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Carbon and nitrogen isotopic compositions of particulate organic matter and biogeochemical processes in the eutrophic Danshuei Estuary in northern Taiwan

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Abstract

The Danshuei Estuary is distinctive for the relatively short residence time (1–2 d) of its estuarine water and the very high concentration of ammonia, which is the dominant species of dissolved inorganic nitrogen in the estuary, except near the river mouth. These characteristics make the dynamics of nitrogen cycling distinctively different from previously studied estuaries and result in unusual isotopic compositions of particulate nitrogen (PN). The $\delta^{15}N_{PN}$ values ranging from −16.4‰ to 3.8‰ lie in the lower end of nitrogen isotopic compositions (−16.4 to +18.7‰) of suspended particulate matter observed in estuaries, while the $\delta^{13}C$ values of particulate organic carbon (POC) and the C/N (organic carbon to nitrogen) ratios showed rather normal ranges from −25.5‰ to −19.0‰ and from 6.0 to 11.3, respectively. There were three major types of particulate organic matter (POM) in the estuary: natural terrigenous materials consisting mainly of soils and bedrock-derived sediments, anthropogenic wastes and autochthonous materials from the aquatic system. During the typhoon induced flood period in August 2000, the flux-weighted mean of $\delta^{13}C_{POC}$ values was −24.4‰, that of $\delta^{15}N_{PN}$ values was +2.3‰ and that of C/N ratio was 9.3. During non-typhoon periods, the concentration-weighted mean was −23.6‰ for $\delta^{13}C_{POC}$, −2.6‰ for $\delta^{15}N_{PN}$ and 8.0 for C/N ratio. From the distribution of $\delta^{15}N_{PN}$ values of highly polluted estuarine waters, we identified the waste-dominated samples and calculated their mean properties: $\delta^{13}C_{POC}$ value of −23.6±0.7‰, $\delta^{15}N_{PN}$ value of −3.0±0.1‰ and C/N ratio of 8.0±1.4. Using a three end-member mixing model based on $\delta^{15}N_{PN}$ values and C/N ratios, we calculated contributions of the three major allochthonous sources of POC, namely, wastes, soils and bedrock-derived sediments, to the estuary. Their contributions were, respectively, 83%, 12% and 5% under non-typhoon conditions, and 9%, 63% and 28% under typhoon conditions. The autochthonous POM had the most varied isotopic compositions, encompassing the full ranges of $\delta^{13}C_{POC}$ (−25.5 to −19.1‰), $\delta^{15}N_{PN}$ (−16.4–3.8‰) and C/N ratio (6.0–11.3). The heavy end of the carbon isotopic composition reflected the typical marine condition and the lower end the estuarine condition, which probably had elevated concentrations of dissolved inorganic carbon with low $\delta^{13}C$ values due to input from decomposition of organic matter. The lack of isotopically heavy PN, as found in larger estuaries, was attributed to isotopically light starting materials, namely, anthropogenic wastes, the slow phytoplankton growth within the estuary and the rather short residence time; the latter two factors made ^{15}N enrichment during ammonia consumption very limited. The most isotopically light

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PN likely originated from phytoplankton incorporating ^{15}N-depleted nitrate near the river mouth, where ammonia inhibition of nitrate uptake probably stopped.

1. Introduction

The Danshuei River (Fig. 1), also known as the Tamshui River, is the largest river in northern Taiwan, where the population density (2380 persons km^{-2}) is the highest in Taiwan. The high population brings a heavy loading of anthropogenic wastes to the river. Until 1990, a large fraction of sewage and surface runoff was discharged into the river with no or primitive treatment due to the inadequate sewer system. Although a sewage treatment plant with a planned capacity of 1.32 Mt d^{-1} was built in the 1990s, its operation never reached its goal because of flawed design and engineering problems (Lo, 2001). Consequently, the Danshuei Estuary is highly eutrophied and polluted (Wen et al., 2007). At some monitoring stations, the mean concentration of dissolved oxygen in surface water dropped to 97 μM, and mean total organic carbon loading rose to 500 μM, mean total nitrogen loading to 570 μM, and mean concentration of total dissolved copper to 60 mgL^{-1} (Sun and Peng, 2001).

The purpose of this study was to trace the origin of particulate organic matter (POM) in the Danshuei Estuary. POM is especially important in the estuarine system because of its capacity to carry trace metals and hydrophobic organic pollutants (Santschi et al., 1997; Ko and Baker, 2004), its high oxygen demand and its potential to release nutrient elements upon degradation. Carbon and nitrogen isotopes have long been used as indicators of different sources of organic matter in aquatic environments (Peters et al., 1978; Wada et al., 1987; Cifuentes et al., 1988; Kao and Liu, 2000; Sigleo and Macko, 2002). The combination of these isotopic signatures or the dual isotope composition has proven useful in differentiating the origins of POM in estuarine and coastal environments (Rau et al., 1981; Cifuentes et al., 1988; McClelland and Valiela, 1998). For this study, we try to understand the
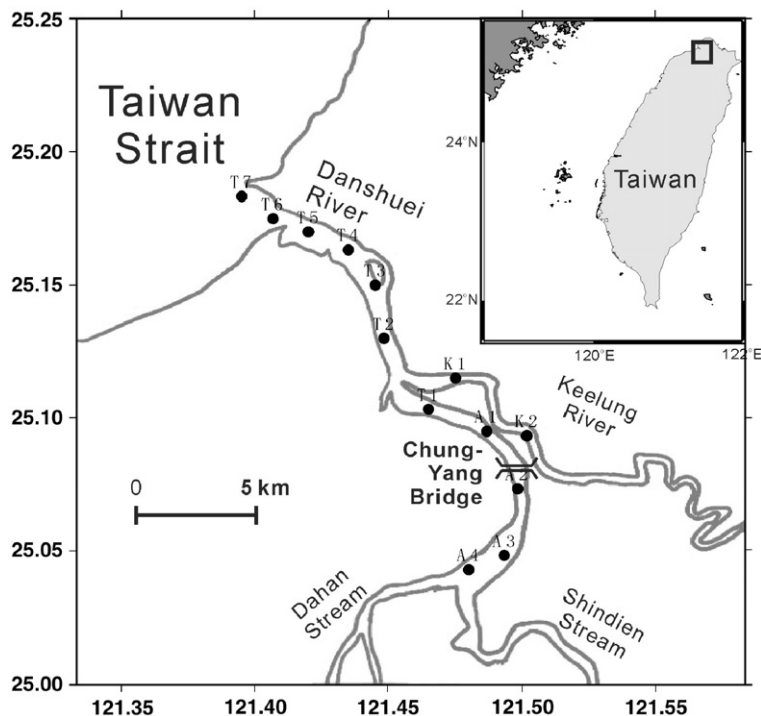

Fig. 1. Locations of sampling sites in the Danshuei Estuary, northern Taiwan.

biogeochemical processes that control the isotopic compositions and distinguish the highly polluted Danshuei Estuary from others. We also attempt to determine the contributions from major external sources of POM to the estuary using carbon and nitrogen isotopic compositions and geochemical characteristics.

2. Materials and methods

2.1. Sampling and area description

Samples were collected from the Danshuei Estuary (Fig. 1) on five occasions between August 2000 and March 2001 (Table 1) covering a wide range of flow conditions, from nearly base flow (March 2001) to flooding (August 2000). For the latter, water samples were collected during and after the invasion of Typhoon Bilis at the Chung-Yang Bridge (Fig. 1). A bucket was lowered from the bridge to collect the water sample 2–5 times every day during the period from 22 August to 24 August and once per day from 28–30 August. On other occasions (Wen et al., 2007), water samples were collected (Fig. 1) on board a small boat cruising in the Danshuei Estuary. Samples were collected using a peristaltic pump system equipped with Teflon tubing inlets and outlets. For sample collection, the tubing was attached to a nonmetallic pole and the tubing inlet oriented into the current at about 0.25 m depth. Prior to sample collection, the sampling system was flushed for 5 to 10 min at a flow rate of approximately 300 ml/min to remove any possible residuals in the tubing. Water column properties were measured with a multi-sensor CTD unit (Hydrolab DataSonde 911). The collected samples were stored in ice chests and returned to the laboratory prior to analysis. Two samples of sewage sludge were collected from the Dihua Waste Water Treatment Plant of Taipei City.

The Danshuei River has three major tributaries, the Dahan Stream, the Shindien Stream and the Keelung River (Fig. 1). The area of the drainage basin is 2,726 km^2, about 7.6% of the total area of Taiwan. The primary soils are Entisol and Inceptisol according to Soil Taxonomy (Soil-Survey-Staff, 1999). The underlying geology is dominated by argillite and slate with sandstone interbeds formed after the Oligocene (Ho, 1975). Montane forest covers about 93% of the watershed land area, agricultural land use comprises 5% and <1% belongs to residential areas and other man-made constructions, including roads.

The length of the main stem is 159 km. The mean annual discharge is 210 m^3 s^{-1}. The headlands of the watershed reach a maximum altitude of 3529 m. The area with altitude less than 250 m comprises approximately 1/3 of the total area; the flat area with altitude less than 20 m in the Taipei basin is only 243 km^2. The length of the tidal excursion along the main channel is about 30 km with a mean tidal range of 2.2 m (Liu et al., 2001). The depth in the lower reach (10 km from the river mouth) of the Danshuei Estuary varies mostly between 4 and 8 m. Due to the shallowness of the estuary, it is well mixed in most areas with the exception for a short section near Station T2 (Fig. 1), where the channel depth reaches 12 m and two layer circulation occurs (Wang et al., 2004). The residence time of the estuarine water was estimated to be only 1–2 d under the mean flow, while the fresh water flush time is about twice this value (Wang et al., 2004). The total population within the drainage basin is about 6.5 million, but the distribution is very uneven due to the hilly topography. The most densely populated region has a population density as high as 9684 km^{-2} in the Taipei Metropolitan area around the Danshuei Estuary. The mean temperature of the estuary water varies between 12 °C in winter and 30 °C in summer (http://wqshow.epa.gov.tw/). Diatoms are usually the most abundant taxonomic group in the entire Danshuei Estuary in every season, whereas the abundance of chlorophytes and cyanobacteria increases towards the upriver region (Wu and Chou, 2003).

2.2. Chemical analyses

Suspended particulate matter (SPM) was obtained by filtering 0.5 to 2 L of water through a Whatman® quartz filter, 47 mm in diameter with mean pore size of 2 μM, for each sample shortly after collection. The quartz filters were preheated at 500 °C in an oven for the removal of organic matter and wrapped in aluminum foil before use. After filtration, the filters were folded and wrapped again

Table 1
Sampling records

Date	Sites	No. of samples	Note
22–24 Aug. 2000	Chung-Yang Bridge	12	Typhoon, 2–5 times per day
28–30 Aug. 2000	Chung-Yang Bridge	3	Post-typhoon, daily
23 Sept. 2000	Along estuary	9	
11 Dec. 2000	Along estuary	16	8 during flood tide, 8 during ebb
17 Mar. 2001	Along estuary	22	11 during flood tide, 11 during ebb

Table 2
Summary of $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values and C/N ratios observed in the Danshuei Estuary

Localities	Types	$\delta^{13}C_{POC}$ (‰)	$\delta^{15}N_{PN}$ (‰)	C/N	Data sources
Danshuei river					
(Non-typhoon)	Estuarine SPM	−25.5 to −19.0 (−23.1)	−16.4 to 3.8 (−2.6)	6.0–11.3 (8.0)	1
(Typhoon)	Estuarine SPM	−24.9 to −23.8 (−24.4)	−2.7–3.0 (2.3)	5.6–11.3 (9.3)	2
Forth Estuary, Scotland	Estuarine sediments	−24.4 to −23.6	4.7–6.2	10–42	3
Schelde Estuary	Terrestrial end-member	−26.0	3.5	21.0	4
	Riverine end-member	−30.0	9.0	7.5	4
	Estuarine end-member	−29.0	15.0	8	4
	Marine end-member	−18.0	9.0	8.0	4
Tokachi River, Japan	Estuarine SPM	−28.8 to −25.2	0.4–4.0	6.0–12.2	5
Delaware Estuary, USA	Estuarine SPM	−25.8 to −16.4	3.7–18.7	5–18	6
Potomac River, USA	Estuarine SPM	−27.5 to −18.4	3.1–12.6	7–12	7
Brantas River, Java, Indonesia	Estuarine SPM	−28.9 to −19.6	−2.3–10	6.4–12.7	8

Values in the parentheses are averages weighted by concentration under non-typhoon conditions or by flux under typhoon conditions. Observations from six other estuaries are also listed for comparison. C/N is the atomic ratio.
1. This study. 2. Chen et al. (2001). 3. Middelburg and Nieuwenhuize (1998). 4. Graham et al. (2001). 5. Usui et al. (2006). 6. Cifuentes et al. (1988).
7. Sigleo and Macko (2002). 8. Jennerjahn et al. (2004).

in aluminum foil and stored in a freezer until analysis. The filtrate was stored in 100 mL polypropylene sample bottles, which were kept in an ice chest for chemical analyses performed immediately after sampling except those collected in August 2000; on that occasion, the filtrates were frozen in liquid nitrogen for later analyses.

Nutrients, including nitrate, nitrite, ammonia, phosphate and silicate were analyzed in the shore-based laboratory at the National Center for Ocean Research. Frozen samples were thawed under tap water. Nitrate and nitrite were analyzed by the standard pink azo dye method adapted for flow injection analyzer (Pai et al., 1990b); ammonium by an improved indophenol blue method (Pai et al., 2001); phosphate and silicate by the standard molybdenum blue method with a flow injection analyzer (Pai et al., 1990a). The precision of the analyses was ±0.3 μM for nitrate and nitrite, ±0.5 μM for ammonia, ±0.05 μM for phosphate and ±0.5 μM for silicate. It is noted that ammonia was analyzed only on samples collected in December 2000 and March 2001.

Chl-a samples were obtained by filtering two liters of waters through GF/F filters (Whatman®, 47 mm) and stored at −20 °C. The phytoplankton pigments retained on GF/F filters were extracted in 90% acetone (Strickland and Parsons, 1972). The Chl-a concentrations in the extracts were measured with a fluorometer (Turner 10-AU-005).

2.3. Isotopic analyses

The filters bearing SPM were dried at 70 °C in an oven, and then acidified with 1 ml of 1N solution of reagent grade HCl for the removal of carbonate. The sewage sludge samples were freeze-dried. About 0.2 g of the freeze-dried samples was treated with 15 ml 1N

HCl for 2 d in pre-combusted (500 °C) glass test-tubes and then centrifuged for removal of solution. The acid-treated samples were dried at 60 °C in an oven for 48 h. The dried samples were processed for the preparation of carbon and nitrogen isotope samples by means of the sealed tube combustion method (Wedeking et al., 1983), followed by gas purification for mass spectrometric analysis. Because inorganic carbon is effectively removed from the solid samples in the pretreatment, the carbon analyzed is referred to as particulate organic carbon (POC) in this study. By contrast, the inorganic nitrogen that may exist in mineral phases of the SPM, albeit in minute amounts, cannot be effectively removed; therefore, the nitrogen analyzed is referred to as particulate nitrogen (PN) in this study.

Each of the decarbonated samples was mixed with 1 g each of CuO and Cu pellets and several inches of silver wire, and then sealed in an evacuated 9-mm quartz tube. Sealed quartz tubes were then heated at 900 °C for 3 h, kept at 650 °C for over 12 h, and cooled to room temperature. N_2 and CO_2 gases were extracted and purified by cryogenic traps in a vacuum line and collected in sealed 6-mm glass tubes. The abundances of carbon and nitrogen were measured manometrically in the vacuum line. This method had been crosschecked previously by Leco® Carbon Analyzer and gave consistent results with a relative standard deviation less than 5% (Chang et al., 1991). Carbon and nitrogen isotopic compositions were determined in a Micromass VG602E mass spectrometer. Results are presented in the standard δ notation with respect to standards of atmospheric nitrogen and Peedee Belemnite (PDB) carbon for $\delta^{15}N$ and $\delta^{13}C$, respectively. The precision of nitrogen and carbon isotopic determination was better

than ±0.2‰ as determined from repeated measurements of a working standard, the reagent grade histidine.

3. Results

All sampling stations are within the tidal reach of the estuary. During the sampling occasions, except the typhoon period in August 2000, the salinity front with 50% seawater in the surface water fluctuated between Station T5 at ebb tide and Station T1 at flood tide (Fig. 1). The mean water temperature was 22.3±0.5 °C in September 2000, 19.9±1.0 °C in December 2000 and

20.2±0.7 °C in March 2001 (http://wqshow.epa.gov.tw/). We first report results obtained on non-typhoon occasions as the "normal" condition, and then report those obtained under typhoon and post-typhoon conditions, which have been partially covered by Chen et al. (2001). The $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values and C/N (organic carbon to nitrogen) ratios of SPM are summarized in Table 2.

3.1. Non-typhoon conditions

In order to focus on the biogeochemical processes controlling nutrient dynamics and isotopic compositions,
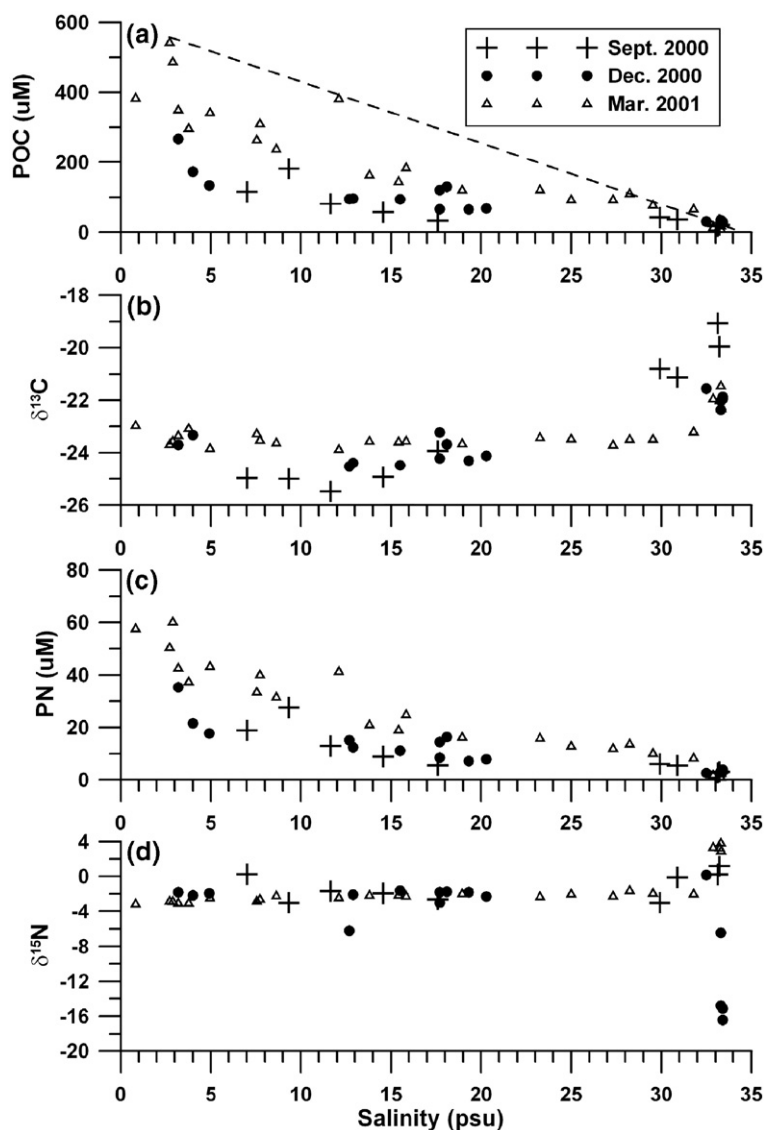

Fig. 2. Properties of suspended particulate matter vs. salinity observed on the three non-typhoon occasions in the Danshuei Estuary. The dashed line is the conservative mixing line for POC in March 2001. (a) For POC concentrations. (b) For $\delta^{13}C_{POC}$ values. (c) Same as Fig. 2a except for PN concentrations. (d) Same as Fig. 2b except for $\delta^{15}N_{PN}$ values.

we report the results of our measurements versus salinity rather than describing the complicated spatial and temporal variations. The POC concentration decreased gradually with increasing salinity towards the river mouth from the peak values around 266–540 μM at the uppermost stations (Fig. 2a). It is obvious that most POC data points fall significantly below the mixing curve, suggesting removal of POC within the estuary. In contrast to the nearly monotonous decrease of POC concentration with increasing salinity, its carbon isotopic composition (Fig. 2b) remained fairly constant with most $\delta^{13}C_{POC}$ value within a narrow range of −25 to −23‰ before salinity reaching 30; beyond that, the $\delta^{13}C_{POC}$ increased abruptly reaching

values as high as −19‰. The variation of PN concentration (Fig. 2c) was quite similar to that of POC concentration with the highest value around 60 μM, and its isotopic composition (Fig. 2d) also remained invariant, mostly between $\delta^{15}N_{PN}$ values of −4 and −2‰, for salinity below 30. Rather than showing an abrupt increase like $\delta^{13}C$ values of POC for salinity above 30, the $\delta^{15}N_{PN}$ value diverged in both directions. The sewage sludge samples displayed $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ ranges of −24.9 to −24.7‰ and 2–3‰, respectively, well within the isotopic composition ranges of the SPM.

Contrary to the rather similar distribution patterns of POC and PN observed on different sampling occasions,
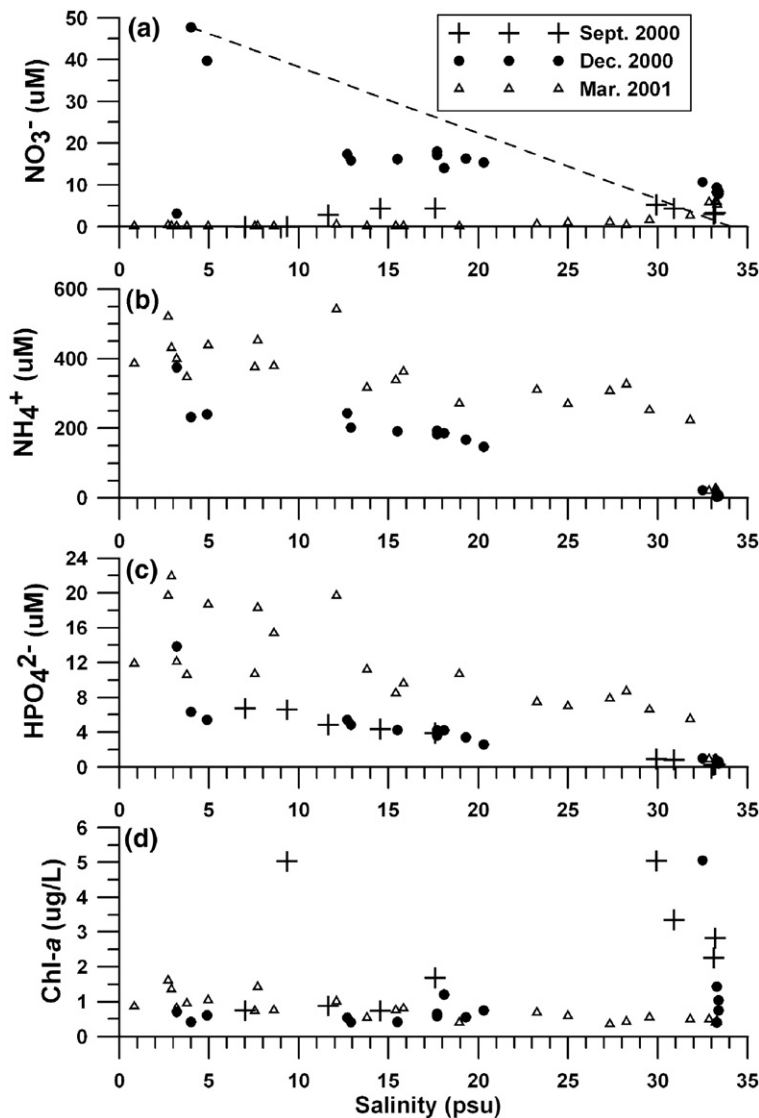

Fig. 3. Same as Fig. 2 except for nutrients and Chl-a concentrations. The dashed line is the conservative mixing line for nitrate in December 2000. (a) Nitrate. (b) Ammonia. (c) Phosphate. (d) Chl-a. It is noted that ammonia was not analyzed on the samples collected in September 2000.

the variation of different species of dissolved inorganic nitrogen across the salinity gradient changed drastically on different occasions (Fig. 3). In most cases ammonia was the dominant species of dissolved inorganic nitrogen (DIN) with an observed maximum concentration of 542 μM (Fig. 3b). Nitrate was usually the second most abundant species of DIN (Fig. 3a), but nitrite concentrations (not shown) exceeded those of nitrate for salinity lower than 18 in September 2000. It is noted that nitrate concentrations in December 2000 were much higher than those observed on the other two occasions (Fig. 3a), but the sample with the lowest salinity had a rather low nitrate concentration, resembling those from the other two occasions. The abrupt change in nitrate concentration suggests multiple sources of nutrients to the estuary, which are worth of exploring. A mixing line (Fig. 3a) is drawn to depict the conservative mixing between the nitrate-rich estuarine water and the coastal surface seawater with a salinity of 34 and nearly no nitrate (Gong et al., 1995). Nitrate deficit in the mid salinity waters indicates removal of nitrate, but nitrate excess in the high salinity waters suggests nitrification occurring near the river mouth. Slight increases of nitrate in the high salinity waters occurred in September 2000 and March 2001 (Fig. 3a), also indicating occurrences of nitrification.

The phosphate concentration (Fig. 3c) showed a similar distribution pattern as that of ammonia. The Chl-a concentration (Fig. 3d) stayed at relatively low values of less than 2 μg/L for all samples with salinity less than 30 except one. The low Chl-a concentrations in the presence of so much nutrients suggest that the short residence time of the estuarine water did not allow the phytoplankton to grow before they were flushed out of the estuary. A similar situation also occurs in the fast flushed Tweed Estuary, England (Uncles et al., 2000). Near the river mouth Chl-a increased abruptly up to 5 μg/L for salinity above 30, resembling the increases of $\delta^{13}C_{POC}$ values. The concurrence of the changes suggests that the ^{13}C-enriched POC and the significant Chl-a increments near the river mouth are closely related. This is to be discussed later. It is worth noting that most of the higher Chl-a concentrations were observed in September 2000, the first sampling occasion after the typhoon flood, suggesting the relatively fresh conditions favored phytoplankton growth.

3.2. Typhoon and post-typhoon conditions

Geochemical variations of the river water under typhoon and post-typhoon conditions have been described in detail (Chen et al., 2001) and are only briefly

presented here. The peak concentrations of POC (4325 μM) and PN (420 μM) corresponded to the peak flow of 3000 m^3 s^{-1}. The positive correlation (Chen et al., 2001) between discharge rate and POC concentration is indicated by the high R^2 value of 0.87; a similar correlation is evident for PN with R^2 value of 0.88.

The carbon isotopic composition of POC fluctuated between δ^{13}C values of −25‰ and −24‰ with no clear trend. By contrast, the $\delta^{15}N_{PN}$ value increased sharply from −2.5‰ to +3‰ as PN concentration increased abruptly responding to the flood. When the flood subsided, the relatively high $\delta^{15}N_{PN}$ value persisted for 1 d and then dropped slightly to +2‰ and remained nearly constant in the post-typhoon condition. Both POC and PN concentrations dropped dramatically after the peak flow, but stayed at levels of 400–1400 μM for POC
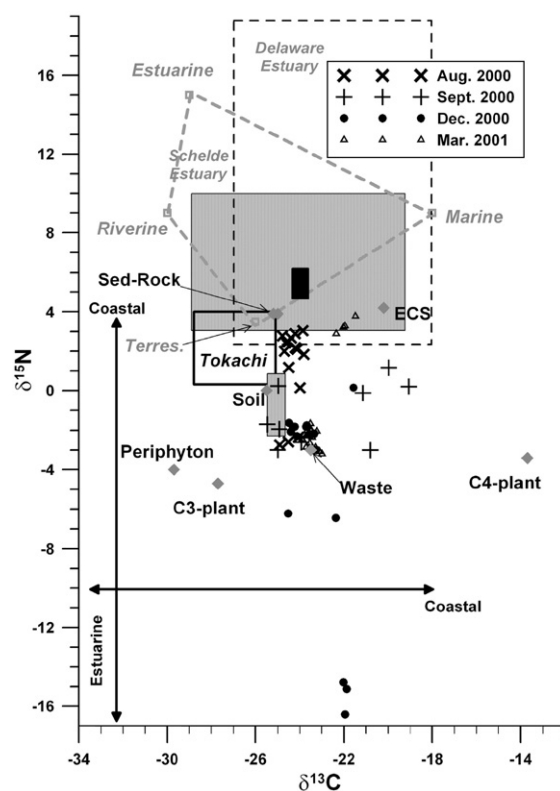

Fig. 4. Plot of $\delta^{15}N_{PN}$ vs. $\delta^{13}C_{POC}$ observed in the Danshuei Estuary. Also plotted are potential end-members (gray diamonds) of organic matter listed in Table 3. (ECS stands for East China Sea.) The two thick lines with arrows indicate the range of δ^{13}C and δ^{15}N values that may be acquired by the newly produced POM in the estuary-coastal zone continuum. For comparison, observed ranges from other estuaries are plotted as the polygon and rectangles (Table 2). Three sites are labeled. The unlabeled are the Forth Estuary (solid black rectangle) and the Brantas River (shaded rectangles); the latter displayed two distinctive areas of data distribution (see text). The open squares at the corners of the dashed polygon represent the four end-members found for the Schelde Estuary.

Table 3
Carbon and nitrogen isotopic and elemental compositions of potential sources of POM in the Danshuei Estuary

Localities	Sample types	$\delta^{13}C_{POC}$ (‰)	$\delta^{15}N_{PN}$ (‰)	C/N	Data sources
Northern Taiwan	Terrestrial plants (C3)	-27.7 ± 1.7	-4.7 ± 1.2	35.3 ± 8.9	1
Northern Taiwan	Terrestrial plants (C4)	-13.7 ± 1.1	-3.4 ± 1.1	36.6 ± 0.6	1
Northern Taiwan	Aquatic plants	-29.7 ± 2.5	-3.97 ± 0.4	13.3 ± 2.0	1
Northern Taiwan	Bedrocks	-25.0 ± 0.2	3.9 ± 0.1	5.8 ± 0.5	1
Northern Taiwan	River sediments	-25.2 ± 0.2	3.9 ± 0.1 (3.9)	5.8 ± 0.5 (6.2)	1
Northern Taiwan	Soils	-25.5 ± 1.3	-0.0 ± 1.3 (1.25)	13.6 ± 4.5 (14.25)	1
East China Sea	Marine SPM	-20.2 ± 1.5	4.2 ± 1.0	8.0 ± 0.3	2
Danshuei River, Taiwan	Anthropogenic wastes	-23.6 ± 0.7	-3.0 ± 0.1 (-3.0)	8.0 ± 1.4 (7.5)	3
Dihua Waste Water Treatment Plant, Taipei	Sludge	-24.8 ± 0.1	2.5 ± 0.7		3
Tay Estuary, Scotland	Sewage	-26.7	2.3	12.57	4
Deer Island, MA, USA	Effluent POM		$1.1–3.3$		5, 6
Providence, RI, USA	Sludge	-23.7			
NY Bight, USA	Sludge	-26.0			7
Yonkers, NY, USA Sludge	Sludge	-21.4	7.2		7
Middlesex, NJ, USA Sludge	Sludge	-24.7	-1.1		7
Bergen, NJ, USA Sludge	Sludge	-23.2	6.1		7
Whites Point, Calif., USA	Sludge	-23.5 to -16.5	1.8 to 2.5		8–10
Hunts Bay, Jamaica	Sewage	-24.8 ± 3.2		12.5 ± 1.0	11

The compositions of the end-members for the model calculation are shown in parentheses. Also listed are compositions of sewage-derived organics from nine other coastal areas. C/N is the atomic ratio.
1. Kao and Liu (2000). 2. Chen et al. (2001). 3. This study. 4. Thornton and McManus (1994). 5. Tucker et al. (1999). 6. Hunt et al. (1995). 7. van Dover et al. (1992). 8. Meyers (1974). 9. Sweeney et al. (1980). 10. Spies et al. (1989). 11. Andrews et al. (1998).

and 75–140 for PN. These levels were generally higher than the normal range of 500 µM or less for POC and 70 µM or less for PN, while the discharge rate fluctuated between 500 and 1000 m^3/s (Chen et al., 2001), which were 2–5 times above the mean level.

Using the hourly discharge rate recorded during the typhoon period, Chen et al. (2001) constructed rating curves for POC and PN as well as for carbon and nitrogen isotopes. The flux weighted mean of $\delta^{13}C_{POC}$ values was found to be -24.4‰ and that of $\delta^{15}N_{PN}$ values was $+2.3$‰. The dual isotope composition fell between the mean compositions of soils and sediments (Fig. 4), suggesting these end-members to be the main sources of POC and PN during flood conditions. Since the sediments analyzed by Kao and Liu (2000) had the same mean isotopic composition as the bedrocks (Table 3), they are referred to as the bedrock-derived sediments.

4. Discussion

The origin of organic matter may be traced through geochemical characteristics, such as C/N ratio and isotopic compositions (Table 2). Observations from other estuarine systems are shown for comparison (Table 2 and Fig. 4). The geochemical characteristics of potential end-members from the watershed–river–estuary system are shown in Table 3 as references. In addition to the known end-members, we discuss other possible sources of organic materials and the processes

that may be responsible for the geochemical characteristics of these source materials.

4.1. Geochemical characteristics

Geochemical characteristics of POC and PN observed in the Danshuei Estuary are discussed for the purpose of delineating their origins.

4.1.1. C/N ratio

The POC and PN concentrations are highly correlated as observed throughout this study. Although the ranges of C/N ratio observed in individual samples obtained during non-typhoon and typhoon periods are nearly identical (Table 2), the slopes of regression analyses differ considerably. Under non-typhoon conditions, the overall regression equation for concentration in units of µM is as follows:

$$PN = 0.117\pm0.004*POC + 1.4\pm0.7 \qquad (1)$$
$$R^2 = 0.96$$

The C/N ratio, which is the reciprocal of the slope, is 8.5 ± 0.3. For samples from typhoon and post-typhoon periods, the regression equation is

$$PN = 0.0919\pm0.003*POC + 15.9\pm5.2, \qquad (2)$$
$$R^2 = 0.988$$
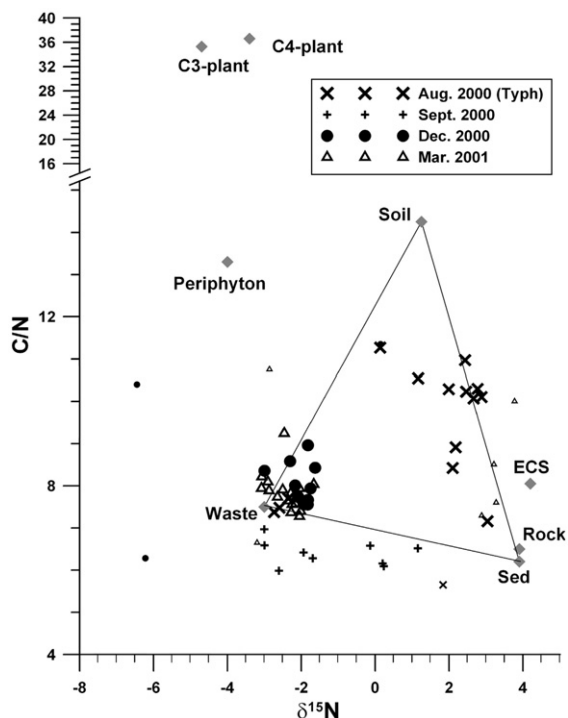
Fig. 5. Same as Fig. 5 except for C/N ratio vs. $\delta^{15}N_{PN}$ value. The triangle represents the field covered by the mixing of the three major allochthonous POM end-members, for which a 3 component mixing model was developed. The normal sized symbols represent the allochthonous POM dominated samples that allowed calculation of end-member contributions, while the smaller symbols, including all samples from September 2000, represent those, which did not allow the model calculation due to significant contribution of autochthonous POM or from other sources (see text). The horizontal axis does not cover the lowest part of the $\delta^{15}N_{PN}$ range (−16.4 to −8‰) occupied by only four samples.

The C/N ratio corresponding to the slope is 10.9 ± 0.3. The difference suggests that the changes in POM concentration were attributed to different types of organic matter under typhoon and non-typhoon conditions.

During the typhoon period, the elevated POM concentration with higher C/N ratio was probably attributed to additional input of soils, which had an average C/N ratio of 13.6 ± 4.5 (Table 3), from the upstream catchment. The low C/N ratios observed during non-typhoon periods resemble the aquatic end-members reported for the Schelde Estuary between the Netherlands and Belgium (Middelburg and Nieuwenhuize, 1998), but the isotopic signatures of POC and PN from the two estuaries are quite different (Table 2) and warrant further discussion to be given in following sections.

4.1.2. Isotopic compositions

The carbon and nitrogen isotopic compositions of POC and PN observed in the Danshuei Estuary are presented in

the dual-isotope plot of $\delta^{13}C$ vs. $\delta^{15}N$ (Fig. 4). The six types of organic source materials observed in the Lanyang Hsi watershed and the adjacent Fu-Shan Natural Preserve, which is located in one of the headlands of the Danshuei River watershed (Kao and Liu, 2000), are potential terrestrial sources. The POM obtained from the southern East China Sea (Chen et al., 2001) represents the potential marine end-member, which is to be discussed in Section 4.3.2. Their compositions are listed in Table 3 and plotted in Fig. 4.

The seven potential end-members cover almost the entire dual-isotope field occupied by the SPM samples of the Danshuei Estuary except the few samples with the unusually low $\delta^{15}N_{PN}$ values (<-6‰), suggesting that these end-members could be significant in this study area. The dual isotope composition of POC–PN obtained during the typhoon and post-typhoon periods extended from the region of non-typhoon samples towards the compositions of soils and bedrock-derived sediments (Fig. 4). During and after the peak flow, the POC–PN compositions fell between soil and bedrock-derived sediments, suggesting that they are the primary sources of SPM during typhoon floods. This is consistent with previous findings (Kao and Liu, 2000).

However, the plot of C/N ratio vs. $\delta^{15}N$ reveals quite a different picture (Fig. 5). It is difficult to account for the observed compositional variation in the C/N-$\delta^{15}N_{PN}$ field in the Danshuei Estuary with the afore-mentioned end-members. More than 2/3 of the data points fell out of the field defined by the potential end-members. Although the plants, including periphyton, may provide isotopically light organic nitrogen to the system, their C/N ratios, 13–38, are much higher than the estuarine POM. Hence, their contributions are probably not significant. An end-member with $\delta^{15}N_{PN}$ value similar to the plants but lower C/N ratio is required to account for the majority of the observations. The samples with unusually low $\delta^{15}N_{PN}$ values, down to −16.4‰, pose an even greater problem. The presence of

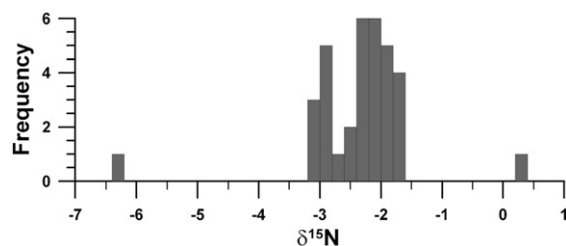Fig. 6. Frequency of occurrences of $\delta^{15}N_{PN}$ values among samples with phosphate concentration above 2.5 μM. The range of lowest $\delta^{15}N_{PN}$ values with high occurring frequencies around −3‰ is considered representative of anthropogenic wastes. (see text).

the ^{15}N depleted SPM in the Danshuei Estuary is worthy of attention.

4.2. Comparison with other estuaries

Observations from six other estuaries, ranging from the tropics (Brantas River, Java) to the cold temperate (Forth Estuary, Scotland), are included for the comparison (Table 2 and Fig. 4). In the Delaware Estuary, USA the isotopic compositions of POM cover the $\delta^{13}C_{POC}$ ranges of −26 to −16.4‰ and the $\delta^{15}N_{PN}$ range of 2.3 to 18.7‰ (Cifuentes et al., 1988). Less than 1/6 of the data points from the Danshuei Estuary fell within this domain (Fig. 4).

Middelburg and Nieuwenhuize (1998) proposed four end-members of organic source materials for the Schelde Estuary, including riverine and estuarine end-members in addition to the traditional terrestrial and marine end-members (Peters et al., 1978). Aside from the terrestrial end-member, the isotopic compositions of other end-members for the POM found in the Schelde Estuary are far from the observed dual-isotopic field in the Danshuei Estuary (Fig. 4). In fact, there is no overlapping between the dual isotope field defined by the four end-members of the Schelde Estuary and our observations.

Most $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ values observed in other estuaries fall within the domains of the two afore-mentioned estuaries, which also show considerable over-lapping. The observations in the Potomac River, USA (Sigleo and Macko, 2002) overlap considerably with the two, and, therefore, are not plotted for clarity of the figure. The only exceptions are data from the Tokachi River, Japan (Usui et al., 2006) and a few sites from the Brantas River, Java, Indonesia (Jennerjahn et al., 2004). The observed $\delta^{13}C_{POC}$ values from these sites lie in the low end of the full range and the $\delta^{15}N_{PN}$ values are considerably lower than the majority, but similar to our observations.

At the Wonokromo Stations 1 II and 2 II of the Brantas River, the rather low $\delta^{15}N_{PN}$ values (−2.3–0.9‰) were attributed to nitrogen fixation performed by cyanobac-teria, which were the dominant group of phytoplankton (Jennerjahn et al., 2004). However, the environmental conditions of these sites were characterized by low salinity (0.3–2.4 psu), high nitrate (98–118 μM) and low ammonium (0.1–0.2 μM), which were very different from the conditions of the Danshuei Estuary. In addition, the low $\delta^{15}N_{PN}$ values occurred only at a few sites in the Brantas River, while such values occurred throughout the Danshuei Estuary. It seems unlikely that the same process was responsible for the very low values $\delta^{15}N_{PN}$ observed in the Danshuei Estuary, because the very high ammo-nium concentration would inhibit nitrogen fixation. The relatively low $\delta^{15}N_{PN}$ values observed in the Tokachi

River, Japan overlap considerably with those observed in the Danshuei Estuary, but no explanation was given by the authors (Usui et al., 2006).

4.3. Organic source materials

The foregoing discussion has illustrated that the geochemical characteristics of POC and PN in the Danshuei Estuary cannot be readily explained by the currently known natural sources of organic matter in northern Taiwan. Observations in other estuaries do not shed much light, either. Here we explore other possibilities.

4.3.1. Anthropogenic wastes

In the urbanized watershed, anthropogenic wastes are a major source of organic matter and nutrients (e.g., Sweeney et al., 1980; Tucker et al., 1999). In view of the very high concentration of dissolved inorganic nitrogen, especially in the Danshuei Estuary one expects anthropogenic wastes as a major end-member of POM. Nitrogen loading is a good indicator of anthropogenic wastes (Cole et al., 1993). Very good positive correlation is found between total loading of nitrogen and phosphate concentration in the Danshuei Estuary. For phosphate concentration above 2.5 μM, the total nitrogen concen-tration increased abruptly, suggesting a strong loading of anthropogenic waste-derived materials. Because ammo-nia was not analyzed for all samples but phosphate was, we use the phosphate concentration to indicate samples with severe pollution of anthropogenic wastes.

Analysis of occurrence frequencies of $\delta^{15}N_{PN}$ values in water samples with phosphate above 2.5 μM (Fig. 6) indicates that most values fell within the range of −3.2 to −1.6‰ with a bimodal distribution. It is hypothesized that the population ($n=8$) with the lower $\delta^{15}N_{PN}$ values, between −3.2 and −2.8‰, represents materials derived mainly from anthropogenic wastes. The mean $\delta^{15}N_{PN}$ value of the population weighted by PN concentration is −3.0‰; the population's weighted mean of $\delta^{13}C_{POC}$ value is −23.5‰ and that of C/N ratio is 8.2. The inferred composition of the anthropogenic waste-derived organic matter is different from that of the sewage sludge samples collected from the Dihua Waste Water Treatment Plant (Table 3). It is suspected that the sewage sludge samples may not be representative. These samples displayed isotopic compositions between those of the bedrock-derived sediments and soil suggesting that they may represent the recalcitrant fraction of the sewage. The contribution of the treated sewage sludge to the SPM in the estuary is probably not important, because of the setback of waste water treatment in the greater Taipei metropolis (Lo, 2004).

The isotopic and elemental compositions of sewage-derived organic matter from 9 other localities are listed for comparison (Table 3). The $\delta^{13}C$ value of the inferred anthropogenic end-member falls well within the range of previously reported values (−26.7 to −16.5‰), whereas its $\delta^{15}N$ value is lower than all the rest, but not much lower than some values (−1.1–1.1‰) reported for sewage sludge from the east coast of the USA (Table 3).

4.3.2. Autochthonous POM

In the Schelde Estuary, algal production is an important source of POM in the river-estuary-coastal zone system (Middelburg and Nieuwenhuize, 1998). Similar process may also happen in the Danshuei Estuary, but the autochthonous POM may not be as significant due to the short residence time of the estuarine water of 1–2 d (Wang et al., 2004). The residence time of the river water above the tidal reach is probably equally short or even shorter (M.-S. Li, personal communication), because the main channel of the Danshuei River is very steep, with a mean slope of 1/45. Consequently, the algal growth before river water enters the estuary is probably very limited. We may assume that most autochthonous POM is produced either in the estuary or in the coastal zone outside the estuary.

The POM collected in the continental shelf north of Taiwan showed considerable variation in carbon and nitrogen isotopic compositions with $\delta^{13}C_{POC}$ ranging

from −24.4 to −19.1‰ and $\delta^{15}N_{PN}$ values ranging from −2.3 to 4.9‰ (Chen et al., 2001), but the two samples with the highest Chl-a concentrations (≥ 1 mg m^{-3}) showed rather consistent $\delta^{13}C_{POC}$ values of −21.2 to −19.1‰ and $\delta^{15}N_{PN}$ values of 3.5–4.9‰. The mean $\delta^{13}C$ value is very close to that of phytoplankton (−20.1±1.8‰) observed in the Otsuchi Bay, Japan (Wada et al, 1984). The mean $\delta^{15}N_{PN}$ value is very close to that of nitrate, $4.7 \pm 0.6‰$, in the Kuroshio upwelling water, which is the main nutrient source to the East China Sea (Liu et al., 1996; Gong et al., 1996). Hence, the mean isotope compositions may represent the marine end-member (Table 3).

Following the approach of Cifuentes et al. (1988), we use the Chl-a to POC ratio to distinguish samples dominated by freshly produced POM from the rest (Fig. 7). The freshly produced POM has Chl-a/POC ratio greater than 1/200 or 5 μg mg^{-1}. It is noted that all freshly produced POM should be autochthonous, but autochthonous POM may not all be fresh. It is shown later that some autochthonous POM have slightly lower Chl-a/POC ratio.

All samples with the ratio greater than 5 μg mg^{-1} had the highest $\delta^{13}C_{POC}$ values (as indicated in Section 3.1), implying the ^{13}C-enriched POC was newly produced. Most $\delta^{15}N$ values of the freshly produced POM fell above the background level. This suggests that the main nitrogen source of the phytoplankton growing in the estuary was a nitrogen source more enriched in ^{15}N than the ammonia regenerated from anthropogenic wastes.
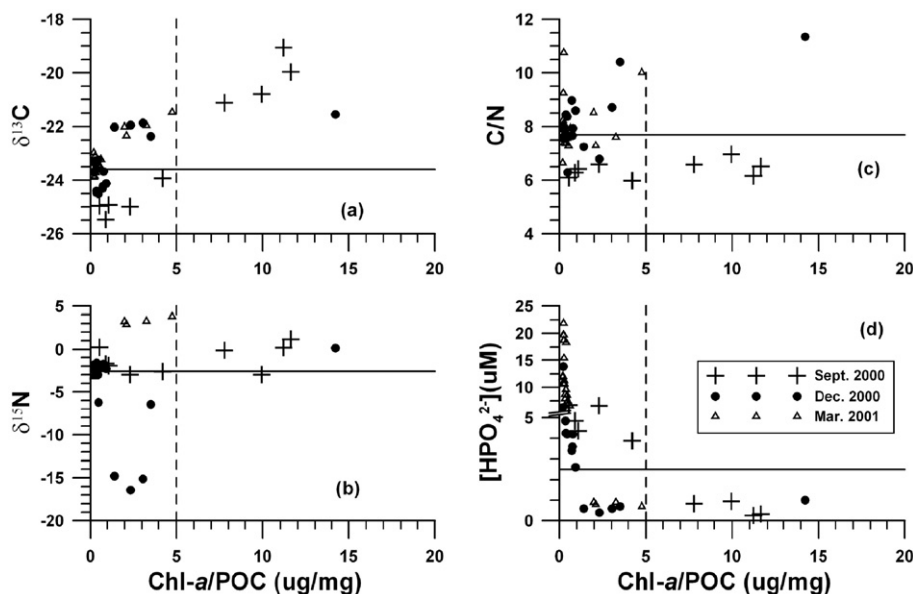

Fig. 7. Properties of estuarine water samples vs. the Chl-a/POC ratio. Samples with the Chl-a/POC ratio above 5 μg mg^{-1} are considered as containing high fraction of freshly produced POM. (a) $\delta^{13}C$ value. (b) $\delta^{15}N$ value, (c) C/N ratio and (d) phosphate concentration. The horizontal line represents the weighted mean in the first three panels; for panel (d), it represents the phosphate concentration (2.5 μM) distinguishing the highly polluted waters from the rest (see text).

This is to be discussed later. By contrast, the C/N ratio (6.0–10.8) of the freshly produced POM covers almost the entire range of observed C/N ratios (Table 2). It is interesting to note that those data points from September 2000 all fell on the lowest level of C/N ratio between 6.0 and 7.0, whereas the two data points from the other two sampling occasions were the highest, suggesting different classes of phytoplankton with different C/N ratios thriving under different estuarine conditions.

4.3.3. Factors affecting the isotopic composition of autochthonous POC

It is noteworthy that both the highest (−19.0‰) and the lowest (−25.5‰) $\delta^{13}C_{POC}$ value occurred in September 2000. The highest value occurred in waters with highest salinity, whereas the lowest value occurred in

the mid salinity of about 12 (Fig. 2b). This trend is worth discussion.

The carbon isotopic composition of phytoplankton produced POM is controlled (Rau et al., 1996; Barth et al., 1998) by that of the starting material and by isotope effect during photosynthesis. The isotope effect has been found to be controlled mainly by the isotope fractionation during carbon fixation and the diffusive process from the ambient aqueous medium, which is mainly controlled by the ambient concentration of dissolved CO_2 (Rau et al., 1996). The higher $[CO_2]_{aq}$ is, the stronger the fractionation gets. The overall isotope fractionation between the phytoplankton produced POM and DIC ranges from −18‰ to −35‰ in aquatic environments (Hofmann et al., 2000, Lehmann et al., 2004) with most values around −20‰. In other words, the phytoplankton POC is isotopically lighter than
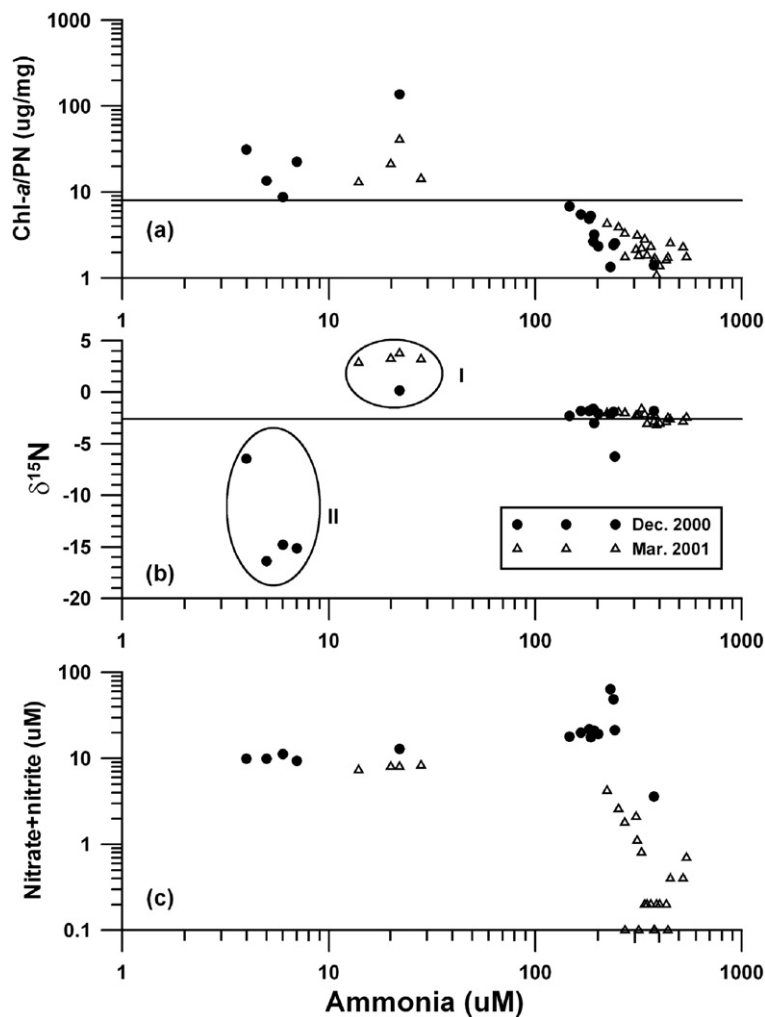

Fig. 8. Properties of estuarine water samples vs. the ammonium concentration. (a) Chl-a/PN ratio., (b) $\delta^{15}N$ value. (c) concentration of nitrate plus nitrite. The sudden drop of $\delta^{15}N$ values for ammonia concentration less than 7.5 µM suggests switch of nitrogen uptake from ammonia to nitrate or nitrite by phytoplankton.

the ambient DIC by about 20‰ on average with variability depending on local conditions.

Sheu et al. (1996) found DIC concentrations between 1900 and 2050 μMol kg^{-1} with $\delta^{13}C$ values around +0.25‰ in the surface water near Taiwan. The POM produced from such ambient DIC would have a $\delta^{13}C$ value around −19.7‰, which is close to the upper limit of the $\delta^{13}C$ values observed at the highest salinity in the Danshuei Estuary (Fig. 2b). The much lower $\delta^{13}C_{POC}$ values found at lower salinity may be attributed to two major factors: the high concentration and the low $\delta^{13}C$ value of ambient dissolved CO_2. The water with lower salinity had higher concentrations of ammonia and phosphate (Fig. 3b, c), and probably also higher DIC concentration due to mineralization of anthropogenic wastes. Sheu et al. (1996) reported $\delta^{13}C$ values of DIC in Taiwanese river waters mostly between −7 and −5‰, which were lower than the surface seawater due to decomposition of isotopically light POC. It is likely that the DIC in the Danshuei Estuary had similarly low $\delta^{13}C$ values.

The most negative $\delta^{13}C_{POC}$ value observed was −25.5‰, which occurred in the estuarine water with Chl-a/POC ratio of 1 μg mg^{-1}. The bulk POC is a mixture of the autochthonous POC and the background material, which may have a $\delta^{13}C$ value close to the mean of allochthonous POC, −23.7‰.. Derivation of this value is to be shown later. If the phytoplankton produced POM has a Chl-a/POC ratio of 5 μg mg^{-1}, a simple mixing relation suggests that this sample contains only 20% of phytoplankton produced POM. Using the same relation we calculated the $\delta^{13}C$ value of phytoplankton produced POC to be −32.7‰. Similarly low $\delta^{13}C$ value (−31.5‰) was observed in the nearshore environment of the St. Lawrence River, where the $\delta^{13}C$ value of DIC reached as low as −13‰ (Barth et al., 1998).

In contrast to the rather wide range of $\delta^{13}C_{POC}$ values occurring in September 2000, the ranges observed on the other two occasions were considerably narrower, with limited expansion away from the background level (Figs. 2b and 7a). The narrower ranges seemed to indicate the stronger background signal contributed by soils, bed-rock derived sediments and wastes, which all have similar $\delta^{13}C$ values (Table 3). However, this could also result from smaller isotope effect during photosynthesis, probably manifested by a different dominant class of phytoplankton, as suggested by the much higher C/N ratio (Fig. 7c). Further study is needed to verify this notion.

4.3.4. Nitrogen uptake and isotope fractionation

The isotopic compositions of PN observed in the Danshuei Estuary cover a wide range of $\delta^{15}N$ values

from −16.4 to +3.8‰. As mentioned in Section 4.3.2, most freshly produced POM had $\delta^{15}N$ values higher than the background level. This enrichment of ^{15}N in the phytoplankton needs an explanation. On the other hand, the very negative lower limit is much lower than those observed in other estuaries (Table 2). A similarly low $\delta^{15}N_{PN}$ value, down to −5‰, was observed in the outflow region of the Lanyang Hsi in the northeastern Taiwan (Hsueh, 1991). Therefore, the unusually low $\delta^{15}N_{PN}$ values deserve attention.

The occurrences of the unusual $\delta^{15}N_{PN}$ values, either higher or lower than the background level, appear to be controlled by nitrogen uptake. Since phytoplankton has a preference for ammonium to nitrate during nitrogen uptake (McCarthy et al., 1977), the nitrogenous species used by phytoplankton was in turn controlled by the ammonium concentration. Nitrogen uptake associated with the production of autochthonous POM is indicated by the Chl-a/PN ratio (Fig. 8a). Nine samples with elevated Chl-a/PN ratio (>8 μg mg^{-1}) occurred at ammonium concentrations below 30 μM. These samples all had $\delta^{15}N_{PN}$ values distinctive from those of the highly polluted samples with very high concentration of ammonium.

The first group of samples that had ammonium concentrations between 10 and 30 μM displayed $\delta^{15}N_{PN}$ values higher than the background level around −2.6‰ (Fig. 8b). The second group that had the lowest $\delta^{15}N_{PN}$ values occurred at the lowest ammonium concentrations, which were all below 8 μM. By contrast, the concentrations of nitrate plus nitrite of these samples all stayed at a fairly constant level around 10 μM, which was probably sustained by nitrification as mentioned in Section 3.1. It is noted that the second group of samples had Chl-a/POC ratio lower than 5 μg mg^{-1}, which does not qualify them as containing a high fraction of freshly produced POM. However, there are good reasons to believe that they contained mostly autochthonous POM. Their Chl-a/POC ratios, though lower than the critical level, were higher than 2/3 of all samples. They had the lowest levels of ammonium and highest salinities (Fig. 3b), suggesting that they might contain the highest proportions of marine materials.

The ^{15}N enrichment in the first group of samples (Fig. 8a) could be due to uptake of isotopically heavy ammonia, which was probably the residual remaining from nitrification, as observed in the Schelde Estuary (Middelburg and Nieuwenhuize, 2001). The sudden drop of the $\delta^{15}N_{PN}$ values of the second group of samples suggests a switch of nitrogen uptake from predominantly ammonia to predominantly nitrate or nitrite during phytoplankton growth. The threshold

concentration of ammonium for inhibition of nitrate uptake by phytoplankton is usually in the range of 0.3–1 µM (Eppley et al., 1969; Wheeler and Kokkinakis, 1990), but the threshold may be elevated by a factor of 10 or more for algae in ammonia replete environments, such as oyster ponds (Maestrini et al., 1986). Culture experiments demonstrated that the threshold concentrations varied between 21 and 44 µM, depending on algal species (Maestrini et al., 1986), where ammonium remained high persistently. Most interestingly, the same experiments showed that the nitrate uptake increased rapidly to maximum rates, when the ambient ammonium concentration dropped to 7.5 µM or lower, which agrees very well with our observations.

The very negative $\delta^{15}N$ values of the autochthonous PN in the second group of samples may be attributed to two factors. The isotopic composition of the products of nitrification, namely, nitrate and nitrite, could be rather low due to preferential oxidation of isotopically light ammonia (Miyake and Wada, 1971). The uptake of nitrate again favors isotopically light nitrate (Wada and Hattori, 1978; Pennock et al., 1996). The superimposed effects must have made the phytoplankton produced PON very depleted in ^{15}N.

4.4. Biogeochemical considerations

The similarities in carbon isotopic compositions of POC in estuaries suggest that they are controlled by similar biogeochemical processes. By contrast, the nitrogen isotopic compositions of PN in estuaries exhibit different ranges in different types of estuaries, suggesting different biogeochemical pathways of nitrogen cycle must be operating in different estuaries. An important manifestation of the different biogeochemical pathways is the presence or absence of isotopically heavy PN in the estuary. The high enrichment of ^{15}N in the Delaware Bay and the Schelde Estuary (Table 2) is attributed to preferential removal of ^{14}N in the uptake of ammonia by phytoplankton and other processes, such as nitrification and denitrification (Owens, 1985; Cifuentes et al., 1988; Middelburg and Nieuwenhuize, 1998). Enrichment of ^{15}N in PN was also observed in the Danshuei Estuary near the river mouth, but the magnitude was very small (Fig. 8b), probably due to the very short residence time of the estuarine water (Wang et al., 2004) and the rather low primary production, 128 mg m^{-2} d^{-1} (Wu and Chou, 2003). By comparison, the residence time of the Delaware Estuary or the Schelde Estuary is several months long (Cifuentes et al., 1988, Middelburg and Nieuwenhuize, 1998); the average

primary production of the Delaware Bay is 840 mg m^{-2} d^{-1} (Pennock and Sharp, 1986). The Tokachi River (Usui et al., 2006) and the Forth Estuary (Graham et al., 2001), where the ^{15}N enrichment was also quite small (Table 2), may serve as test cases for this residence time hypothesis.

The isotopically very light PN observed near the river mouth of the Danshuei Estuary has not been observed in other estuaries. The very low $\delta^{15}N_{PN}$ values, which were attributed to nitrate uptake as discussed above, may occur only in the early stage of nitrification. With increasing degree of reaction, the isotopic composition of the product should become more enriched in the heavier isotope for reactions favoring the light isotopes (Hoefs, 1997). Middelburg and Nieuwenhuize (2001) reported that nitrate is a dominant species in most estuarine waters in three temperate estuaries in Europe. It is also the case in the Delaware Bay (Cifuentes et al., 1988). By contrast, ammonia is generally the dominant species in the Danshuei Estuary. Here nitrification and nitrate uptake occurred only near the river mouth.

4.5. Allochthonous contributions to estuarine POM

It has been shown that the autochthonous POM could be quite variable in isotopic and elemental compositions. By comparison, each of the allochthonous POM sources, namely, anthropogenic wastes, soils and bedrock derived sediments, is probably more uniform in composition. Materials from the same origin may be better homogenized because of the much longer life time, which allows them to be homogenized. Therefore, for samples without significant contribution of autochthonous POM, it is feasible to estimate contributions of different types of allochthonous POM in the estuary. We used two criteria to decide the allochthonous POM dominated samples for the non-typhoon conditions, namely, the Chl-a/POC ratio less than 2 µg mg^{-1} and the phosphate concentration greater than 2.5 µM. In fact, all samples but two that met the second criterion also met the first criterion (Fig. 7d). Out of 49 samples there were 36 that met both criteria. It is also assumed that most samples collected under typhoon conditions were allochthonuos POM-dominated.

The compositions of the three end-members are chosen as within 1 standard deviation from the measured mean (Table 3) such that all but one typhoon samples fall within or near the compositional triangle of mixtures (Fig. 5). Among non-typhoon samples, two thirds also fall within or near the triangle. The notable exceptions mostly are samples obtained in

Table 4
Contributions of different sources to the POC and PN in the Danshuei Estuary calculated from the three end-member mixing model

| Conditions | | End-members | | | | | |
| | | Nitrogen-based | | Fractions | Carbon-based | | Fractions |
		Wastes	Soils	Sediments	Wastes	Soils	Sediments
Non-typhoon	Range	74–95%	0–23%	0–24%	62–91%	0–36%	0–20%
	Mean	87%	7%	6%	83%	12%	5%
Typhoon	Range	0–96%	0–59%	4–81%	0–96%	0–77%	4–70%
	Mean	12%	44%	45%	9%	63%	28%

The calculation was conducted for samples without significant autochthonous POM. (See text.) The mean values are concentration weighted averages.

September 2000, when the phytoplankton flourished after the typhoon season. The contributions of the three major types of POM in each sample were derived from the $\delta^{15}N_{PN}$ value and the C/N ratio. The nitrogen-based fraction of each type may be calculated as follows:

$$f_w = [R(r - r_{sed}) - (d - d_{sed})]/$$
$$[r(r_{soil} - r_{sed}) - (d_{soil} - d_{sed})], \qquad (3)$$

$$f_{soil} = (d - d_{sed})/(d_w - d_{sed})$$
$$- f_w(d_{soil} - d_{sed})/(d_w - d_{sed}) \qquad (4)$$

$$f_{sed} = 1 - f_w - f_{soil} \qquad (5)$$

where f represent the fraction of each end member, r represents the C/N ratio, d represents the $\delta^{15}N_{PN}$ value, and the subscripts, w and sed, stand for wastes and bedrock-derived sediments, respectively. The parameter, R, is defined as follows:

$$R = (d_w - d_{sed})/(r_w - r_{sed}). \qquad (6)$$

For carbon-based fraction (g), the following relationship may be used for the conversion:

$$g_i = f_i \cdot r_i / \sum_i (f_i \cdot r_i), \qquad (7)$$

where i denotes each of the three end-members. Derivations of these relationships are based on mass balance equations Liu and Kao, 2007.

The calculation was carried out for the 36 potentially allochthonous POM dominated samples from the non-typhoon periods and 15 from the typhoon period. However, those samples that fell out of the triangle defined by the three end-members in Fig. 5 could not be properly calculated with the previously shown relationships because negative fractions were obtained for those samples. Such conditions could be caused by three

possible reasons: (1) some samples comprise significant fractions of end-members other than the three assumed here; (2) the isotopic and elemental compositions of the end-members are not as uniform as we assumed; and (3) uncertainties of the measurements. For those samples negative fractions were obtained, we re-did the calculation using the two end-members with non-negative fractions by reducing the fractions proportionally to make the sum 100%. If the differences were within 1/10 of the original results, we retained the new results; otherwise, we rejected the samples. We did so assuming that, for the latter two possibilities, the errors of the calculated fractions should be relatively small. Only 8 samples out of 51 were rejected because of their significant deviation from the compositions defined by the three allochthonous end-members.

The calculated results are summarized in Table 4. Under non-typhoon conditions, the anthropogenic waste was the dominant end-member, contributing 62–91% to the POC in the Danshuei Estuary. The concentration weighted mean fraction of it was 83%. The soil and the bedrock-derived sediment contributed up to 36% and 20%, respectively, but their weighted mean fractions were merely 12% and 5%, respectively. Under typhoon conditions, soil was the dominant source of POC comprising up to 77%. The weighted mean fraction was 63%. The contribution of the bedrock-derived sediment was comparable, ranging from 4% to 70% with a weighted mean of 28%. The mean contribution of the anthropogenic waste was only 9%. The choice of end-member compositions may change the results of the calculation, but the changes are limited. A shift of the $\delta^{15}N_{PN}$ value or the C/N ratio of any end-member by 0.5 unit may cause the calculated mean fractions to change by no more than 1/15 of the original values Liu and Kao, 2007.

The presence of relatively fresh or bedrock-derived organic carbon can be indicated by the ^{14}C contents (Kao and Liu, 1996), which may be estimated from the

organic carbon percentage of the SPM (Komada et al., 2004). The non-typhoon SPM displayed organic carbon contents ranging from 0.64% to 28.4% with a weighted mean of 14.8%. We calculated the $\triangle^{14}C$ values of the samples using the relationship established by Komada et al. (2004):

$$\Delta^{14}C = -517/OC\% + 47 \qquad (8)$$

About 1/3 of the calculated $\triangle^{14}C$ values were positive, suggesting these samples contained significant amount of modern organic carbon. The weighted mean of $\triangle^{14}C$ value of all samples was −27‰. This supports our findings that the dominant component of POM under non-typhoon conditions was derived from anthropogenic wastes. By comparison, under typhoon conditions, the organic carbon contents in SPM ranged from 0.67% to 7.7% with a weighted mean of 1.44%. The weighted mean of $\triangle^{14}C$ value was −471‰, supporting the findings of a significant contribution from bed-rock derived sediments.

5. Conclusions

The major sources of organic matter in the suspended particulate matter in the estuary include anthropogenic wastes, soils, bedrock-derived sediments and phyto-plankton produced POM. The majority (29 out of 49) of non-typhoon samples and all ($n=15$) but one typhoon samples were dominated by allochthonous POM. Using a three end-member mixing model, we found the average contributions of different sources to the allochthonous POC in the estuary: 83% from anthropogenic waste, 12% from soils and 5% from bedrock-derived sediments for non-typhoon conditions. For the typhoon condition, the contributions were 9%, 63% and 28%, respectively.

Only 1/7 of samples from non-typhoon periods, mostly from September 2000 shortly after the typhoon season, showed dominance of phytoplankton produced POM. The autochthonous POM showed the most varied carbon and nitrogen isotopic compositions, attributable to the highly variable biogeochemical conditions. The isotopically heavy POC represented the marine end-member produced in the coastal zone, whereas the isotopically light POC represented the estuarine condition, probably with elevated concentration of dissolved inorganic carbon derived from the isotopically light organic matter.

The lack of isotopically heavy nitrogen in the Danshuei Estuary was attributed to the rather low $\delta^{15}N$ value (−3‰) of the main nitrogen source in the estuary, namely, anthropogenic wastes. Moreover, the short residence time of the estuarine water and the low primary production (Wu and Chou, 2003), limited ammonia uptake, a major pathway for enriching ^{15}N in estuaries (Owen, 1985). The very low $\delta^{15}N_{PN}$ values (−16.4 to −6.4‰) occurred in waters with ammonia concentrations lower than 7.5 µM and relatively high Chl-a/PN ratios, suggesting a switch of the nitrogen source from ammonia to nitrate near the river mouth, where nitrification took place.

Further studies are needed to verify the hypotheses derived from the observations here. Most critical is to identify the nature and origin of anthropogenic wastes. It is also important to investigate the isotopic compositions of dissolved inorganic carbon and different species of dissolved inorganic nitrogen, which are the carbon and nitrogen sources of the autochthonous organic matter. Study is also warranted to examine precursors of nitrogenous materials in the estuary, such as dissolved organic nitrogen, and their transformation. The contrasting C/N ratios and isotopic compositions of autochthonous POM may be attributed to different classes of phytoplankton, which need to be examined under different conditions in the estuary.

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