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

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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- ecosystems (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 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$^{-1}$ (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 ecosystems 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,
leaching were 5.6 – 9.0 kg$\text{ha}^{-1}\text{year}^{-1}$ of surplus N [22]. However, less than half of the fertilizer N applied in China is gradually increased to 130 kg N fertilizer in the world. The average annual application rate of N in China’s total N application [24].

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 flow monitoring sites of the CERN were chosen to represent typical agricultur- forest ecosystems, on water quality. Twenty-eight 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, Yuncheng, Fengqiu), and (2) the Loess Plateau (An sai 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, Yuncheng, Fengqiu, An sai 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 cropping, 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 flow 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 (An sai, Fengqiu, and Chang shu), 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 persul fate 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 ecosystems.
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\(\text{L}^{-1}\) (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 (10\textsuperscript{th} and 90\textsuperscript{th} percentiles in box plots) in the agro-, oasis agro- and forest ecosystems ranged between 0.4 – 8.7 mg\(\text{L}^{-1}\), 0.7 – 15.2 mg\(\text{L}^{-1}\), and 0.2 – 6.6 mg\(\text{L}^{-1}\), respectively for still surface water (Figure 2(A)), and 0.4 – 10.9 mg\(\text{L}^{-1}\), 0.6 – 11.6 mg\(\text{L}^{-1}\), and 0.2 – 3.3 mg\(\text{L}^{-1}\), 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\(\text{L}^{-1}\) and 0.5 mg\(\text{L}^{-1}\), respectively. These concentrations were significantly lower than those of still (1.5 mg\(\text{L}^{-1}\) and 1.8 mg\(\text{L}^{-1}\), respectively) and flowing surface water (2.4 mg\(\text{L}^{-1}\) and 1.8 mg\(\text{L}^{-1}\), 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\(\text{L}^{-1}\) [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 \((> 1.0 \text{mg}\text{L}^{-1})\) 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\(\text{L}^{-1}\), 0.3 – 3.5 mg\(\text{L}^{-1}\), and 0.2 – 6.6 mg\(\text{L}^{-1}\), respectively for still surface water (Figure 3(A)), and 0.4 – 10.9 mg\(\text{L}^{-1}\), 0.6 – 11.6 mg\(\text{L}^{-1}\), and 0.2 – 3.3 mg\(\text{L}^{-1}\), respectively 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\(\text{L}^{-1}\)) were significantly higher than those in the southern (1.2 mg\(\text{L}^{-1}\)) and northwestern regions (1.8 mg\(\text{L}^{-1}\)) \((p < 0.05)\).

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\(\text{L}^{-1}\) [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\(\text{L}^{-1}\) [7]. About 50% of

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**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
### 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          |
| 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    |
|                 | Hallun      | 500-600                 | Black Soil          | Wheat-Maize rotation          | 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    |
|                 | Qianyanzhou | 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    |
| North-West Akesu| 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
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 Anais, Fengjuz, 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, Qiyanzhou, Taoyuan, Yingtai) 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 \(r^2 = 0.225, p = 0.107\).

4.1 Surface water nitrogen pollution in national and international

The median surface water total N concentrations under agroand 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 Changbai       | Beijing                  | 1248          | 612                     | Mountain brown soils       | Man-made Pinus tabulaeformis Forests    | --      | --     | -- | --                          | 9(1)    | 1.0     | 1.4 | 44                          |
| Areas in Temperate Zone         |                          |               |                         |                            |                                          |                     |                      |     |                                 |
| Humid, Sub-humid Areas in Warm  | Maoxian                  | 1826          | 825                     | Cinnamon soil              | Warm temperate coniferous forest        | --      | --     | -- | --                          | 8(1)    | 0.7      | 1.0 | 13                          |
| Temperate Zone                  |                          |               |                         |                            |                                          |                     |                      |     |                                 |
| Humid Areas in North Sub- tropical Zone | Dongga                  | 2950          | 1974                    | Podzolie brown taiga soils | Subalpine dark coniferous forest         | 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
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].

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]. Kvitek 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\(_2\)O 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) species emitted during fossil fuel combustion, have resulted in some of the most pronounced air pollution ever recorded in China, and the increased N emissions may have influenced atmospheric N deposition near the study areas. Research has shown that N deposition in Dinghushan and Beijing exceeds 30 kg ha\(^{-1}\) 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 mgL\(^{-1}\). 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, Et реша) were severely polluted by N with exceedance (\(>1.0\) mgL\(^{-1}\)) frequencies greater than 50%. Fertilizer applications were the main source of N pollution in the flowing surface waters in agro- and oasis agro-ecosystems.

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Author Contributions

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

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