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Degradation dynamics and bioavailability of land-based dissolved organic nitrogen in the Bohai Sea: Linking experiment with modeling

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ABSTRACT

Dissolved organic nitrogen (DON) is the major nitrogen form in the Bohai Sea. Land-based DON is released into the nitrogen pool and degraded by planktonic microbiota in coastal ocean. In this study, we evaluated the degradation of land-based DON, particularly its dynamics and bioavailability, in coastal water by linking experiment and modeling. Results showed that the degradation rate constant of DON from sewage treatment plant was significantly faster than those of other land-based sources ($P < 0.05$). DON was classified into three categories based on dynamics and bioavailability. The supply of dissolved inorganic nitrogen (DIN) pool from the DON pool of Liao River, Hai River, and Yellow River was explored using a 3D hydrodynamic multi-DON biogeochemical model in the Bohai Sea. In the model, large amounts of DIN were supplied from DON of Liao River than the other rivers because of prolonged flushing time in Liaodong Bay.

1. Introduction

With the rapid development of economy and society in coastal zones, large amounts of land-based pollutants are discharged into the coastal ocean, in which nitrogen plays an important role (Ryther and Dunstan, 1971; Vitousek and Howarth, 1991). Human activities are the dominant factor affecting nitrogen export in coastal areas worldwide (Kroeger et al., 2006; Nixon, 1995; Smith, 2003). Humans continuously change land use types into agricultural, industrial, and urban land by burning of fossil fuel, planting of leguminous crops, and increasing fertilizer use; these phenomena rapidly increase nitrogen emissions (Galloway et al., 2014; Howarth et al., 1996; Vitousek, 1997). About 48 million tons of N is discharged into the coastal ocean via rivers (Boyer et al., 2006).

Most studies focused on dissolved inorganic nitrogen (DIN) (Baeyens et al., 1984; Gentilhomme and Lizon, 1997; Radach et al., 1990; Ramírez et al., 2005; Wafar et al., 1983). Only few studies emphasized the importance of dissolved organic nitrogen (DON) in coastal water (Butler et al., 1979; De Galan et al., 2004; Jurgensone and Aigars, 2012; Pellerin et al., 2006; Zee and Chou, 2004). DON is considered refractory to phytoplankton or refractory in a relatively short time scale because of its persistence (Antia et al., 1991; Bronk et al., 2006).

Similar to DIN, DON is critical in coastal ocean ecosystems. Many studies indicated that DON is dominant in coastal catchment (Lønborg and Søndergaard, 2009; Peters and Donohue, 2001; Petrone et al., 2009). In the Bohai Sea, DON comprises 63% of the TDN (Li et al., 2015). DON is also an important nutrient source for primary production in the coastal ocean ecosystem. Moreover, DON can be degraded by microbes into DIN, which is as a nutrient source easily utilized by primary producers. Some phytoplankton directly utilize specific DON as their nutrients (Berman and Bronk, 2003; Berman and Chava, 1999), such as urea (Lisa et al., 2002). Based on the bioavailability of DON and in reference to the study of Badr et al. (2008), DON strongly strains the eutrophication of coastal water. Thus, DON cannot be completely ignored.

Most DON forms are bioavailable. Thus, studying the bioavailability of DON in coastal water may contribute to elucidate this nitrogen form. Seitzinger et al. (2002) reported that the bioavailability of DON range from 0 to 73%, and the bioavailability of DON from urban source is higher than that from agricultural and forest source in New Jersey watershed. The same order (urban > agriculture > forest) was reported in a study about a coastal catchment in South-western Australia (Petrone et al., 2009), where the DON bioavailability ranges from 4% to 44%. In a study on two rivers in Denmark (Lønborg and Søndergaard, 2009), approximately 43% (Horsens Fjord) and 28% (Darss Sill) DON is bioavailable. Bioavailable DON (BDON) also comprises approximately 52% (Horsens Fjord) and 74% (Darss Sill) of BTDN (BDON + DIN). In a study about nine Eastern US rivers (Wiegner et al., 2006), the DON bioavailability was low, with a value of only 23%; this experiment lasted for only 6 days. Moreover, this study indicated that bioavailability is independent of initial DON concentration.

Although the importance of DON distribution and cycling in coastal ecosystems has been recognized, the sources, transport, and

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transformation of DON are not well understood. Generally, DON in coastal ecosystems is derived from two types of sources, namely, allochthonous and autochthonous (Benner, 2003). A major source of allochthonous DON is terrestrially-derived humic substances in a runoff. Studies have focused on DON in human activities (agriculture, intensive animal farming, and treated wastewater), atmosphere, and underground water (Badr et al., 2008; Jickells, 1995; Kroeger et al., 2006). The important contributors of autochthonous DON include microbes, phytoplankton, submerged aquatic vegetation, and sea grass (Bronk et al., 1994). Numerous physical, chemical, and biological processes can produce DON or affect its concentration in the water column; these processes include DON release from sediments (Jen et al., 1998), DON loss caused by photochemical degradation (Hedges and Keil, 1999; Mesfioui et al., 2015), DON production through zooplankton grazing, and bacterial release and uptake (Bronk et al., 1994; Seitzinger et al., 2002).

Marine biogeochemical modeling can be utilized to understand the action of DON in coastal ecosystems. This technique is valuable for numerical simulation of the magnitude of processes that are difficult to measure and observe in the field. Marine biogeochemical models have included DON (Anderson and Pondaven, 2003; Anderson et al., 2007; Druon et al., 2010; Faure et al., 2010; Fouest et al., 2015; Grégoire et al., 2008; Karel et al., 2004; Keller and Hood, 2011; Salihoglu et al., 2008; Schmittner et al., 2005; Van Cappellen et al., 2014; Xiu and Chai, 2014) to simulate and elucidate biogeochemical cycles. These models typically consider autochthonous nitrogen, whilst little considered autochthonous DON. Most of these models are rather complex and have state variables that describe multiple DON classes, such as semi-labile or labile DON. These models also consider DON sources and sinks, such as phytoplankton exudation, zooplankton grazing, breakdown of detritus, and release and uptake by bacteria. Despite the recognized importance of DON cycling in many studies, few coastal biogeochemical models have included autochthonous DON cycling.

In this paper, we present the degradation action of land-based DON from four different sources and the effect of hydrodynamic condition under different stirring rates. Experimental results, including kinetic equation and parameters, were applied to improve the multi-DON biogeochemical model in the Bohai Sea. The model can be further applied to evaluate plans for water quality management.

2. Materials and methods

2.1. Study area

The Bohai Sea is located in the northeast of China (37°07′–41°N, 117°35′–122°15′E). The sea is semi-enclosed and bordered by Bohai Rim (consisting of Shandong Province, Hebei Province, Liaoning Province, Beijing City and Tianjin City) (Fig. 1). The sea is characterized by poor water-exchange capacity and vulnerable marine ecosystem. The Bohai Sea has a surface area of 7.7×10^4 km^2 and an average depth of 18 m. The sea is connected to the Yellow Sea by a ~109-km long channel with a coastline of ~1235 km. The Bohai Sea is increasingly affected by anthropogenic activities. Consequently, eutrophication is a serious problem in the Bohai Sea because of the increasing concentrations of nitrogen and phosphorus since the 1980s (Wang and Li, 2006; Wu et al., 2013). The Bohai Sea receives approximately 36% of terrestrial waste water through ~45 rivers, such as Liao, Yellow, and Hai Rivers, etc. (Wang et al., 2009). Where, Liao River is joined by the East Liao River

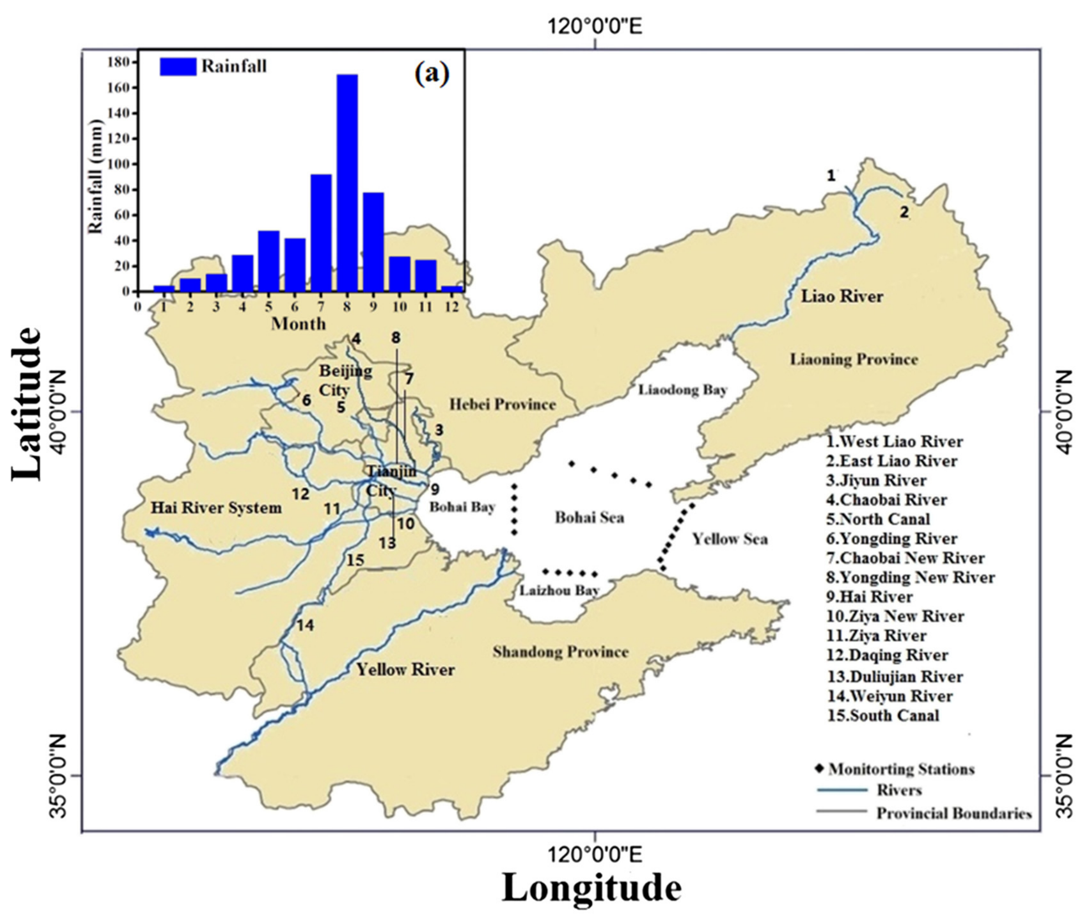

Fig. 1. Location of the Bohai Sea and the average rainfall for the main cities in the basin around Bohai Sea (a).