**) heavily oiled zones at 1- and 2-year observations

The tendency for the oil to remain was also affected by meteorological conditions, topographic features, and physical properties of the oil. A large part of the coastlines of the Noto Peninsula are sheltered. The waves are usually weakened by offshore rocks. However, in the winter a strong northwest wind from the Asian continent hits the west coast of the Japan Islands, causing high energy waves to strike



Picture 16.1 Pictures of long-term heavily oiled coasts. (**a**) Shakuzaki, Suzu, on March 5, 1998. (**b**) Kawaura Beach, Suzu, on March 5, 1998

the coast. In January, waves in the Japan Sea may have deposited oil on the shores over the sheltered rocks. After C-heavy oil is beached, it may have been difficult to remove from either sheltered or exposed types of coasts because the oil hidden within the rocks and of its high viscosity makes contact with waves difficult. Other factors possibly affecting the length of time oil remains on the coasts of the Noto Peninsula might include the steepness of the shores, as well as the lack of volunteer effort due to an areas' remoteness. The above results made it possible to adopt suitable countermeasures including cleanup methods for each type of coast. For this purpose, the Hazardous Materials (HAZMAT) Response and Assessment Division of the US National Oceanic and Atmospheric Administration (NOAA) has published Environmental Sensitivity Index (ESI) maps which describe all environmental elements that mediate the extent of contamination, such as relative exposure to waves and tidal energy, shoreline slope, substrate type, biological productivity, and sensitivity (NOAA HAZMAT 2002). As a lesson from the Nakhodka oil spill, the Japanese Coast Guard made the ESI of the shorelines of Japan (Japan Coast Guard 2009). According to the guidelines, the fragility of coastal bedrock and boulder/cobble/pebble is higher than that of gravel/sandy beaches, and the fragility of sheltered-type coasts is higher than that of the exposed coasts.

16.3 PAHs in Oil Lumps, Sand, and Seawater

Samples of the beached oil, sand, and seawater were collected at five sites: Otani and Nagahashi (Suzu, Ishikawa), Fukami and Kaiso (Monzen, Ishikawa), and Sunset Beach (Mikuni, Fukui) (Fig. 16.1). Their substrate types and the shapes of the coasts of the five sampling sites are as follows: Otani (Suzu), sand, exposed; Nagahashi (Suzu), bedrock, sheltered; Fukami (Monzen), bedrock, pocket; Kaiso (Monzen), boulder/cobble/pebble, sheltered; and Sunset Beach (Mikuni), sand, exposed. Nakhodka C-heavy oil or beached oil lump was weighed, dissolved in benzene, and diluted with acetonitrile. Deuterated PAHs (naphthalene-d_8,

Table 16.2 Concentrations of PAHs in The Nakhodka C-heavy oil

Number of rings	Name	Concentration (μg/g)
2	Naphthalene	410
3	Acenaphthene	27
	Fluorene	106
	Phenathrene	2630
	Anthracene	33
4	Fluoranthene	47
	Pyrene	164
	Benz[*a*]anthracene	210
	Chrysene	336
5	Benzo[*b*]fluoranthene	92
	Benzo[*k*]fluoranthene	14
	Benzo[*a*]pyrene	91
	Dibenz[*ah*]anthracene	110
	Benzo[*ghi*]perylene	217
6	Dibenz[*ah*]anthracene	76

phenanthrene-d_{10}, pyrene-d_{10}, and benzo[*a*]pyrene-d_{12}) were added as internal standards to each sand sample, and PAHs were extracted with *n*-hexane. One half of the solution was evaporated to dryness and dissolved in acetonitrile. Each seawater sample was filtered with a membrane filter (pore size 0.4 μm), and deuterated PAHs were added to the filtrate as internal standards. The solution was applied to a polymethacrylate cartridge. PAHs on the cartridge were eluted with acetonitrile. An aliquot of each solution was injected into an HPLC system for PAH quantification. The 16 US EPA PAHs (minus acenaphthylene) were all detected in the Nakhodka C-heavy oil. Among these PAHs, phenanthrene (Phe), a three-ring PAH, had the highest concentration followed by chrysene (Chr), a four-ring PAH (Table 16.2).

The Nakhodka C-heavy oil contained not only PAHs having two to four rings but also PAHs having more rings such as indeno[1,2,3-*cd*]pyrene (IDP), a six-ring PAH. In aged lumps on the coasts, the concentrations of PAHs were lower than those in the Nakhodka C-heavy oil, suggesting the degradation of PAHs in the environment. Naphthalene (Nap), a two-ring PAH, rapidly disappeared after the spill (Fig. 16.3). By contrast, the decreases of the other PAH concentrations were much slower. This is because Nap (boiling point 217.9 °C, melting point 80.2 °C) is more volatile than PAHs having three rings or more. Nap sublimes easily even on cold winter days. The boiling point of anthracene (Ant) (342 °C), a three-ring PAH, is higher than that of Nap, which might explain why the concentration of Ant did not decrease soon after the spill but decreased gradually. Another reason for the fast decrease of Nap may be its relatively high solubility in seawater. The solubilities of PAHs in water are compared in Table 1.1 in Chap. 1. The solubility of Nap (19–38 mg/L in seawater at 22 °C) is much larger than that of benzo[*a*]pyrene (BaP) (0.003 mg/L in seawater at 22 °C), a five-ring PAH, in seawater (Verschuerene 2001).

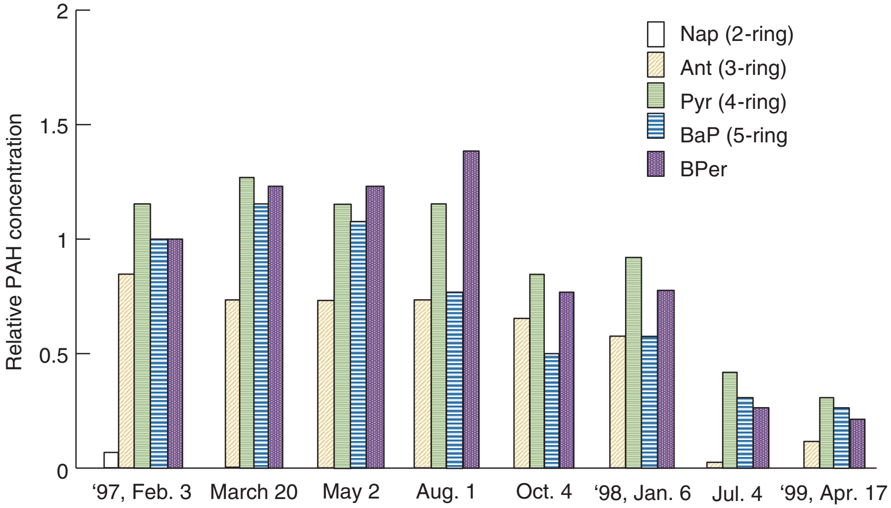


Fig. 16.3 PAH concentrations in beached oil lumps collected on bedrocks at Nagahashi, Suzu Each PAH concentration is the mean value of three samples and is expressed as a value relative to those in the Nakhodka C-heavy oil

Figure 16.3 shows the time course of concentrations of PAHs in beached oil relative to the concentrations in Nakhodka C-heavy oil. Both pyrene (Pyr), a four-ring PAH, and benzo[*ghi*]perylene (BghiPer), a five-ring PAH, increased up to August 1, 1997 (7 months after the spill) and then decreased. This initial increase of the concentrations of Pyr, BaP, and BghiPer might be due to evaporation of the components having low boiling points from the lumps. PAHs having four rings or more could not be easily degraded (Cookson 1995), although bacterial degradation of n-alkanes (Tazaki 1997) and PAHs having two or three rings have been reported (Hayakawa et al. 2000). These results suggest that the gradual decreases in the concentrations of Pyr, BaP, and BghiPer having four rings or more observed on the contaminated coastlines might be mainly due to photolysis (Tebbens et al. 1971). Moreover, among these three PAHs, BaP showed the fastest decrease in the first year, possibly because it is less stable in sunlight (Hayakawa et al. 2002).

The concentrations of BaP in seawater at Nagahashi (Suzu) and Kaiso (Monzen) were 7.5–8 μg/L on February 8, 1997 (1 month after the spill), and the concentrations at Sunset Beach, Mikuni, were lower on May 2, 1997 (4 months after the spill) than those at the other two sites because of the quick recovery operation described above. However, the concentration at Sunset Beach was as high as those of the other sites on January 6, 1998 (1 year after the spill), suggesting transportation of the contamination from other polluted sites. The concentrations decreased gradually at the three sites, reaching sub ng/L levels by April 30, 2000, more than 3 years (40 months) after the spill (Fig. 16.4).

BaP concentrations in seawater at three coasts (Nagahashi, Kaiso, and Sunset Beach) were compared to that of several other coasts that were not affected by the Nakhodka oil spill (Fig. 16.5). Surprisingly, the BaP concentrations in seawater at

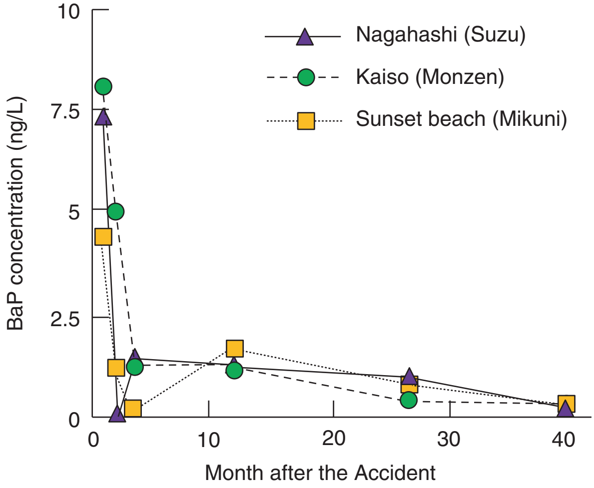


Fig. 16.4 BaP concentrations in seawater at Nagahashi (Suzu), Kaiso (Monzen), and Sunset Beach (Mikuni) after the Nakhodka oil spill
Each point and bar represents the concentration and SD, respectively
Sampling dates: February 8, March 20, May 2, 1997; January 6, 1998; April 17 (May 8 for Sunset Beach), 1999; April 30, 2000

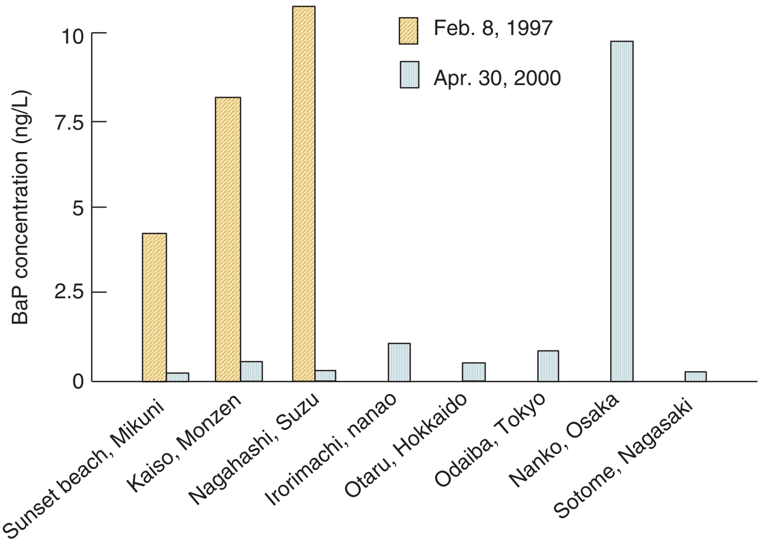


Fig. 16.5 Comparison of BaP concentrations in seawater at Nagahashi (Suzu), Kaiso (Monzen), and Sunset Beach (Mikuni) and other beaches in Japan
Each concentration represents the mean values of two samples

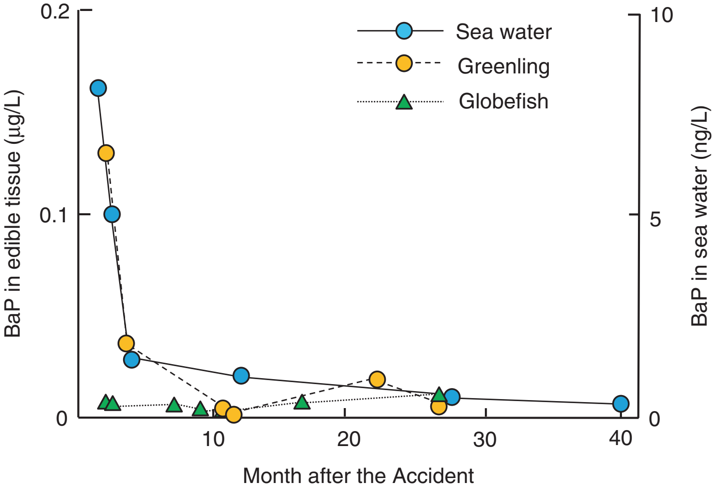


Fig. 16.6 BaP concentrations in edible tissues of greenling and globefish collected at Kaiso, Monzen, Japan, after the Nakhodka oil spill

the three beaches on February 8, 1998 (1 month after the spill) were comparable to that at Nanko, Osaka, whose harbor is well known for its pollution. However, on April 30, 2000 (more than 3 years after the spill), the BaP concentrations at the three coasts (0.20–0.27 ng/L) were as low as those at Sotome (Nagasaki) and Otaru (Hokkaido) which are famous for their cleanness. This suggests that the above three coasts all recovered from the seawater pollution by 3 years after the spill.

16.4 PAHs in Fish

Fish were collected at Kaiso, Monzen (Fig. 16.1), which had the highest BaP concentrations in seawater in the first 2 months after the spill in the three coasts as shown in Fig. 16.4. Two nonmigratory species, greenling and globefish, live in a narrow area near the shoreline, which was polluted with oil. The concentration of BaP in edible tissues of greenling was 0.13 ng/g on March 20, 1997 (2 months after the spill) which was much higher than that in globefish. The concentration was still higher on April 17, 1997 (3 months after the spill). On November 15, 1997 (more than 10 months after the spill), the concentration was as low as the level in unpolluted seawater (0.005 ng/g) (Fig. 16.6). The change in BaP concentrations in the edible tissues of greenling tended to follow the pattern change of BaP concentration in seawater, although the sample number was not large enough to obtain a clear conclusion. On the other hand, the concentration of BaP in edible tissues of globefish was not so high, possibly because this species lives on bedrock near the sea surface while greenling live at the bottom of the sea and/or because globefish do not have as much fatty tissue. Thus, the BaP in greenling might be a biomarker for C-heavy oil contamination of seawater.

High concentrations of PAHs in fish were also observed after the Exxon Valdez crude oil spill (Al-Yakoob et al. 1993). During 4 months after the Exxon Valdez oil spill, the total concentration of PAH subcomponents (naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) in tissues (6.9 + 1.4 μg/g) was much higher than that in the control (0.025 + 0.013 μg/g). The concentration in the pink salmon tissues (0.18 + 0.028 μg/g) was also much higher than that 1 year after the spill (0.051 + 0.007 μg/g) which was as low as the control level (Carls et al. 1996). The tendency for the PAH concentration in fish to be significantly higher just after the spill and to decrease to the control level in a year was similar to what we observed in greenling fish following the Nakhodka oil spill.

More detailed studies of oil on fish eggs and fishes are described in Part VI.

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