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Chemical composition of rainwater and dustfall at Bhubaneswar in the east coast of India

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Abstract

Chemical composition of rainwater and dustfall was studied in two different stations of Bhubaneswar, located in the east coast of India. A wet-only and a bulk collector were placed at Regional Research Laboratory (RRL), a suburban area, during 1995–1997 and in the State Botanical Garden (SBG), a rural forest area, during 1997–1998. Of the rain events, 93% recorded alkaline pH (>5.6) at RRL while at SBG, 57% of the rain events were alkaline and the rest were acidic. Non-sea salt (nss) Ca^{2+} and NH₃ were the primary neutralizing agents of rainwater acidity at both the locations. Low concentrations of alkaline constituents in the dustfall are an important finding in this study under Indian conditions. The Cl^{-}/Na^{+} ratio in rainwater at RRL was same as the seawater ratio (1.167) which indicates that sea salt contribution is local to RRL. It may be of indirect marine origin and resuspended locally. Rainwater samples were enriched with nss SO_4^{2-} , nss Ca^{2+} and nss Mg^{2+} at both the sites. Most of the nss SO_4^{2-} and NO_3^{-} were of anthropogenic origin, while a part of those might be soil derived.

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1. Introduction

Precipitation chemistry is indicative of the changes in chemical composition of the atmosphere over time. Acidic precipitation is primarily caused by incorporation of anthropogenic SO_x , NO_x and other acid precursors. Neutralizing components like carbonates, bicarbonates and ammonia, also influence the final acidity of deposition.

Europe and North America have been adversely affected by acidic deposition (Balasubramanian et al., 1999; Hu et al., 2003; Rodhe et al., 2002). Emission of air pollutants are increasing rapidly in many south and

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east Asian countries (Granat et al., 1996), as well as China (Rodhe et al., 2002) due to faster growth in population and the consequent upward trend in agricultural production, industrialization, energy consumption, transport, housing, etc. Systematic observations on the chemical composition of precipitation has been carried out since several years in Europe and North America (Rodhe et al., 2002) but it is limited in the rest of the world (Rodhe et al., 2002; Granat et al., 1996; Whelpdale et al., 1996), especially under non-urban conditions in the tropical region (Whelpdale et al., 1996; Norman et al., 2001). The rainwater composition data are useful for the validation of Global Chemistry Transport Models (GCTMs) (Rodhe et al., 1995; Langner and Rodhe, 1991) and help in determining global cycling of sulfur compounds, oxidized and

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reduced nitrogen compounds, soil dust, etc. (Rodhe et al., 2002; Langner and Rodhe, 1991).

Several studies on the chemical composition of precipitation in India have been reported in literature. Continuous measurement programs like the Background Air Pollution Monitoring Network (BAPMoN) studies of Global Atmospheric Watch (GAW), (Mukhopadhyay et al., 1992), Precipitation Chemistry monitoring program of Indian Institute of Tropical Meteorology (IITM) Pune, (Khemani et al., 1989b; Rao, 1997; Pillai et al., 2001) and the Indo–Swedish collaboration on atmospheric chemistry (Parashar et al., 1996; Norman et al., 2001 and Granat et al., 2001), etc., have contributed to rainwater chemistry database over considerable periods.

Considering the importance and consequences of acid rain, rainwater studies were carried out initially at the Regional Research Laboratory (RRL), a suburban site, during 1995–1997. Later, the rainwater collectors were operated at the State Botanical Garden (SBG), a rural forest site, during 1997–1998. This paper reports precipitation chemistry data, with objectives of establishing chemical composition of rainwater and dustfall at both sites.

2. Experimental

A wet-only (wo) and a bulk (B1) collector used in this study were fabricated by the Meteorology Institute of Stockholm University (MISU), Sweden, details of which are given in the Manual of EMEP Manual for Sampling and Chemical Analysis (EMEP, 1996). During 1995-1997, the wo and B1 collectors were placed on the roof of a building $\sim 20 \,\mathrm{m}$ above the ground, in the premises of the RRL [latitude: 20°16'N; longitude: 85°50'E; 250 m above MSL] located in the Bhubaneswar township. This is a suburban site considerably influenced by local anthropogenic sources. The collectors were operated at the State Botanical Garden (SBG) [latitude: 20°15' N; longitude: 85°52' E] located in a rural forest area, ~ 30 km north of the city, during 1997–1998. It is an upland area with scanty settlements and free from local influences.

The wo collector collects only rainwater free from dustfall whereas the bulk collectors collect rainwater

along with air blown dusts and gases. The rainwater samples were collected at ~ 1000 h after each rainy day. After collection, the samples were weighed and a part of these was analyzed for pH and conductivity in the laboratory. Rest of the samples were preserved by adding $\sim 200 \text{ mg} \text{ l}^{-1}$ thymol (Gillett and Ayers, 1991) and refrigerated at 4 °C. Preserved samples were shipped to MISU for further chemical analysis using a DIONEX ion chromatograph (model DX4000). The samples were analyzed for pH and conductivity once again at MISU. Cations (NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) were analyzed using Dionex CG12 and CS12 columns isocratic with sulfuric acid eluent, while anions (F⁻, HCOO⁻, CH_3COO^- , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- and PO_4^{3-}) were analyzed with Dionex AG11 and AS11 columns using NaOH gradient elution.

3. Data quality

The quality of chemical analysis can, in part, be assessed by the ion balance (sum of cations versus sum of anions), provided that HCO_3^- is included and there is an agreement between measured and calculated conductivity. Bicarbonate was calculated from pH and also measured by ion chromatograph. HCO_3^- was theoretically calculated from the theoretical relationship between pH and HCO_3^- using the equation $[HCO_3^-]$ $= 10^{(pH-5.05)}$ (Kulshrestha et al., 2003a). A poor agreement was observed between calculated and measured HCO_3^- and so calculated HCO_3^- values have been reported in this paper. All the samples (\sim 341 numbers) collected were included in the ion and conductivity balance. Out of these, 26 samples were rejected as outliers. The sum of anions and cations was well correlated, while the average ion difference was 4% with higher amounts of cations. Similarly, the calculated and measured conductivity were well correlated, with $\sim 4\%$ difference in average conductivity (Table 1). These differences were well below the limits recommended by WMO (1994) for precipitation analysis. Quality control was done with internal standards and external reference samples from the National Institute for Standards and Technology (NIST). A comparison between early and late analysis values of pH and conductivity indicated good stability.

Table 1 Average ion and conductivity difference

Sum cation (C)	Sum anion [A]	C-A/C+A	Measured conductivity [mCond]	Calculated conductivity [cCond]	[m-c] Cond/ mCond
109.4	100.0	0.04	14.36	13.78	0.04

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