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Nitrogen removal rates in a frigid high-altitude river estimated by measuring dissolved N_2 and N_2O

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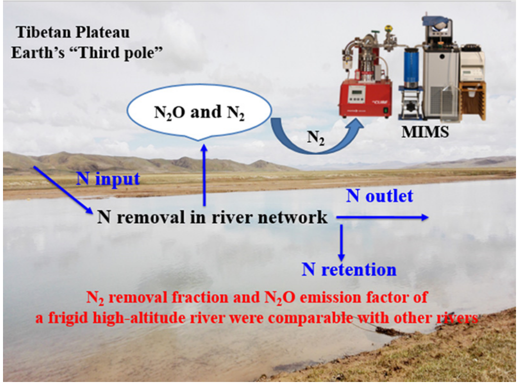
HIGHLIGHTS

- Excess dissolved N_2 and N_2O in the Yellow River source region were lower than other rivers.
- N_2O emission factor increased with the elevation of the Yellow River in its source region.
- N_2 removal fraction and N_2O emission factor in this study were comparable with other rivers.
- The nitrogen removal from the Yellow River source region was about 1.87×10^7 kg N yr^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

Rivers are important sites of both nitrogen removal and emission of nitrous oxide (N_2O), a powerful greenhouse gas. Previous measurements have focused on nitrogen-rich temperate rivers, with cold, low-nitrogen river systems at high-altitude receiving less attention. Here, nitrogen removal rates were estimated by directly measuring dissolved N_2 and N_2O of the Yellow River in its source region of the Tibetan Plateau, a frigid high-altitude environment. We measured the dissolved N_2 and N_2O using N_2:Ar ratio method and headspace equilibrium technique, respectively. Dissolved N_2 in the river water ranged from 337 to 513 μmol N_2 L^{-1}, and dissolved N_2O ranged from 10.4 to 15.4 nmol N_2O L^{-1}. Excess dissolved N_2 ($\triangle N_2$) ranged from −8.6 to 10.5 μmol N_2 L^{-1}, while excess dissolved N_2O ($\triangle N_2O$) ranged from 2.1 to 8.3 nmol N_2O L^{-1}; they were relatively low compared with most other rivers in the world. However, N_2 removal fraction ($\triangle N_2$/DIN, average 21.6%) and EF_{5r} values ($N_2O - N/NO_3 - N$, range 1.6×10^{-4}–5.0×10^{-2}) were comparable with many other rivers despite the high altitude for the Yellow River source region. Furthermore, the EF_{5r} values increased with altitude. Estimated fluxes of N_2 and N_2O to the atmosphere from the river surface ranged from −67.5 to 93.5 mmol N m^{-2} d^{-1} and from 4.8 to 93.8 μmol N m^{-2} d^{-1}, respectively, and the nitrogen removal from rivers was estimated to be 1.87×10^7 kg N yr^{-1} for the Yellow River source region. This is the first report of nitrogen removal for a frigid high-altitude river; the results suggest that N removal and N_2O emission from cold high-altitude rivers should be considered in the global nitrogen budget.

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1. Introduction

Rivers are an important sink in the global nitrogen (N) budget, receiving high N loads (~118 Tg N yr^{-1}) from the terrestrial landscape and converting approximately 40% of this terrestrial input to biologically unavailable dinitrogen gas (N_2) along the drainage network (Galloway et al., 2004). However, a great deal of uncertainty remains in global nitrogen removal from river systems. It is thus important to better quantify the role of riverine N removal in the global N budget. Potential pathways for N removal (production of gaseous end products) include denitrification, nitrification (nitrous oxide, N_2O), anaerobic ammonium oxidation (anammox), and other processes (DNRA) (Xia et al., 2017b; Zhang et al., 2017). Denitrification, which converts nitrate (NO_3^-) to N_2 and N_2O, is the primary N removal pathway in rivers (Galloway et al., 2008; Xia et al., 2017a); anammox, where NH_4^+ is converted to N_2, has recently been discovered to remove N in some rivers (Cheng et al., 2016; Kim et al., 2016; Sun et al., 2014). In streams and rivers, the dominant end product of denitrification is N_2 rather than N_2O (Beaulieu et al., 2011). Nitrous oxide is also produced as a by-product in the nitrification process as well as being an intermediate product in denitrification (Canfield et al., 2010). The N_2O molecule is a powerful greenhouse gas having a global warming potential 296 times greater than carbon dioxide (CO_2) (Stocker et al., 2013) and is expected to remain the largest ozone-depleting emission throughout the 21st century (Ravishankara et al., 2009). Bed-sediments in many rivers are favorable environments for microbial denitrification and anammox (Johannsen et al., 2008; Lansdown et al., 2016; Li et al., 2010) due to the high frequency of low oxygen concentrations. Furthermore, NO_3^- can be denitrified in the suboxic water column (Reisinger et al., 2016; Seitzinger et al., 2006), and even on suspended sediment (SPS) of oxic waters such as turbid rivers (Jia et al., 2016; Liu et al., 2013b).

Direct estimates of N removal rates from rivers are best based on the production of N_2 and N_2O. However, the high atmospheric background levels of N_2 concentration make it difficult to directly quantify the N_2 flux *in situ* with flux chambers. To solve this problem, denitrification rates can be estimated with microcosm experiments that employ various techniques including acetylene inhibition, application of ^{15}N tracers, and mass balance approaches (Herrman et al., 2008; Smith et al., 2006). However, these methods are expensive and time-consuming, and the results obtained may not accurately reflect *in situ* removal rates (Groffman et al., 2006). For instance, the acetylene inhibition technique can lead to underestimation of denitrification rates because the acetylene inhibits the production of NO_3^- by nitrification, which may cause nitrification-denitrification decoupling, and it cannot entirely inhibit nitrous oxide reduction (Bernot et al., 2003). The application of ^{15}N tracers has been limited due to the high cost of isotopic tracer additions *in situ*, and has typically been limited to small streams (Mulholland et al., 2008). The measurement of N_2:Ar by membrane-inlet mass spectrometry (MIMS) is a relatively new approach in quantifying denitrification rates through directly measurement of dissolved N_2 in water samples and correcting for the air saturation concentration. The MIMS method is similar to the approach established by Kana (Kana et al., 1994) and has several advantages, such as rapid analysis (~20 to 30 samples h^{-1}), small sample volume (<7 mL), lack of sample water preparation (*e.g.*, no degassing step), and low coefficients of variation (CVs) of the N_2 to Ar ratios for duplicated samples (<0.03%).

In situ measurements of N_2O fluxes have been conducted for some rivers and streams (Clough et al., 2007; Hinshaw and Dahlgren, 2013); however, there is great uncertainty in estimation of indirect nitrous oxide (N_2O) emissions as defined by the Intergovernmental Panel on Climate Change (IPCC). Measurements of the N_2 production rate have generally been made in microcosm experiments (Herrman et al., 2008; Smith et al., 2006). In addition, these studies have focused on river systems at low altitudes, with a bias toward N-rich rivers and estuaries located in tropical, sub-tropical and temperate regions (Chen et al., 2014a; Hama-Aziz et al., 2016). Less attention has been given to estimations of *in situ* N removal in low-N river systems at high altitudes. Although N_2 and N_2O effluxes tend to increase with N loads (Beaulieu et al., 2010; Chen et al., 2014b; Clough et al., 2011), the trends are usually weak or nonexistent (Soued et al., 2016). The measured N_2 removal fraction (E_d, unit of N_2 produced per unit of N processed) has been observed range from 2 to 94% (Chen et al., 2014b) while the measured N_2O yield (ratio of N_2O generation to ($N_2 + N_2O$) generation) ranged from 0.1% to 6% (Beaulieu et al., 2011). This wide range in the N_2 removal fraction and N_2O yield emphasize the complexity of the microbial processes that regulate riverine N_2 and N_2O production under different biological and hydrologic characteristics, and no clear large-scale patterns have been identified. There remains the need to understand the N_2 and N_2O dynamics for a wide range of river systems.

In this paper, we quantify N removal rates along the high-altitude reaches of the Yellow River in China by directly measuring dissolved N_2 and N_2O. Originating in the Tibetan Plateau, which is often referred to as Earth's "Third pole," the Yellow River source region is a relatively pristine landscape that has been subjected to relatively little human intervention and remains unstudied until now. The objectives of the present study are to (1) investigate gaseous N concentrations in river water of the Yellow River source region; (2) relate gaseous N concentrations in river water to environmental factors (*e.g.*, NO_3^- and NH_4^+ concentration, altitude, atmosphere pressure, and temperature); (3) compare the measured N_2 removal fraction (E_d) and N_2O emission factor (EF_{5r}) with previous studies; (4) estimate N_2 and N_2O fluxes using a water - gas exchange model and N removal. Results of this study provide the first information available for N removal and N_2O emissions for a frigid high-altitude river.

2. Material and methods

2.1. Study area

The study was conducted in the source region of the Yellow River in the Tibetan Plateau. The drainage area (1.22×10^5 km^2) of this region only accounts for 15% of the entire Yellow River basin, but accounts for about 35% (168 mm/a) of the total runoff for the Yellow River (Hu et al., 2011). Therefore, the region is called the "Water Tower" of the Yellow River for millions of people. The source region has no large dams and no large irrigation projects, so it is a relatively pristine area and has been subject to little human intervention (Hu et al., 2011). The climate in this region is cold and semi-humid, with temperatures below 0 °C from October to April and an average annual precipitation of about 530 mm, 75–90% of which occurs between June and September. Elevation in the study region ranges from 1650 m to 4221 m, with a basin-wide average of 3014 m. Glaciers are widespread but are shrinking with climate change; 10.1% of total glacier area has been lost from 1970 to 2000 (Zhang et al., 2012).

2.2. Sample collection

According to the hydrological and geographic conditions, fifteen sampling sites were located along a 2270-km reach in the Yellow River source region; twelve sites were in the mainstem and three sites were in the tributaries (Fig. 1). Each of these sites has a hydrologic station that can provide basic hydrological data. Water samples were collected at each station in May and July of 2016 and 2017. The icebound season in the Yellow River source region is from October to April; May is the month when the ice in the river melts completely and July is the warmest month, with a mean daily air temperature of 8 °C. To avoid contaminating samples by any surface pollutants, water samples were collected at 5 cm below the surface using a 5-L Niskin water sampler. Sampling occurred mainly between 10:00 and 16:00 to minimize any potential variability caused by diel changes in water chemistry or gas concentrations. Triplicate water samples for dissolved N_2 were placed in 12 mL glass vials with a high depth/diameter ratio (Labco Exetainer,