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Soil nitric oxide emissions from terrestrial ecosystems in China: a synthesis of modeling and measurements

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Soils are among the major sources of atmospheric nitric oxide (NO), which play a crucial role in atmospheric chemistry. Here we systematically synthesized the modeling studies and field measurements and presented a novel soil NO emission inventory of terrestrial ecosystems in China. The previously modeled inventories ranged from 480 to 1375 and from 242.8 to 550 Gg N yr^{-1} for all lands and croplands, respectively. Nevertheless, all the previous modeling studies were conducted based on very few measurements from China. According to the current synthesis of field measurements, most soil NO emission measurements were conducted at croplands, while the measurements were only conducted at two sites for forest and grassland. The median NO flux was 3.2 ng N m^{-2} s^{-1} with a fertilizer induced emission factor (FIE) of 0.04% for rice fields, and was 7.1 ng N m^{-2} s^{-1} with an FIE of 0.67% for uplands. A novel NO emission inventory of 1226.33 (ranging from 588.24 to 2132.05) Gg N yr^{-1} was estimated for China's terrestrial ecosystems, which was about 18% of anthropogenic emissions. More field measurements should be conducted to cover more biomes and obtain more representative data in order to well constrain soil NO emission inventory of China.

Nitrogen oxides (NO_x = NO + NO_2) play a crucial role in atmospheric chemistry by controlling the photochemical formation of tropospheric ozone (O_3) and regulating many other oxidizing agents, e.g., hydroxyl radical (OH)[1]. Their end photochemical products HNO_3 and NO_3^- contribute to formation of secondary aerosols, acidification of precipitation and nitrogen (N) deposition[2,3]. Thus, for developing strategies to reduce regional or national levels of O_3, secondary aerosols or N deposition, it is necessary to have reliable estimates of the sources of NO_x other than fossil fuel combustion including soil NO_x emissions, with the predominant form emitted from soils as nitric oxide (NO).

Soils are a major source of atmospheric NO_x, but the source strength of a soil depends on the balance between soil NO production and consumption, which are controlled by both biotic and abiotic processes[4]. Among the processes of soil NO production, nitrification and denitrification are the two major ones[4]. Although some abiotic processes, termed chemodenitrification, can also produce NO, they usually play a trivial role and occur under low pH conditions. Soil NO emissions are regulated by many factors, including N availability, soil water content, soil temperature, soil pH, ambient NO concentration, soil organic carbon[4–6].

The estimated global NO emission inventories for soil ranged from 6.6 to 33 Tg N yr^{-1} (above soil) or from 4.7 to 26.7 Tg N yr^{-1} (above canopy)[7] dependent on whether the studies considered canopy reduction factor, which is adopted to account for canopy uptake of NO_x. Different approaches have been used to estimate regional or global soil NO emissions. One of these approaches simply estimated NO emission inventory by multiplying biome areas in a region by the corresponding mean NO fluxes as proposed by Davidson and Kingerlee[8]. The second approach involves the use of fertilizer-induced NO emission factor (FIE, i.e., soil NO emission from a fertilized site subtracts that from an unfertilized control site divided by the rate of fertilizer N and expressed as percentage) or a combination of FIE and background soil NO emission[9,10]. Empirical models based on the relationship between soil NO emissions and environmental variables or soil properties have been used to estimate regional NO emissions[11,12]. In the simplest case, soil NO emission was only related to soil temperature, and the correlation was then used to upscale NO emission at regional scale[11]. Yienger and Levy[12] adopted a more complicated empirical modeling approach, i.e., YL95 scheme, by taking both soil temperature and soil moisture (using precipitation as a proxy) into account. The YL95 scheme has been applied in numerous global atmospheric chemistry models[13–16]. Statistical models were recently developed on the basis of field measurements[6,17,18]. For example, Yan et al.[18] developed a statistical model to represent the dependence of soil NO emission on soil organic carbon (SOC) content, soil pH, land-cover type, climate, and nitrogen input, and they used the statistical model to estimate the global soil NO emission inventory. The last approach is to employ process-based models such as the biogeochemical model PnET-N-DNDC[19] and the Carnegie-Ames-Standord (CASA) Biosphere model[20]. However, even for the process-based models, empirical relationships are used for some critical processes. In a word, field measurements form the basis for upscaling soil NO emission from site scales to regional or global scales regardless of which kind of approach is used. In fact, one probable cause for the huge discrepancy in soil NO emission estimates is that the previous studies were imbalanced in regions under investigation.

As for China, many air quality or environmental problems including increased tropospheric ozone levels, photochemical smog episodes, elevated N deposition have arisen and been related to increased atmospheric NO_x levels[21–23]. However, atmospheric and NO_x sources other than combustion have not been well understood. Soil NO emissions in China are likely high since (i) the cropland (Note: cropland hereafter includes upland fields and rice fields) are well known to be intensively managed with excess N application rates[2] and (ii) the vast majority of the land is under high N deposition[22,24]. Nevertheless, most modeling estimates of soil NO emissions from China were based on few field measurements from China, since field measurements were conducted only at two sites before 2006. As much more field measurements are available now, it is time to synthesize the existing data to help constrain the NO emission inventory in China.

In this paper, we systematically synthesized the available information of modeling and field measurements regarding soil NO emissions from terrestrial ecosystems in China. The main objectives were to 1) present the state-of-the-art modeling approaches of soil NO emissions in China, 2) synthesize the existing field measurements of soil NO emission from Chinese terrestrial ecosystems, 3) present a novel soil NO emission inventory based on the constrained parameters in China.

Results and Discussion

State-of-the-art modeling approaches of soil NO emission inventories in China. Various approaches have been used to estimate soil NO emissions from China or regions in China (Table 1). Soil NO emissions from all terrestrial ecosystems over China were only clearly presented by three studies[11,18,25]. Tie et al.[11] estimated that the above-soil NO emission was 2750 Gg N yr^{-1}, which was 1375 Gg N yr^{-1} when converted to above-canopy emission using a canopy reduction factor of about 50%[12]. Both values were much greater than those estimated by others. This was likely related to the much simple modeling scheme adopted by Tie et al.[11], i.e., dependence of soil NO emission only on soil temperature, regardless of other important factors like N fertilizer inputs, paddy rice fields, etc. Wang et al.[25] used a similar scheme as that proposed by Yienger and Levy[12], i.e., YL95 scheme, but obtained a much higher inventory of soil NO emissions relative to Yienger and Levy[12]. In fact, the YL95 scheme was criticized to underestimate regional emissions by a factor of up to 3 in regions including eastern China[7], partly because it categorized all the agricultural land within 0–35°N and 80–140°E into rice field[25]. A complicated statistical modeling approach was developed by Yan et al.[18] based on 92 field measurements by relating soil NO emission to SOC, pH, land cover, climate and N input in an exponential way; and canopy reduction effect and pulsing emission were also considered. However, the measurements included by the above modeling studies were almost all conducted outside of China.

Two commonly used methods to upscale the field measurements to regional or national scales in China were: (i) considering background emission and FIE[2,9,26], and (ii) multiplying mean NO fluxes by areas of the corresponding biomes[2,27,28]. Among these studies, Yan et al.[9] estimated FIEs based on 48 measurements from 14 studies (only one from China) and estimated background NO emission based on 5 measurements for uplands. For rice fields, they assumed that the FIE was one-fifths that of uplands and the background NO emission was assumed to be the same as that for uplands[9]. Therefore, the estimation for rice fields was very rough due to lack of data. The other four studies estimated regional[2,27,28] or national[26] NO emissions simply based on measurements from single site. Li and Wang[2] used both approaches and found that the estimates were very similar. Nevertheless, the obtained inventories should be very rough if they were upscaled from measurements of a single site.

Two studies constrained soil NO emission over east China in combination with satellite observations[29,30]. For these studies, the "top-down" inventory of NO_x, or the a posteriori inventory, was constructed using an inversion approach with a global 3-D chemical transport model (GEOS-Chem) with the a priori parameters. The soil NO emission processes are represented using a modified version of the YL95 scheme to get the a priori estimate. Therefore, field measurements are very important to constrain the parameters in order to get reasonable the a priori estimate. According to Wang et al.[30], the a posteriori value for soil emitted NO_x was 0.85 Tg N yr^{-1} (with an uncertainty of 40%) for the three-year period from 1997-2000 over east China (100–123°E, 20–42°N) and the emission peaked in summer when soil emissions accounted for about 43% of the combustion source; while the inventory from fossil fuel combustion and biomass burning were 3.72 Tg N yr^{-1} (±32%) and 0.08 Tg N yr^{-1} (±50%), respectively. Lin[29] reported that the annual budgets for anthropogenic, lightning and soil emissions were 7.1 Tg N (±39%), 0.21 Tg N (±61%), and 0.38 Tg N (±65%), respectively, for east China (101.25–126.25°E, 19–46°N) in 2006. It seemed that there was a big discrepancy even the same approach was used largely due to difference in the adopted parameters which need to be constrained by field measurements.

Synthesis of field measurements of soil nitric oxide emissions in China. The ecosystems involved in the current dataset include forests, grassland, cropland with or without N fertilization and bare soil of cropland (Table S1). However, there was only one location involved for grassland which located in Inner Mongolia (location 14, Fig. 1). For forest, one broadleaf forest and one adjacent pine forest were studied at the same location (location 2, Fig. 1). NO emissions from upland fields and rice fields were conducted at 10 locations and 3 locations, respectively. Although quite a few measurements were conducted for uplands, most of the studies were located in the east China (Fig. 1).

Dynamic flow-through chamber technique was adopted by four studies[26,31–33], while static chamber technique was used by the others. Field comparison indicated that the NO emissions measured by static and flow-through dynamic chamber techniques were comparable in spite of differences in chamber size, plot location, extent of area coverage and random error associated with the measurements[34].

NO fluxes varied greatly with a range from -1.9 to 160.0 ng N m^{-2} s^{-1} in the upland fields (Table S1). The median NO flux was 7.1 ng N m^{-2} s^{-1} and the median annual emissions was 3.07 kg N ha^{-1} yr^{-1} (with a range from 0.29 to 50.46 kg N ha^{-1} yr^{-1}) for the uplands (Table 2). Davidson and Kingerlee[8] reported that NO emissions ranged from 0.2 to 23 kg N ha^{-1} yr^{-1} from uplands globally. The global averaged annual NO emission for uplands was 1.1 kg N ha^{-1} yr^{-1} according to Stehfest and Bouwman[17]. It seems that the annual NO emission from uplands in China were greater than the global average probably due to higher N fertilization rate in China (380 kg N ha^{-1} yr^{-1} in 2012).

Table 1 | Published estimates of soil nitric oxide emissions from China or regions of China (Unit: Gg N yr^{-1})

Reference	Region	Year	Above soil	Above canopy	Approach description
Wang et al. (2005)	China	1999		657	YL95 scheme was used; for different temperature intervals, different empirical models were used: linear (0–10°C), exponential (10–30°C), and optimal(>30°C)
Tie et al. (2006)	China	2004	2750	1375	Exponentially dependent on soil temperature
Yan et al. (2005)	China			480 (310)a	Developed a statistical model based on 92 field measurements by relating emission to SOC, pH, land cover, climate and N input in an exponential way; considered canopy reduction effect and pulsing emission
Yan et al. (2003)	China	1995		242.8b*	Considering background emission and fertilizer N induced emission; separate fertilizer-induced emission factors for upland and rice fields
Zheng et al., 2003	China	mid 1990s		550b	Based on fertilizer-induced NO emission factor and background NO emission from a single rice-wheat rotation site
Wang et al. (2007)	east China	1997–1999		850	YL95 scheme was implemented into GEOS-Chem
Lin et al. (2012)	east China	2006		380	YL95 scheme was implemented into GEOS-Chem
Li & Wang, 2007	Guangdong province	2005		11.7c	Based on the vegetable field area and annual NO emission rate from a single site
Li & Wang, 2007	Guangdong	2005		13.3c	Based on fertilizer-induced NO emission factor and background NO emission from a single site
Fang & Mu, 2007	Yangtze Delta	2006		15.9d	Based on the vegetable field area and NO emission rate from a single site
Fang & Mu, 2009	Yangtze Delta	2004–2006		12.5e	Based on the vegetable field area and NO emission rate from a single site
Yienger and Levy (1995)	China and Japan	1992		310 (220)a	1) Temperature and precipitation dependent; 2) Pulsing emission; 3) Canopy reduction; 4) Linear dependence on N input rate
Bouwman et al. (2002)	East Asia			380b*	Developed a statistical model based on 99 field measurements by relating emission to SOC, N input and drainage in a exponential way

Note:
a: values in the parentheses represent emissions from cropland;
b: emissions from cropland;
c: for vegetable fields;
d: vegetable fields during spring-summer period;
e: cropland during summer-autumn period;
*: It was not pointed out whether the emissions were above-soil or above-canopy ones.

For paddy field, measurements were only conducted at three locations (3, 4 and 6 in Fig. 1) in the Yangtze River Delta. The median NO flux was 3.2 ng N m^{-2} s^{-1} and ranged from 0.2 to 4.2 ng N m^{-2} s^{-1} (Table 2 and Table S1). NO emissions from paddy fields have been rarely measured at the global scale and thus very few data were available. For example, only two measurements were compiled by Stehfest and Bouwman[17] and only one was found by Davidson and Kingerlee[8]. Galbally et al.[35] reported a NO flux of 0.2 ng N m^{-2} s^{-1}, but their measurement only spanned a few days during the water-logged period. Nevertheless, most paddy fields are managed with dry-wet cycles and intense nitrification/denitrification could occur during non-waterlogged periods similar to uplands[9]. Even during the water-logged period, higher fluxes up to 0.95 ng N m^{-2} s^{-1} were observed after application of urea when significant nitrite and nitrate were present in the floodwater[35]. Therefore relatively greater fluxes observed in the rice fields were reasonable considering a complete growing period was covered.

NO emissions were measured at two adjacent systems for both forest and grassland. For forest, measurements were conducted at a broadleaf forest and an adjacent pine forest in subtropical China. Annual NO emissions in the broadleaf forest and the pine forest were estimated to be 6.1–6.9 and 4.0–4.3 kg N ha^{-1} yr^{-1}, respectively[36] with a mean of 5.05 kg N ha^{-1} yr^{-1} (Table 2). The total pulses-induced NO emissions during the dry season were roughly estimated to be 29.4 mg N m^{-2} in the broadleaf forest and 22.2 mg N m^{-2} in the pine forest, or made up of about 5% of the total annual NO emissions for both forests[37]. A simulated N deposition experiment revealed that approximately 2% of the deposited N lost as NO in the two forests[38]. Annual NO emissions in these forests were relatively higher than those from most tropical forests and temperate forests, which usually emit less than 5 and 0.2 kg N ha^{-1} yr^{-1}, respectively[8]. One probable reason is that the atmospheric deposition in this area was much higher (>50 kg N ha^{-1} yr^{-1} in throughfall)[39]. Similarly, soil NO emissions as high as 6.4–9.1 kg N ha^{-1} yr^{-1} were reported in a spruce

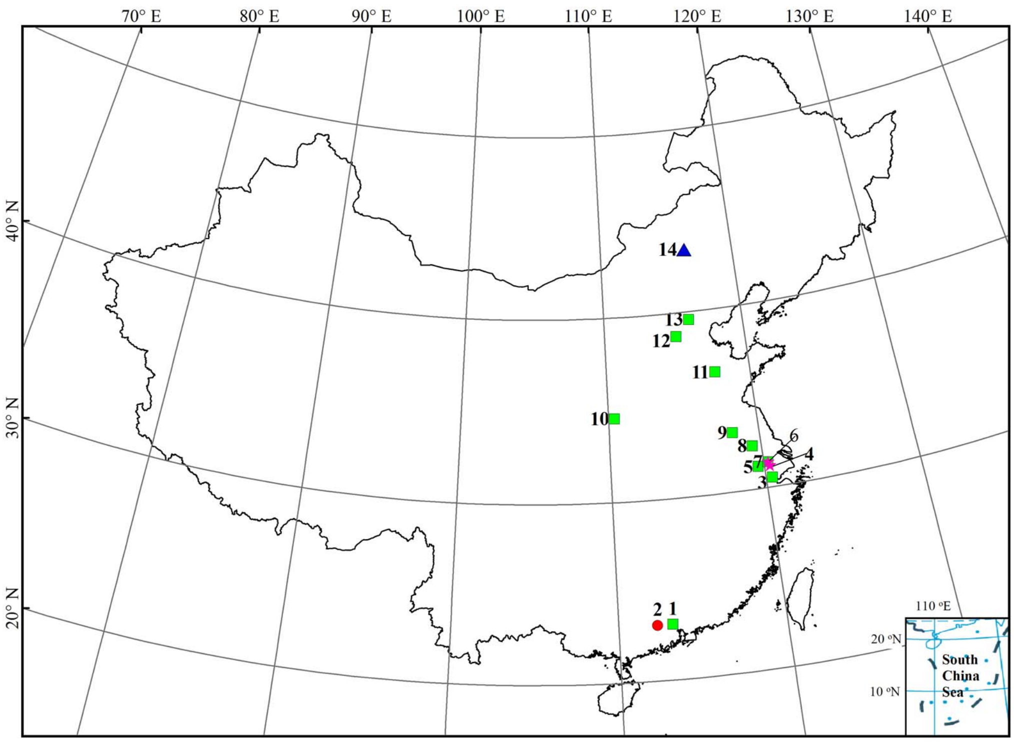

Figure 1 | Schematic map showing the 14 locations which included 130 sampling sites for NO emissions. 1, Suburban of Guangzhou, Guangdong province (Li & Wang, 2007); 2, Dinghu Shan, Guangdong province (Li et al., 2007); 3, Shuangqiao Farm, Zhejiang province (Fang & Mu, 2006, 2007, 2009; Fang et al., 2006; Pang et al., 2009); 4, Suburban of Suzhou city, Jiangsu province (Zheng et al., 2003); 5, Dapu, Jiangsu province (Lan et al., 2013); 6, Wuxi, Jiangsu province (Zhou et al., 2010; Deng et al., 2012); 7, Wuxi, Jiangsu province (Deng et al., 2012); 8, Jiangdu, Jiangsu province (Mei et al., 2009); 9, Lingqiao, Jiangsu province (Lan et al., 2013); 10, Dong Cun Farm, Shanxi province (Liu et al., 2011); 11, Huangtai, Shangdong province (Cui et al., 2012; Yang et al., 2013); 12, Wangdu, Hebei province (Zhang et al., 2011); 13, Suburban of Beijing (Walsh, 2001); 14, Xilin, Inner Mongolia (Holst et al., 2007). The symbols triangle, asterisk, solid cycles and solid squares denote grassland, rice paddy, forest and cropland sites, respectively. The references were presented in Note S1. The map was generated using ArcGIS 9.3 (ESRI, CA).

Table 2 | Statistics results for NO flux (ng N m^{-2} s^{-1}), fertilizer induced NO emission factor (FIE, %) and annual NO emission (kg N ha^{-1} yr^{-1})

		NO flux	FIE, %	Annual emission
Cropland				
Upland	Median	7.1	0.67	3.07
	N	89.0	53.00	54.00
	95% CI_L	4.2	0.48	1.66
	95% CI_U	12.9	1.09	6.59
Rice field	Median	3.2	0.04	1.29
	N	7	4	3
Bare soil control	Median	7.0		2.33
	N	6		5
Planted soil control for upland	Median	1.6		0.73
	N	32		17
	95% CI_L	1.1		0.35
	95% CI_U	2.5		1.23
Planted soil control for rice field	Median	2.2		0.79
	N	3		3
Other biomes				
Forest	Mean	16.0		5.05
	N	2		2
Grassland	Mean	0.1		0.03
	N	2		2

Note:
N: number of measurements;
95% CI_L: Lower limit of 95% CI;
95% CI_U: Upper limit of 95% CI.

forest experiencing N deposition of 30 kg N ha^{-1} yr^{-1} in Germany[40]. NO emissions from the grassland in Inner Mongolia (Table 2) were much lower compared to grasslands in other regions (with means of 0.56–1.22 kg N ha^{-1} yr^{-1})[8,17]. However, due to the limited sites involved, the observed NO emissions from forest and grassland were far from representative of their respective biomes in China.

The FIEs of NO ranged from 0.04% to 4.90% with a median of 0.67% and the lower and upper 95% CI of 0.48% and 1.09%, respectively (Table 2). Several studies have reported FIEs based on the analyses of global dataset. The global averaged FIEs of 0.55% to 0.71% for fertilized uplands and grasslands were reported previously[6,17,41]. Therefore our estimate was well within the range of the reported global averages. A median FIE of 0.02 with a range from 0.02 to 0.20% was found for rice fields and was much lower than that for uplands (Table 2). To our knowledge, these were the only reported FIEs globally for rice fields.

In order to get FIEs, two ways were employed with one way using bare cropland soils (bare control) as control while another way using planted soils without N fertilization as control (planted control) (Table S1). For the rice fields, the median NO flux from planted control was 2.2 ng N m^{-2} s^{-1} (Table 2). Nevertheless, it should be pointed out that this value should be used with carefulness since only three data points were available. For the uplands, the median NO flux for the bare control was 7.0 ng N m^{-2} s^{-1}, much higher than that for planted control (1.6 ng N m^{-2} s^{-1}). There are two possible mechanisms responsible for the discrepancy between the two types of controls. In one hand, crops in the planted control consume a portion of the soil available N and subsequently the available N for nitrifiers and denitrifiers decreases. According to the hole-in-the-pipe model (a conceptual model used to describe the biogenic emissions of NO and N_2O in soils), the decrease of N flowing through the pipe would result in corresponding decrease of NO emission[42]. In another hand, plant canopy plays an important role in mediating soil NO emissions. Once emitted from soils, NO is converted to NO_2 within the plant canopy and may be deposited to the plant canopy in the form of NO_2 and thus reduce the amount of NO fluxes[5]. For example, a global canopy reduction factor of about 50% was proposed[12]. To a less degree, NO itself can be deposited to or emitted from plant canopy but with huge uncertainties yet[5]. Considering the much higher fluxes, using bare soils as control likely lower the estimated FIEs. Therefore, NO fluxes from the planted control should be used as the background emissions.

Many factors affect soil NO emissions, including N availability, soil water content, soil temperature, soil pH, ambient NO concentration, soil organic carbon[4–6]. Since most measurements were conducted at upland fields, we only analyzed the factors regulating soil NO emissions for this land use. These studied sites were located from south subtropical to temperate continental in climate. No significant correlation between latitudes and averaged NO fluxes was observed, implying that apparent change of soil NO emissions along latitude or climate zone did not exist. Similarly, climate was also found to be not important in determining NO flux variation by Bouwman et al.[6]. This was reconfirmed by the fact that the NO fluxes were not significantly related to MAT. Nevertheless, Stehfest and Bouwman[17] reported that factors that significantly influenced agricultural NO emissions were N application rate, soil N content and climate. In field measurements for a given site, soil NO emissions were frequently found to increase exponentially with soil temperature with Q_{10} values (Q_{10} here means change in NO flux for a 10°C difference in temperature) in the range of 2–3[4]. The lack of clear correlation between soil NO emissions and climate or temperature probably due to the masking effects from other factors including soil texture, fertilization, etc.

Total NO emissions for a given sampling period were found to be significantly related to N application rates within the same periods (Fig. 2). Dependence of NO emissions (kg N ha^{-1}) on fertilizer N inputs (N_{Fert}, kg N ha^{-1}) could be quantitatively represented by an Ordinary Least Squares (OLS) linear regression model:

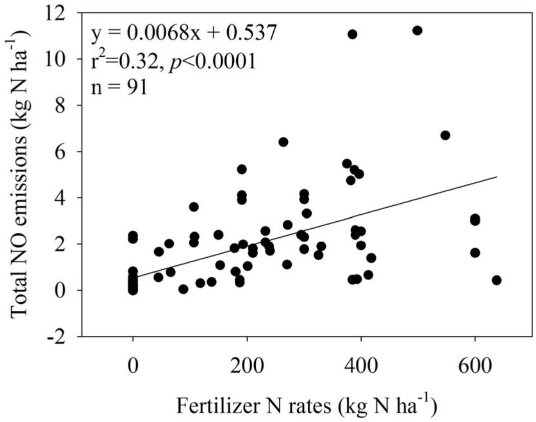

Figure 2 | Dependence of total NO emissions in a sampling period on N fertilizer application rates in the same period for uplands.

$$\mathrm{NO-N} = 0.0068 \times N_{Fert} + 0.537\left(r^2 = 0.32, p < 0.0001, n = 91\right) \quad (1)$$

Based on this model, the FIE was 0.0068 kg NO-N kg^{-1} N_{Fert} with a standard error of 0.001 (Table 2). This FIE value of 0.68% was very close to the median (0.67%) of the dataset. Since the duration of the sampling period ranged from one month to about one year, the parameter 0.537 could not be used as the annual background NO emission.

A novel soil NO emission inventory in China. Cropland, forest, grassland and desert/semi-desert are the four major land cover types by occupying more than 93% of the total land area in China (Table 3). As for soil NO emission measurements, few data were available for forest and grassland and no data were available for desert/semi-desert up to date. In order to get an inventory of NO emissions from terrestrial ecosystems over China, total emission from cropland was estimated according to parameters constrained in the present study (i.e., background emissions and fertilizer N induced emissions for uplands and rice fields, respectively), but emissions from forest, grassland and desert/semi-desert were estimated using parameters from previous studies.

For croplands, total NO emissions from uplands and rice fields were estimated separately according to background emissions and fertilizer N induced emissions. There was no evidence in terms of whether FIE for synthetic fertilizer N differed from that for manure N[6]. For this reason, both synthetic fertilizer N and manure N consumption should be considered in estimating national NO emission inventory for croplands. Total synthetic fertilizer N consumption was 24.00 Tg N yr^{-1} in China for 2012. According to Holland et al.[43], the ratio of synthetic fertilizer N to manure N was 0.63 on average for the period from 1993 to 2002 at the global scale. If this ratio was also applicable to China, then the manure N consumption was estimated to be 38.10 Tg N yr^{-1} for 2012. Therefore the total fertilizer N input to cropland was 62.10 Tg N yr^{-1} for 2012. The areas of uplands and rice fields were 133.28×10^6 ha and 30.14×10^6 ha, respectively, in 2012 (Table 3). Since there were no data about the allocation of fertilizer N inputs between uplands and rice fields, we assumed that fertilizer N allocation was proportionate to their areas. Thus the fertilizer N inputs to uplands and rice fields were 48.06 and 14.03 Tg N yr^{-1}, respectively. The background emission for uplands was 0.73 kg N ha^{-1} yr^{-1} (95%CI: 0.35 to 1.23 kg N ha^{-1} yr^{-1}) (Table 2). Total background emission from uplands was 97.09 Gg N yr^{-1} (95%CI: 53.20 to 116.51 Gg N yr^{-1}). The fertilizer induced NO emission from uplands was 322.01 Gg N yr^{-1} (95%CI: 232.14 to 523.87 Gg N yr^{-1}) using a median FIE of 0.67% (95%CI: 0.48% to

Table 3 | Areas of cropland, forest, grassland and desert/semi-desert in China and soil NO emissions from the four land cover types

	Area	Percentage of total land area	Soil NO emissions	Percentage of anthropogenic NO_x emission
	10^6 ha	%	Gg N yr^{-1}	%
Cropland	163.42[a]	17.02	442.83 (296.67–699.15)	6.51 (4.36–10.28)
Forest	258.26[b]	22.64	371.96 (153.37–747.95)	5.47 (2.26–11.00)
Grassland	191.65[b]	26.15	328.98 (130.33–527.63)	4.84 (1.92–7.76)
Deserts and semi-deserts	262.20[c]	27.31	82.59 (7.87–157.32)	1.21 (0.12–2.31)
Total	875.53	93.12	1226.33 (588.24–2132.05)	18.03 (8.65–31.35)

Note: a, from China Statistical Yearbook 2013 (133.28 × 10^6 ha for upland fields and 30.14 × 10^6 ha for rice fields in 2012); b, from Wu et al.[60]; c, from Zhao et al.,[61].

1.09%). As a consequence, the total NO emission from uplands was 419.10 Gg N yr^{-1} (95%CI: 285.34 to 640.38 Gg N yr^{-1}). With regard to rice fields, there were two distinct periods, i.e., water-logged period with rice and non-waterlogged period without rice. In China, the water-logged period was about 7 months for double rice, while 4 month for single rice[26]. We assumed that the areas for double and single rice were the same, i.e., 1.51 × 10^7 ha each, and the N application rate was similar for each rice period. The background emission for non-waterlogged period was the same to that for uplands (1.37 g N ha^{-1} d^{-1}) while that for waterlogged period was 1.90 g N ha^{-1} d^{-1} (Table 2). Hence the total background NO emission from rice fields was 18.76 Gg N yr^{-1}. The fertilizer induced NO emission from rice fields was 4.96 Gg N yr^{-1} with an FIE of 0.04% and total fertilizer input of 14.03 Tg N yr^{-1}. The total NO emission from rice fields (23.72 Gg N yr^{-1}) was very low compared to that from uplands. Accordingly, the total NO emission from croplands in China was estimated to be 442.83 Gg N yr^{-1} (95%CI: 296.67 to 699.15 Gg N yr^{-1}. Note: instead of 95%CI, median plus minimum and maximum values were used to calculate emissions for rice fields). Our estimate was greater than that calculated by Yan et al.[9], but was in line with others for croplands[18,26] (Table 1).

As for forest, total NO emission was estimated according to the relationship between NO emission and N deposition. Dependence of soil NO emission on N input to forest has been observed either in N addition experiment[38,44,45] or in field survey[46–49]. However, there was uncertainty in terms of whether tree species played a role in determining the responses of soil NO emission to N input. Pilegaard et al.[47] reported that the dependence of soil NO emission on N input was only found for coniferous forests across 14 forest sites in Europe. Nevertheless, strong dependence was also reported for deciduous forests[46,49] or evergreen broadleaf forests[38,44]. Considering that N is the substrate of soil NO production, it is reasonable that there is likely a strong dependence of soil NO emission to N input for all forest types, similar to the strong relationship between NO emission and N application rate in croplands[6]. In the present study, soil NO emissions and the corresponding N deposition rates in different types of forests were collected (Table S2) and a strong relationship ($F_{NO} = 0.1444\ N_{dep} - 0.851$, $r^2 = 0.5548$, $p < 0.0001$, n = 26) between soil NO emission and N deposition was found (Fig. 3). With this relationship, we firstly estimated the NO fluxes (including the mean, minimum and maximum values) for each province using the province-specific N deposition rates[24], and we then estimated the total NO emission for each province with the respective NO fluxes and forest area (Table S3). The total NO emission from forest sector in China was 371.96 (with a range from 153.37 to 747.95) Gg N yr^{-1} (Table 3).

Total NO emission from grassland were estimated according to grassland types and NO fluxes for each type. Grassland in China was roughly divided into four types, i.e., temperate steppe/meadow steppe, alpine steppe/meadow steppe, temperate tussock and tropical tussock (Table S4). Soil NO fluxes for each type were collected from the literature. Total NO emission for a grassland type was calculated by multiplying the area by NO flux. With this method, total NO emission was 328.98 (with a range from 130.33 to 527.20) Gg N yr^{-1} (Table 3, Table S4). NO fluxes in deserts/semi-deserts have been measured in very limited studies, and the measured range of 0.03 to 0.6 (0.315 on average) kg N ha^{-1} yr^{-1} was used for deserts/semi-deserts[50,51]. It turned out that total NO emission from this biome was 82.59 (from 7.87 to 157.32) Gg N yr^{-1}.

Total NO emission from the above terrestrial sources in China was 1226.33 (from 588.24 to 2132.05) Gg N yr^{-1}. This value was within the previous reported range for China but close to the upper limit (Table 1). According to Lin et al.[52], anthropogenic NO_x emission from four major sectors (industry, power plants, mobile and residential) was 6800 Gg N yr^{-1} in China in 2008. Therefore, total NO emission from China's terrestrial ecosystems was 18.03% (8.65%–31.35%) of the anthropogenic emission. Cropland and forest were the two largest contributors to biogenic NO emissions and accounted for 6.51% and 5.47% of the anthropogenic emission.

Regarding the great amount of NO emissions from terrestrial ecosystems, it is necessary to consider this source when developing strategies to reduce regional or national levels of O_3, secondary aerosols or N deposition. In addition, given the much diverse biomes in China, more field measurements should be conducted to obtain more representative data in order to well constrain soil NO emission inventory.

Methods

Data compilation. All modeling studies which presented estimates of soil NO emissions in China or regions of China were included. These studies either used "bottom-up" approaches which use various algorithms for estimating soil NO emission based on soil and climatological parameters, or used "top-down" approaches to optimize NO emissions from various sources including soils[13]. In total 10 studies were found to have estimated soil NO emissions for China or regions of

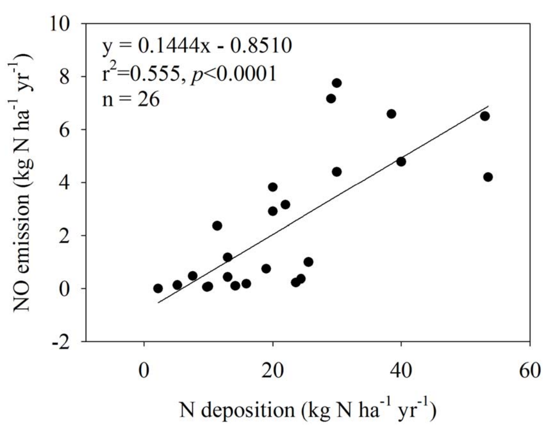

Figure 3 | Dependence of soil NO emission on N deposition for forest. The data and references were presented in Table S2.

China. In addition, two studies which modeled soil NO emissions for both China and Japan[12] or for East Asia[18] were also included for comparison purpose.

For field measurements, the following criteria were used to select studies: (i) soil NO emission measurements should be conducted in the field; (ii) for cropland, measurements should cover at least a complete growing season; (iii) given a cropland field was planted with different batches of crops over a year or consecutive years, each batch was regarded as an independent measurement site; (iv) NO emissions from bare soils of cropland were rejected if the bare soils were fertilized; (v) data were excluded if FIE were greater than 10% since these kind of values were far more than the upper limit of 95% confidence interval (95% CI) of the dataset. Although measurements of soil NO emissions for different land uses were available based on laboratory studies[53–57], they were discarded due to the difficulty to extrapolate these data to field conditions, e.g., no management or vegetation existed for all the incubated soil. In total, 20 peer-reviewed papers were included in the dataset, which composed of 130 measurement sites from 14 locations (Fig. 1, Table S1 and Notes S1).

The raw data were either obtained from tables or extracted by digitizing graphs using the GetData Graph Digitizer (version 2.24, Russian Federation). For each paper, the following information was compiled: location (longitude and latitude), climatic information (mean annual temperature (MAT) and mean annual precipitation (MAP)), vegetation type, soil properties (soil texture, bulk density, soil organic carbon, total N, pH), starting and end dates of sampling, measurement frequency, chamber type and dimension, fertilizer type and rates, mean NO fluxes over the sampling periods, FIE, total emissions over the sampling periods and annual emissions.

Data analyses. Since the data were much skewed, median instead of mean values was used as a measure of statistics[58]. Confidence interval for a median was calculated according to Campbell and Gardner[59]. The n (sample size) sample observations were ranked in increasing order of magnitude and the rth to sth observations in the ranking thus determined the 95% confidence interval (95% CI) for the median. r and s were calculated according to Eqn (2) and (3):

$$\mathrm{r} = \frac{n}{2} - \left(1.96 \times \frac{\sqrt{n}}{2}\right) \quad (2)$$

$$s = 1 + \frac{n}{2} + \left(1.96 \times \frac{\sqrt{n}}{2}\right) \quad (3)$$

However, when the sample size was too small, the 95% CI was not calculated. For forest and grassland, the mean values were presented since only two measurements were available for both biomes.

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Author contributions

D.L. designed the study; Y.H. compiled and analyzed the data. All authors discussed and wrote the manuscript and contributed equally.

Additional information

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