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Atmospheric wet deposition of nitrogen and sulfur to a typical red soil agroecosystem in Southeast China during the ten-year monsoon seasons (2003–2012)

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HIGHLIGHTS

- N and S wet deposition had an increased trend in the monsoon seasons.
- Total N wet deposition ranged from 3.34 to 65.17 kg ha^{-1} N in the monsoon seasons.
- S wet deposition was in the range of 7.17–23.44 kg ha^{-1} S in the monsoon seasons.
- NH_4^+–N and DON contributed 48.5% and 20.8% of the wet deposition of total N, respectively.
- The acid rain type was shifted from sulfur to a mixed one during the five-year monsoon seasons (2008–2012).

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ABSTRACT

Biological processes in agroecosystems have been affected by atmospheric nitrogen (N) and sulfur (S) deposition, but there is uncertainty about their deposition characteristics in the monsoon season. We collected rain samples using an ASP-2 sampler, recorded rainfall and rain frequency by an auto-meteorological experiment sub-station, and determined total N, NO_3^- – N and NH_4^+ – N levels in precipitation with an AutoAnalyzer 3 and SO_4^{2-} – S with a chromatography, in order to characterize the wet deposition of N and S to a typical red soil agroecosystem by a ten-year monitoring experiment in Southeast China. The results indicated that N and S wet deposition had an increased trend with the flux of total N (3.34–65.17 kg ha^{-1} N) and total S (SO_4^{2-} – S) (7.17–23.44 kg ha^{-1} S) during the monsoon seasons. The additional applications of pig mature in 2006 and 2007 led to the peaks of DON (dissolved organic nitrogen) and total N wet deposition. On average, NH_4^+ – N was the major N form, accounting for 48.5% of total N wet deposition and DON was not a negligible N form, accounting for 20.8% during the ten-year monsoon seasons (except 2006 and 2007). Wet deposition of N and S has been intensively influenced by human activities in the monsoon season, and would increase the potential ecological risk in the red soil agricultural ecosystem.

1. Introduction

Atmospheric nitrogen (N) and sulfur (S) deposition is a very topical environmental issue, and captures the attention of policy makers in the world (Kim et al., 2010; Bobbink et al., 2010; Cornell, 2011). Although kinds of protocols on reducing N and S in air have been executed since 1980, the N and S deposition still causes a broad range of detrimental effects and perturbations to ecosystems (Wright et al., 2001; Phoenix et al., 2006; Tørseth et al., 2012; Payne et al., 2013). In China, N and S deposition is increasing although there has been a decline for total emission of N and S (Liu et al., 2013; Song et al., 2013). Prior studies on N and S deposition mostly focused on forest and aquatic ecosystems but neglected agroecosystems due to substantial use of N fertilizers on farmlands

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(Pryor et al., 2001; Cui et al., 2010). In fact, our group found N wet deposition ranged from 10 to 94 kg ha^{-1} yr^{-1} N (Cui et al., 2012), which was significantly greater than the global average of 3.5 kg ha^{-1} $year^{-1}$ N (Phoenix et al., 2006). Moreover, there have been only a few reports on dissolved organic N (DON) deposition for its different chemical families, low concentrations and instability after collection (Cape et al., 2001; Cornell, 2011; Zhang et al., 2012). In fact, DON is of similar bioavailability to inorganic N, plays an important role in N deposition and accounts for a significant fraction (33 ± 19%) of total N deposition (Neff et al., 2002; Zhang et al., 2012). Therefore, it is important to further discuss the characteristics of N and S deposition in agroecosystems for understanding N and S deposition and evaluating their ecological effects.

Red soils are the highly leached soils and usually designated under the orders of Oxisols, Ultisols, occasionally Alfisols, Mollisols and even Inceptisols (Baliger et al., 2004). It is widely distributed in (sub-) tropical regions and potentially constitutes one of the most important soil resources for food production in the world. In China, the red soil regions cover an area of 2.6 million km^2 and account for over 20% of the country's total land area. The red soils of China are highly weathered and inherently infertile, dominated by low mountains and hills, and are typical of similar red soils that occur throughout (sub-) tropical South America, Africa, South and East Asia and other regions.

Red soils are not able to preserve moisture for their poor water holding capacity and as the soils frequently occur in areas subject to droughts at certain times of the year (Baliger et al., 2004). Therefore, crops are cultivated mostly during the monsoon reason. In the red soil regions of China, drought has become more and more frequent and intensive in these regions (He et al., 2001). Hence, the monsoon season, especially rainfall, plays an important role in the regions (Wang, 2006). However, temporal characteristics of N and S deposition have most often been recorded in various regions of the world based on monthly, seasonal, and annual data (Pryor et al., 2001; Cui et al., 2010; Tørseth et al., 2012; Liu et al., 2013), but few studies estimated the N and S deposition in the monsoon season and evaluated its ecological effect on farmlands. In our previous study, we found that inorganic N wet deposition in the monsoon season ranged from 5.0 to 20.2 kg ha^{-1} N, accounting for 17.6–51.9% of annual inorganic N deposition on a farmland during 2005–2012 (Cui et al., 2012). On the same farmland, Yang et al. (2005) also found S wet deposition in the monsoon season contributed 29.7% to the annual S wet deposition. In addition, the monsoon season is very critical for peanut and early rice growth on the farmland. Moreover, red soils are generally acidic in nature and deficient in most essential nutrients (Baliger et al., 2004). Larger amounts of organic matter and nutrients are also lost from the cultivated land (He et al., 2001), making the agroecosystems fragile. Then the N and S deposition in the monsoon season might have a great ecological effect on, for example, the yields, the acidification and alteration of nutrient balances of the agricultural ecosystems. However, now it is still unclear regarding: 1) characteristics of N and S deposition; and 2) proportions of N forms, such as $NH_4^+ - N$, $NO_3^- - N$, and dissolved organic nitrogen (DON) in the long term.

In the present study, we focused on a typical agroecosystem in the red soil region, southeastern China to: 1) determine N and S wet deposition fluxes and trends, and 2) estimate the proportion of N forms in the monsoon season by a long-term observation (2003–2012). The results could not only supply a valuable parameter for assessing the effect of N and S deposition on agroecosystems and an effective policy to reduce N and S deposition, but also attribute to the understanding of N and S cyclings and their nutrient management of red-soil agroecosystems in China and also around the world.

2. Data and methods

2.1. Site description

Yingtan city lies in the northern part of Jiangxi Province, southeast China (116°35′–117°30′ E, 27°35′–28°41′ N), and covers a total area of 3556.7 km^2 (Fig. 1). The primary soil type is red soil. Geomorphologically, the city consists of hills, basins and high, steep, clustered mountains in its northern, central and southern parts. Its ground elevation varies from 16 to 1541 m above sea level. Subtropical humid monsoon climate prevails in the city, with an

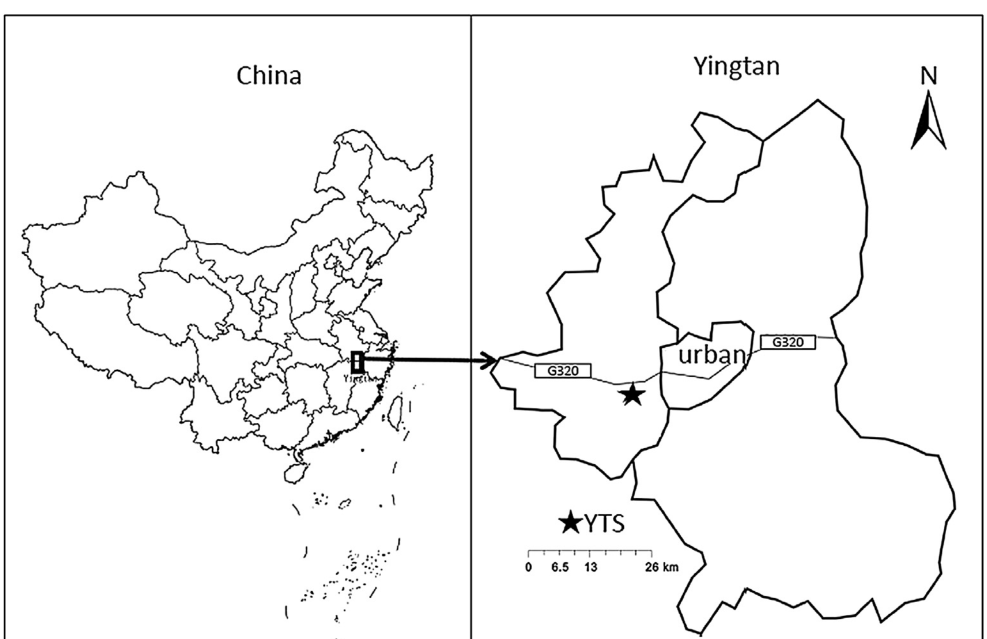

Fig. 1. The study site in Yingtan city, Jiangxi Province, China.

annual mean air temperature of 18 °C, abundant annual rainfall (1750 mm), and a leading wind direction of southwest during June to August while that of east and northeast in other nine months.

Atmospheric precipitation in the present study was collected at the Red Soil Ecological Experiment Station (116°55′E, 28°12′N), Chinese Academy of Sciences (CAS) in the northeast of urban region of Yingtan city, usually known as Yingtan Station (YTS) (Fig. 1). YTS is the typical hilly region of red soil in subtropical China, and has been selected as a long-term agro-ecosystem monitoring site by the CAS, as well as a global environment-climate observation station. It covers a total area of 120 ha, and is composed of 75% farmlands, 15% forestlands, 10% other lands such as water bodies, roads and residential areas. The crops, including peanut and rice, were mainly planted in April, June and August. Usually, the paddy fields in the YTS were subjected to the application of chemical N fertilizers (urea, ammonium bicarbonate and compound fertilizers), with 120–480 kg ha^{-1} year^{-1} N, whereas the drylands were subject to the application of chemical N fertilizers (130–220 kg ha^{-1} year^{-1} N) and pig mature (180–250 kg ha^{-1} year^{-1} N). In addition, the application of 4–5 times pig manure (about 300 kg N per time) in most years was conducted in the study region on April 28th 2006, August 25th 2006 and March 13th 2007, respectively. There are three pig farms within 50 km^2. One pig farm is located in the direction of north-northwest to north and the other two are in the east-southeast to east in the sample site, respectively.

2.2. Deposition sampling and analysis

Wet deposition samples were collected from two sites (1 km from each other) in the YTS at a 4-week interval using ASP-2 samplers (Wuhan-Tianhong Inc., China) from 2005 to 2009 while collected immediately after each rain event during 2003–2004 and 2010–2012. To eliminate the effects of microbial activities on rainwater chemical compositions during the 4-week intervals, some doses of methyl propyl phenol (analytical pure) were added to rainwater samples at the base of the rainfall after every event (ratio of methyl propyl phenol to rainwater sample = 450 mg to 1 L) (Sun et al., 2006). Polyethylene collection bottles were carefully cleaned with acid-washed with 10% HCl solution and deionized water (Anderson and Downing, 2006).

Total N (TN) in water samples was measured by alkaline potassium peroxydisulfate oxidation method (APOM) (Cabrera and Beare, 1993; Huang et al., 2011) while $SO_4^{2-}-S$ was measured by chromatography (Swaluw et al., 2011). Prior to analysis of TN and $SO_4^{2-}-S$, water samples were shaken for 2–3 min to agitate the sunken particles at the bottom of these containers. Then water samples were filtrated through 0.45 μm cellulose membrane filters for the analysis of $NO_3^- - N$ and $NH_4^+ - N$ concentrations, which were performed following the standard procedure with a continuous flow analyzer AutoAnalyzer 3 (Bran-Luebbe Inc., Germany). The DON concentration was calculated by the concentration difference of TN and DIN ($NO_3^- - N + NH_4^+ - N$) (Huang et al., 2011; Walker et al., 2012; Zhang et al., 2012). Moreover, $NH_4^+ - N$ concentration was determined using a 721-100 visible spectrophotometer (Shanghai Changfang Optical Instrument Co., Ltd., China) at 625 nm and $NO_3^- - N$ using a T6-UV spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) at 220 nm and 275 nm in some samples. The recoveries of $NH_4^+ - N$ and $NO_3^- - N$ spiked to rainwater were determined by the AutoAnalyzer 3. The concentrations of $NH_4^+ - N$ and $NO_3^- - N$ standard solutions were both prepared at eight levels: 0.2, 0.4, 0.6, 0.8 1.2, 1.6, 2.4 and 3.2 mg L^{-1} N, and the recoveries of NH_4^+- and $NO_3^- - N$ ranged from 90.3% to 101.8% and from 91.9% to 100.7%, respectively.

In addition, hourly precipitation and wind directions per 10 min were monitored and recorded using an auto-meteorological experiment sub-station (Vaisala, Finland) in the YTS. Rain frequency was used to record the number of raining days (daily rainfall >0 mm). Wind directions (0–360°) were divided into 16 equal parts: N (0°/360°), NNE (22.5°), NE (45°), ENE (67.5°), E (90°), ESE (112.5°), SE (135°), SSE (157.5°), S (180°), SSW (202.5°), SW (225°), WSW (247.5°), W (270°), WNW (292.5°), NW (315°), and NNW (337.5°).

2.3. Simulated experiment

Based on the N wet deposition flux (16 kg ha^{-1} N) in the ten-year monsoon seasons and that (50 kg ha^{-1} N) in the whole year of 2005, five N treatments were made: 0, 15, 30, 45 and 60 kg ha^{-1} N, with each treatment was repeated three times. Red soil samples of 0–20, 20–40 and 40–60 cm below the ground were collected sequentially from a field with 30-year production history in the YTS, and then were homogenized, dried, filtered with a 10-mesh sieve, and placed into a polyvinyl chloride column with an inner diameter of 15 mm and a height of 70 cm, sequentially. A layer of inert quartz sand and medium-speed filter paper was paved at the bottom and on the upper of the column, with the *in-situ* soil solution sampler (Luo et al., 2007) in the middle (20 and 40 cm) of the column. The N liquids at pH4.5 were prepared using NH_4NO_3, HCl and deionized water (15 L), and then added into columns with a leaching rate at 125 ml h^{-1} in the middle and at the end of each month from April to June, 2013. After every leaching process, 50 ml soil solutions of the two layers (20 and 40 cm) were extracted by the *in-situ* soil solution samplers for measuring pH using a portable pH meter (Spectrum Technologies, INC., US).

2.4. Data analysis

Wet deposition was calculated using formulas (1) and (2) as follows:

$$C_w = \sum_{i=1}^{n}(C_iP_i)/\sum_{i=1}^{n}P_i \quad (1)$$

where C_w is the precipitation-weighted mean concentration (mg L^{-1} N, S) calculated from the n valid samples within a month or one monsoon season, and individual valid sample concentration C_i is weighted by the rainfall amount P_i for each sample.

$$F_w = P_tC_w/100 \quad (2)$$

where F_w is the wet-deposition flux (kg ha^{-1} N, S), P_t is the total rainfall (mm), and 100 is the unit conversion factor.

Relative contribution of each N-species was calculated to identify the composition of wet N deposition, whereas one-way Analysis of Variance (ANOVA) was performed to demonstrate seasonal variations in wet N deposition.

3. Results and discussions

3.1. Precipitation fluxes in the ten-year monsoon seasons

In the monsoon seasons during 2003–2012, rainfalls ranged from 478.0 to 1387.3 mm (averaged 821.2 mm) and there were three stages for those years: 1) higher in May while lower in April in 2003–2006, 2) higher in April while lower in May in 2007–2009, and 3) higher in June while lower in April in 2010–2012 (Fig. 2a). Fig. 2b also shows that rain frequency varies from 39 to 65 days and its average is 51 days during the 10-year monsoon seasons. The average values of rainfalls and rain frequency accounted for 47.8% and 32.9% of their corresponding annual mean values, respectively.

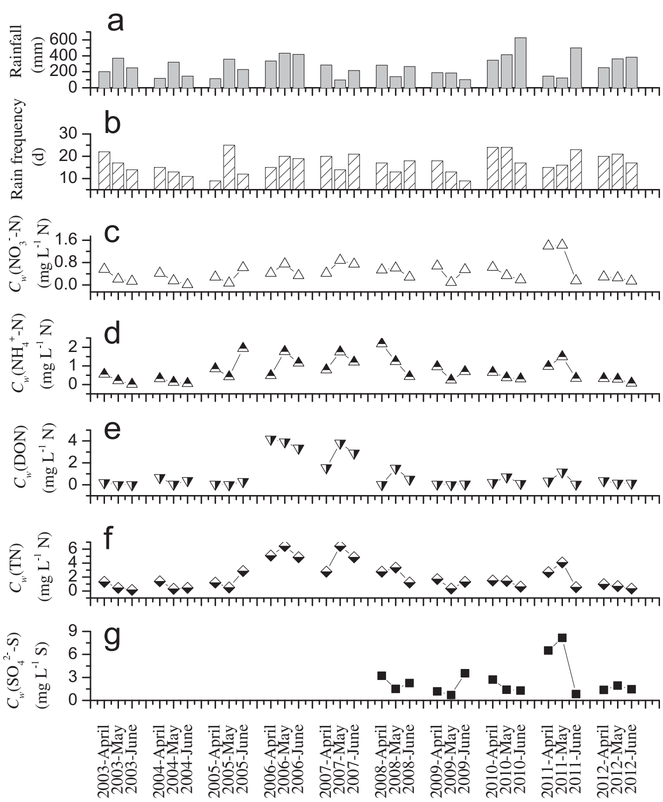

Fig. 2. Monthly variations of C_w(N), C_w(S), rainfall and rain frequency in the ten-year monsoon seasons.

There were significant differences in both rainfalls and rain frequency among years. The maxima of both the rainfalls and rain frequency were recorded in 2010, which were significantly higher than those in 2009 ($p < 0.05$, Table 1).

3.2. Atmospheric wet deposition nitrogen in the ten-year monsoon seasons

3.2.1. Concentrations (C_w) of atmospheric wet deposition nitrogen

In rural and suburb region, $C_w(NO_3^- - N)$ was controlled by the imported NO_x from motor vehicles, power plants and factories (Glasius et al., 1999) while $C_w(NH_4^+ - N)$ mainly originated from the ammonia volatilization loss from N fertilization in agricultural fields and animal production (Zhou et al., 2007; Sun et al., 2007). The application of organic fertilizers including pig mature led to higher DON emission (Schade and Crutzen, 1995; Zhang et al., 2012). In our study, we found there was a slightly fluctuating variation for monthly $C_w(NO_3^- - N)$ in the ten-year monsoon seasons while all of higher $C_w(NH_4^+ - N)$, C_w(DON) and C_w(TN) occurred in the two years (2006 and 2007) when additional pig manure was applied (Fig. 2c–f). Correlations between DON, $NH_4^+ - N$, $NO_3^- - N$ and TN were shown in Table 2 using their monthly concentrations in this study. Statistically, DON had significantly positive linear regressions with $NH_4^+ - N$ and TN but none with $NO_3^- - N$, suggesting that the origin of DON was more closely related to $NH_4^+ - N$ than it to $NO_3^- - N$; i.e. more closely related to reduced rather than oxidized organic N compounds in the study region. Also, $NH_4^+ - N$ had significantly positive linear

Table 1
Means and aggregations in precipitation, and seasonal C_w(N, S) in the ten-year monsoon seasons.

	Rainfall (mm)	Rain frequency (day)	C_w (mg L^{-1} N) C_w (mg L^{-1} S)				
			$NO_3^- - N$	$NH_4^+ - N$	DON	TN	$SO_4^{2-} - S$
2003	822.4abc	53ab	0.27b	0.24abc	0.05c	0.56b	–
2004	585.5bc	39b	0.17b	0.14c	0.25c	0.57b	–
2005	700.6bc	46ab	0.28b	0.99abc	0.11c	1.38b	–
2006	1187ab	54ab	0.51ab	1.19abc	3.79a	5.49a	–
2007	599.4b	55ab	0.61ab	1.10ab	2.40b	4.12b	–
2008	687.4bc	48ab	0.45ab	1.32a	0.51c	2.28b	2.50a
2009	478.0c	40ab	0.42ab	0.63abc	0.04c	1.09b	1.50a
2010	1387.3a	65a	0.34b	0.41abc	0.32c	1.08b	1.67a
2011	766.7bc	54ab	0.59a	0.64abc	0.29c	1.52b	3.06a
2012	997.2ab	58ab	0.22b	0.22bc	0.19c	0.63b	1.61a
Mean [a)]	821.1	51	0.45	0.74	0.90	2.09	2.53
Mean [b)]	821.1	50	0.42	0.63	0.29	1.34	2.53

Note: '–' is not available. Different small letters following the data stand for different significant differences at 5% level in the same column. "Mean [a)]" and "Mean [b)]" above are the average means in the whole ten years (2003–2012) and the eight years (2003–2005, 2008–2012), respectively.

Table 2
Correlations of monthly C_w(N) in the ten-year monsoon seasons ($n = 30$).

	C_w(DON)	$C_w(NH_4^+ - N)$	$C_w(NO_3^- - N)$	C_w(TN)
C_w(DON)	1	0.440*	0.324	0.907**
$C_w(NH_4^+ - N)$	0.440*	1	0.663**	0.757**
$C_w(NO_3^- - N)$	0.324	0.663**	1	0.628**
C_w(TN)	0.907**	0.757**	0.628**	1

Note: '*' and "**" are not available following the data stand for different significant correlations at 5% and 1% level.

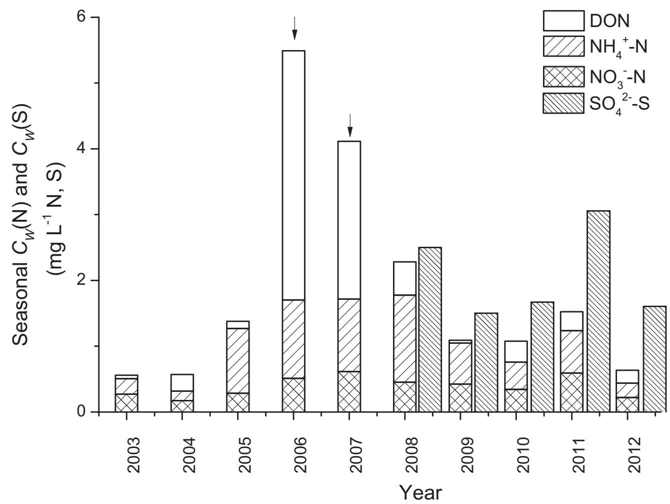

Fig. 3. Seasonal C_w(N) and Cw(S) variations in the ten-year monsoon seasons. The solid arrows represent the additional pig mature applied.

regressions with $NO_3^- - N$ and TN (Table 2) which indicated that part of reduced and oxidized N changed into each other rapidly after they were in rain. These results were in good agreement with those in other farmland ecosystems in China (Zhang et al., 2012).

Significant variations of seasonal C_w(N) were found in the monsoon seasons among the ten years (Fig. 3 and Table 1). The seasonal means were 0.74, 0.45, 0.89 and 2.09 mg L^{-1} N for $C_w(NO_3^- - N)$, $C_w(NH_4^+ - N)$, C_w(DON) and C_w(TN), which were higher than those in another red soil farmland (117°26′E, 26°44′N) reported by Zhang et al. (Zheng et al., 2012). This might be attributed to the applications of pig manure applied and pig farms. In our study site, pig mature was usually applied in drylands during March–April and additional pig manures were applied on April 28th 2006 and March 13th 2007, respectively, which was the primary factor leading to higher seasonal C_w(N) than those reported by Zhang et al. (2012). The other factor was the distribution of pig farms. The prevailing wind direction was east during the ten-year monsoon seasons (Fig. 4). Just in the east-southeast to east in the

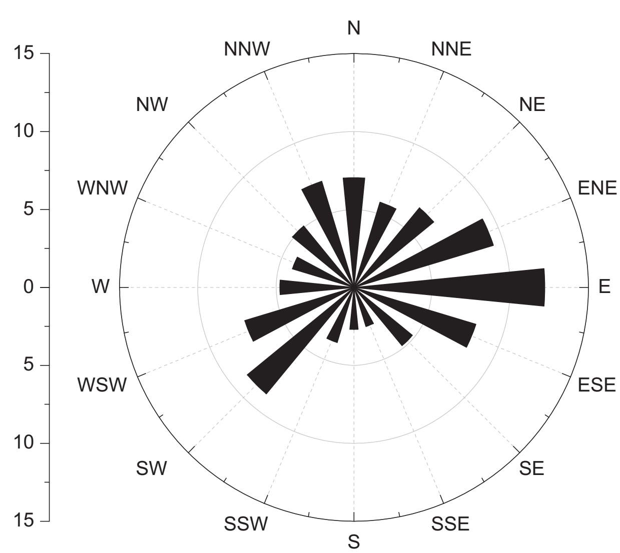

Fig. 4. Means of wind direction frequency in the ten-year monsoon seasons (2003–2012).

Table 3
Seasonal F_w(N, S) in the ten-year monsoon seasons.

	$NO_3^- - N$	$NH_4^+ - N$	DON	TN	$SO_4^{2-} - S$
2003	2.23 (48.6%) bc	1.94 (42.2%) b	0.42 (9.2%) c	4.59 c	–
2004	1.01 (30.3%) c	0.84 (25.3%) b	1.48 (44.4%) c	3.34 c	–
2005	1.99 (20.6%) bc	6.92 (71.6%) ab	0.76 (7.8%) c	9.66 c	–
2006	6.08 (9.3%) a	14.13 (21.7%) a	44.96 (69.0%) a	65.17 a	–
2007	3.69 (14.9%) abc	6.61 (26.8%) ab	14.37 (58.3%) b	24.67 b	–
2008	3.12 (19.9%) abc	9.09 (57.9%) ab	3.47 (22.1%) c	15.69 bc	17.18 ab
2009	2.02 (38.9%) bc	2.99 (57.5%) b	0.19 (3.6%) c	5.20 c	7.17 b
2010	4.77 (31.9%) ab	5.73 (38.4%) ab	4.43 (29.7%) c	14.92 bc	23.17 a
2011	4.55 (39.0%) abc	4.93 (42.2%) b	2.19 (18.8%) c	11.67 bc	23.44 a
2012	2.22 (35.1%) bc	2.16 (34.2%) b	1.94 (30.7%) c	6.31 c	16.01 ab
Mean [a)]	3.17 (19.6%)	5.53(34.3%)	7.42(46.0%)	16.12	17.39
Mean [b)]	2.74 (30.7%)	4.32 (48.5%)	1.86 (20.8%)	8.92	17.39

Note: Percentage in total wet N deposition is given in brackets. Different small letters following both brackets and data stand for different significant differences at 5% level in the same column. '–', "Mean [a)]" and "Mean [b)]" above are same to Table 1.

sample site, there were two pig farms. The prevailing wind of east brought N-species from the two pig farms led to higher seasonal C_w(N) than those reported by Zhang et al. (2012).

3.3. Fluxes (F_w) of atmospheric wet deposition nitrogen

During the ten-year monsoon seasons, seasonal F_w(TN) values fluctuated in the range of 3.34–65.17 kg ha^{-1} N, with its mean 16.12 kg ha^{-1} N (Table 3). Seasonal $F_w(NO_3^- - N)$, $F_w(NH_4^+ - N)$ and F_w(DON) values accounted for 9.3–48.6%, 21.6–71.6% and 3.6–69.0% of corresponding seasonal F_w(TN), respectively. And all the higher values of seasonal wet N deposition were found in 2006 and 2007 under the precipitation conditions (Tables 1 and 3) and agricultural activities especially when additional pig manure was applied in 2006 and 2007. But both the maxima of seasonal rainfall and rain frequency were observed in 2010 and the former was significantly larger than that in 2007 ($p < 0.05$, Table 1). Moreover, DON had significantly positive linear regressions with $NH_4^+ - N$ and TN, and $NH_4^+ - N$ had significantly positive linear regressions with $NO_3^- - N$ and TN (Table 2). This result above indicated that additional pig manure applied made higher seasonal F_w(DON) and $F_w(NH_4^+ - N)$ and further seasonal $F_w(NO_3^- - N)$ and F_w(TN) in the ten-year monsoon seasons.

In order to reflect the common trend, the two monsoon seasons of 2006 and 2007 were excluded. During the other eight-year monsoon seasons, seasonal F_w(N) variations were shown in Fig. 5. Seasonal $F_w(NO_3^- - N)$, $F_w(NH_4^+ - N)$ and F_w(DON) values were in the ranges of 1.01–4.77,0.84–9.09 and 0.19–4.43 kg ha^{-1} N, with averages 2.73, 4.32 and 1.86 kg ha^{-1} N, which accounted for 30.7%, 48.5% and 20.8% of their corresponding seasonal F_w(TN) (8.92 kg ha^{-1} N), respectively (Fig. 5 and Table 3). Fig. 5 also shows that all of seasonal F_w(N) had an increasing trend due to the application of excessive N fertilizers and pig farms.

3.4. Concentrations (C_w) and fluxes (F_w) of atmospheric wet deposition of sulfur

Monthly $C_w(SO_4^{2-} - S)$ was in the range of 0.71–6.50 mg L^{-1} S (Fig. 2g), and had positive correlation with corresponding rainfall and negative correlation with corresponding rain frequency (Table 2). During 2008–2012, seasonal $C_w(SO_4^{2-} - S)$ varied from 1.50 to 3.06 mg L^{-1} S and generally had a decreasing trend (Fig. 3; Table 1) while seasonal $F_w(SO_4^{2-} - S)$ ranged from 7.17 to 23.44 kg ha^{-1} S (averaged 17.39 kg ha^{-1} S) and had an increasing trend (Fig. 5 and Table 3), in good agreement with the results in East Asia (Kuribayashi et al., 2012), which mainly attributed to industrialization in China. With China stepping into the mid-later stage

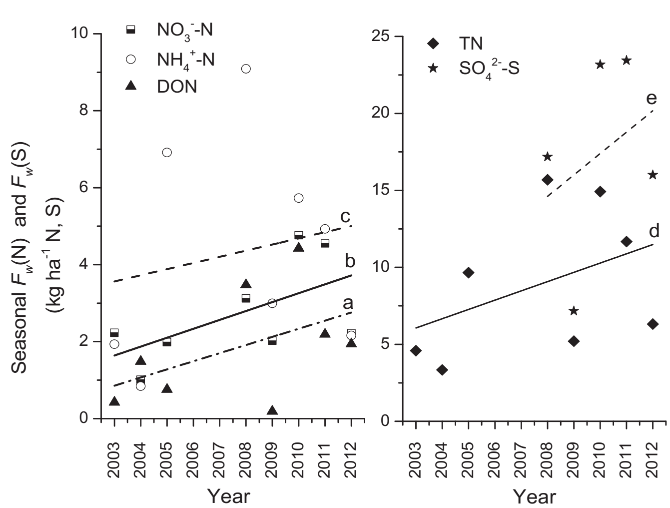

Fig. 5. Seasonal F_w(N) and F_w(S) variations and trends of the monsoon seasons in most years when N fertilizers were applied as usual. Related data in 2006 and 2007 were excluded for the application of 4–5 times pig manure than usual in most years was conducted in the two monsoon seasons. Different linestypes of a–e above show their trends of seasonal F_w(DON), $F_w(NO_3^- - N)$, $F_w(NH_4^+ - N)$ and $F_w(SO_4^{2-} - S)$ in the most years, respectively.

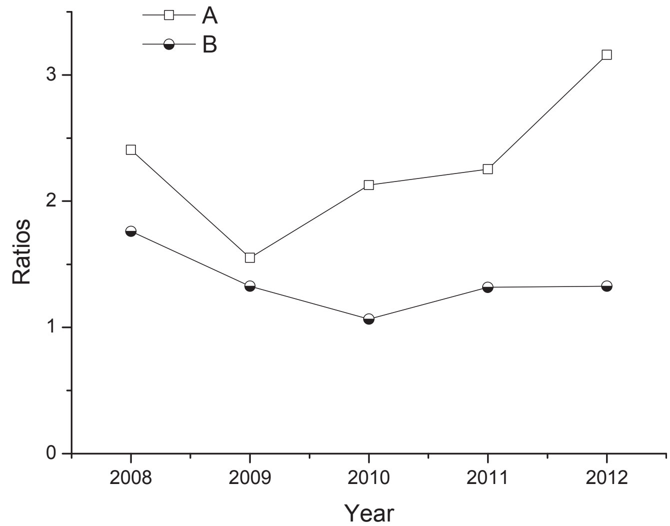

Fig. 6. Seasonal molar ratios of SO_4^{2-} to NO_3^- of (A) rainwater in the present study region and those of SO_2 to NO_2 of (B) air in the urban regions in Yingtan city during 2008–2012. The data of SO_2 and NO_2 concentrations of Yingtan urban regions were from Environmental Quality in Yingtan City (http://www.ythb.gov.cn/hjzk/201304/t20130410_230981.htm).

of industrialization, the economic diffusion effect is becoming more and more significant and the industrialization is also beginning to accelerate. Yingtan city is going through industrialization too. During this process, some pollution-intensive industries are being moved to this city from the Yangtze River Delta Economic Zone, leading to SO_2 emission and further to increased S deposition. The environmental policy in China has set limitations for SO_2 emission. Song et al. (2013) found the total SO_2 deposition still increased after the implementation of the environmental policy in 2003. This was the main factor for increasing S wet deposition in the study.

It should be noted that seasonal $F_w(SO_4^{2-} - S)$ approached the minimum in 2009 (Fig. 6 and Table 3), which was attributed to the financial crisis in 2008 and low precipitation. After 2008, especially in 2009, most of industries surrounding the study site had to be closed due to the financial crisis, which led to a sharp decline in seasonal $C_w(SO_4^{2-} - S)$ in the study. In addition, the minimum rainfall (478.0 mm) and low rain frequency (40 days) occurred in 2009 (Table 1). Those two factors led to the minimum seasonal $F_w(SO_4^{2-} - S)$ in 2009 in the study.

3.5. Changes of the molar ratios of SO_4^{2-} to NO_3^- in rainwaters

The molar ratios of SO_4^{2-} to NO_3^- ranged from 0.76 to 4.52 during the five-year monsoon seasons (Table 4). And inner the 15 months during the five-year monsoon in 2008–2012, four of the ratios was above 3.0 and eleven between 0.5 and 3.0, indicating that the acid rain types shifted from the sulfur types to mixed ones. The change in acid rain type has accelerated the generalization in China (Jie et al., 2012). Moreover, similar variations for the molar ratios of SO_4^{2-} to NO_3^- in the rain samples and those of SO_2 to NO_2 in urban air were found (Fig. 6), which would suggest SO_4^{2-} to NO_3^- had the similar regional source and evoke a new ecological effect. Those above were assigned to regional and national conditions in China. In the present study, N emission has its relatively stable sources (N fertilizers and pig matures) and S emission is from SO_2 in factories such as power plants. Because the farmlands and pig farms are relatively dispersed, it is difficult to control N emission in agricultural regions in China, which would make N emission and deposition continue to increase for a long time. However, S emission and deposition should significantly decline with the development of economy and the implementation of S protocols in China. Tørseth et al. (2012) have found that the implementation of S protocols had led to a marked decline in the emissions of S and thus atmospheric S deposition.

Table 4
Ratio of monthly molar concentrations of SO_4^{2-} to NO_3^- in the five-year monsoon seasons.

	April	May	June
2008	2.60	1.08	3.51
2009	0.76	3.45	2.81
2010	1.88	1.81	2.96
2011	2.03	2.49	2.29
2012	2.08	3.22	4.52

Note: The molar ratio of *currhskip0ptScurrhskip0ptO*$_4^{2-}$ to NO_3^- is the parameter used to denote acid types. For example, the ratios ≥3.0, 0.5–3.0 and ≤0.5 indicate the sulfur, mixed and nitrate types of acid rain, respectively.

3.6. Ecological effects of N and S deposition

Regardless of the increase and decline in N and S deposition, their combined depositions are expected to affect ecosystems continuously (Blake and Goulding, 2002; Clark and Tilman, 2008). Excessive N and S deposition had a negative impact on provisioning, regulating and supporting ecosystem services, e.g. water quality, soil quality and plant species diversity (Blake and Goulding, 2002; Payne et al., 2013).

In the red-soil agroecosytem of our study during the ten-year monsoon seasons, C_w(TN) (except June 2006) surpassed the threshold for water eutrophication (0.2 mg L^{-1} N). A similar result was also found in the Taihu agricultural region (Wang et al., 2004) and Fujian (Zheng et al., 2012). This indicated that more effective and rigorous policies or air-quality standards should be set to protect ecosystems from the damage by excessive N, such as the reduction of N emission in agroecosystems by resorting to scientific fertilization.

In the present study, the sample site is in a seriously acid rain area. During the study period, N and S wet deposition had an increasing trend and the acid rain types shifted from the sulfur types to mixed ones, which might increase soil acidification. Our simulated wet N deposition experiment indicated the more N deposition, the more acidification of red soil solution. Compared with deep layer (40 cm), the response of the surface layer (20 cm) to pH value was more significant especially at the low N wet

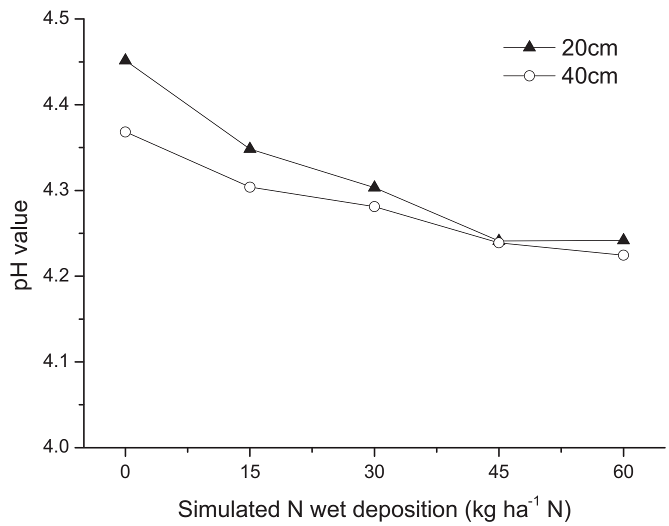

Fig. 7. Effect of simulated N wet deposition on pH of red soil solution.

deposition levels (0–30 kg ha^{-1} N) (Fig. 7). Similar results were also found in red soil in another study (Wang et al., 2012). The mechanisms through which increasing N deposition fluxes and changing NH_4^+-N/NO_3^--N/ rates affect soil acidification will be studied by establishing the relationship between the nitrogen in atmospheric deposition and H^+, aluminum forms, base cations and nitrogen forms in different depths of undisturbed loessal soil cores under laboratory conditions in the future.

4. Summary and conclusions

In the red-soil farmland ecosystem, the application of pig manure especially additional pig manure in 2006 and 2007 led to DON wet deposition and further to the increase of total N (TN) wet deposition during the ten-year monsoon seasons. Generally, both N and S wet deposition had an increasing trend and the acid rain types shifted from the sulfur ones to mixed ones. NH_4^+-N was the main form of N wet deposition and DON was not negligible in wet N deposition. DON and NH_4^+-N had similar sources from agricultural activities such as the application of N fertilizers and the distribution of pig farms. NO_3^--N and $SO_4^{2-}-S$ had a similar regional source from the urban region of Yingtan.

Both N and S are essential elements to plants growth, but their excessive depositions also continue to affect ecosystems negatively. It is critical to balance between the positive and negative effects of N and S deposition. Future assessments and policies should focus on a multi-criterium approach to meeting both anthropogenic needs and rendering ecosystems sustainable.

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