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RESEARCH ARTICLE

Total phosphorus concentrations in surface water of typical agro- and forest ecosystems in China, 2004–2010

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Abstract The concentrations of total phosphorus (TP) from 83 surface water sampling sites in 29 of the Chinese Ecosystem Research Network (CERN) monitored ecosystems, representing typical agro- and forest ecosystems, were assessed using monitoring data collected between 2004 and 2010 from still and flowing surface water. Results showed that, TP concentrations were significantly higher in agro-ecosystems than those in forest ecosystems both for still and flowing surface water. For agro-ecosystems, TP concentrations in the southern area were significantly higher than those in the northern and northwestern areas for both still and flowing surface water, however no distinct spatial pattern was observed for forest ecosystems. In general, the median values of TP within agro- and forest ecosystems did not exceed the Class V guideline for still ($0.2\,\mathrm{mg\cdot L^{-1}}$) or flowing ($0.4\,\mathrm{mg\cdot L^{-1}}$) surface water, however, surface water at some agro-ecosystem sampling sites was frequently polluted by TP. Elevated concentrations were mainly found in still surface water at the Changshu, Fukang, Linze and Naiman monitored ecosystems, where exceedance ($>0.2\,\mathrm{mg\cdot L^{-1}}$) frequencies varied from 43% to 78%. For flowing water, elevated TP concentrations were found at the Hailun, Changshu and Shapotou monitored ecosystems, where exceedance ($>0.4\,\mathrm{mg\cdot L^{-1}}$) frequencies varied from 29% to 100%. Irrational fertilization, frequent irrigation and livestock manure input might be the main contributors of high TP concentrations in these areas, and reduced fertilizer applications, improvements in irrigation practices and centralized treatment of animal waste are necessary to control P loss in these TP vulnerable zones.

Keywords Chinese Ecosystem Research Network (CERN), total phosphorus (TP), surface water, ecosystem type, spatial variation

1 Introduction

Widespread phosphorus (P) enrichment of water bodies caused by urbanization and agricultural intensification has attracted much attention across the world [1–4]. P accumulation in surface water may increase the potential for eutrophication and lead to a range of environmental, social and economic problems [5–7].

To identify at-risk surface water bodies and protect them from eutrophication, the USEPA developed guidelines, which state that phosphorus concentrations should not exceed $0.05\,\mathrm{mg\cdot L^{-1}}$ in streams or $0.025\,\mathrm{mg\cdot L^{-1}}$ in lakes and reservoirs [8]. In China, still surface waters with $\mathrm{TP}>0.2\,\mathrm{mg\cdot L^{-1}}$ or flowing surface waters with $\mathrm{TP}>0.4\,\mathrm{mg\cdot L^{-1}}$ are grouped into Class V, waters that are polluted and can only be used for agricultural or landscape management [9]. According to these criteria, phosphorus pollution of surface water is widespread both nationally and internationally [10–14]. Monitoring data of lowland streams in Britain indicated that the average TP concentrations were consistently higher in catchments with high intensity agriculture when compared with catchments with lower intensity agriculture [15]. Research into runoff losses suggests that higher P application rates to land can result in higher P loads in surface runoff [16]. However, increases in P concentrations in runoff and surface water are not equally distributed across the landscape, meaning that it is impossible to correlate high TP concentrations solely with land use and fertilizer input [17]. Therefore, an understanding of TP hotspots and the identification of TP vulnerable zones in landscapes is important to support the development of effective management practices to protect surface water from eutrophication.

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Despite an awareness of the damaging consequences of excessive P and an urgent need for policy to protect freshwater, until now there has been no comprehensive national assessment of surface water P concentrations within different terrestrial ecosystems in China. To date, studies of P pollution in freshwater in China have generally been limited to the regional level [18,19].

This study provides an assessment of TP concentrations in surface water within representative agro- and forest ecosystems of China, using the Chinese Ecosystem Research Network (CERN) as the monitoring framework. The TP concentrations from 83 surface water sampling sites in 29 of the CERN monitored ecosystems, representing a national scale assessment of TP concentrations within typical agro- and forest ecosystems, were assessed using monitoring data collected from still (lake or pool) and flowing (stream) surface water from 2004 to 2010. The primary objectives of this study were: 1) to determine the occurrence and concentrations of TP in surface water associated with different ecosystem types; and 2) to identify TP vulnerable sites within agricultural ecosystems across China.

2 Methods and materials

2.1 Monitoring sites

Surface water monitoring of the CERN focuses on assessing the effects of typical terrestrial ecosystems, i.e. agro- and forest ecosystems, on water quality. The monitoring network has been designed so that surface water monitoring for TP in typical Chinese ecosystems reflects recent P inputs to the land surface of these different ecosystems. 29 monitored ecosystems of the CERN were chosen to represent typical agriculture and forest ecosystems across a range of climatic zones, geologies, soils and land use types found in China (Fig. 1).

The selected ecosystems represent a wide range of climatic conditions and cover a wide geographical area

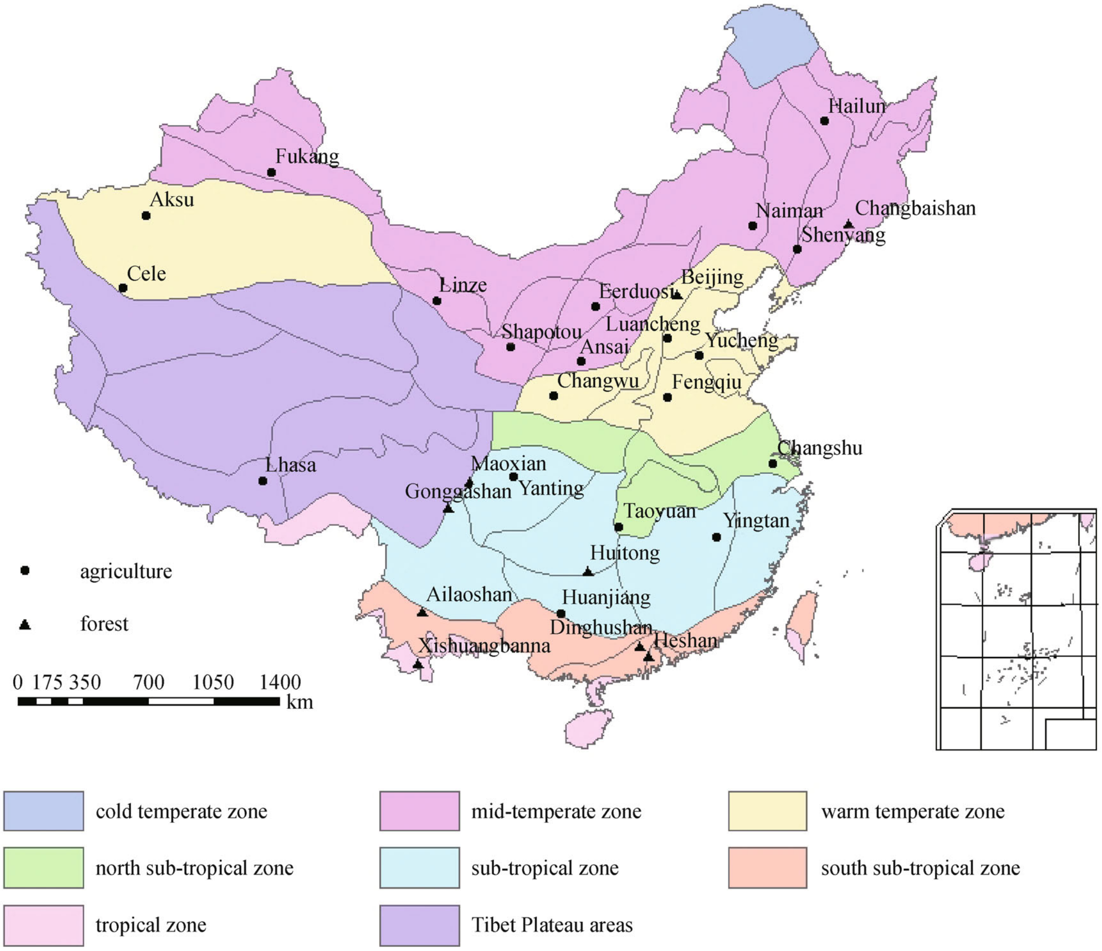
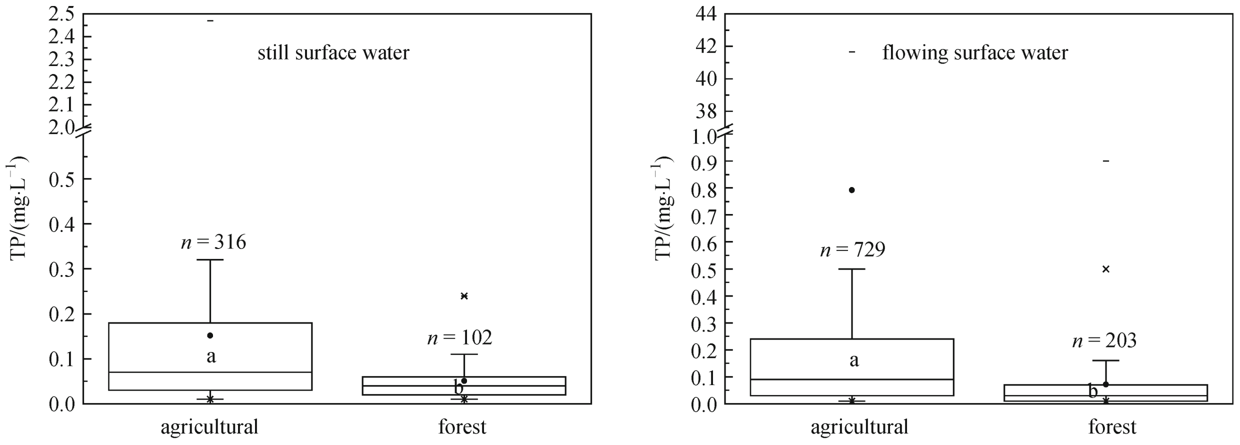


Fig. 1 Distribution map of the terrestrial ecosystem monitored ecosystems in the Chinese Ecosystem Research Network (CERN).The different colors represent different ecotypes

Table 1 Total phosphorus concentrations in surface water within agro-ecosystems

spatial region	monitored ecosystems	geographical location	MAP/ (mm)	soil type	soil AP /(mg·kg^{-1})	land use	application rate/ (kg·hm^{-2})	still/(mg·L^{-1})				flowing/(mg·L^{-1})			
								samples (sites)	median	max	> 0.2 mg·L^{-1} frequency	samples (sites)	median	max	> 0.4mg·L^{-1} frequency
north	Ansai	109°19′12″E 36°51′29″N	500	Loessial	18	Soybean-Millet	75	–	–	–	–	68(1)	0.07	0.59	4%
	Changwu	107°40′59″E 35°14′27″N	584	Loessial	18	Maize-Wheat	75	27(1)	0.04	0.10	0	18(1)	0.02	1.43	6%
	Fengqiu	114°19′43″E 35°00′40″N	597	Fluvo-aquic	11	Maize-Wheat	60-75	–	–	–	–	67(1)	0.09	0.70	9%
	Hailun	126°55′39″E 47°27′15″N	500-600	Black	36	Wheat-Maize	55-82.4	–	–	–	–	21(1)	20.8	41.66	100%
	Shenyang	123°22′05″E 41°31′06″N	650-700	Aquic brown	19	Maize	56.4-75	16(1)	0.09	0.13	0	17(1)	0.05	0.11	0
	Yucheng	116°34′13″E 36°49′ 51″N	582	Fluvo-aquic	27	Maize-Wheat	126.5	–	–	–	–	79(5)	0.05	1.82	13%
south	Changshu	120°25′08″E 31°19′46″N	1038	Red	24	Paddy-Wheat	180	60(1)	0.26	2.47	78%	121(2)	0.31	2.69	35%
	Huanjiang	108°19′12″E 24°43′18″N	1389	Calcareous	6	Maize-Soybean	135	5(1)	0.06	0.12	0	12(2)	0.01	0.42	8%
	Qianyanzhou	115°02′04″E 26°26′40″N	1542	Red	13	Paddy-Paddy	135	22(3)	0.05	0.16	0	13(1)	0.03	0.16	0
	Yanting	105°27′21″E 31°16′18″N	826	Purple	10	Maize-Wheat	160	45(1)	0.07	0.26	4%	88(2)	0.10	1.03	8%
	Taoyuan	111°26′26″E 28°55′46″N	1450	Red	11	Paddy-Paddy	160	12(1)	0.09	0.30	8%	24(2)	0.12	0.73	4%
	Yingtan	116°33′18″E 28°07′23″N	1785	Red	20	Peanut	135	69(7)	0.05	1.30	22%	77(6)	0.01	0.13	0
northwest	Akesu	80°51′40″E 40°37′49″N	45.7	Aeolian sandy	12	Cotton	172	11 (1)	0.02	0.04	0	21(2)	0.02	0.11	0
	Cele	80°43′39″E 37°01′15″N	35	Aeolian sandy	13	Cotton-Maize	126	22(1)	0.01	0.05	0	22(1)	0.02	0.59	5%
	Eerduosi	110°11′29″E 39°29′37″N	348.3	Aeolian sandy	–	Cotton-Maize	121.8	4(1)	0.14	0.18	0	17(1)	0.04	0.13	0
	Fukang	87°55′58″E 44°17′26″N	164	Aeolian sandy	21	Cotton-Maize	121.8	7(1)	0.12	0.34	43%	7(1)	0.14	0.26	0
	Linze	100°07′42″E 39°20′59″N	117	Aeolian sandy	24	Wheat–Maize	225	7(2)	0.18	0.80	43%	8(1)	0.16	0.23	0
	Naiman	120°42′00″E 42°55′47″N	340-450	Aeolian sandy	20	Wheat-Maize	135	9(1)	0.25	0.32	67%	14(2)	0.12	0.25	0
	Shapotou	105°00′01″E 37°16′04″N	180-220	Aeolian sandy	9	Wheat-Maize	105	–	–	–	–	17(1)	0.22	0.74	29%

Note: MAP, mean annual precipitation; soil AP, soil available phosphorus (data came from the monitoring data of CERN, 2004–2010, the soil samples were taken from plots under local typical fertilization treatments); application rate referred to the rate of P_2O_5. "–" indicates no monitoring data



(a) (b)

Fig. 2 Distribution of TP concentrations in surface water within agro- and forest ecosystems ((a) for still surface water, (b) for flowing surface water). Box plots labeled with different letters indicate that the differences in median concentrations between the two groups are significant ($p < 0.05$). Boxes illustrate the 25th, 50th and 75th percentiles, the whiskers indicate the 10th and 90th percentiles, the "–" indicates the max and minimum percentiles, the "×" indicates the 1th and 99th percentiles, the "·" indicates the mean values. These descriptions also apply to Fig. 3 and Fig. 4

(80°43′39″–133°18′03″E, 18°13′01″–47°27′15″ N). The annual average rainfall of the monitored ecosystems varies between approximately 43 mm (Cele) and 1956 mm (Dinghushan) (Table 1), and the average temperature between 1.5°C (Hailun) and 21.8°C (Xishuangbanna).

The 20 agro-ecosystems are located in 1) humid and sub-humid regions in the temperate zone of north-eastern China (Hailun, Shenyang) and the warm temperate zone of northern China (Luancheng, Yucheng, Fengqiu), 2) humid areas in the sub-tropical zone in the Yangtze River Delta (Changshu) and southern China (Huanjiang, Qianyanzhou, Yanting, Taoyuan,Yingtan), 3) the loess plateau (Ansai and Changwu) and 4) arid and semi-arid areas located in the warm temperate zone of north-west and northern China (Akesu, Cele, Eerduosi, Fukang, Linze, Naiman, Shapotou) (Fig. 1). Land use is mainly crop growing, including wheat, maize, soybean, rice and cotton (Table 1).

Nine forest ecosystems are selected to assess the natural background levels of TP, and to act as a control with which to compare the agro-ecosystems. The forest sites are located along the north–south transect of eastern China (Fig. 1), and are representative of old native forests and secondary forests without any fertilization.

2.2 Monitoring and analysis methods

Surface water samples were collected between 2004 and 2010, in accordance with the Monitoring Protocol of the Chinese Ecosystem Research Network [20]. For this study, 29 still water sites (ponds or lakes) and 54 flowing water sites (streams) were sampled, resulting in between 1 and 7 sampling sites for each ecosystem type (details in Table 1). In total 418 and 932 samples were analyzed for still and flowing surface water respectively. The sampling frequency at the sites ranged from 2 to 12 times a year, with sampling distributed evenly through the wet and dry seasons.The maximum sampling frequency was monthly, and the minimum sampling frequency was twice a year, in both the dry and wet seasons.

Water samples were analyzed using standard protocols and methods [20]. Total phosphorus concentrations were determined by the ammonium molybdate spectrophotometric method, following digestion by potassium persulfate, using a detection limit of $0.01\ \mathrm{mg \cdot L^{-1}}$. The CERN water sub-center supplied blind samples to test the quality of the laboratory analyses. If the data of the blind samples were not in the range of standard results, the batch of samples was re-analyzed. The unqualified data were eliminated from the analysis database in this study.

2.3 Statistical analysis

To minimize statistical bias, concentrations below the detection limit (LOD) were reported as half of the limit, rather than as zero [21]. Less than 10% of the measured values of TP were below the LOD.

Data were analyzed with Matlab7.11.0 (Massachusetts, USA). A Lilliefors test was conducted to test the normality of the data. As the data were not normally distributed, the nonparametric Kruskal–Wallis test was used to test for differences between the median TP concentrations among data grouped by ecosystem type (agro- and forest ecosystems) and geographical region (southern, northern and north-western). Where there were differences between data groups, the Kruskal–Wallis test was combined with a multi-comparison method to determine which groups were different ($p < 0.05$). Correlation analysis was conducted to explore the relationship between TP concentrations and fertilizer application rates. Class V of the Chinese National Quality Standards for Surface Waters was used as the guideline to assess the exceedance frequency of P concentrations at the monitored ecosystems, and those with high exceedance frequencies were identified as TP vulnerable zones.

3 Results and discussion

3.1 Total P concentrations under different terrestrial ecosystems

TP concentrations ranged from 0.01 mg·L^{-1} (forest ecosystems) to 2.47 mg·L^{-1} (agro-ecosystems) for still surface water, and from 0.01 mg·L^{-1}(forest ecosystems) to 41.66 mg·L^{-1}(agro-ecosystems) for flowing surface water, respectively.

Between 2004 and 2010, the median TP concentrations were significantly higher in the agro-ecosystems (0.07 mg ·L^{-1}) than those in the forest ecosystems (0.04 mg·L^{-1}) for still surface water, and the median TP concentrations were significantly ($p < 0.05$) higher in the agro-ecosystems (0.09 mg·L^{-1}) than those in the forest ecosystems (0.03 mg·L^{-1}) for flowing surface water.

The median TP concentrations for agro- and forest ecosystems did not exceed the Class V limit of the Chinese National Quality Standards for Surface Waters at the sampling sites (Fig. 2), and the median concentrations of TP within the forest ecosystems were below the Class III limit. However, the 90th percentile concentrations of TP within agro-ecosystems for still and flowing surface water were higher than the corresponding Class V limit (Fig. 2), indicating that more than 10% of the surface water samples were heavily polluted by P.

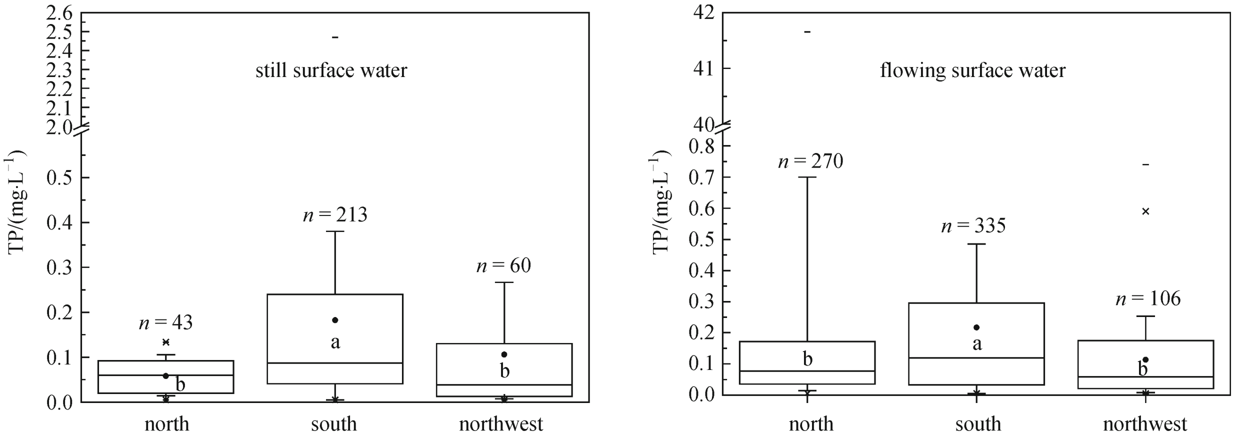
TP concentrations of surface water within different Chinese ecosystems were similar to the findings of a study undertaken in the U.S., which claimed that median TP concentrations in agricultural streams were higher than those in streams with mixed and undeveloped land use [22]. Mouri et al. [23] and Mou et al. [24] also pointed out that TP concentrations were consistently greater in streams draining cultivated areas due to fertilizer use.

For still surface water, the TP concentrations in the CERN agro-ecosystems were similar to those found in the Lower Yangtze floodplain lakes (0.05 – 0.09 mg·L^{-1}) [25], but higher than those in the Lake Hayes catchment, South Island, New Zealand (0.011 – 0.065 mg·L^{-1}) [26]. For flowing surface water, TP concentrations for the agricultural ecosystems of the CERN were close to those in the Xiangxi River, which flows into the Three Gorges Reservoir (0.14 mg·L^{-1}) [27], but much higher than those in rivers draining agricultural areas in Finland (0.014 – 0.064 mg·L^{-1}) [28].

An investigation of management practices showed that the forest ecosystems of the CERN have not been subject to anthropogenic inputs of fertilizer, and in these ecosystems, TP concentrations were comparable to those found in forested headwaters in Japan [21].

3.2 TP concentrations under different geographical regions

There were no significant seasonal (between wet and dry seasons) differences in TP concentrations for agro- (p = 0.78) ecosystems (p = 0.65) (Data not shown). However, there were spatial patterns in the data and TP concentrations for the southern sites were significantly higher than those for the northern and north-western sites (Fig. 3). The median TP concentrations of still surface water were significantly higher in the southern areas (0.09 mg·L^{-1}) than those in the northern (0.06 mg·L^{-1}) and north-western (0.04 mg·L^{-1}) areas. Similarly, TP concentrations for



(a) (b)

Fig. 3 Box plot showing the distribution of TP concentrations in surface water within agro- ecosystems grouped by geographical region (a for still surface water, b for flowing surface water) flowing surface water were significantly higher in the southern areas (0.12 mg·L^{-1}), than those in the northern (0.08 mg·L^{-1}) and north-western areas (0.06 mg·L^{-1}) ($p < 0.05$).

Monitoring data indicated that surface water within agro-ecosystems was frequently polluted by TP. For example, the TP concentration exceedance (> 0.2 mg·L^{-1}) frequencies for still surface water at the Fukang, Linze, Naiman and Changshu monitored ecosystems varied from 43% to 78% (Table 1). For flowing surface water, the TP concentration exceedance (> 0.4 mg·L^{-1}) frequencies at the Shapotou, Changshu and Hailun monitored ecosystems varied from 29% to 100% (Table 1). This indicated that the Fukang, Linze, Naiman, Shapotou, Changshu, and Hailun regions might be TP vulnerable areas.

Generally speaking, surface water within forest ecosystems was relatively free from excessive TP contamination and there were no spatial patterns in TP concentrations. The mean TP concentrations of flowing surface water in the northern areas (0.10 mg·L^{-1}) were not significantly higher than those in the southern areas (0.07 mg·L^{-1}), and the median TP concentrations in the northern and southern areas were the same (0.03 mg·L^{-1}) (Fig. 4).

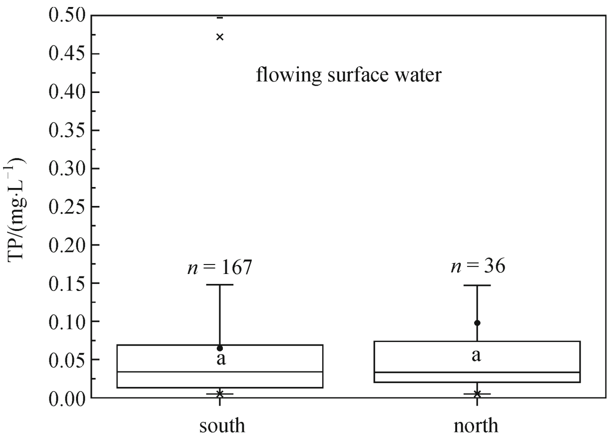


Fig. 4 Box plot showing the distribution of TP concentrations in surface water within forest ecosystems grouped by geographical region

3.3 Factors influencing TP in surface water

Anthropogenic inputs are a main source of phosphorus, and inappropriate agricultural management practices might result in TP pollution. In the southern areas, correlation analysis revealed that TP median concentrations were positively correlated with fertilizer application rates (r = 0.851 and 0.953 for still and flowing surface water respectively, $p < 0.05$), indicating that excessive applications of P fertilizer might be one of the main causes of P pollution of surface water within the agro-ecosystems.

Excessive P fertilizer application in farming systems has led to P accumulation in soil [29–31]. Sharpley et al. [32] considered that, once the available P content in soil exceeded 20 mg·kg^{-1}, extra P input would simply lead to enhanced P runoff and leaching rather than contributing to increased crop production. Wang et al. [33] reported that after long-term fertilization soil test P and surface water TP were significantly and positively correlated in paddy ecosystems. Owens and Walling [34] revealed that fertilized agricultural land had higher TP content of fluvial sediment than moorland, and P in sediment might be released into the surrounding water, posing a potential risk to the surface water. In general, excessive P fertilizer applications resulted in increased soil P levels and led to an enhanced risk of P loss from land to adjacent watercourses via surface runoff or soil erosion, meaning that the potential risks of eutrophication in receiving waters was increased [35–37].

In China, it was estimated that, by 2000, available P enriched arable land (Olsen–P content > 20 mg·kg^{-1}) accounted for 15% of the total arable land [38]. In Hailun, Changshu, Linze and Fukang, soil P concentrations were very high (with available P values of 36, 24, 24 and 21 mg·kg^{-1}, respectively) (Table1), which might explain the higher TP median concentrations and exceedance frequencies observed at these monitored ecosystems. Correlation analysis also showed that soil available P content had a significant positive effect on TP concentrations of flowing surface water (r = 0.631, p = 0.005). Phosphorus fertilizer application management practices based on soil test P should be recommended to reduce the risk of P loss in these areas [39,40].

Changshu is located in the highly developed and densely populated Yangtze Delta and has a long history of high yield, intensive rice farming. Farmers tend to overuse chemical fertilizers in an attempt to improve yield. It was reported that after 20 years fertilization, soil TP and Olsen–P had increased by 15% – 95% and 4% – 19%, respectively [35]. A case study in Changshu [29] demonstrated that further P fertilizer applications would not lead to increases in crop productivity, but rather would increase P loss to waters. In addition, P availability has been shown to increase under high temperature and precipitation conditions [41], thereby further increasing P loss risk by runoff. These factors may help explain the high median TP concentrations and guideline exceedance frequencies in Changshu.

Soil texture could also influence TP loss from soil to surface water and thereby influence TP concentrations of surface water. Aeolian sandy soils in north-western agro-ecosystems are characterized by their low P–retention capacity [42,43]. When fertilizer is added, aeolian sandy soils are more susceptible to P leaching [44,45]. Moreover, successful crop cultivation depends heavily on irrigation in these arid or semi-arid areas, which promotes leaching of P–fertilizer through sandy soils. The combination of the sandy texture and frequent irrigation has meant that surface water in the north-western agro-ecosystems is susceptible to TP pollution, which may help explain the high TP exceedance frequencies in the Fukang, Linze, Naiman and Shapotou agro-ecosystems. Converting irrigation systems from furrow to sprinkler or drip, which can lead to more efficient irrigation, will help to reduce phosphorus loss in these regions [46,47].

Livestock manure was also an important source of P in China [48]. According to our investigation, animal husbandry is one of main sources of income for farmers in Hailun. Animal waste usually contains large amounts of phosphorus [49], which has resulted in extremely high TP concentrations and exceedance frequencies in Hailun. To protect surface water from animal waste pollution, measures such as preventing livestock access to water bodies and centralized treatment of animal waste might be effective [50].

4 Conclusions

Median TP concentrations were significantly higher within agro-ecosystems than those within forest ecosystems. Furthermore, TP concentrations within agro-ecosystems varied geographically, with TP concentrations in the southern sites significantly higher than those in the northern and north-western sites. There were no spatial patterns in TP concentrations within forest ecosystems.

While surface water within forest ecosystems was relatively free from TP pollution, some agro-ecosystems were severely polluted by P when compared with the Class V standard. For still surface water, high exceedance frequencies mainly occurred in Fukang, Linze, Naiman and Changshu, while for flowing surface water, high exceedance frequencies were mainly found in Shapotou, Changshu, and Hailun. Special attention should be paid to these phosphorus vulnerable areas. In Changshu, fertiliser applications should take account of the soil test P levels and actual crop needs so that phosphorus loss from agricultural farmland is reduced. In Fukang, Linze, Naiman and Shapotou, converting furrow irrigation system to sprinkler or drip irrigation system may help to reduce related phosphorus loss, while in Hailun, animal waste should be managed more carefully.

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