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N-Alkanes in an Equatorial Sedimentary Environment: Their Distribution as a Function of Particle Size[†]

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In order to investigate the biogeochemistry of organic matter deposited in an equatorial deltaic environment, the Mahakam delta, Borneo, analysis of geochemical markers has been realised both on various sediments and on sediments separated as a function of particle size.

Sediments were selected from two levels (-150 m and -500 m) of a continuous core sampled in the Mahakam delta in 1981 (Misedor Programme) and represent various lithotypes of the deltaic environment and different diagenetic conditions. After separation into sand size ($> 50 \mu\text{m}$), silt size ($50-5 \mu\text{m}$) and clay size ($< 5 \mu\text{m}$) fractions, free lipids have been extracted and hydrocarbons isolated by micro-column chromatography, and analysed by capillary gas liquid chromatography. Concentrations and carbon number distributions of n-alkanes are discussed in terms of the relationship between the sedimentary environment and the importance of terrigenous inputs.

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The distribution patterns of n-alkanes of different sediment size fractions are characterized by the predominance of high molecular weight compounds in the range C23–C37, which are also encountered for the actual deltaic plain flora: mangrove and nipah-nipah. Carbon Preference Index (CPI) values are higher in the coarse and intermediate fractions reflecting their enrichment in continentally-derived vegetation debris.

KEY WORDS: Deltaic environment, n-alkanes, organic matter, particle size, sediment.

INTRODUCTION

The identification of lipid markers in a sediment may provide important information on its geochemical environment by precisising the nature of the inputs of organic matter and the nature of evolution processes that occur during the transport and deposition of particles. Two recent approaches have been developed in order to obtain more information using organic molecular markers in organic geochemistry: (i) the use of selective extraction procedures for providing and comparing bound versus free extractable lipids^{1–6} and references therein, and (ii) the fractionation of the whole sediment as a function of particle size or density.^{7,8} Thompson and Eglinton⁷ have shown by fractionating a recent lacustrine sediment into five fractions from $<5\ \mu\text{m}$ up to $>250\ \mu\text{m}$ and by using microscopy and XRD, that higher plants debris were concentrated in the coarsest fractions and compounds issued from autochthonous algae were selectively gathered in the finest fractions; these differences are clearly indicated by the distributions of C29–C31 and C17 n-alkanes. More recently, Prahl and Carpenter⁸ have demonstrated, by analysing surficial recent marine coastal sediments sample on the Washington continental shelf, that important information can be obtained from the analysis of aliphatic and polycyclic aromatic hydrocarbons of both whole unfractionated sediment and sediment fractions separated by particle size and density. For these sediments the particles of low density (<1.9), lignin-rich, did not represent more than 1% of the total sediment weight, but they contained 20–25% of the perylene and pyrolytic-like PAH and 50% of the retene measured in the whole sediment. In contrast, a series of methylated phenantrene homologues, possibly of fossil origin, were concentrated in some

components of the more dense, lithic matrix of the sediment. Jocteur Monrozier *et al.*⁹ have developed such grain-size fractionation to study carbon and nitrogen budget in some recent deep-sea sediments; they have found that, in Amazon detrital fan, nitrogen-poor vegetal remains prevailed in coarsest fractions ($>50\ \mu\text{m}$), whereas organic nitrogen-rich components, are concentrated in the colloidal, clay-sized part of these sediments. Such nitrogen-rich components may be considered as of bacterial, animal or planktonic origin more than of higher terrestrial plants.

We examine in this paper how n-alkanes from different sources vary within equatorial deltaic environment as a function of particle size in relation with organic carbon and nitrogen distribution. These samples correspond to the main zones of the deltaic environment (upper and lower deltaic plain, delta front) at different degrees of diagenetic evolution. Although organic inputs are predominantly from terrestrial sources, contribution of freshwater or marine plankton must be considered, according to the biostratigraphic, palynologic and organic geochemistry results of the Misedor programme.

EXPERIMENTAL

Sampling

Sediment samples were selected from a continuous core realised in 1981 in the Mahakam Delta, located on the east coast of Kalimantan (Borneo). The sedimentology of the Mahakam Delta was described by Allen *et al.*¹⁰ Two cores were carried out with a mine corer from a platform near Handil Dua, permitting to reach the level $-638\ \text{m}$. Samples were immediately freeze-dried and kept in sealed metallic containers. Studies were conducted for determining the sedimentary facies: sedimentology, biostratigraphy (Institut de Géologie du Bassin d'Aquitaine, Bordeaux) and palynology (Centre d'Etudes de Géographie Tropicale, Bordeaux).

Sediment fractionation (Figure 1)

The sediments (ca 40 g dry weight) selected for this study were dispersed in 200 ml of distilled water and rolled for one night (16 h)

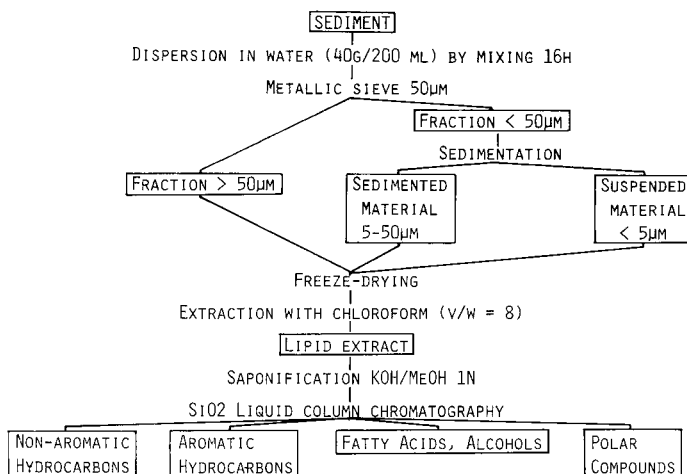


FIGURE 1 Analytical scheme used for the fractionation and analysis of sediments as a function of particle size.

with five agate marbles (diam. 5 mm). Then, the dispersed samples were passed through a stainless sieve, 50 μm mesh-size, by distilled water washing. The material smaller than 50 μm was allowed to settle gently in glass cylinders according to the Stokes' law. The non-sedimented material, composed of particles < 5 μm , was pumped off until turbidity has disappeared. The sedimented part was therefore assumed to be 5–50 μm size. Finally, this fractionation leads to 3 fractions, viz: sands > 50 μm , silts 50–5 μm and clays < 5 μm .^{9,11}

Carbon and nitrogen determinations (whole sediments and fractions)

- Organic carbon was measured by combustion in a Carmograph 12 (Wöstoff) after removal of carbonates by HCl 3N.
- Total carbon and nitrogen determinations were performed on a CHN analyser (Carlo Erba 1104).

Extraction of free lipids

The freeze-dried sample was pulverized during 15" and mixed vigorously with a mixer Turbula. Each fraction was extracted with chloroform in a glass flask respecting the optimum value for the ratio solvent volume: sediment weight of 8, proposed by Monin *et*

*al.*¹² The extraction was realised during one hour with a vigorous mixing. After decantation, the suspension was filtered on vacuum on a Whatman GF/F glass fibre filter. The remaining sediment was washed with chloroform, entirely transferred onto the glass fibre filter which was then washed another two times with chloroform. The chloroformic extract was concentrated in a Büchi rotary evaporator at low temperature ($t < 40^{\circ}\text{C}$) and dried under nitrogen.

Isolation and analysis of hydrocarbons The lipid extract was dissolved in n-hexane and refluxed during one hour. After decantation and elimination of the asphaltenes, the extract was transferred on the top of an activated copper column in order to eliminate sulfur.¹³ The extract was then spiked with an internal standard, n-C22, and saponified with a solution of KOH in MeOH (1N) under Argon. After acidification at pH2 with HCl 6N, the lipid material was extracted three times with a mixture of hexane-ether 9:1. The isolation of non-aromatic hydrocarbons was performed by using a glass micro-column filled with silicic acid Merck G60. The analysis of non-aromatic compounds was achieved by gas-chromatography using a Girdel 3000 gas chromatograph equipped with FID, a Ross type injector and a fused silica column, 25 m long, 0.32 mm internal diameter, wall coated with CP Sil 5 (Chrompack). Conditions were as follows: temperature of the column programmed from 120° to 300°C at 3°C per minute; injector temperature: 250°C ; detector temperature: 320°C ; carrier gas: Helium, flow rate: 2 ml per min. Peak areas were determined using a Varian Vista 401 integrator. N-alkanes were identified by comparison of their retention times with those of authentic standards from n-C11 to n-C36 injected in the same conditions, and quantified with respect to the internal standard n-C22.

Handling precautions

Great care was taken against contamination during the coring operations and laboratory work up. Solvents were distilled twice. Filters and silicic acid were extracted in a Soxhlet with distilled chloroform. Blanks showed that only traces of interfering compounds were present.

RESULTS AND DISCUSSION

An example of the interest of the size fractionation of a highly continentally influenced sediment: K80 (-500 m)

This sediment was chosen as representative of deltaic plain deposition with high contribution of continental material. The total organic carbon content of the sediment is 11.2% dry weight.

Weight, organic carbon and n-alkanes budget

The data of the fractionation of this sediment into $<5\ \mu\text{m}$, $5\text{--}50\ \mu\text{m}$ and $>50\ \mu\text{m}$ are listed in Table I and illustrated in Figure 2. The sediment is essentially composed of fine clay particles accounting for 70% of the whole sediment weight (Figure 2a). The budget of organic carbon (Figure 2b) shows the predominance of the coarse fraction, which represents 50% of the total organic carbon sediment content. This is explained by the high organic carbon content of the $>50\ \mu\text{m}$ fraction, 47% dry weight of the fraction (Figure 3a). n-

TABLE I
Summary of chemical characterization of bulk and fractionated Mahakam delta sediments

Fraction	Characteristics/ whole sediment		Characteristics of sediment and separated fractions				
	Weight %	OC %	OC %	C/N	N-alkanes ($\mu\text{g g}^{-1}$)	C.P.I.	N-alkanes/OC (%)
<i>K80 (-500 m)</i>							
Bulk	100	100	11.2	47	62	4.9	
$<5\ \mu\text{m}$	70.3	24	3.6	26	44.5	4.2	0.12
$5\text{--}50\ \mu\text{m}$	18.6	26	14.5	50	126.6	7.0	0.087
$>50\ \mu\text{m}$	11.1	50	47.0	55	263.4	6.0	0.056
<i>K22 (-150 m)</i>							
Bulk	100	100	1.4	13	3.5	3.8	
$<5\ \mu\text{m}$	64.1	60	1.3	10	4.2	3.2	0.032
$5\text{--}50\ \mu\text{m}$	34.8	33	1.3	19	3.3	2.6	0.025
$>50\ \mu\text{m}$	1.1	7	9.4	31	18.6	3.6	0.020

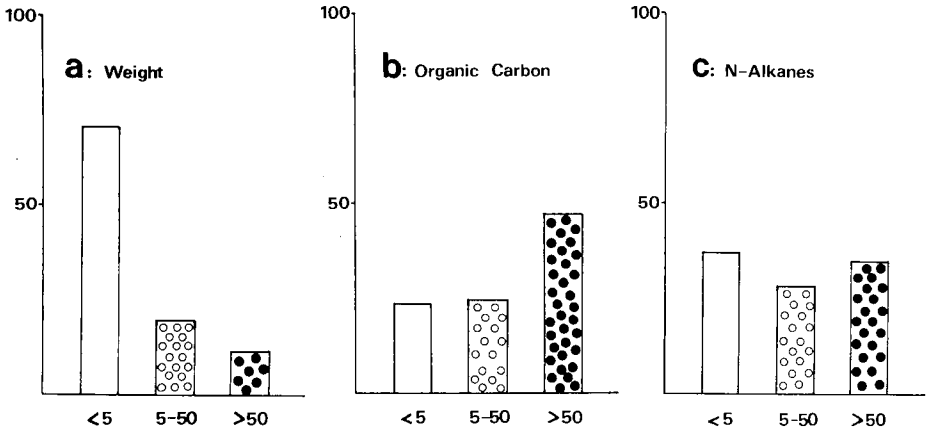


FIGURE 2 Budget of the fractionation of the K80 sediment into three fractions: < 5 μm , 5-50 μm and > 50 μm . Distribution of weight (2a), organic carbon (2b) and n-alkane content (2c). For each parameter, the height of the bars in the histogram represents the percentage of the total measured in each respective sediment fraction, totalling 100% in the sum of the three fractions.

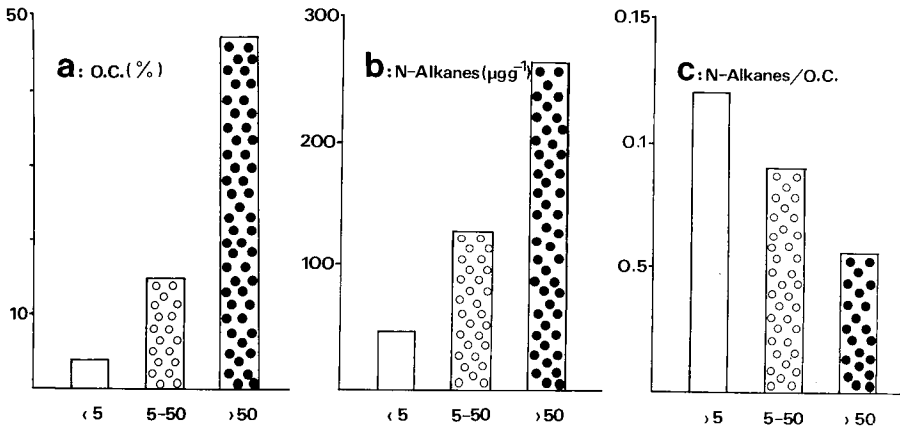


FIGURE 3 Characteristics of each fraction of the K80 sediment: organic carbon content % dry weight fraction (3a); n-alkane concentration, $\mu\text{g g}^{-1}$ (3b) and ratio n-alkanes/organic carbon, % w/w (3c).

Alkanes are regularly distributed by weight within the three fractions (Figure 2c).

Characteristics of grain-sized fractions

Considering now each fraction, they show different characteristics; the coarse fraction has a very high carbon content, 47% d.w. as indicated before, in comparison with other fractions, 14.5% for the silts and 3.6 for the clays. The same trend is observed for the n-alkane concentrations: high content (263 μg per g) in the coarse fraction and low content in the fine fraction (44.5 μg per g). But it must be pointed out that this clay-size fraction exhibits, *with respect to its carbon content*, marked enrichment of n-alkanes (Figure 3c) and nitrogen (Table I). Do these grain-sized fractions change in nature? The distributions of n-alkanes as a function of carbon number are shown in Figure 4 for the three fractions. Although the three patterns exhibit similar trends such as the predominance of high molecular weight compounds in the C23-C37 range, characteristic of higher terrestrial plants,¹⁴⁻¹⁶ and notably of the actual deltaic plain flora (Figure 5),¹⁷ they differ for the Cmax: 31 for the finest fraction and C27 for the coarse one. The value of the Carbon Preference Index (CPI) in the >C23 range varies from 4.2 for the clay size up to 6-7 in the other fractions. The selective concentration of higher plants debris with the coarse particles stock, previously noted in sediments influenced by terrestrial inputs^{7,9} is confirmed

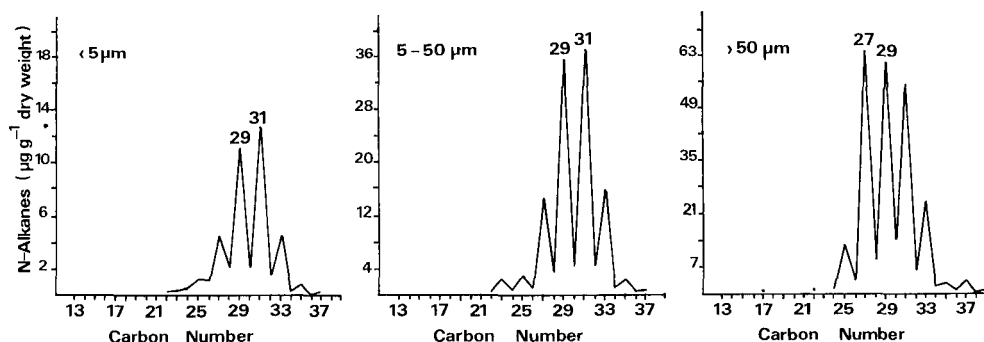


FIGURE 4 N-alkane distribution patterns for the three fractions < 5 μm , 5-50 μm and > 50 μm isolated from the K80 (-500 m) sediment.

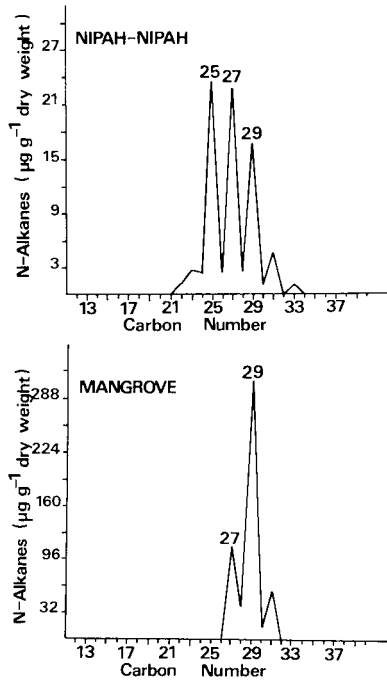


FIGURE 5 N-alkane distribution patterns for the two vegetals predominating in the actual deltaic Mahakam plain: nipah-nipah and mangrove.

here not only by n-alkanes data but also by C:N ratio which reaches 55 (versus 26 in the finest fraction) and by higher CPI values of n-fatty acids ranging from C24 to C36.¹⁸ These trends are observed for several sediments analysed from the Misedor core.

In samples belonging to more marine influenced environments, low molecular weight n-alkanes <C23 carbon range are not present, reflecting the unstability of this class of compounds, among which are found predominant marine derived n-alkanes, n-C15, n-C17,¹⁹ during diagenesis as discussed previously.²⁰

A second example for a sediment with mixed continental and marine organic matter inputs: K22 (-150 m)

This second sediment was chosen as representing a sedimentary environment belonging to the internal delta-front with a marked

marine influence (Carbonnel, pers. comm.) and low C:N value of 13. It is essentially composed of clays and silts (98% of the sediment is in the $< 50 \mu\text{m}$ fraction).

Weight, organic carbon and n-alkanes budget

The data of the physical fractionation of this sediment are listed in Table I and illustrated in Figure 6. This sample is principally constituted by fine particles $< 5 \mu\text{m}$ (64.1% of the sediment) and medium size particles 5–50 μm (34.8%), Figure 6a. The coarse fraction represents only 1.1% of the total sediment; it consists mainly of vegetal remains and minerals. The distribution of total organic carbon in the three fractions is as follows, as particle size increases: 60%, 33% and 7% (Figure 6b). The repartition of n-alkane contents follows the same pattern with the respective fractionation: 66.5%, 28.4% and 5.1% (Figure 6c). Of note, if the coarse fraction represents less than 2% of the total sediment weight, it represents a more important component of the total organic carbon (7%) and n-alkanes (5.1%).

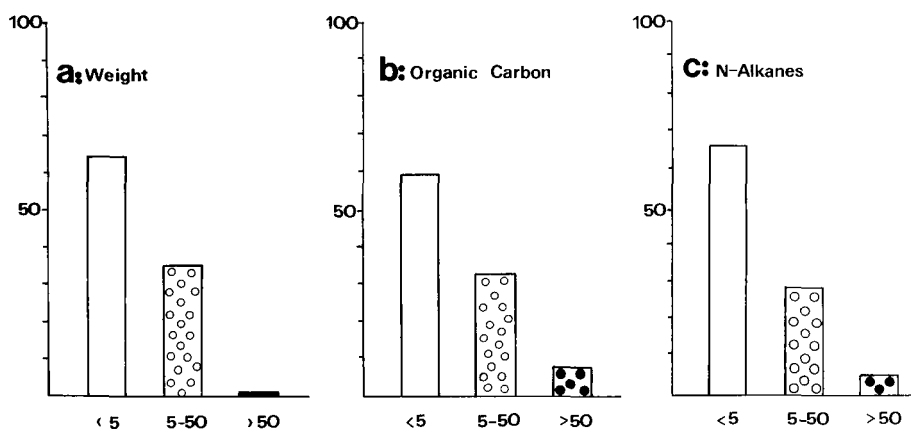


FIGURE 6 Budget of the fractionation of the K22 sediment into three fractions: $< 5 \mu\text{m}$, 5–50 μm and $> 50 \mu\text{m}$. Distribution of weight (6a), organic carbon (6b) and n-alkane content (6c). For each parameter, the height of the bars in the histogram represents the percentage of the total measured in each respective sediment fraction, totalling 100% in the sum of the three fractions.

Characteristics of grain-sized fractions

The different fractions show very specific characteristics: the coarser fraction has a high content in organic carbon (Figure 7a). The n-alkane concentration of the $>50\ \mu\text{m}$ fraction is $18.6\ \mu\text{g}$ per g dry sediment fraction against $3.3\ \mu\text{g}$ per g for the $5\text{--}50\ \mu\text{m}$ fraction and $4.2\ \mu\text{g}$ per g for the $<5\ \mu\text{m}$ fraction. Nevertheless, we have to bear in mind as for other samples, that the global contribution of each fraction to the whole sediment depends essentially of their respective weights (Figure 6a). Do these fractions change in nature? Yes, if we consider the distributions of fatty acids.¹⁸ Briefly, the finest fraction is enriched in monounsaturated components, C16:1 and C18:1, and *iso* and *anteiso* C15 and C17 compounds, reflecting biological activity traces and particularly of microorganisms.^{21,22,23} The CPI value of fatty acids in the $>\text{C}24$ range varies from 3.8 for the $<5\ \mu\text{m}$ fraction up to 5.8 for the coarse fraction, reflecting an enrichment of this latter fraction in higher plants debris. This observation corroborating previous data^{7,9} is confirmed by the distribution of n-alkanes (Figure 8) and C:N ratio variations (Table I). Although, the three distribution patterns show similar trends with the predominance of high molecular weight compounds nC29, nC31 and nC33, the value of the CPI in the $>\text{C}21$ range varies from 2.6 and 3.1 for the finest fractions up to 3.6 for the coarse one.

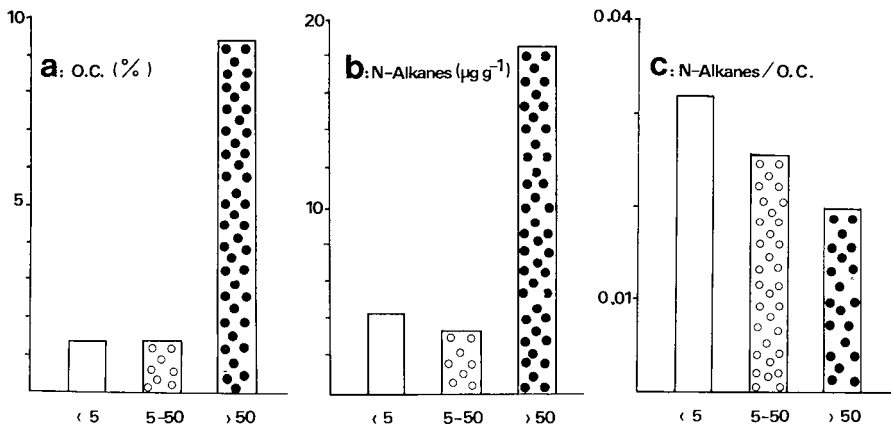


FIGURE 7 Characteristics of each fraction of the K22 sediment: organic carbon contents, % dry weight fraction (7a); n-alkane concentration $\mu\text{g g}^{-1}$ (7b) and ratio n-alkanes/organic carbon, % w/w (7c).

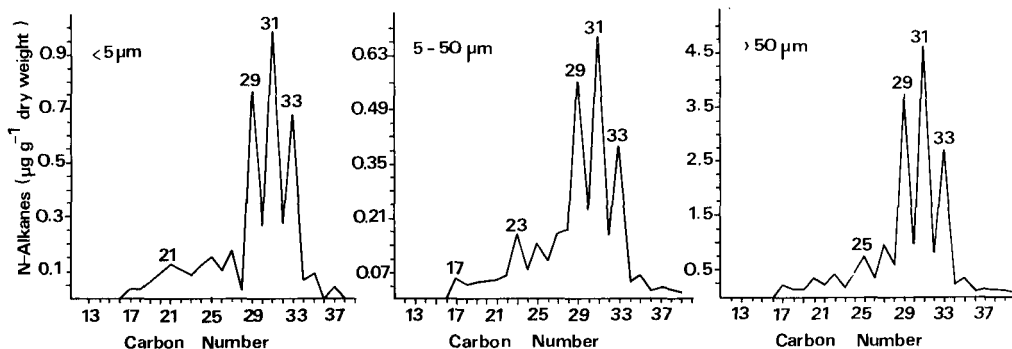


FIGURE 8 N-alkane distribution patterns of three fractions $<5\ \mu\text{m}$, $5\text{--}50\ \mu\text{m}$ and $>50\ \mu\text{m}$ isolated from the K22 ($-150\ \text{m}$) sediment.

CONCLUSION

Particle size fractionation of the equatorial Mahakam delta sediments has shown that plant debris predominated in the coarse fractions as previously shown for lacustrine and detrital deep-sea sediments. This observation based on different criteria issued from biostratigraphy, palynology and microscopic examination, registered for sediments belonging to different depths, degree of evolution and respective importance of continental *versus* marine inputs is corroborated here by organic geochemical studies using the n-alkane marker approach and relates to: an increase of n-alkane Carbon Preference Index and C:N values. The clay size fraction exhibits a depleted n-alkane CPI and lower C:N values, and, for the $-150\ \text{m}$ sediment, a specific evidence of microbial activity, as shown by the identification of significant amounts of *iso* and *anteiso* C15 and C17 fatty acids.

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