Summary and Conclusion
Monitoring of wet-only, bulk and dry deposition holds a promise as an early warning tool in monitoring acidic deposition. Because the ionic components and total acidity are important in determining the effects, the present study aims to characterise the status of Agra in terms of wet-only, bulk and dry depositions.

7.1 SUMMARY

7.1.1 Sampling and Analysis

Sampling was performed at four sites within the city, these were:

a) Dayalbagh (DB): A suburb located in the north, with low residential density and surrounded by areas exclusively devoted to agriculture.

b) Hariparwat (HP): Centrally located, is a residential and a major business and commercial centre.

c) Taj Ganj (TJ): Site of the Taj Mahal, it is also a residential area.

d) Industrial Estate (IE): It is dominated by all kinds of industries, particularly foundries.

Wet-only rain water samples were collected manually using bottle and funnel collectors only at Dayalbagh during the monsoon period of 1991. The collection was on an event basis, where an event may be defined as the span of rain between two consecutive dry periods of greater than one hour.
duration. Collection bottles were installed as soon as the rains began and were also retrieved and stored as immediately as possible, after the end of rain.

Bulk deposition was collected from all four sites on a 24 hour basis during the monsoon (wet period) and non-monsoon (dry period), during the years from 1990-1992, using bottle and funnel collectors. At all the sites clean bottles and funnels were placed each day between 8-10 a.m., retrieving the previous day’s sample.

Dry deposition was collected on perspex trays of defined dimensions on a 10 day basis at all sites for the period November 1990 through January 1992. To prevent contamination by rain and dew they were also protected by a rainshield mounted at about 30 cm above the trays.

Sampling was performed a meter above the roof of buildings about 8-10 meters above ground level. The samples were stored and preserved as per standard procedures. The composition of the water soluble fractions of the three types of deposition were only determined, since its chemical reactivity is important with regard to various atmospheric and biogeochemical cycles. The local soil was also analysed for the water soluble concentrations of most of the ions to make source inferences.

Physical parameters like pH and conductance were determined in unfiltered samples. For the chemical characterisation, the anions F, Cl, NO₂, Br, NO₃, PO₄, SO₄;
Cations Na, K, Ca, Mg, NH4 and a few trace metal ions Fe, Cu, Zn, Si, As, Mn, Pb were determined. The anions were determined by Suppressed Ion Chromatography and cations by Atomic Emission, Atomic Absorption, Inductively Coupled Plasma and Colorimetric techniques.

Editing of the data has been done by a F ratio test and also by an inspection of the cation-to-anion ratio (Section 4.1, 5.1, 6.1). Enrichment factor and principal component methods have been used to obtain source inferences.

7.1.2 Wet-Only Deposition

The concentrations of ions in the wet-only samples follow a lognormal distribution. The concentrations depend on factors like precipitation rates, antecedent periods and atmospheric conditions. To account for these, concentrations have been weighted by volume of rain collected. The average relative magnitude of ionic species concentration from the data follows the order Ca > HCO3 > Na >SO4 > Mg > Cl > NO3 > NH4 > K > F >H [Section 4.2 and Fig.4.1]. Despite accounting for concentrations of organic ions, formate and acetate an appreciably high cation excess is observed, the cation-to-anion ratio being 1.15. The Volume Weighted (VW) mean pH is 6.9 (Section 4.3 and 4.4).

The RMA technique was employed to determine both sea salt contributions and ion pair correlations. As one would expect, these were indicative of an absence of sea salt...
contribution and a presence of a continental influence. Significant correlations were obtained for the ion pairs NO$_3^-$ and SO$_4^{2-}$ ($r=0.96$), Na and NO$_3^-$ ($r=0.85$); Ca and Cl ($r=0.75$); Mg and SO$_4^{2-}$ ($r=0.74$); Na and SO$_4^{2-}$ ($r=0.75$); Ca and Mg ($r=0.70$); Mg and Na ($r=0.42$); Ca, Mg and Cl ($r=0.75; 0.58$ respectively) and NH$_4^+$ and NO$_3^-$ ($r=0.59$). The correlations between Ca and Mg, Ca and SO$_4^{2-}$, Mg and SO$_4^{2-}$, Ca and NO$_3^-$, Mg and NO$_3^-$ showed that wind carried dust and soil play an important role in precipitation chemistry. Correlation between NH$_4^+$ and NO$_3^-$ was indicative of a greater dominance of ammonium nitrate over ammonium sulphate compounds (Section 4.5 and 4.6).

The natural and anthropogenic contributions of SO$_4^{2-}$ and NO$_3^-$ were evaluated by regressing NO$_3^-$ concentration with SO$_4^{2-}$ concentration. The regression equation gave a positive intercept revealing the presence of some NO$_3^-$ free SO$_4^{2-}$ [Fig. 4.4], which has been attributed to both primary sulphate of soil origin and from water-logged paddy fields in the region during the monsoon.

The contribution of locally eroded soil was evaluated by a comparison of the ratios of Ca/Mg and Ca/K in local soil with that of precipitation. About 10 percentile rain samples corresponded to these ratios. Higher ratios suggested the contribution of other similar sources (Section 4.7).

Acid neutralizing capacities of Ca, Mg, NH$_4^+$ were determined by neutralization factor calculations. The
factors were greater for Ca and Mg indicating that they neutralize a larger fraction of the available acid. This has further been corroborated by correlations between various cation-anion combinations and a stepwise multiple regression analysis [Section 4.8]. On the basis of the above results, it has been postulated that,

a) $SO_2$ is adsorbed by soil particles,
b) $SO_4$ is present as primary aerosol, and
c) $H_2SO_4$ in the liquid aerosol reacts with soil components.

Factor analysis of the data could group ions into four factors that are known to occur together for chemical, meteorological, physical and microphysical reasons as well as due to common sources (Section 4.9).

7.1.3 Bulk Deposition

The bulk deposition samples revealed a higher cation-to-anion ratio at the four sites. The VW mean pH was above 6.5 at the four sites. The contribution of dry deposition to these samples was estimated to be about 27% (Section 5.2).

The four studied sites could be ranked in order of higher volume weighted concentrations, and significant inter-site differences for each variable were evaluated. Among the anions, $Cl$ was dominant at all four sites while $SO_4$ concentration exceeded $NO_3$ at DB, HP and TG and were almost equal at IE. Among the cations, Ca was the abundant species and decreased in the order Ca > Na > Mg > NH4 > K at
DB, HP and IE while at TG the species decreased in the same order except that K exceeded NH$_4$ (Section 5.2 and Fig.5.1). Mean concentrations of Cl, SO$_4$, Na, Ca, K and Mg were uncharacteristically high at the TG site. It is surmised that elevated levels are due to the influence of emissions from the cremation ground and dhobighats located nearby. Ranking of sites were also confirmed by calculating the ratio of mean concentration of an ionic species to that of Ca [Table 5.2]. However, an analysis of variance ANOVA revealed no significant inter-site differences in total composition of bulk samples (Table 5.3).

Positive correlations between rain depth and cations Ca, Mg, Na and K revealed the effect of greater solubility. The elements Fe, Cu and Zn were well correlated but a lack of uniform correlation between these and soil components indicated both natural and anthropogenic sources for them (Section 5.3).

A comparison between bulk samples of wet and dry periods showed high concentrations in the dry period. The ionic inputs of F, NO$_3$, SO$_4$ and K were higher in the dry period against those of NH$_4$, Na, Ca and Cl which were high in the wet period. This is suggestive of an influence of maritime air masses (Section 5.5).

Lean enrichments were found for most of the species with respect to local soil, suggesting multiple sources. The factor matrix obtained after a principal component analysis
of the data indicated a mixed source effect. It is surmised that plausibly this is due to a diversity of sources in Agra that inject similar elements into the atmosphere and possibly also due to the impact of the dry deposition phenomenon (Section 5.6).

7.1.4 Dry Deposition

The water extracts of dry deposition were alkaline in nature. The dry deposition rate was maximum for Ca and decreased in the order $\text{SO}_4 > \text{NO}_3 > \text{Cl} > \text{Na} > \text{K} > \text{Mg} > \text{Si} > \text{NH}_4 > \text{F} > \text{Fe} > \text{Zn} > \text{Cu} > \text{As} > \text{Mn}$ [Section 6.2]. The deposition rates of $\text{SO}_4$ and $\text{NO}_3$ were of the same order as for Ca, Na, Mg and K. This has led to hypothesize that $\text{SO}_4$ and $\text{NO}_3$ are either the primary aerosols derived from soil or are associated with soil components by chemical conversion of their gaseous precursors in the atmosphere.

An analysis of variance showed spatial and temporal variations in deposition rates for most of the species, which appeared to be a characteristic of the dominant activity at the site as well as of the season. The soil derived species Cl, $\text{SO}_4$, Na, Ca, Mg and Si showed neither significant spatial nor temporal variations. Nitrate fluxes had significant inter-site differences but no seasonal differences. The fluxes were high at TG and HP and can be attributed to greater vehicular pollution in these regions. In contrast, K fluxes exhibits significant difference.
between seasons but not between sites. The flux of K is higher in winter, twice that of the summer flux at all sites. This is possibly due to greater biomass combustion in winter. NH\textsubscript{4} fluxes on the other hand, show both seasonal and site differences which could be explained by its sources; animal wastes and nitrogenous material used in foundry moulds. Maximum deposition rates are observed during monsoon followed by winter and summer. F deposition seems to be of special concern, indicating that substantial amounts are released during roasting of clays in the brick industry.

Enrichment factors showed lean enrichments for most of the ions, and indicated site differences supporting the ANOVA results (Table 6.4). However, the rotated factor matrices on the dry deposition data showed a mingling of natural and anthropogenic components reflecting a mixed or a multiple source effect. This is probably due to the fact that the various industrial and natural sources in Agra bear similar source signatures. On the basis of the measured species and variables included in the factor analysis step, it is difficult to assign a marker element which may best represent the source characteristics (Section 6.6).

A comparison of annual deposition rates of wet-only, bulk and dry deposition, indicated greater bulk deposition rate. It has also demonstrated the importance of dry deposition process in the context of Indian climatic conditions (Section 6.7 and Table 6.5).
7.2 CONCLUSIONS

On the basis of the chemical characterization of the three types of depositions it may be concluded that depositions are alkaline dominated by Ca, Na, Mg, SO₄ and Cl. As such, acidity of rainwater is completely neutralized by alkaline dust and ammonia, the former which are of non-sea salt origin, have a greater ameliorating effect. It therefore appears that neutralization is brought by adsorption of both SO₂ and HNO₃ on soil particles and chemical reactions of H₂SO₄ and HNO₃ with soil components. This is corroborated by the finding that the dry deposition rates of SO₄ and NO₃ compare with those of Ca, Mg and Na.

Enrichment factor calculation with respect to local soil indicated marginal enrichments for both the crustal and anthropogenic elements indicating multiple sources. For the crustal components like Ca, it appears that the enriched fraction is either transported Ca or derived from industrial processes or both. With these inferences it was further attempted to apportion the sources by a multivariate analysis of the data using Factor analysis by the Principal Component Method. Application of factor analysis on the wet deposition data could separate a soil factor, anthropogenic influences of the industrial processes in Agra and other man-made activities like biomass combustion. However, when applied to bulk and dry deposition the factors obtained, showed a mingling of natural and anthropogenic elements.
reflecting a multiple source effect. It is felt that this is probably due to the typical emission inventory of the city where several industrial processes and the natural source soil have common chemical signatures. It is therefore realised that, first emissions at the sources should be monitored, the relative proportions of elements in these emissions should be determined. On this basis a marker element to trace a particular source should be assigned or a chemical mass balance approach should be applied in conjunction with factor analysis. Also, since each observation (sample) of dry deposition was of a longer period, meteorological parameters could not be included as other variables to support the factors.

Both spatial and temporal variation in deposition fluxes of individual species were observed, indicating the influence of the dominant activity of a site and season. But, with respect to the total composition of deposition there were no perceivable spatial differences.

Lastly, a comparison of the annual fluxes of the major ionic components obtained from wet-only, bulk and dry deposition data, indicates that unlike in temperate countries, deposition by the dry deposition phenomenon is a significant fraction of the total deposition. This probably reflects the influence of tropical meteorology and climatic conditions which tend to maximise dry deposition rates.
Although this piece of work intends to describe the factors affecting alkaline deposition and classifies the probable contributors, it is envisaged in future to focus and perceive the problem in a wider aspect including:

1. A detailed monitoring of rain chemistry within individual events and if possible monitoring of fog and cloud water should also be pursued.

2. Dry deposition deserves special attention. New approaches to dry deposition collection, measurement of deposition velocities and air concentrations are of utmost importance.

3. Besides these, monitoring of gas phase concentrations of pollutant species like $\text{SO}_2$, $\text{HNO}_3$ and $\text{HF}$ is needed.

4. In a place like Agra with a diversity of sources bearing common chemical signatures, a better resolution of sources by the multivariate techniques would require size segregated aerosol measurements, and if applied to dry deposition total ionic concentrations should also be determined.

5. Finally, given existing knowledge about deposition processes, a reliable inventory of emission sources including both anthropogenic and natural should be compiled.