4. Summary and conclusions

From an integrated study on geochemistry of rain, river and ground waters, the results are summarised (Figure 4 1) along with the following conclusions

The pH of rainwater has been highly variable and no definite trend noticed with respect to seasonal changes. The fallout of acid rains was recorded at many stations during the summer monsoon 1999 and to some extent spring intermonsoon 2000 The main reason for the acidification of rain water is by the relative dominance of anions over cations and anthropogenic contribution of acidic species Rain water samples falling in the acid rain category (pH <5 6) are characterised by three-fold higher concentrations of non-sea-salt SO$_4^{2-}$, Cl$^-$ and NO$_3^-$ relative to those for the alkaline rains Anthropogenic components of these ions were highest in the monitoring stations near industrial and urban activity centres like petroleum refinery, pesticide factory, chemicals and fertilizers, copper sulphate plant, rare earth element extraction plant, alkali plant, zinc smelters etc., but lowest at the proximity of cement factory The fallout of H$^+$ in the study area has been considerably higher by factors of 2 to 19 as compared to coastal BAPMoN stations of India, rains around Mangalore, acid rains recorded cities along the west coast of India, like Mumbai, Trivandrum and, both low and high rainfall regions in the tropics The principal cause for the formation of acid rains in the study area has been explained as due to local anthropogenic activities rather than regional atmospheric contributions from the Indian sub-continent.

Shift of pH from acidic rainwater to alkaline river water and alkaline groundwater has been very prominent at most of monitoring stations, implying that neutralization of acidic rainwater occurs
Fig 4.1 Schoeller diagram illustrating the relative abundances of elements in natural waters of the study area.
through the catchment/weathered material. Increase of ionic concentrations and electrical conductivity of river and ground waters in relation to those for rainwater supports this interpretation.

R-mode factor analysis of ionic concentrations of rainwater suggests that mineral aerosol together with sea-salts form an important source of ions. Anthropogenic inputs such as biomass/garbage burning, long-range transport of nitrate-rich mineral aerosol from the arid regions and neutralization of acidic components have been other minor factors explaining the observed variance in the data set.

The concentrations of $\text{K}^+$, $\text{NH}_4^+$, $\text{NO}_3^-$, and $\text{SO}_4^{2-}$ to the natural waters of the study area appear to have been essentially controlled by the atmospheric input, whereas significant proportions of $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{SiO}_2^{3-}$, and iron were contributed through the weathering processes. The river waters of the study area have been characterised by higher concentrations of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{SiO}_2^{3-}$, and $\text{HCO}_3^-$ as compared to those for rain and ground waters suggesting that they have been derived from headward erosion of Western Ghats. Processes like evapotranspiration and uptake of ions by plants may often result in the discrepancy in the abundance of ions; however, the build up of alkalinity in river waters suggests that mobilization of ions from the catchment material during neutralization of acid rains.

Geochemical mass balance calculations indicate that atmospheric contribution of major cations was less than 5%, for most of cations ($\text{Na}^+$, $\text{K}^+$, and $\text{Ca}^{2+}$) with the exception of $\text{Mg}^{2+}$ ($\sim$18%) to the rivers of the study area. The chemical weathering rates estimated from the dissolved ions concentrations of the study area are also slower by factors of about 14-28 to 5-10 as compared to the Congo-Zaire basin, that has been recorded the lowest weathering rate recorded.
among the 60 world major rivers and their average respectively. Similarly, the rates of chemical denudation were also lower as compared to Congo–Zaire river and the average of 60 world major rivers (0.84 – 1.69 mm/kyr and 16 mm/kyr respectively). The slow rate of chemical weathering has been explained as due to short, swift and high gradient nature of rivers of the study area, where not much of time available for water-rock interactions. The decreasing order of elemental abundance from silicate weathering has been arranged as Na⁺, followed by K⁺, Ca²⁺ and Mg²⁺. Ion balance calculations suggested that Ca²⁺ flux from carbonate weathering was about four-fold higher than that for Mg²⁺ flux. The sum of these ions flux has been higher than a factor of two as compared to those from silicate weathering, reflecting differential stability of minerals during weathering processes. The sequestration of CO₂ also appears to have been much slower during the weathering processes in the area of investigation as compared to the lowest rate of 60 world major rivers and their average (38 – 52 mol/km²/yr, 68 mol/km²/yr and 246 x 10³ mol/km²/yr respectively). Furthermore, the chemical denudation rates estimated in this study are nearly the same for rivers of igneous and metamorphic terrain as compared to the global average (42 tons/km²/yr respectively).

Rivers of the study area fall under precipitation dominance category as per the Gibbs (1970) chemical classification of rivers. However, according to the revised chemical classification (Stallard and Edmond, 1983; Berner and Berner, 1996) of rivers of the study area indicates that most of the samples are clustered in triangular diagram towards the alkalinity corner, to some extent towards Si and Cl⁻ + SO₄²⁻ corners, suggesting the weathering of silicate rocks. Plots of Mg/Na against Ca/Na and HCO₃/Na against Ca/Na further support weathering of silicates to some extent carbonate rocks. This
would agree with the major rock types in the drainage basins of the study area.

R-mode factor analysis of the chemical data of river waters indicates that weathering of fresh rocks and sea-salt are the major contributing factors. Impact of anthropogenic activity on river water chemistry can be noticed through biomass burning and acid neutralization along with industrial contamination.

Majority of groundwater samples belong to alkaline category with the exception of acidic type in the vicinity of industrial monitoring stations. The concentrations of major ions $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{SiO}_2^{3-}$, and $\text{HCO}_3^-$ were marginally higher than those for the rain water due to neutralization taking place in the soils/weathered material. The groundwaters of the study area thus can be classified as alkaline, non-carbonate type with the dominance of $\text{SO}_4^{2-}$. Among cations, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ predominate over $\text{Na}^+$ and $\text{K}^+$.

R-mode factor analysis of the groundwater indicates that weathering and neutralization, together with sea-salts are important factors for the mobilizing ions to the groundwater. Anthropogenic impacts can be noticed in the form of $\text{SO}_4^{2-}$ and effect of biomass burning. Remobilization of Fe and Mn, and to some extent Cu from the particulate phase which yield higher concentrations of these ions possibly due to the depletion of dissolved oxygen in the groundwater. The levels of major ions and some of the measured trace elements are well below the maximum permissible limits prescribed by the WHO and other standards of water quality. However, the pollution indices of $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ have been higher in the urban groundwater probably due to contamination through sewage and urban industrial effluents.