

Situation of sewage input reflected by nitrogen isotopic composition in a sediment core of Hongfeng Lake

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Abstract Nitrogen in Hongfeng South Lake water mainly comes from sewage with high N concentrations from Pingba Chemical Fertilizer Plant (PCFP). Studies on the sediment core HF010427 sampled in the lake showed that the upward increase of nitrogen isotopic composition of sedimentary organic nitrogen ($\delta^{15}\text{N}_{\text{org}}$) accorded with the trend of industrial total production (TP) of PCFC. On the contrary, diagenesis will theoretically cause an upward decrease of $\delta^{15}\text{N}_{\text{org}}$. Because no treatment of sewage water was carried out, TP corresponds with sewage emission, indicating that sedimentary $\delta^{15}\text{N}_{\text{org}}$ can reflect well the total trend of sewage input. The very similar profile shape between nitrogen isotopic composition of sedimentary absorbed ammonium ($\delta^{15}\text{NH}_4^+$ absorbed) and TP of PCFP suggests that $\delta^{15}\text{NH}_4^+$ absorbed can be used to reconstruct more detailed situation of sewage input. The study has a reference to history investigation of sewage input.

Keywords: lacustrine sediments, organic nitrogen, absorbed ammonium, nitrogen isotopes, situation of sewage input.

Nitrogen isotopic ratios have been widely used to reconstruct past changes in marine and lacustrine environments^[1-4]. Several factors are believed to control the ratios in sediments, including early diagenesis^[5,6] and sources of organic matter, such as primary productivity^[7] and external organic nitrogen input^[8].

The impact of lake primary production on sedimentary $\delta^{15}\text{N}_{\text{org}}$ is related to inorganic N input in lakes. Owing to $\delta^{15}\text{N}$ values of nitrate higher in sewages (>10‰) than in natural water (<10‰)^[9,10], sewage N input will increase $\delta^{15}\text{N}$ values of inorganic N in lakes, and then $\delta^{15}\text{N}_{\text{org}}$ values of aquatic life. In recent several

hundred years economics rapidly develops in most areas of the world. More anthropogenic N such as industrial and domestic sewage has been produced and enters lacustrine environments. This influences $\delta^{15}\text{N}_{\text{org}}$ values in lakes. Although some effects of sewage on sedimentary $\delta^{15}\text{N}_{\text{org}}$ values in lakes have been recognized^[11,12], there are no reports of whether sedimentary $\delta^{15}\text{N}_{\text{org}}$ values can reflect situation of sewage input. Additionally, studies on lacustrine paleo-environments via $\delta^{15}\text{NH}_4^+$ absorbed data are few. Here we take advantage of a core sampled from a modern lake with relatively detailed sewage input data to acquire variation rule of sedimentary nitrogen isotopic ratios under different sewage input conditions and examine the possibility of using sedimentary nitrogen isotopic ratios to record the history of sewage input.

1 Experimental methods

Hongfeng Lake is a modern man-made lake, formed on May 29, 1960. Water in rivers from rain is the main water source of the lake. The largest river is the Yangchang River, which lies to the south of the lake. The lake water flows from the south to the north. There is no extensive human-being destroy such as forest clearing in the lake drainage area since the formation of the lake, and so flux of external particle inputs is stable. The lake is seasonally anoxic and benthic fauna cannot survive in sediments. It suggests that effects of bioturbation on sediments can be ignored. Owing to its abundant water source and good geographical position, some chemical plants (e.g. PCFC, a compound fertilizer plant and lies in the downstream of the Yangchang River) were built up contemporarily close to the lake. Sewage water from these plants entered the lake without any treatment for a long time. Thus the quantity of N inputted into the lake is large and sewage is the main N source of the lake^[13]. Flux of sewage water input from these plants corresponds to their TP and so TP can reflect the situation of sewage input.

A 22cm long sediment core HF010427 (22 m water depth, formed in 1960) was obtained in 2001 at Houwu site, Hongfeng Lake (26°33'N, 106°25'E) (Fig. 1), and sub-sampled with an interval of 1cm in the field. All samples were wrapped in PVC tubes and stored at 4°C before treatment in the laboratory.

Weight percents of organic carbon and nitrogen were determined using PE 2400 II CHNS elemental analyser, after removing inorganic carbon with 0.1 mol/L HCl and inorganic nitrogen with 2 mol/L KCl and dried with

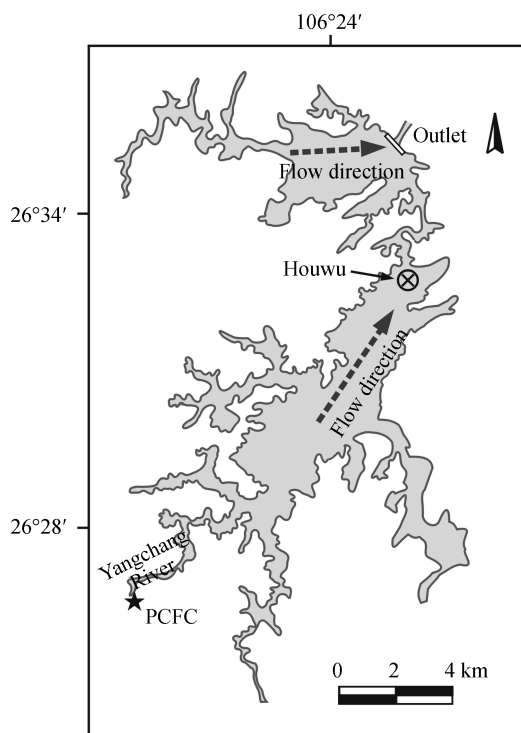


Fig. 1. Sketch map showing the main N polluted sources and the sampling site (Houwu) in Hongfeng Lake. PCFC refers to Pingba Chemical Fertilizer Company.

a cool drier. Analytical precision is better than $\pm 1\%$ for both organic carbon and nitrogen. Absorbed ammonium was extracted from sediments using 30 mL of 2 mol/L KCl^[15]. Ammonium concentrations were determined in solution by spectrophotometer after being treated with Nessler's reagent, with a detection limit of 0.02 mg/L. $^{15}\text{N}/^{14}\text{N}$ ratios of organic nitrogen and absorbed ammonium were prepared for isotopic analysis following the methods described by Kendall and Grim^[14] and Xiao and Liu^[15]. The results are reported in the δ notation,

$$\delta^{15}\text{N} = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right] \times 10^3, \text{ in units of per mil, where the standard is atmospheric nitrogen. The precision for both the measurements is better than } \pm 0.2\text{‰.}$$

Chronological control of core HF010427 is based on ^{210}Pb and ^{137}Cs dating by Wan *et al.*^[16,17] and direct estimation. Wan *et al.*^[17] reported that annual accumulation rate of core HF8801 (sampled in 1988) was about 0.092 g/cm/a, which is very close to the value (0.086 g/cm/a) obtained by dividing mass depth (3.515 g/cm²) of core HF010427 within 41 years. Additionally, the external particle input is stable since the formation of

the lake. These two suggest that stable-stage sediment accumulation occurred in the Hongfeng Lake and the direct estimated chronology is right.

2 Results and discussion

Two stages (stable and variable) can be recognised in the profiles of organic carbon content (C_{org}), organic nitrogen content (N_{org}) and $C_{\text{org}}/N_{\text{org}}$ atomic ratio (C/N ratio) of the core HF010427. For these 3 profiles, stable stage is from the bottom of 22cm (1960) upward to 17cm (1978) of the core. The C_{org} , N_{org} and C/N ratios keep constant during the stage. From 17cm upward to the surface of the core is the variable stage. C_{org} increased from 3% to 6.85% (Fig. 2(a)), N_{org} from 0.2% to 0.57% (Fig. 2(b)), while the C/N ratios decreased

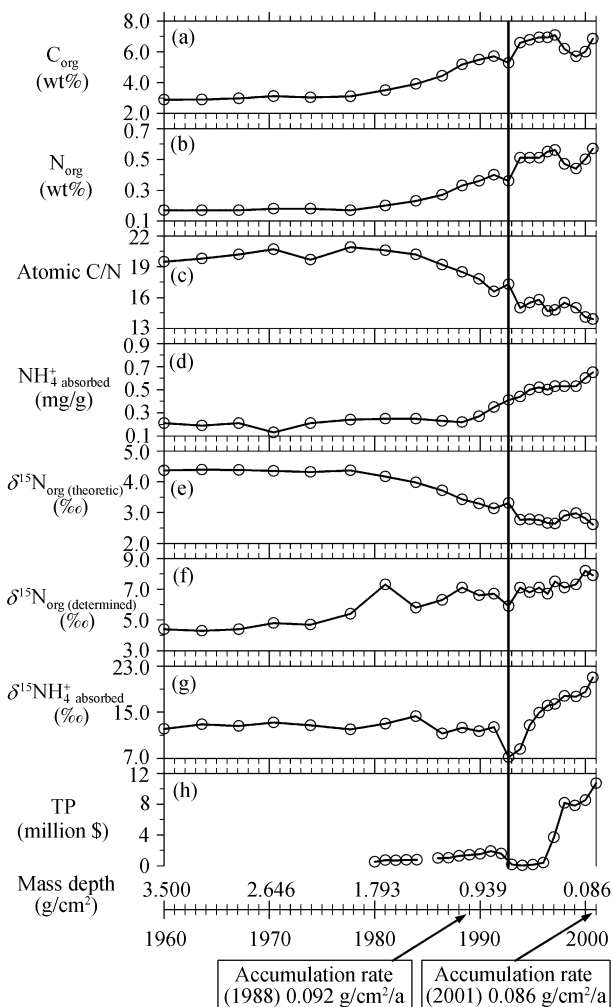


Fig. 2. Profile variations of weight percent of organic carbon and nitrogen (a) and (b), $C_{\text{org}}/N_{\text{org}}$ atomic ratios (c), absorbed ammonium concentrations (d), theoretical (e) and determined (f) $\delta^{15}\text{N}$ values of organic nitrogen, $\delta^{15}\text{N}$ values of absorbed ammonium (g) in core HF010427 and TP of PCFC during 1980–2001 (h).

from 21 to 14 (Fig. 2(c)). The shape of sedimentary absorbed ammonium concentration (NH_4^+ absorbed) (averaging about 0.3 mg/g) profile is similar to that of both C_{org} and N_{org} (Fig. 2(d)), but NH_4^+ absorbed concentrations are kept stable longer.

The composition profiles of organic matter in core HF010427 imply that either the sources or the diagenetic history of organic matter in the core has changed over the past 41 years. External organic matter input^[8] and aquatic productivity^[7] are believed to be two most important organic sources in lakes. Although change of high level aquatic organism flux is generally large during developing course of a new lake, its effects are negligible due to less production as compared to primary productivity. Because there are good correlations between C/N ratios and C_{org} or N_{org} (Fig. 3), no obvious changes occurred to external organic input flux into the core. In spite of more anthropogenic nitrogen into the lake, enhanced primary productivity has not been observed yet due to the limitation of low phosphorus contents in the lake (0.01–0.03 mg/L, N/P>30)^[13]. Except for the above, early diagenesis can also change the sedimentary C/N ratios. Our former studies^[18] showed that intensive organic degradation occurred during organic matter settling to the sediment surface and their C/N ratios increased. Because the C/N ratio of surface sedimentary organic matter is only 14 and organic N is often preferentially removed relative to organic C, the initial ratios of those not degraded may be less than 10. It indicates that aquatic organisms, whose ratios are often believed less than 10^[19,20], predominate in the core. This is consistent with the long distance between the sampling site and the river inlets (about 10 km). Additionally, C_{org} will fit well the double exponential decay model^[21,22] when their variations are due to degradation. As showed in Fig. 4, degradation is the

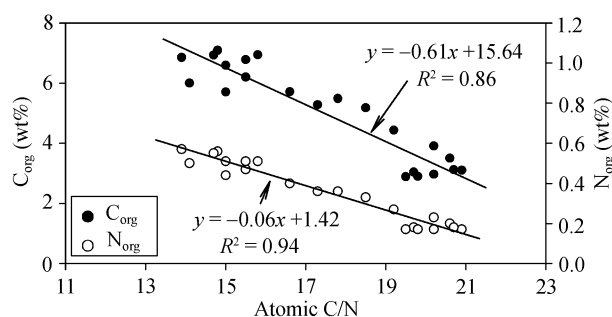


Fig. 3. Correlation between C/N ratios and C_{org} or N_{org} in core HF010427.

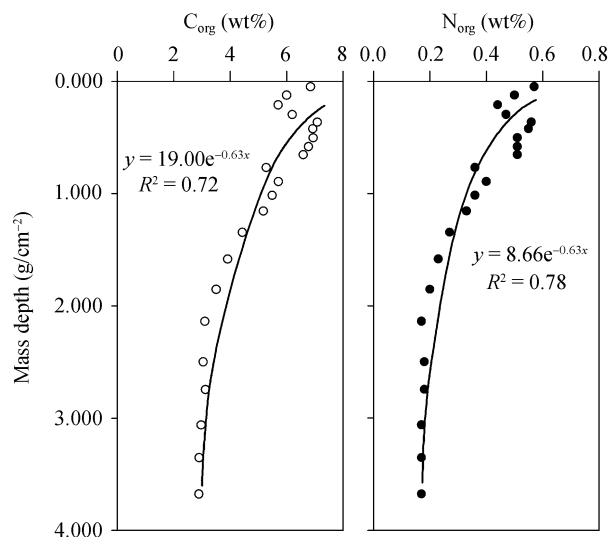


Fig. 4. Double exponential decay models of C_{org} and N_{org} in core HF010427.

main cause leading to the variations of C_{org} , N_{org} and C/N ratios.

The sedimentary $\delta^{15}\text{N}_{\text{org}}$ data shows an upward increase from 4.4‰ to 8.2‰, with an average of 6.3‰ (Fig. 2(f)). Being not the same as those C_{org} , N_{org} and C/N ratios, $\delta^{15}\text{N}_{\text{org}}$ increased slowly below 17cm of the core (before 1978). The classical explanation is that early diagenesis has an impact on the $\delta^{15}\text{N}_{\text{org}}$ values because in most cases an increase in $\delta^{15}\text{N}_{\text{org}}$ was observed during organic matter degradation^[5,23,24]. Based on degradation degree of organic matter and the nitrogen isotopic fractionation factor ϵ (1.48) during diagenesis reported by Freudenthal *et al.*^[5], theoretical changes of sedimentary $\delta^{15}\text{N}_{\text{org}}$ caused by only early diagenesis can be calculated as follows:

We assume that the surface sedimentary N_{org} is the initial content before diagenesis ($N_{\text{org}}(2001)$) and relative proportion of not degraded organic matter of No. i year is $N_{\text{org}}(i)/N_{\text{org}}(2001)$. When only nitrogen isotopic fractionation during diagenesis is considered, according to Rayleigh fractionation theory, the theoretic $\delta^{15}\text{N}_{\text{org}}$ value in No. i year is $\delta^{15}\text{N}_{\text{org}}(i)$:

$$\delta^{15}\text{N}_{\text{org}}(i) = \delta^{15}\text{N}_{\text{org}}(\text{initial}) - \epsilon \ln(f_i),$$

where $\delta^{15}\text{N}_{\text{org}}(\text{initial})$ is the initial $\delta^{15}\text{N}_{\text{org}}$ value of 2001, different from the determined value of the said year. The theoretic $\delta^{15}\text{N}_{\text{org}}$ value of the bottom of the core (1960) is the determined one after $N_{\text{org}}(1960)/N_{\text{org}}(2001)$ of organic N degraded. So $\delta^{15}\text{N}_{\text{org}}(\text{initial})$ can be calculated using the following equation:

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$$\delta^{15}\text{N}_{\text{org}}(\text{initial}) = \delta^{15}\text{N}_{\text{org}}(1960) + \varepsilon \ln[\text{N}_{\text{org}}(1960)/\text{N}_{\text{org}}(2001)].$$

Theoretic sedimentary $\delta^{15}\text{N}_{\text{org}}$ values ($\delta^{15}\text{N}_{\text{org}}(\text{theoretic})$) controlled only by early diagenesis show a downward decrease (Fig. 2(e)). Obviously, its trend is contrary to that of the determined $\delta^{15}\text{N}_{\text{org}}$ values ($\delta^{15}\text{N}_{\text{org}}(\text{determined})$) (Fig. 2(f)), indicating that the upward increase of the determined value is not due to early diagenesis. The difference in profile shapes of $\delta^{15}\text{N}_{\text{org}}$ and N_{org} also suggests that although diagenesis caused the C_{org} , N_{org} and C/N ratio variations, other factors resulted in the $\delta^{15}\text{N}_{\text{org}}$ variations in core HF010427.

Based on the difference in $\delta^{15}\text{N}$ values of contaminated and uncontaminated sediments^[11], nitrogen isotopic technique has been used to trace contaminated sediment dispersal^[25]. When more sewage (including industrial and domestic sewage) with ^{15}N -enriched inorganic N (nitrate and ammonium) enters lakes, $\delta^{15}\text{N}$ values of organic matter produced in these lakes will increase^[26]. Although the $\delta^{15}\text{N}_{\text{org}}$ values are not conservative during settling and burial diagenesis, the values have been shown to be reliable for use as a sediment tracer^[27]. Ruiz - Fernández *et al.*^[12] found that the $\delta^{15}\text{N}_{\text{org}}$ values in sediments contaminated with sewage water are considerably higher than those less contaminated. As a whole, the profile trends are similar between sedimentary $\delta^{15}\text{N}_{\text{org}}$ values of core HF010427 and TP of PCFC, suggesting that sedimentary $\delta^{15}\text{N}_{\text{org}}$ values can reflect the whole variation trend of TP. Because flux of sewage corresponds to TP, the TP variation of PCFC is consistent with that of sewage flux. Therefore, the upward increase of sedimentary $\delta^{15}\text{N}_{\text{org}}$ values of core HF010427 can be explained by larger flux of sewage (mainly industrial sewage) input now than before. Although we had no TP data before 1980, it is easily recognised that TP before 1980 should be less than that after 1980 according to the slow increase of sedimentary $\delta^{15}\text{N}_{\text{org}}$ values before 1978 (below 17cm) (Fig. 2(f)). However, the corresponding valley in TP profile is not found in the sedimentary $\delta^{15}\text{N}_{\text{org}}$ profile, that is, in 1993–1995, there is a lower TP value of PCFC but no corresponding one occurred in the sedimentary $\delta^{15}\text{N}_{\text{org}}$ profile. The discrepancy may be due to mixing with a small quantity of external organic N, which has a different $\delta^{15}\text{N}_{\text{org}}$ value^[28]. Therefore, sedimentary $\delta^{15}\text{N}_{\text{org}}$ value of core HF010427 can reflect well the whole variations of TP of PCFC.

Ammonium produced during organic matter de-

composition (ammonification) is immediately absorbed to the surface of clay minerals because of their different charges and significant adsorption capacities^[29]. Ammonium absorbed in sediments (absorbed ammonium) can be extracted by 2 mol/L KCl solution. Absorbed ammonium keeps a kinetic equilibrium with free ammonium in porewater. In core HF010427, absorbed ammonium concentrations, upward increasing from 0.2 to 0.7 mg/g and averaging 0.36 mg/g (Fig. 2(d)), are much higher than those reported by Freudenthal *et al.*^[5]. The comparably higher concentrations of absorbed ammonium may be attributed to the predominance of aquatic organic matters in the core^[18]. In the surface sediment, ammonium is consumed by diffusion due to concentration gradient and by nitrification due to high concentrations of dissolved oxygen.

Compared to $\delta^{15}\text{N}_{\text{org}}$ values, $\delta^{15}\text{NH}_4^+$ absorbed values are much higher (averaging 13.7‰) in the core. Except for the fractionation during early diagenesis of organic N, fractionation during nitrification and diffusion can also bring on $\delta^{15}\text{NH}_4^+$ absorbed changes. It has been shown previously^[30] that ammonium absorbed by clay minerals generally has $\delta^{15}\text{N}$ values not significantly different from those of the source N_{org} if thermal maturation did not occur. Increasing thermal maturation tends to produce heavier $\delta^{15}\text{NH}_4^+$ values^[31], yet it did not occur in core HF010427 because of burial temperatures lower than 40°C. Therefore, the upward increase of $\delta^{15}\text{NH}_4^+$ absorbed is the results of both nitrification and diffusion, both of which bring on enrichment of ^{15}N in residual ammonium^[32].

$\delta^{15}\text{NH}_4^+$ absorbed values of core HF010427 keep relatively stable from the bottom of 22cm upward to 17cm (1978). At 10cm (1978), a minimum (7.2‰) occurs and upward increases to 21.0‰ (Fig. 2(g)). Because both occurring time and intensity of nitrification and diffusion are less in surface sediment than in the layer below, the downward decrease of $\delta^{15}\text{NH}_4^+$ absorbed values in the above 10cm cannot be explained by nitrification and diffusion. The downward decrease is also not due to degradation of organic N, in spite of that degradation preferentially produces $^{14}\text{NH}_4^+$ absorbed^[5]. If so, the downward decrease of $\delta^{15}\text{NH}_4^+$ absorbed values needs more ammonium absorbed downward. Obviously, this does not agree with the fact showed in Fig. 2(d).

Since $\delta^{15}\text{NH}_4^+$ absorbed values are at least under the influence of 3 factors: $\delta^{15}\text{N}_{\text{org}}$, nitrification and diffusion, the relationship between $\delta^{15}\text{NH}_4^+$ absorbed values and TP

is normally worse than that between $\delta^{15}\text{N}_{\text{org}}$ and TP. To our surprise, there is a large similarity in shape between the formers. The lowest $\delta^{15}\text{NH}_4^+$ absorbed values in core HF010427 just occurred in those years when TP decreased (1993–1995). $\delta^{15}\text{NH}_4^+$ absorbed other than $\delta^{15}\text{N}_{\text{org}}$ better matches with TP because of mixing with external organic N— $\delta^{15}\text{N}$. Because external organic N is often drastically ammonified before settling, the survived one is now more resistant to degradation (ammonification). This fraction of organic N is important for $\delta^{15}\text{N}_{\text{org}}$ [28], but not for $\delta^{15}\text{NH}_4^+$ absorbed. This is because NH_4^+ absorbed in core HF010427 is predominantly derived from nitrogen—rich aquatic organic matter, so the effects of external organic N on $\delta^{15}\text{NH}_4^+$ absorbed are negligible. Although both nitrification and diffusion increase $\delta^{15}\text{NH}_4^+$ absorbed values, the profile trend is kept. Therefore, the ammonium— $\delta^{15}\text{N}$ data maybe more reliably reflected N sources (sewage) to the lake.

3 Conclusions

The upward increase of $\delta^{15}\text{N}_{\text{org}}$ in core HF010427, sampled in Hongfeng Lake, Guizhou Province, is neither the result of external organic N mixing nor early diagenesis. N input in sewage water changed inorganic nitrogen isotopic composition, and then affected that of aquatic organisms in the lake. The total profile trend of sedimentary $\delta^{15}\text{N}_{\text{org}}$ is the same as that of TP of PCFC, indicating that sedimentary $\delta^{15}\text{N}_{\text{org}}$ can reflect well situation of sewage input.

Influenced by nitrification and diffusion, sedimentary $\delta^{15}\text{NH}_4^+$ absorbed values are much higher than $\delta^{15}\text{N}_{\text{org}}$, but the initial trend of $\delta^{15}\text{NH}_4^+$ absorbed is kept. The large similarity in profile shape between $\delta^{15}\text{NH}_4^+$ absorbed and TP of PCFC suggests that sedimentary $\delta^{15}\text{NH}_4^+$ absorbed can be used to record the history of sewage input. The study based on $\delta^{15}\text{NH}_4^+$ absorbed values shows that sewage input stably and slowly increased at the early stage, a little decreased in the middle and late of 1980s, and much rapidly lifted again after 1990s in the lake.

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