

Biomarkers in the Siak River System, E. Sumatra, Indonesia

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Abstract: A total of 33 plant species and 122 surface sediments were obtained from March 2004 to November 2008 in the Siak River system including its major tributaries and coastal areas. Grain size distribution shows the sediments to be sands to silt with a general trend of coarser sediments in the upper reaches and finer ones in the estuary. The expected linear relationship between the content of organic carbon and the mud fraction of the sediments ($<63\ \mu\text{m}$) is distorted by input of (a) clay-sized, organic-poor material from river bank erosion and (b) input of coarse plant detritus. All samples were analysed for n-alkanes and steroids. For all plant samples and a limited number of sediment samples, fatty acids were also determined. The data indicate a variety of organic carbon sources, the dominant one being river bank vegetation. Urban and industrial discharges, peat erosion and atmospheric deposition of black carbon and biomarkers might also play a role in controlling the lipid composition of the sedimentary organic carbon pool.

Key words: Siak river (Sumatra), grain size distribution, steroids, fatty acids, alkanes. Blackwater river, peat,

Introduction

Lipid biomarkers, although usually representing only a small fraction of the sedimentary organic carbon pool, are robust molecular indicators of organic matter sources. This feature is due to the specificity of their biosynthesis as well as the changes in lipid compositions with environmental conditions (Saliot et al., 1991; Colombo et al., 1996). Furthermore, they are, either in their original form or with recognisably altered structures, relatively resistant towards degradation. Lipid classes considered in this survey of plants and sediments of the Siak River system, E. Sumatra, encompass *n*-alkanes, fatty acids and steroids.

n-Alkanes are almost exclusively synthesised by higher land plants as part of their epicuticular waxes. Accordingly, they serve as indicators for the contribution of terrestrial plants to aquatic sediments (e.g., Rommerskirchen et al., 2006). In addition, the chain length distribution and stable isotope composition

of these compounds are assumed to vary with respect to vegetation composition and hydrologic conditions (e.g., Bi et al., 2005; Tierney et al., 2010). Plant-derived alkanes are dominated by odd-carbon-chained compounds due to their biochemical origin from the decarboxylation of even-carbon-chain fatty acids. Furthermore petroleum-derived hydrocarbons may contribute to the sedimentary pool. In this case, both odd and even compounds are present in similar proportions. A distinction between natural and fossil sources can be made e.g. via the Carbon Preference Index (CPI) (Bray and Evans, 1961) which related the relative abundances of odd- and even-chain *n* alkanes.

Carboxylic acids in recent sediments originate from a variety of sources. Although the *n*-C₁₆ and *n*-C₁₈ alkanic and alkenic acids occur ubiquitously in biota, the even chain C₂₄ to C₃₀ *n*-alkanoic acids originate mainly from the waxy coatings of land plants (Cranwell, 1974). As carboxylic acids are more sensitive to degradation and modification than other types of lipid biomarkers (e.g.,

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Meyers and Ishiwatari, 1993; Ficken et al., 2002), they can be useful indicators of the amount of organic matter recycling in sedimentary environments.

Sterols are significant components of the sedimentary lipid fraction. Within this group of specific and diverse lipid biomarkers, contributions from algae, higher animals, vascular plants, and sewage contamination can be ascertained (Volkman, 1986; Leeming et al., 1996). This feature, coupled with the relatively high resistance of the sterol carbon skeleton to extensive degradation after release into the environment, makes them valuable as biomarkers.

Sterol molecular biomarkers have been extensively used to characterise the source and fate of organic matter in aquatic sedimentary environments (Volkman, 1986, 2003, 2005). Furthermore, several estuaries have been evaluated for their organic matter sources through the use of sterols as biomarkers, among them the Mackenzie River estuary in Canada (Yunker et al., 1993), the Changjiang mesotidal estuary in China (Sicre et al., 1993), the macrotidal Seine estuary of France (Thoumelin et al., 1997) and the Conwy Estuary of North Wales (Mudge and Norris, 1979).

In the present investigation, 12 sterols were investigated (Table 1). These include the commonly occurring cholesterol and various phytosterols as well as their corresponding stanols.

Table 1: Sterols investigated, carbon numbers and symbols. Trivial names are given in italics.

<i>Compound</i> <i>Trivial name</i>	<i>Number of C atoms</i>	<i>Symbol</i>
<i>Cholest-5-en-3β-ol</i>		
<i>Cholesterol</i>	27	S1
<i>5α(H)-cholestan-3β-ol</i>		
<i>Cholestanol</i>	27	S2
<i>24-methyl-cholesta-5,22-dien-3β-ol</i>		
<i>Brassicasterol</i>	28	S3
<i>24-methylcholest-22E-en-3β-ol</i>	28	S4
<i>24-ethyl-5β(H)-cholestan-3β-ol</i>	29	S5
<i>24-ethyl-5β(H)-cholestan-3α-ol</i>	29	S6
<i>24-methylcholest-5-en-3β-ol</i>		
<i>Campesterol</i>	28	S7
<i>24-methyl-5α(H)-cholestan-3β-ol</i>		
<i>Campestanol</i>	28	S8
<i>24-ethylcholesta-5,22-dien-3β-ol</i>		
<i>Stigmasterol</i>	29	S9
<i>24-ethyl-5α(H)-cholest-22-en-3β-ol</i>		
<i>Stigmastanol</i>	29	S10
<i>24-ethylcholest-5-en-3β-ol</i>		
<i>Sitosterol</i>	29	S11
<i>24-ethyl-5α(H)-cholestan-3β-ol</i>		
<i>Sitostanol</i>	29	S12

Coprostanol (5 β (H)-cholestan-3 β -ol) will not be considered here as a report on the compound in Siak River sediments has already appeared (Wöstmann and Liebezeit, 2010). Other sterols were present in trace quantities only and were hence not quantified.

Material and Methods

Dominant Plant Species

As no detailed information is available on the vegetation of the Siak River and its tributaries, a field campaign to comprehensively sample the dominant species was conducted. Botanical identification was successfully done for only 33 out of 69 plant specimens collected (Table 2). This limitation was particularly evident for grasses growing abundantly in the upper reaches of the Siak. None of the grasses sampled in the upper reaches of the Siak could be unambiguously identified. The only abundant aquatic macrophyte found was the water hyacinth *Eichhornia crassipes*.

Neither qualitative nor quantitative data are available for the distribution of vegetation along the Siak banks. Only in the estuarine reaches, a dominance of mangroves (*A. alba*, *B. gymnorhiza*, *R. apiculata*, *X. granatum*) was noted. *Cerberamanghas* occasionally occurred in larger numbers in the middle reaches while *Pandanusodoratissimus* was a dominant part of the vegetation along the Mandau banks. Visual inspection of coarse plant debris in surface sediments did not provide information on its origin. Hence, during field sampling attempts were made to sample plant species that were dominant both from own estimates and local knowledge provided by e.g. boat drivers.

There is only limited information on phytoplankton in the Siak River and its tributaries. Husnah and Rastina (2009) report on the dominance of bacillariophyceae and Chlorophyceae in the middle reaches but do not provide quantitative data. Given the fact that the Siak is a blackwater river with low transparencies (mean about 25 cm) (Husnah and Rastina, 2009), extremely low transparencies have also been reported by Siegel et al. (2009) without, however, giving actual values.

Sediments

A total of 122 surface sediments were obtained with a van Veen-type hand-operated grab from the tributaries of the Siak, Tapung kanan and Tapung kiri, to the estuary (Figure 1). In addition, coastal samples were taken off Dumai into Selat Panjung.

In a number of samples larger identifiable plant remains such as leaves, twigs or seeds were found. These were manually removed prior to further treatment

Table 2: Plant species analysed

Species	Family	Common name	Plant part analysed
<i>Acanthus ilicifolius</i>	<i>Acanthaceae</i>	Seaholly	Leaf
<i>Acrostichum speciosum</i>	<i>Polypodiaceae</i>	Mangrove fern	Leaf
<i>Artocarpus communis</i>	<i>Moraceae</i>	Bread fruit	Leaf
<i>Avicennia alba</i>	<i>Avicenniaceae</i>	White mangrove	Leaf
<i>Bambusa vulgaris</i>	<i>Poaceae</i>	Common bamboo	Leaf
<i>Barringtonia asiatica</i>	<i>Lythridaceae</i>	Fish poison tree	Leaf
<i>Bruguiera gymnorhiza</i>	<i>Rhizophoraceae</i>	large-leafed mangrove	Leaf
<i>Calamus rotang</i>	<i>Palmae</i>	Rattan palm	Leaf
<i>Caryota forficata</i>	<i>Palmae</i>	Fishtail palm	Leaf
<i>Cerbera manghas</i>	<i>Apocynaceae</i>	Sea mango	Leaf
<i>Cordia dichotoma</i>	<i>Boraginaceae</i>	Indian cherry	Leaf
<i>Cycas circinalis</i>	<i>Cycadaceae</i>	Queen sago	Leaf
<i>Eichhornia crassipes</i>	<i>Pontederiaceae</i>	Water hyacinth	Leaf, stem, root
<i>Elaeis guineensis</i>	<i>Arecaceae</i>	Oil palm	Leaf, fruit
<i>Elocharis congesta</i>	<i>Cyperaceae</i>	Spike rush	Leaf
<i>Ficus</i> sp.	<i>Moraceae</i>	Fig tree	Leaf
<i>Gleichenia linearis</i>	<i>Gleicheniaceae</i>	Bracken fern	Leaf
<i>Heritiera littoralis</i>	<i>Sterculiaceae</i>	Looking-glass mangrove	Leaf
<i>Hevea brasiliensis</i>	<i>Euphorbiaceae</i>	Rubber tree	Leaf, bark
<i>Hymenachne acutigluma</i>	<i>Graminae</i>		Leaf
<i>Imperata cylindrica</i>	<i>Graminae</i>		Leaf
<i>Nepenthes</i> sp.	<i>Nepenthaceae</i>	Pitcher plant	Leaf
<i>Nypa fruticans</i>	<i>Arecaceae</i>	Mangrove palm	Leaf
<i>Ochrospermatigralania</i>	<i>Palmae</i>		Leaf
<i>Pandanus odoratissimus</i>	<i>Pandanaceae</i>	Thatchscrew pine	Leaf, green, leaf, brown
<i>Panicum repens</i>	<i>Graminae</i>	Torpedo grass	Leaf
<i>Rhizophora apiculata</i>	<i>Rhizophoraceae</i>	Red mangrove	Leaf
<i>Sonneratia alba</i>	<i>Sonneratiaceae</i>	Mangrove apple	Leaf
<i>Xylocarpus granatum</i>	<i>Meliaceae</i>	Cannonball mangrove	Leaf
<i>Zingiber</i> sp.	<i>Zingiberaceae</i>		Leaf
<i>Zizania caducifolia</i>	<i>Graminae</i>		Leaf

and hence were not included in organic carbon determinations. Sediments were initially air-dried after recovery, then freeze-dried after transport to the home laboratory, and ground with an agate ball mill at 200 rpm for 30 min.

Sediment total carbon (TC) was determined by high temperature combustion (LECO SC 444), and total inorganic carbon (TIC) was measured by coulometry after acidification (UIC). Total organic carbon (TOC) was calculated as the TC – TIC difference. All values reported are averages of duplicate measurements and have a reproducibility of $\pm 0.2\%$.

Larger plant remains were not further analysed as neither leaf remains nor twig parts could be related to a specific plant source.

Black carbon (BC) was calculated as difference between TOC and TOC determined after the sample had been combusted at 375 °C (Gustafsson et al., 2001).

Sample Work-up and Analysis

Extracts were prepared by ultrasonic extraction using solvents of sequentially increasing polarity: fraction 1 – *n*-hexane, fraction 2 – *n*-hexane/dichloromethane (50:50, v/v), fractions 3 to 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, 5 α -androstanol, 5 α -androstanone and erucic acid was added to provide internal standards. The *n*-alkanes were separated from the total extracts using a 1.0 \times 20 cm glass chromatography column packed with activated silica gel (100-200 mesh). On top of the silica gel, about 10 mm of anhydrous Na₂SO₄ 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

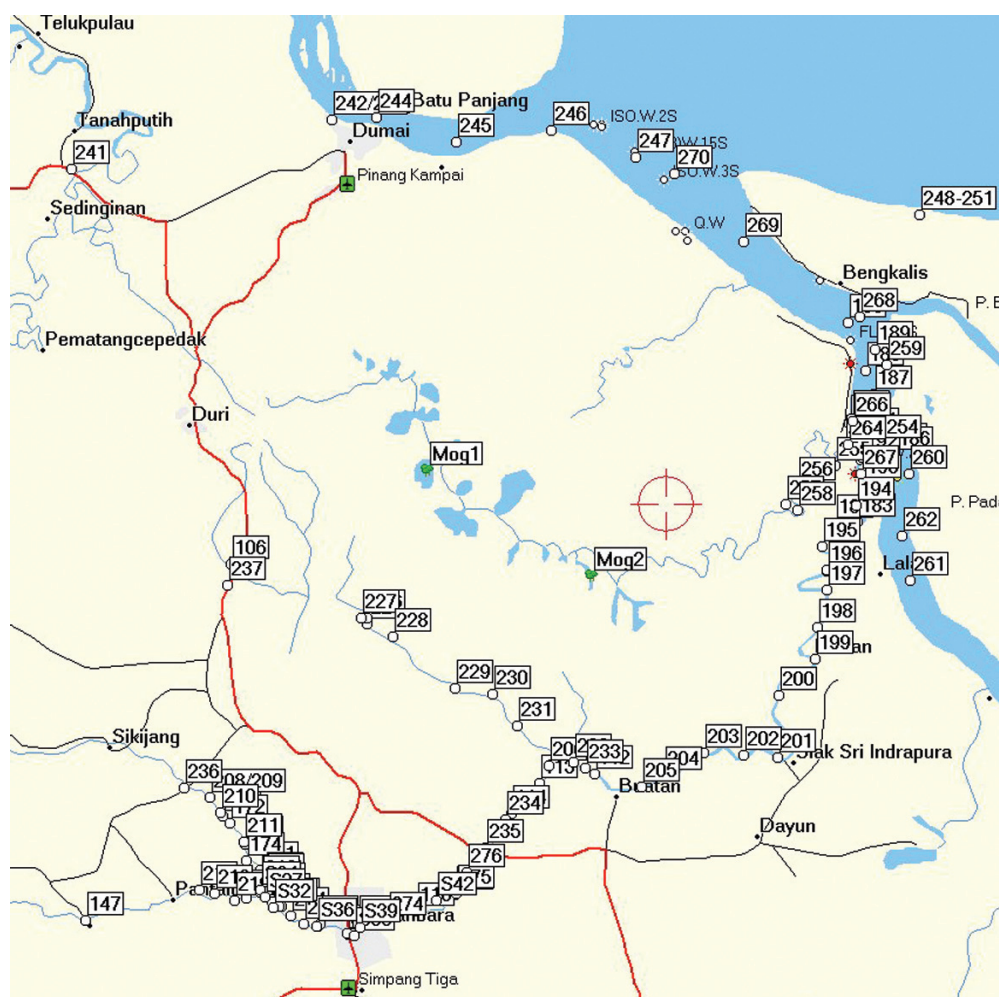


Figure 1: Stations sampled in the Siak River system.

mL of *n*-hexane while polar compounds were eluted with a mixture of 40 mL dichloromethane/methanol (90:10, v/v).

Long chain *n*-alkanes ($n\text{-C}_{16}$ to $n\text{-C}_{39}$) were analysed 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 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at a rate of 6 $^{\circ}\text{C}/\text{min}$ and held at 300 $^{\circ}\text{C}$ 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 times of authentic standards. Concentrations were calculated by comparison to the response of the corresponding internal standard (squalane).

Polar compounds were analysed using an Agilent 5973 GC-MS System operating at 70 eV with a m/z

range of 50-650 in the scan mode. The GC was equipped with a fused silica capillary column of the same specifications as described above. The carrier gas was helium. The same temperature program as above was used. Before measurement the polar compounds were derivatised to trimethylsilyl ethers by adding 50 μL of *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA) to each sample. Components were identified by comparison of their mass spectra and retention times with synthetic standards or published data. The different internal standards added prior to the sample extraction were used for quantification.

Grain Size Distribution

Air-dried samples were subjected to laser diffraction analysis (Laser Particle Sizer, Analysette 22, Fritsch). All samples were measured in triplicate. Mean grain size composition had a reproducibility of $\pm 2\%$.

Results and Discussion

Grain Size Composition and Relation to Total Organic Carbon

Surface sediments of the Siak and its tributaries are dominated by grain sizes in the sand to silt fractions (Figure 2 left). About 55% of the samples had median grain sizes in the silt range whereas pure clay sediments were absent (Figure 2 right). Fine to coarse sands made up the remainder.

The absence of finer grained surface sediments can be attributed to the relatively high current velocities (our field observations). Besides river sediments, estuarine sediments and samples of the close-by coastal environment were also analysed. Here also no fine-grained sediments were encountered. This finding suggests that this grain size fraction will be exported to the coastal ocean. Furthermore, in the Siak estuary the normal processes leading to sedimentation of

fine-grained sediments, such as colloid flocculation, apparently do not lead to deposition in the estuary itself. However, because the particulate and possibly also of the colloidal fraction are predominantly organic in origin, formation of particles with sufficient density to sink out of the water column might be prevented. In addition, as shown by Jennerjahn et al. (2004), high river discharge, in this case by the Brantas River, East Java, during rainy seasons also leads to a pronounced export of sediment and particulate organic matter to the coastal ocean.

Closer inspection of the grain size frequency curves shows that in almost all samples a bimodal distribution exists (Figure 3). Bimodality typically indicates the presence of two distinct particle-size populations supplied from different lithological sources with each population exhibiting different transport behaviour. This feature is particularly evident in the examples on the left and right of Figure 3. Here the coarse

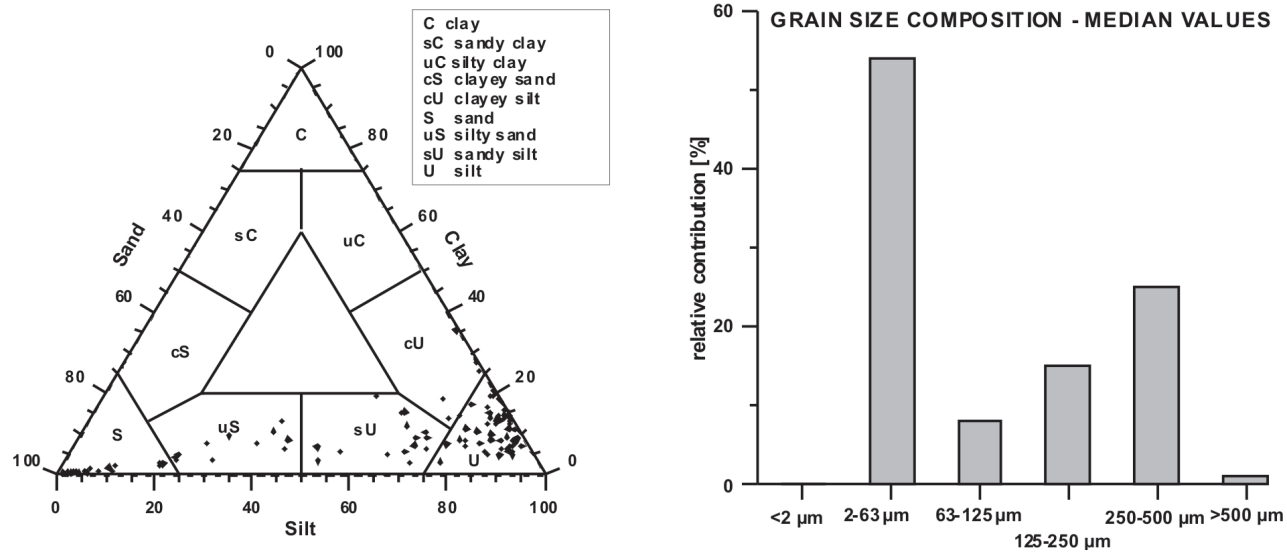


Figure 2: Grain size distribution in Tapung kanan, Tapung kiri, Mandau and Siak surface sediments. Left: Shepard plot (Shepard, 1954), right: frequency distribution.

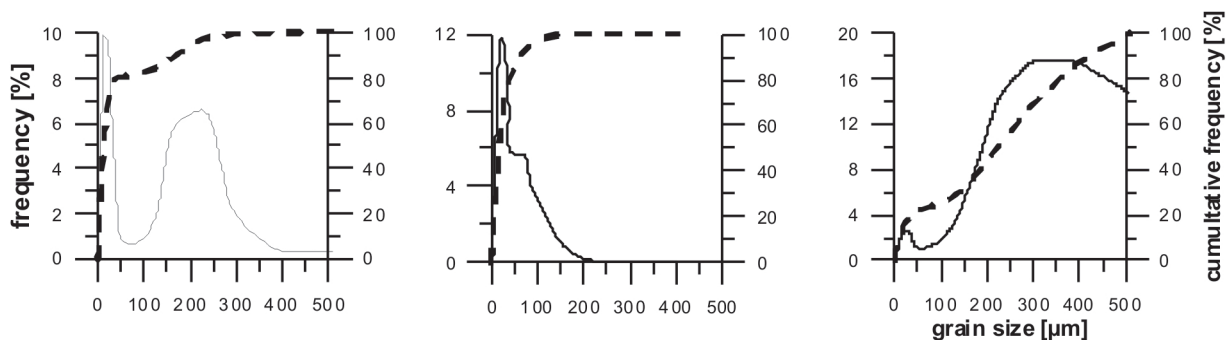


Figure 3: Examples of grain size frequency distributions.

fraction dominates and is transported as bedload. The silt fraction, which is usually less prominent, may be transported in suspension but also as bedload when flow velocities are too low for sand transport.

The interpretation of grain size distributions in the present case is hampered by the fact that neither the riverbed morphology is well known nor are good data on current velocities available. Nevertheless, the geographical distribution of median grain sizes allows identification of the tributaries Tapung kanan and Tapung kiri as dominated by sands, while mainly silts are found in the lower reaches of the Siak River (Figure 4). This downstream trend from coarse to finer sediments is augmented by the effects of river bank erosion contributing mainly fine material.

This general picture is, however, distorted by morphological effects. Preliminary echo soundings indicate an irregular bed morphology both along and across the river. Thus, finer grained sediments in the upper reaches might be due to the presence of patchy “sediment traps” in the river bed. The few available echo sounding support his hypothesis but are presently not sufficient to lend unambiguous support to it.

Typically, in aquatic sediments, there is a positive relation between the fine grain size fraction and total organic carbon content (e.g., Mayer, 1994; Hedges and Keil, 1995; Pelletier et al., 2011). This association is also seen in the present sample suite (Figure 5 left). However, especially in the region with higher mud,

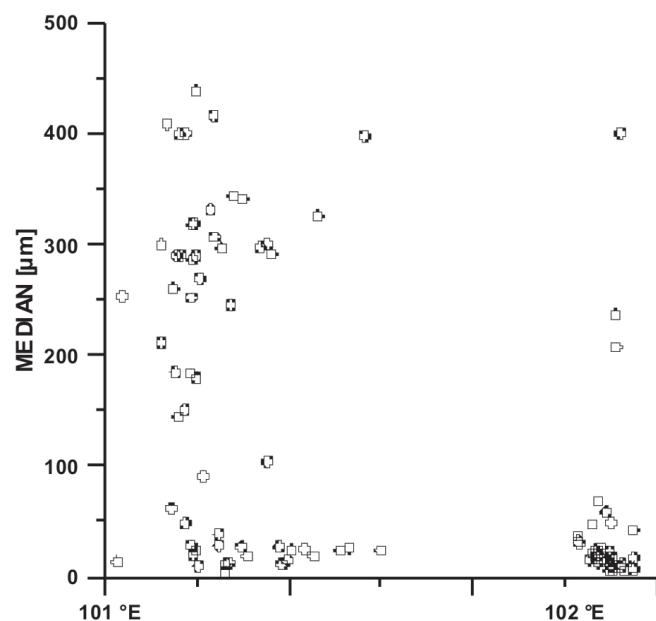


Figure 4: Median grain size as function of longitude.

i.e. <63 µm fraction, contents there is more organic carbon present than can be expected from a simple linear relation. Furthermore, there is more scatter than in other sedimentary environments such as the Jade Bay (Rinne et al., 2005). These deviations suggest that in the Siak system fine-grained organic material is not only present in the form of sorbed compounds but also as intact detrital material.

The presence of organic debris becomes evident when the TOC-median grain size relation is considered (Figure 5 right). Here two effects can be seen: higher TOC contents in coarse sediments as an indication of the presence of intact organic material and lower TOC contents in finer grained sediments as indication of the dilution by eroded river bank clays.

Identifiable organic detritus such as leaf, twig or bark fragments was frequently encountered during sediment sampling. Although larger items were moved prior to analysis, these findings are in accordance with a number of reports on the presence of plant remains in deltaic sediments (cf. Gastaldo, 1986). More detailed taphonomic analyses have been carried out microscopically identifying distinct phytoclasts e.g., in the Mahakam Delta, Indonesia (Gastaldo and Huc, 1992). Furthermore, Kamaruzzaman et al. (2009) also reported high TOC contents for some coarse grained sediments of the Pahang estuary, Malaysia. Thus, in riverine and estuarine settings the phytoclast fraction obviously plays a significant role in carbon cycling of sandy sediments.

On the other hand, fine grained material is introduced to the system from the erosion of river banks. This process is largely brought about by waves from regular traffic by fast boats. Field observations indicate this eroded material to consist of whitish clay with low organic carbon contents. This dilution is evident from the TOC-clay plot (shaded area in Figure 6A).

In addition, fine-grained debris originating from erosion of peats was also found to be present. This material gives rise to high TOC contents at low median grain size values. Peat erosion has been reported as an important source for both dissolved and particulate organic carbon in river systems (e.g., Alkhatib et al., 2007; Baum et al., 2007; Pawson et al., 2008).

n-Alkanes

All plant species analysed had maxima at chain lengths from 29 to 35 carbon atoms. With the exception of *Cerberamanghas* the C_{31} compound was the most prominent one followed by C_{29} and C_{33} (Figure 7).

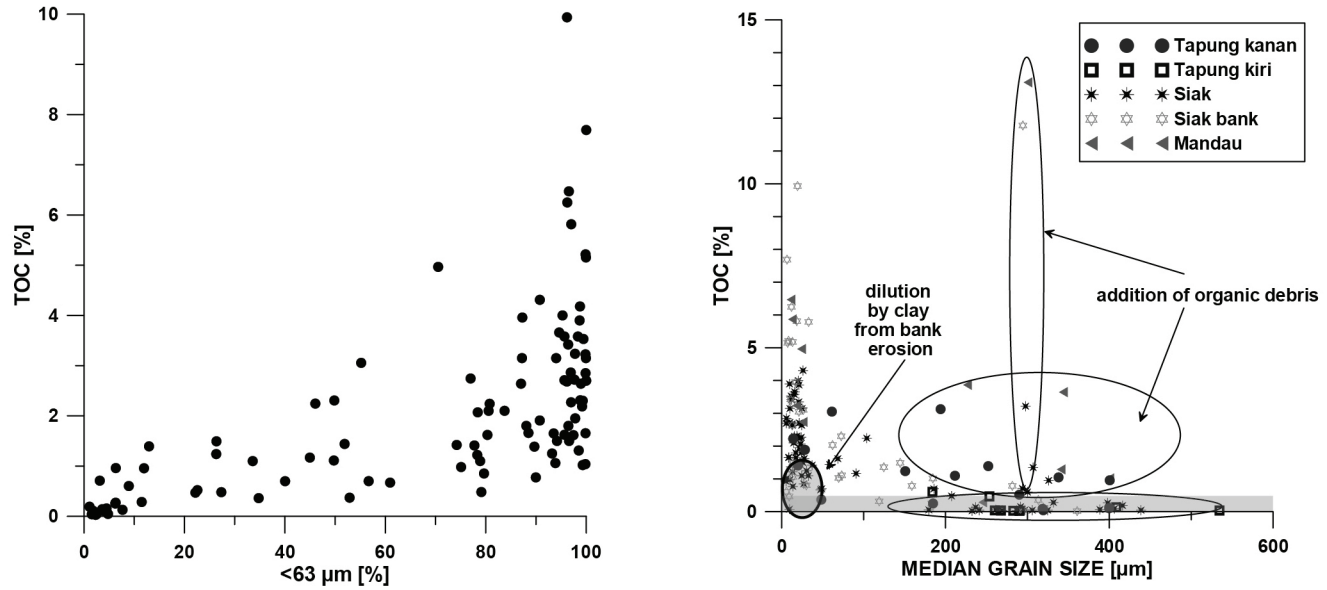


Figure 5: Left: Relationship between TOC and mud (<63 µm) content in surface sediments of Tapung kanan, Tapung kiri, Mandau and Siak rivers. Right: Relationship between TOC and median grain size.

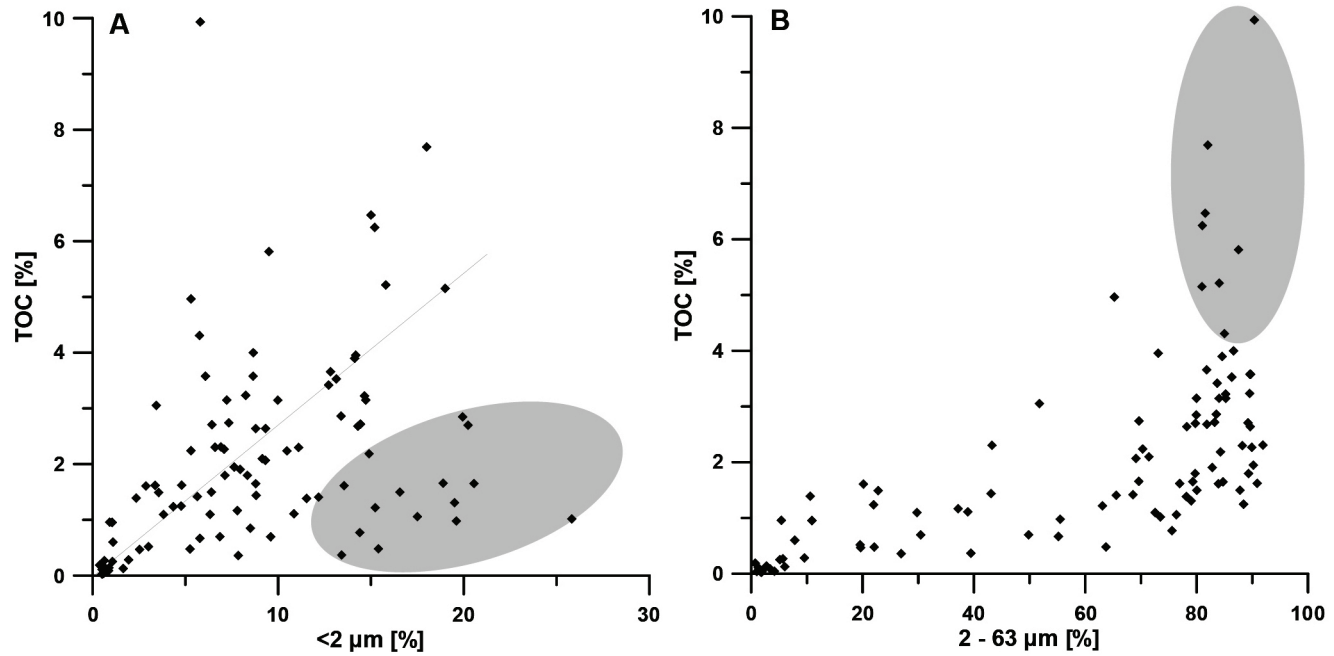


Figure 6: Relations of clay (A) and silt (B) to total organic carbon (TOC) for Siak River system surface sediments.

The following derived parameters were calculated from the alkane data set: Carbon Preference Index (CPI_{23-33}), Average Chain Length (ACL_{27-33}) and Higher Vegetation Index (HVI) according to equations 1 to 3.

$$CPI_{23-33} = \frac{(C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{(C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}) + (C_{23})}$$

$$\frac{+ C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{+ C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} \times 0.5 \quad (1)$$

$$ACL_{27-33} = \frac{((27 \times C_{27}) + (29 \times C_{29}) + (31 \times C_{31}) + (33 \times C_{33}))}{(C_{27} + C_{29} + C_{31} + C_{33})} \quad (2)$$

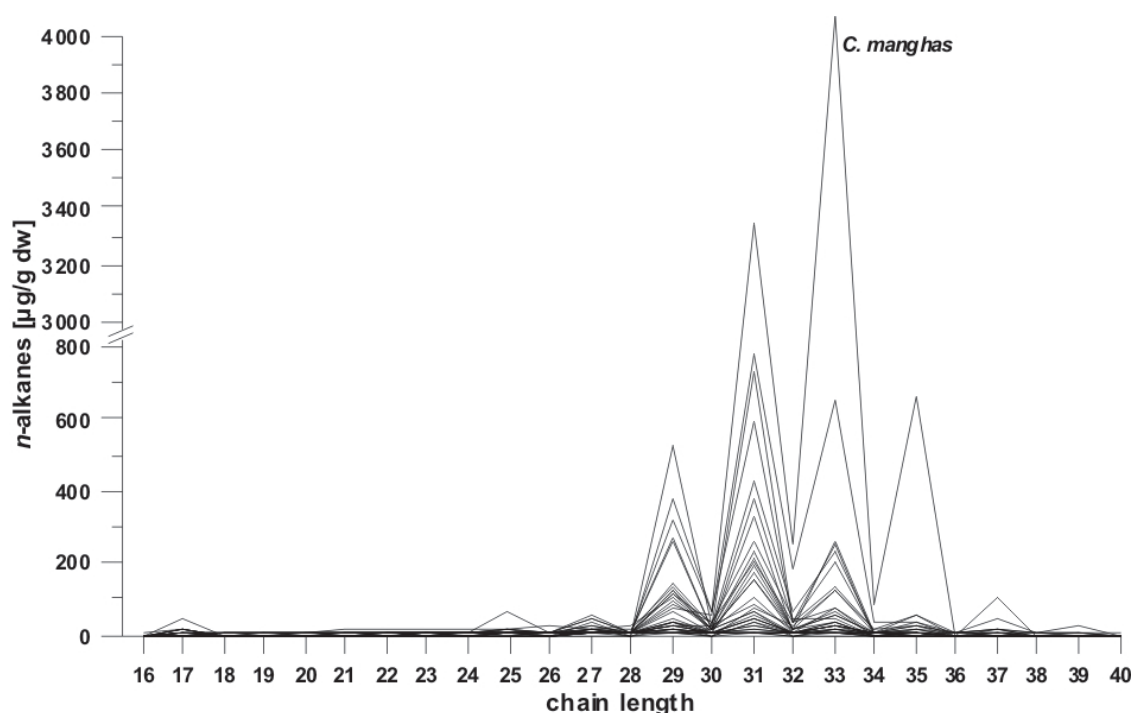


Figure 7: *n*-Alkane distribution in Siak vegetation.

$$\text{HVI} = (C_{27} + C_{29} + C_{31}) / (C_{17} + C_{19}) \quad (3)$$

All three indices have been used to differentiate between terrestrial and aquatic sources of *n*-alkanes (CPI – Bray and Evans, 1966; ACL – Poynter, 1989, HVI – Cranwell, 1973).

A comparison between the derived indices for plants and sediments indicates marked similarity (Figure 8) suggesting that the overwhelming majority of *n*-alkanes in riverine sediments is plant-derived.

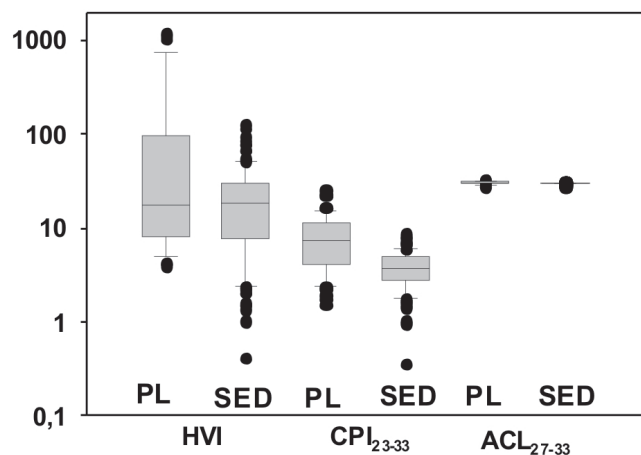


Figure 8: Derived parameters for the *n*-alkane data set. PL – plant, SED – sediment.

Based on the assumption that short chain compounds are predominantly derived from aquatic producers and long-chain ones from higher plants, a ternary plot can be used to further elucidate possible contributions from these sources (Figure 9). Most plant and sediment samples fall indeed into one region clearly indicating a plant source.

On the other hand, some plants and sediments show a distinctly different signal indicating higher contributions of the short- and medium-chain compounds. This difference might indicate an additional contribution from aquatic sources. However, only five out of the ten samples labelled in Figure 9 are located in the Siak estuary; three (stations 148, 236, 237) originate from the tributary Tapung kanan, one from downstream Pekanbaru (116) and one from the coast of Bengkalis Island (248). As some grasses also had a similar composition, it can be assumed that, at least for the Tapung kanan samples, the *n*-alkane distribution is related to an input from this source. On the other hand, the Bengkalis island sample was an eroded peat washed ashore. Taking into account other eroded peats (Liebezeit and Wöstmann, 2012; Figure 9) it is evident that this source may also contribute to sedimentary *n*-alkanes. On the other hand, two outcropping peats—both upstream in the Siak and in its estuary—had relatively long-chain *n*-alkane

contents >80 %, thus making it impossible to distinguish plant and peat derived *n*-alkanes.

In a previous communication, *n*-alkanes were used to assess contamination of the Siak River system by petroleum-derived compounds (Liebezeit et al., 2009). Because the CPI₂₃₋₃₃ values of some plants were <3, only a combination of this ratio and the presence of an unresolved complex mixture (UCM) in the gas chromatograms indicated presence of oil contamination. In the present sample suite an UCM was present in samples 236, 237, 248 and 259 (Figure 9).

Furthermore, sawdust that is discharged into the river from numerous saw mills from Pekanbaru to Perawang also contains appreciable quantities of short- and medium-chain *n*-alkanes (E in Figure 9).

Thus, while plant sources appear to be the most likely and dominant source for the *n*-alkane fraction in Siak surface sediments, other sources such as peats, sawdust or petroleum-derived compounds also have to be taken into account. This suggests that the indices used are, in this case, not useful for differentiating plant from other sources.

Fatty Acids

The Siak vegetation is characterised by a fatty acid distribution dominated on an absolute basis by

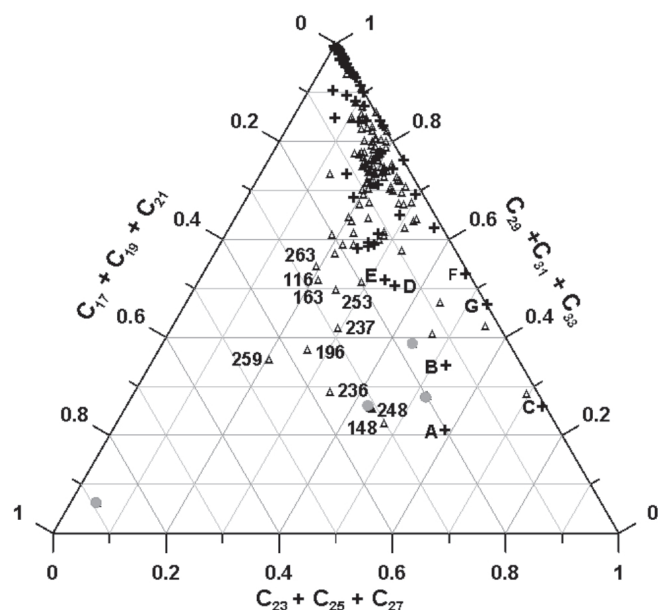


Figure 9: Ternary plot of short, medium and long chain *n*-alkanes. Crosses – plants: A – unknown, B, D – unidentified grasses, C – *Nypafruticans*, E – sawdust, F – *Bambusa vulgaris*, G – *Eichhornia crassipes* stem; triangles – sediments: numbers refer to stations (Figure 1), grey dots – eroded peats, coastal samples (Liebezeit and Wöstmann, subm.).

C₁₆, followed by C_{18:1}, C_{18:2}, C₁₈ and C₁₄ compounds (Figure 10). Although chain lengths of up to 30 were determined the longer chain fatty acids are of minor importance.

Using a normalisation to stearic acid (C₁₈) two plants have an unusual contribution of even fatty acids: *Zingiber* sp. had a high relative contribution of the C₂₀ acid while *Gleichenialinearis*, a fern, had an extremely high content of the C₂₆ and also higher contents of the C₂₈ and C₃₀ acids (Figure 11).

Capric acid (C₁₀) was found only in *E. guineensis* leaf while heneicosanoic acid (C₂₁) was found in *E. crassipes* stem and *A. alba* and *S. alba* leaves. The C₁₅, C₁₇, C₂₃ and C₂₅ compounds occur more frequently, being present in 24, 27, 23 and 19, respectively, of the 33 species investigated.

Fatty acids with chain lengths >24 carbon atoms are synthesized mostly by vascular plants (Volkman et al., 1980), and can hence be considered as indicators of terrestrial inputs to aquatic sediments (e.g., Scribe et al., 1991; Colombo et al., 1996; Carrie et al., 1998). However, in the Siak samples sedimentary FAs are lacking the longer-chain compounds (Figure 12) suggesting a rapid degradation of the plant-derived compounds. Based on the data of e.g. Hu et al. (2006) it can be assumed that the majority of fatty acids are actually of bacterial origin.

On the other hand, the fact that the rare C₂₁-FA was found in sediments suggests that the source species, i.e. *E. crassipes*, *A. alba* or *S. alba*, may contribute to sedimentary fatty acids. Which of these species are actually responsible for this cannot be unambiguously

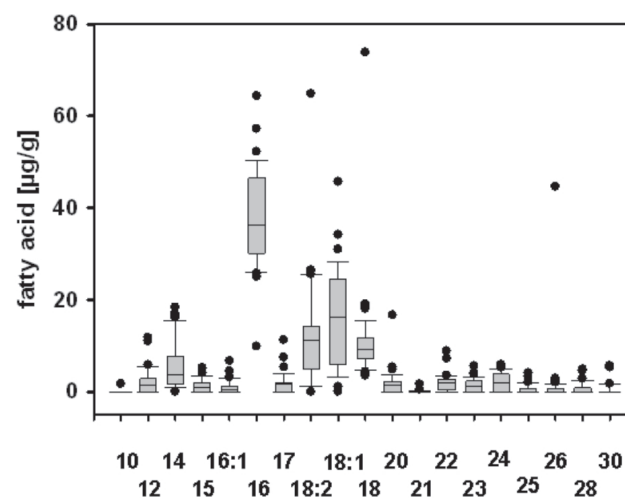


Figure 10: Box-whisker plot for absolute contents of plant fatty acids. Order of compounds as derived from GC retention times.

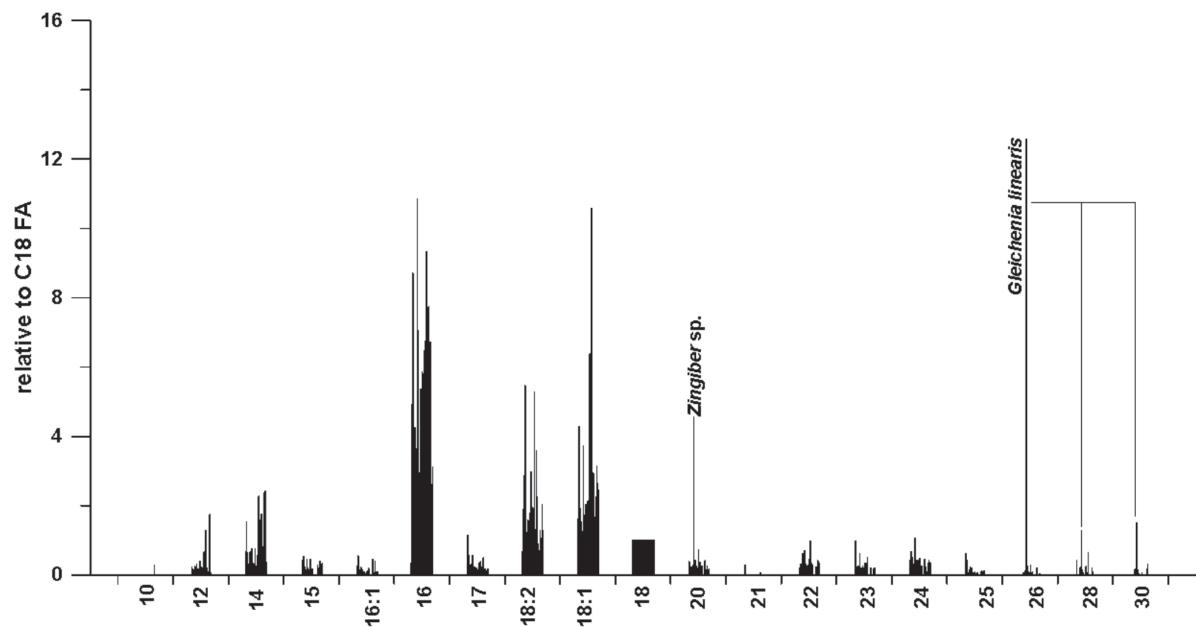


Figure 11: C₁₈-normalised fatty acid composition of Siak vegetation.

established from the FA data alone as of the five stations with C₂₁-FA presence three are located in the Siak estuary where contributions from the mangrove species *A. alba* and *S. alba* can be expected while two are located upstream the Siak and in the Tapung kanan. Here water hyacinth is presumably the dominant source of the C₂₁-FA.

Sterols

Of the 12 sterols investigated (Table 1) four were completely absent in the 36 plant species, two were

present only in two plants, one in seven plants and only three sterols, i.e. campesterol, stigmasterol and sitosterol, were encountered with higher frequencies (Figure 13). With the exception of a few isolated occurrences, stanols were absent in the plant samples.

Particularly noticeable is the limited presence of cholesterol (S1) in the plants, being detectable in only 25% of the species analysed (Figure 13). A notable

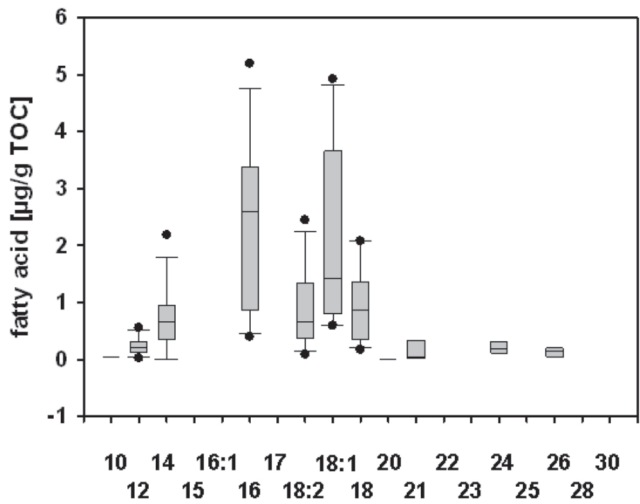


Figure 12: Box-whisker plot for sedimentary fatty acids. Order of compounds as derived from GC retention times.

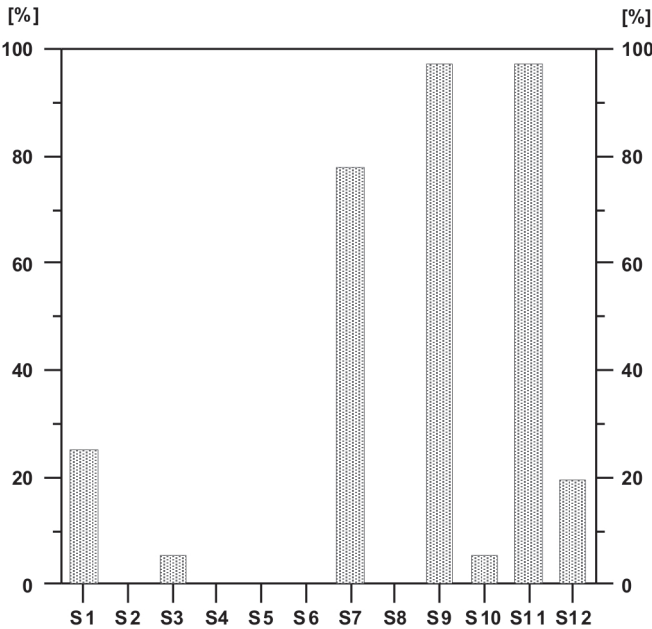


Figure 13: Relative distribution of sterols in the 36 plant species analysed. For compound identification see Table 1.

exception is the water hyacinth *Eichhornia crassipes* where cholesterol was found in all parts, i.e. root, stem and leaf (Liebezeit, subm.) (Figure 14).

A ternary plot of ΣC_{27} - ΣC_{28} - ΣC_{29} sterols is often used to distinguish sources (Huang and Meinschein, 1979). All plant species plot, as expected, in this ternary diagram in the terrestrial region (Figure 14).

In the sediments reduction from sterols to stanols is observed (Figure 15), e.g., cholesterol (S1) to

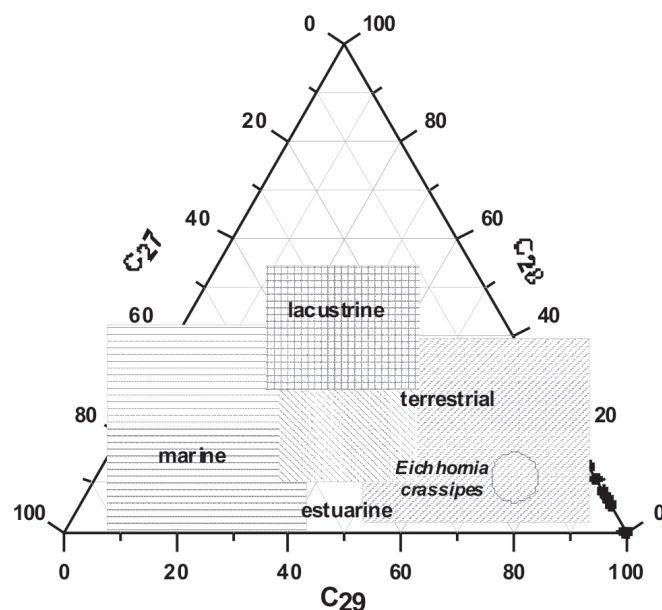


Figure 14: Huang-Meinschein diagram for plant sterols.

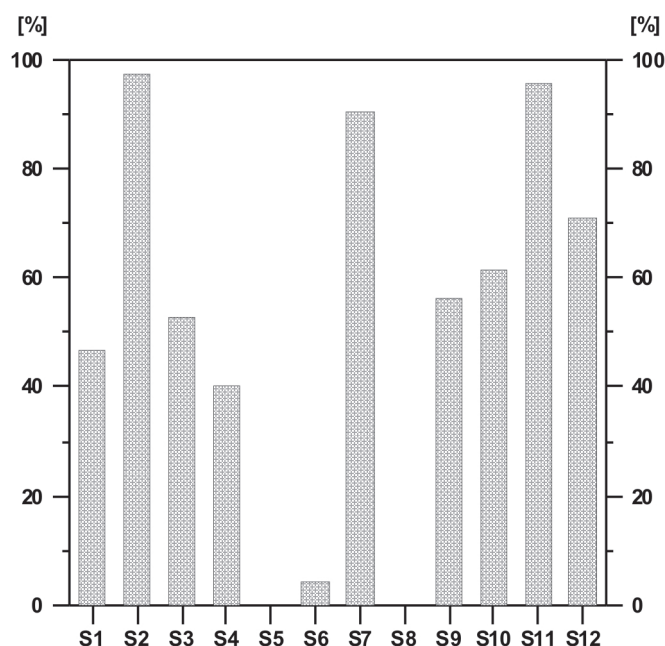


Figure 15: Relative occurrence of sterols in Siak sediments. For compound identification see Table 1.

cholestanol (S2), stigmasterol (S9) to stigmasterol (S10) and sitosterol (S11) to sitostanol (S12). As stanols are produced in the sediment by anaerobic bacteria the dominance of this compound class indicates suboxic to anoxic conditions in river surface sediments. Although truly anoxic sediments were not noted during field sampling, suboxic conditions are likely to occur, being favoured by the low oxygen contents (12-170 $\mu\text{mol/L}$) of the river water itself (Rixen et al., 2008; 2010).

Relative sterol contents range from <10 to >10,000 $\mu\text{g/g}$ TOC (Figure 16). These values are comparable e.g., with the 239 to 3285 μg total sterols/g TOC recalculated for surface sediments from Guanabara Bay, Brazil, which receives a direct input of domestic effluents and other associated contaminants from human activities to its watershed (Santos et al., 2008). For Mississippi River sediments, they report values from 500 to 2300 μg total sterols/g TOC. In contrast to the Siak samples 24-ethylcholest-5-en-3 β -ol (compound S11) had the highest abundances in these samples.

Using the Huang-Meinschein plot (Figure 17) it is evident that the majority of sedimentary sterols is derived from plant sources. There are, however, also samples that fall in the aquatic sources region. This difference is particularly evident for estuarine and coastal samples.

This finding does not necessarily imply that aquatic sources such as phytoplankton contribute to the sedimentary sterol pool. The shift towards this source is largely brought about by variations in the relative C_{27} contribution, i.e. mainly caused by higher cholesterol contents. Liebezeit and Wöstmann (2010) showed that

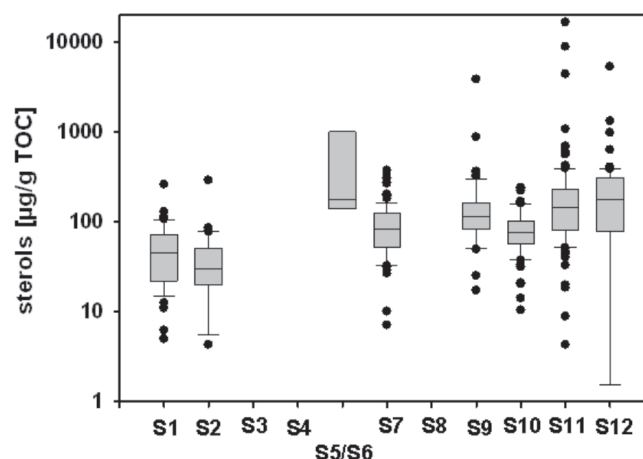


Figure 16: Sterol contents in Siak River system sediments normalised to total organic carbon. For compound identification see Table 1.

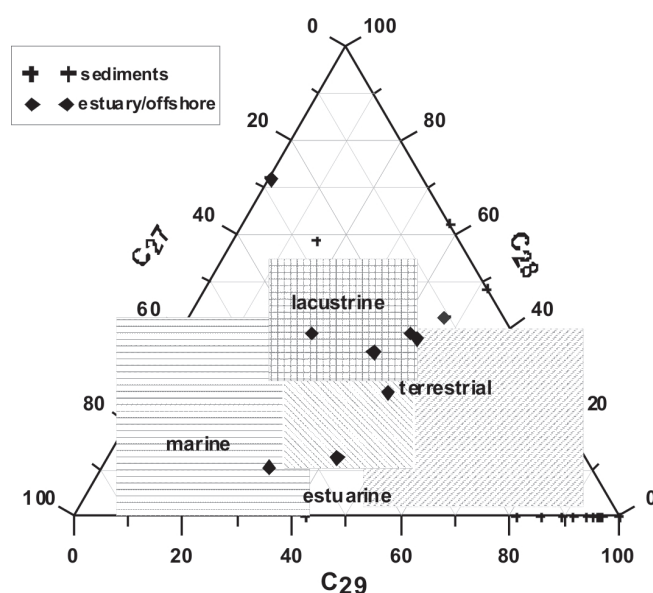


Figure 17: Huang-Meinschein diagram for sedimentary sterols.

discharge of untreated sewage, a common occurrence along Siak and its tributaries, introduces cholesterol and coprostanol (5 β -cholestan-3 β -ol). Depending on the redox conditions in the sediment cholesterol can also be microbially reduced to 5 β -cholestan-3 α (H)-ol or remain intact.

Biomass Burning as Additional Source of Organic Compounds

Black carbon

The term black carbon (BC) is used to describe a relatively inert and ubiquitous form of condensed carbon produced by incomplete combustion of a variety of fossil fuels such as coal or petroleum and from biomass burning, i.e. forest fires and vegetation burnt for agricultural purposes. BC particles range from partly charred plant material through char and charcoal to soot and graphite-like particles. These pyrogenic particles produced play important roles in a number of geochemical processes. BC is an important component in the preservation of sedimentary carbon (e.g., Goldberg, 1985; Dickens et al., 2004) and may be employed to reconstruct the history of global wildfires (e.g., Bird and Cali, 1998).

Aquatic sediments also receive combustion by-products via atmospheric deposition in addition to direct inputs of organic material. With respect to the global carbon cycle, black carbon has been recognised as important as its formation results in transfer of carbon from the fast biological-atmospheric carbon cycle to

the slower geological cycle. Since black carbon cannot be readily oxidised it can be considered to be a “sink” for CO₂.

The importance of black carbon in global cycles is evident from an early study of Andreae (1991) who estimated that 19 Tg C yr⁻¹ of elemental carbon emission could derive from biomass burning, which would represent more than 85% of the total global elemental carbon emission. More recent estimates are somewhat lower: 7.2 Tg C yr⁻¹ (Lioussé et al., 2004), 4.8 Tg C yr⁻¹ (Andreae and Merlet, 2001), 4.9 Tg C yr⁻¹ (Bond et al., 2004), and 5.5 Tg C yr⁻¹ (Ito and Penner, 2005). According to Ramanathan and Carmichael (2008), approximately 20% of global black carbon emissions derive from biofuels, 40% from fossil fuels and another 40% from open biomass burning.

Given the fact that vegetation burning and uncontrolled peat fires occur frequently in E Sumatra (e.g., Levine, 2000; Heil and Goldammer, 2001; Page et al., 2002; Streets et al., 2003; Langmann and Heil, 2004), the presence of black carbon in river sediments is not surprising. This is also supported by the pronounced presence of pyrogenic polycyclic aromatic hydrocarbons in Siak sediments (Lukman, 2010).

Absolute black carbon contents ranged from 0.01 to 1% sediment dry weight with the majority of values lying between 0.01 and 0.1% (Figure 18). These contents are in line with data for Rawa Danau, west Java, Indonesia (0.01 to 0.24%) (Tareq et al., 2005). There is no significant relation to median grain size; thus finer grained sediments do not necessarily have more BC incorporated.

On an average black carbon accounts for 6.7% of total organic carbon with relative contributions ranging from 0.2 to 100% (Figure 19). Higher values in TOC-poor coarse sediments are presumable due to the fact that in these sediments absorption sites for organic carbon are lacking and that this carbon may be present predominantly in particulate form. Most values, however, are found in the range 1 to 10%.

Besides black carbon, intact and heat-altered organic compounds are also components of smoke clouds from biomass burning (e.g., Simoneit and Elias, 2000; Simoneit, 1999, 2002; Oros et al., 2002; Akagi et al., 2011). These include a large variety of compounds, e.g., saturated and unsaturated hydrocarbons, acids, phenols, terpenes, sterols and saccharide derivatives. On the other hand, other anthropogenic and biogenic sources such as emissions from traffic, higher plant waxes, food cooking and biomass and domestic refuse burning may also

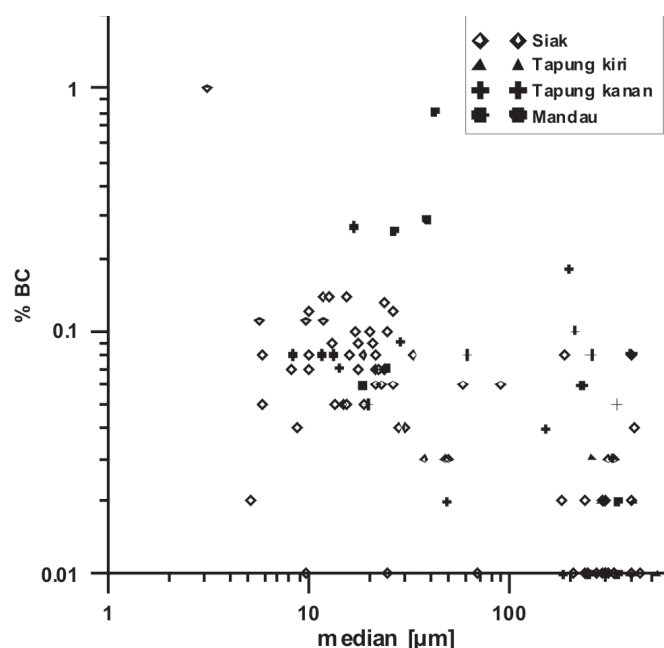


Figure 18: Absolute black carbon contents in surface sediments of the Siak River system. Note that the detection limit of TOC determination is 0.01%.

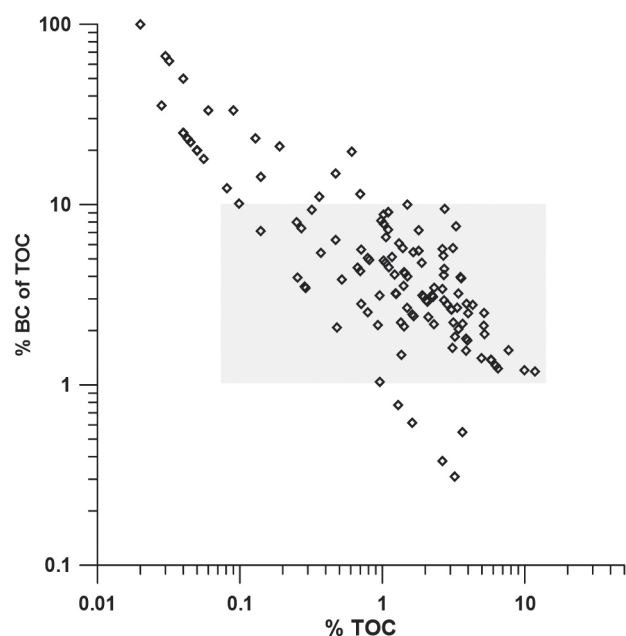


Figure 19: Relative black carbon content in relation to total organic carbon.

contribute to the organic matter content of atmospheric dust particles.

Indonesian peat was found to produce both *n*-alkanes and *n*-alkenes in the C_{20} to C_{34} range, polycyclic aromatic hydrocarbons, lignin degradation products, nitrophenols and sugar derivatives (Iinuma et al., 2007).

Terpenes and sterols were not investigated. In aerosol samples collected in Kuala Lumpur, Malaysia, during the 1997 haze event in Sumatra Fang et al. (1999) found *n*-alkanes, *n*-alkanoic acids, *n*-alkanols, hopanoids and terpenoids to be present while See et al. (2007) reported the presence of polycyclic aromatic hydrocarbons in atmospheric particulates for several sites in Sumatra.

Given the extent of biomass burning in E. Sumatra (e.g., Heil and Goldhammer, 2001; Radojevic, 2003) it is highly likely that atmospheric particles loaded with organic compounds from this source are deposited in river and estuarine sediments also. The relative importance of burning-derived biomarkers can, however, not be assessed with the data at hand.

Conclusions

The analysis of biomarker compounds in both river bank vegetation and river sediments indicates that the majority is derived from plants. Additional sources such as petroleum contamination predominantly from boat traffic, urban and industrial discharges, peat erosion and biomass burning do however contribute to the overall organic carbon pool of riverine sediments of the Siak system.

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