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n-Alkanes as Indicators of Natural and Anthropogenic Organic Matter Sources in the Siak River and its Estuary, E Sumatra, Indonesia

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Abstract Along the Siak River and its estuary a total of 100 sediment and 57 plant samples were taken for the analysis of *n*-alkanes from 2003 to 2005. Sediment *n*-alkanes exhibit in the majority of samples a pronounced odd over even predominance with maxima at C29 and C31 indicative of a plant origin. Plant *n*-alkanes analysed have chain lengths up to C39. These compounds are also present in the river sediments. In some plants the Carbon Preference Index (CPI) has extremely low values normally only found in petroleum-contaminated samples. A distinction between vegetation- and petroleum-derived *n*-alkanes is therefore only possible by a combination of CPI and and the absence/presence of a prominent unresolved complex mixture. Based on these criteria only a limited number of the 100 sediments analysed exhibit clear indications of a petroleum contamination.

Keywords Hydrocarbon · Alkane · Organic matter sources · River · Estuary · Coastal ocean · Sumatra · Indonesia

Homologous series of *n*-alkanes, *n*-alcohols and *n*-alkanoic acids are abundant constituents of epicuticular waxes found on leaves of terrestrial higher plants (Eglinton and Hamilton 1963, 1967). Plant-wax *n*-alkanes typically contain between 25 and 35 carbons, with a strong predominance of odd- over even-carbon-numbered chain lengths. This predominance is often expressed as the carbon preference index (CPI), where terrestrial higher plant waxes yield high values, usually greater than four (Collister et al. 1994). Waxes on plant leaf surfaces are removed by rain and wind, especially by a sand-blasting effect (Simoneit 1977), and can then reach coastal and offshore sediments through fluvial and aeolian transport (e.g., Schefuß et al. 2003).

The presence of *n*-alkanes in aquatic sediments has been widely used as a proxy to identify possible sources of organic matter, i.e., to distinguish between inputs from terrestrial higher plants and aquatic primary producers (e.g., Schubert and Stein 1997). In addition, oil-derived pollution also leaves a noticeable mark on the *n*-alkane distributions (e.g., Zegouagh et al. 1998).

The Siak River, Province Riau, East Sumatra, with a total length of 370 km drains a catchment area of 11.500 km^2 (Fig. 1). About 45% of this area are peat soils. Estimated discharge in March is 642 $m^3\ s^{-1}$, in September 99 $m^2\ s^{-1}$ (*A. Baum, T. Rixen, personel communication, 2006*).

Pekanbaru, the capital of Riau Province, discharges untreated sewage of an estimated 2 million inhabitants and has, in addition, a number of saw mills and latex drying plants which release saw dust and organic- and particle-rich waters. In Perawang (Fig. 1) paper and pulp industry is located also discharging large amounts of untreated production waters. In the area of the tributaries Tapung kanan and Tapung kiri palm oil plantations are the most abundant form of land use.

The Siak river estuary and the coasts around Dumai and the island of Bengkalis are fringed by mangroves, mainly *Avicennia* spp. and *Rhizophora* spp. while in the upper and middle reaches of the Siak a large number of different plant

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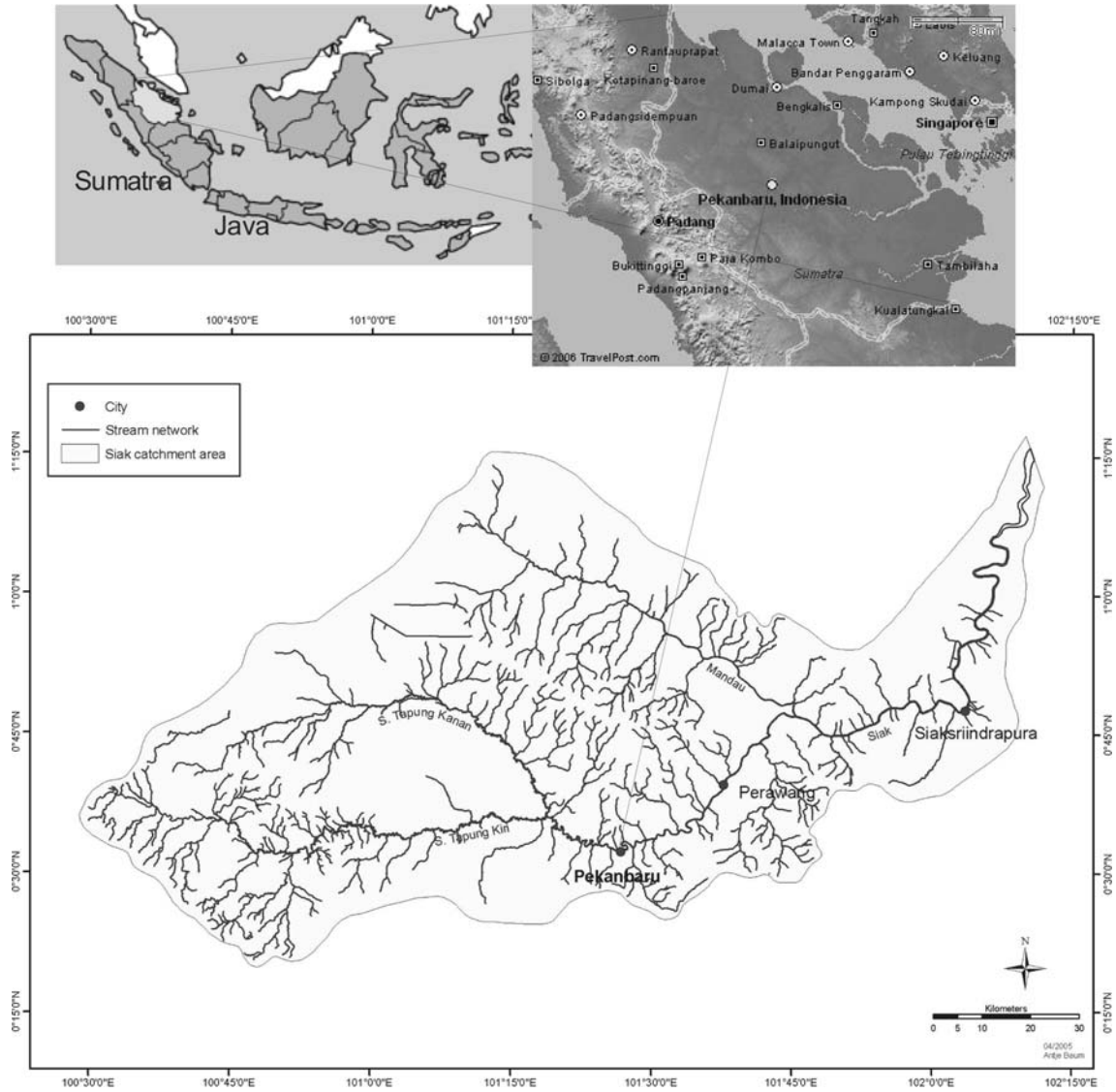

Fig. 1 Drainage basin of the Siak River, Province Riau, E Sumatra

species grow along the banks of the river with no species being dominant.

Sediments in the estuary and the lower reaches are fine-grained (median 5–30 μm) while sands dominate in the middle and upper reaches (*Liebezeit and Wöstmann, unpubl. data*). During incoming tide a flow reversal is observed at the water surface making tidal effects noticeable as far as Pekanbaru although salinity changes can only be observed up to the mouth of the Mandau (Fig. 1). This suggests that sedimentation of particulate material originating from the upper parts of the Siak drainage basin is deposited from this point on downstream.

In the present communication we report on the *n*-alkane contents and composition of sediments from the Siak River system in an attempt to elucidate sources, transport and sedimentation of terrestrial organic material in its estuary and coastal area.

Materials and Methods

Surface sediments and plant samples were obtained in March 2004, September/October 2005, February and September 2006. Sediments were sampled with a van Veen-type hand-operated grab from the tributaries of the Siak, Tapung kanan and Tapung kiri, to the estuary (Fig. 1).

After recovery sediments were first air-dried, after transport to the home laboratory freeze-dried and ground in an agate ball mill at 200 rpm for 30 min. Extracts were prepared by ultrasonic extraction using solvent systems of

sequentially increasing polarity: (1) *n*-hexane, (2) *n*-hexane/dichloromethane (50:50 v/v), (3–5) dichloromethane/methanol (90:10 v/v) corresponding in polarity to hydrocarbons, alcohols and polar N,S,O compounds, respectively. The combined lipid extracts were rotary-evaporated to dryness and a mixture of squalane, 5α-androstanol, 5α-androstanone and erucic acid was added as internal standards. The *n*-alkanes were separated from the total extracts using a 1.0 × 20 cm glass chromatography column packed with activated silica gel (100–200 mesh). On top of the silica gel, about 10 mm anhydrous Na_2SO_4 was added to retain remaining water. After adding an aliquot of the redissolved total lipid extract to the column, *n*-alkanes were eluted with 15 mL of hexane.

Long chain *n*-alkanes (*n*-$C_{16–39}$) were analyzed with a Hewlett Packard 5890 series II gas chromatograph equipped with a cold injection system (KAS 3, Gerstel), a FID detector and a J&W DB 5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) programmed from 60 to 300°C at a rate of 6°C/min and held at 300°C for 30 min. Helium was used as carrier gas with a flow rate of 1.2 mL/min. Individual *n*-alkanes were identified based on the retention time of authentic standards. Concentrations were calculated by comparison to the response of the corresponding internal standard (squalane).

Total carbon (TC) was determined by high temperature combustion (LECO® SC 444), total inorganic carbon (TIC) by coulometry after acidification (UIC®). Total organic carbon (TOC) was calculatesd as difference TC–TIC. All values reported are averages of duplicate measurements and have an average reproducibility of ±0,2%.

The Carbon Preference Index ($CPI_{25–33}$) was calculated according to Bray and Evans (1961).

The average chain length (ACL) was calculated for the range 27–37 according to

$$ACL_{27-37} = \frac{(27 \times C27) + (29 \times C29) + (31 \times C31) + (33 \times C33) \times (35 \times C35) + (37 \times C37)}{(C27 + C29 + C31 + C33 + C35)}$$

Results and Discussion

n-Alkane contents in surface sediments ranged from 3.9 to 3113.1 μg/g TOC (mean 355.3) while the analysed plants contained from 5.6 to 9,000 μg/g. CPI values in sediments range from 3 to 9 indicating significant contributions from higher terrestrial plants with average chain lengths between C_{30} and C_{32} (Fig. 2). Twenty-two samples had $CPI_{25–33}$ values <3 which, using the conventional assessment, would indicate the presence of oil-derived hydrocarbons. In sediments the *n*-alkane distribution varies between the extremes depicted in Fig. 3, i.e., on one hand a clear dominance of odd-chain alkanes typical for oil-derived contamination and on the other hand a distribution reminiscent of plants (Fig. 4).

The majority of the 57 plant samples analysed had $CPI_{25–33}$ values >3 as exemplified by *Cerbera manghas* (Fig. 4). There are seven exceptions: leaf material from *Calamus rotang* (rattan palm), *Nypa fruticans*, *Elaeis guineensis* (oil palm) and an unidentified grass, bark of *Hevea brasiliensis* (rubber tree), nuts from an unidentified hardwood tree and saw dust (Fig. 4). This is in accordance

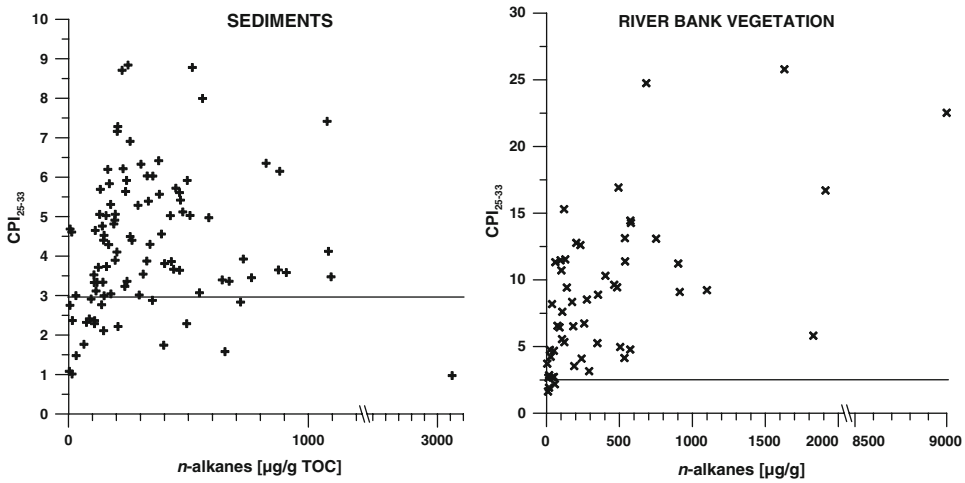

Fig. 2 $CPI_{25–33}$ versus total alkanes for all sediment (*left*) and plant samples (*right*)

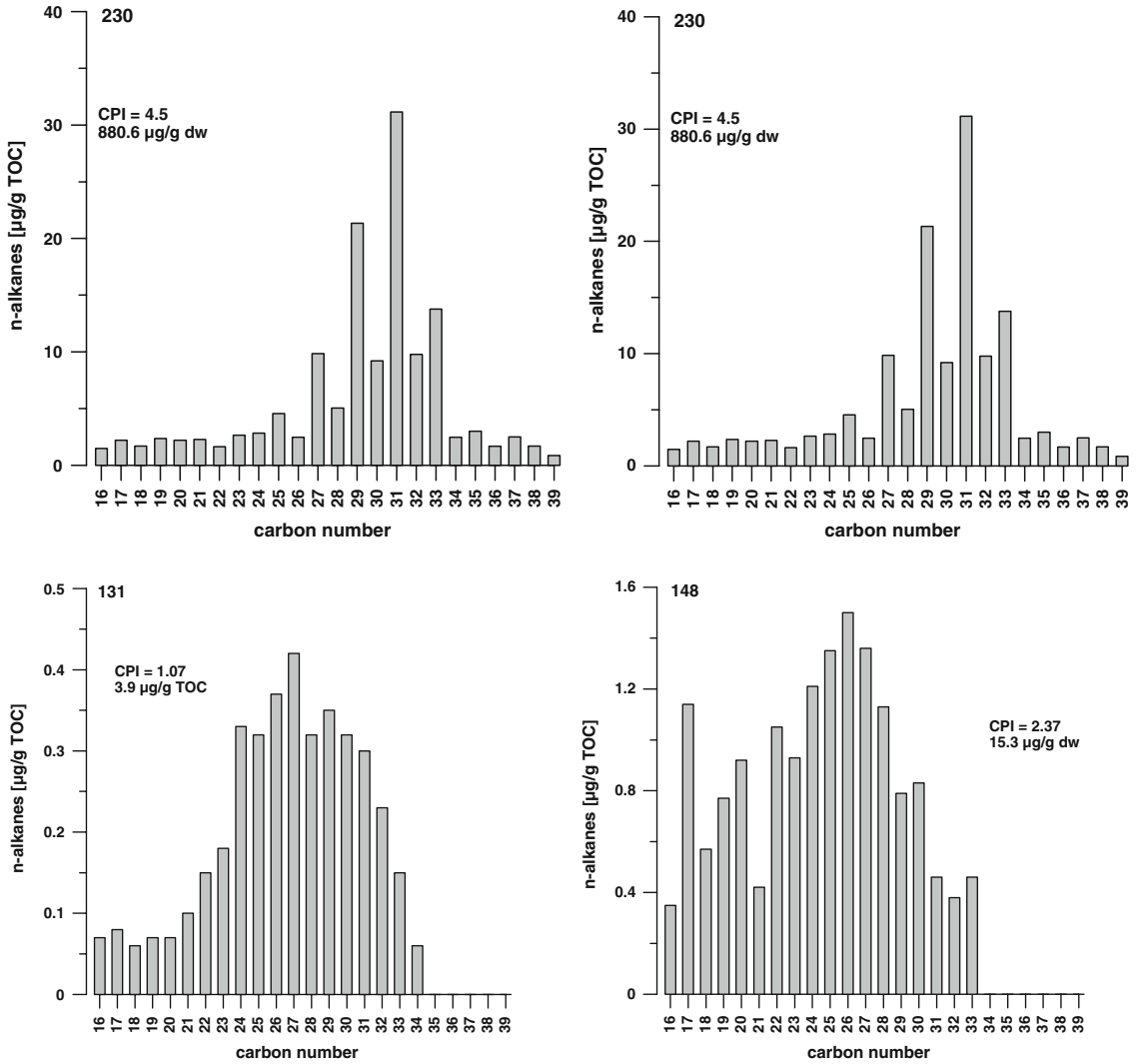

Fig. 3 Examples of *n*-alkane distribution patterns in surface sediments. *Numbers* in *upper left hand corner* are station numbers

with data provided by Brassell et al. (1978) who report CPI values of 3–10 for fresh organic material from terrestrial sources.

While sawdust might have been contaminated with oil products during its production grasses (Fig. 4) are important components of the river bank vegetation especially in the tributaries Tapung kanan and Tapung kiri and the upper reaches of the Siak and can be expected to contribute significantly to the organic matter load of the Siak.

Based on the $CPI_{25–33}$ values alone 22 out of 100 samples show signs of an oil contribution, i.e., with CPI values <3 (Farrington et al. 1977), while a further three samples had CPI values <3.1. These samples generally also had low total *n*-alkane contents with the exception of station 236 (Fig. 2 left). Thus, for the present suite of samples the CPI alone cannot provide evidence for the presence of oil-derived *n*-alkanes in the sediments analysed as plants may also have contributed to the low $CPI_{25–33}$ values.

In addition to external inputs from terrestrial vegetation and oil, aquatic primary production has also to be taken into account as a possible source of *n*-alkanes, especially in the Siak estuary and the adjacent coastal ocean. Marine phytoplankton has high contents of short chain *n*-alkanes, especially C15, C17 and C19 with the C17 compound usually being the dominant one (e.g., Han et al. 1968; Blumer et al. 1969; Gelpi et al. 1970; Youngblood and Blumer 1973). Odd long-chain *n*-alkanes maximising at C27, C29, or C31 are often employed as indication of a higher-plant input to the sediment, as these alkanes usually predominate in higher-plant leaf waxes (Eglinton and Hamilton 1963, 1967; Fig. 5).

The long chain/short chain ratio (C27 + C29 + C31)/(C17 + C19) LC/SC is hence used to identify sediments with *n*-alkane distributions suggesting input from an aquatic source. Of the plants analysed only 58% had C17 and C19 compounds with ratios ranging from 4 to 566

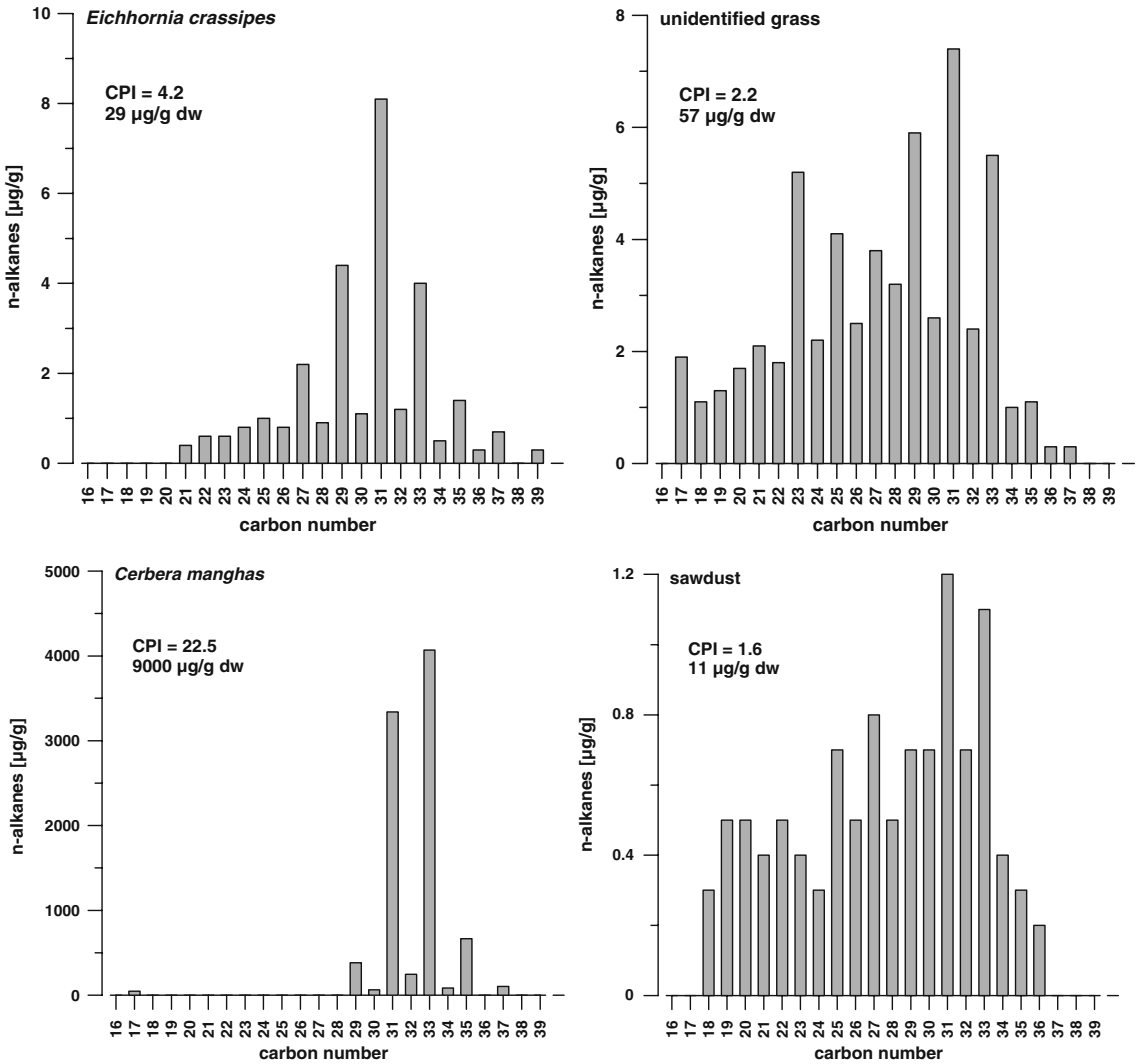

Fig. 4 Examples of *n*-alkane distribution patterns in plants

(Fig. 5). Thus a value of three will be used to distinguish terrestrial and aquatic *n*-alkane sources. The majority of sediments had LC/SC values >3 indicating a dominant terrestrial organic matter source (Fig. 5). Of the 11 stations with lower values five are located in an estuarine or coastal setting, four in the upper reaches and one each in the Mandau tributary and the middle reaches of the Siak. Field observations indicate that planktonic biomass is low in the river and its tributaries due to the strong discolouration of the water by humic compounds and consequently low light availability. However, especially in the Mandau and the Tapung kanan a large production of the water hyacinth *Eichhornia crassipes* can be observed. This plant drifts with the river flow from the upper to the middle and lower reaches of the river, usually in large mats. It is conceivable that disintegration and sedimentation takes place when the mats are temporarily stopped, e.g., in river bends or by obstacles. The LC/SC ratio of *E. crassipes* is, however, 46.5 and hence the water hyacinth cannot be the source of the aquatic primary producer signal in the river sediments. Whether other floating macrophytes such as *Lemna* spp. are responsible for the planktonic signal in the LC/SC ratio is presently under investigation.

As discussed above CPI values alone cannot be employed to identify oil-derived *n*-alkanes in riverine, estuarine and coastal sediments, especially in cases where river bank vegetation supplies abundant organic matter to the sediment. This will mask oil contamination to a significant degree as is evident, e.g., at station 236 where the C_{29} and C_{31} *n*-alkanes had the highest contents.

Input from an oil source also expresses itself through the presence of an unresolved complex mixture (UCM). The UCM is composed of a mixture of hydrocarbons, present in significant quantities in petroleum, which are resistant to weathering and biodegradation processes (Farrington et al. 1977). An examination of all 100 GC traces indicates

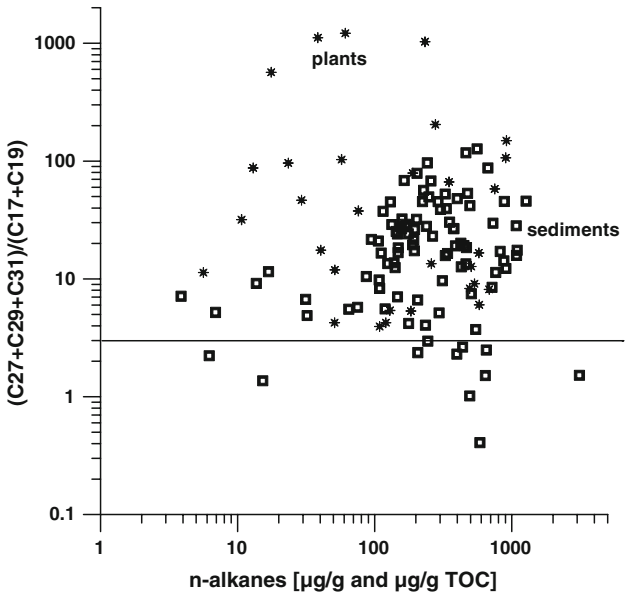

Fig. 5 Ratio of long chain versus short chain *n*-alkanes for plants and sediments in relation to total alkanes

pronounced UCMs to be present in 15 samples while another 32 had only weak UCMs. Some plant samples, on the other hand, also exhibited weakly expressed UCMs. In only four out of 100 sediment samples both the $CPI_{25–37}$ and a pronounced UCM co-occur (Table 1) giving rise to the assumption that here an oil input can be positively established. It is noticeable that these oil-contaminated sediments are found in distinct areas only, one in the upper part of the Bengkalis Strait towards the port of Dumai, one on the N coast of Bengkalis Island and two in the tributary Tapung kanan.

Despite the fact that in the middle and lower parts of the Siak heavy ship traffic is present and small oil and diesel slicks were regularly observed on the water surface no marked oil contributions were found in riverine and estuarine sediments. This may be due to either rapid degradation of spilled oils and fuel or specific sedimentation conditions such as river bed depressions which may serve as sediment traps. On the other hand, given the low $CPI_{25–33}$ values of some plants samples (Fig. 2 right) it appears more likely that the oil signal is not derived from a direct oil input but rather from oil-contaminated saw dust or grass-derived material. Bengkalis Strait, on the other hand, experiences heavy ship traffic while Dumai port is also used for oil shipping and hence local oil contaminations are likely.

In the majority of sediment samples analysed *n*-alkanes, derived from terrestrial sources, are dominant independent of the location in the Siak River itself, its estuary and the adjacent coastal waters. Straight chain hydrocarbons may provide first clues on the origin of this fraction but the

Table 1 Stations with $CPI_{25–33}$ values <3 and pronounced UCMs

Station	$CPI_{25–33}$	UCM
111	3,0	+++
116	2,8	
131	1,1	
137		+++
138	2,4	
139		+++
148	1,0	
163		+++
164		+++
168		+++
170	2,9	
173	2,8	
177		+++
178		+++
233		+++
234		+++
236	1,0	+++
237	1,6	+++
240	2,2	
241	2,1	
243	1,8	
245	2,9	
246	2,4	
247	2,4	
248	1,5	+++
250	3,0	
259	2,3	+++
262		+++
263	1,7	
270	2,3	
271	2,8	
272	2,3	
273		+++

interpretation of the data is beset with a number of difficulties due to the fact that already the terrestrial source material shows a wide range in CPI and LC/SC ratio, parameters commonly employed to differentiate terrestrial and aquatic organic matter sources and oil-derived contamination. Nevertheless, it can be stated that aquatic and anthropogenic (oil) sources do not contribute significantly to the *n*-alkane fraction of the sediments analysed. This might be due to the fact that contamination in the Siak is usually from point sources, i.e., from the cities of Pekanbaru and Perawang. Removal of this load during downstream transport appears to be rapid, either by microbial degradation or by adsorption to the high particulate load of the river and subsequent sedimentation. Our sediment grain size data indicate that sedimentation largely takes place in

the lower reaches and in the estuary of the Siak. As in these sediments almost no contamination signal was found it can be assumed that biological activity is largely responsible for the low levels of oil-derived *n*-alkanes found.

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