PLOS ONE

Total Nitrogen Concentrations in Surface Water of Typical Agro- and Forest Ecosystems in China, 2004-2009

Zhiwei Xu, Xinyu Zhang*, Juan Xie, Guofu Yuan, Xinzhai Tang, Xiaomin Sun, Guirui Yu

Key Laboratory of Ecosystem Network Observation and Modeling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China

Abstract

We assessed the total nitrogen (N) concentrations of 28 still surface water (lake and pond), and 42 flowing surface water (river), monitoring sites under 29 typical terrestrial ecosystems of the Chinese Ecosystem Research Network (CERN) using monitoring data collected between 2004 and 2009. The results showed that the median total N concentrations of still surface water were significantly higher in the agro- (1.5 mg·L^{-1}) and oasis agro- ecosystems (1.8 mg·L^{-1}) than in the forest ecosystems (1.0 mg·L^{-1}). This was also the case for flowing surface water, with total N concentrations of 2.4 mg·L^{-1}, 1.8 mg·L^{-1} and 0.5 mg·L^{-1} for the agro-, oasis agro- and forest ecosystems, respectively. In addition, more than 50% of the samples in agro- and oasis agro- ecosystems were seriously polluted ($>$1.0 mg·L^{-1}) by N. Spatial analysis showed that the total N concentrations in northern and northwestern regions were higher than those in the southern region for both still and flowing surface waters under agro- and oasis agro- ecosystems, with more than 50% of samples exceeding 1.0 mg·L^{-1} (the Class III limit of the Chinese National Quality Standards for Surface Waters) in surface water in the northern region. Nitrogen pollution in agro- ecosystems is mainly due to fertilizer applications, while the combination of fertilizer and irrigation exacerbates nitrogen pollution in oasis agro- ecosystems.

Introduction

Nitrogen (N) pollution, leading to eutrophication of inland waters, has resulted in an increase in global algal biomass and photosynthesis, such that primary production is approximately 60% higher than expected background levels in lakes [1], streams and rivers [2]. As a major contributor to eutrophication of water bodies, non-point losses of N (e.g. in runoff) have received particular attention. N pollution causes water eutrophication, which disrupts ecology and causes, among other problems, toxic algal blooms, loss of oxygen, loss of biodiversity (including species that are important for commerce and recreation) [3–5]. Eutrophication can also seriously affect our ability to use water for drinking, industry, agriculture, recreation, and other purposes.

Total N concentrations in surface water have been classified in China and other countries to control water eutrophication and improve water quality. To identify at-risk surface water bodies and protect them from eutrophication, the US EPA developed guidelines, which state that N concentrations should not exceed 0.3 mg·L^{-1} in streams and rivers or 0.1 mg·L^{-1} in lakes and reservoirs [6]. Water has been divided into 14 distinct aggregate nutrient ecoregions in the U.S. according to total P and total N concentrations, chlorophyll a and turbidity. In China surface water has been divided into five categories according to the Chinese National Quality Standards for Surface Water. Water categorized as class I to III can be used as drinking water, while class IV and V water is only suitable for industrial and agricultural uses. The total

N values for categories I – V are $<$ 0.2 mg·L^{-1}, 0.2 – 0.5 mg·L^{-1}, 0.5 – 1.0 mg·L^{-1}, 1.0 – 1.5 mg·L^{-1} and 1.5 – 2.0 mg·L^{-1}, respectively [7].

In China, stream total N concentrations have tended to increase since the 1980s as a consequence of demographic, industrial and agricultural development [8,9]. Rivers and lakes in the Taihu Lake region are polluted to varying degrees by N [10], with 80% of samples having concentrations exceeding 1.0 mg·L^{-1}, meaning that the water is only suitable for industrial, agricultural and landscape uses according to the Chinese National Quality Standards for Surface Water [11]. Cai et al. [12] reported that eutrophication of lakes is serious in southern China, but that it is worse across a large part of northern China. Rural rivers in eastern China are severely polluted [13]. As a general rule, water pollution in China tends to intensify from tributaries to the main stems of river systems, from urban to rural areas, from surface water to groundwater and from the regional to the basin scale [12].

Natural and anthropogenic sources both contribute to surface water N inputs [14,15]. Now that point-source pollution has been controlled effectively, non-point source pollution, especially that which results from agricultural land management, has become the main influence on surface water and is an important environmental issue worldwide [16,17]. Crop production is by far the largest cause of human alteration of the global N cycle. Global industrial N fixation for fertilizers has increased rapidly to 80×10^6 Mg·year^{-1} [18]. In the United States (US) and Europe, only 18% of the N input in fertilizer is removed from farms in produce,

leaving behind, on average, 174 kg·ha^{-1}·year^{-1} of surplus N [19,20]. This surplus may accumulate in soils, from where it may be either eroded and transported to surface water, leached to surface and ground water, or lost to the atmosphere [18]. Inorganic fertilizers now contribute 80 Tg N year^{-1} to the environment, while 32 – 45 Tg year^{-1} of inorganic fertilizers find their way into freshwater (from leaching and erosion) [21].

Fertilizer consumption has grown rapidly in China since 1978, and China recently became the biggest producer and consumer of N fertilizer in the world. The average annual application rate of N in China gradually increased to 130 kg·ha^{-1} in 1985, then rapidly increased to 236 kg·ha^{-1} in 1995 and then to 262 kg·ha^{-1} in 2001 [22]. However, less than half of the fertilizer N applied in China is taken up by crops [23]. The losses of total N through runoff and leaching were 5.6 – 9.0 kg·ha^{-1} from paddy fields and 12.5 – 19.5 kg·ha^{-1} from upland fields, accounting for 2.6 – 4.2% and 7.6 – 12.3% of the total applied N [24]. It is estimated that as much as 0.644 Tg of total N is leached, accounting for 2.8% of China's total N application [24].

Because of the increasing incidence of surface water N pollution, many countries are beginning to be concerned about sustainable water management. The European Union has implemented the Water Framework Directive, which aims to recover good status in water resources by 2015 [25]. Canada (both at the national and provincial levels) and the US have begun to take an effective and integrated approach to land-use management with respect to protection of drinking water sources. On a national level, Canada has established aboriginal water systems, while at the provincial level; British Columbia has established a water policy, similar to that developed by the US Environmental Protection Agency [26]. The Chinese government has published many water environmental protection measures such as the Water Pollution Prevention Program of Yangtze River basin (2011–2015) and other measures for important river basins (Yellow River, Huaihe River, Weihe River, Liaohe River, Haihe River, Songhuajiang River, Chaohu and Dianchi) [27]. Until now however, there have been few national scale assessments of N concentrations in surface water in China.

Using the Chinese Ecosystem Research Network (CERN) as the monitoring framework, total N concentrations at 28 still, and 45 flowing, surface water monitoring sites of 28 CERN monitoring stations were assessed from 2004 to 2009. The aims of this study were: (1) to assess surface water total N pollution under agro-, oasis agro- and forest ecosystems and (2) to identify sites vulnerable to N pollution in agro- and oasis agro- ecosystems. Findings from this study will provide key information that will be useful in controlling N pollution in surface water in China.

Materials and Methods

2.1 Ethics statement

The authors declare that no specific permits were required for the described field studies. The authors also declare that no specific permissions were required for these locations/activities. Locations are not privately-owned or protected in any way. We confirm that this study did not involve endangered or protected species and no protected species were sampled during the monitoring campaign.

2.2 Monitoring sites

Surface water monitoring of the CERN focuses on assessing the effects of typical terrestrial ecosystems, i.e. agro-, oasis agro- and forest ecosystems, on water quality. Twenty-eight monitoring stations of the CERN were chosen to represent typical agricultur-

al, oasis agricultural and forest ecosystems, geology, soils, and land use types found across a wide range of climatic zones in China (Figure 1). The annual average rainfall of the monitoring ecosystems (80°43′39″-133°18′03″E, 18°13′01″-47°27′15″N) varied from approximately 35 mm (Cele) to 1956 mm (Dinghushan), while the annual average temperature ranged from 1.5°C (Hailun) to 21.8°C (Xishuangbanna).

The 12 agro- ecosystems were located in (1) humid and sub-humid regions in the temperate zone of northeastern China (Hailun, Shenyang) and the warm temperate zone of northern China (Luancheng, Yucheng, Fengqiu), and (2) the Loess Plateau (Ansai and Changwu), (3) humid areas in the sub-tropical zone in the Yangtze River Delta (Changshu) and southern China (Huanjiang, Qianyanzhou, Yanting, Taoyuan,Yingtan), respectively (Figure 1). Based on geographical and climatic zones, we designated Hailun, Shenyang, Luancheng, Yucheng, Fengqiu, Ansai and Changwu agro- ecosystems as the northern group, while the Changshu, Huanjiang, Qianyanzhou, Yanting, Taoyuan and Yingtan agro- ecosystems were designated as the southern group. Land use in these agro- ecosystems was mainly crop growing, including wheat, maize, soybean, rice and cotton (Table 1).

Seven oasis agro- ecosystems (Akesu, Cele, Eerduosi, Fukang, Linze, Naiman, Shapotou) were located in the warm temperate zone of northwest and northern China in arid and semi-arid areas. The oasis agro- ecosystem is unique and found only in arid agricultural areas. Unlike agro- ecosystems in other areas represented in this study, crop cultivation depends heavily on irrigation. Land use in the oasis agro- areas was mainly cotton, maize and wheat growing (Table 1). Therefore, we classified these ecosystems as an independent group and called it oasis agro-ecosystem. We designated these seven oasis agro- ecosystems as the northwestern group.

Total N concentrations in surface water in forest ecosystems were assessed. The forest ecosystems were located along the north-south transect of eastern China (Figure 1), and were representative of native and secondary forests and were free from human fertilization and irrigation activities.

2.3 Monitoring and analysis methods

CERN surface water quality samples were collected according to the Water Monitoring Protocol of the Chinese Ecosystem Research Network [28]. 530 samples were collected from the still surface water sites, and 703 samples were collected from the 45 flowing surface water monitoring sites. The monitoring frequency ranged from 2 to 12 times per year, with sampling distributed evenly through the wet and dry seasons. The maximum sampling frequency was monthly (Ansai, Fengqiu, and Changshu), and the minimum sampling frequency was twice a year (for most of the other monitoring ecosystems), in both the dry and wet seasons. Water samples were analyzed at the Chinese Science Academy's laboratory following standard protocols and methods [28]. Total N was determined by spectrophotometry after potassium persulfate digestion. Information about crop rotation, soil type and fertiliser application rate was recorded for each sampling event at each monitoring station.

2.4 Statistical analysis

Data were analyzed with Matlab 7.11.0 (Massachusetts, USA). A Lilliefors test was conducted to test the normality of the data. Data were not normally distributed, so the nonparametric Kruskal-Wallis test was used to test for differences between the median total N concentrations for data grouped by ecosystem type (for agro-, oasis agro- and forest ecosystems) and geographical region (southern, northern and northwestern) for agro- and oasis

Figure 1. Distribution map of total nitrogen monitoring sites in agro- , oasis agro- and forest ecosystems of the Chinese Ecosystem Research Network (CERN).
doi:10.1371/journal.pone.0092850.g001

agro- ecosystems. Where there were differences between data groups, the Kruskal-Wallis test was combined with a multi-comparison method in Matlab R 2010b to determine which groups were different ($p < 0.05$). We used linear regression to test for relationships between total N concentrations and soil N application rates using SPSS 19.0 for Windows. We used $p < 0.05$ as the significance level. We used Origin 8.0 software for box plots.

1.0 mg·L^{-1} (Class III limit of the Chinese National Quality Standards for Surface Waters) was used as the guideline to assess the exceedance frequency of total N concentrations at the monitoring sites in agro-, oasis agro- and forest ecosystems. Sites with high exceedance frequencies were identified as total N vulnerable zones.

Results

3.1 Total N concentrations under different ecosystems

Total N concentrations in the agro- and oasis agro- ecosystems were significantly higher than in the forest ecosystems. The typical total N concentrations (10th and 90th percentiles in box plots) in the agro-, oasis agro- and forest ecosystems ranged between $0.4 - 8.7$ mg·L^{-1}, $0.7 - 15.2$ mg·L^{-1}, and $0.2 - 6.6$ mg·L^{-1}, respectively for still surface water (Figure 2(A)), and $0.4 - 10.9$ mg·L^{-1}, $0.6 - 11.6$ mg·L^{-1}, and $0.2 - 3.3$ mg·L^{-1}, respectively for flowing surface water (Figure 2(B)). The median total N concentrations of still and flowing surface water in forest ecosystems were 1.1 mg·L^{-1} and 0.5 mg·L^{-1}, respectively. These concentrations were significantly lower than those of still (1.5 mg·L^{-1} and 1.8 mg·L^{-1}, respectively) and flowing surface water (2.4 mg·L^{-1} and 1.8 mg·L^{-1}, respectively) in the agro- and oasis agro-ecosystems ($p < 0.05$).

The surface water in agro- and oasis agro- ecosystems was seriously polluted by N. The median concentrations of total N under the agro- and oasis agro- ecosystems exceeded 1.0 mg·L^{-1}

[7] (Figure 2), indicating that more than 50% of surface water samples were heavily polluted by N in these ecosystems.

The total N concentrations in surface water were higher in Beijing, Huitong, Heshan and Dinghushan forest ecosystems than the other forest ecosystems. The exceedance frequencies (> 1.0 mg·L^{-1}) of flowing surface water total N concentrations in Huitong and Dinghushan were about 100%, which indicates that surface water in some forest ecosystems is eutrophic. The water quality standard was not exceeded for either still or surface water in Gongga, Ailao and Xishuangbanna (Table 2).

3.2 Total N concentrations of agro- and oasis agro- ecosystems in different regions

The surface water total N concentrations in northern and northwestern regions in China were higher than those in the southern region. The typical total N concentrations of still surface water in northern, southern and northwestern regions ranged from $0.6 - 4.3$ mg·L^{-1}, $0.3 - 3.5$ mg·L^{-1}, $0.6 - 15.6$ mg·L^{-1} (Figure 3(A)) and $0.9 - 39.1$ mg·L^{-1}, $0.3 - 4.4$ mg·L^{-1}, $0.8 - 12.2$ mg·L^{-1} for flowing surface water (Figure 3(B)). There were no significant differences between total N concentrations in still surface water for the different regions. However, the total N concentrations in flowing surface water in the northern region (3.8 mg·L^{-1}) were significantly higher than those in the southern (1.2 mg·L^{-1}) and northwestern regions (1.8 mg·L^{-1}) ($p < 0.05$).

Surface water in northern, southern and northwestern regions showed varying levels of N pollution, with median total N concentrations of still and flowing surface water all exceeding 1.0 mg·L^{-1} [7] (Figure 3). Results indicate that more than 50% of surface water samples were heavily polluted by N in northern agro- ecosystems, especially flowing surface water samples. The median total N concentrations for surface water in the southern and northwestern regions exceeded 1.0 mg·L^{-1} [7]. About 50% of

Table 1. TN concentrations in still and flowing surface water under agro- and oasis agro- ecosystems.

Spatial Regions	Station	Mean Precipitation (mm)	Soil type	Land use	N application rate (kg·ha⁻¹·year⁻¹)	Still surface water				Flowing surface water			
						n	Median	Max	>1.0 mg·L⁻¹ frequency(%)	n	Median	Max	>1.0 mg·L⁻¹ frequency(%)
North	Ansai	500	Loessial Soil	Soybean-Millet	120	—	—	—	—	56(1)	2.8	13.8	96
	Changwu	584	Loessial Soil	Maize-Wheat	345	24(1)	3.0	9.7	100	17(2)	1.6	3.9	65
	Fengqiu	597	Fluvo-aquic Soil	Maize- Wheat	345	—	—	—	—	57(1)	3.3	39.1	96
	Hailun	500-600	Black Soil	Wheat-Maizerotation	120	—	—	—	—	19(1)	57.0	84.8	100
	Shenyang	650-700	Aquic brown Soil	Maize	75	13(1)	0.8	9.4	23	11(1)	0.3	0.4	0
	Yucheng	582	Fluvo-aquic Soil	Maize-Wheat	510	—	—	—	—	75(2)	5.4	27.8	91
South	Changshu	1038	Red Soil	Paddy-Wheat	466	46(2)	1.9	7.9	80	96(1)	1.8	12.3	75
	Huanjing	1389	Calcareous soil	Maize-Soybean	—	5(1)	0.6	9.0	20	10(2)	0.3	10.3	20
	Qianyanhzou	1542	Red Soil	Paddy-Paddy	320	19(2)	1.0	7.3	53	9(1)	0.9	2.0	44
	Yanting	826	Purple Soil	Maize -Wheat	300	32(1)	1.7	4.5	84	—	—	—	—
	Taoyuan	1450	Red Soil	Paddy-Paddy	270	9(2)	1.0	4.4	44	20(2)	0.9	8.0	40
	Yingtan	1785	Red Soil	Peanut	150	44(2)	0.6	3.0	9	43(6)	0.8	34.8	35
Northwest	Akesu	45.7	Aeolian sandy soil	Cotton	160	15(2)	0.9	1.6	40	7(1)	0.8	1.8	43
	Cele	35	Aeolian sandy soil	Cotton-Maize rotation	468	18(1)	1.0	3.2	39	19(1)	2.8	13.4	84
	Eerduosi	348.3	Aeolian sandy soil	Cotton-Maize rotation	—	4(1)	1.0	1.2	50	21(1)	2.2	4.3	95
	Fukang	164	Aeolian sandy soil	Cotton-Maize rotation	275	9(1)	1.5	17.4	89	8(1)	1.6	91.0	63
	Linze	117	Aeolian sandy soil	Wheat–Maize rotation	122	8(2)	23.3	69.5	100	10(1)	12.2	72.0	100
	Naiman	340-450	Aeolian sandy soil	Wheat-Maize rotation	207	8(1)	1.4	8.3	75	14(2)	0.9	1.3	36
	Shapotou	180-220	Aeolian sandy soil	Wheat-Maize rotation	256	10(1)	11.5	43.0	100	—	—	—	—

Note: The "n" values represent the number of sampling sites and the monitoring sites (within brackets). "–"s illustrate that no detection data were available.
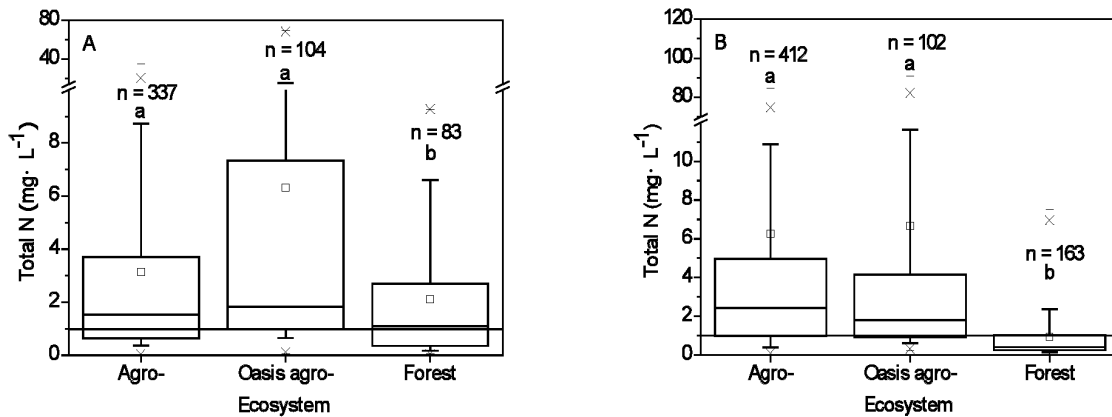doi:10.1371/journal.pone.0092850.t001

Figure 2. Total nitrogen concentrations in still surface water (A) and flowing surface water (B) of the agro-, oasis agro- and forest ecosystems between 2004 and 2009. Box plots illustrate the 25th, 50th, and 75th percentiles, the whiskers indicate the 10th, 90th percentiles, the "-"s indicate the maximum and minimum percentiles, the "×"s indicate the 1th and 99th percentiles, the "□"s indicate the mean values. Box plots labeled with different letters (a, b) indicate that differences in median values among the three ecosystem types are significant at $p < 0.05$. "—" illustrate the Class III guideline of 1.0 mg·L^{-1} for total nitrogen according to the national quality standards for surface waters of China. doi:10.1371/journal.pone.0092850.g002

surface water samples were seriously polluted by N in northwestern oasis agro- ecosystems.

The total N concentrations varied by station. The flowing surface water total N concentration was highest in the Hailun agro- ecosystem located in northern China, with a median value of 57.0 mg·L^{-1} (Table 1). The flowing surface water total N concentrations in the northern agro- ecosystems, except Shenyang, all exceeded 1.0 mg·L^{-1}. Exceedance frequencies at Ansai, Fengqiu, Hailun and Yucheng were 90 – 100%. In addition, the still surface water at Changwu was heavily polluted by N and had an exceedance frequency of 100%.

In southern agro- ecosystems, the two highest still and flowing surface water total N concentrations occurred in Changshu, the median values of which were 1.9 mg·L^{-1} (still) and 1.8 mg·L^{-1} (flowing). At this station about 80% of total N concentrations in still surface water and 75% of total N concentrations for flowing surface water exceeded 1.0 mg·L^{-1} (Table 1). The still and flowing surface water total N concentrations of other stations (Huanjiang, Qianyanzhou, Taoyuan, Yingtan) were about 1.0 mg·L^{-1}, and the exceedance frequencies varied from 20% to 50%.

The total N concentrations in the northwestern oasis agro-ecosystems were highest in Linze and Shapotou. The still and flowing surface water median total N concentrations were 23.3 mg·L^{-1} and 12.2 mg·L^{-1}, respectively, in Linze, while for still surface water in Shapotou, the median total N concentration was 11.5 mg·L^{-1}. The total N concentrations all exceeded 1.0 mg·L^{-1} in these two stations, indicating that the surface water was heavily polluted by N (Table 1).

3.3 Correlations between total N concentrations and N fertilizer application rates in agro- and oasis agro- ecosystems

Correlation analysis between the surface water total N concentrations and N application rates showed that the flowing surface water total N concentrations and N application rates were significantly correlated ($r^2 = 0.415$, $p = 0.009$) (Figure 4). Results indicated that total N concentrations tended to increase as N application rates increased. While there was a similar trend for still surface water and N application rates, the correlation was not significant ($r^2 = 0.225$, $p = 0.107$).

Discussion

4.1 Surface water nitrogen pollution in national and international

The median surface water total N concentrations under agro- and oasis agro- ecosystems of the CERN were lower than those in the Tai Lake region (6.4 mg·L^{-1}) [29], but similar to those in surface water in northern China [30,31]. Compared with studies in other countries, the total N concentrations for this study were higher than those of surface water for a Japanese agro- ecosystem [32], but similar to the total N concentrations of the Calapooia River Basin in a Western Oregon agro- ecosystem, where they ranged from 0.5 to 43 mg·L^{-1}[33]. Generally, total N concentrations in northern and northwestern regions were higher than in the southern region of China. A spatial assessment of lakes in China from 1990 to 2010 showed that total N concentrations decreased with rising latitude, but were not related to longitude [12]. Different farming practices, irrigation practices and crop rotations may influence N leaching [34]. For instance, total N losses due to leaching were 9.875 kg·ha^{-1} in the wheat growing season, but were only 1.868 kg N·ha^{-1} in the rice growing season [29]. Li et al [35]. However, reported that nitrate-N concentrations in surface water from rice growing land were significantly higher than those in corn land. In addition, the dilution effect of precipitation could decrease the total N concentrations in the southern region, as precipitation is much higher than in the northern region.

The total N concentrations in surface water under the forest ecosystems were lower than in agro- and oasis agro- ecosystems. This result is similar to what was observed for surface water total phosphorus concentrations in the same study area [36]. Larned et al. [37] also indicated that dissolved N concentrations in pastoral and urban ecosystems were 2 – 7 times higher than in native and plantation forest ecosystems. Total N concentrations were higher in Chinese typical forest ecosystems than in surface water in Japanese forest ecosystems, where they ranged from 0.01 to 1.3, with a median value of 0.14 mg·L^{-1} [38]. In the US, total N concentrations in surface water in northern Californian national forests ranged from 0.03 to 0.1 mg·L^{-1} [39]; these concentrations are also lower than those in China.

Table 2. TN concentrations and background information of still and flowing surface water under the 9 forest ecosystems.

Ecotype	Station	Altitude (m)	Mean Precipitation (mm)	Soil type	Vegetation	Still surface water				Flowing surface water			
						n	Median	Max	>1.0 mg·L⁻¹ frequency (%)	n	Median	Max	>1.0 mg·L⁻¹ frequency (%)
Humid, Sub- humid Areas in Temperate Zone	Changbai	740	695	Dark Brown soil	Broad-leaved korean pine forest	—	—	—	—	9(1)	1.0	1.4	44
Humid, Sub-humid Areas in Warm Temperate Zone	Beijing	1248	612	Mountain brown soils	Man-made Pinus tabulaeformis Forests	—	—	—	—	9(1)	1.6	5.7	56
Humid Areas in North Sub-tropical Zone	Maoxian	1826	825	Cinnamon soil	Warm temperate coniferous forest	—	—	—	—	8(1)	0.7	1.0	13
	Gongga	2950	1974	Podzolie brown taiga soils	Sulbalpine dark coniferous forest	—	—	—	—	54(7)	0.3	0.8	0
	Huitong	541	1079	Yellow soil	Broad-leaved Trees Mixed Forests	11(1)	1.5	3.5	100	13(1)	1.8	3.7	92
Humid Areas in South Sub- tropical Zone	Ailao	2481	1880	Yellow Brown soil	Subtropical mid mountain humid evergreen broadleaved forest	18(1)	0.3	0.9	0	19(1)	0.2	0.5	0
	Heshan	90	1927	Ferrisols	Acacia mangium pure forests	12(1)	0.8	3.3	42	19(1)	1.6	7.5	63
	Dinghu	90	1700	Lateritic Red Soil	Broad-leaved Trees Mixed Forests	30(3)	5.2	9.3	100	10(1)	1.3	7.0	70
Humid Areas in tropical Zone	Banna	560	1539	Red soil	Tropical seasonal rain forest	12(1)	0.3	0.5	0	23(1)	0.2	0.9	0

Note: The "n" values represent the number of sampling sites and the monitoring sites (within brackets). "–"s illustrate that no detection data were available.
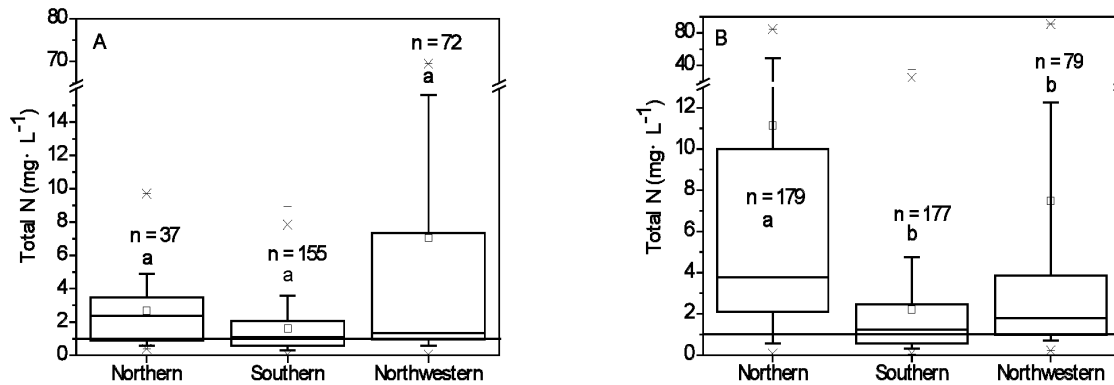doi:10.1371/journal.pone.0092850.t002

Figure 3. Total nitrogen concentrations of still surface water (A) and flowing surface water (B) under agro- and oasis agro-ecosystems in northern, southern and northwestern areas. The illustrations about Box plots are the same as those in figure 2.
doi:10.1371/journal.pone.0092850.g003

Increasing N concentrations have been observed in many watersheds in the US, Europe, New Zealand and Canada because of land use change, atmospheric deposition, fertilizer application and burning fossil fuels [40–43]. Total N at the Konza Prairie Biological Station (Konza), located in the Flint Hills region of the Great Plains in Kansas, increased from 0.4 mg·L^{-1} to 1.2 mg·L^{-1} due to land use change [44]. There are concerns about N exports from streams in the US midwest because of excessive nutrient enrichment and eutrophication [45,46]. In agro- ecosystems in Baltimore, the annual total N exports were about 30 kg N ha^{-1} during 2005 [47]. The annual total N export rates from the world's rivers in different geographical areas between 76 °N and 43 °S ranged from 1 – 20 630 kg N ha^{-1} year^{-1} [48].

4.2 Factors influencing TN in surface water

Climate, hydrology, soil properties, geomorphology, topography, soil cover and land use are the main factors that influence nutrients in stream water [49-51]. As we were restricted by the sampling frequency, we did not explore relationships between mean annual precipitation and total N in surface waters. However, a significant inverse relationship between total N concentrations and precipitation was reported by a study which examined seasonal variation of total N in the Beijing urban ecosystem [52].
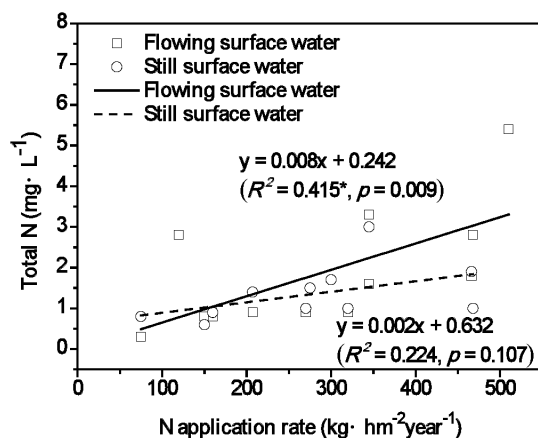

Figure 4. Correlations of total nitrogen concentrations and soil N fertilizer application rates in agro- and oasis agro- ecosystems ($p < 0.05$, n = 15). The total nitrogen concentrations in this figure were the median values of agro- and oasis agro- ecosystems.
doi:10.1371/journal.pone.0092850.g004

Land use change can influence N concentrations. The N concentrations in rural residential areas and cultivated land were much higher than those in grass and forest ecosystems [53,54]. Kvítek et al. [55] reported that, as ploughed land in the catchment increased, nitrate contamination of surface water also increased. Studies of N pollution in the US and the Netherlands showed that 60% – 80% of N came from agricultural non-point sources [56–58]. Alvarez-Cobelas [48] also reported that exports of total N were four times higher from catchments dominated by crops than from forested catchments.

Nitrogen fertilizer, as a non-point source pollutant, is a critical source of pollution in agro- and oasis agro- ecosystems. Surface water N pollution in agro- ecosystems was closely related to agricultural activity. China surpassed the US and the European Union in its production and use of N fertilizers in approximately 2000. However, less than half of the fertilizer N applied in China was taken up by crops [23]. The rest was largely lost to the environment in gaseous (NH_3, NO, N_2O and N_2) or dissolved (NH_4^+ and NO_3^-) forms [59,60]. Leaching is the most important pathway for water eutrophication and poor N fertilizer management could lead to N leaching into the drainage water through run off and drainage [61,62]. In spite of considerable controls on point source pollution, water quality standards have not reached the criterion of the US and European countries due to the increasing contribution of non-point pollution [63]. In general, the waters under the agro- ecosystems have been widely polluted by total N, while only been polluted by total P in a few agro- ecosystem sites [36]. Therefore, the surface water eutrophication under the agro-ecosystems was P limited, which indicated that N fertilizer should generally be reduced and P fertilizer should only be controlled in the P polluted areas of the agro-ecosystems.

Soil textures differ according to location; therefore, losses of N fertilizer through leaching, drainage and runoff are also variable [64]. The relatively high total N concentrations in surface water in northwestern regions may be attributed to soil types. Studies in France have shown that leached N varied from 31 mg·L^{-1} in deep loamy soils to 92 mg·L^{-1} in shallow sandy soils [34]. Soils in the northwestern region of China are mainly aeolian sandy soils, and have low water-holding capacity, meaning that N fertilizer is likely to be lost from soil to surface water. Combined with frequent irrigation, serious soil losses in this region may contribute to the high total N concentrations [65].

Atmospheric N deposition may be an important source of surface water N [66]. While its effects may be weaker than other factors [69], it may still aggravate water eutrophication and affect

ecosystem stability [67,68]. The 9 forest ecosystems in our study showed eutrophication tendencies, especially the Beijing, Huitong, Heshan and Dinghushan forest ecosystems. The reactive nitrogen (N_r) species emitted during fossil fuel combustion, have resulted in some of the most pronounced air pollution ever recorded in China, and the increased N_r emissions may have influenced atmospheric N deposition near the study areas. Research has shown that N deposition in Dinghushan and Beijing exceeds $30 \text{ kg} \cdot \text{ha}^{-1} \text{ year}^{-1}$. These rates are higher than those recorded for the other forest ecosystems in China [70–72]. Therefore, the higher atmospheric N deposition may contribute to the higher total N concentrations in the Beijing and Dinghu forest ecosystems.

Conclusions

The total N concentrations of surface water under agro- and oasis agro- ecosystems were much higher than those under forest ecosystems. About 50% of median total N concentrations exceeded $1.0 \text{ mg} \cdot \text{L}^{-1}$. There was an obvious spatial pattern in surface water total N concentrations, with much higher total N concentrations in the northern region of China, especially in flowing surface water. The surface water of some agro- ecosystems (Ansai, Changwu, Fengqiu, Hailun) and oasis agro- ecosystems (Cele, Linze, Eerduosi) were severely polluted by N with exceedance ($> 1.0 \text{ mg} \cdot \text{L}^{-1}$) frequencies greater than 50%. Fertilizer applications were the main source of N pollution in the flowing surface water in agro- and oasis agro- ecosystems.

Author Contributions

Conceived and designed the experiments: ZX XZ XS GY. Performed the experiments: ZX XZ XS. Analyzed the data: ZX XZ JX. Contributed reagents/materials/analysis tools: JX. Wrote the paper: ZX XZ JX GY XT XS GY.

References

1. Lewis WM Jr (2011) Global primary production of lakes: 19$^{\text{th}}$ Baldi Memorial Lecture. Inland Waters 1(1): 1–28.
2. OECD (1982) Eutrophication of Waters-monitoring, Assessment and Control; Paris, France: Organization for Economic Co-operation and Development.
3. Tian YH, Yin B, Yang LZ, Yin SX, Zhu ZL (2007) Nitrogen runoff and leaching losses during rice-wheat rotations in Taihu Lake region, China. Pedosphere 17(4): 445–456.
4. Lassaletta L, García-Gómez H, Gimeno BS, Rovira JV (2009) Agriculture-induced increase in nitrate concentrations in stream waters of a large Mediterranean catchment over 25 years (1981–2005). Science of the Total Environment 407(23): 6034–6043.
5. Mian IA, Begum SM, Ridealg M, McClean CJ, Cresser MS (2010) Spatial and temporal trends in nitrate concentration in the river Derwent, North Yorkshire and its need for NVZ status. Science of the Total Environment 408(4):702–712.
6. US EPA (2002) National Recommended Water Quality Criteria: 2002. Office of Water, EPA-822-R-02–047, U.S. Environmental Protection Agency, Washington DC. http://www.epa.gov/waterscience/standards/wqcriteria.html.
7. China Ministry of Environmental Protection, China General Administration of Quality Supervision and Quarantine (2002) Environmental Quality Standards for Surface Water. GB3838-2002.
8. Yang AL, Zhu YM (1999) Study on nonpoint source pollution in surface water environment. Advance of Environmental Sciences 7(5):60–67.
9. Bao QS, Wang HD (1996) Perspective on water environment and nonpoint source pollution in China. Geographical Sciences 16(1): 66–71.
10. Xu H, Liu ZP, Jiao JG, Yang LZ (2008) Nitrogen pollution status of various types of passing-by water bodies in upper reaches of Taihu Lake. Chinese Journal of Ecology, 27(1): 43–49.
11. Liu ZD, Yu XG, Wang ZX (2003) The current water pollution of Taihu drainage basin and the new management proposals. Journal of Natural Resources 16(4): 467–474.
12. Cai LY, Li Y, Zheng ZH (2010) Temporal and spatial distribution of nitrogen and phosphorus of lake systems in China and their impact on eutrophication. Earth and Environment 38 (2):235–241.
13. Wang LX, Lü JL, Zhuang SY, Hu ZY (2009) Characteristics of phosphorus adsorption on paddy soil and river sediment in east China. Soils, 41(3):402–407.
14. He B, Oki K, Wang Y, Oki T (2009b) Using remotely sensed imagery to estimate potential annual pollutant loads in river basins. Water Science and Technology 60 (8): 2009–2015.
15. He B, Oki T, Kanae S, Mouri G, Kodama K, et al. (2009a) Integrated biogeochemical modelling of nitrogen load from anthropogenic and natural sources in Japan. Ecological Modelling 220(18): 2325–2334.
16. Galloway JN, Cowling EB (2002) Reactive nitrogen and the world: 200 years of change. Ambio 31(2): 64–71.
17. Galloway JN, Schlesinger WH, Levy II H, Michaels A, Schnoor JL (1995) Nitrogen fixation: anthropogenic enhancement-environmental response. Global Biogeochemical Cycles 9(2): 235–252.
18. Vitousek PM, Aber JD, Howarth RW, Likens GE, Matson PA, et al. (1997) Human alteration of the global nitrogen cycle: Sources and consequences. Ecological Applications 7(3):737–750.
19. Isermann K (1991) Share of agriculture in nitrogen and phosphorus emissions into the surface waters of Western Europe against the background of their eutrophication. Fertilizer Research 26(1–3):253–269.
20. National Research Council (1993b) Soil and water quality: an agenda for agriculture. National Academy Press, Washington, D.C., USA.
21. Smil V (1999) Nitrogen in crop production: An account of global flows. Global Biogeochemistry Cycles 13(2): 647–662.
22. Zhang D, Li G, Yang YS, Zhang X, Guo H (2009) Bio-geological processes of nitrogen transport and transformation in the aeration zone and aquifer. Hydrological Sciences Journal 54(2): 316–326.
23. Zhang FS, Wang YQ, Zhang WF, Cui ZL, Ma WQ, et al. (2008) Nutrient use efficiencies of major cereal crops in China and measures for improvement. Acta Pedologica Sinica 45(5):915–924.
24. Hu YT, Liao Qian JH, Wang SW, Yan XY (2011) Statistical analysis and estimation of N leaching from agricultural fields in China. Soils 43 (1): 19–25.
25. Letcher RA, Giupponi C (2005) Policies and tools for sustainable water management in the European Union. Environmental Modeling & Software 20(2):93–98.
26. Davies JM, Mazumder A (2003) Health and environmental policy issues in Canada: the role of watershed management in sustaining clean drinking water quality at surface sources. Journal of Environmental Management 68(3): 273–286.
27. The Central People's Government of the People's Republic of China (2012) Water pollution prevention program of Yangtze River basin (2011-2015). Gazette of the State Council of the People's Republic of China 11:51–60.
28. Yuan GF, Tang DY, Sun XM (2007) Water Monitoring Protocol of Chinese Ecosystem Research Network. Beijing: China Environmental Science Press.
29. Xie YX, Xiong ZQ, Xing GX, Sun GQ, Zhu ZL (2007) Assessment of nitrogen pollutant sources in surface waters of Taihu Lake region. Pedosphere 17(2): 200–208.
30. Chen LD, Peng HJ, Fu BJ, Qiu J, Zhang SR (2005) Seasonal variation of nitrogen-concentration in the surface water and its relationship with land use in a catchment of northern China. Journal of Environmental Science 17(2): 224–231.
31. Meng LY, Shi MW, Yan XX, Lu H, Zhu XL (2009) Evaluation of Nonpoint Source Pollution on Nitrogen and Phosphorus of Surface Water of Hutuo River Valley under Background State. Geography and Geo-information Science 25(3): 95–98.
32. Mouri G, Takizawa S, Oki T (2011) Spatial and temporal variation in nutrient parameters in stream water in a rural-urban catchment, Shikoku, Japan: Effects of land cover and human impact. Journal of Environmental Management 92(7):1837–1848.
33. Mueller-Warrant GW, Griffith SM, Whittaker GW, Banowetz GM, Pfender WF, et al. (2012) Impact of land use patterns and agricultural practices on water quality in the Calapooia River Basin of western Oregon. Journal of Soil and Water Conservation 67 (3): 183–201.
34. Beaudoin N, Saad JK, Laethem CV, Machet JM, Maucorps J, et al. (2005) Nitrate leaching in intensive agriculture in Northern France: Effect of farming practices, soils and crop rotations. Agriculture, Ecosystems and Environment 111(1–4): 292–310.
35. Li J, Lu WX, Zeng XK, Yuan JH, Yu FR (2010) Analysis of spatial-temporal distributions of nitrate-N concentration in Shitoukoumen catchment in northeast China. Environmental Monitoring and Assessment 169(1–4): 335–345.
36. Xie J, Zhang XY, Xu ZW, Sun XM, Ballantine D (2013) Total Phosphorus concentrations in surface water of Typical Chinese Ecosystems, 2004–2010. Frontiers of Environmental Science & Engineering, DOI: 10.1007/s11783-013-0601-5.
37. Larned ST, Scarsbrook MR, Snelder TH, Norton NJ, Biggs BJF (2004) Water quality in low-elevation streams and rivers of New Zealand: recent state and

trends in contrasting land-cover classes. New Zealand Journal of Marine and Freshwater Research 38(2): 347–366.

38. Zhang Z, Fukushima T, Shi PJ, Tao FL, Onda Y, et al. (2008) Baseflow concentrations of nitrogen and phosphorus in forested headwaters in Japan. Science of the Total Environment 402(1): 113–122.

39. Roche LM, Kromschroeder L, Atwill ER, Dahlgren RA, Tate KW (2013) Water quality conditions associated with cattle grazing and recreation on national forest lands. PLoS ONE 8(6): e68127.

40. Stoddard JL (1994) Long-term changes in watershed retention of nitrogen: Its causes and aquatic consequences. Environmental Chemistry of Lakes and Reservoirs 237: 223–284.

41. Boesch DF, Brinsfield RB, Magnien RE (2001) Chesapeake Bay eutrophication: Scientific understanding, ecosystem restoration, and challenges for agriculture. Journal of Environment Quality 30(2): 303–320.

42. Dayyani S, Prasher SO, Madani A, Madramootoo CA (2012) Impact of climate change on the hydrology and nitrogen pollution in a tile-drained agricultural watershed in eastern Canada. Transactions of the Asabe 55(2): 389–401.

43. Duggan IC, Collier KJ, Champion PD, Croker GF, Davies-Colley RJ, et al. (2002) Ecoregional differences in macrophyte and macroinvertebrate communities between Westland and Waikato: are all New Zealand lowland streams the same? New Zealand Journal of Marine and Freshwater Research 36(4): 831–845.

44. Kemp MJ, Dodds WK (2001) Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams. Biogeochemistry 53(2): 125–141.

45. Dodds WK, Welch EB (2000) Establishing nutrient criteria in streams. Journal of the North American Benthological Society 19(1): 186–196.

46. US Environmental Protection Agency (USEPA) (2000) US Environmental Protection Agency (USEPA) Nutrient criteria technical guidance manual: rivers and streams, EPA-822-B-00-002. US Government Printing Office, Washington, DC.

47. Kaushal SS, Groffman PM, Band LE, Elliott EM, Shields CA, et al. (2011) Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environmental Science & Technology 45(19): 8225–8232.

48. Alvarez-Cobelas M, Angeler DG, Sánchez-Carrillo S (2008) Export of nitrogen from catchments: A worldwide analysis. Environmental Pollution 156(2): 261–269.

49. Ometto JPHB, Martinelli LA, Ballester MV, Gessner A, Krusche AV, et al. (2000) Effects of land use on water chemistry and macroinvertebrates in two streams of Piracicaba river basin, southeast Brazil. Freshwater Biology 44(2): 327–337.

50. McKee LJ, Eyre BD, Hossain S, Pepperell PR (2001) Influence of climate, geology and humans on spatial and temporal nutrient geochemistry in the subtropical Richmond River catchment, Australia. Marine and Freshwater Research 52(2): 235–248.

51. Likens GE, Buso, DC (2006) Variation in streamwater chemistry throughout the Hubbard Brook Valley. Biogeochemistry 78(1): 1–30.

52. Ren YF, Xu ZW, Zhang XY, Wang XK, Sun XM, et al. (2013) Nitrogen pollution and source identification of urban ecosystem surface water in Beijing. Frontiers of Environmental Science & Engineering, DOI: 10.1007/s11783-012-0474-z.

53. Zhu B, Wang T, Xu TP, Kuang FH, Luo ZX, et al. (2006) Nonpoint-source nitrogen movement and its environmental effects in a small watershed in hilly area of purple soil. Journal of Mountain Science 24(5):601–606.

54. Zhang XY, Xu ZW, Sun XM, Dong WY, Ballantine DJ (2013) Nitrate in shallow groundwater in typical agricultural and forest ecosystems in China, 2004–2010. Journal of Environmental Sciences 25(5): 1007–1014.

55. Kvítek T, Žlábek P, Bystřický V, Fučík P, Lexa M, et al. (2009) Changes of nitrate concentrations in surface waters influenced by land use in the crystalline complex of the Czech Republic. Physics and Chemistry of the Earth 34(8–9):541–551.

56. Boer PM (1996) Nutrient Emissions from agriculture in the Netherlands: causes and remedies. Water Science Technology 33(4–5): 183–189.

57. Kronvang B, Graesbøll P, Larsen SE, Svendsen LM, Andersen HE (1996) Diffuse nutrient losses in Denmark. Water Science technology 33(4–5):81–88.

58. Shepard R (2000) Nitrogen and phosphorus management on Wisconsin farms: Lessons learned for agricultural water quality programs. Journal of Soil and Watershed Conservation 55(1): 63–68.

59. Zhu ZL, Chen DL (2002). Nitrogen fertilizer use in China: contributions to food production, impacts on the environment and best management strategies. Nutrient Cycling in Agroecosystems 63(2–3): 117–127.

60. Ju XT, Xing GX, Chen XP, Zhang SL, Zhang LJ, et al. (2009). Reducing environmental risk by improving N management in intensive Chinese agricultural systems. Proceedings of the National Academy of Sciences of the United States of America 106(9): 3041–3046.

61. Barton L, Colmer TD (2006) Irrigation and fertilizer strategies for minimising nitrogen leaching from turfgrass. Agricultural Water Management 80(1–3):160–175.

62. Cang HJ, Xu LF, Li Z, Ren H (2004) Nitrogen losses from farmland and agricultural nonpoint source pollution. Tropical Geography, 24: 332–336.

63. Novotny V (2005) Diffuse pollution from agriculture in the world. In: Proceedings from the International Workshop on Where Do Fertilizers Go? Belgirate, Italy.

64. Nie SW, Gao W, Chen YQ, Sui P, Eneji AE (2009) Review of current status and research approaches to nitrogen pollution in farmlands. Agricultural Sciences in China 8(7):843–849.

65. Zhao SZ (2003) Ecological environmental problems resulting from exploitation of water resources in Northwest China. Northwestern Geology 36(3):92–96.

66. Krusche AV, de Camargo PB, Cerri CE, Ballester MV, Lara LBLS, et al. (2003). Acid rain and nitrogen deposition in a sub-tropical watershed (Piracicaba): ecosystem consequences. Environmental Pollution 121(3): 389–399.

67. Schindler DW (1988) Effects of acid rain on freshwater ecosystems. Science 239(4836): 149–157.

68. Bergström A, Jansson M (2006) Atmospheric nitrogen deposition has caused nitrogen enrichment and eutrophication of lakes in the northern hemisphere. Global Change Biology 12(4): 635–643.

69. Gorham E (1998). Acid deposition and its ecological effects: a brief history of research. Environmental Science & Policy 1(3): 153–166.

70. Huang ZL, Ding MM, Zhang ZP, Yi WM (1994) The hydrological processes and nitrogen dynamics in a monsoon evergreen broad-leafed forest of Dinghushan. Acta Phtoecologica Sinica 18(2): 194–199.

71. Zhou GY, Yan JH (2001) The influence of region atmospheric precipitation characteristics and its element inputs on the existence and development of Dinghushan forest ecosystems. Acta Ecologica Sinica 21(12): 2002– 2012.

72. Zhang Y, Liu XJ, Zhang FS, Ju XT, Zhou GY, et al. (2006) Spatial and temporal variation of atmospheric nitrogen deposition in North China Plain. Acta Ecologica Sinica 26(6): 1633–1638.