



Research Article

Trace metal composition of rainwater and aerosol from Kolkata, a megacity in eastern India



Aditi Majumdar¹ · Jaydeep Satpathy¹ · Jariya Kayee² · Reshmi Das^{1,3} 

Received: 21 August 2020 / Accepted: 20 November 2020 / Published online: 1 December 2020

© Springer Nature Switzerland AG 2020

Abstract

India is one of the world's wettest countries receiving over 1000 mm of rainfall annually and also one of the countries experiencing regular floods and droughts. This study quantifies elemental composition of rainwater and aerosol collected simultaneously during 2019 monsoon season from Kolkata, a megacity in Eastern India marred by air pollution to understand sources and estimate wet deposition flux. Elemental composition (Na, Ca, Mg, Al, Fe, Mn, V, Cr, Ni, Cu, Zn, Cd, Pb) of rainwater was measured in ICP MS along with pH, conductivity, chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) ions. Trace metal composition of PM_{10} collected in between rain events were also analysed to understand anthropogenic sources and atmospheric leaching of metals. Crustal enrichment factors (EFs) identified anthropogenic sources for Ni, Cu, Zn, Pb and Cd in PM_{10} . Principal component analysis (PCA) identified three anthropogenic sources, industrial emission, traffic emission and waste incineration in addition to the natural background from the crustal dust for the aerosol metals. Majority of rainwater samples had almost neutral pH (average 6.81 ± 0.74 , 1SD), with a range of 5.4 to 8.0. In rainwater, Na and Cl^- had marine origin and majority of SO_4^{2-} had non-marine sources. Cu, Zn, Cd, V, Cr and Pb concentrations of rainwater follow the trend in PM_{10} most likely because part of the metals are derived from aerosol leaching. The EFs indicated that all the metals except Fe had anthropogenic origin in rainwater. The wet deposition fluxes were in the order of $\text{Ca} > \text{Na} > \text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Mn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cr} > \text{V} > \text{Cd}$. Overall, the results show significant influence of anthropogenic sources on rainwater chemistry in addition to natural soil dust and marine aerosols. In spite of anthropogenic influence, the trace metal and anion concentrations in rainwater are well within the limits prescribed by World Health Organization (WHO), European Union (EU), USA and Indian Drinking Water Standards.

Keywords Rainwater · Trace element · PM_{10} · Enrichment factor · Principal component analysis · Wet deposition flux

1 Introduction

Anthropogenic activities are constantly altering the natural chemical composition of the atmosphere. Air pollutants are mainly produced from combustion of fossil fuels, smelting and roasting of ores for metal refining, endless urban constructions and waste incineration [84, 111, 126].

Atmospheric pollutants often have long-range transport pathways that have an important contribution on regional climate and pollution levels, since air masses passing through industrially developed regions are heavily loaded with anthropogenic pollutants [60, 115].

Atmospheric wet and dry depositions are the major processes that remove contaminants from the atmosphere [6].

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s42452-020-03933-2>) contains supplementary material, which is available to authorised users.

✉ Reshmi Das, reshmidas.sest@jadavpuruniversity.in | ¹School of Environmental Studies, Jadavpur University, Kolkata, India. ²Department of Marine Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. ³Earth Observatory of Singapore, Nanyang Technological University, Nanyang, Singapore.



SN Applied Sciences (2020) 2:2122 | <https://doi.org/10.1007/s42452-020-03933-2>

The continuous process of dry deposition is predominant in areas of low precipitation [86]. In contrast, episodic wet deposition is the most effective process of atmospheric cleansing [41, 129]. The cleansing of the atmosphere by wet and dry depositions ultimately results in the transfer of both nutrients and contaminants from atmosphere into soil and aquatic ecosystem [32, 48]. The study of metals in rainwater has gained interest due to increasing air pollution and concern about the adverse environmental and human health effects of the deposited pollutant, particularly metals that become potentially toxic after entering the terrestrial and aquatic environments [95].

Chemical composition of rain water is affected by the local and regional characteristics of air pollutants [96]. Rainwater pH is controlled by the ionic composition such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- and NH_4^+ [66, 90, 106]. For example, presence of atmospheric gases such as SO_2 and NO_x which are precursors of major acids H_2SO_4 and HNO_3 , respectively, results in acidic precipitation [7, 24, 74]. In contrast, CaCO_3 in airborne dust and/or presence of ammonia released from anthropogenic or natural sources can neutralize acidity in rainwater [36, 98]. Thus, substances of anthropogenic origin (industry, agriculture and fertilizers, combustion of fossil fuels) such as SO_2 , NO_x , ammonia, and toxic metals, and those of natural origin (sea salt and terrestrial aerosols) such as Na^+ , Mg^{2+} , Ca^{2+} , Cl^- [14] are present in atmospheric precipitation.

Globally, studies pertaining to geochemistry of rainwater have gained tremendous momentum primarily due to two reasons [9, 29, 64, 73, 124]. First, due to the toxicity of certain metals (such as Pb, Cd, Cr, As, Hg), their capability to bioaccumulate and biomagnify and carcinogenic properties, high concentrations of such metals in precipitation are perilous for both terrestrial and aquatic ecosystems [62, 92, 122]. Hence understanding the chemical composition of rainwater, particularly the pollutants are important for the environment and ecosystem. Second, water shortage has become a pressing issue nowadays, and rainwater harvesting (RWH) is considered a viable water supply for urban regions [12, 38]. In many regions, RWH is the only sustainable way to obtain drinking water and used for crop irrigation and the recharging of aquifers [51, 77]. Thus, chemical characterization of rainwater is required to determine the treatment necessities.

There have been numerous studies on the major ion composition of rainwater in India [17, 39, 53, 67, 97, 109, 114, 119] to understand the undergoing processes such as pH control, "in cloud" and below-cloud scavenging and understanding natural versus anthropogenic sources ([61, 66, 81, 89]). However, none of the studies quantified trace metal concentrations simultaneously in rainwater and aerosol and measure their wet deposition fluxes. Additionally, in India, compliance with the rainwater harvesting

has become a necessary requirement for major construction projects to be fulfilled when receiving environmental clearance [31, 67]. Hence, knowledge about the chemistry of the rainwater that is harvested is of utmost importance. To fill in the knowledge gaps, this pilot study investigates trace metal concentrations in aerosol and rainwater during monsoon season in an Indian megacity, Kolkata. Previous studies investigated trace metals in atmospheric particulate matter (PM_{10} and $\text{PM}_{2.5}$) from Kolkata [25, 57]; however, these studies did not quantify rainwater metal concentrations from the megacity. The main objectives of this study are to understand aerosol leaching, quantify trace metal in rainwater and understand the sources of trace metals and quantify the atmospheric wet deposition (AWD) fluxes.

2 Methods

2.1 Sampling

Aerosol and rainwater sampling was carried out in Kolkata [22° 29' 57.53" N, 88° 22' 18.66" E.], the capital of the state of West Bengal and the only megacity in eastern India. The major industries around the city are jute mills, paper and pulp industries, tanneries, textile mill, thermal power plants and oil refineries. The city experiences a tropical wet-and-dry climate [25]. Generally, monsoon commences in June and lasts till September. In 2019, monsoon was delayed by a month and commenced in July, lasted till October and supplied the city with most of its annual rainfall (Fig. 1). 72 h of air mass back trajectories at 500 m above ground level (a.g.l) terminating at Kolkata during the sampling period showed that majority of the air mass originated over Arabian Sea and blew over the Indian landmass before reaching the city (Fig. 1).

Rainwater and aerosol were collected on the roof top of School of Environmental Studies building, Jadavpur University, approximately 24 m a.g.l. The building has no wet laboratories; hence, there are no ventilation exhausts on the rooftop to contribute blanks from acid fumes. The rainwater samples were collected in 500 ml high density polyethylene (HDPE) bottles through HDPE funnel covered with nylon net. The bottles, funnels and the net were pre cleaned with 2% reagent grade HNO_3 and thoroughly washed several times with ultrapure water followed by overnight drying at 60 °C in a convection oven. The bottles were placed on the rooftop several minutes after commencement of rain and immediately removed either after rain stopped or the bottle filled up, whichever was earlier to avoid any dust or dry deposition. A total of thirteen rain water samples and two blanks were collected between July and October

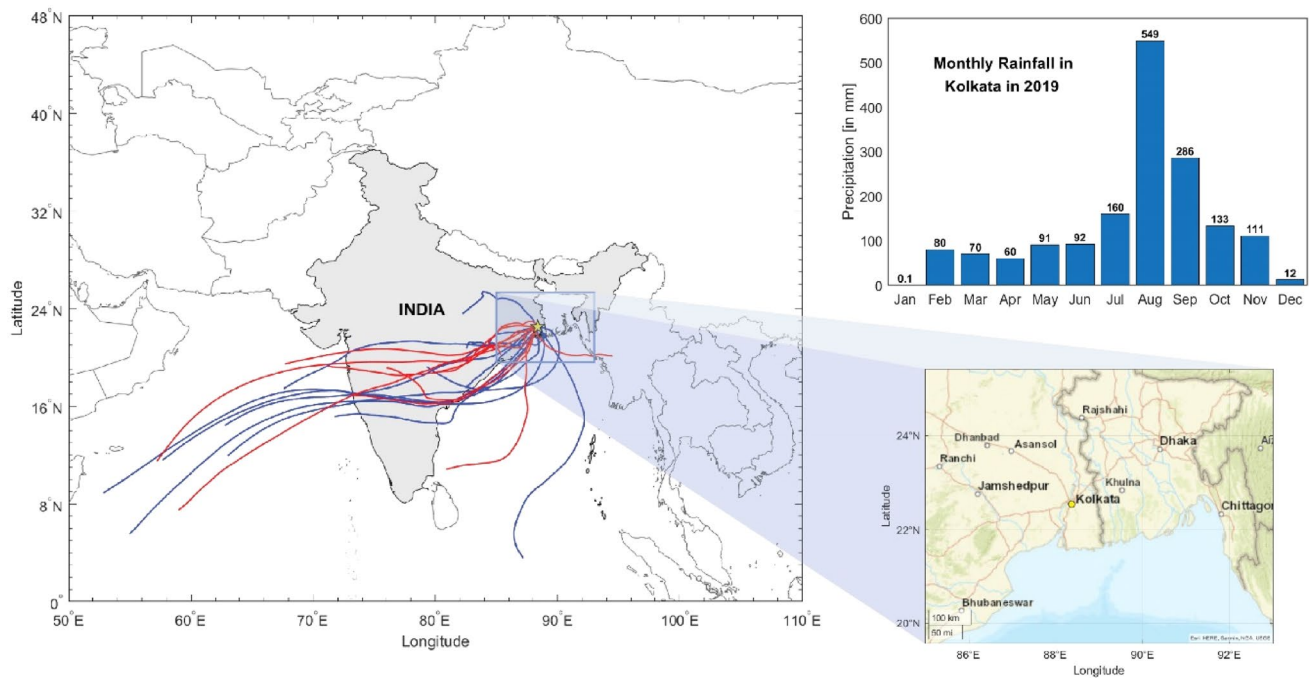


Fig. 1 Backward air mass trajectories terminating at Kolkata back-traced for 72 h at 500 m above mean sea-level using the HYSPLIT model during the sampling days. Red trajectories are for days when

aerosol (PM_{10}) was collected and blue trajectories are for rainwater collection days. The inset bar diagram shows monthly distribution of rainfall over Kolkata in 2019

2019. For the procedural blanks, the bottles with the funnels covered by net were taken to the rooftop and ultrapure water was poured inside the bottles. The blanks samples were treated similar to the rainwater samples.

A total of ten PM_{10} samples were collected in between rain events using a deployable particulate sampler (DPS) pump from Leland Legacy operating at 10 L/min. 24-h samples (usually starting at 8 AM) were collected on prewashed 47-mm PTFE (polytetrafluoroethylene) filters. The PTFE filters were prewashed in acid and blanks collected as described in [26] to minimize filter blanks. The filters were weighed and sealed immediately in a petri dish and stored inside a desiccator after the collection. Concentrations of PM_{10} were assessed gravimetrically.

2.2 Chemical analysis

Trace metal analysis of rainwater and aerosol samples was carried out at the Earth Observatory of Singapore, Nanyang Technological University (NTU), Singapore, in a Class 100 metal-free clean chemistry laboratory. Anions were analysed at the Central Environmental Science and Engineering Laboratory at NTU.

2.2.1 Rainwater

Immediately after sampling approximately 10 ml of rainwater was filtered through prewashed 0.45 μm Acrodisc® Syringe Filters with PTFE membrane into 15-ml HDPE bottles. The filtrates were acidified with several drops of 14 N ultrapure HNO_3 to prevent absorption of trace metals on the bottle wall and preserved for trace element analysis. In the remaining water, pH and electrical conductivity (referred to as conductivity herein) were immediately measured and the remaining preserved for ion chromatography analysis for anions. pH was determined using Eutech pH 700 from Thermo Scientific and cross-checked using Toshcon digital pH meter. Both the pH meters were calibrated with NIST buffer sets with pH 4.01 and pH 6.86 and the electrode cleaned with distilled water before measuring the unknown samples. The difference in reading between the two instruments was within 0.09 of each other, and the average value was taken. The conductivity of the rainwater samples was measured by using a Systronics conductivity meter. Standard KCl solutions (0.01 M, 0.001 M concentrations) were used for calibrating the instrument. The conductivity and the temperature probes were rinsed thoroughly with distilled water before calibration. The different standard KCl solutions were used for calibrating the instrument before measuring the unknown

rainwater sample. Temperature of the instrument was adjusted as closely as possible to 30 ± 2 °C.

The rainwater and blank samples were analysed for anions (Cl^- , SO_4^{2-} , NO_3^-) using ion chromatography (Dionex ICS-1000 Ion Chromatography System (ICS-1000)). Before running the samples, the ion chromatography system was calibrated using a standard solution (Dionex Seven Anion Standard from Thermo Scientific). All samples were filtered through 0.45- μm cellulose acetate syringe filters before being injected into the IC column. By comparing the data obtained from a sample to that obtained from the known standard, sample ions were quantified. The final concentrations were blank-corrected using the average procedural blank concentrations. Averages of the procedural blank were 1.3% (for SO_4^{2-}), 1.9% (for NO_3^-) and 2% (for Cl^-) of the average signal intensity of the samples.

2.2.2 Particulate matter (PM_{10})

For determination of trace metal concentration, filters were cut into small pieces using a ceramic scissor and placed inside pre-cleaned PTFE vials. The scissor was first washed with ultrapure water followed by methanol before cutting the next sample to prevent any contamination. Trace metals were extracted in 50% (v/v) 3:1 HNO_3 : HF mixture. The vials were first placed in an ultrasonic bath at 60 °C for an hour. Then the vials were placed on the hot plate at 150 °C for 12 h. After cooling down the vials, caps were opened and the filter papers were washed with ultrapure water inside the vials and discarded. The digested samples were then evaporated to dryness and re-dissolved in 5 ml of 50% HNO_3 and dried again. The evaporation and re-dissolving procedure were then repeated a couple of times to ensure complete evaporation of HF. Finally, the dried metal extract was dissolved in 5 ml of 2% HNO_3 and transferred to pre-cleaned vials for ICPMS analysis. Procedural blank was measured on two filters that were taken to the field and brought back and were treated in the same way as the samples. SRM 2783 of Urban Particulate Matter standard was used to test the extraction efficiency and validate the method [25].

2.3 ICP MS measurements

Trace metals (Na, Ca, Mg, Al, Fe, Mn, V, Cr, Ni, Cu, Zn, Cd, Pb) were determined in the acidified rainwater samples and aerosol extracts using ICPMS (Inductively Coupled Plasma Mass Spectrometry, Thermo Element 2, USA). High-purity multi-element standard solution (IV-ICPMS-71A from Inorganic Ventures) diluted to appropriate concentrations depending on the signal range was used to measure the metal concentrations. One ppb of indium (In) was used as an internal standard to correct for instrument

drift. Samples were measured using sample standard bracketing technique. The procedural blank intensities that ranged from 1 to 3% of the average signal intensity of the samples were subtracted from the sample signal intensities. SRM 2783 of Urban Particulate Matter samples were used for method validation. Recoveries for all metals were found to be > 90% [25]. The limit of detections (LODs) of all analysed elements was calculated based on three times of the standard deviation (SD) of blank. The value of LOD ranged from 0.0023 (Pb) to 2.2717 (Ca) ppb ($n = 12$) (Kayee et. al., 2020). Chemical composition of all the samples (rainwater and aerosol) is given in Table S1 in the supplementary information section. Further details of the analytical procedures are documented in [25, 26] and [59].

2.4 Chemical data analysis

The measured metal and anion data were further used to calculate the enrichment factor (EF), sea salt component, and wet deposition flux (WDF) and statistical analysis.

2.4.1 Statistical analysis of the data

Pearson's correlation coefficient (r) is used to measure the strength of the association between the two variables. The correlation coefficient is considered to be statistically significant if the p values were ≤ 0.05 .

To identify the probable sources of the trace elements in aerosol, principal component analysis (PCA) with varimax rotation and Kaiser normalization is used. In PCA, a multivariate data table is represented as smaller set of variates that have similar patterns in the real world such as source, atmospheric dispersion pathways, etc. Factors with eigenvalues ≥ 1 are only considered. Eigenvalues < 1 are negligible from a variance point of view. To select the significant features for the interpretation of each component, factors loadings greater than 0.5 are considered.

All statistical analyses were performed using SPSS for Windows V. 16.0.1.

2.4.2 Crustal enrichment factor (EF)

Crustal enrichment factor (EF) is often used to identify anthropogenic sources of metals over natural background. Metal ratios are generally compared with the average upper continental crustal (UCC) composition. In this study, we use UCC composition from Rudnick and Gao [93]. The EF of an element in a PM and rainwater sample is defined as: Enrichment Factor = $\frac{(\text{metal conc./ref.metal conc.})_{\text{aerosol/rainwater}}}{(\text{metal conc./ref.metal conc.})_{\text{crust}}}$.

Elements that generally have typically crustal origin such as Fe, Al and Ti are chosen as reference metal. Ti was not

measured in this study and Fe behaves differently in oxic and anoxic environment, [8]. Hence, we choose a conservative element with high crustal abundance such as Al, as the reference metal in this study [25, 26].

2.4.3 Marine and non-marine sources and marine enrichment factor

Ionic composition of rainwater helps to understand the relative contribution of marine and non-marine sources. Generally, Na is taken as reference element with the assumption that all Na is of marine origin. The equation for the non-sea salt contribution can be written as

$$[NSS - X]_i = [X]_i - [Na^+]_i \left[\frac{[X]}{[Na^+]} \right]_{sea\ salt}$$

$[NSS - X]_i$ is the concentration of non-sea salt concentration of species X in sample i, $[X]_i$ is the total measured concentration of chemical species X in sample i, $[Na^+]_i$ is the concentration of Na^+ in sample i, and $\left\{ \frac{[X]}{[Na^+]} \right\}_{sea\ salt}$ is ratio of these species measured in sea water [66]. Furthermore, marine enrichment factors of the anions with respect to Na are estimated as follows: $EF = \frac{[X/Na^+]_{rain}}{[X/Na^+]_{seawater}}$ where X is the ion of interest.

2.4.4 Wet deposition flux (WDF)

The volume-weighted mean concentrations (VWM) of trace metals ($mg\ L^{-1}$) and wet deposition fluxes (mgm^{-2}) were determined using Eqs. (1) and (2), respectively:

$$C_{VWM} = \frac{\sum_{i=1}^n (C_i \times P_i)}{\sum_{i=1}^n P_i} \tag{1}$$

$$WDF = C_{VWM} \times P_t / 1000 \tag{2}$$

where C_{VWM} is the concentration of VWM, C_i ($mg\ L^{-1}$) are the concentrations of the measured TE, P_i (mm) are the rainfall amount of individual precipitation event, and WD is the wet deposition.

WDF refers to the monthly/seasonal/annual wet deposition flux expressed in mgm^{-2} , which is calculated by multiplying the C_{VWM} ($mg\ L^{-1}$) by the volume of monthly/seasonal/annual rainfall amount in mm. For the present study, seasonal P_t in mm will be for the months of July to October 2019, i.e. those during which the samples were collected and annual P_t for the entire year [18, 127]. Precipitation data were obtained from archive of *Regional Meteorological Centre Kolkata*, via the online portal at <http://imdco.lkato.gov.in/>.

3 Results and discussion

3.1 PM_{10} concentration and trace metal composition

The PM_{10} concentrations ranged between 42 and 69 $\mu g/m^3$ (average $56 \pm 9\ \mu g/m^3$, 1SD) during the sampling period which is well within the National Ambient Air Quality Standards (NAAQS) [121] prescribed value of 100 $\mu g/m^3$ for 24 h.

The overall trend of the average elemental composition of PM_{10} is (Na, Al, Ca, Fe and Mg) > 100 ng/m^3 , (Zn, Mn and Pb) > 10 ng/m^3 , and (Ni, Cu, V, Cr and Cd) < 5 ng/m^3 (Fig. 2, Table 1). Concentrations reported in this study

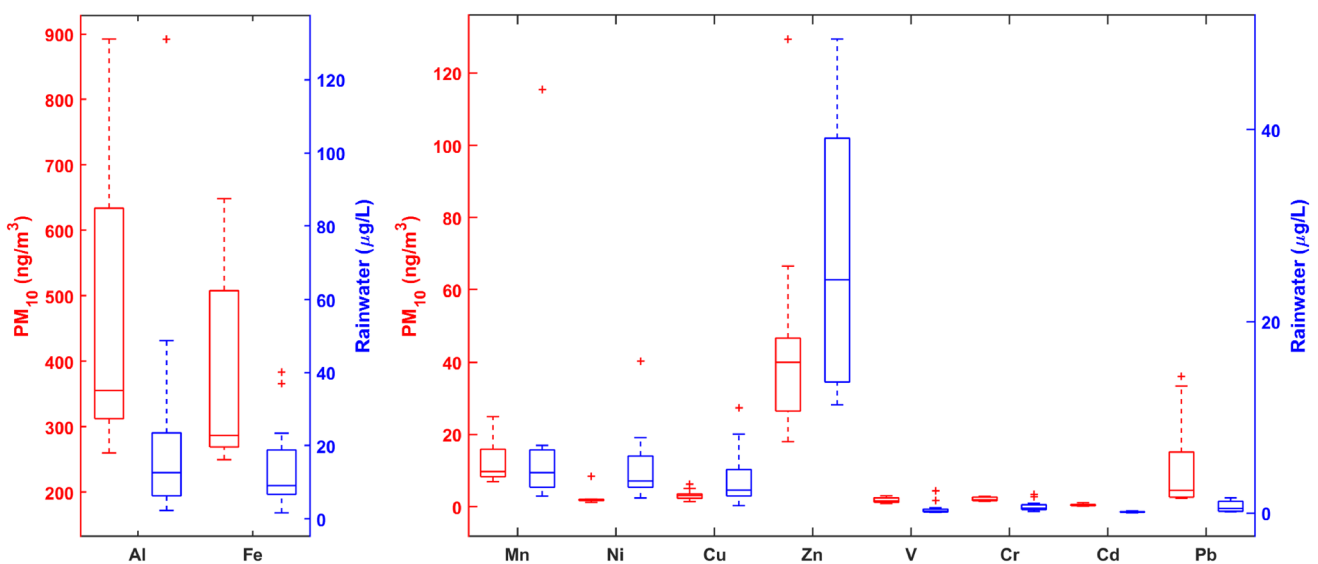


Fig. 2 Box plot of metal concentrations in PM_{10} (red box) and rainwater (blue box) from Kolkata

Table 1 Summary statistics of major ions and trace metals in rainwater ($n = 13$) and PM_{10} ($n = 10$) measured during the study period

RAINWATER	Unit	Mean	1SD	Median	Min	Max	AEROSOL	Unit	Mean	1SD	Median	Min	Max
pH		6.8	0.74	7.0	5.4	8.0	PM_{10}	$\mu\text{g}/\text{m}^3$	56	9.3	56	42	69
Conductivity	$\mu\text{S}/\text{cm}$	55	46	38	13	188							
Cl^-	$\mu\text{eq}/\text{L}$	68	35	61	18	126							
NO_3^-	$\mu\text{eq}/\text{L}$	202	190	136	20	614							
SO_4^{2-}	$\mu\text{eq}/\text{L}$	65	63	40	25	218							
Na^+	$\mu\text{g}/\text{L}$	1381	619	1303	393	2440	Na	ng/m^3	496	274	517	117	855
Ca^{2+}	$\mu\text{g}/\text{L}$	1231	1475	514	152	4597	Ca	ng/m^3	441	178	417	217	731
Mg^{2+}	$\mu\text{g}/\text{L}$	198	127	162	52	470	Mg	ng/m^3	188	81	164	81	372
Al	$\mu\text{g}/\text{L}$	24	35	13	2.3	131	Al	ng/m^3	459	206	356	260	893
Fe	$\mu\text{g}/\text{L}$	14	12	9.1	1.6	40	Fe	ng/m^3	385	159	287	250	648
Mn	$\mu\text{g}/\text{L}$	7.2	11	4.2	1.8	44	Mn	ng/m^3	12	6.0	9.7	6.9	25
V	$\mu\text{g}/\text{L}$	0.45	0.65	0.19	0.08	2.3	V	ng/m^3	1.8	0.73	1.6	0.85	3.0
Cr	$\mu\text{g}/\text{L}$	0.71	0.55	0.51	0.18	1.9	Cr	ng/m^3	2.0	0.54	1.9	1.4	2.8
Ni	$\mu\text{g}/\text{L}$	4.8	3.8	3.4	1.6	16	Ni	ng/m^3	2.4	2.1	1.8	1.1	8.4
Cu	$\mu\text{g}/\text{L}$	3.7	3.2	2.4	0.79	11	Cu	ng/m^3	3.2	1.4	3.0	1.4	6.3
Zn	$\mu\text{g}/\text{L}$	26	14	24	11	49	Zn	ng/m^3	47	32	40	18	129
Cd	$\mu\text{g}/\text{L}$	0.12	0.06	0.12	0.03	0.22	Cd	ng/m^3	0.40	0.29	0.31	0.10	1.0
Pb	$\mu\text{g}/\text{L}$	0.68	0.54	0.48	0.14	1.6	Pb	ng/m^3	12	13	4.5	2.3	36

are less than those reported in previous studies from Kolkata [25, 57]. Generally, the pollution levels have a seasonality and are minimum during the monsoon due to washout effect. The previous studies reported trace elements in PM during winter [25] when pollution is highest due to thermal inversion and annual average [57], which is generally higher than monsoon minima. Hence, absolute concentrations are inadequate to understand the sources, and thus we use the crustal enrichment factor (EF).

As per the EF calculations, any element with natural origin should have $EF \sim 1$. However, to account for the local variability of upper continental crustal composition which forms the immediate precursor of the aerosol metals, $EF \leq 10$ is, considered to have a natural origin [25–27, 57, 59]. In PM_{10} , Na, Mg, Al, Ca, V, Cr, Mn and Fe have $EF < 10$ indicating natural origin. Ni and Cu have EF between 10 and 100 indicating moderate enriched by anthropogenic sources. Very high EF ($EF > 100$) of Pb, Cd and Zn are most likely associated with industrial, high-temperature combustion and vehicular emissions (Fig. 3b). The general trend of EFs observed in our study is consistent with those reported from Kolkata by [25] indicating the presence and similar intensity of anthropogenic sources. Though EF can differentiate between crustal and anthropogenic origins, source apportionment of PM is difficult to achieve solely based on EF and elemental concentrations. Thus, principal component analysis (PCA) and elemental ratios are used to better understand the anthropogenic sources of the metals.

As the objective of the study is to understand sources of trace metals in rainwater, we exclude the major ions in rainwater such as Na, Ca and Mg from PCA analysis in both the PM_{10} and rainwater samples. Four factors can explain 92% of the total variation in the PM_{10} metal dataset (Table S2, Fig. 4). Communalities of all metals ranged between 0.85 and 0.99 which is an indication of satisfactory apportionment of each element to the identified factors. Physical interpretation of each factor or source was based on its association with strong loading of marker elements, typically emitted from that source.

The first factor is associated with Al, Fe, Mn, and Cr and can explain 41.8% of the total variance. Al and Fe are typically crustal metals, and all the metals have $EF < 10$. Hence factor 1 represents crustal source [5, 21, 113].

Factor, associated with Ni, Cd and Zn explains 27.8% of the total variance. The largest sources of atmospheric Ni are coal and liquid fuels consumption [118]. Other minor sources include non-ferrous metal smelting, cement production, brick production, glass manufacturing. The ferrous and non-ferrous metal industries and fuel combustion are estimated to account for the largest emissions of atmospheric Cd [52, 85]. Cd has the highest EF and can also originate from the production and recycling of Ni–Cd batteries [117]. Major anthropogenic sources of Zn are coal combustion and industrial activities [75, 84]. Hence factor 2 represents coal combustion and industrial emissions.

The third factor, with marker elements Pb and V, explains 13% of the total variance. Both Pb and V are characteristics of road traffic or vehicular emissions [5, 42, 71].

Fig. 3 A) Concentration trends of the measured elements in PM₁₀ and rainwater. B) Enrichment factors (EF) of metals, calculated using Al as reference. EF is calculated with respect to average upper continental crust (UCC) composition from [93]. Metals with values of EFs < 10 have crustal sources, and those with values of EFs > 10 indicate anthropogenic influence

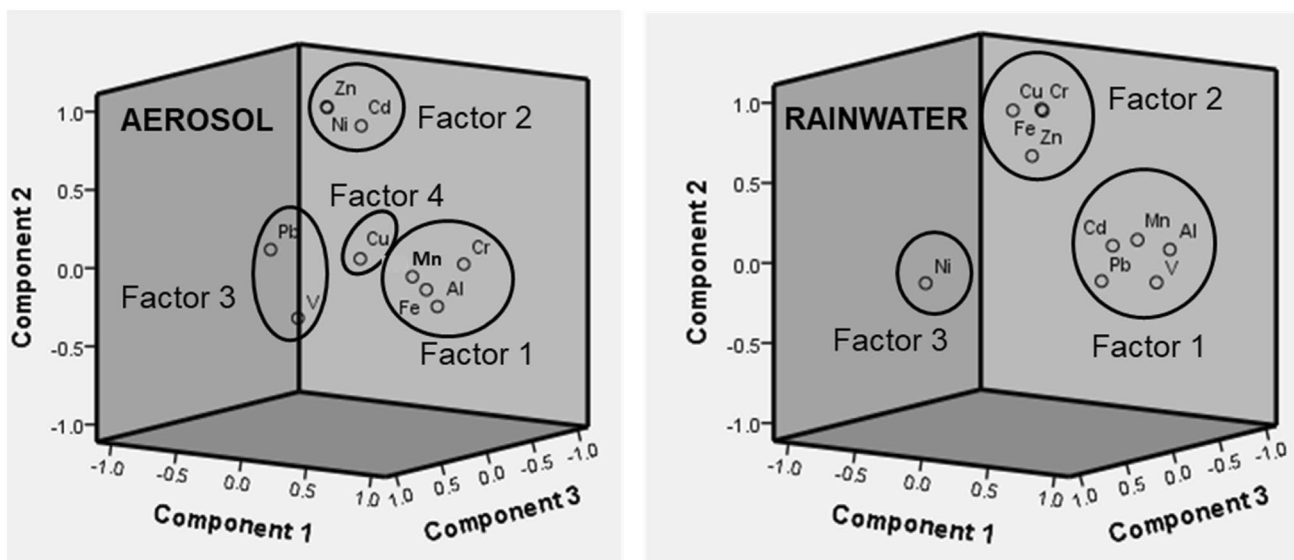
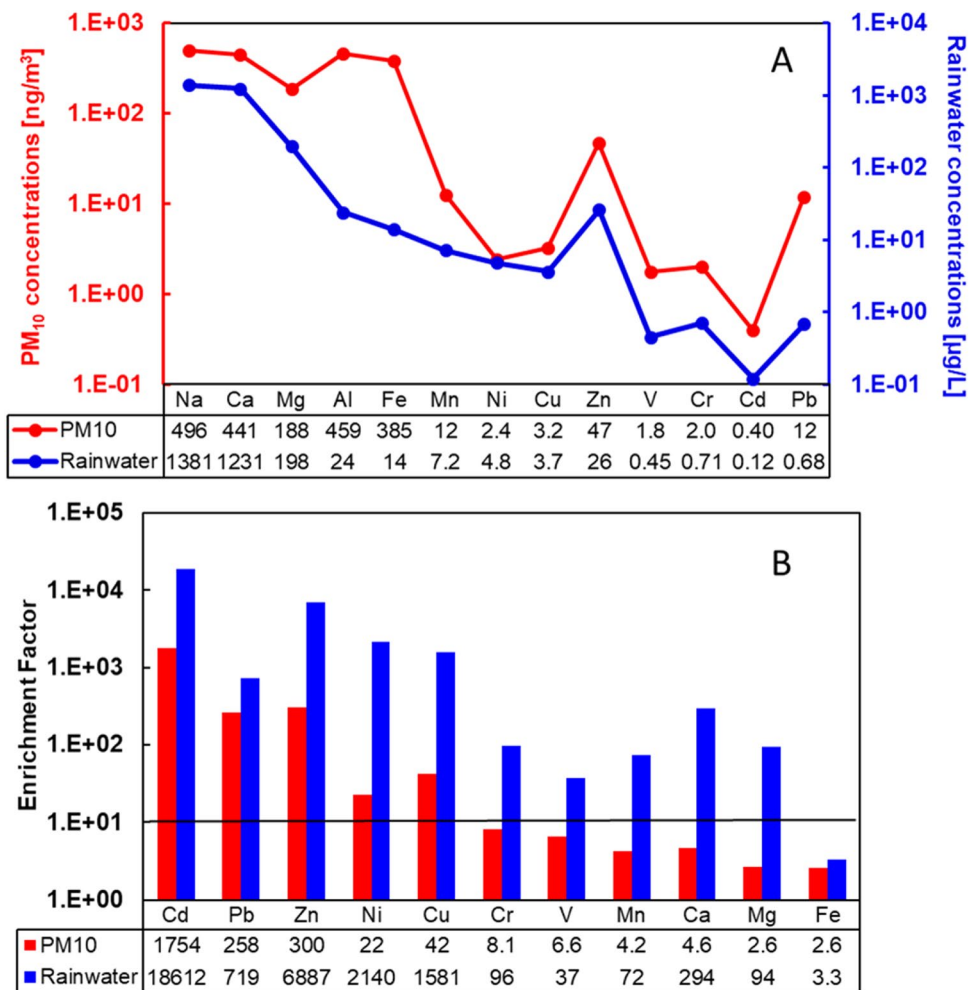


Fig. 4 Principal component analysis (PCA) loading three-dimensional plot for 10 trace elements in aerosol (PM₁₀) and rainwater

Though leaded gasoline was completely phased out from India in the year 2000, present-day diesel and unleaded gasoline still contain trace amounts of Pb [22]. The large fleet of vehicles on city roads magnify Pb emission to the atmosphere. V/Pb ratios can differentiate vehicular sources from coal combustion and industrial emissions. Coal is generally enriched in V (mg/g level) resulting in V/Pb ratio of > 1 , whereas non-coal burning industrial sources have V/Pb ratio < 1 [40]. V/Pb ratio of vehicle exhaust is in between and is usually < 1 . The Kolkata aerosols have average V/Pb ratios of 0.30 ± 0.20 , 1SD (range 0.08–0.59), indicative of vehicle exhaust emission.

Finally, the fourth factor, primarily loaded with Cu, explains 9.4% of the total variance. Fossil fuel combustion, commercial metallurgical processes and waste incineration are the major sources of atmospheric Cu emission [63].

3.2 pH and conductivity of rainwater

The pH of the rainwater from this study ranged from 5.4 to 8.0 (average 6.8 ± 0.74 , 1SD). Out of 13 rainwater samples, approximately 15% were acidic (pH < 5.61), 15% were slightly acidic (pH 5.6–6.5) and 54% of the samples were alkaline with pH > 7 . The pH of natural precipitation in pristine environment is 5.6 and is controlled by interaction between water droplets and atmospheric CO_2 [19]. However, in polluted settings, the pH of rainwater is mainly regulated by the abundance of acids forming chemical species such as SO_4^{2-} and NO_3^- , and basic gas such as NH_3 . Soil dust containing Ca^{2+} , Mg^{2+} and K^+ can balance acidification, due to their buffering capacity [60, 72, 99, 101, 110, 120]. The average pH of the present study (pH = 6.8) is slightly higher than the Indian average of 6.5 [17]. The pH range of the present study is comparable with those reported in earlier studies from Kolkata [17] but less alkaline than those reported by [68] (Table 2). The sulphate ion showed strong negative correlation with pH ($r^2 = -0.8$) but not the nitrate. The almost neutral pH of the precipitation is due to the neutralization caused by different cations. When the sum of ($[\text{Ca}^{2+}] + [\text{Mg}^{2+}]$) is fitted against $[\text{SO}_4^{2-}]$, the correlation coefficient is 0.73, indicating that Ca and Mg carbonate is the major neutralizing base [5]. Slightly alkaline pH has been reported from many other cities and states of India as well as places around Asia (Table 2). In general, Indian precipitation has higher pH than natural rainwater resulting from high loading of alkaline rich atmospheric particulate matter though acid rain has been reported from coal mining city of Dhanbad and the national capital of Delhi due to the influence of SO_4^{2-} ions [91, 109].

Conductivity in the present study ranged from 12.6 to 188 $\mu\text{S}/\text{cm}$ (average 55 ± 46 $\mu\text{S}/\text{cm}$, 1SD). Low conductivity

in precipitation is an indicator of good environmental quality in the atmosphere [125]. The common conductivity range of precipitation is 5–1000 $\mu\text{S}/\text{cm}$ [4]. There were two previous studies from Kolkata. One reported similar conductivity (47.87 $\mu\text{S}/\text{cm}$) [17], and the other study reported much higher conductivity (370 ± 297 $\mu\text{S}/\text{cm}$) that was attributed to industrial emissions of cations and anions in the megacity atmosphere [68]. The conductivity of the present study is compared to other Indian cities given in Table 2. Precipitation conductivity is attributed primarily to the total soluble ionic components present in the rainwater hence reflecting the impact of atmospheric particulate matter on rainwater chemistry [80]. In this study, the conductivity strongly correlates ($r^2 = 0.85$) with Ca most likely due to presence of CaCO_3 as a significant solute [3].

3.3 Chemical composition of rainwater

Inorganic composition of rainwater comprises the major anions (Cl^- , NO_3^- , SO_4^{2-}), NH_4^+ from anthropogenic emissions, major elements (Ca, Mg, Na, K) and trace metals. In this study, K and NH_4^+ were not measured. Concentrations in rainwater follow the order of (Na and Ca) > 1000 $\mu\text{g}/\text{L}$, Mg > 100 $\mu\text{g}/\text{L}$, (Al, Fe and Zn) > 10 $\mu\text{g}/\text{L}$ and (Mn, Ni, Cu, V, Cr, Cd and Pb) < 10 $\mu\text{g}/\text{L}$ (Fig. 2).

The marine and non-marine contributions of the anions Cl^- and SO_4^{2-} were determined. The ratios of Cl^- and SO_4^{2-} with respect to Na^+ in sea water are 1.16 and 0.125, respectively [66]. Average Cl^-/Na^+ ratio of rainwater samples (1.12 ± 0.17) is similar to sea water ratio of 1.16. Significant correlation between Cl^- and Na^+ ($r = 0.96$) confirmed sea salt origin. Average $\text{SO}_4^{2-}/\text{Na}^+$ ratio of rainwater samples (1.132 ± 0.90) is higher than sea water. Calculations show sea salt fraction of SO_4^{2-} is only 12%. Furthermore, marine enrichment factor of Cl^- is 1 indicating marine source and that of SO_4^{2-} is 9 indicating contribution of non-marine sources. The non-sea salt fraction of SO_4^{2-} may be sourced from soil dust containing gypsum, pyrite or may be derived from anthropogenic processes, primarily combustion [10, 35, 65, 83, 112].

Removal of aerosols by wet deposition occurs primarily by two mechanisms, below-cloud scavenging and within-cloud scavenging [43]. For below cloud scavenging, trace metal composition of the ambient aerosol controls the composition of rainwater. Relative abundance of metals in rainwater depends on emission sources and solubility of metals. The general concentration trend of the major elements in rainwater followed the aerosol Na, Ca, Mg trend (Fig. 3a). The overall concentration trend of the metals Cu, Zn, Cd, V, Cr and Pb follows the trend in PM_{10} indicating at least part of the metals are derived from aerosol leaching (Fig. 3a). However, Al and Fe do not follow the trend indicating limited leaching of these two elements from

Table 2 Comparison of pH of rainwater of the sampling site in Kolkata with some other selected sites of India and the world

Site	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Reference
Kolkata, India	6.81 ± 0.74	55 ± 46	Present Study
Kolkata, India	6.77	48	[17]
Kolkata, India	7.23 ± 0.68	370 ± 30	[68]
Delhi, India	5.70	–	[91]
Dhanbad, India	5.37 ± 0.78	27 ± 26	[109]
Nagpur, India	6.30 ± 0.30	–	[97]
Roorkee, India	7.05	–	[53]
Mumbai, India	5.70	–	[88]
Comba, South Goa	6.25 ± 0.28	–	[39]
Bongaigaon, India	5.68	25	[17]
BGR Township, India	6.01	22	[17]
Dolaigaon, India	5.35	30	[17]
Irongmara, India	5.58	24	[17]
Kharagpur, India	6.06	11	[17]
Varanasi, India	5.72	18	[119]
Ballia, India	6.03	24	[119]
Kanpur, India	5.81	26	[119]
Manali, India	5.76	29	[119]
Meerut, India	5.65	30	[119]
Gorakhpur, India	5.44	34	[119]
Delhi, India	5.81	39	[119]
Kurukshetra, India	5.61	44	[119]
Tharamani, India	7.14 ± 0.64	75 ± 24	[68]
Tirunelveli, India	7.63 ± 0.41	403 ± 702	[68]
Kakinada, India	7.53 ± 0.98	111 ± 702	[68]
Belgaum, India	7.53 ± 0.24	134 ± 29	[68]
Bangalore, India	6.42 ± 1.32	82 ± 62	[68]
Patna, India	6.93 ± 0.096	51 ± 7	[68]
Sagar, India	7.40 ± 0.47	89 ± 52	[68]
Lucknow, India	7.36 ± 0.33	95 ± 66	[68]
Jammu, India	7.07 ± 0.48	153 ± 66	[68]
Gangotri, India	6.30	8	[68]
Dabrani, India	5.90 ± 0.21	59 ± 68	[68]
Uttarkashi, India	6.83 ± 0.92	88 ± 63	[68]
Devprayag, India	6.25 ± 0.21	37 ± 24	[68]
Danum Valley Malaysia	5.17	8.30	[114]
Loess plateau, Northwest China	7.82 ± 0.43	124 ± 67.30	[128]
Nanping Mangdang Mountain, Eastern China	4.81	20	[21]
Guangzhou, South China	4.49	–	[16]
Beijing, China	5.12	–	[128]

aerosol. Natural sources of Al and Fe in aerosol are crustal dust, and these two elements are mostly locked inside aluminosilicate structures [93] that are difficult to leach in rainwater. The sampling location is on the alluvium of the Indo Gangetic Plain (IGP). The common aluminosilicates that are found in the IGP soil are illite/mica, smectite, kaolinite and feldspars. The EFs of trace elements in rainwater of Kolkata are shown in Fig. 3b and compared with the EF

of PM_{10} trace elements. Out of all the trace elements measured, Fe is the only non-enriched element with $\text{EF} < 10$. The major element Ca and Mg in rainwater have high EF indicating anthropogenic influences. In cities, the sources of Ca and Mg can be cement from construction dust and road dust because of the abundance of alkaline materials in road coverings [37]. V, Mn, and Cr are moderately enriched with EF between 10 and 100. Cu, Ni, Zn, Pb and

Cd were highly enriched with $EF > 100$ indicating strong anthropogenic sources.

Cu, Ni, Zn, Pb and Cd have $EF > 10$ in PM_{10} collected in between rain events and were identified to have anthropogenic sources related to non-ferrous metal industry, waste incineration and coal combustion [63, 84, 85]. V, Mn, Co and Cr in aerosol have EF between 4 and 9. However, their EF in rainwater increases to greater than 10 but less than 100 in rainwater.

Figure 4 presents the three dissolved trace metal clusters for rainwater during monsoon period. Varimax-rotated PCA identified three sources of trace metals in the rainwater and can explain 79% of the variance in the data (Table S3). The first factor explains 38.6% variance and is loaded with crustal element such as Al, and the rest are anthropogenic metals such as Mn, V, Cd and Pb. Factor 1 can be attributed to vehicular emission and road dust [107]. Factor 2 accounts for 27% of the variance and has strong loadings of Fe, Zn, Cu and Cr and is possibly soil dust mixed with industrial emission. Factor 3 explains 13.7% variance and has strong loading of Ni and moderate loading of Zn and is possibly related to coal combustion emission [84].

VWM and average concentrations of trace elements in our study were compared with those reported from India and worldwide (Table 3). Selected worldwide stations are either large urban centres and/or stations close to the coast like Kolkata. A remote station in Lhasa, Tibet, is also

chosen for comparison. Trace elements in two successive rain events from the Indian city of Lucknow reported higher concentrations of Cu, Zn, Cr, Cd and Pb. This is possibly because concentrations of these elements are several times higher in Lucknow PM_{10} compared to Kolkata during monsoon [103]. However, the trace element concentrations in the Kolkata rainwater are in the same order of magnitude with those reported from global rainfall data over urban centres. The concentrations of Ca were higher than those reported from both the stations in Brazil and Europe. The high concentration of Ca in Kolkata rain is primarily due to the influence of soil dust and endless constructions which contains large fractions of $CaCO_3$. The concentration of marine elements such as Na and Mg in rainwater of Kolkata is higher than most of the compared cities but lower than that of Coastal Station in Western Europe and comparable with Northern & Southern Jordan [3, 5, 28]. The Bay of Bengal coast is approximately 125 km south of Kolkata and presumably influences the rainwater composition. Concentrations of crustal elements such as Al and Fe measured in Kolkata precipitation are low relative to other sites. Anthropogenic elements such as Zn and Pb were significantly lower than Kolkata rainwater compared to cities in Greece, Iran, Jordan, China and Lucknow. Pb shows large variation in the global dataset. In Jordan, high concentrations of Pb are attributed to biomass burning and industrial activities [3, 5]. High Pb was also reported from China and Singapore. While Pb in China was due to

Table 3 The volume-weighted mean (VWM) concentrations of major ions and trace metals ($\mu\text{g/L}$) in this study are compared to those obtained from other parts of the world

Location		Na	Ca	Mg	Al	Fe	Mn	V	Cr	Ni	Cu	Zn	Cd	Pb	Reference
Kolkata, India	VWM	1686	1748	275	46	19	14	0.76	0.82	3.7	4.1	31	0.14	1.0	This study
Kolkata, India	Average	1381	1231	198	24	14	7.2	0.45	0.71	4.8	3.7	26	0.12	0.68	This study
Lucknow, India (1st rainfall)	Average	-	-	-	-	-	2.0	-	121	-	1.0	122	11	33	[103]
Lucknow, India (2nd rainfall)	Average	-	-	-	-	-	3.0	-	17	-	10	85	46	62	[103]
Acegua, Brazil ^a	Average	349	156	66	-	2.4	2.2	-	0.15	0.64	0.30	10	0.06	0.13	[117]
Tres lagoas, Brazil ^a	Average	206	181	37	-	2.9	1.6	-	0.07	0.02	0.50	6.8	0.01	0.15	[117]
Athens, Greece ^b	Average	-	-	-	5.8	4.4	3.6	-	1.3	4.14	15	33	0.20	0.88	[56]
Shiraz, Iran ^{a,b}	Average	-	-	-	430	306	24	-	1.6	4.12	13	63	-	10	[76]
Pensacola, Florida ^b	VWM	985	-	-	53	26	1.1	0.27	0.10	0.37	4.6	2.2	0.01	0.31	[69]
Northern Jordan ^a	Average	1150	2166	373	382	92	2.1	4.2	0.77	2.6	3.1	6.5	0.42	2.6	[5]
Southern Jordan ^a	Average	1614	2513	734	115	87	20	-	-	-	36	33	-	39	[3]
Singapore ^b	VWM	-	-	-	18	24	2.7	3.5	1.6	3.9	-	-	0.33	7.2	[49]
Tangshan, Northern China ^a	VWM	-	-	-	248	291	28	1.4	1.0	1.4	5.4	89	0.30	18	[130]
Nanjing, China ^a	Average	-	-	-	113	19	24	4.6	11	1.4	-	28	3.30	13	[116]
Coastal Station in Western Europe ^b	VWM	13794	461	827	-	-	-	-	-	-	0.70	16	0.10	2	[28]
Tibet, Lhasa ^c	VWM	-	-	-	131	221	7.7	0.31	0.43	0.58	1.7	14	0.03	1.6	[43]

^a Polluted cities

^b Coastal location

^c Remote location

industrial emission, high Pb in Singapore rain was due to atmospheric scavenging of gasoline Pb released from neighbouring Indonesia. Interestingly, though India is the second largest emitter of atmospheric Pb in Asia, after China [70], Pb concentration in rainwater is < 1 ppb indicating low solubility of atmospheric Pb over Kolkata and hence limited bioavailability of the toxic metal. Most of the metals (except the crustal elements Al and Fe) in Kolkata are higher than in Tibetan rainfall as expected, but interestingly, Pb concentrations are comparable and only ~ 0.5 times higher in Kolkata rain.

3.4 Comparison of precipitation chemistry with groundwater and surface water

With increasing population pressure, there is growing reliance on groundwater for farming and drinking purposes. Human activity has threatened freshwater reserve by polluting and depleting groundwater reserve by overdrawing [123]. Rainwater is relatively free from impurities and may be one of the alternative sources of drinking water.

The drinking water standards of India consist of several criteria such as: (1) perceptible parameters and inorganic constituents, (2) organic substances, (3) pesticides, (4) disinfectant and disinfectant by-products, (5) radioactive constituents, and (6) micro-organisms [46]. The present study focuses only on the inorganic components of the rainwater. In Table 4, we have compared rainwater chemistry with other sources of drinking water such as untreated groundwater and river water from India. Kolkata rainwater meets the Indian and the WHO standards for drinking water, while the concentrations of toxic metals such as Pb and Ni of river and groundwater are higher than the guideline values. Pb is long known to affect physical or mental development in infant and children and causes high blood pressure and kidney problems in adults [15, 20]. Ni is a well-known human carcinogen that affects the activity of α -tocopherol, the most common lipid soluble antioxidant in human body [58]. The concentration of major ions such as Na, Ca and Mg is higher in river and groundwater compared to rainwater, but they are within the limits prescribed by WHO and Indian standards. Fe exceeds safe limits for drinking water in the ground and surface water. All the measured anions (chloride, sulphate and nitrate) are significantly higher in the ground and surface water as compared to the rainwater and exceeds the WHO and Indian Standards. Nitrate in drinking water is often reduced to nitrite in the stomach by gastric acids and with subsequent reactions with amines and amides results in the formation of N-nitroso compounds that have been linked to different types of cancer [30]. Nitrate (12.5 ± 11.8 ppm) in the rainwater meets the Indian, WHO and EU standards, but fails to meet the US EPA standard of

10 ppm. Therefore, rainwater needs a bare minimum treatment with respect to inorganic constituents before use as opposed to groundwater and river water, and this makes the use of rainwater more convincing as a drinking source.

3.5 Wet deposition flux (WDF) of the trace metals

The WDF calculated during the current study are shown in Table 5 and compared with the WDF data in different Asian countries from the literature. The atmosphere includes a variety of nutrient ions and trace metals adsorbed onto particulate matter that are scavenged by rain. Some of these ions and metals are plant nutrients (such as nitrate, ammonium, K, Ca, Mg, Fe) and some of them are toxic such as Cr, Cd, Pb, which affect the physico-chemical properties of the soil [32, 48].

WDF depend on the solubility of the trace metals and particle size distribution [86]. In Kolkata, the magnitude of the concentrations and fluxes of the different elements were in the order of: $\text{Ca} > \text{Na} > \text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Mn} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Cr} > \text{V} > \text{Cd}$. Of the primary crustal elements, Ca exhibited the highest flux of $242 \text{ mg/m}^2/\text{yr}$ followed by Na, Mg, Al and Fe. Al, Fe and Mn represent higher loadings because of their high concentrations in dust derived from crustal materials [23] and Na has a sea salt origin and comparable with the WDF over IGP. Higher flux values of Ca and Mg over IGP compared to Kolkata are due to enhanced anthropogenic emissions from power plants, refineries, stone crushing units and numerous medium and small-scale industries over IGP [119]. Among the anthropogenic metals, Zn had the highest WDF, followed by Cu, Ni, Pb, Cr, V and Cd. Despite differences in sampling periods reported in previous studies and the probability of inter-annual variability, WDFs of elements like Cd, V, Cr, Ni and Cu are in good agreement with those recorded from other sites. The deposition fluxes of Ni, Cu and Zn at Kolkata were more or less similar to Izmir, Turkey, and Singapore both of which are large coastal urban centres where the sources are attributable to local emissions from anthropogenic activities [47, 102]. V and Cr fluxes of this study are comparable with different cities of China and Japan but much less than those reported from Turkey and Singapore. Leather tanning, textiles industries and electroplating are significant anthropogenic sources of Cr in soil, whereas fossil fuel (both coal and oil combustion) and waste incineration releases Cr in the atmosphere [50]. V is released from combustion of fossil fuels. Wet deposition of Cd is comparable with global data. Cd is primarily released from coal combustion, vehicle emissions and industries. Pb flux is lower than all the compared sites. Post-phasing out of leaded gasoline the largest anthropogenic sources of Pb is coal combustion followed by nonferrous metal smelters and vehicle exhaust, besides the natural background

Table 4 Comparative table showing rainwater, river and groundwater and water quality standards. Units of trace elements are in ppb (µg/L) and those of the anions are in ppm (mg/L)

Trace element and anions	Na	Ca	Mg	Al	Fe	Mn	V	Cr	Ni	Cu	Zn	Cd	Pb	Cl ⁻	NO ³	SO ⁴⁻	References
Indian Standard 1983	-	75000	30000	30	300	100	-	50	20	50	5000	3	10	250	45	200	(BIS)
WHO Standard 1993	200000	-	-	200	-	500	20	50	20	2000	3000	3	10	500	50	500	[82]
EU Standard 2000	200000	-	-	200	200	50	-	50	20	50	3000	5	10	250	50	250	[34]
US Standard 1996	-	-	-	-	-	-	-	100	-	1300	-	5	0	4	10	-	(EPA, 2009)
Rainwater																	
Kolkata (Mean)	1381	1231	198	24	14	7.2	0.45	0.71	4.8	3.7	26	0.12	0.68	2.4	13	2.9	This study
Lucknow (1st Rainfall)						2.0		121		1.0	122	11	33				[103]
Lucknow (2nd Rainfall)						3.0		17		10	85	46	62				[103]
Groundwater																	
Hyderabad	91	185	36	71	48	596	4.3	5.4	9.1	9.7	35	0.2	49	225	8.0	104	[100]
Uppinangadi, SW India	30337	8260	3396	63190	-	-	-	-	3520	-	-	-	-	25410	23498	8928	[45]
Ponnaiyar River Basin	112	90	40	-	1020	70	-	-	80	-	710	-	70	220	144	9.7	[54]
Western Bengal Basin	88366	49600	12984	-	52	5.7	-	-	-	2.9	-	-	-	120890	967	11947	[79]
Dhanbad, Damodar River Basin	61	98	39	-	-	-	-	-	-	-	-	-	-	84	14	150	[108]
River water																	
Mahi River Basin	270	76	45	-	2781	364	71	27	16	48	1822	1.0	-	330	25	127	[104]
Rangit River Water Basin, West Bengal	4.4	8.9	3.6	-	1060	0.15	-	-	-	7.4	-	-	47	8.5	0.88	17	[44]
Deoria District, Ganga Plain	36	21	18	-	495	55	-	-	-	10	213	0.11	0.62	38	24	135	[11]
Godavari River Basin	19941	13960	4236	-	-	-	-	-	-	-	-	-	-	21840	1060	5520	[55]
Neyyar River Basin, 2006	12	2.3	0.70	-	-	-	-	-	-	0.01	-	-	-	14	0.34	0.41	[105]

Table 5 The wet deposition fluxes (WDF) in mg/m²/year from this study compared with those reported for other locations in Asia. As sampling was conducted from July to October 2019, WDF for those four months are also reported for comparison

Area	Sampling period	Na	Ca	Mg	Al	Fe	Mn	V	Cr	Ni	Cu	Zn	Cd	Pb	References
Kolkata	2019 (annual)	243	243	38	6.4	2.6	1.9	0.11	0.11	0.52	0.57	4.3	0.02	0.14	This Study
Kolkata	2019 (Jul–Oct)	492	492	78	13	5.2	3.9	0.21	0.23	1.1	1.2	8.7	0.04	0.28	This study [119]
Indo Gangetic Plain	2009	270	1740	350	650	1010									
	2010	610	2440	650											
	2011	480	2680	1010											
Wanzhou, China	2015–2016	-	-	-	10	5.3	3.4	0.47	0.18	0.18	0.95	10	1.4	4.1	[87]
Ligiang, China	2012	-	-	-	27	12	1.7	0.26	0.14	0.09	0.24	3.6	0.04	30	[43]
Northern China	2007–2010	-	-	-	45–120	60–149	8–19	0.4–0.9	0.3–0.7	0.5–2.0	1.8–3.8	22–90	0.18–0.31	5–28	[86]
Mt. Qomolangma, China	2009–2010	-	-	-	0.85	1.3	0.16	0.01	0.02	0.04	0.02	0.13	0.01	0.01	(Cong et al., 2015)
Noshiro, Japan	2003–2005	-	-	-	-	-	8.0	0.78	0.41	0.86	2.3	-	0.3	9.0	[78]
Izmir, Turkey	2003–2004	-	-	-	-	-	-	-5	5.8	4.9	10	45	1.3	3.8	[94]
Singapore	2000	-	-	-	48	62	7.2	9.1	4.2	10	15	19	0.78		[49]

from regional and local soil. Among the compared sites, Mt. Qomolangma in China which is regarded as a remote background site has the least WDF for almost all the trace elements.

3.6 Limitations of the study

The current study collected rainwater and aerosol in between rain events during the monsoon season only. In 2019, the total rainfall over Kolkata was 1642 mm out of which 1127 mm or 69% occurred during the sampled monsoon months between July and October. The remaining months of the year except November received less than 100 mm rainfall. Hence, seasonality of rainwater chemical composition could not be measured in this pilot study. Furthermore ammonia (NH₄⁺) in rainwater was not measured in this study; thus, neutralization factors could not be analysed. Future study plans to focus on seasonal variation of rainwater metal and major ions concentrations in urban centres and compare it with a less polluted rural site to better understand sources of pollutants in rainwater.

Access to safe drinking water remains an urgent requirement in India, as a large fraction of Indian households (30% of urban and 90% of rural households) are still dependent on either groundwater or untreated surface water [2]. Though access to drinking water has improved in India over the last decade, the enormous adverse health effects of contaminated water continue. Generally, contaminants in harvested rainwater are derived primarily from the atmosphere; however, rainwater quality deterioration may occur during harvesting, storage and household use [77]. To correctly assess the treatment needs of harvested rainwater for drinking purpose, both harvesting conditions and rainwater quality with respect to chemical (organic and inorganic constituents, pesticides, radioactive components, disinfectants), physical and microbiological components should be assessed [1]. Identifying pollutants that are incorporated from the harvesting process and organic and microbiological pollutants quantification of rainwater was not within the scope of this study.

4 Conclusions

The present work is a pilot study to assess metal concentrations and major anions in rainwater and quantifying wet deposition flux of the trace metals from a polluted megacity in India. Trace metal chemistry of rainwater is gaining importance as rain water harvesting is one of the strategies that the water sector is increasingly adopting to cope with future climate change. In many areas in China and Middle East, Pb exceeds WHO guideline limits for safe

drinking water. In Lucknow, India, several toxic trace metals such as Pb, Cr and Cd exceeds Indian Standards. Kolkata in spite of having poor air quality experienced rainfall with all the trace elements and anions within WHO guideline limits. Hence the rainwater is deemed suitable for drinking purpose with respect to metal content and anions and does not require pre-treatment to remove toxic metals. Comparison of concentration trends and crustal enrichment factor for the trace metals of PM₁₀ and rainwater shows preferential leaching of metals such as Cu, Zn, V, Cd and Pb. A soluble fraction of the metals enter the ecosystem through wet deposition. The annual WDF for Pb was much less when compared to other sites around the globe. However, WDF of the remaining metals are comparable to the global data.

Acknowledgement This research was partially supported by UGC Start Up Grant and RUSA 2.0 (Project No: P-11/720/19) awarded to RD. We thank Dr. Tarit Roychowdhury of Jadavpur University, Dr. Xianfeng Wang, Dr. Jeffrey Oalman, Ms. Lin Ke, Ms. Maria Chong, Ms. Beng Choo and Ms. Pearlyn See Shen Yen at Nanyang Technological University for their help and support in the laboratory.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Abbasi T, Abbasi SA (2011) Sources of pollution in rooftop rainwater harvesting systems and their control. *Crit Rev Environ Sci Technol* 41:2097–2167
- Agapitova, N, Navarrete MC., Barkatky, R. (2017). Waterlife: improving access to safe drinking water in India. World Bank, Washington, DC. © World Bank. <https://openknowledge.worldbank.org/handle/10986/27664> License: CC BY 3.0 IGO
- Al-Khashman OA, Jaradat AQ, Salameh E (2013) Five-year monitoring study of chemical characteristics of Wet atmospheric precipitation in the southern region of Jordan. *Environ Monit Assess* 185:5715–5727
- Allan, MA. (2004). Manual for the GAW precipitation chemistry programme: guidelines, data quality objectives and standard operating procedures (World Meteorological Organization Geneva (Switzerland))
- Al-Momani I (2003) Trace elements in atmospheric precipitation at Northern Jordan measured by ICP-MS: acidity and possible sources. *Atmos Environ* 37:4507–4515
- Amodio M, Catin S, Dambruoso PR, de Gennaro G, Di Gilio A, Giungato P, Laiola E, Marzocca A, Mazzone A, Sardaro A et al (2014) Atmospheric deposition: sampling procedures, analytical methods, and main recent findings from the scientific literature(Hindawi). *Adv Meterol* 2014:1–27
- Anatolaki Ch, Tsitouridou R (2009) Relationship between acidity and ionic composition of wet precipitation: a two years study at an urban site, Thessaloniki, Greece. *Atmos Res* 92:100–113
- Barbieri M, Sappa G, Vitale S, Parisse B, Battistel M (2014) Soil control of trace metals concentrations in landfills: a case study of the largest landfill in Europe, Malagrotta, Rome. *J Geochem Explor* 143:146–154
- Berg T, Røyset O, Steinnes E (1994) Trace elements in atmospheric precipitation at Norwegian background stations (1989–1990) measured by ICP-MS. *Atmos Environ* 28:3519–3536
- Bhanarkar AD, Rao PS, Gajghate DG, Nema P (2005) Inventory of SO₂, PM and toxic metals emissions from industrial sources in Greater Mumbai, India. *Atmos Environ* 39:3851–3864
- Bhardwaj V, Singh DS (2011) Surface and groundwater quality characterization of Deoria district, Ganga plain, India. *Environ Earth Sci* 63:383–395
- Bhattacharya S (2015) Traditional water harvesting structures and sustainable water management in India: a socio-hydrological review. *Int Lett Nat Sci* 37:30–38
- BIS IS: 10500 (2012) Indian Standard: Drinking Water–Specification, first revision. Bureau of Indian Standards, New Delhi, India
- Budhavant KB, Rao PSP, Safai PD, Ali K (2011) Influence of local sources on rainwater chemistry over Pune region, India. *Atmos Res* 100:121–131
- de Burbure C, Buchet J-P, Leroyer A, Nisse C, Haguenoer J-M, Mutti A, Smerhovský Z, Cikrt M, Trzcinka-Ochocka M, Razniewska G et al (2006) Renal and neurologic effects of cadmium, lead, mercury, and arsenic in children: evidence of early effects and multiple interactions at environmental exposure levels. *Environ Health Perspect* 114:584–590
- Cao Y-Z, Wang S, Zhang G, Luo J, Lu S (2009) Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. *Atmos Res* 94:462–469
- Chakraborty B, Gupta A (2014) Rainwater quality analysis in selected areas of eastern and northeastern India. *Int J Environ Eng* 1:5
- Chance R, Jickells TD, Baker AR (2015) Atmospheric trace metal concentrations, solubility and deposition fluxes in remote marine air over the south-east Atlantic. *Mar Chem* 177:45–56
- Charlson RJ, Rodhe H (1982) Factors controlling the acidity of natural rainwater. *Nature* 295:683–685
- Chaudhary S, Firdaus U, Ali SM, Mahdi AA (2018) Factors associated with elevated blood lead levels in children. *Indian Pediatr* 55:38–40
- Cheng Y, Liu Y, Huo M, Sun Q, Wang H, Chen Z, Bai Y (2011) Chemical characteristics of precipitation at Nanping Mangdang Mountain in eastern China during spring. *J Environ Sci* 23:1350–1358
- Chifflet S, Amouroux D, Bérail S, Barre J, Van TC, Baltrons O, Brune J, Dufour A, Guinot B, Mari X (2018) Origins and discrimination between local and regional atmospheric pollution in Haiphong (Vietnam), based on metal(loid) concentrations and lead isotopic ratios in PM₁₀. *Environ Sci Pollut Res* 25:26653–26668
- Cong Z, Kang S, Zhang Y, Li X (2010) Atmospheric wet deposition of trace elements to central Tibetan Plateau. *Appl Geochem* 25:1415–1421
- Das N, Das R, Chaudhury GR, Das SN (2010) Chemical composition of precipitation at background level. *Atmos Res* 95:108–113
- Das R, Khezri B, Srivastava B, Datta S, Sikdar PK, Webster RD, Wang X (2015) Trace element composition of PM_{2.5} and PM₁₀ from Kolkata – a heavily polluted Indian metropolis. *Atmos Pollut Res* 6:742–750
- Das R, Mohtar BM, TRakshitShome ADDX, Wang (2018) Sources of atmospheric lead (Pb) in and around an Indian megacity. *Atmos Environ* 193:57–65
- Das R, Wang X, Itoh M, Shiodera S, Kuwata M (2019) Estimation of metal emissions from tropical peatland burning in Indonesia by controlled laboratory experiments. *J Geophys Res: Atmos* 124:6583–6599

28. Deboudt K, Flament P, Bertho M-L (2004) Cd, Cu, Pb and Zn Concentrations in atmospheric wet deposition at a coastal station in Western Europe. *Water Air Soil Pollut* 151:335–359
29. Deguillaume L, Leriche M, Desboeufs K, Mailhot G, George C, Chaumerliac N (2005) Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters. *Chem Rev* 105:3388–3431
30. Dkhar EN, Dkhar PS, Anal JMH (2014) Trace elements analysis in drinking water of Meghalaya by using graphite furnace-atomic absorption spectroscopy and in relation to environmental and health issues (Hindawi). *J chem* 2014:1–7
31. Domínguez I, Ward S, Mendoza JG, Rincón CI, Oviedo-Ocaña ER (2017) End-user cost-benefit prioritization for selecting rainwater harvesting and greywater reuse in social housing. *Water* 9:516
32. Duan L, Song J, Xu Y, Li X, Zhang Y (2010) The distribution, enrichment and source of potential harmful elements in surface sediments of Bohai Bay, North China. *J Hazard Mat* 183:155–164
33. EPA U (2009). National primary drinking water regulations. Arsenic and Clarifications To
34. Flanagan PJ (1988). Parameters of water quality: interpretation and standards (Environmental Research Unit)
35. de Foy B, Krotkov NA, Be N, Herndon SC, Huey LG, Martinez AP, Ruiz-Suarez LG., Wood EC, Zavala M, Molina LT (2009). Hit from both sides: tracking industrial and volcanic plumes in Mexico City with surface measurements and OMI SO₂ retrievals during the MILAGRO field campaign. *Copernicus*
36. Gheorghe IF, Ion B (2011) The effects of air pollutants on vegetation and the role of vegetation in reducing atmospheric pollution. The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources
37. Gillette DA, Stensland GJ, Williams AL, Barnard W, Gatz D, Sinclair PC, Johnson TC (1992) Emissions of alkaline elements calcium, magnesium, potassium, and sodium from open sources in the contiguous United States. *Global Biogeochem Cycles* 6:437–457
38. Glendenning CJ, van Ogtrop FF, Mishra AK, Vervoort RW (2012) Balancing watershed and local scale impacts of rain water harvesting in India—A review. *Agric Water Manag* 107:1–13
39. Gobre T, Salve PR, Krupadam RJ, Bansiwai A, Shastry S, Wate SR (2010) Chemical composition of precipitation in the coastal environment of India. *Bull Environ Contam Toxicol* 85:48–53
40. Gowd SS, Reddy MR, Govil PK (2010) Assessment of heavy metal contamination in soils at Jajmau (Kanpur) and Unnao industrial areas of the Ganga Plain, Uttar Pradesh, India. *J Hazard Mater* 174:113–121
41. Grantz DA, Garner JHB, Johnson DW (2003) Ecological effects of particulate matter. *Environ Int* 29:213–239
42. Guagliardi I, Buttafuoco G, Cicchella D, De Rosa R (2013) A multivariate approach for anomaly separation of potentially toxic trace elements in urban and peri-urban soils: an application in a southern Italy area. *J Soils Sediments* 13:117–128
43. Guo J, Kang S, Huang J, Zhang Q, Tripathi L, Sillanpää M (2015) Seasonal variations of trace elements in precipitation at the largest city in Tibet, Lhasa. *Atmos Res* 153:87–97
44. Gupta S, Nayek S, Chakraborty D (2016) Hydrochemical evaluation of Rangit river, Sikkim, India: using water quality Index and multivariate statistics. *Environ Earth Sci* 75:567
45. Gurusurthy GP, Balakrishna K, Tripti M, Riotte J, Audry S, Braun J-J, Lambs L, Udaya Shankar HN (2015) Sources of major ions and processes affecting the geochemical and isotopic signatures of subsurface waters along a tropical river, Southwestern India. *Environ Earth Sci* 73:333–346
46. Halder D, Halder S, Das (Saha), P., and Halder, G. (2016) Assessment of water quality of Damodar River in South Bengal region of India by Canadian Council of Ministers of Environment (CCME) Water Quality Index: a case study. *Desalination Water Treat* 57:3489–3502
47. Hjortenkranz DST, Bergbäck BG, Hæggerud AV (2007) Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. *Environ Sci Technol* 41:5224–5230
48. Hovmand MF, Kemp K, Kystol J, Johnsen I, Riis-Nielsen T, Pacyna JM (2008) Atmospheric heavy metal deposition accumulated in rural forest soils of southern Scandinavia. *Environ Pollut* 155:537–541
49. Hu G-P, Balasubramanian R (2003) Wet deposition of trace metals in Singapore. *Water Air Soil Pollut* 144:285–300
50. Hu Y, Cheng H (2013) Application of stochastic models in identification and apportionment of heavy metal pollution sources in the surface soils of a large-scale region. *Environ Sci Technol* 47:3752–3760
51. Huston R, Chan YC, Gardner T, Shaw G, Chapman H (2009) Characterisation of atmospheric deposition as a source of contaminants in urban rainwater tanks. *Water Res* 43:1630–1640
52. Hutton M (1983) Sources of cadmium in the environment. *Eco-toxicol Environ Saf* 7:9–24
53. Jawad AI Obaidy AHM, Joshi H (2006) Chemical composition of rainwater in a tropical urban area of northern India. *Atmos Environ* 40:6886–6891
54. Jeevanandam M, Kannan R, Srinivasulu S, Rammohan V (2006) Hydrogeochemistry and groundwater quality assessment of lower part of the Ponnaiyar River Basin, Cuddalore district, South India. *Environ Monit Assess* 132:263–274
55. Jha PK, Tiwari J, Singh UK, Kumar M, Subramanian V (2009) Chemical weathering and associated CO₂ consumption in the Godavari river basin, India. *Chem Geol* 264:364–374
56. Kanellopoulou EA (2001) Determination of heavy metals in wet deposition of Athens. *Global Nest J* 3:45–50
57. Karar K, Gupta AK (2007) Source apportionment of PM₁₀ at residential and industrial sites of an urban region of Kolkata, India. *Atmos Res* 84:30–41
58. Kasprzak KS, Sunderman FW, Salnikow K (2003) Nickel carcinogenesis. *Mutat Res/Fundam Mol Mech Mutagen* 533:67–97
59. Kayee J, Sompongchaiyakul P, Sanwlan N, Bureekul S, Wang X, Das R (2020) Metal concentrations and source apportionment of pm_{2.5} in Chiang Rai and Bangkok, Thailand during a biomass burning season. *ACS Earth Space Chem* 4:1213–1226
60. Keresztesi Á, Nita I-A, Boga R, Birsan M-V, Bodor Z, Szép R (2020) Spatial and long-term analysis of rainwater chemistry over the conterminous United States. *Environ Res* 188:109872
61. Khare P, Goel A, Patel D, Behari J (2004) Chemical characterization of rainwater at a developing urban habitat of Northern India. *Atmos Res* 69:135–145
62. Kibria G, Hossain MM, Mallick D, Lau TC, Wu R (2016) Monitoring of metal pollution in waterways across Bangladesh and ecological and public health implications of pollution. *Chemosphere* 165:1–9
63. Kim ND, Fergusson JE (1994) The concentrations, distribution and sources of cadmium, copper, lead and zinc in the atmosphere of an urban environment. *Sci Total Environ* 144:179–189
64. Kim G, Scudlark JR, Church TM (2000) Atmospheric wet deposition of trace elements to Chesapeake and Delaware bays. *Atmos Environ* 34:3437–3444
65. Kitayama K, Murao N, Hara H (2010) PMF analysis of impacts of SO₂ from Miyakejima and Asian continent on precipitation sulfate in Japan. *Atmos Environ* 44:95–105
66. Kulshrestha UC, Kulshrestha MJ, Sekar R, Sastry GSR, Vairamani M (2003) Chemical characteristics of rainwater at an urban site of south-central India. *Atmos Environ* 37:3019–3026

67. Kumar D, Katoch SS (2014) Harnessing 'water tower' into 'power tower': a small hydropower development study from an Indian prefecture in western Himalayas. *Renew Sustain Energy Rev* 39:87–101
68. Kumar B, Rai SP, Kumar US, Verma SK, Garg P, Kumar SVV, Jaiswal R, Purendra BK, Kumar SR, Pande NG (2010) Isotopic characteristics of Indian precipitation. *Water Resour Res*. <https://doi.org/10.1029/2009WR008532>
69. Landing WM, Caffrey JM, Nolek SD, Gosnell K (2009) Atmospheric wet deposition of mercury and other trace elements in Pensacola. *Florida Atmos Chem Phys Discuss* 9:27649–27674
70. Lee J-M, Boyle EA, Suci Nurhati I, Pfeiffer M, Meltzner AJ, Suwargadi B (2014) Coral-based history of lead and lead isotopes of the surface Indian Ocean since the mid-20th century. *Earth Planet Sci Lett* 398:37–47
71. Li X, Lee S, Wong S, Shi W, Thornton I (2004) The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. *Environ Pollut* 129:113–124
72. Menz FC, Seip HM (2004) Acid rain in Europe and the United States: an update. *Environ Sci Policy* 7:253–265
73. Meyer C, Diaz-de-Quijano M, Monna F, Franchi M, Toussaint M-L, Gilbert D, Bernard N (2015) Characterisation and distribution of deposited trace elements transported over long and intermediate distances in north-eastern France using Sphagnum peatlands as a sentinel ecosystem. *Atmos Environ* 101:286–293
74. Migliavacca D, Teixeira EC, Wiegand F, Machado ACM, Sanchez J (2005) Atmospheric precipitation and chemical composition of an urban site, Guaíba hydrographic basin, Brazil. *Atmos Environ* 39:1829–1844
75. Mijic Z, Stojic A, Perisic M, Rajsic S, Tasic M (2012) Receptor modeling studies for the characterization of PM10 pollution sources in Belgrade. *CI and CEQ* 18:623–634
76. Mirzaei S, Hashemi H, Hoseini M (2018) Concentration and potential source identification of trace elements in wet atmospheric precipitation of Shiraz. *Iran J Environ Health Sci Eng* 16:229–237
77. Morrow AC, Dunstan RH, Coombes PJ (2010) Elemental composition at different points of the rainwater harvesting system. *Sci Total Environ* 408:4542–4548
78. Muezzinoglu A, Cizmecioglu SC (2006) Deposition of heavy metals in a Mediterranean climate area. *Atmos Res* 81:1–16
79. Mukherjee A, Bhattacharya P, Shi F, Fryar AE, Mukherjee AB, Xie ZM, Jacks G, Bundschuh J (2009) Chemical evolution in the high arsenic groundwater of the Huhhot basin (Inner Mongolia, PR China) and its difference from the western Bengal basin (India). *Appl Geochem* 24:1835–1851
80. Niu H, He Y, Lu XX, Shen J, Du J, Zhang T, Pu T, Xin H, Chang L (2014) Chemical composition of rainwater in the Yulong Snow Mountain region, Southwestern China. *Atmos Res* 144:195–206
81. Norman M, Das SN, Pillai AG, Granat L, Rodhe H (2001) Influence of air mass trajectories on the chemical composition of precipitation in India. *Atmos Environ* 35:4223–4235
82. Organization WH (2017) Guidelines for drinking-water quality: first addendum to the, 4th edn. First Addendum to the Fourth Edition, Guidelines for Drinking-Water Quality
83. Ozkurt N, Sari D, Akalin N, Hilmioğlu B (2013) Evaluation of the impact of SO₂ and NO₂ emissions on the ambient air-quality in the Çan-Bayramiç region of northwest Turkey during 2007–2008. *Sci Total Environ* 456–457:254–266
84. Pacyna JM, Pacyna EG (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ Rev* 9:269–298
85. Pacyna JM, Pacyna EG, Aas W (2009) Changes of emissions and atmospheric deposition of mercury, lead, and cadmium. *Atmos Environ* 43:117–127
86. Pan YP, Wang YS (2015) Atmospheric wet and dry deposition of trace elements at 10 sites in Northern China. *Atmos Chem Phys* 15:951–972
87. Peng Y-L, Wang Y-M, Qin C-Q, Wang D-Y (2014) Concentrations and deposition fluxes of heavy metals in precipitation in core urban areas, Chongqing. *Huan Jing Ke Xue* 35:2490–2496
88. Prathibha P, Kothai P, Saradhi IV, Pandit GG, Puranik VD (2010) Chemical characterization of precipitation at a coastal site in Trombay, Mumbai, India. *Environ Monit Assess* 168:45–53
89. Rajeev P, Rajput P, Gupta T (2016) Chemical characteristics of aerosol and rain water during an El Niño and PDO influenced Indian summer monsoon. *Atmos Environ* 145:192–200
90. Rao PSP, Tiwari S, Matwale JL, Pervez S, Tunved P, Safai PD, Srivastava AK, Bisht DS, Singh S, Hopke PK (2016) Sources of chemical species in rainwater during monsoon and non-monsoonal periods over two mega cities in India and dominant source region of secondary aerosols. *Atmos Environ* 146:90–99
91. Ravichandran C, Padmanabhamurty B (1994) Acid precipitation in Delhi, India. *Atmos Environ* 28:2291–2297
92. Rivera-Rivera DM, Escobedo-Urías DC, Jonathan MP, Sujitha SB, Chidambaram S (2020) Evidence of natural and anthropogenic impacts on rainwater trace metal geochemistry in central Mexico: a statistical approach. *Water* 12:192
93. Rudnick RL, Gao S (2003) Composition of the continental crust. *Treat Geochem* 3:659
94. Sakata M, Asakura K (2009) Factors contributing to seasonal variations in wet deposition fluxes of trace elements at sites along Japan Sea coast. *Atmos Environ* 43:3867–3875
95. Sakata M, Marumoto K, Narukawa M, Asakura K (2006) Regional variations in wet and dry deposition fluxes of trace elements in Japan. *Atmos Environ* 40:521–531
96. Sakihama H, Ishiki M, Tokuyama A (2008) Chemical characteristics of precipitation in Okinawa Island, Japan. *Atmos Environ* 42:2320–2335
97. Salve PR, Maurya A, Wate SR, Devotta S (2008) Chemical composition of major ions in rainwater. *Bull Environ Contam Toxicol* 80:242–246
98. Samara C, Tsitouridou R (2000) Fine and Coarse ionic aerosol components in relation to wet and dry deposition. *Water Air Soil Pollut* 120:71–88
99. Santos PSM, Otero M, Santos EBH, Duarte AC (2011) Chemical composition of rainwater at a coastal town on the southwest of Europe: What changes in 20years? *Sci Total Environ* 409:3548–3553
100. Satyanarayanan M, Balaram V, Al Hussin MS, Al Jemali MAR, Rao TG, Mathur R, Dasaram B, Ramesh SL (2007) Assessment of groundwater quality in a structurally deformed granitic terrain in Hyderabad, India. *Environ Monit Assess* 131:117–127
101. Seinfeld, J.H., and Pandis, S.N. (2016). Atmospheric chemistry and physics: from air pollution to climate change (John Wiley and Sons)
102. Shao X, Cheng H, Li Q, Lin C (2013) Anthropogenic atmospheric emissions of cadmium in China. *Atmos Environ* 79:155–160
103. Sharma P, Rai V (2018) Assessment of rain water chemistry in the Lucknow metropolitan city. *Appl Water Sci* 8:67
104. Sharma A, Singh AK, Kumar K (2012) Environmental geochemistry and quality assessment of surface and subsurface water of Mahi River basin, western India. *Environ Earth Sci* 65:1231–1250
105. Sheeja RV, Sheela AM, Jaya S, Joseph S (2020) Assessment of water quality of a tropical river with special reference to ions. *Current J App Sci Technol* 97–116. <https://doi.org/10.9734/cjast/2020/v39i1830779>
106. Shukla SP, Mukesh S (2010) Neutralization of rainwater acidity at Kanpur, India. *Tellus B: Chem Phys Meteorol* 62:172–180

107. Shukla SP, Sharma M (2010) Neutralization of rainwater acidity at Kanpur, India. *Tellus B* 62:172–180
108. Singh AK, Mondal GC, Kumar S, Singh TB, Tewary BK, Sinha A (2008) Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin. *Environmental Geology, India*. <https://doi.org/10.1007/s00254-007-0860-1>
109. Singh AK, Mondal GC, Kumar S, Singh KK, Kamal KP, Sinha A (2007) Precipitation chemistry and occurrence of acid rain over Dhanbad, Coal City of India. *Environ Monit Assess* 125:99–110
110. Singh KP, Singh VK, Malik A, Sharma N, Murthy RC, Kumar R (2007) Hydrochemistry of wet atmospheric precipitation over an urban area in northern Indo-Gangetic plains. *Environ Monit Assess* 131:237–254
111. Singh N, Murari V, Kumar M, Barman SC, Banerjee T (2017) Fine particulates over South Asia: review and meta-analysis of PM_{2.5} source apportionment through receptor model. *Environ Pollut* 223:121–136
112. Smith SJ, van Aardenne J, Klimont Z, Andres RJ, Volke A, Delgado Arias S (2011) Anthropogenic sulfur dioxide emissions: 1850–2005. *Atmos Chem Phys* 11:1101–1116
113. Song F, Gao Y (2009) Chemical characteristics of precipitation at metropolitan Newark in the US East Coast. *Atmos Environ* 43:4903–4913
114. Sumari SM, Muhamad-Darus F, Kantasamy N, Urban Sinyaw S, ak, (2010) Rainwater characterization at global atmospheric watch in Danum valley, Sabah. 2010 International Conference on Science and Social Research (CSSR 2010), (Kuala Lumpur. IEEE), Malaysia, pp 479–484
115. Szép R, Bodor Z, Miklóssy I, Niță I-A, Oprea OA, Keresztesi Á (2019) Influence of peat fires on the rainwater chemistry in intra-mountain basins with specific atmospheric circulations (Eastern Carpathians, Romania). *Sci Total Environ* 647:275–289
116. Tang X (2007) The studies and analyses of precipitation acidity and chemical composition in industriale state locates in north bank of the Yangtze River. Nanjing. Nanjing University of Information Science & Technology, Nanjing
117. Teixeira EC, Migliavacca D, Pereira Filho S, Machado ACM, Dallarosa JB (2008) Study of wet precipitation and its chemical composition in South of Brazil. *An Acad Bras Ciênc* 80:381–395
118. Tian HZ, Lu L, Cheng K, Hao JM, Zhao D, Wang Y, Jia WX, Qiu PP (2012) Anthropogenic atmospheric nickel emissions and its distribution characteristics in China. *Sci Total Environ* 417–418:148–157
119. Tiwari S, Hopke PK, Thimmaiah D, Dumka UC, Srivastava AK, Bisht DS, Rao PSP, Chate DM, Srivastava MK, Tripathi SN (2016) Nature and sources of ionic species in precipitation across the Indo-Gangetic Plains. *India Aerosol Air Qual Res* 16:943–957
120. Topçu S, Incecik S, Atimtay AT (2002) Chemical composition of rainwater at EMEP station in Ankara, Turkey. *Atmos Res* 65:77–92
121. Vahlsing C, Smith KR (2012) Global review of national ambient air quality standards for PM₁₀ and SO₂ (24 h). *Air Qual Atmos Health* 5:393–399
122. Varol M, Şen B (2012) Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *CATENA* 92:1–10
123. Velis M, Conti KI, Biermann F (2017) Groundwater and human development: synergies and trade-offs within the context of the sustainable development goals. *Sustain Sci* 12:1007–1017
124. Vlastos D, Antonopoulou M, Lavranou A, Efthimiou I, Dailianis S, Hela D, Lambropoulou D, Paschalidou AK, Kassomenos P (2019) Assessment of the toxic potential of rainwater precipitation: first evidence from a case study in three Greek cities. *Sci Total Environ* 648:1323–1332
125. Wetang'ula GN, Wamalwa HM. Trace elements in rainfall collected around Menengai Area Kenya. In: *Proceedings World Geothermal Congress*, pp 13–25
126. Wu Y-S, Fang G-C, Lee W-J, Lee J-F, Chang C-C, Lee C-Z (2007) A review of atmospheric fine particulate matter and its associated trace metal pollutants in Asian countries during the period 1995–2005. *J Hazard Mat* 143:511–515
127. Xing J, Song J, Yuan H, Wang Q, Li X, Li N, Duan L, Qu B (2017) Atmospheric wet deposition of dissolved trace elements to Jiaozhou Bay, North China: fluxes, sources and potential effects on aquatic environments. *Chemosphere* 174:428–436
128. Xu Z, Li Y, Tang Y, Han G (2009) Chemical and strontium isotope characterization of rainwater at an urban site in Loess Plateau, Northwest China. *Atmos Res* 94:481–490
129. Yang F, Tan J, Shi ZB, Cai Y, He K, Ma Y, Duan F, Okuda T, Tanaka S, Chen G (2012) Five-year record of atmospheric precipitation chemistry in urban Beijing, China. *Atmos Chem Phys* 12:2025–2035
130. Ym L, Yp P, Ys W, Yf W, Xr L (2012) Chemical characteristics and sources of trace metals in precipitation collected from a typical industrial city in Northern China. *Huan Jing Ke Xue* 33:3712–3717

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.