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Carbon and nitrogen isotopes analysis and sources of organic matter in the upper reaches of the Chaobai River near Beijing, China

LU FengYun[1], LIU ZhuQing[2] & JI HongBing[1,3*]

[1] *Key Laboratory of Metropolitan Eco-Environment Processes, College of Resource Environment and Tourism, Capital Normal University, Beijing 100048, China;*
[2] *College of Water Conservancy & Civil Engineering, China Agricultural University, Beijing 100083, China;*
[3] *The State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*

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The carbon and nitrogen isotopes in the surface sediments, plants, and soil in the upper reaches of the Chaobai River have been researched. The results showed −27.75‰ – −21.58‰ and 1.32‰–6.74‰ for carbon and nitrogen isotopic ratios in the surface sediments, respectively. The sources of sedimentary organic matter in this area are soil organic matter, aquatic vascular plants, and riverine plankton, respectively, and a significant contributor to sediment in the Chaohe River, the Baihe River, and the Miyun Reservoir areas is soil organic matter. Furthermore, part of sedimentary organic matter in the Miyun Reservoir is attributed to the input from the Chaohe River and the Baihe River, the other is from C4 vegetation growing around individual point stations at the Miyun Reservoir. Compared with the situation in Hebei Province, the contribution of soil organic matter decreased significantly and river plankton and aquatic vascular plants increased significantly in Beijing municipal areas. This study reveals that the source of organic matter has a close relationship with the soil erosion.

carbon isotopes, nitrogen isotopes, organic matter, Chaobai River, material source

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Rivers play an important role in land-sea interactions. They are important channels for transporting materials from the terrestrial ecosystem to the marine ecosystem, whereas the content of materials in the river also reflects biogeochemical processes in the basin [1, 2]. Based on this, it is very important to study the organic matter in the river to assess the states of the river and the basin. The reasons for using organic matter in the river to assess the ecosystem of basin are based on the following principles. The sources of organic matter in river are divided into external and internal matter. While the origins of external organic matter include terrestrial plant debris and soil organic matter, the main origins of organic matter are river plankton, algae and aquatic vascular plants [3, 4]. Terrestrial organic matter are related to the ecological characteristics and soil types in the basin which can reveal the types of watershed vegetation and changes of soil erosion [5]. At the same time, origins of internal organic matter can reflect the conditions of water quality and record human activities [6], further infer the impact on global change, and provide a theoretical basis and technical support to agriculture, forestry, and water conservancy [7, 8]. Therefore, it is important and timely to study the origins, fate, and migration and transformation process of organic matter in river ecosystems for material circulation problems in a complex river environment [9].

In general, the composition of stable isotopic C, N (δ^{13}C,

*Corresponding author (email: jih_oooo@126.com)

δ^{15}N) and C/N ratios from different origins of organic matter in the natural river environmental system is significantly different. These geochemical indicators are widely used in the study of the origins of sediment organic matter in river and estuarine ecosystems [10–12]. The application of stable isotopes in trace for organic material sources has two main basic assumptions: (1) stable isotope ratios in organic matter have conservative characteristics, and (2) physical mixing of organic matter with different origins controls the distribution of stable isotopes [13]. Carbon isotopes are widely used to explore the origins and the migrating principles of materials in a variety of ecological environments whereas nitrogen isotopes are widely used in the study of biological tracing of the nitrogen cycle, but the fractionation in the absorption process of inorganic nitrogen will be fed back to the nitrogen isotope composition in organic matter, which reflects the provenance information and biogeochemical processes [8, 14]. Therefore, it is customary to use C/N and δ^{13}C together to determine the origins of organic matter. This indicator should be carefully applied in case that the early diagenesis process changes the value of C/N.

The Miyun Reservoir is one of the largest reservoirs located on the Chaobai River. It is the main source of water for the municipality of Beijing. However, over nearly four decades the water quantity in The Miyun Reservoir has been reduced, the water quality has deteriorated, and the ecological environment has been further destroyed. Therefore, the study of the source of organic matter and the ecological situation in watershed has great practical significance, and has not so far been reported. This paper takes the Chaobai River, an important tributary of the Haihe River, as its focus, analyzes the watershed vegetation, soil and the geochemistry characters of stable isotope, such as C, N, found in the surface sediments, uses a multiple mixed model to simulate the relationships among the organic geochemical indicators of the sources of sedimentary organic matter, and thus analyzes and discusses the sources of organic matter in the watershed quantitatively, and provides references and evidence for the study of the ecological environment situation in the watershed and the biogeochemical cycling of carbon and nitrogen elements.

1 Overview of regional environment

The Chaobai River originates from north of Yanshan Mountain, flows through Hebei Province and the municipalities of Beijing and Tianjin, and empties into to the Haihe River. The northern section of the Chaobai River (the upper-stream of the Miyun Reservoir) is divided into two tributaries, the east branch is called Chaohe River, and the west branch is called Baihe River. At the down-stream of the Miyun Reservoir, the Chaohe River joins the Baihe River near the Hechao Village in southwest Miyun County. The Chaohe River originates in Fengning County, Hebei Province, runs south through Gubeikou Village into Miyun County, and empties into the Miyun Reservoir near Xinzhuang Village; the watershed area is 6960.59 km^2. Its main tributaries include the Xiaotang River, Andamu River, Qingshui River, and the Mangniu River. The Baihe River originates in Guyuan County, Hebei Province, runs south through Chongli and Chicheng County, flows into the Baihepu Reservoir in Yanqing County, Beijing, and empties into the Miyun Reservoir near Zhangjiafen Village; the watershed area is 8827.41 km^2. Its main tributaries are the Heihe River, the Tanghe River, and the Baimaguan River. The study area in this paper is the upstream of Chaobai River, which refers to the part of Chaobai River flows through Beijing but above the Miyun Reservoir. The total watershed area is 3514 km^2, including 400 km^2 of the Chaohe River, and 3114 km^2 of the Baihe River. The basin belongs to the Yanshan Mountain range, and the physiognomy is dominated by mountainous and hilly landscape. The terrain is high in the northwest and low in the southeast, and more than 60% of the areas in the region has a slope greater than 25°. The basin has a warm temperate zone semi-humid monsoon climate, which experiences an average annual rainfall of 660 mm. Land utilizations is dominated by forest (65.2%), grassland (16%), and arable land (17.5%) respectively, and the remaining land is water (0.4%) and construction sites (0.7%) [15]. The soils in this region are divided into three categories: brown soil, cinnamon soil, and calcareous soil. Brown soil is distributed in middle mountainous areas that are more than 700–800 m above sea level. Cinnamon soil is distributed mainly in the low mountain area and hilly area, which is the largest area, and thus this is the most widely distributed soil. Calcareous soil is located in bottom and high floodplain of the river valley. Brown soil and the cinnamon soil account for 80% or more of the total area.

The study area belongs to a warm-temperature zone deciduous broad-leaved forest belt. The main vegetation types are deciduous broadleaf forest and temperate coniferous forests. In middle mountainous areas with altitude above 800m, the shady slope dominated by birch, oak, aspen, linden, maple, and other deciduous broad-leaved secondary forest with a shrub understory. The sunny slope is dominated by deciduous shrub, scattered with pine, cypress, and other coniferous trees. In low-elevation mountainous areas with altitudes below 800 m, the shady slope is dominated by mixed shrubs. There are broad-leaved oak forests in some areas, and Chinese pine plantations in some locations with more favorable water and temperature conditions. The sunny slope suffers serious soil erosion in most areas, which has resulted in shallow soil and low vegetation coverage. There are few trees and mainly shrubs. Hilly areas are dominated by shrub, with different size vegetation including pine, acacia and others. Local crops are dominated by xeric grasses (mostly are maize and sorghum), with some legumes.

The Miyun Reservoir is the most important water source of Beijing and is located in Central Miyun County, across the main channel of Chaohe River and Baihe River. However, in recent years, soil erosion has become very serious among the area upstream of the reservoir. The causes are due to the mountainous region, where water is more developed, with a high concentration of precipitation in summer, and the lithology consists mainly of metamorphic rocks, igneous rocks and volcanic rocks, which are weak in weather-resistance. The geological structure, especially the faulted structure, is relatively well-developed. However the mining, tourism and agriculture and other human activities are more strongly related to soil erosion in the areas [16]. The illustrations below show the Chaobai River drainage basin subarea map and the percentage of soil erosion (erosion area to their proportion of watershed area) (Figure 1).

2 Sampling and analysis

2.1 Sample collection

Sample collections of plants, soil, and surface sediments were initiated in August, 2009, in the study area of the Chaobai River. The sampling sites covered the Chaohe River (Gubeikou Village to the Miyun Reservoir), the main stream of the Baihe River (from Xishan Village, Houcheng Township, Hebei Province to the Miyun Reservoir) and the Miyun Reservoir. The point stations of sampling for surface sediments are shown in Figure 2. The samples were sent back to the laboratory one day after their collection, placed into a vacuum freeze-drying machine, ground sieved and screeed using 100 mesh (149 microns) after they were completely dry, and then sealed in polyethylene plastic bags prepared for experimental analysis.

We collected different types of plants along the densely covered areas of the river bank. Aquatic plants (18 items), were collected such as cattail, reed, sedge brown scales, and barnyard grass. The collected terrestrial C3 vegetation (7 items), mainly included pine, black locust, poplar, and similar samples. Collected terrestrial C4 vegetation (7 items), mainly included maize and sorghum. The samples collected were mainly plant leaves and grass, with only a small amount of stems. After plant samples were collected, they were washed of soil, freeze-dried, crushed with micro-mill plants, ground sieved and screened using 100 mesh, and freeze-dried for use later.

Soil samples (13 items) are surface soil (0–20 cm), collected from the riverbank and the reservoir nearby, and mainly include brown soil and cinnamon soil. The soil samples were cryo-preserved in −20°C immediately after 12 h, freeze-dried when they were sent back to the lab, then plant debris and large stones were picked out from the soil sample, which was then ground sieved and screened using 100 mesh before being freeze-dried again for use.

2.2 Sample treatment and analysis

A total of 0.5 g sediment and soil samples were taken, inorganic carbonates were removed using 0.5 mol/L HCl for acidification, and samples were then rinsed with deionized water until the filtrate was neutral. Silver nitrate solution was used to detect the presence or absence of Cl-residues, and then samples were freeze-dried and inorganic carbon was removed. Sample analysis was conducted in the Test Center of the China Academy of Geological Sciences, Key Laboratory of Geochemistry, using an elemental analyzer (FLASH EA1112, Thermo) and mass spectrometer (MAT253) spectrometry to determine organic carbon and nitrogen content and stable isotope composition. The formulas are

$$\delta^{13}\mathrm{C}\ (\%)=[(R_{\mathrm{sample}}-R_{\mathrm{standard}})/R_{\mathrm{standard}}]\times 1000,\quad R={}^{13}\mathrm{C}/{}^{12}\mathrm{C};$$

$$\delta^{15}\mathrm{N}(\%)=[(R_{\mathrm{sample}}-R_{\mathrm{standard}})/R_{\mathrm{standard}}]\times 1000,\quad R={}^{15}\mathrm{N}/{}^{14}\mathrm{N}.$$

The $^{13}C/^{12}C$ and $^{15}N/^{14}N$ correspond to international standards Vienna PDB and atmospheric nitrogen standard, and

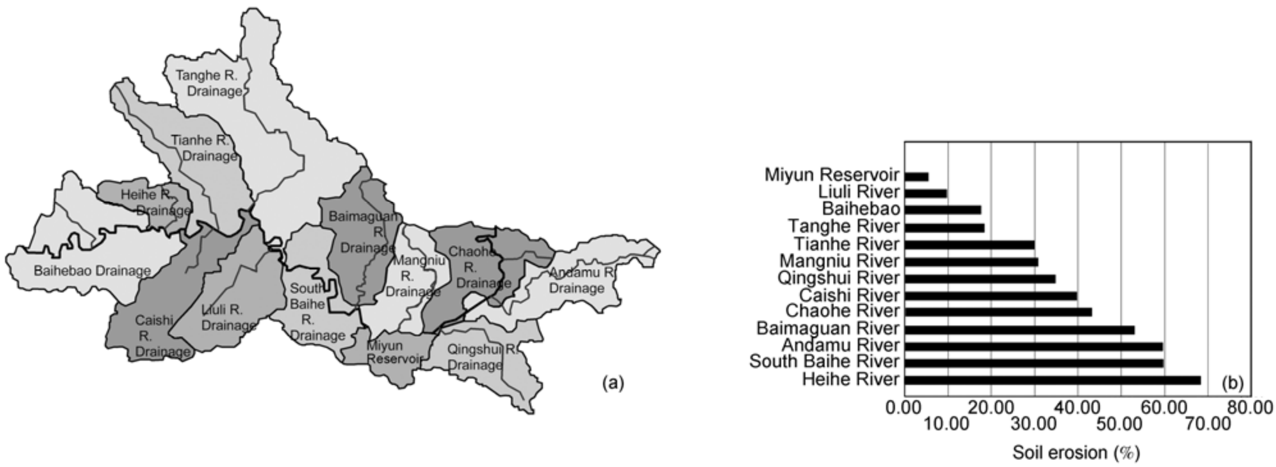

Figure 1 The drainage basin subarea map (a) and the percentage of soil erosion in the upstream region of the Chaobai River (b). The data are from footnote 1).

1) Beijing Institute of Geology. The General Survey Report of Comprehensive Geological Environment for Main Water Sources in Beijing. 2003. 87–92.

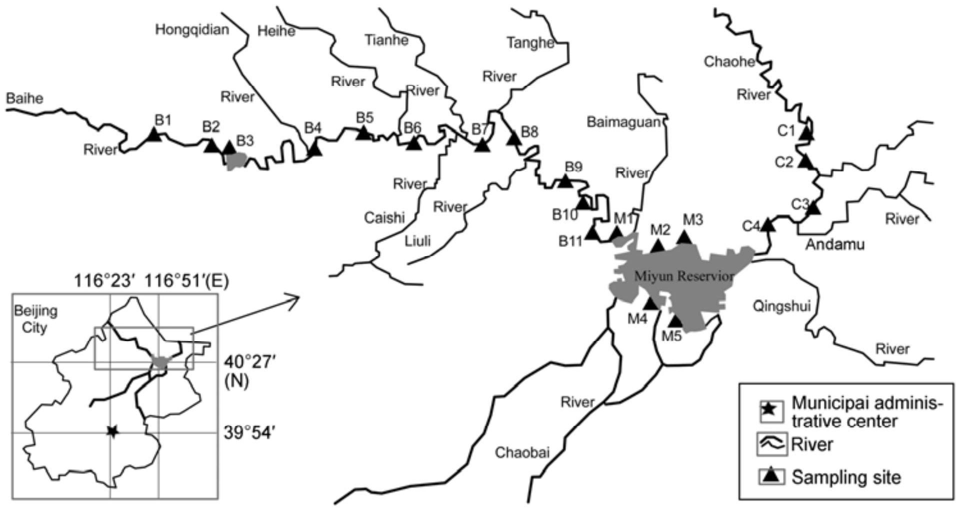

Figure 2 Diagram of the sampling point stations of Chaohe River (C), Baihe River (B), and Miyun Reservoir (M).

analytical error is ±0.3%.

The concentration of nitrate ions was determined by ion chromatograph ICS-90 produced by DIONEX.

3 Results and discussion

3.1 Carbon and nitrogen isotope analysis of sedimentary organic matter in Chaobai River

Total organic carbon (TOC) content of surface sediments in the basin (Table 1) is between 0.11% and 1.76%, with an average of 0.64%±0.47% (n = 20). The organic carbon content of samples from C1and C3 in Chaohe River is significantly higher than that of other point stations in the basin. And the organic carbon content of samples from B2, B4, and B6 of the Baihe River and M5 of the Miyun Reservoir is also higher. Previous studies have shown that the erosion was moderate along the Chaohe River; however, water loss and soil erosion are more serious upstream of the Baihebao Reservoir, Qianjiadian Township, Baoshan Temple, and Changshaoying Village, due to human activities and different natural factors. High organic carbon content areas (except M5) in the study areas overlap with the water loss and soil erosion area, which demonstrates that the inputs of organic carbon in these point stations may come from a large number of terrigenous organic carbons. Although the situation of soil and water conservation around the Miyun Reservoir is better, high organic carbon content in M5 may be related to human activities locally.

C/N ratio is often used to determine the origin of organic matter. Some research shows that the C/N ratio of terrestrial higher plants is generally > 15 [3], the C/N ratio of soil organic matter is usually between 10 and 13 [17, 18] , and the C/N ratio of aquatic plants is generally 6 to 8 or 10 to 30 [3]. The C/N ratio of sediment in the Chaobai River is between 8.50 and 13.68, with an average of 10.37±1.42 (20 samples), which reflects that the sources of sedimentary organic matter are mixed; in other words, the sources are both exogenous and indigenous to the river itself.

Many scholars use the C, N isotopes of organic matter to better identify its origins . Generally, they consider the δ^{13}C values of terrestrial C3 and C4 plant debris to be −23‰ to −30‰ and −17‰ to −9‰ [19], the δ^{13}C value of soil organic matter is −22‰ – −25‰ [20], the δ^{13}C value of aquatic vascular plants is −18‰ to −28‰ [21, 22], and the δ^{13}C value of plankton is −24‰ to −42‰ [21, 23]. For aquatic plants, NO_3^- is its major nitrogen sources for utilizing, and terrestrial plants mainly uptake soil inorganic ammonium and nitrate ions through root to obtain nitrogen [24]. The dissolved δ^{15}N value of NO_3^- ranges from 7‰ to 10‰ [25], and the δ^{15}N value of soil N ranges from −6‰ to 16‰ [24]. The δ^{13}C value of organic matter in Chaobai River ranges from −27.75‰ to −21.58‰ with an average of −25.29‰±1.73‰ (20 samples); the δ^{15}N value ranges from 1.32‰ to 6.74‰ with an average of 3.60‰±1.5‰ (20 samples). This reflects the diversity of sources of organic matter in sediment of the Chaobai River.

From the juncture of Hebei Province and Beijing to the Miyun Reservoir, there is no significant change in regular trend (Figure 3) on the organic carbon content (TOC), C/N ratio and the δ^{13}C value, which again demonstrates the diversity of sources of organic matter in sediments of Chaobai River.

3.2 Qualitative analysis of the source of sedimentary organic matter in Chaobai River basin

The relationship diagram of C/N and δ^{13}C is an effective qualitative analysis method for the sources of organic matter. The precondition for accurately applying this method is the reasonable range of the different sources (end-members)

Table 1 Measured values of TOC, TN, δ^{13}C, δ^{15}N and C/N in surface sediment of upper reaches of Chaobai River

Study area	Point station	TOC (%)	TN (%)	δ^{13}C (‰)	δ^{15}N (‰)	C/N
Chaohe River	C1	1.71	0.16	–25.17	4.30	10.46
	C2	0.42	0.04	–24.18	2.37	10.14
	C3	1.76	0.18	–26.06	6.74	9.87
	C4	0.97	0.08	–27.27	6.19	11.97
Baihe River	B1	0.33	0.03	–25.32	1.32	9.92
	B2	0.86	0.09	–25.24	2.83	9.77
	B3	0.34	0.04	–23.19	4.86	8.56
	B4	0.90	0.08	–27.75	5.17	11.92
	B5	0.23	0.02	–26.32	4.37	13.68
	B6	0.82	0.08	–26.26	3.26	10.03
	B7	0.38	0.04	–26.20	2.29	10.26
	B8	0.60	0.06	–26.49	4.77	10.51
	B9	0.11	0.01	–26.24	4.45	8.27
	B10	0.12	0.01	–27.75	2.97	9.32
	B11	0.70	0.08	–24.62	4.27	8.50
Miyun Reservoir	M1	0.34	0.03	–21.94	2.65	10.38
	M2	0.73	0.06	–24.62	1.75	11.72
	M3	0.25	0.03	–21.58	2.66	8.79
	M4	0.26	0.02	–23.58	1.66	12.57
	M 5	0.94	0.09	–25.97	3.15	10.80

organic matter C/N and δ^{13}C. Potential sources of organic matter in the river include: terrestrial higher plants (C3 and C4 plants), soil organic matter, aquatic vascular plants, plankton, and algae [3, 4]. Previous studies have summarized the ranges of δ^{13}C for the sources of sedimentary organic matter and C/N ratio. Our study determines the plants and soil in the basin (Table 2). The conclusion reached through comparison and analysis (Table 3) is that the plants and soil organic carbon in the basin are broadly consistent with the results of previous studies. However, there is no previous research on the end-members value for organic carbon of plankton in basin water, and this study has not determined its value, either. Redfield's study has shown that freshwater plankton has C/N ratio similar to marine phytoplankton, which is generally between 6 to 8 [26], and a typical δ^{13}C value for freshwater plankton is between –24‰ – –42‰ [21, 23]. Of course, due to the different environmental changes in rivers around the world (such as temperature, nutrients, CO_2 in water), the δ^{13}C values and C/N ratio of water plankton will appear significantly different. Samples taken at different periods along the river show that there are minimal water algae in the basin so we can ignore the contribution of algae. Therefore, we discuss only the remaining five possible end-members: C3 plants, C4 plants, soil organic matter, aquatic vascular plants and river plankton. Little amount of C3 and C4 plant samples were collected in this study. Thus, we cited results in previous research for δ^{13}C values for C3 and C4 plants [19], the δ^{13}C values for C3 plants are in the range of –23‰ – –30‰, and the values for C4 plants are in the range of –17‰ – –9‰. Due to the wide variation of C/N ratios for different plants, the C/N ratio for C3 and C4 plants in this article uses the measuring values that C3 plants > 18, C4 plants > 15. Since the vegetation types are different in different areas, and the δ^{13}C values and C/N ratios of soil organic matter exhibited significant differences, this article uses the measured value δ^{13}C in the range of –21.0‰ to –26.0‰, and C/N in the range of 9.0–12.5. While the differences around the aquatic environment and the δ^{13}C values and C/N ratios of aquatic vascular plants are quite different, this article uses the following measured values: δ^{13}C is between –16.0‰ and –30.0‰, and C/N is between 12.6 and 18.5. For the end-member values for planktons, the previous findings are used that δ^{13}C is between –24‰ and –42‰, C/N is 6–8.

The δ^{13}C values and the C/N ratio of surface sediment (0–2 cm) represent the organic matter input to the river over the short term [27]. Figure 4(a) clearly shows that there are three main sources of sedimentary organic matter in Chaobai River basin: soil organic matter, river plankton, and aquatic vascular plants; the contribution of C3 and C4 plants is small. Figure 4(b) shows that the main sources of sedimentary organic matter can be divided into three types: (1) the main sources are soil organic matter (C1, C2, B1, B2, B3, M1, M2, M3); (2) the main sources are aquatic vascular plants and river plankton (C4, B4, B10); (3) a combination of the above two types, with a larger contribution by soil organic matter (C3, M5, B6, B7, B8 , B9). In addition, the sources of organic matter in B5 are mainly from aquatic vascular plants, the main sources in B11 are soil organic matter and river plankton, and the sources in M4 are mainly from soil organic matter and vascular plants in the river. From the above results, it can be seen that the main sources of organic matter are soil organic matter for 70% of the

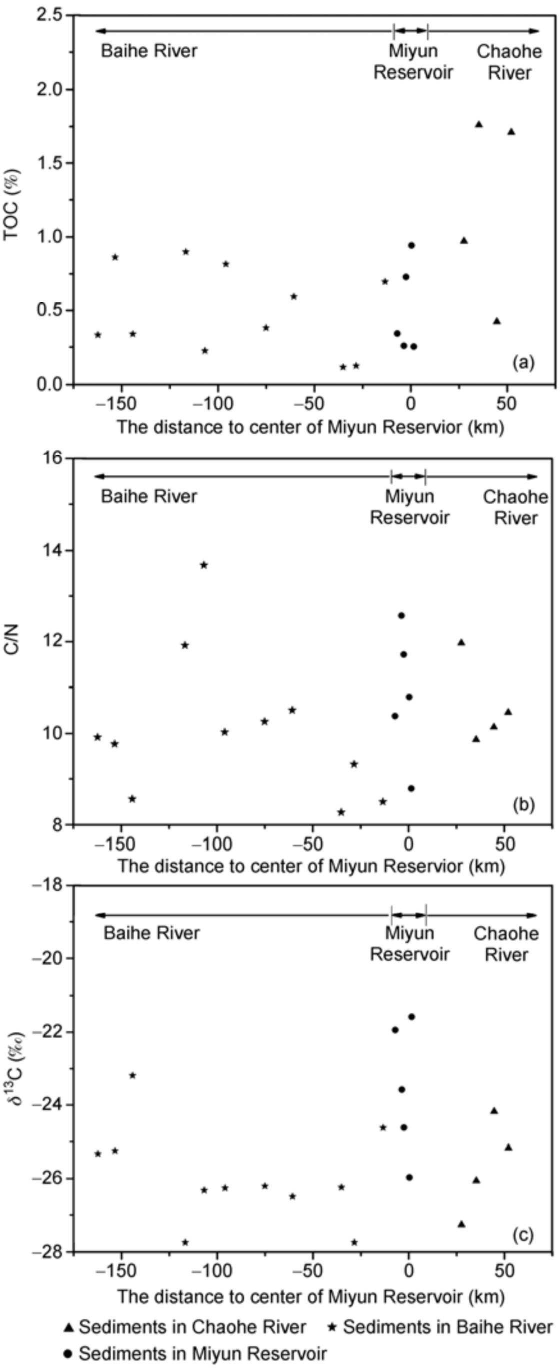

Figure 3 Distribution of values of TOC, C/N and $\delta^{13}C$ in the surface sediment of the Chaohe River, Baihe River and Miyun Reservoir.

basin point stations, which indicated that the main sources of sedimentary organic matter are external. It is consistent with the conclusions for the Schelde estuary by Middelburg [28].

In the Chaohe River basin, the sources of sedimentary organic matter in C1 and C2 belong to the first type, while the situations in C3, C4 belong to the third and the second and third types. Soil organic matter are the dominant contributor in 75% of point stations.C1 and C2 are located near Gubeikou Village. Gubeikou is situated at the entrance of the Chaohe River into Beijing Municipality and reflects the basin situation in Hebei Province. The soil erosion is more serious within Hebei Province due to the low vegetation cover, which results in the erosion of a large number of terrestrial materials, so the contributions of soil organic matter in these two point stations are larger. C3 and C4 are located downstream of Gubeikou. There have been remarkable results in Beijing Municipality, so the contributions of soil organic matter are relatively increased.

As observed in the Chaohe River, the sources of sedimentary organic matter in the Baihe River are divided into three types: B1, B2, and B3 belong to the first type; B4 and B10 belong to the second type; B6, B7, B8, and B9 belong to the third type. The main sources of B5 are vascular plants in the river, while soil organic matter and river plankton are the main sources in B11. It can be seen that the soil organic matter make a larger contribution to sedimentary organic matter in 63% of point stations. Since the ecological damage within Hebei Province is more serious, the water quality in the main stream of the Baihe River is poor. After entering Beijing Municipality the poor quality water is blocked by the Baihepu Reservoir's upstream without further flooding into the Baihe River. In the downstream of the Baihepu Reservoir, the water quality gradually improved over time due to the precipitation and the better ecological environment within Beijing. B1, B2, and B3 are located upstream of the Baihepu Reservoir, and the contribution of soil organic matter has a direct relationship with serious soil erosion. In the point stations located below the Baihepu Reservoir, the contribution of soil organic matter to sedimentary organic matter decreased while the contribution of aquatic vascular plants and river plankton increased, which is connected with the healthier ecological environment in Beijing.

Compared with the Chaohe and Baihe Rivers, the contribution of soil organic matter to organic matter in the Miyun Reservoir is much larger. The sources of organic matter in three point stations (M1, M2, M3) belong to the first type, one point station (M5) belongs to the third type, and the sources of sedimentary organic matter at M4 are soil organic matter and vascular river plants . It can be seen that the contributions of soil organic matter are greater in 80% of point stations. The Miyun Reservoir is the meeting point of the Chaohe River and the Baihe River. Due to the good soil and water conservation around the Miyun Reservoir (Figure 1), it can be concluded that the majority of soil organic matter in the Miyun Reservoir sediment comes from the terrigenous sediment carried by the Chaohe River and Baihe River. This further demonstrates that the contribution of sedimentary organic matter to the Miyun Reservoir by the Chao and Baihe Rivers is much larger than the contribution of sedimentary organic matter by the Miyun Reservoir itself. It should be noted that the point stations in this research are

Table 2 Measured values of C/N, carbon and nitrogen isotopes in the source of sedimentary organic matter[a)]

End member No.	C3 plants			C4 plants			Soil organic matter			Aquatic vascular plants		
	δ^{13}C (‰)	δ^{15}N (‰)	C/N	δ^{13}C (‰)	δ^{15}N (‰)	C/N	δ^{13}C (‰)	δ^{15}N (‰)	C/N	δ^{13}C (‰)	δ^{15}N (‰)	C/N
1	−27.86	−1.96	18.01	−12.89	2.41	19.13	−26.02	2.05	12.41	−15.87	4.70	13.79
2	−28.93	−0.78	18.40	−13.50	7.00	26.25	−23.95	2.21	11.65	−12.60	5.97	13.21
3	−28.60	−0.59	18.11	−17.40	−17.4	29.29	−24.84	−0.22	11.78	−28.58	8.87	16.46
4	−21.84	−2.20	18.37	−14.89	4.50	15.20	−24.72	4.79	12.46	−22.21	8.24	12.85
5	−27.93	−2.75	38.03	−12.56	5.83	15.02	−25.63	−0.66	11.61	−26.40	9.99	12.23
6	−27.97	−2.33	27.50	−11.28	5.25	15.33	−21.18	−0.15	10.84	−17.78	5.34	13.37
7	−26.68	−1.80	18.68	−13.23	1.36	15.27	−23.84	0.97	9.38	−18.01	6.34	16.00
8							−23.84	4.22	10.38	−28.54	1.85	14.00
9							−23.81	4.78	10.88	−14.12	2.28	18.49
10							−24.48	3.90	9.37	−28.79	6.31	14.67
11							−21.47	0.15	9.45	−29.32	6.20	14.04
12							−23.80	1.40	10.98	−29.25	7.00	17.79
13							−25.97	0.22	10.13	−27.56	5.72	17.71
14										−28.30	7.34	18.68
15										−27.67	-2.92	37.91
16										−29.56	6.28	9.02
17										−28.91	4.37	12.58
18										−30.05	10.85	7.95

a) C3 plants consisted mostly of *Pinus massoniana*, *Pinus tabulaeformis*, jujube tree, and cypress trees; C4 plants consisted mostly of maize, sorghum, and bean. Aquatic vascular plants consisted mostly of reed, cattail, sedge, barnyard grass, cress, *Potamogeton crispus*, water crowfoot. The soil samples are collected from the corresponding growing region of C3 and C4 plants.

Table 3 The distribution of δ^{13}C and C/N for the sedimentary organic matter[a)]

Sources of sedimentary organic matter	δ^{13}C (‰)		C/N	
	Previous studies	Current study	Previous studies	Current study
C3 plants	−30 – −23 [20]	−28.93 – −21.84 (n=7)	>15 [17]	18.01–38.03 (n=7) (>18)
C4 plants	−17 – −9 [20]	−17.40 – −11.28 (n=7)	>15 [17]	15.02–29.29 (n=7) (>15)
Soil organic matter	−25 – −22 [21]	−26.0 – −21.18 (n=13) (−26.0 – −21.0)	10–13 [18, 19]	9.37–12.46 (n=7) (9.0–12.5)
Aquatic vascular plants	−28 – −18 [22, 23]	−30.0 – −12.60 (n=18) (−30.0 – −16.0)	10–30 [3]	7.95–37.91 (n=7) (12.6–18.5)
River plankton	−42 – −24 [22, 24]	–	6–8 [26]	–

a) Compare the results of previous studies and the measurement data of this study. n represents the number of samples for determination, and the numbers in parentheses are focused range for determining data in this study.

limited to the perimeter of the reservoir and that this limits the conclusions.

In the analysis above, soil organic matter is the main source of sedimentary organic matter in the upper reaches of the Chaobai River. The contribution of soil organic matter to sedimentary organic matter in the Chaobai River is reduced in Beijing Municipality compared to that in Hebei, while the contribution of aquatic vascular plants and the river plankton is relatively increased. The sedimentary organic matter in the Miyun Reservoir is derived mainly from the Chaohe River and the Baihe River, while the contribution from the reservoir area itself is small.

3.3 Quantitative analysis of sources of sedimentary organic matter in Chaobai River basin

In order to quantify the sources of organic matter in the upper reaches of Chaobai River, a tri-mixed model was developed to determine the contributions of different sources based on the principle of a conservative mixture of different end-members values for δ^{13}C and C/N in the water and the law of mass conservation. As shown in Figure 4(a), three end-members were selected, i.e. soil organic matter, aquatic vascular plant and river plankton. Due to their small contribution to the sedimentary organic matter, the C3 and C4 plant debris was neglected. The end-member models are

$$\delta^{13}C_{sample}=\delta^{13}C_{soil}\cdot f_{soil}+\delta^{13}C_{M}\cdot f_{M}+\delta^{13}C_{P}\cdot f_{P},$$

$$C/N_{sample}=C/N_{soil}\cdot f_{soil}+C/N_{M}\cdot f_{M}+C/N_{P}\cdot f_{P},$$

$$1=f_{soil}+f_{M}+f_{P},$$

where δ^{13}C is the stable carbon isotope compositions of organic matter; C/N is the atomic ratio of carbon and nitro-

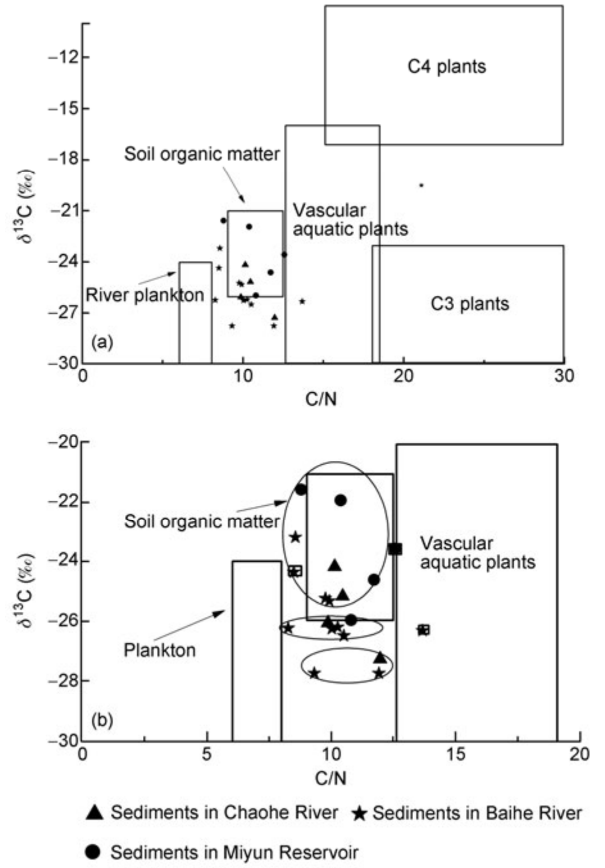

Figure 4 The relationship diagram of the δ^{13}C and C/N for the sedimentary organic matter in the Chaobai River. The solid points represent the data points of sedimentary organic matter, the rectangles represent the range of different end-member values for δ^{13}C and C/N, and the ellipses represent the three types of origins of the organic matter. (a) five-end-member diagram; (b) three-end-member diagram.

gen in organic matter; f is the percentage of different source contribution; and the subscripts of soil, M, and P represent the end-members of soil organic matter, aquatic vascular plants and river plankton respectively.

Determination of the values of different end-members is as follows. (1) Soil organic matter: The distribution of soil δ^{13}C in this basin is between −21.18‰ – −26.02‰ (n=13) with a majority in −23‰ – −24‰ (n=5), and the average value of C13 of the samples distributed in −22‰ – −25‰ (n=8) was taken as the eigenvalue of soil C13. The range of soil C/N is within 12.46–9.37 (n=13) with a majority of 10–11 (n=5), and the average C/N of 9–12 (n=11) of the samples was taken as the eigenvalue of soil C/N. Based on calculation, the C13 and C/N were determined to be −24.2‰ and 10.6 respectively. (2) Aquatic vascular plants: C13 of the aquatic vascular plants in this basin was distributed within −12.60‰ – −30.05‰ (n=18) with a majority in −27‰ – −30‰ (n=10), and average δ^{13}C in the samples of −26‰ – −31‰ (n=12) was taken as the eigenvalue of soil δ^{13}C. C/N of the aquatic vascular plants was distributed within 7.95–37.91 (n=18) with a majority in 13–18 (n=10), and average C/N in the samples of 12–19 (n=15) was taken as the eigenvalue of soil C/N; the δ^{13}C and C/N were determined to be −28.6‰ and 15.1 respectively. (3) River plankton: the amount of plankton was not directly measured in this paper, and the data reported in previous studies were used. The δ^{13}C and C/N of plankton were determined to be −30‰ [3, 28] and 7.3 [29] respectively based on the findings of Kendall, Middelbur, and Canuel.

As shown in Table 4 and Figure 5, the organic matter in C1 to C3 in the Chaohe River basin were mainly from the soil, the plankton made a smaller contribution, while the aquatic vascular plants made little contribution (about 5%). In C1 and C2 , soil organic matter accounted for 81.86% and 102% respectively, while the contributions of plankton in C1 and C2 were 12.27% and zero respectively. The contribution of soil organic matter in C3 decreased to 66.8%, while the plankton increased to 28.51%. In C4, the contribution of aquatic vascular plants was 44.49%, and soil organic matter was 36.33%, followed by 19.18% of plankton. In the Chaohe River, the contribution of soil organic matter decreased gradually from C2 to C4, while aquatic vascular plants and plankton increased. This finding generally

Table 4 Percentage of organic matter in different sources for the Chaohe River, the Baihe River and the Miyun Reservoir[a)]

River/reservoir	Location	f_{soil} (%)	f_M (%)	f_P (%)	River/reservoir	Location	f_{soil} (%)	f_M (%)	f_P (%)
Chaohe River	C1	81.86	5.87	12.27	Baihe River	B1	80.84	−0.87	20.03
	C2	102.00	6.86	−8.86		B2	82.89	−3.40	20.51
	C3	66.80	4.69	28.51		B3	126.43	−37.35	10.92
	C4	36.33	44.49	19.18		B4	27.28	47.70	25.02
Miyun Reservoir	M1	144.16	−21.52	−22.64		B5	48.68	61.18	−9.86
	M2	88.07	19.42	−7.49		B6	62.41	8.59	29.00
	M3	156.55	−47.14	−9.41		B7	62.77	11.38	25.85
	M4	105.12	23.07	−28.19		B8	56.34	17.31	26.35
	M5	65.32	17.25	17.43		B9	68.86	−16.71	47.85
						B10	36.24	10.58	53.18
						B11	99.17	−26.56	27.39

a) f_{soil}, f_M and f_P representing the parts of soil, aquatic vascular plant, and plankton.

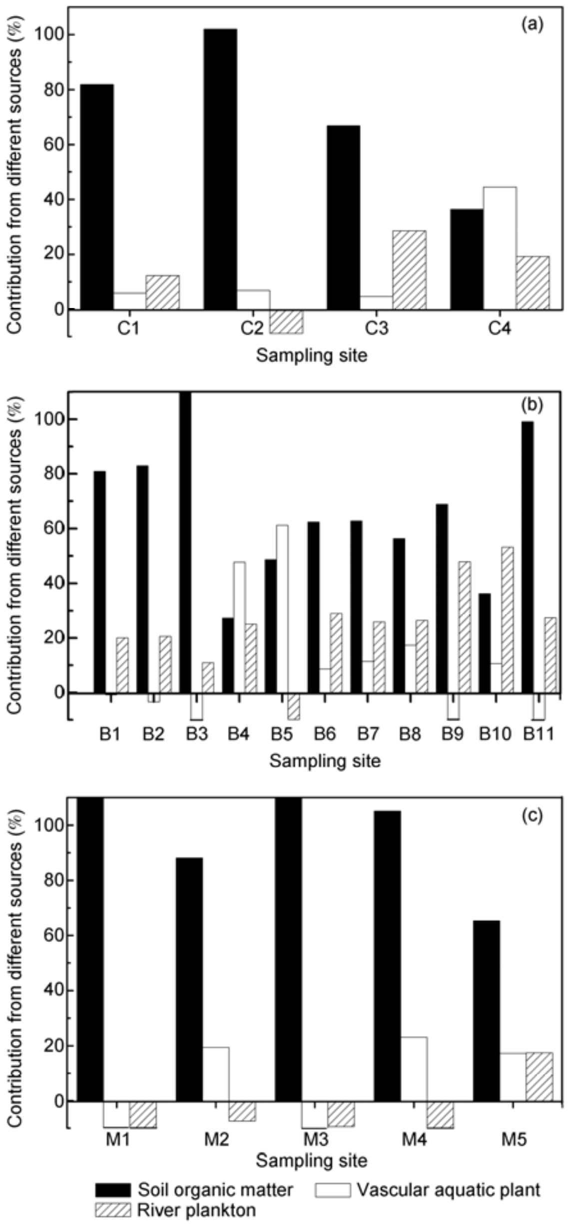

Figure 5 Percentages of organic matter in different locations along the Chaohe River (a), Baihe River (b), and Miyun Reservoir (c).

matches the qualitative analysis. From C1 to C3, the contribution of aquatic vascular plants is close to zero, while in C4 it becomes a major part, indicating a good productivity in this area.

In the Baihe River basin, a major contribution of soil organic matter, aquatic vascular plants and plankton was found in 8, 2, and 1 point stations, respectively. The results show that the soil organic matter is the major source of sedimentary organic matter. Based on the distribution and contribution of different organic matter in the Baihe River shown in Figure 5, the point stations can be assigned into four different categories: (1) B1–B3; (2) B4 and B5; (3) B6 to B8; and (4) B9–B11.

From B1 to B3, the major source in the sedimentary organic matter is soil. The distribution of organic matter sources in B1 and B2 is similar where the greatest contribution is from soil organic matter (81%), plankton is less with approximately 20% of contributed matter, while aquatic vascular plants contribute nothing. In B3, the organic matter mostly from soil, and nearly nothing from the other two types. This result agrees with the qualitative analysis.

In contrast to B1, B2, and B3, the biggest contribution of organic matter in B4 and B5 is from aquatic vascular plants, and the contribution of soil is significantly decreased. In B4, the aquatic vascular plants contribute about 47.70% of organic matter, and the contributions from soil and plankton are roughly the same (accounting for 27.28% and 25.02% respectively). An increase of organic matter from aquatic vascular plants and soil in B5 was observed, accounting for 61.18% and 48.68% respectively, and plankton contributed nothing. As shown in Figures 1 and 2, the water and soil erosion is relatively small in Baihebao basin where B4 and B5 are located. Water from the main stream of the Baihe River in Hebei Province is introduced to the Baihebao Reservoir, and therefore the terrestrial organic matter is relatively reduced, which explains the decrease of soil organic matter and the increase of aquatic vascular plant material. In B5 the measured result differs from the qualitative analysis, which indicates that the organic matter is completely derived from aquatic vascular plants, but the quantitative analysis results show that there is still a significant contribution from soil. This demonstrates that quantitative analysis can clearly distinguish between organic matter sources.

From B6 to B8, the measured results roughly agree with the qualitative analysis, showing that the major organic matter are from soil (60%) and less is from plankton (26%). Although the aquatic vascular plants contribute the smallest part, their contribution gradually increases from 8.59% to 17.31%. It might be because these three point stations are located in the lower reaches of Haihe River, which is originally from Chicheng County, Hebei Province. Because of its low vegetation ratio (less than 30% in most places) and severe rock effloresce, the Haihe River basin is one of the regions with a significant water and soil loss (69%), and carries a significant amount of terrestrial matter and pollutants, resulting in pollution. The Haihe River has a bigger effect on B6 and B7, and the sources of organic matter are also much similar. The contributions of soil organic matter and plankton are stabilized at approximately 62% and 27%, respectively, while the contribution of aquatic vascular plants is about 10%. Meanwhile, the Liuli River basin where B8 is located has a healthy water and soil conservancy condition (soil erosion level is about 9.68%). After settling for a long time, the pollution level was significantly alleviated in B8 and the ratio of soil organic matter was reduced to 56.34%, while aquatic vascular plants increased to 17.31%.

The main sources of organic matter in B9 and B11 are soil organic matter and plankton, and the contribution of aquatic vascular plants is negligible. B9 and B11 are located in the south section of the Baihe River basin, where the soil erosion is also very severe but less than along the Haihe River. The soil organic matter accounts for 68.86%, which is similar to the ratio (62.41%) of the soil organic matter in Haihe River basin. The contribution of soil organic matter is almost 100% in B11, roughly equaling to that of B3. It may be partially due to the severe water and soil erosion caused by the heavy rain in summer. In B10 the source of the organic matter in sediment is mainly from plankton (53.18%), and soil contributes less (36.24%) while the aquatic vascular plant accounts for 10.58%. This may be affected by local tourism. A filed survey showed that many restaurants and hotels were built along the rivers to the Miyun Reservoir. The inadequately treated waste water and solid waste are discharged directly into the rivers, resulting in a light eutrophication and increasing plankton growth. In the Baihe River basin, plankton makes the largest contribution to organic matter (more than 47%) in B9 and B10.

Compared with the Chaohe River and Baihe River, the Miyun Reservoir has more point stations where the major organic matter contribution is from soil (100%), while aquatic vascular plants and plankton have almost no contribution. At location M1, M3 and M4, the organic matter is 100% from soil, while for the other two point stations it accounts for 88.07% and 65.32% respectively, and the ratio of aquatic vascular plants increases to 19.42% and 17.25%, respectively. Organic matter from aquatic vascular plants and plankton accounts for a small part of organic matter in M2 and M5, while it is almost zero at other locations. The results agree with the qualitative analysis.

Table 4 shows that the contribution of a source could be over 100% or below 0 in individual point stations. For those in controlled ranges, the percentages were amended to 100% or 0. But in M1 and M3, the percentage of soil organic matter was much larger than 100% (144% and 156% respectively), while the ratio of aquatic vascular plant contributions were much less than 0 (–21% and –47% respectively). This was due to the δ^{13}C in organic matter of the sediment or C/N being over their thresholds, neglecting other pollutants in the water. For M1 and M3, the C4 plant was a source of organic matter. Previous studies showed that crops, maize in particular, were planted in the Miyun Reservoir basin.

To validate the assumption, a quaternary mixed model adding the C4 plant was utilized to calculate the contributions of organic matter sources for M1 and M3. The nitrogen isotope is also treated as an index. The values of the end-members were determined as followings. The values of δ^{13}C or C/N for soil organic matter, aquatic vascular plants and plankton used for above calculation were applied in this model as well. δ^{15}N in the soil was within –0.66‰–4.79‰ and the average value of 1.8 was used for calculation. δ^{15}N in aquatic vascular plant was –2.92‰–10.85‰ with a majority of 4–8 (n=11), and the average value of 6.4 in the samples of 3–9 (n=13) was determined. The δ^{15}N in plankton was taken as 5‰, based on measurements by Owen [30] and Wada [31]. δ^{13}C in C4 plant samples were within −11.28‰ – −17.40‰ (n=7), and the average value of −13‰ in the samples of −11‰ – −15‰ (n=6) was used. C/N in C4 plant was within 15.02 – 29.29 (n=7), and the average value of 16 in the samples (15–19, n=5) was used. δ^{15}N in C4 samples was within 1.36‰–7.00‰ (n=7), and the average value of 4.7 in the samples was taken. The result of the model calculation was shown in Table 5. For M1 and M3, the C4 plant has some contribution to sedimentary organic matter, while the soil still was the major source, which proves the previous assumption.

Table 5 Percentage of organic matter in different sources for M1 and M3 in Miyun Reservoir a)

Point station	f_{soil} (%)	f_{C4} (%)	f_M (%)	f_P (%)
M1	63. 13	27.33	−17.71	27.25
M3	51.33	35.49	−42.20	55.38

a) f_{soil}, f_{C4} , f_M and f_P represent the contribution percentage of sources in terms of soil organic matter, C4 plant, aquatic vascular plant and plankton, respectively.

The results of the quantitative analysis show that the major source of organic matter in sediment at 80% of point stations is from the soil. The similar results could be found for most rivers, namely, it is mainly comes from the soil through water and soil loss as well as the erosion [32]. For some point stations in the Miyun Reservoir, a small part of the organic matter is from C4 plant. Comparing sections of the Chaohe River and the Baihe River in Hebei Province with sections in Beijing Municipality shows that the percentage of organic matter from external sources, is decreased, while the percentage of organic matter from internal sources namely aquatic vascular plants and plankton, increases, particularly in the Baihe River. It is partly because of the river environment. The water and soil loss is severe in the upper reaches of the Chaohe River in Hebei, and a large amount of sand was excavated, which results in a higher sand content in the water. Furthermore, there is no reservoir regulation for the main streams of the Chaohe River, therefore water containing large amounts of sand and pollutants flushes into the Miyun Reservoir during flood periods. Hence the water quality is poor. The Baihebao Reservoir along the Baihe River results in much higher water quality.

4 Conclusions

According to the elemental analysis of organic matter and the studies of stable isotope of C, N for sediment in Chaobai River basin, following conclusions can be drawn:

(1) The total organic carbon content in the Chaobai River

sediment is in the range of 0.11% to 1.76%, with an average of 0.64%. The organic carbon contents are high in locations C1 and C3 along the Chaohe River, B2, B4 and B6 of the Baihe River, and M5 in Miyun Reservoir. With the exception of M5, the point stations above are located in the vicinity of severe soil erosion, which indicates that the organic carbon in these point stations may come largely from terrestrial organic carbon. The conditions in M5 may be due to local human activities.

(2) Joint end-member analysis of δ^{13}C and C/N ratios shows that the sedimentary organic matter in basins has mixed sources. The external source is soil organic matter, and the internal sources are aquatic vascular plants and river plankton.

(3) The sedimentary organic matter in the Chaohe River, Baihe River, and Miyun Reservoir is derived mainly from soil organic matter. The sedimentary organic matter in Miyun Reservoir comes mainly from organic matter carried by the Chaohe River and the Baihe River, while the contribution of organic matter by the reservoir itself is lower, while some point stations have a small amount of C4 plants as sources.

(4) The contribution of soil organic matter to sedimentary organic matter within Beijing is lower than in Hebei Province, while the contribution of aquatic vascular plants and plankton is higher, especially in the Baihe River basin, which demonstrated that the sources of organic matter can reflect the status of watershed soil erosion.

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