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Research Article

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Pollution characteristics of thermally-stratified reservoir: A case study of the Heihe reservoir in Xi'an city, China

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ABSTRACT

Reservoirs are important water sources for most large cities. Many problems are attributed to their thermal stratification and inherent pollution characteristics. So the pollution characteristics of a typical thermally-stratified reservoir in Xi'an City, China were studied by field investigation and laboratory simulation. The results showed that: (1) The Heihe Reservoir was stably thermally stratified, particularly during summer months and that the deeper the water layer, the lower the oxygen concentration. Thus, the bottom layer became completely devoid of oxygen. (2) The water quality problems of this reservoir were mainly caused by internal pollutant release from the sediments. (3) The simulation experiment in the laboratory proved that the pollutants in the Heihe Reservoir sediment could be easily released into the overlying water. (4) The stratification broke up at seasonal changes. Hence, the pollutants released from the sediment transported to the upper layer as the layer became mixed. The pollutants supplied algae with sufficient nutriment, and harmful algae bloomed accordingly, especially in summer. Thus to destroy the stratification, aerate the bottom layer would be effective method to solve the water quality problems for thermally-stratified reservoir.

Key words: internal pollution, pollution characteristic, pollutant release, thermal stratified reservoir, water quality

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INTRODUCTION

As a result of the growing population, increasing industry, agriculture, and urbanization, inland water bodies are confronted with increasing water demand and are facing extensive anthropogenic inputs of nutrients and sediments, especially the lakes and reservoirs [1]. As large cities expanded continuously during the last century, they relied on local water resources, but as demand grew they were forced to invest in reservoirs often quite remote from the point of use. Examples include reservoirs built in Germany, e.g. the Wahnbach Reservoir [2], in China, e.g. the Three Gorges Reservoir [3] ， in Whales [4] and so on. Therefore reservoirs play a more and more important role in urban water supply. Once the reservoirs were brought into use for supply purposes, they must be carefully managed. But the quality of reservoir water has deteriorated in many countries in the past few decades [5].

Thermal stratification caused by variations in the density of the water is mainly a common phenomenon of deep reservoirs and lakes [4, 6, and 7]. Thermal stratification is one of the most important environmental issues for deep waters, due to its strong effects on physical, chemical, and biological processes [8]. Vertical stratification causes weak mixing, which in fact prevents the surface water from supplying substances to the bottom layer. Therefore, nutrients and Dissolved Oxygen (DO) are often confined only in the epilimnion layer, causing a series of water quality problems such as hypoxia [9, 10]. In particular, water temperature stratification may speed up the eutrophication and create favorable conditions for algal blooms [11], which may pose a significant adverse impact on the ecosystems in water [8]. As the hypolimnion has no source of oxygen to replace that already used, its water may become completely devoid of oxygen. On the other hand, microbial respiration also commonly results in oxygen depletion in the lower portion of the water column, especially in eutrophic waters; anoxia near the sediments, in turn, can lead to increased release of nutrients from the sediments. Thus under anaerobic conditions iron, manganese, ammonia, sulphides, phosphates and silica are released from the sediments into the overlying water. During a mixing event after a long period of stratification, nutrients, sulfide, and other dissolved constituents are mixed to the upper portion of the water column, where they can fuel potential algae blooms, odors, and fish kills[12]. Furthermore, when the whole water body turns over at the season alternation, the water layers become mixed and the pollutants are transported to the upper layer [4]. In particular the catchments area of major high dam reservoirs is often covered with mountainous forest area and the water quality of the reservoirs has been acted by a seasonal migration of diffuse pollution during monsoon rainfall [13]. Before the 1970s, sediment was simply regarded as the "sink" of pollutants in aquatic environments. With the increasingly effective control of point pollution sources in the aquatic environment, the polluted sediment has become one of the non-negligible non-point sources. It has become the sink and source of transfer and transformation of various pollutants [14]. Attributed to these phenomenons, more and more notorious problems such as eutrophication, harmful algal blooms (HABs), and pollutants periodic eruptions and so on [15-17] have arisen in thermally stratified reservoirs all over the world in recent years. In order to solve these problems effectively, the pollution characteristics and causes must be studied. Consequently, a case study of the Heihe Reservoir in Xi'an city was carried out in this research.

EXPERIMENTAL SECTION

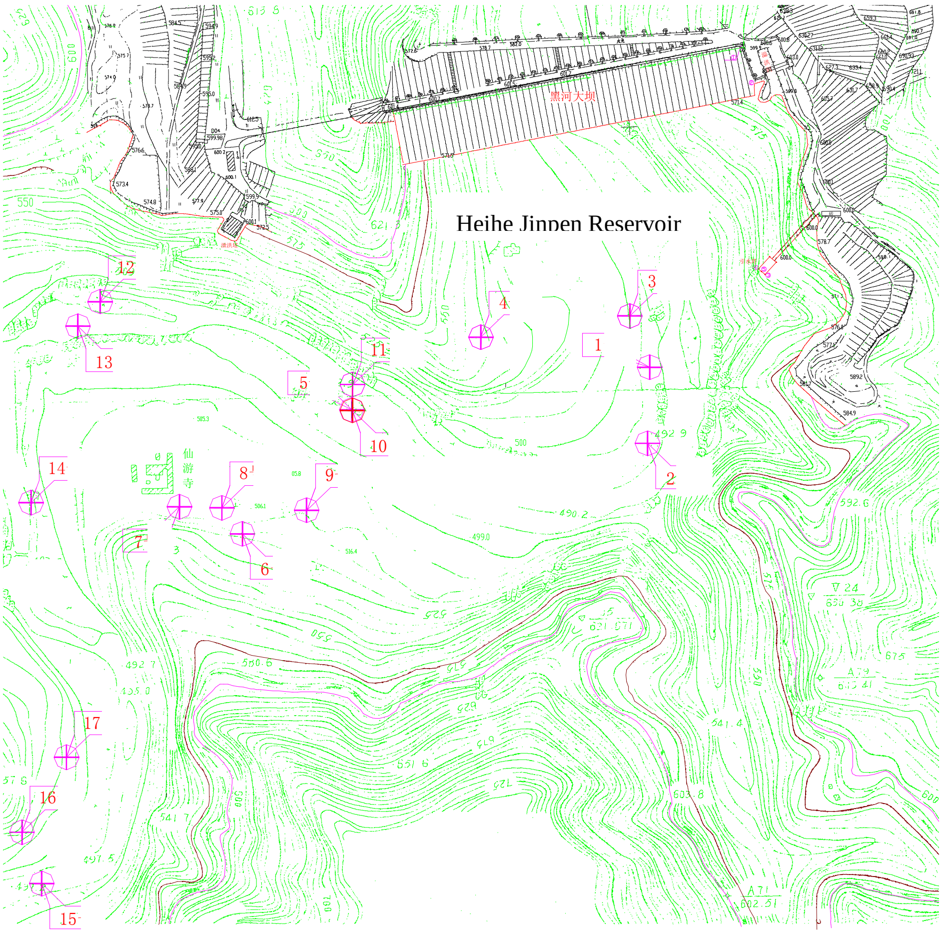


Fig.1 Map of the study area and sampling locations in research area (17 samples (1-17) in the Heihe Reservoir)

1. Sampling

The Heihe Reservoir, the most important water supply source of Xi'an, is a typically thermally stratified reservoir. It supplies 1.1 million steres of water to Xi'an each day, covering 70% of the total water supply. The maximum depth of this reservoir is about 95 meters and the mean depth is about 75 meters. The Heihe Reservoir pollution characteristics and pollutant release caused by internal origin pollution were systematically investigated and analyzed in this study.

Surface sediment samples were collected 30cm above the bottom at 17 different representative sites (labeled from 1 to 17, Fig.1) using a core sampler in July 2007. These selected sites whose locations were surveyed using a hand GPS locator were located near the water intake, at sites with different depth and in the main flow area of the original watercourse respectively. This was according to the Heihe Reservoir's characteristics such as its great depth, long renewing periodicity, long retention time and so on. Water samples were also collected at these 17 sites 5cm above the water-sediment interface. These sediment and water samples were stored in brown wild-mouth bottles at a low temperature until they were returned to the laboratory. Then the sediments were sieved to remove large pieces of stones and sand particles through a Standard Testing Sieve. They were divided into two parts. One part of 17 samples was mixed thoroughly for the release experiment use. The other part of the 17 samples were each dried by a freeze drier and stored at 4℃.

Also, vertical water samples in the reservoir centre area were collected each month from July 2007 to December 2008. All the collected water samples were filtered (0.45 μm) and analyzed as soon as possible. In order to investigate the causes of pollution, water samples from upstream (labeled from U1 to U7) were also collected and tested in different seasons.

2. Vertical analysis

The pollutant vertical distributions in the reservoir centre were studied by monitoring the water quality each month from July 2007 to December 2008. The parameters included temperature (T), dissolved oxygen concentration (DO), Chl-a, algae cell density, total phosphorus (TP), total nitrogen (TN), and ammonia nitrogen (NH_3^+-N). T, pH, DO and Chl-a were monitored using a multifunction water quality monitoring instrument Hydrolab DS5 made by HACH company(USA) which is specially used for field monitoring. The measurement range, precision and resolution of this instrument are listed in Table 1.

Table 1 Performance parameters of Hydrolab DS5

Index	Range	Precision	Resolution
depth	0-10m 0-100m 0-200m	±0.003m ±0.05m ±0.1m	0.001m 0.01m 0.1m
pH	0-14pH unit	±0.2 unit	0.01 unit
DO	0-20mg L^{-1}	±0.1mg/L DO<8 mg L^{-1} ±0.2mg/L DO>8 mg L^{-1}	0.01mg L^{-1}
T	-5-50℃	±0.1℃	0.01℃
Chl-a	Dynamic range low：0.03-500μg L^{-1} medium：0.03-50μg L^{-1} high：0.03-5μg L^{-1}	±3%	0.01mg L^{-1}

3. Chemical analysis

The analytical water samples parameters were measured according to methods of the China Environmental Protection Agency (2002), as shown in Table 2.

The total phosphorus and organic matter content in sediment samples were tested by a molybdate and L-ascorbic acid colorimetric method after Perchloric acid digestion [18] and a potassium bichromate titrimetric method according to methods of the China Environmental Protection Agency (2002) respectively.

Table 2 Analytical items and method of water samples

Item	NH_3^+-N	TN	WSIP and TP	Fe^{2+}	Mn	COD	Algae cell density
Method	Nessler's reagent colorimetric method	Ultraviolet spectrophoto-metry	molybdate and L-ascorbic acid colorimetric method	10-phenanthroline colorimetric method	Potassium periodate colorimetric method	HACH method 8000	Method of microscopic field

4. Release experiment design

The mixed sediments were put into a series of brown wild-mouth glass incubators whose volume capacity and in radius were 250mL and 6cm. Three parallel groups (G1, G2 and G3) were designed and each group contained 8 incubators labeled from G1-1# (or G2-1#, G3-1#) to G1-8# (or G2-8#, G3-8#). In each incubator, 100ml mixed sediments were filled into the bottom. The overlying water (150mL, DO≤0.5mg/L), which was collected from the

reservoir and deoxydated by high-purity nitrogen, was injected into each incubator slowly and carefully to avoid disturbing the sediments. Then all of these incubators were airproofed and cultured in the dark at 7～8℃. After some time, three incubators of the same labeled number (for example: G1-1#, G2-1# and G3-1#) in each group were opened and the overlying water qualities were tested to research the release characteristics of the internal pollution.
The release rates of pollutants from the sediment were calculated according to the following formula [19]: where *V* (L) is the volume of overlying water. The analyzed time is expressed as "n". C_n (mg/L) is the concentration of pollutants measured every time. C_0 (mg/L) is the original concentration of pollutants in the overlying water. γ (mg) is the release quantity measured every time. *R* (mg/ (d•m^2)) is the release rate. The release time is described as *t* (d). The touch area of sediment and water A (m^2) in this experiment is 0.0113 m^2.

$$\gamma = V(C_n - C_0) \quad R = \gamma / tA \qquad (1)$$

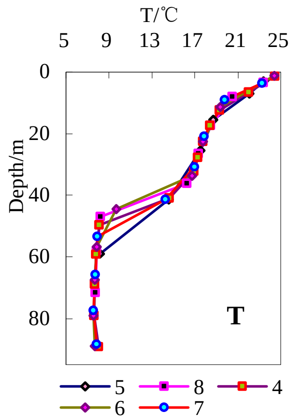
RESULTS AND DISCUSSION

1. Vertical, seasonal distributions of water quality indexes and investigation of the reasons for the pollution

According to Formula (2) [20], the Heihe Reservoir is a stable thermally-stratified reservoir (a=18.58/2.0=9.29).

$$\begin{cases} \text{a=reservoir inflow/total storage capacity} \\ \text{if a<10, stable stratified} \\ \text{if a>20, completely mixed} \end{cases} \qquad (2)$$

The field testing results (Fig. 2) of some typical sampling sites showed that the Heihe Reservoir was a stably thermally-stratified reservoir. In the summer months, the temperature of the surface water was 23~25℃, while the bottom layer was only 7.6~8.3℃. The epilimnion, from the surface to the depth of 40 meters, was much warmer than the hypolimnion, from the depth of 50 meters to the bottom. Owing to the differences in density, the two layers were separated by a static boundary layer known as the metalimnion (from the depth of 40 meters to 50 meters). On one hand, because of the steady stratification, the oxygen transfer was restrained. On the other hand the chemical and biological oxygen consumption was still happening. So the bottom layer became completely devoid of oxygen. The oxygen concentration distribution showed similar regularity with the thermal stratification, i.e. the deeper the water layer, the lower the oxygen concentration. The oxygen concentration of the surface layer was 8mg/L, while it was only 0.1~0.2mg/L at the deepest point.



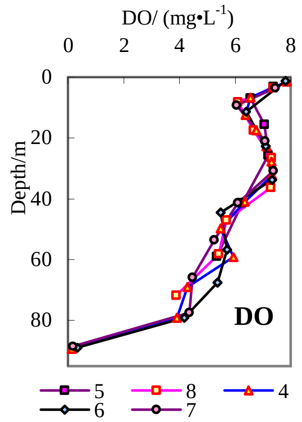


Fig. 2 Vertical distribution of T and DO in Jul. 2007

The distributions of the water quality parameters in the reservoir area were continuously monitored on the spot from July 2007 to December 2008 in order to learn more about the pollution characteristics of this reservoir in different seasons (Fig. 3).

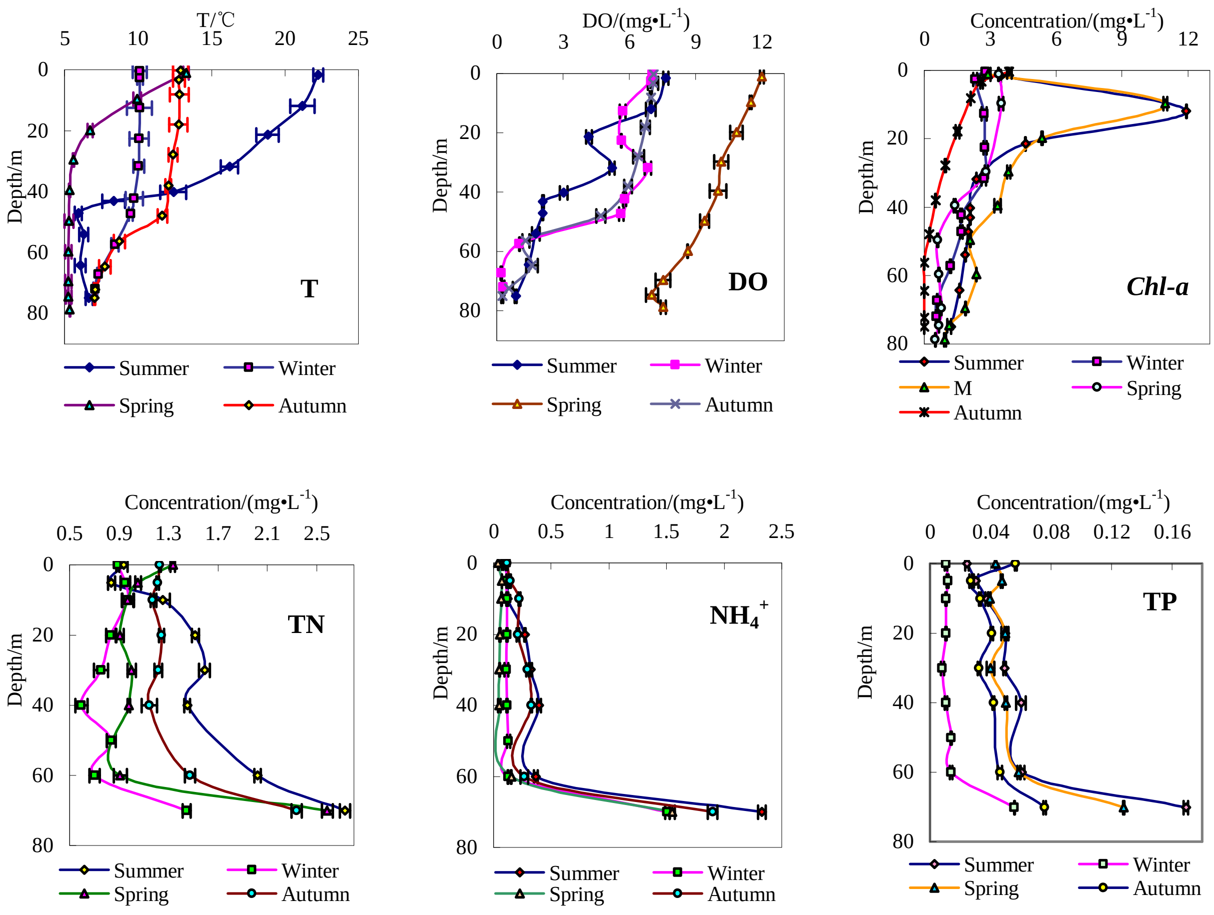


Fig. 3 Vertical and seasonal distribution of water quality (from Nov.2007 to Dec. 2008)

It was proved again that the Heihe Reservoir was stably thermally-stratified, particularly during the summer months. Although the metalimnion was absent in autumn, the layered structure of temperature, i.e. the temperature of the upper layer being higher than the bottom layer, still existed. The temperature vertical distributions in winter and spring were relatively more homogeneous. This was attributed to the mix happening as seasons change. But in spring, the temperature of the upper layer (<20m) was higher than the lower layer because of the air temperature increase. The DO decreased as the depth increased in all seasons. The great increase of TN, NH_4^+ and TP in the bottom layer supplied good evidence proving that the internal pollutants released from sediments greatly deteriorated the water. The TN and NH_4^+ increased a little as the depth increased (the bottom layer was not included) in summer and autumn. This phenomenon was not obvious in winter and spring. The TP of the water in spring, summer and autumn showed a similar vertical distribution, i.e. comparatively higher value appearing at the depth of about 20m and 40m. At the same depth, the concentration of TP in the water in four seasons was sequenced as follows: summer>spring>autumn>>winter. This phenomenon was attributed to the factors which can influence the internal pollutants release, such as temperature and concentration gradient. The *Chl-a* in the water appeared “inverse-S” shape along the vertical direction and increased to the maximum at the depth of 10m at the alternation between spring and summer and during the whole summer. In the other three seasons, the *Chl-a* decreased as the depth increased. The *Chl-a* concentration, which can reflect the algal growth, was influenced by the factors such as sun-light, temperature, N and P.

Table 3 Water qualities of upstream (content/ (mg L^{-1}))

No.	Spring				Summer				Autumn				Winter			
	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD
U1	0.67	0.06	0.02	3.96	0.37	0.104	0.017	3.31	0.538	0.175	0.017	2.78	0.959	0.089	0.038	2.75
U2	0.96	0.03	-*	3.69	0.49	0.172	0.014	3.74	0.854	0.118	0.017	2.62	1.055	0.049	0.010	4.99
U3	0.29	0.05	0.01	3.59	0.35	0.078	0.003	2.86	1.246	0.112	0.017	2.54	0.710	0.037	0.021	1.72
U4	0.41	0.05	0.01	3.59	0.25	0.115	0.007	3.62	0.394	0.152	0.010	2.95	0.758	0.031	0.017	1.63
U5	0.56	0.03	0.01	3.68	0.42	0.094	0.003	2.73	0.586	0.123	0.003	2.29	0.930	0.037	0.017	3.44
U6	0.53	0.02	-*	3.41	0.46	0.078	0.010	3.15	0.557	0.140	0.007	2.78	1.055	0.043	0.010	1.29
U7	0.48	0.01	0.03	3.78	0.27	0.089	0.000	2.97	0.480	0.181	0.007	2.05	0.815	0.060	0.010	4.47

*Not detected

Table 4 Water qualities of upper layer in reservoir area (content/ (mg L^{-1}))

No.	Spring				Summer				Autumn				Winter			
	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD	TN	NH_4^+	TP	COD
1	1.86	0.12	0.01	3.68	0.89	0.104	0.024	2.54	1.361	0.135	0.010	3.19	1.068	0.079	0.001	2.49
2	1.2	0.03	0.02	3.59	0.73	0.078	0.014	2.47	0.882	0.140	0.003	2.86	1.238	0.076	0.003	2.46
3	1.2	0.06	0.01	4.14	0.59	0.089	0.014	2.31	1.447	0.146	0.021	2.95	1.218	0.066	0.002	2.91
4	0.84	0.01	0.02	3.51	0.74	0.078	0.014	2.39	0.796	0.140	0.021	3.03	1.091	0.062	0.004	2.75

As analyzed above, the internal pollutants release was the main cause of seasonal water quality problems of the Heihe Reservoir. In order to demonstrate this conclusion much better, a stricter study and investigation was carried out. The upstream and upper layer water qualities in different seasons were tested and compared (Table 3 and Table 4).

Surface waters can be contaminated by human activities in two ways : (1) by point sources , such as sewage treatment discharge and storm water runoff ; and (2) by non-point sources , such as run off from urban and agricultural areas [21]. The investigation results of upstream showed that there were no obvious point or non-point pollution sources. Further more as shown in Tables 3 and 4, the upper layer water was much dirtier than that of upstream, which proved that the reservoir water pollution was not caused by the external pollution but the internal pollution. The field testing results of water quality at the 17 sites in the bottom layer can illuminate this conclusion much better (Tables 5 and 6). The DO was influenced by the water depth greatly: the deeper the water, the lower the DO. As shown in Table 5, the DO was lower than 2mg/L when the water was more than 80m deep. Furthermore, the DO in 8 of 17 sampling sites was lower than 1mg/L. The correlation analyses showed that the DO was negatively related to the water depth (R^2=0.8571). According to other scholars' reports, if the DO was very low, the internal pollutants were easily released from the sediments [22-24], which was also proved by the testing results of bottom water quality (Table 6).

Table 5 Field testing results of bottom water quality

No.	Location of sample sites longitude latitude		Depth (m)	T (℃)	pH	ORP (mV)	SpCond (μS cm^{-1})	DO (mg L^1)	*Chl-a* (μg L^{-1})
1	N34°02.739'	E108°12.429'	65.8	8.1	7.4	265.5	191.7	2.34	0.37
2	N34°02.676'	E108°12.344'	92.9	7.7	7.3	255.8	198.4	0.91	4.33
3	N34°02.772'	E108°12.338'	89.5	7.8	7.1	189.2	240.7	0.18	0.00
4	N34°02.753'	E108°12.220'	49.7	8.3	7.6	245.8	191.4	6.02	0.78
5	N34°02.694'	E108°12.121'	90.3	7.9	7.5	100.9	370.7	0.12	0.00
6	N34°02.611'	E108°12.030'	58.9	8.2	7.7	252.6	191.7	5.35	0.75
7	N34°02.636'	E108°11.977'	65.8	7.7	7.6	276.0	195.0	4.53	0.71
8	N34°02.632'	E108°12.022'	71.7	7.7	7.5	284.0	194.8	3.88	0.91
9	N34°02.634'	E108°12.087'	76.7	8.1	7.5	272.0	192.3	3.60	11.62
10	N34°02.704'	E108°12.133'	89.2	8.0	7.3	178.3	201.3	0.14	0.00
11	N34°02.715'	E108°12.124'	89.4	7.7	7.5	282.0	216.3	0.39	2.30
12	N34°02.762'	E108°11.914'	88.9	7.7	7.4	287.9	205.7	0.34	1.36
13	N34°02.753'	E108°11.905'	87.4	7.7	7.4	298.5	204.7	0.45	1.45
14	N34°02.631'	E108°11.869'	88.4	7.8	7.4	299.8	210.6	0.18	2.81
15	N34°02.384'	E108°11.884'	87.2	7.8	7.5	286.5	197.7	1.71	2.03
16	N34°02.415'	E108°11.864'	84.7	7.7	7.6	295.2	194.2	2.23	1.64
17	N34°02.469'	E108°11.904'	79.6	7.5	7.6	296.5	191.5	2.79	1.33

Table 6 Laboratory testing results of bottom water quality content/(mg L^{-1})

Items	Sampling sites No.													
	2	3	4	5	6	7	8	9	10	11	12	13	14	16
NH_4^+	0.82	1.28	0.35	2.89	1.31	2.45	1.47	2.29	2.86	2.97	2.92	2.86	4.09	2.56
TN	1.54	2.49	2.30	2.94	1.66	2.91	1.90	2.46	3.07	2.97	2.98	2.95	4.67	2.94
WSIP	0.02	0.02	0.02	0.01	0.04	0.04	0.03	0.03	0.02	0.02	0.02	0.02	0.04	0.02
TP	0.04	0.04	0.06	0.04	0.06	0.07	0.05	0.08	0.03	0.04	0.06	0.09	0.05	0.05
Fe	0.10	0.12	0.12	0.13	0.12	0.14	0.12	0.15	0.14	0.13	0.12	0.17	0.14	0.12
Mn	2.71	4.42	0.46	2.74	0.61	2.10	1.53	2.10	2.81	3.38	3.51	3.89	2.94	2.16
COD	43	56	107	51	84	149	85	98	74	70	60	85	68	63

The water quality of the bottom layer was so poor that most parameter value was over the value prescribed by the state standard. The worst one was 44 times greater than the state standard value. The TP content in the sediment was (692.325±34.142) ug/g and the organic matter OC was (2.332±0.091) %, which were both higher than the equivalent value of most Chinese source water reservoirs. The high load of internal pollutants in the sediments was the potential cause of the seasonal water quality problems in the Heihe Reservoir. In a word, the internal pollution was the main cause of the problems. Although it cannot directly influence the water quality of the upper layer, the internal pollutants released from the sediments can indirectly deteriorate the upper layer water by diffusion caused by the concentration gradient and the mix happening as the season changes because of the density difference.

2. Internal pollution release characteristics analysis

Extra work, a simulated experiment (Fig.4), was carried out in the laboratory to find more information about the internal pollution characteristics of the Heihe Reservoir. The simulation lasted 158 hours. Six kinds of pollutants were tested and they all released at different times and in different ranges. After reaching the release balance, the concentration of each pollutant was much higher than the initial value.

The maximum and mean release intensities of these six pollutants were comparatively high (Table 7). At the condition of DO<0.5mg/L, pollutants in great quantities were released into the overlying water in a short time. Also, the final pollutants' concentrations were coincident with the field investigation of the bottom layer water, which once again proved that the internal pollution was the main cause of water quality problems. So it can be concluded that the controlling of internal pollution has great importance to improve the reservoir water quality.

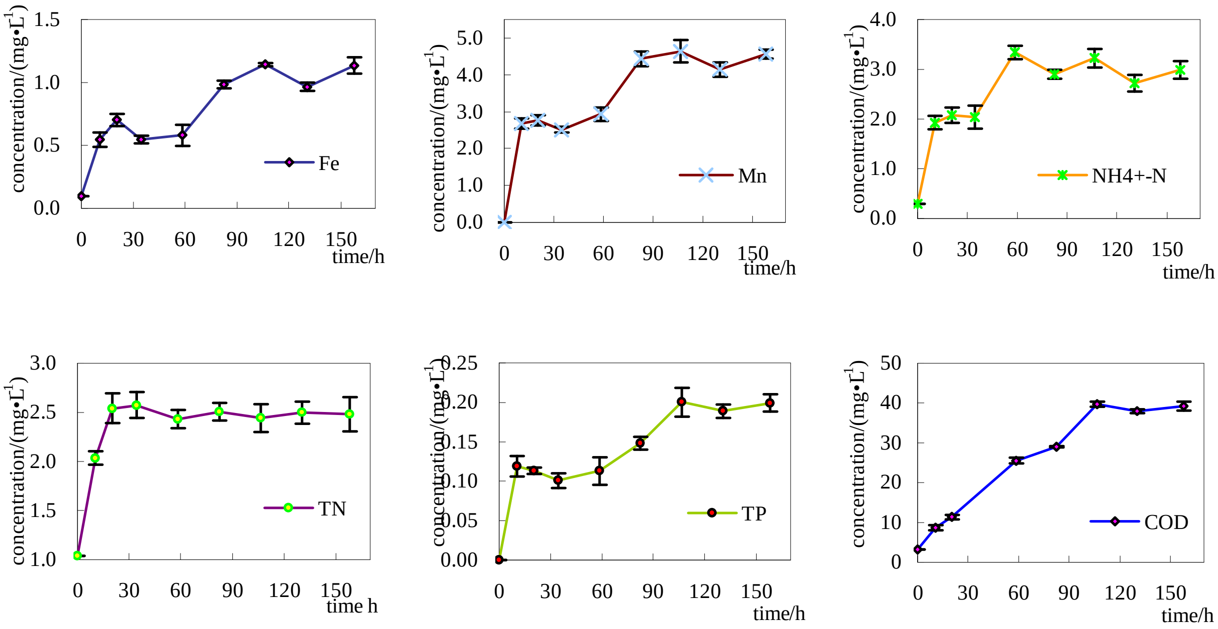


Fig. 4 Release curves of six pollutants

Table 7 Sediments release characteristics

Items	Balance release time (h)	Initial concentration (mg L^{-1})	Final concentration (mg L^{-1})	Maximum release rate (mg (d·m^2)$^{-1}$)	Mean release rate (mg (d·m^2)$^{-1}$)
NH_4^+	58.5	0.296	3.345	13.68	6.96
TN	34.5	1.037	3.572	30.24	5.52
TP	106.5	-*	0.148	3.6	0.38
Fe	106.5	0.094	1.076	13.68	1.78
Mn	106.5	-*	4.642	81.36	10.01
COD	106.5	3.170	39.900	166.8	68.64

**Not detected*

3. Algae investigation: growth status and dominant algae

The upper layer and bottom layer will be mixed at the seasonal changes of autumn-winter and winter-spring. The pollutants released from the sediments will be transported into upper layer water, which can supply great quantities of nutrients. The temperature will decrease greatly when winter is coming, which is not good for algal growth. So the algal bloom usually happened in summer following the change from winter to spring when the temperature was comparatively high. Unfortunately, algal blooms have also been observed in recent years in the central area of the bay in spring season due to the poor hydrodynamics [25].

Similar to the classical theory, the algal bloom of the Heihe Reservoir also happened in summer. But differently, there were two peak values appearing in May and July respectively (Fig.5). This was because that after spring, the temperature increased gradually and the nutrients especially P (Fig.3) was abundant. The algae cells increased at these advantage conditions and reached the first peak value in May. Then, although the temperature increased continually, the rain fall in Xi'an city became frequent, which was bad for algal growth. Besides, according to the common regularity of algae kinds' conversion, the quantity of algae cells in the water will not be very high at this time. After the beginning of July, the temperature and sun-light were both good for algal growth. So the second peak value appeared in July. The dominant algae subkingdoms in the Heihe Reservoir were Chlorophyta and Cyanophyta. Their percentages in different months were shown in Table 8. The microscope pictures of some algae are shown in Fig.6.

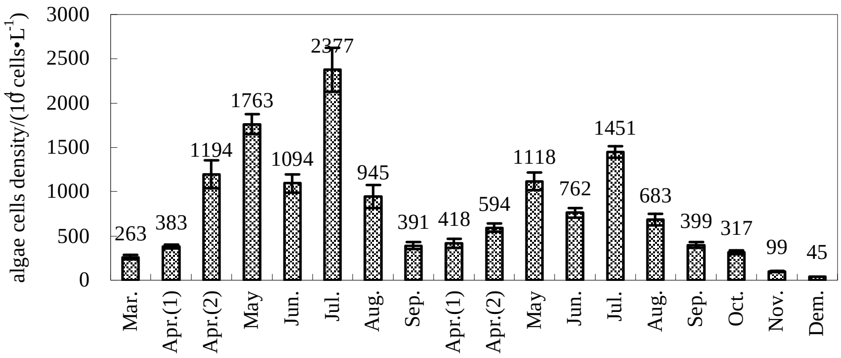


Fig. 5 Algae cells density distribution in different months

Table 8 Dominant algae percentage in different months

Date(Y.M)	Dominant subkingdom	Percentage (%)	Date(Y.M)	Dominant subkingdom	Percentage (%)
07.05	*Chlorophyta*	78.5	08.6	*Chlorophyta*	42.91
07.06	*Cyanophyta*	74.3	08.7	*Cyanophyta*	63.19
07.07	*Cyanophyta*	66.9	08.8	*Chlorophyta*	62.28
08.4	*Chlorophyta*	52.06	08.9	*Chlorophyta*	78.50
08.5	*Chlorophyta*	45.83	08.10	*Chlorophyta*	70.09

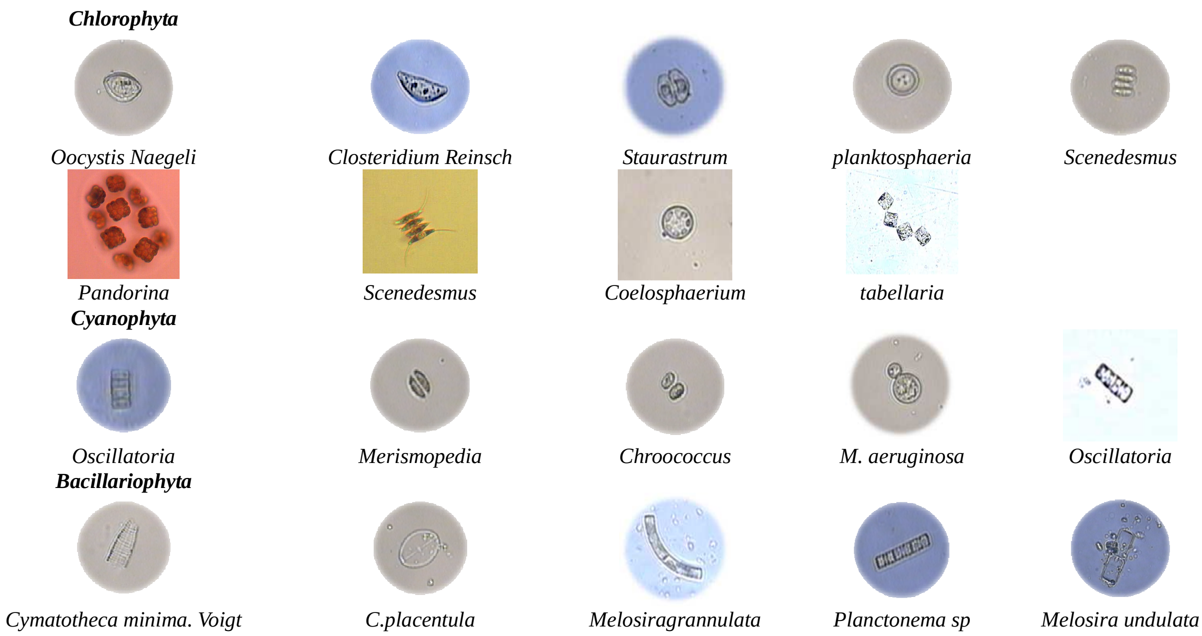


Fig. 6 Some algae microscope pictures

CONCLUSION

The field investigation which lasted about two years and the simulation experiment in the laboratory were used to study the pollution characteristics of thermally-stratified reservoir and the internal pollution effect on water quality problems. The results showed that: (1) The Heihe Reservoir was stably thermally-stratified, particularly during the summer months. (2) The water quality problems of this reservoir were mainly caused by internal pollutants released from the sediments. (3) The pollutants in the Heihe Reservoir sediment could be easily released into the water. (4) The pollutants released from the sediment were transported to the upper layer as the layers became mixed. The pollutants supplied alga with sufficient nutriments, and harmful alga bloomed accordingly, especially in summer. It is suggested that a technology, such as water lifting aerator, which can not only destroy the stable stratification by mixing the layers but also supply the bottom layer with sufficient oxygen by aerating should be taken into use to solve the water quality problems of thermally-stratified reservoir.

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