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Effects of land use on the concentration and emission of nitrous oxide in nitrogen-enriched rivers☆

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ABSTRACT

Nitrous oxide (N_2O) is a potent greenhouse gas that contributes to climate change and stratospheric ozone destruction. Nitrogen-enriched rivers are significant sources of atmospheric N_2O. This study conducted a one-year field campaign in seven N-enriched rivers draining urban, rural, and agricultural land to determine the link between the production, concentrations, and emissions of N_2O and land use. Estimated N_2O fluxes varied between 1.30 and 1164.38 μg N_2O-N m^{-2} h^{-1} with a mean value of 154.90 μg N_2O-N m^{-2} h^{-1}, indicating that rivers were the net sources of atmospheric N_2O. Concentrations of N_2O ranged between 0.23 and 29.21 μg N_2O-N L^{-1} with an overall mean value of 3.81 μg N_2O-N L^{-1}. Concentrations of ammonium and nitrate in urban and rural rivers were high in the cold season. The concentrations were also high in agricultural rivers in the wet season. N_2O concentrations and emissions in rural and urban rivers followed a similar pattern to ammonium and a similar pattern to nitrate in agricultural rivers. A strong link between the concentrations and emissions of N_2O and land use was observed. N_2O concentrations in and emissions from the rivers draining the urban and rural areas were significantly higher than the rivers draining the agricultural areas ($P < 0.01$). Stepwise regression analysis indicated that dissolved N_2O were primarily influenced by NH_4^+ in agricultural rivers and by NO_3^- in rural rivers; while dissolved N_2O in urban rivers was primarily predicted by temperature and reflected the integrated impact of sewage input and river hydrology. Nitrate-N and NO^{3-}-O isotope data and linear regression of N_2O and river water variables strongly indicated that dissolved N_2O was mainly derived from nitrification in agricultural rivers and denitrification in rural and urban rivers.

1. Introduction

Nitrous oxide (N_2O) is an atmospheric trace gas and a strong ozone-depleting substance that has attracted considerable scientific attention (Garnier et al., 2009; Ravishankara et al., 2009). N_2O is the third most important greenhouse gas with a global warming potential approximately 298 times that of carbon dioxide (CO_2) over a 100-yr period (IPCC, 2013). Global nitrogen (N) enrichment has resulted in an increase in the concentration of atmospheric N_2O, which increased from ~270 parts per billion by volume (ppbv) in pre-industrial times to 321 ppbv at a rate of 0.25% yr^{-1} (IPCC, 2013). N_2O emissions are expected to remain at high levels throughout the 21st century and aquatic systems are estimated to contribute to 25%–30% of total global N_2O emissions (Ravishankara et al., 2009).

River systems receiving increased anthropogenic N loading from agricultural fertilizers and human waste are important sources of N_2O (Alvim et al., 2014; Seitzinger et al., 2000; Yan et al., 2012). High saturation and emission of N_2O has been measured from rivers in many studies globally (Seitzinger and Kroeze, 1998; Stow et al., 2005). Generally, riverine N_2O is produced as a byproduct of microbially mediated denitrification and nitrification. Under anaerobic conditions, denitrification can permanently remove nitrate-nitrogen (NO_3^--N), producing N_2O and N_2; annually; <1% of denitrified N is converted to N_2O (Beaulieu et al., 2010; Weier et al., 1993). Increased concentrations of NO_3^- may contribute to higher rates of denitrification and alter the ratio of N_2O to N_2 but may not increase the N_2O yield (Zhu et al., 2010). N_2O is also produced as a byproduct of nitrification where ammonium (NH_4^+) is oxidized to NO_3^- and N_2O under oxic conditions (Stein and Yung, 2003). Coupled nitrification–denitrification can be an important source of

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N_2O in large, N-limited rivers (Allen et al., 2007; De Wilde and De Bie, 2000).

Thus, N_2O production is a function of both nitrification and denitrification. However, simple relationships between the rates of N cycling and N_2O production may not exist because of the uncertainty associated with spatial and temporal variations in environmental conditions. It is generally assumed that the dissolved inorganic nitrogen (DIN) load within a river is linearly related to riverine N_2O yield. However, this result seems to merit further study. Land use reflects the heterogeneity of a watershed and exerts a strong influence on river chemistry. The influence of land use categories on water parameters often varies with the spatial scale and seasons. Thus, biochemical processes of N in rivers also change with the heterogeneity of the watershed because of which riverine N_2O concentrations are linked to the land use (Harrison and Matson, 2003). Surface waters impacted by urbanization and anthropogenic activities exhibit individual hydrochemical characteristics; as a result, the factors controlling N_2O production and emissions may differ. Numerous investigations have found strong correlations between dissolved N_2O and NO_3^- concentrations in some agricultural or N-limited rivers (Harley et al., 2015; Herrman et al., 2008; Reay et al., 2003; Turner et al., 2016; Yan et al., 2012). However, the relationship between dissolved N_2O and nitrogen might be different in rural and urban rivers. A study by Wang et al. (2015a) found a significant positive relationship ($r^2 = 0.22$, $P < 0.001$) between NH_4^+ and N_2O production; NH_4^+ and dissolved oxygen (DO) explained 64% of the variability in N_2O production in urban rivers. Land use strongly affects water quality and sediment characteristics, which in turn enhance sediment denitrification and N_2O production (Garcia-Ruiz et al., 1998; Liu et al., 2015a). A study in a severely polluted urban river found that sediments were the sources of N_2O in river water (Wang et al., 2015b). Sediment denitrification in rivers can play an important role in riverine N_2O production; riverine N_2O concentration and emission dynamics vary greatly with the changes in land use. However, little is known about how N_2O changes with the land use type.

Understanding the linkage between the concentrations and emissions of riverine N_2O and land use can provide a scientific reference for establishing an inventory of greenhouse gases and land use management. This study reports the results of a 12-month investigation of seven N-enriched tributaries (including urban, rural, and agricultural rivers) in the Chao Lake basin, which is ideal for the purpose of this study because of the heavy water pollution and diversity of land use types in the basin. The objective of this study is to understand the effect of land-use on the seasonal dynamics of riverine N_2O concentrations and emissions.

2. Materials and methods

2.1. Site description

This research was conducted in the Chao Lake basin (E116°30′20″-118°0′0″, N30°58′40″–32°6′0″) in southeastern China with a watershed area of 13,500 km^2. This basin is located in a typical subtropical monsoon area. The annual average rainfall, wind speed, and temperature of this basin are 1100 mm, 3.5 m s^{-1}, and 18.8 °C, respectively. The rainy season is generally from June to August (Zhou and Wu, 2009).

The Chao Lake basin is one of the most densely populated areas in China, with a population of 61 million people. With local and regional development, N loading of the basin has increased continuously. Annually, approximately 1.2 billion tons of sewage enters the basin's urban rivers. This basin is also typical of agricultural production areas in central China, which are subject to heavy agricultural activity. Chemical fertilizers have been used extensively in agricultural lands in recent years with a mean N fertilizer rate of 960 kg km^{-2} yr^{-1} across the Chao Lake basin; as a result, about 1900 tons of N leached to the rivers from various sources. Consequently, water quality in this basin has degraded substantially and the basin waterways are known to experience eutrophication and algal blooms.

Nutrient concentrations vary greatly among the tributaries flowing into the Chao Lake due to the differences in land use and human activities. In this study, seven major tributaries, the Nanfei (NR), Ershibu (ER), Dianbu (DR), Shiwuli (SR), Pai (PR), Fengle (FR), and Hangbu (HR) rivers were investigated (Fig. 1) and one sampling site was set up on each river. Rivers were categorized as urban, rural, and agricultural rivers according to the land-use type. In this study, agricultural rivers refer to the rivers that drain cropland areas; in those rivers, nutrients are mainly derived from surface runoff. Rural rivers drain populated areas in villages and towns and nutrients are mainly derived from the effluent of rural domestic sewage. Because the urban areas are larger, N concentrations in urban rivers could vary greatly between upper and lower reaches. To collect the representative water samples from urban rivers where sewage is well mixed with river water, the sampling sites in NR and ER are located in the downriver section and in city proper (Hefei City). Sampling sites in SR, DR, and PR were located in rural areas and sites in FR and HR in cropland areas (mainly for rice cultivation). The categories of land use for each river watershed are obtained via remote sensing and GIS (Table 1).

Based on the land-use data in Table 1, the percentages of developed land around the Nanfei, Ershibu, Shiwuli, and Dianbu rivers are close to each other (Table 1). The Nanfei and Ershibu rivers are classified as urban rivers, while Shiwuli and Dianbu rivers are classified as rural rivers. The developed land involves both urban and rural built-up areas. Although the percentages of developed land are close to each other, the Nanfei and Ershibu rivers (especially the sampling sites on those two rivers) are mainly located in urban areas (Hefei City) and the Shiwuli and Dianbu rivers are mainly located in rural areas (Cuozhen and Longtang).

2.2. Sample collection and chemical analysis

Monthly sampling to measure dissolved N_2O, water quality parameters, and abundance of nitrate isotopes was conducted from January to December 2013. Triplicate samples of surface river water were collected at a depth of 0.2 m using a water sampler. In the field, collected water samples were filtered through glass fiber filters (0.45 μm) and stored in acid-washed plastic bottles before the measurement of NH_4^+, NO_3^-, TP, BOD_5, COD_{Mn}, SO_4^{2-}, Cl^-, $\delta^{15}N\text{-}NO_3^-$, and $\delta^{18}O\text{-}NO_3^-$ in the laboratory. DO, pH, and water temperature were measured *in situ* using a portable meter (HQ30D, U.S.). Other chemical analyses were conducted based on the standard methodology. The concentrations of NH_4^+, NO_3^-, TP, BOD_5, COD_{Mn}, SO_4^{2-}, and Cl^- were measured using an indophenol blue colorimetric method, an ultraviolet spectrophotometry method, an alkaline potassium persulfate digestion method, a dilution inoculation method, a standard titrimetric method, a gravimetric method, and mercury nitrate titration, respectively.

Samples were collected in serum bottles (60 mL, FIS#06-406H) tightly sealed with butyl-rubber stoppers to determine dissolved N_2O and preserved with the addition of a few drops of saturated mercuric chloride solution to prevent biological activity (Kirkwood, 1992). Samples were stored in a cooler during transport and analyzed within 24 h. The headspace-equilibrium method was used to measure the initial dissolved N_2O concentrations in river water (Clough et al., 2007; Crill et al., 1995; Huttunen et al., 2002). Then, 20 mL of highly purified N_2 (purity > 99.999%) was injected into the sampling bottle using an air-tight syringe and 20 mL of the water