Chapter 6

Synthesis and Scope of future research

This work described in this thesis is an attempt to understand and quantify chemical weathering of various lithologies in the southern slopes of the Himalaya in contributing to the riverine budgets of major cations, trace elements (Sr, Ba, Re, U and Os) and isotopes ($^{87}Sr/^{86}Sr$). A part of this also deals with characterization of processes in regulating the stable isotope composition of the YRS waters. These objectives have been achieved by extensive measurements of major ions, Sr, Ba, Re, stable isotopes ($\delta^{18}O$ and δD) and $^{87}Sr/^{86}Sr$ in the YRS waters and sediments collected during three different seasons. The results and findings of this study have been integrated with those available for other rivers, the Ganga, the Indus and rivers draining the Nepal Himalaya, to achieve a synoptic scenario on the contemporary chemical weathering and erosion rates and associated CO_2 consumption in the southern slopes of the Himalaya. In the following, the results obtained in this study are summarized and important conclusions drawn from them are presented.

6.1 Stable isotopes in the Yamuna River System

The Yamuna and its tributaries in the Himalaya have been extensively sampled and analyzed for their oxygen and hydrogen stable isotopes. These data, in conjunction with those available on rainwater at New Delhi, has been used to infer about various meteorological and hydrological processes regulating their isotopic composition. Further, these results have been integrated with those from the Ganga, the Indus and Gaula catchment in the Himalaya to understand the processes controlling the river water stable isotopic composition in this region

The river waters show seasonal and altitudinal variations in $\delta^{18}O$ and δD, with more depleted values during the monsoon and at higher altitudes. Such variations can be explained by "amount effect", more pronounced during monsoon season and possible evaporation of rainwater during their fall during summer. The river waters during monsoon season have a slope of 7.71 in $\delta^{18}O$-δD space, quite similar to that for rainwater of New Delhi during the same period, suggesting that the rainwater signature is well preserved in the rivers and not altered by processes such as evaporation. A reduced slope of ~6 for the YRS waters during summer and post-monsoon is also similar to that for New Delhi rainwater during June, suggesting that rivers receive waters from precipitation which have already undergone evaporation during their fall. This inference is further attested by the lower deuterium excess in rivers and rainwater during June. The higher d values in the YRS during October can be due to an inherent signature of a source with a significant component of recycled moisture. The "altitude effect" in $\delta^{18}O$ in the YRS samples is derived to be 0.11‰ per 100 m, about a factor of two less than that reported for the Ganga headwaters. Large variability in the altitude effect among adjacent river catchments in the Himalaya is intriguing and is attributable to amount effect on isotope fractionation. This needs to be understood in greater detail, as it has implications to reconstruction of paleoelevation in the Himalaya. The relation between $\delta^{18}O$ and cations of the YRS has been used to assess the altitudinal variation of dissolved cation load in the Yamuna mainstream and shows that major cation abundance doubles as the Yamuna flows about 1.4 km. downstream. The altitudinal dependence of cation concentrations mainly results from variation in lithology and temperature with altitude.

6.2 Major ions, Sr, Ba and $^{87}Sr/^{86}Sr$ in the Yamuna River System

Knowledge on contemporary rates of silicate and carbonate weathering and CO_2 consumption via silicate weathering in the Himalaya is important to assess the role of Himalayan uplift and its influence on global climate change. This requires determination of various sources and quantification of their relative contributions to the cation budgets of the rivers in the Himalaya. Mass balance of Sr and its isotope (^{87}Sr) in rivers in the Himalaya has implications to use of $^{87}Sr/^{86}Sr$ in rivers as a potential tracer for silicate weathering and hence interpretation of marine strontium isotope record. This study, based on extensive measurements of major ions, Sr, Ba and $^{87}Sr/^{86}Sr$ in the YRS waters and sediments, aims at identifying sources of major cations, Sr and its isotope (^{87}Sr) and Ba to these waters. Further, these data have been used to estimate rates of silicate and carbonate weathering and CO_2 consumption in the basin.

Silicate contributions to cation budget, $(\Sigma Cat)_s$, have been estimated using Na* (Na corrected for atmospheric and cyclic contributions) as an index of silicate weathering. For carbonate weathering, *upper limit* of carbonate cations $(\Sigma Cat)_{carb}$ have been estimated assuming *all* non-silicate Ca is derived from carbonates. *Lower limits* of $(\Sigma Cat)_{carb}$ have been estimated assuming *all* SO_4 to be of evaporite origin. This provides *upper limits* of evaporite contributions to YRS cation budget. Using estimates of $(\Sigma Cat)_s$ and $(\Sigma Cat)_{carb}$, river discharge and drainage area, contemporary rates of silicate and carbonate weathering and CO_2 consumption by silicate weathering have been determined.

Similar approaches have been adopted to quantify contributions of Sr and Ba from silicates, carbonates and evaporites. Water chemistry and available information on catchment lithology have been used to evaluate the relative importance of various lithologies in regulating high radiogenic Sr isotopic composition of river waters. The study also addresses to an issue of recent debate, i.e. the role of vein-calcites, occurring in granites, in contributing to the Sr budget and $^{87}Sr/^{86}Sr$ of YRS waters. The main conclusions are:

1. The YRS waters demonstrate the control of lithology on their chemistry. The rivers draining predominantly silicates in the upper reaches, have low TDS, Sr, Ba and high $^{87}Sr/^{86}Sr$. In the lower reaches, the tributaries draining more easily weatherable lithologies such as carbonates, evaporites and phosphates have high TDS, Sr, Ba and low $^{87}Sr/^{86}Sr$. ,
2. Major ion chemistry of YRS waters is dominated by carbonate weathering, Ca and alkalinity being the most abundant. Evidence of dolomite weathering, which has significant volumetric abundance in the Lesser Himalaya, is also seen. Many of the samples are supersaturated with calcite, however, no evidence of calcite precipitation has been observed in this study. The estimated lower and upper limit of carbonate contributions to the YRS cations average ~50% and ~70%. The impact of carbonate weathering on the YRS dissolved Sr load, average ~15%. The carbonates with low Sr/Ca and $^{87}Sr/^{86}Sr$ than the YRS waters, are not an important source for the high radiogenic Sr isotopic composition in many of the rivers. The upper limit of carbonate contributions to the YRS dissolved Ba average ~30%.
3. Silicate weathering is an ongoing process in the Himalaya, as evident from abundances of Si, K and Na* in the YRS waters. Their contributions to the YRS cations is lower than the carbonates and average ~25%. Their average contribution to the YRS Sr is roughly the same ~25%. Silicate weathering is the dominant contributor to the ^{87}Sr load in the waters, an inference drawn from the observation that streams draining predominantly silicates have high $^{87}Sr/^{86}Sr$ and that $^{87}Sr/^{86}Sr$ shows strong linear correlation with silicate cations $(\Sigma Cat)_s$, (Na^*+K/TZ^+) and (SiO_2/TDS). Our estimates of upper limit of vein-calcite contributions to the dissolved Sr in rivers show that they can be significant, however, proper evaluation of their role in regulating the river water Sr and $^{87}Sr/^{86}Sr$ needs more detailed work.

4. Minor lithologies such as evaporites and phosphorites, more abundant in the lower reaches, seem to be contributing significantly to the dissolved Sr and Ba of the YRS waters as evident from the observation that the streams draining them have high Sr and Ba. They however, dilute the high radiogenic Sr isotopic composition of the river waters.
5. Silicate weathering in the YRS basin is not so intense, as evident from the low values of chemical index of alteration ~60 and Si/(Na*+K) in the rivers (~1.2). This is likely to be caused by high physical erosion rates, at least an order of magnitude higher than the chemical weathering rates. The carbonate weathering rates, ~31-46 mm ky^{-1} is three to four times higher than the silicate weathering rate in the catchment, ~10 mm ky^{-1}. The CO_2 drawdown via silicate weathering in the Yamuna and the Ganga basins are roughly similar but significantly higher than those reported in other major river basins in the world. This enhanced drawdown is unlikely to have pronounced impact on the global CO_2 consumption, as the Ganga and the Yamuna in the Himalaya constitute only low proportion of the global drainage area and water discharge. If such high drawdown is also characteristic of other rivers draining the Himalaya, then weathering in the Himalaya can be important in regulating the atmospheric CO_2 in a million-year time scale.
6. This study brings out the influence of climatic parameters such as temperature on silicate weathering. From relations of Si and Na* (silicate Na) with water temperature, the activation energy for overall silicate weathering in the catchment is estimated to be ~50-75 kJ mol^{-1}, similar to those reported for granitoid weathering.

6.3 Dissolved Re in the Yamuna River System

In this study, extensive measurements of Re has been carried out in YRS waters and some of the source rocks (granites and Precambrian carbonates). These data, along with those available on black shales from the Lesser Himalaya, have been used to calculate contributions of Re to the YRS from various sources. In addition to these data, these estimates also rely on certain assumptions on the release of Re to the rivers.

Further, dissolved Re in rivers has been used as an index to quantify the role of black shale weathering in contributing to trace metal budgets of rivers such as Os and U. For the first time, an attempt has been made to estimate the rate of CO_2 release via oxidation of organic rich sediments, using dissolved Re as a proxy for weathering of these sediments. The salient features of this study are as the following:

1. The average dissolved Re in the YRS, 9.4 pM is much higher than the global average river water value, 2.1 pM. The dissolved Re flux from the Ganga and the Yamuna in the Himalaya, ~270 moles y^{-1} is disproportionately higher compared to their drainage area and water discharge.
2. Based on Re measurements in granites in the Yamuna basin and Precambrian carbonates in the Lesser Himalaya, it is estimated that their contributions to the dissolved Re budget of the YRS waters is only minor on a basin wide scale.
3. Higher Re concentrations in rivers flowing through black shale occurrences and mine waters dripping through black shale-phosphorite-carbonate layers and significant Re-SO_4 correlation in the YRS waters, all suggest that organic rich sediments can be a major contributor to dissolved Re in the YRS. Using average Re concentration in the LH black shales, it is estimated that all Re from ~60 mg black shales have to be released per liter of water to account for the measured average Re in the YRS waters. Data on the distribution of organic rich sediments in the drainage basin and Re abundance in them are needed to determine if such a requirement can be met.
4. Weathering of black shales can also account for the reported dissolved Os and U concentrations in the rivers in the Himalaya, as shown by estimates using dissolved Re in rivers and Re, U and Os in black shales.
5. Using Re in river as an index of weathering of organic rich sediments, it has been estimated that $(6\text{-}9)\times10^8$ kg of such sediments are weathered in the YRS and the Ganga basins annually. If their weathering results in oxidation of all organic carbon to CO_2, then it would release a maximum of $(1\text{-}3)\times10^5$ moles km^{-2} y^{-1} of CO_2. This flux is roughly similar to the CO_2 consumption via silicate weathering in the basin.

6.4 Scope of future research

This study has used mass balance calculations to assess the importance of various components in contributing to the budgets of major cations, Sr, Ba and Re to river waters. These calculations critically depend on the end member compositions and the validity of the assumptions involved. A case to be emphasized is the role of vein-calcites in contributing to Sr and $^{87}Sr/^{86}Sr$ of rivers. Evaluation of the impact of this lithology on river water Sr isotope budgets needs proper sampling and analysis of them from granites in the Himalaya. Available data on major ions and Sr in the vein calcites are based on leaching of granite samples. It is essential that "pure" vein-calcites be separated from granites to avoid interference from silicates to the contribution of Ca and Sr during leaching.

Another issue addressed in this study is uncertainties in the assessment of sources of Ca and Sr from evaporite dissolution and pyrite oxidation. Considering the very large range in the sulphur isotopic values ($\delta^{34}S$) in the pyrites associated with the black shales and phosphorites in the Lesser Himalaya, analysis of pyrites for sulphur isotopes to determine the source of SO_4 to rivers may not be very rewarding. The oxygen in dissolved SO_4 would carry in them signatures of evaporite oxygen (marine value at time of their formation) and of weathering solution (a mixture of surface water and atmospheric O_2). These components of oxygen involved have very different isotopic compositions. Hence analysis of oxygen isotopes in dissolved SO_4 may provide better handle to discriminate the contribution of evaporite and pyrites to dissolved SO_4. This in turn can help in better assessing the riverine Ca and Sr budgets. Data on areal distribution of minor lithologies such as evaporites and phosphates are needed to support the inferences drawn from the geochemical evidence that they may be dominant contributors to the dissolved Sr and Ba in the YRS.

It has been shown that preferential release of Re over Na (and other cations) to solution from black shales can significantly change their contribution to the dissolved Re budget in the rivers. This has implications to the quantity of black shales being weathered and hence to the CO_2 budget of the atmosphere. Hence experiments of stepwise leaching of black shales should be carried out to determine the relative ease with which the elements are released from them. In this context, sampling and analysis of streams exclusively passing through black shales should also be carried out to couple the laboratory experiments with field observation. Further, volumetric abundance of organic rich sediments in the drainage basin should be assessed in more detail to determine if they can be dominant contributor to dissolved Re in many of the streams throughout the catchment.

Proper assessment of mechanism regulating "altitude effect" in the Himalaya requires sampling and analysis of rain and fresh snow at a number of places spanning over different seasons in a year and also during different years. These should be coupled with river water data to determine the extent of "averaging effect" in rivers and the utility to derive "altitude effects".