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Studies on the oil pollution of sediments in the Seto Inland Sea

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Oils are supplied from various sources to the ocean. Then released oils are spread on the surface and degenerated by evaporation or solubilization, and the residual oil adheres to the detritus or small clay particles suspending in the sea, being accumulated to the bottom sediments afterwards.

The oily substances are mainly supplied to the ocean through two pathways. The first one is the decomposition of marine organisms and the second one is the influx from the land or ships. It is estimated by NISHIMURA [1] that the oil influx to the Seto Inland Sea amounts approximately 13300-31600 ton per year. The discharge from the land and industry occupies about 57-69% of total released oil, the bilge from ships occupies 10-23%, spilling from the oil transport occupies 2-5% and the accident of tanker occupies 4-32%. Therefore, it is obvious that most of the oils are discharged from the land and industry.

The lipids extracted from the bottom sediments contain biogenetic components.[2] Therefore, in order to estimate whether the marine environment is polluted by oil or not, it is very significant to separate the biogenetic components from the petroleum components. The intent of this paper is to estimate the degree of pollution of bottom sediments in the Seto Inland Sea by analyzing the composition of hydrocarbons extracted from mud.

The data utilized in this manuscript were acquired in the surveys on the influence of the discharged oil to the marine ecosystem and on the influence of the reclamation to fisheries.

Materials and Methods

The area investigated: The Seto Inland Sea is an area surrounded by the western parts of Honshu, Shikoku and Kyushu Islands. The distance of the Seto Inland Sea from the east to west is about 445 Km and from the north to the south is 18-55 Km, and the area is about 17107 Km^2. There are about 3000 islands, and the Seto Inland Sea is divided into several regions by channels. In this study, the surveys were carried out in the eastern part of the Seto Inland Sea and in Beppu Bay. The industries are developed along the coast of Seto Inland Sea, big ports are located at Kobe and Osaka and many steamers navigate

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to the area.

Survey: The surveys were carried out during 25th, Jan. - 3rd, Feb., 1975 in the eastern part of the Seto Inland Sea and during 13th - 14th, Mar., 1975, 4th - 7th, July, 1975, 8th - 11th, Oct., 1975, 24th - 25th, Feb., 1976 in Harima Nada. The survey was also done during 27th - 30th, Nov., 1975 in Beppu Bay. The sediments were collected with Eckman - Berge dredge and stored at - 20°C until the laboratory work.

Analytical procedure: Lipids were extracted from sediments with chloroform-methanol (1:1, v/v), then the hydrocarbon fraction was obtained by a silicic acid column chromatography[3], and analyzed by gas liquid chromatography.

Gas liquid chromatography: A Hitachi 073 gas chromatograph was used. The column was 2m in length, 3mm in internal diameter, packed with 1 % Dexil-300 on Celite 545 (80-100 mesh, acid washed and siliconized). The oven temperature was programmed from 100°C to 340°C at a rate of 5°C per minute. The injector and detector were at 350°C. The carrier gas (N_2) flow rate was 60ml/min. The detector was a flame ionization detector. The hydrocarbons were identified by the comparison of the retention time of authentic hydrocarbons and of residual fuel oil (C grade), and by the internal standard methoh.

Ignition loss (Crude organic matter): Ignition loss is determined by burning the dry mud at 750°C until the weight become constant.

Results

The distribution of lipid content is shown in Fig. 1 and 2. The area where

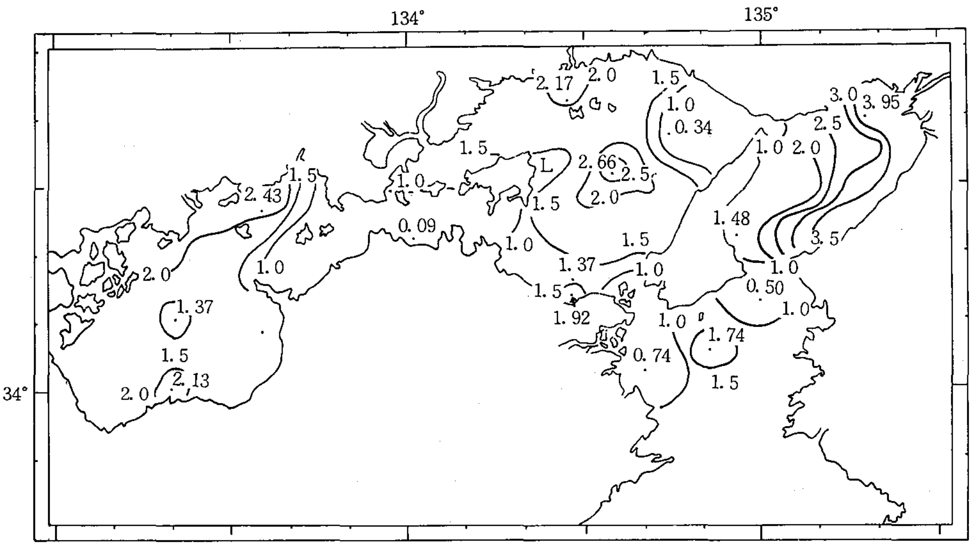


Fig. 1. The distribution of lipid content in the eastern part of the Seto Inland Sea. (mg/g dry mud) (Jan., 1975.)

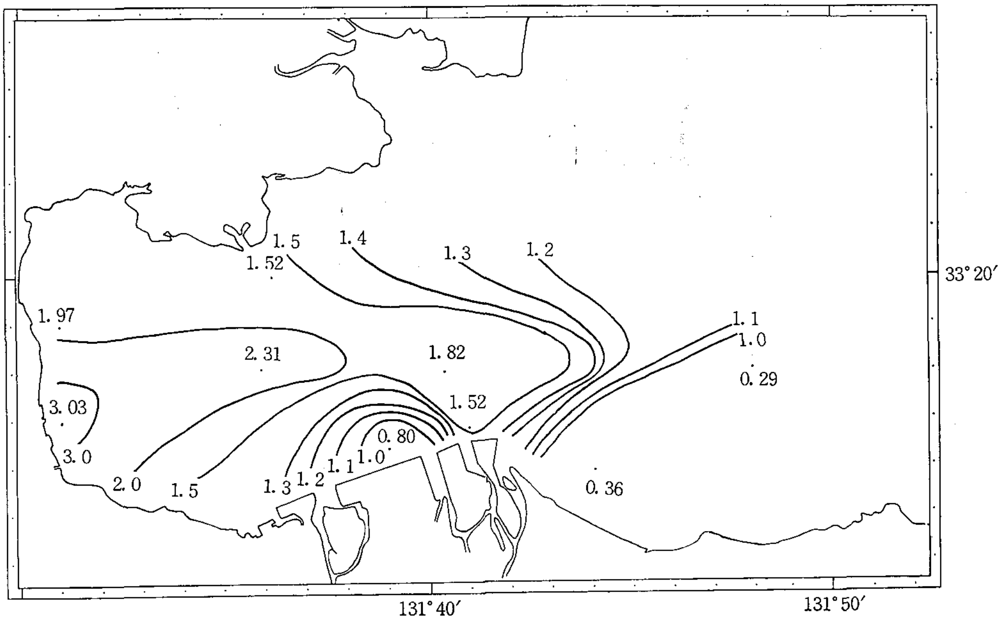
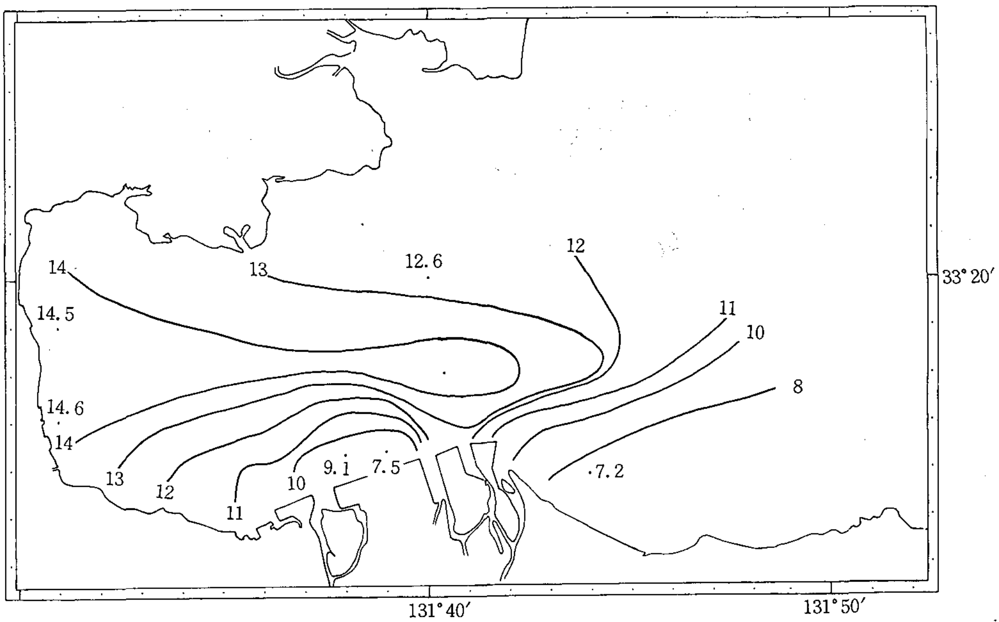


Fig. 2. The distribution of lipid content in Beppu Bay.
(mg/g dry mud) (Nov., 1975.)



Fig, 3. The distribution of the ignition loss in Beppu Bay.
(%) (Nov., 1975.)

the lipid content is over 2 mg/g dry mud are located at Osaka Bay, the northern and central parts of Harima Nada, the northern part of Bingo Nada and also the central part of Beppu Bay. As seen in Fig. 3 on the distribution of the ignition loss at Beppu Bay, the high value (14.8%) is obtained at the central part of this area, and the distribution patterns are coincident with those of lipid and hydrocarbon content in Fig. 4.

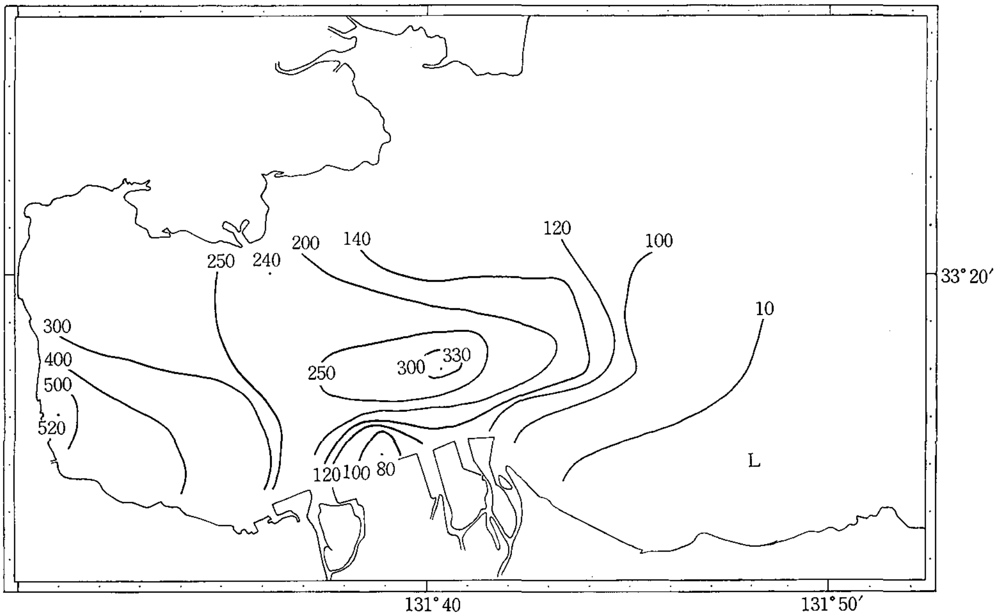


Fig. 4. The distribution of hydrocarbon content in Beppu Bay.
(ppm) (Nov., 1975.)

The gas chromatogram of authentic hydrocarbons is shown in Fig. 5, and that of the residual fuel oil is shown in Fig. 6. The occurrence of n-alkanes ranging from n-hexadecane to n-pentatetracontane was comfirmed in the residual fuel oil. Under gas chromatographic conditions previously described, the peak of n-heptadecane and pristane, and of n-octacosane and squalene were not separated completely.

The gas chromatogram of hydrocarbons extracted from mud is shown in Fig. 7. The presence of pristane, squalene and n-alkanes was comfirmed as reported previously.[4] The long chain n-alkanes (n-C_{36} to n-C_{40}) were detected at the

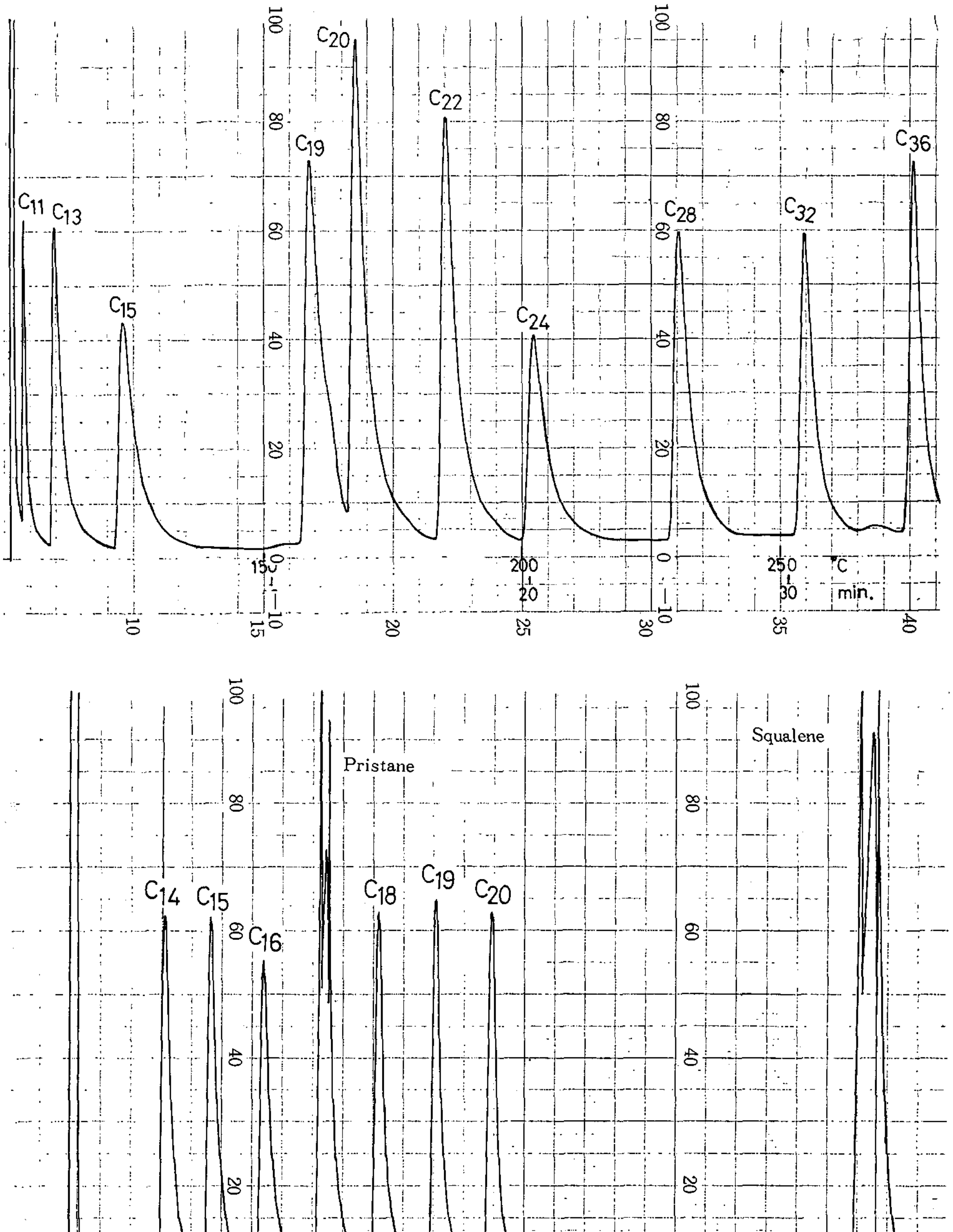


Fig. 5. The gas chromatogram of the authentic hydrocarbons.

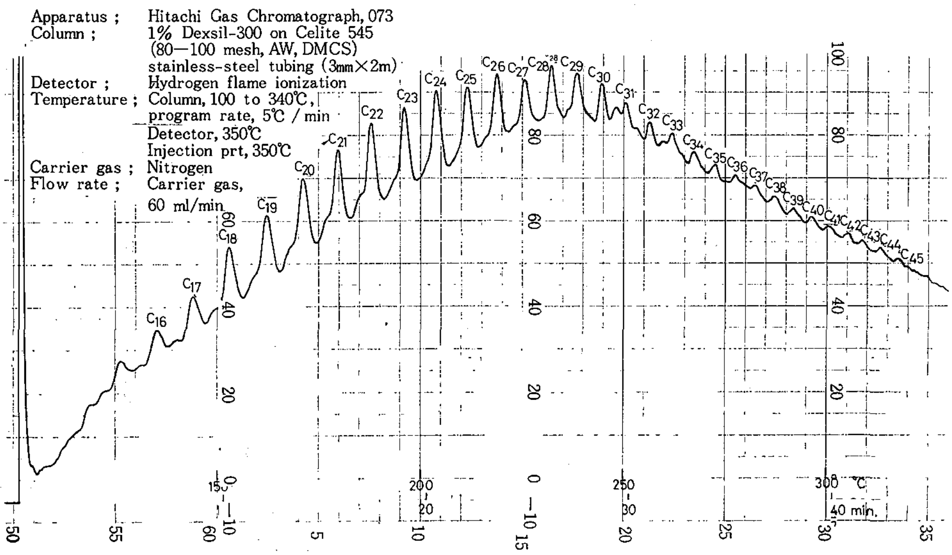


Fig. 6. The gas chromatogram of the residual fuel oil.

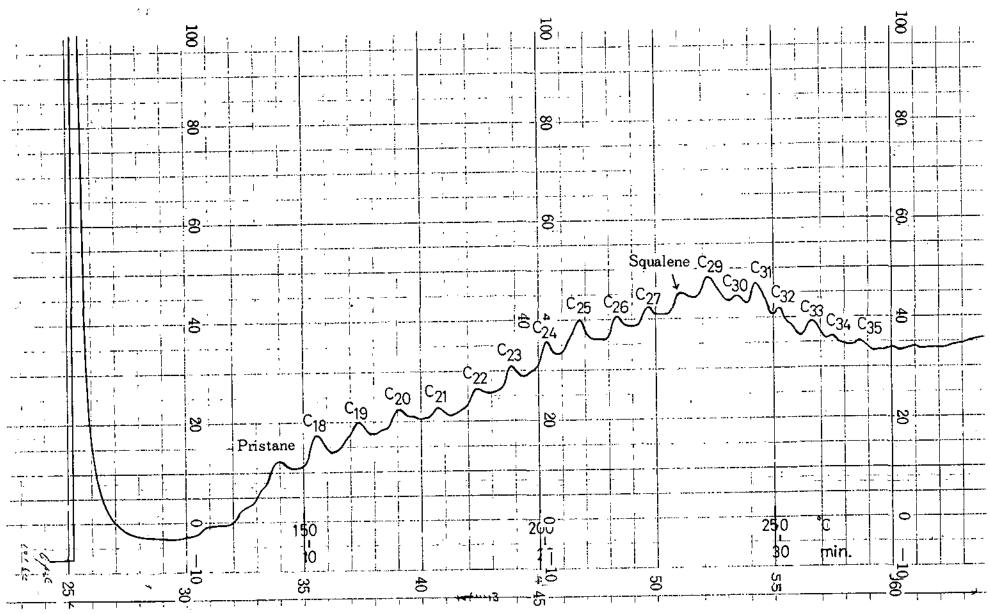


Fig. 7. The gas chromatogram of hydrocarbons extracted from mud.

southern region of Harima Nada. However, n-C_{29}, n-C_{31} and n-C_{32} were major components.

The distribution of n-alkanes/pristane and squalene ratio is shown in Fig. 8, 9

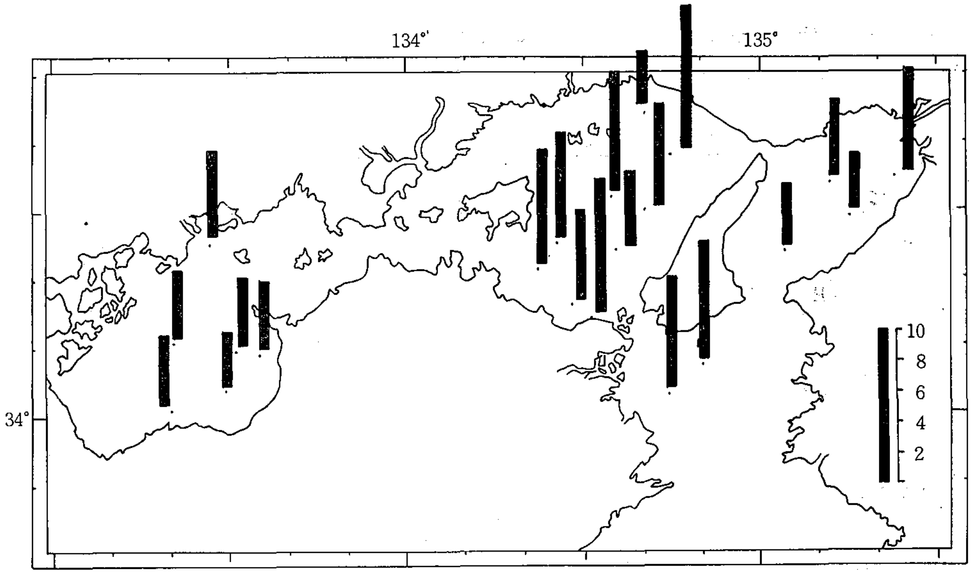


Fig. 8. The distribution of n-alkanes/pristane and squalene ratio in the eastern part of the Seto Inland Sea. (Jan., 1975.)

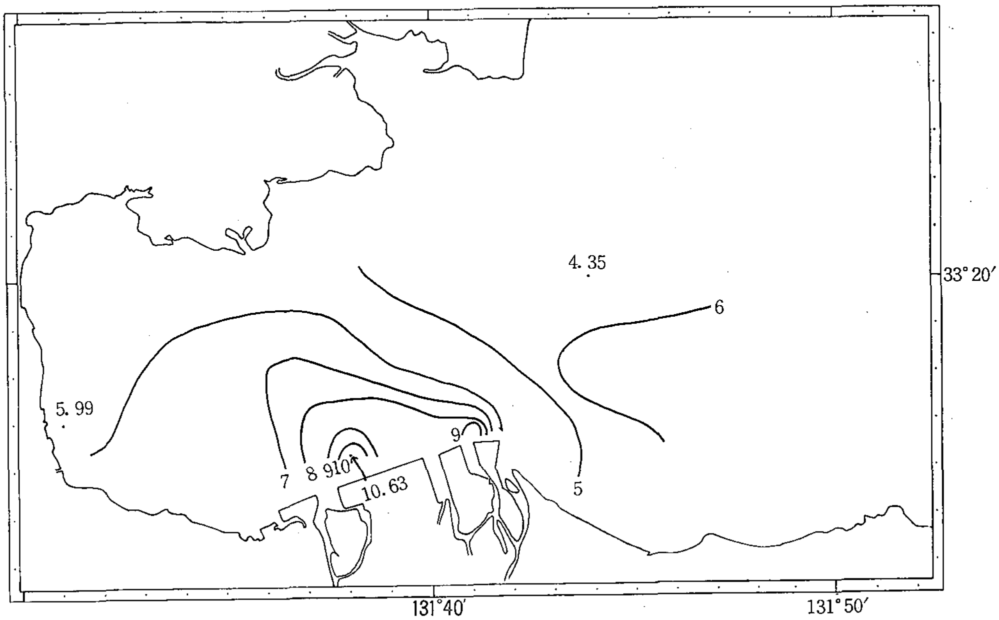


Fig. 9. The distribution of n-alkanes/pristane and squalene ratio in Beppu Bay. (Nov., 1975.)

and 10. The value of this ratio was large at Harima Nada, Kii Suido, the southern area of Beppu Bay and the northern coast of Osaka Bay, on the contrary was small at Hiuchi Nada, the central part of Osaka Bay and the northern area of Beppu Bay.

At the southern coast of Harima Nada, the value of this ratio was larger at the shore than at the offshore at the first time (Jan., 1975 - July, 1975), and then

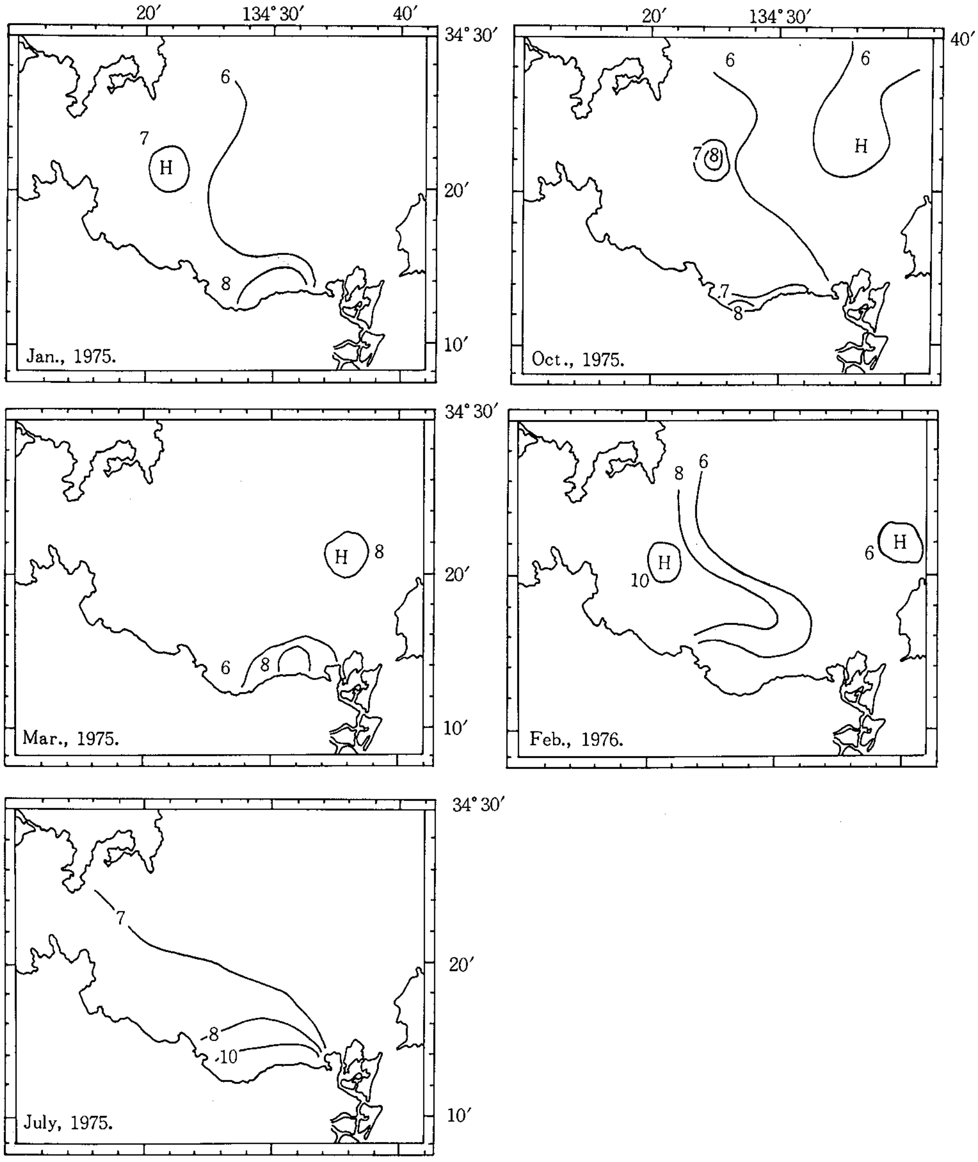


Fig. 10. The distribution of n-alkanes/pristane and squalene ratio at the southern part of Harima Nada.

the area where the ratio was large become narrow gradually, the region exhibiting the large value of this ratio has transfered from the coast to the offshore at the last time (Feb., 1976).

Discussion

The distribution of lipid content is very similar with that of the ignition loss. Since it is thought that the area where the ignition loss is large is the stagnant region, the suspensoids or particles adhering oil are tend to accumulated at this area. The relationship between lipid content and the ignition loss was observed in the Seto Inland Sea as shown in Fig. 11. From this result, it is obvious that

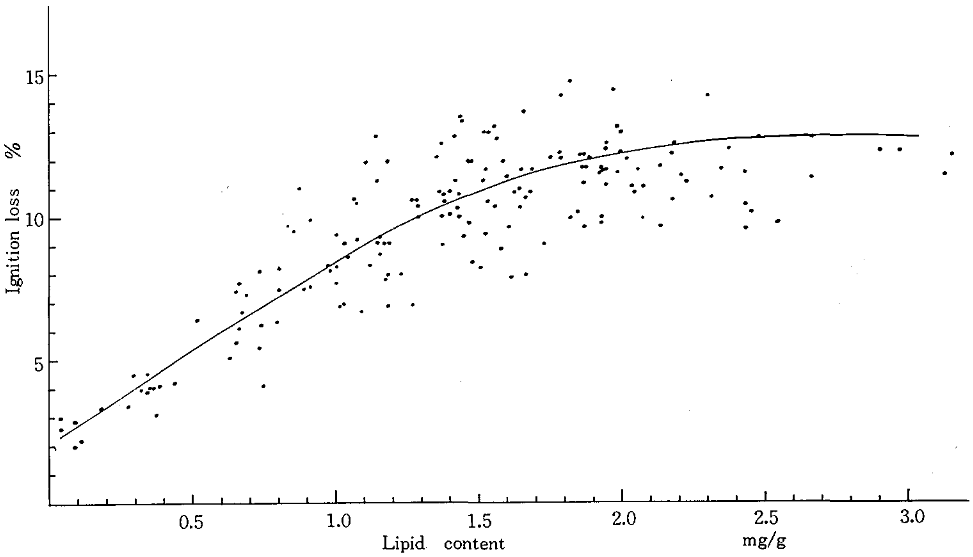


Fig. 11. The relaitonship between the ignition loss and the lipid content.

the lipid content is paralleled with the ignition loss at the area where the lipid content was below 1.5 mg/g, but in the case where the lipid content was over 2.0 mg/g, the variation of lipid content is independent of the ignition loss. Considering that the ignition loss is the amount of the organic compounds in sediments, and that the organic compounds in sediments are mainly derived from endogenous compounds (mainly synthesized by marine organisms) and exogenous compounds (supplied to the ocean as pollutants), it is thought that the area where lipid content was over 2.0 mg/g is polluted by oil. Because the endogenous organic compounds has a certain proportion of lipids.

Many researchers suggested that pristane and squalene in the ocean are biogenetic hydrocarbons. The ocurrence of pristane was reported by INOUE *et al*[5] in salmon, trout and carp, by SHINMA, Y., and H. SHIMMA[6] and KAYAMA *et al*[7] in shark liver oil and by SANO[8] in the sperm whale blubber oil. Squalene is also a major constituent of hydrocarbons in organisms[7]. The hydrocarbons of marine benthic algae was studied by YOUNGBLOOD *et al*[9], and they reported that n-pentadecane, n-heptadecane and n-heneicosahexaene were predominant components. Moreover, since the hydrocarbons of marine phytoplankton contained n-heneicosahexaene, n-heneicosane, n-heptadecane and n-pentadecane (summarized in Table 1 from the article by BIUMER *et al*[10]), those are also biogenetic hydrocarbons in the marine environment. Under the gas chromatographic condition

Table 1. Hydrocarbons of the marine phytoplankton. (after BIUMER, M., R.R.L. GUILLARD, and T. CHASE.[10])

Class	Major component
Bacillariophyceae	n - Heneicosahexaene
exception *Rhizosolenia setigera*	n - Heneicosahexaene n - Heneicosane n - Heptadecane
Dinophyceae Cryptophyceae Haptophyceae	n - Heneicosahexaene
Euglenophyceae	n - Heneicosahexaene n - Heptadecane n - Pentadecane
Rhodophyceae Xanthophyceae Chlorophyceae	n - Heptadecane n - Pentadecane

used, the peak of pristane and squalene contains n-heptadecane and n-octacosane respectively, and n-heneicosahexaene is not identified from the gas chromatogram of sediments. Nevertheless, n-alkanes/pristane and squalene ratio exhibit the degree of oil pollution of sediments. The n-alkane/pristane and squalene ratio was small at the south - eastern part of Hiuchi Nada[4], and the content of phaeopigment in mud was large at this region as reported by SHAZUKI *et al*[12] (Fig. 12.). As the distribution of n-alkane/pristane and squalene ratio is related with that of phaeopigment derived from phytoplankton, it is supposed that this ratio explain the characteristic of lipids extracted from mud.

As shown in Fig. 8 and 9, this ratio was small at the central part of Hiuchi Nada and Osaka Bay and at the northern part of Beppu Bay. Therefore, it is considered that the biogenetic compounds are accumulated at these regions, or that the lipids of mud are influenced by high productivity at these regions. On the contrary, it is thought that the large proportion of lipids extracted from mud

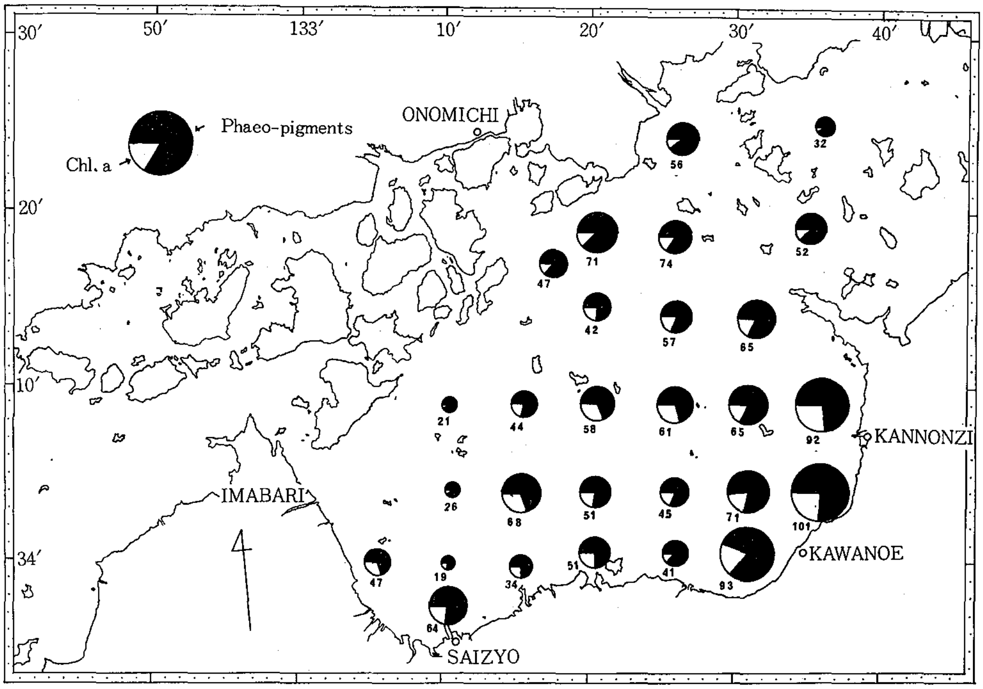


Fig. 12. The distribution of phaeopigments content in mud of Hiuchi Nada. (mg/g dry mud)
(Feb., 1975.) (after by SHAZUKI K. and K. TAKESUE, 12))

derives from petroleum oil at the coastal area of the Seto Inland Sea. In Beppu Bay the area high in this ratio was located at the southern coast. As many industries (e.g., steel work, oil refinery and petrochemical enterprises) are located at this coast, it is supposed that the discharged water from these industries may be one of the sources of oil pollution in Beppu Bay. Therefore, in order to estimate the oil pollution of mud, it is insufficient to determine the amount of lipids alone.

When the oil spill from a tank occured at Mizushima on 18th, Dec., 1974, 7500-9500 Kl of residual fuel oil was spread to the Seto Inland Sea, and a part of spilled oil was stranded also at the southern coast of Harima Nada. The distribution of n-alkanes/pristane and squalene ratio has been observed from Jan., 1975 to Feb., 1976. At the first time, this ratio was large at the coast, and then the higher ratio area was becoming narrower gradually, and the high value of this ratio was observed as far as 14 Km off the shore. It is surmised that the stranded oil was transferred from the shore to offshore by current, and perhaps accumulated to the sediments of the stagnant area.

Summary

1. The relationship between the lipid content and ignition loss is recognized in the Seto Inland Sea. It is obvious that the lipids as well as other organic compounds are accumulated to the sediments of stagnant area.

2. The n-alkanes/pristane and squalene ratio explains the contribution of petroleum oil in sediments. Observing this ratio, it is supposed that the lipids extracted from mud at the northern part of Osaka Bay, Harima Nada, Kii Suido and the southern part of Beppu Bay contain larger proportion of petroleum hydrocarbons than other areas.

3. From the results of n-alkanes/pristane and squalene ratio, it is surmised that the oil stranded at the southern coast of Harima Nada is moving to the sediments of the stagnant area.

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瀬戸内海，底泥の油汚染に関する研究

山田　久・鹿山　光

今日，石油類の流出による海域の汚染は深刻な問題になっている。1975年1月から1976年2月までの6回の調査により得られた瀬戸内海（主として東部海域，別府湾）の底土に含まれる炭化水素を検討した結果を報告する。

1）底泥の強熱減量と炭化水素含量には相関が得られ，油も他の有機化合物同様，停滞域に沈降する。脂質含量が2㎎/g以上の海域では，強熱減量はほぼ一定値を示し，底泥への鉱油の影響が推定される。

2）n―アルカン/(プリスタン＋スクアレン）の比は底泥への鉱油の堆積を示すと考えられる。この比の値は大阪湾北部，播磨灘，紀伊水道，別府湾南部沿岸で大きく，他の海域に比較して鉱油の影響を受けていると考えられる。

3）1974年12月，水島より流出したC重油は播磨灘南部海岸に漂着した。n―アルカン/(プリスタン＋スクアレン）比の分布の変化より漂着した油は次第に停滞域へ移動していることが推察される。