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Use of $\delta^{13}C$ and $\delta^{15}N$ as Indicators to Evaluate the Influence of Sewage on Organic Matter in the Zhangjiang Mangrove–Estuary Ecosystem, Southeastern China

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Abstract: Organic matter in the productive mangrove–estuary ecosystem plays an important role in global climate changes. In recent years, the eutrophication in such areas caused by anthropogenic inputs of sewage has been revealed, highlighting the need to understand its influence on organic matter. In this study, $\delta^{13}C$ and $\delta^{15}N$ were used to reveal the effects of sewage on organic matters in the Zhangjiang mangrove–estuary ecosystem. Our results indicate that sewage contributed the most of the total particulate organic matter (41%) in the Zhangjiang estuary, while mangrove plants contributed most of the soil organic matter (45%) in the neighboring Yunxiao mangrove. Phytoplankton was another important source of organic matter, accounting for about 21.8% and 49.8% of the particulate and soil organic matter, respectively. Sewage was also a major source of dissolved inorganic nitrogen, providing 28.9%, 12.2%, and 100% of the total NO_3^-, NO_2^-, and NH_4^+ in the Zhangjiang estuary, respectively. This may be the major reason for the productive phytoplankton here, which contributed 21.8% and 49.8% of the total particulate and soil organic matter in the study area. Our results reveal the direct contribution and the potential effects of sewage on the contents and bioavailability of organic matter in mangrove–estuary ecosystems, providing new insights into understanding the response of coastal areas to the influence of human activities.

Keywords: organic matters; carbon and nitrogen isotopes; estuary; mangrove

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1. Introduction

As the areas with the highest population density, estuaries have great significance in understanding the effects of human activities on marine environments [1,2]. In southeastern China, estuaries are usually fringed by mangroves [3]. This integrated mangrove–estuary ecosystem has been reported to be strongly influenced by the influx of agricultural, industrial, and domestic waters, causing several problems such as the eutrophication of waters [4–6], the degradation of mangroves, and the emission of greenhouse gases [7–10]. As the most productive ecosystem, the mangrove–estuary ecosystem has been reported to export about 29 Tg C year^{-1} of particulate organic carbon and 14 Tg C year^{-1} of dissolved organic carbon to the ocean [1], hence playing important roles in the marine carbon cycle and global climate change [8,9,11]. This highlights the need to understand the influence of anthropogenic sewage on the biogeochemical processes of organic matter in these areas.

The influx of sewage may effect organic matter in the mangrove–estuary ecosystem through the following paths: 1. the organic residues in industrial water and the residual baits, as well as the animal waste in agriculture water, may directly increase the amount of organic matter [4,5]; 2. the large amounts of nutrients transported by sewage may promote the production of mangroves and algae [5,8,12], hence increasing the amount of biogenic organic matter, which is usually characterized by higher bioavailability [13,14];

and 3. the simultaneous increase in the content and bioavailability of organic matter may accelerate the coupling cycles of carbon (C) and nitrogen (N) in such areas by facilitating the heterotrophic microbial processes [5,8,13]. This will further increase the release of greenhouse gases, which may largely offset the carbon sink function of the mangrove–estuary ecosystem [9,15,16]. Hence, it is urgent to distinguish the influence of sewage on organic matter in such areas, and the $\delta^{13}C$ and $\delta^{15}N$ of organic matter may provide help. In past years, the $\delta^{13}C$ and C:N ratio were widely used as indicators in the source analysis of organic matter [17–19]. However, the variable C:N ratio caused by the microbial preference for N may raise the uncertainty of the source analysis. In comparison, $\delta^{15}N$ may be more suitable, as the isotopic fractionation during the biogeochemical cycle of N is relatively small [20–23]. In recent years, $\delta^{15}N$ has been used instead of the C:N ratio to analyze the source of organic matter in many areas [20,24,25]. Therefore, $\delta^{13}C$ and $\delta^{15}N$ may be helpful to distinguish the effects of sewage on organic matter in the mangrove–estuary ecosystem.

The Zhangjiang estuary (117.40–117.50° E, 23.88–23.93° N) is a semienclosed estuary in southeastern China, occupying 2360 ha and fringed by 117.9 ha of natural mangroves [10]. The dominant mangrove species here include *Kandelia obovata*, *Aegiceras corniculatum*, and *Avicennia marina* [9,10]. The eutrophication caused by the influx of agricultural and domestic water has been reported here for several years [3,4,9,10], while its influence on organic matter has not been well understood. The main aims of this study are as follows: 1. to observe the contents and the isotopic distribution ($\delta^{13}C$, $\delta^{15}N$) of organic matter in the Zhangjiang mangrove–estuary ecosystem, 2. to observe the direct contribution of sewage to organic matter here, and 3. to reveal the potential influences of anthropogenic sewage on the organic matter in such mangrove–estuary ecosystems. Our results build upon previous knowledge of the response of C and N cycles in coastal areas to the influences of human activities.

2. Materials and Methods

2.1. Sample Collection

A field sampling was carried out in December 2021, and the sampling locations are shown in Figure 1. Surface water (~0.5 m) in the Zhangjiang estuary and surface sediments (~5 cm) in the neighboring Yunxiao mangrove were collected to measure the contents and the isotopic values ($\delta^{13}C$, $\delta^{15}N$) of organic matter. In addition, the primary productions on the surface of the Zhangjiang estuary were also measured. All water samples were collected by Niskin bottles and kept at 4 °C before analysis. The temperature (T), salinity (S), the contents of dissolved oxygen (DO), and phycoerythrin and chlorophyll *a* (Chl *a*) in the Zhangjiang estuary were measured in situ using YSI 6600 multiprobe sensors (Yellow Springs Instrument Co., Yellow Springs, OH, USA). Mangrove sediments were collected by a core sampler and kept at −20 °C before analysis.

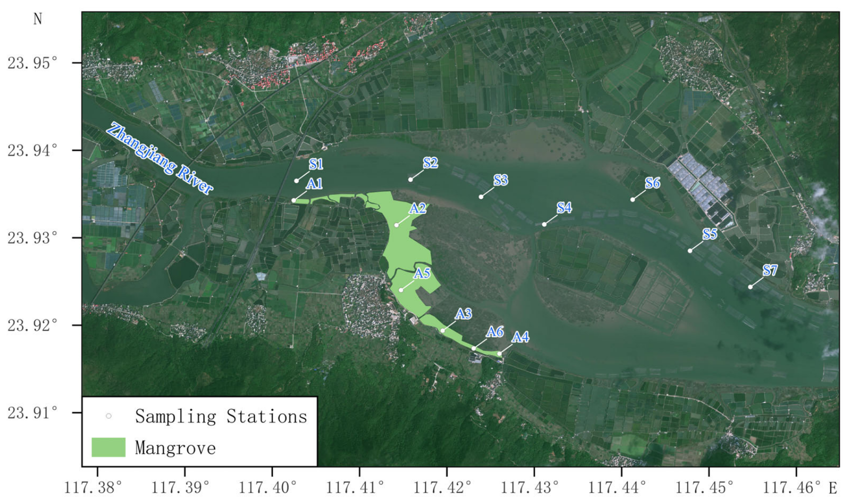


Figure 1. The sampling stations in Zhangjiang mangrove–estuary ecosystem.

2.2. Dissolved Inorganic Nutrients

Concentrations of nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), and silicate (SiO_3^{2-}) were analyzed by a Lachat QuickChem 8500 autoanalyzer (Lachat Instruments, Loveland, CO., USA) after standard colorimetric methods. The content of phosphate (PO_4^{3-}) was measured using a spectrophotometer via the standard molybdenum blue method. The nutrient detection limits were 0.05 μmol L^{-1} (NO_3^-), 0.02 μmol L^{-1} (NO_2^-), 0.03 μmol L^{-1} (NH_4^+), 0.02 μmol L^{-1} (PO_4^{3-}), and 0.45 μmol L^{-1} (SiO_3^{2-}), respectively.

2.3. Organic Carbon and Nitrogen

Particulate organic matter (POM) in water samples were collected by filtering 4 L of water through GF-75 filters (47 mm, 0.3 μm pore size). The filters were previously combusted for 4 h at 450 °C to remove organic matter. All water samples were then filtered through a 200 μm mesh sieve to remove large detritus. Then, water samples (without large detritus) were filtered by the precombusted GF-75 filters to collect particulate organic carbon (POC) and nitrogen (PN). The GF-75 filters were quickly washed using Milli-Q water following filtration and frozen at −20 °C until analysis. In the laboratory, the filters were treated with HCl vapor (48 h) to remove inorganic carbon and then dried at 60 °C. The contents of POC, PN, and the $\delta^{13}C$, $\delta^{15}N$ of POM ($\delta^{13}C_{POM}$, $\delta^{15}N_{POM}$) were measured using a Finnigan Delta V Advantage isotope ratio mass spectrometer interfaced with a Carlo Erba NC 2500 elemental analyzer. The contents of the soil organic matter (SOM) in Yunxiao mangrove sediments and its $\delta^{13}C$, $\delta^{15}N$ in ($\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$) mangrove sediments were measured by the same method. The analytical precision is <0.2‰ in this study.

2.4. Primary Production

Primary production (PP) of phytoplankton was determined by a ^{13}C uptake method: after collection, water samples were immediately transferred into three 125 mL pre-cleaned Nalgene polycarbonate bottles. After the addition of $NaH^{13}CO_3$ (the ^{13}C concentration in the dissolved inorganic carbon was about 10 at-%), the bottles were incubated in an on-deck incubator filled with circulating water under the surface irradiance. Incubation experiments were started during the daytime and continued for 6–8 h. $ZnCl_2$ was used to end the incubation and the particulate matter was filtered onto precombusted (450 °C, 4 h) GF-75 filters (47 mm, 0.3 μm pore size). The concentration and the ^{13}C at-% of particulate organic carbon (POC) were determined by EA-IRMS, and the PP of phytoplankton was calculated as the follow equation:

$$PP = C \cdot \frac{(A_f - A_0)}{t\,(A_{DIC} - A_0)} \cdot f \quad (1)$$

where t is the incubation duration (h), C is the concentration of POC at the end of incubation, A_f and A_0 represent the abundance of ^{13}C at the end and the start time of incubation, A_{DIC} is the abundance of ^{13}C substrate (measured by a Finnigan Delta V Advantage isotope ratio mass spectrometer interfaced with GasBench II), and *f* (1.025) is the correction coefficient [26].

2.5. Statistical Analysis

Pearson's correlations analysis was conducted using the Statistical Package for Social Sciences program (version 19.0). The source analysis of organic matter based on $\delta^{13}C$, $\delta^{15}N$ values was conducted by IsoSource (version 1.3), with an increment of 1% and a tolerance of 0.1%.

3. Results

3.1. Physicochemical Parameters

The basic physicochemical parameters of the Zhangjiang estuary are shown in Table 1. Surface temperatures (T) ranged from 17.5 to 17.9 °C (17.7 ± 0.2 °C, n = 7), with the maximum observed at station S6 and the minimum at S3. Surface salinity (S) and dissolved oxygen (DO) ranged from 19.2 to 22.3 (20.4 ± 0.9, n = 7) and 5.8 to 7.8 mg L^{-1} (6.4 ± 0.6 mg L^{-1}, n = 7), respectively, and slightly increased from upstream to downstream. The contents of phycoerythrin and Chl *a* ranged from 0.699 to 4.940 μg L^{-1} (2.630 ± 1.350 μg L^{-1}, n = 7) and 1.765 to 4.028 μg L^{-1} (2.779 ± 0.765 μg L^{-1}, n = 7), with higher values observed upstream.

Table 1. The physicochemical parameters at the sampled stations in the Zhangjiang estuary.

Station	T (°C)	S	DO (mg L^{-1})	Phycoerythrin (μg L^{-1})	Chl *a* (μg L^{-1})
S1	17.7	20.0	5.81	4.94	4.03
S2	17.6	20.3	6.04	3.27	3.40
S3	17.5	19.1	6.43	3.85	3.31
S4	17.5	20.4	6.08	2.19	2.48
S5	17.6	20.5	6.30	1.71	2.51
S6	18.0	20.3	7.79	1.75	1.76
S7	17.6	22.3	6.51	0.699	1.96

3.2. Nutrients Concentrations

The concentrations of NO_3^-, NO_2^-, and NH_4^+ ranged from 51.0 to 73.8 μmol L^{-1} (60.0 ± 8.0 μmol L^{-1}, n = 7), 0.10 to 0.12 μmol L^{-1} (0.11 ± 0.01 μmol L^{-1}, n = 7), and 605.6 to 1898.8 μmol L^{-1} (1050.2 ± 467.8 μmol L^{-1}, n = 7), respectively (Table 2). The concentration of dissolved inorganic nitrogen (DIN) ranged from 664.4 to 1967.8 μmol L^{-1} (1117.9 ± 469.2 μmol L^{-1}, n = 7), and NH_4^+ accounted more than 90% of the total DIN at most stations. Generally, the concentrations of DIN decreased from upstream to downstream. The concentration of PO_4^{3-} and SiO_3^{2-} ranged from 2.9 to 3.7 μmol L^{-1} (3.2 ± 0.3 μmol L^{-1}, n = 7) and 77.4 to 101.5 μmol L^{-1} (90.0 ± 8.8 μmol L^{-1}, n = 7), with the maximum observed at S3 and the minimum at S2 and S6, respectively. The spatial variations in PO_4^{3-} and SiO_3^{2-} were less than that of DIN. A notable feature of nutrient stoichiometry is that the ratios of N: P (352.2 ± 150.9, n = 7) were significantly higher than the Redfield ratios at all stations.

Table 2. The concentration of dissolved inorganic nutrients at the sampled stations.

Station	NO_3^-	NO_2^-	NH_4^+	PO_4^{3-}	SiO_3^{2-}
S1	73.8	0.118	621.7	3.34	98.6
S2	61.0	0.112	1067.0	2.91	89.9
S3	65.4	0.112	1427	3.73	101.5
S4	61.3	0.109	1899	3.03	92.4
S5	55.9	0.107	895.3	3.07	89.5
S6	51.8	0.0986	605.6	2.99	77.4
S7	51.0	0.0993	836.3	3.22	80.3

Note: The unit of the concentration of nutrients is μmol L^{-1}.

3.3. The Contents and the Isotopic Characters of Organic Matter

The concentrations of POC and PN in the Zhangjiang estuary ranged from 20.7 to 38.7 μmol L^{-1} (29.5 ± 8.2 μmol L^{-1}, n = 7) and 2.0 to 6.9 μmol L^{-1} (4.4 ± 1.4 μmol L^{-1}, n = 7), respectively, with both maximums observed at S1 and the minimum at S7 (Figure 2a). The C:N ratio of POM ranged from 5.6 to 7.7 (6.9 ± 0.9, n = 7), with the maximum observed at S5 and the minimum at S2 (Figure 2a). The $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ in the Zhangjiang estuary ranged from −27.4 to −24.1‰ (−25.5 ± 1.0‰, n = 7) and 1.9 to 4.1‰ (3.0 ± 0.7‰, n = 7), respectively, with both maximums observed at S5 and the minimum at S1 (Figure 2b).

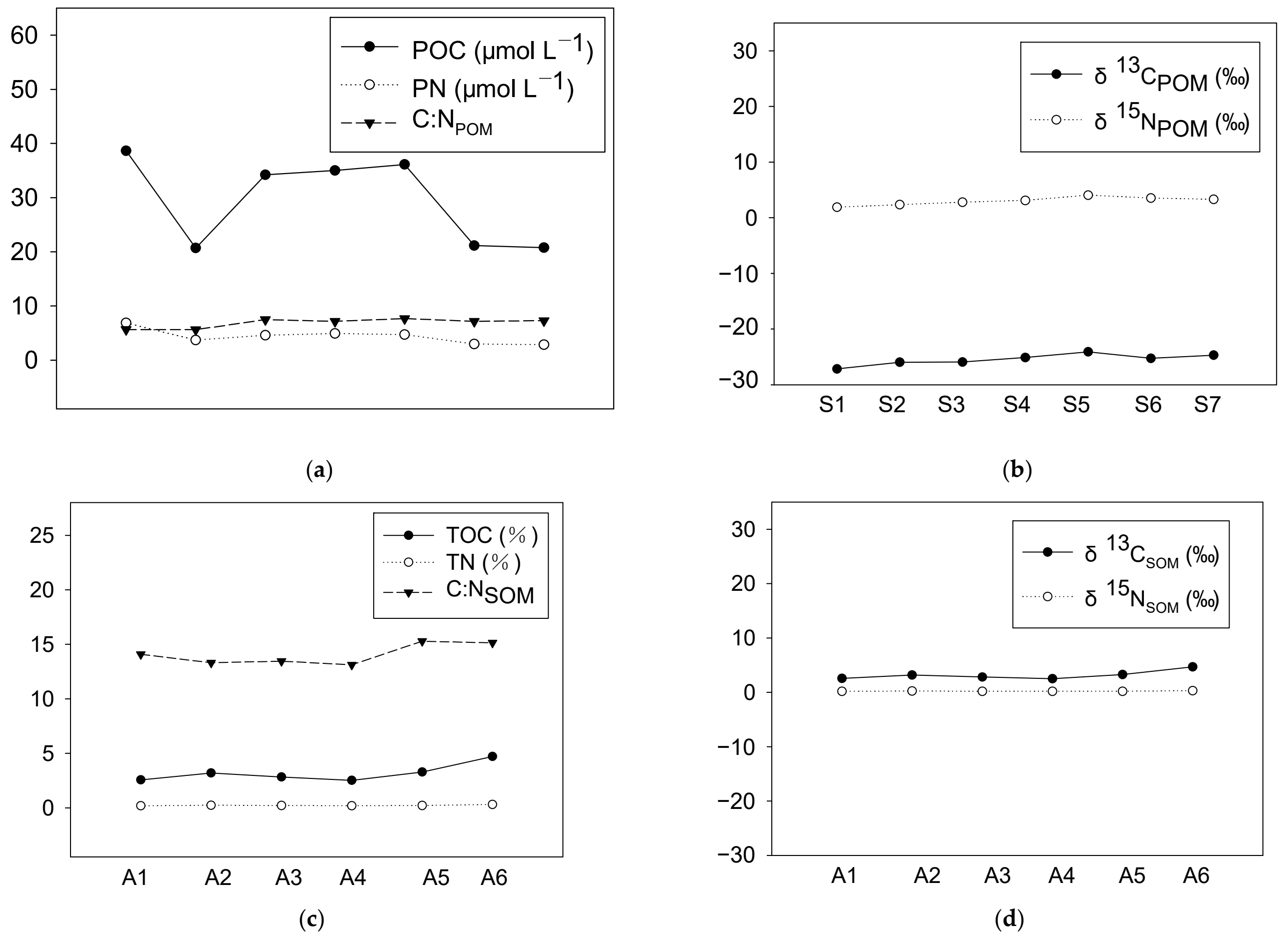


Figure 2. The contents, C:N ratios, and the isotopic characters of organic matter: (**a**) the contents and the C:N ratio of particulate organic carbon and nitrogen; (**b**) the $\delta^{13}C$ and $\delta^{15}N$ of particulate organic matter; (**c**) the contents and the C:N ratio of soil organic carbon and nitrogen; and (**d**) the $\delta^{13}C$ and $\delta^{15}N$ of soil organic matter.

The contents of total organic carbon (TOC) and nitrogen (TN) in the mangrove sediments ranged from 2.52 to 4.71% (3.19 ± 0.71%, n = 6) and 0.18% to 0.31% (0.23 ± 0.05%, n = 6), with both maximums observed at A6 and the minimum at A1 and A2, respectively (Figure 2c). The C:N ratio of SOM ranged from 13.1 to 15.3 (14.1 ± 0.9, n = 6), with relatively small variation (Figure 2c). The $\delta^{13}C$ and $\delta^{15}N$ of the SOM in the surface mangrove sediments ($\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$) ranged from −28.6 to −23.2‰ (−26.5 ± 1.8‰, n = 6) and 6.3 to 10.7‰ (9.2 ± 1.6‰, n = 6), with the maximum observed at A4 and A6 and minimum at A6 and A2, respectively (Figure 2d).

3.4. Primary Production

Surface PP in the Zhangjiang estuary ranged from 0.05 to 0.28 μmol C L^{-1} h^{-1} (0.13 ± 0.07 μmol C L^{-1} h^{-1}, n = 6). The sample observed at S6 was lost. The highest PP was observed at S1, where a bloom of algae was also observed, and the lowest PP was observed at S2. Except for the maximum at S1, PP downstream was higher than that upstream (Figure 3).

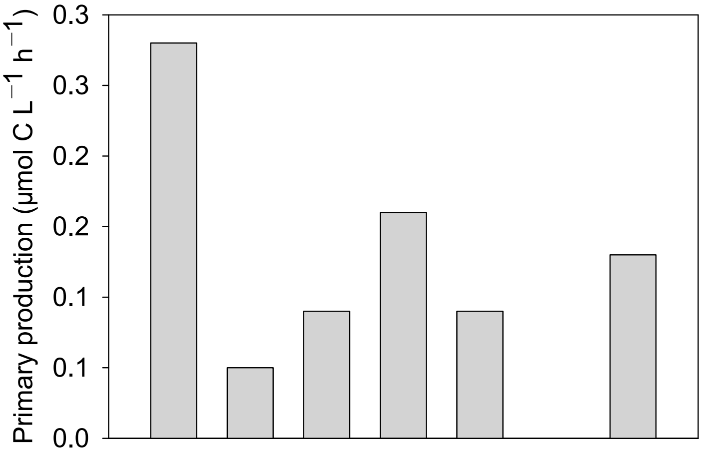


Figure 3. The surface primary production in the Zhangjiang estuary.

4. Discussion

4.1. Contribution of Sewage to Organic Matter

Generally, the observed $\delta^{13}C$ and $\delta^{15}N$ in this study fell in the range of the reported values in similar areas (Tables 3 and 4). Covariance between the organic C and N (POC and PN: r = 0.855 $p < 0.01$ $n = 7$, TOC and TN: r = 0.947 $p < 0.01$ $n = 6$) was observed during our investigation, indicating that $\delta^{15}N$ may be more suitable than the widely used C:N ratio for the source analysis of organic matters. Hence, $\delta^{13}C$ and $\delta^{15}N$ were used to distinguish the contribution of anthropogenic sewage to organic matter in this study.

Table 3. $\delta^{13}C$ and $\delta^{15}N$ of soil organic matter in mangrove sediments.

Research Areas	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	References
Yunxiao mangrove sediments	−28.6–−23.2	6.3–10.7	This study
Yunxiao mangrove sediments	−25.5–−21.6	4.7–7.8	[27,28]
Gaoqiao mangrove sediments	−26.68 ± 0.38	-	
Dongzhai harbor mangrove sediments	−24.87 ± 1.76	-	
Wenchang mangrove sediments	−26.29 ± 1.02	-	
Jiulong River estuary mangrove sediments	−28.2–−23.0	2.4–11.2	[29]
Futian mangrove sediments	−28.0 ± 0.3	-	[30]

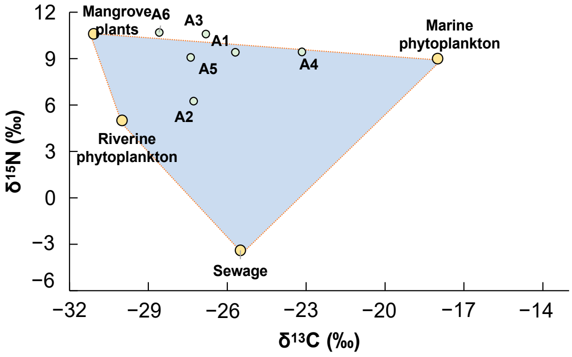
Table 4. $\delta^{13}C$ and $\delta^{15}N$ of particulate organic matter in estuaries and gulfs.

Research Areas	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	References
Zhangjiang esturay	−27.1~−24.1	1.9 ~ 4.1	This study
Danshuei estuary	−25.5~−19.0	−16.4~3.8	[17]
Yangtze river	−29.2~−25.8	2.4~7.0	[31]
Daya bay	−25.7~−16.9	−6.3~10.4	[32]
Jiaozhou bay	−28.6~−21.2	−3.1~13.2	[33]
Potomac river	−27.3~−18.4	3.1~11.6	
Chesapeake bay	−26.9~−17.5	5.0~9.5	
San Francisco bay	−26.4~−26.0	0.7~1.0	
Boston harbor	−26.9~−17.5	5.0~9.5	[34]
Delaware estuary	−23.1~−18.7	5.5~12.2	[21]
Conception bay	−27.2~−21.6	3.7~8.4	[35]
Traverse bay	−30.7~−23.9	1.7~11.6	[36]
Lugao bay	−29.9~−26.9	4.7~7.0	[37]
Yellow river	−25.6~−23.1	-	[38]
Pearl river	−25.6~−24.3	-	[39]
Amazon river	−28.4~−17.5	3.6 ± 1.5	[40,41]

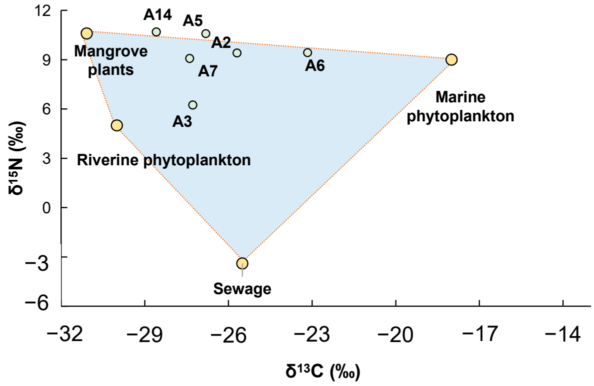
The major sources of POM in estuaries include the production of phytoplankton, the transport of sewage, and the influx of terrestrial soil [34–41]. For the Zhangjiang estuary, the inputs of the neighboring Yunxiao mangrove sediment may be the major source of terrestrial organic matter [27,28]. Hence, we propose that the POM in the Zhangjiang estuary was mainly composed of organic matter derived from phytoplankton production, sewage, and mangrove sediment. For the Yunxiao mangrove sediment, the production of mangrove plants may be the major source of SOM [2,27,28]. It has been reported that mangrove plants contributed more than 50% of the total carbon storage (95.9 Mg C ha^{-1}) of the Yunxiao mangrove sediment [27]. The influences of anthropogenic sewage may also not be ignored, which may increase the content of SOM by directly importing external organic matter or by promoting the production of mangrove plants and algae [2,8,13]. Hence, SOM in the Yunxiao mangrove may mainly come from the production of mangrove plants, algae, and the inputs of sewage. However, as the benthic algae in Yunxiao mangrove was not collected, and its $\delta^{15}N$ value was rarely reported, the contribution of benthic algae was not considered in this study.

Generally, organic matter derived from marine phytoplankton is characterized by higher $\delta^{13}C$ (−16–−20‰) and $\delta^{15}N$ (6–10‰) [42,43], while that from riverine phytoplankton is characterized by lower $\delta^{13}C$ (−34–−26‰) but relatively higher $\delta^{15}N$ (~5‰) [2,44]. The $\delta^{13}C$ and $\delta^{15}N$ of organic matter derived from terrestrial C3 plants (such as mangrove plants) range from −33‰ to −22‰ and 0‰ to 3‰, respectively [45,46], while that derived from terrestrial soil ranges from −27‰ to −24‰ and 0‰ to 2‰, respectively [47,48]. Organic matter in anthropogenic sewage has a similar range of $\delta^{13}C$ (−28–−23‰) to terrestrial soil but a larger range of $\delta^{15}N$ (−16.4–3‰) [17,23,49,50]. Based on the stable isotope conservation model, the contribution of different sources to the total organic matter can be observed by IsoSource [51]. In this study, the $\delta^{13}C$ and $\delta^{15}N$ of organic matters derived from mangrove plants ($\delta^{13}C$ = −31.1‰, $\delta^{15}N$ = 10.6‰, unpublished data, Table S1) and mangrove sediment ($\delta^{13}C$ = −26.5‰, $\delta^{15}N$ = 9.2‰) were observed by field measurement, while those of organic matters derived from anthropogenic sewage ($\delta^{13}C$ = −25.5‰, $\delta^{15}N$ = −3.4‰), marine ($\delta^{13}C$ = −18‰, $\delta^{15}N$ = 9‰), and riverine phytoplankton ($\delta^{13}C$ = −30‰, $\delta^{15}N$ = 5‰) were set with the median of the reported values [17,23,42–50].

According to Figure 4a, all the observed $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$ fell into the coverage area of the four end elements. The contributions of the four members to POM, POC, and PN were calculated by IsoSource, respectively, and the results are as follows: 1. anthropogenic sewage was the major source of POM in the study area, accounting for about 35.5–46.5% (41.1 ± 4.0%, n = 7) of the total POM (Figure 5), with a higher contribution to PN (40.2 ± 6.8%, n = 7) than POC (29.5 ± 4.0%, n = 7); 2. riverine phytoplankton was another important source of POM, accounting for about 16.3–44.2% (23.4 ± 9.6%, n = 7) of the total POM, with a similar contribution to POC (23.6 ± 9.1%, n = 7) and PN (25.9 ± 3.1%, n = 7), and the calculated concentration of the POC derived from riverine phytoplankton (POC_{rphy}) had a positive correlation with the contents of phycoerythrin (r = 814, $p < 0.05$, n = 7), Chl *a* (r = 771, $p < 0.05$, n = 7), and PP (r = 856, $p < 0.05$, n = 7), indicating the reliability of the source analysis; and 3. mangrove sediments and marine phytoplankton had similar contributions to POM (mangrove sediments: 17.1 ± 8.8%, n = 7; marine phytoplankton: 18.5 ± 5.4%, n = 7), while the contribution of mangrove sediments to the POC (27.6 ± 4.1%, n = 7) was obviously higher than that of marine phytoplankton (18.5 ± 8.4%, n = 7).



(**a**)



(**b**)

Figure 4. The relationship between $\delta^{13}C$ and $\delta^{15}N$ of organic matter: (**a**) particulate organic matter in the Zhangjiang estuary; (**b**) soil organic matter in the Yunxiao mangrove.

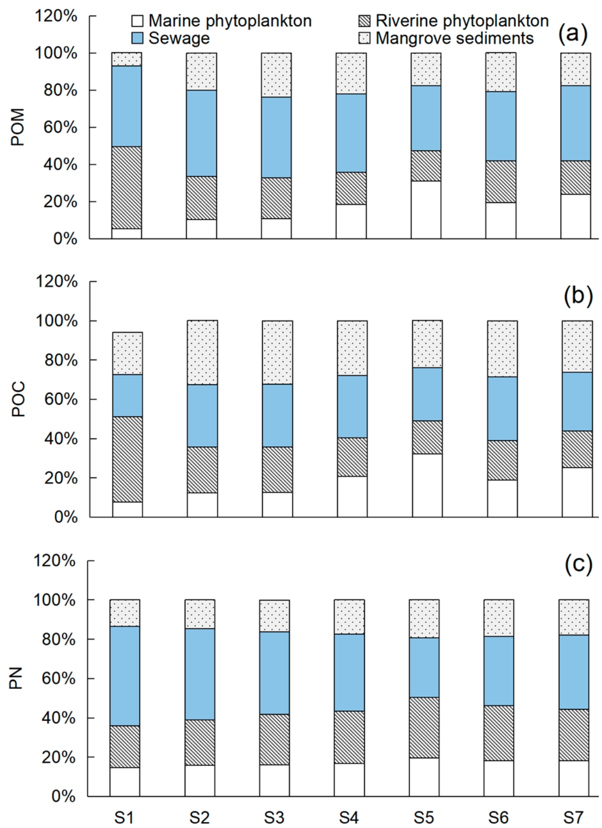


Figure 5. The contribution of the major sources to particulate organic matters: (**a**) particulate organic matters (POM); (**b**) particulate organic carbon (POC); and (**c**) particulate nitrogen (PN).

The source of SOM in the Yunxiao mangrove was also analyzed. Most of the observed $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ fell into the coverage area of the four end elements, except for the $\delta^{15}N_{SOM}$ observed at A3 and A6 (Figure 4b). Hence, the source of SOM and TN at A3 and A6 was not analyzed. The high values of $\delta^{15}N_{SOM}$ observed at A3 and A6 also indicate another potential source of SOM, most likely the production of benthic algae, which needs to be considered in future research. According to the calculated results, mangrove plants were the major contributor of SOM in the Yunxiao mangrove, accounting for about 21.1–62.4% (45.0 ± 15.4%, n = 4) of the total SOM (Figure 6), with a higher contribution to TN (51.9 ± 18.4%, n = 4) than TOC (24.9 ± 8.0%, n = 6). The production of marine algae was another important source of SOM (Figure 6), accounting for about 36.4 ± 17.6% (n = 4) of the total SOM. In comparison, the contributions of riverine algae (13.5 ± 16.7%, n = 4) and sewage (5.2 ± 5.9%, n = 4) were small. However, when considering the TOC and TN separately, the results are different. For the TOC, the average contribution ratios of the four sources were similar to each other, among which the contribution of sewage was slightly higher than the others (Figure 6). A significant contribution of marine phytoplankton was observed at A4, which is located at the seaward side and is under the strong effect of tide (Figure 1). For TN, the contribution ratio of the sewage was only 6%, which may be due to the following reasons: (1) A large portion of N imported by sewage to the mangrove may be removed by the water exchange between the mangrove and its fringe water. It has been reported that the mangrove ecosystem may be one of the major sources of nitrogen nutrients for its fringe water [10]. (2) The imports of external C may also facilitate the microbial denitrification and anaerobic ammonia oxidation [1,5,8,9,13], most of which are heterotrophic processes [8], which may further accelerate the removal of N from mangroves. Hence, most of the N imported by sewage may be removed from mangroves before being converted to the organic state. In comparison, the organic carbon in sewage, both in the dissolved or particle phase, seems to be more easily conserved in mangrove sediments, mostly due to its higher bioavailability and sedimentation rates [1,8,13,14].

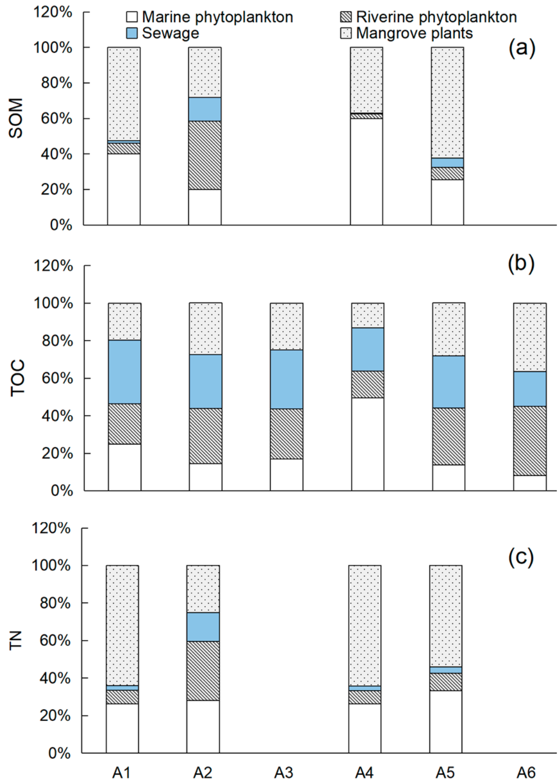


Figure 6. The contribution of the major sources to soil organic matters: (**a**) soil organic matters (SOM); (**b**) total organic carbon (TOC); and (**c**) total nitrogen (TN).

Generally, anthropogenic sewage was the most important contributor to the POM in the Zhangjiang estuary, while mangrove plants were the major source of the SOM in the Yunxiao mangrove sediment. The production of algae (including marine and riverine species) was another important source of organic matter, which contributed about 21.8% of the total POM in the Zhangjiang estuary and 49.8% of the total SOM in the Yunxiao mangrove sediment. In addition, the production of benthic algae may be another source of SOM for the Yunxiao mangrove, which needs to be further investigated in the future.

4.2. Potential Effects of Sewage on Organic Matters

The contents and the $\delta^{13}C$ and $\delta^{15}N$ of organic matter in coastal areas are influenced by many factors, such as the mixture of freshwater and seawater, biological production and degradation, and anthropogenic activities [52,53]. For the eutrophic Zhangjiang mangrove–estuary ecosystem, anthropogenic inputs of sewage may be one of the major regulators of the biogeochemical processes of organic matter. The direct contribution (41.1 ± 4.0%, n = 7) of sewage to the POM in the Zhangjiang estuary was observed in this study, while its potential effects should also be realized. We propose that sewage may potentially impact the contents, the $\delta^{13}C$ and $\delta^{15}N$ values, and the bioavailability of organic matter in the Zhangjiang mangrove–estuary ecosystem by regulating the biological production and degradation of organic matter.

For the POM in the Zhangjiang estuary, the active production of phytoplankton was closely related to the excess nutrients caused by sewage. It has been reported that the phytoplankton in the Zhangjiang estuary are mainly composed of riverine species [54]. During our investigation, positive correlations between the contents of NO_3^-, Chl *a*, and POC derived from riverine phytoplankton ($POC_{riverine}$) were observed (Table 5), indicating the obvious effects of the nutrient availability on the production of local phytoplankton. In addition, the positive correlations between the PN derived from sewage (PN_{sewage}) and the contents of NO_3^- and NO_2^- and those between the POC derived from sewage (POC_{sewage}), dissolved organic carbon (DOC, unpublished data, Table S1), and NH_4^+ were also observed in this study (Figure 7). Hence, we hypothesize that the inputs of PN_{sewage} were closely accompanied by the inputs of NO_3^- and NO_2^-. After setting the value of PN_{sewage} to zero, the contents of the NO_3^- and NO_2^- derived from sources other than sewage were observed. Then, the contribution of the sewage to the total NO_3^- and NO_2^- was observed. Similarly, the contribution of sewage to the total NH_4^+ was observed based on the statistical correlations between the DOC, POC_{sewage}, and NH_4^+. The results indicate that sewage contributed about 28.9% of the total NO_3^-, 12.2% of the total NO_2^-, and almost 100% of NH_4^+ in the Zhangjiang estuary. This indicates the strong effects of sewage on the nutrient condition in the study area. The promoted production of phytoplankton caused by the excess nutrients can further influence the $\delta^{13}C_{POM}$ and $\delta^{15}N_{POM}$, as it may accelerate the accumulation of lighter isotopes (^{12}C and ^{14}N) in biogenic organic matter [55,56]. In this study, the lowest $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ were observed at S1, at which a bloom of algae was observed, combined with the maximum of the POC, PN, and PP. In addition, the negative correlation between $\delta^{13}C_{POC}$, $\delta^{15}N_{PN}$, and the content of Chl *a* was also observed (Table 5). Hence, the influx of nutrients in sewage may promote the production of phytoplankton and hence potentially influence the contents and the isotopic composition of POM in the Zhangjiang estuary [1,8,13,55,56].

Table 5. The results of Pearson's correlation analysis.

	Chl *a* ($\mu g\ L^{-1}$)	**NO_3^- ($\mu mol\ L^{-1}$)**
$POC_{riverine}$	r = 0.771 $p < 0.01$ n = 7	r = 0.896 $p < 0.01$ n = 7
$\delta^{13}C_{POM}$	r = −0.802 $p < 0.05$ n = 7	r = −0.833 $p < 0.05$ n = 7
$\delta^{15}N_{POM}$	r = −0.835 $p < 0.05$ n = 7	r = −0.810 $p < 0.05$ n = 7

For the SOM in the Yunxiao mangrove, anthropogenic sewage may produce potential effects through the following paths: 1. the external C and N may stimulate the microbial activities in mangrove sediments, such as the degradation of organics, the production of methane, and microbial denitrification [1,8,9], causing the isotope fractionation of C and N [55,56]; 2. the imported nutrients may also promote the production of mangrove plants and algae (planktonic or benthic) in mangroves, potentially increasing the carbon storage of the Yunxiao mangrove [27,28]. In addition, the increasing amounts of biogenic organic matter with higher bioavailability may further facilitate microbial activity [1,8,13], further impacting the isotopic characteristics of SOM. However, the nutrient condition of the Yunxiao mangrove sediment was not directly investigated in this study. Its relationship with the anthropogenic inputs of sewage, combined with its effects on SOM, need to be further investigated in future studies.

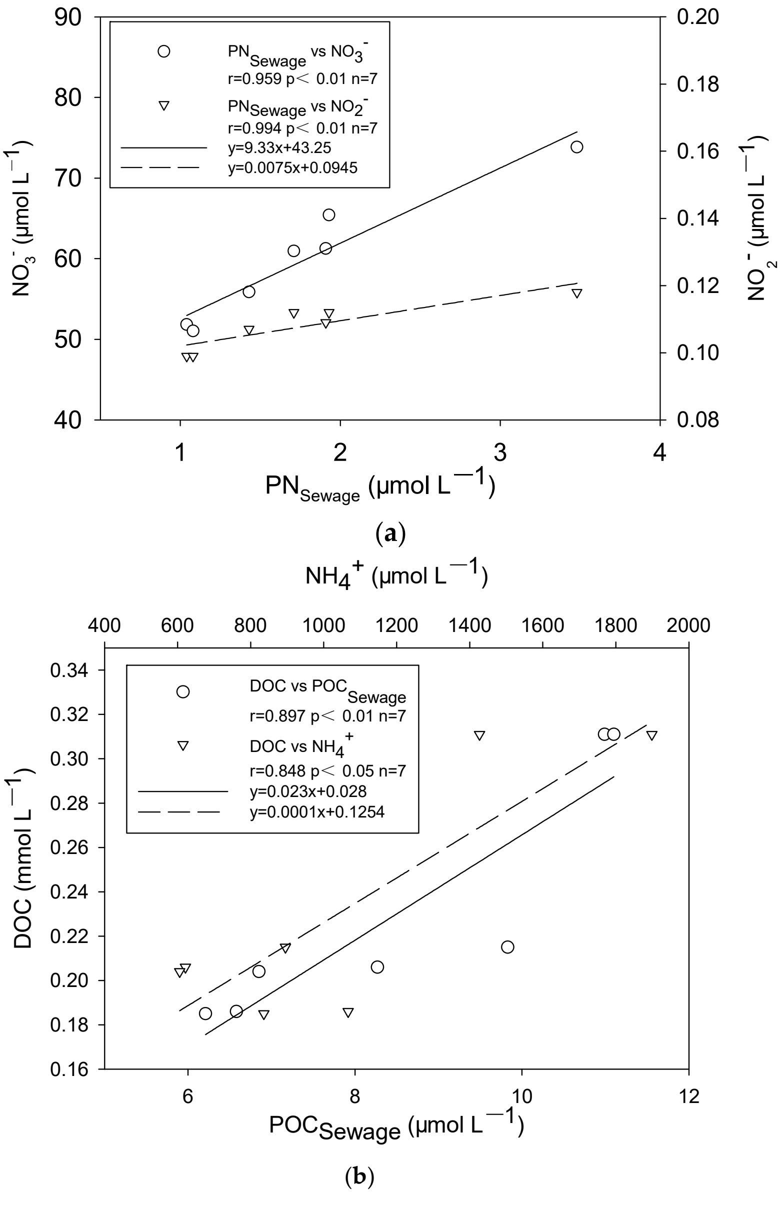


Figure 7. The results of Pearson's correlation analysis: (**a**) the correlations between particulate nitrogen derived from sewage (PN_{sewage}) with NO_3^- and NO_2^-; (**b**) the correlations between particulate organic carbon derived from sewage (POC_{sewage}) with dissolved organic carbon (DOC, unpublished data) and NH_4^+.

5. Conclusions

This study revealed the influences of anthropogenic sewage on the contents and the isotopic characteristics of organic matter in the Zhangjiang mangrove–estuary ecosystem. The major conclusions are as follows: 1. sewage was the major contributor of POM (~41% of the total POM) in the Zhangjiang estuary, while mangrove plants were the major contributor of SOM (~45% of the total SOM) in the Yunxiao mangrove; 2. the production of phytoplankton (including marine and riverine species) was another important source of organic matter in the Zhangjiang mangrove–estuary ecosystem, accounting for about 21.8% of the total POM in the Zhangjiang estuary and 49.8% of the total SOM in the Yunxiao mangrove sediments; and 3. sewage may impact the contents and the isotopic characters of organic matter in the study area by the direct import of organic matter or by promoting the biological production or degradation of organic matter. This study indicates that the $\delta^{13}C$ and $\delta^{15}N$ of organic matter can efficiently indicate the influences of anthropogenic sewage on the coastal C and N cycles and may provide new insights in understanding the response of coastal areas to the influence of human activities.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/w15203660/s1, Table S1: The $\delta^{13}C$, $\delta^{15}N$ of mangrove plants in the Yunxiao mangroves. Table S2: The concentration of dissolved organic carbon in the Zhangjiang estuary.

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