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The application of sterol biomarkers to the study of the sources of particulate organic matter in the Solo River system and and Serayu River, Java, Indonesia

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Abstract. Sterols were analyzed in suspended particles collected in January 1991 in the Solo River system and in the Serayu River, Java, Indonesia. Free sterols were extracted from particles larger than 0.7 μm and analyzed, after derivatization into their trimethylsilyl esters, by GC and GC/MS. Concentrations of total sterols ranged from 438 to 7922 ng/l, or from 2.4 to 183.8 ng/mg of total suspended matter, which varied from 3.3 to 400 and 471 mg/l, respectively in the Serayu River and at the downstream station in the Solo River. POC concentrations also varied in a wide range, from 0.91 to 4.72 and 6.13% of TSM, respectively at the above stations, and were associated with sterol/POC values ranging from 0.15 to 1.75 μg/mg. Eleven structures of C_{27}, C_{28} and C_{29} stenols and associated stanols were identified. $28\Delta^{5,22}$ was only found at downstream stations in the Solo River and in the Serayu River. This unique distribution, different from that of other C_{27}, C_{28} and C_{29} sterols, suggests a predominantly autochthonous origin for these compounds associated with an increased planktonic biosynthesis near the estuary. Concentrations of $28\Delta^5$, $29\Delta^{5,22}$ and $29\Delta^5$ showed similar spatial distributions and increased downstream, reflecting the significant accumulation of organic matter originating from the vegetation of the various drainage basins.

Values of the autochthonous versus terrigenous sterol index, defined as $27\Delta^5/29\Delta^{5,22}$ + $29\Delta^5$ were in the 1.4–1.9 range at upstream stations, whereas at downstream stations lower values were found, 0.4–0.6, which also corresponded to higher concentrations of TSM and lower POC values.

Insofar as the stanol/stenol values can be used to estimate the bacterial activity of oxic waters, simultaneous variations of C_{27} and C_{29} stenol/stanol pairs suggest rather different bacterial degradation capacities of autochthonous versus allochthonous organic matter. The wide differencies between the values of the stenol/stanol pairs observed in one of the main tributaries and in downstream stations of the Solo River is evidence that allochthonous organic matter is much more resistant than autochthonous matter. The low index value observed in the Serayu River indicates the highly refractory nature of both autochthonous and allochthonous organic material.

Key words: sterol biomarkers, particulate organic matter, Indonesia

Introduction

Particulate organic matter in rivers plays an important role in biogeochemical processes occurring at the continent-ocean interface. Consequently, particu-

late organic carbon (POC) is one of the key bulk parameters for evaluating the standing stocks of allochthonous and photosynthetic carbon and for understanding carbon circulation in coastal marine ecosystems. Apart from this global viewpoint, organic carbon is composed of a large number of organic compounds produced by autochthonous biological activity and derived from terrigenous inputs. Within this large inventory of hundreds of molecules, specific molecular markers can be used to study physical, chemical and biological processes which control production, circulation, adsorption, flocculation, deposition, and degradation of organic matter in both freshwater and marine environments, and particularly at the highly active river/ocean boundary.

Sterols are biosynthetic compounds, which can be used as tracers of various inputs and transformation processes thanks to their structural diversity and stability. Sterol fingerprints have been extensively recognized as potential records of vegetal, both continental and marine, and animal organic matter inputs (Huang & Meinschein 1976; Volkman 1986; Saliot et al. 1991). Most studies dealing with sterols have been carried out on marine sediments (Nishimura & Koyama 1977; Lee et al. 1979; Volkman et al. 1987; Saliot et al. 1988; Lajat et al. 1990; Conte et al. 1994) and in the seawater column (Saliot & Barbier 1973; Gagosian 1975, 1976; Saliot et al. 1982; Wakeham & Lee 1989). Recently a few biogeochemical studies have been carried out in estuaries and adjacent coastal seas by means of sterol markers (Bayona et al. 1989; Grimalt & Albaiges 1990; Lajat & Saliot 1990; Tian et al. 1992; Laureillard & Saliot 1993; Yunker et al. 1995). Most of them have been performed in temperature areas, whereas equatorial environments have been little studied.

The first criteria of origin based on sterol distributions have been established from various observations. Cholesterol (a C_{27} sterol) and 24-methylenecholesterol (a C_{28} sterol) were found to be the major compounds in phytoplankton (Boutry & Barbier 1974). Higher plants were characterized by sterol distributions different from those of lower plants: main features were the predominance of C_{29} sterols such as β-sitosterol and presence of C_{28} sterols (Heftmann 1971). Cholesterol and 22-dehydrocholesterol (C_{27} sterols) were observed to account for more than 60% by weight of total sterols in plankton, whereas β-sitosterol and stigmasterol (C_{29} sterols) were the most abundant sterols in freshwater sediments from the Aransas River and Yellowwood Lake which were predominantly composed of terrigenous plant debris (Huang & Meinschein 1979).

Further studies have demonstrated the structural diversity of sterols in the side chain, mainly at $_{24}$, but also in rings A and B. This underlines the limits of GC/MS analysis versus biogeochemical interpretation (Maxwell et

al. 1980; Volkman 1986), especially when mixed, terrigenous and algal inputs of organic matter are concerned.

In the framework of the French "Dynamics and Budgets of the Earth" program, particulate samples were collected in the Solo and Serayu rivers, Java, Indonesia, and analyzed for sterols. Sterol distribution patterns are used in this manuscript to give insight into the origins of suspended organic matter and biogeochemical processes occurring in this equatorial aquatic environment.

Sampling Sites

The Solo River, classified as a mountain (1000-3000 m) monsoon-dominated river, is the largest river in Java Island, Indonesia, with a length of 540 km. The river flow presents wide variations (7-2700 m^3/s) with a mean of 440 m^3/s from November to April and at 95 m^3/s from May to October. It receives major inputs from a highly vegetation-rich drainage basin (0.016 $\times$ 10^6 km^2). The yield is estimated at 1200 $t/km^2/y$ and the total sediment load at 19 $\times$ 10^6 t/y (Hoekstra 1990). Although relatively pristine, it also receives discharge from a few small and medium-sized cities, before flowing eastward into the Indian Ocean. Suspended matter samples were collected in January 1991 at 7 stations, where domestic and industrial waste pollution might be significant (Fig. 1). Stations 2, 3 and 5 were located near three small towns above the Gajahmungkur Reservoir. Stations 9 and 12 were sited on two main tributaries close to but upstream of the cities of Madium and Bojonegoro, whereas stations 8 and 13 were located on the main stream. Another sampling site, station 20, was also located on the Serayu River, near to but upstream of the city of Rawalo.

Methods

River water (5–12 l) was collected in 20 l glass bottles and filtered within a few hours, through pre-extracted, 293 mm diameter, glass fibre filters (Whatman GF/F, 0.7 μm pore size). Filters were stored frozen in clean aluminium foils until analysis in the laboratory.

For analytical details, see Lajat et al. (1990). Filters were extracted for 24 hours using a mixture of dichloromethane-methanol (3:1, v/v). The lipid extract was evaporated to a few ml under vacuum at low temperature ($T < 40\,^{\circ}C$). The extract was then evaporated under a stream of pure argon. After dissolution of the extract in hexane, half of the fraction was submitted to thin

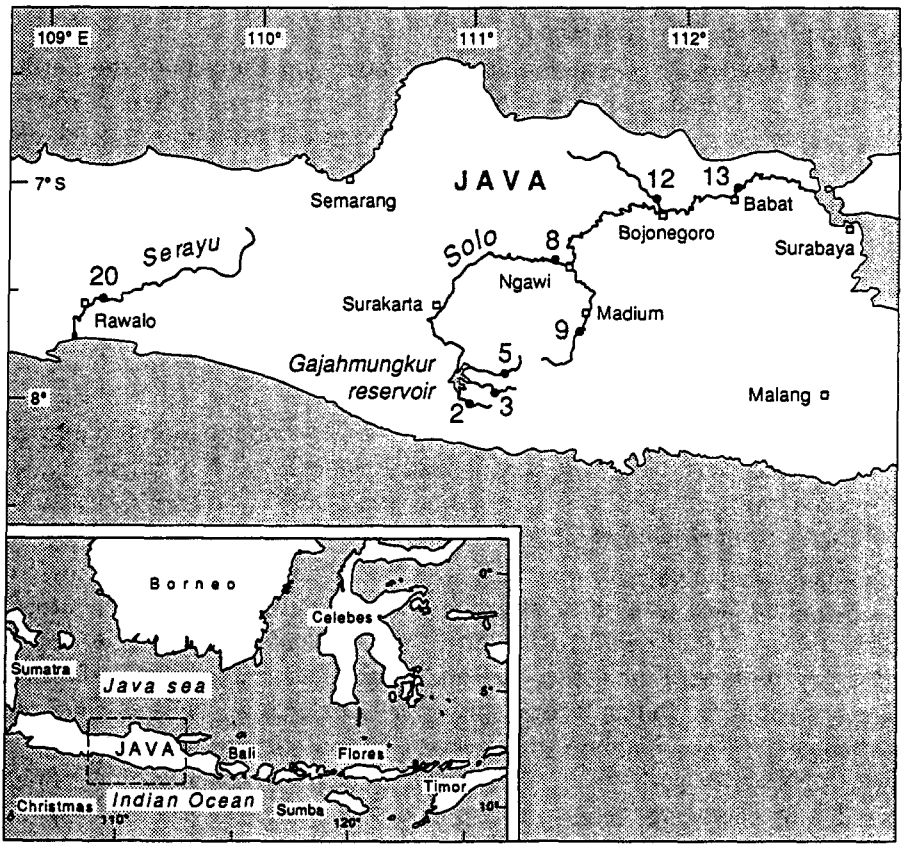

Fig. 1. Location of sampling sites in January 1991 on the Solo River system and Serayu River, Java, Indonesia.

layer chromatography. Elution was performed using a mixture of hexane-ether (9:1, v/v). Two fractions (sterols and wax esters) were recovered after detection of lateral spots of authentic standards by vizualisation under U. V., after spraying with phosphomolybdic acid and washing the silica-gel with methanol and dichloromethane.

After concentration, sterols were converted into their trimethylsilyl esters (TMS) by using bis(trimethylsily)-trifluoroacetamide in trimethylchlorosilane. The extract was spiked with a known amount of 5α-cholestane, as external standard.

The analyses of TMS sterols were performed by capillary gas chromatography using a Varian 6000 (Orsay, France) gas chromatograph equipped with a 30 m x 0.32 mm, i. d., fused silica column and a flame ionization detector. Molecular structure was elucidated by GC/MS using a Girdel 30 (Delsi-

Nermag, Argenteuil, France) gas chromoatograph interfaced with a Nermag (Delsi-Nermag, Argenteuil, France) R 10/10C quadrupole mass spectrometer/ PDP 11/23 data processing system.

Results and Discussion

Eleven molecular structures of sterols were confirmed by GC/MS and quantified. The concentrations of individual sterols from the Solo River and main tributaries and the Serayu River at station 20 are listed in Table 1.

Concentrations of total sterols ranged from 438 to 7922 ng/l. This range appears to be among the highest encountered in various riverine, estuarine and adjacent coastal waters as summarized in Table 2.

Concentrations of total suspended matter (TSM) varied in a wide range, from 3.3 mg/l at station 3 to 471 mg/l in the main stream of the Solo River at station 13 (Table 1). Concentrations of sterols expressed in ng/mg of TSM varied in the range 2.4–183.8. These values are comparable to those observed in the Chang Jiang Estuary during a high river flow period by Sicre et al. (1994): 1.3–2221 ng/mg for TSM values varying in the range 1.1–282.7 mg/l.

C_{27} sterols

Concentrations of cholesterol, cholest-5-en-3β-ol ($27\Delta^5$), varied from 92.1 to 1961 ng/l. Higher concentrations were observed in the upstream major tributary at station 12 and in the main stream of the Solo River at station 13 (Fig. 2). Concentrations of 5 α-cholestan-3β-ol ($27\Delta^{0,5\alpha}$) ranged rom 52.4 to 468.3 ng/l and showed variations similar to those of $27\Delta^5$.

Coprostanol, 5 β-cholestan-3β-ol ($27\Delta^{0,5\beta}$), is the principal sterol in human and higher animal feces. It is usually found in environments contaminated by urban wastes (Pocklington et al. 1987; Grimalt et al. 1990; Laureillard & Saliot 1993). Although $27\Delta^{0,5\beta}$ cannot by itself be unambiguously attributed to fecal matter inputs, when the relative concentration of $27\Delta^{0,5\beta}$ is higher than that of the corresponding 5α epimer, its presence can be considered a confident criterion of urban sewage pollution (Grimalt et al., 1990). With the exception of station 13, values of 5β/5α + 5β epimers varied in the range 0.7–0.9 which belongs to the urban pollution range. Concentrations of coprostanol showed a very different distribution from those of other sterols (Fig. 2). They were high in some tributaries, at station 12 (679.9 ng/l; 7.8 ng/mg), station 2 (561.6 ng/l; 8.6 ng/mg), and station 9 (188.2 ng/l; 1.7 ng/mg). $27\Delta^{0,5\beta}$ was not detected at stations 3 and 5 or on the Serayu River. A stricking feature is that in the main stream coprostanol concentrations were

Table 1. Solo and Serayu Rivers, Indonesia; concentrations of particulate individual sterols (in ng/l) and percentages with respect to total sterols (in brackets). Concentrations of total sterols (in ng/l, in ng/mg of total suspended matter (TSM) and in ng/mg particulate organic carbon (POC)), TSM and POC, in mg/l and % of TSM.

	Sterols	Carbon number and abbreviation	Stations upstream of the Gajahmungkur reservoir			Tributaries		Solo (main stream)		Serayu
			2	3	5	9	12	8	13	20
Coprostanol	5β-Cholestan-3β-ol	27$\Delta^{0,5\beta}$	561.6 (38.1)	n.d.	n.d.	188.2 (31.2)	679.9 (25.4)	425.8 (23.0)	14.6 (0.2)	n.d.
Cholesterol	Cholest-5-en-3β-ol	27Δ^{5}	270.3 (18.3)	280.7 (46.3)	203.7 (46.5)	92.1 (15.2)	526.1 (19.7)	311.7 (16.8)	1961 (24.8)	503.9 (24.2)
	5α-Cholestan-3β-ol	27$\Delta^{0,5\alpha}$	80.8 (5.5)	55.6 (9.2)	59.2 (13.5)	52.4 (8.7)	150.0 (5.6)	148.2 (8.0)	468.3 (5.9)	72.1 (3.5)
Brassicasterol	24-Methylcholesta-5,22E-dien-3β-ol	28$\Delta^{5,22}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	591.5 (7.5)	99.5 (4.8)
	24-Methyl-5α-cholest-22-en-3β-ol	28$\Delta^{0,22}$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24.1 (1.2)
Campesterol	24-Methylcholest-5-en-3β-ol	28Δ^{5}	312.4 (21.2)	66.8 (11.0)	37.5 (8.6)	153.6 (25.4)	369.3 (13.8)	465.0 (25.1)	946.6 (12.0)	237.9 (11.4)
	24-Methyl-5α-cholestan-3β-ol	28Δ^{0}	n.d.	n.d.	n.d.	n.d.	184.6 (6.9)	17.8 (1.0)	261.3 (3.3)	46.6 (2.2)
Stigmasterol	24-Ethylolesta-5,22E-dien-3β-ol	29$\Delta^{5,22}$	69.0 (4.7)	74.3 (12.3)	50.7 (11.6)	55.5 (9.2)	431.8 (16.2)	221.0 (22.9)	1562 (19.7)	403.5 (19.4)
	24-Ethyl-5α-cholest-22-en-3β-ol	29$\Delta^{0,22}$	n.d.	12.0 (2.0)	11.4 (2.6)	n.d.	25.7 (1.0)	n.d.	n.d.	44.8 (2.2)

Table 1. Continued.

	Sterols	Carbon number and abbreviation	Stations upstream of the Gajahmungkur reservoir			Tributaries		Solo (main stream)		Serayu
			2	3	5	9	12	8	13	20
Sitosterol	24-Ethylcholest-5-en-3β-ol	29Δ^5	123.9 (8.4)	91.2 (15.0)	58.8 (13.4)	43.3 (7.2)	305.4 (11.4)	264.6 (14.3)	1640 (20.7)	568.8 (27.4)
Sitostanol	24-Ethyl-5α-cholestan-3β-ol	29Δ^0	57.6 (3.9)	25.8 (4.3)	16.6 (3.8)	19.1 (3.2)	n.d.	n.d.	476.4 (6.0)	78.0 (3.7)
	Total sterols (ng/l)		1476	606.6	438.0	604.1	2673	1854	7922	2079
	Total sterols (ng/mg TSM)		22.7	183.8	2.4	5.5	30.7	13.0	16.8	5.2
	Total sterols (ng/mg POC)		1450	666.6	156.4	262.6	1747.0	882.8	1292	440.5
	TSM (mg/l)		65	3.3	179	110	87	142	471	400
	POC (mg/l)		1.18	0.91	2.80	2.30	1.58	2.10	6.13	4.72
	POC (% of TSM)		1.95	3.23	1.54	2.01	1.90	1.48	1.28	1.29
	27$\Delta^{0,5\alpha}$/27Δ^5		0.3	0.2	0.29	0.57	0.29	0.48	0.24	0.14
	29Δ^0/29Δ^5		0.46	0.26	0.28	0.44			0.29	0.14
	27Δ^5/28Δ^5		3.92	3.78	4.02	1.66	1.22	1.41	1.26	1.25
	27Δ^5/29Δ^5		2.18	3.08	3.46	2.13	1.72	1.18	1.20	0.89
	27Δ^5/28Δ^5 + 29Δ^5		1.40	1.70	1.86	0.93	0.71	0.64	0.61	0.52

n.d.: not detected.

Table 2. Sterol concentrations reported for rivers, estuaries and adjacent coastal waters.

Sterols analyzed	Area	Concentration range (ng l^{-1})	Reference
Rhone delta, Mediterranean Sea			
Particulate free sterols sampled in July 1988	River Marine Coastal area	17–60 370	Scribe et al. (1989)
Particulate free sterols sampled in December 1988 and January 1989	River Marine Coastal area	380–3100 150–2500	Scribe et al. (1991)
Ariake Sea, Kyushu, Japan			
Dissolved and particulate free and esterified sterols sampled in September 1971 and June 1972	Marine coastal area	6200–84500	Kanazawa & Teshima (1978)
Bedford basin, Nova Scotia Dissolved and particulate free and esterified sterols sampled from July 1983 to August 1984	Marine coastal area	300–5000	Pocklington et al. (1987)
Krka estuary, Adriatic Sea			
Particulate free and esterified sterols sampled in May 1988	River Marine waters	441–724 77–497	Laureillard & Saliot (1993)
Dissolved free and esterified sterols sampled in May 1988	River Marine waters	1220–1566 432	Laureillard & Saliot (1993)
Changjiang estuary			
Particulate free and esterified sterols sampled in July 1986	River Coastal area	280–1020 64–5900	Lajat & Saliot (1990) Sicre et al. (1994)
Mackenzie River, Arctic Beaufort Sea			
Particulate free and esterified sterols samples from late winter to summer in 1987	River Mid shelf Outer shelf	3.5–570 1.2–150 0–19	Yunker et al. (1995)

Table 2. Continued.

Sterols analyzed	Area	Concentration range (ng l^{-1})	Reference
Amazon River			
Particulate free and esterified sterols sampled in June 1989	River	16–320	Dagaut et al. unpublished data
Solo River, Serayu River, Indonesia			
Particulate free sterols sampled in January 1991	River	438–7922	This work

high at station 8 (425.8 ng/l; 3.0 ng/mg) and very low at the most downstream station 13 (14.6 ng/l; 0.03 ng/mg). The data suggest that the degradation rate of urban sewage derived organic matter is high downstream both in the Solo and Serayu Rivers under high temperatures and oxic conditions. This also suggests that the use of coprostanol as indicator of fecal material is rather limited in equatorial aquatic environments.

C_{28} *sterols*

Brassicasterol, 24-methylcholesta-5,22E-dien-3β-ol ($28\Delta^{5,22}$), was surprisingly found only at downstream stations in the Solo River (st. 13, 591.5 ng/l; 1.2 ng/mg) and in the Serayu River (st. 20, 99.5 ng/l; 0.2 ng/mg) (Fig. 3). This unique distribution with regard to other C_{28} and C_{29} sterols indicates that this compound originates predominantly from algae and not from higher plants as documented by Volkman (1986). This could be explained by an increased biosynthesis from planktonic algae near the estuary.

Campesterol, 24-methylcholest-5-en-3β-ol ($28\Delta^5$), whose origin is commonly attributed to higher plant biosynthesis (Volkman 1986), showed increasing concentrations downstream, with highest levels in the main stream at stations 8 (465 ng/l; 3.3 ng/mg) and 13 (946.6 ng/l; 2 ng/mg) (Fig. 3; Table 1). Thus campesterol appears to be the best index for appreciating the accumulation and transport of continental organic matter inputs in equatorial rivers. The associated stanol, 24-methyl-5α-cholestan-3β-ol ($28\Delta^0$), was encountered at lower levels in the main stream at stations 8 and 13 and at station 12 (184.6 ng/l; 2.1 ng/mg) and in the Serayu River at Station 20.

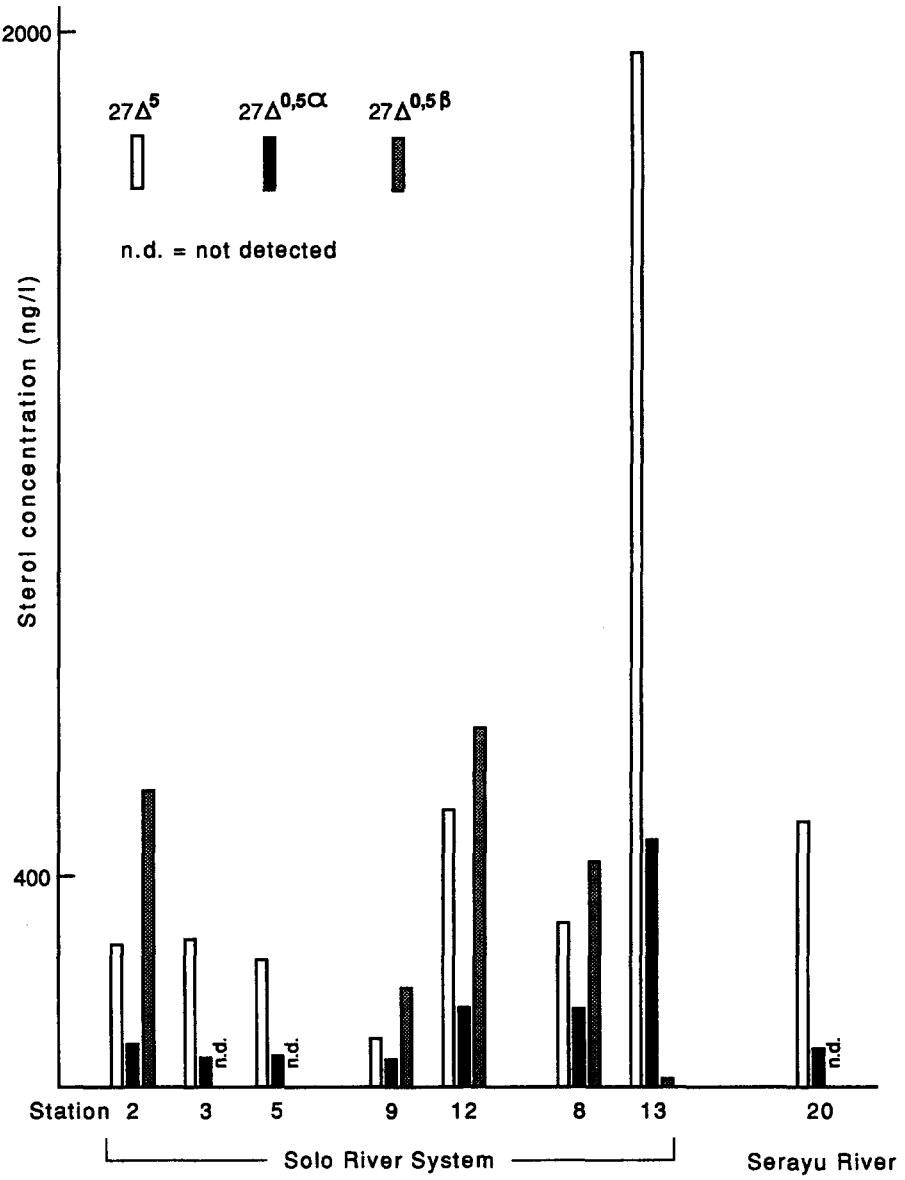

Fig. 2. Spatial distribution of C_{27} sterols in the Solo River system and the Serayu River.

C_{29} sterols

Two C_{29} sterols, stigmasterol (24-ethylcholesta-5,22 (E)-dien-3β-ol; 29$\Delta^{5,22}$) and sitosterol (24-ethylcholest-5-en-3β-ol; 29Δ^{5}), show spatial distributions

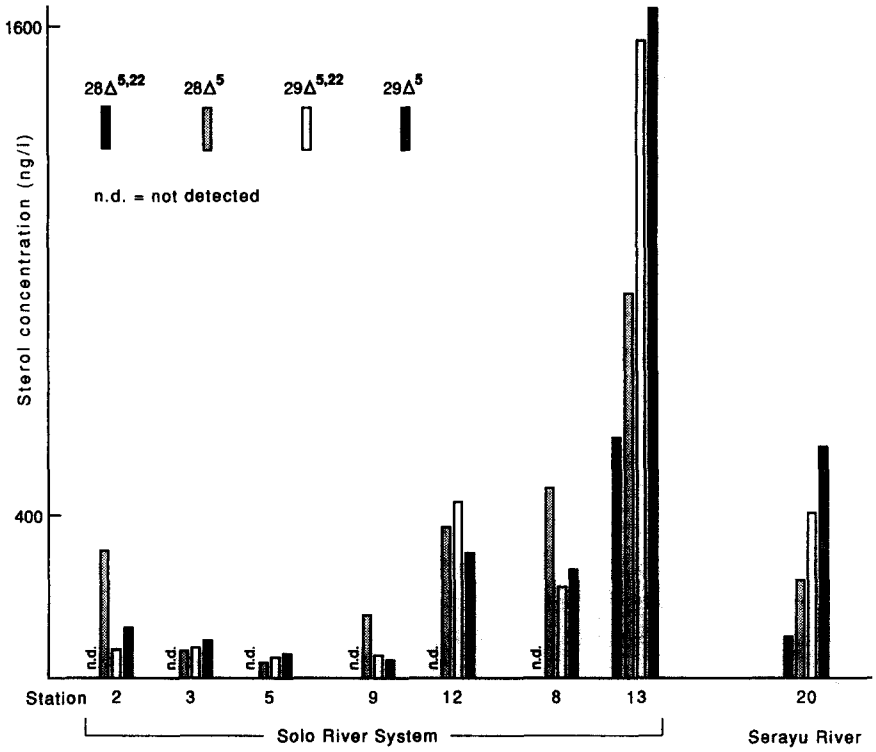

Fig. 3. Spatial distribution of C_{28} and C_{29} sterols in the Solo River system and the Serayu River.

close to that observed for campesterol (Fig. 3). Highest concentrations were found at station 13: 1562 and 1640 ng/l, respectively. Much lower concentrations of the associated stanols ($29\Delta^{0,22}$ and $29\Delta^{0}$) were encountered at all the other stations. 24α-$28\Delta^{5}$ (campesterol), 24α-$29\Delta^{5,22}$ (stigmasterol) and 24α-$29\Delta^{5}$ (β-sitosterol) are usually considered confident markers of terrigenous contributions especially when present in precise relative proportions (Heftmann 1971; Huang & Meinschein 1976, 1979; Lee et al. 1979; Laureillard & Saliot 1993). In this study, due to the minute amounts of organic material obtained, we were unable to distinguish the 24 sterol configurations, that can be identified by nuclear magnetic resonance or long capillary column gas chromatography (Maxwell et al. 1980). If the stereochemistry of the 24 sterols is known, interpretation of the origin of 28 and 29 sterols is much more precise. For example, 24α-$29\Delta^{5}$ mainly originates from vascular plants whereas 24β-$29\Delta^{5}$ (clionasterol) is derived predominantly from plankton (Volkman 1986).

Nevertheless, despite their limits, the present analyses provide an index of abundance of organic matter of terrigenous origin in this type of environment.

This index is of course a combination of $28\Delta^5$, $29\Delta^{5,22}$ and $29\Delta^5$ sterols. The $28\Delta^5 + 29\Delta^{5,22} + 29\Delta^5$ index is highest near the estuary at station 13: 4.15 μg/l or 8.8 ng/mg of TSM which is also highest at this point. At this station the three reference compounds represent up to 52% of total sterols, ahead of cholesterol, 24.7%.

Relative abundance of $C_{27}C_{28}C_{29}$ sterols

The relative abundances of individual particulate sterols with respect to total sterols are listed in Table 1. Cholesterol ($27\Delta^5$) predominates at stations 3, 5 and 13 (46.3, 46.5 and 24.8%, respectively), whereas coprostanol ($27\Delta^{0,5\beta}$) is the major sterol at stations 2, 9 and 12, (38.1, 31.2 and 25.4%, respectively). Other predominant sterols are campesterol ($28\Delta^5$) in the main stream of the Solo River at station 8 (25.1%), and sitosterol ($29\Delta^5$) in the Serayu River at station 20 (27.4 %).

The C_{27}, C_{28}, C_{29} sterol abundance ratio has been used to distinguish between autochthonous and allochthonous organic matter inputs in estuarine environments (Huang & Meinschein 1976; Saliot et al. 1983; Sicre et al. 1994) and in lake sediments (Matsumoto et al. 1982, 1983).

Although concentrations of both terrigenous and partly autochthonous sources increase downstream in the Solo River, $27\Delta^5/29\Delta^{5,22}$ and $27\Delta^5/29\Delta^5$ show higher values at upstream stations 2, 3 and 5, but lower values in the main stream at stations 8 and 13 (Table 1).

Values of the autochthonous versus terrigenous sterol index defined as $27\Delta^5/29\Delta^{5,22} + 29\Delta^5$ are 1.40, 1.70 and 1.86 at stations 2, 3 and 5, respectively, whereas lower values of 0.4 and 0.6 are found at stations 8 and 13, respectively, which also correspond to increasing concentrations of TSM and decreasing POC % values (Table 1).

Stanol/sterol

Although to be considered with caution (Gaskell & Eglinton 1975), stanol/sterol values have been proposed as a potential index for estimating the biohydrogenation efficiency leading to the transformation of stenols into stanols (Eyssen et al. 1973; Saliot & Tusseau 1984; Tian et al. 1992, among others). Insofar as the index can be used to estimate bacterial activity of oxic waters, examination of simultaneous variations of 27 and 29 pairs reveals several discrepancies. This suggests that the bacterial degradation of autochthonous versus allochthonous organic matter could differ depending on local conditions (Fig. 4). At stations 2, 3 and 5, upstream of the Gajahmumgkur reservoir, values of $27\Delta^{0,5\alpha}/27\Delta^5$ and $29\Delta^0/29\Delta^5$ are similar, with a mean of 0.3 and a slightly higher value at station 2 for the 27

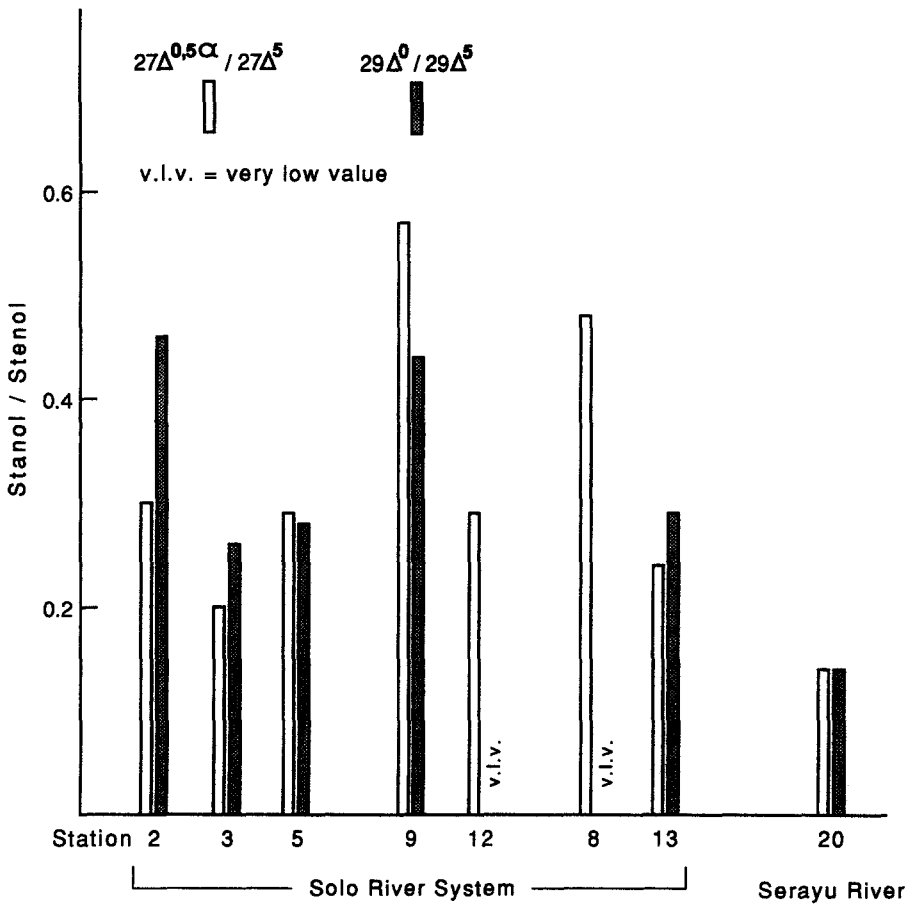

Fig. 4. Distribution of cholestanol/cholesterol ($27\Delta^{0,5\alpha}/27\Delta^{5}$) and sitostanol/sitosterol ($29\Delta^{0}/29\Delta^{5}$) values in the Solo River system and the Serayu River.

ratio, 0.46. In the tributaries, there is no relation between station 9 where similar high values are observed for 27 and 29 pairs and station 12 where a value of 0.3 is observed for the 27 pair and a very low value for the 29 pair, which suggests that allochthonous organic matter is much more resistant than autochthonous matter. The same disagreement is observed in the main stream at stations 8 (high value for the 27 pair, very low for the 29 one) and 13 (similar values for 27 and 29 pairs, 0.24 and 0.29), respectively.

A rather low value is observed in the Serayu River for the two 27 and 29 pairs, 0.14, indicating the rather high refractory nature of both autochthonous and allochthonous organic material.

Conclusions

This is a first attempt to identify the different contributions of organic matter, natural, autochthonous, allochthonous, and anthropogenic in equatorial aquatic environments by assay of selected particulate samples from two Indonesian rivers, the Solo and Serayu. Three sterol indicators or indexes are described. The first index of autochthonous algal biosynthesis is linked to cholest-5-en-3β-ol ($27\Delta^5$) and 24-methylcholesta-5,22(E)-dien-3β-ol ($28\Delta^{5,22}$). $27\Delta^5$ accounts for between 15.2 and 46.5% of total sterols and highest concentrations were found downstream near the estuary, 1961 ng/l or 4.2 ng/mg TSM. $28\Delta^{5,22}$ was found only at downstream stations in the Solo River system and in the Serayu River.

The second index permits evaluation of terrigenous inputs; it is the sum of 24-methylcholest-5-en-3β-ol ($28\Delta^5$), 24-ethylcholesta-5,22(E)-dien-3β-ol ($29\Delta^{5,22}$) and 24-ethylcholest-5-en-3β-ol ($29\Delta^5$). Highest concentrations were clearly observed at the most downstream station in the Solo River, 946.6, 1562 and 1640 ng/l, or 2, 3.3 and 3.5 ng/mg TSM respectively. At this station the three terrigenous index compounds represented up to 52% of total sterols.

The third index is representative of urban waste pollution and is attributed to the presence of 5β-cholestan-3β-ol ($27\Delta^{0,5\beta}$). The distribution of $27\Delta^{0,5\beta}$ was very different from that of other sterols, high in some tributaries, very patchy in the main downstream, absent at some locations and in the Serayu River. It suggests a high degradation rate of organic matter within these environments characterized by high temperature and oxic conditions.

Although concentrations of both partly autochthonous algal and terrigenous sources increased downstream in the Solo River, $27\Delta^5/29\Delta^{5,22}$ and $27\Delta^5/29\Delta^5$ showed high values at upstream stations, but lower values at downstream stations. Mean values of the autochthonous versus terrigenous sterol index, defined as $27\Delta^5/29\Delta^{5,22} + 29\Delta^5$, were 1.65 and 0.5 at upstream and downstream stations, respectively, suggesting an increase in algal inputs by a factor of $\sim$ 3 along the Solo River.

Assuming that stanol/stenol values reflect the potential microbial biohydrogenation capacity, large discrepancies found at various stations between $27\Delta^{0,5\alpha}/27\Delta^5$ and $29\Delta^0/29\Delta^5$ suggest that terrigenous organic matter is much more resistant than autochthonous algal material. The highest microbial hydrogenation capacity was found at the most downstream station, near the estuary, as also attested by the low concentration of coprostanol.

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