Spatial and Temporal Variations of Water Quality and Trophic Status in Xili Reservoir: a Subtropics Drinking Water Reservoir of Southeast China

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Abstract: Controlling of water quality pollution and eutrophication of reservoirs has become a very important research topic in urban drinking water field. Xili reservoir is an important water source of drinking water in Shenzhen. And its water quality has played an important role to the city's drinking water security. A fifteen-month's field observation was conducted from April 2013 to June 2014 in Xili reservoir, in order to analyze the temporal and spatial distribution of water quality factors and seasonal variation of trophic states. Xili reservoir was seriously polluted by nitrogen. Judged by TN most of the samples were no better than grade VI. Other water quality factor including WT, SD, pH, DO, COD, TOC, TP, Fe, silicate, turbidity, chlorophyll-a were pretty good. One-way ANOVA showed that significant difference was found in water quality factors on month (p<0.005). The spatial heterogeneity of water quality was obvious (p<0.05). The successions of water quality factors were similar and the mainly pattern was Pre-rainy period > Latter rainy period > High temperature and rain free period > Temperature jump period > Winter drought period. Two-way ANOVA showed that months rather than locations were the key influencing factors of water quality factors succession.TLI (Σ) were about 35--52, suggesting Xili reservoir was in mycotrophic trophic states. As a result of runoff pollution, water quality at sampling sites 1 and 10 was poor. In the rainy season, near sampling sites 1 and 10, water appeared to be Light-eutrophic. The phytoplankton biomass of Xili reservoir was low. Water temperature was the main driving factor of phytoplankton succession. The 14 water quality factors were divided into five groups by factor analysis. The total interpretation rate was about 70.82%. F1 represents the climatic change represented by water temperature and organic pollution. F2 represents the concentration of nitrogen. F3 represents the phytoplankton biomass. F4 represents the sensory indexes of water body, such as turbidity, transparency.

1. Introduction

With the development of economy and the increase of population scale, many cities are faced with the shortage of drinking water \cite{1-3}. Shenzhen, the most densely populated city in China, is particularly deficient in fresh water resources. In 2016, more than 80% of the drinking water needed to be retrieved from the Pearl River. External water is stored in the local reservoir after arriving at Shenzhen,
and then supplied to the waterworks. Xili reservoir is one of the most important drinking water storage reservoir and plays a key role in the safety of drinking water in Shenzhen. In recent years, the population expansion brings serious pollution caused a severely impact on the water quality of Xili reservoir. Therefore, it is necessary to strengthen the monitoring of water quality, grasp the dynamic changes of water quality, and find out the main pollutants and their distribution law. This is of great significance to control water pollution, prevent water eutrophication and ensure the safety of drinking water.

In order to analyze the spatial and temporal distribution of water quality factors and seasonal variation of trophic states, a fifteen-month's field observation was conducted from April 2013 to June 2014 in Xili reservoir. Monitoring factors include WT, SD, pH, DO, COD, TOC, TN, NH$_4^+$-N, NO$_3^-$-N, TP, Fe, silicate, turbidity, chlorophyll-a, and so on. Through the stratified monitoring of 10 sampling points, the evolution path of water environment in Xili reservoir was studied. Our research can provide basic data for the protection of the ecological safety of water environment and safeguard the safety of drinking water in Shenzhen.

2. Materials and Methods

2.1. The layout of the study area and sampling sites
The Xili reservoir is located in the Northeast of Shenzhen City, Guangdong Province, China (Figure 1). The reservoir is the principal potable water source for the people of Baoan District. There were a total of 10 sampling sites (Table 1). For each sampling site, the samples were collected within 3 layers from top to bottom. The surface layer was the water layer approximately 10 cm below the surface, the photic layer was the water layer corresponding to the depth of the transparency measurement, and the bottom layer was the water layer approximately 10 cm above the sediment.

![Fig.1 Sampling sites at Xili reservoir](image_url)

Table 1 General characteristics of sampling stations with coordinates in Xili reservoir

| Sampling sites | Approximate sampling location | Description of sampling sites |
|----------------|------------------------------|-----------------------------|
2.2. Sampling and analysis
The samples were collected using a ZPY-1 water collector and stored separately. The water samples were transferred to the laboratory within 2 hours after collected and kept at 4°C. The chemiluminescence detection of the permanganate index (COD$_{Mn}$) and determination of ρ(Chla), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), ammonia nitrogen (NH$_4^+$-N), nitrate nitrogen (NO$_3^-$-N), iron (Fe) and silicate were carried out within two days. Chlorophyll-a was measured by using a modulated fluorometer (WALZ Phyto-PAM, Germany) that was periodically calibrated by acetone extraction spectrophotometry. The depth of the water, WT, pH, DO and turbidity were measured in-site using a multi-parameter water quality analyzer (YSI 6600V2, USA). The transparency (SD) was measured in-site using a secchi disk. COD was measured by the acidic potassium permanganate method; TP was determined by ammonium molybdate spectrophotometry; silicate was determined by silicon molybdenum blue spectrophotometry; TN, NH$_4^+$-N and NO$_3^-$-N were analyzed by a flow analyzer (AMS-Alliance-Futura, French); and TOC was determined using a TOC analyzer (GE-Siever 5310C).

2.3. Climate period
According to the weather characteristics, sampling time was divided into five periods. Pre-rainy period was from April to June 2013 and 2014. Latter rainy period was from July to September 2013. High temperature and rain free period was from October to November 2013. Winter drought period was from December 2013 to February 2014. Temperature jump period was March 2013.

2.4. Method of Water quality evaluation
On the basis of "surface water environmental quality standard" (GB3838-2002) and the "surface water environmental quality assessment methods", WT, pH, DO, COD, TN, NH$_4^+$-N, NO$_3^-$-N, TP were used for water quality evaluation. Water quality was measured by water quality index (WQI). Single factor evaluation method was used. The final water quality was determined by the highest category in the participating index. Water quality was divided into 6 levels, including I, II, III, IV, V, VI (see Table 3).

2.5. Method of Synthetic evaluation of nutritional status
Chl-a, TN, TP, SD, and COD were used for quantitative evaluation of trophic level for eutrophication, as measured by trophic level index (TLI).

Trophic level index TLI (Σ) was calculated according to the equations and the parameters given below:
\[ TLI(\sum_j) = \sum_{j=1}^{n} W_j \cdot TLI(j) \]  

where \( W_j \) is correlative weighted score for trophic level index of \( j \); \( TLI(j) \) is the trophic level index of \( j \); \( j \) present Chla, TP, TN, SD, or CODMn;

\[
W_j = \frac{r_{ij}^2}{\sum_{j=1}^{n} r_{ij}^2}
\]

where \( r_{ij} \) is relative coefficient between Chl-a and other parameters \( j \); \( r_{ij}, r_{ij}^2 \), and \( W_j \) is the value for parameters with Chl-a of lakes in China was shown in Table 2.

**Table 2** \( r_{ij}, r_{ij}^2 \) and \( W_j \) value for parameters with Chl-a of lakes in China

| Parameter (j) | Chl-a | TP    | TN    | SD    | CODMn |
|---------------|-------|-------|-------|-------|--------|
| \( r_{ij} \)  | 1     | 0.84  | 0.82  | -0.83 | 0.83   |
| \( r_{ij}^2 \) | 1     | 0.7056| 0.6724| 0.6889| 0.6889 |

According to the assessed standard values of the trophic state for Chl a, TP, TN, SD and CODMn in different lake regions, the single trophic state index was calculated according to the equations given below.

The single trophic state index was calculated as follow equations:

\[
TLI(\text{Chl a}) = 10 \left[2.5 + 1.086 \ln(\text{Chl a})\right] 
\]

\[
TLI(\text{TP}) = 10 \left[9.436 + 1.624 \ln(\text{TP})\right] 
\]

\[
TLI(\text{TN}) = 10 \left[5.453 + 1.694 \ln(\text{TN})\right] 
\]

\[
TLI(\text{SD}) = 10 \left[5.118 - 1.94 \ln(\text{SD})\right] 
\]

\[
TLI(\text{CODMn}) = 10 \left[0.109 + 2.66 \ln(\text{CODMn})\right] 
\]

**Table 3** Lake trophic state for corresponding designated uses of water body

| WQI | Trophic state  | TLI (\(\Sigma\)) | Designated uses |
|-----|----------------|------------------|-----------------|
| I   | Oligotrophic   | 0-30             | National natural protection region and rural distributed life drinking water source, etc. |
| II  | Mesotrophic    | 30-50            | The first-grade protection zone of centralized drinking water source, rare aquatic habitats, fish and prawn production field, etc. |
| III | Light-eutrophic| 50-60            | The second-grade protection zone of centralized drinking water source; fish and prawn wintering grounds, migration channel, aquaculture etc. |
| IV  | Mid-eutrophic  | 60-70            | Industrial water and human indirect contact recreation water |
| V   | High-eutrophic | 70-80            | Agricultural irrigation water and general landscape water |
| VI  | Hypereutrophic | >80              | Loss of water ecological functions; with poor function except regulating local climate |

2.6. Statistical analysis

Pearson correlation analysis, one-way ANOVA, two-way ANOVA and factor analysis were performed on SPSS20. The distribution chart of trophic level was generated on ArcMap10.2 by the Kriging interpolation method based on the mean of the TLI (\(\Sigma\)) of several months at each sampling site in the corresponding climatic period. Other graphics were prepared using Origin9.0.

3. Results and Discussion

3.1. Spatiotemporal characteristics Physical chemical factors
Figure 2 shows the seasonal variations of the water quality factors. Water temperature (WT) in Xili reservoir was 14.61-31.59°C. The average WT of surface layer, transparent layer and bottom layer were 25.44, 24.96, 23.39°C. WT was highest during July to September, and declined rapidly since November. WT reached the lowest in February and then raised sharply in March. From March to April, WT jumped from 16 °C to 28 °C. From March to early April, it was called "temperature jump period". During this period, algae recovered rapidly, and spread upward from the bottom to the surface. Xili reservoir was located in the subtropical regions. WT was more than 25 °C each year in nearly 6 months. Continuous high temperature in summer and autumn made the algae outbreak risk in Xili reservoir much higher than that in the north Chinese reservoirs. SD in Xili reservoir was 0.47~1.95 m. In January and February, SD was higher than 1.45m, while in other months SD was about 0.5~0.8m. During the preceding flood season, a large amount of sediment and pollutants were accompanied by rainfall, which was the main reason for the decrease of transparency. The decline of phytoplankton in winter has led to a marked increase in transparency. COD and TOC were 1.38~2.57 mg/L and 1.65~4.12 mg/L respectively which showed that organic pollution was not serious in Xili reservoir. Xili reservoir is arranged around the nature reserve. So the organic pollution is much lower than that of natural lakes such as Taihu Lake[6, 7]. DO was 6.85~12.13 mg/L in surface and euphotic layers. The change of DO was not obvious between the months. The high DO illustrated a good state water quality and ecological system. DO in bottom layer fluctuated violently for 0.56~6.32 mg/L. Usually, when the water depth exceeded 6 m, DO fell to about 2 mg/L. When the water depth exceeded 8m, DO fell to less than 1 mg/L. When DO was below 1 mg/L, the bottom of reservoir would form an anaerobic zone. At this time, nutrients and organic matter in the sediment may be released by the action of anaerobic microorganisms, which will bring internal pollution to the reservoir. pH was 6.3~8.8, showing the characteristics of being high in summer and low in winter.Xili reservoir was seriously polluted by nitrogen. TN was 1.33-2.88 mg/L. NO3--N was 0.95-2.61 mg/L and NH4+-N was 0.05-0.32 mg/L. Like most of the southern China rivers, Xili reservoir pollution TN. TN was the main pollutant. There were two sources of TN. First, Dongjiang water was the main water source of Xili reservoir. TN in Dongjiang water was 1.25~3.52 mg/L, much higher than that of Xili reservoir. Nitrogen mainly came from the surrounding runoff pollution, such as Makan River and Baiamng River. Some cash crops such as litchi and longan had been planted around the reservoir. Rivers brought large amounts of agricultural non-point source pollutants into the reservoir. Phosphorus pollution was light in Xili reservoir. The concentration of TP was 0.01~0.05 mg/L and the seasonal variation was not obvious. The concentration of Fe in was 0.05-0.42 mg/L. The concentration of silicate was 4.35~18.63 mg/L. Both Fe and silicate showed the characteristics of lower in flood season than in dry season. Chlorophyll a is an important pigment in photosynthesis of phytoplankton. Chlorophyll a is commonly used to characterize the algal biomass, and then to describe the degree of eutrophication in water bodies [6-8]. Chlorophyll a concentration was 3.56-31.62 μg/L in Xili reservoir. The successions of chlorophyll-a and turbidity were similar and the mainly pattern was Pre-rainy period > Latter rainy period > High temperature and rain free period > Temperature jump period > Winter drought period.

One-way ANOVA showed that there were significant differences between the physical and chemical factors such as Chl-a, WT, SD, COD, TOC, silicate, NO3--N, TN and Fe on month (p<0.005). The distribution pattern of Chl-a, WT, TOC, Silicate, NO3--N, TN and Fe were pre-rainy period > latter rainy period > high temperature and rain free period > temperature jump period > winter drought period, while SD Show the contrary. Seasonal variation of DO, pH, NH4+-N and TP were not obvious. The spatial differences of Chl-a, DO, SD, COD, TOC, TN, NH4+-N and Fe were significant at different sampling points(p<0.01). Concentration of Chl-a, COD, TOC, TN, NH4+-N and Fe raised gradually from southeast to northwest, while DO and TN reduced gradually in the country direction. The water quality of the southern part of Xili reservoir near the No.5 and No.6 sampling sites was better than other area. The water quality around the No.10 sampling site was the worst as a result of the runoff of Baimang River. No.1 sampling site is located near the Jiuwei River, so the water quality was relatively poor. As a result of the dilution of Dongjiang water from nearby No.2 sampling site, the water quality was better than that of No.10 sampling site area. The spatial difference of WT, pH,
Silicate, TP, and NO$_3$-N were not significant. TN was the primary pollutant in Xili reservoir. The average concentration of TN was 1.76 mg·L$^{-1}$. The highest TN concentration was 2.88 mg·L$^{-1}$, which appeared on the surface layer of the No. 10 sampling site on June 21, 2013. The lowest TN concentration was 1.33 mg·L$^{-1}$, which appeared on the bottom layer of the No. 6 sampling site on February 192, 2014. According to the evaluation results of surface water environment evaluation method, TN of all sampling points in the monitoring period were no better than grade VI. Judged by TN, 53% of the samples were grade V, and 21% of them were grade VI. Xili reservoir was a nitrogen polluted water body. Other pollutants concentration was low. DO, COD and TP have reached the surface water environmental quality standard class I~II.

Two-way ANOVA shows that there was a statistically significant interaction between the effects of location and month on the surface and photic water temperature of Xili reservoir. The variation of environmental factors can be explained by the interaction effect between month and sampling point ($R^2$, 24.5 % - 70.8 %). Month was the most important factor affecting environmental factors, which had significantly effects on Chl-a, WT, SD, COD, TOC, Silicate, NO$_3$-N and Fe($p<0.01$). Month also has a certain correlation with TN ($p=0.061$), but had little effect on pH, DO, NH$_4$-N, TP. Sampling points had a significant effect on SD ($p<0.01$) and Chl-a ($p<0.01$), which had little effect on other environmental factors ($p>0.3$). The interaction between the month and the sampling point had a slight effect on Fe and SD, but had little effect on other environmental factors ($p>0.8$). On the whole, the main influencing factors of the environmental factors were month, which showed that the temporal heterogeneity of environmental factors was higher than that of spatial heterogeneity.
3.2. Water quality evaluation

Xili reservoir was seriously polluted by total nitrogen. In April and May in the year 2013, average TN concentration was higher than 2.0mg/L, and WQI was at grade VI. From June to October in the year 2013 and April, May, June in the year 2014, average TN concentration was 1.5~2.0mg/L, and WQI was at grade V. In other months average TN concentration was 1.0~1.5mg/L, and WQI was at grade IV.

Considering that TN concentration was too high, the results of single factor water quality assessment was only the reflection of total nitrogen. Besides, TN was listed as the reference index by "surface water environmental quality assessment method". So the water quality was re-evaluated using pH, DO, NH4+-N, TP and permanganate index (Figure 3). The result of figure 3 showed that the water quality of Xili reservoir was good, and the WQI were mainly at grade I~II in surface layer and photic layer. TP or NH4+-N was the decisive factor of water quality. When the water depth was more than 5 meters, DO decreased significantly in the bottom layer, resulting in WQI at grade III~VI. For surface layer of water bodies, 6.67% of the sampling sites were at grade I, 76.67% of them were at grade II, and 16.67% of them were at grade III. For photic layer of water bodies, 2.67% of the sampling sites were at grade I, 76.33% of them were at grade II, and 18% of them were at grade III. For bottom layer of water bodies, 26.67% of the sampling sites were at grade II, 46.67% of them were at grade III, and 31.33% of them were at grade VI, and 1.33% of them were at grade V. The spatial heterogeneity of water quality was obvious. Water quality in sampling site 4, site 5 and site 6 were pretty good. Especially from January to February 2014, the WQI was at grade I level. Water quality in sampling sites 1 and 10 were poor. In rainy seasons the WQI was at grade III~IV level.
There are 10 columns every month and each column from left to right represents sampling sites 1 to 10.

3.3. Synthetic evaluation of nutritional status

The single factor evaluation method used in water quality evaluation chose the worst water quality to calculate the WQI. Its quantization ability was relatively poor and the water quality difference was not obvious. The integrated trophic status index provides a more accurate response to water quality [9, 10]. Therefore, comprehensive assessment of water quality was carried out using comprehensive nutrition status evaluation method (Figure 4). Evaluation indicators include five water indexes including chlorophyll-a, TP, TN, SD and COD. The distribution chart of trophic level was generated by the Kriging interpolation method based on the mean of the TLI (Σ) of several months at each sampling site in the corresponding climatic period (Figure 5).

Figure 4 and Figure 5 clearly show the temporal and spatial succession of the trophic state of Xili reservoir. Overall, Xili reservoir was in mycotrophic state. Except for sampling sites 1, 10 in flood season, the TLI (Σ) of other points were less than 50. The succession pattern of TLI (Σ) was pre-rainy period > latter rainy period > high temperature and rain free period > temperature jump period > winter drought period. In rainy season, the TLI (Σ) of sampling sites 1, 10 were more than 50, indicating that there was a slight eutrophication in these area. In January and February, TLI (Σ) were
about 35–40, suggesting water quality was very good. The spatial distribution pattern of TLI (Σ) was rising gradually from south to north. Vertically, there was little difference between the surface layer and the euphotic layer in TLI (Σ). TLI (Σ) in bottom layer was much smaller than that of surface layer and euphotic layer. Compared with Xili reservoir, TLI (Σ) of Xili reservoir was much lower. The main reason is the Chl-a concentration in Xili reservoir was low. Algae blooming risk in Xili reservoir was low.
Table 4 shows the result of the person correlation between 14 water quality factors. Chlorophyll a reflected the biomass of phytoplankton. The WT was positively correlated with chlorophyll a, and the correlation coefficient was 0.619. It indicated that water temperature is the primary driving factor for phytoplankton growth. Beside, chlorophyll a had positive correlation with TOC, ammonia nitrogen and COD. Water temperature was positively related to multiple water quality factors. The main correlated factors in descending order of the absolute value of the correlation coefficient were TOC > Chl-a > COD > SD > pH, in which the SD and Fe were negatively correlated. There are two reasons for WT positively related to the TOC (0.740). On the one hand, in the beginning of summer, the surface runoff brought the non-point source pollutants into the reservoir, rising the organic matter concentration in the water. On the other hand, when the temperature raised, algae blooms leading to the rising of TOC. Do was positively correlated with COD, and the correlation coefficient was 0.436. In organic polluted water, microorganisms need to consume large amounts of oxygen to decompose organic matter. SO DO and COD are usually negatively correlated. However in Xili reservoir Do was positively correlated with COD, and the correlation coefficient was 0.436. This is mainly because COD in Xili reservoir was low and the consumption of DO was less. Transparency was negatively correlated with turbidity, and the correlation coefficient was -0.497. Silicate was negatively correlated with Fe, and the correlation coefficient was -0.402. Nitrate nitrogen and total nitrogen were significantly positive correlation, the correlation coefficient was 0.798.
3.5. Factor analysis of water quality factors

Factor analysis can convert a large number of water quality factors that may be related to each other to a small number of synthetic indicators that are not related to each other. In Environmental Science, factor analysis is often used to identify key pollutants. In order to further understand the water quality of Xili reservoir, factor analysis was used to identify potential pollutant factors. KMO and Bartley sphere tests were performed before factor analysis. When the KMO test coefficient >0.5 and p<0.05, it indicated that the data is taken from a normal distribution. Thus the correlation between variables was recognized, and that the original data is suitable for principal component analysis. KMO and Bartley Sphere Tests results showed that KMO test coefficient is 0.575, p<0.01, so it is suitable to use factor analysis to identify the main pollutants in Xili reservoir.

The eigenvalues of the first five factors are larger than 1, and the Cumulative % of the first five factors is 70.82%, so these five factors can be used to represent the 14 environmental factors. In order to facilitate the interpretation of factors, factor rotation is required. The rotation method is Varimax with Kaiser Normalization. Table 5 gives the factor loading values after rotation. Factor analysis showed that the 14 water quality factors can be divided into 5 categories. The total contribution rate of the five factors was 70.82%. F1 accounted for 24.33% of the total contribution rate, which was positively correlated with WT (0.873), COD (0.801), and TOC (0.784). F2 accounted for 16.48% of the total contribution rate, which was strongly correlated with nitrate nitrogen (0.954) and total nitrogen (0.875). F3 accounted for 10.99 accounted for 12.93% of the total contribution rate, which was positively correlated with Chl-a (0.779) and pH (0.662). F4 accounted for 10.19 of the total contribution rate, which was positively correlated with Turbidity (0.778) and negatively correlated with SD (-0.738). F5 accounted for 8.83% of the total contribution rate, which was negatively correlated with Silicate (-0.797) and positively correlated with Fe (0.782). F1 represents the climatic change represented by water temperature and organic pollution. F2 represent the concentration of nitrogen. F3 represent the phytoplankton biomass. F4 represent the sensory indexes of water body, such as turbidity, transparency.

| Water quality factors | Component |
|-----------------------|-----------|
|                       | F1 | F2 | F3 | F4 | F5 |
| pH                   | -0.076 | -0.009 | 0.662 | -0.212 | -0.203 |
| DO                   | 0.719 | -0.282 | -0.206 | -0.005 | -0.093 |
| SD                   | -0.153 | -0.242 | -0.182 | **0.738** | -0.030 |
| Turbidity            | -0.092 | 0.097 | -0.007 | **0.778** | 0.311 |
| COD                  | **0.801** | 0.087 | 0.116 | 0.038 | 0.111 |
| TOC                  | **0.784** | 0.185 | 0.442 | 0.015 | -0.002 |
| Silicate             | 0.005 | 0.120 | -0.067 | 0.117 | **0.797** |
| Ammonia              | 0.025 | -0.168 | 0.469 | 0.261 | 0.274 |
| Nitrate              | -0.033 | **0.954** | -0.048 | -0.011 | -0.086 |
| Fe                   | 0.099 | 0.277 | 0.010 | 0.218 | **0.782** |
| TN                   | 0.038 | **0.875** | 0.020 | 0.265 | 0.181 |

Table 5 Matrix of rotated factor loadings
4. Conclusion
The results indicated that water quality in Xili reservoir is generally good. Xili reservoir was seriously polluted by nitrogen. Judged by TN, most of the samples were no better than grade VI. Other water quality factor including WT, SD, pH, DO, COD, TOC, TP, Fe, silicate, turbidity, chlorophyll-a were pretty good. One-way ANOVA showed that significant difference was found in water quality factors on month (p<0.005). The spatial heterogeneity of water quality was obvious (p<0.05). Two-way ANOVA showed that months rather than locations were the key influencing factors of water quality factors succession. TLI (Σ) were about 35–52, suggesting Xili reservoir was in mycotrophic trophic states. As a result of runoff pollution, water quality at sampling sites 1 and 10 was poor. In the rainy season, near sampling sites 1 and 10, water appeared to be Light-eutrophic. The phytoplankton biomass of Xili reservoir was low. WT was the main driving factor of phytoplankton succession. The 14 water quality factors were divided into five groups by factor analysis. The total interpretation rate was about 70.82%. F1 represents the climatic change represented by water temperature and organic pollution. F2 represents the concentration of nitrogen. F3 represents the phytoplankton biomass. F4 represents the sensory indexes of water body, such as turbidity, transparency.

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