Changes in carbon and nitrogen with particle size in bottom sediments in the Dan River, China

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Abstract

Understanding the composition and changes in nutrients in sediments and soil will enable a better description of sedimentation and environmental processes. In this study, soil from the source (Ss) of the Dan River and sediments along the river were sampled. The particle size distribution (PSD) of sediment and soil was analyzed, together with the total nitrogen (TN), total organic carbon (TOC) and the C/N ratio. The dominant particle size of Ss was <0.05 mm, while the sediments showed no obvious dominant particles. Concentrations of TN and TOC in sediments were significantly lower than in Ss. The <0.05 mm fraction of sediments manifested good ability to maintain TN and TOC, as indicated by average levels of 0.59 g N/kg and 13.85 g/kg, respectively. In the downstream portion of the Dan River, the TN contents decreased, while the TOC contents remained stable throughout the river. Cluster analysis indicated that TN division became simpler as the particle size decreased, while it became more complicated for TOC. There was no significant difference in the C/N ratio of Ss among particle sizes, and the ratio was below 25:1 for all groups. Conversely, the C/N ratio of sediments increased obviously with decreasing distance to the Danjiangkou reservoir. The nitrogen levels in particles <0.05 mm were preserved relatively well so that the C/N ratio of this fraction was relatively stable. The enrichment ratio of nutrients in sediments of the upstream portion of the river also showed that a finer fraction was associated with a greater capacity for holding nutrients, especially particles <0.05 mm. Overall, comprehensive control of sediments in rivers should focus on large particle sediments.

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1. Introduction

Sediments in rivers have been gaining increased attention worldwide owing to their importance in biogeochemistry, engineering, fluvial geomorphology and land–ocean interactions (Walling and Fang, 2003; Dai et al., 2009). Due to their capacity to reserve or release different materials from the water column, sediment acts as both a sink and source of nutrients (Aigars and Carman, 2001; Southwell et al., 2010, 2011; Liang and Zhang, 2011). Additionally, investigations of sediments can be used to evaluate the anthropogenic influence on aquatic systems (Rognerud and Fjeld, 2001). Sediments can determine the quality of overlying water by absorbing pollutants from water (Yi et al., 2008). As potential contaminant sources, sediments can exert adverse effects on water through the release of pollutants such as nutrients, heavy metals and other organic micro-pollutants (Junakova and Balintova, 2012), leading to eutrophication of rivers and lakes (Abrams and Jarrell, 1995; Xie et al., 2003; Tian and Zhou, 2007). Wu et al. (2012) reported that the sediment of the Haihe River is a potential threat to river ecology because of its phosphorus, nitrogen and organic matter (OM) contents. Additionally, an enclosure experiment conducted in a hypereutrophic subtropical Chinese lake indicated that the release of phosphorus from sediments led to eutrophication of overlying water when external loading was reduced (Xie et al., 2003). In sediment, the regeneration of dissolved inorganic nitrogen (DIN), PO4 and SiO4 plays a vital role in nutrient equilibrium mechanisms and the global biogeochemical cycle (Gle et al., 2008; Llebot et al., 2010). Rivers and lakes can
recover slowly owing to the large amount of easily releasable nitrogen and phosphorus, even though pollution controls are implemented (Wu et al., 2011). Zhang et al. (2013) considered sediment to be the source of DIN in summer and winter, but to act as a sink in spring. Various bio-availabilities and potential to impact eutrophication exist when there are different bound-forms of phosphorus in sediments (Hua et al., 2000).

Furthermore, sediment transport and off-site transport of nutrients from sediments markedly impacts the water quality, ecological environment (Sanchez et al., 2012), global geochemical cycle and transport of organic carbon from land to the oceans (Ludwig et al., 1996). The type of sediment, OM, dissolved oxygen (DO), benthic organisms and hydrodynamics affect the transformation of nitrogen in sediment dramatically (Liu et al., 2012; Rigaud et al., 2013). Xiang and Zhou (2011) studied the sediments of Poyang Lake and found that the spatial distribution of phosphorus decreased from the outlet to the entrance, and this transformation resulted from geographical factors and sediment types.

Particle size distribution (PSD) can respond to the characteristics of deposition and transportation (Folk and Ward, 1957; Sahu, 1964; Friedman, 1979). Additionally, the initial motion of sediment can be affected by particle shapes (Wang and Dittrich, 1999). Therefore, analyzing PSD may help us understand the origin, transportation and deposition of sediment nutrients (Watson et al., 2013). To date, many studies have been conducted to investigate nutrients and particle size of sediments (Beck and Jones, 1996; Kaiserli et al., 2002; Makarova et al., 2004; Wang et al., 2006). Multiple contaminants in water are highly correlated with sediments, especially fine sediments (Garcia, 2008). In the sediment samples from Kashiung Harbor (Taiwan), the concentrations of polycyclic aromatic hydrocarbons and polychlorinated biphenyl with a low density fraction were much higher than those of particles with a high density fraction (Huang et al., 2011). In urban sediments, an inverse relationship between heavy metals and particle size was found (Selbig et al., 2013). However, few studies have investigated the carbon, nitrogen and ratio of carbon to nitrogen with different particle sizes in sediments along rivers. Further information regarding these relationships could expand our understanding of sediments control and fractal theory.

Recognizing the source materials in sediment is crucial to a thorough understanding of carbon (C) cycling in water environments. Extensive studies of the carbon—nitrogen ratio (C/N) have been conducted to illuminate the source and fate of organic matter (Tyson, 1995; Ogawa and Ogura, 1997; Cloern et al., 2002; Goni et al., 2003; Usui et al., 2006; Ramaswamy et al., 2008). Low nitrogen levels and a high C/N ratio could slow the digestion rate (Rughoonundun et al., 2012). A low C/N ratio of sediments goes against nitrogen mineralization, resulting in the sediment contributing little to biogeochemical cycles (Rao et al., 2007). The optimal C/N ratio for anaerobic digestion is 25–30 (Kayhanian and Tchobanoglous, 1992). After waste water is drained into rivers, eutrophication occurs and changes the nature and C/N ratio of the system (Gao et al., 2012).

The sediment enrichment ratio (SER) can be defined as the ratio of the amount of particles in sediment divided by the amount in the original soil; therefore, the ratio can express the composition of the size distribution of the eroded sediment (Defersha and Melesse, 2012). The nitrogen enrichment ratio (NER) or carbon enrichment ratio (CER) is based on similar concepts, but refers to nutrient loss. The concentration of nutrients associated with sediment increases as more fine particles are washed from upstream to downstream owing to the large surface area of clay-sized sediment (http://www.sciencedirect.com/science/article/pii/S0341816211001949FAO, 1996).

The South to North Water Transfer Project (SNWTP) was conducted to address water shortage problems in China. As the water source of the middle route of the SNWTP, the Yangtze River has attracted increasing attention because it is adjacent to a population center and exposed to unsustainable overuse (Nilsson et al., 2005). The Dan River, a tributary of the Yangtze River, is deeply affected by increasing anthropogenic influences. For satisfactory analysis of river and lake pollution, it is important to observe sediment particles and nutrients (Mccauley et al., 2000; Hawa Bibi et al., 2007; Li et al., 2007). As the transformation model of river sediments has not yet been investigated (Topalova et al., 2009), samples were collected from along the Dan River to offer data and a theoretical foundation.

2. Materials and methods

2.1. Study area

The research area is located in the watershed (33°12′–34°11′ N, 109°30′–111°1′ E) of the Dan River in Shaanxi Province (Fig. 1). The Dan River originates in the southern part of Shaanxi Province and flows into the Danjiangkou Reservoir at Wuhan, where it supplies water to Beijing and Tianjin Municipalities in He'nan and Hubei provinces (CWRPI, 2005). The basin covers a watershed area of 7769.15 km², 24.51% (1904.24 km²) of which is farmland. The subtropical and temperate climate cause uneven rainfall, with 44.8% falling from July to September. The river has an average runoff of 82 million m³ and a sediment concentration of 4.52 kg/m³.

The principal vegetation in the watershed is broad-leaved forest, coniferous forest, mixed coniferous and broad-leaved forest, shrubs and herbs (Shen et al., 2006). The crops are dominated by rice (Oryza sativa L.), maize (Zea mays L.), wheat (Triticum aestivum L.), and forest by-products including shitake (Lentinula edodes) (Li et al., 2008). Yellow brown soil and cinnamon soil dominate this zone, while azonal soil development is influenced by human economic activity and natural regional conditions.

2.2. Sampling

A total of 44 sample points (Fig. 1, white circular points) in the bottom sediment of the Dan River at five kilometer intervals and 30
samples of source soils (Ss) (Fig. 1, black triangular points) were selected in July, 2013. The distances from every point to the Danjiangkou Reservoir ranged from 31.3 km to 171.5 km, and the points were encoded as 1–44 (Fig. 1, white numbers). The undisturbed samples were loaded into polyethylene bags, frozen immediately, and then transported to the laboratory, where they were dried and homogenized. For further analysis of total nitrogen, total phosphorus and total organic carbon with different particle sizes, the samples were hand-sieved into six size fractions, the samples were loaded into polyethylene bags, frozen immediately, and then transported to the laboratory, where they were dried and homogenized. For further analysis of total nitrogen, total phosphorus, and total organic carbon with different particle sizes, the samples were hand-sieved into six size fractions, <0.05 mm, 0.05–0.15 mm, 0.15–0.25 mm, 0.25–0.5 mm, 0.5–1 mm and 1–2 mm.

2.3. Methods

The particle distribution was measured using a Malvern laser particle analyzer (Mastersizer 2000), while total nitrogen was analyzed using the Kjeldahl digestion procedure (Foss 8400), and total organic matter was determined using a total organic carbon analyzer (Multi N/C 3100), SPSS 16.0 was used for statistical analyses, such as variance analysis (ANOVA), cluster analysis (CA).

3. Results

3.1. Particle size distribution of soil and sediments

Significant differences (p < 0.01) in the size distribution of Ss and sediment samples were observed (Table 1). Specifically, the results revealed a clear dominance of clay and silt (51.53%), followed by the 0.05–0.15 mm size fraction (18.65%). In contrast, the sediment size fractions were distributed relatively equally, with a maximum value of 23.36% (0.25–0.5 mm). These findings indicate that erosion primarily removed particles smaller than 0.05 mm while causing deposition of large particles. The sediment enrichment ratios (SER) were computed as well. Fine particles showed a tendency to decrease, while the larger particles increased. As the size increased, the enrichment became more pronounced, reaching 685.44% for particles >1 mm.

3.2. Nutrient characteristics of sediment particles

The average contents of TOC and TN of sediments and Ss were measured for the six particle sizes (Table 2). The medium size Ss particles contained more nutrients, while the content of TSN and SOC in the 0.15–0.25 mm fraction was 1.65 g N/kg and 24.98 g/kg, respectively. However, for sediments, the finest particles contained the most nutrients, with the content of TSN and SOC in particles <0.05 mm being 0.60 g N/kg and 13.81 g/kg, respectively. When compared with Ss, the nutrient concentrations of sediments were significantly lower. For different particle sizes, the TN levels in sediments were 70.62%, 74.59%, 80.17%, 79.43%, 80.01% and 52.91% lower than in Ss samples for the respective particle size fractions (from largest to smallest), while the TOC levels were 41.78%, 40.67%, 46.71%, 50.09%, 53.77% and 18.00% lower, respectively. Furthermore, TN and TOC loss of the 0.05–0.25 mm fractions was more serious than that of any other fractions. Additionally, the proportion of nutrient loss from the <0.05 mm fraction was smallest, illustrating the relatively good nutrient retention capacity.

The nearest reservoir of the Dan River to the sample points is the Danjiangkou reservoir. For further analysis of the sediment nutrient, the changes with distance from sample sites to the Danjiangkou reservoir were analyzed (Fig. 2). The TN contents showed decreasing fluctuation from upstream to downstream, while the TOC remained stable in most parts of the river. The coefficient of variation (CV) of TOC was larger than that of TN, while the mean CV of TOC and TN was 141.65% and 65.15%. As the particle size increased, the variability of TOC increased from 126.75% to 149.65%, while that of TN decreased from 82.42% to 58.80%. In addition, the ranges of TN contents for particles <0.05 mm along the river were highest, while those for TOC were lowest.

3.3. Cluster analysis of TN and TOC of sediments

Cluster analysis (CA) was applied to detect multivariate similarities in TN and TOC using the ward method. A dendrogram

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle size (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ss</td>
<td>&lt;0.05 0.05–0.15 0.15–0.25 0.25–0.5 0.5–1 1–2</td>
</tr>
<tr>
<td>Sediments</td>
<td></td>
</tr>
<tr>
<td>Sediment</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Source</th>
<th>Nutrients</th>
<th>Particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TN (g N/kg)</td>
<td>&lt;0.05 0.05–0.15 0.15–0.25 0.25–0.5 0.5–1 1–2</td>
</tr>
<tr>
<td>Ss</td>
<td>1.24 1.41 1.54 1.65 1.49 1.27</td>
<td></td>
</tr>
<tr>
<td>SOC (g/kg)</td>
<td>22.36 21.25 24.54 24.98 24.66 16.84</td>
<td></td>
</tr>
<tr>
<td>Sediments TN (g N/kg)</td>
<td>0.36 0.36 0.31 0.34 0.30 0.60</td>
<td></td>
</tr>
<tr>
<td>SOC (g/kg)</td>
<td>11.02 12.61 13.07 12.47 11.40 13.81</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Variation of TN (a) and TOC (b) in sediment along the river with different particle sizes.
(Fig. 3) of particles 1.0–2.0 mm was generated based on the rescaled distance cluster method. Clear divisions in the sampling points for TN and TOC were obtained. Specifically, all points were divided into two clusters, one characterized by lower TN and TOC contents and another by higher contents. These divisions for sampling points were consistent with hydrological and sedimentation processes (Reczynski et al., 2010). As the particle size decreased, the points division of TN became simpler, while for TOC the division became increasingly complicated. The dendrograms of particles <0.05 mm are shown in Fig. 4.

3.4. Carbon–nitrogen ratio (C/N)

As shown in Fig. 5, the average rates of total nitrogen (TN) and total organic carbon (TOC) of source soil were all less than 25:1, indicating that the decomposition and mineralization of organic matter could be high, and that the moderate degree of mineralization of Ss resulted in accumulation of nitrogen. For all soil samples, the C/N ratio ranged from 2.86 to 107.00. Based on one way ANOVA, the C/N ratio did not differ between groups (different particle sizes) (P > 0.05). These findings illustrate that the particle size of soil had little effect on the C/N ratio. The moderate C/N ratio of the source in the study area likely results in increased microflora and better soil fertility.

The C/N ratio of sediment increased with distance to the Danjiangkou reservoir (Fig. 6). The average C/N ratio of each size fraction was 47.50 (1.0–2.0 mm), 36.72 (0.5–1.0 mm), 53.94 (0.25–0.5 mm), 44.71 (0.15–0.25 mm), 48.20 (0.05–0.15 mm), and 28.70 (<0.05 mm). Sampling points closer to the Danjiangkou reservoir showed greater changes in the C/N ratio. The maximum CV of the C/N ratio (263.77) occurred in the 0.15–0.25 mm fraction, while the lowest CV (136.23) was observed for the <0.05 mm fraction. These results show that the nitrogen could be maintained relatively well in the <0.05 mm fraction when compared with the other fractions. Although the organic carbon in sediment decreased, the TN contents decreased more during the erosion process from land to the river (Fig. 2). Consequently, the C/N ratio of sediment was obviously greater than that of Ss.

4. Discussion

Sediment generated by erosion of land accumulates in rivers and wetlands (Keddy, 2000). Accordingly, sequestering nutrients in sediment can improve the water quality of rivers (Wang et al., 2004). The particle size characteristics of sediment are also important to model predictions for related hydrological and ecological processes (Saye and Pye et al., 2006). The distributions of TOC and TN in particle-size fractions are of great significance for
analysis of how sediments influence water quality in the river, including nutrient accumulation and release (Reddy et al., 1993).

Although the CV of TOC contents in sediment tended to increase with increasing particle size, the greatest variation was observed for the 0.05–0.15 mm fraction. This may indicate that microorganisms have intense activities that lead to more frequent release and accumulation of organic carbon relative to other particle sizes, which corresponds with the results of a study conducted in Taihang Mountain (Qin et al., 2010).

To evaluate the integral level, the TN and SOC contents were calculated based on the PSD and the corresponding nutrient

![Fig. 4](image1.png)  
**Fig. 4.** Cluster analysis of TN (a) and TOC (b) contents for particles <0.05 mm.

![Fig. 5](image2.png)  
**Fig. 5.** Carbon–nitrogen ratio of source soil of different particle sizes (mm).

![Fig. 6](image3.png)  
**Fig. 6.** C/N ratio along the Dan River for different particle sizes.
concentrations. The average TN and SOC content of bottom sediment in Dan River was 9.73 g/kg and 0.37 g/kg, respectively. The concentration of SOC and CV value (48.11%, 55.36%, respectively) of the nutrients was lower than that in individual size fraction (See Table 2). Conversely, with the exception of the 0.05 mm fraction, the TN content was higher for all sizes, supporting the theory that fine particles better retain nutrients. The changes in overall contents along the river are shown in Fig. 7. Comparison of the changes in particles revealed that the amplitude of TOC was reduced downstream. Consequently, the influence of the external factors was more obvious on individual sediment particle size fractions than on sediment as a whole.

Large changes in the TOC along the Dan River were only observed in the downstream portions (samples 29–44). This section of the river was far from the expressway, while the upstream area was located close to the highway. Accordingly, the residential land was widely distributed in the downstream area and frequent anthropogenic activities exerted a great effect on water quality. Although the highway could play a role in water pollution (Stagge et al., 2012), the random dispersion of anthropogenic activities induced large variations in nutrient concentrations (Sylvan et al., 2007; Diaz and Rosenberg, 2008; Selman and Greenhalgh, 2009). Fertilizer use, as well as industrial and residential sewage on farm land could lead to nutrient loss (Huang et al., 2014), resulting in large changes in the TOC contents in sediment.

Cluster analysis (CA) was carried out on group sediments of the sample facies and confirms the correlation between TOC and TN (http://www.sciencedirect.com/science/article/pii/S0883292712001011Einax et al., 1998). The main purpose of CA is to
classify the objects into categories based on similarities (Ramaswamy et al., 2014); however, the results obtained are only qualitative (Giela et al., 2012). As particle size decreased, the cluster of TN (Figs. 3 and 4) in sediments along the Dan River tended to become simpler, indicating that the concentration of TN was highest in several specific intervals (0.1–0.5 g/kg; 0.55–1.0 g/kg). Conversely, the division of TOC contents decreased as the particle size of sediments declined. These findings inferred that carbon is more active between sediments and the aquatic environment, which corresponds to the release, absorption and transformation process. All identified groups reflected the function and location within the geomorphic setting (Maghsoudi et al., 2014).

Soil nutrients are influenced by factors such as soil characteristics, vegetation type and topography (Stewart et al., 2014), and that the nutrients released by rainfall or wind transport (Caon et al., 2014) have direct or indirect effects on sediment. To determine the impact of terrain factors on TOC and TN, cluster analysis was executed after injecting altitude data. In contrast to the original results, including altitude data resulted in the clusters of TOC and TN being similar among different particle size fractions (Fig. 8). Therefore, dendrograms generated using particles <0.05 mm were listed as an example. Furthermore, the samples within a certain range of altitude were classified into one group. For example, the altitude of samples 27–32 ranged from 322 m to 398 m, which was relatively small; accordingly, they were placed into the same cluster as indicated in the figure. The prevailing fluid flow driven by different terrain has the potential to develop a diverse composition of underlying sediment (Turnewitsch et al., 2013), indicating that the TOC and TN contents in sediment were significantly influenced by topographic factors.

To compare the nitrogen and carbon contents between the Ss and sediments, sample points in the upstream portion of the Dan River (samples 1–16) were used to calculate the enrichment ratios (ER, %) and the ratio of nutrients (nitrogen and carbon) in sediment to those in Ss (Fig. 9). As the distance from the Danjiangkou reservoir decreased, the nitrogen enrichment ratio (NER) declined. At the head of the river, sediments nutrient loss was not very serious; however, it became greater as the distance from Danjiangkou reservoir decreased due to the release from sediments, which led to even less than 10% of nitrogen being left in some particles. Analysis of the carbon enrichment ratio (CER) showed a similar trend. The relatively higher release of nutrients may be correlated with the better water quality, which contained a lower concentration of nutrients. As the particle size increased, the CER and NER both increased, suggesting that the finer particles had a greater capacity to hold nutrients. Overall, TN reduction was more severe than TOC and therefore requires greater attention when managing water pollution.

Even though the soil loss for particles <0.05 mm was highest (69.73%), the nutrient loss and C/N ratio was lowest. When compared to other sizes, the clay fraction tended to erode and the nutrients (N and C) became more likely to adsorb onto this fraction (Zhang et al., 2011). Several investigators (Kiem and Kögel-Knabner, 2003; Wright and Hons, 2005; Yang et al., 2007) also observed higher C/N ratios in micro-aggregates, while Tripathi et al. (2014) obtained the opposite results. Due to the wealth of the clay fraction with more micro-aggregates, the C/N ratio decreased as the particle size decreased (Kandeler et al., 1999).

5. Conclusions

Bottom sediments and source soil (Ss) collected in July of 2013 from the Dan River were analyzed for particle size distribution, C and N. The following conclusions can be drawn from the results of this study:

1. The PSD of sediments was more even than that of Ss. As the particle size increased, the TSN and SOC contents increased, then decreased. The TN and TOC contents of sediments were lower than that of Ss, but particles <0.05 mm were capable of maintaining nutrient levels. From the up to downstream portion of the Dan River, the TN contents decreased, while the TOC contents remained stable.

2. Cluster analysis indicated that TN division became simpler as the particle size decreased, while it became more complicated for TOC. These findings correspond to the hydrological and sedimentation processes.

3. The C/N ratios of Ss were all below 25:1, and the differences among the six particle sizes were not significant (P > 0.05). As the distance to Danjiangkou reservoir decreased, the C/N ratio of sediments increased obviously, but the nitrogen in particles <0.05 mm was preserved relatively well so that the C/N ratio remained more stable than for other sizes.

Overall, fine sediments, especially those smaller than 0.05 mm, could be retained within the river ecosystem. Accordingly, larger particles should receive greater attention because the fine sediments appear to be more effective at preserving nutrition.

Acknowledgments

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