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Dissolved Inorganic Nitrogen and Phosphate in the Human Affected Blackwater River Siak, Central Sumatra, Indonesia

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Abstract: Increases in domestic, industrial and agricultural effluents have nearly doubled global riverine N and P fluxes into the coastal ocean during the last few decades. Indonesian rivers were modelled to be one global "hot spot" with respect to N and P yields (kg km^{-2} yr^{-1}) as a consequence of large-scale deforestation, intensive agriculture, urbanization and wastewater disposal. The objectives of this field study were (i) to identify sources of dissolved nutrients and (ii) to investigate the impact of anthropogenic activities on nutrient levels in the peat-draining blackwater river Siak. During seven expeditions between 2004 and 2009 dissolved inorganic nutrients (NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}), chlorophyll-a (chl a), particulate and dissolved organic matter (POM, DOM) and stable carbon isotopes ($\delta^{13}C_{org}$) of POM were determined along the river continuum as well as in urban sewage channels. The results showed that the Siak is a classical blackwater river characterized by high levels of dissolved organic matter (DOM) and low nutrient concentrations. Nevertheless, compared to other tropical blackwater rivers, nutrient concentrations are enriched indicating that the Siak is eutrophied. Decomposition of DOM leached from the surrounding peat soils is one factor controlling the DIN and the PO_4^{3-} concentration in the Siak. Wastewater discharges increased especially the PO_4^{3-} concentrations, which exceed the background concentration locally by a factor >4. The washout of N-fertilizers from palm oil estates seems to be a main factor influencing the DIN concentration and could even double the riverine DIN concentration as seen in March, 2004.

Key words: Blackwater river, peat, dissolved inorganic nutrients, wastewater, fertilizer.

Introduction

Population growth increases the pressure on terrestrial and aquatic ecosystems (Smith et al., 1999) and enforces an ever growing food production for which the use of fertilizers is mandatory. As a consequence cycling of nutrients such as nitrogen (N) and phosphorus (P), which control the productivity of many ecosystems worldwide, has strongly been altered (Gruber and Galloway, 2008).

Significant fractions of the anthropogenic mobilized nutrients were leached through soils or eroded from the landscape, thus increasing the fluxes of growth-limiting nutrients from land to surface waters, rivers and finally the coastal ocean (Smith, 2003). In addition to agricultural nutrient inputs, the disposal of domestic and industrial wastewaters contributes significantly to the riverine nutrient load that has increased by a factor of 1.5 to 2 over the last decades (Meybeck and Ragu, 1995; Rabouille et al., 2001).

Indonesian rivers, which play an important role in the water cycle contributing ~11% to the global freshwater discharge (38,540 km^3 yr^{-1}) into the coastal ocean, seem to follow this global trend as indicated by model studies identifying Indonesia as one global "hot spot" with respect to N and P yields (kg km^{-2}

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yr^{-1}) (Seitzinger et al., 2005; Syvitski et al., 2005). Morphological conditions (high relief) and high runoff in combination with a high anthropogenic impact (large scale deforestation, intensive agriculture, urbanization, wastewater disposal) strongly affect nutrient cycling in Indonesian rivers (Seitzinger et al., 2005; Suwarno et al., 2013). Although eutrophication has been reported in Indonesian rivers (Astirin et al., 2002; Jennerjahn et al., 2004), there are only few studies investigating dissolved inorganic nutrients in Indonesian blackwater rivers (Alkhatib et al., 2007; Rixen et al., 2010).

Considering the fact that ~10% of the Indonesian landmass is covered by peatlands, peat draining blackwater rivers contribute significantly to the overall Indonesian river discharge. In order to investigate the impact of human activities on the biogeochemistry of tropical blackwater rivers, seven expeditions to the Siak in Central Sumatra were conducted between 2004 and 2009. The major objectives of this study were to (i) identify sources of dissolved inorganic nutrients (DIN and PO_4^{3-}) and to (ii) investigate the impact of anthropogenic activities on riverine nutrient levels in tropical blackwater rivers.

Study Area

The Siak is located in the province of Riau. With a catchment size of ~10,500 km², a total length of 370 km and a mean annual freshwater discharge of 498 $m^3\ s^{-1}$, the Siak is one of the main rivers draining Central Sumatra (Baum et al., 2007; Rixen et al., 2008). The climate is dominated by the meridional migration of the Intertropical Convergence Zone (ITCZ). Seasonal variations are weakly pronounced with a dry season between May and September and elevated precipitation rates between October and April (Rixen et al., 2010). On inter-annual time scales precipitation rates are influenced by the climate anomaly El Nino Southern Oscillation (ENSO) (Ropelewski and Halpert, 1987).

The Siak originates from the confluence of the headstreams S. Tapung Kanan and S. Tapung Kiri (km ~155), and passes through the adjacent lowlands with the cities of Pekanbaru (km ~180), Perawang (km ~220) and Siaksriindrapura (km ~285) before discharging into the Strait of Malacca (km ~370) (Figure 1). The S. Tapung Kanan as well as the main tributary Mandau originate in peat swamps covering vast areas of the river

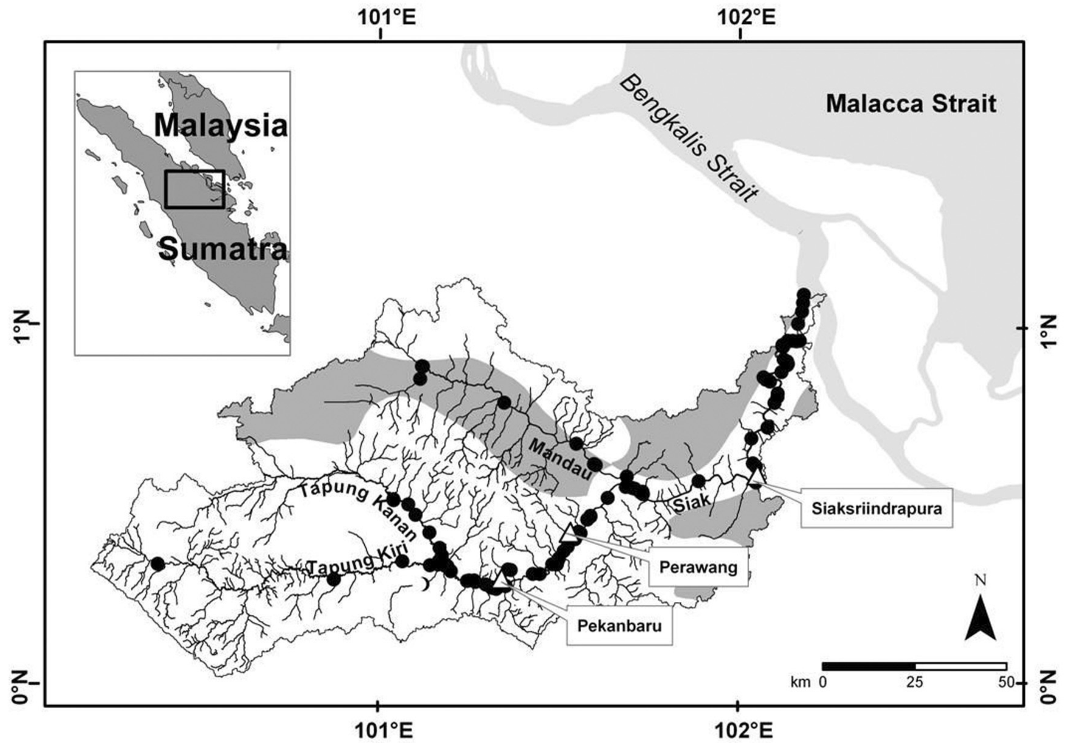

Figure 1: The Siak with its headstreams S. Tapung Kanan and S. Tapung Kiri and its major tributary Mandau. The river catchment is marked by the black line. The main cities along the Siak are indicated by triangles. Peat soils (obtained from FAO/UNESCO, 2003) are coloured dark grey. Sampling stations of the seven expeditions between March 2004 and October 2009 are presented by the black circles.

catchment (Baum et al., 2007; Figure 1). Since the last decades these peatlands have been heavily affected by drainage, deforestation and conversion into oil palm and rubber estates (Hooijer et al., 2006; Laumonier, 1997). Peat soil leaching was identified to mainly control the riverine DOC concentrations, which are with a mean value of ~1940 µmol L^{-1} (348-4167 µmol L^{-1}) among the highest reported worldwide (Baum et al., 2007; Hope et al., 1994; Ludwig et al., 1996; Rixen et al., 2008; Spencer et al., 2007). In turn, decomposition of dissolved organic matter and the resulting oxygen consumption were considered to be the main factors influencing oxygen concentrations along the Siak (Rixen et al., 2008).

Since the last decades, the population within the Siak catchment has increased dramatically, particularly in the cities like the province capital Pekanbaru (672,000 inhabitants in 2006). According to local authorities, a further population increase up to 1.3 million inhabitants is estimated for Pekanbaru for the year 2031. In addition to increasing population densities, an expansion of oil, paper and rubber processing industries, which are mainly located between the cities Perawang and Siaksriindrapura (Figure 1), has been noticed during the last years.

Methods

Sampling

The Siak was sampled for water and suspended matter in March and September 2004, August 2005, March 2006, March and November 2008 and October 2009. Water samples were taken with a Niskin bottle at a sampling depth of ~1 m in the middle of the river. The river estuary, except March 2004, was sampled along the salinity gradient during increasing and high tide. Plant samples were collected mainly within the riverine vegetation and in the floodplain.

Dissolved Inorganic Nutrients

Water samples for the determination of dissolved inorganic nutrients (NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-}) were filtered through single-use syringe filters (0.45 µm), fixed with $HgCl_2$ and stored cool until analysis. Dissolved inorganic nutrients were analyzed spectrophotometrically as a coloured complex using a continuous flow autoanalyzer (Skalar-SAN-plus). The absorption of the colour-complexes was measured at different wavelengths (NO_3^-, NO_2^-, = 540 nm; NH_4^+ = 630, PO_4^{3-}= 820 nm). The absorptions were corrected for the absorptions of the pure samples at the indicated wavelengths. Detailed descriptions of the methods can be found in Grasshoff et al. (1999).

Particulate Organic Carbon (POC) and Nitrogen (PON)

In order to determine POC and PON concentrations river water was filtered through pre-combusted glass-fibre filters directly after sampling and dried. Filters were acidified with 1 N HCl to remove inorganic carbon and dried at 40 °C. Filters were oxidized at 1100 °C in a Carlo Erba NA 2100 elemental analyzer. Evolving CO_2 and N_2 were quantified by a thermal conductivity detector.

Chlorophyll-*a*

Samples for the determination of chlorophyll-*a* were taken below the water surface and filtered through Whatmann glass-fibre-filters (GF/F). The filters were suspended in 90% aqueous acetone. After immediately destroying the plankton cells on the filter surface using a Bandelin Sonoplus HD 2200 ultrasonic device, the samples were stored in the refrigerator for 12 hours to extract the chlorophyll. After clarifying in a centrifuge the samples were determined spectrophotometrically by measuring the absorbance of the extract at various wavelength (750, 665, 663, 645 and 630 nm, using 90% aqueous acetone as blank) in a "Libra S11" spectrophotometer. Detailed descriptions of the methods can be found in ESS (1991).

Stable Carbon Isotopes ($\delta^{13}C$)

Stable carbon isotopic compositions ($\delta^{13}C$) of filter and plant samples were analyzed with a Finnigan Delta Plus gas isotope ratio mass spectrometer following high temperature combustion in a Flash 1112 EA elemental analyzer. Carbonate was removed prior to the combustion from the samples by adding 1 N HCl. The $\delta^{13}C$ values are reported in ‰ relative to PDB standard.

Box Diffusion Model

A box diffusion model was applied in order to assess the role of peat-soil leaching and DOM decomposition as source for DIN in the Siak (Equation 1). As described by Rixen et al. (2008) the water column of the river was divided into 50 cm thick layers (Δz).

$$\frac{\partial O_2}{\partial t} = \frac{\partial}{\partial z}\left(A_V \frac{\partial O_2}{\partial z}\right) + S_{\text{Oxygen}} + C_{\text{Oxygen}} \quad (1)$$

A_V is the diffusion coefficient for which a value of 370 $cm^2\ s^{-1}$ was selected. This implies a rapid mixing and results in a well-mixed water body as seen in the salinity and temperature profiles presented by Rixen et al. (2008). S_{Oxygen} is the oxygen source term in the surface layer derived from the oxygen flux through the air-water interface (F_{Oxygen}) by means of $S_{Oxygen} = F_{Oxygen}/\Delta z$. The F_{Oxygen} is

$$F_{Oxygen} = k \times \alpha\ (pO_{2\text{-Atmosphere}} - pO_{2\text{-River}}) \quad (2)$$

where α is the temperature and salinity-dependent solubility coefficient of oxygen (Benson and Krause Jr., 1984) and k is the piston velocity, which according to our previous model studies varied between 22.9 and 28.1 cm hr^{-1}.

Based on our previous DOC decomposition experiment exponential decreasing DOC concentration observed was described as follows (Rixen et al., 2008):

$$DOC(t) = (DOC_{t0} \times 0.27) \times \exp(-0.016 \times t) + (DOC_{t0} \times 0.73) \quad (3)$$

DOC(t) and DOC_{t0} were the DOC concentrations at a certain time (t) and at the beginning of the experiment (t0). The decay constant (λ) was –0.016 hr^{-1}. The first derivative of equation (3) describes the DOM decomposition rate ($DOM_{decomposition}$), which was converted into oxygen consumption (C_{oxygen}) by multiplying it by 0.8:

$$C_{Oxygen} = 0.8 \times \frac{\partial DOC(t)}{\partial t}$$

The factor 0.8 indicates that only 0.8 mol of dissolved oxygen is used to oxidize 1 mol of DOM (DOM + 0.8 $O_2 \geq CO_2$) because oxygen organically bound within the dissolved organic matter could also be used to oxidize DOC in addition to oxygen dissolved in the river water (Rixen et al., 2008 and references therein). Since peat-samples collected within the Siak catchment reveal a mean molar C/N ratio of 48.7 we assumed here that the decomposition of one mol DOC is associated with the release of 1/48.7 mol DIN. For the release of P an N/P ratio of 16 (Redfield et al., 1963) was assumed. During the model runs the DOC_{t0} as given by the red line in Figure 2a were given in order to calculate the DOC decomposition. DOC losses were assumed to be balanced by DOC inputs from soils. Oxygen, DIN and PO_4^{3-} concentrations (see red lines Figure 2b, c, and Figure 3) were calculated and compared to measured data.

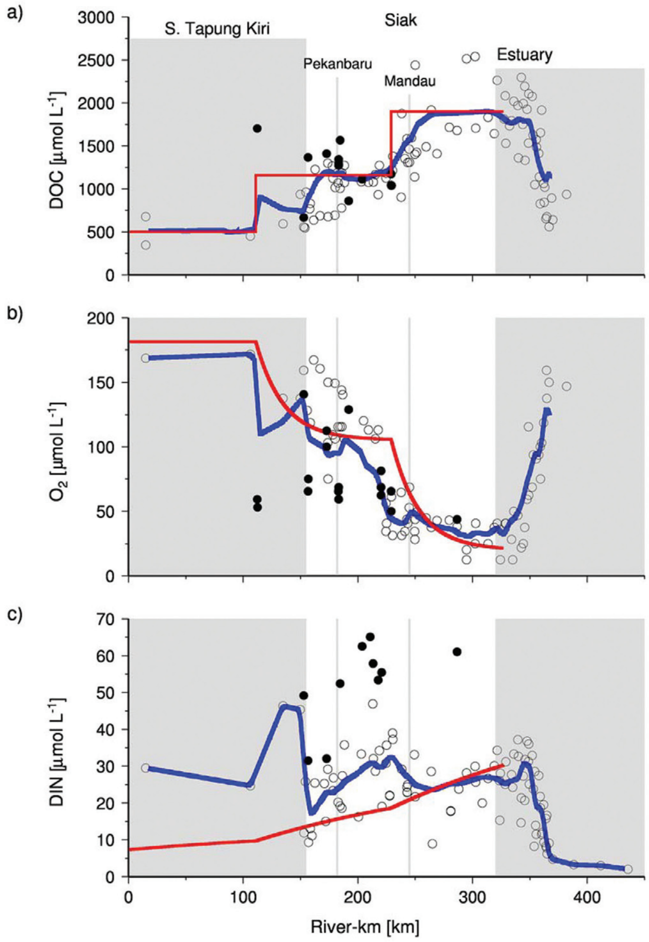

Figure 2: DOC (a), oxygen (b), and DIN (c) concentrations measured at a water-depth of 1 m versus river-km (circles). Black circles indicate data measured during the expedition in March 2004. The blue lines show the DOC, oxygen and DIN concentrations averaged for all expeditions. The red line in figure (a) indicates the DOC concentrations used to run the model. The red lines in figures (b) and (c) indicate the resulting oxygen and DIN concentrations.

Results and Discussion

Dissolved Inorganic Nitrogen (DIN)

In the Siak river system, DIN concentrations ranged between 2 and 54 µmol L^{-1} during all expeditions except in March 2004, where they reached values up to 65 µmol L^{-1} (Table 1; Figure 4a). Ignoring this exceptional period in 2004, which will be discussed later, the mean DIN concentration in the Siak mainstream falls with ~25 µmol L^{-1} below the mean DIN concentration (49.6 µmol L^{-1}) measured in other tropical non-blackwater rivers (Figure 5). The Siak is a classical blackwater river owing its dark water colour to high concentrations of

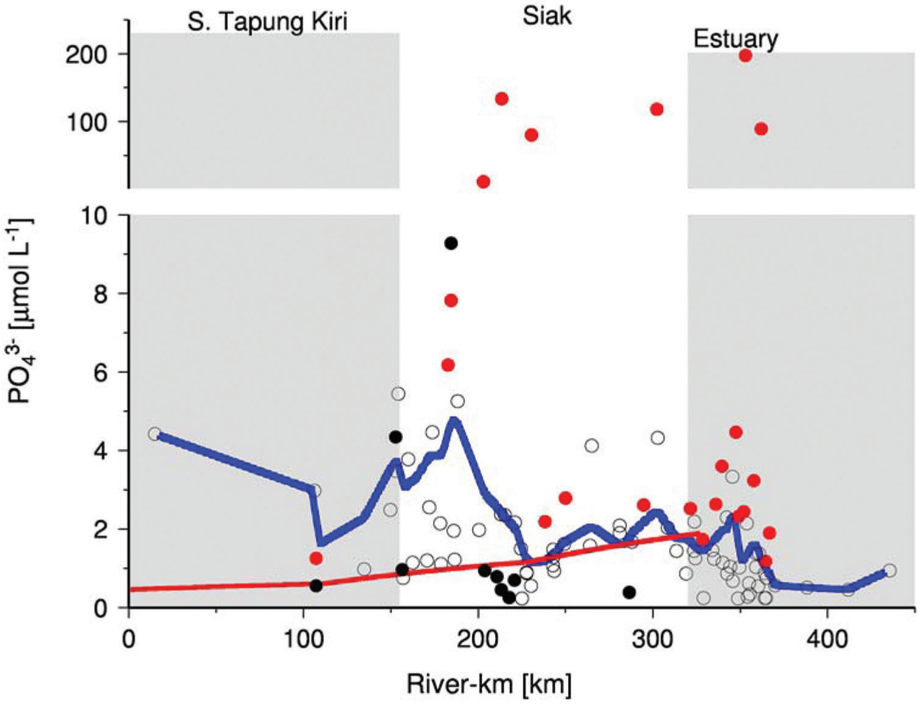

Figure 3: Phosphate (PO_4^{3-}) measured at a water-depth of 1 m versus river km (circles). Black and red circles indicate data measured during the expedition in March 2004 and September 2004. The blue line shows the PO_4^{3-} concentrations averaged for all expeditions except the one in September 2004. The DOC concentrations used to run the model are given in Figure 2 and the red line indicates the calculated PO_4^{3-} concentrations.

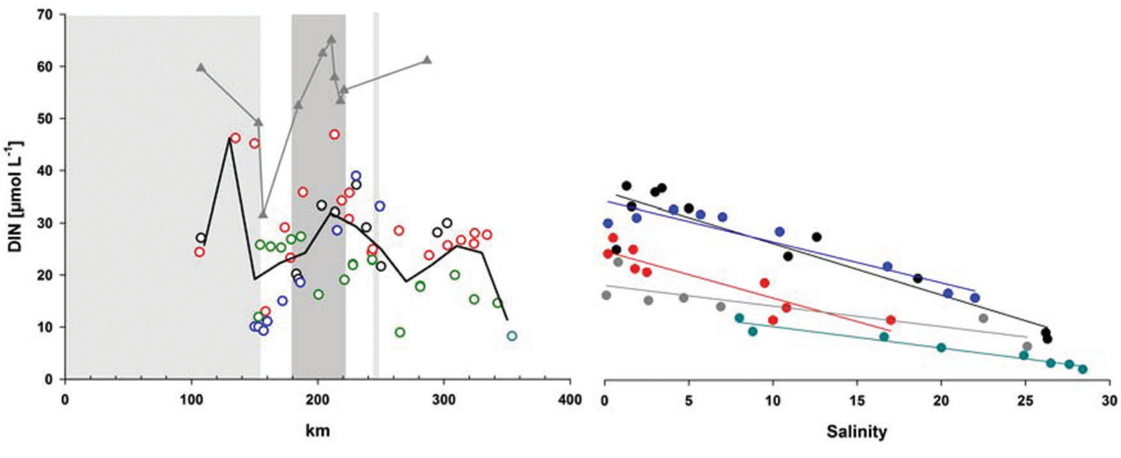

Figure 4: (a) DIN concentrations along the S. Tapung Kiri (km 0-155, coloured in light grey) and Siak without estuary (km 155-345) in March 2004 (grey triangles), September 2004 (black circles), August 2005 (red circles), March 2006 (blue circles), November 2008 (green circles) and October 2009 (cyan circle). The black line presents the mean DIN concentrations of the samplings in September 2004, August 2005 and March 2006, November 2008 and October 2009 averaged every 20 km along the S. Tapung Kiri and Siak. The industrial area between Pekanbaru and Perawang (river km 180-220) is coloured dark grey. The Mandau discharge (river km 245) is marked by the light grey line. b) Salinity versus DIN concentrations of water samples taken in the Siak estuary in September 2004 (black dots), August 2005 (red dots), March 2006 (blue dots), March 2008 (grey dots) and October 2009 (cyan dots).

Table 1: Minimum, maximum and mean dissolved inorganic nitrogen (DIN) and phosphate (PO_4^{3-}) concentrations measured in the headstreams Sungai Tapung Kanan and Sungai Tapung Kiri, the Siak mainstream and the tributary Mandau

		DIN			*PO_4^{3-}*		
		min	*max*	*mean*	*min*	*max*	*mean*
March 2004	Kiri	49.1	59.7	54.4	0.6	4.3	2.4
	Siak	31.5	65.1	54.9	1.2	197.4	32.3
	Kanan	25.2	40.2	32.7	1.0	5.2	3.1
	Mandau	5.8	8.1	6.9	0.6	0.9	0.7
September 2004	Kiri	-	-	27.2*	-	-	1.3*
	Siak	7.9	37.2	27.4	1.2	197.4	32.3
	Kanan	-	-	62.8*	-	-	2.1*
	Mandau	15.5	28.1	21.8	2.2	15.4	8.8
August 2005	Kiri	24.4	46.2	33	0.9	4.4	2.7
	Siak	11.5	46.9	25.4	<0.01	5.3	1.7
	Kanan	24.9	53.9	36.9	1.1	3.7	2.8
	Mandau	5.9	11.5	8.9	1.5	13.9	4.8
March 2006	Kiri	10.0	10.1	10.1	0.7	3.5	2.1
	Siak	9.3	38.9	25.4	0.2	3.8	1.2
	Kanan	10.6	13.7	12.2	15.8	17.7	16.7
	Mandau	-	-	-	-	-	-
March 2008	Kiri	-	-	-	-	-	-
	Siak	6.5	22.7	14.6	<0.01	0.9	0.4
	Kanan	-	-	-	-	-	-
	Mandau	-	-	-	-	-	-
November 2008	Kiri	-	-	-	-	-	-
	Siak	8.9	27.4	20.1	0.9	5.4	2.0
	Kanan	-	-	-	-	-	-
	Mandau	-	-	19.2*	-	-	1.9*
October 2009	Kiri	-	-	-	-	-	-
	Siak	2.1	11.9	6.4	0.5	2.2	0.9
	Kanan	-	-	-	-	-	-
	Mandau	-	-	-	-	-	-

*Only one station sampled.

DOM leached from the surrounding peat soils (Baum et al., 2007). Tropical blackwater rivers are known to be nutrient-poor revealing average DIN concentrations <10 µmol L^{-1} (Figure 5). The Dumai, a relatively short peat-draining river located a few hundred km north of the Siak, even shows DIN concentrations of ~1 µmol L^{-1} (Alkhatib et al., 2007). Compared to these blackwater rivers, the Siak is nutrient-enriched (Figure 5).

Spatial Distribution of DIN along the River

Spatial distribution of DIN along the river was similar during all expeditions with enhanced concentrations in the lower reaches of the S. Tapung Kiri (river km 0 to 155) and the densely populated zone between Pekanbaru and Perawang (river km 180 to 220, Figures 2 and 4). Lower DIN concentrations were measured at the confluence of the headstreams S. Tapung Kiri and S. Tapung Kanan (river km 155), after the Mandau junction (river km 245) and in the Siak estuary (river km 345). As indicated by the linear relation between salinity and DIN (Figure 4b), mixing of nutrient-poor ocean water with river water seems to decrease the DIN concentrations in the Siak estuary in a conservative way. Decreasing DIN concentrations after the Mandau/Siak junction can be explained by dilution of the Siak with Mandau water showing a mean DIN concentration of 12.6 µmol L^{-1} (Table 1). The S. Tapung Kiri and S. Tapung Kanan revealed mean DIN concentrations up to 63 µmol L^{-1} (Table 1), which indicates that mixing of the two water masses cannot explain the observed decrease in DIN at the S. Tapung Kiri and S. Tapung Kanan junction in March 2004 and August 2005 (Figure 4). Water hyacinths (*Eichhornia crassipes*) which are known for their high nutrient uptake (Reddy

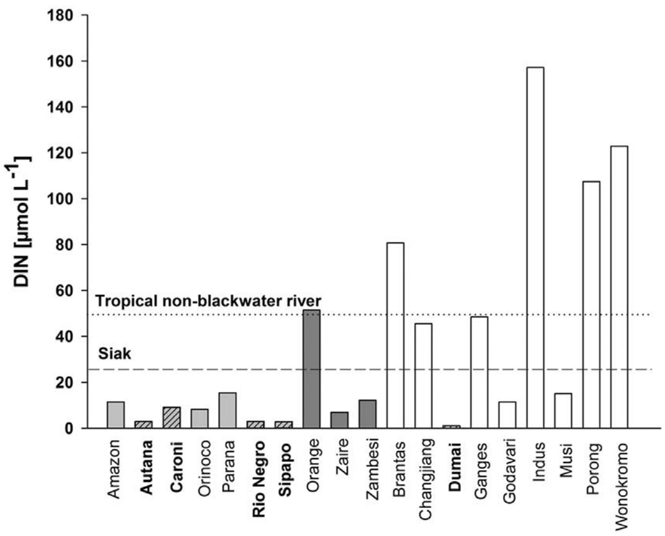

Figure 5: Mean DIN concentrations of the Siak (dashed line) compared to other tropical rivers in South America (grey bars), Africa (dark grey bars) and Asia (white bars). DIN concentrations comprise NO_3^- and NH_4^+ concentrations (Alkhatib et al., 2007; Castillo et al., 2004; Jennerjahn et al., 2004; Lewis Jr. et al., 1999; Lewis Jr. and Weibezahn, 1981; Meybeck and Ragu, 1995; Sarkar et al., 2007). Blackwater rivers are presented by the striped bars. Mean DIN concentration of the tropical non-blackwater rivers is presented by the dotted line.

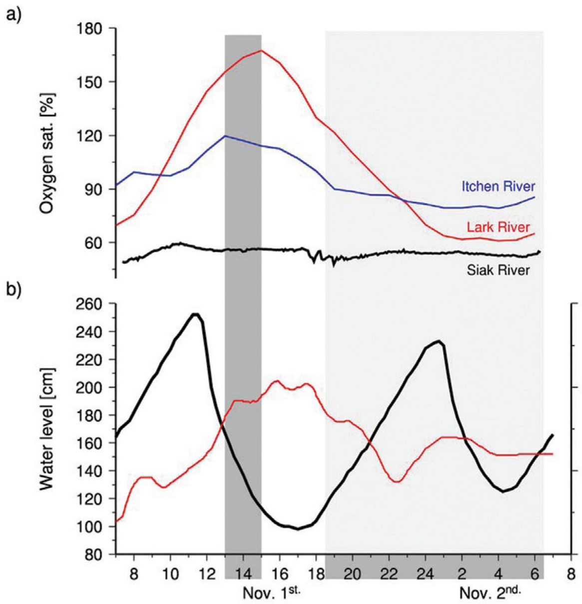

Figure 6: (a) Oxygen saturation measured in the Siak at Pekanbaru (black line) versus time. For comparison the mean diurnal variations of oxygen measured in the small temperate non-blackwater rivers Itchen and Lark in 1927 are given. The Lark river was polluted and Itchen river was considered unpolluted (Butcher et al., 1927). (b) The water level and the water temperature measured as well as the oxygen concentration at Pekanbaru on November 1st and 2nd, 2008. The light grey bar shows the night-time and the dark grey bar the early afternoon when photosynthesis reached its maximum in the Lark and Itchen rivers.

and D'Angelo, 1990) occurred at this site and thus could have been responsible for the observed low DIN concentrations.

Sources of DIN

In well-drained peat soils small quantities of nitrate are present, which are formed by the oxidation of organic matter (Andriesse, 1988). In order to assess the impact of the DOM decomposition on the concentration of nitrate in the Siak we used a box-diffusion model which was developed by Rixen et al. (2008; 2010) to study the oxygen dynamic in the Siak. The previous results show in line with measured data that the decomposition of DOM leached from the peat soils is the main factor controlling the concentration of dissolved oxygen in the Siak. Photosynthesis appeared to be an insignificant oxygen source due to the lack of light caused by the dark brown water-colour reducing the light penetration to water-depth <20 cm (Siegel et al., 2009). Accordingly the oxygen concentrations reveal contrary to non-blackwater rivers no diurnal variations (Figure 6). These results are supported by measurements made in March 2008 showing chl-*a* concentrations which fall with mean values of 0.28 µg L^{-1} (0-0.64 µg L^{-1}) much below values measured in Indonesian non-blackwater environments (0.2-22.2 µg L^{-1}) (Damar, 2012; Schröder et al., 2004).

Furthermore, C/N (mean 16.4) and stable carbon isotope ratios ($\delta^{13}C$; -28.8‰) of the POM (Table 2) exceed those determined in riverine algae (6-7) (Hedges et al., 1997; Meybeck, 1982); –30 to –40‰ (Hamilton and Lewis Jr., 1992; Middleburg and Herman, 2007). This strongly indicates that aquatic plankton hardly contributes to the POC. POC, which is with a mean concentration of 243 µmol L^{-1} in general by factor 5 to 10 lower than DOC (Table 2, Figures 2a and 7), seems to be rather derived from peat and plant material showing C/N and stable carbon isotope ratios ranging between 26.1 and 75.2 (mean 48.7) and –29.3‰ to –30.6‰ (–29.8‰) and 15.7 to 103.2 (mean 35.9) and –26.9‰ to –33.2‰ (mean –29.3‰), respectively (Table 2). Accordingly, POC concentrations are enhanced at river km ~345 where a small peat-draining channel discharges into the Siak. This channel is known for high current velocities and

Table 2: Minimum, maximum and mean values of chlorophyll-*a* (chl-*a*), particulate organic carbon (POC), C/N and δ^{13}C of particulate organic matter (POM), peat and plant samples

		min	*max*	*mean*
Chl-*a*	µg L^{-1}	0	0.64	0.28
POC	µmol L^{-1}	39.1	1461.6	242.9
C/N POM		9.4	25.1	16.6
δ^{13}C POM	‰	–29.4	–27.9	–28.8
C/N peat		26.1	75.2	48.7
δ^{13}C peat	‰	–30.6	–29.3	–29.8
C/N plants		15.7	103.2	35.9
δ^{13}C plants	‰	–33.2	–26.9	–29.3

enhanced erosion along the channel banks (Figure 7). However, since the low concentrations of chl-*a* and POC as well as the absence of diurnal variations of oxygen suggest that photosynthesis of freshwater plankton is quantitatively of minor importance, it was ignored as DIN sink in the model. Consequently the DIN released during the decomposition of DOM accumulates in the river water on its way from the origin towards the estuary of the Siak (Figure 2c). Between river km 0 and 150 the discrepancy between the modelled and measured DIN concentrations could be caused by leaching from non-peat soils and/or washout from DIN from palm oil estates, both dominating this part of the catchment. From river km 160 to 340 increasing DOC concentrations show that peat soil leaching is becoming more important. Between river km 260 and 340 calculated DIN concentrations agree quite well with values measured in the river while from km 160 to 260, which is the most industrialized and urbanized region along the Siak, the measured values exceed the modelled ones. This might imply an anthropogenic perturbation of the nutrient cycle within this part of the river.

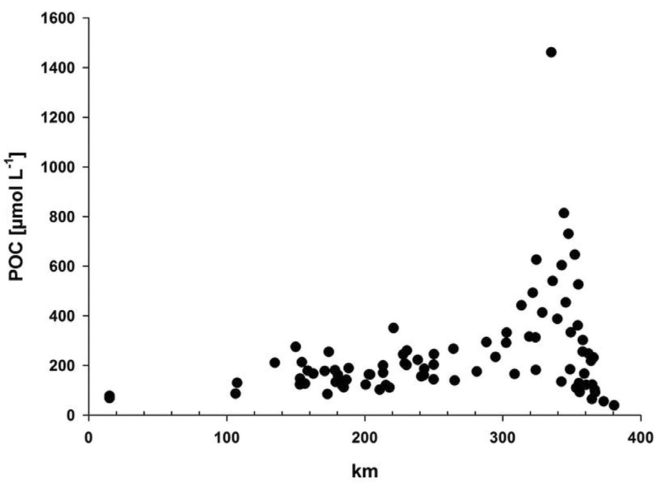

Figure 7: Particulate organic carbon (POC) concentrations of the seven sampling expeditions versus river km.

Wastewater Influence: In the study area sewage purification hardly exists so that domestic wastewaters are discharged untreated via wastewater channels into the Siak. During the expeditions in March and September 2004, seven wastewater channels draining Pekanbaru were sampled and analyzed for DIN showing extremely high concentrations ranging between 565 and 1877 µmol L^{-1} (mean = 1170 µmol L^{-1}) in March 2004 and 374 to 921 µmol L^{-1} (mean = 548 µmol L^{-1}) in September 2004, respectively (Table 3A). Considering a population of Pekanbaru of 671,777 and a water consumption per capita of 95 L d^{-1} as stated by local authorities for the year 2006, the amount of wastewater accounts for 6.4×10^7 L d^{-1} (740.7 L s^{-1}, Table 3B). Multiplied with mean DIN concentrations of 1170 and 548 µmol L^{-1} suggests mean wastewater DIN inputs of 0.87 and 0.40 mol N s^{-1} in March and September 2004, respectively (Table 3B).

In order to estimate the contribution of domestic wastewater to the DIN load of the Siak in the area of Pekanbaru, the riverine nutrient load before the city of Pekanbaru was calculated. Therefore, the tidal unaffected freshwater discharge (268.3 m^3 s^{-1}) measured approximately 20 km before Pekanbaru (Baum et al., 2007) was multiplied by the mean DIN concentration (19.2 µmol L^{-1}) measured during all expeditions at a sampling station located between the confluence of the two headstreams and the municipal area of Pekanbaru. The resulting riverine DIN load of 5.14 mol s^{-1} and the wastewater DIN inputs of 0.87 and 0.40 mol N s^{-1} imply that wastewater effluents could increase the riverine DIN concentration by up to 3.24 µmol L^{-1} in the area of Pekanbaru. The modelled DIN concentration accounts for 16.7 µmol L^{-1} suggesting that domestic wastewater discharges could increase the DIN concentration by ~20%, which is still insufficient to explain the deviation between the calculated and measured DIN concentrations of ~13 µmol L^{-1} (Figure 2c). Along the Siak petroleum, natural gas, rubber, palm oil and fibre plantations are located. Studies investigating the exposure and treatment of industrial sewage (Agamuthu, 1999; Korhonen et al., 2004) indicate that wastewaters from rubber and paper processing industries are heavily enriched in nitrogen components. Thus it could be assumed that industrial wastewater discharges contribute

Table 3: (A) DIN and PO_4^{3-} concentrations and loads of wastewater channels draining the city of Pekanbaru in March and September 2004 and (B) DIN and PO_4^{3-} loads of the Siak upstream Pekanbaru

A	*DIN (µmol L⁻¹)*	*PO_4^{3-} (µmol L⁻¹)*
Wastewater channels Pekanbaru March 2004		
Il. Karag	1377	106.2
S. Sail Cont.	772.6	63.7
S. Sail	633.9	58.4
Il. Riau	1481.8	86.8
Il. Riau 2	1482.6	77.7
S. Hitam	564.4	51.6
Il. Juanda	1877.1	99.9
Average	1169.9	77.8
Wastewater channels Pekanbaru September 2004		
Riau	373.5	192.1
Karag	722.4	179.4
Juanda	920.5	170.5
Average	548.0	185.8
B		
Capita Pekanbaru		671,777
Water consumption per capita	($L\ d^{-1}$)	95
Wastewater discharge	($L\ d^{-1}$)	6.4×10^7
Wastewater discharge	($L\ s^{-1}$)	740.7
DIN load wastewater March 2004	($mol\ s^{-1}$)	0.87
DIN load wastewater September 2004	($mol\ s^{-1}$)	0.40
PO_4^{3-} load wastewater March 2004	($mol\ s^{-1}$)	0.057
PO_4^{3-} load wastewater September 2004	($mol\ s^{-1}$)	0.137
River discharge Pekanbaru#	($m^3 s^{-1}$)	268.3
DIN concentration Siak upstream Pekanbaru	($\mu mol\ L^{-1}$)	19.2
PO_4^{3-} concentration Siak upstream Pekanbaru	($\mu mol\ L^{-1}$)	2.1
Riverine DIN load	($mol\ s^{-1}$)	5.14
Riverine PO_4^{3-} load	($mol\ s^{-1}$)	0.56

Tidal unaffected discharge measured ~20 km upstream Pekanbaru (Baum et al., 2007).

to the enhanced nutrient levels in the Siak between Pekanbaru and Perawang.

Fertilizer Influence: In March 2004, DIN concentrations in the Siak mainstream are with an average concentration of 55 $\mu mol\ L^{-1}$ more than twice as high as the mean DIN concentration calculated for the expeditions between September 2004 and October 2009 (25 $\mu mol\ L^{-1}$) (Figure 4a, Table 1). As already mentioned the Siak catchment is heavily affected by the industrial plantation of oil palm. In the Riau province, oil palm plantations cover an area of 16,000 km^2 (~19.97% of the Riau province, Table 4), and even exceed the catchment area of the Siak (~10,500 km^2). In general, each palm tree receives 2.5 kg N-fertilizers per year, which is ~5 times higher than N-fertilization at other oil palm estates in Indonesia and elsewhere (FAO, 1977; FAO, 2005; Omoti et al., 1983; Schroth et al., 2000). This intensive N fertilization is required to meet the nitrogen demand of oil palms growing on the nutrient-poor peat soils. To avoid the washing out of fertilizer March/April (end of the rainy season) is the point of time when oil palm plantations usually get fertilized (plant manager, pers. comm.). Considering a mean oil palm density of 0.028 oil palms m^{-2} (280/ha, Table 4), the N fertilization accounts for 5 mol N $m^2\ yr^{-1}$ (0.028 oil palms $m^{-2} \times 2.5$ kg N oil $palm^{-1}\ year^{-1}$ / 0.014 kg mol^{-1}) in the Riau Province. However, assuming that similar to the entire Riau Province ~20% of the Siak catchment (2112.4 km^2) is covered by oil palm plantations, 10.562 $\times 10^9$ mol N would be added to the Siak catchment. Assuming a river-length of 370 km, a mean depth of 8 m, a mean width of 220 m (Rixen et al., 2008) and a mean DIN concentration of ~25 $\mu mol\ L^{-1}$, implies that

Table 4: Estimate on the amount of N-fertilizer used in the Riau province and calculation of riverine DIN-load

		Data source	
Area Riau province	(km^2)	80,701	
Area oil palm plantations Riau province	(km^2)	16,114	BPS, 2009
Area oil palm plantations Riau province	(%)	19.97	
Palm trees per plantation	(plants m^{-2})	0.028	Plant manager, pers comm.
N fertilizer per plant	(kg yr^{-1})	2.5	Plant manager, pers comm.
Fertilized N in Riau province	(mol m^{-2} yr^{-1})	5	
River length Siak	(km)	370	Baum et al., 2007
Mean river depth Siak	(m)	8	Rixen et al., 2008
Mean river width Siak	(m)	220	Rixen et al., 2008
Water mass Siak (length × width × depth)	(L)	6.5×10^{11}	
Mean DIN concentration Siak	(µmol L^{-1})	25	This study
DIN load Siak	(mol)	1.63×10^{7}	

the Siak holds on average 1.63×10^7 mol N (Table 4). Accordingly, we suggest that the washout of <1% of the total annual application rate of N fertilizer in the Siak catchment could significantly influence the riverine DIN concentration, particularly when fertilization coincides with the rainy season as observed in March 2004.

Dissolved Inorganic Phosphate (PO_4^{3-})

Most of the samples taken along the S. Tapung Kiri and Siak show PO_4^{3-} concentrations <5 µmol L^{-1} (Figure 3). In September 2004, PO_4^{3-} concentrations of up to 197 µmol L^{-1} were observed at single stations along the Siak (Table 1, Figure 3). Neglecting these peaks, which will be discussed later, PO_4^{3-} concentrations follow a trend similar to that of DIN, including the decrease in the estuary due to mixing with ocean water (Figures 3 and 4). Similar to the trend seen in the DIN concentrations, also the measured PO_4^{3-} concentrations exceed the model predictions within the industrialized and urbanized region between river km 140 and 220. In order to quantify the possible contribution of domestic wastewater discharges to this deviation, PO_4^{3-} concentrations were also measured in the wastewater channels draining the city of Pekanbaru. Mean PO_4^{3-} concentrations of 77.8 µmol L^{-1} in March and 185.8 µmol L^{-1} in September multiplied by the amount of wastewater (740.7 L s^{-1}, Tables 3A and B) result in PO_4^{3-} discharges of 0.057 and 0.137 mol s^{-1}, which contribute 10.2 and 24.5%, respectively, to the PO_4^{3-} load (0.56 mol s^{-1}) of the Siak upstream Pekanbaru. Thus, wastewater discharges could increase the PO_4^{3-} concentrations in the area around Pekanbaru up to ~5.5 µmol L^{-1} which would be sufficient to explain the difference between the modelled and the measured PO_4^{3-} concentrations representing a PO_4^{3-} increase of ~470%. Domestic wastewater discharges are an important PO_4^{3-} source in the Siak, which implies that the PO_4^{3-} concentrations up to 197 µmol L^{-1} could have been measured in wastewater plumes entering the Siak during the expedition in September 2004.

As discussed in preceding sub-heading, washout of N-fertilizers is likely to cause a doubling of riverine DIN concentrations in March 2004. Interannual variations in riverine PO_4^{3-} concentrations, however, could not be observed although every oil palm gets fertilized with 2.25 kg P-fertilizer every year (plant manager, pers. comm.). One possible explanation could be the high P adsorption capacity of oxisols (Lawrence and Schlesinger, 2001) which are dominant in the tropics and cover, in addition to peat, huge areas in the Siak catchment. In contrast to N, P gets adsorbed rapidly on minerals (mainly iron (Fe) and aluminum (Al)) and is thus rather immobile in soils. The adsorbed P has furthermore the tendency to occlude in the interior of Al and Fe minerals as, therefore, P losses due to the washout of soils are quite small (Lawrence and Schlesinger, 2001 and references therein; Wild, 1950).

Summary

The results of this study show that the Siak is a classical blackwater river characterized by high DOC levels and low concentrations of POC, oxygen, DIN and PO_4^{3-}. However, compared to data available from other tropical blackwater rivers the Siak can be considered as nutrient-enriched. Nutrient concentrations are controlled by the decomposition of dissolved organic matter leached from the surrounding peat soils. Domestic wastewater discharges could increase PO_4^{3-} concentrations by more than 470% and DIN concentrations by 20%. The main anthropogenic factor controlling the DIN concentrations in the Siak is the washout of fertilizers from palm oil estates whereas adsorption of PO_4^{3-} in soils seems to prevent an associated PO_4^{3-} enrichment in the river.

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