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Surface water pH variations and trends in China from 2004 to 2014

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Abstract With economic development and the increase of energy consumption, surface water acidification has been a potential environmental concern in China. Here, we analyzed variations and trends in surface water pH of 73 sites from ten river basins in China from 2004 to 2014 with nonparametric Seasonal Kendall test method. Our analysis showed that the variations of surface water pH in China ranged from 6.5 to 9.0 in the past decade (2004–2014), which satisfied the water quality criteria in pH for protection of aquatic ecosystems in China (6.0–9.0) and USA (6.5–9.0). However, significant decreasing trends in surface water pH were found in 31 monitoring sites, which were mainly located in Haihe River, Taihu Lake and Yangtze River, while the pH value showed significant increasing trends in 22 sites, which mainly were located in Songhua River and Pearl River. Our results suggested the increased potential acidification of susceptible water bodies in China. Besides the control policy of sulfur dioxide (SO_2) emissions, the emissions of nitrous oxides (NO_x) should also be reduced to protect the aquatic systems in China.

Keywords Surface water · pH · Acidification · Seasonal Mann–Kendall · Space distribution

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Introduction

Surface water acidification caused by acidic deposition could lead to soil acidification (Matzner 1995), forest vitality reduction (Fischer 2007), disturbance of aquatic animals' metabolic systems, reduction of hatchability, and even the extinction of fish population (Haines and Baker 1986). In addition to biological effects, pH can also affect the solubility of chemical constituents such as nutrients and heavy metal toxicity in the water (EPA 2012). Therefore, pH is an important parameter for understanding biological consequences of acid deposition (Matsubara et al. 2009).

Acidification in surface water has been an environmental problem in Europe and North America. However, the acidity of precipitation has declined over large portions of eastern North America and Western Europe due to more stringent air pollution emission laws, widespread availability of improved pollutant removal technologies, and energy conservation in the past two decades (Skjelkvale et al. 1998; Stoddard et al. 1999; Driscoll

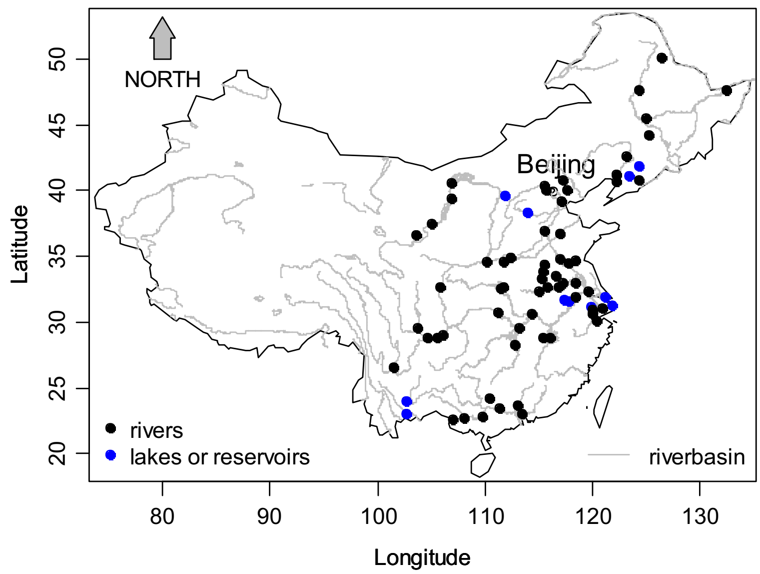

Fig. 1 Map showing location of the monitoring stations including rivers, lakes, or reservoirs in the study area. The *black points* indicate monitoring sites are located in rivers and the *blue points* indicate the monitoring sites are located in lakes or reservoirs

2001; Evans et al. 2001; Kvaeven et al. 2001). The goals of these acid deposition-related emission laws, such as the Clean Air Act Amendments of 1990 in the USA and the 1994 Oslo Protocol in Europe, are to reduce the acidity of precipitation and allow the chemical and biological recovery of previously impacted waters and ecosystems (Burns et al. 2006). Decreases in pH have been clarified in lakes and rivers of northern USA (Charles et al. 1987), Canada (Watt et al. 1983), and Scandinavia (Wright et al. 1976) by analyzing the long-term records.

Due to the increased emissions from mining and fossil fuel consumption in the past 30 years, China has become the third largest acid rain district after Europe and North America (Nordberg 2003), and acid rain pollution is one of the important environmental problems currently in China (Zhang et al. 2007; Ouyang et al. 2008). The economic loss caused by acid rain pollution was about 110 billion yuan every year in China (Zhang et al. 2010). Several studies have been conducted on regional surface water acidification in recent years in China (Zhang et al. 2007; Duan et al. 2011; Xu et al. 2013; Fang et al. 2013). However, the national surface water acidification trend in China is still not clear. In our study, by the data from 73 national monitoring sites in ten water basins, we initially analyzed the surface water pH variations and trends from 2004 to 2014 and evaluated the possible effects of air pollutant emission control policy on the restoration of surface water acidification in China.

Materials and methods

Data source and study area

Weekly water pH data for the 73 monitoring sites in ten major river basins were obtained from the China Ministry of Environment Protection. These data are publicly accessible through the China Ministry of Environment Protection data center (available via http://datacenter.mep.gov.cn). The basins include 7 rivers (Yellow River, Liaohe River, Haihe River, Huaihe River, Yangtze River, Pearl River, Songhua River) with 62 sites and 3 lakes (Taihu Lake, Dianchi Lake, Chaohu Lake) with 11 sites (Fig. 1). For the rivers, there are 30 sites in the main stream and 32 sites in the tributary. Sixty-five sites have an 11-year period of record (2004 to 2014), 6 sites have a 10-year record (2005 to 2014), and 2 sites have an 8-year record (2007 to 2014).

Statistical analysis

Trend analysis was undertaken by the Seasonal Mann–Kendall test (SMK) (Hirsch et al. 1982; Hirsch and Slack 1984). SMK is a nonparametric method by which data are grouped within seasonal blocks and tested for monotonic trends within each block using a ranking procedure. Further, the method can be used on data that are not normally distributed, which is commonly the case with environmental data. It is also robust for extreme values and possible outliers (Helsel and Hirsch 1992).

Assuming that a time series is formed by n data (Y_1, Y_2, Y_3, Y_n), Kendall's S statistic is computed from each data pair:

$$S = P - N \tag{1}$$

where P is the number of $Y_i < Y_j$ for all $i < j$ and N is the number of $Y_i > Y_j$ for $i < j$. S is asymptotically normal, with a mean of 0. The variance of S is

$$Var(S) = n(n-1)(2n+5)/18 \tag{2}$$

The SMK test accounts for seasonality by computing the Mann–Kendall test on each of m seasons separately and then combining the results. No comparisons are made across seasons. The SMK statistic S_k is simply the sum of individual Kendall's S statistics (S_L) for each of the "$L = 1$ to m" seasons.

$$S_k = \sum_{L=1}^{m} S_L \tag{3}$$

When the product of number of seasons and number of years is more than about 25, the distribution of S_k will be approximated quite well by a normal distribution (Hirsch et al. 1982).

The resulting statistic (Z_{Sk}) is evaluated against a table of the standard normal distribution.

$$Z_{S_k} = \begin{cases} \frac{S_k - 1}{\sigma_{S_k}} \; if \; S_k > 0 \\ 0 \; if \; S_k = 0 \\ \frac{S_k + 1}{\sigma_{S_k}} \; if \; S_k < 0 \end{cases}$$

where

$$\mu_{S_k} = 0$$

$$\sigma_{S_k} = \sqrt{\sum_{L=1}^{m} (n_L/10)(n_L - 1)(2n_L + 5)}$$

and

n_L = number of data in the n_L season

The overall SMK trend slope for Y over time is computed as the median of all slopes between data pairs within the same season. Furthermore, the slope is unaffected by seasonality and less affected by extreme values than is a linear regression slope (Hirsch et al. 1982).

All analyses were performed using R software ("rkt" package) at a 0.05 significance level (R Core Team. R 2014).

Results

pH variations

We used annual value to reflect the variations of surface water pH in China. The annual data were calculated from the weekly pH data in all sites of each basin in 2004 and 2014. The annual pH values from the 65 stations of ten surface water basins were shown in Figs. 2 and 3. The variations of pH level ranged from 6.5 to 9.0 in 2004 and 2014. The national mean pH

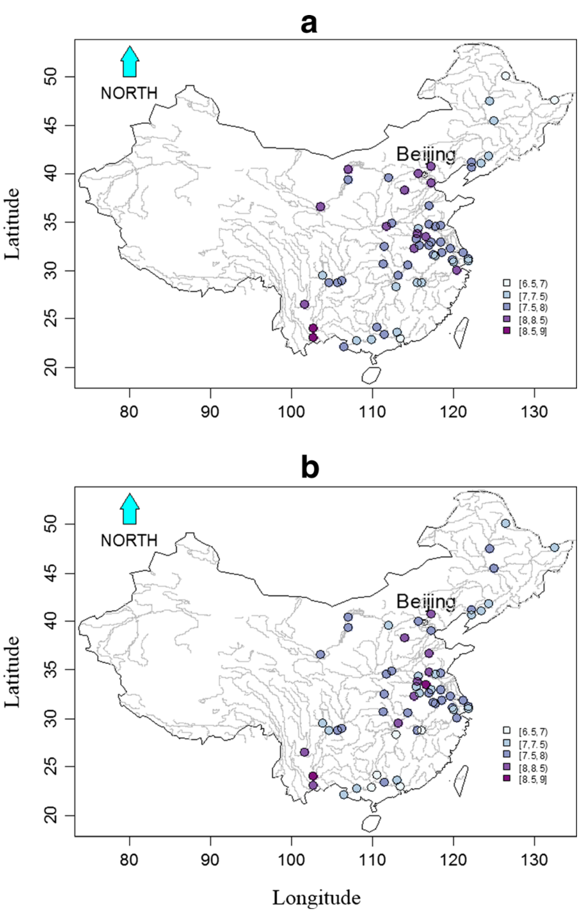

Fig. 2 Distributions of mean pH in 2004 (**a**) to 2014 (**b**) in the main river basins of China

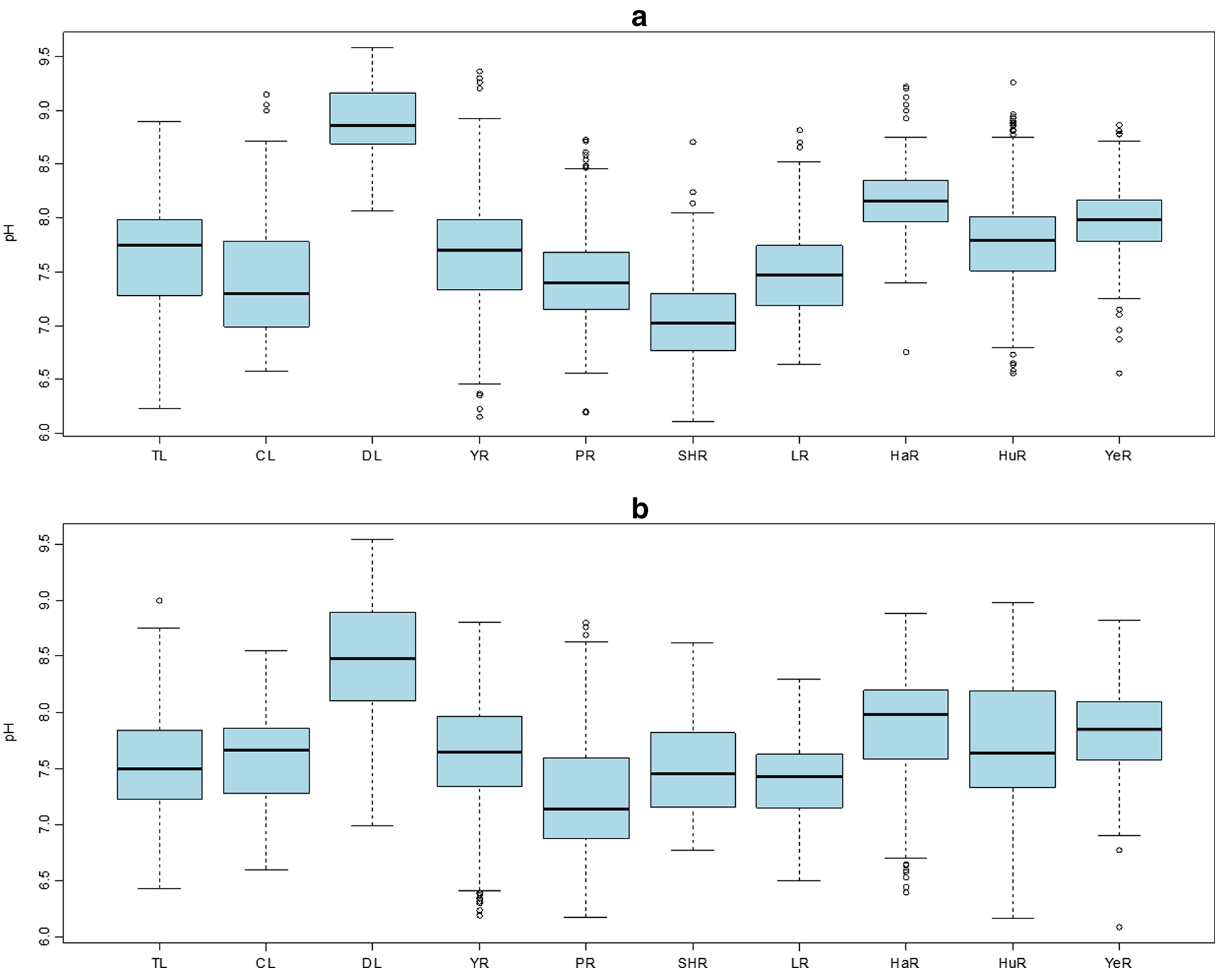

Fig. 3 Comparison of the basins' mean pH in 2004 (**a**) and 2014 (**b**) in China. The order from *left* to *right*: *TL* (Taihu Lake), *CL* (Chaohu Lake), *DL* (Dianchi Lake), *YR* (Yangtze River), *PR* (Pearl River), *SHR* (Songhua River), *LR* (Liaohe River), *HaR* (Haihe River), *HuR* (Huaihe River), and *YeR* (Yellow River)

value was 7.70 ± 0.43 in 2004 and decreased to 7.64 ± 0.41 in 2014. The lowest pH (6.60 ± 0.16) was found at the Tongjiang station in Songhua River, and the highest pH (8.94 ± 0.37) was seen at the Xiyuan tunnel in Kunming in Dianchi Lake in 2004 (Fig. 2). While in 2014, the lowest pH (6.54 ± 0.19) was found at the Nanchang station in Jiangxi province in Yangtze River and the highest pH (8.61 ± 0.65) was seen at the Guanyin Mountain in Kunming in Dianchi Lake.

For the pH variations in basin scale, the lowest mean pH values in 2004 (7.04 ± 0.30) and 2014 (7.25 ± 0.34) were found in Songhua River and Pearl River, respectively (Fig. 3). However, the pH value of Dianchi Lake (8.90 ± 0.05 and 8.41 ± 0.29) was the highest both in 2004 and 2014.

Long-term trends

Although no significant difference was found in the mean pH value in national scale between 2004 and 2014, the water pH for some sites showed significant increasing or decreasing trends (Fig. 4).

Table 1 showed the results of the seasonal Mann–Kendall tests for long-term trends in surface water pH at the 73 points in the ten basins of China. Details of results for the SMK test were shown in Table 2. Significant decreased trends ($p < 0.05$) in river water pH were observed at 31 points, while we detected significant increasing trends ($p < 0.05$) at 22 points (Table 1 and Fig. 5). The sites which showed significant decreasing trends were mainly located in Haihe River (6/7; among a total of seven

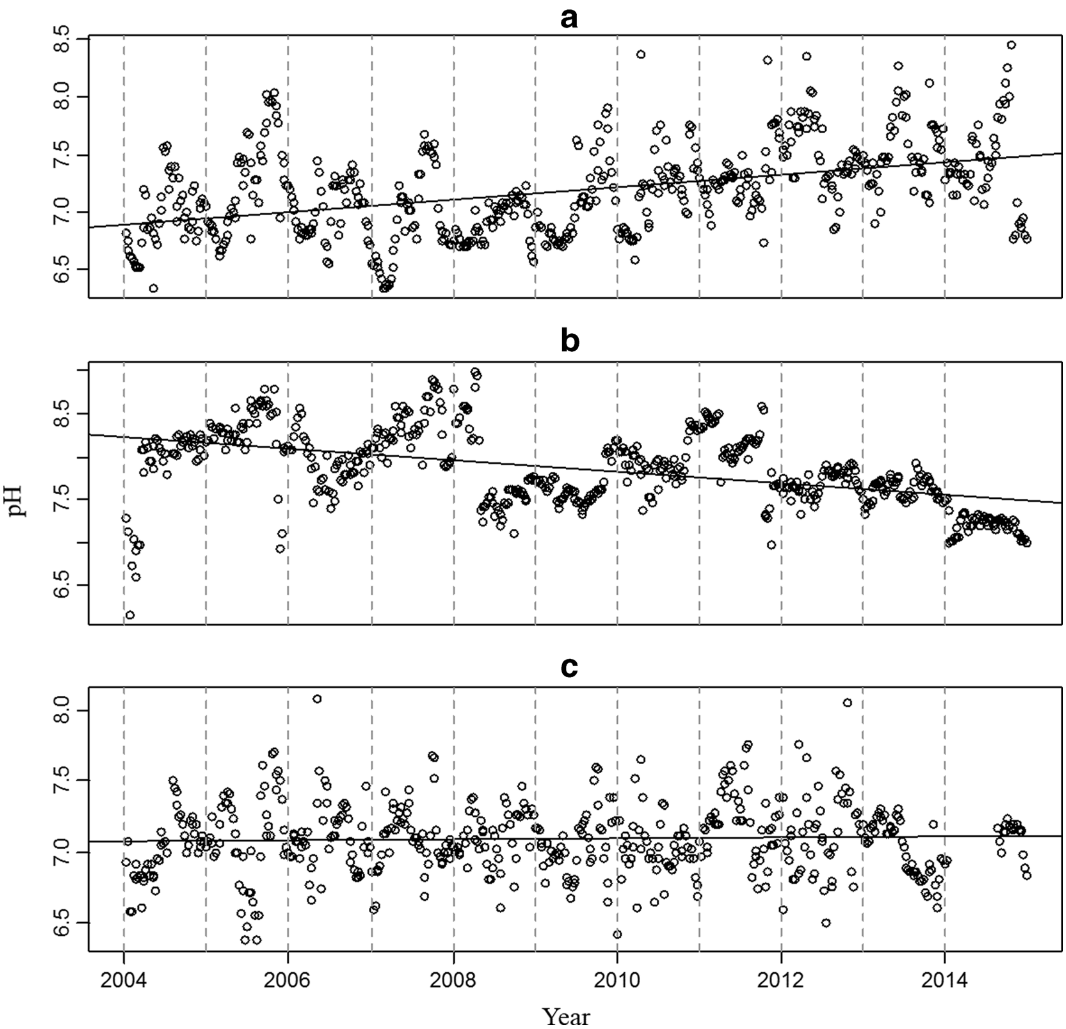

Fig. 4 Examples of the three long-term surface water pH trends in China: **a** significant increase (the Heihe monitoring sites of Heilongjiang province in Songhua River), **b** significant decrease (the Yibin monitoring sites of Sichuan province in Yangtze River), and **c** nonsignificant (the Changchun monitoring sites of Jilin province in Songhua River)

monitoring sites, six showed significant decreasing trends), Taihu Lake (4/7), and Yangtze River (10/16). The sites showing significant increasing trends belong to Songhua River (4/5) which is the northernmost basin and Pearl River (4/7) which is the southernmost basin in China (Fig. 5).

Discussion

Surface water acidification in China

Excessively low or high pH can be detrimental for the use of water. The water with a low pH (<6.5) could be acidic and contain high levels of heavy metals which are harmful to aquatic organisms. Some surface waters are in serious water acidification, for example in Scandinavia, where waters (typically inland lakes and streams) with pH below 5.0 are common (Menz and Seip 2004). In an assessment of the effect of plantation forestry on the recovery of surface waters from acidification, Malcolm et al. (2014) found that streams ranged from highly acidic (median annual pH 4.1) to circumneutral (pH 7.1) in the Loch Ard area of Central Scotland. Our analysis showed that the variations of surface water pH in China ranged from 6.5 to 9.0 in the past decade (2004–2014), which satisfied the water quality criteria in pH for protection of aquatic

Table 1 Number of sites with different pH trends ($p < 0.05$) from 2004 to 2014 in the main surface water basins of China

Basins	Long-term trends (2004–2014)			
	Increase	Decrease	Not significant	Total
Taihu Lake	1	4	2	7
Chaohu Lake	1	0	1	2
Dianchi Lake	0	1	1	2
Yangtze River	1	10	5	16
Songhua River	4	0	1	5
Pearl River	4	2	1	7
Yellow River	4	3	2	9
Haihe River	0	6	1	7
Liaohe River	2	2	2	6
Huaihe River	5	3	4	12
Total	22	31	20	73

ecosystems in China (6.0–9.0) and USA (6.5–9.0, US-EPA 2009).

Water pH in Songhua River and Pearl River showed lower levels than in other basins. The possibility of water acidification still exists in Songhua River due to the widely distributed acidic forest soils, and the water body is less able to buffer acidity in this region (Xu et al. 2013). Some regions in Pearl River, especially those in Jiangxi and Guangdong province, are more susceptible to acidification than those in northeastern China, which attribute to their soil types and geological and acid deposition conditions (Hao et al. 2001).

Dianchi Lake showed the highest water pH, which is possibly caused by the plateau geological condition, climate condition, terrestrial heat flow, and the interaction between planktonic algae growth and change of dissolved oxygen content in the process of eutrophication (Li et al. 2007).

The trends of surface water pH and possible effects of control policy

Long-term trends of surface water pH in the world were summarized in Table 3. Acidification in surface water has been a serious environmental problem in Europe and North America. However, widespread recoveries of surface water acidification in Europe and North America have been reported since the 1990s (Garmo et al. 2014). For example, the water acidification in the UK (Battarbee et al. 2014; Murphy et al. 2014), Sweden (Wällstedt et al. 2009; Oni et al. 2013), Spain (Bouza-Deaño et al. 2008), and the USA (Kahl and Center for the Environment, 2004) have been recovering slowly following considerable emission abatement of sulfur dioxide (SO_2) and nitrogen oxide (NO_x) since the 1990s. In the lakes and their catchments of western Japan and Bohemia, the decline of total acid input in precipitation and regrowth of vegetation could lead to further increase of the water pH (Yamada et al. 2007; Oulehle et al. 2013). Lake Peipsi water (Estonia/Russia) has experienced a significant increase of pH due to combination of climate change and eutrophication over the last three to four decades (Minella et al. 2013). In addition, a disturbing eutrophication of the reservoir after the spraying of fertilizers and industrial wastewater had an impact on water pH of the Grouz dam in Eastern Algeria (Guerraiche et al. 2015). In contrast, a significant long-term declining trend in river water pH was found in several watersheds in Central Japan and the Maroon River in Iran. The reason for the acidification of the river waters could be the cumulative acid loading from the atmosphere to the soil due to the development of the region economy during the last several decades (Matsubara et al. 2009; Tabari et al. 2011).

Acid deposition caused by sulfur dioxide (SO_2) and nitrogen oxide (NO_x) emissions has become a major concern in China (Tang 2006). Although we did not find water acidification in our analysis (Fig. 3), the pH in many monitoring sites showed significant decreasing trends, especially in Haihe River, Taihu Lake, and Yangtze River (Fig. 5). To protect the aquatic ecosystems and improve the air quality further, the Chinese government has established compulsory targets to reduce SO_2 emissions by 10 % during 2005–2010 and a further 8 % by 2015 and reduce NO_x emissions by 10 % during 2010–2015. The SO_2 emissions generally showed decreasing trends resulting from the compulsory policy (Fig. 6a). However, the NO_x emissions showed different trends in different regions. Decreasing trends of NO_x emissions were found in Guangdong (Pearl River) and Liaoning province (Songhua River), while increasing trends of NO_x emissions were found in other three basins (Fig. 6b).

Water pH trends are usually related to anthropogenic pollutions, such as acid rain which comes from the reaction of water with nitrogen oxides, sulfur oxides, and other acidic compounds. Direct correlations were found between sulfur emissions and sulfur deposition, including sulfur dioxide and nitrogen oxides (Lynch

Table 2 Results of trend analysis of surface water pH in China from 2004 to 2014

Type	Basin	Site	Number	Slope	Trend
River	Songhua River	Zhaoqing	572	+0.029***	Increase
		Tongjiang	572	+0.058***	Increase
		Changchun	572	+0.002	–
		Heihe	572	+0.058***	Increase
		Baicheng	572	+0.030***	Increase
	Liaohe River	Xingan	572	+0.003	–
		Yingkou	572	+0.000	–
		Tieling	572	−0.023**	Decrease
		Dahuofang	572	+0.028***	Increase
		Liaoyang	572	+0.016**	Increase
		Dandong	520	−0.014***	Decrease
	Haihe River	Guoheqiao	572	−0.011*	Decrease
		Liaocheng	520	−0.047***	Decrease
		Mentougou	572	−0.038***	Decrease
		Miyunkou	572	−0.008	–
		Sanchakou	572	−0.050***	Decrease
		Shijiazhuang	572	−0.017***	Decrease
		Zhangjiakou	520	−0.056***	Decrease
	Huaihe River	Fengbu	572	+0.011	–
		Bunan	572	+0.009*	Increase
		Huaibei	572	+0.006	–
		Xuyi	572	+0.041***	Increase
		Huainan	572	+0.035***	Increase
		Jieshou	572	−0.026***	Decrease
		Linyi	572	−0.014	–
		Luyi	572	+0.036***	Increase
		Peizhou	572	+0.010	–
		Zaozhuang	572	−0.021**	Decrease
		Zhoukou	572	+0.036***	Increase
		Zhumadian	572	−0.060***	Decrease
	Pearl River	Changzhou	572	+0.011***	Increase
		Guigang	572	−0.016**	Decrease
		Laokou	572	−0.028***	Decrease
		Pingerguan	572	−0.009	–
		Qixinggang	572	+0.020***	Increase
		Wuzhou	572	+0.014**	Increase
		Yangshuo	572	−0.041***	Increase
	Yellow River	Lanzhou	572	+0.014*	Increase
		Zhongwei	416	−0.002	–
		Wuhai	572	+0.004	–
		Baotou	572	−0.008*	Decrease
		Xinzhou	572	−0.042***	Decrease
		Jiyuan	572	+0.043***	Increase
		Jinan	572	+0.033***	Increase

Table 2 (continued)

Type	Basin	Site	Number	Slope	Trend
		Yuncheng	572	−0.032***	Decrease
		Weinan	520	+0.052***	Increase
	Yangtze River	Panzhihua	572	−0.012***	Decrease
		Zhutuo	572	+0.002	–
		Yichang	572	−0.017***	Decrease
		Yueyang	572	+0.010	–
		Jiujiang	572	−0.021***	Decrease
		Nanjing	572	+0.023***	Increase
		Leshan	572	−0.008**	Decrease
		Yibin	572	−0.074***	Decrease
		Luzhou	572	−0.003	–
		Guangyuan	416	−0.035***	Decrease
		Wuhan	572	−0.030***	Decrease
		Danjiangkou	572	+0.004	–
		Nanyang	520	+0.003	–
		Changsha	572	−0.040***	Decrease
		Nanchang	572	−0.047***	Decrease
		Yangzhou	572	−0.038***	Decrease
Lake	Dianchi Lake	Guanying Mountain	572	+0.003	–
		Xiyuan Tunnel	572	−0.087***	Decrease
	Chaohu Lake	Hubin	572	−0.035***	Increase
		Yuxikou	572	+0.006	–
	Taihu Lake	Suzhou	572	−0.013*	Decrease
		Wuxi	572	−0.018***	Decrease
		Yixing	572	−0.022**	Decrease
		Huzhou	572	−0.036***	Decrease
		Qingpu	572	−0.003	–
		Wangjiangjin	572	−0.008	–
		Xielugang	520	+0.033***	Increase

Positive slopes by seasonal Mann–Kendall tests indicate increasing trend, whereas negative slopes indicate decreasing trend

*$p < 0.05$; **$p < 0.01$; ***$p < 0.001$ (significant trends ($p < 0.05$))

et al. 2000). Our analysis suggested that the increasing trends of water pH in Songhua River and Pearl River are possibly caused by the reductions of SO_2 and NO_x emissions in the two basins. However, the increased NO_x emissions in Haihe River, Taihu Lake, and Yangtze River may counteract the reductions of the SO_2 emissions, which caused the decreased water pH in these three basins. It seems that the increase of N deposition would delay the recovery of stream water from acidification due to control of S deposition in these catchments in China in recent years. Therefore, to prevent the potential acidification of susceptible water bodies, the NO_x emissions should be also controlled at the basin scale. In addition to the atmospheric deposition, the source pollutant emissions which come from agricultural runoff, wastewater discharge, or industrial runoff could also affect the water pH (Matsubara et al. 2009). Our analysis suggested that China is also facing an increased potential acidification of susceptible water bodies. Besides the control policy of sulfur dioxide (SO_2) emission, the emission of nitrous oxides (NO_x) and other factors like point source pollution should also be reduced to protect the aquatic systems in China.

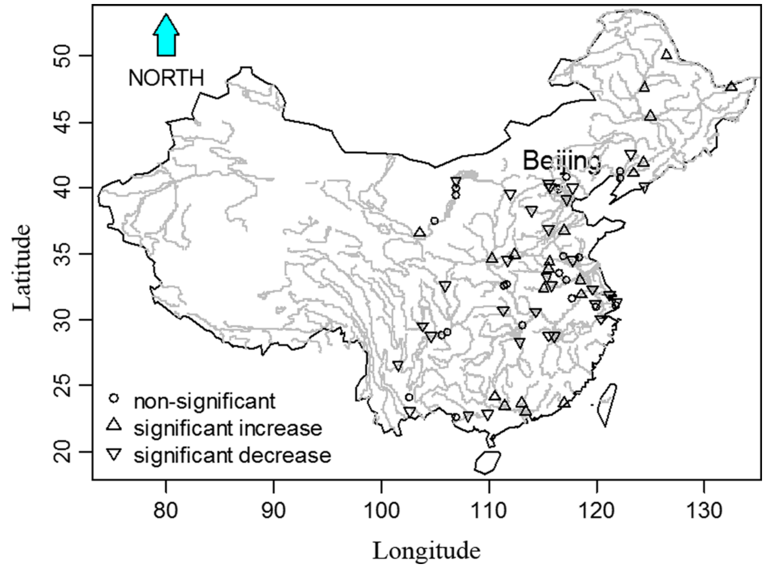

Fig. 5 Map showing the trends of surface water pH in 73 stations for 2004 to 2014 in main river basins of China

Other factors could also have an impact on pH changes in surface water, e.g., changes in hydrological regime, land use, or wastewater emissions. The agricultural nonpoint source pollution caused by land use change in the upper reaches of Yellow River is becoming the main pollution source of Yellow River, which threatens the water quality including pH in the lower reaches of the Yellow River basin (Hu et al.

Table 3 Comparison of surface water pH trends in other regions

Period	Region	Trend	Reference
1990–2000	USA	Increase	(Kahl and Center for the Environment 2004)
1981–2004	Ebro River (Spain)	Increase	(Bouza-Deaño et al. 2008)
1992–2007	Lake Årsjön (Sweden)	Increase	(Wällstedt et al. 2009)
1987–2011	Svartberget catchment (Sweden)	Increase	(Oni et al. 2013)
1990–2008	North Nordic	Increase	(Garmo et al. 2014)
1990–2008	South Nordic	Increase	(Garmo et al. 2014)
1990–2008	West Central Europe	Increase	(Garmo et al. 2014)
1990–2008	East Central Europe	Increase	(Garmo et al. 2014)
1990–2008	Maine and Atlantic Canada	Increase	(Garmo et al. 2014)
1990–2008	Vermont and Quebec	Increase	(Garmo et al. 2014)
1990–2008	Adirondacks	Increase	(Garmo et al. 2014)
1990–2008	Ontario	Increase	(Garmo et al. 2014)
1990–2008	UK	Increase	(Battarbee et al. 2014; Murphy et al. 2014)
1988–1997	Western Japan	Increase	(Yamada et al. 2007)
1986 –2003	Central Japan	Decrease	(Matsubara et al. 2009)
1989–2008	Maroon River (Iran)	Decrease	(Tabari et al. 2011)
1972–2010	Lake Peipsi (Estonia/Russia)	Increase	(Minella et al. 2013)
2007–2010	Grouz dam waters (Algeria)	Decrease	(Guerraiche et al. 2015)
1984–2012	Bohemian lakes	Increase	(Oulehle et al. 2013)

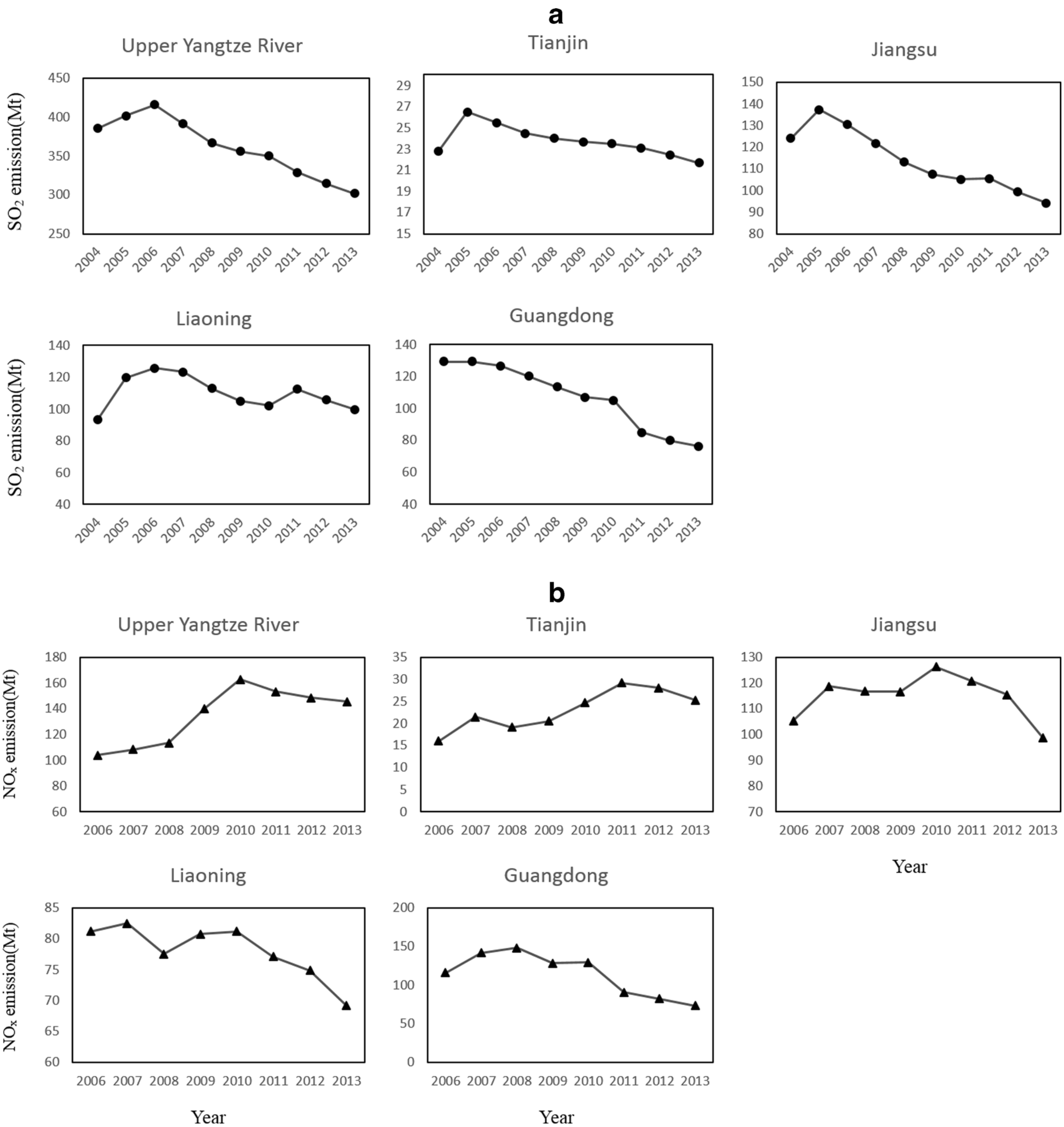

Fig. 6 Trends in emissions of **a** sulfur dioxide (2004–2013) and **b** nitrogen oxides (2006–2013). It includes five regions: Upper Yangtze River, Tianjin (Haihe River), Jiangsu (Taihu Lake), Liaoning (Songhua River), and Guangdong (Pearl River)

2013). Nutrients from farmland fertilizers and urban wastewater discharged into rivers contribute main pollutants to the surface water in Chaohu and Dianchi Lake, thereby tending to induce serious ecological problems such as eutrophication, which interrelates with the water pH (Zhang et al. 2012; Tanaka et al. 2013; Jiang et al. 2014). The water in the Liaohe River Estuary area has been seriously polluted by discharges of wastewater containing petroleum pollutants and nutrients (Ye et al. 2013). In recent years, many industries developed rapidly along the main and branch streams of Huaihe River, which have discharged a number of wastewater and led to the deterioration of water quality (Dou et al. 2016).

Conclusion

In this study, with the nonparametric Seasonal Kendall test method, the surface water pH trends were analyzed in 73 sites from ten river basins in China from 2004 to 2014. The variations of surface water pH in China ranged from 6.5 to 9.0 in the past decade (2004–2014), with relative lower levels in Songhua River and Pearl River but higher levels in Dianchi Lake. Significantly decreasing trends in surface water pH were found in 31 monitoring sites, which were mainly located in Haihe River, Taihu River, and Yangtze River. In contrast, the pH value showed significantly increasing trends in 22 sites, which were mainly located in Songhua River and Pearl River. Decreasing trends of NO_x emissions were found in Guangdong (Pearl River) and Liaoning province (Songhua River), while increasing trends of NO_x emissions were found in other three basins. Our results suggested that the increasing trends of water pH in Songhua River and Pearl River are possibly caused by the reductions of SO_2 and NO_x emissions in these two basins. However, the increased NO_x emissions in Haihe River, Taihu Lake, and Yangtze River may counteract the reductions of the SO_2 emissions. To effectively protect the aquatic systems, the emission of nitrous oxides (NO_x) should also be controlled in China.

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