Atmospheric Environment 43 (2009) 3786–3798

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric nitrogen fluxes at the Belgian coast: 2004–2006

László Bencs [a,b,*], Agnieszka Krata [a], Benjamin Horemans [a], Anna J. Buczyńska [a], Alin C. Dirtu [a,c], Ana F.L. Godoi [a,d], Ricardo H.M. Godoi [a,d], Sanja Potgieter-Vermaak [a,e], René Van Grieken [a]

[a] Micro and Trace Analysis Centre, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium
[b] Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, P.O. Box 49, H-1525 Budapest, Hungary
[c] Department of Inorganic and Analytical Chemistry, University "Al.I. Cuza" of Iassy, 700506, Romania
[d] Department of Environmental Engineering, Federal University of Parana States, Curitiba, Paraná, Brazil
[e] Molecular Science Institute, School of Chemistry, University of the Witwatersrand, 2050 Johannesburg, South Africa

ARTICLE INFO

Article history:
Received 19 June 2008
Received in revised form
31 March 2009
Accepted 1 April 2009

Keywords:
Gaseous
Aerosol
Wet nitrogen flux
Atmospheric deposition
Inorganic N-nutrients
Dissolved organic nitrogen
Coastal eutrophication
North Sea

ABSTRACT

Daily and seasonal variations in dry and wet atmospheric nitrogen fluxes have been studied during four campaigns between 2004 and 2006 at a coastal site of the Southern North Sea at De Haan (Belgium) located at coordinates of 51.1723° N and 3.0369° E. Concentrations of inorganic N-compounds were determined in the gaseous phase, size-segregated aerosol (coarse, medium, and fine), and rainwater samples. Dissolved organic nitrogen (DON) was quantified in rainwater. The daily variations in N-fluxes of compounds were evaluated with air-mass backward trajectories, classified into the main air-masses arriving at the sampling site (i.e., continental, North Sea, and Atlantic/UK/Channel).

The three, non-episodic campaigns showed broadly consistent fluxes, but during the late summer campaign exceptionally high episodic N-deposition was observed. The average dry and wet fluxes for non-episodic campaigns amounted to 2.6 and 4.0 mg N m^{-2} d^{-1}, respectively, whereas during the episodic late summer period these fluxes were as high as 5.2 and 6.2 mg N m^{-2} d^{-1}, respectively.

Non-episodic seasons/campaigns experienced average aerosol fluxes of 0.9–1.4 mg N m^{-2} d^{-1}. Generally, the contribution of aerosol NH_4^+ was more significant in the medium and fine particulate fractions than that of aerosol NO_3^-, whereas the latter contributed more in the coarse fraction, especially in continental air-masses. During the dry mid-summer campaign, the DON contributed considerably (~15%) to the total N-budget.

Exceptionally high episodic aerosol-N inputs have been observed for the late summer campaign, with especially high deposition rates of 3.6 and 2.9 mg N m^{-2} d^{-1} for Atlantic/UK/Channel and North Sea-continental (mixed) air-masses, respectively. During this pollution episode, the flux of NH_4^+ was dominating in each aerosol fraction/air-mass, except for coarse continental aerosols. High deposition of gaseous-N was also observed in this campaign with an average total N-flux of 2–2.5-times higher than in other campaigns.

1. Introduction

The Greater North Sea, a regional sea of North-Western Europe, has a water surface of approximately 775,800 km^2, including the British Channel with an area of 89,620 km^2 (De Leeuw et al., 2003a). Its importance is manifested by a long history of multiple uses by people from several surrounding nations. For the past decades, the growing anthropogenic activities have significantly increased the terrestrial input of nitrogen-containing nutrients to coastal North Sea waters (Spokes and Jickells, 2005). The overload of coastal waters with biologically available nitrogen compounds occurs especially during seasonal pollution episodes. It can cause proliferation of harmful algal blooms and other eutrophication phenomena, which affect the marine ecosystem, thus the fishery and the tourism (Lancelot et al., 1994; Regnier and Steefel, 1999). This is a worldwide environmental problem (Owens et al., 1992; Jickells, 1998).

Atmospheric deposition of nitrogen compounds has been shown to represent a significant terrestrial input to coastal waters, especially, in summer and autumn, when riverine inputs are low (De Leeuw et al., 2003a). Moreover, it also triggers input to mid-oceanic regions removed from riverine sources (Galloway et al., 1994), and can be distributed over spatial scales from tens to hundreds of kilometres (Owens et al., 1992). According to recent

* Corresponding author at: Micro and Trace Analysis Centre, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium.
E-mail addresses: laszlo.bencs@ua.ac.be, bencs@szfki.hu (L. Bencs).

1352-2310/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2009.04.002

reviews, the atmosphere plays the major role in the distribution of reactive nitrogen on regional and global scales (Duce et al., 2008; Galloway et al., 2008). Also, the nitrogen cycle along with the carbon cycle and the climate are expected to become an increasingly important determinant of the Earth system (Gruber and Galoway, 2008).

In relation to these environmental problems, the regional OSPAR Convention has been formulated for the protection of the marine environment of the Northeast Atlantic, to which the European Community and several other countries are contracting parties (Bartnicki and Fagerli, 2006). One of its objectives, organized as "Eutrophication Strategy", is to achieve and maintain a healthy marine environment by 2010, where eutrophication does not occur. This strategy is implemented through measures including reduction of anthropogenic emissions, discharges, and losses of nutrients in all areas from which nutrient input is possible, directly, or indirectly. Recent reports suggest that atmospheric nitrogen inputs play a major role for certain OSPAR Convention waters, including the North Sea (Bartnicki and Fagerli, 2003, 2004; OSPAR Commission, 2005a,b). Emission sources of this atmospheric nitrogen are mostly from the national NO_x and ammonia emissions, including the ship traffic (Bartnicki and Fagerli, 2006).

Atmospheric nitrogen deposition to the North Sea has been shown to occur mostly in the forms of nitrate and ammonium salts, and in addition, its extent is comparable to that of riverine inputs (Rendell et al., 1993). Although the dissolved organic nitrogen (DON) has been reported to be an insignificant component of total N-aerosol loading over coastal waters of the North Sea, it makes up 14% of the total nitrogen in rainwater, on average (De Leeuw et al., 2003b). On the other hand, DON has been reported to be a more significant contributor (20–80%) in other coastal marine areas (Cornell et al., 1995). It is therefore critical to assess the main atmospheric nitrogen fluxes in terms of inorganic and organic nitrogen compounds to get an insight into the extent of eutrophication in coastal regions, and its relation with the biological productivity (De Leeuw et al., 2003b).

The role of atmospheric nitrogen in the total nutrient fluxes to the North Sea and the related chemical and biological processes have been the subject of several experimental and model studies, documented in the relevant literature on marine research (e.g., Rendell et al., 1993; Beddig et al., 1997; Hertel et al., 1995, 2002; Peierls and Paerl, 1997; De Leeuw et al., 2003a,b). However, neither particle-size distributions of N-compounds in aerosols, nor the atmospheric transport of nitrogen compounds from diverse regions surrounding the North Sea on the base of using air-mass backward trajectories (BWTs) have been fully investigated. The BWTs are also useful in assigning various polluted air-masses contributing to coastal eutrophication episodes.

The main objectives of this study is to determine the fluxes of nitrogen compounds at the coastal site of the Southern North Sea at De Haan (Belgium) in terms of wet and dry deposition from atmospheric samples (gaseous, aerosol, and precipitation); to compare and contrast temporal and seasonal differences in fluxes of nitrogen compounds atmospherically deposited at De Haan; and to quantify the concentration and the contribution of the major nitrogen compounds, such as nitrite, nitrate, ammonium and DON to atmospheric deposition.

2. Experimental

2.1. Description of the sampling site and campaigns

Four sampling campaigns were organized between 2004 and 2006, to cover the yearly/seasonal variations in the deposition of nitrogen compounds, scheduled as follows:

- Autumn/early winter campaign (August 21st, 2004–January 31st, 2005)
- Late summer campaign (August 8th–21st, 2005)
- Late winter/spring campaign (February 14th–April 30th, 2006)
- Mid-summer campaign (June 12th–August 8th, 2006)

The sampling site selected for this study, De Haan, in Belgium, is a seaside resort at the coast of the Southern Bight of the North Sea (Fig. 1), located at coordinates 51.1723° N and 3.0369° E. The area at which the sampling equipment was deployed is a small research

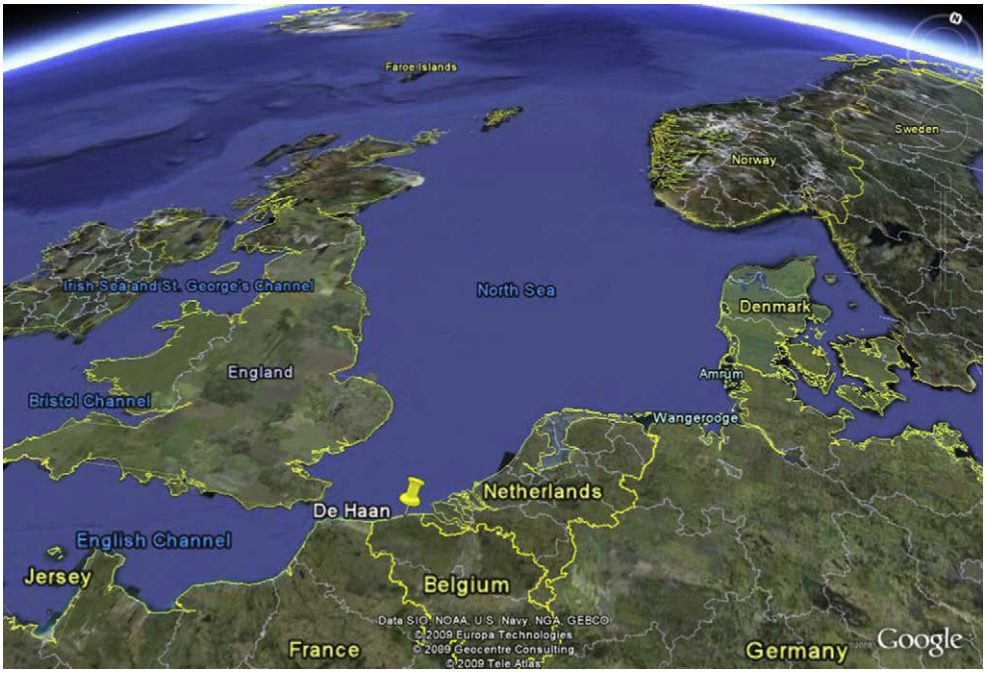

Fig. 1. Map of the North Sea with the sampling area marked at De Haan, Belgium (source: Google Earth).