

Identifying organic matter provenance in sediments using isotopic ratios in an urban river

HUA-YUN XIAO* and CONG-QIANG LIU

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

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To provide a better understanding of potential hazard of effluent detritus, both at the present and in the future, the dispersal and accumulation of sewage-derived materials in the receiving river should be addressed. For the goals, we determined concentrations and isotopic compositions of sedimentary organic carbon (SOC) and nitrogen (SON) and those of effluents in an urban river (Nanming River, China). In the river, the two major sources of sedimentary organic matter (SOM) are effluent detritus ($\delta^{13}\text{C}$: -25.0‰ ; $\delta^{15}\text{N}$: $+8.5\text{‰}$; C/N: 8.1) and C3 plants growing along the river bank ($\delta^{13}\text{C}$: -27.7‰ ; $\delta^{15}\text{N}$: -0.9‰ ; C/N: >28). Isotopic difference between the two end-members was observed to be 9.4‰ for nitrogen, compared with 2.7‰ for carbon, and hence nitrogen isotopic difference between end-members is large enough to be used as a tracer for source recognition of SOM. Using a mixing model, we found that at outfalls sewage-derived SON accounted for $>60\%$ of the bulk SON. At site 40 km far from outfall, fraction of sewage-derived SON was still high to 50% . But at most sites, though about $450,000\text{ m}^3$ sewage effluents per day discharge into the river, effluent detritus and C3 plants contributed nearly the same to SOM, indicated that natural contribution from C3 plants should be also paid attention to.

Keywords: riverine sediment, isotopic ratios, effluent, C3 plants, sources

INTRODUCTION

Raw human wastewater usually contains high concentrations of nitrogen, phosphorus, and numerous other chemicals. Through the estuarine food web, sewage-associated contaminants would transfer to aquatic consumers (McClelland *et al.*, 1997; McClelland and Valiela, 1998). In order to assess the potential hazard of effluents, the dispersal and accumulation of sewage-derived materials in the receiving river should be addressed.

Various geochemical data help identify source of organic matter and the stable isotopic ratios have been reported to be most diagnostic. Considerable attention has been focused on the utilization of organic carbon and nitrogen stable isotopic ratios, in addition to C/N elemental ratios, as natural tracers identifying organic matter provenance in near-shore marine, estuarine, lacustrine and riverine environments (e.g., Mariotti *et al.*, 1984; Meyers and Eadie, 1993; Prahll *et al.*, 1994; Thornton and McManus, 1994; Andrews *et al.*, 1998; Kao and Liu, 2000). The analysis of carbon and nitrogen stable isotopic ratios provides information on the relative contri-

tribution of different sources. Because terrestrial organic matter ($\delta^{13}\text{C}$: -28‰ ~ -25‰ ; $\delta^{15}\text{N}$: $+0.2\text{‰}$ ~ $+4\text{‰}$) is more ^{13}C - and ^{15}N -depleted than marine organic matter ($\delta^{13}\text{C}$: -23‰ ~ -18‰ ; $\delta^{15}\text{N}$: $+4\text{‰}$ ~ $+9.7\text{‰}$), near-shore marine or estuarine organic matter from these two end-members are relatively easy to be identified using a single mixing model (Cifuentes *et al.*, 1988; Thornton and McManus, 1994; Middelburg and Nieuwenhuize, 1998). In freshwater environments, $\delta^{13}\text{C}$ versus C/N ratios can effectively separate land-derived organic matter (C3 and C4 plants) from aquatic plants and, thus, allow distinction between the end-members (Meyers, 1994, 1997).

In human disturbed watershed (e.g., contaminated estuaries), distinguishing between marine and sewage-derived materials ($\delta^{13}\text{C}$: -27‰ ~ -25‰ ; $\delta^{15}\text{N}$: $+1.4\text{‰}$ ~ $+3.3\text{‰}$) can be actualized because carbon and nitrogen isotopes are significantly distinct between them (Sweeney *et al.*, 1980; Cifuentes *et al.*, 1988; Gearing *et al.*, 1991; Bachtiar *et al.*, 1996; Waldron *et al.*, 2001; Ruiz-Fernández *et al.*, 2002). Sewage effluent is usually believed an important source of light (^{15}N -depleted) nitrogen and heavy (^{13}C -enriched) carbon in estuarine waters relative to marine organic matter (Bachtiar *et al.*, 1996). Terrestrial organic matter, however, overlap sewage-derived materials in the $\delta^{13}\text{C}$ versus $\delta^{15}\text{N}$ diagram. Therefore, organic matter provenance in contaminated waters is relatively difficult to be identified.

*Corresponding author (e-mail: xiaohuayun@vip.skleg.cn)

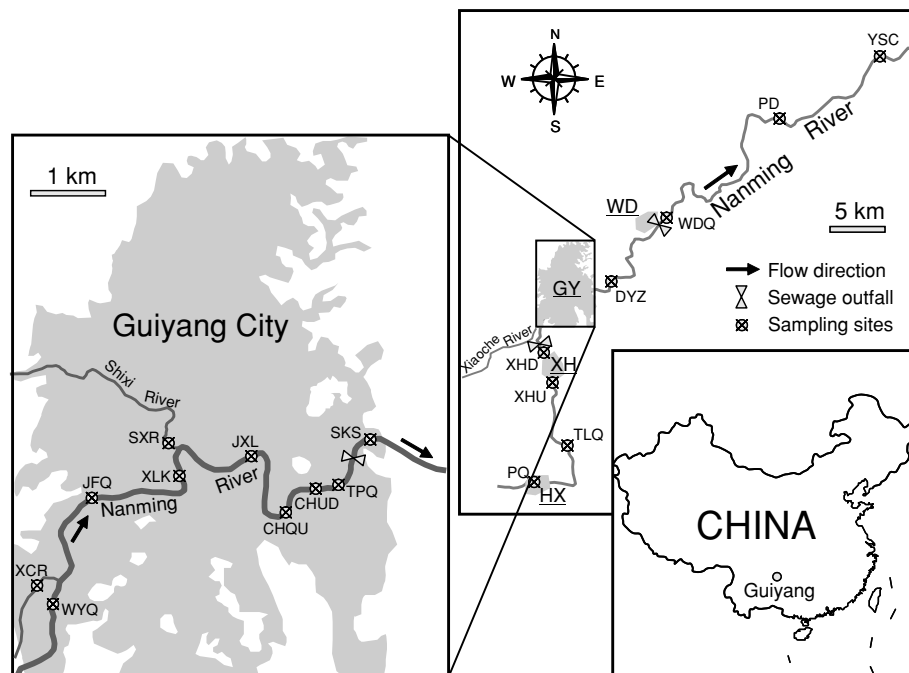


Fig. 1. Location of the sampling sites along the Nanming River. HX, XH, GY, WD represents Huaxi town, Xiaohe town, Guiyang city and Wudang town, respectively.

Due to increasing pressure from urbanization for most urban river watershed, it is important to better understand how sewage effluents, both at the present and in the future, influence the river environments. In order to assess the potential hazard of effluent detritus from outfalls which is in operation or closed, pervasiveness and persistence of sewage-derived OM in the receiving river should be examined. Additionally, we attempt to find an effective geochemical indicator for source recognition of sedimentary OM.

SITE DESCRIPTIONS AND METHODS

Study area

The Nanming River watershed is shown in Fig. 1, with a small catchment area of 1433 km². Headwaters are in the relatively pristine area of Huaxi town, about 30 km from Guiyang city (around 1.5 million people). Nanming River passes through Huaxi Town, Xiaohe Town, Guiyang city and Wudang Town. Within Guiyang domain, because trees (mainly C3 plants) are planted along the river, large numbers of tree leaves fall into the river in autumn. Beyond Wudang Town, the river, running northeast, finally flows into Wujiang River, a major branch of Yangtze River.

About 5.2 m³s⁻¹ sewage effluents discharge into the Nanming River without any treatment, accounting for about 40% of the annual flowing flux of the river (Guizhou

Environmental Protection Bureau, 2003). The sewage outfall at Shuikousi (SKS) has been in operation since 2003 and before at Tuanpoqiao (TPQ). In addition, two smaller outfalls are located at the downstream of Xiaohe Town (XHD) and Wudang Town (WDQ). The XHD outfall was located at the upstream of sampling site XHD before 1998 but now at the downstream.

Sampling and analysis

Surface sediment samples were collected from 16 sites along the Nanming River (Fig. 1) and its two tributaries in 2003. We collected 5–10 subsamples at each site and combined them into one representative sample. Sampling was performed at sites with a distance interval of 5–10 km (1–2 km within Guiyang city) and at effluent outfalls. In addition, sewage effluent wastewater was also sampled by a Niskin water sampler (General Oceanics, Inc., Florida) from the SKS outfall and then filtered (pre-combusted Whatman GF/F) to collect enough suspended material.

After removing inorganic carbon with chlorhydric acid of 2 mol L⁻¹, sediment samples were freeze-dried and then frozen to -20°C prior to elemental and isotopic determination. Nitrogen and carbon isotopic ratios were prepared using sealed-tube combustion and measured in a Finnigan MAT-252 mass spectrometer after purification with liquid nitrogen. Isotopic measurements are expressed as δ values, which are ‰ deviations from standard reference

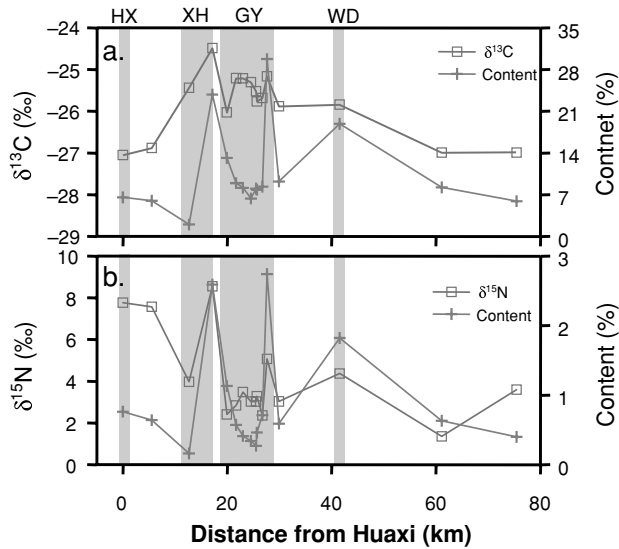


Fig. 2. Changing stable isotopic ratios with distance from Huaxi in Nanming River sediments. a. SOC; b. SON.

materials:

$$\delta X = [(R_{\text{sample}}/R_{\text{ref}}) - 1] \times 10^3 \quad (1)$$

where $X = {}^{13}\text{C}$ or ${}^{15}\text{N}$ and $R = {}^{13}\text{C}/{}^{12}\text{C}$ or ${}^{15}\text{N}/{}^{14}\text{N}$. Analysis of potassium nitrate standard (MOR2386-01, $\delta^{15}\text{N} = +1.92\text{‰}$) provided by Shoko Co., LTD, Tokyo, Japan, gave a mean ($\pm\text{SD}$) $\delta^{15}\text{N}_{\text{air}}$ value of $+1.9 \pm 0.2\text{‰}$ ($n = 5$). IAEA-C3 ($\delta^{13}\text{C} = -24.91\text{‰}$, cellulose) was used as a standard for $\delta^{13}\text{C}$ and the analytical precision ($n = 5$) was $<0.1\text{‰}$. Because we did not collect enough bacterial biomass, nitrogen isotopic ratios of bacteria were not determined.

Organic C and N contents of sediment and effluent detritus were determined by elemental analyzer (PE2400II, USA) with an analytical precision of 0.1% before removal of inorganic carbon with acid.

RESULTS

In Nanming River, C/N ratios of effluent detritus ranged from 7.3 to 8.9, lower than that (12.5) reported by Andrews *et al.* (1998) and Thornton and McManus (1994), reflecting an enrichment of N in effluent detritus. The SOC and SON contents within GY were $<1\%$ and $<0.1\%$ (Fig. 2), respectively, at most sites, while at outfalls, high contents of SOC and SON were found (e.g., 29.73% and 2.74% at SKS, respectively). Benthic surface sediments showed highly variable C/N ratios varying from 10 to 34.5 (Table 1) with a mean of 16.7 ± 6.2 , within the range between the typical value of the terrestrial organic matter (>20 ; Meyers, 1994) and freshwater phytoplankton ma-

Table 1. Isotopic values and C/N ratios of SOM in Nanming River and effluents

Sampling sites	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	C/N
PQ	-27.1	7.8	10.0
TLQ	-26.9	7.6	10.9
XHU	-25.4	4.0	14.5
XHD	-24.5	8.5	10.7
WYQ	-26.0	2.4	13.6
JFQ	-25.2	2.8	18.4
XLK	-25.2	3.5	23.3
JXL	-25.3	3.0	21.7
CHQU	-25.5	3.0	34.5
CHQD	-25.8	3.3	19.9
TPQ	-25.7	2.4	13.7
SKS	-25.2	5.1	12.7
DYZ	-25.9	3.0	18.2
WDQ	-25.8	4.4	12.1
XB	-27.0	1.4	15.2
YSC	-26.9	3.6	17.4

terials (6–9; Coffin *et al.*, 1989) or effluent SPOM (7.3–8.9; Fig. 2). The low C/N ratios at outfalls (10.7–12.7) revealed high N inputs from sewage effluents, consistent with the observed high N contents of effluent detritus (3.5–11.2%).

The $\delta^{13}\text{C}$ in effluent detritus at Guiyang was $-25.0 \pm 2.2\text{‰}$, much close to that reported by Andrews *et al.* (1998: $-24.8 \pm 3.2\text{‰}$), but slightly heavier than that by Thornton and McManus (1994: -26.7‰) while lighter than that by Lee Van Dover *et al.* (1992: $-22.8 \pm 2.9\text{‰}$). The $\delta^{15}\text{N}$ values of effluent detritus ($+8.5 \pm 1.1\text{‰}$) were heavier than those reported by Thornton and McManus (1994: $+2.3\text{‰}$), Lee Van Dover *et al.* (1992: $+3.3\text{‰}$) and Owens and Law (1989: $\delta^{15}\text{N} \approx +1.4\text{‰}$) and Sweeney and Kaplan (1980: $\delta^{15}\text{N} \approx +2.5\text{‰}$).

Table 1 showed that the $\delta^{13}\text{C}_{\text{SOC}}$ and $\delta^{15}\text{N}_{\text{SON}}$ values changed from -24.9‰ to -27.1‰ (averaging $-25.8 \pm 0.8\text{‰}$) and from $+1.4\text{‰}$ to $+7.8\text{‰}$ (averaging $+4.1 \pm 2.1\text{‰}$), respectively. There is similar spatial variation between element contents and isotopic ratios ($\delta^{13}\text{C}_{\text{SOC}}$ and $\delta^{15}\text{N}_{\text{SON}}$) of benthic surface SOM (Fig. 2). Three obvious peaks occurred at XHD (old outfall of XH), SKS and WDQ, being closely associated with the three sewage outfalls. Because of large discharge fluxes from sewage outfalls ($\sim 40\%$ of the river flowing flux) and lower C/N ratios while higher $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, effluent detritus may be an important SOM source.

DISCUSSION

Potential sources

Organic carbon and nitrogen stable isotope ratios, in addition to C/N elemental ratios, are practical to trace organic matter provenance in the aquatic environments,

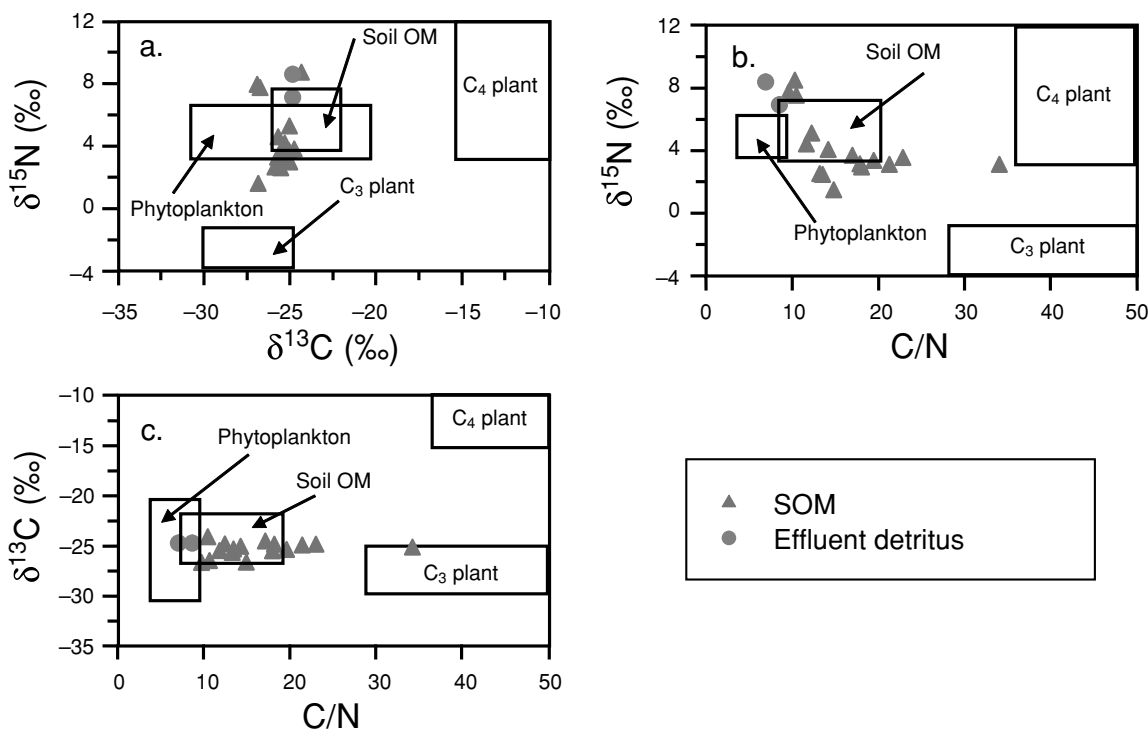


Fig. 3. Plots of $\delta^{15}\text{N}$ vs. $\delta^{13}\text{C}$ (a), $\delta^{15}\text{N}$ vs. N/C (b) and $\delta^{13}\text{C}$ vs. C/N (c).

allowing to discriminate the origin of SOM (e.g., Thornton and MacManus, 1994; Kao and Liu, 2000; Sigleo and Macko, 2002). The potential sources for particulate organic matter buried in rivers usually include aquatic plants (e.g., phytoplankton), zooplankton, terrestrial plants (C3 and C4), soil OM and effluent OM. Data of all these potential sources except aquatic animals, along with SOM in this study, were plotted in Fig. 3.

Chen and Wang (2005) observed 31 species of benthic animals in Nanming River during an investigation. Macroinvertebrate was found predominant at JXL. In general, consumers of both carbon and nitrogen isotopic values are slightly more positive than their food due to trophic fractionation (Gearing *et al.*, 1984; Peterson and Fry, 1987). Considering the relatively low $\delta^{15}\text{N}_{\text{SON}}$ at JXL (+3.0‰), we concluded that benthic animal-derived OM was not an important component for SOM.

We did not collect phytoplankton samples in this study for elemental and isotopic determination due to the difficulty in isolating phytoplankton from other suspended particulates. Generally, discrimination of phytoplankton from land-derived OM can be obtained because phytoplankton has atomic C/N ratio between 4 and 10, whereas vascular land plants have C/N ratios of ≥ 20 (C3 and C4 plants: Meyers, 1994). Freshwater phytoplankton typically have $\delta^{13}\text{C}$ values from -35.0‰ to -25.0‰ (Boutton, 1991), while $\delta^{15}\text{N}$ values around +5‰ (Owens

and Law, 1989). Even so, phytoplankton was not an important contributor for sedimentary OM because of the relatively low contents of suspended materials in river water ($<15 \text{ mg L}^{-1}$) in most sampling sites.

The $\delta^{15}\text{N}$ values of soil OM sampled at Guiyang, reported by Liu *et al.* (2006), averaged $+5.7 \pm 2.0\text{‰}$. OM in surface soils (0–20 cm) of Huaxi (HX) has atomic C/N ratios between 9.3 and 19.5, and $\delta^{13}\text{C}$ values between -26.4‰ and -22.3‰ (Zhu, 2006). Although soil OM has a similar characteristic to that of SOM (Liu *et al.*, 2006), most of it was accepted by effluent channels and then enter the river. So soil OM was only a component of OM in effluents. In this study, we assumed that the effluent OM was an integrated mixer of several land-derived OM including soil OM.

Several researchers (Zhu, 2006; Yang, 2007) analyzed the isotopic ratios of >10 species of C3 land plants sampled at HX, with $\delta^{13}\text{C}$ values in the range -29.9‰ – -25.4‰ . They found that they were depleted in ^{15}N (-4.1‰ to -0.8‰) relative to the previous reported C3 plants in other urban areas (-1‰ – $+6\text{‰}$: Pearson *et al.*, 2000), reflecting the dominance of atmospheric NH_x deposition (-12.2‰ ; Xiao and Liu, 2002) as N sources for terrestrial ecosystems in the area. Similar ^{15}N -depleted C3 plants were also observed in Taiwan (China) by Kao and Liu (2000). For SOM buried in Nanming benthic riverine sediments, C3 plants growing on the river bank,

should be one of the major contributors. The higher C/N ratios for SOM at XLK, JXL and CHQU (C/N > 20) revealed a greater contribution of terrestrially derived OM (C3 plants), which is further confirmed by its lower $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values.

Isotopic fractionation

Nitrogen isotopic fractionation Source recognition should consider kinetic isotopic fractionation effects because source $\delta^{15}\text{N}$ signatures are subject to radical modification during processes like DIN uptake, denitrification, remineralization, and nitrification (Heaton, 1986). Generally, breakdown of pure organic matter preferentially mineralizes ^{14}N , potentially causing an enrichment in ^{15}N in that which is left (e.g., Thornton and McManus, 1994). Preferential mineralization of more labile algal materials relative to terrestrial materials can also affect chemical and isotopic signatures of OM. This may cause a decrease in ^{15}N contents because algal materials tend to be more ^{15}N enriched ($\sim+8\%$) and more labile than terrestrially derived materials ($\sim+1\%$) (Meyers and Ishiwatari, 1993). But some researchers hold a different issue, who believed that isotopic fractionation during release of amino compounds or ammonia as a consequence of bacterial degradation of organic detritus can be negligible (Sweeney *et al.*, 1980).

In Nanming River sediments with much high or low organic matter contents, isotopic fractionation did not occur during SON decomposition as comparing $\delta^{15}\text{N}$ of exchangeable ammonium ($\text{NH}_4^+_{\text{ex}}$) with $\delta^{15}\text{N}$ of SON (Xiao *et al.*, 2009). In the paper, we found that at those sites having <1 mg/g $\text{NH}_4^+_{\text{ex}}$ contents, no obvious difference was observed between them. And there was no obvious trend between $\Delta\delta^{15}\text{N}$ and f [$=\text{NH}_4^+_{\text{ex}}/(-\text{NH}_4^+_{\text{ex}} + \text{SON})$] for all the samples. But for those having <1 mg/g $\text{NH}_4^+_{\text{ex}}$ contents, $\Delta\delta^{15}\text{N}$ was $\sim 0\%$ when f varied from 0.06 to 0.34. These indicated that small nitrogen isotopic fractionation occurred during parent SON degradation in sediments.

Carbon isotopic fractionation Selective loss of components during degradation is also an important process changing carbon isotopic ratios of bulk organic carbon in aquatic environments. Organic matter mineralization is usually believed generate small carbon isotopic fractionation (McArthur *et al.*, 1992; Fogel and Cifuentes, 1993; Hayes, 1993). But preferential degradation of ^{13}C -enriched organic compounds can cause an isotopic shift in bulk organic carbon. Generally, lipids have significantly lower $\delta^{13}\text{C}$ values than total biomass, while the $\delta^{13}\text{C}$ of carbohydrates and amino acids are higher (Hayes, 1993). Because isotopically heavy components like carbohydrates and amino acids are decomposed more rapidly than other components (Harvey *et al.*, 1995; Benner *et al.*, 1987), decomposition changes the $\delta^{13}\text{C}$ of bulk organic

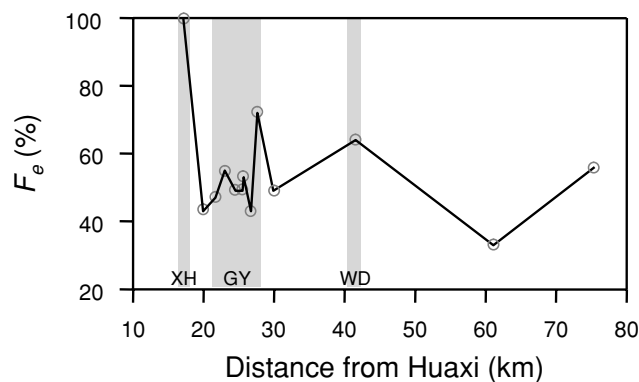


Fig. 4. Sewage contribution (F_e) to the bulk SOM.

matter (e.g., Benner *et al.*, 1987), leading to mask the original source signatures. Bada *et al.* (1989) found that hydrolysis of reactive compounds was associated with ^{13}C enrichment in the residual materials. But minimal change in the $\delta^{13}\text{C}$ of organic detritus occurs following extensive and prolonged (>2 years) microbial decomposition (Gearing *et al.*, 1984). In this study, we believed that there was small carbon isotopic change during SOC decomposition because at SKS, a site where intensive decomposition occurred, undegraded SOC contained similar ^{13}C content to that of sewage detritus (Fig. 2).

Source identification

For which one between nitrogen and carbon isotopic ratio to be successfully used as a tracer to determine the relative contribution between two sources, it must satisfy two requirements:

(1) Isotopic ratios should be conservative and the distribution in natural systems reflects only physical mixing of materials from end-member sources. Source recognition is often compounded by potential modification of end-member signatures by biogeochemical processes which are known to alter the isotopic and elemental composition of organic matter pools in estuaries (Cifuentes *et al.*, 1988; Owens and Law, 1989).

(2) The end-members are isotopically distinct. When identifying sources of organic matter in estuarine sediments, carbon isotopic difference between end-members is usually enough large to be used as a tracer (Middelburg and Nieuwenhuize, 1998).

As discussed above, we believed that only the two end-member (C3 plant and effluent OM) were important in Nanming River. Phytoplankton and soil-derived OC were not important because content of the first is low and soil-derived OC joined effluent OM (effluent channel accept most of soil-derived OC). The isotopic difference between the end-members (C3 plants and sewage detritus) was observed to be 9.4% for nitrogen, compared with 2.7%

for carbon (Fig. 3). Therefore, $\delta^{15}\text{N}$ was an effective and sensitive indicator of SON origins relative to $\delta^{13}\text{C}$, as reported by Ostrom *et al.* (1997). Fractions of sewage-derived SON (F_e) in bulk SON can be calculated using the mixing equation:

$$F_e = (X - X_p)/(X_e - X_p) \quad (2)$$

where X , X_e and X_p are the $\delta^{15}\text{N}$ of the sample, effluent detritus end-member and C3 plant end-member, respectively, and F_e and F_p (given by $1 - F_p$) are the respective fractions of sewage-derived SON and C3 plants in the sample.

Our results showed that effluent detritus contribution was comparable to that of C3 plants at most sites while >60% at outfalls (Fig. 4). At XHD, an old outfall where no C3 plants are observed, fraction of sewage-derived SON in bulk SON was almost 100%. Sewage-derived SON can be found >50% at site 40 km far from the outfall. The relatively low fraction of sewage-derived SON at PD site (a forested site) may be due to high input of C3 plants. In the domain of Guiyang, many C3 plants (mainly trees) grow along the river bank and large quantities of large-sized leaves enter the river in autumn. These C3 plant detritus deposited fast and were buried into sediments. Because C3 plant detritus is large enough in size and effectively held up by man-made dams, most of them should be kept in the original sites they deposited. Therefore, the fluctuating change in fractions of sewage-derived SON may be attributed to accident delivery episodes of C3 plant leaves.

CONCLUSIONS

Effluent detritus, having the highest isotopic ratios ($\delta^{13}\text{C}$: -25.0‰ ; $\delta^{15}\text{N}$: $+8.5\text{‰}$; C/N: 8.1), was one of the major contributors to both riverine SOM. Another important end-member was C3 plants growing along the river bank, which had lower isotopic ratios ($\delta^{13}\text{C}$: -27.7‰ ; $\delta^{15}\text{N}$: -0.9‰ ; C/N > 28). Nitrogen isotopic difference between the two end-members was observed to be 9.4‰, compared with 2.7‰ for carbon. When identifying OM provenance, nitrogen isotopic ratio was an effective signature because nitrogen isotopic difference was large enough. According to an estimation using a mixing model, contributions of components from effluent detritus and C3 plants (mainly tree leaves) are comparable in sediments. Sewage-derived SON at outfalls accounted for >60% of the bulk N. At site 40 km far from outfall, fraction of sewage-derived SON was still high to 50%.

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