

CHEMICAL COMPOSITION OF PRECIPITATION IN INDIA AND NEPAL
A PRELIMINARY REPORT ON AN INDO-SWEDISH PROJECT ON
ATMOSPHERIC CHEMISTRY

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ABSTRACT

Rainwater and dustfall are being collected for chemical analysis at five sites in India and one in Nepal on an event basis with wet-only and bulk collectors. Special attempts are made to obtain regionally representative values and in particular to avoid local sources of alkaline dust. Sampling and analysis are described and data are given from four of the stations, Delhi, Pune, Sinhgad and Goa. Rainwater is on the average alkaline (contains more bicarbonate than hydrogen ion) with a pH of between 6.2 and 6.8 based on mean hydrogen and bicarbonate concentrations. Major acidifying and neutralizing components have rather similar concentrations at three of the four sites (except Delhi): SO_4^{2-} (12-18 $\mu\text{eq/L}$), NO_3^- (5-7 $\mu\text{eq/L}$) and nss Ca^{2+} (32-40 $\mu\text{eq/L}$). Concentration of NH_4^+ varies from 5 at the coastal Goa to 12 $\mu\text{eq/L}$ at the inland stations and nss Mg^{2+} from 2 to 8 $\mu\text{eq/L}$. Sea salt components very clearly decreases with increasing distance from the coast. Delhi deviates in a peculiar fashion with higher concentrations of SO_4^{2-} , NH_4^+ and K^+ and lower in Ca^{2+} and Mg^{2+} . Amount of dustfall (as collected by funnels which probably only give a fraction of dry deposition to real surfaces) was estimated at Delhi. The dustfall greatly exceeded wet deposition of Ca^{2+} and Mg^{2+} , made a significant contribution in case of NO_3^- and was rather unimportant in case of NH_4^+ (20%).

1. INTRODUCTION

Acid precipitation, caused by man, has long been recognised in Europe and North America where acidifying components dominates over neutralising ones. This has led to ecological damage adding to the effects of other components of anthropogenic origin (Rodhe *et al.*, 1995a, Havas and Rosseland, 1996, Matzner and Murach, 1996) and inflict irreversible damage on buildings including some of the most treasured monuments (Kucera and Fitz, 1995). Increasing emissions of sulfur dioxide in Asia have the potential to create an acid deposition problem also here (Galloway, 1995) and is recognised as one of the key issues in IGAC (International Global Atmospheric Chemistry Programme) and especially addressed in subproject CAAP (Composition and Acidity of Asian Precipitation) within the DEBITS Activity of IGAC. Acid precipitation has been reported in China (Zhao *et al.*, 1988) and in India near large point sources of SO₂ (Khemani *et al.*, 1989). During the last two decades, a number of studies have been carried out on the chemical composition of precipitation in India (Khemani *et al.*, 1985, 1987 a, b, 1989, 1992; Handa *et al.*, 1982; Naik *et al.*, 1988; Mahadevan *et al.*, 1989; Kulshrestha *et al.*, 1991; Saxena *et al.*, 1991; Kumar *et al.*, 1993; Varma 1989 a,b). Samples of rain water were collected manually using funnels and bottles and these studies revealed pH in rainwater of between 6 and 7, which is higher than those reported from most other places of the world. A crucial question is whether the results are regionally representative due to large scale deposition of neutralizing compounds or may be locally biased by activities stirring up (alkaline) dust in the vicinity of the collectors. Precipitation data are very useful for estimating part of the deposition (wet deposition) and for validating global scale model simulations of sulphur and nitrogen compounds (Rodhe *et al.*, 1995b).

This report presents preliminary results from a joint Indian-Swedish project to determine deposition of some major components related to acidification with special emphasis to regional representativity. The project is carried out in co-operation between the following laboratories: National Physical Laboratory in Delhi (NPL), Department of Meteorology at Stockholm University and International Meteorological Institute in Stockholm (MISU),

Indian Institute of Tropical Meteorology in Pune (IITM) and National Institute of Oceanography in Panjim (NIO). Measurements have also been attempted at a site in Nepal as a special co-operation with Tribhuvan University, Kathmandu.

2. OBJECTIVES

The primary objective was to study the atmospheric deposition of SO_4^{2-} , NO_3^- , H^+ and other major ions in India with sampling sites representative for larger areas. Also included was a comparison with previous long term measurements in the country. An effort is also made to model deposition based on meteorological data, land use patterns and anthropogenic emissions in southern Asia. Such a model, if properly validated against observations, can be used to predict changes and possible damages from future emission scenarios.

3. EXPERIMENTAL

3.1 Site description

In India climatic and topographical conditions vary as well as the emission strength of both neutralising and acidifying components. This will of course influence the rain water composition. The sampling sites have been selected to represent certain conditions as follows. Their location is also given in Figure 1.

3.1.1 Delhi ($26^\circ 38' N$, $77^\circ 12' E$)

The metropolitan city of Delhi is a continental, highly polluted, urban site. The precipitation study at Delhi will be useful for understanding the contribution due to anthropogenic pollution as well as dust particle interference (which may be partly natural, partly of anthropogenic origin).

Collectors are located in the NPL area which has a suburban character located about 4 km NNE of the centre of the city. Seen from the sampling site the surroundings include green areas, houses and a few major roads (within 0.7 km). One wet-only and one bulk collector are located at 1.6 m above the roof of a narrow tower (5x5m), 30 m above the ground. A second bulk collector is located 1.6 m above a lower, large flat roof 12 m above ground and near the tower. Rain is not likely to drip from the high tower but dust may come off.

15 daily samples and 19 samples of equal volume from two convective showers were collected and analysed during the 1994 monsoon.

3.1.2 Pune ($18^{\circ} 32' N, 73^{\circ} 51' E$)

Pune is located 130 km east of the Arabian Sea shielded by the a ridge known as the Western Gats. Rain (typically 800 mm/year) falls almost exclusively during the SE monsoon (July to October) with occasional rain events during the rest of the year. The city has about 1 million inhabitants and includes several suburban areas within 30 km radius from the centre.

Collectors are located on the roof of the IITM building which is some 6 km N of the city centre. The surroundings contain houses and quite large green areas. The site is shielded from the city by a hilly area. A major road (mostly trucks) passes within some 300 m. One wet-only and one bulk collector are located on the highest part of the building, a small platform some 15 m above ground. The second bulk collector is located some 3 m lower in the middle of a large flat roof some 50 m away. The site was selected in order to make a connection to previous long term measurements (Khemani *et al.*, 1989 b). The location may, with wet-only collector approach a regional value. 12 daily events are examined below which is however only a small selection of data available from this site.

3.1.3 Sinhagad ($18^{\circ} 21' N, 73^{\circ} 45' E$)

The station is located on a mountain peak in the Western Gats at 1400 m above sea level among other equally high mountain peaks. There is an open view towards W while there is still some 100 km to the coast with more mountains in between and the station can not be regarded as a coastal site, although slightly more exposed to westerly winds than Pune. Nearest city is Pune at some 18 km distance. The area is sparsely populated, with no agriculture. The ground is covered by forest (dense to scattered trees) and some understorey. At the summit two bulk collectors are located at 10 m distance within a fenced area of a TV transmitter station. A few people live at the summit and some tourists visit the area (by foot). The only noticeable local source of pollution is a reserve power generator (seldom in operation) and wood burning in connection with cooking, the latter not closer than 200 m. A few cars and buses enter the mountain but can not come closer than one km. This can be considered to be a remote site and is operated by IITM with great effort. 17 samples of rain water are examined below.

3.1.4 Goa ($15^{\circ} 31' N, 57^{\circ} 57' E$)

The station is located on the premises of National Institute of Oceanography on the peninsula NW of Panjim. One wet-only and one bulk collector are located on the roof of the computer building some 20 m above ground and 0.5 km from the coast. The other bulk collector is located 20 m from and 10 m above the sea and surrounded by vegetation. The area between the buildings is mainly covered by vegetation. Traffic does not come close to the collectors and the nearest city is Panjim 20 km away. This is an extreme coastal site (during the SE monsoon) with 160 degree sea horizon. It may thus be representative with regard to marine air during on-shore winds, while some influence from locally originating dust can not be ruled out during easterly winds. 5 daily rain events are examined below.

3.1.5 Dulikhel/Kathmandu ($26^{\circ} 42' N, 85^{\circ} 12' E$)

The site is situated some 25 km east of Kathmandu but in a different valley. Nearest town is Dulikhel 5 km to the east. The site is located halfway up a mountain covered with dense vegetation some 200 m above the bottom of the valley. There are a few settlements and agriculture (rice fields) in the valley. One wet-only and two bulk collectors are located in a small natural clearing in the vegetation with the second bulk collector some 50 m below also in a small opening in the vegetation. The area is a forest reserve with no access to the public. Measurements in this region are motivated by the location downstream of Indian emissions (during the rainy period) and the sensitivity of the Himalayan ecosystems.

3.1.6 Bhubaneswar ($20^{\circ} 15' N, 85^{\circ} 52' E$)

The collectors are temporarily located on the premises of Regional Research Laboratory (RRL) 20 km from the centre of Bhubaneswar awaiting transfer to a rural location. The present location is suburban. Wet-only and one bulk collectors are located on the roof of a building 10 m above ground while the other bulk collector is located on the roof of a private house in a vegetation covered area.

3.2 Sample collection

Rain is collected with wet-only collectors, open only during rain, and so called bulk

collectors, which are open all the time. A brief description is given of the merits of the two sampling principles and construction of collectors.

3.2.1 Wet-only collector

This device will prevent collection of dust fall and absorption of gases during dry periods and will considerably decrease the risk of contamination from insects and other debris. The wet-only collector minimises the influence from local sources during dry periods and will therefore give more regionally representative samples, although influence from local sources during rain is, of course, not eliminated.

The sampling funnel of the wet-only collector is, in absence of rain, covered with a lid that makes an almost air tight seal. The lid is held with a spring against a collar surrounding the collecting funnel. One drop of rain (on 20 cm²) is enough to activate a mechanism that opens the collector. Two double arms move the lid to the side of and below the opening, where it is tilting slightly outwards. When no rain drops are encountered for more than two minutes the lid is again closed. The sampling funnel has a cylindrical upper part with diameter of about 200 mm. A net is fastened in the lower part of the funnel. A collection bottle of 2 L capacity can be attached by screwing from beneath. Connection between funnel and bottle is a narrow bore that will prevent evaporation from water in the bottle. Total time of opening and number of openings are recorded. The instrument runs on a 12 V completely sealed battery continuously recharged by a solar cell panel. The equipment has been designed and constructed at the Department of Meteorology, Stockholm University, Sweden.

3.2.2 Bulk collector

Bulk collector is the common name of a collector that is open all the time. It thus collects rain as well as some particulate matter deposited by sedimentation or impaction when air is moving over the opening. It is also open for insects and other material of biogenic origin. The collection efficiency for this kind of "dry deposition" is usually substantially different from that of any surface in nature or in urban areas and can thus not represent real dry deposition. Bulk collectors can, however, give useful information on rain chemistry (which in some areas is very close to that from wet-only collectors) and on "dustfall".

Bulk collectors are made of a polyethylene funnel, 20 cm in diameter with a small cylindrical upper part, connected to a 2 L (or 5 L) bottle. The connection is water tight from outside (to prevent contamination from outside water) and with a restriction (a 2 mm ID tubing) which prevents evaporation from collected water even in hot and windy conditions. The bottle should as far as possible be kept dark (i.e. wrapped in aluminium foil) to decrease light stimulated biological activity in collected water. The collector is placed in a simple stand on a pole.

3.2.3 Collection procedure

If possible, the site should be visited every day. It has, however, been difficult to always make daily visits. When rain has fallen the bottle is removed. The funnel is washed with deionized (DI) water. If necessary, an all plastic brush is also used. The wash water is normally discarded and a clean bottle is then connected to the funnel. Specific samples of dust fall were collected during dry days on some occasions (two week periods). Dust samples are obtained by washing the funnel with 60 ml of DI water with a clean spray bottle and collecting the water in the collection bottle.

Sampling conditions were recorded and the amount of water measured with a simple digital balance. At the field sites (not near a laboratory) the samples were transferred to smaller, prewashed polyethylene bottles for transport to laboratory and chemical analyses. Samples were preserved with thymol to avoid biological activity and associated changes in chemical composition. Recommended minimum is 200 mg/l (Gillett and Ayers, 1991) but usually more was added.

3.3 Analysis

Samples were analysed at NPL, IITM and IMI. pH and electrolytic conductivity were measured shortly after the collection. Several different instruments were used by the different laboratories. pH was measured with a glass electrode, Ross normal type or one for low ionic strength solutions, with e.g. Scandinovata, Model 102 pH meter. The anions, Cl^- , NO_3^- and SO_4^{2-} were analysed either by ion chromatography (Dionex 2000i/SP or 4000)

using Dionex AS4A column, $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent and H_2SO_4 as regenerant at NPL and MISU or by colourimetric methods (IITM). Na^+ , K^+ , Ca^{2+} , Mg^{2+} were analysed by atomic absorption spectrophotometry. NH_4^+ was analysed colourimetrically by the indo-phenol method using a UV-VIS spectrophotometer (NPL and IITM) or FIA with ammonia gas diffusion (MISU).

4. RESULTS AND DISCUSSION

4.1 Composition of rain

The mean concentration in rain samples obtained from the wet-only and bulk collectors are given in Tables 1a and 1b. Data from bulk collectors at Sinhagad is also included in table 1a since no wet-only collector was operated there. A representative pH is obtained from the mean difference in concentration of H^+ and HCO_3^- . Since no direct measurements of HCO_3^- were available the concentration was estimated from the theoretical relation between pH and HCO_3^- when the pH is above 5.6 and sample is in equilibrium with atmospheric carbon dioxide pressure as

$$[\text{HCO}_3^-] = 10^{-11.2+\text{pH}}$$

with HCO_3^- concentration in mol/L. Previous comparisons between measured concentrations of HCO_3^- and estimated as above indicated that concentrations of HCO_3^- was underestimated in this way (Granat, 1972). The HCO_3^- values might thus be too low while the representative pH will have less bias.

The mean concentration of HCO_3^- is clearly higher than that of H^+ with typical pH values of between 6.2 and 6.7 at all four stations. The rain is thus alkaline rather than acid. Events with slightly acid rain do however occur - in particular in Delhi - which also, on the other hand, experienced some of the most alkaline rain so far recorded from any station in the study. The frequency distribution of daily samples is shown in Figure 2 based on 23 wet-only samples at Delhi. In more than 82% of these events, the pH was above 5.6. The first acidic event of the monsoon season occurred on 20-21 July 1994. It was the ninth rain event of the season and was preceded by two days of continuous rain. A total of 131 mm rainfall was

recorded before this event which comprised 28% of the total rainfall during this monsoon season. These results can in part be due to high rainfall that reduced the emission of dust from soil and removed pre-existing aerosol in the atmosphere.

The acidic / alkaline nature of the precipitation is the result of a balance between acidifying and neutralising components. We can speculate that the major part of the non seasalt (nss) sulfate and nitrate was formed from corresponding sulfur and nitrogen oxides and thus gave rise to hydrogen ions and that some (possibly a major) fraction of the base cations were in the form of carbonates. Ammonium may have been introduced as ammonia, generally considered to be emitted from urine in Europe (mainly from cattle) and to a lesser degree from microbiological activity in the soil (especially fertilized soils). The present study with so far rather few samples can however not yet verify this scenario and rule out the possibility that some of the sulfate and nitrate might be emitted in particulate form and not pass through an acid producing gas phase.

The pH at Delhi can thus be seen as a result of antropogenic SO_2 and NO_x emissions, a substantial contribution of ammonia and only a small amount of alkaline dust or fly ash (judging from the Ca^{2+} and Mg^{2+} content). Some yet unidentified compound must have given the high pH encountered and the unusually large discrepancy in the ion balance.

The concentrations of acidifying compounds, SO_4^{2-} and NO_3^- , are rather similar at Goa, Pune and Sinhagad especially if non seasalt fractions (nss) are considered (see further below and Table 16) which is also the case for neutralizing components indicated by nss Ca. Ammonia concentration at Goa is lower by a factor two compared to the two other stations.

Concentration of sea salt components very clearly decreases with increasing distance from the sea.

The higher concentration of nss SO_4^{2-} compared to NO_3^- at all the sites (a factor of 3 or more) indicates that SO_2 is presently much more important for the (potential) acidity of rain water than NO_x . At Delhi, the concentrations of NH_4^+ and SO_4^{2-} are much higher than those of the

other species. Higher concentrations of NH_4^+ can be explained by agricultural activities in the neighbouring farms while SO_4^{2-} may originate from SO_2 emitted in the city of Delhi and in the region. The concentration of K^+ at Delhi is higher as compared to that reported earlier (Khemani *et al.*, 1989). The higher contribution of K^+ in Delhi may be due to biomass combustion or some not yet recognized source in Delhi or agricultural fields in the adjoining area (Safai *et al.*, 1993).

4.2 Influence of dust particles

4.2.1 Comparison of results from wet-only and bulk collectors

Results from bulk collectors are given in Table 2 and the difference between bulk and wet-only are given in Table 3. The concentration of most components is generally higher in samples from the bulk collectors and the pH is also higher. The relative difference varies very much between components and between stations for a given component. At Goa the relative difference in Ca^{2+} concentration, calculated as:

$$(\text{bulk minus wet-only})/\text{wet-only},$$

is only about 8% while at Pune it is 60%. Difference in SO_4^{2-} varies from very low 2% at Delhi to 36% at Pune. In Figure 3 the pH in samples from wet-only and bulk collectors are compared (23 daily samples from NPL, Delhi). The difference is obviously due to deposition of particulate material. Deposition of this material is more efficient for coarse particles (due to sedimentation and impaction by turbulence created over the collector). Gases may also be deposited either to the walls themselves or to material already deposited in the funnel. Large amounts of Ca^{2+} and Mg^{2+} may either originate from the soil, made airborne by eolian processes, or from industrial activities. Extra sulfate may come from SO_2 deposited in the funnel, from SO_2 reacting with alkaline dust in the atmosphere or from soil derived CaSO_4 . The relative magnitude of these different sources depends i.a. on the strength of local pollution sources.

The concentration of NH_4^+ is equal in the two types of collectors or even lower in the bulk collectors except at Goa. Lower NH_4^+ concentration in bulk samples has been explained as

due to higher pH of the bulk samples (Seinfeld, 1988) but it can also be an effect of higher biological activity in these samples which reduces the amount of ammonium, when the samples are not treated with a biocide.

The relative importance of neutralising components can be visualised by computing the following ratios (neutralisation factors, NF), which are given in Table 4 .

$$[NF_{(NH_4)}] = \frac{[NH_4^+]}{[NO_3^-] + [nss SO_4^{2-}]}$$

$$[NF_{(Ca)}] = \frac{[nss Ca^{2+}]}{[NO_3^-] + [nss SO_4^{2-}]}$$

$$[NF_{(Mg)}] = \frac{[nss Mg^{2+}]}{[NO_3^-] + [nss SO_4^{2-}]}$$

In both wet-only and bulk samples, the order of neutralising factors are, with the simplifying assumptions of originating compounds given above, $Ca^{2+} > Mg^{2+} > NH_4^+$ at Goa and Pune but $NH_4^+ > Ca^{2+} > Mg^{2+}$ in Delhi. This feature shows that in both wet-only and bulk depositions, the major neutralisation occurred by Ca^{2+} and Mg^{2+} compounds at Goa and Pune while at Delhi ammonia was more important for neutralisation.

4.2.2 Bulk deposition at two different heights

At Delhi, bulk samples were collected at two different heights, 13 and 30 m, and wet-only samples at one height 30 m. At 30 m the difference between wet-only and bulk collector is

less than 10% for NO_3^- , SO_4^{2-} , NH_4^+ and Na^+ , higher in bulk collector by 16% in case of Cl^- and much higher (a factor of 1.3 to 2.1) in case of K^+ , Ca^{2+} and Mg^{2+} as can be seen from the data in Table 5. At 13 m concentrations were higher, compared to 30 m, of Ca^{2+} and Mg^{2+} (about double), of NH_4^+ (20%) and of NO_3^- (30%), while concentrations of remaining compounds were lower at 13 m compared to that at 30m.

The difference may be explained by predominance of Ca^{2+} and Mg^{2+} in locally generated particles possibly from the large roof, large enough to have a significant fall velocity and therefore not so easily transported to the 30 m level. Some alkaline dust may also blow off from the nearby 30 m (concrete) tower and deposit in the funnel at 13 m. The lower concentrations at 13 m can not be easily explained.

4.2.3 Dustfall rates

The amount of material accumulating in the bulk collectors during dry periods is likely to also deposit on any other surface (vegetation, ground, buildings) as a part of the total dry deposition. One may call this "dustfall" to distinguish it from "dry deposition" which is normally used for deposition to surfaces in the environment (manmade or natural surfaces). The so called "dustfall" can be particulate material deposited by sedimentation and impaction or gaseous compounds depositing to the walls of the funnel or on already collected material. The dustfall rate for the components can be of interest as a lower limit of the dry deposition to a given surface. Table 6 shows measured dustfall rates at the Delhi site. Although calculated from a few events the units are given as deposition per annum and compared with a rough estimate of yearly wet deposition (obtained from concentrations in Table 1 and 0.6 m of precipitation valid for Delhi region). This qualitative comparison shows that dustfall of Ca^{2+} and Mg^{2+} is likely to be very important for neutralising acid rain (present or future). An important contribution is also obtained for SO_4^{2-} and NO_3^- , about equal to wet deposition, while that of NH_4^+ is rather small. The sum of NO_3^- and SO_4^{2-} is clearly less than half of the sum of Ca^{2+} and Mg^{2+} which means a significant net addition of alkaline material (carbonate or bicarbonate). The rather large deposition rate for K^+ may be due to dust from soil and biomass burning.

4.2.4 Short-time sampling within the showers

Samples of equal volume of 50 ml (1.5 mm rain) were collected from two convective showers on July 28, 1994 and August 23, 1994 on the terrace of the National Physical Laboratory, New Delhi at a height of 13 m above the ground. The time intervals between the first and last samples were 250 and 190 minutes respectively for the two showers. The concentration of major ions, pH and conductance are given in Table 7. Concentration levels and temporal variations were very different between the two showers. The first shower had a preceding dry period of only 2-3 hours while the second shower occurred after 14 dry days. The Ca^{2+} concentrations were, despite differences in length of preceding dry period, rather similar and had no obvious trend during the event. Decreasing concentrations during the events were most pronounced for H^+ , NO_3^- and SO_4^{2-} in the first event and for NH_4^+ in the second. Whether this can be related to wind direction (trajectories) or scavenging processes can not be easily evaluated since no meteorological data are available.

4.3 Marine contribution

4.3.1 Ratios with respect to marine Na and non-seasalt (nss) fraction

Table 8 presents the equivalent ratios of Cl^- , Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} with respect to Na^+ at Delhi, Goa, Pune and Sinhadgad in rain water and it also gives the comparison with corresponding ratios in sea water. These ratios are highest at Delhi indicating a dominating non-marine contribution. Even part of the Na^+ can be of non marine origin here. At Goa, being a coastal site, the ratios are close to those in sea water except for Ca^{2+} . At Pune and Sinhadgad the ratio for Cl/Na is still close to that in sea water while the others are higher and in particular Ca^{2+} .

In order to exclude the contributions from sea salt to the rain water, different ratios and sea salt fractions have been calculated using Na (Keene *et al.*, 1986) as the reference element and assuming that all Na is of marine origin.

$$f_{\text{nss}} = \frac{[X] - [Na]r}{[X]}$$

where f_{nss} is the non seasalt fraction, $[]$ denotes concentration of component X and r is the ratio X/Na in sea water.

Table 9 shows that nearly all the SO_4^{2-} , Ca^{2+} and K^+ and a part of Cl^- (33%) and Mg^{2+} (64%) appears to be of non-marine origin at Delhi, while the maritime influence is only slightly larger in Pune. Ca^{2+} has dominating, non sea sources even at Goa (90%).

4.4 Sources of components in rain

Examples of correlation matrices of concentrations found in wet-only and bulk collectors are shown in Tables 10 to 12. The degree of individual contribution varied from place to place depending upon the nature of site. At Pune, Goa and Sinhagad the strong correlation between Cl^- and Na^+ indicates a significant marine contribution. In Pune and Delhi, NH_4^+ has strong correlation with SO_4^{2-} , and NO_3^- . It is likely that this correlation is indirect via meteorological influence and it can not be taken as an indication that these components are emitted together (e.g. as NH_4SO_4 which is also precluded by the stoichiometry of rainwater composition). At each site, Ca^{2+} and Mg^{2+} have significant correlations which may indicate that they are derived from a common source material. It is however difficult to distinguish between man-made and natural emissions from concentration data alone. The weak correlation with pH is in line with previous discussion. Only if either an acidifying or an alkaline component dominates there will be a high correlation with this component and acidity.

5. CONCLUSION

From the limited data so far obtained on rain water composition and dustfall some features can be seen clearly.

On the average rain water is alkaline at all sites (more bicarbonate than hydrogen ion) with a pH in the range of 6.2 to 6.8. Concentration of both acidifying and neutralizing compounds are quite similar at Pune, Sinhagad and Goa and within a factor of 2 or less if Delhi is also included. The variation from day to day can, however, be very large (a factor of 10).

Compared to two rural sites in Thailand (Granat et al., 1996) the concentration of sulfate is some 50% higher while concentrations of neutralizing compounds are some 5 times higher.

Sulfate dominates over nitrate (3 times higher) as indicator of acidifying components while Ca^{2+} seems to be much more important than NH_4^+ for neutralizing, except at Delhi where the opposite is the case.

Dustfall - as judged from deposition in collection funnels, which is only a fraction of dry deposition to real land surfaces - is an important pathway for deposition of neutralizing compounds and contributes almost as much as wet deposition.

6. RECOMMENDATIONS

The present study needs to be continued to enable estimates of the variations during a year and to give some indication of year-to-year variability in relation to variations in meteorological conditions.

Further dustfall measurements will contribute to the understanding of dry deposition but parallel estimates of dry deposition to actual ground surfaces are clearly needed - both to estimate potential neutralizing capacity of the atmosphere and deposition of acidifying gases.

In view of the important role of alkaline particulate matter in this region, there is a need for quantitative estimates of dust emission from the ground as well as from industrial sources. Better estimates of natural and anthropogenic emissions (from both industrial and agricultural activities, including biomass burning) of gaseous and particulate compounds are required for future modelling of the dispersion of acidifying and neutralizing species in the

region.

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Table 1a Mean concentrations and sum of cationes (P) and aniones (N) of samples from wet-only collectors at Delhi, Goa and Pune and from bulk collectors at Sinhagad

Site	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH	cond	HCO ₃	Σ P	Σ N
.....	μeq/L	μS/cm	μeq/L
Delhi (n=15)	27.7	2.2	5.9	30.5	1.3	10.2	0.8	7.5	6.7	16.2	31	50	67
Goa (n=5)	27.4	113.4	5.5	5.5	97.2	2.5	24.5	41.5	6.3	16.2	13	171	159
Pune (n=12)	16.4	40.3	5.3	11.7	31.0	1.1	14.7	33.6	6.5	12.6	20	92	82
Sinhagad (n=17)	23.4	51.0	6.9	13.0	45.5	1.6	16.8	36.3	6.2	15.5	10	114	91

Table 1b Non seasalt concentrations from the same collectors as in Table 1 a

Site	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH	cond	HCO ₃	Σ P	Σ N
.....	μeq/L	μS/cm	μeq/L
Delhi (n=15)	27.5	0.7	5.9	30.5	-	10.2	0.5	7.4			31	49	65
Goa (n=5)	15.3	0.6	5.5	5.5	-	0.4	2.4	37.2			13	46	34
Pune (n=12)	12.5	4.3	5.3	11.7	-	0.4	7.7	32.2			20	52	42
Sinhagad (n=17)	17.7	-1.8	6.9	13.0	-	0.6	6.5	34.3			10	54	33

Table 2 Mean concentrations of samples from bulk collectors at the same four sites as in Table 1.

Site	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH	EC* μS/cm	HCO ₃	Σ P	Σ N
 μeq/L												
Delhi (n=15)	28.3	2.8	6.4	28.3	1.3	6.4	1.6	15.0	6.8	20.6	45	53	83
Goa (n=6)	30.5	134.7	5.9	7.1	115.3	3.4	28.7	44.7	6.5	25.3	21	199	192
Pune (n=12)	22.3	49.6	8.1	11.0	40.7	1.7	17.6	54.0	6.5	17.3	20	125	100
Sinhagad (n=17)	23.4	51.0	6.9	13.0	45.5	1.6	16.8	36.3	6.2	15.5	10	114	91

Table 3 Relative difference between bulk and wet-only collectors.
Calculated as (bulk-wet)/wet.

Site	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	HCO ₃
Delhi (n=15)	0.02	0.27	0.08	-0.07	0.00	-0.37	1.00	1.00	0.45
Goa (n=5)	0.11	0.19	0.07	0.29	0.19	0.36	0.17	0.08	0.62
Pune (n=12)	0.36	0.23	0.53	-0.06	0.31	0.55	0.20	0.61	0.00

Table 4 Neutralization factors (NF), see explanation in text.

	NH ₄	Ca	Mg
Delhi			
Wet-only	0.91	0.25	0.02
Bulk30m	0.82	0.48	0.04
Bulk13m	0.61	0.83	0.08
Goa			
Wet-only	0.27	1.26	0.12
Bulk	0.32	1.22	0.11
Pune			
Wet-only	0.66	1.64	0.43
Bulk	0.43	1.89	0.33

Table 5 Comparison between bulk collectors at 13 and 30 m height and with wet-only collector at 30 m.

	Ratios	
	Bulk30m / Wet-only30m	Bulk30m / Bulk13m
Cl	1.16	1.46
NO ₃	1.08	0.70
SO ₄	1.02	1.21
NH ₄	0.93	0.82
Na	1.01	1.42
K	1.30	1.59
Ca	2.03	0.45
Mg	2.06	0.59
H	0.63	3.15

Table 6. Dustfall - and wet deposition rates of major ions at Delhi. See text for further details. Values in meq m⁻² a⁻¹

	Dustfall rates obtained from some funnel washings	Estimated wet deposition rate
Cl	11	1
NO ₃	4	4
SO ₄	12	18
NH ₄	4	20
Na	3	1
K	9	7
Ca	30	5
Mg	14	1

Table 7 Changes in composition during two rain events in Delhi.
Each sample corresponds to 1.5 mm of rain.

	pH	cond μS/cm	Cl	NO ₃	SO ₄	NH ₄	Na	K	Ca	Mg
		 μeq l ⁻¹							
July 28, 1994										
E1	4.42	48.2	20.2	46.0	127.3	65.2	3.8	37.8	47.1	10.7
E2	4.53	24.5	10.8	23.2	30.7	44.0	0.9	26.7	9.3	-
E3	4.65	21.7	4.0	7.2	9.2	8.3	0.8	28.8	10.8	-
E4	5.27	9.6	5.3	6.8	34.0	14.0	1.7	30.6	55.7	-
E5	5.51	8.2	9.0	5.2	14.5	9.1	0.9	24.5	34.2	-
E6	5.29	8.4	11.5	6.6	40.1	30.3	1.2	27.4	61.3	-
E7	5.28	6.9	6.8	3.3	15.9	11.0	1.1	32.1	21.1	-
E8	5.34	7.8	2.9	7.9	13.3	25.5	1.9	32.6	12.2	-
E9	5.51	8.8	13.6	6.8	13.4	29.0	2.0	34.0	14.1	-
August 23, 1994										
E1	5.76	16.8	3.8	7.2	27.1	38.0	1.0	1.2	34.7	3.5
E2	5.87	8.1	1.7	2.1	7.3	12.5	0.9	0.2	32.6	0.8
E3	5.95	6.1	7.6	2.4	6.1	8.8	1.0	1.0	29.0	1.0
E4	5.94	4.6	6.4	4.3	5.2	6.6	0.8	0.4	30.9	0.6
E5	5.93	3.6	0.7	4.7	5.3	5.1	0.9	0.4	25.7	-
E6	5.85	2.6	2.5	5.2	4.0	3.3	0.8	2.2	24.6	0.6
E7	5.89	3.3	1.9	6.4	2.6	1.2	1.0	1.0	28.4	-
E8	5.92	2.4	2.3	4.2	2.6	3.2	0.9	0.6	26.3	0.6
E9	5.49	5.6	7.2	6.8	7.4	3.6	1.2	1.6	32.6	1.2
E10	5.06	8.6	4.0	4.3	11.3	6.0	0.0	0.0	25.2	-

Table 8 Equivalent concentration ratios of various species to Na wet-only collector

	Cl\Na	Mg\Na	K\Na	Ca\Na	SO ₄ \Na
Delhi	1.69	0.62	7.85	5.77	21.3
Pune	1.30	0.47	0.04	1.08	0.53
Goa	1.17	0.25	0.07	0.43	0.28
Sea water *	1.16	0.227	0.0218	0.0439	0.125

* Keene et al., 1986

Table 9 Percent non-sea salt (nss) fraction estimated from Na

	Cl	SO ₄	Mg	K	Ca
Delhi	31	99.4	63	99.7	99.2
Pune	11	76	52	39	96
Goa	1	56	10	15	90

Table 10 Wet-only correlation matrix at Delhi

	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH
SO ₄	1.00								
Cl	0.47	1.00							
NO ₃	0.95*	0.28	1.00						
NH ₄	0.73*	0.25	0.85*	1.00					
Na	0.62	0.22	0.66	0.29	1.00				
K	0.35	0.20	0.59	0.55	0.40	1.00			
Mg	0.49	0.82*	0.33	0.43	0.89	0.49	1.00		
Ca	0.61	0.75	0.38	0.41	0.89	0.41	0.95*	1.00	
pH	0.59	0.30	0.45	0.52	0.24	0.32	0.51	0.59	1.00

1-tailed significance * .01

Table 11 Wet-only correlation matrix at Pune

	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH
SO ₄	1.00								
Cl	.67*	1.00							
NO ₃	.61	.09	1.00						
NH ₄	.66*	.16	.88**	1.00					
Na	.67*	.99**	-.09	.16	1.00				
K	.81**	.78*	.22	.39	.78*	1.00			
Mg	.45	.46	.04	.15	.50	.23	1.00		
Ca	.60	.43	.27	.32	.46	.34	.93**	1.00	
pH	.65	.52	.31	.46	.55	.44	.85**	.87**	1.00

1-tailed significance * .01, ** .001

Table 12 Wet-only correlation matrix at Goa

	SO ₄	Cl	NO ₃	NH ₄	Na	K	Mg	Ca	pH
SO ₄	1.00								
Cl	0.92	1.00							
NO ₃	0.96*	0.84	1.00						
NH ₄	0.33	0.40	0.05	1.00					
Na	0.91	0.99**	0.83	0.39	1.00				
K	0.87	0.94*	0.76	0.51	0.94*	1.00			
Mg	0.94*	0.99**	0.88	0.34	0.99**	0.94*	1.00		
Ca	0.99**	0.91	0.98*	0.21	0.89	0.84	0.93*	1.00	
pH	0.64	0.65	0.41	0.92	0.64	0.76	0.61	0.55	1.00

1-tailed significance * .01, ** .001

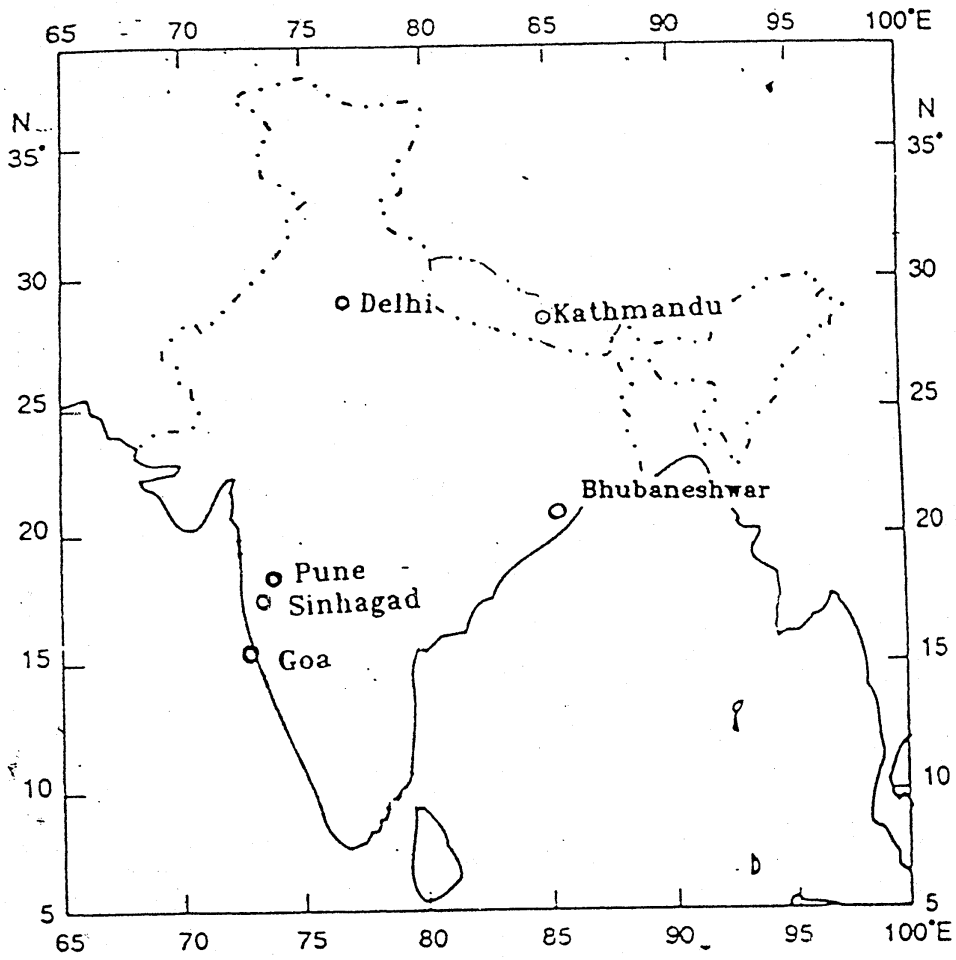


Figure 1 Location of sampling sites

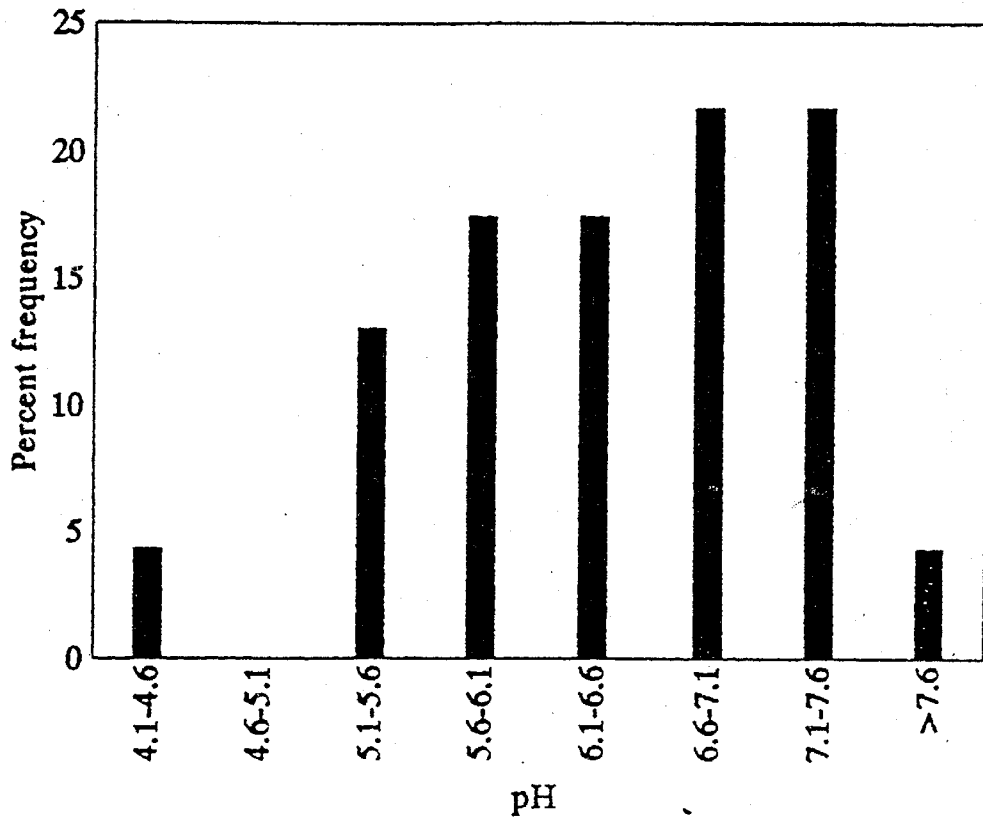


Figure 2 Frequency distribution of pH in wet-only samples at Delhi

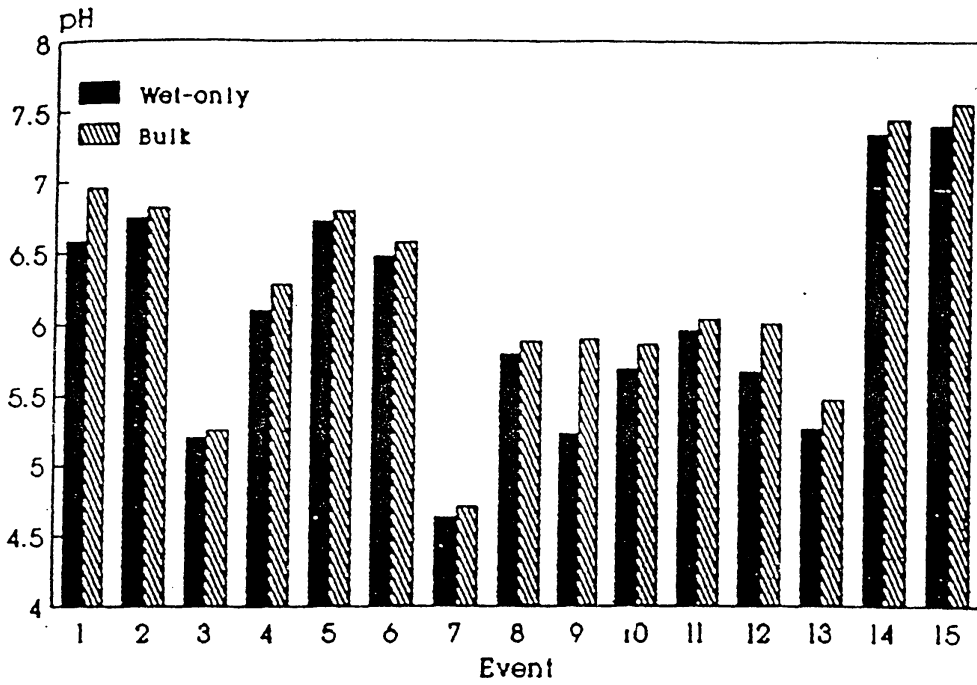


Figure 3 pH of wet-only and bulk samples at Delhi