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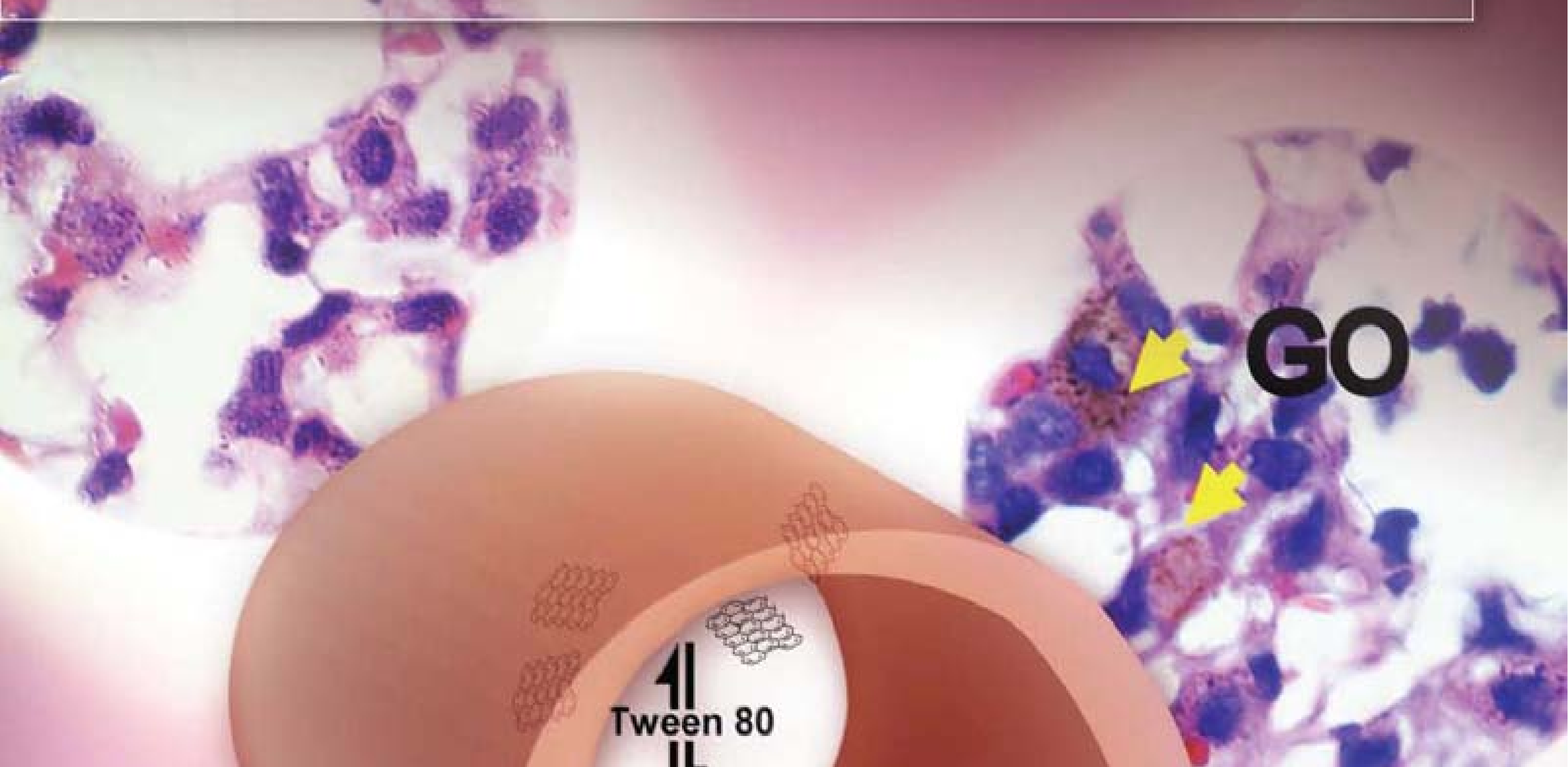

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Nitrate in shallow groundwater in typical agricultural and forest ecosystems in China, 2004–2010

Xinyu Zhang[1], Zhiwei Xu[1], Xiaomin Sun[1,*], Wenyi Dong[1], Deborah Ballantine[2]

1. Key Laboratory of Ecosystem Network Observation and Modelling, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China. E-mail: zhangxy@igsnrr.ac.cn
2. National Institute of Water and Atmospheric Research, Hamilton, New Zealand

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Abstract

The nitrate-nitrogen (NO_3^--N) concentrations from shallow groundwater wells situated in 29 of the Chinese Ecosystem Research Network field stations, representing typical agro- and forest ecosystems, were assessed using monitoring data collected between 2004 and 2010. Results from this assessment permit a national scale assessment of nitrate concentrations in shallow groundwater, and allow linkages between nitrate concentrations in groundwater and broad land use categories to be made. Results indicated that most of the NO_3^--N concentrations in groundwater from the agro- and forest ecosystems were below the Class 3 drinking water standard stated in the Chinese National Standard: Quality Standard for Ground Water ($\leq$ 20 mg/L). Over the study period, the average NO_3^--N concentrations were significantly higher in agro-ecosystems (4.1 ± 0.33 mg/L) than in forest ecosystems (0.5 ± 0.04 mg/L). NO_3^--N concentrations were relatively higher (> 10 mg N /L) in 10 of the 43 wells sampled in the agricultural ecosystems. These elevated concentrations occurred mainly in the Ansai,Yucheng, Linze, Fukang, Akesu, and Cele field sites, which were located in arid and semi-arid areas where irrigation rates are high. We suggest that improvements in N fertilizer application and irrigation management practices in the arid and semi-arid agricultural ecosystems of China are the key to managing groundwater nitrate concentrations.

Key words: Chinese Ecosystem Research Network; shallow groundwater; agricultural; forest ecosystems; nitrate concentration

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Introduction

It is universally recognized that nitrate contamination of groundwater can affect human health. Ingestion of NO_3^- in drinking water can lead to Methemoglobinemia in infants (Macilwain, 1995; Knobeloch et al., 2000). It can also increase the incidence of various cancers (Gulis et al., 2002). Because of the risks to human health associated with elevated nitrate concentrations, and to help identify at-risk waters, international and national thresholds have been established for nitrate in ground and surface waters. For example, the World Health Organization (WHO) drinking water criterion states that the NO_3^- concentration should be less than 50 mg/L (i.e. NO_3^--N of 11.3 mg/L) (WHO, 2006), while the US EPA maximum permissible concentration for drinking water is 10 mg/L of NO_3^--N (US EPA, 2002). In China the permissible NO_3^--N concentration in groundwater is 20 mg/L (Department of Geology and Mineral Resources, 1994), while in surface water and central drinking water sources it is less than 10 mg/L (China Ministry of Environmental Protection, China General Administration of Quality Supervision and Quarantine, 2002). Although the national and international guideline values are higher, it has been reported that long-term exposure to nitrate at concentrations of 2 to 4 mg/L in drinking waters has possible links to bladder and ovarian cancer (Weyer et al., 2001).

It is assumed that groundwater closer to the soil surface is at greater risk of contamination by nitrate pollution. According to the US EPA and WHO criteria, nitrate pollution of shallow groundwaters under agricultural ecosystems is widely reported internationally (Burow et al., 2010; Ju et al., 2006; Macilwain, 1995; Spalding and Exner, 1993; Zhang et al., 1996; Zhu et al., 2003). Monitoring data from the US indicates that nitrate concentrations are highest in shallow groundwater beneath agricultural land with well-drained soils and oxic geochemical conditions, and lowest in deep groundwater with reduced conditions, or where groundwater is older and concentrations reflect a historically low nitrogen (N) application rate (Burow et al., 2010). A study of decadal-scale changes of nitrate

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* Corresponding author. E-mail: sunxm@igsnrr.ac.cn

concentrations in groundwater in the U.S. demonstrated that nitrate concentrations increased in response to the increased use of N fertilizer, and that nitrate in groundwater from wells with reduced conditions had significantly smaller decadal-scale changes in nitrate concentrations than oxidized and mixed waters (Rupert, 2008). However, elevated groundwater nitrate concentrations are highly variable across the landscape and it is sometimes difficult to link high nitrate concentrations in groundwater directly to land use activities and N inputs at the surface (Liu et al., 2005; Morari et al., 2012). Therefore, identification of nitrate vulnerable zones can help in the development of effective management practices for groundwater protection.

Groundwater resources play an important role in human activity. In China, the groundwater supply accounts for about 18% of the total water supply, however dependence on groundwater supplies varies regionally. For example, in northern China, 65% of domestic water, 50% of industrial water and 33% of irrigation water comes from groundwater resources and out of 657 cities of China, more than 400 use groundwater as a source of drinking water (China Ministry of Land and Resources and China Ministry of Environmental Protection, 2011).

However, human alterations to the N cycle have led to approximately a doubling of the N input rates into the terrestrial N cycle, and these rates are still increasing (Vitousek et al., 1997). Globally, fertilizers are identified as a principle source of nitrate in groundwaters in intensely cultivated areas. In China, the average annual N-fertilizer application is over 200 kg N/ha, and high groundwater nitrate concentrations have been identified in agricultural ecosystems, especially in northern China (Zhang et al., 1996; Ju et al., 2006; Huang et al., 2011). Excessive N input was more pronounced in intensive vegetable ecosystems, where fertiliser applications of up to 1881 kg N/ha have been recorded, leading to more serious nitrate pollution of groundwater (Ju et al., 2006). However, manure and crop residues are also thought to contribute significantly to nitrate in groundwater (Savard et al., 2010). An identification of nitrate vulnerable ecosystems constitutes a key step in supporting informed decisions for protecting water resources.

To date, there has been no comprehensive national assessment of groundwater nitrate concentrations in China. Previous studies in China have focused on localized areas. Little work has been done to systematically record nitrate concentrations over extended periods of time from a wide geographical area and different land use types. While data exists for single sampling events, we know that this data may not be reliable, and cannot be assumed to be representative either in time or space, and therefore should be interpreted with care.

This study provides a national scale assessment of groundwater nitrate concentrations in representative agro- and forest ecosystems of China, using the Chinese Ecosystem Research Network (CERN) as the monitoring framework, and will contribute to our understanding of the extent of nitrate contamination of shallow groundwater.

1 Methods

1.1 Monitoring sites

Groundwater quality monitoring of the CERN focuses on assessing the water quality of shallow groundwater beneath typical terrestrial ecosystems, i.e. agriculture and forest ecosystems. The monitoring network has been designed according to the ‘representativeness’, ‘consistency’, and ‘long-term’ criteria (Yuan et al., 2007) so that groundwater monitoring for nitrate in the Chinese agro- and forest ecosystems reflects recent N inputs by N application and deposition to the land surface of these different ecosystems.

Twenty agro-ecosystems, distributed across a range of climatic zones, were selected as study areas. These agro-ecosystems were representative of (1) humid and sub-humid regions in the temperate zone of north-eastern China (Hailun, Sanjiang, Shenyang) and the warm temperate zone of northern China (Luancheng, Yucheng, Fengqiu), (2) humid areas in the sub-tropical zone in southern China (Changshu, Yanting, Taoyuan,Yingtan, Qianyanzhou), (3) arid and semi-arid areas in the warm temperate zone of northwest and north China (Naiman, Shapotou, Linze, Fukang, Akesu, Cele), (4) the loess plateau (Ansai and Changwu), and (5) the Tibet plateau (Lasa) (**Fig. 1**). Land use was mainly crop growing, including wheat, corn, soybean, rice and cotton (**Table 2**).

Nine forest ecosystems were selected to assess the possible effect of N deposition on shallow groundwater in forest areas, and to act as control to compare with the agro-ecosystems. The forest sites were located along the north-south transect of eastern China (**Fig. 1**), and were representative of old native forests and secondary forests without any fertilization. The monitoring wells were selected using consistent criteria and standards (Fu et al., 2010).

For this study, 62 groundwater monitoring wells were selected as being representative of groundwater quality in the selected agro- and forest ecosystems as follows: 43 wells under agro-ecosystems and 19 wells beneath forest ecosystems.

As well as representing typical land use types, a wide range of physical conditions was also represented in the groundwater wells selected. The altitude of the selected monitoring wells ranges from 3 m (Changshu) to 3688 m (Lasa) (80°43′39″–133°18′03″E, 18°13′01″–47°27′15″N). The average rainfall ranges from approximately 43 mm (Cele) to 1956 mm (Dinghushan) per year (Yu et al., 2008), and the average temperature ranges from 1.5° in the north (Hailun) to 21.8° in the southern areas (Xishuangbanna). The groundwater level varied from 0.2

Table 1 Nitrate-N concentrations and background information of the monitoring wells in the 9 forest ecosystems

Ecotype	Station name	Geographical location	Altitude (m)	Mean precipitation (mm)	Soil type	Vegetation	Average groundwater level (m)	n	NO_3^--N (mg/L) (mean ± SE)
Humid, sub-humid areas in temperate zone	Changbaishan	128°05′24′′E, 42°24′09′′N	740	695	Dark brown soil	Broad-leaved korean pine forest	8.8 ± 0.15	10	0.5 ± 0.09
Humid, sub-humid areas in warm temperate zone	Beijing	115°25′683′′E, 37°57′583′′N	1248	500–650	Mountain brown soil	Man-made pinus tabulaeformis forest	2.8 ± 0.22	21	0.7 ± 0.11
Humid areas in north sub-tropical zone	Maoxian	103°53′33′′E, 31°41′41′′N	1826	825	Cinnamon soil	Warm temperate coniferous forest	1.1 ± 0.04	10	0. 4 ± 0.13
	Gonggashan	101°59′51′′E, 29°34′27′′N	2950	1974	Podzolie brown taiga soil	sulbalpine dark coniferous forest	1.3 ± 0.07	14	0.9 ± 0.10
	Huitong	109°36′30′′E, 26°50′50.1′′N	541	1079	Yellow soil	Broad-leaved tree mixed forest	2.2 ± 0.29 0.9 ± 0.02	17 17	0.5 ± 0.08 0.6 ± 0.10
Humid areas in south sub- tropical zone	Ailaoshan	101°1′40.8′′E, 24°32′49.2′′N	2481	2350	Brown soil	Subtropical mid mountain humid evergreen broad leaved forest	3.9 ± 0.22 2.2 ± 0.15	12 16	0.1 ± 0.01 0.1 ± 0.01
	Heshan	113°30′32′′E, 23°08′31′′N	90	1761	Ferrisols	Acacia mangium pure forest	0.2 ± 0.05	11	0.6 ± 0.28
	Dinghushan	112°32′30′′E 23°10′21′′N	90	1996	Lateritic red soil	Broad-leaved tree mixed forest	1.8 ± 0.13	13	0.2 ± 0.06
Humid areas in tropical zone	Xishuangbanna	101°3′00′′E, 21°51′00′′N	560	1412	Red soil	Tropical seasonal rain forest	2.0 ± 0.11 0.9 ± 0.14	14 14	0.1 ± 0.01 0.1 ± 0.01

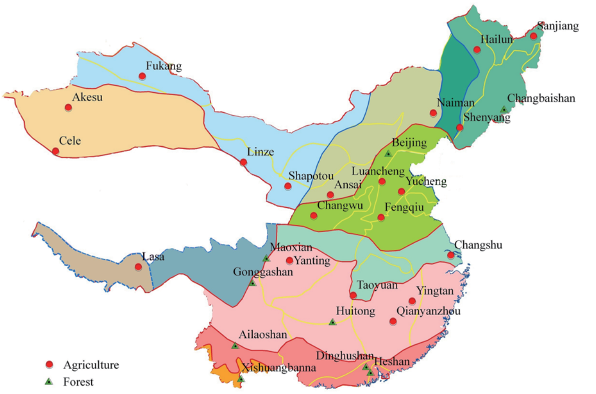

Fig. 1 Distribution map of the groundwater well network of the agro- and forest ecological stations in the Chinese Ecosystem Research Network (CERN). The different colors represent different ecotypes.

to 18.7 m (**Table 2**).

1.2 Survey of groundwater nitrate concentrations

CERN groundwater quality samples were collected according to the Water Monitoring Protocol of the Chinese Ecosystem Research Network (Yuan et al., 2007). The monitoring frequency at the wells 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 (Yuan et al., 2007). Nitrate was measured by ion chromatography or Pbenoldisulfonic acid spectrophotometry (BranLubbe, AA3, Germany). Total N was digested by potassium persulfate and measured by spectrophotometry (Shimadzu, UV-1700, Japan). Information about groundwater level, crop rotation, soil type and fertiliser application rate was recorded for each sampling event at each monitoring well.

A three-tier (i.e. the field stations, water sub-centre, and synthesis centre) data quality control and assurance system were used for the CERN monitoring data (Fu et al., 2010). The field stations do the groundwater sampling and analysis according to the laboratory quality control standards. The CERN water sub-centre supplies blind

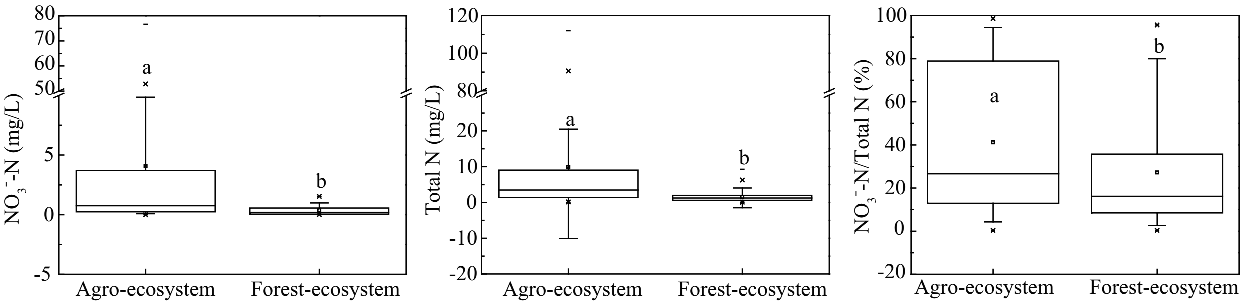

Fig. 2 Nitrate and total nitrogen concentrations, and ratios of nitrate concentration to total nitrogen concentrations in shallow groundwater of agro- and forest-ecosystems of CERN during 2004–2010. Boxplots illustrate the 25th, 50th, and 75th percentiles, the whisker indicates the 10th, 90th percentiles, the "–" indicates the max and minimum percentiles, the "×" indicates the 1th and 99th percentiles, the "□" indicates the mean values ($n = 504$ for agro-ecosystem, $n = 294$ for forest-ecosystem). Box plots labeled with different letters indicate that differences between the two ecosystem types are significant at $p < 0.05$.

samples to the field station to test (1) the quality of the laboratory analyses and (2) the data for quality control and quality assurance (Yuan et al., 2012). The blind samples are standard nitrate and total N samples (analyses results are not disclosed to the field laboratory by the water sub-centre). If the data of the standard samples were not in the range of standard results, the batch of samples were needed to re-analysis. The synthesis centre assesses the data quality. Where the nitrate N content is larger than the total N content for any sample, data are eliminated from the analysis database (Yuan et al., 2012).

Monitoring data for 798 samples from 62 shallow groundwater wells collected between 2004 and 2010 were assessed. Nitrate, total N values and nitrate: total N ratios were statistically analyzed with Matlab R2010b. Non-parametric methods were used because the data were not normally distributed. The Kruskal-Wallis test was used to test the differences between the agricultural and forest ecosystems for the entire data set. The significance level used was $p < 0.05$. The Kruskal-Wallis test was also used to test the differences between the dry and wet season in each monitoring ecosystem, but no significant differences were found (data not shown). The US EPA maximum threshold level for nitrate in drinking water (less than 10 mg N/L) and the Class 3 drinking water standard from the Chinese National Standard: Quality Standard for Ground Water (≤ 20 mgN/L) were used to assess the exceedance frequency of NO_3^--N concentrations in each monitoring well.

2 Results and discussion

2.1 Nitrate concentrations under different terrestrial ecosystems

Of the 29 typical terrestrial ecosystems sampled, most of the shallow groundwater wells (all of those beneath forest (**Table 1**) and the majority of those beneath agricultural ecosystems) were relatively free from excessive NO_3^--N contamination, with high NO_3^--N concentrations (i.e. > 10 mg N/L) found beneath 8 agricultural ecosystems (**Table 2**). Between 2004 and 2010, average NO_3^--N concentrations were significantly higher in agricultural ecosystems (4.1 ± 0.33 mg/L) than in the forest ecosystems (0.5 ± 0.04 mg/L). The groundwater total N concentrations (9.5 ± 0.61 mg/L), and the NO_3^--N:total N ratios (41% ± 1%) for the agricultural ecosystems were significantly higher than the total N concentrations (1.5 ± 0.11 mg/L), and the NO_3^--N:total N ratios (28% ± 2%) for the forest ecosystems ($p < 0.05$) (**Fig. 2**).

Based on the threshold value of 3 mg/L NO_3^--N mentioned by Andrade and Stigter (2009) as the lowest NO_3^--N concentration that indicates contamination due to human activities, the ranges of NO_3^--N values found in the shallow groundwater of the forest ecosystems indicate little incidence of anthropogenic contamination (**Table 1**).

An investigation of management practices showed that there were no fertiliser inputs to the forest areas. Mean N deposition ranged from 12.96 to 30.76 kg N/(ha·yr) along the north-south transect of eastern China (Lü and Tian, 2007). The total rates of wet and dry deposition peaked over central south China, with maximum values of 63.53 kg N/(ha·yr), and an average value of 12.89 kg N/(ha·yr)(Lü and Tian, 2007). Further, NO_3^--N concentrations suggest that atmospheric N deposition in the forest ecosystems did not cause serious NO_3^--N pollution in shallow groundwater.

In contrast, NO_3^--N, total N values and NO_3^--N to total N ratios found in the shallow groundwater of the agro-ecosystems all indicate the presence of anthropogenic contamination. As well as being high when compared to the NO_3^--N concentrations in the forest ecosystems of the CERN, the NO_3^--N concentrations in groundwater under agricultural ecosystems of the CERN were higher than those found in groundwater sampled in an intensively cultivated district of India, where the concentrations ranged from 0.12 to 6.58 mg/L, mean concentrations ranged from 0.73 to 2.17 mg/L, and only 8.7% of samples had concentrations greater than 3.0 mg/L (Kundu et al., 2009). This suggests that the relatively high concentrations in shallow groundwater of Chinese agro-ecosystems are the result of intensive agricultural management practices in NO_3^--N vulnerable zones.

2.2 Nitrate concentrations under different agro-ecosystems

Results indicated that in spite of intensive cultivation and the present rate of heavy fertilization, the NO_3^--N concentrations in groundwater of the monitored CERN agro-ecosystems were mostly below the permissible limits for drinking water (**Table 2**). Of the 43 wells sampled beneath the 20 agro-ecosystems, NO_3^--N concentrations were high (>10 mg N/L) in 10 wells located in 8 agro-ecosystems, in which the mean and maximum NO_3^--N concentrations ranged from 28.5 to 1.9 mg/L, and 76.6 to 10.9 mg/L, respectively (**Table 2**). For wells where the mean concentrations were in excess of the EPA threshold value (>10 mg N/L), about 20% of samples were in exceedance of the threshold value. Ansai and Yucheng were the only two wells at which the concentrations exceeded the Chinese threshold value (≥ 20 mg N/L).

The mean NO_3^--N concentration at the Ansai monitoring well, located in the Loess Plateau, was 28.5 mg/L (the highest mean concentration for the monitored ecosystems). The > 10 mg/L exceedance frequency was 86%, while the ≥ 20 mg/L exceedance frequency was 61%. The mean NO_3^--N concentration at the Yucheng monitoring wells, in the Yellow-Huai Riverplain, was 3.0 mg/L.

Here, 29% of samples exceeded the > 10 mg/L threshold and 24% exceeded the ≥20 mg/L threshold. At the Yanting and Qianyanzhou monitoring wells in the humid areas of

Table 2 Nitrate-N concentrations and percent above threshold of shallow groundwater in agro-ecosystems of CERN

Ecotype	Station	Geographical location	Altitude (m)	Mean precipitation (mm)	Soil type	Land use type	Average groundwater level (m)	N application rate (kg/hm^2)	*n*	NO_3^--N (mg/L) (Mean ± S.E.)	> 10 mg/L Frequency (%)	Maximum (mg/L)
Humid, sub-humid areas in temperate zone	Hailun	126°55′39′′E, 47°27′′15′′N	236	500–600	Black soil	Maize-soybean rotation	18.7 ± 0.37	120	14	0.3 ± 0.01	0	0.4
	Sanjiang	133°18′′03′′E, 47°21′07′′N	55	600	Boggy soil	Soybean	11.4 ± 0.31	0	30	0.2 ± 0.18	0	3.8
	Shenyang	123°22′05′′E, 41°31′06′′N	49	650–700	Aquic brown soil	Maize	8.0 ± 0.81	75	17	0.2 ± 0.04	0	0.5
Humid, sub-humid areas in warm temperate zone	Luancheng	114°24′47′′E, 37°53′26′′N	50	537	Aquic cinnamon soil	Summer maize -winter wheat	33.1 ±1.58	390	10	4.5 ± 0.18	0	5.1
	Yucheng	116°34′13′′E 36°49′51′N	22	582	Fluvo-aquic soil	Summer maize -winter wheat	2.3 ± 0.14	510	20	3.0 ± 0.78	29	41.1
	Fengqiu	114°19′43′′E, 35°00′40′′N	68	597	Fluvo-aquic soil	Summer maize -winter wheat	4.2 ± 0.43	345	70	0.8 ± 0.07	0	7.6
Humid areas in north sub-tropical zone	Changshu	120°25′08′′E, 31°19′46′′N	3	1038	Paddy soil	Paddy-wheat	0.4 ± 0.08	466	21	0.7 ± 0.12	0	2.9
	Yanting	105°27′21′′E, 31°16′18′′N	420	826	Purple soil	Maize - wheat	2.3 ± 0.15	300	81	5.8 ± 0.35	12	10.9
	Taoyuan	111°26′26′′E, 28°55′46′′N	106	1450	Red soil	Paddy-paddy	2.5 ± 0.25	270	8	0. 6 ± 0.12	0	1.1
	Yingtan	116°33′18′′E, 28°07′23′′N	45	826	Red soil	Peanut	1.6 ± 0.63	150	10	1.3 ± 0.52	0	2.2
	Qianyanzhou	115°02′04′′E, 26°26′40′′N	76	1542	Red soil	Paddy-paddy	3.2 ± 0.48	320	16	1.9 ± 0.70	5	12.0
Arid and semi-arid areas in in warm temperate zone	Naiman	120°42′00′′E, 42°55′47′′N	363	340-450	Aeolian sandy soil	Wheat-maize rotation	7.6 ± 0.15	207	12	1.1 ± 0.23	0	4.0
	Shapotou	105°00′01′′E, 37°16′4′′N	1350	180-220	Aeolian sandy soil	Wheat - maize rotation	15.2 ± 0.37	256	10	4.3 ± 0.59	0	6.4
	Linze	100°07′42′′E, 139°20′59′′N	1375	117	Aeolian sandy soil	Wheat – maize rotation	4.3 ± 0.61	122	12	3.9 ± 1.41	8	18.6
	Fukang	87°55′58′′E, 44°17′26′′N	460	164	Aeolian sandy soil	Cotton- maize rotation	3.4 ± 0.38	275	9	2.6 ± 0.88	22	13.4
	Akesu	80°51′40.8′′E, 40°37′49.2′′N	1028	42-94	Aeolian sandy soil	Cotton	2.5 ± 0.20	160	9	7.0 ± 1.24	22	13.6
	Cele	80°43′39′′E, 37°01′15′′N	1306	35	Aeolian sandy soil	Cotton- maize rotation	14.5 ± 0.14	468	40	6.0 ± 0.59	25	13.3
Loess plateau areas	Ansai	109°19′12′′E, 36°51′29′′N	1083	500	Loessial soil	Soybean-millet	11.9 ± 0.06	120	55	28.5 ± 2.66	86	76.6
	Changwu	107°40′59′′E, 35°14′27′′N	1200	584	Malan soess	Maize -wheat	84.5 ±1.22	345	47	1.3 ± 0.19	0	4.3
Tibet plateau areas	Lasa	91°12′20′′E, 29°24′22′′N	3688	400	Meadow soil	Wheat - barley-rape	2.8 ± 0.47	144	13	0.3 ±0.06	0.00	1.0

For the Luancheng, Shapotou, and Cele, the data was during 2005 and 2010. For the Akesu, the data was during 2008 and 2010.

southern China, the mean NO_3^--N concentrations varied from 5.8 to 1.9 mg/L, respectively, and 12% and 5% of samples exceeded the > 10 mg/L threshold, respectively.

The Linze, Fukang, Aksu, and Cele monitoring wells were in the oasis areas of Xinjiang and Gansu. At these wells, the mean NO_3^--N concentrations ranged from 2.6 to 7.0 mg/L, and the percentage of samples exceeding the > 10 mg/L threshold ranged from 8% to 25% (**Table 2**).

Analysis of the relationship between NO_3^--N concentrations and groundwater levels for the ecosystems with relatively high monitoring frequency showed that the groundwater NO_3^--N concentrations were significantly and negatively correlated with groundwater levels in the Fengqiu ($r = –0.496$, $p < 0.001$), Yanting ($r = –0.604$, $p < 0.001$), and Changshu ($r = –0.483$, $p = 0.026$) agro-ecosystems. For the Yucheng agro-ecosystem, groundwater NO_3^--N concentrations were negatively but not significantly correlated with groundwater levels ($r = –0.263$, $p = 0.324$), while for the Changwu ($r = 0.138$, $p = 0.561$) and Ansai ($r = 0.053$, $p = 0.684$) agricultural-ecosystems, groundwater NO_3^--N concentrations were not significantly correlated with groundwater levels (**Fig. 3**).

The high NO_3^--N concentrations were likely the result of high nitrogen inputs and soil conditions which promote NO_3^--N transport to groundwater in the agro-ecosystems (Burow et al., 2010). The exceedance frequency of the > 10 mg/L limit in the shallow groundwater wells of the CERN agro-ecosystems across all of the monitoring wells (20%) included in this assessment was higher than that found in the general assessment of groundwater quality in both typical agricultural land in the US (8% or 19%) (Burow et al., 2010) and intensive agricultural areas of northeastern Australia (8.7% greater than 3 mg/L) (Thorburn et al., 2003), but lower than that found in northern China (54%) (Zhang et al., 1996). High N applications are known to be one of the main causes of NO_3^--N pollution of ground and drinking water in northern China (Zhang et al., 1996; Ju et al., 2006). The average N-fertilizer application rate to the agricultural land in the Yucheng region was 510 kg N/ha, where summer corn (*Zea mays* L.) and winter wheat (*Triticum aestivum* L.) are the major crops grown. Permeable soils make the region susceptible to groundwater pollution by NO_3^--N due to high rates of N fertilizer application. The shallow groundwater table under soil layers which are enriched with NO_3^--N during the growing season is extremely susceptible to NO_3^--N contamination (Zhao et al., 2007).

In the Yanting monitoring wells, the intensive vegetable and crop cultivation caused obvious NO_3^--N pollution of shallow groundwater (Wang et al., 2006). The significantly negative relationship between NO_3^--N concentrations and groundwater levels in the Yanting agro-ecosystems also highlighted the influence of rainfall and fertilizer on the shallow groundwater NO_3^--N contents. Sandy textured soils and the practice of frequent irrigation make the groundwater in the oasis agro-ecosystems susceptible to NO_3^--N pollution (Yang and Su, 2008). Indeed Yang and Su (2008) reported that groundwater under long-term oasis gro-ecosystems was seriously contaminated by NO_3^--N, with a mean NO_3^--N concentration of 10.7 ± 0.19 mg/L.

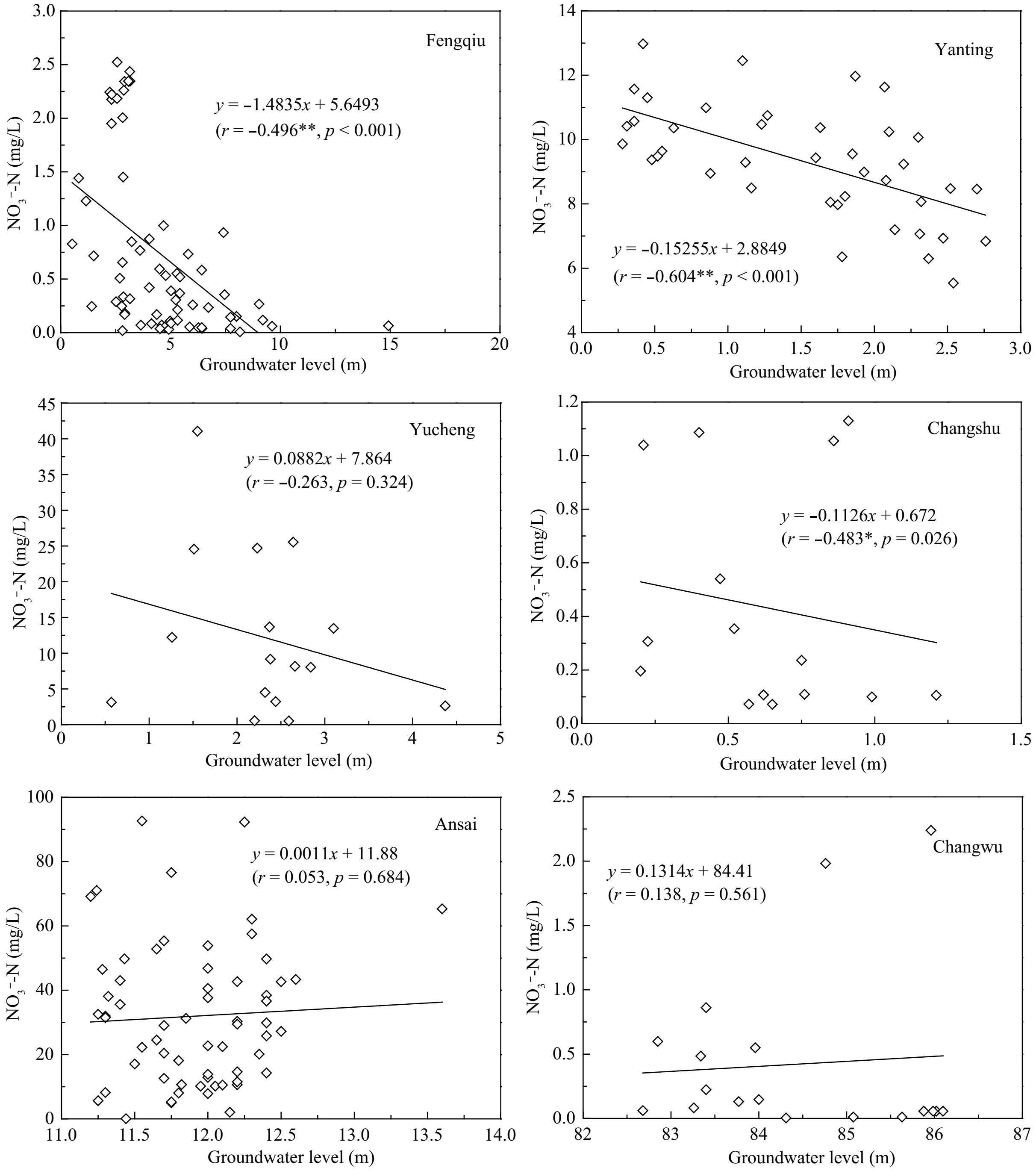

Fig. 3 Plot of NO_3^--N concentrations versus groundwater levels in the Fengqiu, Yanting, Yucheng, Changshu, Changwu and Ansai agro-ecosystems.

For example, in the Cele oasis agro-ecosystem, where highly profitable cotton (*Gossypium* spp.) is the major crop grown in rotation with corn (*Zea mays* L.), the average N-fertilizer application rate was 468 kg N/ha and the mean NO_3^--N concentration was 6.0 ± 0.59 mg/L.

High groundwater NO_3^--N concentrations and exceedance frequencies can however occur where N-fertiliser applications are relatively low. For example, the average annual N-fertilizer application rates were relatively low at the Linze and Akesu oasis sites (122, and 160 kg N/ha, respectively), but the corresponding mean NO_3^--N concentrations (3.9 and 7.0 mg/L, respectively) were relatively high. This may be due to the oxic conditions which tend to occur in soils in the northwest of China where the climate is arid or semi-arid and soil is sandy. Crop planting in arid and semi-arid agro-ecosystems depends heavily on irrigation, which promotes easy leaching of N fertilizer into the shallow groundwater.

There were no significant relationships between NO_3^--N concentrations and groundwater level in the loess plateau. However, the highest NO_3^--N concentration in the monitored ecosystems was found in the Ansai (28.5

± 2.66 mg/L) agro-ecosystem, where the N application rate was only 120 kg N/ha, which suggests that there maybe have some factors other than N fertilization causing the NO_3^--N pollution in this agro-ecosystem. The Ansai monitoring sites are in the floodplain, where groundwater levels are relatively low, and where people are inclined to dig drinking wells. In the future, the drinking wells in this area should be monitored often to assess the NO_3^--N concentrations. Such frequent monitoring is valuable for long-term trend assessment. For national assessments however, we would recommend that the number of sampling sites in a typical CERN ecosystem is increased, so as to give a more representative network. However, some of the wells with high N inputs have low NO_3^--N concentrations, an indication that factors other than N inputs influence NO_3^--N concentrations in groundwater. For example, in the paddy ecosystems with higher N fertilizer application rates (ranging from 270 to 466 kg N/ha in Taoyuan and Changshu, respectively), NO_3^--N levels under rice were lower and were associated with a reduced environment, finer-grained sediments, a higher water table and a humid climate. Denitrification is found to be an important NO_3^--N attenuation process (Zhu et al., 2003), as is dilution by surface water irrigation and precipitation (Andrade and Stigter, 2009). This suggests that the paddy soils, especially in the saturated zone, may possess some self-purification properties which can reduce NO_3^--N contamination (Zhu et al., 2003).

3 Conclusions

Shallow groundwater in typical Chinese forest ecosystems, as represented by groundwater monitoring wells in forest areas along the north-south transect of eastern China, was relatively free from excessive NO_3^--N contamination by human activities and N deposition. Shallow groundwater in agro-ecosystems may however be contaminated with NO_3^--N from agricultural management practices. Nitrate was the main form of N in shallow groundwater of the agro-ecosystems.

Nitrate concentrations in shallow groundwater in the wheat, corn and cotton planting agro-ecosystems in the arid and semi-arid areas, such as at Ansai in the Loess Plateau, Yucheng in the Yellow-Huai River plain and in the oasis ecosystems (Linze, Fukang, Akesu and Cele), were high, suggesting the presence of NO_3^--N vulnerable zones. Improvement of nitrogen fertilizer and irrigation management practices in the arid and semi-arid areas of China is the key in managing groundwater NO_3^--N concentrations. Nitrate beneath paddy soils in humid areas (even with high N applications) on the other hand were lower, suggesting that the paddy soils may possess some self-purification capabilities for nitrate contamination.

In the Fengqiu, Changshu and Yanting agro-ecosystems there were significant negative relationships between shallow ground water levels and NO_3^--N concentrations, suggesting that rainfall or irrigation combined with fertilizer may increase groundwater NO_3^--N contamination. Farmers should drill deeper drinking wells in these areas to reduce the risk of high NO_3^--N contamination.

In the future, it may be better to have samples analysed by one central laboratory with built-in quality control standards. Further, to have a more representative network, we recommend increasing the number of groundwater monitoring wells. In addition, to permit trend analysis (both seasonal and longer term), we recommend increasing the frequency of monitoring of the CERN agro-ecosystems to 12 times per year.

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