Chapter III

RESULTS OF CHEMICAL ANALYSIS OF RAIN WATER AND AEROSOLS
Numerous experimental studies conducted on the metal ion catalysed aqueous phase oxidation of S(IV) by O₂ (Hoffman and Boyce, 1983; Hoffman and Jacob, 1984; Martin, 1984) as well as modelling studies (Gradel et. al., 1985, 1986; Seigneur and Saxena, 1984) suggest that the transition metal ions present in wet deposition (Penkett et. al., 1979; Clarke and Radojevic, 1987) and in dry deposition (Grgic et. al., 1993; Cohen et. al., 1981) play an important role in the atmospheric oxidation of SO₂ to H₂SO₄, i.e., acid formation. As discussed in Chapter I, it is clear that only water soluble components of transition metal ions play a positive role in acid rain formation. Higher the concentration of heavy metals along with high SO₂ emission, higher will be the acidity, but, higher the concentration of alkali and alkaline earth metals, lower will be the acidity. Whereas, the alkali metals and alkaline earth metals present in the atmosphere reduce the acidity of rain water due to their neutralizing effect.

This Chapter deals with the concentration of heavy metals and alkaline earth metals along with the concentration of SO₄²⁻ in wet deposition and dry deposition at the selected sites.

3.1 CHEMICAL COMPOSITION OF THE RAIN WATER

Figures 3.1 and 3.2 show the spatial and monthly variation of the concentration of alkali metals, (Na and K), in rain water respectively. From these two figures it is clear that I.T.O. has higher concentration of both these metals than at J.N.U. Further, the concentrations of
Fig. 3.1: Spatial & monthly variation of Na⁺ in rainwater

Fig. 3.2: Spatial monthly variation of K⁺ in rainwater
Fig. 3.3: Spatial & monthly variation of $SO_4^{2-}$ in rainwater

Fig. 3.4: Spatial & monthly variation of $Ca^{2+}$ in rainwater
Fig. 3.5: Spatial & monthly variation of Mg$^+$ in rainwater

Fig. 3.6: Spatial & monthly variation of Fe ions in rainwater
both metals at I.T.O. are found maximum in September (16.73 and 7.5 mg/l respectively). The minimum concentrations for Na (8.35 mg/l) and K (2.09 mg/l) are observed in the month of August and September respectively. In comparison to I.T.O., the rain water at J.N.U. has the highest concentration of Na (4.2 mg/l) and K (1.605 mg/l) in February. The concentration of K at J.N.U. decreases gradually from 1.61 mg/l in February to 0.424 mg/l in September. The concentration of K at I.T.O. gradually increases from 2.09 mg/l July to 7.5 mg/l in September.

Figure 3.3, shows the spatial and monthly variation of SO$_4^{2-}$ (acid radical) in rain water. This also has similar trend as that of Na and K, i.e., the month of September has the highest concentration of SO$_4^{2-}$ (192.93 mg/l) for I.T.O.; whereas, the month of June has the lowest one (18.896 mg/l). In case of J.N.U., it decreases gradually from 29.16 mg/l in June to 12.63 mg/l in September. Here, the opposite trend at the two places is significant. The high concentration of SO$_4^{2-}$ at I.T.O. (due to the oxidation of SO$_2$ to SO$_4^{2-}$) is expected due to high traffic density and industrial units running in the vicinity of I.T.O., specially, the Iridraprastha Thermal Power Plant.

Spatial and monthly variation of Ca$^{2+}$ and Mg$^{2+}$ in rain water at I.T.O. and J.N.U. are plotted in figures 3.4 and 3.5, respectively. These two metal ions also show the same trend as Na$^+$, K$^+$ and SO$_4^{2-}$. The month of September has the highest Ca$^{2+}$ (37.64 mg/l) and Mg$^{2+}$ (4.31 mg/l) concentrations at I.T.O. The general trend at I.T.O. shows that the concentrations these two metal ions increases from June to September [except Ca$^{2+}$ which has the lowest concentration 14.29 mg/l in July] at
Fig. 3.7: Spatial & monthly variation of Mn ions in rainwater

Fig. 3.8: Spatial & monthly variation of Cu ions in rainwater
Fig. 3.9: Spatial & monthly variation of Co ions in rainwater

Fig. 3.10: Spatial & monthly variation of Cd ions in rainwater
I.T.O. For J.N.U., the lowest levels of Ca\(^{2+}\) and Mg\(^{2+}\) 2.784 mg/l and 0.506 mg/l, respectively in September, whereas, the respective maximum levels are observed 8.31 and 3.325 mg/l in February.

J.N.U., being a residential-cum-educational area, has lower concentration of Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and SO\(_4^{2-}\) as compared to at I.T.O., which is a commercial-cum-industrial area, having high traffic density and industrial units (in the vicinity). The decreasing trend of the alkali and alkaline earth metals and SO\(_4^{2-}\) at J.N.U. from February to September may be associated with the wind born soil dust, which is alkaline in nature. The alkaline dust mainly consists of Na\(^+\), K\(^+\), Ca\(^{2+}\), and Mg\(^{2+}\). The concentration of the dust decreases with the arrival of the monsoon. The opposite trend of these metal ions and sulphate at I.T.O. indicates that there should be some origin of these metals and sulphate other than the soil dust in the atmosphere. The high traffic density and the industrial units nearby I.T.O. may be the expected sources for these ions. The high sulphate load in the atmosphere at I.T.O. during the monsoon period may be associated with the high rate of oxidation of SO\(_2\) in aqueous phase. This leads to the acidification of the atmosphere, which, in turn is being neutralized by the alkali and alkaline earth metals of the atmosphere resulting in the formation of the sulphates of these metals.

Figures from 3.6 to 3.10 show the spatial and monthly distributions of water soluble parts of some transition metal ions, which are important from atmospheric environment point of view, such as, Fe, Mn, Cu, Co, Cd and Zn. From the Figure 3.6, it is clear that JNU has higher concentration of Fe than that at I. T.O., except for the month of August.
concentration of Fe than that at I.T.O., except for the month of August. It has a general decreasing trend from June to September at J.N.U.. It has the highest levels 0.39 mg/l at I.T.O. in July and the lowest in September (0.27 and 0.18 mg/l at J.N.U. and I.T.O. respectively). Fig. 3.7 shows the distribution of Mn, which has approximate an decreasing trend from June (0.38 mg/l) to September (0.26 mg/l) for J.N.U., whereas, I.T.O. has the highest Mn levels in the month of June (0.44 mg/l) and the lowest in July (0.27 mg/l). Figure 3.8, which depicts the distribution of Cu shows that I.T.O. has the highest concentration in September. Whereas, the highest value of Cu is observed in the month of June and the least in September at J.N.U.. Figure 3.9 shows the spatial and monthly variation of Co ion in rain water. The concentration of Co in rain water is higher at J.N.U. than at I.T.O. in the month of August and September. There is an increasing trend of Co concentration from February to September at J.N.U.. But I.T.O. does not have such type of trend. The Co levels at I.T.O. are approximately same in June, August and September except in the month of July when the maximum level 0.37 mg/l has been observed. Fig. 3.10 shows the monthly variation of Cd, which is similar at the two sites. From this diagram it is evident that its concentration was maximum in July at both the sites. In the month of August and September, Cd concentration is more at I.T.O. than at J.N.U.. From Figure 3.11, which shows the distribution of Zn at JNU and I.T.O., it is clear that at I.T.O. the Zn levels are highest in the month of August (0.09 mg/lit.) and at J.N.U in the month of September.
3.2. CHEMICAL COMPOSITION OF AEROSOLS

Figure 3.12 shows the spatial variation concentrations of Na and K ions in aerosols (expressed in weight percentage) at J.N.U., I.T.O., Hauz Khas and Janakpuri. From this diagram, it is clear that Janakpuri has the highest Na\(^+\) levels (0.67%) followed by J.N.U., Hauz Khas and I.T.O. respectively. The highest concentration of K\(^+\) was observed at I.T.O. (1.2%) followed by Janakpuri, Hauz Khas and J.N.U. The wind born soil is supposed to be responsible for the high Na\(^+\) and K\(^+\) ions concentrations at Janakpuri. The high K\(^+\) levels at I.T.O. may also be due to industrial sources (Other than wind born soil erosion). J.N.U. and Hauz Khas have moderate Na\(^+\) and K\(^+\) concentrations. Figure 3.13 shows the spatial distribution of Ca\(^{2+}\) and Mg\(^{2+}\) concentration in the aerosols at all the four sites. This diagram reveals the highest level of Ca\(^{2+}\) has been observed at I.T.O. followed by J.N.U., Janakpuri and Hauz Khas, in decreasing order. Again the wind born dust is supposed to be the principal source of Ca\(^{2+}\) at all the sites except at I.T.O., where nearby industrial sources also contribute significantly. The percentage concentration of Mg\(^{2+}\) (Figure 3.13) is maximum at and the least at Hauz Khas. J.N.U. and I.T.O. are found to have moderate concentrations of Mg\(^{2+}\).

Figure 3.14 shows the percentage concentration of water soluble portion of Fe and Mn cations in the aerosols at all the four sampling locations. The concentrations of Fe and Mn, though low, are approximately equal at J.N.U. and I.T.O. followed by Hauz Khas but very low at Janakpuri. These concentrations of Fe and Mn seem to be associated with wind born soil erosion. Figure 3.15 contains the
Fig. 3.11: Spatial & monthly variation of Zn ions in rainwater

Fig. 3.12: Spatial variation of Na\(^+\) & K\(^+\) in aerosols
Fig. 3.13: Spatial variation of water soluble Ca & Mg in aerosols

Fig. 3.14: Spatial variation of water soluble Fe & Mn ions in aerosols
Fig. 3.15 Spatial variation of water soluble Co & Cu ions in aerosols

Fig. 3.16 Spatial variation of water soluble Cd & Zn ions in aerosols
Fig. 3.17: Spatial variation of $SO_4^{2-}$ in aerosols
four places. J.N.U. has highest concentration of Co followed by Hauz Khas, I.T.O. and Janakpuri. The highest concentration of Cu is found at Janakpuri followed by Hauz Khas. The other two places have very low concentration of Cu$^{2+}$ cations. The concentrations of Cd and Zn are too low (< 0.1 %) at all the four places (Figure 3.16) to be significant.

Figure 3.17 shows the concentration of SO$_4^{2-}$ anions at the four sites. J.N.U. and I.T.O. have very high (~16 %) followed by Hauz Khas (~10 %) and Janakpuri (~8%) the lowest of its concentration. The higher SO$_4^{2-}$ concentration at J.N.U. and I.T.O. indicate a high rate of conversion of SO$_2$ to SO$_4^{2-}$. The strong presence of Mn and Fe cations at all the sites leads us to believe that they play a significant role in the oxidation of SO$_2$ to SO$_4^{2-}$. To summarise, the results of the chemical analysis presented above indicate high concentration of alkali and alkaline earth metals, high concentration of SO$_4^{2-}$ and significant concentration of Fe and Mn ions in both rain water and aerosols.