# Source apportionment of rainwater chemical composition in wet precipitation at Kelaniya in Sri Lanka



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## Abstract

Rainwater quality is of utmost importance as it can be used to predict atmospheric quality which of course governs, to some extent, the health of the ecosystem. In this regard, the research reported here was to study chemical characteristics of precipitation in Kelaniya, Gampaha District, one of the most populated and most urbanized districts in Sri Lanka. This study was conducted during the period from 2012 to 2014, and wet precipitation was analyzed for pH, conductivity, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Pb, Cu, Mn, Al, Zn, and Fe for a total of seventy-eight (78) samples. Volume-weighted average concentrations of the major ionic species present in precipitation samples were in the order of Na<sup>+</sup> > Ca<sup>2+</sup> > Cl<sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > NH<sub>4</sub><sup>+</sup> > Mg<sup>2+</sup> > NO<sub>3</sub><sup>-</sup> > K<sup>+</sup> > F<sup>-</sup>. Neutralization of the acidic species would take place due to the presence of NH<sub>4</sub><sup>+</sup> and CaCO<sub>3</sub>. When considering marine contribution, SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>, Ca<sup>2+</sup>/Na<sup>+</sup>, and Mg<sup>2+</sup>/Na<sup>+</sup> ratios are higher than the reference value suggesting that contribution of sources be possible other than marine. Among metallic constituents, the concentration of Al is the highest while that of Mn is the lowest. Significant correlation is observed among certain ions and elements (Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, Al, Cu, Fe, Zn, and H<sup>+</sup>) which indicates their source of origin and chemical interaction. This study reveals that chemical composition of rain water depends on both anthropogenic activities and natural phenomena.

Keywords Chemical characteristics · Atmospheric pollution · Wet precipitation · Ions · Correlation · Pollution

# Introduction

The chemical composition of rain water has become a major concern in the cities with high pollution level (Liu et al. 2018). Urbanization is a process which involves economic and industrial development, and consequently, concentration of population into mega cities would be an end result (Singh et al. 2018; Czerwińska and Wielgosiński 2019). In addition, investigation of chemical composition of the atmosphere in a certain area is very important as it would lead to take air pollution control measures (Martins et al. 2019). As dissolution of pollutants would change the chemistry of rainwater, and therefore, determination of the chemical composition of

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rainwater with respect to pollutants present is an indirect measure of the extent of pollution (Alkhashman 2005; Huang et al. 2008).

Among various sources of atmospheric pollution, the prominent source of aerosols is the dust formed in arid regions, followed by soil and marine erosion, and anthropogenic sources (Romero Orué et al. 2019; Carvalho et al. 2014; Rao et al. 2016; Deusdará et al. 2017; Lin et al. 2019; Ouyang et al. 2019). Wet deposition which occurs through rain events is defined as the process by which atmospheric compounds attached to and dissolved in cloud and precipitation droplets followed by their delivery to the earth's surface by rain, hail, or snow. Thus, dry deposition is predominantly associated with the transfer of particulate matter, total phosphorous,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $K^+$ , whereas wet deposition dominates the atmospheric delivery of Na<sup>+</sup> and nitrogen-containing species (Akkoyunlu and Tayanc 2003; Staelens et al. 2005; Cao et al. 2009; Huston et al. 2009).

In coastal areas, the Na<sup>+</sup>/Cl<sup>-</sup> ratio and the contents of  $SO_4^2$ <sup>-</sup>,  $Mg^{2+}$ , and  $Ca^{2+}$  in the atmosphere are useful in evaluating the influence of both anthropogenic and natural sources (Park et al. 2015; Bhaskar and Rao 2017). Chemical characteristics of rainwater at a Southeastern site of Brazil have identified the

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presence of Mg<sup>2+</sup>, K<sup>+</sup>, Ca<sup>+2</sup>, and HCO<sub>3</sub><sup>-</sup> in the atmosphere due to soil contribution; Na<sup>+</sup> and Cl<sup>-</sup> to sea-salt contribution; and NO<sub>3</sub><sup>-7</sup>, SO<sub>4</sub><sup>-2</sup>, and NH<sub>4</sub><sup>+</sup> to anthropogenic sources. Some studies conducted in India indicate that atmospheric particulates, which contain significant amounts of basic cations, and rich in metal particulate matter, could affect physicochemical properties and microbial interactions in soil. The metals deposited may enter living body through dietary intake and subsequently cause adverse health effects (Chakraborty et al. 2016; Rao et al. 2016; Bhaskar and Rao 2017; Bisht et al. 2017; Chakraborty and Gupta 2018; Singh et al. 2018). Influence of pollutant sources on rainwater chemistry is investigated at an industrial coastal site in Iran and has revealed that nearly all NO<sub>3</sub><sup>-</sup> and most Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, and Mg<sup>2+</sup> have been originated from non-marine and local sources (Rastegari et al. 2019). Further, rainwater chemistry, investigated at a semirural site in Ya'an, Sichuan basin in China has revealed that pH values ranged from 3.25 to 6.86, with an annual volumeweighted mean (VWM) of 4.38, with a high acid rain frequency of 74%. Such a severe acidification of the total events has shown pH < 4.0, which was attributed to the deficiency of  $Ca^{2+}$ , a basic cation which would have neutralized acidity to some extent. This rainy pattern in this area is contributed by significant anthropogenic pollution. The annual VWM of total ionic concentration was determined to be 477.19 µeg/l, where  $NH_4^+$  was the most abundant ionic species, followed by  $SO_4^2$ <sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and F<sup>-</sup> in descending order (Li et al. 2016).

Sri Lanka, being an island, has both positive and negative impacts with regard to atmospheric pollution (Ileperuma 2015). Kelaniya, located close to the busiest and economically strong Western Province of the country, has much intense industrial activities including power plants, oil refineries, and many industrial zones in the vicinity. However, Kelaniya being situated somewhat close to the coast would be beneficial to diffuse some pollutants out.

Few isolated studies have been reported in Sri Lanka with regard to rain water composition. Among them, heavy metals and microorganisms present in atmospheric deposition have been characterized in Kandy, Sri Lanka, together with health implications (Weerasundara et al. 2018). It has been reported that Al and Fe are at uncontaminated levels, and other metals investigated, Cr, Mn, Ni, Cu, Zn, Cd, and Pb, are in the range of uncontaminated to contaminated levels. However, these metals have the potential to increase their levels in the long term (Weerasundara et al. 2017). It has also been implicated that traffic and land use influence atmospheric metal concentrations (Liyandeniya et al. 2020). Further, comparative studies of atmospheric deposition in areas having different geography, industrial activities, and anthropogenic activities are rare in the Sri Lankan context.

Due to anthropogenic activities, the environment has become polluted to an extent of being irreparable with respect to some aspects. Although the total environment cannot be compartmentalized, it has become the practice to investigate pollution aspects of water, air, and soil separately. Among these, water pollution studies and its remedial measures have taken a lead, probably due to ease of following water quality monitoring protocols. On the other hand, atmospheric monitoring and modeling would be of great importance as the general public should be aware of the air they breathe although not much attention has been given in this aspect.

It is important that rain water quality guidelines should be met for rain water to be used in harvesting (Mosley 2005). Nevertheless, rapid industrialization and urbanization of surrounding area lead to air pollution thus changing the chemical composition of rain water, and further, regular rain water quality measurement programs are not much practiced. This project thus aims to fill this void by investigating composition of rain water collected in Kelaniya, Sri Lanka, for selected chemical parameters which will lead to establish baseline data.

# **Material and methods**

## Study area

The sampling site is at the University of Kelaniya (GPS coordinates—latitude 6.973701, longitude 79.915256) located in Gampaha District of the Western Province of Sri Lanka (Fig. 1) where high industrialization and urbanization are prevalent; the University of Kelaniya is located by the Kandy-Colombo (A1) highway where high traffic congestion is present in many parts of the daytime. Additionally, the only oil refinery of the country, Bandaranayake International Airport, and a number of thermal power plants are located in close proximity to the sampling site.

## Sampling apparatus

Wet deposition samples were collected using a manual collector [high density polyethylene (HDPE) container with a funnel], which was placed 120 cm above the ground level (Fig. 2). Diameter of the funnel was 20.6 cm. Containers and collectors were pre-washed with ASTM type 1 deionized water before being used. Sampling was done after each precipitation event starting from October 2012 to July 2014. Collectors were fully opened to the air during the total collection time period.

The volume of each wet deposition sample collected was measured to determine the rainfall. Prior to reinstallation of sample containers and funnels, they were washed thoroughly with ASTM type I deionized water. Conductivity and pH of wet samples were measured soon after sampling, and thereafter, the samples were filtered using 0.45-µm nylon filters and divided into two parts; one part was stored in pre-cleaned polyethylene bottles and refrigerated at 4 °C prior to ion

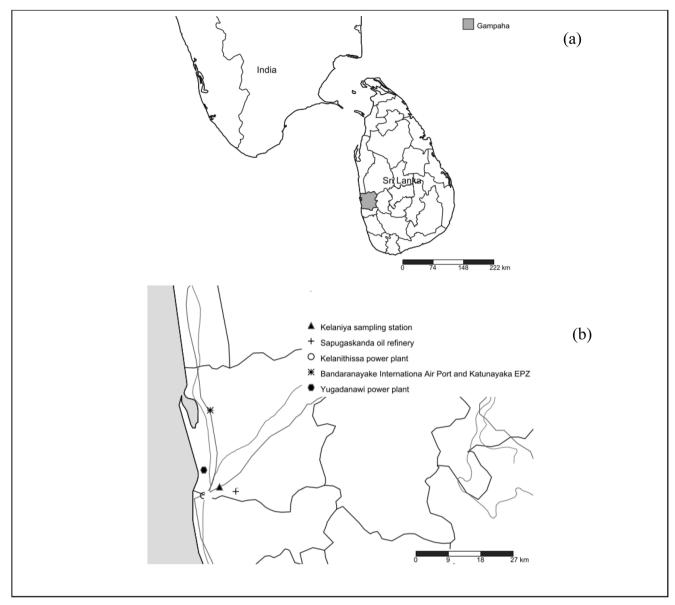


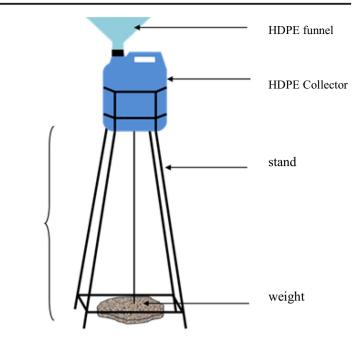
Fig. 1 Map of location of Sri Lanka in the Indian sub-continent (a) Kelaniya sampling station (GPS coordinates—latitude 6.973701, longitude 79.915256) and (b) possible sources located in Gampaha district

analysis. The other part was preserved by acidification to bring pH below 2 by adding analytical grade conc. HNO<sub>3</sub> (BDH VWR), refrigerated at 4 °C prior to metal analysis and stored in pre-cleaned polyethylene bottles. Acidification is needed to all metallic species to soluble form.

# Materials and instrumentation

All chemicals used for sample collection, preservation, and analysis were of analytical grade with certifications. All preparation and final washing were done with freshly prepared deionized water which complied with the standards of ASTM type I water. All standard solutions were prepared using certified standard materials. Trace metal standards (Al, Fe, Mn, Zn, Cu, and Pb) were Sigma-Aldrich, and standards used for ion chromatography were Thermo Dionex. Eluent required for anion determination was prepared by diluting IC grade 0.45 M Na<sub>2</sub>CO<sub>3</sub> and 0.08 M NaHCO<sub>3</sub> (Thermo Dionex) while 1.0 M sulfuric acid (Thermo Dionex) was used to regenerate the anionic suppressor. Eluent required for cation determination was prepared by diluting IC grade methanesulfonic acid (Thermo Dionex) while tetrabutylammonium hydroxide solution (TBAOH) (Thermo Dionex) was used to regenerate cationic suppressor.

Rainfall data were measured using Watchdog 2700 automated weather station located at the premises of the University of Kelaniya. **Fig. 2** Rain water collector use for bulk deposition sampling and wet deposition sampling



H = 120 cm

Conductivity and pH were determined using HACH Sens ION+ EC5 portable conductivity meter and Thermo Orion 3 Star pH meter, respectively. Selected cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>+2</sup>, Ca<sup>+2</sup>) and anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) were quantified using Thermo Dionex ICS 900 ion chromatograph with chemical suppression mode. For anion analysis, Dionex ionpack AS23 (4 × 250 mm) analytical column was used, while Dionex ionpack CS12A (4 × 250 mm) column was used for cation analysis. Each column was equipped with a separate guard column for the protection of the analytical column. The detection limits of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> ions were found to be 1.6, 1.1, 1.0, and 2.0 µeq l<sup>-1</sup>, respectively, and those of Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> were 2.2, 2.8, 1.5, 6.5, and 6.0 µeq l<sup>-1</sup>, respectively.

Trace metals (Al, Fe, Mn, Zn, Cu, and Pb) were determined using a graphite furnace atomic absorption spectrometer (GFAAS) equipped with an autosampler (Thermo electron M5 GF95 Graphite Furnace System) with deuterium background correction. Detection limits for elements were within the range of 0.1–2.0  $\mu$ g l<sup>-1</sup>.

Quality of the analysis was achieved by running known standard with the same matrix as analyte (both ions and elements) between 20 sample intervals to check reproducibility of analytical results, and 95% confidence level was maintained for all analytes studied.

## Statistical analysis

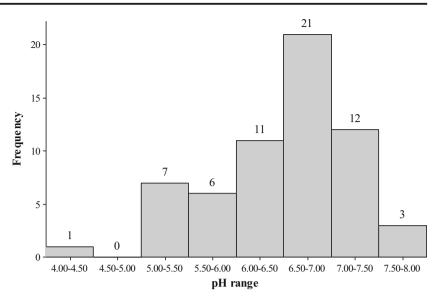
Seventy-eight (78) samples were collected on a weekly basis throughout the sampling period from the sampling station at the University of Kelaniya, and results were analyzed statistically. Spearman's correlation coefficient, a statistical measure of the strength of a monotonic relationship between paired data, was also evaluated for the results of the rainwater samples. Interpretation of Spearman's correlation coefficient is similar to that of Pearson's.

# **Results and discussion**

## Investigation of pH variation of depositions

Figure 3 shows the frequency histogram of pH for samples of atmospheric precipitation collected. Only eight acid precipitation events with pH less than 5.60 were recorded during the entire sampling period from Kelaniya which accounted for 10% of total precipitation events. The average pH was 6.54 and the volume-weighted average (VWA) pH was 5.70 within the pH range between 4.38 and 8.69 at Kelaniya. This pH variation reflects the large number of anthropogenic activities in Kelaniya. The only oil refinery in the country with 500 barrels of crude oil capacity and a number of thermal power plants run on fossil fuel are located in the vicinity of the sampling points. These operations may emit acid rain precursors, such as oxides of sulfur and nitrogen. Most of the acid precipitation events were recorded during February and March where dry weather prevails. During this time period, much of the wind blows from the seaward side which prevents neutralization of pollutants in the atmosphere. On the other hand, neutralization would occur due to the presence of considerable amounts of  $Ca^{2+}$  and  $NH_4^+$  in the atmosphere, leading to pH values of rain water higher than that would be due to acidic pollutants.

**Fig. 3** Frequency histograms of pH values in wet precipitation at Kelaniya



## **Chemical composition**

Table 1 presents VWA values, ranges obtained for pH, conductivity, and inorganic ions, namely  $F^-$ ,  $CI^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Ca^{2+}$  along with chemical elements for a total of seventy-eight (78) samples collected. The VWA value and the range for conductivity were 25.45  $\mu$ S cm<sup>-1</sup> and

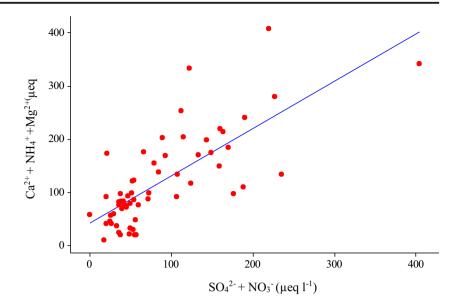
**Table 1** Average, range, volume-weighted average (VWA) in samples of atmospheric precipitation at Kelaniya in Sri Lanka for pH, conductivity ( $\mu$ S cm<sup>-1</sup>), and major ion concentration. Except for pH and conductivity, values of other major ions are given in  $\mu$ eq  $\Gamma^{-1}$ . Elemental concentrations are given in  $\mu$ g  $\Gamma^{-1}$ 

		Kelaniya			
Variable	Avg	Range	VWA		
pН	6.54	4.38-8.69	5.70		
Conductivity	47.70	4.00 241.23	25.45		
$F^{-}$	<mdl< td=""><td><mdl-17.21< td=""><td>1.17</td></mdl-17.21<></td></mdl<>	<mdl-17.21< td=""><td>1.17</td></mdl-17.21<>	1.17		
Cl	54.82	<mdl-329.03< td=""><td>36.98</td></mdl-329.03<>	36.98		
$NO_3^-$	18.76	<mdl-148.75< td=""><td>13.21</td></mdl-148.75<>	13.21		
$SO_4^{2-}$	54.36	<mdl-255.18< td=""><td>35.53</td></mdl-255.18<>	35.53		
Na <sup>+</sup>	221.21	<mdl-725.25< td=""><td>94.02</td></mdl-725.25<>	94.02		
$\mathrm{NH_4}^+$	23.49	<mdl-217.12< td=""><td>18.70</td></mdl-217.12<>	18.70		
K <sup>+</sup>	15.54	<mdl-106.46< td=""><td>9.15</td></mdl-106.46<>	9.15		
Mg <sup>2+</sup>	26.00	<mdl-137.07< td=""><td>16.16</td></mdl-137.07<>	16.16		
Ca <sup>2+</sup>	91.06	<mdl-453.96< td=""><td>54.95</td></mdl-453.96<>	54.95		
Pb	<mdl< td=""><td><mdl-19.04< td=""><td><mdl< td=""></mdl<></td></mdl-19.04<></td></mdl<>	<mdl-19.04< td=""><td><mdl< td=""></mdl<></td></mdl-19.04<>	<mdl< td=""></mdl<>		
Cu	7.71	<mdl-44.00< td=""><td>4.81</td></mdl-44.00<>	4.81		
Al	77.03	<mdl-302.33< td=""><td>75.30</td></mdl-302.33<>	75.30		
Zn	30.32	<mdl-70.10< td=""><td>27.83</td></mdl-70.10<>	27.83		
Fe	10.50	<mdl-78.68< td=""><td>6.78</td></mdl-78.68<>	6.78		
Mn	4.75	<mdl-21.08< td=""><td>3.70</td></mdl-21.08<>	3.70		

4.00–241.23  $\mu$ S cm<sup>-1</sup>, respectively. The VWA concentrations of the major ionic species present in precipitation samples were in the order of  $Na^+ > Ca^{2+} > Cl^- > SO_4^{2-} > NH_4^+ >$  $Mg^{2+} > NO_3^- > K^+ > F^-$ . This order could vary with weather and intensity of anthropogenic activities. Nevertheless,  $Ca^{2+}$ ,  $Na^+$ ,  $Cl^-$ ,  $NH_4^+$ , and  $SO_4^{2-}$  are found to be the dominant ions. Further, Na<sup>+</sup> and Cl<sup>-</sup> are predominant because this sampling station is close to the coast. Fluoride was present in some of the samples collected, and most of the F<sup>-</sup> were recorded during dry months of January to March. Atmospheric F<sup>-</sup>, even if present at very low concentrations, is much harmful to vegetation. Principal anthropogenic sources for fluoride include aluminum smelters; industrial activities such as brick, tile, pottery and cement works; ceramic industries; and glass manufacturing. These industries are located in Kelaniya, indicating atmospheric F<sup>-</sup> pollution in the area. The most abundant cations in the sampling sites are Ca<sup>2+</sup> and Na<sup>+</sup>, which are probably due to dust particles which contain Ca<sup>2+</sup> and marine contribution of Na<sup>+</sup>. Further, the Ca<sup>2+</sup> ion plays a major role along with NH4<sup>+</sup> in neutralization of acidified rain. More importantly, these ions are mainly found in dry months during November to February where South-East monsoon is not occurred.

Concentrations of elements (Pb, Cu, Al, Zn, Fe, and Mn) determined in rainwater are shown in Table 1. Few rainfall events detected for Pb and these events were recorded in the dry season of the area where less amounts of rain fall were recorded. Low levels of Pb observed could probably be due to the lack of Pb sources in these areas and abandoning the usage of leaded gasoline which had been used many years ago. The element having the highest concentration was Al, followed by Zn, Fe, Cu, and Mn. Many anthropogenic activities can be found in the surrounding areas of the Kelaniya sampling site which may lead to atmospheric elemental constituents other than natural sources. Aluminum and its compounds are

**Fig. 4** Linear regression between  $(SO_4^{2-} + NO_3^{-})$  and  $(Ca^{2+} + NH_4^{+})$  Kelaniya station



mainly originated from natural sources, such as crustal origin, while other elements are originated from anthropogenic activities, such as waste incineration, biomass burning, fossil fuel burning, mass scale civil constructions, and some industries. The elements, Mn and Cu, were moderately enriched compared with mean crustal elements indicating the presence of other sources. Apart from the above-stated contributions, Sri Lanka, being a small island in the middle of the Indian Ocean, trans-boundary pollution would play an important role for elevated levels of the above elements. Through this phenomenon, impact of pollution that originates in one country is able to cause damage in another country's environment as a result of transportation of pollutants via air or water.

#### Acidification and neutralization potentials

Acidity of precipitation is mainly controlled by strong acids, such as  $H_2SO_4$  and  $HNO_3$ , and to lesser extent by weak organic acids. Neutralization of these species would take place due to the presence of  $NH_4^+$ ,  $MgCO_3$ , and  $CaCO_3$ . As stated earlier, the pH of precipitation is strongly controlled by the presence of these acids and bases, and neutralization reactions among them. Figure 4 shows the linear regression analysis applied to the variables with acidification and those with neutralization potential. The correlation coefficient is found to be 0.56 for Kelaniya.

Table 2 shows the results of regression coefficient analysis, and approximately 99.0% of  $SO_4^{2^-}$  and 42.1% of  $NO_3^-$  were able to be explained by the two independent variables,  $Ca^{2+}$ ,  $NH_4^+$ , and  $Mg^{2+}$  at Kelaniya. Of 99.0% of  $SO_4^{2^-}$  explained, 55.6% appears as  $CaSO_4$ , 33.6% as  $MgSO_4$ , and 9.8% as  $(NH_4)_2SO_4$ . As for  $NO_3^-$ , it is found as  $Ca(NO_3)_2$  in 28.6% of the cases and as  $NH_4NO_3$  in only 10.3% followed by  $Mg(NO_3)_2$  in only 3.2% of the cases in wet precipitation. Further, neutralization of acidity of precipitation is much more related to  $CaCO_3$  than to  $NH_3$ , and  $MgCO_3$ . This is further supported by high content of  $Ca^{2+}$  ions in both locations. Sources of  $NH_3$  are mainly the application of fertilizers and biomass burning.

## Marine contribution

Table 3 shows the ratio between the ions and the Na<sup>+</sup> analyzed in the rain water samples, and the ratio of the ions and Na<sup>+</sup> in sea water. Ratio of the respective ion and Na<sup>+</sup> is higher than that of the ratio of the same two ions for sea water indicating negligible marine contribution. When considering the ratio between  $SO_4^{2^-}/Na^+$ ,  $Ca^{2^+}/Na^+$ ,  $K^+/Na^+$ , and  $Mg^{2^+}/Na^+$  in rain water samples collected in Kelaniya, values obtained for  $SO_4^2$  $^-/Na^+$ ,  $Ca^{2^+}/Na^+$ , and  $Mg^{2^+}/Na^+$  being higher than the value obtained for sea water in that location indicate that the marine contribution of those ions are negligible. However, the ratios

<b>Table 2</b> Fractions of $SO_4^{2-}$ and $NO_3^{-}$ explained by $Ca^{2+}$ and $NH_4^{+}$ in samples	Kelaniya	SO4 <sup>2</sup>	% explained by (Ca <sup>2+</sup> ) 55.6	% explained by NH4 <sup>+</sup> 9.8	% explained by Mg <sup>2+</sup> 33.6	Total explained 99.0
		NO <sub>3</sub> <sup>-</sup>	28.6	10.3	3.2	42.1

Table 3 Average ratio for several ions in association with Na<sup>+</sup>

	SO4 <sup>2-</sup> /Na <sup>+</sup>	Cl <sup>-</sup> /Na <sup>+</sup>	Ca <sup>2+</sup> /Na <sup>+</sup>	K <sup>+</sup> /Na <sup>+</sup>	Mg <sup>2+</sup> /Na <sup>+</sup>	
Sea water	0.12	1.16	0.02	0.23	0.04	
Kelaniya	0.38	0.39	0.58	0.10	0.18	

of Cl<sup>-</sup>/Na<sup>+</sup> and K<sup>+</sup>/Na<sup>+</sup> are 0.39 and 0.10, respectively, which are less than the sea water ratio indicating the significant marine contribution of those elements. The marine contribution of Kelaniya is much stronger as a result of close proximity of the location to the cost.

#### Correlation between analytes and probable sources

In order to find a possible relationship among ions and elements in rain water samples collected as wet deposition samples from Kelaniya, and to predict probable sources of pollutants, correlation between ions in the rain water was calculated based on statistical analysis. According to the results of Spearman's correlation coefficient shown in Table 4, a very strong correlation between conductivity and Na<sup>+</sup> (0.881) observed is indicative of a positive correlation between the two parameters. It is a clear indication of high conductivity of samples collected from Kelaniya contributed mainly from Na<sup>+</sup> ions. Further, positive correlations among conductivity and pH (0.686),  $Ca^{2+}$  and pH (0.439), and  $Mg^{2+}$  and pH (0.559) observed provide a clear indication of increasing pH with the presence of some neutralization ions, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>. According to Table 4, significant positive correlations among conductivity and ions can be observed, probably due to the fact that the presence of

these ions increases the conductivity of rain water. A moderate positive correlation of 0.654 determined between  $SO_4^{2-}$  and  $NO_3^{-}$  can also be explained using a similar argument that these two species come from the same source probably vehicular emission. A significant correlation between Na<sup>+</sup> and Ca<sup>2+</sup>/  $Mg^{2+}$  also indicates that natural contribution of these ions. The same argument can be made for the correlation between Na<sup>+</sup> and Cl<sup>-</sup>, that the source is marine. There were significant correlations between acidic anions  $(SO_4^{2-})$  and cations  $(Ca^{2+}/$  $Mg^{2+}$ ) indicating that interaction between this acidic anion and cations which would lead to neutralization. Moderate positive correlation observed between Na<sup>+</sup> and Fe is indicative of increase in corrosion in the presence of Na<sup>+</sup> which enhances the corrosion of steel which is widely used during construction activities. The elements, Fe, Al, Cu, and Zn, which show weak to moderate positive correlations, would have been originated from natural sources, such as crustal erosion, and from anthropogenic activities, such as brass industry, construction activities, and vehicular emissions. Among these, Fe shows moderate correlation between Cu, Al, Zn, and Mn, which are widely used in alloy manufacturing to enhance different properties. It should also be considered that many industries in Sri Lanka are located in the Districts of Gampaha and Colombo, close to the Kelaniya sampling site.

# Conclusion

This study characterizes certain ions and selected elements for a period of 16 months starting from 2012 to 2014 in precipitation at Kelaniya in Gampaha District, Sri Lanka. Analysis of samples harvested soon after each precipitation event indicates that

 Table 4
 Spearman's correlation coefficients for precipitation samples collected from Kelaniya. Values given in italics are relatively high correlation coefficients

	pН	Cond	$F^{-}$	Cl	$NO_3^-$	$\mathrm{SO_4}^{2-}$	Na <sup>+</sup>	$\mathrm{NH_4}^+$	$K^+$	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Cu	Al	Zn	Fe	Mn
Cond	0.686															
$F^{-}$	-0.087	0.064														
$Cl^{-}$	0.459	0.490	0.198													
$NO_3^-$	0.122	0.248	0.570	0.286												
$\mathrm{SO_4}^{2-}$	0.415	0.559	0.353	0.618	0.654											
$Na^+$	0.123	0.881	0.148	0.348	0.186	0.436										
$\mathrm{NH_4}^+$	- 0.125	- 0.038	0.125	- 0.002	0.328	0.312	- 0.010									
$K^+$	0.403	0.369	0.391	0.482	0.243	0.637	0.333	0.183								
$Mg^{2+}$	0.439	0.443	0.010	0.787	0.186	0.602	0.260	0.017	0.322							
Ca <sup>2+</sup>	0.559	0.674	0.108	0.514	0.417	0.636	0.567	0.436	0.393	0.531						
Cu	0.323	0.439	0.281	0.109	0.412	0.309	0.144	0.221	0.463	- 0.056	0.501					
Al	0.117	0.360	- 0.018	-0.037	0.028	-0.048	- 0.063	0.023	- 0.105	- 0.162	0.322	0.355				
Zn	- 0.206	- 0.001	- 0.116	- 0.164	0.013	- 0.128	- 0.011	- 0.026	- 0.220	0.015	0.173	0.154	0.270			
Fe	0.183	0.409	0.018	-0.028	0.224	0.043	0.461	0.005	0.076	- 0.105	0.315	0.643	0.491	0.406		
Mn	- 0.034	0.194	0.052	- 0.082	0.309	0.160	0.159	- 0.011	- 0.075	0.027	0.383	0.312	0.294	0.481	0.589	

the volume-weighted average (VWA) concentrations of the major ionic species present in precipitation samples were in the order of  $Na^+ > Ca^{2+} > Cl^- > SO_4^{2-} > NH_4^+ > Mg^{2+} >$  $NO_3^- > K^+ > F^-$ . The pH of precipitation samples was ranged between 4.38 and 8.69 with less than 10% events of acidic precipitation in which pH < 5.60. In the wet precipitation in Kelaniya, approximately 68.4% of  $SO_4^{2-}$  and 38.9% of  $NO_3^{-}$ were able to be explained by the two independent variables, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup>. The ratios of SO<sub>4</sub><sup>2-</sup>/Na<sup>+</sup>, Ca<sup>2+</sup>/Na<sup>+</sup>, and Mg<sup>2+</sup>/Na<sup>+</sup> were higher than the reference values suggesting that marine contribution be negligible and contribution of anthropogenic sources be predominant for these ions. The ratios of Cl<sup>-/</sup> Na<sup>+</sup> and K<sup>+</sup>/Na<sup>+</sup> were less than the reference values indicating marine influence of Cl<sup>-</sup> and K<sup>+</sup> ions. It was also found that Al is the most predominant element while Mn was the least. Investigation of correlation between major ionic species and elements (Ca<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup>, Al, Cu, Fe, Zn, and H<sup>+</sup>) in the wet precipitation samples identified probable anthropogenic sources, heavy traffic, oil refinery activities, thermal power plant activities, biomass burning, waste incineration, and industrial activities. This study reveals that influencing human activities on chemical composition of rain water depends on both anthropogenic activities and natural phenomena.

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