Fluxes of dissolved and nonfossil particulate organic carbon from an Oceania small river (Lanyang Hsi) in Taiwan

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Accepted 12 May 1997

Key words: DOC, flux, fossil carbon, Lanyang Hsi, Oceania, POC, river, Taiwan

Abstract. Concentrations of dissolved and particulate organic carbon (DOC & POC) in river waters were measured during 1993–1994 in the Lanyang Hsi watershed, which represents a typical small Oceania river. The DOC concentrations varied in the range of 0.5–4 mg/l during non-typhoon period, but rose to as high as 8 mg/l during Typhoon Tim in July, 1994. Based on the log-linear relationship between the DOC load and the discharge rate, we estimated the DOC export to be 3.4 ± 0.6 ktC/yr, and the DOC yield to be 4.1 ± 0.7 gC/m²/yr, which is considerably higher than a former estimate (ca. 0.1 gC/m²/yr) for the Oceania. On the other hand, the DOC yield is less than the concurrent POC yield (21.7 ± 4.7 gC/m²/yr) by a factor of five, but most of the exported POC is fossil carbon. Under the assumption that the suspended sediments contain a mean fossil POC content of 0.5%, the nonfossil POC yield was calculated to be 4.6 ± 3.0 gC/m²/yr, comparable to the DOC yield. Since DOC and nonfossil POC are directly related to the ecosystem, their combined fluxes give a biogenic organic carbon yield of 8.7 ± 3.1 gC/m²/yr.

Introduction

The riverine fluxes of carbon to the oceans represent a major link in the global carbon cycle (Kempe 1979), which cannot be neglected when studying the problem of the "missing carbon" (Siegenthaler & Sarmiento 1993). Recently, small mountainous rivers of Oceania have attracted much attention due to their significance in exporting particulate organic carbon (POC) to the oceans (Degens & Ittekkot 1985; Ittekkot 1988; Milliman & Syvitski 1992). However, Kao and Liu (1996) demonstrated that the extraordinarily high POC flux in Lanyang Hsi, a typical Oceania small river, is attributable to human disturbance, and much of the exported POC is fossil carbon. By contrast, the Oceania rivers' contribution of dissolved organic carbon (DOC) to the oceans receives little attention. In fact, the average yield of DOC in Oceania has been estimated to be negligibly small, ca. 0.1 gC/m²/yr (Degens & Ittekkot 1985).

Since many of the Oceania rivers are on the tropical islands of the western Pacific, the high precipitation and high temperature of the tropical climate favor high primary productivity, which may provide high output flux of organic carbon in both particulate form and dissolved form (Whittaker & Likens 1973). Despite the small total area of Oceania, about 13% of the total water discharge to the oceans occurs via the rivers of Oceania (Milliman 1991). High precipitation also enhance DOC yield in the watershed (Spitzy & Leenheer 1991; Ludwig et al. 1996). Thus, significant contribution of DOC from Oceania is conceivable. The purpose of this paper is to determine the DOC yield in Lanyang Hsi watershed, to calculate the nonfossil POC yield from previously published data (Kao & Liu 1996), and to estimate the flux of biogenic organic carbon.

Lanyang Hsi (Figure 1) in northeastern Taiwan originates from an altitude of 3535 m with a drainage area of 820 km² and the length of 70 km. The mean annual precipitation is 3000 mm. In summer, typhoons often bring torrential rains with them and account for 38% of the annual precipitation of Lanyang Hsi on average (Chang et al. 1992). The mean annual occurrence of typhoon in Taiwan is 3.5 (Liu et al. 1996), but less than half may cause local flooding. The basement rock in the watershed is composed mainly of Tertiary argillite-slate and metasandstone (Ho 1975). The denudation rate is very high in the same manner as the rest of Taiwan (Li 1976). There is no dam blocking the river. In the main stem, the mean gradient is 1/21. The population in the drainage area is about 500 thousand.

This paper presents DOC data from a continuous monitoring at a gauge station near the river mouth over a 12-month period, including intensive sampling during a typhoon, and also data from repeated sampling at eight other stations. The yearly DOC flux calculated from the time-series data is only about 1/5 of the POC flux reported previously (Kao & Liu 1996), but is similar to the nonfossil POC flux which was calculated from measurements on particulate matter obtained concurrently.

Materials and methods

River waters were sampled at nine stations in the study area (Figure 1). Four sampling stations were along the main channel, and another four were along tributaries near their confluences with the main channel. Station 9 locates in the nearby Fushan Experimental Forest, a natural preserve. The discharge rate of the Lanyang Hsi at a gauge station (Station 8) was provided by the Water Resources Planning Committee (WRPC) of the Republic of China. During typhoon invasion, hourly discharge values were available.

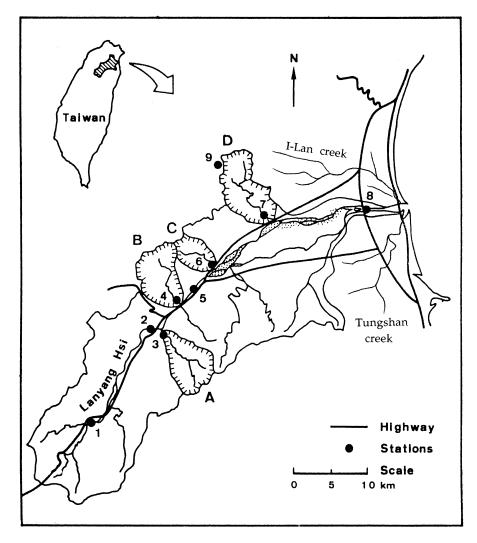


Figure 1. Map of the Lanyang Hsi drainage area. There were eight sampling stations (Stations 1-8) in this watershed and one (Station 9) in an adjacent natural preserve. Stations 2 and 8 are gauge stations.

Sampling for POC, DOC and total suspended matter (TSM) was done at Station 8 about every five days from September 1993 to August 1994 to monitor the temporal variation over a year's course. Sampling was also done at the other eight stations every one to two months from June 1993 to August 1994 to assess the spatial variation. During the invasion of typhoon Tim on July 9–11, 1994, sampling was performed every 4–6 hours so that the rapid change of the flow condition was captured.

Water samples were collected using polyethylene bottles and filtered with preheated (at 450 °C) GF/F filters. The filtration was done by drawing sample water into a 200 ml plastic syringe, which had been rinsed several times with the sample before hand, and filtering the water through the filter mounted in a holder attached to the syringe. The filtrates were divided into two preheated 50 ml glass bottles, added 0.3 ml of concentrated phosphoric acid, stored in an ice chest during transport and stored in a freezer upon return to the laboratory.

DOC concentration was determined in a Shimadzu TOC 5000 analyzer. Filtered and acidified water samples were purged with pure oxygen to remove inorganic carbon. The sample was subsequently combusted at $680\,^{\circ}\text{C}$ and the released CO_2 was measured with an IR detector. The instrument was calibrated using potassium phthalate as the standard. The precision was better than $\pm 5\%$ in the range of 0.5–5 mg/l. Detailed description of POC and TSM analyses has been reported elsewhere (Kao & Liu 1996).

Results and discussion

Continuous monitoring

The daily discharge rate (Figure 2a) of the Lanyang Hsi varied in the range of 8 to 1500 m³/s with the total discharge amounting to an annual value of $1.65 \, \mathrm{km}^3/\mathrm{yr}$, which is very close to the mean discharge of $1.68 \pm 0.52 \, \mathrm{km}^3/\mathrm{yr}$ for 1970–1991. Typhoon occurred three times in the summer of 1994 as indicated by the three peaks in discharge rate plot (Figure 2a). Among the three typhoons, the one in July by the name Tim caused the highest precipitation.

The DOC concentrations at Station 8 during non-typhoon period were in the range of 0.5–4 mg/l, which was similar to the range observed for POC during the same period (Figure 2c). Rather low concentrations of DOC (<2 mg/l) were observed in winter (during December, 1993–January, 1994). The lowest concentration (0.5 mg/l) occurred in January, 1994. Higher DOC concentrations mostly occurred in summer. The highest DOC concentrations (up to 8 mg/l) were observed during Typhoon Tim, but the increase was not as dramatic as that for POC, which increased 30 fold (Figure 2c). The detail obtained by intensive observations (Figure 3) revealed that the maximum concentration occurred at peak flow rate, suggesting that DOC may have been purged or flushed out of soil column during flooding (Brinson 1976; Lewis & Saunders 1989). Other than high concentrations during typhoon, the DOC variation showed no clear trend dependent on discharge rate (Figure 4a).

The daily DOC load (L_{DOC}) was calculated by multiplying the daily discharge rate by the DOC concentration. DOC load is well correlated with the

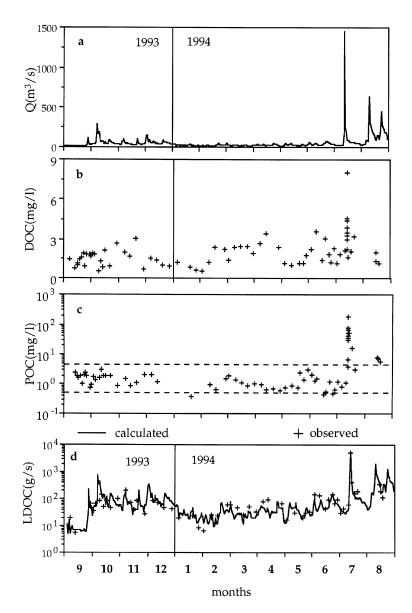


Figure 2. Results of continuous monitoring at the gauge station near the river mouth (Station 8) from September 1993 to August 1994. (a) Daily discharge rate. (b) Observed DOC concentrations: 0.5–4 mg/l during non-typhoon period, and up to 8 mg/l during invasion of Typhoon Tim in July 1994. (c) Concurrent POC concentrations (Kao & Liu 1996) presented for comparison. Note the concentration in logarithmic scale. The two dashed lines indicate the DOC concentration range during non-typhoon period. (d) DOC flux. The abscissa represents months from September 1993 to August 1994. Solid line indicates values calculated from the discharge rate by regression function and the symbols (+) represent the fluxes calculated from observed values.

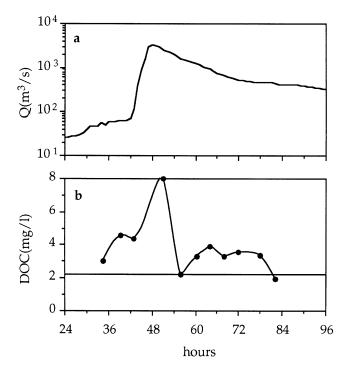


Figure 3. Results of intensive sampling at Station 8 during Typhoon Tim in July, 1994. (a) Hourly discharge rate. (b) DOC concentration. The horizontal line indicates the annual mean.

daily discharge rate (Q) in a log-log plot (Figure 4b). The logarithmic-linear regression is the following:

$$\begin{split} \log L_{DOC} &= -0.199 + 1.248 \times \log Q \\ r^2 &= 0.90, n = 66, \text{and } p < 0.001 \end{split} \tag{1}$$

where L_{DOC} is in g/s and Q is in m³/s. From this relationship, the daily DOC load (Figure 2d) was calculated from the discharge rate for every day during the study period. The DOC loads from measured data are also plotted for comparison. The transport of DOC over the one-year study period was calculated to be 3.4 ± 0.6 ktC/yr. The estimated error was determined from the mean relative deviations between the observed and the calculated values of the daily loads (Figure 2d). The mean relative deviation is defined as the root of the weighted mean square of the coefficient of variation, where the weighting is by the respective daily loads.

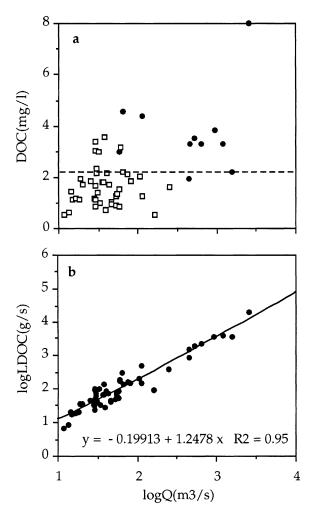


Figure 4. (a) Relationship between DOC concentration and discharge rate at Station 8. The solid dots represent typhoon conditions. (b) Relationship between DOC load $[L_{DOC}]$ and discharge rate at Station 8. The regression line is for all data from both non-typhoon and typhoon conditions.

Spatial variation

In order to understand the spatial variation of DOC concentration (Figure 5), we grouped the sampling stations into four subsets to represent different parts of the catchment basin. Station 1 represents the upper segment of the main channel, Stations 2 and 5 the middle segment, Station 8 the lower segment, and Stations 3, 4, 6, and 7 the undisturbed tributaries, where paved roads are rare. Kao and Liu (1996) showed that a massive road construction during 1975–80

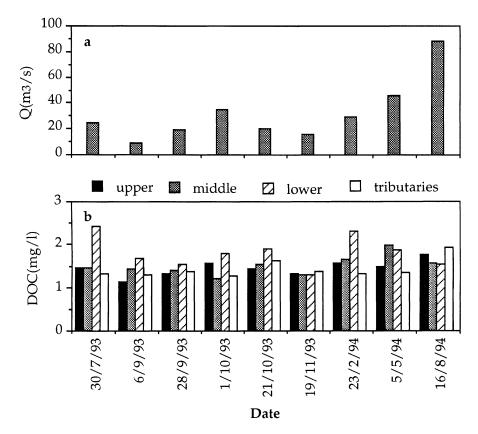


Figure 5. Results from repeated sampling at all stations in the Lanyang Hsi drainage area. The upper reach is represented by Station 1, the middle segment by Stations 2 and 5, the lower stem by Station 8, and the undisturbed tributaries by Stations 3, 4, 6 and 7. (a) Discharge rate at Station 8. (b) DOC concentration in different parts of the river.

along the main channel and the subsequent traffic could be the main cause of a three-fold increase in the sediment load in the Lanyang Hsi in recent years. Therefore, the lack of paved roads may significantly limit human perturbation. In fact, the TSM and POC concentrations in the undisturbed tributaries, that are usually 1–2 orders of magnitude lower than those in the main channel (Kao & Liu 1996), serve as an evidence.

Contrary to the large variability of POC concentration in different parts of the river (Kao & Liu 1996), the spatial variation of DOC was small. Repeated samplings showed that the DOC concentrations in the lower reach were mostly higher than other sites (Figure 5b). Compared to DOC concentrations observed in the upper and middle segments, the DOC concentration observed at Station 8 on the same day was higher by $23 \pm 10\%$ (n = 26, p < 0.05);

Table 1. The fossil POC contents in suspended sediments calculated from percentages of modern carbon derived from the ¹⁴C based apparent ages (Kao & Liu 1996)

Sta No.	Sampling Date	Apparent age	Modern carbon*	Non- fossil carbon [#]	POC Conc.	TSM Conc.	POC in TSM	Fossil POC in TSM
		(yr)	(%)	(%)	(mg/l)	(mg/l)	(%)	(%)
2	1 Oct. 1993	12960	19.8	18.3	1.35	245	0.55	0.45
5	30 Jul. 1993	16620	12.6	11.6	1.75	253	0.69	0.61
8	21 Oct. 1993	10000	28.6	26.5	1.14	156	0.73	0.54
9	1 Oct. 1993	-670	108.1^{\dagger}	100	0.206	1.1	19.5	

^{*}The percentage of modern carbon, which is defined by the ¹⁴C concentration in atmospheric CO₂ in 1950, was calculated from the apparent age with the equation of Stuiver and Polach (1977):

compared to those in the undisturbed tributaries, it was higher by $33 \pm 14\%$ (n = 36, p < 0.05).

The slight enrichment in DOC in the lower reach may have been caused by local agricultural activities and urban wastes. On the other hand, the enrichment could also be attributable to higher DOC yield in the rather flat deltaic region (Mulholland & Kuenzler 1979; Eckhardt & Moore 1990; Clair et al. 1994). It is not clear whether human activities of the relatively small population (about 500 thousand) of the Lanyang Hsi watershed may have caused increase of DOC in the river water. If the slight excess of DOC in the lower reach had been entirely due to human activity, the natural DOC flux would be reduced by 1/3. Further study is needed to determine the actual causes for such an enrichment.

Total organic carbon flux

The total organic carbon flux comprises of the dissolved and the particulate from. The concurrent POC export from Lanyang Hsi has been estimated at 19 ± 6 ktC/yr (Kao & Liu 1996), which is much larger than the DOC export, but most of it is fossil carbon as indicated by the rather old apparent ages (>10000 yr) of POC samples from the main channel (Table 1). The percentages of modern carbon in these samples were calculated from their apparent ages (Stuiver & Polach 1977). However, the sample from Station 9, which contains almost 20% of organic carbon, is more enriched in $^{14}\mathrm{C}$ than

 $pM = 100 \times exp-[t + (y - 1950)/1.03]/8033,$

where t is the apparent age, and y is the year of analysis.

^{*}The percentage of nonfossil carbon was calculated by normalizing the percentage of modern carbon to that of the sample from Station 9 (See text).

[†]The sample contains bomb ¹⁴C.

the modern carbon, indicating inclusion of bomb ¹⁴C (Table 1). Under the assumption that the nonfossil carbon in the other three samples contains the same ¹⁴C concentration as in the Station 9 sample, the percentages of nonfossil carbon were calculated by normalizing the percentages of modern carbon to that of the Station 9 sample. In turn, the fossil carbon contents in the suspended sediments were calculated using the following equation:

$$POC_f(\%) = (100\% - C_{nf}) \times [POC]/[TSM]$$
 (2)

where C_{nf} is the percentage of nonfossil carbon, and [POC] and [TSM] are concentrations in mg/l. The calculated percentages of fossil carbon fall in the range of 0.45–0.61% (Table 1) with a mean of 0.53 \pm 0.08%.

This mean value is an direct evidence supportive of Meybeck's (1993) proposition of an almost uniform fossil carbon content of 0.5% in riverine suspended sediments. The universal trend of decreasing organic carbon content in suspended matter with increasing TSM concentration (e.g., Ludwig et al. 1996) is evident in Lanyang Hsi (Kao & Liu 1996), and the lower limit of the carbon content at given TSM concentration approaches a constant value of 0.5% for high TSM concentrations (> 200 ppm). Therefore, the observed background value of 0.5% POC in suspended sediments is also consistent with the notion of a rather uniform fossil carbon content. Under this assumption, we calculated the load of nonfossil POC (L_{POCnf}) as follows:

$$L_{POCnf} = L_{POC} - L_{TSM} \times 0.5\% \tag{3}$$

where L_{POC} and L_{TSM} are the loads of POC and TSM. A few samples with the POC content lower than 0.5% were ignored in the discussion. Then, the correlation between nonfossil POC load in gC/s and the discharge rate in m^3/s was found to be:

$$logL_{POCnf} = -1.411 + 1.781 \times logQ$$

$$r^{2} = 0.94, n = 54, and p < 0.001$$
(4)

Using this relationship, we calculated the daily nonfossil POC load from the daily discharge rate for each day from September 1993 to August 1994 and obtained a yearly transport of 3.8 ± 2.4 ktC/yr. The daily loads of fossil POC were estimated from the TSM loads (Kao & Liu 1996), which yield a yearly transport of 14.5 ± 4.0 ktC/yr. The relative importance of DOC, nonfossil and fossil POC and the contribution of typhoons to the organic carbon fluxes are illustrated in the plot of the cumulative loads (Figure 6). The three stepwise jumps in July and August, 1994 corresponded to occurrences of typhoons.

Table 2. Transports, mean concentrations and yields of DOC, nonfossil POC (POC_{nf}) and fossil POC (POC_f) in Lanyang Hsi. Biogenic organic carbon is the sum of DOC and nonfossil POC. POC is the sum of nonfossil and fossil POC

	Transport (ktC/yr)	Mean Concentration (mg/l)	Yield (gC/m²/yr)
DOC	3.4 ± 0.6	2.1 ± 0.4	4.1 ± 0.7
POC_{nf}	3.8 ± 2.4	2.3 ± 1.5	4.6 ± 3.0
POC_{f}	14.5 ± 4.0	8.8 ± 2.4	17.7 ± 4.9
Biogenic organic Carbon	7.2 ± 2.5	4.3 ± 1.5	8.7 ± 3.1
POC	18.3 ± 4.7	11.1 ± 2.8	22.2 ± 5.7
Total organic carbon	21.7 ± 4.7	13.1 ± 2.9	26.4 ± 5.8

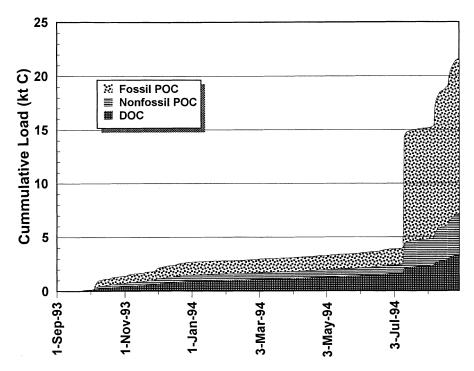


Figure 6. Cumulative loads (in kilotons of carbon) of DOC, nonfossil POC and fossil POC observed at Station 8 from September 1993 to August 1994.

The most striking one was during Typhoon Tim's invasion, which accounted for 17%, 54% and 61% of the yearly transports of DOC, nonfossil POC and fossil POC, respectively.

The fluxes of all types of organic carbon are summarized in Table 2. The POC transport is 18.3 ± 4.7 ktC/yr, which agrees with the previous estimate of 19 ± 6 ktC/yr (Kao & Liu 1996). The fossil carbon accounts for $79 \pm 30\%$ of POC export, while the nonfossil POC accounts for $21 \pm 14\%$, which is consistent with the range (3–30%) proposed by Kao and Liu (1996). The total organic carbon export is 21.7 ± 4.7 ktC/yr, 2/3 of which belongs to fossil POC (14.5 ± 4.0 ktC/yr). If sediments exported from other Oceania islands also contain 0.5% of fossil carbon, the total fossil POC export could be as much as 45 MtC/yr, which is calculated from the Oceania sediment transport of 9 Gt/yr (Milliman & Syvitski 1992). This is quite significant as compared to the estimated global POC transport of 170 MtC/yr (Meybeck 1993; Ludwig et al. 1996).

The DOC/POC ratio of the export fluxes, 0.19 ± 0.06 , is anomalously low as compared to values (0.5--4.7) reported for other parts of the world. However, the DOC to nonfossil POC ratio (DOC/POC_{nf}), 0.9 ± 0.6 , is fairly close to the ratio of 1.1 estimated for the tropical wet regions (Ludwig et al. 1996), suggesting that the fossil POC should be excluded in comparison of organic carbon fluxes. Only the two lesser fluxes, namely the DOC and nonfossil POC fluxes, represent organic carbon export from the ecosystem, and their combined fluxes are collectively named the biogenic organic carbon flux. The fossil POC flux is merely a recycled flux of sedimentary organic carbon.

Mean concentrations and yields

From the yearly transports, the mean concentrations of DOC, nonfossil POC and fossil POC were calculated by dividing the transports with the total discharge of 1.65 km³/yr., and the yields were calculated by dividing them with the watershed area of 820 km². The results are listed in Table 2. The mean concentrations of DOC (2.1 \pm 0.4 mg/l) and nonfossil POC (2.3 \pm 1.5 mg/l) are considerably lower than the global average concentrations of DOC (5.4 mg/l) and POC (4.5 mg/l) estimated by Ludwig et al. (1996), whereas their respective yields $(4.1 \pm 0.7 \text{ and } 4.6 \pm 3.0 \text{ gC/m}^2/\text{yr})$ are among the highest values observed in different parts of the world and more than twice as high as the respective global average yields, 1.9 and 1.6 gC/m²/yr, for DOC and POC (Spitzy & Leenheer 1990; Ludwig et al. 1996). The DOC yield is much greater than the yield (ca. 0.1 gC/m²/yr) formerly estimated for Oceania by Degens and Ittekkot (1985), but is similar to the average (3.8 gC/m²/yr) for the tropical wet regions as determined from the DOC export and the area reported by Ludwig et al. (1996). Similarly, the yield of nonfossil POC yield is also close to the average POC yield (3.4 gC/m²/yr) for the tropical wet regions.

The DOC yield has been shown correlated with environmental conditions such as discharge rate, topography, and soil organic carbon content. Ludwig et al. (1996) proposed the following equation to calculate the DOC yield (F_{DOC}) in gC/m²/yr:

$$F_{DOC} = 0.0040Q - 8.76Slope + 0.095soilC$$

where Q is the runoff depth (mm/yr), Slope is in radian, and soilC is the amount of organic carbon per cubic meter (kgC/m³). For Lanyang Hsi drainage area, Q was 2012 mm/yr during the study period, and soilC was assumed to be 20 kgC/m³. For the upper, middle and lower segments of the river basin, where the slopes are 0.13, 0.021 and 0.005, the yields was calculated to be 8.8, 9.8 and 9.9 gC/m²/yr, respectively. These values are all significantly higher than the DOC yield estimated from our observations. Such discrepancy is understandable in light of the fact that few of the data used for linear regression by Ludwig et al. (1996) are from areas with precipitation as heavy as the study area. Besides, the rapid runoff during torrential rains in Oceania islands also makes DOC production less effective. A different relationship between DOC yield and the environmental conditions is required for Oceania islands.

Because the biogenic organic carbon flux is supported by primary production of the ecosystem, its ratio to the net primary production (NPP) may be compared to those observed for other ecosystems. The Lanyang Hsi watershed, due to its high relief, covers several ecotypes, from temperate cypress forest to tropical woodland. The mean NPP may be roughly estimated by averaging the NPP of three ecotypes reported by Warnant et al. (1994): the needle leaf (419 gC/m²/yr), the temperate broadleaf deciduous and mixed forest (659 gC/m²/yr) and the tropical deciduous forest (711 gC/m²/yr). The mean value, $600 \, \text{gC/m²/yr}$, is taken as the estimate for the NPP. This is consistent with the range ($600-800 \, \text{gC/m²/yr}$) predicted by the modified Chikugo model, which makes use of data from 76 weather stations in the Oceania (Seino & Uchijima 1992). The biogenic organic carbon export per unit area is $8.7 \pm 3.1 \, \text{gC/m²/yr}$ (Table 2), which represents $1.5 \pm 0.5\%$ of the estimated NPP. This is in agreement with those (1.1% and 1.2%) estimated for the Congo and Amazon river basins (Probst et al. 1994).

Conclusions

Based on direct observations, we calculated the mean yield of DOC exported from the Lanyang Hsi drainage area to be 4.1 \pm 0.7 gC/m²/yr, which is considerably higher than the DOC yield (0.1 gC/m²/yr) formerly estimated

for the Oceania. The observed DOC yield is only about 1/5 of the POC yield (22.2 \pm 5.7 gC/m²/yr), which comprises mostly of fossil POC. Assuming a mean fossil POC content of 0.5% in suspended sediments, we estimated the nonfossil POC yield at 4.6 \pm 3.0 gC/m²/yr, which is comparable to the DOC yield. Combining the DOC and nonfossil POC fluxes, we got a biogenic organic carbon yield of 8.7 \pm 3.1 gC/m²/yr. The DOC and nonfossil POC yields are similar to the average values for the tropical wet regions, and the exported fraction of NPP, 1.5 \pm 0.5%, is also similar to those (1.1–1.2%) obtained for other tropical river basins. In contrast to the extraordinarily high POC flux attributable to human perturbation in the Lanyang Hsi watershed, the export of biogenic organic carbon seems rather normal.

Acknowledgements

This paper benefits from constructive and encouraging comments from two anonymous reviews. This study was supported by grants (NSC 81-0209-M001-146, 82-0209-M001-146, 83-0209-M001-146) from the Natural Science Council of the Republic of China. We are grateful for the data provided by the Water Resources Planning Commission.

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