1.1 Natural water and its characteristics

The term “Natural Water” includes oceans, freshwater lakes, ponds, streams, rivers and springs and all these acts as an active interface among the atmosphere, lithosphere and the biosphere. Again, at the scale of a watershed, the natural waters act as the fundamental link amongst the various components of the catchment ecosystem. Although natural waters are comparatively dilute aqueous solutions, they are chemically very complex and dynamic systems comprising of different components - various solutes, organic matter and colloidal or particulate material. These constituents interact chemically with other dissolved materials. A number of chemical processes occur between the various trace elements dissolved in very low amounts and each of the above mentioned components in the aquatic reservoirs. The geochemical and biological reactivity of trace metals is determined by their distribution across the different chemical species and fractions. All the factors that determines the characteristics and composition of natural waters can be said to be under the three dominant controls- climatic, lithogenic and biogenic. Some of the chemical processes that occur due to these controls are those of concentration, dissolution, precipitation, ion exchange, redox reactions, sorption and consumption. The chemical composition of river waters, lakes and springs is mainly due to atmospheric and lithological sources. Processes of chemical weathering and solute transport provide most of important link between the atmosphere, lithosphere, and biosphere. The relative contribution of solutes to surface waters from the various sources is a function of climate which is being increasingly modified by human activity. Importance of solute study lies in the fact that it allows for calculating rates of chemical denudation and for gaining an understanding of the controls on the river water chemistry. Thus, for a complete characterization of natural waters an appropriate monitoring and assessment of the above processes and components is required and this comes under the ambit of hydro-geochemistry.
1.1.1 Contamination of natural waters

Contamination of natural waters is a matter of public health concern. Natural waters are frequently contaminated by chemical contaminants of numerous origins and also through microbial pathogens. However, it is often observed that the microbial contaminants are given more priority than the chemical contaminants in the natural waters that are being used directly for domestic purposes. This is because the symptoms of adverse health effects due to chemical contaminants are generally observed after long-term exposures, whereas the effects from microbial contaminants usually observed immediately after short exposures. Nonetheless, health hazard due to chemical contaminants in water supplies can cause fatal conditions in humans. According to World Health Organization, the various sources of chemicals in natural water can be categorized as follows:

- Naturally occurring chemicals: Weathering and leaching of rocks, minerals and soils
- Chemicals from agricultural activities: Application of manure, fertilizer and pesticides; intensive livestock and animal husbandry practices
- Chemicals from human settlements: Sewage and waste disposal, urban runoff,
- Chemicals from industrial activities: Manufacturing, processing and mining
- Chemicals from water treatment: Water treatment chemicals; corrosion of, and distribution and leaching from, storage tanks and pipes

According to Ako et al., (2012) the two most important criteria for identifying specific chemicals of concern to public health are:

(i) High probability of consumer exposure from drinking-water
(ii) Significant hazard to health.

Water quality data in the developing countries are limited or non-existent and this is particularly true for the rural areas of these countries. In absence of such data, it is difficult to determine priorities for risk management. As such based on the probability of exposure only, the risk management priorities are formulated. Further, such operations also depend upon the various pathways of contaminants and the factors affecting the concentration along the pathways.
1.1.2 Pathways of contamination

Human exposure to any particular contaminant requires a pathway from the source to the consumer. The pathway for the transport of the contaminants may be direct or very complex in nature. The transport may occur through aquifers, surface water bodies, rocks, runoff etc. Very often such pathway includes the public water supply systems.

![Pollutant contamination pathways in aquatic ecosystems](image)

Figure 1: Pollutant contamination pathways in aquatic ecosystems (Source: WHO)

1.1.3 Factors affecting chemical concentrations along pathways

It is pertinent to point out here the major processes that affect the concentration of contaminants along its pathways. This is because these processes can effectively reduce the concentration of the chemical on its path from its source to its fate. The major factors affecting chemical concentration along the pathways can be categorized as follows:

- Mixing and dilution of source waters
- Volatilization of organic compounds
- Adsorption of inorganic and organic compounds to soil, sediments or rocks
- Chemical environment- alkalinity, acidity of water affecting transformation of minerals and other chemical compounds
- Biological degradation/transformation/adsorption of chemicals
1.2 River sediments

Hydro-geochemical studies of natural water systems are never accomplished without studying the associated sediments of the system. This is because the sediments not only provide nutrients for living organisms but also act as sinks for harmful chemicals and so sediments are rightly considered as one of the basic components of our environment. Taking the case of river sediments, they act as source of persistent bioaccumulative chemicals even after the point and non-point sources have stopped releasing those chemicals. The river sediment contaminants can cause serious ecological damages. Some of the documented adverse effects include skin lesions, reproductive disorders and ailments in fishes and fish-eating birds and mammals. Further, toxicity due to the contaminants can cause decreased biodiversity in the riverine ecosystems. Metal contaminants released from sediments can bioaccumulate in fish and other aquatic organisms. These organisms when consumed by human beings pose a direct threat to human health (Mülligan et al., 2001; Lasheen, 2008). Thus, river sediments can act as both carrier and source of chemical contamination. Further, the sediments can be analyzed to learn about the rivers’ past pollution history (Tsai et al., 2003). Studying the concentration and distribution of heavy metals in the river sediments allows the researchers to identify the source of anthropogenic impact on the aquatic ecosystem.

Among the various chemical reactions, those involving the association of trace elements with suspended and bottom sediments are the most important processes in the cycling of trace metals in natural waters on a wide range of timescales. It has been found that trace metals occurring in most rivers are predominantly carried by suspended particles and only a small fraction is transported in the soluble form (Moore and Ramamoorthy, 1984, Horowitz, 1991).
1.3 Chemical fractionation or speciation of trace elements in sediments

Natural sediments are a mixture of different physico-chemical phases which can be broadly categorized as – residues of weathering, erosion and products of biological activity. Clays, alumino-silicates, iron and aluminum oxy-hydroxides and sulfides are examples of the first category. On the other hand biological activity produces substances like detritus and humus, carbonates, phosphates and silica (Tessier, 1992).

Understanding the behavior and concentration of trace metals in sediment is an important aspect of detection of the source and degree of pollution and also the distribution mechanisms in aquatic systems. As compared to the total concentration of the metals in sediments, the study of chemical form of the metal is more relevant in determining its bioavailability, reactivity and mobility which render chemical speciation study of metals an utmost necessity (Morrison, 1989).

The notion that all the chemical forms of a trace metal have the same impact on the environment has led to the use of total metal concentration as a criterion in sediment pollution assessment. However, according to Tessier et al., (1979) such an assumption does not hold well. It is evident from various works that the different forms of trace metal pollutants attached with the various sediment phases have specific impact on the environment. Sequential extraction procedure is a common method of speciation and extraction of different trace metal-sediment phase associates. Such procedures are base on the principle of partition of solid material into different fractions which are further selectively extracted alongwith associated trace metals using appropriate reagents (Tessier et al., 1979; Tessier et al., 1980; Horowitz, 1991; Tessier, 1992; Langen et al., 1994). Based on the same principle, a number of sequential extraction schemes have been devised by several authors and have been applied to assess the bioavailability and mobility of trace metals in sediments of aquatic systems throughout the world (Pardo et al., 1993; Tack and Verloo 1995; Lim and Kiu 1995; Lopez-Sanchez et al., 1993; Abollino et al., 2000; Lasheen and Ammar, 2009).
1.4 Understanding chemical weathering processes in river basins through major ion composition

Many studies on major ion composition of rivers is aimed at determining chemical erosion rates of river basins, particularly silicate and carbonate erosion rates and the factors which regulates them. Due to chemical weathering processes in river basins, major ions are supplied to solutions from the entire lithology in the basin (Sharma and Sarma, 2011). This is particularly relevant in terms of the silicates, carbonates and also minor amounts of evaporites. It is necessary to characterize the source of major ions to rivers and acids involved in the weathering reactions to determine chemical and silicate erosion rates of the basin and CO$_2$ drawdown by silicate erosion (Singh, 2005).

Chemical weathering reactions in the river basins appear to be the primary source of solutes to rivers (Bhardwaj et al., 2010). These reactions can be either congruent dissolution of minerals (e.g. halite, gypsum) or reactions that are mediated through acids. However, acid mediated weathering reactions can be also be both congruent and incongruent. Reactions involving carbonate minerals are congruent whereas weathering of alumino-silicate minerals is generally incongruent resulting in the formation of secondary solids such as clays and oxides of iron and aluminum (Berner and Berner 1996; Drever, 2002). In the acid mediated reactions, rocks and minerals of the drainage basin react with hydrogen ions (H$^+$) in rivers releasing a number of cations and anions to solution. Solutions of CO$_2$ drawn from the atmosphere and from soil gas forming carbonic acid is believed to be the most common source of H$^+$ in rivers. In highly vegetated river basins, the pCO$_2$ in soil gas is higher than the pCO$_2$ in atmosphere. This is due to the oxidation of biogenic matter in the upper soil horizon. Thus, the river in densely vegetated area derives higher amount of CO$_2$ for the formation of carbonic acid from soil gas. Some other sources of H$^+$ ions for the weathering reactions are sulphuric acids, humic acids, fulvic acids and organic acids. Sulphuric acid results from oxidation of pyrites and organic acid are formed from oxidation of vegetation in upper layer of soil. The H$^+$ ion liberated from sulphuric acid reacts with the various minerals, yielding cations from them and SO$_4^{2-}$ ions (Berner and Berner, 1996; Drever, 2002). Chemical weathering of silicates with carbonic acid...
releases Na\(^+\), K\(^+\), Mg\(^+\), Ca\(^+\) from them to solution along with HCO\(^3-\). These reactions are a key component of atmospheric CO\(_2\) balance and therefore of global temperature. A major topic of research on river geochemistry is to determine basin scale silicate erosion rates and their impact on atmospheric CO\(_2\) drawdown. It has been suggested that the uplift of the Himalaya during the Cenozoic enhanced global silicate erosion and this in turn contributed to global cooling via increased CO\(_2\) drawdown (Raymo and Ruddiman, 1992; Ruddiman, 1997).

1.5 Statement of the problem

Kameng river in the western Arunachal Pradesh is susceptible to various forms of environmental problems owing to its natural characteristics and also due to some human interference. Anthropogenic activities such as jhum cultivation along the river valley cause disruption in watershed hydrology. Accelerated natural degradation due to erosion, runoff, and nutrient losses are consequences of such human negligent attitude towards nature. This also leads to heavy load of suspended sediment into the river and thereby changing the natural geochemical composition of the river. Additionally due to addition of animal wastes, human faecal matter, fertilizer and pesticide application in agricultural lands brings about nutrient and toxic problems into the river valley.

Geologically, heavy metal contamination in river water is a bigger possibility due to rock-water interaction and base metal mineralization. Therefore while Kameng river flows from its pristine source to the confluence zone at Bhalukpong, the quality of the river water and nature of the streams become altered continuously by both natural and anthropogenic changes.

Although heavy metal contamination have been reported in downstream stretches of Kameng river (also known as Jia Bhareli) in some recent works (Hoque et al., 2011; Khound et al., 2012), no systematic research has been carried out in this regard in the upper reaches of the river basin. Some consultancy reports in respect of hydroelectric projects in the river basin are available at the public domain, but these lack the scientific authenticity.
Rivers being dynamic systems serve to transport or store contaminants which are brought in from outside sources. If contaminants are readily transported, the rivers provide a means by which contaminants can migrate and adversely impact downstream. Again when contaminants are stored, it may result in adverse localized problems or form a contaminant reservoir which may be released at a later time (Solo Gabriele, 1995). Therefore it becomes imperative to understand the underlying hydrogeochemical processes which actually control the transport and fate of contaminants in the river. The health and livelihood of downstream people are severely affected due to deterioration of water quality. Due to this fact, in our country a specific law in the form of Water (Prevention and Control of Pollution) Act, 1974 (6 of 1974) has been enacted. Thus to maintain and restore the “wholesomeness” of the river water quality is also a requirement under the law of the land. Furthermore, knowledge of such processes allows successfully designing and implementing future control measures.

1.6 Objectives

Keeping in mind the different hydrogeochemical aspects of the Kameng river basin, the following objectives have been taken into consideration for this study:

1. To study the major ion chemistry of the Kameng river water
2. To study the heavy metal distribution in Kameng river water
3. To study the environmental geochemistry of bed sediments of Kameng river
4. To study the chemical fractionation of selected heavy metals in the bed sediments of Kameng river
1.7 Scope of study

This study focuses on the middle and lower stretches of Kameng river within the geographical boundary of Arunachal Pradesh. Sampling was carried out in the Kameng main channel along with its tributaries, namely – Tenga, Bichom, Papu. Geographically the sampling locations were at Tenga valley and Bhalukpong circle within the West Kameng district and at Seppa, Bana and Papu valley within the East Kameng district. Sampling in higher altitude areas and remote areas of the river basin could not be done due to inaccessibility and hard conditions. Further sampling was limited only to pre-monsoon and post-monsoon season owing to frequent landslides and blockage of the motorable roads during the rainy season. The sampling locations were chosen based on its proximity to anthropogenic activities along the river stretches. A total of 27 numbers of surface water and equal number of sediment samples were collected during each sampling trip in both seasons. During the study period the following parameters were investigated:

For water samples: pH, Conductance, TDS, Turbidity, DO, BOD, TH, Chloride, Sulphate, Nitrate, Bicarbonate, Sodium, Potassium, Calcium, Magnesium, Fluoride, Copper, Zinc, Manganese, Iron, Cadmium, Lead and Arsenic

For sediment samples: pH, Conductance, Bulk Density, Organic Matter, Trace elements quantification (using XRF technique) and Mineral identification (using XRD and FTIR techniques).