African Journal of Biotechnology Vol. 10(54), pp. 11206-11213, 19 September, 2011
Available online at http://www.academicjournals.org/AJB
DOI: 10.5897/AJB11.1932
ISSN 1684–5315 © 2011 Academic Journals

Full Length Research Paper

Relationship of phosphorus content in carp otoliths with that in ambient water in Xiaoxi Port of the Taihu Lake, East China

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Accepted 22 August, 2011

It has been of high concern that the phosphorus pollution is getting serious after lake eutrophication in the Taihu Lake, the third largest freshwater lake in China. As a sensitive recorder of the ambient water and fish exposures, fish otolith has been studied as a potential dynamic monitor of water quality by many biologists and mineralogists. In order to work out the correlation of phosphorus enrichment in carp otoliths to the ambient water of the carps, the phosphorus concentration in carp otoliths was measured *in situ* using laser ablation plasma mass spectrometry (LA-ICP-MS) and comparison with the relevant data of the water was conducted. Significant positive correlation was found for phosphorus concentration in carp otoliths to the ambient water in the corresponding time. Therefore, the wild carp otoliths have the potential to act as an environmental indicator of water phosphorus pollution and lake eutrophication.

Key words: Carp otoliths, environmental pollution, lake eutrophication, phosphorus enrichment, mineral monitoring, Taihu Lake.

INTRODUCTION

Water is a natural resource for human survival. 70% of the river water has been polluted and 40% almost has lost its basic function. The worst part however, is that more than 95% was polluted when flowing through cities (Jiang, 2010). Water environmental degradation has become a great threat to human health including the human living environment and food safety. As China's third largest freshwater lake, Taihu Lake flows through Shanghai, Suzhou, Wuxi, Changzhou and Hangzhou. With the increasing utilization of The Taihu Lake and a large number of domestic sewage (nitrogen, phosphorus and other pollutants) emissions, the organic pollution and lake eutrophication are getting worse and worse. Particularly, there is lack of drinking water for millions of people in Wuxi because of the bloom of blue-green algae in the Taihu Lake in 2007, with more concern focused onthe lake eutrophication. Therefore, it is necessary to explore more economical, efficient and effective approach for dynamic monitoring and evaluation of water quality.

Fish otoliths are pearl-like calcium carbonate concretions found in the membranous labyrinth of most fishes. There are three pairs of otoliths for each fish, namely lappillae, sagittae and asteriscae in utricular, saccular and lagena, respectively, functioning in hearing and balance systems (Qiu et al., 2009). Typically, chemical elements intake into fish is through direct absorption from water and indirect intake from food, and then deposit into otoliths and other organs after a series of physical activities. The special nature of the otoliths, on one hand, is their stability, which means that once laid down in a fish, otoliths remain chemically inert and no evidence of diagenetic alteration has been found (Gao, 1999). On the other hand, otoliths begin to form before hatching and grow continuously through the entire life of a fish (Schwarcz et al., 1998), forming annual, seasonal, and even daily growth layers (Xie, 1995), thus preserving an uninterrupted record of the internal and external environment of the fish. Previous studies of otoliths have

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mainly focused on few elements such as strontium (Sr) and barium (Ba), and the oxygen and carbon isotopes to disclose the related marine environment (Kalish, 1991; Thorrold et al., 1997; Gao and Beamish, 2003). Using otolith as a potential tool to monitor the lake water quality is innovative and pioneering, which might be an important supplement to the traditional approach.

Based on the basic knowledge of some biominerals about their continuity and periodicity in growth and sensitivity to environment (Li et al., 2008a), wild carp lappillae from Xiaoxi port of the Taihu Lake in Eastern China were used for phosphorus enrichment analysis, and the phosphorus concentration in the ambient water was compared for correlation analysis. In this way, we tried to make out the bioconcentration factors (BCF) of phosphorus in fish otoliths, and to reveal the relationship of phosphorus enrichment between otoliths and ambient water. We think this work is of great significance in exploring potential long-time mineralogical tools for water environment monitoring.

Sampling location

Taihu Lake (119°53'~ 120°36', 30°55'~ 31°33'), located in the southern margin of the Yangtze River Delta, is China's third largest freshwater lake with the total lake area of approximately 2428 km^2 and shoreline length of 393.2 km. Average depth is about 1.29 m, and the maximum depth is about 2.60 m. Taihu Lake is a good catchment water lake, with total water of about 4.7 billion m^3. The water level is relatively stable, with the average water level of 2.89~3.27 m and annual amplitude of 1.10~1.80 m generally, and it changes significantly dependent on seasonal precipitation, showing a year-round spring up and fall winter trend. The annual average temperature is 17.0 ℃, with the highest monthly average temperature in August and the lowest in January (Zhu and Xu, 2008).

Taihu Lake plays a huge role in agro-industrial water supply, flood control and water storage, tourism, shipping, climate regulation, keeping the ecological balance and so on. However, impacted by the heavy population density around the lake (according to statistics, 1,000 people / km^2), reduction of natural vegetation, water reclamation and over-development, and agro-industrial and domestic sewage discharge, the water environment is deteriorating and lake eutrophication (Qin, 1998) is becoming an increasing problem in the Taihu Lake. The large outbreak of blue-green algae happened twice in May 2007 and 2008, respectively (Wu, 2008; Deng, 2010).

Hydrochemical characteristics

Xiaoxi port is located at Li River (crossing over the tributary of Beijing-Hangzhou Grand Canal) in Wuxi. The water flows from north to south, ending to the Taihu Lake, and it is the locality of key assessment section of national government and Jiangsu provinces (Figure 1). The data of water quality as shown in Table 1, is supplied by the Environmental Monitoring Center at Wuxi. The indicators of eutrophication given by the Chinese government are as below: nitrogen> 0.2 mg/L, phosphorus> 0.01 mg/L, BOD> 10 mg/L, the total number of bacteria > 100,000 /ml in fresh water with pH from 7.0 to 9.0, chlorophyll content> 10.000 μg/L (Fang, 2011). As showed in Table1, the water is characterized by overweight of total nitrogen and total phosphorus in Xiaoxi port. 39% of nitrogen data is 2 orders of magnitude higher than the eutrophication indicator, 56% is 1 order of magnitude higher than the indicator and 5% is 4 times higher than the indicator. Also, 94% of phosphorus data is 1 order of magnitude higher than the eutrophication indicator and 6% is 8 times higher than the indicator. Apparently, the lake eutrophication is very serious in Xiaoxi port.

The total phosphorus concentration in the water of Xiaoxi Port from July 2005 to May 2008 was plotted over time in Figure 2(A). It was noticed that from March to May 2007, the phosphorus in the water of Xiaoxi port was abnormally accumulated with its content been 57 to 63 times higher than the eutrophication indicator, and 60 times higher on average. From March 2006 to January 2007, the phosphorus content in the water was 17 to 29 times higher than the eutrophication indicator and 25 times higher on average while from July 2005 to January 2006 and from July 2007 to May 2008, the phosphorus content in the water was 8.6 to 24 times higher than the eutrophication indicator, and 15.5 times higher on average.

On the whole, the phosphorus concentration in the water of Xiaoxi port was low in 2005, two years before the large bloom of blue-green algae in the Taihu Lake in 2007. However, the concentration of phosphorus was significantly higher during 2006 and the first half of 2007, which might be the prelude to the large bloom of blue-green algae in 2007. The water phosphorus decreased during late 2007 and early 2008, which might be the late coming effect of the blue-green algae "blooms" with a lot of phosphorus absorbed.

MATERIALS AND METHODS

Sample collection

Carp, a very common freshwater fish, was chosen to collect otoliths in this work primarily because of its wide distribution, easy for sampling, and convenient to carry out comparison analyses of different regions (Li et al., 2008a; Li et al., 2011). Totally, 47 wild carps were collected from Xiaoxi port in the Taihu Lake in June 2008, following with physiological measurement, image digitized and scale collection in the field. Otoliths were extracted, ultrasonic cleaned with 75% alcohol and then allowed to air-dry for 24 h in the laboratory.

Age determination

The age determination of carps was mainly based on the scale-

Figure 1. Location of the study area.

identification method, with otolith-identification method described by Liu (1995), Yin (1995) and Ye and Zhang, (2002). This method is described as follows: the scale was put on a glass slice, covered with a thin glass slice and fixed with adhesive tape. Observation was made under OLYMPUS microscope. According to the indexes of annual ring for scales of sparse-dense type, incision type and fragment type, the locations and number of annual rings were determined. Taking into consideration the forming time of the annual rings of the scale and otoliths of the carps from the Dongjiang River, Guangdong Province, which is February to March for the first ring and mainly March to April for the second and the other rings, respectively (Ye et al., 2002), the time of the ring can be estimated. Considering the distances of the first ring to the second ring and to the core, the starting time for the growth of the scale can be estimated; similarly, based on the distance of the outer ring to the margin, the closing time for the growth of the scale can be estimated. Other time-spots can be deduced from the fixed ones simply on equal distance rule.

Measurement of phosphorus content in lappillae

Trace elements in lapilli were measured by laser ablation plasma mass spectrometry (LA-ICP-MS), which has wide detection range, high sensitivity and low detection limit (0.010 μg/g) which can effectively detect some elements that cannot be detected by EPMA (Li et al., 2008b; Gao et al., 2008). The phosphorus content of three lapillus slices was determined using LA-ICP-MS at the State Key Laboratory for Continental Dynamics, Northwest University in December 2009. The beam diameter was 30 μm. The equidistant measurement spots were ablated from the otolith core to the margin and there was a standard measurement spot every five spots, with

Table 1. Hydrochemistry of the water in Xiaoxi Port of the Taihu Lake from 2005 to 2008.

Year-Month	T℃	pH	DO (mg/L)	COD_{MN} (mg/L)	BOD_5 (mg/L)	ρ_N (mg/L)	Total-P (mg/L)	Total-N (mg/L)	S (mg/L)
2005 - 07	4.1	7.0	2.5000	8.4000	5.2000	2.3900	0.2210	5.5600	0.0025
2005 - 09	8.5	7.2	2.3000	8.3000	2.4000	2.1300	0.1500	3.0500	0.0025
2005 - 11	23.0	7.6	6.0000	5.8000	6.1000	0.4800	0.0860	3.1900	0.0025
2006 - 01	2.85	7.3	10.7000	7.0000	4.9000	1.3220	0.1800	32.0000	0.0060
2006 - 03	14.5	7.7	8.5000	6.4000	3.0000	1.9900	0.2720	35.0000	0.0025
2006 - 05	15.2	8.3	4.6000	9.7000	5.9000	0.9660	0.1720	48.0000	0.0025
2006 - 07	26.1	7.5	4.0000	12.0000	12.0000	1.3400	0.2580	50.0000	0.0130
2006 - 09	15.2	7.2	2.3000	7.1000	4.7000	2.7520	0.2910	33.0000	0.0100
2006 - 11	14.3	7.3	5.1000	2.4000	4.0000	1.4860	0.2560	56.0000	0.0020
2007 - 01	6.0	7.9	5.3000	6.0000	4.2000	1.1700	0.2500	9.1000	0.0050
2007 - 03	8.0	8.0	5.1000	5.8000	3.9000	0.9700	0.6300	11.3000	0.0050
2007 - 05	22.0	7.2	5.0000	5.9000	3.6000	0.8900	0.5700	8.6300	0.0050
2007 - 07	29.0	7.7	5.4000	7.3000	6.9000	0.5300	0.2400	2.4900	0.0050
2007 - 09	25.5	6.8	5.6000	4.5000	2.2000	0.5100	0.1100	2.1700	0.0050
2007 - 11	15.6	7.9	6.3000	5.2000	2.0L	0.2900	0.2000	1.0200	0.0050
2008 - 01	4.7	8.3	11.9000	4.5000	3.7000	0.3800	0.1000	1.1300	0.0050
2008 - 03	11.4	8.6	11.0000	3.5000	4.0000	0.2100	0.1300	0.8100	0.0100
2008 - 05	23.0	7.5	6.4000	3.7000	2.7000	0.2200	0.1300	1.9900	0.0020

T, temperature; DO, dissolved Oxygen; COD, chemical oxygen demand; BOD, biochemical oxygen demand.

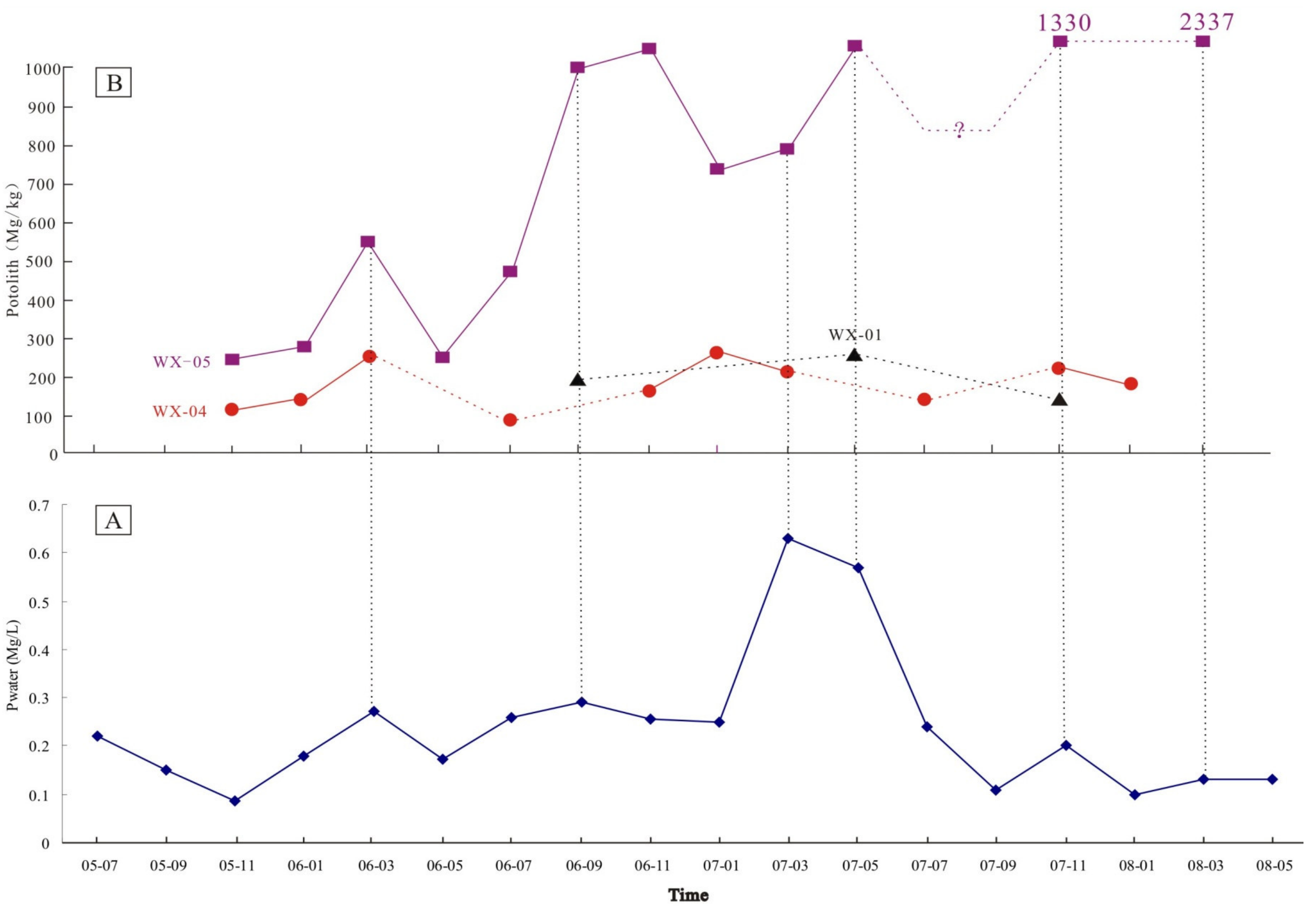

Figure 2. Comparison of diagrams of the total phosphorus content over time in the water of Xiaoxi Port (A) and phosphorus content over time in the carp lapilli from Xiaoxi Port (B).

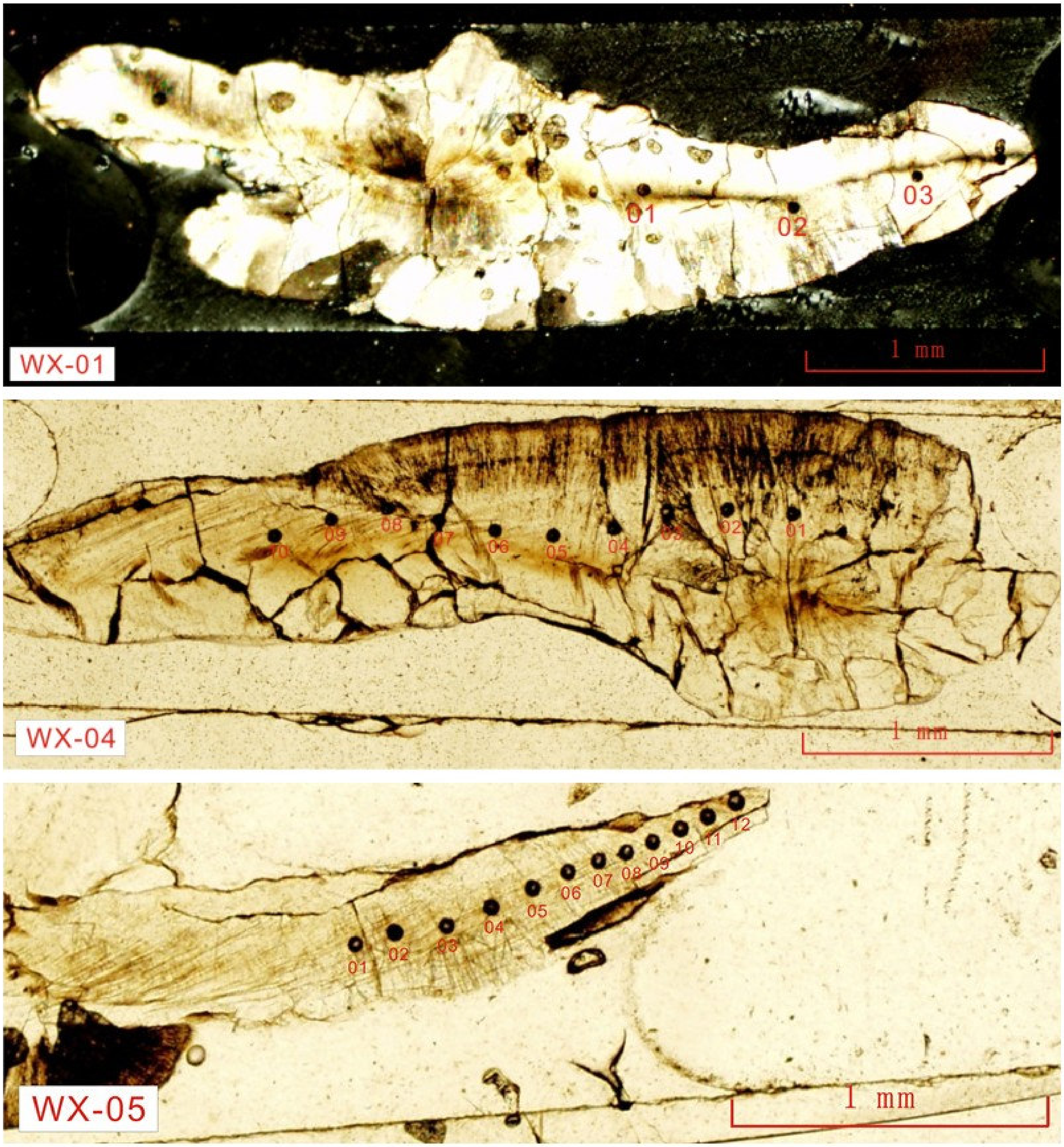

Figure 3. Ablation spots in lappillae WX-04, WX-05 and WX-01(their corresponding age determinations are shown in Table 2). WX is the abbreviation of the Xiaoxi port in Wuxi; WX-01,WX-04 and WX-05 refers to the first, fourth and fifth numbers of carp otolith samples, respectively.

a total of 59 spots obtained.

RESULTS AND DISCUSSION

The age of fish

Combining identification by fish scales and otoliths, the age of fish was determined which ranged from 3 to 4 years. The first month was November 2005, and the last month was March 2008. The determination results are shown in Figure 3 and Table 2.

Phosphorus content in lappillae

The phosphorus content in the three lappillae samples

Table 2. The phosphorus content of sample WX-01 in different ablation spots/different time periods.

Sample number	Ablation spot	Year-month	P (mg/kg)
WX-01	WX-01-01	2006-09	190.1600
	WX-01-02	2007-05	260.0300
	WX-01-03	2007-11	149.7500
	Average		199.9800

Table 3. The phosphorus content of lappillae sample WX-04 in different ablation spots/different time periods.

Sample number	Ablation spot	Year-month	P (mg/kg)
WX-04	WX-04-01	2005-11	121.4800
	WX-04-02	2006-01	145.7600
	WX-04-03	2006-03	259.5500
	WX-04-04	2006-07	90.7200
	WX-04-05	2006-11	165.7400
	WX-04-06	2007-01	265.2100
	WX-04-07	2007-03	235.3000
	WX-04-08	2007-07	142.0900
	WX-04-09	2007-11	225.0400
	WX-04-10	2008-01	185.0700
	Average		183.6000

Table 4. The phosphorus content of lappillae sample WX-05 in different ablation spots at different time period.

Sample number	Ablation spot	Year-month	P (mg/kg)
WX-05	WX-05-01	2005-11	246.2900
	WX-05-02	2006-01	280.1900
	WX-05-03	2006-03	550.8600
	WX-05-04	2006-05	252.5700
	WX-05-05	2006-07	477.4700
	WX-05-06	2006-09	1002.6600
	WX-05-07	2006-11	1053.2700
	WX-05-08	2007-01	743.6000
	WX-05-09	2007-03	793.5400
	WX-05-10	2007-05	1059.9000
	WX-05-11	2007-11	1300.5800
	WX-05-12	2008-03	2337.0100
	Average		841.5000

(WX-01, WX-04 and WX-05) was obtained through different growth rings (periods) using LA-ICP-MS *situ* analysis, as shown in Tables 2, 3, and 4, respectively.

Comparing Tables 1 and 2 and Tables 3 and 4, phosphorus content in lappillae was 2 to 4 orders of magnitude higher than that in the water, indicating that there was strong phosphorus enrichment in carp lappillae from the water. Although there was a big difference from individual samples, the trend of phosphorus content in the same time period was consistent. The BCF of phosphorus in carp lappillae reached 1134 to 3709. Therefore, it is much more convenient to determine phosphorus content in lappillae than in water, and this lays a foundation for further correlation study between phosphorus content in lappillae and in water.

It can be seen from Table 2 that in lappillae sample WX-01, the phosphorus content was much lower in September 2006 and November 2007 than that in May 2007. From Table 3, it is also noticed that in lappillae sample WX-04, phosphorus content showed three increase cycles from November 2005 to March 2006, July 2006 to March 2007 and from July 2007 to January 2008. The data in Table 4 shows that the phosphorus content in lappillae sample WX-05 also gives three increase cycles from November 2005 to March 2006, May 2006 to November 2006 and January 2007 to March 2008.

Comparing the data of phosphorus content in lappillae shown in Tables 2 to 4 to the data of phosphorus content in water shown in Table 1 (Figure 2), the variability of phosphorus content in water (Figure 2A) was consistent with that in lappillae (Figure 2B) from late 2005 to late 2007 in general. It indicates the relatively low phosphorus content both in water and in lapilli in 2005; two years before the large bloom of blue-green algae in The Taihu Lake in 2007. The phosphorus content increased significantly in 2006 and the first half year of 2007, which was one year before the large bloom of blue-green algae. It however dropped slightly both in water and in lappillae during late 2007. Figure 2 shows that the fluctuation of phosphorus content in water and in lappillae displays the same trend on several critical time points. The preliminary findings show that phosphorus content in lapilli can be used for determining the varying tendency of phosphorus content in ambient water and to predict the blue-green algae pollution in the future. Furthermore, the phosphorus content tended to increase both in water and in lapilli in early 2008, which might be a sign of the next outbreak of “bloom” in 2008 (it has been proven).

Geochemistry study on carp lapilli in Lianhuanhu and Longhupao lakes near Qiqihar city of Heilongjiang Province, supports that elements in carp lapilli correlate well to the corresponding elements in water (Gao et al., 2010). Linear relationship of trace elements was found between lapilli and water in Baiyangdian lake and Miyun reservoir near Beijing (Yang et al., 2006; Cao et al., 2008). Good correlation of trace elements was also found in cultural carp (Gao et al., 2008). Other studies validate the same conclusion as well: there was sensitive response between carp otolith chemistry and hydrochemistry in different waters, and the content of some trace elements in carp otoliths correlated well to the corresponding elements in water (Tzeng, 1994; Thorrold et al., 1998; Bath et al., 2000; Anadon et al., 2002; Bacon et al., 2004; Yang et al., 2006; Luo et al., 2008; Li et al., 2011).

The traditional monitoring method for water quality based on hydrochemical analyses, has some dis-advantages, such as, non-continuity of sampling, instantaneity of hydrochemistry, high cost, time-consuming, difficulty in storing samples and so on. It might be possible to apply carp otoliths as a monitor for water eutrophication, considering its good correlation of phosphorus in lapilli to the ambient water. This new method can provide history record of ambient water environment as it does not need to collect a large number of samples and is easy to store samples. Undoubtedly, the correlation of fish otoliths to environment is still waiting for further studies.

Conclusions

Based on the aforesaid, the following conclusions were arrived at;

1. Strong enrichment of phosphorus in lappillae from water was found in Xiaoxi port of the Taihu Lake, and the phosphorus content in lappillae was 2 to 4 orders of magnitude higher than that in the water. Also, the BCF of phosphorus in carp lappillae reached 1134 to 3709 and it is much more convenient to measure phosphorus content in lappillae than in water.
2. Although there is a big difference in phosphorus content from individual lappillae samples, the trend of phosphorus content in the same time period was broadly consistent for all samples; therefore it is possible to set a correlation model for phosphorus content in lappillae and in water.
3. An almost same trend of phosphorus content was found in lappillae and in water from latter half of 2005 to late 2007 in the Taihu Lake, showing relatively lower phosphorus content in 2005 and higher phosphorus content during 2006 to early 2007, but lower content in late 2007 again. The result reveals that phosphorus accumulated gradually for about two years before the large bloom of blue-green algae in 2007 to provide nutrition for the algae growth; the phosphorus content reached maximum during the large bloom of blue-green algae and then decreased because the phosphorus was absorbed by the large amount of algae.
4. Phosphorus content in lappillae might be used as potential recorder for organic or phosphorus pollution of water.

ACKNOWLEDGEMENTS

We wish to thank Dr. Gao Yongwen, Makah fisheries Management, USA, and Dr. Chang Jianbo, and Institute of hydrobiology, Chinese Academy of Sciences for their support during the research. This paper was financially supported by the Chinese State Basic Research Program (“973” project, Grant No. 2007CB815604), NSFC project (Grant No.40473044) and the National Laboratory of Mineral Materials, China University of Geosciences, Beijing, China (Grant No.06004).

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