Nutrient sources and composition of recent algal blooms and eutrophication in the northern Jiulong River, Southeast China

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Abstract
The natural process of eutrophication is accelerated by human activities worldwide that interrupt nutrient biogeochemical cycles. Three algal bloom events have been monitored in the northern tributary of the Jiulong River since 2009. The inflection points in a robust locally-weighted regression analysis (LOESS) of the relationship between TN and TP concentrations in the river water, and a TN:TP comparison with nutrient source loadings, suggested that both external loading and internal nutrient cycling contributed to these algal blooms. Nutrient release from the sediments may have played an important role in regulating the nutrients in the overlying water column. In particular, excessive nutrient inputs from various sources and ubiquitous river damming caused further accumulation of the nutrient loading. In-situ autochthonous primary production was enhanced in this relatively stable “river” to “lake” water body. Thus, attention must be paid to the effects of river damming and the consequent internal nutrient release.

1. Introduction
Although algal blooms, whether harmless or toxic, can be seen as a natural aging process of aquatic ecosystems, their frequency and extent in rivers, lakes and coastal areas worldwide have been enhanced, thus encouraging more attention to the potential causes (Paeerl, 1997; Anderson et al., 2002; Glibert et al., 2005). Biological studies have emphasized more on nutrient composition and concentration for phytoplankton growth (Smith, 1983; Sterner, 1990; Sterner and Hessen, 1994; Smith et al., 1995), while chemical studies had nutrient cycling and fluxes as the key points. Recently, human-derived sources have been highlighted, because people have realized that the natural cycling has been accelerated under the interruption of anthropogenic activities. Studies have shown that the sources could be atmospheric deposition, agriculture runoff, groundwater, and sewage (Nixon and Pilson, 1983; Anderson et al., 2002; Vitousek et al., 2008). Although the relationship between nutrient sources and phytoplankton production is relatively clear in many study sites, the direct factors effecting nutrient sources, composition, and limitation in water bodies, which result in excessive phytoplankton production, might be different (Guildford and Hecky, 2000).

In this study, current insights into the relationship between nutrient sources and eutrophication, focusing on the effects of damming along a river and consequent nutrient retention, are addressed and a new understanding of internal nutrient release and algal blooms within a river system is presented.

2. Materials and methodology
2.1. Study site
The study site is located in a northern tributary of the Jiulong River (hereafter referred to as the northern Jiulong River), which is the second largest river in Fujian province, Southeast China. The whole watershed of the northern river is divided into 27 sub-watersheds based on tributaries and monitoring gauges (Fig. 1). Recently, three algal blooms (Peridiniopsis spp.) occurred, with the first within the Xizaikou hydro-power station (XZK) sub-watershed in late January 2009, the second within the Jiangdongqiao reservoir (JDQ) in early February, and the third in the Longtan (LT) Lake in December. The LT Lake is an upstream artificial lake located in a scenic part of a sub-watershed (for location, see ‘9’ in Fig. 1).

2.2. Data sources and analysis
The bulk of the data on loadings of total nitrogen (TN) and total phosphorus (TP) for each sub-watershed was derived from the first national pollution source census in China. The river water quality data were collected from monitoring gauges maintained by the Fujian Environmental Protection Bureau (FJEPB) during the first
3 months and December of 2009 and January 2010. Sediment samples from the LT Lake were taken with a grab sampler. The samples were first digested, and then TN and TP were analyzed using Kjeldahl and spectrophotometric methods. Organic matter content was analyzed titrimetrically. The water samples for NO$_3^-$-C$^{15}$N natural abundance analysis were stored immediately on ice, and measured using an improved ion exchange-diffusion method.

Spearman correlation analysis was used to examine any relationships between chlorophyll-$a$ (Chl-$a$) concentrations and other physical and chemical parameters, including water temperature, pH, dissolved oxygen (DO), COD$_{MN}$, TN, TP, TN:TP mass ratio (TN:TP), NH$_4^-$-N and water transparency for the XZK and JDQ sub-watersheds and the LT Lake during the algal blooms. The relationship between log$_{10}$TN and log$_{10}$TP in the river waters was analyzed using robust locally-weighted regression analysis (LOESS) and piecewise polynomial regression analysis based on the least-squares technique (Cleveland, 1979; Downing and McCauley, 1992).

The efficiency of dissolved N (DN) and dissolved P (DP) retention was calculated using the following equations (Kronvang et al., 2004):

\[
R_p = \left(1 - \frac{1}{1 + 1.86 \cdot \text{HRT}}\right),
\]

\[
R_N = \left(1 - \frac{1}{1 + 7.3 \cdot \text{HRT}/z}\right)
\]

where $R_p$ and $R_N$ are the retention efficiencies of DP and DN; HRT is the hydraulic retention time of the water body; and $z$ is the depth of water.

3. Results and discussion

3.1. Variations of hydrochemistry during algal blooms

Water in JDQ, XZK and LT Lake during blooms had similar concentration ranges of DO and COD$_{MN}$; however, nutrient concentrations varied (Fig. 2). The range of TP concentration were around 0.02–1.10 mg L$^{-1}$ in XZK, while the corresponding values were about 0.03–0.99 mg L$^{-1}$ for JDQ, and 0.01–0.20 mg L$^{-1}$ for LT Lake. The TN concentrations in LT Lake were only about one-eighth of those in JDQ and XZK (0.1–7.0 mg L$^{-1}$ for both). The maximum concentration of Chl-$a$ in LT Lake was also relatively low, about 18 mg m$^{-3}$, compared with those in the JDQ and XZK water bodies, which were 878 and 424 mg m$^{-3}$ (Fig. 2).

The relationship between Chl-$a$ concentrations and other parameters during blooms were examined using Spearman correlations. Results showed that the associated factors differed from site to site (Table 1). In general, the correlation was most noticeable for nutrients, such as TN and TP. Despite the fact that the correlated factors were not both TN and TP for all sites, Chl-$a$ concentrations were all significantly related with TN:TP. Thus, these data suggested that TN:TP were statistically critical for these bloom events and, for the river water in JDQ and XZK, the low TN:TP would stimulate algal blooms.

3.2. Nutrient sources from the sub-watersheds

Many sources can contribute to eutrophication, including agricultural runoff, livestock manure, sewage and aquaculture. The data in our study site revealed that point sources, including intensive livestock farms and urban domestic wastes, might generally be more important nutrient contributors than non-point sources in the sub-watersheds, when considered on an annual basis,
although non-point sources were often of greater concern because of the difficulty in controlling them (Fig. 3). To more closely examine the influence of point source TN inputs on the TN concentrations in river water, the natural abundance of NO$_3^-$/C0$_3$/$\Delta^{15}$N from five sub-watersheds was measured. The average NO$_3^-$/C0$_3$/$\Delta^{15}$N values in river water exiting the sub-watersheds increased from +1.9‰ to +21.4‰, while the proportion of river water nitrogen contributed by point sources increased from 61% to 95% (Fig. 4). As the point sources were mainly composed of wastewater which enriched the NO$_3^-$/$\Delta^{15}$N, the positive correlations (P < 0.05 for both regression lines) presented sufficient evidence to suggest that it might be the increase in the proportion of point source-derived TN contributing to the TN pool in the river water that led to the increased concentration of TN in the water body.

According to the dataset, the external sources had a relatively low TN:TP (ranging from 5.4 to 15.2) compared with the river water average of 34 (Fig. 3). These ratios tended to increase from the upstream sub-watersheds to the downstream ones, whereas the large loading of TN and TP were focused mainly on the upstream sub-watersheds, which were more affected by livestock husbandry (Fig. 3). In terms of the eutrophic sub-watersheds, the river water in XZK received a loading with the second lowest TN:TP values (5.7), although the loading quantity was not large. This pattern might suggest it was not the quantity of nutrient loading, but the composition (which was reflected in the decreased TN:TP in the loading to the river water) that resulted in the algal blooms. However, the TN:TP in the eutrophic water at the JDQ site was relatively high annually. It was speculated, therefore, that the outbreaks of algal blooms in JDQ might be more related to hydrological conditions. The change from “river” to “reservoir” at the JDQ site as a result of damming might have decreased the flow rate, and caused particle settling, turbidity decreases and light transmissivity increases. Furthermore, these changes would enhance in situ autochthonous primary production, and fuel high biomass algal blooms.

Compared with the terrestrial loading within the sub-watersheds, the effect of nutrients coming from the upstream water body was relatively insignificant. This was because the ubiquitous damming significantly decreased the discharge and nutrient loadings from the upstream.

### 3.3. Nutrient composition and eutrophication

In order to get a deeper understanding of the development of eutrophication, LOESS and piecewise polynomial regression on log$_{10}$TN and log$_{10}$TP were applied to offer a simple explanation for the observed variation in TN:TP in the river water.

The four-part regressive polyline showed different rates of increase along the line (Fig. 5). The values of log$_{10}$TN increased with log$_{10}$TP at a constant rate when TP concentrations were between 0.031 and 0.051 mg L$^{-1}$, and then the concentration of TN had little change. But when the concentration of TP reached 0.091 mg L$^{-1}$, the slope increased again until the concentration of TP reached 3.389 mg L$^{-1}$. In general, these slopes followed a pattern of values less than one, indicating a faster rate of TP than TN accumulation in the river water.

Before the first inflection, the TN:TP in the river water was almost constant at 55. This suggested that these low concentrations of TN and TP might have been due to natural runoff from less fertile terrestrial ecosystems, such as forests (Fig. 5). According to the measured data, the values around the first inflection were indeed almost all from the relatively undisturbed sub-watersheds (such as JDQ – shown in solid dots – which is a source of drinking water).

According to Fig. 5, the TN:TP values in this oligotrophic water decreased rapidly with increased TP because the TN and TP were quickly overwhelmed by meso- and eutrophic nutrient sources, such as precipitation, groundwater and sewage (Uttormark et al.,

### Table 1

<table>
<thead>
<tr>
<th>Sites</th>
<th>Water temperature</th>
<th>pH</th>
<th>DO</th>
<th>COD$_{BOD}$</th>
<th>TP</th>
<th>TN</th>
<th>TN-TP (mass)</th>
<th>NH$_4$-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>JDQ</td>
<td>r</td>
<td>0.773$^{a}$</td>
<td>0.596$^{b}$</td>
<td>0.177</td>
<td>0.801$^{b}$</td>
<td>0.596$^{b}$</td>
<td>0.622$^{b}$</td>
<td>-0.539$^{b}$</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.773$^{a}$</td>
<td>0.177</td>
<td>0.801$^{b}$</td>
<td>0.596$^{b}$</td>
<td>0.622$^{b}$</td>
<td>-0.539$^{b}$</td>
<td>0.533$^{b}$</td>
</tr>
<tr>
<td>XZK</td>
<td>r</td>
<td>0.657$^{a}$</td>
<td>0.187</td>
<td>0.502</td>
<td>0.358</td>
<td>0.713$^{a}$</td>
<td>0.007</td>
<td>-0.757$^{a}$</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.657$^{a}$</td>
<td>0.187</td>
<td>0.358</td>
<td>0.713$^{a}$</td>
<td>0.007</td>
<td>-0.757$^{a}$</td>
<td>-0.081</td>
</tr>
<tr>
<td>LT Lake</td>
<td>r</td>
<td></td>
<td>0.134</td>
<td>0.093</td>
<td>0.206</td>
<td>-0.316</td>
<td>0.567$^{b}$</td>
<td>0.585$^{b}$</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>0.134</td>
<td>0.093</td>
<td>0.206</td>
<td>-0.316</td>
<td>0.567$^{b}$</td>
<td>0.585$^{b}$</td>
<td>0.546$^{a}$</td>
</tr>
</tbody>
</table>

$^{a}$ Significant at the 0.05 level.

$^{b}$ Significant at the 0.01 level.
1974), which had TN:TP values that differed greatly (about 2–10-fold) from those in the runoff from the less fertile terrestrial ecosystems. This was why TP concentrations in the river water increased, whereas the variation in TN concentration was relatively small in the second part of the polyline.

However, the difference between the rates of change in TN and TP concentrations decelerated from the second inflection of 25. This might have arisen from the relatively small differences in TN:TP in various nutrient sources of eutrophic rivers. Under the effects of various nutrient sources with low TN:TP, the TN:TP in the

![Fig. 3. Loadings of TN and TP to sub-watersheds in the northern Jiulong River watershed. Indicates the main sub-watersheds in the Jiulong River.](image)

![Fig. 4. δ15N of nitrate in the sub-watersheds under different percentage N contributions by point sources.](image)

![Fig. 5. Relationship between mean TN and TP concentrations (mg L⁻¹) in river water (dots) and the TN:TP in terrestrial nutrient loadings (lines) in the northern Jiulong watershed. TN and TP concentrations were analyzed during the algal blooms in 2009 and the first 3 months of 2010. The TN:TP of runoff from unfertilized fields, precipitation and eutrophic lake sediment are cited from Loehr (1974), Allen et al. (1968) and Fukushima et al. (1991), whilst the other ratios were values from the northern Jiulong watershed.](image)
The two inflection points were clearly visible (Fig. 6). Early studies by Hodgkiss and Ho (1997) and Hodgkiss (2001) demonstrate that dinoflagellate cell numbers increase whenever the TN:TP falls below about 10:1. This was related to the superior ability of dinoflagellates to acquire nitrogen from both the atmosphere and the water when nitrogen becomes growth-limiting. However, how did the P enriched river water form?

The stretch of the river turned into a reservoir changed the internal nutrient cycling at our study sites. Evidence in support of this internal mechanism included the high contents of TN and TP (0.13% and 0.05%) in the sediment of the LT Lake, and the fact that the sediment TN:TP was below 4, whilst the value in the lake water was as high as 43. Under a long term high P loading and increased retention by damming, a chronic saturation of the sediment P formed and reduced the assimilation capacity for P (Smith et al., 1995). Most of the P loading thus remained in the water column, and so depressed the in-lake TN:TP. Meanwhile, the construction of dams elevated the water level along the river, and stable thermal stratification could easily form and anoxic bottom waters develop. Once reduced compounds, such as nitrate, iron (hydr)oxides and sulfate, accumulated in the deep water, this would favor P release from the sediment (Cooke and Carlson, 1989; Olila and Reddy, 1993; Havens et al., 1996). As a result, in situ autochthonous primary production would be enhanced during wind induced sediment re-suspension. In addition, the anoxic conditions would provide suitable conditions for denitrification, thus leading to the loss of the N from the water column and depression of the TN:TP (Friedl and Wüst, 2002).

4. Conclusions

From the parallel increases in Chl-α alongside the increases in TN and TP concentrations, there was no doubt that nutrients could stimulate algal blooms. Here, external and internal nutrient contribution played different roles. Historical external nutrient loading
could be a potential cause of river eutrophication and so the algal blooms, while the internal release of TP and loss of TN might be the direct inducements. Under the effect of a series of dams, the hydrological conditions were altered to accelerate internal nutrient cycling and to change nutrient composition, and this fueled eutrophication and algal blooms in the northern Jiulong River. Although it is difficult to predict precisely an algal bloom due to the complexity of the internal nutrient cycle, attention must be paid to the effects of river damming and the consequent internal nutrient release.

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