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Atmospheric nitrogen deposition in the Yangtze River basin: Spatial pattern and source attribution☆

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ABSTRACT

The Yangtze River basin is one of the world's hotspots for nitrogen (N) deposition and likely plays an important role in China's riverine N output. Here we constructed a basin-scale total dissolved inorganic N (DIN) deposition (bulk plus dry) pattern based on published data at 100 observational sites between 2000 and 2014, and assessed the relative contributions of different reactive N (N_r) emission sectors to total DIN deposition using the GEOS-Chem model. Our results show a significant spatial variation in total DIN deposition across the Yangtze River basin (33.2 kg N ha^{-1} yr^{-1} on average), with the highest fluxes occurring mainly in the central basin (e.g., Sichuan, Hubei and Hunan provinces, and Chongqing municipality). This indicates that controlling N deposition should build on mitigation strategies according to local conditions, namely, implementation of stricter control of N_r emissions in N deposition hotspots but moderate control in the areas with low N deposition levels. Total DIN deposition in approximately 82% of the basin area exceeded the critical load of N deposition for semi-natural ecosystems along the basin. On the basin scale, the dominant source of DIN deposition is fertilizer use (40%) relative to livestock (11%), industry (13%), power plant (9%), transportation (9%), and others (18%, which is the sum of contributions from human waste, residential activities, soil, lighting and biomass burning), suggesting that reducing NH_3 emissions from improper fertilizer (including chemical and organic fertilizer) application should be a priority in curbing N deposition. This, together with distinct spatial variations in emission sector contributions to total DIN deposition also suggest that, in addition to fertilizer, major emission sectors in different regions of the basin should be considered when developing synergistic control measures.

1. Introduction

In the past few decades, human activities associated with agricultural and industrial production emitted large amounts of nitrogen (N) oxides ($NO_x = NO + NO_2$) and ammonia (NH_3) to the atmosphere (Galloway et al., 2008). They can be transported in downwind direction and transformed in the atmosphere to nitric acid (HNO_3) and to particulate ammonium (NH_4^+) and nitrate (NO_3^-) via chemical reactions, and eventually return to earth surface by wet and dry deposition processes. As a consequence, atmospheric N deposition has dramatically increased globally, and this increase is expected to continue over China (Kanakidou et al., 2016). Meanwhile, a considerable portion of deposited N in land can also be transported to coastal waters and the open ocean via river flow (Fowler et al., 2013). Excessive N inputs into aquatic ecosystems can cause negative environmental and ecological effects, e.g.,

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eutrophication of water body (Bergström and Jansoon, 2006), hypoxia (Diaz and Rosenberg, 2008), breakout of red tide (Dai et al., 2010), and a loss of biodiversity (Clark and Tilman, 2008).

The Yangtze River basin is a region characterized by rapid economic development and population growth, and generates as much as half of China's gross domestic product (GDP) (Lin et al., 2005). This, in turn, makes the basin suffered from serious reactive nitrogen (N_r) pollution (Gu et al., 2012). The Yangtze River is the largest river in the Euro-Asian continent and is the third longest river in the word. It is responsible for significant N discharges into its estuary and the adjacent East China Sea, leading to negative ecological effects (Dai et al., 2010). Dissolved inorganic nitrogen (DIN), which includes oxidized (e.g., NO_x, HNO_3, NO_3^-) and reduced (e.g., NH_3, NH_4^+) forms, is often the most abundant and bioavailable form of N and thereby contributes significantly to coastal eutrophication (Veuger et al., 2004; Dumont et al., 2005). Using a mass balance model, Wang et al. (2014) estimated that the contributions of bulk DIN deposition (i.e. wet plus some dry deposition, measured by open rain collectors) to total N input to the basin increased from 3% in 1980 to 5% in 2000. Furthermore, Chen et al. (2016) reported that atmospheric DIN deposition accounts for on average approximately 13% of human-controlled N inputs into the basin during the period of 1980–2012. Using principal components analysis, Xu et al. (2013) estimated that DIN deposition contributed 25–28% of total DIN loads in the river between 1972 and 2010. These estimated contributions, however, are inherently uncertain mainly due to the scarcity of complete observational data on dry N deposition, which accounted for approximately 40% of total N deposition in the Yangtze River basin (Shen et al., 2013; Xu et al., 2015; Kuang et al., 2016), compared with 60% of that in northern China (Pan et al., 2012). Indeed, long-term measurement of dry N deposition at a regional scale remains a major challenge because of the wide range of N-containing compounds in gaseous and aerosol phases, and technical difficulties associated with measurement of their deposition, especially in remote areas (Xu et al., 2015). An alternative and widely accepted approach uses a spatial interpolation technique to yield continuous estimates of dry N deposition from discrete data points on a spatial scale (Nowlan et al., 2014; Jia et al., 2016). However, to date, no study (based on the interpolation method) has provided any information on the magnitude and spatial pattern of total (wet plus dry) DIN deposition over the Yangtze River basin, significantly limiting our knowledge of the N cycle in the basin.

Chemical transport models (CTMs) are capable of simulating the magnitude and spatial pattern of total DIN deposition, and have been employed at the national scale (Zhang et al., 2012a) and on a global scale (Vet et al., 2014; Kanakidou et al., 2016). Recent advances in N deposition modeling include improved estimates of DIN deposition at a continental scale using a nested modeling approach with the GEOS-Chem global chemical transport model to estimate DIN deposition in China (Zhao et al., 2017). However, few studies modeled the spatial distribution patterns of total DIN deposition at a regional scale (Huang et al., 2015), mainly due to lack of resolution in model input data, such as spatial emissions. In addition, modeled total DIN deposition should be compared to surface observations to validate and improve models, but few of these datasets are available (Pan et al., 2012; Xu et al., 2015). Thus, application of the interpolation method and comparison with a modeling method can provide reliable information on the magnitude and spatial pattern of total DIN deposition at a regional scale.

To develop emission control strategies to conserve ecosystem health, the emission sources of N deposition needed to be determined. Using the moss $\delta^{15}N$ method, a previous study determined that the main atmospheric N sources in the Yangtze River basin were excretory wastes for most of the cities and soil emission for forests (Xiao et al., 2010). However, large uncertainties may exist in the results from Xiao et al. (2010), since relevant analysis was built on the $\delta^{15}N$ signatures of potential atmospheric N sources established for other countries (e.g. Germany); it is unsure whether there is spatial variability of $\delta^{15}N$ signatures. Fortunately, CTMs by simulating physical and chemical processes of atmospheric N pollution are useful in providing insights into the relative contribution of emissions sources to N deposition. Existing CTMs such as the Goddard Earth Observing System with chemistry (GEOS-Chem) model (Lee et al., 2016; Zhao et al., 2017), the Community Multiscale Air Quality (CMAQ) model (Qiao et al., 2015) and the European EMEP model (Simpson et al., 2014) have capability to link N sources with deposition. For example, Zhao et al. (2017) used the GEOS-Chem model to show that in China total N deposition is predominantly contributed by domestic anthropogenic sources (86%), followed by *trans*-boundary import of anthropogenic sources (7%) and natural sources (7%). However, relative contributions from different emission sectors (e.g., fertilizer, manure, industry, power plants, and other) to N deposition were not quantified. Source attribution data calculated with CTMs may be used in an integrated assessment modeling framework to calculate the cost-benefit of reduced nitrogen deposition from targeted emission reduction policies (Oxley et al., 2013).

In the present study, we use the spatial interpolation technique and available published data to map the spatial distribution of total DIN deposition in the Yangtze River basin. In addition to this, an attempt is made to quantify contributions from different emission sectors (i.e. fertilizer use, livestock, industry, power plant, transportation, and others) to total DIN deposition using the GEOS-Chem model. A comparison of spatial patterns of total DIN deposition obtained with interpolation technique and the GEOS-Chem model is also made using provincial deposition totals. The outcomes of this study are expected to provide the scientific basis for developing an effective policy for N pollution abatement in the basin.

2. Methodology and data collection

2.1. Study area

The Yangtze River basin is located between 24°-35°N and 90°-122°E, originating from the Tibetan Plateau, cross the country from west to east, and finally flowing into the East China Sea (Fig. 1). The basin has a total drainage area of approximately 1.8×10^6 km^2, covering about 20% of the total land area of mainland China. The areas of the Hubei, Hunan, Jiangxi, and Sichuan provinces, which are totally located within the basin, account for about 65% of the total basin area, while areas of the other 13 provinces (Qinghai, Gansu, Yunnan, Tibet, Shaanxi, Guizhou, Guangxi, Henan, Anhui, Jiangsu, Shanghai, Guangdong, Fujian) account for 35% of the total basin area (Yan et al., 2003). The climate in large parts of the basin is subtropical monsoon. The long-term mean annual precipitation in this region is approximately 1070 mm, but the spatial and temporal distributions are highly uneven, ranging from 500 mm in the west to 2500 mm in the east, and more than 60% of the annual precipitation occurs in summer (June, July and August) (Xu et al., 2008).

There are nearly 440 million inhabitants in the basin. The main land use types are forest, farmland and grassland (Fig. 1), of which the areas accounted for 40%, 30% and 24% respectively, of the total basin area over the 1980–2012 period (Chen et al., 2016). Agriculture is well developed in the Sichuan basin and corresponding regions in the middle and lower reaches of the Hunan, Hubei, Anhui and Jiangsu provinces, where regional NH_3 emissions are concentrated compared with low NH_3 emissions in the northwest remote area of the basin (e.g., Qinghai and Xizang) (Huang et al., 2012). In these regions, a turning cultivation system of rice-wheat, rice-rape,

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