Atmospheric outflow of nutrients to the Bay of Bengal: Impact of anthropogenic sources

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A B S T R A C T

The air–sea deposition of nutrients (N, P and Fe) to the oceanic regions located downwind of pollution sources in south and south-east Asia is gaining considerable attention in the present-day scenario of climate change. We report here a case study on the atmospheric outflow of nutrients from the Indo-Gangetic Plain (IGP) to the Bay of Bengal (BoB). Air mass back trajectories suggest conspicuous downwind transport of chemical constituents from the IGP to the BoB during the late NE-monsoon (January–April); thus, representing BoB as one of the unique oceanic regions influenced by anthropogenic sources over a short span of 3–4 months. During the course of this study (November'09–March'10), nutrient (NO_3^-, NH_4^+, N_{Org}, PO_4^{3-} and Fe_{ws}) concentrations in the atmospheric outflow show pronounced temporal variability. The inorganic nitrogen (NH_4^+-N: ~90% of N_{Inorg}) dominates the total soluble nitrogen (N_{Tot}). Although the contribution of organic nitrogen is not significant, the mass ratio of N_{Org}/N_{Tot} in the outflow varied from 0.07 to 0.40. The abundances of P_{Inorg} and Fe_{ws} varied from 0.4 to 4.8 nmol m^{-3} and 0.2 to 0.6 nmol m^{-3}, respectively. The high abundance of K^+ and significant (P-value < 0.05) correlation with P_{Inorg} and Fe_{ws} suggest their significant contribution from biomass burning emissions (BBEs). The characteristic mass ratios of nutrients (N_{Inorg}/N_{Tot}: 0.92 ± 0.13, N_{Org}/N_{Tot}: 0.21 ± 0.11, and P_{Inorg}/nss-Ca^{2+}: 0.35 ± 0.23) in the IGP-outflow show striking similarity with those reported over the BoB. These results have implications to further increase in the atmospheric deposition of nutrients and their impact on biogeochemistry of surface Bay of Bengal.

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1. Introduction

In the present-day scenario of growing anthropogenic activities, atmospheric transport and deposition of nutrients (N, P and Fe) to the oceanic regions located downwind of pollution sources are gaining considerable attention due to their potential impact on biogeochemistry of ocean surface (Duce, 1986; Duce et al., 1991, 2008; Jickells et al., 2005; Mahowald et al., 2011; Prospero et al., 2009). A significant increase in the eutrophication caused by atmospheric deposition of reactive nitrogen (Paerl and Whitall, 1999; Paerl et al., 2002) further emphasizes the need to assess the impact of air–sea deposition of nutrients to oceanic regions. The increasingly growing use of fertilizers, emissions from biomass burning and fossil-fuel combustion, and animal live stock are the potential sources of this macronutrient. Until recently, studies on the atmospheric deposition of nitrogen have mainly focused on the soluble inorganic species (Duce et al., 2008 and references therein). However, studies on the atmospheric deposition of organic nitrogen and its bioavailability in sea water are rather sparse (Cornell, 2011;

Lesworth et al., 2010; Mace et al., 2003; Neff et al., 2002; Russell et al., 1998; Spokes et al., 2000; Violaki et al., 2010), making it difficult to assess its global significance in the reactive nitrogen cycle.

In addition to the deposition of N, the atmospheric source of phosphorus (P) has been also suggested to significantly influence the biogeochemical cycle of nutrients in the ocean surface (Mahowald et al., 2008; Paytan et al., 2009). Owing to the lower abundance of P in the atmosphere, earlier studies have suggested its minor role on ocean biogeochemistry, largely based on small contribution from mineral dust (Froelich et al., 1982; Smil, 2000). However, recent estimates have addressed to the concept of mobilization of P from other sources such as mining of phosphate rocks, increase in the use of fertilizers (Benitez-Nelson, 2000; Mahowald et al., 2008; Paytan and McLaughlin, 2007), biomass burning emissions (Mahowald et al., 2005; Migon and Sandroni, 1999) and fossil-fuel combustion (Anderson et al., 2010). It is suggested that atmospheric supply of N is far more higher compared to the input of soluble inorganic phosphorus. Under these conditions, the atmospheric deposition (high N and low P) can perturb the Redfield ratio (N:P = 16:1) in the surface waters (Duce et al., 2008; Jickells, 2006). In this context, P-limitation is documented in the Mediterranean Sea (Herut et al., 2002; Markaki et al., 2010; Migon et al., 2001) and open ocean waters of Atlantic (Ammerman et al., 2003; Mills et al., 2004;

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Sanudo-Wilhelmy et al., 2001). These studies emphasize the need to assess the atmospheric sources of phosphorus with respect to present-day increase in contribution from anthropogenic sources.

In contrast to N and P, much of the open ocean waters are limited by the availability of iron (Boyd et al., 2010; Coale et al., 1996; Martin et al., 1990). The significance of mineral dust as a dominant source of this micronutrient to the surface ocean is well recognized (Baker and Croot, 2010; Boyd and Ellwood, 2010; Jickells et al., 2005; Mahowald et al., 2009; Schulz et al., 2012). However, recent studies have emphasized the importance of anthropogenic combustion sources (fossil-fuel and bio-mass burning) as a potential source of soluble iron to the seawater (Chuang et al., 2005; Guieu et al., 2005; Kumar et al., 2010; Luo et al., 2008; Schroth et al., 2009; Sholkovitz et al., 2009, 2012; Srinivas et al., 2011a). These observations further emphasize the need to assess the atmospheric input of nutrients on a regional scale.

The widespread dispersal of airborne pollutants, from South and South-east Asia, over the pelagic Indian Ocean has gained much attention in recent years (Lamarque et al., 2010; Lawrence and Lelieveld, 2010; Lelieveld et al., 2001; Quinn and Bates, 2005; Ramanathan et al., 2001). Furthermore, modeling studies are projecting enhanced deposition of reactive nitrogen to the surface waters from pollution sources in south Asia (Duce et al., 2008; Galloway et al., 2004). However, there is no clear consensus on the source specific contribution of P and Fe (i.e., anthropogenic vis-à-vis natural) to the Northern Indian Ocean (Kumar et al., 2010; Srinivas and Sarin, 2012; Srinivas et al., 2011a). It is, thus, relevant to assess the long-range transport of nutrients in the continental outflow and their subsequent deposition to the downwind oceanic regions.

During the late NE-monsoon (January–April), atmospheric outflow from the Indo-Gangetic Plain (IGP) is a conspicuous feature and dominant source of chemical constituents to the marine atmospheric boundary layer (MABL) of the Bay of Bengal (Kumar et al., 2010; Sarin et al., 2010; Srinivas and Sarin, 2012). These studies have essentially characterized the chemical composition of particulate matter ($PM_{2.5}$ and PM_{10}), and have documented the abundances of nutrients (N, P and Fe) within the MABL of Bay of Bengal (Srinivas and Sarin, 2013a). These studies have emphasized the dominant role of anthropogenic sources (biomass burning emissions, BBEs) in supplying the soluble P and Fe to the Bay of Bengal (Kumar et al., 2010; Srinivas and Sarin, 2012). In addition, dominance of inorganic nitrogen (mainly as NH_4^+-N; >90% of N_{Inorg}) to total aerosol water-soluble nitrogen is noteworthy over the Bay of Bengal associated with the outflow from the Indo-Gangetic Plain (Srinivas et al., 2011b). This observation is further supported by long-term observation of aerosols (2001–2009) from the Bay of Bengal (Srinivas et al., 2011b). However, it is relevant to state that these studies have relied mainly on air-mass back trajectory analyses to assess the transport of nutrients and chemical species from the Indo-Gangetic Plain. Therefore, the study reported in this manuscript aims to investigate the temporal variability in the atmospheric outflow of anthropogenic nutrients from the Indo-Gangetic Plain to the Bay of Bengal; and to establish the diagnostic ratios of nutrients vis-à-vis those reported over the Bay of Bengal.

2. Methodology

In this study, fine mode ($PM_{2.5}$, N = 46) aerosols were collected during November'09–March'10 from a downwind site (Kharagpur: 22.3 °N, 87.3 °E) in the Indo-Gangetic Plain (IGP). A high-volume air sampler (HVS, Thermo Anderson) was set up on the roof top of geology department in the campus of IIT Kharagpur (Fig. 1). The flow rate of air sampler was periodically calibrated and ascertained as ~1.07 m^3 min^{-1}. All samples were collected on pre-combusted (~450 °C) tissuquartz filters (PALLFLEX®™) for a total time period of 20–22 h; filters were sealed in plastic Zip-lock bags and stored at −19 °C until the time of analysis. Prior to the assessment of gravimetric mass, samples were equilibrated for ~24 h under a clean laminar flow bench (Class − 1000) and $PM_{2.5}$ concentration was ascertained from the tare weight of the filters.
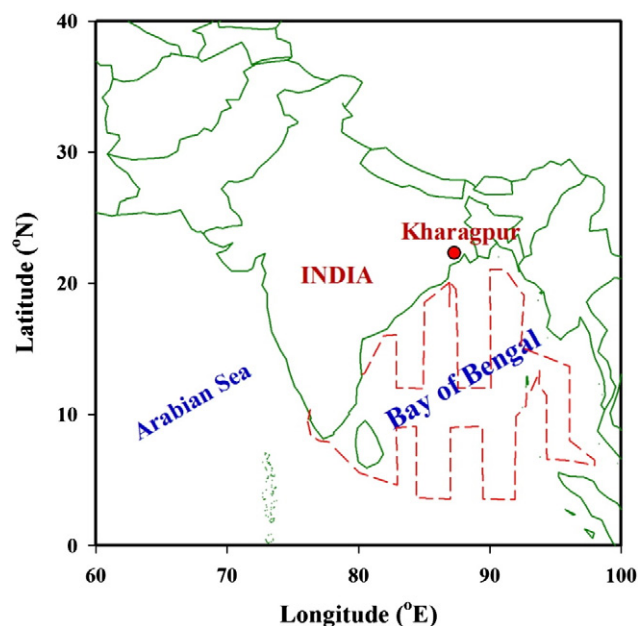

Fig. 1. Map showing downwind sampling site at Kharagpur in the Indo-Gangetic Plain. Also shown is a cruise track conducted in the Bay of Bengal (Kumar et al., 2010).

Subsequently, aerosol samples were analyzed for water-soluble nutrients using analytical protocols described in our earlier publications (Srinivas and Sarin, 2013a and references therein).

We have defined the water-soluble inorganic nitrogen (N_{Inorg}) as the sum of mass concentrations of NH_4^+ and NO_3^-. In order to assess the contribution of N_{Inorg}, a 1/8th portion of the filter was extracted with 50 ml of Milli-Q water (Millipore Co., Specific resistivity > 18.2 MΩ-cm) and analyzed for NO_3^- and NH_4^+ on Dionex-500 Ion chromatograph equipped with a suppressed conductivity detector. Likewise, another aliquot of filter (i.e., 1/8th portion) was extracted in 30 ml of Milli-Q and filtered through pre-combusted GF/F filters (Whatman®™, pore size: 0.45 μm). These extracts were subsequently analyzed for water-soluble organic carbon (WSOC) and total soluble nitrogen (N_{Tot}) on a TOC-TN analyzer (Model: Shimadzu, TOC-5000a). The water-soluble organic nitrogen (N_{Org}) was, then, estimated by subtracting the contribution of N_{Inorg} from N_{Tot}. Along with aerosol samples, filter blanks were also extracted and analyzed for WSOC and N_{Tot}. The procedural blank contributes to ~1.6 and 0.2% of minimum and maximum signal of N_{Tot} measured on a TN analyzer. Likewise, the contribution of blank varies from 14 to 2% of min–max signal measured during the analysis of WSOC. The analytical accuracy of the measurements of N_{Inorg} and N_{Tot} has been ascertained by analyzing the Merck standard solutions (Srinivas and Sarin, 2013a; Srinivas et al., 2011b).

An aliquot of water extract was filtered through a 0.45 μm Millipore filter (Millipore Co.,) and analyzed for water soluble inorganic phosphorus ($P_{Inorg} = PO_4^{3-}$) using 2 m long liquid-core waveguide capillary cell (LWCC from World Precision Instruments, WPI Inc.) coupled to a USB-4000 spectrophotometer (from Ocean Optics Inc.). The absorption of phospho-molybdenum blue complex was measured at a wavelength of 710 nm (Srinivas and Sarin, 2012) with respect to calibration standards made from suitable dilution of stock solution of 2 mM $KHPO_4$. The analytical accuracy of the measurement (i.e., ≤5%) was ascertained from the independent analysis of the 1000 ppm Merck commercial standard solution. For further details on analytical measurements reference is made to our earlier publication (Srinivas and Sarin, 2012).

For water soluble iron (Fe_{ws}), 8–10 filter punches (ca. 2.0 cm diameter) were extracted with Milli-Q water and filtered through 0.45 μm Millipore filters. Subsequently, extracts were acidified with 2 N distilled HNO_3 to a pH of 2 and analyzed for soluble iron on GF-AAS (Perkin