

行政院國家科學委員會專題研究計畫成果報告

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一、中文摘要

本計畫分析東海陸棚 11 個總懸浮物與 9 個表層沈積物中之脂肪族烴類、脂肪醇與固醇的濃度為了探討它們的區域分布，以及懸浮物與沈積物之相關。結果顯示：總懸浮物標本中 n -C₁₇, pristane, n -C₁₈, n -C₁₉, n -C_{19:1}, n -C_{21:6} 及 squalene 佔極強勢，它們皆由浮游生物所衍生之碳氫化合物故簡稱為 PDHCs 並且佔絕大部分總碳氫化合物，含高百分比 PDHCs 的測站位置靠近長江口，另外，含有 n -C_{21:6} 最高濃度的三個測站位於文獻所報告含有最高濃度的葉綠素區內。脂肪醇中以葉綠素醇與 C_{20:1} 與 C_{22:1} n -alkenols 佔優勢，顯示浮游生物貢獻。總懸浮物中含固醇量最多者依次為 24-methylcholesta-5,22E-dien-3 β -ol (brassicasterol/diatomsterol), cholest-5-en-3 β -ol (cholesterol), cholesta-5,22E-dien-3 β -ol (22-dehydro-cholesterol), 及 27-nor-24-methylcholesta-5,22E-dien-3 β -ol。來自長江陸源脂質在總懸浮物中並不扮演角色因長江流入東海主要向南傳輸。比較總懸浮物與沈積物中之 PDHCs 顯示其分解依序為

n -C_{21:6} > n -C_{19:1}, n -C₁₉ 及 n -C₁₇ > n -C₁₈, pristane 及 squalene；脂肪醇分解依序為 C_{20:1} 與 C_{22:1} n -alkenols > phytol。懸浮物的碳優指數變化範圍是 1.04~1.82 平均值為 1.41；而沈積物的碳優指數變化範圍是 1.82~3.74 平均值為 2.81，此結果可歸因於粒度效應。

關鍵詞：脂質、懸浮物、沈積物

Abstract

Total suspended matter (TSM) and sediment samples from the East China Sea (ECS) Shelf were analyzed for aliphatic hydrocarbons, alkanols and sterols in order to explore their area distribution and relations between TSM and sediments. TSM samples showed a strong predominance of n -C₁₇, pristane, n -C₁₈, n -C₁₉, n -C_{19:1}, n -C_{21:6} and squalene; they were planktonically-derived hydrocarbons (PDHCs) and accounted for most of total hydrocarbons. Stations with high percentages of PDHCs were generally situated near the Changjiang. In addition, three stations with highest

concentrations of n -C_{21:6} were located in the hot spot of chlorophyll reported in the literature. Phytol (the most abundant alcohol in TSM) along with C_{20:1} and C_{22:1} n -alkenols were dominant in the alcohol fraction, indicating plankton contribution. The sterol composition of TSM was dominated by, in decreasing order, 24-methylcholesta-5,22E-dien-3 β -ol (brassicasterol/diatomsterol), cholest-5-en-3 β -ol (cholesterol), cholesta-5,22E-dien-3 β -ol (22-dehydro-cholesterol), and 27-nor-24-methylcholesta-5,22E-dien-3 β -ol. Terrigenous lipids from the Changjiang did not play a role in TSM since they were transported mainly southward.

A comparison of PDHCs in TSM and in sediments showed that degradation is in the following order: n -C_{21:6} > n -C_{19:1}, n -C₁₉, and n -C₁₇ > n -C₁₈, pristane, and squalene. The order for degradation of alcohols was C_{20:1} and C_{22:1} n -alkenols > phytol.

Carbon preference indices (CPIs) of suspended matter varied from 1.04 to 1.82 with an average of 1.41, and those of sediment ranged between 1.82 and 3.74 with a mean of 2.81. The CPI difference could be attributed to grain size effect.

Keywords: Lipids, Suspended Matter, Sediment

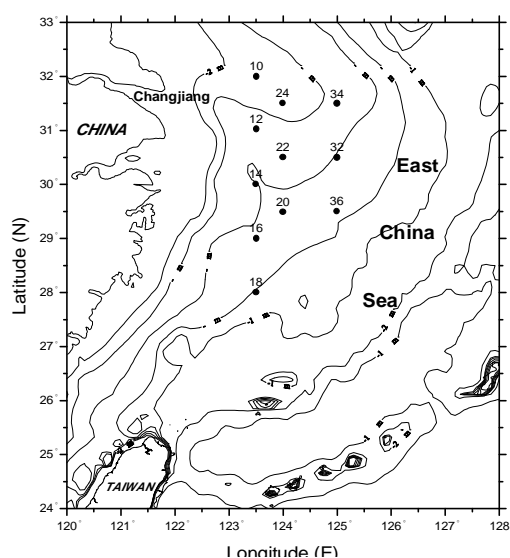
二、緣由與目的

Several studies on lipids in the Changjiang Estuary have been made by the French team. Analyzing non-aromatic hydrocarbons in suspended matter from the Changjiang Estuary, Qiu et al. (1991) have found that anthropogenic and/or petrogenic inputs extend over a larger area from the river mouth in winter than in summer and that the contamination level in the river mouth and in the adjacent ECS is low in both winter and summer 1986. Sicre et al. (1993a) have studied n -alkanes and polycyclic aromatic hydrocarbons in the suspended particles from the Changjiang Estuary, and have concluded that terrestrial and anthropogenic inputs are prevailing and that a high total suspended particle concentration is observed during the ebb, pointing out stronger contamination of the water after crossing the highly populated and industrialized area of Shanghai. Bouloubassi et al. (2001) have examined hydrocarbons in surface sediments from the Changjiang Estuary, and have concluded that the overall levels of anthropogenic hydrocarbons are low compared to relevant areas worldwide. It is indicated by factor analysis that 24-ethyl-cholesta-5,22-dien-3 β -ol is a tracer of terrigenous inputs whereas other sterols appear to be essentially produced by autochthonous sources in

the suspended particles of the Changjiang Estuary and adjacent ECS (Sicre et al., 1994). Using correspondence factorial analysis, the sterols in suspended particles of the Changjiang Estuary can be classified into three groups--marine, continental and diatomaceous origins (Sicre et al., 1993b), and sterols in Changjiang Estuary sediments can be divided into two groups: autochthonous and allochthonous (Tian et al., 1992).

Several questions are addressed in the present study. In the ECS, what are the important lipid biomarkers in suspended matter? What are the area distributions of these markers? The Changjiang discharges into the ECS, do terrigenous lipids from the river play a role in ECS suspended matter? Because marine lipids are selectively destroyed than terrigenous lipids, do marine biomarkers degrade similarly? Are there compositional differences in lipids between suspended matter and sediments?

Sampling locations in the East China Sea for this study is shown in the following figure.



三、結果與討論

1. Aliphatic hydrocarbons

Seven most predominant components were *n*-C₁₇, pristane, *n*-C₁₈, *n*-C_{19:1}, *n*-C₁₉, *n*-C_{21:6} and squalene; other *n*-alkanes up to C₃₅ were minor ones. This pattern was similar to that reported by Qiu et al. (1991) with the exception of squalene. The seven hydrocarbons are produced chiefly from plankton (Winters et al., 1969; Blumer et al., 1971) and are termed planktonically derived hydrocarbons (PDHCs). High percentages (80-94%) of the seven PDHCs were observed at stations 10, 12, 14, 16, 22, 24, 32 and 36, but relatively low percentages (45-61%) were found at stations 18, 20 and 34. Two other samples located ca. 110 km east of stations 16 and 18 exhibited hydrocarbon distribution with little or no sign of enhanced plankton contribution (unpublished data). It appears that stations with high percentages of PDHC were located close to the Changjiang. As to aliphatic hydrocarbon distribution in the GC range, there are five types recognized in the Changjiang Estuary (Qiu et al., 1991). However, the present study area was farther away from the estuary; only two types of aliphatic distribution patterns were

observed. This may suggest that input sources to the open sea become simpler than the estuary with anthropogenic input (e.g., oil pollution).

In general both photosynthetic algae and bacteria contain n -C₁₇ or n - Δ -C₁₇ as the most abundant component (Oro et al., 1967; Han et al., 1968; Winters et al., 1969), whereas non-photosynthetic bacteria have major components $>n$ -C₁₇ such as n -C₁₈ in *E. coli*, n -C₁₉ in *Micrococcus lysodeikticus*, and n -C₂₀ in yeast (Han et al., 1968). Either n -C₁₈ or n -C₁₉ concentration higher than n -C₁₇ concentration was observed in 7 samples. A substantial contribution might be from non-photosynthetic bacteria. It is also known that n -C_{19:1} accounts for 85-98% of hydrocarbons in three species of marine blue-green algae (Winters et al., 1969) and occurs in some zooplankton species (*Eucalanus sp.*) (Saliot, 1981). Higher concentrations of n -C_{19:1} than n -C₁₇ were observed in 6 samples, and contribution from blue-green algae is suggested. Four classes of planktonic algae are found to contain trace amounts of pristane (Blumer et al., 1971); in fact, pristane undoubtedly derives largely from zooplankton such as calanus-type copepods (Blumer et al. 1963). Squalene is absent in green and blue-green algae and non-photosynthetic bacteria, and is present in most cases in photosynthetic

bacteria at high percentages (92-95%) (Han and Calvin, 1969). Squalene has been commonly found in diatom blooms (Osterroht and Petrick, 1982; Matsueda et al., 1986) although it has been identified in planktonic and benthic algae (Clark and Blumer, 1967; Blumer et al., 1971) and in some fish and their feces (high in squalene and dietary pristane; Prahel et al., 1985).

The compound *cis*-heneicosahexa-3,6,9,12,15,18-ene (n -C_{21:6}) is known to predominate in five classes of marine phytoplankton, notably, but not exclusively, diatoms (Blumer et al., 1971; Nichols et al., 1988), and can be related to primary productivity (Schultz and Quinn, 1977; Osterroht and Petrick, 1982), which is usually determined by measuring chlorophyll *a*. For comparison, three highest n -C_{21:6} concentrations of 56.7, 48.5 and 104 μ g/g found at stations 22, 24 and 32, respectively, are located within the "hot" spot (approximately between 124° and 125°30' in longitude and between 30° and 32°N in latitude) with a 0.2 m⁻² contour of chlorophyll *a* (Gong et al., 1996). This agreement implies that the "hot" spot is a common occurrence with respect to space and time (summer) in this region.

Besides the predominant PDHCs, land plant waxes in suspended particles from the Changjiang might play a role in TSM distribution. Carbon preference index (CPI) in the range of

C₂₅~C₃₃ was used to investigate the possible influence of terrigenous lipids from the river. If CPI values are plotted, no systematic spatial variation can be observed. This implies that the terrigenous input from the Changjiang doesn't appear to influence the TSM distribution. This is probably because the Changjiang discharges most freshwater and sediment southward during regular periods (Beardsley et al., 1985).

2. Fatty alcohols

The distribution of *n*-alkanols observed in suspended matter was similar among stations, and was dominated by shorter chain (<C₂₂) alcohols with phytol being the most significant constituents, reflecting a major contribution from marine sources. In contrast, saturated alcohols from higher plant waxes (>C₂₂) constituted a minor proportion, indicating that terrigenous alcohols played a minor role. However, among the shorter chain alcohols, monounsaturated *n*-alkenols C_{20:1} and C_{22:1} can be derived from marine zooplankton especially calanoid copepods (Sargent and Lee, 1975; Saito and Kotani, 2000). Both C_{20:1} and C_{22:1} *n*-alkenols generally were not detected at 3 or 4 stations close to land and were present at much higher concentrations at the other six stations farther offshore. This result appears to suggest that the stations farther from

land may contain relatively high proportions of zooplankton than those close to land.

3. Sterols

The GC traces of sterols observed in the suspended matter were very similar among samples. The major feature is that the four predominant sterols of marine origin were, in general order of decreasing abundance, 24-methylcholesta-5,22E-dien-3 β -ol (brassicasterol-diatomsterol), cholest-5-en-3 β -ol (cholesterol), cholesta-5,22E-dien-3 β -ol (22-dehydro-cholesterol), and 27-nor-24-methylcholesta-5,22E-dien-3 β -ol. In the suspended matter, sterols common to diatoms, dinoflagellates and zooplankton make up the major proportion of the sterol fraction (Goad and Withers, 1982; Volkman, 1986). It is difficult to assign specific sterols to given algal classes because one biomarker specific to one species of plankton is also found in another; many examples are given by Wakeham (1995). In the light of this, stations 22 and 32 were distinguished from other stations by their high concentrations of 24-methyl-cholesta-5,24(28)-dien-3 β -ol and 4 α ,23,24-trimethyl-5 α -cholest-22E-en-3 β -ol (dinosterol); a major contribution from dinoflagellates (Volkman, 1986) could not be conclusive.

4. Degradation of lipids

The distributions of aliphatic hydrocarbons in nine sediment samples were quite similar. Among PDHCs, unsaturated hydrocarbons (n -C_{19:1} and n -C_{21:6}) except squalene were in trace to minor quantity in the sediment. By characterizing aliphatic hydrocarbons in plankton, sediment trap particulates and sediments from Dabob Bay, most pronounced decreases have been found for pristane and two unsaturated compounds (Prahl et al., 1980). In a deltaic environment, unstable hydrocarbons of both algal (C_{15:1}, C_{17:1} and C_{21:6} etc.) and terrestrial (C₂₅-C₂₉ n -alkenes) origin have not been found in the underlying sediments (water depths <20 m) due to prevailing oxic conditions (Albaiges et al., 1984). The present result could be attributed to the oxic conditions (shallow shelf water < 80 m) of the ECS which contribute to the easy degradation of unstable hydrocarbons of algal (n -C_{19:1} and n -C_{21:6}) origin and to marine components being selectively destroyed relative to terrigenous components (Meyers et al. 1984; Gagosian and Peltzer; 1986). However, most 7 PDHCs were generally detected with varying amounts in ECS surface sediments. This allows us to make rough estimates about their relative degradation by assuming these 7 PDHCs in sediment all were deposited from the overlying suspended matter. Because of

different matrices, the concentration difference between TSM and sediment is generally three orders of magnitude. For comparing the degradation of lipid biomarkers, it is more appropriate to divide the PDHC data by a normalizer; here n -C₂₃ was chosen since it is neither a major component of marine plankton nor a dominant component of higher plants. Each PDHC concentration was normalized and then summed for all TSM and sediment samples separately. The ratio for each PDHC was obtained using the averages of TSM and of sediments. Calculated ratios for 7 PDHCs vary by two orders of magnitude; high ratios represent rapid degradation. The relative degradation was n -C_{21:6} > n -C_{19:1}, n -C₁₉ and n -C₁₇ > n -C₁₈, pristane and squalene. This result is similar to that of Albaiges et al., (1984), but further indicates that degradation varies with different compounds. It is worthy of note that squalene is apparently of marine origin (discussed above) but was observed to be present at high levels in sediments, which appears to indicate that squalene (containing 6 double bonds in its molecule) is more refractory to degradation than n -C_{19:1} and n -C_{21:6}. Other studies lending support to this result are that squalene did not change with time in a sediment core from Halifax Harbor (Gearing et al., 1991) and that it has been found in various petroleum asphaltenes (Samman et al., 1981). Additional

contribution from benthic animals also containing squalene to the sediments can not be ruled out.

For comparison of alcohol degradation, *n*-C₂₀OH was used as a normalizer since it is not substantially enhanced by inputs of land or marine plants. Both C_{20:1} and C_{22:1} *n*-alkenols degrade faster than phytol by factors of 3-4 although they all contain one double bond in each molecule. Compared to *n*-alkanols, phytol is relatively unstable in sediment. For instance, in a sediment core (sedimentation rate 0.33 cm/y) from off southwestern Taiwan, extractable phytol decreases abruptly from 1049 ng/g (0-4 cm) to 375 ng/g (4-8 cm), but bound phytol increases sharply from 43 to 58%. This might suggest that part of the extractable phytol is transformed into the bound form (Jeng et al., 1997). In a field study, Sun et al. (1998) demonstrate that solvent-extractable phytol is rapidly converted into highly-bound phytol (in sediment matrix) after deposition.

Compared with the 7 PDHCs, estimated degradation of 9 important sterols showed low values and varied over a small range--within the same order of magnitude. These low values indicate that sterols are relatively resistant to degradation, which is in agreement with those reported by Saliot et al. (1991) and Quemeneur and Marty (1992). It is

noted that the three most readily degraded sterols were 24-methylcholesta-5,22E-dien-3 β -ol (brassicasterol-diatomsterol), 27-nor-24-methylcholest-5,22-dien-3 β -ol and 24-methylcholesta-5,24(28)-dien-3 β -ol (24-methylenecholesterol).

5. Stanol/stenol ratios

The stanol/stenol ratios of three selected sterol pairs for suspended matter and sediment samples in the study area are compared. Significant differences exist between the ratios of stanol to stenol in suspended matter and those in sediments. Similarly, lower stanol/stenol ratios of suspended particles compared to those of surface sediments from the shelf off north Taiwan have been reported by Jeng and Huh (2001). Suspended matter, which probably represents the ratios of stanol-containing marine plankton (Volkman, 1986), has the lower stanol/stenol ratios because the conversion of stenol to stanol by bacteria is expected to be slow in the oxic surface waters. The high stanol/stenol ratios of the shelf sediments may be caused by selective degradation of stenols relative to stanols at the sediment/water interface (Nishimura and Koyama, 1977). On the other hand, relatively higher stanol/stenol ratios for the sediments might also be due to microbiological hydrogenation of stenols (Edmunds et

al., 1980; Taylor et al., 1981) and some input of terrestrial material.

四、計畫成果自評

主持人對本計畫研究成果感到很滿意。

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