



Risk assessment and source apportionment of wet bulk deposition in three typical sites of Gampaha District, Sri Lanka

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Abstract

Scavenging of pollutants emitted to the atmosphere from natural resources and anthropogenic activities changes the chemical composition of rainwater. However, determination of the extent of atmospheric pollution and identification of pollution sources have not been regularly carried out in Sri Lanka. The objective of this research is therefore to analyze bulk deposition samples collected during a 7-month period from 10 June 2017 to 6 January 2018 in three different locations in Sri Lanka, Katunayake, Gampaha and Lunugama, followed by analysis of rainwater quality parameters including anions and cations using standard methods. These locations differ from each other in geography, industrialization and urbanization. Acid rain was not encountered in any of the three locations during the sampling period according to the pH measurements. The volume-weighted mean ion concentration in the three locations determined by ion chromatography varied as $K^+ < NH_4^+ < Mg^{2+} < Ca^{2+} < Na^+$. The dominant cations were Ca^{2+} and Na^+ , while Cl^- and SO_4^{2-} were identified as the dominant anions in all locations. The ratios between Na^+ and the ions Cl^- , SO_4^{2-} , Ca^{2+} , K^+ and Mg^{2+} , calculated using the enrichment factor, indicate that some ions from marine and anthropogenic activities contribute to the rainwater. The Katunayake sampling location showed the highest Pearson correlation between Na^+ and Cl^- because of the sea breeze, while Ca^{2+} and Mg^{2+} showed the highest Pearson correlation in the Gampaha and Lunugama locations because of soil dust. Although rainwater is not acidic according to pH measurements, it can be neutralized by calcium salts. This masking effect should thus be considered in risk assessment strategies. Continuous monitoring of rainwater quality is necessary to reach sound conclusions and make predictions about atmospheric quality.

Keywords Rainwater quality · Sri Lanka · Metal ions · Anions · Cations · Statistical analysis

1 Introduction

Air is mainly polluted by anthropogenic activities. Hence, air quality problems are increasing because of the rapid development of the industrial and agricultural sectors, which emit various types of pollutants into the atmosphere [1]. Consequently, air quality monitoring plays a key role in air pollution management programs. It has been reported that in Sri Lanka SO_2 and O_3 levels have exceeded the WHO permitted standards in certain atmospheric samples [2].

Primary air pollutants, such as carbon monoxide, sulfur dioxide and suspended particulate matter, which exist in the atmosphere in the same form as in source emissions, are emitted directly into air in harmful forms [3]. On the other hand, secondary air pollutants, when released into the air, become hazardous after reacting with substances in the atmosphere. They form in the atmosphere as a result of hydrolysis, oxidation and/or photochemical oxidation [3]. Acidic mists, chlorofluorocarbons and photochemical oxidants such as ozone are some examples.

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Atmospheric deposition, the removal of gases and particulates from the atmosphere, has two types, wet and dry deposition, which are collectively called bulk deposition. Wet deposition of any form of precipitation removes pollutants from the atmosphere and delivers it to the Earth's surface, while dry deposition occurs in the absence of precipitation. Both wet and dry deposition events are scavenging processes that remove both inorganic and organic pollutants from the atmosphere [4–6]. Major ions found in bulk deposition are Na^+ , K^+ , Mg^{2+} , Ca^{2+} , NH_4^+ , F^- , Cl^- , Br^- , NO_3^- and SO_4^{2-} . Therefore, the extent of atmospheric pollution, and hence the chemical composition of rainwater, varies depending on many factors, including the influence of local sources, rain events, transport of atmospheric pollutants and geographical location [7–11]. Determination of quantitative changes of these parameters thus helps to understand the relative contribution of different sources of atmospheric pollution.

Atmospheric deposition leads to acid rain if the pH of rainwater is < 5.6 [12]. Acid rain is a potential environmental hazard, especially in highly industrial and urban areas, due to the emission of acidic pollutants to the atmosphere. The two types of gases contributing most to acid rain are sulfur dioxide and nitrogen dioxide. Sulfur dioxide normally comes from burning coal in thermal power plants and roasting of metal sulfides, while nitrogen oxides come from the combustion of nitrogenous compounds in fossil fuels and direct combination of nitrogen and oxygen in motor vehicle engines. When sulfur dioxide and nitric oxide are introduced into the atmosphere, they are oxidized, forming sulfuric acid and nitric acid, respectively [13]. In addition to the above gases, the pH of rainwater decreases to < 7.0 because of the ionization of carbonic acid, which occurs when atmospheric carbon dioxide is dissolved in rainwater. Acid rain and other pollutants can be contributed by neighboring countries as a result of transboundary air pollution, which has become a severe regional atmospheric environmental problem [14]. For instance, neighboring countries in South and South-East Asia can contribute to the acidity of the rain in Sri Lanka [15].

Acid rain affects all components of the ecosystem. Acidification of soil causes an increase in the exchange between H^+ and nutrient cations, such as K^+ , Mg^{2+} and Ca^{2+} , in the soil. Consequently, acidic water contributes to the washout of nutrients and other useful minerals before they can be absorbed by flora, leading to nutrient deficiency of the soil, thereby weakening trees and crop plants [16]. The main atmospheric pollutants that affect trees are nitrates and sulfates. Mixing of acidic water with soil also causes the release of toxic substances, such as aluminum, into the soil, harming the vegetation [17]. Furthermore, the decomposition rate and the nitrogen cycle are also

negatively affected because of the acidity of the soil. It has been reported that photosynthesis is decreased at acidic pH values [18]. In fish, acid rain increases the mortality rate and reproductive failure, and reduces the growth rate, causing skeletal deformities [13]. Deterioration of concrete structures is also caused by acid deposition, and the impact on structures made of marble and limestone is high. For instance, the Taj Mahal in India, the Acropolis in Greece and Renaissance buildings in Italy have already been affected by severe acid rain damage [19]. In some parts of Poland, railway tracks have been damaged by acid rain [20].

Sri Lanka is an island surrounded by the Indian Ocean. Therefore, its climate changes rapidly because of the wind. The inter-monsoon period (March–mid May), South-West monsoon period (mid May–September), second inter-monsoon period (October–November) and North-East monsoon period (December–February) are the main climatic seasons in Sri Lanka [21]. Pollutant levels are affected by the seasonal climate of the area where the impact of the relatively high North-East monsoon is strongly felt compared to the South-West monsoon. Despite the global need for a rainwater quality database, reports on rainwater analysis and atmospheric modeling in Sri Lanka are limited. Nevertheless, with the expansion of economic activities in Sri Lanka, particularly urbanization and industrialization, levels of atmospheric pollution need monitoring. In this context, the objectives of this research were to study the chemical composition of rainwater, the variation of the chemical composition of rainwater at selected locations in Gampaha District of Sri Lanka and the effect of human activities that alter the chemical composition of rainwater. Investigation of the chemical composition of rainwater will be useful for formulating remedial measures to reduce the extent of air pollution due to anthropogenic activities.

2 Materials and methods

2.1 Description of sampling points

Sampling locations used in this study were Katunayake, Gampaha and Lunugama, which were selected because of their industrialization, urbanization and geographical variation. Katunayake is an industrialized as well as urbanized area. Katunayake export processing zone (KEPZ), which has various atmospheric pollution-emitting industries, Bandaranaike International Airport and the ocean are near the Katunayake site. Environmental pollution caused by aircraft operations is an important issue to consider regarding atmospheric pollution in this area [22]. Gampaha is a major urban city in the Western Province situated northeast of the capital city, Colombo. It has

been reported that the annual average NO_2 and SO_2 levels in 2014 in Gampaha exceeded the 24-h guideline value [23]. The many diesel-powered trains frequently traveling through Gampaha may have a significant impact on air pollution. Lunugama, a rural area, is the third sampling point, located in Dompe Divisional Secretariat. In rural areas, air pollution is caused by natural sources, such as forest and coal fires [18]. Meteorologic factors also play an important role in the air quality in rural areas, and winds help disperse and dilute pollutants. In this study, it is expected that few anthropogenic activities take place in the Lunugama area.

The GPS coordinates of the Katunayake sampling point are (44 N) 377647 E 796236 N. Distances from KEPZ, Bandaranaike International Airport and the beach to the sampling point are 3.5 km, 1.0 km and 6.0 km, respectively (Fig. 1). Negombo lagoon and Negombo town are located within 6.0 km of the sampling point. As sea wind can come to this area, sea salt (Na^+ and Cl^-) can be deposited, changing the chemical composition of the bulk deposition.

The GPS coordinates of the Gampaha sampling point are (44 N) 388907 E 784316 N. As shown in Fig. 2, the location adjoins the railway tracks opposite the railway station and near a bus stand. The other bus stands of Gampaha city are also located within 300 m from the sampling point. Road traffic mostly occurs because of the narrow roads and high density of vehicles. Therefore, vehicular emission levels are very high in this area. The contribution from

vehicular emissions to the acidity of rain is probably more in this area than in the other study areas.

The GPS coordinates of the Lunugama sampling point are (44 N) 399168 E 771975 N. Lunugama is a rural area, and neither industries nor vehicle traffic is encountered in the area. There are many paddy fields in the areas surrounding the sampling point (Fig. 3). In this research, Lunugama is considered an environmentally safe area compared to the other two sample areas.

2.2 Sampling and materials

A 20.6-cm-diameter funnel was attached to a polyethylene bucket and kept on a stand for collection of bulk deposition samples. A cotton wool plug was placed in the funnel mouth to prevent particulate matter and insects from entering the sample, and the bucket was placed 150 cm above the ground. The funnel and bucket were thoroughly washed using deionized water followed by ultrapure water before being placed in the sampler. Bulk precipitation was collected once a week during a 7-month period from 10 June 2017 to 6 January 2018 at the three locations. Samples from all three locations were collected on the same day.

The sampler that contained rainwater was considered wet deposition. The sampler with no rainwater was considered dry deposition. The rainfall at each event was calculated using the total volume of rain and the



Fig. 1 Google map of the sampling point in Katunayake. The ocean, international airport and export processing zone are in the vicinity



Fig. 2 Google map of the sampling point in Gampaha. This point is in a highly urbanized area



Fig. 3 Google map of the sampling point in Lunugama. It is much less urbanized and is surrounded by agricultural fields

surface area of the funnel. During the sampling period, 30 samples were collected from each location. Seven dry deposition samples were obtained at the 5th, 6th, 7th, 8th, 10th, 12th and 30th weeks in Katunayake. Four dry deposition samples were obtained at the 5th, 8th, 24th

and 30th weeks in Gampaha. During the sample period, only one dry deposition sample was obtained at the 30th week in Lunugama.

Tetrabutylammonium hydroxide (TBAOH) (2.06 M, Dionex cation regenerant concentrate), sulfuric acid (2.0

M, Dionex anion regenerant concentrate), 0.4 M methanesulfonic acid (Dionex CS12A eluent concentrate), 4.5 mM sodium carbonate and 0.8 mM sodium bicarbonate (Dionex AS23 eluent concentrate) were purchased from Thermo Fisher Scientific Inc. Buffer solution of pH 10.00 (potassium carbonate-potassium borate-potassium hydroxide buffer, 0.05 M), pH 7.00 (potassium phosphate monobasic-sodium hydroxide buffer, 0.05 M) and pH 4.00 (potassium acid phthalate buffer, 0.05 M) was purchased from Wisconsin Inc. Buffer solutions of HI7030L 12,880 $\mu\text{S cm}^{-1}$ and HI7031L 1413 $\mu\text{S cm}^{-1}$ were purchased from Hanna Instruments.

2.3 Research methodology

Samples collected from all the three locations were brought to the laboratory to determine the relevant chemical and physical parameters. Each sample was divided into two parts. One part was used to measure the conductivity and pH. The other part was filtered through a 0.45- μm cellulose acetate filter paper and stored in the dark at 4 °C until ion analysis was performed.

The mass of each sample was measured using an electric balance. The volume of each sample was measured using a graduated measuring cylinder. Conductivity and pH were measured using 6820 VZ (Multiparameter Water Quality Sonde). Before taking measurements, 6820 VZ (Multiparameter Water Quality Sonde) was calibrated using standard solutions. A Thermo Scientific Dionex ICS-900 Ion Chromatography System was used to determine the anions (Cl^- , NO_3^- , F^- and SO_4^{2-}) and cations (Na^+ , K^+ , Ca^{2+} , NH_4^+ and Mg^{2+}). For anions, a Dionex ion pack AS23 (4 × 250 mm) column was used, and a Dionex ion pack CS12A (4 × 250 mm) column was used for cations.

2.4 Statistical analysis

Minitab 16 (Minitab Inc., State College, PA, USA) and IBM SPSS statistical softwares were used to analyze ions and other parameters. Regression analysis and Pearson correlation methods were also used for data analysis.

3 Results and discussion

3.1 Variation of rainfall

As shown in Fig. 4, the highest rainfall values of 144.92 mm and 158.60 mm were obtained in the 19th week for Katunayake and Gampaha, respectively, and the corresponding lowest values of 4.5 mm and 5.1 mm were obtained in the 1st week with the exception of dry depositions. The highest rainfall amount for the above two sampling

locations occurred in the second inter-monsoon period. On the other hand, the highest rainfall of 160.00 mm was obtained in the 14th week and the lowest of 7.08 mm in the 10th week in Lunugama with the exception of dry depositions. The rainfall in Katunayake in general was lower than that in the other two locations during the entire sampling period with the exception of the 26th week.

3.2 Variation of pH at the three locations

According to the results shown in Fig. 5, the highest pH value of depositions in Katunayake was obtained in the 1st week and the lowest in the 14th week. On the other hand, the highest pH value of depositions in Gampaha was obtained in the 24th week and the lowest of 5.8 in the 14th week. Figure 5 also shows that the highest pH value of depositions in Lunugama was obtained in the 8th week and the lowest in the 14th and 22nd weeks.

It would be expected that emission of smoke from airplanes at Bandaranaike International Airport, the largest airport in Sri Lanka, and stack emissions from the industries in KEPZ, one of the biggest export processing zones, could cause a decrease of the pH of depositions in Katunayake because the above operations emit acidic fumes such as CO_2 and SO_2 into the atmosphere, which subsequently dissolve in rainwater. On the other hand, it would also be expected that the high level of vehicular traffic and train smoke could lead to decreased pH levels in the depositions in Gampaha. Furthermore, many metal-melting industries are located near the Gampaha sampling location, which release SO_2 into the atmosphere contributing to the decrease in the pH of depositions. In contrast, volatilization of ammonia as a result of excessive use of nitrogen fertilizers in paddy fields in the Lunugama area increases the pH of rainwater in depositions in Lunugama [20]. Nevertheless, the pH of rainwater in general is lower in Lunugama than in the other two locations. It can thus be argued that acidic fumes released from operations in the Katunayake area diffuse out toward the ocean, thereby minimizing their effect. This phenomenon could be effective to some extent in Gampaha. It can also be argued that acidic pollutants can diffuse into the Lunugama area causing the depositions to be more acidic. However, extensive research on long-term atmospheric monitoring and modeling is necessary to arrive at a sound conclusion.

An important fact is that both the lowest pH of 5.7 and the highest rainfall occurred in the 14th week in Lunugama, showing a correlation between the rainfall and pH. Such a direct correlation was not observed in the other two locations, probably because of the complexity of many factors influencing the pH of wet depositions. Nitric oxide produced in lightning events during rainy days also oxidize to HNO_3 , causing a decrease of

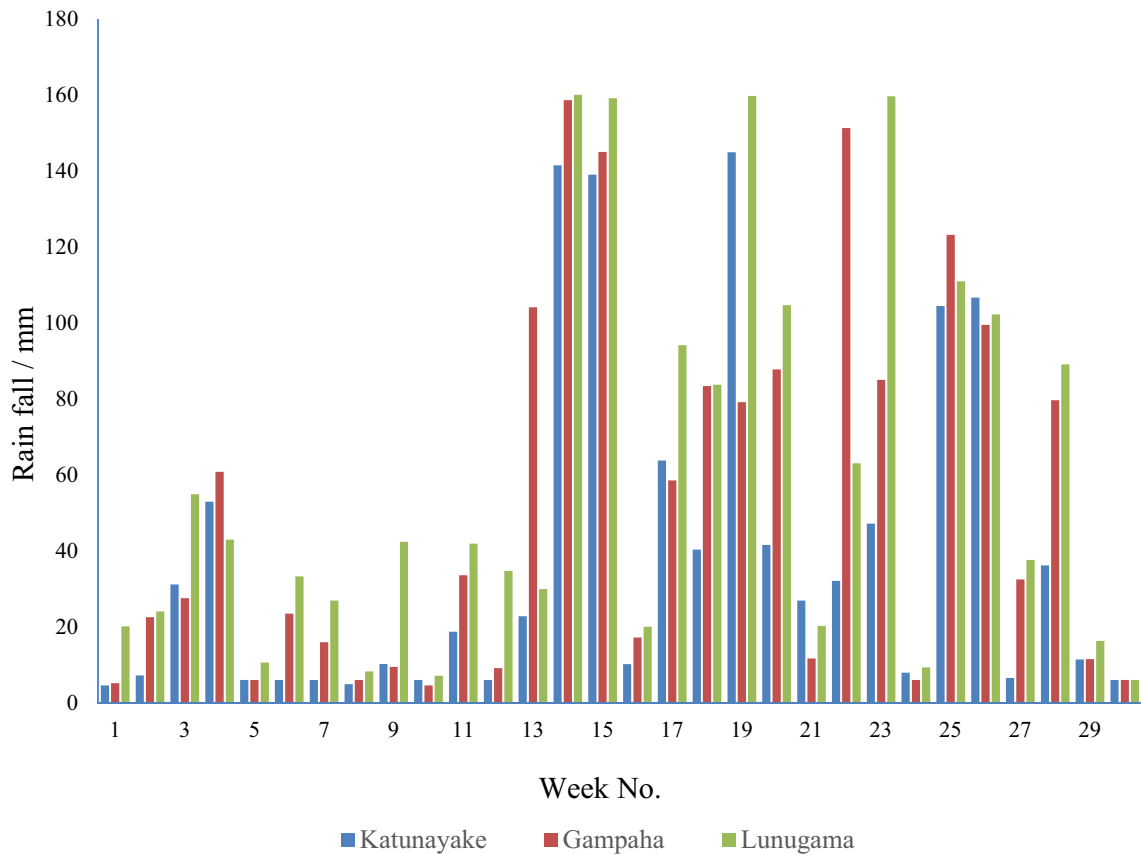


Fig. 4 Variation in rainfall in the Katunayake, Gampaha and Lunugama locations

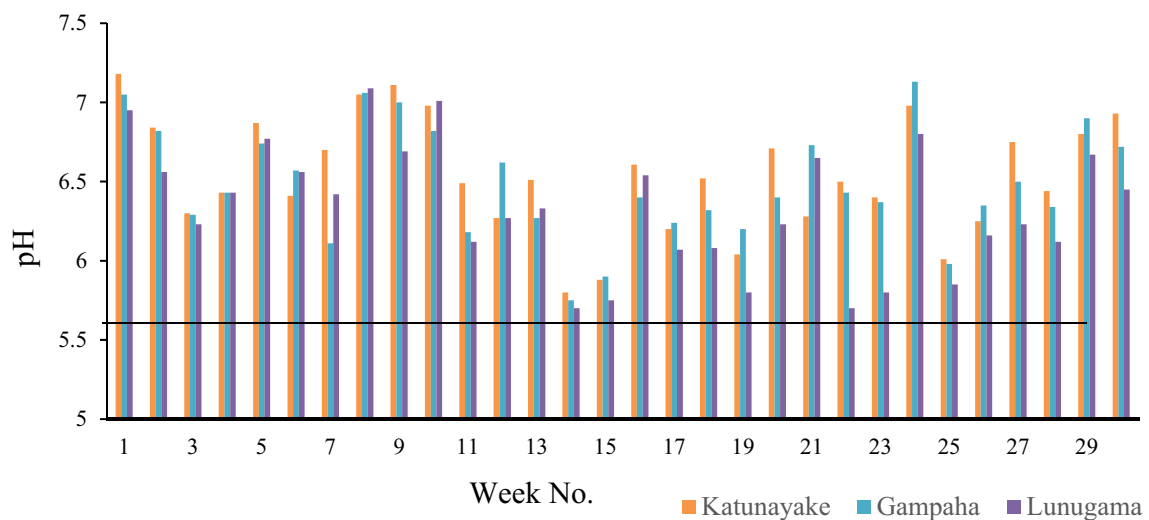


Fig. 5 Variation of pH at three locations. The solid line represents the limit of pH below which the rain is considered to be acidic

the pH of depositions. The solid horizontal line in Fig. 5 corresponds to the pH value of 5.6 indicating the margin level of acid rain. The pH values of all the depositions at all locations were determined to be above the solid line

during the sampling period, indicating that no acid rain events occurred as per pH measurements.

3.3 Variation of conductivity at three locations

According to the results shown in Fig. 6, the highest conductivity of Katunayake depositions was obtained in the 8th week and the lowest in the 25th week. The lowest rainfall occurred in the 8th week in Katunayake, indicating that the concentration of ions is high when the rainfall level is low, increasing conductivity, which is an accepted fact. On the other hand, the highest conductivity of Gampaha depositions was obtained in the 24th week and the lowest in the 10th and 28th weeks. Conductivity of dry deposition usually results in high values because of dust particles derived from the soil that can adsorb atmospheric pollutants. This fact is consistent with the observation of the highest conductivity in the 24th week, within which only dry deposition was observed. The Lunugama location also showed the highest conductivity in the 24th week and the lowest in the 14th week.

In general, the Lunugama location showed low conductivities in depositions compared to the other two locations, indicating less atmospheric pollution. The comparatively high conductivities recorded in samples collected in the

10th and 24th weeks can be attributed to the low rainfall level recorded. Previous studies also showed that conductivity decreases in high rainfall periods because of the dilution effect of dissolved gases and particulate matter [24].

3.4 Determination of anions and cations in rainwater

3.4.1 Variation of cations

Ion concentrations in rainwater mainly depend on anthropogenic activities in a particular area; consequently, there is a clear variation of anions and cations depending on both the topography and temporal nature. The dominant cations are Ca^{2+} and Na^+ in depositions of all three locations (Figs. 7, 8 and 9), and the highest concentration of Ca^{2+} in both Katunayake and Gampaha locations was obtained in the 26th week. However, the lowest concentrations in Katunayake and Gampaha locations were recorded in the 10th and 20th week, respectively. On the other hand, the highest concentration of Na^+ was obtained in the 19th week and the lowest in the 9th week in Katunayake, and

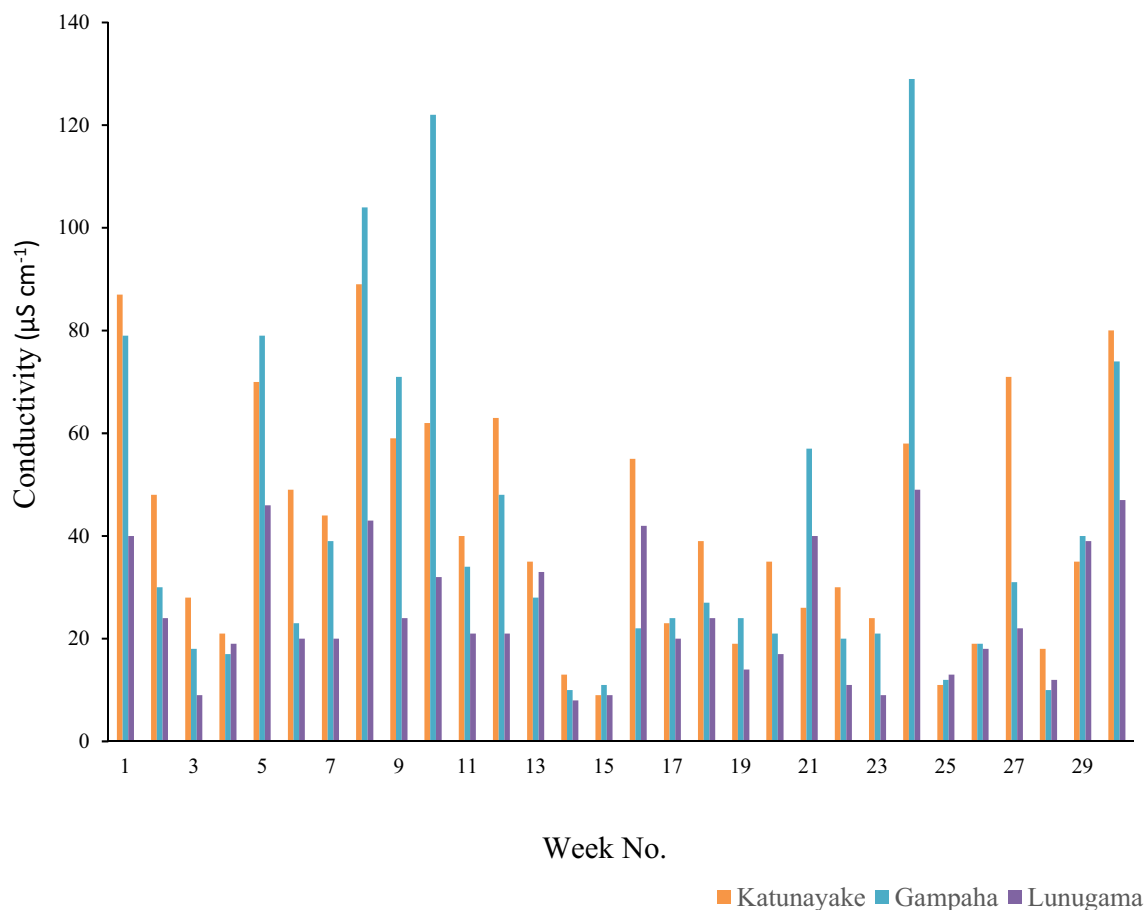


Fig. 6 Variation of conductivity at the three locations

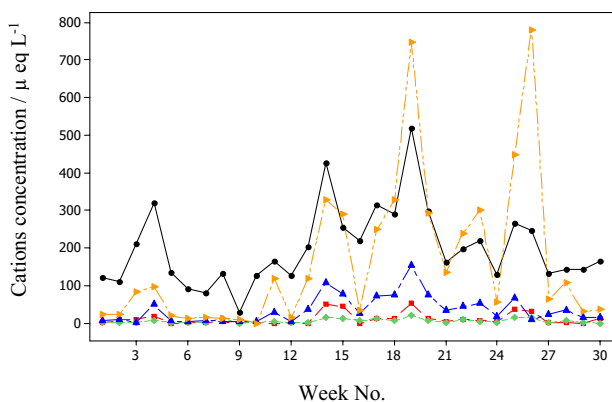


Fig. 7 Variation of cations in Katunayake (—●— Na⁺, —■— NH₄⁺, —◆— K⁺, —▲— Mg²⁺ and —▶— Ca²⁺)

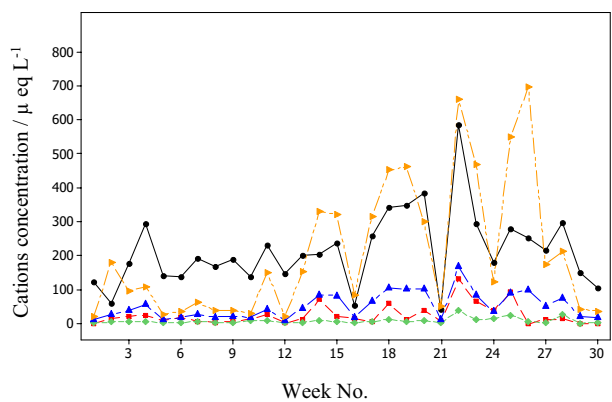


Fig. 8 Variation of cations in Gampaha (—●— Na⁺, —■— NH₄⁺, —◆— K⁺, —▲— Mg²⁺ and —▶— Ca²⁺)

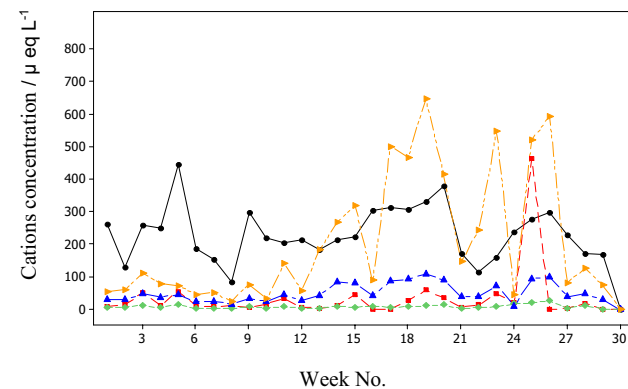


Fig. 9 Variation of cations in Lunugama (—●— Na⁺, —■— NH₄⁺, —◆— K⁺, —▲— Mg²⁺, and —▶— Ca²⁺)

the respective observations in Gampaha were recorded in the 22nd and the 21st weeks, respectively. Figure 9 indicates that, in Lunugama, the highest concentration of Ca²⁺ was obtained in the 19th week and the lowest was obtained in the 8th week. The highest concentration of Na⁺ was obtained in the 5th week and the lowest in the 8th week.

On average, the volume-weighted mean (VWM) concentrations of cations in depositions of all three locations were increased in the same order, K⁺ < NH₄⁺ < Mg²⁺ < Ca²⁺ < Na⁺, as shown in Fig. 10. Among the three locations, the highest concentration of both Na⁺ and K⁺ was in the Katunayake location. This sampling point, being located in close proximity to the coast, receives sea breezes containing salts contributing to elevated levels of Na⁺ in depositions to a great extent and K⁺ to some extent, as shown in the figure. Observations made on the reasonably high levels of Na⁺ in depositions in Gampaha and Lunugama could be partly attributed to the sea breezes, as these locations are not far from the coast. Diffusion in sea breeze containing mainly Na⁺ ions toward the sampling locations is supported by the argument that acidic pollutants diffuse out from the Katunayake and Gampaha locations as pointed out earlier.

The high level of Ca²⁺ in rainwater in these locations is probably due to dust particles containing Ca²⁺-bearing minerals. Low rainfall causes an increase in soil dust in the Katunayake region. In rainy periods, soil is relatively wet, and surface dusts are not easily incorporated into the air. Furthermore, the presence of Ca²⁺ and Mg²⁺ is caused by burning lime biomass. Figure 10 also shows that the concentration of Ca²⁺ is increased in the order Lunugama < Gampaha < Katunayake, indicating that the amount of dust particles derived from the soil in the atmosphere in the Katunayake area is higher than that in the other two areas. It should be highlighted that Lunugama depositions show the highest NH₄⁺ concentration with respect to the other two locations due to agricultural activities, especially paddy fields, in this area, where dissolution of NH₃ from nitrogenous fertilizer produces NH₄⁺.

3.4.2 Variation of anions

The dominant anions are Cl⁻ and SO₄²⁻ in all three sampling locations (Figs. 11, 12 and 13). Average anion concentrations in depositions of all three locations are as follows: Katunayake: NO₃⁻ < F⁻ < SO₄²⁻ < Cl⁻, Gampaha: F⁻ < NO₃⁻ < SO₄²⁻ < Cl⁻, Lunugama: NO₃⁻ < SO₄²⁻ < Cl⁻. The highest VWM concentration of Cl⁻ (together with Na⁺) in the Katunayake location is attributed to sea salt being swept by the wind from the sea to the ground (Fig. 14). Although the sea is not as close as in the Katunayake area, sea salt deposits Na⁺ and Cl⁻ in the

Fig. 10 Variation of VWM concentrations of cations at three locations (Katunayaka, Gampaha and Lunugama)

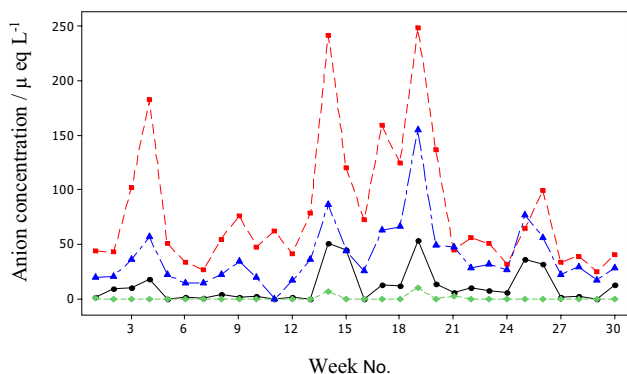
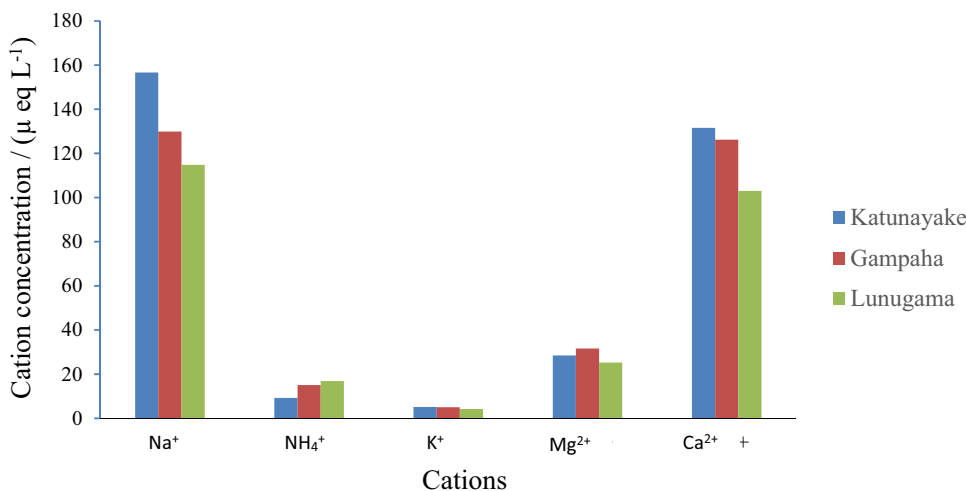


Fig. 11 Variations of anions in the Katunayaka location (—●— F⁻, —■— Cl⁻, —◆— NO₃⁻ and —▲— SO₄²⁻)

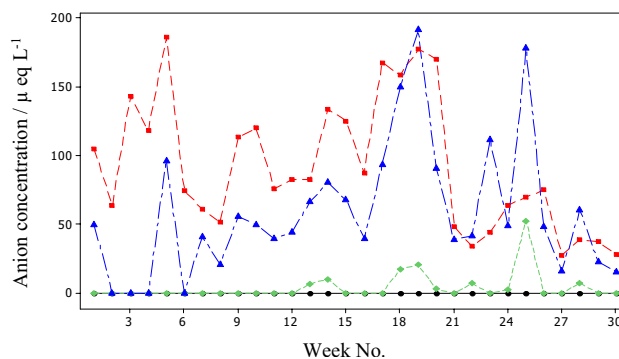


Fig. 13 Variations of anions in the Lunugama location (—●— F⁻, —■— Cl⁻, —◆— NO₃⁻ and —▲— SO₄²⁻)

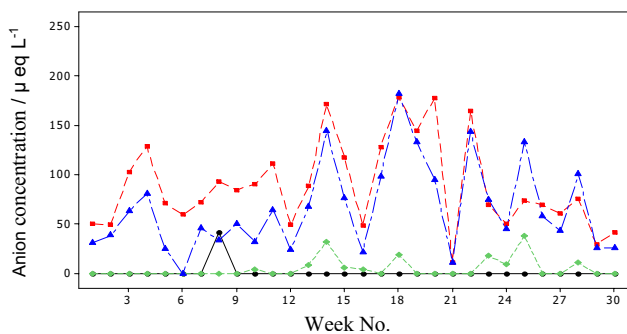


Fig. 12 Variations of anions in the Gampaha location (—●— F⁻, —■— Cl⁻, —◆— NO₃ and —▲— SO₄²⁻)

Gampaha and Lunugama areas as well. The presence of SO₄²⁻ in rainwater may be due to the release of SO₂ from anthropogenic activities in the KEPZ and vehicular

and railway emissions. Vehicular emission is significant in both the Katunayaka and Gampaha locations, being close to the respective city, while railway emissions are higher in Gampaha. High levels of SO₄²⁻ are contributed by the Sapugaskanda oil refinery, which emits SO₂ during operation. This is probably a major reason for the high levels of SO₄²⁻ in depositions in the Lunugama location, which is closer to the oil refinery than the other two locations.

The relatively low concentrations of F⁻ in Katunayaka and Gampaha are contributed by natural sources mainly marine and anthropogenic sources, such as aluminum smelters, fertilizer factories, cement works, ceramic industries and glass manufacturing industries [25]. These factors provide a clear indication of the higher concentration of F⁻ in Katunayaka than in the Gampaha location. Furthermore, the concentration of NO₃⁻ in Gampaha is higher than that in the other two locations, probably because of emissions from trains, which are not present in the other two locations (Fig. 14).

Fig. 14 Variation of VWM concentrations of anions at the three locations

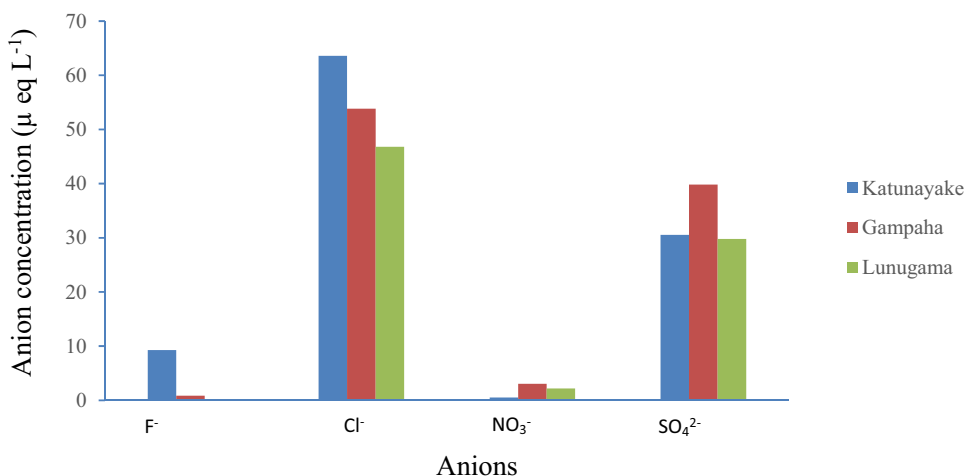
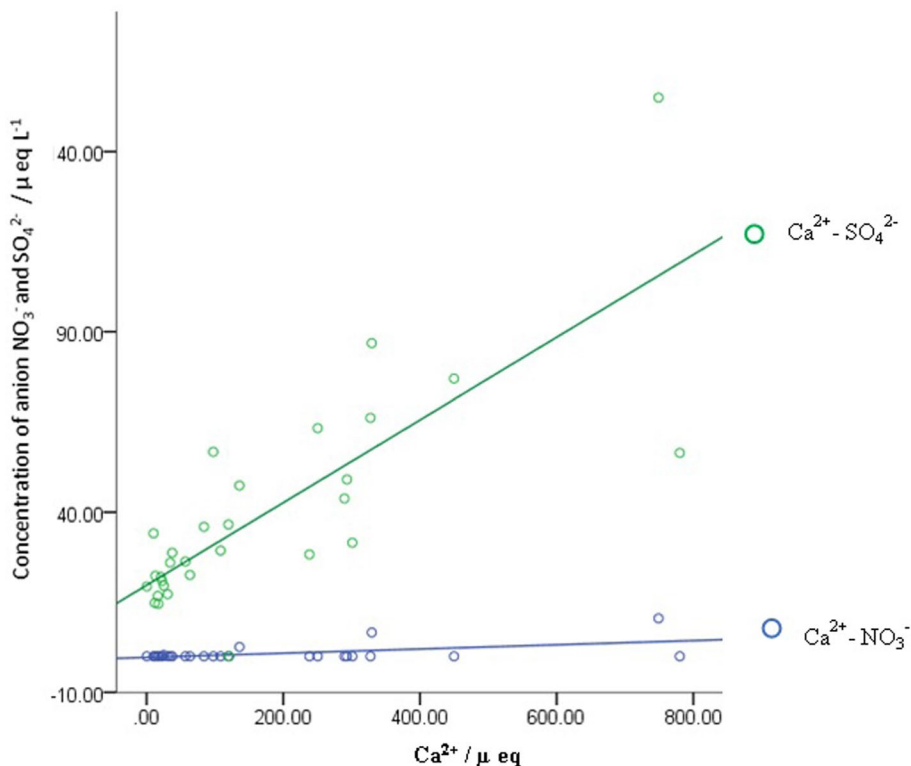


Fig. 15 Regression analysis for the concentration of Ca²⁺ with concentrations of NO₃⁻ and SO₄²⁻ in Katunayake (○ Ca²⁺-SO₄²⁻ (top) and ○ Ca²⁺-NO₃⁻ (bottom))



3.4.3 Acidification and neutralization of rainwater

Ions present in rainwater affect compositional changes leading to pH changes in rainwater. The main ions responsible for such changes are Na⁺, Mg²⁺, Ca²⁺, K⁺, NH₄⁺, NO₃⁻ and SO₄²⁻. Among them, Ca²⁺ and NH₄⁺ are the dominant constituents decreasing rainwater acidity, while NO₃⁻ and SO₄²⁻ lead to high levels of acidity. The presence of Ca²⁺ and SO₄²⁻ in combination is found to be more probable than the combination of Ca²⁺ and NO₃⁻;

furthermore, the presence of the NH₄⁺ and SO₄²⁻ combination is more probable than the NH₄⁺ and NO₃⁻ combination in Katunayake (Figs. 15 and 16). Similar patterns in regression analysis were found in the depositions in Gampaha and Lunugama locations as well. It should also be stated that pH was not the sole parameter used in the risk assessment because of the acidity of depositions because basic cations, such as Ca²⁺ and Mg²⁺, through the buffering action, have an opposing effect in increasing pH.

Fig. 16 Regression analysis for the concentration of NH_4^+ with concentrations of NO_3^- and SO_4^{2-} Katunayake (○ $\text{NH}_4^+ - \text{NO}_3^-$ (bottom) and ○ $\text{NH}_4^+ - \text{SO}_4^{2-}$ (top))

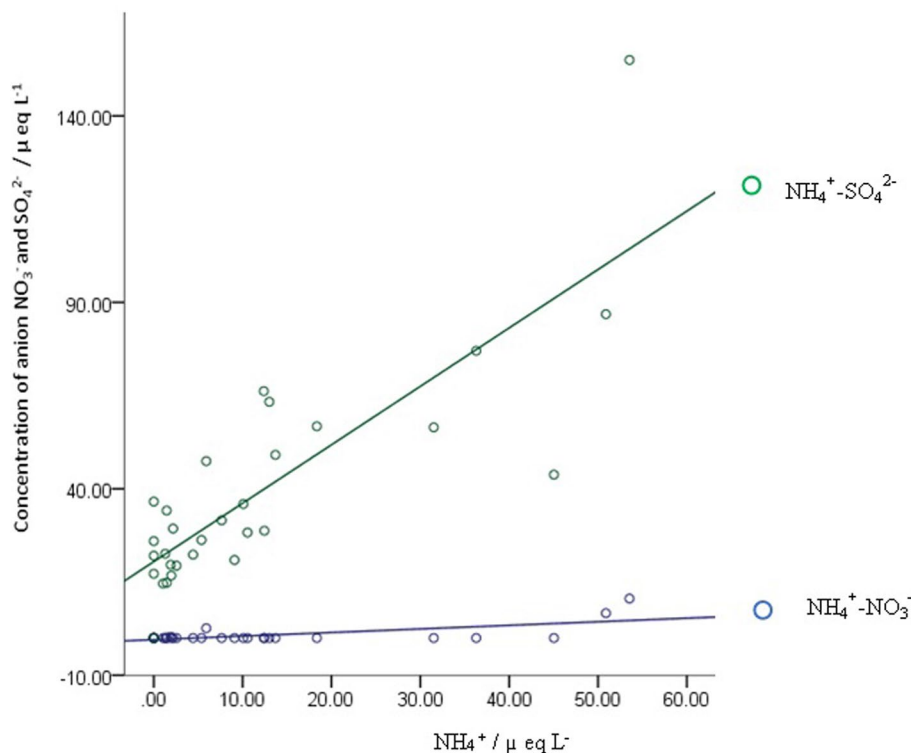


Table 1 Percentages of NO_3^- and SO_4^{2-} with concentrations of Ca^{2+} and NH_4^+ in three locations

	NO_3^- (%)	SO_4^{2-} (%)	Total (%)
Katunayake location			
$[\text{Ca}^{2+}]$	27.8	62.0	89.8
$[\text{NH}_4^+]$	21.2	58.0	79.2
Gampaha location			
$[\text{Ca}^{2+}]$	18.4	56.1	74.5
$[\text{NH}_4^+]$	36.2	48.0	84.2
Lunugama location			
$[\text{Ca}^{2+}]$	21.3	59.6	80.9
$[\text{NH}_4^+]$	20.2	77.4	97.6

Table 1 shows the results of the regression analysis coefficients, which indicate that, in the Katunayake location, 89.8% of Ca^{2+} can be explained by the two variables: 27.8% as $\text{Ca}(\text{NO}_3)_2$ and 62.0% as CaSO_4 . The percentage of NH_4^+ (79.2%) can be explained by two variables: 21.2% as NH_4NO_3 and 58.0% as $(\text{NH}_4)_2\text{SO}_4$. Therefore, the percentage of Ca^{2+} participating in the neutralization process is higher than that of NH_4^+ . This can be attributed to the fact that depositions are contaminated by soil dust particles. As Katunayake usually has a dry climate, soil dust is frequently formed.

In the Gampaha location, 74.5% of Ca^{2+} can be explained by two variables, 18.4% as $\text{Ca}(\text{NO}_3)_2$ and 56.1% as CaSO_4 (Table 1). The percentage of NH_4^+ (84.2%) can be explained

Table 2 Average ratio for ions and enrichment factors for three locations

	Cl^-/Na^+	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$	K^+/Na^+	$\text{Mg}^{2+}/\text{Na}^+$
Sea water	1.16	0.25	0.03	0.03	0.12
Katunayake					
Mean	0.41	0.33	0.84	0.03	0.18
EF	<i>0.35</i>	<i>1.32</i>	<i>28.00</i>	<i>1.00</i>	<i>1.50</i>
Gampaha					
Mean	0.41	0.31	0.02	0.04	0.24
EF	<i>0.35</i>	<i>1.24</i>	<i>32.33</i>	<i>1.33</i>	<i>2.00</i>
Lunugama					
Mean	0.40	0.26	0.90	0.04	0.22
EF	<i>0.34</i>	<i>1.04</i>	<i>30.00</i>	<i>1.33</i>	<i>1.83</i>

Enrichment factor values are in italics

by two variables, 36.2% as NH_4NO_3 and 48.0% as $(\text{NH}_4)_2\text{SO}_4$. In the Lunugama location, 80.9% of Ca^{2+} was explained by two variables, 21.3% as $\text{Ca}(\text{NO}_3)_2$ and 59.6% as CaSO_4 . The percentage of NH_4^+ (97.6%) can be explained by two variables, 20.2% as NH_4NO_3 and 77.4% as $(\text{NH}_4)_2\text{SO}_4$. Accordingly, the percentage of NH_4^+ participating in the neutralization process is higher than the participation of Ca^{2+} . The presence of paddy fields near the Gampaha sampling site and widespread agricultural activities including paddy fields in the vicinity of the Lunugama location cause an increase of the contribution of NH_4^+ to neutralizing the acidity of rainwater

in the two areas with the highest contribution of NH_4^+ in Lunugama at 97.6% among the three sites.

3.5 Enrichment factor (EF)

In the absence of anthropogenic activities, the anions and cations observed in rainwater samples should be contributed by natural resources. Obvious natural sources include sea breezes and weathering of the earth's crust. As the ocean is the major source of Na^+ in rainwater, it is used as a reference element to estimate the ocean's contribution of any ion component of marine aerosols. The enrichment factor, as shown in Eq. (1), can be used to describe sources of such ions that come into the selected precipitation site [26],

$$\text{Enrichment Factor(EF)} = \frac{X/C_{\text{(Precipitation)}}}{X/C_{\text{(Reference)}}} \quad (1)$$

where X is the concentration of the selected ion and C is the concentration of the reference ion.

3.5.1 Marine source contribution to the rainwater sample

To represent the marine source contribution, every ion should be compared with the ionic components in the ocean. If $\text{EF} < 1$, this indicates that the presence of the ion in rain is caused by marine activities, and $\text{EF} > 1$ indicates

that the ion is caused by both the marine source contribution and anthropogenic activities. According to Table 2, EF values of Cl^- in each of the three locations are < 1 , indicating that all Cl^- comes predominantly from marine sources. Furthermore, the EF of SO_4^{2-} in the three locations increases in the order, Lunugama $<$ Gampaha $<$ Katunayake, which can be explained by the previously described anthropogenic facts.

3.6 Statistical analysis: Pearson correlation

Pearson correlation is a number between -1 and 1 that indicates the extent to which two variables are linearly related. This is also known as the "product movement correlation coefficient" given in the following equation,

$$r = \frac{N \sum xy - (\sum x)(\sum y)}{\sqrt{[N \sum x^2 - (\sum x)^2][N \sum y^2 - (\sum y)^2]}} \quad (2)$$

where N is the number of pairs of scores, $\sum xy$ is the sum of the products of paired scores, $\sum x$ is the sum of x scores, $\sum y$ is the sum of y scores, $\sum x^2$ is the sum of squares of x scores, and $\sum y^2$ is the sum of squares of y scores.

The " r " is the measurement of the calculation of the strength of a linear relationship between two variables,

Table 3 Pearson correlation coefficient applied to bulk precipitation in the Katunayake site

	Cl^-	SO_4^{2-}	NO_3^-	F^-	Na^+	Ca^{2+}	Mg^{2+}	K^+
SO_4^{2-}	<i>0.835</i>							
NO_3^-	0.691	0.797						
F^-	0.765	0.784	0.721					
Na^+	<i>0.908</i>	<i>0.879</i>	0.692	<i>0.805</i>				
Ca^{2+}	0.610	0.787	0.527	0.774	0.749			
Mg^{2+}	<i>0.817</i>	<i>0.860</i>	0.712	0.762	<i>0.905</i>	0.689		
K^+	0.670	0.757	0.527	0.798	0.765	<i>0.800</i>	0.725	
NH_4^+	0.765	<i>0.823</i>	0.663	0.765	0.732	0.782	0.774	<i>0.823</i>

Values > 0.8 (marked in italics) are considered to indicate a very strong relationship

Table 4 Pearson correlation coefficient applied to bulk precipitation in the Gampaha site

	Cl^-	SO_4^{2-}	NO_3^-	F^-	Na^+	Ca^{2+}	Mg^{2+}	K^+
SO_4^{2-}	<i>0.812</i>							
NO_3^-	0.229	0.576						
F^-	0.751	0.481	0.609					
Na^+	0.741	0.780	0.176	0.676				
Ca^{2+}	0.512	0.749	0.429	0.400	0.740			
Mg^{2+}	0.716	<i>0.850</i>	0.356	0.404	<i>0.910</i>	<i>0.919</i>		
K^+	0.381	0.651	0.456	<i>0.910</i>	<i>0.910</i>	0.626	0.721	
NH_4^+	0.519	0.693	0.602	0.682	0.682	0.653	0.732	<i>0.817</i>

Values > 0.8 (marked in italics) indicate a very strong relationship

Table 5 Pearson correlation coefficient applied to bulk precipitation in the Lunugama site

	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺
SO ₄ ²⁻	0.466						
NO ₃ ⁻	0.101	0.726					
Na ⁺	0.785	0.491	0.187				
Ca ²⁺	0.359	0.773	0.513	0.392			
Mg ²⁺	0.539	0.752	0.504	0.565	<i>0.931</i>		
K ⁺	0.274	0.423	0.413	0.579	0.519	0.555	
NH ₄ ⁺	0.028	0.548	<i>0.880</i>	0.188	0.373	0.367	0.445

Values > 0.8 (marked in italic) indicate a very strong relationship

and the “*r*” value is denoted by the Pearson correlation. In the positive correlation, one variable is increased, then the respective other variable is increased, and vice versa. If there is no correlation between a pair of variables, one variable does not increase or decrease with respect to the other. These correlations can be summarized as follows:

- 0.00 < *r* < 0.19 very weak
- 0.20 < *r* < 0.39 weak
- 0.40 < *r* < 0.59 moderate
- 0.60 < *r* < 0.79 strong
- 0.80 < *r* < 1.00 very strong

Results of anions and cations of depositions at the Katunayake location analyzed using Pearson correlation indicate that the highest positive correlation value of 0.908 is between Na⁺ and Cl⁻ (Table 3). The major sources of Na⁺ and Cl⁻ can be both natural and anthropogenic. The marine contribution is one of the natural sources of both ions, and the other contribution could be from water purification plants in KEPZ. Relationships among Mg²⁺-Na⁺, SO₄²⁻-Cl⁻, Mg²⁺-Cl⁻, Mg²⁺-SO₄²⁻, Na⁺-SO₄²⁻, K⁺-Ca²⁺, NH₄⁺-SO₄²⁻, Na⁺-F⁻ and NH₄⁺-K⁺ are also strong.

Table 4 shows that, for the Gampaha location, the highest positive Pearson correlation coefficient of 0.919 is between Ca²⁺ and Mg²⁺, which is a very strong relationship. Both of these ions probably originate from soil dust. Relationships between Mg²⁺-Na⁺ and K⁺-Na⁺ are also very strong, indicating that these two pairs have the same sources. The relationships among SO₄²⁻-Cl⁻, Mg²⁺-SO₄²⁻, K⁺-F⁻ and NH₄⁺-K⁺ also have very strong correlations.

Among the ions in the bulk deposition in the Lunugama site, Mg²⁺-Ca²⁺ represents the highest positive Pearson correlation coefficient (Table 5), showing a very strong relationship. This may be due to mining activities, metal quarries and soil dust in that area. The relationship

between NH₄⁺-NO₃⁻ is also very strong, and both of these ions would probably be due to the emission of NH₃ from paddy fields.

4 Conclusion

The pH of all the samples collected weekly during a 7-month period in three locations, Katunayake, Gampaha and Lunugama, having different geographical characteristics and different anthropogenic activities, was > 5.6, the limit below which rainwater is considered acidic. The volume weighted mean (VWM) pH of Katunayake, Gampaha and Lunugama depositions is 6.08, 6.05 and 6.03, respectively, while the VWM conductivity of the three locations is 22.93 μS cm⁻¹, 31.39 μS cm⁻¹ and 17.05 μS cm⁻¹, respectively. According to the data obtained, conductivity, in general, decreased in the order Katunayake > Gampaha > Lunugama. However, a relationship between pH and conductivity cannot be predicted directly because the conductivity depends on the concentration of anions and cations in the sample. Cations determined at all three sites vary in the order of K⁺ < NH₄⁺ < Mg²⁺ < Ca²⁺ < Na⁺. The dominant cations in Katunayake are Na⁺ and Ca²⁺. The average anion concentrations in the depositions of all three locations are as follows: Katunayake: NO₃⁻ < F⁻ < SO₄²⁻ < Cl⁻, Gampaha: F⁻ < NO₃⁻ < SO₄²⁻ < Cl⁻, Lunugama: NO₃⁻ < SO₄²⁻ < Cl⁻. The enrichment factor demonstrates the marine source contribution. Furthermore, according to the enrichment factors determined for Cl⁻/Na⁺, SO₄²⁻/Na⁺, Ca²⁺/Na⁺, K⁺/Na⁺ and Mg²⁺/Na⁺, it is clear that Cl⁻ and K⁺ are from marine sources only and Ca²⁺, Mg²⁺ and SO₄²⁻ are from both marine and non-marine sources. Sea breeze plays a significant role in dissolving ions in rainwater samples. The acidification and neutralization potential, determined from regression analysis, indicates that rainwater is neutralized by Ca(NO₃)₂, CaSO₄, NH₄NO₃ and (NH₄)₂SO₄. According to the Pearson correlation analysis in the Katunayake location, Na⁺-Cl⁻, Mg²⁺-Na⁺, SO₄²⁻-Cl⁻, Mg²⁺-Cl⁻, Mg²⁺-SO₄²⁻, Na⁺-SO₄²⁻, K⁺-Ca²⁺,

$\text{NH}_4^+ - \text{SO}_4^{2-}$ and $\text{NH}_4^+ - \text{K}^+$ have very strong relationships. The highest correlation of $\text{Na}^+ - \text{Cl}^-$ is probably due to the marine contribution. The relationship among $\text{Mg}^{2+} - \text{Na}^+$, $\text{K}^+ - \text{Na}^+$, $\text{SO}_4^{2-} - \text{Cl}^-$, $\text{Mg}^{2+} - \text{SO}_4^{2-}$ and $\text{NH}_4^+ - \text{K}^+$ is very strong in Gampaha. A very strong correlation with $\text{Ca}^{2+} - \text{Mg}^{2+}$ and $\text{NH}_4^+ - \text{NO}_3^-$ can be seen in Lunugama. The relationship between $\text{NH}_4^+ - \text{NO}_3^-$ is caused by agricultural activities in that area.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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