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Chemical composition of rainwater around an industrial region in Mumbai

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Chemical analysis of rainwater samples collected at Kalyan, a downwind location of a large industrial belt, and at Alibag and Colaba, the upwind locations, during the southwest monsoon seasons of 1994 and 1995 and comparison with similar data of 1973–74 reveal that pH of rainwater at Kalyan which was alkaline 20 years ago became acidic due to long-term effect of pollutants. A decreasing trend in excess SO_4 was observed at Colaba and Kalyan, which is attributed to the pollution control measures adopted by industries and switching over from coal to natural gas which contains low sulphur. Whereas the increasing trend in NO_x observed at Kalyan and Colaba, is attributable to increased automobile emission.

RAINWATER serves as a collector of many minor constituents of the atmosphere. Hence, the results of rainwater analysis help to reveal the chemical state of the air in which the rain-bearing clouds have formed. In addition, chemical composition of rain plays a critical role in defining the level of acid deposition and the state of some important bio-geochemical cycles of the earth–atmosphere system.

Sulphur dioxide and nitrogen dioxide emitted by burning of coal, natural gas, fuel oil and petrol, are oxidized and hydrolysed to sulphuric acid and nitric acid which subsequently give rise to acid rain. The acid content of rain in many parts of the world has steadily risen for the past several years, as the countries have become more and more industrialized and have increased the use of fossil fuel. Vast areas of the northern hemisphere, including Central Europe, Scandinavia, Northeast United States and Canada have been reported to be affected by acid rain. Asia is a region of rapid population growth and industrialization, and one with increased requirement for energy. Thus industrial development and higher standards of

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living in Asian countries in the future, might repeat the alarm of acidification as has happened in Europe and North America. Southern China is already in the grip of acid rain due to rapid industrialization.

There are very good reasons to consider environmental problems facing developing tropical countries such as India, where significant rates of population growth cause large increase in SO_2 and NO_2 emissions. According to estimates of Streets *et al.*[1], the emission of SO_2 in India was 4437.2 Gg yr^{-1} in 1990, which increased by 21% up to 1995 and 29% up to 1997. Similarly emission of NO_2 was 3235.5 Gg yr^{-1} in 1990, which increased by 28% up to 1995 and 34% by the end of 1997.

In India, studies relating to the acid rain are limited[2–11]. The common feature in most of the studies on the chemistry of Indian precipitation is the high pH value all over the country. The acid rain is reported only in a few industrial pockets[12–14].

Mumbai is one of the most important commercial and industrial centres in India. Kalyan, a large urban area in Mumbai region, comes under downwind of a large industrial belt during the southwest monsoon (SW) season. In order to see the effect of anthropogenic pollutants on precipitation at Kalyan, rainwater samples were collected there during SW monsoon seasons of 1994 and 1995, and at two other locations in the upwind, namely, Alibag and Colaba. In this paper, the main objective is to study the precipitation chemistry over industrial and non-industrial regions and compare the same with the past data.

The magnitude of wet deposition of pollutants is of considerable importance as it indicates the intensity and local impact of the pollution source. Thus, this type of study is useful in assessing the air quality in industrial areas and in implementing emission-reduction policies.

Location of sampling sites

Location of the sampling sites, namely Alibag (18°38′N, 72°52′E), Colaba (18°52′N, 72°47′E) and Kalyan (19°15′N, 73°07′E) is shown in Figure 1. Alibag, Colaba and Kalyan are located in Raigad, Brahan Mumbai and Thane districts respectively in Maharashtra. The area that includes a portion of the three districts (shown in Figure 1) is called the Mumbai region in the present study. All the three sampling sites are situated on the windward side of the Western Ghats. Alibag and Colaba are situated on the west coast of India and Kalyan on the northeastern side of the Mumbai region. There are about 40,000 large, medium and small-scale industries existing in the vicinity of Mumbai city[15]. Majority of them are situated in the Chembur–Thane–Belapur belt which is reported to be a highly industrialized area of the city. Solid strips in Figure 1 represent the areas of major industrial establishments. Major industrial establishments located in the above areas are refineries, petrochemical complexes, cotton mills, textile factories, synthetic material plants, thermal power stations, chemical and fertilizers factories, etc.

Alibag is located at about 30 km away to the south of Colaba and is relatively free from industrial pollution. Colaba, which is located on the southwestern tip of the urban industrial complexes, is no doubt in the upwind side of pollution sources. But, being situated in the immediate vicinity of some of the pollution sources, Colaba may not be free from industrial pollution. Kalyan is surrounded by industrial complexes and is most likely to be affected by the pollutants through transport process.

The sampling sites – Alibag, Colaba and Kalyan – come under the influence of the SW monsoon during June to September. The country as a whole receives nearly 80% of its annual rainfall during this season.

During the SW monsoon season, the winds over this region are normally from the SW in the lower troposphere. The depth of this monsoon current is about 6 km on the west coast. The daily meteorological data for surface wind direction and speed for Alibag and Colaba were taken from India Meteorological Department for the monsoon months (June–September) of 1994 and 1995. Wind roses are then plotted for Alibag and Colaba and are shown in Figure 2. However, meteorological data are not available for Kalyan. Hence, wind roses could not be plotted for Kalyan.

Sampling and analysis

About 125, 141 and 71 rainwater samples were collected at Alibag, Colaba and Kalyan respectively during the two

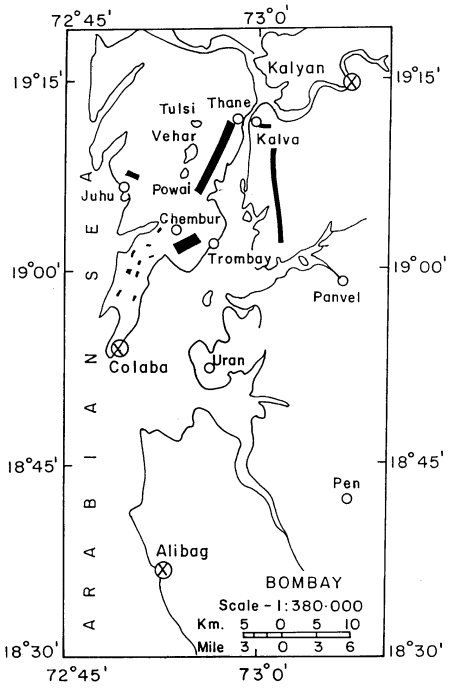

Figure 1. Location of sampling sites.

monsoon seasons of 1994 and 1995 using stainless-steel funnels of 30 cm diameter fitted onto one-litre capacity polyethylene bottle.

Rainwater samples were collected on the terrace of the Abhinav Vidhya Mandir School at Kalyan at the height of about 10 m above the ground. The samples were collected at the campus of Regional Meteorological Centre, Colaba and at the Geo-magnetic Observatory, Alibag. The sampling height was about 1 m above the ground, at these two sites.

To avoid dry deposition, the funnels were washed with distilled water in the morning and evening. However, contamination due to dry deposition could not be completely avoided. The sample was removed at 0830 h, if it rained during the previous night or at 1730 h if it rained during the daytime. The rainwater samples were periodically brought to the Institute, filtered through Whatman-41 filter paper and refrigerated at 4°C in the chemistry laboratory till all ionic components were analysed.

The concentrations of Na, K, Ca and Mg in the above samples were determined using Perkin-Elmer 373, double-beam Atomic Absorption Spectrophotometer with air–acetylene flame. The concentrations of SO_4, NO_3, NH_4 and Cl were determined using colorimetric methods. SO_4 was determined by barium iodate method[16] and NO_3 was determined by brucine sulphate method[17]. The concentration of Cl was determined by mercuric thiocynate method[18] and that of NH_4 was determined using Berthelate colour-reaction procedure[19]. The pH values were measured with a digital pH meter, using reference (KCl) and glass electrodes, standardized with pH of 4.0 and 9.2 reference buffers before pH determination.

The calibrations for different chemical constituents were obtained by preparing low-level standard solutions using AR-grade chemicals. These calibrations were periodically repeated to check the accuracy. The analytical errors were nominal and varied within ± 10%.

The data obtained using the above methods of analysis were subjected to statistical filtering technique described elsewhere[20], to identify and eliminate data from samples that may have been heavily contaminated.

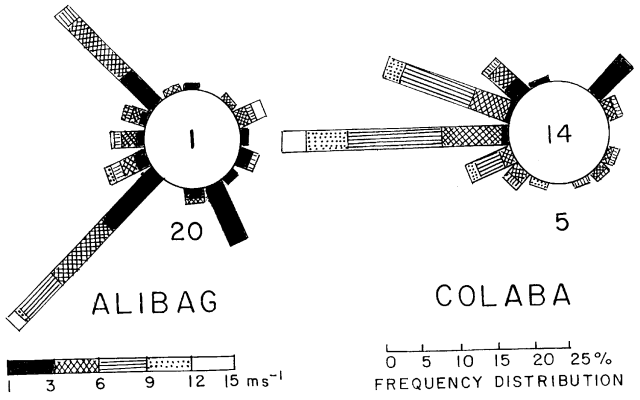

Figure 2. Wind roses for Alibag and Colaba for the period June–September 1994–95.

Results and discussion

Chemical composition of rainwater

The average concentration (mg l^{-1}) of major ionic components, pH value and standard deviation (SD) in rainwater at Alibag, Colaba and Kalyan during monsoon seasons of 1994 and 1995 are given in Table 1. The chemical composition of rainwater at Chembur[21] is also included for comparison. The relative percentage contribution of different anions and cations to the total ionic content at the three locations was calculated from the average composition of Alibag, Colaba and Kalyan, and plotted in Figure 3. Relative percentage contribution was also calculated from the composition at Chembur[21] and plotted. From Figure 3, it is seen that in rainwater at Alibag and Colaba, sea salt (Na and Cl) contributed the most (69% and 54%) to total ionic content. The concen-

Table 1. Average ionic concentration (mg l^{-1}), pH, and standard deviation (SD) in rainwater at Alibag, Colaba and Kalyan during 1994–95

Location	Cl	SO_4	NO_3	NH_4	Na	K	Ca	Mg	pH
Alibag									
Average	8.37	1.77	0.57	0.15	5.07	0.32	2.66	0.77	6.74
SD	5.97	1.50	0.47	0.13	4.39	0.27	1.90	0.50	0.46
Colaba									
Average	6.10	2.48	2.08	0.22	4.12	0.35	3.10	0.71	6.38
SD	3.96	2.12	1.19	0.11	2.47	0.21	1.78	0.50	0.50
Kalyan									
Average	4.75	5.30	4.10	0.26	3.40	0.39	2.60	0.58	5.28
SD	3.07	2.07	1.87	0.15	2.11	0.32	1.23	0.41	0.96
Chembur*									
Average	5.00	20.20	N.R.	2.10	2.20	1.10	3.10	0.68	4.80

*From Sequeira[21].

tration of NO_3 was low at Alibag (3%) and Colaba (11%). On the contrary, at Kalyan, SO_4 and NO_3 together (SO_4 + NO_3) contributed the most (44%) to the total ionic content followed by Cl, Na and Ca. The percentage contribution of SO_4 alone (NO_3 was not reported) was maximum (59%), followed by those of Cl, Ca, Na at Chembur, which reflects the influence of industrial activity in the region.

The average concentration of SO_4 is maximum at Chembur (20.2 mg l^{-1}), a highly industrialized location in Mumbai and minimum at Alibag (1.77 mg l^{-1}) (Table 1). Although Colaba is situated upwind of the industrial belts on the west coast, the average concentration of SO_4 (2.48 mg l^{-1}) was higher (one and a half times more) than that at Alibag (1.77 mg l^{-1}). This could be due to the proximity of Colaba to the industrial complexes. Low concentration of SO_4 at Alibag indicates that the location is relatively free from pollution. The second maximum concentration was observed at Kalyan (5.3 mg l^{-1}) which is situated downwind of industrial complexes. Sulphate in rain arises mainly from anthropogenic emission, which is indicated by the above observations. The sulphate from sea spray is neutral and does not increase the acidity of rainwater[22]. However, SO_4 from anthropogenic sources is considered as a major component which increases the H-ion concentration in rainwater and hence decreases its pH. The average concentration of NO_3 was minimum at Alibag (0.57 mg l^{-1}) and maximum at Kalyan (4.1 mg l^{-1}). The presence of NO_3 in rainwater is considered to be responsible for the increase of H-ion concentration.

With growing energy consumption, the NO_x emissions are expected to rise. If NO_2 is differentiated according to its sources, the substantial part is found to be due to traffic in urban areas.

The average concentration of NH_4 was maximum at Kalyan (0.26 mg l^{-1}) and minimum at Alibag (0.15 mg l^{-1}). The important sources of atmospheric NH_3 are considered to be animal wastes, fertilizers and some industrial activities[23,24].

It is surmised that observed concentrations of some ionic species at Mumbai (Table 1) reflect the impact of pollution sources. Hence, ionic concentrations of rainwater at the three locations (Table 1) were compared with data from Gopalpur near Agra[9] and Hyderabad in India[25], Izmir (industrial area) in Turkey[26], and Seoul in Korea[27] (Table 2).

The area around Gopalpur is predominantly in agricultural use and there are no other point sources at the site. Hyderabad is growing industrially and there is exponential increase in the population and vehicular pollution. The industrial establishments located near Izmir are a refinery, petrochemical complex, iron work plant, paper and pulp factory and fertilizer plant. Seoul is an urban station in Korea.

It is evident from Table 2 that the concentrations of acidic components SO_4 and NO_3 are higher at Kalyan than those reported at other locations. The concentration of Ca at Kalyan is similar to that at Gopalpur, but higher than other reported locations. Since concentrations of acidic components SO_4 and NO_3 were double at Kalyan compared to that at Seoul, the pH value at Kalyan was expected to be more acidic than that at Seoul. On the contrary, pH at Seoul is more acidic. This may be due to the fact that concentration of Ca, which neutralizes the acidity, is four times higher at Kalyan than that at Seoul.

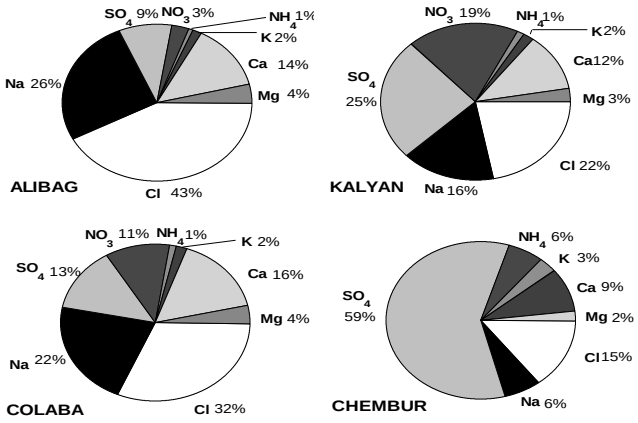

Figure 3. Percentage contribution of ionic components to the total ionic content of rainwater.

Ratios of major components to sodium

The ionic constituents such as SO_4, K, Ca and Mg in precipitation are derived either from marine or from non-marine origins, such as anthropogenic and natural emis-

Table 2. Ionic concentration of rainwater (μeq l^{-1}) at different geographical locations

Area	Period	pH	Cl	SO_4	NO_3	NH_4	Na	K	Ca	Mg
Gopalpur, India*	1996	6.1–7.4	31	15	43	43	19	3	134	78
Hyderabad, India[@]	1999	6.34	73	30	29	–	38	8	41	20
Izmir, Turkey[#]	1994	5.64	117	66	23	43	117	17	81	101
Seoul, Korea[$]	1996–1998	4.7	18	71	30	66	11	3.5	35	7
Present study										
Kalyan	1994–1995	5.28	134	110	66	14	147	6	130	48
Colaba	1994–1995	6.38	171	52	34	12	179	6	155	59
Alibag	1994–1995	6.74	236	36	9	8	220	5	133	64

*From Satsangi *et al.*[9]; [@]From Srinivas *et al.*[25]; [#]From Al-Momani *et al.*[26]; [$]From Lee and Pacyna[27].

sions. Hence, it is necessary to discriminate sea salt (ss) SO_4, K, Ca and Mg from non-sea salt (nss) SO_4, K, Ca and Mg for a city like Mumbai, which has a marine environment. The non-marine components of these elements were evaluated from the Na concentration on an assumption that all the Na ions originated from the sea. The marine (ss) and non-marine (nss) contributions and their percentage to the total ionic content in rain were calculated using ratios like Cl/Na, K/Na, Ca/Na, Mg/Na and SO_4/Na in bulk sea water[28], and using the following formulae[29].

$$\text{nss } X = \text{Total } X_{\text{rain}} - \text{ss } X,$$

where

$$\text{ss } X = [\text{Na}]_{\text{rain}} \times \left\{ \frac{X}{\text{Na}} \right\}_{\text{sea}},$$

X is an ionic component in rain and X/Na the standard sea–water ratio.

The percentage contributions of SO_4, K, Ca and Mg were 28, 42, 92 and 21 from non-marine (nss) sources at Alibag and those at Colaba were 58, 58, 95 and 30, respectively. However, percentage contributions of SO_4, K, Ca and Mg from non-marine sources at Kalyan (84, 69, 95 and 30, respectively) were higher than those obtained from Alibag and Colaba. Using the above equations, reported percentage contribution from non-marine sources[8] for Delhi, Pune and Goa showed similar results and varied from 56 to 99.4% for SO_4, 15 to 99.7% for K, 90 to 99.2% for Ca and 10 to 63% for Mg. This shows that although sea water is the primary source of SO_4, K, Ca, and Mg, there is another source for Ca, K, Mg and SO_4 at Alibag, Colaba and Kalyan. The non-marine sources of K, Ca and Mg in rainwater samples are mainly crustal, soil or construction-generated calcium oxide, hydroxide and carbonate[30]. The other sources are point-source emissions from fuel combustion and industrial processes, as well as open-source emissions associated with traffic on unpaved roads, agricultural tillage practices and natural particle emissions from forest fires or wind erosion of arid soils[31]. The main industrial sources identified for Ca are cement plants, iron and steel plants[32]. For urban areas, anthropogenic emissions are of importance, whereas for the other places, soil is the major contributor. These elements (K, Ca and Mg) are potentially basic in nature and their presence in high concentrations in rainwater helps in neutralizing the acidic effects of anthropogenic emissions (SO_4 and NO_3) and in maintaining the pH of rainwater in the alkaline range.

The nss SO_4 was minimum (28%) in rainwater at Alibag. However, at the other coastal station of Colaba, which has proximity to the industrial complexes the nss SO_4 was 58%, indicating that it is affected by pollutants from the nearby industrial complexes. The nss SO_4 was found to be high at Kalyan (84%) and Chembur (97%). This observation suggested that the rainwater at Kalyan is influenced by pollutants emitted by anthropogenic sources.

Chemical composition of first rain event

The chemical composition of the first rain event at Kalyan which occurred on 3 June 1995 was compared with that of a successive rain event which occurred on 4 June 1995. It was found that the concentrations of Cl, Na, NO_3, K, Mg, SO_4 and Ca were higher in the first rain event compared to those in the next successive sample. The concentrations of Cl, Na, NO_3, K and Mg decreased by about 31–34% and those of SO_4 and Ca by 28 and 41%, respectively in the next successive rain event. This may be due to rapid below-cloud scavenging of components that are of mere local origin. There are, however, other factors that could explain the same phenomenon: higher evaporation rate during the initial phase due to entrainment of dry air, relatively low precipitation rate and change in origin of the air mass that is scavenged[33]. However, the concentration of NH_4 did not decrease, but increased by 17% in the next successive rain event. This suggests that below-cloud scavenging of NH_4 is not the only process that is contributing to rain, but other processes such as diffusion of gaseous NH_3 or rainout also contribute[34].

pH of rainwater

The reference level commonly used to compare acid precipitation to natural precipitation is pH 5.65, the value that results from the equilibration of atmospheric carbon dioxide with precipitation. The pH values in the present study are interpreted in the light of the carbon dioxide equilibrated value (5.65).

As seen from Table 1, the average pH value at Alibag was alkaline (6.74) and it varied from 6.0 to 8.0. The pH value at Colaba was also alkaline (6.38) and varied from 5.46 to 7.50. However, the average pH value at Kalyan was acidic (5.28) and varied from 4.0 to 7.50. In order to see the pH distribution, the pH values of all rainwater samples for each site (Alibag, Colaba and Kalyan) were classified into nine categories, namely 4.0 to 4.49, 4.50 to 4.99, 5.00 to 5.49, etc. The frequency distribution of pH values for these nine categories was plotted for the three sites (Figure 4). The standard deviations in each category of pH values were calculated and they varied from 0.10 to 0.23.

As seen from Figure 4, all the samples at Alibag had pH > 6.0. In case of Colaba, a large fraction of the samples had pH > 5.65 but only 4% of the samples had values which varied from 5.46 to 5.65. However, pH distribution at Kalyan was different from that at the above two stations and values showed wide variation (4.0 to 7.50). About 55% of the samples at Kalyan had pH > 5.65, 30% of samples were acidic (< 5.65), and the remaining samples appeared with pH ≅ 5.6.

Acidic pH values reveal the presence of strong acids in rainwater, while neutral or alkaline pH values are attri-

buted to the effect of soil dust, predominantly $CaCO_3$ and $MgCO_3$, and ammonia[9]. The pH values are, by and large, alkaline in India[10,11,25,35]. However, acid rain is reported only at a few places[13,36,37].

It is assumed that acidic precipitation originates from H_2SO_4 and HNO_3. Atmospheric alkaline species such as Ca, Mg and K mostly originate from the soil and NH_4 is able to neutralize the acidity. In order to study the impact of acidic and alkaline species on rainwater, the correlation coefficients were worked out between H (hydrogen ion) and SO_4, NO_3, K, Ca and Mg from individual samples for the three stations for two years (1994–1995). A significant (> 5% level) negative correlation was found between H and K, Mg and Ca at Alibag and Colaba. This result shows that K, Ca and Mg play a major role in buffering the acidity present in the atmosphere. The influence of alkaline components such as Ca, Mg and K on the pH of rainwater, snow and cloud in India has been reported[3–6]. The high concentration of alkaline components (K, Ca and Mg) is responsible for high pH of rainwater in India[9,38].

The H ion did not show any specific relationship with K, Ca and Mg at Kalyan but it showed significant positive correlation with SO_4 ($r \approx 0.28$) and NO_3 ($r \approx 0.27$). This observation suggests that rainwater at Kalyan is influenced by secondary pollutants such as SO_4 and NO_3. The major industrial establishments in the upwind of Kalyan include a refinery, petrochemical complex, thermal power plant, etc. Therefore, it is likely that the rainwater samples collected at Kalyan have been influenced by anthropogenic emissions, turning rainwater acidic.

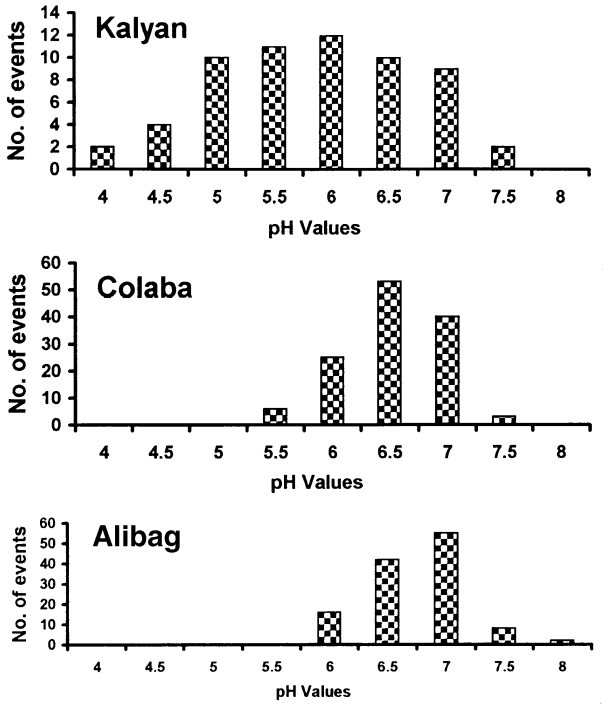

Figure 4. Frequency distribution of pH at Alibag, Colaba and Kalyan.

Long-term change in precipitation chemistry

Industrialization and urbanization processes have been accelerated in the Mumbai region during the past 20 years with installation and expansion of industries and growth of urban centre eastward along the north-south direction. The number of industrial establishments and vehicles in Thane district has increased by 350% from 1987 to 1995 (ref. 39). Population has doubled within the ten-year period from 1981 to 1991, and forest cover has reduced by 19% in 1994 compared to 1972.

It is known that industrialization, urbanization, number of vehicles and population in an area grow together. It has been found through graphical representation of industrial establishments (I) and number of vehicles (V) that, V and I are approximately linearly related.

The correlation coefficient between V and I ($r = 0.91$) is significant at 1% level. The equation of variation is given below.

$$V = 1956 + 82.66I.$$

In order to examine the long-term change in rainwater due to pollutants at Alibag, Colaba and Kalyan, the concentrations of major ions (SO_4, NO_3 and Ca) and pH values of the present work were compared with those reported in the rainwater of 1973 and 1974 (ref. 40). Table 3 shows the concentration of NO_3, nss Ca and nss SO_4 along with pH values at Alibag, Colaba and Kalyan during 1973–74 and 1994–95.

The comparison showed that the concentration of nss Ca had increased at the three locations. It increased by 18, 27 and 11% at Alibag, Colaba and Kalyan respectively. The concentration of SO_4 had decreased at all the three sites. It decreased by 6% at Alibag, 40% at Colaba and 15% at Kalyan. However the concentration of NO_3 increased at all locations, but significantly at Colaba (292%) and at Kalyan (132%). The pH value at Alibag and Colaba decreased by about 0.4 and 0.8 units, respectively, during the two decades. But pH value, which was close to neutral at Kalyan during 1972–73, became acidic in 1994–95.

The observed increase in concentration of Ca at Alibag, Colaba and Kalyan may be due to urban development, road construction and traffic on unpaved roads. Similar sources were reported for Ca[31]. The observed decreasing

Table 3. Concentrations of nss Ca, nss SO_4, NO_3 ($\mu eq\ l^{-1}$) and pH values during 1973–74 and 1994–95

Location	Period	nss Ca	nss SO_4	NO_3	pH
Alibag	1973–74	2.10	0.53	0.47	7.10
	1994–95	2.47	0.50	0.57	6.74
Colaba	1973–74	2.32	2.43	0.53	7.20
	1994–95	2.94	1.45	2.08	6.38
Kalyan	1973–74	2.23	5.23	1.77	5.70
	1994–95	2.47	4.45	4.10	5.28

trend in concentration of SO_4 at Colaba and Kalyan may be due to the change in the use of fuel from coal to natural gas which contains less sulphur, and also the pollution control measures taken by industries. Similar decreasing trend was observed during 1976–1990 at Chembur[41]. The significant increase in NO_3 observed at Colaba and Kalyan may be due to increasing emission of NO_2 due to combustion of fossil fuel by vehicles and by other industries. Thus SO_4 and NO_3, which originated from anthropogenic sources showed opposite trend. Similar decreasing trend in the sulphate and increasing trend in nitrate concentration were reported for different countries like Central and Western Europe and North America[42–46].

Conclusions

The study of chemical composition of rainwater collected at Alibag, Colaba and Kalyan during 1994 and 1995 suggested that the alkaline pH values observed at Alibag and Colaba may be due to influence of alkaline components that originated from the soil. The observed acid rain at Kalyan is due to emissions of sulphur and nitrogen from combustion of fossil fuel by vehicular traffic and other industries. The long-term change in chemical composition was observed during a 20-year period. SO_4 and NO_3 which originated from anthropogenic sources showed opposite trend, i.e. decreasing and increasing, respectively in the 20-year period. The average pH at Kalyan which was alkaline 20 years ago became acidic. The pH values at Alibag and Colaba have also decreased, but they are still in the alkaline range.

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