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Biomarkers from Latex Drying Plants in Siak River Sediments

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Abstract: In Pekanbaru, Riau Province, Sumatra, two latex processing plants discharge wastewater rich in particulate and dissolved organic matter to the Siak river. The immediate effect is a marked enrichment of total organic carbon in the sediment adjacent to the discharge point. Biomarkers specific for *Hevea brasiliensis* were also found in the discharged process water. These compounds could be detected up to 25 km downstream.

Key words: *Hevea brasiliensis*, latex, biomarker, sediment, river, Siak, Sumatra, Indonesia.

Introduction

In Pekanbaru, the capital of Riau Province, Indonesia, two latex processing plants discharge wastewater into the Siak river. Effluent from rubber and latex processing factories contain small amounts of uncoagulated latex and also contain dissolved organic compounds such as proteins, carbohydrates and lipids. The water-soluble proteins are known allergens (see http://www.latexallergyresources.org/ResourceManual/PDF/sec9_latexallergens.pdf for a list of compounds including references). Since large amounts of acid are used in the processing, the effluent is usually acidic and also contains high proportions of suspended solids and nitrogen (http://www.arabis.org/documentation/whitepaper/MSIA_Environment.shtml). High biological and chemical oxygen demands were also noted, e.g. Asia and Akporhonor (2007) report 2.6 and 3.1 mg/L, respectively. Padmini (no date) notes for Sri Lanka plants that "foul odours resulting from decomposing latex serum proteins are the cause of frequent complaints by people living near latex processing plants".

Latex of *Hevea brasiliensis* (Euphorbiaceae) also contains a number of phenolic compounds, a.o. scopoletin (7-hydroxy-6-methoxy coumarin) which is of interest as a possible agent against various plant-pathogenic fungi, especially *Microcyclus ulei*. In addition, lanosterol and its derivatives euphol and euphorbol (24-methylenelanost-8-en-3-β-ol) have been identified in the latex of *H. brasiliensis* (Nishimura et al., 1977). Ubiquinone homologues have also been isolated from *Hevea* latex (Law et al., 1970).

Apart from the olfactory impact to the immediate vicinity of the discharge point the fact that latex drying wastewater carries potential allergens and other substances of unknown effects merits further investigation. Given the fact that traditional usage of the river for personal hygiene purposes or cloth washing still takes place all along the Siak river and hence also in the direct neighbourhood of the discharge points in Pekanbaru, a yet undefined environmental burden may exist for the population living on the river banks.

In addition, the discharge of easily degradable dissolved organic matter and ammonium adds to the already stressed oxygen balance of the river itself.

Environmental Setting of the Siak River System

The Siak river with a total length of 370 km drains a catchment area of 11.500 km² (Figure 1). About 45% of

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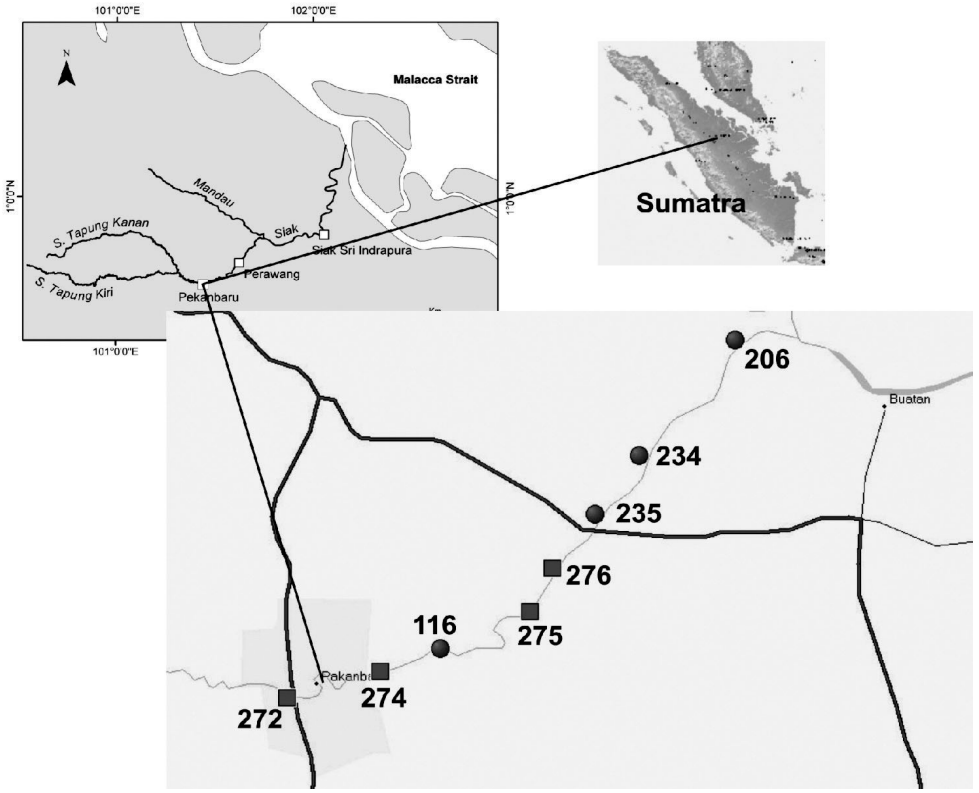

Figure 1: Sediment samples checked for *Hevea* tetraterpenoids: squares – positive, dots – negative.

this area are peat soils. The estimated discharge in March is 642 m^3s^{-1}, while in September it is 99 m^2s^{-1} (A. Baum, T. Rixen, pers. comm., 2007).

Pekanbaru, the capital of Riau Province, discharges untreated sewage of an estimated two million inhabitants and has, in addition, a number of saw mills and two latex drying plants which release saw dust and organic- and particle-rich waters.

Material and Methods

Surface sediment samples were taken in February 2004 with a 150 cm^2 van Veen-Type grab (Figure 1). Samples were initially air dried and lyophilised after transport to the home laboratory. After recovery sediments were first air-dried and after transport to the home laboratory the samples were freeze-dried and ground in an agate ball mill at 200 rpm for 30 minutes.

Grain size distribution was determined by laser diffraction (Particle Sizer Analysette 22, Fritsch) on untreated samples.

Sediment and plant extracts were prepared by ultrasonic treatment using solvent systems of sequentially increasing polarity: (1) *n*-hexane, (2) *n*-hexane/dichloromethane (50:50 v/v), and (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 while polar compounds were eluted with a mixture of 40 ml dichlormethane/methanol (9:1 v/v).

Polar compounds were analysed using a Agilent 5973 GC-MS System operating at 70 eV with a mass range of m/z 50-650 in the scan modus. The GC was equipped with a J&W DB 5 capillary column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness). A temperature programme was run from 60 °C to 300 °C at a rate of 6 °C/min and held at 300 °C for 30 min. The carrier gas was helium. 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.

Total carbon (TC) was determined by combustion analysis with LECO® SC 444 element analyser, and total inorganic carbon (TIC) after acidification and determination by CO_2-coulometer (UIC®). The total organic carbon (TOC) was determined by subtracting the amount of carbon present as carbonate (TIC) from the total amount of carbon. All values reported are averages of duplicate measurements and have an average reproducibility of ±0.2%.

Results and Discussion

The grain size composition of the sediments is dominated by the silt fraction with minor clay and sand contributions. Only stations 275 and 276 have to be addressed as silty sand and sand, respectively (Figure 2). Total organic carbon varies from 0.16 to 31.13% (Figure 3) with station 272 showing the highest value. Out of a total of 151 sediment samples taken in the Siak and its tributaries station 272 is the only one that does not fit the TOC-<63 µm fraction relation exhibited by the rest of the sample suite (Figure 4). From this relation a TOC content of about 2.8% is expected for station 272.

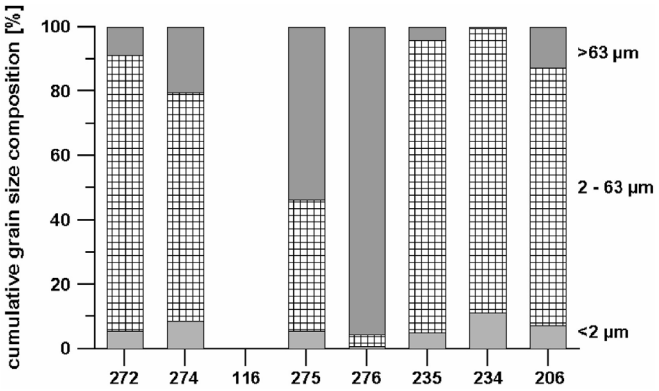

Figure 2: Grain size composition of Siak river sediment samples.

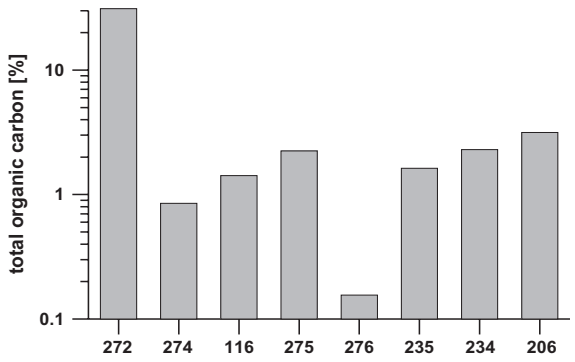

Figure 3: Total organic carbon contents of the Siak river sediment samples. Note logarithmic scale.

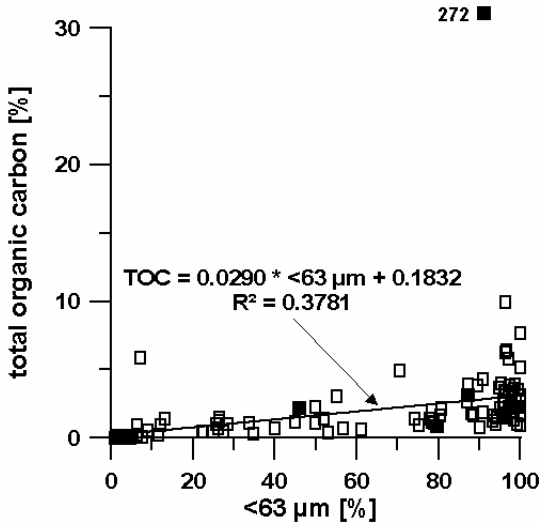

Figure 4: Relationship between mud (<63 µm) and TOC contents for 151 Siak river sediment samples.

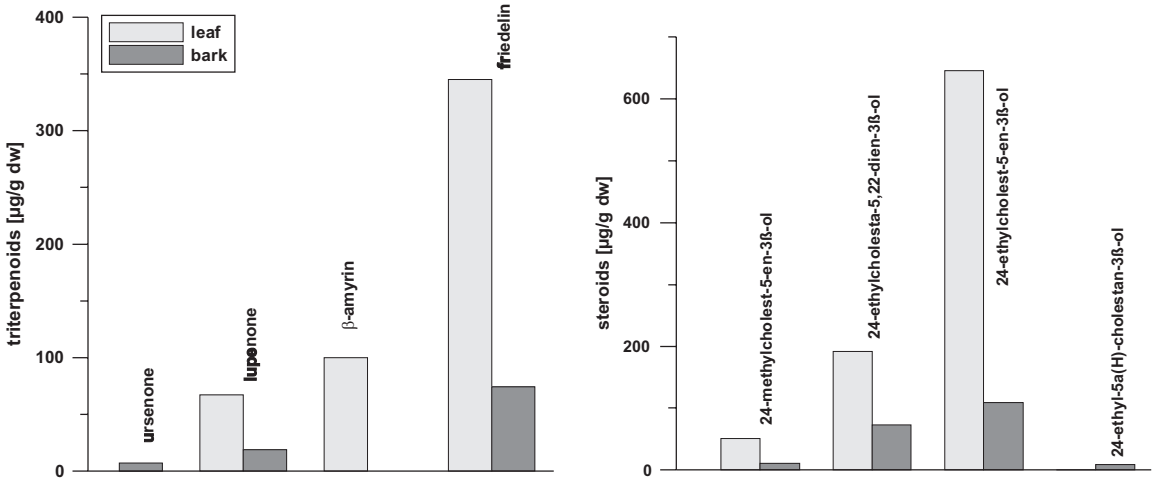

Figure 5: Tetracyclic triterpenoid and steroid compounds in *Hevea brasiliensis* leaf and bark.

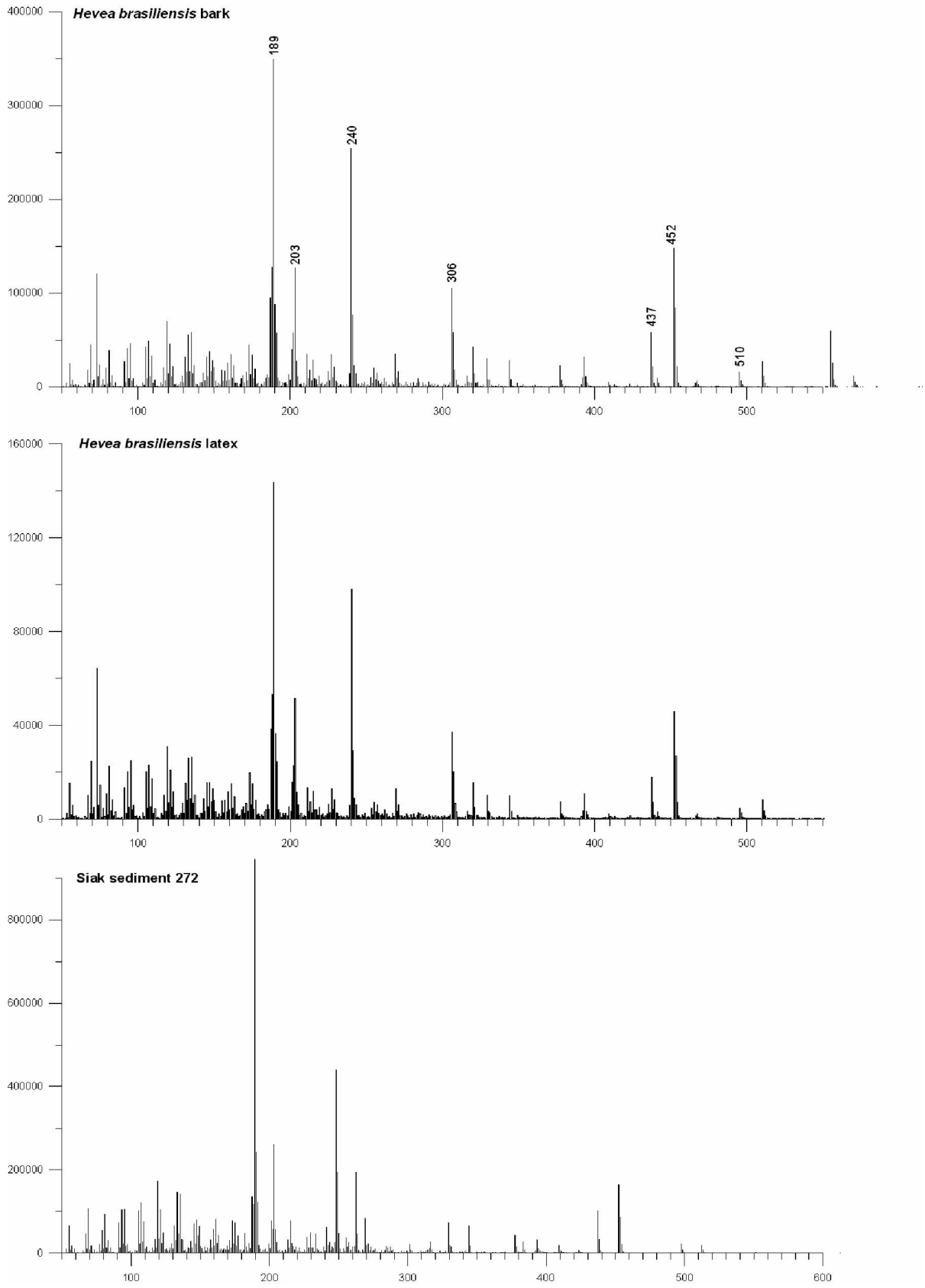

Figure 6: Mass fragmentograms of the unknown triterpenoid alcohol in *Hevea brasiliensis* bark and leaf and the reduced compound in Siak river sediment.

Thus, in the direct vicinity of the latex processing plant discharge point the river sediment receives an extremely high organic carbon load. This input is not detectable some 7 km downstream at station 274 suggesting either rapid dilution of the particle load or rapid sedimentation. The second explanation is supported by the observation that after extraction of sediment sample 272 the extract became a solid, rubber-like mass during solvent evaporation. This indicates a massive input of relatively heavy latex particles.

Bark and leaf material from *Hevea brasiliensis* showed a characteristic composition of steroid alcohols and terpenoid alcohols (Figure 5). Most of these compounds were also found in the sediments analysed. As they are, however, also present in a number of other plants of the Siak vegetation (Wöstmann and Liebezeit, unpubl. results), they cannot be used to unambiguously identify inputs from latex processing to natural aquatic systems. In addition, a yet uncharacterised triterpenoid alcohol (TTA; TMS derivative) with m/z 510 is present in the *H. brasiliensis* bark and latex extracts. Reference data for this compound could not be found. Mass spectral data (Figure 6) indicate the A and B rings to bear a hydroxy group in position 3 and two methyl groups in position 4. This suggests a possible relationship to lanosterol, euphol or euphorbol isolated earlier from *H. brasiliensis* (Nishimura et al., 1977).

Particulate matter sampled directly at the discharge point showed a strong enrichment of this TTA compound with a comparable relative composition as in the plant material. In sediment samples taken further downstream the compound with m/z 510 was missing while a second TTA with m/z 512 and a similar fragmentation pattern (Figure 6) increased suggesting reduction of one double bond. Therefore this compound can be used as tracer for the input of untreated wastewater discharge of latex processing industries at the Siak river banks. The m/z 512 compound could be detected to station 276, i.e. about 25 km downstream from the discharge point.

Conclusions

Discharge from raw latex processing is detectable both in the direct vicinity of the wastewater inlet, in the sediment as well as in the water column, and in surface sediments up to 25 km downstream of the discharge point. Particularly the extremely high organic carbon content in the near vicinity of the discharge point indicates a similarly high oxygen demand of the process water entering the Siak river.

Given the fact that input of untreated sewage already burdens the oxygen budget of the Siak river at Pekanbaru and downstream any additional inputs will aggravate this situation. In addition, the high allergenic potential of the discharged wastewater has also to be taken into account. Although there are at present no data on any allergic reactions of the river population an assessment of this exposition appears to be urgently needed.

There are suggestions in the literature to overcome this problem, e.g. Kantachote et al. (2005) suggest treatment of latex drying wastewater with anoxygenic phototrophic bacteria while Vijayaraghavan et al. (2008) tested electrolytic production of hydrochlorous acid as oxidation agent.

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