CHAPTER 1

INTRODUCTION
1. General Introduction

The goal of studying geochemistry is to understand the cycling of chemical elements between various reservoirs such as continents, oceans and atmosphere and to identify the mechanisms which control the geochemical cycling. The elemental transfer is a continuous process and can happen at global, regional or smaller (between soil and soil horizons) scales. An understanding of interaction between different compartments anticipates a thorough study of the role of continental erosion and mode of transport of chemical elements and their ultimate fate. During the continental weathering, elements may remain in-situ in the form of newly formed minerals and can be an important part of the weathered soil together with primary minerals. Some elements are transferred to different reservoirs by the activity of geological agents. The fluvial activity is the most important geological agent which transfers about 90% of the elements from the continents to oceans (Gaillardet et al., 2003). The fluvial transfer could be in dissolved (<0.22µm) or particulate (>0.22µm) form but on a global scale the particulate form dominates the fluvial transfer process (Viers et al., 2009).

Primarily chemical weathering of rock minerals contributes to the dissolved composition, and physical weathering contributes to particulate composition of the river water. Thus chemical and physical denudation is a landscape building process. During the journey of weathered products from their source to destination (ocean), the chemical elements are subjected to various hydrological and geochemical processes which determine their behaviour, and fate. To understand this, a thorough study on the geochemical, hydrological and biological processes in the riverine and estuarine environments is essential. The estuaries are most dynamic aquatic system with varying physical, chemical and biological activity which can act as source or sink to the chemical elements brought by the rivers and thereby, affecting the transfer of chemical elements to the oceans.

1.1. Chemical weathering and its implications to global cooling

The chemical weathering is one among the continuous landscape building process which plays an important role in the global climate study on longer time scales. The chemical weathering process involves utilization of atmospheric carbon dioxide (CO₂) in the form of fixed soil organic carbon for dissolution and fixation of CO₂ during precipitation as respective salts (Berner, 1991). The interaction of rain water and atmospheric carbon
dioxide with the crustal material results in the dissolution of soluble primary rock minerals, leaving behind the insoluble components as secondary minerals (White and Brantley, 1995). The weathering of silicates is of significant interest because, for every equivalent of silicate cation dissolution there will be a net consumption of one mole of carbon dioxide (Berner, 1991). Hence, it plays an important role in global cooling on a million year time scale. However, it is worth noting that the weathering kinetics of carbonate minerals is faster than the silicate minerals and hence, on a global scale, the carbonate mineral weathering dominates the total elemental transport (Gaillardet et al., 1999).

The weathering reactions are given below:

**Silicate weathering of rocks:**

\[
\text{CaSiO}_3 + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{SiO}_2
\]  
(1)

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2
\]

**Carbonate weathering of rocks:**

\[
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \]  
(2)

\[
\text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2
\]

Several studies have demonstrated the interrelationship between tectonic uplift, increase in the chemical weathering and global cooling (Raymo and Ruddiman, 1992). It was thought that tectonic upliftment of Himalayas and increase in chemical weathering flux was the principal reason for global cooling during the Cenozoic Era. Since then several studies have been carried out on global (Gaillardet et al., 1999) to regional scale (White and Blum, 1995, Gurumurthy et al., 2012) to quantify the carbon fixation during the chemical weathering and its relationship with the global warming. However, there is still uncertainty in the carbon fixation budget during the chemical weathering. The simple reason could be geographical variation in the chemical weathering process which is governed by several multiple inter-dependent geological, climatological & meteorological and biological parameters (Gaillardet et al., 1999; Millot et al., 2002; West et al., 2005). The relative dominance of each of the above mentioned factors in controlling the silicate weathering needs to be evaluated at different climatic and geological settings.
Therefore, the study of river geochemistry provides insight into the contemporary elemental cycle, their sources, fate in the oceans, the chemical denudations rates of the basin, and most importantly, the present day atmospheric CO$_2$ drawdown. Further, with additional data on physical weathering and climatic parameters, it is also possible to constrain the factors influencing chemical weathering and erosion, particularly, the coupling between chemical-physical weathering and erosion.

1.2. Hydrogeochemistry of groundwater

Groundwater is the major source of water for drinking and agricultural purposes in India in addition to abundant surface water resources. However, most of the rivers in India are dependent on the monsoon, and hence the groundwater plays an important role in fulfilling the human needs throughout the year. Over the last four decades (between 1960 and 2000), the groundwater utilization has been amplified 19 times as the number of tube wells and dug wells in India multiplied similarly (Shah et al., 2003) which is posing a threat to water quality and longevity of the resources. Worldwide research often relates the deterioration of water quality to the impact of changing climatological, meteorological conditions (Perrin et al., 2011). Also, acidification of the surface and subsurface water in response to increased industrial and automobile emission is seriously affecting the water resources. Therefore, the study of impact of climate change, urbanization and industrial growth on the groundwater chemistry is urgently needed. An understanding of groundwater quality requires knowledge on the hydrogeochemical processes and the source contribution of chemical elements. Groundwater chemistry is primarily controlled by the weathering of source rock and atmospheric deposition. In addition, climate, soil characteristics, circulation pattern through various rock types, topography of the area, saline water intrusion and human activity have significant effect on the chemistry of water. Apart from these, the exchanges of groundwater back and forth across channel beds of rivers have significant impact on the overall water quality (Harvey and Fuller, 1998). Therefore, a thorough understanding of hydrogeochemistry of groundwater and surface water is needed for the better management of water resources on a basin scale.

1.3. Biogeochemistry of trace elements in riverine and estuarine environment

Understanding metal behaviour in the environment is especially important in a changing world where human activities are perturbing many natural cycles which will have impacts on our food sources, health, and climate. In addition, to an inherent ecological importance
of metals i.e., their role as nutrients or toxins, the chemistry of metals is often linked to, or plays a controlling role in, environmental processes including carbon cycling, ocean circulation, and weathering and transport of chemicals in nature.

Most of the trace elements are nutrients to the living organism, but toxic when it exceeds the concentration limit. The toxicity of trace elements is not just a measure of concentrations in the aquatic system but it is a total effect of speciation, complexation, mobility and sorption behaviour of elements during its cycling. Thus, an understanding of partitioning, complexation, mobility and speciation would help in better constraining the biogeochemical cycling of metal. The trace elements and rare earth elements are also used as tracers to constrain weathering process and elemental mobility in the catchment (Braun et al., 1998). The trace element, major ion and organic carbon data along with ancillary data like discharge, precipitation, alkalinity, pH, conductivity, and temperature will be helpful for better interpretation of the geochemistry of metals in the river. The study of metal and metalloid fluxes are the need of the day as rapid increase in the industrialization led to increased fluxes of trace elements to the nearby freshwater sources (Yan et al., 2000). In addition to discharge of metal pollutants to the freshwater source, in-situ biogeochemical processes affect the abundance and behaviour of metals in the river water. A time series monitoring of metal chemistry and physicochemical parameters in the river would help in better understanding the metal transport from continents to the oceans (Shiller, 1997).

Estuaries are dynamic fluvial system which connects the continental rivers with the open ocean. The estuaries can exhibit profound effect on the chemistry of continental chemical elements because of rigorous in-situ physical, biological and geochemical processes. The estuaries are also an efficient trap for sediment and associated chemical elements. The study of estuarine chemistry (particulate and dissolved) and the geochemical processes are an important aspect of geochemistry to establish the mass balance of chemical elements. The coupling of physical processes and biogeochemistry occurs at many spatial scales in estuaries (Geyer et al., 2000). Estuarine circulation, fresh water discharge (submarine groundwater and river water), tidal activity, resuspension of particle, and exchange flow with adjacent marsh systems (Leonard and Luther, 1995) all constitute important physical variables that exert some level control on estuarine biogeochemical cycles.
1.4. Why Nethravati-Gurupur river basin is chosen as a study area?

The Nethravati-Gurupur river basins are smaller in terms of catchment size but due to their close proximity to the Arabian Sea, they experience warm temperature and humid climate with intense precipitation (~4000mm; 2\textsuperscript{nd} highest in the country) which are known to induce rapid chemical weathering and erosion. Importantly, these rivers have steep gradients, which make rapid transport of sediments and water to the Arabian Sea. These rivers discharge about 8\% of the total discharge of water by the west flowing rivers (Rao, 1979). It is also noted that about 94\% of total discharge of the Nethravati River is mainly during the monsoon. The surface runoff in these rivers is 3300mm and 3550mm respectively. These characteristic features make it interesting to delineate the controlling factors of silicate weathering and associated carbon dioxide consumption.

The river Nethravati-Gurupur, is the primary drinking water source for Mangalore and its adjacent areas. In addition, water is used for industries like Mangalore Refinery and Petrochemicals Limited (MRPL)-Oil and Natural Gas Corporation (ONGC), Mangalore Chemicals and Fertilizers (MCF) and Badische Anilin- und Soda-Fabrik (BASF) dyes and for agriculture. The demand for water is set to increase as the government of India plans to setup two Special Economic Zones (SEZ) in the study area very soon. So, there is a need to generate baseline data on the quality of water. On the other hand, the river receives untreated sewage and domestic wastes from the urban and suburban regions. The effect of these wastes on the biotic and abiotic components needs to be studied.
1.5. Objectives and importance of the research investigation

Objectives

[1] To estimate the Silicate Weathering Rate (SWR), associated Carbon dioxide Consumption Rate (CCR) and its controlling parameters in a humid tropical silicate dominated terrain having higher surface runoff and warm temperature.

[2] To understand the sources of major ions and hydrogeochemistry of subsurface water in a humid tropical river basin.

[3] To understand the fractionation and elemental redistribution of chemical elements during weathering and transportation process in a humid tropical river basin.


[5] To understand the distribution and elemental abundance of metals in the particulate and bed sediments in a tropical estuary.

Importance

[1] Chemical weathering process at regional as well as global scale is important to better understand the past climate and its relation to geological processes.

[2] Geochemical processes controlling the water chemistry, and identification of source of contamination of groundwater in a highly populated region of west coast is important in setting up water resource management practices and policies.

[3] The fractionation of elements during weathering and subsequent redistribution by the geochemical processes occurring in the riverine environment is important, as elemental tracers are being used in paleo-climate and pollution research studies.

[4] Effect of physiochemical parameters on the sedimentary metal characteristics and metal abundance is important to evaluate the geochemical behaviour of metals in the estuary along the salinity gradient.

[5] The geochemical data generated in this study is baseline for monitoring the impact of industries on the river water and it helps to assess the anthropogenic influence at various locations.
1.6. Structure of the thesis

The thesis has been divided into eight chapters

Chapter 1 gives a general introduction to the geochemical research and the need of studying the geochemical aspects in riverine and estuarine environment. This chapter introduces and explains the scope of geochemical research carried out to meet the set objectives of the thesis. The chapter gives overall information on chemical composition of river-estuary-ground water, sources of chemical composition of these samples and what makes the chemical composition to vary through space and time.

Chapter 2 gives a detailed description of the study area, sampling and the analytical procedures. The description of the study area includes information on their general geology, major and minor lithologies of the drainage basin, vegetation, rainfall and temperature in the region. The sampling and analytical procedures include the techniques of sample collection, preparation and chemical treatment (particularly for particulate and isotopic composition measurement), measurement procedures, precision and accuracy.

Chapter 3 discusses the major ion composition of the rivers sampled in this study, chemical/silicate weathering and associated CO$_2$ consumption in the river Nethravati-Gurupur river basin. Further, a comparison has been made with other tropical/silicate basement watersheds to derive the possible controlling factor on the silicate weathering rate.

Chapter 4 focuses on the groundwater chemistry with respect to major ions and the hydrogeochemical processes governing the chemistry. In addition, temporal and spatial variations in the groundwater chemistry are discussed. The sources of water and chemical elements are evaluated. In addition, the interaction of groundwater with surface water is discussed with the help of stable isotopic composition.

Chapter 5 focusses on the temporal variation of dissolved major ions, trace elements and strontium isotopic composition, and particulate and bed sediment chemistry in the Nethravati-Gurupur river basin. The weathering conditions and the elemental mobility during the weathering process are discussed.
Chapter 6 focusses on the biogeochemistry of dissolved trace elements and their variation in space and time. The redox reaction, adsorption/desorption reaction control on the dissolved trace elements has been explained in this chapter.

Chapter 7 focusses on the metal chemistry of particulate matter in the river and sea interface environment. The variation metals in particulate matter and sediments along the salinity gradient at different physicochemical conditions has been explained. Finally, an attempt has been made to evaluate the fate of chemical elements/contaminants in the estuarine region. Also, the level of pollution has been evaluated using enrichment factor and geo-accumulation indexes.

Chapter 8 is a synthesis of the results obtained in this study on chemical weathering, hydrogeochemistry of groundwater and biogeochemistry metals using multi-element and isotopes as geochemical tracers. Based on the results, future directions and scope of further research has been proposed.
References


Chapter 1


Yan XP, Kerrich R, Hendry MJ (2000). Distribution of arsenic (III), arsenic (V) and total inorganic arsenic in pore waters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. Geochimica et Cosmochimica Acta, 64, 2637-2648.