Abstract

The major emphasis of this thesis is to understand and quantify chemical weathering and transport in the southern slopes of the Himalaya. This goal has been achieved through a detailed geochemical and isotopic investigation of river waters and sediments of the Yamuna River System (YRS) in the Himalaya, one of the major rivers in this region. Based on these measurements, this study aims at assessing the role of major lithologies such as silicates and carbonates, and minor lithologies such as evaporites and phosphates, in regulating the major ion chemistry, dissolved Sr and Ba budgets, $^{87}Sr/^{86}Sr$ of the rivers and CO_2 consumption by silicate weathering. The study also determines the impact of weathering of a trace lithology, organic rich sediments, on the riverine trace metal budgets of Re, Os and U, and CO_2 in the atmosphere.

River waters and sediments have been sampled from the YRS in the Himalaya for three different seasons and analyzed for major ion chemistry, Sr, Ba, stable isotopes ($\delta^{18}O$ and δD) and $^{87}Sr/^{86}Sr$. For the first time, a comprehensive geochemical study on Re geochemistry in a river system in the Himalaya has been undertaken through extensive measurements of dissolved Re in the YRS waters and Re in various source rocks.

The spatial and temporal variations in the stable isotopic composition of the YRS waters are regulated by source composition, i.e. monsoon precipitation which in turn is dictated by 'amount effect', recycling of moisture in the region and evaporation of rain during fall. Further, mixing of snow/glacial melt with rainwater and mixing of rivers during their flow all contribute to the isotopic composition of these rivers. The 'altitude effect' in the Himalaya, derived from the YRS water isotopic compositions, is 0.11 ‰ per 100m. This varies among the river basins in the Himalaya and seems to be dictated by the 'amount effect'.

Catchment lithology exerts strong control on the abundances of major ions, Sr and Ba, and $^{87}Sr/^{86}Sr$ of the YRS waters. Rivers in the upper reaches, draining predominantly silicates, have low TDS, Sr, Ba and high $^{87}Sr/^{86}Sr$. Downstream, they drain easily weatherable lithologies such as carbonates, evaporites and phosphates with a consequent increase in the concentrations of major ions, Sr and Ba, and a decrease in $^{87}Sr/^{86}Sr$.

Carbonate weathering contributes dominantly to the major ion chemistry of the YRS, the estimated upper and lower limits of their contributions to the cations average ~70% and ~50% respectively. Silicates contribute, on average, ~25% to the YRS cation budgets. Sulphuric

acid, generated via oxidation of pyrites, acts as an important agent of chemical weathering in the catchment.

Silicate contributions to the YRS Sr budget is in proportion to the silicate cations (~25%). $^{87}Sr/^{86}Sr$ show wide range, 0.7142 to 0.7932, with lower values typical of rivers in the lower reaches draining sedimentaries dominated by Precambrian carbonates and minor amounts of evaporites. The observation, that there is a strong correlation between silicate derived cations and $^{87}Sr/^{86}Sr$ and that rivers draining predominantly silicates have high $^{87}Sr/^{86}Sr$, suggest that silicate weathering regulates the high radiogenic Sr isotopic composition in these rivers. Precambrian carbonates, with lower Sr/Ca and $^{87}Sr/^{86}Sr$ than the YRS waters, is not a major component of Sr budget and high $^{87}Sr/^{86}Sr$ on a basin wide scale. On average, they can account for ~15% to the Sr of the YRS. Minor lithologies such as evaporites and phosphates, with relatively higher Sr concentrations and Sr/Ca also seem significant contributors to the YRS Sr budget. The high $^{87}Sr/^{86}Sr$ of the rivers, inherent from silicate weathering, is diluted by the Sr contributions from these lithologies, especially in the lower reaches. Vein-calcites occurring in granites can be an important source of Sr to the YRS, however, critical evaluation of their significance in influencing river water $^{87}Sr/^{86}Sr$ needs further detailed work on their Sr abundance and $^{87}Sr/^{86}Sr$.

Silicates and carbonates in the YRS basin contribute, on average, ~30% each, to the dissolved Ba in the YRS waters. They can be dominant contributors to the streams with low Ba concentrations. In the lower reaches, for tributaries with higher Ba, sources such as phosphorites have to be invoked.

The average dissolved Re concentrations in the YRS, 9.4 pM, is much higher than the reported global average, 2.1 pM. Estimations based on Re and major ion abundances in the crystallines and Precambrian carbonates show that, on average, they contribute insignificantly to the YRS dissolved Re budget. A very likely source for high Re in these waters is organic rich sediments such as black shales. Based on available data on Re in the black shales of the Lesser Himalaya, it has been estimated that Re from ~60 mg of black shales has to be released per liter of water to account for the measured average Re in the YRS. Currently no data is available on the distribution of organic rich sediments in the Yamuna catchment to determine if such requirement can be met. Using Re in rivers as an index of weathering of organic rich sediments, it has been shown that their weathering can account for the measured concentrations of dissolved Os and U in the rivers draining the Himalaya. The dissolved Re flux from the Ganga and the

Yamuna in the Himalaya is disproportionately higher compared to their contributions to the global water discharge.

Silicates though contribute ~25% of cations and Sr to the YRS waters, and major source for radiogenic $^{87}Sr/^{86}Sr$, their weathering in the Yamuna basin in the Himalaya is not intense, as evident from the water and sediment chemistry. The chemical index of alteration in the YRS sediments is ~60. This is most likely caused by higher rate of physical weathering, about an order of magnitude more than chemical weathering rate. The rate of chemical weathering of carbonates in the Yamuna and Ganga basins in the Himalaya is about four times higher than the rate of silicate weathering.

The contemporary CO_2 consumption rates via silicate weathering in the Ganga and Yamuna basins in the Himalaya, $(2\text{-}7)\times10^5$ moles km^{-2} y^{-1}, are significantly higher than those reported for other major river basins in the world. Together, they account for ~0.1% of the global CO_2 consumption via silicate weathering compared to ~0.1% and ~0.03% of their contribution to the global water budget and drainage area. The CO_2 consumption via silicate weathering in the Ganga and the Yamuna basins in the Himalaya, is roughly balanced by the release of CO_2 by oxidation of organic rich sediments, estimated using dissolved Re as an index of their weathering.

This study brings out possible dependence of silicate weathering on temperature, supportive of the hypothesis that silicate weathering is dependent on climate. Using the major ion data (silicate Na and Si) in the river waters, activation energy for overall silicate weathering in the catchment has been estimated to be 50-75 kJ mol^{-1}.

The present work, based on a very comprehensive measurements of several chemical and isotopic species in the YRS waters and solid phases from drainage basins, has quantified contributions from various lithologies to riverine budgets of these elements and isotopes and has addressed to some of the issues of recent debate. Further, influence of lithology and temperature on chemical weathering of silicates has been demonstrated.