

SPATIAL DISTRIBUTION OF MARINE SALTS IN COASTAL REGION USING WET CANDLE SENSORS

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ABSTRACT

The results of a study to evaluate the spatial distribution of marine salts from sea spray in relation to the distance from the sea are presented. The study monitored the deposition rate of chlorides and sulfates from sea spray in wet candle sensors, located at twelve sampling stations scattered around the metropolitan region of the port city of Chittagong in Bangladesh which is situated on the coastline of the Bay of Bengal. The type and amount of salts captured in the solution from the wet candle sensors were determined by ion chromatography. The data collected showed that the marine salt deposition is significant up to a distance of about 200 m from the seashore. From this point onward, the amount of chlorides drops sharply and in the case of sulfates, other emission sources become more critical than the sea spray. Relationships between the concentration of marine salts and the distance from the sea are established. The results of this study can be used to evaluate the potential aggression of salt deposition on marine systems, and as such should be useful in infrastructure planning and management.

Keywords: *Sea spray; Marine salts; Wet candle sensors, Ion chromatography.*

1. INTRODUCTION

Excessive salt in terrestrial environments can lead to accelerated corrosion of human assets, salinization of agricultural soils, elevated water stress, leaf necrosis, and growth inhibition of plants that have low salt tolerance. In coastal regions, the atmosphere is enriched with particles that are naturally generated by the action of wind on the seawater surface. The sea spray, composed primarily of seawater along with these particles, introduces ionic species into the atmosphere, principally chlorides and sulfates (Campos et al. 2006, Carlos et al. 2003, Davidson et al. 1989).

The enriched air containing sea spray causes accumulative deposition of ions (on the external surface of structures) which are able to penetrate to the interior of the material through ionic diffusion causing its degeneration. Such environments that are charged with salts are extremely dangerous to construction materials as they can penetrate and crystallize inside the material, causing deterioration of the physical structure (Soroka and Carmel 1987). Research work has been conducted to evaluate the deterioration of structures exposed to atmospheric aerosol and/or to acid deposition. Many of these researches concentrated on the mechanisms of interaction between atmospheric substances and those present in construction materials (Sabbioni et al. 2003, Perry and Duffy 1997, Leysen et al. 1989, Zappia et al. 1992). Others were concentrated on the production/distribution of salts from marine aerosols as well as their interaction with structures (Meira et al. 2007, Meira et al. 2006, Lee and Moon 2006, Cole and Paterson 2004, Cole et al. 2003, Morcillo et al. 2000, Petelski and Chomka 2000, Gustafsson and Franzen 1996).

Bangladesh is a country which has a large coastal area with the Bay of Bengal (Fig. 1). Some major cities including Chittagong are situated on the coastline where the action of sea spray creates an aggressive atmosphere for materials and products used in construction. Chittagong is the second largest city, the Commercial Capital, the chief sea port and the main centre of export and import of Bangladesh. From the last decade, the city is expanding rapidly with the establishment of heavy, medium and light industries. The population of the city also increased with the rapid expansion of its metropolitan region. In the city of Chittagong, an intense presence of sea spray can be detected along the coastal line and over the greater metropolitan area of the city. The atmosphere of this area has a strong presence of marine aerosol that has high levels of chloride ions like other regions of the world (Hossain 2001). Such aggressive environment has caused tremendous deterioration/damage to local structures (such as buildings and bridges) and reduced their service life. Very little research has been conducted to measure and evaluate the quantity of airborne sea salt in the context of Bangladesh. Such studies can provide important data for the design and maintenance of seashore infrastructures in Bangladesh.



Figure 1: Map of Bangladesh and location of the Metropolitan Region of Chittagong

The purpose of this study was to establish the spatial distribution of marine salts in the greater Chittagong metropolitan region. An experimental program was conducted to measure the concentration of marine salts in the atmosphere using wet candle sensors at 12 sampling stations (located within 7 km from the sea) and to develop correlations between the concentration of marine salts and the distance from the sea.

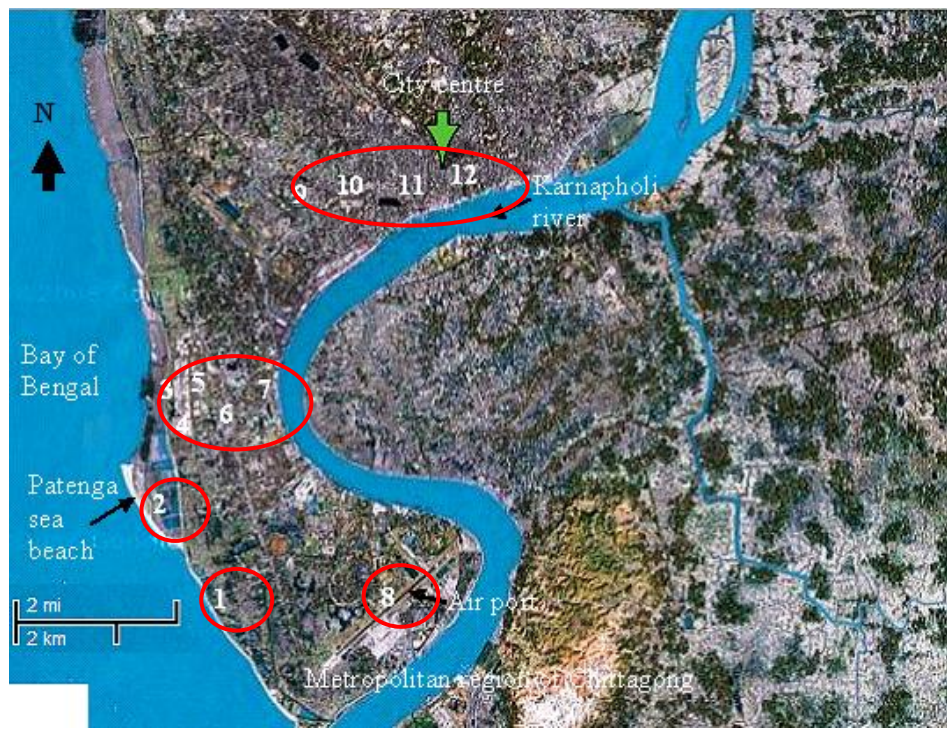


Figure 2: Sampling stations on enlarged satellite map of the Metropolitan Region of Chittagong

2. EXPERIMENTAL PROGRAM

An experimental program was designed to determine the concentration of marine salts in the atmosphere over a period of 25 weeks. The program consisted of three main tasks: selecting the sampling stations at different locations of the city, sampling procedures, and method of analysis.

2.1 Selection of Sampling Stations

The experimental program involved 12 sampling stations that were chosen in areas with high growth state in the city of Chittagong and its metropolitan region. A satellite map showing the locations of the sampling stations in the region is presented in Fig. 2. The sampling stations were designated and identified by their distance from the coastal line that varied from 50 m to approximately 7 km. The sampling stations were selected based on such criteria as availability of an open area with cover, absence of interference from objects (e.g. walls, trees, or other elements), and better wind circulation.

2.2 Sampling Procedures

To sample the atmospheric aerosol and determine its main ionic components, a device based on the Wet Candle Method as per ASTM G 140 (1996) was used (Fig. 3). The wet candle device captured the sea salts from the atmosphere on a prescribed exposed area of the apparatus. The device basically consisted of a 500 mL Erlenmeyer flask containing deionized water. A test tube wrapped in gauze whose lower end immersed in water was fitted to the flask through a perforated rubber stopper. The gauze lining the tube remained permanently moistened through capillary ascension. The ionic components of the atmospheric aerosol were deposited onto the gauze and moved towards the aqueous solution by diffusion where they remained, until their removal for the analysis.

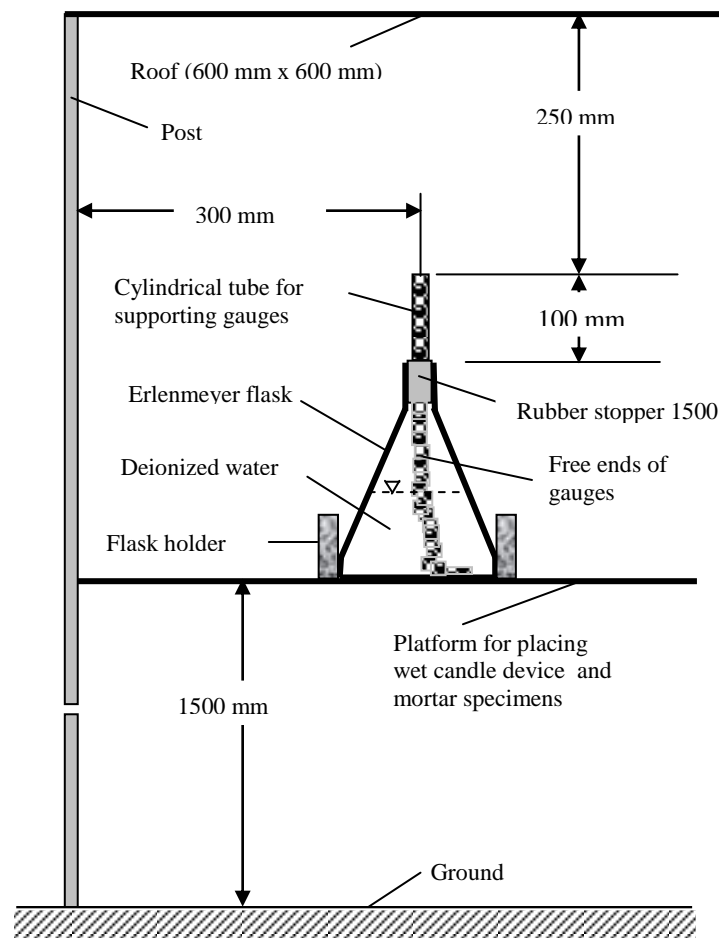


Figure 3: Typical wet candle sensor at a sampling station

As per ASTM G 140 (1996) and ISO 9225 (1992) specifications, a wet candle device was installed (as shown in Fig. 3) at each of the sampling stations in covered balcony/roof for protection against rain, at a distance of 1.5 m from the

soil/ground and away from walls that could hinder free circulation of air. The wet candle sensors remained exposed to the local atmosphere for a duration of 6 months (25 weeks) from April to September 2000 for sampling. The entire duration was divided into various periods that consisted of four periods of one week, two periods of two weeks, three periods of three weeks, and two periods lasting four weeks. The shorter time intervals were chosen at the beginning to determine the minimum quantities of ions that would be sampled on the wet candle. This was necessary to ensure the collection of enough samples for the subsequent analytical method employed, in terms of the concentration of the ions of interest. Besides, it was necessary to determine the performance of the sampling devices and to select sampling periods that would maintain the integrity of the samples. The level of the deionized aqueous solution was maintained at a reasonably constant level by refilling periodically during the wet candle sensor's exposition time to compensate for the losses incurred by evaporation. The positioning of the wet candle sensor was kept constant in relation to the prevailing direction of the local wind.

2.3 Method of Analysis

At the end of the exposure periods, the piece of gauze with the component of the wet candle sensor was incorporated into the solution, and the device was substituted by a new one. The solution containing the ionic components of atmospheric aerosol was then stored in polyethylene flasks of 20 mL and immediately analyzed for chlorides, nitrates, and sulfates by ion chromatography using QuikChem 8000 (Lachat Instruments 2007). The device accommodates up to eight analytical channels and enables the operation of both flow injection analysis (FIA) and ion chromatography (IC) simultaneously and independently on the same platform. The method of analysis of salts by IC provided results that were equivalent to that of ISO method 10304 (2007).

The quantity of sodium in the samples was also analyzed by flame photometry (Skoog et al. 2004) and used as a marine tracer that enabled to distinguish the fraction of sulfate ions from the sea spray (ss) from that of other sources (other). This is accomplished using the following equation (Skoog et al. 2004):

$$\text{SO}_4^{2-}(\text{other}) = \text{SO}_4^{2-}(\text{total}) - 0.06024 \times [\text{Na}^+] \quad (1)$$

where $\text{SO}_4^{2-}(\text{total})$ = molar concentration of total sulfate deposition, $\text{SO}_4^{2-}(\text{other})$ = molar concentration of sulfate deposition not originating from the sea spray, $[\text{Na}^+]$ = molar concentration of the sodium deposition in the sample, and 0.06024 = the molar ratio between the concentrations of SO_4^{2-} and Na^+ in the seawater.

3. RESULTS AND DISCUSSION

3.1 Influence of Meteorological Factor

Marine aerosols may be generated either by the ocean or from the surf through the bursting of bubbles generated by ocean whitecaps, particles torn from the crests of ocean whitecaps or breakers on the shore (Cole et al. 2003, Fitzgerald 1991). Production of salt in the ocean adjacent to the coast depends on whitecap activity and general ocean wind. Because of the lower whitecap coverage and ocean wind speed (average 5.5 m/s) near the equator, the salt production and associated corrosion problems are expected to be considerably less in equatorial regions compared with those with high or low latitudes (Cole et al. 2003). Many factors influence the mechanism of dry deposition of atmospheric components, involving the transport of material through the air, which is controlled mainly by diffusion processes. These factors are affected especially by meteorological variables that control the transfer of chemical species to surfaces at different levels of efficiency. Meteorological factors such as wind velocity, relative air humidity, wind direction, and air temperature can contribute to increase the particle fall velocity by increasing its mass and density (Cole et al. 2003, Morcillo et al. 2000, Petelski and Chomka 2000, Gustafsson and Franzen 1996, Fitzgerald 1991). The higher the wind velocity, the richer is the marine atmospheres with salts - a condition that favours the generation and emission of sea spray into the atmosphere. Besides meteorological factors, other factors such as surface roughness due to forests and urban landscapes can cause a dramatic fall off salt concentration in the air [Cole and Paterson 2004, Cole et al. 2003]. Two areas with similar sea states (thus similar aerosol production) can have significantly different aerosol distribution from the coast because of the varying meteorological and surface roughness conditions. Thus, the meteorological data were recorded during the entire monitoring period.

Bangladesh is situated between 20°34'-26°38' North Latitude and 88°01'-92°41' East Longitude. The country has a 724 km long coast line and many small islands in the Bay of Bengal. As the country is situated close to the equator, aerosol production in the Bay Bengal is expected to be lower compared to those at high or low altitudes such as Australia and Europe. The weather in Bangladesh is largely governed by the monsoon. In Chittagong, wind blows from north-east direction (from land to sea) in the winter season and from the south east direction (sea to land) during the summer season. So the duration of April through September (used in this study) is critical because the prevailing wind from the south (Sea) to the south east (Land) brings more sea aerosol to the land from the sea. The wind speeds exhibit strong seasonal cycle, lower in the September-February period and higher in the March-August

period. It also exhibits a diurnal cycle, generally peaking in the afternoon and weakest at night. Frequency greater than 4 m/sec was above 70% in June compared with less than 7% in November.

During the duration of this study (April to September), the wind speed ranged from 2.9 to 5.8 m/s (with a mean of 4.6 m/s), the temperature ranged from 27 to 32°C, the humidity ranged from 78 to 88%, and the total rainfall was around 210 cm. The meteorological parameters such as temperature, humidity and rainfall did not considerably vary during the duration of study. The Wind speed also did not vary significantly between May and September.

The sampling duration of 6 months “April through September (used in this study)” is critical and justifiable because of the prevailing wind from the south (sea) to the south east (land) and the higher wind speed bring more sea aerosol to the land from the sea. As the study was concentrated on the cumulative deposition of marine salts during the whole study duration at the sampling stations, it did not address the effect of varying meteorological conditions or the correlation between the deposition of atmospheric salts and the meteorological parameters as well as parameters associated with ocean’s aerosol production.

3.2 Variation of Deposition of Marine Salts

The data collected through atmospheric aerosol deposition of chlorides, nitrates and sulfates using the wet candle sensors permitted a spatial evaluation of the aggressive potential of the atmosphere. The aggressive potential was expressed as the weighted mean value of the dry deposition in the wet candle sensor as a function of the number of corresponding days to each sampling period (Table 1).

Table 1 Time weighted mean dry depositions from sea spray at different distances of the sea

Sampling Station No.	Distance from the Sea (L) (m)	Time Weighted Mean Dry Deposition						
		Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻ (total)	SO ₄ ²⁻ (ss)	SO ₄ ²⁻ (other)		
		mg m ⁻² d ⁻¹	mg m ⁻² d ⁻¹	mg m ⁻² d ⁻¹	mg m ⁻² d ⁻¹	% of Total	mg m ⁻² d ⁻¹	% of Total
1	93	54.02	0.90	10.90	8.20	75.2	2.70	24.8
2	152	16.10	0.89	3.90	2.40	61.5	1.50	38.5
3	207	13.22	1.20	3.50	2.10	60.0	1.40	40.0
4	452	4.71	1.10	4.22	1.32	31.3	2.90	68.7
5	811	3.93	1.00	4.12	0.92	22.3	3.20	77.7
6	1222	3.11	0.90	4.25	0.85	20.0	3.40	80.0
7	2105	2.62	1.00	4.30	0.80	18.6	3.50	81.4
8	3216	2.10	0.90	2.48	0.68	27.4	1.80	72.6
9	4019	1.71	1.10	4.81	0.51	10.6	4.30	89.4
10	5013	1.42	1.10	4.86	0.46	9.5	4.40	90.5
11	6105	1.31	1.20	4.65	0.45	9.7	4.20	90.3
12	7012	1.32	1.10	4.89	0.39	8.0	4.50	92.0
Deposition up to 207 m (%)*		79.0	24.1	32.2	66.6	-	14.8	-

SO₄²⁻(total) = Total sulfate deposition = SO₄²⁻(ss) + SO₄²⁻(other)
SO₄²⁻(ss) = sulfate deposition from sea spray (ss); SO₄²⁻(other) = sulfate deposition from other sources
* Deposition up to 207 m as % of total deposition along the entire sampling network

The variation of dry deposition of atmospheric salts that deposited on the wet candle sensors during the six-month sampling period with respect to the distance from the sea is presented in Figs. 4, 5, 6 and 7. Figs. 4 to 7 include the atmospheric salts that originated from the sea spray (chlorides Cl⁻ and part of the sulfates SO₄²⁻(ss)) and from other sources (nitrates NO₃⁻ and other sulfates SO₄²⁻(other)). The best fit curves (Figs. 4 to 7) show the trend of the variation of various salt ions with the distance from the seashore. The values of R (correlation coefficient) indicate that only the deposition of ions originating from the sea spray (Cl⁻ and SO₄²⁻(ss)) show a strong correlation with the distance from the sea. The developed regression equations are as follows:

$$\text{Cl}^- = 4.478 \text{ L}^{-0.744} \quad (\text{R}^2 = 0.93) \quad (2)$$

$$\text{SO}_4^{2-}(\text{ss}) = 1.094 \text{ L}^{-0.553} \quad (\text{R}^2 = 0.90) \quad (3)$$

where L = distance from the sea (km) and the units of Cl^- and $\text{SO}_4^{2-}_{(\text{ss})}$ are $\text{mg m}^{-2} \text{d}^{-1}$. The other ions, incorporated into the atmospheric aerosol via mixed traffic exhaust/industrial emissions and sea spray ($\text{SO}_4^{2-}_{(\text{total})}$) or mixed traffic exhaust/industrial emissions ($\text{SO}_4^{2-}_{(\text{other})}$, NO_3^-), do not correlate well with the distance from the seashore (Eqs. 4 to 6).

$$\text{SO}_4^{2-}_{(\text{total})} = 4.511 L^{-0.065} \quad (R^2 = 0.09) \quad (4)$$

$$\text{SO}_4^{2-}_{(\text{other})} = 2.838 L^{0.191} \quad (R^2 = 0.48) \quad (5)$$

$$\text{NO}_3^- = 1.022 L^{0.028} \quad (R^2 = 0.14) \quad (6)$$

where the units of the emissions are $\text{mg m}^{-2} \text{d}^{-1}$.

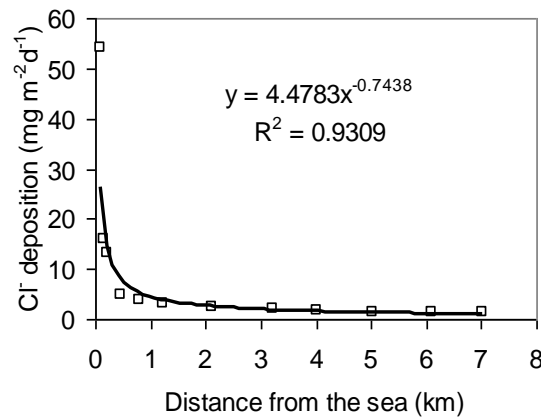


Figure 4: Variation of dry deposition of marine salts along the sampling network (Cl^-)

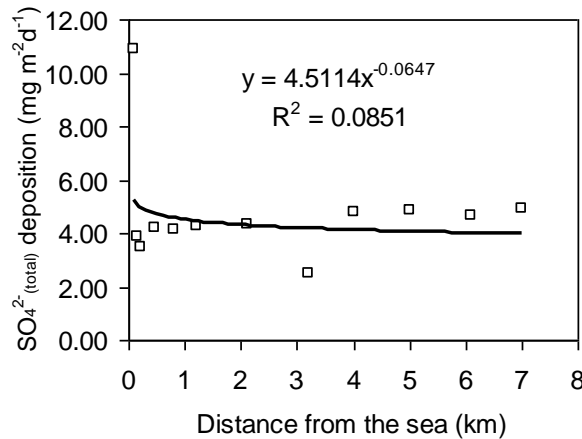


Figure 5: Variation of dry deposition of marine salts along the sampling network ($\text{SO}_4^{2-}_{(\text{total})}$)

The chloride deposition rates (Fig. 4) show a trend of decrease with the increase in the distance from the sea. Considering the data of Table 1, significant deposition was seen up to about a distance of 207 m (sampling station 3). This can be attributed to the fact that a large part of the sea spray is generated in the form of coarse particles (larger than $2 \mu\text{m}$), which are deposited in the proximities of the emission source. In this study, it was found that 79% of the Cl^- which represents the sea spray in the atmosphere was deposited within a distance of about 207 m from the sea (Table 1). Note that Cl^- was calculated in relation to the total deposition that occurred along the sampling network up to the last station, about 7 km from the seashore. A decrease of nearly 70% on chloride concentration was also observed in the first hundred meters from the sea in other research studies (Lee and Moon 2006, Meira et al. 2006).

For the case of $\text{SO}_4^{2-}_{(\text{other})}$, the expected trend of the decrease in deposition with the increase in the distance from the sea was not observed (Fig. 5). This was due to the fact that a very small portion of this ion (incorporated into the local atmospheric aerosol) had its origin from the sea spray. However, the concentration of $\text{SO}_4^{2-}_{(\text{ss})}$ in the atmosphere decreased with the increase in the distance from the sea (Fig. 6). Similar to Cl^- , 66.6 % of the $\text{SO}_4^{2-}_{(\text{ss})}$ deposition occurred within a distance of 207 m from the seashore (Table 1). This can be attributed to the increased

deposition of coarse particles in the proximity of the seashore as well as the interception of these particles by building surfaces (during the air borne transportation).

As expected, the concentration of $\text{SO}_4^{2-}(\text{other})$ in the atmosphere did not show a trend of decrease (rather showed a trend of increase) as the distance from the sea increases (Fig. 6). For the case of NO_3^- deposition, no significant trend was observed in relation to the distance from the sea (Fig. 7). The main local sources of NO_3^- and $\text{SO}_4^{2-}(\text{nss})$ are believed to be the oxidation processes of NO_x and SO_2 emitted from other sources. The trend of increase with the increase in distance from the sea for $\text{SO}_4^{2-}(\text{nss})$ is associated with the presence of industries and traffic in the sampling stations (4 to 7 and 9 to 12). Sampling station 8 was an exception as it was situated in an area of relatively lower traffic and no industries. Little variation in $\text{SO}_4^{2-}(\text{nss})$ (specifically over sampling stations 9 to 12) and NO_3^- (over all sampling stations) can be due to the homogeneity of the traffic intensity and concentration of industries along the sampling network. The deposition of NO_3^- varied within a narrow range between 0.89 and 1.2 $\text{mg m}^{-2} \text{d}^{-1}$ throughout the network. The variation in the $\text{SO}_4^{2-}(\text{nss})$ deposition along the network was higher than that of NO_3^- .

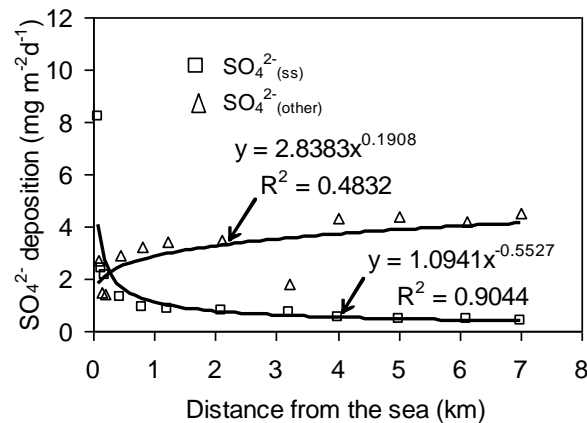


Figure 6: Variation of dry deposition of marine salts along the sampling network (SO_4^{2-})

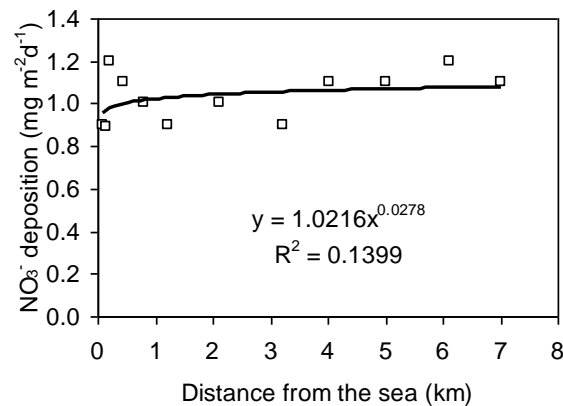


Fig. 7: Variation of dry deposition of marine salts along the sampling network (NO_3^-)

4. CONCLUSIONS

Spatial distribution of marine salts from sea spray within the metropolitan area of Chittagong city, Bangladesh was evaluated using wet candle sensors at 12 sampling stations situated at various distances from seashore. Based on this study, the following conclusions are offered:

1. The aggressive potential of marine salt was found to be significant up to a distance of about 200 m from the seashore. It was also found that 79% of the total chloride and 66.6 % of the total sulfate deposition originated from sea spray along the 7 km long sampling network were deposited within a distance of 207 m from the seashore. From this point onward, the amount of chlorides drops sharply and, in the case of sulfates, other emissions such as vehicular and industrial, become more important than the sea spray. The deposition of NO_3^- did not vary significantly probably due to the homogeneity of the vehicular traffic along the sampling network.
2. Only the deposition of ions originating from the sea spray (Cl^- and $\text{SO}_4^{2-}(\text{ss})$) shows a strong correlation with the distance from the sea. The other ions, which were, incorporated into the atmospheric aerosol via mixed traffic

exhaust and industrial emissions and sea spray or mixed traffic exhaust and industrial emissions alone, had no correlation with the distance from the sea.

3. The study revealed the potential high deposition of sea salt on structures within the proximity (especially within the 200 m) of the sea shore. This can be useful for local authorities in adopting practical measures to prevent aggression of sea salts and deterioration of infrastructures close to the sea.
4. Future studies should focus on determining the performance of materials and service life of structures exposed to various environmental impacts. In this context, the hazard potential of marine salts on the mortars normally used as external renders in concrete structures should be examined.

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