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The 2007 water crisis in Wuxi, China: Analysis of the origin

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ABSTRACT

An odorous tap water crisis that affected two million residents for several days occurred in Wuxi, China in the summer of 2007. Volatile sulfide chemicals including methyl thiols, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide were the dominant odorous contaminants in Lake Taihu and in tap water during the crisis. These contaminants originated from the decomposition of a massive cyanobacterial bloom that was triggered by illegal industrial discharges and inadequately regulated domestic pollution. A specific emergency drinking water treatment process was quickly developed using a combination of potassium permanganate oxidation and powdered activated carbon adsorption. The emergency treatment process removed the odor from the tap water and solved the crisis successfully in several days. This experience underscores the suggestion that a combination of stresses associated with eutrophication and industrial and domestic wastewater discharges can push an aquatic system to the tipping point with consequences far more severe than would occur if the system were subjected to each stress separately.

1. Introduction

An odorous drinking water crisis occurred in the city of Wuxi, China between May and early June of 2007. During this crisis, the drinking water delivered to roughly two million people by water treatment plants became colored and foul-smelling. The crisis was initially attributed to a bloom of the cyanobacterium *Microcystis aeruginosa* in Lake Taihu, which is the source of drinking water for the city [1]. However, Yang et al. [2] subsequently argued that the intrusion of an unknown black water agglomerate into the main water intake in Lake Taihu was the likely cause of the crisis, but that the visible bloom and black water were actually separate incidents that affected the aesthetic quality of water in Wuxi.

The chemicals responsible for the foul smell in the tap water were later identified as volatile organic sulfur compounds (VOSCs). The production of VOSCs from cyanobacteria or algae has been reported for many years. Ginzburg et al. [3] reported an odorous problem caused by *Peridinium gatunense* in Lake Galilee in Israel. Specifically, that algal bloom stored up to 5.5 pg/cell of dimethylsulfoniopropionate (DMSP) and released dimethyl sulfide into the lake water at concentrations of approximately 0.1 mmol/(m^2 month). During a 1-year study, Hu et al. [4] found concentrations of dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and carbon disulfur (CS_2) in Linsley Pond, Connecticut that were as high as 80, 10, and 5 nM, respectively (5.3, 0.98, and 0.38 μg/L, respectively).

However, the situation during the Wuxi water crisis was very complex. A large cyanobacterial population has existed in Lake Taihu for about 20 years [5], and the biomass of cyanobacteria just before the 2007 crisis was about 1×10^8 cell/L, equals to 60 mg/L fresh weight, which was lower than the highest on record (2×10^8 cell/L). The death of cyanobacterial blooms is usually a lengthy process [6] associated with the release of VOSCs. In Lake Taihu, the demise of blooms is typically evidenced by discolored mats of cyanobacteria floating on the surface (Fig. 1). An unusual characteristic of the 2007 episode was the fact that almost all floating cyanobacteria in the vicinity of the water intake disappeared within 1 day (Fig. 2), which is not characteristic of natural processes.

Here, we present evidence that the crisis was the result of a combination of stresses associated with extreme eutrophication and the discharge of industrial and domestic wastewater that pushed the Lake Taihu ecosystem to a tipping point *sensu* Scheffer et al. [7]. The emergency drinking water treatment process developed at that time is also presented to help guide the response to similar problems in the future.

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Fig. 1. Dead and naturally decomposing cyanobacteria, turning into a yellow or blue floating scum on the surface (taken near the shore on July 18, 2007).

Fig. 2. The source water in the crisis, black in color with few algae floating on the surface (taken at the water intake on June 1, 2007). This is the black water agglomerate cited by Yang et al. [2].

2. Materials and methods

2.1. Basic situation of Wuxi water supply

Wuxi is a large city located on the north shore of Lake Taihu and in the heart of the Yangtze Delta in East China that has a population of more than two million. Three large water treatment plants (WTPs) serve the majority of this city, and there were two main water intakes affected during the water crisis (Fig. 3). The Nan-quan water intake is located at the end of a peninsula that provides source water to the Zhong-qiao and Xue-lang WTPs via 16 and 14 km long pipes, respectively. The Xi-dong water intake is located in the northeast portion of Lake Taihu and provides source water to the Xi-dong WTP on the shore. The Zhong-qiao WTP has a capacity of 600,000 m^3/d and supplies most of the urban area. The Xue-lang WTP has a capacity of 250,000 m^3/d and supplies the southern part of Wuxi. The Xi-dong WTP has a capacity of 300,000 m^3/d and supplies the sub-district of east Wuxi.

2.2. Profile of the Wuxi water crisis in 2007

Public recognition of the crisis was triggered by the smell of tap water. Specifically, beginning on the evening of 28 May 2007, residents in Wuxi found their tap water to be swampy, light yellow in color and offensive, with characteristics similar to drainage water. On the afternoon of 28 May, the engineers of the Wuxi Water Company found that hundreds of square meters of the lake surface around the Nan-quan water intake had turned brown and smelled odorous, indicating that Lake Taihu was the source of the odorous tap water (Fig. 2). The water in this area was termed the “black water agglomerate.” It should be noted that this phenomenon was associated with far fewer cyanobacteria floating on the surface than are commonly found in the lake. The monitoring staff also reported

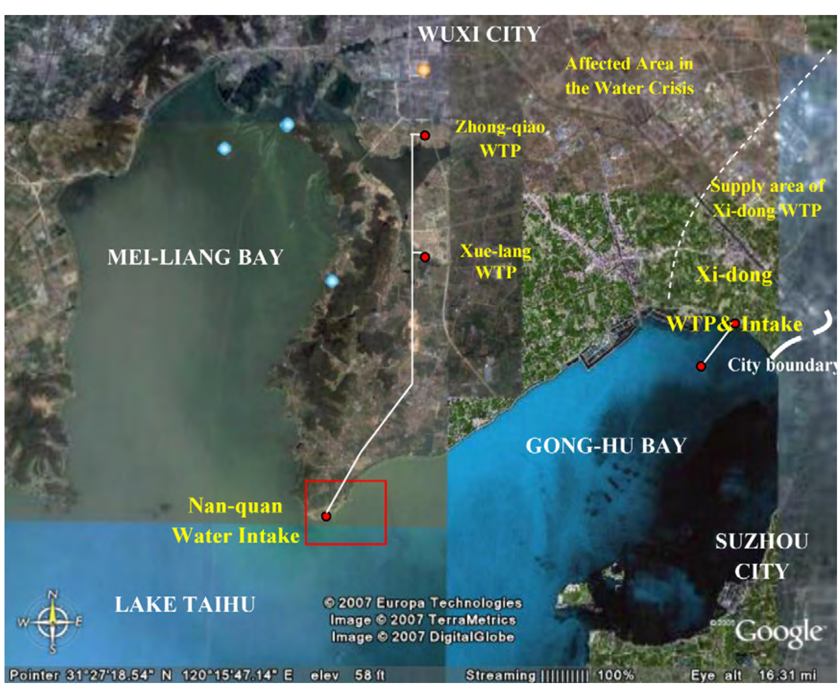

Fig. 3. Overview of the northern part of Lake Taihu, the main water treatment plants (WTP) and their water intakes in Wuxi city.

Table 1
Main compounds detected in the source water at the intake during the crisis and their basic characteristics.

Compound	Concentration (μg/L)*		Type of odor	Odor threshold [11,12]
	May 30	June 2		
VOSCs**				
H_2S	+	N.D.	Rotten eggs	0.62 ng/L in air
MeSH	204/+++	N.D.	Rotten onions	0.15 ng/L in air
DMS	93.9/+++	0.01/+	Rotten cabbage or algae	8.3 ng/L in air
DMDS	2.51/++	46.1/+++	Pulp mill or rotten cabbage	9.2 ng/L in air; 0.2–5 μg/L in water
DMTS	N.D.	17.17/+++	Rotten onions	10 ng/L in water
$CH_3S_4CH_3$	N.D.	+	Garlic or seaweed	–
Other VOCs**				
β-cyclocitral	8.14/++	21/++	Tobacco	19 μg/L in water
toluene	0.46/++	0.44/++	–	–
2-MIB	N.D.	N.D.	Musty	9 ng/L in water
Geosmin	N.D.	N.D.	Earthy	4 ng/L in water
Semi- or non-volatile chemicals***				
Polysulfides (S_6, S_8)	+	N.T.	–	–
3,5-di-t-butyl phenol	+	N.T.	–	–
Indole & derivatives	++	N.T.	Septic	300 μg/L in water
1-hexanal	+	N.T.	Lettuce heart	4.5 μg/L in water
1-octanal	+	N.T.	–	–
3-hexanone	+	N.T.	–	–
Cyclohexanone	+	N.T.	–	–
Microcystin-LR	7.59	0.73	–	–
Microcystin-RR	9.43	0.60	–	–

Note: (*) Some of the detected chemicals were not quantified due to the lack of pure chemicals. The comparative abundances of these chemicals were assessed by their peak area from several analyses of P&T-GC/MS, SPME-GC/MS and LLE-GC/MS. "+" indicates trace; "++" indicates much; "+++" indicates abundant. (**) Determined by P&T-GC/MS; N.D., not detected. (***) Determined by LLE-GC/MS; N.T., not tested. Microcystin-LR and RR were determined by LC/MS.

a burst of filamentous bacterial aggregates in the polluted source water. Morphological characterization of the bacteria indicated that they were affiliated with the genus *Sphaerotilus*; however, due to the emergency situation, no bacterial samples were stored properly for physiological studies.

The severe deterioration of lake water quality by the black water agglomerate exceeded the water purification ability of the Zhong-qiao and Xue-lang WTPs by a wide margin. Indeed, only the Xi-dong sub-district maintained regular drinking water quality because the source water quality around the Xi-dong water intake remained normal. In the following days, engineers attempted various methods of coping with the situation; however, the odor in the treated water was only minimally reduced and the threshold odor number (TON) value remained in the thousands. The deterioration of source water quality triggered a chain reaction that led to a water crisis throughout most of the city. Specifically, due to the offensive tap water there was a shortage of bottled drinking water and juice, public panic, and severe social and economic impacts.

2.3. Evaluation of water quality

The source water in the water intake, the influent and effluent of the water treatment plants, the tap water in residential houses, and the surface water around the northern area of Lake Taihu was sampled and analyzed for basic quality parameters, such as chemical oxygen demand by $KMnO_4$ titration (COD_{Mn}), ammonia nitrogen (NH_4–N), dissolved oxygen (DO), and algal concentrations twice daily and every 2 h during the water crisis by the monitoring staff of the Wuxi Water Company. Fig. 4 and Table 1 show the parameters of source water at the intake.

Identification of contaminants in the water was made several times during the crisis with the cooperation of the Wuxi Environmental Monitoring Station, Tongji University in Shanghai, Beijing Water Co. Ltd. and Dong-jiang Water Works Co. Ltd. The volatile contaminants in these water samples were determined by GC/MS analysis with Purge and Trap (P&T) pretreatment following U.S. EPA method 524.2 or using the solid-phase micro-extraction (SPME) pretreatment method developed by Nielson and Jonnson [8]. Semi-volatile or non-volatile contaminants were determined by GC/MS analysis with liquid–liquid extraction (LLE) pretreatment following EPA method 525. Volatile sulfur compounds were measured by GC analysis using an FPD detector. The instrument information was included in the Supplementary materials.

3. Results and discussion

3.1. Identification of VOCs

Initial efforts to address the water quality crisis focused on identification of the contaminants responsible for the odor problem. MeSH, DMS, DMDS, DMTS, β-cyclocitral, and toluene were identified as the dominant pollutants (Table 1). Liquid–liquid extraction pretreatment and GC/MS analysis were used to detect semi- or non-volatile chemicals including indole and its derivates as well as some aldehydes and ketones (Table 1). In addition to the presence of these individual contaminants, poor intake water quality was demonstrated by the high COD_{Mn} and turbidity, high concentrations of NH_4–N, and low DO (Fig. 4). Indeed, the concentration of COD_{Mn} and turbidity almost doubled after May 28, while the DO was depleted quickly to near zero and the NH_4–N increased by 10 to 20-fold when compared with the normal conditions before May 28.

The olfactory characteristics of thiols and thioethers matched those of the water [9,10], and their concentrations were dominant among VOCs (Table 1), indicating that they were the immediate cause of the offensive taste and odor in the tap water. MeSH (204 μg/L) and DMS (93.9 μg/L) were the dominant VOSCs in the first assay on May 30 and presumably contributed the most to the odor. Small concentrations of H_2S and DMDS were also detected at that time, but no DMTS was found. The second assay was conducted on June 2, when the DO level had risen to ~5 mg/L, at which time the MeSH and DMS were found to have almost entirely disappeared and been replaced by the more oxidized DMDS (46.1 μg/L) and DMTS (17.2 μg/L). β-cyclocitral was also detected in the source and tap water during the crisis, but contributed little to the odor due to its limited concentration and high odor threshold concentration.

Geosmin and 2-methylisorboneol (2-MIB), the most common odorous chemicals in algae-laden lake water [11,12], were detected, but not above the drinking water standard of 10 ng/L, indicating that these compounds were not responsible for the odor of the water during the crisis.

These results differ from those of a study conducted by Yang et al. [2,13], who identified DMTS as a major contributor to the odor of the Wuxi tap water. This discrepancy is probably due to the time of sampling by the two groups. Specifically, Yang et al. conducted sampling on June 4, which was 4 days after our samples were collected, at which time the DO concentration had returned to normal (see Fig. 4) and the source water quality had started to improve.

3.2. Emergency water treatment process

Based on our chemical analyses, we developed an emergency water treatment process that effectively solved the odor problem within 1 day [14]. In this process, potassium permanganate ($KMnO_4$) was added to the intake of the influent pipeline at 3–5 mg/L to oxidize VOSCs during the 6-h transit to the treatment plant. After the source water reached the water treatment plant, powdered activated carbon (PAC; 30–50 mg/L) was added into the mixing well to adsorb other pollutants and decompose the residual $KMnO_4$. The doses of $KMnO_4$ and PAC were adjusted rapidly according to the values measured by the online oxidation–reduction potential (ORP) meter that was used to monitor fluctuations in the

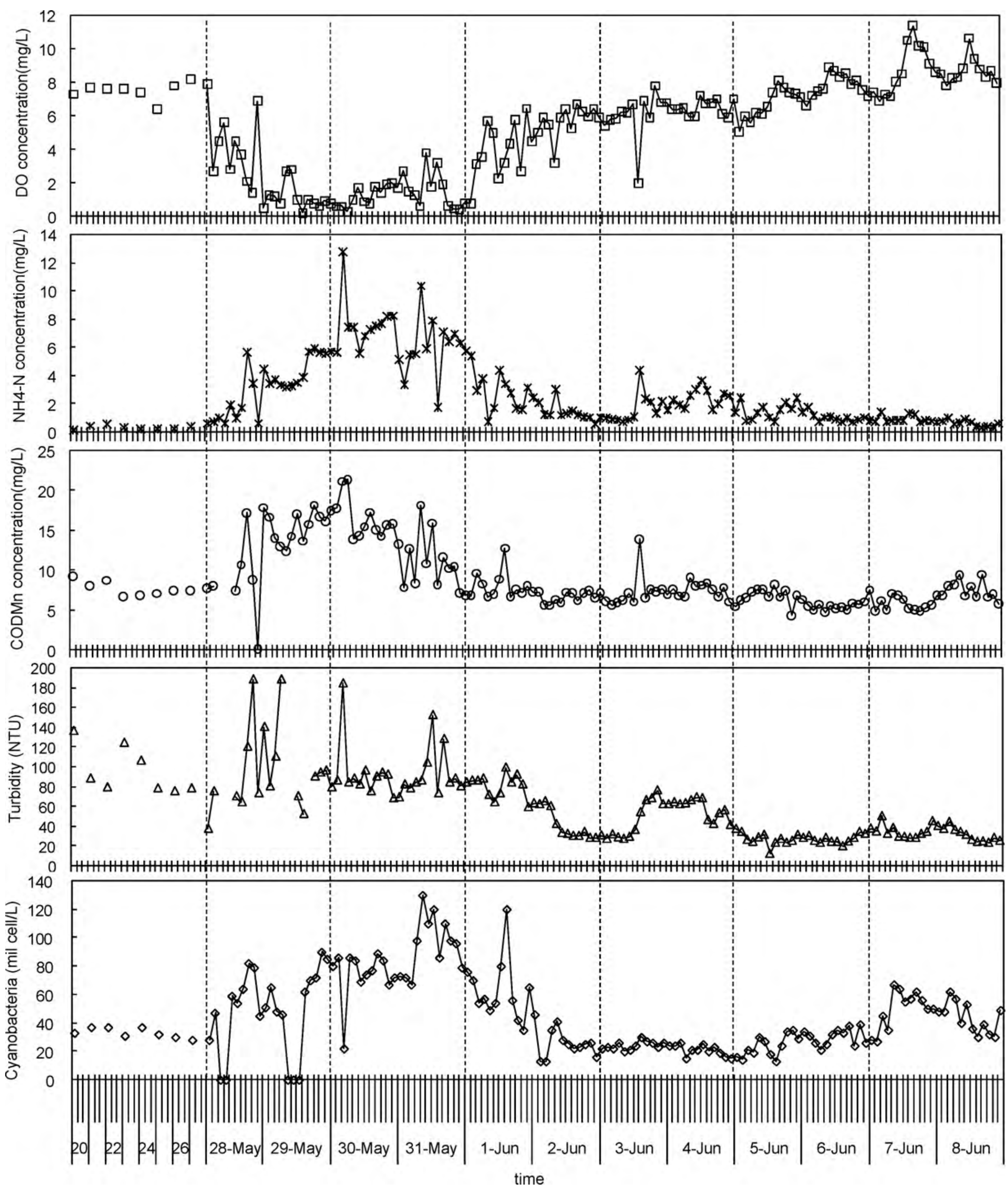

Fig. 4. Fluctuations in basic water quality parameters during the 2007 Wuxi water crisis.

source water quality. The Wuxi Water Company implemented the treatment process on the morning of June 1, and the quality of the treated water met all 106 items of the Chinese Standard for Drinking Water Quality (GB5749-2006), which is similar to the standard of the WHO, according to the determinations made by two licensed water quality monitoring stations from Beijing and Shanghai. In addition, microcystins were detected at levels far below the criteria (1 μg/L) in the treated water.

3.3. Origin analysis of VOSCs

Several questions arose following this crisis, including the need to identify the source of the contaminants, the mechanism of the formation of the black water agglomerate, and measures to avoid a similar crisis in the future. The chemicals detected in the source water were an important clue to the cause of the crisis. These chemicals can be classified into four categories according to their likely sources: VOSCs, cyanobacterial metabolites, industrial contaminants, and domestic contaminants.

VOSCs, including thiols and thioethers, have complex production routes [15–21]. MeSH, DMS, and DMDS can be produced in the decomposition pathway of sulfur-containing amino acids, predominantly methionine, which may originate from proteins present in domestic wastes. However, the main contaminants in domestic waste are COD, N, and P. The amount of sulfur in domestic waste near the intake to the water treatment plants was negligible when compared to the massive cyanobacterial mat in the lake and should not be regarded as the main source of sulfur.

A substantial cyanobacterial bloom associated with hot and dry weather since April 2007 resulted in the accumulation of a great deal of organic matter [22] and sulfur-containing compounds in the water and sediments of Lake Taihu prior to the crisis. Since VOSCs can also originate from the decomposition of algal blooms [23,24], it seems possible that the decomposition of that bloom was the primary cause of the high VOSC concentrations in Lake Taihu. The death and decay of cyanobacterial blooms is often associated with high concentrations of VOSCs and accompanied by drastic increases in organic matter, nitrogen, and phosphorus. To confirm this mechanism, we simulated the decomposition of a cyanobacterial mat in the laboratory by adding wastewater from the local wastewater treatment plant and we observed the release of VOSCs and β-cyclocitral as well as the deterioration of water quality (data not shown). A burst of filamentous bacterial aggregates in the source water noted by Wuxi Water Company engineers on May 28 may have been an indication of the extremely rapid decay of the cyanobacterial bloom.

Reports demonstrated that β-cyclocitral and several other types of aldehydes and ketones are the metabolites of *Microcystis* [18,25]. These chemicals will be released during the growth of *Microcystis* and the disruption of cell integrity as well. High concentrations of these compounds in the source water in Lake Taihu are consistent with a massive decay of algae and concomitant formation of large amounts of VOSCs via cyanobacterial decomposition in the water.

In terms of manufacturing output, Wuxi ranks among the top 10 cities in China, and its industrial structure is heavily skewed toward the chemical sector. There is a large number of small chemical companies along the city's more than 3000 watercourses and rivers, many of which have been discharging waste directly into nearby rivers that eventually flow into Lake Taihu [22]. Among the industrial pollutants is toluene, an important industrial compound in Wuxi and other nearby cities that is often detected in canals and rivers in urban areas.

Indole is often linked to the decomposition of feces, and an investigation by Xie et al. [24] showed that the main source of N pollution of surface waters in the Lake Taihu region was not N fertilizer applied to farmland, but urban domestic sewage and rural human and animal excreta discharged directly into the water bodies without treatment. The presence of these compounds in the source water suggests that industrial and domestic wastes intruded into the water intake in Lake Taihu via the web-like system of canals and rivers in the area. Furthermore, their presence suggests that this water crisis was not just a simple natural disaster.

The co-existence of VOSCs, β-cyclocitral, toluene, and indole along with other phenomena such as DO depletion, high COD, and increased NH_4–N in the source water indicate that the 2007 drinking water crisis was caused by the rapid decomposition of a cyanobacterial bloom triggered by illegal chemical discharges from industries and the absence of adequate controls on domestic wastewater discharges. Lake Taihu, after suffering from cyanobacterial blooms for decades as a result of enrichment by nutrients from industrial and domestic discharges and agricultural run-off, had been at risk in recent years. Indeed, the annual duration of cyanobacterial blooms lengthened each year from 1987 to 2007 in conjunction with substantial increases in the frequency of the occurrence of cyanobacterial blooms in spring and summer months.

The introduction of industrial and domestic wastes with high concentrations of organic matter appears to have brought about a sharp deterioration of water quality, depleted the DO, and nourished heterotrophic microorganisms. The substances present in the industrial wastes very likely poisoned or killed the cyanobacteria, whose decomposition was accelerated by the large resident population of heterotrophic bacteria. The heterotrophic community played an important role in decomposition of the cyanobacteria, whose organic sulfur reserves were then transformed into VOSCs. In addition, multiplication of the heterotrophic decomposer community likely produced the filamentous congeries discovered by local engineers. Anoxic conditions also probably induced the release of sulfur compounds from the sediments into the water column. Large amounts of VOSCs released from the decomposing cyanobacteria and sediments formed the odorous black water agglomerate, which, pushed by the wind, polluted the water intake and eventually triggered the water crisis in Wuxi.

3.4. Influence on local environmental protection work

The Wuxi water crisis may prove to be a turning point in the local environmental movement. Following the crisis, the local government promulgated stringent measures to protect Lake Taihu from further pollution. These measures included strict standards for waste discharges, the elimination of discharges from major industrial polluters, and efforts to restore wetlands along the shore of the lake. In addition, the city's environmental protection bureau has ordered the closure of sewage drain outlets along the river channels into the lake so that companies are forced to discharge their wastewater into the city's sewage collection system to ensure treatment at the wastewater treatment plant. Statistics from the municipal economic and trade committee show that some 600 small chemical companies were shut down in 2007.

Hopefully, these stringent protection measures will be sufficient to prevent a repetition of the water crisis of 2007. The central government of China has recently become more environmentally vocal by advocating more stringent environmental protection and encouraging resource-saving and environmentally friendly modes of development. The People's Congress and the State Council elevated the State Environmental Protection Agency to Ministry of Environmental Protection in March 2008, and gave it more power to implement more strict policies. The punishment for water pollution accident in Water Pollution Control Law was elevated from no more than 200,000 RMB in old version to as much as 30% of the direct loss due to the accident in the 2008 revision. A large fund of billions of yuan has also been earmarked for environmental protection, ecological remedies, and industrial upgrading around Lake Taihu and other areas.

4. Conclusion

This analysis of the causes of the 2007 Wuxi water crisis demonstrates that the combined effects of nutrient enrichment and industrial pollution pushed water quality in Lake Taihu to a tipping point that led to a rapid and massive die-off of cyanobacteria. The decomposition of these organisms in turn released large amounts of odorous chemicals into the water. In this case, the combined effect of multiple stresses produced consequences far more severe than would have been the case had the lake been subjected to each stress separately.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.06.006.

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