

# Chemical Composition and Source Identification of Fog Water at an Indo-Gangetic Plain (IGP) Outflow Location (Coastal Bhola Island), Bangladesh

Ahmed M<sup>1</sup>, Hossain A<sup>1</sup>, Akther T<sup>1</sup>, Shohel M<sup>2</sup> and Salam A<sup>1\*</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, University of Dhaka, Dhaka, Bangladesh

<sup>2</sup>Department of Chemistry, University of Iowa, Iowa City, IA-52242, United States

**\*Corresponding author:** Salam A, Department of Chemistry, Faculty of Science, University of Dhaka, Dhaka-1000, Bangladesh, Tel: +880-1817061160, E-mail: asalam@gmail.com

**Citation:** Ahmed M, Hossain A, Akther T, Shohel M, Salam A (2018) Chemical Composition and Source Identification of Fog Water at an Indo-Gangetic Plain (IGP) Outflow Location (Coastal Bhola Island), Bangladesh. J Environ Pollut Manag 1: 104

**Article history:** Received: 21 June 2018, Accepted: 15 August 2018, Published: 16 August 2018

## Abstract

With the objective of understanding fog water chemistry and sources contribution at an IGP outflow location (coastal Bhola Island, Bangladesh), we have collected fifteen fog water samples during winter 2016-17. Major ions, trace metals with physical properties (pH and electrical conductivity) were measured. The pH ( $7.12 \pm 0.20$ ) was slightly alkaline, which was much higher than rest of the world, but consistent with IGP region.  $\text{Ca}^{2+}$  containing species were the main contributor to the neutralization process of fog water, followed by  $\text{K}^+$  and  $\text{Mg}^{2+}$ . The neutralizing species were derived mainly from soil dusts with a minor contribution from sea salt. HYSPLIT trajectory analysis revealed that substantial influences of the contaminated air mass in fog water from IGP. However, higher enrichment factors and parentage source contribution of  $\text{SO}_4^{2-}$  (76.9),  $\text{NO}_3^-$  (99.3) and trace metals (Mn, Cu, and Zn) suggested significant anthropogenic contribution in the fog water at this Indo-Gangetic Outflow Location.

**Keywords:** Fog Water; Trace Metals; Enrichment Factor; Percentage Source Contribution; Air Mass Trajectory Analysis

## Introduction

Indo-Gangetic Plain (IGP) has been experiencing long periods of dense foggy events stretching across vast regions from northern India and southern Nepal and Bhutan to the whole Bangladesh during wintertime [1,2]. Persistent winter fog has been adversely impacting the quality of health life, ecosystem and economy which encompasses vast agricultural land. Prolonged fog episodes and haze in IGP region is believed to be caused from fossil fuel consumption by motorized transport, biomass burning, thermal power plants, industrial and construction activities [3,4]. Fog is formed at low temperature and high relative humidity in the lower atmosphere, which contain high level of pollutants than cloud [5]. But the exact mechanism for formation of persistent fog in IGP and chemical species responsible are still unknown. High aerosol concentrations were reported in recent years in many studies in fog droplets [6-11]. Aerosol particles act as a condensation nuclei for fog and dew formation [12]. Fog plays a vital role in transferring aerosol particles to wet deposition, and causes change in physical and chemical properties of the aerosol particles [13,14]. The presence of water soluble inorganic, organic and scavengers of insoluble species (e.g., black carbon, trace metals) in fog can also alter the aerosol properties [15]. Chemical characterization of fog water have been carried out in different cities of India at IGP and other locations of the world [8-11,16-24]. Both active and passive fog collector with various design and materials have been used in previous studies [9-11]. pH of fog water in Agra, Raipur and Delhi were found higher (6.61-7.20) than other studies around the world. Cations derived from crustal sources ( $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$ ) found dominated over the anthropogenically produced acidic anions in fog water in these cities [9]. Anthropogenic contribution was found in chemical species like  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and trace metals. The probable anthropogenic sources were inferred as biomass burning, coal burning, mineral roasting, industrial emissions etc. Fog water collected from two major Chinese cities (Shanghai and Nanjing) had higher concentration of ionic species including anthropogenically derived  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  [5,18]. The main sources of anthropogenic species in those two cities were vehicular emission, industries, biomass burning and construction.

In IGP, during wintertime north east (NE) monsoon (December –April) period, the prevailing low level air mass is influenced by the uptake of regional air pollutant and flows from the polluted land in the north to the ocean in the south, finally mixes with the

relatively pristine air over the oceans [25]. Therefore, current sampling location, coastal Bhola Island, is very important sampling site for the atmospheric outflow from IGP to the Bay of Bengal during winter period. Shohel, *et al.* studied on dew water chemical composition at this Island and found high level of water soluble ions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ ) and trace metals (Zn, Fe, Mn, Cu) [26]. Anthropogenic activities and long range transport were responsible for the elevated concentration chemical species in the dew water [26]. Relatively high concentration of aerosol particulate matters (especially black carbon and trace metals) were also been reported previously at this outflow location [26-28]. Unfortunately, there is no systematic study regarding fog water chemical characterization and source identification at this important location. Therefore, we have collected fog water samples using a passive collector for the chemical composition and source characterization during December, 2015 to February, 2016 at this IGP outflow location. Water soluble ions and trace metals have been analyzed for the possible sources (natural and anthropogenic) based on enrichment factor and percentage source contribution. Influence of long range transported pollutants on the fog water chemical composition have also been studied.

## Experimental

### Sampling site – Bhola, Bangladesh

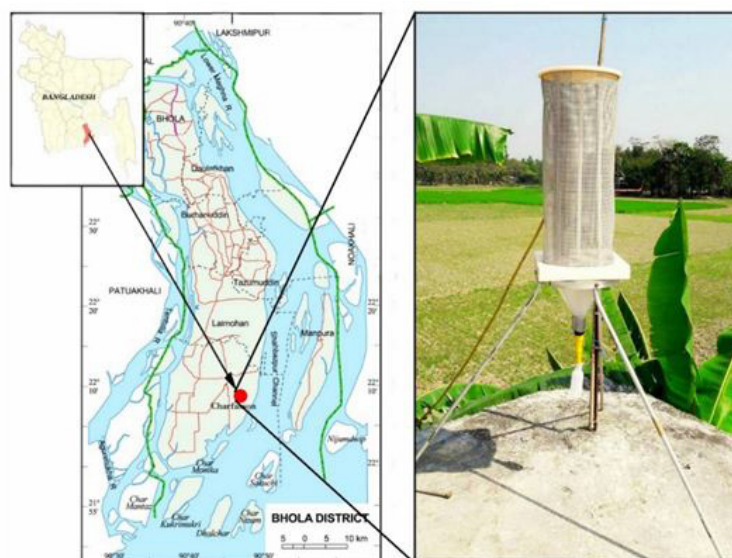
Fog samples were collected in coastal Bhola ( $22^\circ 10' 01''$  N,  $90^\circ 45' 00''$  E), a delta Island of Bangladesh, which is located in the most southern part of the Bangladesh (Figure 1). This island is an important monitoring station as it situated in the outflow path for pollutants from the Indo Gangetic Plain to the Bay of Bengal. It is located in the Barisal Division and has an area of  $3403 \text{ km}^2$  with a population of about 2 million. Most of the people live on agriculture and the influence of traffic and industry are very limited. Most of them use biomass for their cooking purpose, making it the main source of local air pollution. We have built an observatory at Bhola Island with the help of Organization of Naval Research (ONR) Global, USA. It has been operating since 2013 in collaboration with NASA, USA and Stockholm University, Sweden for atmospheric science research.

### Weather condition in coastal Bhola, Bangladesh

Weather condition plays a vital role for the collection of fog samples [7]. Collection volume of fog samples is directly proportional to fog situation. Covering of cloud and fog, water vapor and aerosol optical depth (AOD) are the important factors for weather condition [29]. Four seasons have been characterized as pre monsoon (March–May), monsoon (June–September), post monsoon (October–November) and winter (December– February) in Bangladesh. The average temperature in Bhola is  $25.9^\circ \text{C}$  with an annual rainfall of 2960 mm [28]. However, no precipitation events occur during winter fog water collection.

### Sample Collection and Analysis

Fifteen fog water samples were collected with a fog collector in selected foggy days during December, 2015 to February, 2016 at the IGP outflow, Bhola Island, Bangladesh (Figure 1). The fog sampler used in current study was around 71 cm tall and was fixed in a stand. The base, roof and supporting rod were made of Teflon (Figure 1). A nylon mesh was wrapped around the sampler. Water droplets that were collected on the mesh run downwards in a PET bottle due to gravity at the bottom of collector. The fog water collector was placed on the top of the tower (height=9 meters) in Bhola observatory. The sampling period was about 9 to 10 hours during night as there was no fog during day time. The yield of collecting fog samples were around 25-35 mL (per sample) and stored



**Figure 1:** Map of Bangladesh and Coastal Bhola (red circle indicates the sampling location). Inset at right hand side is a fog collector

in the early morning (around 6:00 am) to avoid any evaporation due to sunlight. The samples were filtered using membrane filters (pore size 0.45 μm) and stored in a freezer until chemical analysis. Half parts of the fog samples were used for physical properties (pH and electrical conductivity) and soluble ions analysis. Other half's were acidified with ultra-pure nitric acid (1% V/V) for trace metal analysis and stored separately in the refrigerator with sealed container. Field blanks were collected and analyzed using the same procedure using for fog water to minimize errors.

Major soluble cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) and trace metals (Mn, Fe, Cu, Zn, Cr, Pb, Ni) were determined by flame atomic absorption spectroscopy (model: Analyst 800, Perkin Elmer). Concentrations of major water-soluble anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) were analyzed by ion chromatography (model: 881 compact IC pro, Metrohm). A pH meter (pH 211, Hanna Instruments) was used for measuring pH with a difference of <0.03 between duplicate analysis was acceptable. For electrical conductivity, a conductivity meter (CM-5S, DKKTOA Corporation) was used and a value <2μS/cm was acceptable for duplicate analysis. Concentration of HCO<sub>3</sub><sup>-</sup> was calculated as follows from pH [26]:

$$[HCO_3^-] = 10^{-11.2+pH} \quad (1)$$

## Results and Discussion

### pH and Electrical Conductivity (EC)

The value of pH and EC are fundamental characteristics of fog water as it reflects the total ionic content and also acid/base balance in the fog water [5]. Table 1 summarizes the pH and EC of the current study and other cities around the world. The pH of fog water was found alkaline (pH range = 6.92 to 7.32, average=7.12) by taking 5.6 as the neutral pH of fog water [30,31]. The alkaline nature of fog water indicates the effective neutralization of the acid forming anions (SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>) by the soluble cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) and NH<sub>4</sub><sup>+</sup> ions [32]. The high concentration of ammonia from agricultural activities can increase the pH value in California fogs [22,23]. The average value of pH in fog samples (7.12) is within the guideline value of WHO (6.5-8.5) [33]. The pH value of fog water (7.12) was almost similar to dew water (6.81) in Bhola and also that of Delhi (6.61) and San Joaquin Valley (6.49) [9,22,23,26].

Table 1 shows the average EC of the collected fog water was 324±144 μScm<sup>-1</sup> ranging from 180 to 470 μScm<sup>-1</sup> in Bhola. Average EC in fog water was 2.10 times higher than dew water collected in Bhola, which is 6.0 times lower than that of Shanghai and also 2.0 times lower than Nanjing but higher than Daekwanreung, Baton Rouge and Mt. Niesen [5,16,17,20,24,26].

	Bangladesh		China		Poland	Japan	S Korea	Canada	USA		IGP			Switze rland
	Bhola Current study	Bhola <sup>a</sup> Dew Water	Shan ghai <sup>b</sup>	Nan jing <sup>c</sup>	Szre nica <sup>d</sup>	Rokko Mt. <sup>e</sup>	Daek w-anre ung <sup>f</sup>	Round top Ridge <sup>g</sup>	San Joaquin Valley <sup>h</sup>	Baton Rouge <sup>i</sup>	Delhi <sup>j</sup>	Raipur <sup>k</sup>	Agra <sup>l</sup>	Mt. Ni esen <sup>m</sup>
pH	7.12±0.2	6.81	5.97	5.9	5.44	3.8	5.0	4.0	6.49	5.0	6.61	6.95	7.2	6.4
EC	324±144	154.8	2050	681	NA	NA	109.8	NA	NA	255	NA	180	NA	34.4
NH <sub>4</sub> <sup>+</sup>	NA	NA	4005	6654	210	171.8	360.3	183.6	1008	2077	307	296	1700	143.5
Na <sup>+</sup>	678.7±226.7	243.8	809	1282	100	82.6	117	5.0	5	114	169.8	490	175	43.0
K <sup>+</sup>	316.7±145.7	135.6	224	383	45	7.7	19.7	2.6	12	6	21.3	301	235	5.0
Ca <sup>2+</sup>	736±361.3	693.3	2064	3772	49	25	78.4	32.6	9	30	105.4	805	338	46.8
Mg <sup>2+</sup>	225.8±11.7	205.1	318	347	140	24.7	50.5	7.4	3	26.7	42.3	471	146	12.6
Cl <sup>-</sup>	856.6±300.5	291.2	1178	1010	100	110	96.3	5.8	14	109	75.6	845	382	10.6
NO <sub>3</sub> <sup>-</sup>	201.9±102.7	223.2	2416	945	240	124.2	170.3	89.3	483	180.8	32	259	494	87.0
SO <sub>4</sub> <sup>2-</sup>	425.2±251.5	264.1	2430	6969	200	64.5	388.5	140.7	117	1791	243	946	691	72.3
HCO <sub>3</sub> <sup>-</sup>	188.3±64.8	63	5.97	NA	NA	NA	NA	NA	NA	NA	28.3	NA	148	NA

<sup>a</sup>NA= Not Analyzed <sup>BDL</sup>= Below Detection Limit

<sup>a</sup>Shohel et al. 2017; <sup>b</sup>Li et al. 2011; <sup>c</sup>Lu et al. 2010; <sup>d</sup>Blaś et al. 2010; <sup>e</sup>Alkawa et al. 2001; <sup>f</sup>Kim et al. 2006; <sup>g</sup>Schmenauer et al. 1995; <sup>h</sup>Collett et al. 1999a,b; <sup>i</sup>Raja et al. 2008; <sup>j</sup>Ali et al. 2004; <sup>k</sup>Ambade et al. 2014; <sup>l</sup>Lakhani et al. 2007; <sup>m</sup>Michna et al. 2015

**Table 1:** Fog water chemical composition collected from different locations of the world. All units are in μeqL<sup>-1</sup>, except EC (μScm<sup>-1</sup>)

### Chemical Composition

**Water soluble ions :**The average concentrations of major chemical components with standard deviations were summarized in Table 1. Ca<sup>2+</sup> had the highest concentration (736 μeqL<sup>-1</sup>) among the all measured cations followed by Na<sup>+</sup> (678.8 μeqL<sup>-1</sup>), K<sup>+</sup> (316.7 μeqL<sup>-1</sup>), and Mg<sup>2+</sup> (225.8 μeqL<sup>-1</sup>). Suspended soil and dust transport by wind can reach the lower layer of the atmosphere which can be a major source of Ca<sup>2+</sup> and Mg<sup>2+</sup> in fog samples. Biomass burning could be the major contributor of K<sup>+</sup> in Bhola. Among all anions, chloride had the highest concentration followed by sulfate, nitrate and bicarbonate with concentrations 856.6, 425.2, 201.9

and 188.3  $\mu\text{eqL}^{-1}$ , respectively. Conversion of  $\text{SO}_x$  to  $\text{SO}_4^{2-}$  ion could be the one reason of high sulfate concentration suggested by many researchers [34,35].

Concentration of measured total cation ( $1.95 \times 10^3 \mu\text{eqL}^{-1}$ ) was 1.2 times higher than total anion ( $1.67 \times 10^3 \mu\text{eqL}^{-1}$ ). Due to the unmeasured concentration of other ionic species e.g.,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ ,  $\text{F}^-$ , etc. ion balance was not done in this study.  $\text{Na}^+$  and  $\text{Cl}^-$  having a total contribution of 42.3% to the total ions due to the fact that Bhola is surrounded by the Bay of Bengal, demonstrating a significant marine contribution. The ratio of  $\text{Cl}^-/\text{Na}^+$  was 1.26 which is higher than sea water fraction (1.17), consistent with marine emission but also influenced by anthropogenic activities.  $\text{Ca}^{2+}$  was the highest concentration among the total cations which accounted for 20.3%, while  $\text{K}^+$  and  $\text{Mg}^{2+}$  contributed for 8.73% and 6.22%, respectively. The second highest contributor among the anions after chloride was  $\text{SO}_4^{2-}$  with 11.7%. The percent contribution for  $\text{NO}_3^-$  and  $\text{HCO}_3^-$  were 13.8% and 2.0%, respectively.

The average concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  were higher than most other sites, but comparable with China, demonstrating a significant marine contribution. The exceptionally high concentration of  $\text{K}^+$  was observed with a value of 121 times higher than Roundtop Ridge (Canada), 63 times higher than in Mt. Niesen (Switzerland), 52 times higher than in Baton Rouge (USA), and several times higher than in other sites except Nanjing (China) – Table 1. The concentration  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were comparable to that of Shanghai and Nanjing, but much higher than those in Roundtop Ridge, San Joaquin Valley and Mt. Niesen. In Bhola, the concentration of  $\text{NO}_3^-$  was 1.5–6.5 times higher than in Rokko Mt. (Japan), Roundtop Ridge (Canada), Mt. Niesen (Switzerland) and IGP while 4.5–12 times lower than Shaghnai and Nanjing (China). High concentration of  $\text{SO}_4^{2-}$  was observed in all the sites except Baton Rouge, USA and in China. The ratio ( $\text{SO}_4^{2-}/\text{NO}_3^-$ ) was  $2.06 \pm 0.71$ , which was lower than urban cities in IGP (e.g., Delhi, Raipur) and China (Nanjing). The total concentration of ionic species in fog water was found higher than dew water in Bhola because fog remain suspended in atmosphere for a long time thus scavenge more aerosol and gases [26].

**Trace metals:** Trace metal element like Fe and Mn played an important role in the catalyzed oxidation of the S (IV) in cloud [36]. Previous studies showed that heavy metal elements of Pb, Cd and Zn are detrimental to human health [37]. The concentration order (in  $\mu\text{eqL}^{-1}$ ) of trace metals followed the sequence  $\text{Zn} (540) > \text{Fe} (260) > \text{Mn} (210) > \text{Cu} (120)$ . The Bangladesh guideline value ( $\mu\text{g/L}$ ) for Zn, Fe, Mn and Cu were 5000, 1000, 100 and 1000, respectively [33]. All the values of trace metal were below BD guideline value except Mn. The concentrations of Cr, Pb, and Ni were below detection limit. The instrumental detection limits for Ni Cr and Pb were 60.0, 100.0 and 200.0  $\mu\text{g L}^{-1}$ , respectively. Concentration of Fe and Zn was also high in aerosol samples previously collected at the coastal Bhola site [38].

### Fractional acidity

Fractional Acidity (FA) of fog water was computed by Balasubramanian, *et al.* according to following equation [39].

$$\text{FA} = \frac{[\text{H}^+]}{[\text{SO}_4^{2-}] + [\text{NO}_3^-]} \quad (2)$$

If FA is 1, it is considered as not neutralized. The average value of FA was 0.005 (highest: 0.009, lowest: 0.001), indicating that effective acidic constituents ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  etc.) were neutralized by basic component ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ). The relative contribution of  $\text{NO}_3^-$  to the acidification was calculated using a ratio  $[\text{NO}_3^-]/([\text{NO}_3^-] + [\text{SO}_4^{2-}])$  reported by Cao, *et al.* and its average value was 0.347, suggesting 34.7% of acidity of fog water was due to  $\text{NO}_3^-$  and 65.3% were for  $\text{SO}_4^{2-}$ .

### Neutralization factor

The neutralization Factors (NF) of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  were calculated to determine the contribution of basic component in the neutralization process. NF was calculated with respect to sulfate and nitrate (as they are largely responsible for acidity in the fog water samples) by following equation [32]:

$$\text{NF}_x = \frac{[\text{X}]}{[\text{NO}_3^-] + [\text{SO}_4^{2-}]} \quad (3)$$

Where, X is the species whose neutralization factor is to be calculated. The order of neutralization factor (calculated with average concentration) found in fog water of Bhola was  $\text{NF}_{\text{Ca}} (1.17) > \text{NF}_{\text{K}} (0.50) > \text{NF}_{\text{Mg}} (0.36)$ , indicating that  $\text{Ca}^{2+}$  was the dominant neutralization components in the fog water.

### Enrichment factor of major ions and trace metal

The enrichment factors (EFs) for individual trace metals and ions were used to identify their origin in fog water as general crust, sea salt and anthropogenic source [7]. Na is taken as a reference element for marine sources since Bhola is a coastal area. For continental crust, Al, Fe and Ca are normally used as reference elements [40]. We used Ca as a reference element for soil origin [41–43]. Using Na and Ca as reference element,  $\text{EF}_{\text{sea water}}$  and  $\text{EF}_{\text{crust}}$  of major cations and anions were calculated by following equations:

$$EF_{\text{sea water}} = (X/Na)_{\text{fog}} / (X/Na)_{\text{sea}} \quad (4)$$

$$EF_{\text{crust}} = (X/Ca)_{\text{fog}} / (X/Ca)_{\text{crust}} \quad (5)$$

Where X is the concentration of individual elements,  $(X/Na)_{\text{sea}}$  is the ratio of elemental concentration to the Na concentration from seawater composition, and  $(X/Ca)_{\text{crust}}$  is the ratio of the elemental concentration to the Ca concentration from crustal composition [44,45]. Table 2 describes  $EF_{\text{sea water}}$  and  $EF_{\text{crust}}$  values.

Ions/Elements	$EF_{\text{sea water}}$	$EF_{\text{crust}}$
K <sup>+</sup>	2.07	0.93
Ca <sup>2+</sup>	49.5	-
Mg <sup>2+</sup>	7.6	0.55
Cl <sup>-</sup>	1.09	374.2
NO <sub>3</sub> <sup>-</sup>	15000	133.3
SO <sub>4</sub> <sup>2-</sup>	5.04	30.9
Mn	-	40.3
Cu	-	416.5
Zn	-	1516.5

**Table 2:** Enrichment factor of major ions and trace metal in fog water

An EF value much less than or much higher than 1 is considered to be diluted or enriched respectively, relative to the reference source [41]. Cl has  $EF_{\text{sea water}}$  value of 1.09 but has an  $EF_{\text{crust}}$  374.2, which clearly indicates its marine origin than compared to soil source. EF value of K<sup>+</sup> and Mg<sup>2+</sup> suggested that it was concentrated compared to seawater and diluted to soils indicating its terrestrial source. SO<sub>4</sub><sup>2-</sup> had an  $EF_{\text{sea water}}$  value of 5.04 and  $EF_{\text{crust}}$  value of 30.9 showed highly enriched for soil source. NO<sub>3</sub><sup>-</sup> had high EF value for crust and sea ( $EF_{\text{crust}} = 133.3$ ,  $EF_{\text{sea water}} = 15000$ ), indicating highly enriched compared to natural sources. High EF value for SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in fog water compared to soil and sea indicated that they are mainly originated from the anthropogenic source.

EFs for trace metals were measured based on the earth's crust abundance of individual element to evaluate the degree of anthropogenic influence [46-48]. Iron (Fe) was used as a reference material to calculate the EFs by the following equation [49].

Where X/Fe is the concentration ratio of element X to a reference metal, Fe. The ratios of  $(X/Fe)_{\text{crust}}$  are taken from [50].

$$EF = (X/Fe)_{\text{fog}} / (X/Fe)_{\text{crust}} \quad (6)$$

Based on EF trace metals were classified into three main groups with the following standard: EFs < 10 was considered to be non-enriched (crust or sea salt sources); 10 < EFs < 100 was classified as moderately enriched (crust or sea salt and anthropogenic sources); and EFs > 100 was believed to be highly enriched (air pollution mainly comes from anthropogenic sources) [51]. Enrichment factors of trace metals in fog water suggested that their source was mainly anthropogenic (EF > 10) (Table 2). EF of Mn was 40.3, considered as moderately enriched. Whereas, Cu and Zn had an EF value of 416.5 and 1516.5 respectively, indicating highly enriched conditions, suggesting severe contamination from anthropogenic source in Bhola [52]. Similar enrichment for Cu and Zn were also observed in dew water of Bhola [26].

## Source Contributions

**Marine contribution:** Sea salt fraction (SSF) and non-sea salt fraction (NSSF) have been calculated to determine the marine contribution to the chemical species present in fog water samples. Significant marine contribution is expected in the fog samples in Bhola as it is surrounded by the Bay of Bengal. The following equations are used by Kulshrestha *et al.* to calculate the SSF and NSSF [53].

$$\%SSF = (X/Na)_{\text{sea}} / (X/Na)_{\text{fog}} \quad (7)$$

$$\%NSSF = 100 - (\%SSF) \quad (8)$$

Where, X is the concentration of the individual element,  $(X/Na)_{\text{sea}}$  is the ratio from seawater composition. From the value of %SSF, it can be inferred that marine contribution was found highest for Cl<sup>-</sup> (92.06%) followed by K<sup>+</sup> (48.29%), SO<sub>4</sub><sup>2-</sup> (19.84%), and Mg<sup>2+</sup> (13.30%), reflecting sea spray aerosol, as Bhola is an Island of the Bay of Bengal. Sea salt aerosol is mainly constituted of sodium

chloride (NaCl) but other chemical ions which are common in sea water, such as  $Mg^{2+}$ ,  $K^+$ ,  $Ca^{2+}$ ,  $SO_4^{2-}$  can also be found [54]. Higher %NFSS value of  $NO_3^-$  (99.99%),  $Ca^{2+}$  (97.98%),  $Mg^{2+}$  (86.70%),  $SO_4^{2-}$  (80.16%) and  $K^+$  (51.71%) suggested that these mainly appeared to be from non-marine origin (sum of crust and anthropogenic fraction - Table 3).

Ion	Sea salt fraction (%)	Terrestrial fraction	
		Crust fraction (%)	Anthropogenic fraction (%)
$Cl^-$	92.06	0.50	7.52
$SO_4^{2-}$	19.84	3.24	76.9
$NO_3^-$	-	0.75	99.3
$Mg^{2+}$	13.30	86.7	-
$Ca^{2+}$	2	98	-
$K^+$	48.29	51.71	-

Table 3: Percent Source contributions of ionic species in fog water

**Crustal and anthropogenic contribution:** The crust and anthropogenic sources of ionic components in fog water were computed respectively using the following equations [26].

$$\%CF = 100(X/Ca)_{soil} / (X/Ca)_{fog} \quad (9)$$

$$\%AF = ((100 - SSF(\%)) - CF(\%)) \quad (10)$$

Where X was the concentration of the desired species. CF and AF indicates crust fraction and anthropogenic fraction, respectively.

Table 3 summarizes the contributions of different possible sources of ionic species in fog water. The results revealed that  $Ca^{2+}$ ,  $Mg^{2+}$  and  $K^+$  were originated mainly from crustal origin. It has shown that  $K^+$  originated in coarse particles in soil, while fine particles occurs mainly from biomass burning [39,55]. Potassium might also come from fertilizers as most of the people in Bhola lives on farming. In the current study,  $K^+$  is considered as a terrestrial fraction as it was difficult to distinguish between crustal and biomass/wood combustion in the fog water. Very tiny crustal contribution was observed for  $SO_4^{2-}$ ,  $Cl^-$ , and  $NO_3^-$  in fog water, indicating manmade source. The value of %AF for  $Cl^-$  (7.52%), suggested that a small fraction of  $Cl^-$  comes from the anthropogenic source. A very small contribution for  $SO_4^{2-}$  and  $NO_3^-$  from crustal source, and about 76.9% for  $SO_4^{2-}$  and 99.3% for  $NO_3^-$  were due to the anthropogenic source.  $SO_x$  and  $NO_x$  enters into the atmosphere from different pollution sources such as coal combustion, vehicular exhaust, biomass burning, long range transport, etc. were believed to be a high anthropogenic contributor of  $SO_4^{2-}$  and  $NO_3^-$  in fog water [7,32,56,57].

### Air mass trajectories analysis

Frequency of Backward air mass trajectories was calculated for winter season during fog sampling with NOAA HYSPLIT model

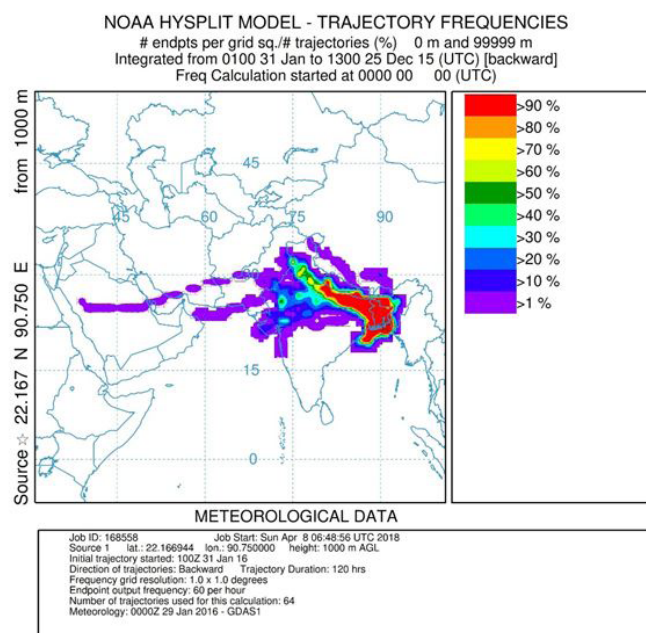


Figure 2: Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) backward frequency trajectories (30 days average) arriving sampling location (coastal Bhola, Bangladesh) during fog collection period (Winter 2016-17)

(hybrid single-particle lagrangian integrated trajectory model) (<http://www.arl.noaa.gov/>) to identify the source region and transport pathways. The 120 h back trajectories were calculated at our sampling site (22°10'01" N, 90°45'00" E) and with ending time corresponding to the end of each sample collection period (around 0 UTC). The result showed that during December and January air masses were mainly originated from the northeast part of India and travel the whole IGP region to reach Bhola. As Bhola is a remote island of Bangladesh, it has very less contribution of anthropogenic activities. Air masses from different part of IGP region could have been the main influence for the chemical species in fog water.

## Conclusion

Fog water samples were collected in winter from a remote island Bhola, Bangladesh from December 2015 to February 2016. The average pH (7.12) of the fog water was alkaline in nature, varied from 6.92 to 7.32. The electrical conductivity of fog water ranged from 180 to 470  $\mu\text{Scm}^{-1}$ . Dominant anions in the fog water were  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  while dominant cations were  $\text{Ca}^{2+}$  and  $\text{Na}^+$ .  $\text{Ca}^{2+}$  was supposed to be the main contributor for neutralization of fog water. 92.06% of  $\text{Cl}^-$  accounted for marine source as Bhola Island is surrounded by Bay of Bengal. High enrichment factor for  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{SO}_4^{2-}$  relative to sea water suggested that these ions originate from non-marine source. Similarly, high enrichment factor for  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cu}$  and  $\text{Zn}$  revealed that they were coming from the anthropogenic source. Additional source contribution analysis reflected that  $\text{NO}_3^-$  (99.3%) and  $\text{SO}_4^{2-}$  (76.9%) were contributed by anthropogenic source and  $\text{Ca}^{2+}$  (98%) and  $\text{Mg}^{2+}$  (86.7%) were contributed by crustal source. Air mass trajectory analysis supported that fog water in Bhola is greatly affected by air masses coming from IGP.

## Acknowledgements

The authors would like to acknowledge the Naval Research Global (ONRG), USA, for giving the financial support to establish the Bhola Observatory. The Authors are grateful to ICMOD for providing us the fog sampler. Thanks to the Centre for Advanced Research in Sciences (CARS), University of Dhaka, for supporting with the chemical analysis. Special thanks to the sampling crews of Bhola Observatory.

## References

1. Gautam R, Hsu NC, Kafatos M, Tsay SC (2007) Influences of winter haze on fog/low cloud cover over the Indo-Gangetic plains. *J Geophys Res* 1112: 207.
2. Kar J, Deeter MN, Fishman J, Liu Z, Omar A, et al. (2010) Wintertime pollution over the Eastern Indo-Gangetic Plains as observed from MOPITT, CALIPSO and tropospheric ozone residual data. *Atmos Chem Phys* 10: 12273-83.
3. Girolamo LD, Bond TC, Bramer D, Diner DJ, Fettinger F, et al. (2004) Analysis of multiangle imaging spectro-radiometer (MISR) aerosol optical depths over greater India during winter 2001–2004. *Geophys Res Letter* 31: 115.
4. Nair VS, Moorthy KK, Alappattu DP, Kunhikrishnan PK, George S, et al. (2007) Wintertime aerosol characteristics over the Indo-Gangetic Plain (IGP): impacts of local boundary layer processes and longrange transport. *J Geophys Res* 112: 205.
5. Li P, Li X, Yang C, Wang X, Chen J (2011) Fog water chemistry in Shanghai. *Atmospheric Environ*, 45: 4034-41.
6. Rajput P, Singh DK, Singh AK, Gupta T (2018) Chemical composition and source-apportionment of sub-micron particles during wintertime over Northern India: New insights on influence of fog-processing. *Environ Pollut* 233: 81-91.
7. Xu X, Chen J, Chao Z, Li J, Sui X, et al. (2017) Fog composition along the Yangtze River basin: Detecting emission sources of pollutants in fog water. *J Environ Sci*.
8. Nath S, Yadav SA (2018) A Comparative Study on Fog and Dew Water Chemistry at New Delhi, India. *Aerosol Air Quality Res* 8: 26-36.
9. Ali K, Momin GA, Tiwari S, Safai PD, Chate DM, et al. (2004) Fog and precipitation chemistry at Delhi, North India. *Atmospheric Environ* 38: 4215-22.
10. Ambade B (2014) Characterization and source of fog water contaminants in central India. *Natural Hazards*, 70: 1535-52.
11. Lakhani A, Parmar RS, Satsangi GS, Prakash S (2007) Chemistry of fogs at Agra, India Influence of soil particulates and atmospheric gases. *Environ Monitoring Assessment* 133: 435-45.
12. Polkowska Ż, Błaś M, Klimaszewska K, Sobik M, Małek S, et al. (2008) Chemical characterization of dew water collected in different geographic regions of Poland. *Sensors* 8: 4006-32.
13. Biswas KE, Ghauri BM, Husain L (2008) Gaseous and aerosol pollutants during fog and clear episodes in South Asian urban atmosphere. *Atmospheric Environ* 42: 7775-85.
14. Kaul DS, Gupta T, Tripathi SN, Tare V, Collett JL (2011) Secondary organic aerosol: a comparison between foggy and nonfoggy days. *Environ Sci Technol* 45: 7307-13.
15. Gilardoni S, Massoli P, Giulianelli L, Rinaldi M, Paglione M, et al. (2014) Fog scavenging of organic and inorganic aerosol in the Po Valley. *Atmospheric Chem Phys* 14: 6967-81.
16. Raja S, Raghunathan R, Yu X, Lee T, Chen J, et al. (2008) Fog chemistry in the Texase Louisiana Gulf Coast corridor. *Atmospheric Environ* 42: 2048-61.
8. Nath S, Yadav SA (2018) A Comparative Study on Fog and Dew Water Chemistry at New Delhi, India. *Aerosol Air Quality Res* 8: 26-36.
9. Ali K, Momin GA, Tiwari S, Safai PD, Chate DM, et al. (2004) Fog and precipitation chemistry at Delhi, North India. *Atmospheric Environ* 38: 4215-22.
10. Ambade B (2014) Characterization and source of fog water contaminants in central India. *Natural Hazards*, 70: 1535-52.
11. Lakhani A, Parmar RS, Satsangi GS, Prakash S (2007) Chemistry of fogs at Agra, India Influence of soil particulates and atmospheric gases. *Environ Monitoring Assessment* 133: 435-45.
12. Polkowska Ż, Błaś M, Klimaszewska K, Sobik M, Małek S, et al. (2008) Chemical characterization of dew water collected in different geographic regions of Poland. *Sensors* 8: 4006-32.

13. Biswas KF, Ghauri BM, Husain L (2008) Gaseous and aerosol pollutants during fog and clear episodes in South Asian urban atmosphere. *Atmospheric Environ* 42: 7775-85.
14. Kaul DS, Gupta T, Tripathi SN, Tare V, Collett JL (2011) Secondary organic aerosol: a comparison between foggy and nonfoggy days. *Environ Sci Technol* 45: 7307-13.
15. Gilardoni S, Massoli P, Giulianelli L, Rinaldi M, Paglione M, et al. (2014) Fog scavenging of organic and inorganic aerosol in the Po Valley. *Atmospheric Chem Phys* 14: 6967-81.
16. Raja S, Raghunathan R, Yu X, Lee T, Chen J, et al. (2008) Fog chemistry in the Texase Louisiana Gulf Coast corridor. *Atmospheric Environ* 42: 2048-61.
17. Lu C, Niu S, Tang L, Lv J, Zhao L, et al. (2010) Chemical composition of fog water in Nanjing area of China and its related fog microphysics. *Atmospheric Res* 97: 47-69.
18. Błaś M, Polkowska Z, Sobik M, Klimaszewska K, Nowinski K, et al. (2010) Fog water chemical composition in different geographic regions of Poland. *Atmospheric Res* 95: 455-69.
19. Alkawa M, Hiraki T, Shoga M, Tamaki M (2001) Fog and precipitation chemistry at Mt. Rokko in Kobe, April 1997–March 1998. *Water, Air, and Soil Pollut* 130: 1517-22.
20. Kim MG, Lee B-K, Kim HJ (2006) Cloud/Fog Water Chemistry at a High Elevation Site in South Korea. *J Atmos Chem* 55: 13-29.
21. Schemenauer RS, Banic CM, Urquiza N (1995) High elevation fog and precipitation chemistry in southern Quebec, Canada. *Atmos Environ* 29: 2235-52.
22. Collett Jr JL, Hoag KJ, Sherman DE, Bator A, Richards LW (1999a) Spatial and temporal variations in San Joaquin Valley fog chemistry. *Atmospheric Environ* 33: 129-40.
23. Collett Jr JL, Hoag KJ, Rao X, Pandis SN (1999b) Internal acid buffering in San Joaquin Valley fog drops and its influence on aerosol processing. *Atmospheric Environ* 33: 4833-47.
24. Michna P, Werner RA, Eugster W (2015) Does fog chemistry in Switzerland change with altitude? *Atmospheric Res* 151: 31-44.
25. Niranjana K, Sreekanth V, Madhavan BL, Krishna MK (2006) Wintertime aerosol characteristics at a north Indian site Kharagpur in the Indo-Gangetic plains located at the outflow region into Bay of Bengal. *J Geophys Res*, 111: 209.
26. Shohel M, Simol HA, Reid E, Reid JS, Salam A (2017) Dew water chemical composition and source characterization in the IGP outflow location (coastal Bhola, Bangladesh). *Air Quality, Atmosphere Health* 10: 981-90.
27. Salam A, Bauer H, Kassim K, Ullah SM, Puxbaum H (2003) Aerosol chemical characteristics of an island site in the Bay of Bengal (Bhola-Bangladesh). *J Environ Monit* 5: 483-90.
28. Shohel M, Kistler M, Rahman MA, Kasper-Giebl A, Reid JS, et al. (2018) Chemical characterization of PM<sub>2.5</sub> collected from a rural coastal island of the Bay of Bengal (Bhola, Bangladesh). *Environ Sci Pollut Res* 25: 4558-69.
29. Kulshrestha UC, Kulshrestha MJ, Sekar R, Sastry GSR, Vairamani M (2003) Chemical characteristics of rainwater at an urban site of south-central India. *Atmospheric Environ* 37: 3019-26.
30. Galloway J, Likens GE, Edgerton E (1976) Acid precipitation in the northeastern United States: pH and acidity. *Sci* 194: 722-4.
31. Collett JL, Bator A, Sherman DE, Moore KF, Hoag KJ, et al. (2002) The chemical composition of fogs and intercepted clouds in the United States. *Atmos Res* 64: 29-40.
32. Yadav S, Kumar P (2014) Pollutant scavenging in dew water collected from an urban environment and related implications. *Air Quality Atmos Health* 7: 559-66.
33. Islam MA, Higuchi T, Sekine M, Karim MR, Sakakibara H (2014) Comparison of the trace metal concentration of drinking water supply options in southwest coastal areas of Bangladesh. *Appl Water Sci* 4: 183-91.
34. Cass GR (1981) Sulphate air quality control strategy design. *Atmos Environ* 15: 1227-49.
35. Munger JW, Waldman DJ, Hoffman MR (1983) Fog water chemistry in an urban atmosphere. *J Geophys Res* 88: 5109-23.
36. Harris E, Sinha B, van Pinxteren D, Tilgner A, Fomba KW, et al. (2013) Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO<sub>2</sub>. *Sci* 340: 727-30.
37. Viard B, Pihan F, Promeprat S, Pihan JC (2004) Integrated assessment of heavy metal (Pb, Zn, Cd) highway pollution: bioaccumulation in soil, Gramineae and land snails. *Chemosphere* 55: 1349-59.
38. Salam A, Bauer H, Kassim K, Ullah S, Puxbaum H (2003) Aerosol chemical characteristics of a mega-city in Southeast Asia (Dhaka–Bangladesh). *Atmos Environ* 37: 2517-28.
39. Balasubramanian R, Victor T, Chun N (2001) Chemical and statistical analysis of precipitation in Singapore. *Water, Air, and Soil Pollution*, 130: 451-6.
40. Cao YZ, Wang S, Zhang G, Luo J, Lu S (2009) Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. *Atmos Res* 94: 462-9.
41. Safai PD, Rao PSP, Momin GA, Ali K, Chate DM, et al. (2004) Chemical composition of precipitation during 1984–2002 at Pune, India. *Atmos Environ* 38: 1705-14.
42. Das R, Das SN, Misra VN (2005) Chemical composition of rainwater and dustfall at Bhubaneswar in the east coast of India. *Atmos Environ* 39: 5908-16.
43. Zhang M, Wang S, Wu F, Yuan X, Zhang Y (2007) Chemical composition of wet precipitation and anthropogenic influence at a developing urban site in Southeastern China. *Atmos Res* 84: 311-22.
44. Kidron GJ, Starinsky A (2012) Chemical composition of dew and rain in an extreme desert (Negev): cobbles serve as sink for nutrients. *J Hydrol* 420-1: 284-91.
45. Taylor SR (1964) Abundance of chemical elements in the continental crust: a new table. *Geochim Cosmochim Acta* 28: 1273-85.
46. Cong Z, Kang S, Zhang, Y, Li X (2010) Atmospheric wet deposition of trace elements to central Tibetan Plateau *Appl Geochem* 25: 1415-21.
47. Huang J, Kang S, Zhang Q, Guo J, Chen P, et al. (2013) Atmospheric deposition of trace elements recorded in snow from the Mt. Nyainqentanglha region, southern Tibetan Plateau. *Chemosphere*, 92: 871-81.
48. Kyllonen K, Karlsson V, Ruoho-Airola T (2009) Trace element deposition and trends during a ten year period in Finland. *Sci Total Environ* 407: 2260-9.



49. Tripathee L, Kang S, Huang J, Sillanpää M, Sharma CM, et al. (2014) Ionic composition of wet precipitation over the southern slope of central Himalayas, Nepal. *Environ Sci Pollut Res Int* 21: 2677-87.
50. Islam MF, Majumder SS, Mamun AA, Khan MB, Rahman MA, et al. (2015) Trace metals concentrations at the atmosphere particulate matters in the Southeast Asian Mega City (Dhaka, Bangladesh). *Open J Air Pollut* 4: 86-98
51. Shridhar V, Khillare, PS, Agarwal T, Ray S (2010) Metallic species in ambient particulate matter at rural and urban location of Delhi. *J Hazard Mater* 175: 600-7
52. Duce RA, Hoffman GL, Zoller WH (1975) Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural? *Sci* 187: 339-42
53. Kulshrestha UC, Sarkar AK, Srivastava SS, Parashar DC (1996) Investigation into atmospheric deposition through precipitation studies at New Delhi (India). *Atmos Env* 30: 4149-54.
54. O'Dowd CD, Facchini MC, Cavalli F, Ceburnis D, Mircea M, et al. (2004) Biogenically driven organic contribution to marine aerosol. *Nature* 431: 676-80.
55. Zunckel M, Saizar C, Zarauz J (2003) Rainwater composition in northeast Uruguay. *Atmos Env* 37: 1601-11.
56. Xu Y, Zhu H, Tang J, Lin Y (2015) Chemical Compositions of Dew and Scavenging of Particles in Changchun, China. *Adv Meteorol* Article ID 104048.
57. Rubio MA, Lissi E, Villena G (2002) Nitrite in rain and dew in Santiago city, Chile. Its possible impact on the early morning start of the photochemical smog. *Atmos Env* 36: 293-97.