Chemical composition of rain water over Bhubaneswar, Orissa

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ABSTRACT. Monsoon rain water over Bhubaneswar were collected and analysed during 1988, 1989 and 1991 for CO₂, HCO₃, Cl, SO₄, NO₃, Na, K, Ca, Mg, SiO₂, EC and pH. The data shows that the chemical composition of rain water is greatly affected by meteorological conditions, viz, intensity, quantity and interval between successive showers and also on wind velocity. It was found that with some exception the initial showers are generally more saline than the subsequent ones, the ratios between various constituents vary quite irregularly. The sources of various constituents have been discussed and the amount of various plant nutrients though small in relation to overall requirements of plants brought down by rain have been calculated in kg/hec.

Key words — Aerosol, Anthropogenic sources, Sea salt nuclei, Marine origin, Solute load.

1. Introduction

Rainfall is the primary source for ground water recharge and instrumental incycling metals and non-metals in hydrological cycle. The chemical characteristics of rain water are indicators of the pollution effects from various sources on earth and also influence the chemical composition of ground water. Some major and minor constituents in the rain water are of utmost significance to agriculture. In India only limited studies have been carried out on the chemical composition of rain water. A systematic study of the chemical constituents of the monsoon rain water over Bhubaneswar was undertaken during 1988, 1989 and 1991 with the following objectives:

(i) To determine the chemical composition of rain water.

(ii) To find out the role of air borne salt in hydrogeochemical cycle.

(iii) To assess the significance of some major ions to agriculture.

(iv) To find out the degree of pollution in the atmosphere, if any.

2. Rain water interactions with atmospheric gases

Aerosol is one of the most important factors affecting atmospheric gases which is dispersion of solid or liquid matter. They are formed either by vapour or gases dispersed into or condensed from the atmosphere and from chemical reactions producing ion volatile substances. The common components of gases in the air are oxides of carbon, sulphur and nitrogen. The local variations in atmospheric composition are produced by activities of human, plants and animal metabolism, decay, gases from volcanoes and particulates carried into air by dry fall out from smoke stacks and sea salt nuclei.

Carbon-di-oxide and carbon-monoxide are the two gaseous pollutants produced by natural and anthropogenic sources. The pH of rain water is affected by the dissolved CO₂. The carbon-monoxide is produced by internal combustion engine and by oxidation of CH₄ which is produced by anaerobic oxidation of organic matter. SO₂ is a primary pollutant and SO₃ is a secondary pollutant. H₂S emitted by the biological processes on land in coastal areas and decomposition of waste product rapidly oxidises to SO₂ in atmosphere producing H₂SO₄. Among the oxides of nitrogen in atmosphere nitrous and nitric oxides are most important. The principal source of NO is by photo dissociation of N₂O. Nitrates in the rain water are produced as a result of oxidation of N₂ during lightening and in most of the vehicle engines.

3. Methodology

Rain water samples over Bhubaneswar were collected in cleaned polythene bottles. These bottles were...
Fig. 1. Variation of EC with time in rain water over Bhubaneswar

| S. No | Date of collection | pH | EC (μS/cm) | HCO₃ | Cl | SO₄ | NO₃ | Ca | Mg | Na | K | Cations (A) | Anions (B) | Difference (A-B) |
|-------|--------------------|----|------------|------|----|-----|-----|----|----|----|---|-------------|-------------|------------------|
| 1     | 13 May '88         | 7.50 | 50      | 0.197 | 0.150 | 0.016 | 0.012 | 0.225 | 0.055 | 0.087 | 0.008 | 0.375 | 0.375 | 0.000 |
| 2     | 14 May '88         | 7.10 | 45      | 0.180 | 0.130 | 0.012 | 0.010 | 0.200 | 0.060 | 0.065 | 0.008 | 0.333 | 0.332 | 0.001 |
| 3     | 17 May '88         | 6.60 | 25      | 0.080 | 0.079 | 0.010 | 0.013 | 0.110 | ND   | ND   | 0.052 | 0.010 | 0.162 | 0.184 | 0.022 |
| 4     | 22 May '88 (51)    | 6.55 | 35      | 0.070 | 0.099 | 0.008 | 0.023 | 0.130 | ND   | ND   | 0.035 | 0.005 | 0.170 | 0.200 | 0.030 |
| 5     | 31 May '88         | 7.10 | 90      | 0.344 | 0.299 | 0.066 | 0.024 | 0.475 | 0.026 | 0.187 | 0.051 | 0.738 | 0.733 | 0.005 |
| 6     | 2 Jun '88          | 7.20 | 50      | 0.197 | 0.161 | 0.018 | 0.023 | 0.220 | 0.030 | 0.070 | 0.010 | 0.340 | 0.399 | 0.059 |
| 7     | 4 Jun '88 (51)     | 7.10 | 75      | 0.295 | 0.210 | 0.031 | 0.047 | 0.300 | 0.099 | 0.087 | 0.033 | 0.520 | 0.573 | 0.053 |
| 8     | 8 Jun '88          | 7.20 | 56      | 0.125 | 0.124 | 0.012 | 0.016 | 0.175 | 0.025 | 0.040 | 0.005 | 0.245 | 0.277 | 0.032 |
| 9     | 9 Jun '88          | 7.19 | 48      | 0.130 | 0.079 | 0.008 | 0.003 | 0.140 | 0.020 | 0.040 | 0.005 | 0.205 | 0.220 | 0.015 |
| 10    | 10 Jun '88         | 7.10 | 36      | 0.098 | 0.079 | ND   | ND   | ND   | ND   | ND   | 0.010 | 0.005 | 0.055 | 0.073 | 0.018 |
| 11    | 21 Jun '88         | 7.00 | 19      | 0.039 | 0.039 | 0.004 | 0.002 | 0.050 | 0.010 | 0.015 | 0.005 | 0.080 | 0.084 | 0.004 |
| 12    | 22 Jun '88         | 6.85 | 17      | 0.039 | 0.030 | ND   | ND   | ND   | ND   | ND   | 0.010 | 0.005 | 0.055 | 0.073 | 0.018 |
| 13    | 7 Jul '88          | 6.95 | 22      | 0.061 | 0.079 | ND   | ND   | ND   | ND   | ND   | 0.020 | 0.005 | 0.095 | 0.146 | 0.051 |
| 14    | 9 Jul '88          | 6.90 | 19      | 0.061 | 0.099 | ND   | ND   | ND   | ND   | ND   | 0.020 | 0.005 | 0.085 | 0.164 | 0.079 |
| 15    | 11 Jul '88         | 6.83 | 23      | 0.070 | 0.099 | 0.014 | 0.002 | 0.030 | 0.020 | 0.026 | 0.030 | 0.106 | 0.185 | 0.079 |
| 16    | 12 Jul '88         | 6.75 | 19      | 0.100 | 0.059 | 0.014 | 0.026 | 0.050 | ND   | ND   | 0.020 | 0.050 | 0.120 | 0.249 | 0.129 |
| 17    | 15 Jul '88         | 6.98 | 23      | 0.070 | 0.099 | 0.014 | 0.015 | 0.075 | 0.025 | 0.022 | 0.005 | 0.127 | 0.198 | 0.071 |
| 18    | 17 Jul '88         | 6.85 | 19      | 0.051 | 0.161 | 0.006 | 0.000 | 0.040 | 0.010 | 0.040 | 0.003 | 0.093 | 0.218 | 0.125 |
| 19    | 24 Jul '88         | 6.75 | 22      | 0.100 | 0.059 | 0.018 | 0.008 | 0.050 | ND   | ND   | 0.041 | 0.003 | 0.094 | 0.185 | 0.091 |
| 20    | 26 Jul '88         | 6.65 | 20      | 0.100 | 0.059 | 0.020 | 0.005 | 0.050 | ND   | ND   | 0.050 | 0.005 | 0.105 | 0.184 | 0.079 |

ND — Not detected
CHEMICAL COMPOSITION OF RAIN WATER

TABLE 2

Chemical analysis results of rain water during 1989

| S. No | Date of collection | pH | EC (µS/cm) | HCO₃⁻ | Cl⁻ | SO₄²⁻ | NO₃⁻ (in mg/l) | Ca | Mg | Na | K | Cations (A) | Anions (B) | Difference (A—B) |
|-------|--------------------|----|------------|-------|-----|-------|--------------|----|----|----|---|-------------|------------|------------------|
| 1     | 17 May '89         | 6.38 | 54 | 0.230 | 0.099 | 0.078 | 0.113 | 0.400 | 0.025 | 0.080 | 0.032 | 0.537 | 0.520 | 0.017 |
| 2     | 18 May '89         | 6.20 | 17 | 0.038 | 0.099 | 0.016 | 0.023 | 0.075 | 0.025 | 0.013 | 0.031 | 0.144 | 0.176 | 0.032 |
| 3     | 24 May '89         | 7.20 | 61 | 0.050 | 0.099 | 0.088 | 0.150 | 0.300 | 0.100 | 0.063 | 0.031 | 0.494 | 0.387 | 0.107 |
| 4     | 25 May '89         | 6.60 | 16 | 0.050 | 0.076 | 0.008 | 0.006 | 0.075 | 0.025 | 0.013 | 0.005 | 0.118 | 0.140 | 0.022 |
| 5     | 26 May '89         | 6.15 | 12 | 0.038 | 0.076 | 0.010 | ND | 0.038 | 0.013 | 0.043 | 0.003 | 0.096 | 0.124 | 0.028 |
| 6     | 4 Jun '89 (DS)     | 6.80 | 87 | 0.328 | 0.251 | 0.039 | 0.075 | 0.500 | 0.040 | 0.120 | 0.021 | 0.681 | 0.693 | 0.012 |
| 7     | 13 Jun '89         | 6.84 | 45 | 0.246 | 0.090 | 0.010 | 0.014 | 0.225 | 0.055 | 0.043 | 0.013 | 0.336 | 0.369 | 0.033 |
| 8     | 14 Jun '89         | 6.88 | 15 | 0.025 | 0.076 | 0.020 | ND | 0.050 | 0.026 | 0.004 | 0.003 | 0.083 | 0.121 | 0.038 |
| 9     | 17 Jun '89         | 6.87 | 19 | 0.075 | 0.076 | 0.010 | 0.009 | 0.100 | 0.026 | 0.022 | 0.004 | 0.152 | 0.170 | 0.018 |
| 10    | 20 Jun '89         | 7.05 | 25 | 0.025 | 0.099 | 0.020 | 0.093 | 0.175 | 0.025 | 0.011 | 0.003 | 0.214 | 0.237 | 0.023 |
| 11    | 24 Jun '89         | 7.44 | 50 | 0.295 | 0.150 | 0.049 | 0.071 | 0.375 | 0.025 | 0.087 | 0.017 | 0.504 | 0.565 | 0.061 |
| 12    | 28 Jun '89         | 6.70 | 26 | 0.075 | 0.076 | 0.039 | 0.001 | 0.075 | 0.063 | 0.004 | 0.009 | 0.208 | 0.191 | 0.017 |
| 13    | 5 Jul '89          | 6.80 | 71 | 0.149 | 0.200 | 0.078 | 0.061 | 0.300 | 0.013 | 0.165 | 0.018 | 0.503 | 0.488 | 0.015 |
| 14    | 14 Jul '89 (Day)   | 7.45 | 23 | 0.075 | 0.076 | 0.020 | 0.012 | 0.100 | 0.026 | 0.028 | 0.006 | 0.160 | 0.183 | 0.023 |
| 15    | 14 Jul '89 (Night) | 7.40 | 22 | 0.049 | 0.099 | 0.020 | 0.009 | 0.100 | 0.050 | 0.033 | 0.003 | 0.186 | 0.177 | 0.009 |
| 16    | 22 Jul '89         | 7.42 | 32 | 0.062 | 0.200 | 0.020 | ND | 0.088 | 0.012 | 0.163 | 0.014 | 0.277 | 0.282 | 0.005 |
| 17    | 26 Jul '89         | 7.26 | 13 | 0.038 | 0.050 | 0.007 | 0.001 | 0.075 | ND | 0.013 | 0.003 | 0.091 | 0.096 | 0.005 |

ND — Not detected

placed on a raised platform (0.8 m high), on the top of roof (around 20 m from ground level) to avoid contamination due to splashing of rain drops from the surface or from rain water pools. The samples were filtered immediately (if not clear) through whatman No. 542 filter paper and analysed for pH, EC, carbonate, bicarbonate, chloride, sulphate, nitrate, calcium, magnesium, sodium, potassium and silica by standard methods (APHA 1985).

4. Results

Results of chemical analysis of 20 water samples collected in 1988, 17 in 1989 and 18 in 1991 are presented in Tables 1-3 respectively along with quantity of daily rainfall. The study brings out the following salient points:

1. The chemical composition and ionic ratios are dependent on the meteorological conditions, i.e., lightening and cyclonic conditions.

2. EC seems to be greatly affected by the intensity and total quantity of rainfall, as the salinity generally decreases with successive showers. An inverse relationship is observed between the dissolved mineral content and the quantity of rainfall. The time interval between successive rains has also a significant role as evident from Fig. 1.

3. At the beginning of the monsoon season the bicarbonate ions are dominant but later the bicarbonate content greatly reduces with significant increase of chloride ions.

4. Nitrate ions are always present in the rain water which is due to the presence of oxides of nitrogen in the atmosphere.

5. The chloride ion exceeds the sulphate ion.

6. Silica is universally present in the rain water.
**Fig. 2.** Regression analysis and correlation between Na vs Cl and Ca vs HCO₃ in rain water during 1988-89 and 1991

**TABLE 3**

Chemical analysis results of rain water during 1991

| S. No. | Date of collection | pH | EC (µS/cm) | HCO₃ (in mg/l) | Cl | SO₄ | NO₃ | Ca | Mg | Na | K | Cations (A) | Anions (B) | Difference (A−B) |
|--------|--------------------|----|------------|----------------|----|-----|-----|----|----|----|----|------------|------------|------------------|
| 1      | 5 Jun '91          | 6.85 | 82 | 0.393 | 0.339 | 0.039 | 0.026 | 0.065 | 0.020 | 0.200 | 0.010 | 0.870 | 0.797 | 0.073 |
| 2      | 6 Jun '91          | 6.90 | 33 | 0.180 | 0.124 | 0.024 | 0.011 | 0.150 | 0.050 | 0.100 | 0.010 | 0.310 | 0.339 | 0.029 |
| 3      | 7 Jun '91          | 7.05 | 22 | 0.120 | 0.099 | 0.005 | 0.004 | 0.150 | 0.050 | 0.020 | 0.005 | 0.225 | 0.228 | 0.003 |
| 4      | 20 Jun '91         | 6.74 | 64 | 0.295 | 0.251 | 0.029 | 0.031 | 0.400 | 0.082 | 0.100 | 0.010 | 0.590 | 0.606 | 0.016 |
| 5      | 24 Jun '91         | 6.84 | 48 | 0.213 | 0.141 | 0.078 | 0.060 | 0.160 | 0.020 | 0.139 | 0.018 | 0.337 | 0.492 | 0.155 |
| 6      | 4 Jul '91          | 6.15 | 30 | 0.151 | 0.099 | 0.029 | 0.034 | 0.150 | 0.050 | 0.100 | 0.020 | 0.320 | 0.313 | 0.007 |
| 7      | 8 Jul '91          | 6.32 | 32 | 0.197 | 0.099 | 0.008 | 0.018 | 0.125 | 0.025 | 0.252 | 0.012 | 0.292 | 0.322 | 0.030 |
| 8      | 16 Jul '91         | 7.05 | 36 | 0.125 | 0.099 | 0.008 | 0.013 | 0.150 | 0.025 | 0.052 | 0.018 | 0.246 | 0.245 | 0.001 |
| 9      | 21 Jul '91         | 7.10 | 28 | 0.100 | 0.099 | 0.010 | 0.004 | 0.125 | 0.025 | 0.100 | 0.015 | 0.265 | 0.213 | 0.052 |
| 10     | 22 Jul '91         | 6.85 | 21 | 0.120 | 0.099 | 0.005 | 0.005 | 0.100 | 0.025 | 0.100 | 0.010 | 0.236 | 0.229 | 0.007 |
| 11     | 25 Jul '91         | 6.90 | 19 | 0.100 | 0.079 | ND | 0.004 | 0.060 | 0.020 | 0.052 | 0.005 | 0.137 | 0.183 | 0.046 |
| 12     | 27 Jul '91         | 6.87 | 17 | 0.070 | 0.051 | ND | 0.004 | 0.070 | 0.010 | 0.061 | 0.001 | 0.142 | 0.125 | 0.017 |
| 13     | 11 Aug '91         | 6.68 | 33 | 0.100 | 0.200 | 0.020 | 0.006 | 0.125 | 0.025 | 0.152 | ND | 0.302 | 0.326 | 0.024 |
| 14     | 22 Aug '91         | 7.20 | 45 | 0.246 | 0.175 | 0.024 | 0.003 | 0.220 | 0.040 | 0.139 | 0.041 | 0.440 | 0.446 | 0.008 |
| 15     | 27 Aug '91         | 7.12 | 34 | 0.115 | 0.150 | 0.008 | 0.016 | 0.170 | 0.050 | 0.100 | 0.018 | 0.338 | 0.289 | 0.049 |
| 16     | 12 Sep '91         | 6.85 | 35 | 0.151 | 0.150 | 0.003 | 0.023 | 0.150 | 0.029 | 0.122 | 0.005 | 0.207 | 0.327 | 0.120 |
| 17     | 2 Oct '91          | 7.30 | 40 | 0.125 | 0.150 | 0.039 | 0.052 | 0.210 | 0.050 | 0.100 | 0.018 | 0.378 | 0.366 | 0.012 |
| 18     | 4 Oct '91          | 7.26 | 23 | 0.100 | 0.076 | 0.014 | 0.002 | 0.125 | 0.025 | 0.052 | 0.010 | 0.212 | 0.192 | 0.020 |

ND — Not detected
CHEMICAL COMPOSITION OF RAIN WATER

TABLE 4
Range of different chemical parameters in rain water over Bhubaneswar

| Parameter | 1988 (n=20) | | | 1989 (n=17) | | | 1991 (n=18) | |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
|           | Minimum     | Maximum     | Average     | Minimum     | Maximum     | Average     | Minimum     | Maximum     | Average     |
| pH        | 6.00        | 7.20        | 6.95        | 6.15        | 7.45        | 6.89        | 6.15        | 7.26        | 6.89        |
| EC (μS/cm) | 17          | 90          | 37          | 12          | 87          | 34.6        | 17          | 82          | 35.66       |
| HCO₃⁻ (mg/l) | 24         | 18          | 7.3         | 1.5         | 20          | 6.62        | 4.3         | 24          | 9.83        |
| Cl        | 1.06        | 10.6        | 3.86        | 1.8         | 8.9         | 3.96        | 1.8         | 12          | 4.87        |
| SO₄²⁻      | ND          | 3.25        | 0.84        | 0.34        | 4.32        | 1.54        | ND          | 38          | 1.04        |
| NO₃⁻      | 0.01        | 4.70        | 0.92        | ND          | 9.30        | 2.32        | 0.2         | 37          | 1.08        |
| TH        | 2.0         | 25          | 7.4         | 3.75        | 27          | 10.9        | 6.3         | 33          | 10.83       |
| Ca        | 0.6         | 9.5         | 2.56        | 0.75        | 8.0         | 2.53        | 1.2         | 13          | 3.62        |
| Mg        | ND          | 1.2         | 0.32        | 0.15        | 1.2         | 0.39        | 0.12        | 1.0         | 0.42        |
| Na        | 0.23        | 4.3         | 1.10        | 0.25        | 3.75        | 1.25        | 0.46        | 4.6         | 2.31        |
| K         | 0.12        | 2.0         | 0.53        | 0.10        | 1.25        | 0.48        | ND          | 1.6         | 0.57        |
| SiO₂       | 0.30        | 1.8         | 0.75        | —           | —           | —           | 0.3         | 2.0         | 0.88        |

(7) Among the cations the Ca ions are generally prominent and all other ions like, sodium, potassium and magnesium play subordinate role.

(8) The water type is basically calcium bicarbonate type with chloride ions occasionally present in high percentage which may be due to the sea salt nuclei.

5. Discussion

The chemical composition of rain water over Bhubaneswar is likely to be affected by the following factors:

(1) The chemical composition of the sea salt nuclei brought by the monsoon clouds.

(2) Waste gas emission by local industries.

(3) Burning of fossil fuels, wood, coal gas, petrol, diesel etc.

(4) Emanations from the land, particularly agriculture lands and lands submerged for varying periods resulting in anaerobic conditions.

No specific information is available on the input from the various sources listed above. The composition of the suspended material over Bhubaneswar is also not available. The combustion of coal, petroleum, coal gas and cow dung etc are likely to release considerable quantity of H₂S, HCl, NH₃ and other carbonaceous materials including hydrocarbons. Similarly, the dust storms which precede the monsoons, or the dust storms which sometimes occur during the rains or before the rains may also have some effect on the composition of rain water. The proximity of sea near Bhubaneswar may also be a contributing factor, particularly when cyclonic condition prevails. However, the study clearly indicates the unpolluted nature of rain water at Bhubaneswar as compared to the other big cities.

The maximum and minimum values of different ionic compositions of rain water with average values are given in Table 4.

The pH of rain water is in the normal range of 6-7.5 and there is no incidence of 'Acid rain' over Bhubaneswar. This is to be expected as there is no big industries nearby emitting gaseous pollutants. The contribution of H⁺ in ionic balance is negligible (.00071 mg/l at 6.15 pH which is lowest observed pH value). The chloride ions are primarily of marine origin. The high concentration of chloride (10.6 and 8.9 mg/l during 1988 & 1989 respectively) coincides with occurrence of dust storms. Fig 2 (a) shows the relation of chloride with sodium. Sulphate is mostly below 1 mg/l. The main sources may be fuel and sea salt
nuclei. The source of nitrate may be lightening, fuel and soil particles containing nitrogenous fertilizers.

The soil dust is the main source of calcium in rain water. The non-marine origin of calcium ion can be confirmed from the plot of Ca ions versus HCO₃ [Fig. 2(b)]. Calcium is mainly associated with bicarbonate. The concentration of magnesium is much less than calcium. The sodium ions are mostly from marine origin and is comparatively more during storms and cyclonic days. The K ions owe their origin mainly from marine. The ratio of Na/K is found to be high. The average values of ionic ratios in the rain water as compared to sea water is given in Table 5 and the solute load in rain water in kg/hec is given in Table 6.

It is observed that the rain over Bhubaneswar shows contribution from both atmosphere and sea salt nuclei. The ratio of Cl/SO₄ is quite near to the sea water whereas HCO₃/Cl ratio is otherwise. The Ca/K and Ca/Na ratio also shows contribution of Ca from atmosphere.

6. Conclusion

The chemical analysis results of rain water samples over Bhubaneswar show that the dissolved mineral concentration differs from shower to shower depending upon the weather conditions, e.g., cyclonic or dust storm and also depends upon the quantity of rain. Generally high values of dissolved salts are recorded with low precipitation. The interval between successive rains is also important. The data also reveals that the proximity of the sea is a contributory factor. The basic type of water encountered is a calcium bicarbonate type but relative high values of chloride and high ratio between Cl and SO₄ confirm the sea salt nuclei contribution.

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