# SEDIMENT-BOUND HEAVY METALS IN HIMALAYAN STRETCH OF GANGA

**A Project Dissertation Submitted in the Partial Fulfilment of the Requirements for the Degree of**

## MASTER OF TECHNOLOGY

**IN**

## ENVIRONMENTAL ENGINEERING


**Submitted by**

**Naveen Radhakrishnan**

**(2K14/ENE/11)**

**Research Supervisor**

**Dr. A. K. HARITASH**

**Department of Environmental Engineering**

# Delhi Technological University


**June 2016**

# CERTIFICATE

This is to certify that Mr. NAVEEN RADHAKRISHNAN, M. Tech. student in the Department of Environmental Engineering has submitted a dissertation on "SEDIMENT-BOUND HEAVY METALS IN HIMALAYAN STRETCH OF GANGA" in partial fulfillment of the requirement for award of degree of Master of Technology in Environmental Engineering, during the academic year 2015-16.

It is a record of the student's research work prepared under my supervision and guidance.

Naveen Radhakrishnan
(Candidate)

(Dr. A. K. Haritash)

Assistant Professor
Environmental Engineering
Delhi Technological University

Date :

Place: Delhi

# Declaration of Originality

I hereby undertake that I am the sole author of this report. I undertake that this report neither infringes upon anyone's copyright nor violates any proprietary rights to the best of my knowledge. Any ideas, techniques, quotations, or any other material form of work of other people included in this report, published or otherwise, are fully acknowledged in accordance with the standard referencing practices.

I declare that this is the true copy of my report, including all revisions, as approved by my advisor and supervisor, and that this report has not been submitted for any other degree to any other University or Institution.

(Naveen Radhakrishnan)

# Acknowledgement

*The dissertation is an important part of the degree of M. Tech. in Environmental Engineering. No research can be accomplished without the guidance of research supervisor, cooperation of faculty members and friends. We would like to thank all those who helped us directly or indirectly in getting this task of research through.*

*It gives me immense pleasure to take this opportunity to thank our Head of Department of Environmental Engineering, Dr. A.K Gupta for providing the lab facilities required to carry out the project.*

*I feel greatly privileged to express my sincere thanks and regards to the Project mentor, Dr. A. K. Haritash, Assistant Professor (Environmental Engineering), DTU, who not only guided me but also took great effort in making the project a success. I thank him for his keen interest, moral support, invaluable suggestions and guidance. I also express a sincere thanks to Dr. M.K.Sharma, Scientist 'D', National Institute of Hydrology, Roorkee, for his constant support and guidance throughout the project.Help provided by Mr. Shyamlal, a Ph.D scholar of NIH, Roorkee is also acknowledged*

*A special word of thanks to Mrs. Vandana Shan, Ms. Manisha Verma, Ms. Deepika, Mrs. Navita, Mr. Jai and Mr. Sahil. I would also like to thank all the faculty members along with the officials of Delhi Technological University for assisting us in the realization of this project.*

(Naveen Radhakrishnan)

# Abstract

Analysing the sediment quality of rivers is vital while assessing the quality of rivers. The sediments of river Ganga in the Himalayan region are assessed for different heavy metals - Cd, Cr, Cu, Ni, Pb and Zn at 7 different locations. The concentrations of Al and Fe, two of the conservative metals were also analysed for comparison. The sediments collected were sieved, to classify them into 8 different sizes - 0-75µm, 75-150µm, 150-200µm, 200-250µm, 250-300µm, 300-450µm, 450-600µm and >600µm. The concentration of heavy metals are found for each of these particle size. The concentration of all the metals except Al and Fe showed an increase as we moved from Gomukh to Rishikesh. In general, the order of the metal concentration in the study area was Al > Fe > Cr > Zn > Pb > Ni > Cu > Cd. It was also observed that the concentration of heavy metals was also dependent on particle size as a strong negative correlation was found between particle size and concentration. A strong positive correlation also existed between various metals like Al-Fe, Cr-Pb, Zn-Cu, Zn-Cd, Cu-Cd and Ni-Cd indicating a common source for these metals. Various factors like Contamination Factor and Metal Enrichment Factor showed that the sediments at the downstream locations i.e. Chinyalisaur, Devaprayag and Rishikesh were contaminated and enriched with many toxic metals. Geo-accumulation index showed that the sediments of Chinyalisaur were uncontaminated to moderately contaminated with Pb and Ni and moderately contaminated with Cd; the sediments of Devaprayag were moderately contaminated with Pb and Cd and the sediments of Rishikesh were uncontaminated to moderately contaminated with Cu and Ni, moderately contaminated with Pb and moderately to strongly contaminated with Cd. Other indices such as Sediment Pollution Index and Pollution Load Index revealed that the sediments of Chinyalisaur, Devaprayag and Rishikesh were polluted to different degrees. Most of the pollution in these centres are mainly attributed to anthropogenic sources as human activities in these areas have been on a rise since the past few decades. The increased concentration and increasing relative mobility of metals with respect to distance from origin also confirms the addition and higher ecotoxicological effects to the aquatic system in the Himalayan stretch of River Ganga.

# Contents

# List of Figures

# List of Tables

# List of Abbreviations and Symbols

| | |
|---|---|
| UEPPCB | Uttarakhand Environment Protection and Pollution Control Board |
| WHO | World Health Organisation |
| DO | Dissolved Oxygen |
| Al | Aluminium |
| Fe | Iron |
| Cd | Cadmium |
| Cr | Chromium |
| Cu | Copper |
| Ni | Nickel |
| Pb | Lead |
| Zn | Zinc |
| Se | Selenium |
| Mn | Manganese |
| Hg | Mercury |
| As | Arsenic |
| µg/L | microgram per Litre |
| USEPA | United States Environmental Protection Agency |
| E.*coli* | *Escherichia coli* |
| mg/l | milligram per litre |
| EC | Electric Conductivity |
| SAR | Sodium Absorption Ratio |
| BIS | Bureau of Indian Standards |
| BOD | Biological Oxygen Demand |
| D/s | Downstream |
| U/s | Upstream |
| OC | Organic Carbon |

| | |
|---|---|
| TOC | Total Organic Carbon |
| µg/g | microgram per gram |
| mg/Kg | milligram per kilogram |
| DNA | Deoxyribonucleic Acid |
| ppm | parts per million |
| $HNO_3$ | Nitric Acid |
| HCl | Hydrochloric Acid |
| $H_2SO_4$ | Sulphuric Acid |
| $CrO_3$ | Chromium Trioxide |
| AAS | Atomic Absorption Spectrophotometer |
| EF | Enrichment Factor |
| GAI | Geo-accumulation Index |
| SPI | Sediment Pollution Index |
| CF | Contamination Factor |
| PLI | Pollution Load Index |
| M/Al | Metal to Aluminium ratio |

# Chapter 1

# INTRODUCTION

Water is an important resource needed to support life. It constitutes the hydrosphere which is an important part of biosphere. Almost three-fourth of the Earth's surface is water. 97% of the water is a part of oceans which cannot be used for regular needs of humans. Only the remaining 3% of the water is fresh. Even this is not fully accessible to us as around 68.7% of the fresh water is trapped as ice in polar regions and as glaciers. 30.1 % of the water is present underground, as groundwater. A mere 0.3% of the fresh water is present as surface water. 98% of the surface water is lakes, ponds and swamps and the remaining 2% constitute the rivers. So despite the Earth having plentiful amount of water, scarcity of water do exist in large part of the world (Igor *et al.*, 1993). The fresh water that is available for human consumption and usage is very less. The major sources of water are lakes, rivers, ponds, streams, ground-water etc. This small portion of water was sufficient to support life, long back. But presently with the ever increasing population, industrialisation, urbanisation and various other human activities there has been a shortage of fresh water in many parts of the world. The existing sources of water are getting deteriorated day by day.

River systems add up to about 0.0001% of Earth's water. This may not seem to be a large amount, but rivers drain as much as 75% of Earth's land surface. Rivers are often referred to as Earth's circulatory system. This is because river water is highly influenced by the surroundings. The river water takes with it the sediments, nutrients or any kind of pollutant that is present and transports them along with it till it drains into the oceans. It thus provides imperative linkages between land, lakes, wetlands and oceans. The rivers have been an important sources from time immemorial. Most of the civilisations originated near the bank of rivers, stressing on the importance of rivers for human development. In fact even in the present world, rivers support most of the important cities of the world like New York is located near Hudson River, London is located near Thames, Alexandria is located near Nile, New Delhi is located near Yamuna and so on. Unlike lakes and ponds, rivers are flowing water bodies and hence their self purification capacity is much more. This is one of the major reason why rivers scores over lakes. They tend to dilute and disperse the pollutants that enter into them. The self purification capacity depends on a lot of factors like flow of river, temperature etc. The quality of rivers is often monitored through various river monitoring programmes. The data obtained from monitoring rivers are used to characterise rivers, identifying emerging problems, identifying the trends in the quality with respect to time and space, determining whether the pollution control programmes are working or not, respond to emergencies such as floods and spills, effect in direct control of pollution wherever needed.

The Ganga is a trans-boundary river in South Asia, flowing through the countries India and Bangladesh. The length of the river is 2525 Km with catchment area of 10,80,000Km$^2$. It originates in the Indian state of Uttarakhand from the Gangotri Glacier of Western Himalayas. From there it flows to south and east through the Northern Plains of India, crosses the boundaries to reach Bangladesh and empties into Bay of Bengal. The Ganga River Basin is one of the largest living river systems in the world. It flows through 5 states of India, but its catchment provides water to a total of 11 states. It supports a population of 500 million which is same as the population of USA, Canada and Russia combined. The river supports a variety of ecosystems starting from the alpine forests of Uttarakhand to the plains of Northern India to the mangrove forests of West Bengal.

The river Ganga was once synonymous with purity. The water of the river was known for its self purifying capacity. But over the years, with the increase in human population and activities near the river, it has undergone rapid changes. These activities include industrial discharge, disposal of untreated sewage, mining activities, tourism and religious activities, and various domestic activities. The water of river Ganga kept on getting polluted especially in the Northern Plains. The river flows through many of the important cities of North and East India like Kanpur, Varanasi, Allahabad, Patna and Kolkata. A lot of tanneries, chemical plants, textile mills, distilleries, slaughter houses discharge their partially treated or untreated wastes into the rivers thereby polluting it. Mining, disposal of treated and untreated toxic wastes and metal chelates from different industries resulted in deterioration of water quality rendering serious environmental problems. Discharge of heavy metals with industrial effluent of pulp and paper mills and distilleries were also reported in many studies. Inadequate urban sanitary infrastructure, lack of formulation of plans and ineffective implementation of necessary pollution control measures are making the situation worse. These materials are often non-biodegradable and toxic. A lot of studies revealed that the condition of the river is not as sound as what it was earlier. The same scenario is true for all the other cities as well and also all other rivers including Yamuna, Gomti, Hindon, Chambal etc. But of late, even the water in the Himalayan ranges has started to get polluted. The tourism sector, agricultural activities and industries have a major role in this. Due to these factors, deterioration of water quality of Himalayan rivers has been suspected. As per Uttarakhand Environment Protection and Pollution Control Board report (UEPPCB, 2007) submitted to Central Pollution Control Board of India, paper industries discharge nearly 141,620 KLD effluent, sugar industries discharge nearly 24,137 KLD, and distilleries discharge nearly 6,000 KLD effluent into river bodies of Uttarakhand. Along with these, 97.37 MLD of sewage either in treated or untreated form find their way into water bodies of Uttarakhand (UPJN, 2009). Following these a lot of studies have been carried out on the water bodies of Uttarakhand. Most of the above studies have reported that the Himalayan rivers are no more of the superior quality as they earlier were. Their condition isn't as alarming as the state of rivers in the plain, but still needs constant attention so that they don't end up with the same fate as the later.

The degrading quality of water in these water bodies can have lots of adverse effects on living beings directly and indirectly. It will affect the availability of good water sources as the water that is polluted won't be able to put to use for drinking purposes. In addition to this, its usage for various domestic purposes will also get affected. The water also may not satisfy the requirements for usage in industries as well as for agricultural purposes. The inclusion of nutrients into the water body can accelerate the process of eutrophication. This in turn will have its effect on the plants and aquatic life around and in the water body. The natural beauty of the water bodies will be destroyed and the aesthetic appeal will be lost. Other than these, problems related to biomagnification can also effect the living beings especially the ones at the top of the food chain. The non-biodegradable part of the waste especially the toxic compounds and heavy metals get biomagnified as it moves from one trophic level to another. Humans who normally exist at the top most part of any trophic level have to bear the brunt of it. These toxic compounds may create many physiological and psychological problems. Their concentration keeps on increasing in the body as they don't get degraded very easily (bioaccumulation). When the concentration reaches a limit, various symptoms are seen and further accumulation of the toxic compounds or metals ultimately leads to death. From the discussion that has been made above, we can see that just how important it is to control the deterioration of our water bodies.

A measure of deterioration of water bodies can be given by the sediments present at the bank or river bed of the river. The sediments unlike water are comparatively less affected by various seasonal changes that occur. It is therefore believed that sediments in the river systems are a true representative of the pollution status of the river. Sometimes the river water may not be polluted but the sediments might be, which always poses a threat especially when there is a mobilisation of the toxic compounds from the sediments to the water column. Thus study of river water quality is not complete without the analysis of sediments. Sediment analysis is imperative for contamination study. One of the important parameter that is studied in sediments is the heavy metal content. Heavy metals can be added to the river systems from industrial waste water, sewage, wastes from chemical plants and hospitals, agricultural and highway run off and leachates from mines that make their way into the river systems. Along with these there are various natural reasons. Weathering of rocks is one of the major cause for this. Heavy metals are bio-accumulative in nature. Once they enter the biotic system they have a tendency to get retained in the body, thus increasing their concentration with time. Heavy metals that are normally of concern are Cd, As, Hg, Pb, Cu, Ni, Zn, Cr and Mn. These toxic metals have a huge tendency to get adsorbed on to the surface of soil sediments especially when the flow is low. When a favourable condition arises, these metals get mobilised from the sediments to the water. Thus, sediments are the most important source as well as sink of heavy metals. Hence their study is vital for studying the effects of heavy metals. The concentration of these toxic metals has to be kept in check, as they can enter the body of humans through water and food. Direct consumption of water can make way for the entry of these toxic metals into our body. Sometimes the water would be so much contaminated with heavy metals that even proper treatment may not be able to deal with them. The heavy metals can also enter through food. The metal concentration in plants and fishes living in such conditions will be relatively high. It increases when someone consumes them i.e.

biomagnifies and they keep on magnifying as we move from one trophic level to another. The animals at the top of the trophic levels are adversely effected with this. The detrimental effects of these heavy metals are large in number and these dealt with in detail in the coming sections.

With due concern to all of the above aspects, the present study was carried out, with the following objectives:

- To determine the metal concentration in the sediments of River Ganga from different locations in the Himalayas with respect to particle size.
- To evaluate Metal Enrichment Factor and Contamination Factor for different metal to understand their respective enrichment and contamination status in the sediments at different locations.
- To evaluate Geo-accumulation Index, Sediment Pollution Index and Pollution Load Index to assess the quality of sediments at a particular location.
- To find the Relative Mobility of Metals and to classify the source of pollution, if any.

# Chapter 2

# LITERATURE REVIEW

The distribution of water has been dealt in the previous chapter. From that it can be seen that even with so much of water around us, all of that cannot be used to meet our needs. The water that can be put to use is much lesser than the actual quantity of available water. To this limited supply of water when we add other factors like growing population, urbanisation and industrialisation into consideration, a problem related to water shortage can arise. Along with this if the existing sources of water gets polluted it can create even more stress on the limited supply on the water and that has just been the case in the past few decades. More number of cities around the world have become mega cities with a population of more than 10 million. The population directly effects the domestic demands of water. Water demand for agriculture also increases as more food is required to feed the increased population. Rapid industrialisation and urbanisation which is a typical feature of any growing city adds to the hassle of water shortage. The effluents from these industries, domestic wastes, mine wastes, agricultural wastes go on to pollute the water bodies. All these lead to a reduction of both quantity of wholesome water and quality of water. The sources of water pollution are discussed below.

## 2.1. SOURCES OF WATER POLLUTION

### 2.1.1. Run Off from Agricultural Fields

Agricultural pollution is one of the major sources of river water pollution. It can cause both direct and indirect impacts on human health. The WHO reports that nitrogen levels in groundwater have increased in many parts of the world as a result of intensification of farming practice (WHO, 1993). This phenomenon is well known in parts of Europe. Nitrate levels have grown in some countries to the point where more than 10% of the population is exposed to nitrate levels in drinking water that are above the 10 mg/l guideline. Although WHO finds no significant links between nitrate and nitrite and human cancers, the drinking water guideline is established to prevent methaemoglobinaemia to which infants are particularly susceptible (WHO, 1993). The pollution can be due to the run off from agricultural fields which are high in nutrients like nitrates and phosphates. These tend to accelerate the plant growth including many unwanted weeds, shrubs and plants. Upon dying, these increase the organic matter content of the rivers and decreases the D.O. content in water. Another problem that is exerted by agricultural run offs are the pesticides present in them. An analysis of pesticidal pollution in river Ghaggar in Haryana showed that the water was having high contents of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT). These two were traceable in all the collected water samples and their concentration were above the permissible limit specified by European Commission Directive for drinking purposes (Kaushik *et al.*, 2010).

### 2.1.2. Run Off from Mining Sites

Mining sites are another major sources of water pollution. Desertion of mines are causes of many environmental distress (Mileusnic *et al.*, 2014). Mines are abandoned due to various reasons. These include technical reasons (adverse geotechnical problems and problems with equipments), regulatory reasons (environmental violation or safety violation), social and community pressure, geological surprises (low grade or size of ore body), economic reasons (low commodity price or high production cost), closure of downstream markets and industries. Wastes from these deserted and active mines act as continuous source of heavy metals. These tend to pollute and degrade the quality of soil, water and also the living biota (Fernandez-Caliani *et al.*, 2009; Mileusnic *et al.*, 2014). Mostly they are homogeneous, loose and fine. These wastes have very low moisture holding capacity and bulk density and are devoid of any kind of nutrients. Because of this, they don't allow plants to thrive in that area restricting the plant colonisation. Further problems are caused during the rains and at the time of strong winds (Mileusnic *et al.*, 2014; Kumar & Maiti 2014). The contact between serpentine rocks and natural water can cause the water to get enriched with heavy metals (Apollaro *et al.*, 2011). These heavy metals can get easily adsorbed onto sediments which then goes on to get accumulated with time. Under favourable conditions, they move from the sediments into the water thus enriching the water with heavy metals. For instance, extensive open cast and underground mining carried out in Chibasa district of Jharkhand has lead to severe pollution of nearby agricultural fields, the run off of which has contaminated the water sources with heavy metals (Kumar & Maiti, 2015). The abondoned chromite-asbestos mine wastes were found to be acting as a perennial source of contamination for the nearby agricultural fields. The concentration of both Cr and Ni were found to be way above the limits of toxicity for soils. The CF and GAI were also found to be very high for these to metals. This high concentration of metals was found for considerable depth indicating a thick deposition of heavy metals. In addition to this, other metals like Mn, Zn, Co, Cu and Pb were also detected with concentration varying from low to moderate. Water flowing through these mining sites and agricultural fields were also effected as Cr and Ni concentration was found to be above the critical drinking water total concentration. Cr concentration above toxicity limit was found in the sediment and water sample of tributary flowing close to the sites.

### 2.1.3. Atmospheric Deposition

Some recent observations have indicated that air-borne heavy metals are increasingly becoming an important source of contamination of soil and plant produce even for those areas situated away from the emission sources (Sharma *et al*., 2007). Urban and peri-urban areas are worst affected by air-borne contaminations (Pandey & Pandey, 2009). The impacts of long-range atmospheric transport and deposition of pollutant aerosols on terrestrial systems are well documented from long-back (Pandey & Agrawal, 1994), impact of such depositions on aquatic habitats especially on river systems have received attention only recently (Thornton & Dise, 1998). Some earlier studies have indicated sizable atmospheric input of trace metals to lake systems (Eisenreich, 1980; Bragazza, 2006). Recent researches have indicated rising trends in atmospheric deposition of toxic metals in different parts of the world including the Indian sub-continent (Azimi *et al*., 2003; Singh & Agrawal, 2005). For developing countries in particular, this problem is rapidly rising due to newly establishing industries coupled with fastened urban growth and lack of efficient control measures (Borbely–Kiss *et al*., 1999; Pandey & Pandey, 2009). Furthermore, unlike most of the surface discharge sources which contaminate soil and water bodies under limited spatial range, aerial emission often follows long-range atmospheric transport and contaminates wider range of ecosystems down-wind of the emission sources. In river systems, where the stream-flow restricts mid-stream access of land-borne contaminants, atmospheric deposition directly adds contaminants on to the water surfaces. Thus, despite all efforts to minimize environmental contamination, atmospherically driven toxic metals will continue to contaminate ecosystems including surface water resources. A study was conducted on the concentration of 5 heavy metals (Cd, Cr Cu, Ni and Pb) in mid-stream water of Ganga with respect to their inputs through atmospheric deposition at Varanasi (Pandey *et al*., 2009). It was found that atmospheric deposition was highest for Pb (1.80 - 124.00 g/ha/y). A similar result was obtained when a study was conducted on air deposition for various sites in Indian tropics (Singh and Agarwal, 2005; Pandey and Pandey, 2009). In the case of mid-stream water the concentration of Ni was found to be highest (1.2 - 60.00 µg/L). Correlation analysis indicated significant relationships between the mean levels of heavy metals in water and their respective deposition, suggesting that at least some of the observed variability could be attributed to variations in atmospheric deposition recorded at different locations.

### 2.1.4. Sewage

Discharge of sewage into water bodies acts as another major source of water pollution. According to 2013 figures from the World Health Organization, some 780 million people (11 percent of the world's population) don't have access to safe drinking water, while 2.5 billion (40 percent of the world's population) don't have proper sanitation (hygienic toilet facilities); although there have been great improvements in securing access to clean water, relatively little progress has been made on improving global sanitation in the last decade. Sewage disposal affects people's immediate environments and leads to water-related illnesses such as diarrhoea that kills 760,000 children under five each year (WHO, 2013). Back in 2002, the World Health Organization estimated that water-related diseases could kill as many as 135 million people by 2020. In developed countries, most people have flush toilets that take sewage waste quickly and hygienically away from their homes. Yet the problem of sewage disposal does not end there. When you flush the toilet, the waste has to go somewhere and, even after it leaves the sewage treatment works, there is still waste to dispose of. Sometimes sewage waste is pumped untreated into the sea. Until the early 1990s, around 5 million tons of sewage was dumped by barge from New York City each year.
According to 2002 figures from the UK government's Department for the Environment, Food, and Rural Affairs (DEFRA, 2002), the sewers of Britain collect around 11 billion litres of waste water every day, some of it still pumped untreated into the sea through long pipes. The New River that crosses the border from Mexico into California once carried with it 20–25 million gallons (76–95 million litres) of raw sewage each day; a new waste water plant on the US-Mexico border, completed in 2007, substantially

solved that problem. Unfortunately, even in some of the richest nations, the practice of dumping sewage into the sea continues. In early 2012, it was reported that the tiny island of Guernsey (between Britain and France) has decided to continue dumping 16,000 tons of raw sewage into the sea each day (USEPA, 2013).

### 2.1.5. Waste Water from Industries

Waste water that comes from various industries, tanneries, power plants, chemical plants etc are perhaps the most important contributor of pollutants to waste bodies. Each year, the world generates perhaps 5–10 billion tons of industrial waste, much of which is pumped untreated into rivers, oceans, and other waterways (Spalding, 1998). In the United States alone, around 400,000 factories take clean water from rivers, and many pump polluted waters back in their place. However, there have been major improvements in waste water treatment recently. Since 1970, in the United States, the EPA has invested about $70 billion in improving water treatment plants that, as of 2015, serve around 88 percent of the US population (compared to just 69 percent in 1972). A similar type of action however has not been taken in other developing countries like India. Infact, the discharge of waste water is rarely monitored and partially treated as well as untreated waste water find their way into water bodies. An analysis of the sediments of Kazipalli lake which flows through Kazipalli Industrial Development Area, was carried out in 2011. The results showed that the sediments in the lake was moderately polluted with respect to Cu and Ni, moderate to heavy pollution occurred due to Cr, whereas the pollution due to As and Pb was heavy (Krishna and Mohan, 2012). This pollution was mainly attributed to the fact that most of the wastes from the industries Kazipalli IDA were let into this lake. Even the groundwater in the area have shown heavy metal contents because of the percolation of effluent into the aquifer through leaching and other processes from sediment surface. Even in the case of river Ganga, 13% of the pollution is due to chemical wastes from industries. Kanpur, which is the centre of multinational leather industries is considered to be the hot spot region of pollution in the Ganga Plain. More than 50% of the contents of Cd, Co, Cr, Cu, Hg, Ni, Pb, Sn, Zn and of organic carbon in sediments and soils of this region are derived from anthropogenic sources in which industrial effluents have a major role to play Ansari *et al.*, 1998). Other than heavy metals, many other chemical wastes are also discharged into rivers and lakes. The chemical plants are contributors of toxic wastes like any other industries. Highly toxic chemicals such as polychlorinated biphenyls (PCBs) were once widely used to manufacture electronic circuit boards, but their harmful effects have now been recognized and their use is highly restricted in many countries. Nevertheless, an estimated half million tons of PCBs were discharged into the environment during the 20th century. In a classic example of transboundary pollution, traces of PCBs have even been found in birds and fish in the Arctic. They were carried there through the oceans, thousands of miles from where they originally entered the environment. Although PCBs are widely banned, their effects will be felt for many decades because they last a long time in the environment without breaking down (Jorgensen *et al.*, 2006).

## 2.2. RIVER WATER QUALITY

As discussed earlier rivers are an important source for drinking water, other domestic, agricultural and industrial activities. The amount of water from rivers that supports so many cities of the world is a mere 2% of the total surface water (Igor, 1993). River water is an important source considering its self purification capacity compared to other still sources like lakes and ponds. The flow of the river ensures that the pollutants get transported to a larger distance and hence more effective dilution. The discharges from the big cities however have tested the self purification capacity of many rivers. The discharge is so high in pollutants - degradable as well as non-biodegradable, toxic as well as non-toxic, that the water is not able to dilute it properly. This has lead to the reduction in water quality at the downstream of any city, in general.

### 2.2.1. River Water Quality of International Rivers

In China, studies were carried out in the upper Han River for seasonal variation of dissolved trace elements and heavy metals (Li & Zhang, 2010). The river serves as the water source area for the middle route of China's South-to-North Water Transfer Project diverting water to northern China including Beijing and Tianjin city for various usages. During the period of 2005-06, 6 sampling campaigns (June, August and November 2005 and April, June and October 2006) were conducted and water was sampled from 42 sites. From each site, 3 samples were collected from different depths. When compared with drinking water guidelines by WHO (2006), China (2007) and

USEPA (2006), there were a number of metals with concentration higher than the levels for drinking water in different sampling times - Al, Cd, Pb, Sb and Se in June 2005, while As, Cd, Se and Sb in June 2006, Al and Cd in August 2005, As in October 2006 and As, Pb and Sb in Novemver 2005. These results shows the difference in concentration of metals with respect to season. This can be due to sesasonal anthropogenic activities and varying seasonal inputs to river water due to hydrological regime. The highest total concentration was in June 2005 which can be attributed to summers resulting in evaporation and intense anthropogenic activities like agriculture and mining during that month. During the rainy season (July - November), the dilution effect resulted in the decrease in the concentration of 15 metals. In terms of dry and rainy seasons, the average levels of Al, As, Cd, Pb and Se were above the permissible limits. Their findings were similar to the results reported in Danjiangkou Reservoir on the Han River (Li & Zhang *et al.*, 2010). When we take into account the priority toxic pollutants (As, Cd, Cr, Cu, Pb, Ni and Se) which were listed in the USEPA 2006 for aquatic life protection, the average concentration of Cu and Cd were beyond the Criteria Maximum Concentration (CMC) and Se, Al and Pb were higher than the Criterion Continuous Concentration (CCC) values of USEPA water quality criteria. Also, the mean metal concentrations in the river were much greater than the world average bacKground values. The water of river Bindare Stream of Chikaji Industrial Area Zaria, in the northern part of Nigeria was also found to be polluted with metals like Cu, Zn, Ti, Fe and Al (Abolude et al., 2013). Bindare Stream flows in a west-east direction along a gulley situated to the North-West of Sabon-Gari and Chikaji Industrial Area of Zaria. Bindare Stream which is about 6Km long took its source from Kwangila hills and empties into River Galma. The concentration of the metals obtained were compared with Nigerian Industrial Standards (NIS, 2007). The concentration of the above metal were not showing any compatibility with the NIS and hence they concluded that a continuous check should be made by NIS on the discharges made by industries. The value obtained for these metals coincided with the values for a nearby dam in Zaria, Nigeria (Oniye *et al*., 2002). Similarly a research done on Tembi River in Iran showed many metals having concentration greater than the permissible limits. The sampling was done for 4 seasons (Summer 2011, Autumn 2011, Winter 2011 and Spring 2012). Two sampling points were selected one at upstream and the other one at downstream. The analysis showed that there was a tremendous increase in the concentration of metals like Cd, Cu, Zn, Pb and Fe at the downstream when compared with that of upstream. The increase was much more than the normal one that one would expect. This was attributed to the fact that a lot of untreated sewage was discharged into it and the due to leaching of the solid wastes into the water. It was also noted that the concentration of the metals were maximum in summer and least in spring. They concluded that the water of the Tembi River were contaminated by heavy metals and, therefore, using this water for recreational purposes, washing, and fishing is detrimental to human health and the environment (Saeed *et al.*, 2014).

### 2.2.2. River Water Quality in India

The problem of river water getting polluted is equally of concern to the Indian rivers. Even the Himalayan ranges which ones were excellent sources of drinking water are now getting effected. This was proved by various studies which showed that the water may not be suitable for drinking throughout the year (Joshi *et al*., 2009). A study was conducted in Haridwar to test the quality of river Ganga for drinking purpose. They collected 90 water samples from 5 sampling stations and analysed them for physico-chemical parameters. The test was carried out in 2007 and 2008 in 3 different seasons i.e. summer, winter and rainy. The analytical data of various physicochemical parameters indicates that some parameters like pH, electrical conductivity, total dissolved solids , total suspended solids, turbidity and sodium are found to be in excess than the prescribed limit in some water samples of the study areas. The WQI value indicates that water samples of some sampling stations are quite unfit for drinking purpose because of high value of dissolved solids and sodium. It was also observed that the water in the year 2007 was of a better quality than in the year 2008. The water was however found to be of very good quality in the winter season at all 5 sampling sites. However the WQI increases from sinter to summer and again from summer to rainy season. The water had poor quality in the rainy season. Another study carried out in nearby area of Rishikesh, revealed that water quality of River Ganga was good at most parts in Rishikesh (Haritash *et al*., 2014). The water samples were collected in the December month of 2008 from 20 stations to assess the suitability of water for drinking, irrigation and industrial usages by the usage of various indices. The water in upper segment was found to be of Class A (CPCB, 2008) i.e. it can be used for drinking after disinfection. The middle segments were of Class B i.e. they can be used as outdoor bathing source and the lower segments were Class C i.e. they can be used as drinking water source. All the parameters assessed were found to be within the specified limits for drinking water quality except E.*coli*. MPN was a parameter that had to be kept in check. Night soil deposition in river bed and waste water discharge through open channels needed attention to control MPN and the organic load.

A lot of such studies have been carried out on water quality of rivers in the Himalayan ranges. A study on heavy metal content and their relationship with various physico-chemical parameters, of the rivers in Uttarakhand was carried out by Kansal *et al.* (2012). Their study was conducted in 4 systems - River Ganga system having 15 monitoring stations, River Yamuna system having 5 monitoring stations, River Ramganga system with 8 monitoring stations and finally at Naini Lake with 2 monitoring stations, adding up to a total of 30 monitoring stations. On each of these stations the samples were collected from upstream and downstream. The samples were collected January 2010 representing winters, April 2010 representing spring, July 2010 representing monsoon as well as summer and October 2010 representing autumn. There weren't much of a temporal variation, however variation existed with respect to spatial variation especially in Ramganga River system. Lead was detected in 96 samples out of 120 in Garhwal and Kumaon regions. The highest concentration of 6.98 mg/l was found in river Bhela Kashipur in Kumaon region The Pb concentration in this region was found to be similar to concentration of Pb in water bodies of Delhi (Zaherrudin and Shabber, 1996). Cu was detected in 111 samples out of 120. The highest concentration was detected in Kosi river where the concentration was 7.30 mg/l. This was mainly because this river carries the industrial effluent load coming from most of the industries in the state. The Garhwal, the highest value for Cu was observed in river Bhagirathi, downstream of Uttarkashi. This was mainly because of the fact that the area was influenced by large construction activities related to hydroelectric projects. It was found that most of the Uttarakhand river bodies had a Cu content greater than that of river Yamuna in Delhi (Zaherrudin and Shabber, 1996) and river Kaveri (Ayyadui *et al.*, 1994). The Zn and Fe concentration didn't show much of a variation which indicated that their origin could be lithological. All these metals also showed a negative correlation with pH and and D.O. This shows that more the organic load, more will be the heavy metal content in the water body because organic matter provides surface for leachation of metals in acidic conditions. The values were compared to the WHO standard for drinking water and it showed that all observed values of Pb, 2 values of Cu and 59 observations of Fe were above the limits (WHO, 1998). The values were also compared to BIS and 83 observations of Pb, 110 observations of Cu and 59 observations of Fe exceeded the limits specified.

These were some the cases of the Himalayan rivers in the Himalayan range. If their condition is deteriorating with time, one can assume that the condition for the rivers flowing through the plains will be much worse. Enormous number of research and studies have been carried out in this thickly populated and industrial areas of North, Central and East India. Most of them revealed that the water in the rivers are used to dilute the wastes coming from chemical plants, sewage systems, industries, mines and agricultural fields. The surface water at various locations of Ganga river around Kolkata in West Bengal were rich in micronutrients like Mn, Zn and Cu (Md. Wasim *et al.*, 2008). They conducted a study from November 2005 to October 2006 to evaluate the surface water quality of river Ganga near Kolkata. They chose 4 different sampling stations and collected water from 2 points - middle of the river and discharge point. Out of 96 samples, they detected Ni, Zn, Cu, Mn and Fe in 45, 60, 38, 47 and 71 samples respectively. Their concentration varied from 0.045 - 0.240, 0.005 - 0.293, 0.003 - 0.033, 0.022 - 1.780, 0.013 - 5.49 mg/l. Pb and Cd were also detected in 21 and 6 samples with concentration ranging from 0.05 - 0.53 and 0.005 - 0.006 mg/l respectively. Cr was not detected in any of the samples. The metal concentration showed almost no relationship with respect to sampling locations as well as discharge points. However some relation was seen with respect to sampling seasons especially in the case of Cu, Mn and Ni. Their concentration was more during the rainy seasons. Whereas Fe had its highest concentration in winters. Another relation was seen between pH and certain metal concentrations. It was noted that when the pH was less, the concentration of metal was comparatively higher than the case when pH was low. This was mainly because low pH would help in the movement of metals from the bound form in sediments into the water. Other than this, it was also observed that the EC and SAR of sewage water samples exceeded the standard value for irrigation as prescribed by FAO and hence, the river water is not suitable for irrigation if we take these two parameters into consideration. The surface water requires treatment before it is used for irrigation. Another study was carried on river Ganga by D. Kar *et al.* (2006). They also analysed various physico-chemical parameters and heavy metal concentration in West Bengal during 2004-05. Water samples were collected once in every month from 4 monitoring stations - Berhampore, Palta, Daksineswar and Uluberia during the time period April 2004 to March 2005. The pH was mostly alkaline with the lowest pH recorded in rainy season. The values were however with the limits prescribed for drinking purpose (WHO, 1973) as well as for crop production (FAO, 1975). The same was the case with conductivity. The lowest conductivity was again in rainy season mostly because of dilution effect. The highest value of conductivity was observed in Uluberia. The 4 essential micronutrients - Cu, Zn, Mn and Fe were detected in 36, 95, 93 and 95 out of the samples with mean concentrations of 0.005, 0.716, 0.266 and 1.052 mg/l. Toxic heavy metals - Ni, Cr, Cd and Pb were also detected in 93, 93, 20 and 93 samples with mean concentrations of 0.450, 0.170, 0.002 and 0.140 mg/l. The mean concentration of the metals in the ascending order was Cd < Cu < Zn < Pb < Cr < Ni < Mn < Fe. A similar result was also observed in Ganga - Brahmaputra - Meghna estuary (Khan *et al*., 1998). The seasonal variation was found to be significant for Cd, Fe, Mn and Cr. The maximum mean concentration of Fe (1.520 mg/l) was observed in in summer, Mn (0.423 mg/l) in monsoon, Cd (0.003 mg/l) and Cr (0.020 mg/l) in winters season. Cd, Fe and Mn showed variation with change in sampling locations. The highest mean concentration in mg/l for Fe (1.485), Cu (0.006) and Zn (0.085) were observed in Palta, for Mn (0.420) and Ni (0.054) were recorded in Berhampore, for Pb (0.024) and Cr (0.018) were seen in Uluberia. A significant positive correlation was also found between metals like Cr and Cd with conductivity. However conductivity showed a negative correlation with Mn. They concluded that water from the river was not at all suitable for drinking purposes because of the excess concentration of heavy metals like Ni, Pb, Fe and Mn. It also may not be suitable for irrigational purposes as well considering the excess concentration of Mn. The excess heavy metal in this region can be attributed to the presence of many industries which discharge their effluents into it. Even the municipal waste is also partly responsible for the present condition of the river. There is a need to renovate the sewage treatment plants in this area and also to adsorb the he heavy metals from the industrial wastes coming from the industry.

The condition of the  Peninsular rivers in India is also the same owing to various sources of pollutants that get discharged into them. For instance, the water quality meets the desired water quality criteria with respect to DO, pH, Conductivity, Fecal coliform and Total coliform at all locations but the BOD is not meeting the criteria in River Sabarmati at Gandhi Nagar Chiloda Bridge (7 mg/l) and River Shedhi at Kheda (26 mg/l) in Gujarat (CPCB Water Status Report 2012). Even in the case of Narmada, many of the parameters have values beyond the prescribed range. Narmada river is comparatively less accessible because of its flow through hilly terrains and still the pH criteria is not met at Chandod (8.8); Bharuch, Hoshangabad D/s & Hoshangabad U/s (8.7) and Sethanighat & Korighat (8.6). High BOD is observed at Saraswatighat Jabalur (7.9 mg/l); Mandla (7.8 mg/l); Sethanighat (3.3 mg/l); Hoshangabad U/s (4.5 mg/l); Korighat Hoshangabad & Hoshangabad D/s (4.2 mg/l); Garudeshwar (6.0 mg/l) and Bharuch (5.0 mg/l). The Total Coliform count in the river ranges from 0-9000 MPN/100ml whereas the Faecal Coliform count varies from 0-5000 MPN/100ml and is not meeting the desired criteria at Bharuch (9000MPN/100 ml and 5000 MPN/100ml respectively). The water quality study reveals that the water of Mahanadi is comparatively less polluted compared to the other similar rivers in the country. However, certain stretches like the D/s portion of river Ib at Brajrajnagar, D/s of Sambalpur and Cuttack have comparatively higher degree of pollution. The pollution of Ib river is easily attributable to the discharges from a large paper industry situated in Brajrajnagar. In the majority of the other locations the BOD and the total coliform are the two parameters that are mainly responsible for lowering the water quality. While at places like Tikarapara this could be due to run-off from the areas adjoining the riverbanks that are generally used by the village people for defection. At the urban centres, the high BOD and coliform levels are obviously due to the discharges into the river from domestic sources either directly or indirectly. None of the towns small or large, on the banks of Mahanadi have any regular sewerage system or sewage treatment plants and the domestic wastes find their way mostly through small storm water drains which join the D/s of the Ib river at Brajrajnagar causing serious depletion of oxygen level along the whole stretch which cause serious threat to the aquatic lives. Even the river Krishna has problems with values of D.O. and conductivity being out of range at many points in the river. Thanagadi at Mahaboobnagar & Gadwal Bridge has a D.O.

content of close to 0mg/l & Ramalingeshwarnagar (Vijayawada) has a D.O, of 1.8 mg/l in Andhra Pradesh. B.O.D. levels were really high at some places. The maximum value of 24 mg/l was noted at Thanagadi at Mahaboobnagar in Andhra Pradesh & Islampur D/s in Maharashtra (CPCB Water Status Report, 2012).

## 2.3. HEAVY METAL POLLUTION IN RIVER WATER

The river water around the world have been facing some strong challenges to maintain their quality due to human intervention. A lot of its physical, chemical and biological parameters have been altered in the past few decades effecting its overall quality. One of the parameters that is of enormous importance are the presence of metals in the river water. As seen in the previous section, in many rivers the increase in the concentration of metals above certain limits, put restriction on their usage. Some of the metals are required by plants and microorganisms as nutrients whereas some of them are pure toxic substances. The ones that are needed by living beings are micronutrients like Cu, Fe, Mn, Zn and Ni. There are some other metals which serve no particular physiological activity. Although they can prove to be detrimental if present beyond certain limits. These include metals like Pb, Cd and Cr (Marschner, 1995; Bruins *et al*., 2000). The limits for these metals are very narrow. The deadlier diseases like edema of eyelids, tumour, genetic malfunctions, congestion of nasal mucous membranes and pharynx, stuffiness of head and gastrointestinal, muscular, reproductive and neurological problems caused by some of these metals have been recognized (Abbasi *et al*., 1998; Johnson, 1998). Therefore monitoring these metals is necessary for safety evaluation of the environment and human health especially. A study of metal content in rivers are made by evaluating the metal content in the river water as well as the metal content in the bed sediments of the river. While the river water will give an idea about the present condition of the water with respect to the metals present, the analysis of bed sediments for metal concentration will throw light on the metal that is present in the soil layers which could later get diffused into the water under favourable conditions. The soil sediments thus gives a picture of the amount of pollution that the river body would undergo under adverse conditions. Hence an analysis of both water and sediments are done for analysing metal and toxic substance concentration in the water.

### 2.3.1. Heavy Metals in Water

In the previous section it the problems associated with rivers bodies around the world were addressed. It was seen that heavy metals were of a major concern in many of the water bodies. A lot of these was discussed earlier. The rivers had a high metal concentration in them owing to industrial effluents coming from the industries, the waste water from chemical factories, mining activities, agricultural and irrigational practices and run offs from various sources of these metals. Even natural weathering is a process by which metal concentration increases in these river water. While the natural processes cannot be controlled, the anthropogenic activities leading to the increase in metallic contents have to be controlled. The studies carried out in upper Han river of China revealed that a lot of metal concentration were above the permissible limit when compared with various standards like WHO 2006, USEPA 2006. The levels exceeded for Al, Cd, Pb, Sb and Se in June 2005, while As, Cd, Se and Sb in June 2006, Al and Cd in August 2005, As in October 2006 and As, Pb and Sb in Novemver 2005 (Li and Zhang, 2010). Similarly the case of Tembi river was seen in which the there was a tremendous increase in the concentration of metals like Cd, Cu, Zn, Pb and Fe at the downstream when compared with that of upstream. The increase was much more than the normal one that one would expect. This was attributed to the fact that a lot of untreated sewage was discharged into it and the due to leaching of the solid wastes into the water. They concluded that the water of the Tembi River were contaminated by heavy metals and, therefore, using this water for recreational purposes, washing, and fishing is detrimental to human health and the environment (Saeed *et al*., 2014). The water of river  Bindare Stream of Chikaji Industrial Area Zaria, in the northern part of Nigeria  was also found to be polluted with metals like Cu, Zn, Ti, Fe and Al (Abolude *et al*., 2013). Even the Himalayan rivers had metals like Pb, Cu and Fe above the permissible limit when compared with various standards like WHO 1998 (Kansal *et al*., 2012). The case is even more worse in the case of the river Ganga while flowing through metropolitan cities like Kolkata. Many of the micronutrients were present above the permissible limits for drinking, but many toxic metals were also found. Metals like Ni, Zn, Cu, Mn were present in excess amount and toxic metals like Cd and Pb were also detected at such concentrations that would render the water unsafe not only for drinking purposes but also for agricultural usage. All these cases have been discussed in detail. Indian Standards for drinking water gives the desirable and permissible limits for most of these metals. BIS also specifies the maximum allowable limit for these metals.

**Table 2.1.** Specification and BIS Guidelines for Drinking Water (IS 10500:2012)

| Element | IS 10500:2012 Specification | |
|---|---|---|
| | Desirable Limit (mg/l) | Permissible Limit (mg/l) |
| Fe | 0.3 | 0.3 |
| Mn | 0.1 | 0.3 |
| As | 0.01 | 0.05 |
| Cr | 0.05 | 0.05 |
| Cu | 0.05 | 1.5 |
| Pb | 0.01 | 0.01 |
| Hg | 0.001 | 0.001 |
| Zn | 5 | 15 |
| Al | 0.03 | 0.2 |
| Cd | 0.003 | 0.003 |
| Ni | 0.02 | 0.02 |

### 2.3.2. Heavy Metals in Sediment

Natural addition of trace metals occurs into riverine system through various ways such as chemical weathering of rocks and soil, accelerated rate of soil erosion in the source catchment area due to deforestation, through rill erosion in the riverine zones, wet and dry fall out of atmospheric particulate matter (Macklin *et al*., 2003; Kraft *et al*., 2006). A significant amount of trace metals also gets added into the river by anthropogenic sources such as industrial and vehicle discharges, agricultural run off, untreated domestic waste water etc. Depending on hydrodynamics, biogeochemical processes and environmental conditions of rivers like pH, salinity, temperature and redox, sediments are considered as an important sink of heavy metals in aquatic systems as well as potential non-point source which may directly affect the overlying water (Thornton *et al.*,1975; Calmano *et al*., 1993). Fine grained suspended particle can scavenge contaminants due to their sorptive nature (Gibbs *et al*., 1973). Under favourable hydraulic conditions, suspended particles with contaminants get deposited on the river bottom making ita n important reservoir. Changes in sediment chemistry can result in contaminant remobilisation. Subsequently exposure to a different chemical environment could result in desorption and transformation of contaminants into more bio-available or toxic chemical forms (Zoumis *et al*., 2001). Therefore, Horowitz pointed out that the strong association of numerous trace metals in aquatic environment cannot be evaluated solely through the sampling and analysis of river water samples. In river systems, the sediments from the rivers are often used as environmental indicators and their chemical analysis can provide sufficient information for proper understanding of anthropogenic activities in that area. These sediments also play a vital role in the environmental studies of rivers as well, as they have long residence time for interaction with biotic components of the river's ecosystem (Muller, 1979; Forstner and Wittmann, 1983). Also revealed in certain studies were the fact that the metal concentration in sediments don't undergo that much changes with seasons as undergone by the water samples. This was seen in the case of Tembi River in Iran where heavy metal concentration showed very high variation with respect to different seasons whereas the values for sediments didn't vary much (Saeed *et al*., 2014). This makes the analysis of sediment a more accurate way of understanding the metal pollution in rivers as they represent the true metal concentration in that area. In most rivers, sediments are known to act as sinks or reservoirs for heavy metals and other pollutants. They have much higher heavy metal concentration than in river water (Horowitz, 1991). Sediment analysis thus provides record of physical, chemical and biological conditions of the river, which allows researchers to evaluate the environmental quality of the stream sediments. Thus river sediments act as both source and sink for heavy metals and is an important source for the assessment of manmade contamination of rivers (Forstner and Wittmann, 1983).

During the last decade, some research works have been carried out mainly on elemental concentrations in water, suspended and bed sediments of the Ganga River and its tributaries. The magnitude of suspended loads and their elemental concentrations in the Himalayan rivers has been the focus of several works (Abbas and Subramanian 1984, Jha *et al*., 1988). Ajmal *et al.* (1985) demonstrated that waste effluents of major cities like Delhi, Agra, Mathura and Allahabad on the bank of the Yamuna River (a tributary of Ganga) have deteriorated the quality of water and sediments by the addition various metals, such as, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Subramanian *et al.* (1987)

analysed heavy metals (Fe, Mn, Ni, Cr, Cu and Zn) in suspended and bed sediments of Ganga and Brahamaputra Rivers. They report on the pronounced temporal and spatial variations in heavy metal distributions in Ganga River. Another study of Subramanian and others (1987) demonstrates that the increase of the contents of Mn (40%), Fe (76%), Cu (62%), Zn (90%) and Pb (50%) in sediments of an urban stretch of the Yamuna River around Delhi is caused by the anthropogenic contribution from the wastes of the city drains. Kumar (1992) analysed heavy metals in the clay fraction of river sediments from the middle section of the Ganga River from Kanpur city to Patna city in 1984. Chander and others (1994) demonstrate that river sediments of the Pandu River (a tributary of Ganga near Kanpur city) are contaminated by fly ash derived copper from a coalbased thermal power plant. Singh (1996) has carried out a study on the status of heavy metal pollution in sediments of the urban river stretches of Delhi, Agra, Kanpur, Allahabad, Varanasi and Lucknow from natural and anthropogenic sources. Markedly elevated concentrations of Cr, Ni, Cu, Zn, Cd and Pb in sediments of the Ganga River were found in comparison to the natural bacKground concentrations. The average enrichment factors of the sediments from urban centres were 1.5 for Cr and Ni, 3 for Cu, Pb and Zn, and 14 for Cd. These high factors are attributed to the anthropogenic inputs of metal-rich wastes from the urban centres. Singh and others (1997) report that the freshly deposited Gomati River sediments around the Lucknow urban centre are polluted with several heavy metals due to human activities. In most of these studies it can be seen that, they haven't considered the particle size of sediments. Heavy metal concentration generally decrease with increase in particle size (Sakai *et al.*, 1986). Higher quantities of metals generally accumulate in the fine grained sediment fractions because of higher surface to grain size ratio (Gibbs, 1973). A grain size fraction comprising of fine silt and clay would be fine enough to accumulate higher quantities of heavy metals in river sediments. Mobility and dispersion of metals is also controlled by mineralogy of sediments. Heavy metals generally show an increase in concentration with the decrease in quartz content in the sediments. (Singh *et al.*,2002).

A lot of studies have been carried out in the last few decades on various Indian rivers for evaluating the metal concentration in sediments. C.K. Jain and others assessed for the concentration of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the Hindon river which flows through western Uttar Pradesh. The river originates in from the Lower Himalayas and flows through the districts of Saharanpur, Muzaffarnagar, Meerut and Ghaziabad. It joins Yamuna downstream of Delhi. Sediment samples were collected from 13 locations on the River Hindon on alternate months during April 1997 to February 1999. The sediments with size 0 - 210μm were analysed for heavy metals. Higher concentration of Fe and Mn occurred in upstream section of the river, which indicates the possibility of of the presence of Mn and Fe minerals instead of hydroxides. In the middle section the concentration of Fe and Mn was almost the same. However in the downstream section of the river, the concentration increases below the confluence of Kali and Krishni rivers which carries wastes from different industries. The maximum concentration of Fe was observed at Mohan Nagar. This was mostly due to impoundment of water for longer periods and site specific activities. The concentration of metals in sediments mostly followed the same trend as their corresponding concentration in water samples. The concentration of heavy metals followed the following order - Fe > Mn > Zn > Pb > Cr > Ni > Pb > Cd. The concentration was found to be higher in the summer months. During monsoon, the flow of water would displace the sediments and similar to the metal concentration in water, here also the metal concentration decreases. However, post - monsoon, the concentration of heavy metals was found to increase slightly. Overall it was observed that during the low flow period, the concentration was high and during the high flow period the concentration was low. The variation observed in sediments was much less than the variation that was seen in the water samples, thus reinforcing the fact that bottom sediments provide a more stable base for contaminative studies. A correlation matrix was also formed to study the correlation between any of the metals. There existed a strong correlation between Ni - Cr and Ni - Zn which goes onto show that they might have a common source. Whereas no other correlation was seen among the metals indicating that their concentration is dependent on many factors and a common source many not be responsible for the metal concentration in sediments. All the metals showed a positive correlation towards organic matter even though it was not that strong. Fe and Zn had the highest correlation coefficient with organic matter showing that they have more affinity towards the organic matter than other metals. Partition Coefficients, which is the ratio of metals in solid to metals in water was also evaluated. It was seen that the coefficient increased in the downstream section indicating that there is an increase in the adsorption capacity of sediments. This can be due to the presence of fine fraction of sediments present in the downstream portion. The relative mobility of metals were also calculated in which the concentration of each of the metal were compared with that of Al. Al was chosen as the conservative metal because of its abundance in Earth's crust. It is assumed that it has reached a steady state and is not being accumulated by soil layer and is only obtained from land erosion i.e. anthropogenic source is assumed to be non-existent. The order of relative mobility was Fe > Mn > Zn > Cr > Ni > Pb > Cu > Cd. They finally concluded that the river Hindon is subjected to varying degree of pollution caused by numerous untreated and/or partially treated waste inputs of municipal and industrial effluents. The river is highly influenced by heavy metals and these enter by direct discharges of municipal and industrial effluents and surface run off. As per their observation, Santagarh was the most polluted site in the entire 200 Km course of the river (C.K.Jain *et al*., 2005).

A lot of such studies related to sediment analysis of rivers have been done on the River Ganga and its tributaries as well. For instance, the sediment quality was monitored at Delhi and Agra through which Yamuna river flows. A 30 Km stretch of River Yamuna in Delhi and 15 Km stretch in Agra was considered. 31 sediment samples were collected during the dry months of 1993. Granulometric and mineralogical analysis was carried out which showed that the sediments were mainly composed of very fine sand, silt and clay derived from Himalayan region. After proper digestion of the samples they were analysed for Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd. The concentration of each metal showed a wide range of values. The mean values of Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd were 394, 695, 40500, 18, 159, 275, 561, 76 and 4.5 in Delhi and 263, 718, 37700, 18.7, 101, 339, 554, 168 and 32.5 in Agra. The maximum levels for Cr, Mn, Co, Fe and Ni were found in Delhi, whereas the maximum levels for Cu, Zn, Pb and Cd were observed in Agra. The metal enrichment values were > 1 for all metals except Mn and Fe. It showed high values for Cr, Ni, Cu, Zn and Pb and very high value for Cd. These high ratios indicate the concentration of metals in sediments is mostly due to anthropogenic sources. It was estimated that 70% Cr, 59% Zn, 90% Cd, 74% Cu, 46% Pb in Delhi and 61% Cr, 71% Cu, 63% Pb, 23% Ni, 72% Zn, 94% Cd concentrations were derived from anthropogenic sources. There also existed high positive correlations between Cr - Ni, Ni - C, Zn - Cu, Cd - Cu, Cu - C, Zn -C, indicating their common sink in the river sediments. The Yamuna River sediments were classified as unpolluted with Mn, Fe and Co; moderately polluted with Cr and Ni; highly polluted with Cu, Zn and Pb and very highly with Cd in Delhi and unpolluted with Fe, Mn and Co; moderately polluted with Cr, Ni; highly polluted with Zn and very highly polluted with Cu, Cd and Pb in Agra. The study supports the concept that urban effluents have a great influence on the concentration and distribution of toxic heavy metals in river sediments (Singh, 1999). The above study was further expanded by Singh *et al.* (1997) by analysing sediments of other important cities in the Ganga Plain - Kanpur and Varanasi (through which Ganga flows), Lucknow (through which Gomti flows) and Allahabad (the point of confluence of Yamuna and Ganga). They chose a 20Km stretch of Gomti river (Lucknow), 11 and 12Km stretches of Ganga River (Kanpur and Varanasi) and 10Km stretch of the confluence of Ganga and Yamuna (Allahabad). Sampling was done during the pre-monsoon period at Kanpur, Varanasi and Allahabad in 1993 and at Lucknow in 1995. Yamuna was found to have the most concentration of Pb, Cd, Cr, Ni, Cu and Zn in its stream sediments. There were certain locations in Kanpur and Delhi which showed sudden and isolated increase in the concentration of Pb. This was related to atmospheric deposition of metals on to the sediments. The Metal Enrichment Factor was calculated for all the metals by comparing with average shale concentration (Turekian *et al*., 1961). The maximum values for Cr, Ni, Cu, Zn, Pb and Cd were 3.8, 1.6, 3.9, 3.9, 4.1 and 34 respectively. It is generally believed that when EF is greater than 1.5, it is mostly due to the influence of anthropogenic sources. Cd in particular, showed a very high value indicating heavy pollution because of anthropogenic source. In the Urban Ganga Sediments, 59% Cr, 49% Cu, 52% Zn, 51% Pb and 77% Cd of total heavy metal concentrations were derived from anthropogenic source. A similar result was seen in the lower Rhine river in Germany, where more than 90% of Cu, Zn and Pb and about 99% of Cd were coming from anthropogenic sources (Forstner and Muller, 1981). High percentage of anthropogenic source indicates the high amount of availability of these toxic metals to the sediments. Under favourable conditions, they can get diffused into water and thus pollute the water. They can also enter the food chain, exposing millions of people in one way or the other. After studying the correlation among the metals it was observed that a very high positive correlation existed between Cr-Ni, Cu-Zn and Cu-Cd. High positive correlation existed between

Cu-Cr, Zn-Cr, Fe-Co, Zn-Ni and Cd-Pb. Moderately positive correlation existed between Mn-Co, Ni-Cu, Pb-Cu and Pb-Zn. The probable order of binding strength with TSC (Total Sediment Carbon) and TSS (Total Sediment Sulphur) increases in the order Ni < Cr < Cu < Zn and Ni < Cr < Zn < Cu respectively. A high positive correlation was found between TSS and TSC contents with Zn, Cr, Cu and Ni concentrations in stream sediments, indicating them as significant concentrator of these heavy metals. The overall sediment quality was analysed by considering 3 indices - Geo-accumulation Index, Sediment Pollution Index and Pollution Load Index. As per Geo-accumulation Index, The Ganga Plain was found to be very highly polluted with Cd, moderately to highly polluted with Cu and Zn, moderately polluted with Ni, Cr and Pb. No major pollution was observed with respect to Co, Fe and Mn. SPI was a multi-metal approach for overall quality assessment of sediments. The sediments were grouped into 5 classes - Natural sediments, Low polluted sediments, Moderately polluted sediments, Highly polluted sediments and Dangerous sediments. It was found that 6 stations in Delhi and 4 stations in Agra had dangerous sediments with SPI >20. The PLI is a reflection of urbanisation. It was calculated for each urban centre to understand the impact of urbanisation activities on sediment quality (Tomlinson *et al.*, 1980). The values for Kanpur, Allahabad, Varanasi, Lucknow, Agra and Delhi were found to be 1.71, 1.13, 1.20, 1.64, 4.4 and 3.61 respectively. When the PLI values were plotted against population of those urban centres a linear relationship was observed except for Agra, which had an unusually high PLI for the population it had. They concluded their study by that the sediments are adversely affecting the ecological functioning of rivers due to heavy metal mobilisation from urbansphere into biosphere. The areas downstream of the above areas were analysed for sediment quality by Singh *et al.* (2010). They chose 3 urban areas - Ghazipur, Buxar and Ballia in Eastern Uttar Pradesh and Western Bihar. A total of 30 monitoring stations were established with 10 stations in each centre. The study was carried out in 2010 during the pre-monsoon season in May. They analysed the sediments for Cr, Co, Ni, Cu, Zn, Cd and Pb. The heavy metal concentration had the following range in mg/Kg - 113-230, 11-29, 32-75, 39-73, 72-140, 0.45-0.95 and 15-27 for Cr, Co, Ni, Cu, Z, Cd and Pb respectively. The maximum concentration of Cu, Cr and Ni were recorded at Buxar, Zn and Cd at Ghazipur and Pb at Ballia. The river sediment at Buxar is moderatley toxic for Cu, Cr and Ni due to the point of addition of industrial efluents from various types of point sources. River is highly polluted by Zn and Cd at Ghazipur, whereas river sediments at Ballia had deposition of Pb in them. The GAI class was found to be between 0 and 1 for all trace metals in the area indicating uncontaminated to moderately contaminated sediments. The maximum values were noted as 0.77 for Cr at Buxar, 0.10 for Co at Buxar, 0.34 for Cu at Ghazipur, 1.08 for Cd at Ghazipur. These values indicate that the river bed sediments are moderately contaminated by Cd, Cr and Cu which may contribute to sediment toxicity in the freshwater ecosystem of the river. Several metals showed negative values for GAI suggesting that the area doesn't have much of a concern with respect to these metals. EF was also evaluated for checking the enrichment of metals. All the values lied between 0 and 3. The maximum EF was recorded as 1.182, 1.18, 0.87, 1.33, 1.15, 2.43 and 1.05 for Cr, Co, Ni, Cu, Zn, Cd and Pb respectively. It was noted that exceptionally high values of EF was recorded for Cd in all 3 sampling stations. The average percentage of heavy metals added through anthropogenic sources was 43, 12, 19, 57 and 53 for Cr, Co, Cu, Zn and Cd. It was suggested that toxicity of these metals might increase considerably in  the future considering the urban activities that is being carried out in the area (Singh *et al.*, 2012 ).

A study (Pandey and Pandey, 2015) was conducted in Varanasi to determine the heavy metal concentrations in the Ganga River during the period from March 2012 to February 2013 (Pandey *et al.,*2015). Nine sites - Chunar, Adalpura, Ramna Ghat, Gadwa Ghat, Ravidas Park, Assi Ghat, Dashashwamedh Ghat, Manikarnika Ghat and Rajghat respectively. It was found that the metal concentrations increased consistently down the study gradient and were highest at site 9. Seasonally, metal concentrations in general were highest in summer followed by winter and rainy season.   In summer at site 1, concentrations of Fe, Zn, Ni, Mn, Pb, Cd, Cu, and Cr were 35,623.2, 61.7, 14.9, 282.1, 14.9, 1.3, 15.4, and 54.9 $\mu g\ g^{-1}$, respectively. The respective concentrations at site 9 were 41, 170.1, 92.5, 44.9, 43.0, 32.6, 71.1, 40.8, and 93.3 $\mu g\ g^{-1}$. Concentrations at site 2 were almost comparable to the values observed at site 1. Sites 1 and 2 are located in city upstream and receive rural and suburban influences. Downstream sites with urban influences showed concentrations higher by 1.8 - 4.10 fold. As the river flow declines in summer, the rate of sedimentation and consequently the concentration is enhanced. In rainy season, on the other hand, increased river flow causes a dilution effect, and consequently, metal concentration in sediment declines. Although at the onset of rainy season the first flush effect may enhance the concentration, the dilution effect predominates as the season progresses. When concentrations were regressed with river discharge, significant negative relationships were observed, indicating that the increased river discharge reduces metal concentration in rainy season. Higher concentrations in winter than rainy season was linked similarly to decreased river flow during winter. Similar seasonal patterns have been reported (Kumar *et al*., 2013). On spatial scale, a rising trend was observed along the pollution gradient irrespective of season. Mann–Kendall time series analysis with Sen's slope statistics showed significant seasonality and a rising trend along the study gradient, indicating the influence of local control. Such trend could be expected due to urban releases of sewage and industrial effluents together with agricultural runoff. Further, the atmospherically deposited substances also reached the river directly or indirectly through land surface runoff (Pandey *et al.*, 2015). Highest concentrations of heavy metals at site 9 was considered a possible effect of these sources. Relatively sharp increase in the concentration of heavy metals, especially Mn and Cu at site 3, was believed to be due to wastewater, in addition to domestic and agricultural causation, flushed from Bhagwanpur sewage treatment plant (10 MLD) situated close to the study site. Further, Cu is an important component of pesticide entering to river through agricultural runoff. The overall trend in metal concentration was found to be: Fe > Mn > Zn > Cr > Cu > Ni > Pb > Cd. Iron (Fe) appeared the most abundant element in Ganga River sediment with mean concentration ranging from 21,924 to 41,170 $\mu g\ g^{-1}$. The Fe abundance in these systems has been attributed, in addition to weathering, erosion and other natural sources, large-scale human activities such as urban–industrial release, municipal solid waste, construction and demolition wastes, and agricultural activities. enrichment factor (EF) used to predict the level of contamination and possible anthropogenic impact on the sediment (Esen *et al*., 2010 ). A metal with EF between 0.5 and 1.5 is considered in a crustal state, whereas EF > 1.5 indicates anthropogenic disturbances (Zhang & Liu 2002 ). In this study, except for Cd and Pb, the EF remained <1, indicating relatively smaller enrichment. A comparison of their data with Chen et al., (2007) indicates Cd at Rajghat has moderate to severe enrichment, and at sites 4, 5, 6, and 7, it has moderate enrichment. Lead (Pb) at sites 5, 6, 7, 8, and 9 showed small to moderate enrichments. Ghrefat *et al*., (2011) and Singh *et al*., (2005) also showed high enrichment of Pb and Cd in sediments receiving anthropogenic influences. When compared with USEPA (1999) and CCME 1999 (Canadian Water Quality Guidelines for Protection of Aquatic Life), concentrations of all the metals except Zn, in most of the cases, were found higher than the threshold values. Concentrations although remained below the world averages (Martin & Meybeck 1979) of Cd, Ni, Cu, and Cr did exceed WHO (2004) standards. Accumulation of Zn in Ganga River was found higher than those reported in Tapti River (Marathe *et al*., 2011), and Pb, Cu, and Cr were higher than those reported in Cauvery (Raju *et al.,* 2012) and Euphrates River (Salah *et al*., 2012). These observations indicate relatively higher input of heavy metals in Ganga River in Varanasi region. It was also found that there exists positive correlation between organic carbon (OC) and study metals. Metal pairs such as Fe–Zn, Pb–Fe, Pb–Zn, Ni–Fe, Ni–Zn, Ni–Pb, Cd–Fe, Cd–Zn, Cd–Pb, Cd–Ni, Cd–Mn, Cr–Fe, Cr–Zn, Cr–Pb, Cr–Ni, and Cr–Cd also showed significant positive relationships. Relationship with organic carbon indicates possible chelation (Jayaprakash et al., 2008) while those between metal pairs show common sources of origin or similarity in geochemical behaviour. Similar observations have been made by Dhanakumar *et al*., (2011) and Kumar *et al*., (2013). Principal component analysis (PCA) was used to identify principal drivers regulating spatial and temporal distribution patterns of heavy metals in the river sediments. This multivariate technique analyzes the interrelations between explanatory variables and response variables and extracts principal drivers by reducing the contribution of factors with minor significance. The PCA ordinates segregated sites into four groups. Relatively less polluted sites such as Chunar, Adalpura, and Ramna appeared in one group. Gadwa, which receives higher pollution input than the first three upstream sites, appeared separate from the rest of the sites. This site receives, in addition to surface-borne inputs, massive amount of atmospherically deposited materials from the bypass highway. The analysis separates Ravidas Ghat, Assi Ghat, Dashashwamedh Ghat, and Manikarnika Ghat as third group showing the influence of urban release in downstream contamination. The most polluted site Rajghat did appear separately indicating the influence of urban input and downstream factors.

## 2.4. HEAVY METAL CONCENTRATION IN OTHER SYSTEMS

The problem related to heavy metals is not something that is unique to rivers. It effects all water bodies as the sediments under them are the main source and sink for these metals. The degree of danger can be different for different water bodies. For lakes, with lesser volume of water, the heavy metal may not get properly distributed and hence their concentration will be high when such kind of discharges are made into lakes. Also since the lakes are still, their self-purification capacity is much lesser than rivers. The lakes are one of the most important sources of water, so it can be a bit dangerous if the heavy metal concentration in lakes increases as it will pollute an important source. In other water body systems like seas and oceans, the heavy metal concentration can affect the living beings in certain other ways. If the concentration of metals are high, they can enter the food chain and undergo biomagnification. Once they enter the human body they will get bioaccumulated leading to increasing concentration with time. The danger of exposure will be more in the case of those people who consume sea food. As humans are at the top of the food chain the concentration of the heavy metal would have increased manifold. Thus it becomes important to monitor even the other water bodies as well.

### 2.4.1. Sediment Quality of Lakes

As discussed earlier, lake sediments have a larger risk of getting accumulated with heavy metals than rivers as they remain still. These sediment, under favourable physico-chemical conditions pass on the toxic heavy metals to water column above them. This can be quite dangerous as lakes don't have the same volume and flow as rivers to dilute the pollutants. Many studies have been carried out in different lakes around the world to understand the heavy metal concentration in the sediments and to study their toxicity.

A sediment quality analysis was carried out in Akkulam-Veli lake in January 2009 by (Swarnalatha *et al.*, 2012) The lake is situated around 5 Km northwest of Thiruvananthapuram. The stations were almost uniformly distributed. The AV lake was chosen because presently it is a stressed and fragile ecosystem. Apart from a huge sewage load, the lake receives hospital wastes, industrial wastes, tourism by-products and wastes from other developmental activities. The tidal phenomena in the area is weak, infrequent and insufficient, complete flushing of watewater from the lake is scanty. the surrounding areas have been developed into tourist spots with potential of further development. The population in the area has also increased due to rapid urbanisation. 10 sampling stations were chosen with 5 stations in Akkulam side and the rest 5 in Veli side. The variation in concentration of heavy metals (mg/Kg) varied as follows: Ni (25-77), Zn (86-397), Pb (39-105), Cr (107-194), Cu (16-187), Co (10-42) and Mn (17-426). As per USEPA (1991), all selected stations can be considered as heavily polluted with Cr. Station 1,2,3,5 and 6 are heavily polluted with respect to Ni, Cu and Pb. Station 2, 3 and 5 are heavily polluted with Cu. Station 2 and 3 are heavily poluted with Zn. The average concentrations of all metals except Cr where found to be more on the Akkulam side. This was mainly due to discharge of untreated sewage effluents into lake through Kannammoola stream on the Akkulam side. The inter relationship between elements and particle size were studied. There existed a positive relation between TOC and heavy metals and between Clay particles and heavy metals. Whereas, the heavy metals share a negative correlation with sand particles. Cu and Zn had the maximum positive correlation with TOC. Other significant correlation was seen between Ni and Pb indicating a common source. The average Enrichment Factors were found to be greater than 1 for all metals. the order was seen increasing as Ni < Co < Cu < Zn < Cr < Pb. The most enriched metal was Pb and its values were found to be high throughout the lake. Although an unusually high value of 25.2 was observed at station 6. This was attributed to localised pollution. Contamination Factor was also evaluated and it showed the contamination levels for Ni as "low", for Cr, Zn, Cu and Co as "moderate" and Pb as "considerable" . From CF values, PLI was also evaluated. All the stations had PLI >1 except station 4 and 10. This indicates deteriorated sediment quality. The most deteriorated sediment was at station 5 on the Akkulam region and the lowest value was found at station 6 on the Veli region. They concluded that the sediment quality of the lake is of concern. Considering the future development that is taking place around the area, it is very likely that the concentrations could further increase resulting in further deterioration of samples (Swarnalatha *et al.*,2012).

Spatial distribution and temporal variation studies were carried out by P. K. Govil et al., at Katedan Industrial Development Area (KIDA) near Hyderabad. The area consists of 5 lakes - Chilan Lake, Ura Cheruvu, Narsabaigunta, Noor Mohammad and

Devullama Cheruvu. These lakes are connected by small streams. 95 sediment samples were collected during pre-monsoon and post-monsoon season from a depth of 1-3m from the lake. The maximum concentration observed for potentially toxic matels like As, Cr, Cu, Ni, Pb, Zn, Zr were 400, 500, 1486, 271, 2000, 3327 and 827 mg/Kg respectively. They showed high concentration of As, Zn, Pb and Cu in particular. Higher concentrations of Cr, Cd and Ni are located in the lower stretches of one of the feeder streams. During the period of monsoon, the concentration of Zn and Pb was found to be high whereas the concentration of Cr, As, Ni, Cu and Cd were reduced. Severe metal enrichment was observed in lake sediments of Noor Mohammad and Narsabaigunta. Noor Mohommad was observed to be acting as a sink for contaminants with 4 - 10 times higher concentration than other lakes downstream. The correlation coefficient was also evaluated for all the trace metals. A strong positive correlation > 0.8 was found for As-Pb, Cr-Ni, Cu-Zn revealing their common source i.e. industrial contamination. Concentration of toxic metals observed in their study were much higher than similar studies carried out by other researchers on Lake Geneva and Lake Texoma (Pote *et al*., 2008).

### 2.4.2. Sediment Quality of Oceans and Seas

As mentioned earlier, the sediment quality of oceans and seas have to be monitored even though they are not used as regular sources of water. The sediments in the ocean beds can be rich in toxic heavy metals which will be passed on to the aquatic plants and fishes. Once they enter the food chain, they get biomagnified as they pass on from one trophic level to another. The concentration will be really high in the top most trophic level which normally includes humans as well. Once they get into the body they keep on getting accumulated causing many problems. Hence even the coastal areas, a lot of such studies are carried out to analyse the heavy metal concentration in sediments.

Udaykumar *et al.* (2014), conducted a study on the southwest coast of India in 2008. 5 sampling sites were chosen - Kochi, Chettuva, Ponnani, Calicut and Kasargod. Samples were taken from each of these stations at a depth of 1, 3, 5, 7.5, and 10Km from the shore and also from the shore. These stations were selected because of the fact that they are primary fishing locations. Seasonal sampling was carried out in

January, April and September representing post-monsoon, pre-monsoon and monsoon seasons. The sediments were mostly fine grained (clay and silt). The sand content decreased as one moves away from the shore. This was attributed to the fact that particle grains gets eroded by the strong waves. Low organic matter was observed in the pre-monsoon period due to less riverine flow, low nutrients and thus low phytoplankton biomass etc. As the flow increases in the post-monsoon period and the monsoon period the organic matter increased. The organic matter content was more near the shore. This was believed to be because of the rapid deposition of coarser inorganic constituents in relation to organic material. The central coast (Kochi and Chettuva) had more organic matter content than the northern coast (Ponnani, Calicut and Kasargod). The enrichment of organic matter in the case of Kochi and Chettuva was mainly due to the 260 $m^3$ of domestic wastes, which the city generates per day which get released into the coastal water without proper treatment (Balachandran *et al*., 2006). The order of abundance of metals increased in the following order : Hg < Cd < Pb < Cu < Ni < Cr < Zn. Pb, Cd and Hg showed the lowest concentration for all seasons, while there was much spatial and temporal variation in the concentration of Cr, Ni, Zn and Cu among seasons. It was also observed that as one moved away from the shore the concentration of the heavy metals increased. This was mainly because of finer sediment particles offshore than near shore. The Pollution Load Index was also evaluated for all 5 monitoring stations. The increasing order for PLI were : Kasargod < Chettuva < Ponnani < Calicut < Kochi. The comparatively less values of PLI at Kasargod and Chettuva was because of low anthropogenic activities. GAI values were calculated for all metals at all the 5 locations. It was observed that the coastal areas of Kochi were strongly polluted by Cd. The Cd deposits were mainly coming from the number of industries present near the city of Kochi. Infact most of the other metals had their maximum values at Kochi itself. It was thus concluded that Kochi had the most deteriorated sediments of all the 5 locations (Udaykumar *et al*., 2014).

### 2.4.3. Sediment Quality in Estuaries

Estuarine sediments can be a sensitive indicator of both spatial and temporal trends when monitoring contaminants in estuarine environments (Ergin *et al*., 1991; Balls, 1997). Estuaries around the world receive a large amount of waste from the catchments that surround them and have become repositories for heavy metals, hydrocarbons and pesticides.

Jayaraju *et al.* (2008), studied the sediment quality of the Tambaraparni River Estuary in 2008. Estuarine sediments in the < 63 µm size fraction were collected from 15 stations within the Tambaraparni River Estuary, located on the east coast of India. The distribution of the heavy metals Cd, Co, Cr, Cu, Ni, Pb and Zn was recorded. analysis distinguished two groups of elements. First, Cd, Pb and Zn, which occurred in higher than expected concentrations indicative of pollution, and second, Co, Cr, Cu and Ni, which occurred at bacKground levels. The highest metal concentration found in the study area was for Zn (1200 µg/g), and the lowest was for Cd (0.42 µg/g). It is presumed that river run-off, industrial waters and untreated domestic waters are major contributors to heavy metal pollution in the Tambaraparni River Estuary. It is presumed that road traffic, run-off, industrial waters, untreated domestic waters and other anthropogenic sources are major contributors of heavy metals in the Tambaraparni Estuary. The metal concentration data indicate that the surface sediments are moderately to strongly contaminated, probably as a result of anthropogenic activities, and provide a useful means of distinguishing between natural and anthropogenic sources of metals entering the coastal zone through river inputs. Comparison of the metal levels from the estuary indicated that there is a detectable anthropogenic input into the Tambaraparni Estuary. Cu and Zn showed the influence of organic waste from municipal sewage entering the estuary. It is proposed that continuous monitoring and further studies in the area should be carried out in the near future to ascertain the long-term effects of anthropogenic impacts and to assess the effectiveness of minimising human activity to upgrade the marine environment in the estuary.

## 2.5. TOXICITY OF HEAVY METAL

Heavy metal toxicity has proven to be a major threat and there are several health risks associated with it. The toxic effects of these metals, even though they do not have any biological role, remain present in some or the other form harmful for the human body and its proper functioning. They sometimes act as a pseudo element of the body while at certain times they may even interfere with metabolic processes. Few metals, such as aluminium, can be removed through elimination activities, while some metals get accumulated in the body and food chain, exhibiting a chronic nature. Various public health measures have been undertaken to control, prevent and treat metal toxicity occurring at various levels, such as occupational exposure, accidents and environmental factors. Metal toxicity depends upon the absorbed dose, the route of exposure and duration of exposure, i.e. acute or chronic. This can lead to various disorders and can also result in excessive damage due to oxidative stress induced by free radical formation.

### 2.5.1. Study of Toxicity in Aquatic Life

The mechanism by which heavy metals enter the food chain have been discussed earlier. They have a tendency to biomagnify and then bioaccumulate in organisms. A lot of studies have been carried out on the toxicity of these metals, by checking the concentration in aquatic plants and fishes. One such study was carried out by Rajeshkumar *et al.* (2013). This was done to assess the concentration of Cd, Zn, Cu and Pb in different tissues of C. *chanos.* The species were collected from Kaattuppalli Island and they were compared to the fishes collected from Kovalam coast. The heavy metal concentration were also measured in the water and sediments. The concentration of Cu, Zn, Cd and Pb in water and sediment were, 2.075, 1.136, 1.185 and 1.412 µg/l and 3.765, 1.900, 0.367 and 0.178 µg/g. The metal concentration was measured in muscles, gills and liver of the fish species. The relative abundance of metals in muscle, liver and gills were in the order : Cu > Zn > Cd > Pb, Zn > Cu > Cd > Pb and Zn > Pb > Cd > Cu respectively. A high degree of organ specificity was seen in these organisms, where liver exhibited greater accumulation compared to the gills and muscles. Of the metals studied , Pb concentration was low and Zn, Cd and Cu concentration were high. The heavy metal accumulation was found to be high in the summer season and low during monsoon season. Heavy metals mainly accumulate in the metabolic organs such as liver that store metals for detoxification by producing metallothioneins (Hogstrand and Haux, 1991). Thus the liver and gills are mostly recommended as environmental indicator organs of water pollution than other fish organs (Al-Yousuf *et al*., 2000; Canli & Atli, 2003). The measurement of metal concentration in muscles are equally important because it is an edible part and it is through food that they get carried onto other organisms. The mean concentration of heavy metals from fishes in Kovalam coast was found to be less compared to the fishes in their study area. The mean concentration was also higher than the maximum permissible limit specified by FAO (1993). Thus there is a danger of such toxic metals entering the food chain and causing problems to other organisms as well. This condition in the study area is bound to get worse in future as the population is increasing rapidly and a number of industries are coming up near the Kaattuppalli coast (Rajeshkumar *et al*., 2013).

A lot of such studies showed the presence of heavy metals in organisms at different trophic levels. A study conducted near the South coast of Japan showed the biomagnification of heavy metals in big fishes when compared to that of small fishes. There was an increase of threefold in the concentration of Cd in certain big fishes with respect to the smaller ones. Such studies on biomagnification and bioaccumulation shows that the heavy metals entering our body through food can be of a great concern. Since they don't get digested, they are keep on accumulating in the body with problems arising in the later stage.

### 2.5.2. Effect of Heavy Metals on Human Beings

There are 35 metals that are of concern for us because of residential or occupational exposure, out of which 23 are heavy metals: antimony, arsenic, bismuth, cadmium, cerium, chromium, cobalt, copper, gallium, gold, iron, lead, manganese, mercury, nickel, platinum, silver, tellurium, thallium, tin, uranium, vanadium, and zinc (Mosby *et al.,* 1996). These heavy metals are commonly found in the environment and diet. In small amounts they are required for maintaining good health but in larger amounts they can become toxic or dangerous. Heavy metal toxicity can lower energy levels and damage the functioning of the brain, lungs, kidney, liver, blood composition and other important organs. Long-term exposure can lead to gradually progressing physical, muscular, and neurological degenerative processes that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy. Repeated long-term exposure of some metals and their compounds may even cause cancer (Jarup, 2003). The toxicity level of a few heavy metals can be just above the bacKground concentrations that are being present naturally in the environment. Hence thorough knowledge of heavy metals is rather important for allowing to provide proper defensive measures against their excessive contact (Ferner, 2001). Toxic effects of some of the metals on humans are given below:

### Arsenic

Arsenic concentration have been on rise due to anthropogenic and natural sources. The exposure to Arsenic can occur from air, water as well as food. Still, water is believed to be the most common mode by which Arsenic enters the human body. In more than 30 countries of the world, the major reason for Arsenic toxicity is water being contaminated by As (Chowdhury *et al.*, 2000). If the concentration of As in groundwater is 10 to 100 times the value that is prescribed by WHO (10µg/L), then it can be harmful to the health of human beings (Hoque *et al.*2011). One of the major problem that is associated with As is that it is carcinogenic. It can cause the skin, liver, bladder and lung cancer. Lower levels of exposure to As can cause abnormal heart beat, nausea and vomiting, damage to blood vessels and pricking sensations to hands and legs. Long-term exposure can lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease and diabetes mellitus (Smith *et al.,* 2000). Infact most of the chronic effects of Arsenic are skin on the skin as they are skin specific. Pigmentation is one of the major skin problem that can be caused due to Arsenic toxicity (Martin & Griswold, 2009).

### Lead

The concentration of Pb has seen an upward trend because of various reasons. Some of it can be attributed to natural weathering. But the major reason for increasing Pb concentrations are anthropogenic activities. Human activities such as various manufacturing processes, burning of fossil fuels and mining processes are one of the major reason for this. Lead is also used for production of various materials like batteries, metal products, cosmetics etc (Martin & Griswold, 2009). Lead is a highly toxic heavy metal and because of this a lot of their usage especially in products such as gasoline, paints etc have been restricted. Exposure to Lead can be due to paints, gasoline, cosmetics, toys, household dust, contaminated soil, industrial emissions (Gerhardsson *et al.*, 2002). Most of the problem related to Pb can be seen in Central Nervous System (CNS) and also in gastro-intestinal tracts (Markowitz,2000). Another major source of Pb is the drinking water. One of the common mechanisms by which Lead enters the drinking water system is through the pipes which are made of Pb or compounds of Pb. As per USEPA (1993), Lead is a carcinogen. Lead can show various harmful effects on different parts of the body. Lead distribution in the body initially depends on the blood flow into various tissues and almost 95% of lead is deposited in the form of insoluble phosphate in skeletal bones (Papanikolaou 2005). The toxicity of Pb is often called Lead Poisoning. This can have acute as well as chronic effects. Acute exposure to Pb mainly occur at workplaces or some factories were Pb or its compounds are used. Acute exposure can cause headache, loss of appetite, hypertension, arthritis, sleeplessness, fatigue, hallucinations, abdominal pain, renal dysfunction and vertigo. Chronic exposure of lead on the other hand can result in birth defects, mental retardation, kidney damage, braindamage psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness and in severe cases may even cause death (Martin & Griswold, 2009). Even though Lead Poisoning can be prevented, it is still considered as a dangerous disease which can effect a lot of organs of our body. The plasma membrane moves into the interstitial spaces of the brain when the blood brain barrier is exposed to elevated levels of lead concentration, resulting in a condition called edema (Teo *et al.,* 1997). It disrupts the intracellular second messenger systems and alters the functioning of the central nervous system, whose protection is highly important.

**Mercury**

Mercury is considered to be one of the most toxic heavy metals. Industries and mining activities are one of the major anthropogenic sources of Hg. Industries which release Hg include paper and pulp industry, agricultural industry, pharmaceutical industry, chlorine and soda production industry (Morais *et al.*, 2012). Mercury is known to easily form organic and inorganic forms of Hg by combining with various other metals. Brain damage, kidney damage and damage to the developing foetus can occur upon exposure of humans to such metallic, organic and inorganic forms of Mercury (Alina *et al.*, 2012). Mercury toxicity is normally called pink disease or acrodynia. Many studies have shown that one of the common mechanism by which Mercury enters our body is through food. The Mercury content in marine food is normally on the higher side (around 50 μg/Kg). Since Mercury is lipophillic it gets accumulated in the fat tissues of fish and also in the liver of fish. Micro-organisms can also convert the mercury present in soil sediments into different forms like methyl mercury and mercuric chloride. These get accumulated in the body of fish as the time passes and get passed onto other organisms when they consume it. The process of biomagnification has been encountered a lot in the case of Mercury. In addition to causing problems like blue baby disease, methyl mercury and mercuric chloride are also classified as carcimogens by USEPA. The nervous system is very sensitive to all types of mercury. Increased exposure of mercury can alter brain functions and lead to shyness, tremors, memory problems, irritability, and changes in vision or hearing. Exposure to metallic mercury vapours at higher levels for shorter periods of time can lead to lung damage, vomiting, diarrhoea, nausea, skin rashes, increased heart rate or blood pressure. Symptoms of organic mercury poisoning include depression, memory problems, tremors, fatigue, headache, hair loss, etc. Due to the excess health effects associated with exposure to mercury, the present standard for drinking water has been set at lower levels by WHO.

**Cadmium**

Cadmium is a new-age metal. Its usage started in $20^{th}$ century. It is a by-product of zinc production. Soils and rocks, as well as coal and mineral fertilizers, have some amount of cadmium. Cadmium has many purposes, like in batteries, pigments, plastics and metal coatings. It is widely used in electroplating (Martin & Griswold, 2009). Cadmium and its compounds are classified as Group 1 carcinogens for humans by the International Agency for Research on Cancer (Henson & Chedrese, 2004). Cadmium is released into the environment through natural activities such as volcanic eruptions, weathering, river transport and also through some human activities like smelting mining, tobacco smoking, burning of municipal waste, and production of fertilizers. Even though cadmium release have been noticeably reduced in most industrialized countries, it is a remaining source of problem for workers and people living in the polluted areas. Cadmium can cause both acute and chronic intoxications (Chakraborty *et al.*, 2013). Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations. Cadmium can cause bone mineralization either through bone damage or through renal dysfunction. Studies on humans and animals have revealed that osteoporosis (skeletal damage) is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hypercalciuria. The Cadmium ions replace the Calcium ions in the bone leading to a reduction in the strength of bones. Inhaling higher levels of cadmium can cause severe damage to the lungs. If cadmium is ingested in higher amounts, it can lead to stomach irritation and result in vomiting and diarrhoea. On very long exposure time at lower concentrations, it can become deposited in the kidney and finally lead to kidney disease, fragile bones and lung damage (Bernard, 2008). Cadmium and its compounds are highly water soluble compared to other metals. Their bioavailability is very high and hence it tends to bioaccumulate.

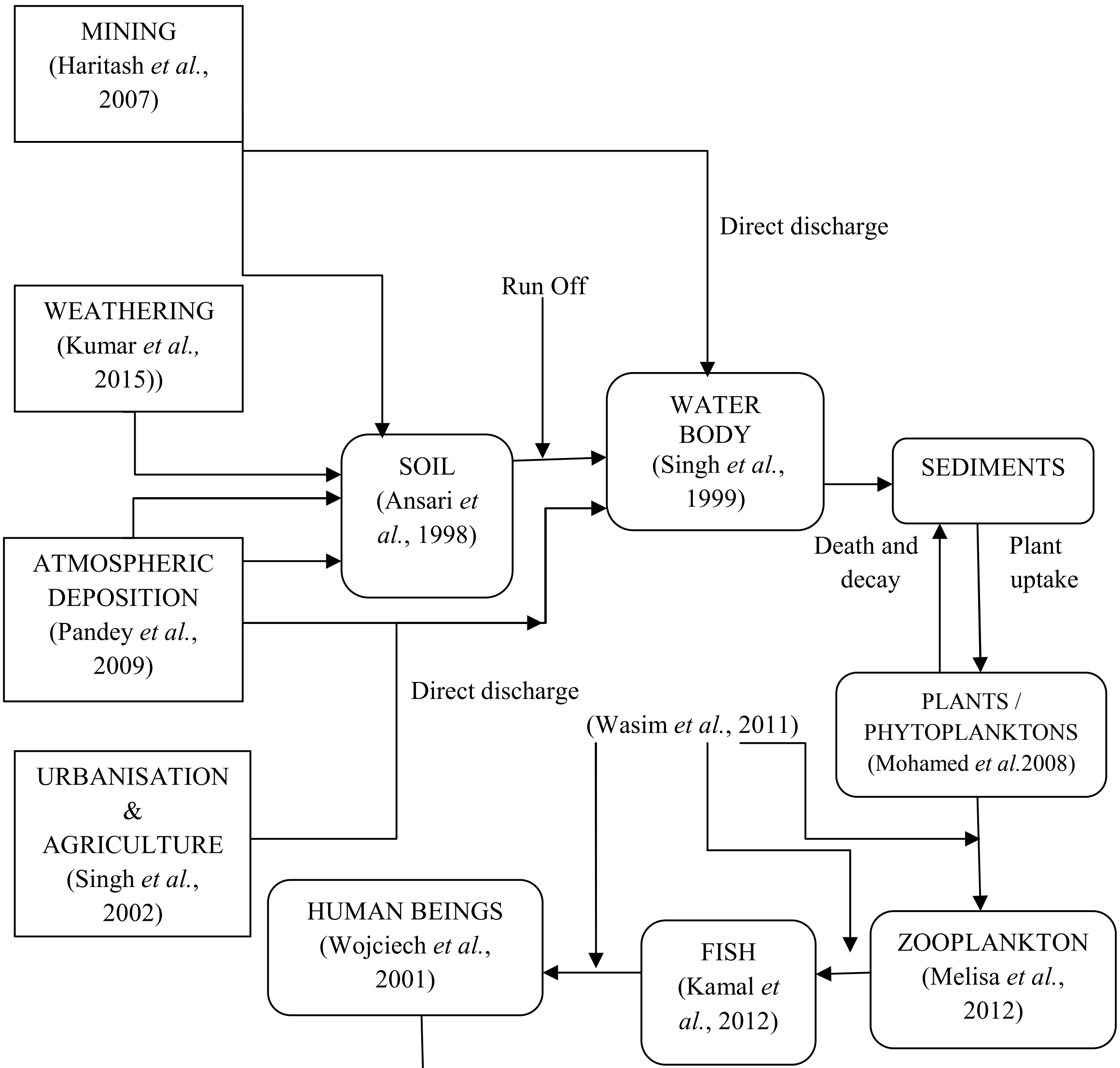
**Chromium**

Chromium is present in rocks, soil, animals and plants. It can be solid, liquid, and in the form of gas. Chromium compounds are very much persistent in water sediments. They can occur in many different states such as divalent, four-valent, five-valent and hexavalent state. Cr(VI) and Cr(III) are the most stable forms and only their relation to human exposure is of high interest (Zhitkovich, 2005). Chromium(VI) compounds, such as calcium chromate, zinc chromates, strontium chromate and lead chromates, are highly toxic and carcinogenic in nature. Chromium (III), on the other hand, is an essential nutritional supplement for animals and humans and has an important role in glucose metabolism. When broken skin comes in contact with any type of chromium compounds, a deeply penetrating hole will be formed. Exposure to chromium compounds can result in the formation of ulcers, which will persist for months and heal very slowly. Ulcers on the nasal septum are very common in case of chromate workers. Exposure to higher amounts of chromium compounds in humans can lead to the inhibition of erythrocyte glutathione reductase, which in turn lowers the capacity to reduce methemoglobin to haemoglobin (Koutras *et al.*, 1965; Schlatter & Kissling, 1973). Results obtained from different in vitro and in vivo experiments have shown that chromate compounds can induce DNA damage in many different ways and can lead to the formation of DNA adducts, chromosomal aberrations, sister chromatid exchanges, alterations in replication and transcription of DNA (O'Brien et al., 2001; Matsumoto *et al*., 2006).

**Iron**

Iron is the most plentiful transition metal in the earth's crust. Biologically it is the most important nutrient for most living creatures as it is the cofactor for many vital proteins and enzymes. Iron mediated reactions support most of the aerobic organisms in their respiration process. If it is not shielded properly, it can catalyze the reactions involving the formation of radicals which can damage biomolecules, cells, tissues and the whole organism. Iron poisoning has always been a topic of interest mainly to pediatricians. Children are highly susceptible to iron toxicity as they are exposed to a maximum of iron-containing products (Albretsen, 2006). Excess iron uptake is a serious problem in developed and meat eating countries and it increases the risk of cancer. Formation of free radicals is the outcome of iron toxicity (Ryan & Aust, 1992). During normal and pathological cell processing, byproducts such as superoxide and hydrogen peroxide are formed, which are considered to be free radicals (Fine, 2000). These free radicals are actually neutralized by enzymes such as superoxide dismutase, catalase and glutathione peroxidase but the superoxide molecule has the ability to release iron from ferritin and that free iron reacts with more and more of superoxide and hydrogen peroxide forming highly toxic free radicals such as hydroxyl radical (McCord, 1998). Hydroxyl radicals are dangerous as they can inactivate certain enzymes, initiate lipid peroxidation, depolymerize polysaccharides and can cause DNA strand breaks. This can sometimes result in cell death (Hershko *et al.*,1998).

Figure 2.1. shows the movement of these toxic metals from various sources to reach the human body. Heavy metal containing waste water from industries and other anthropogenic activities and from natural weathering processes end up in soil or get directly discharged into water bodies. From the soil, these metal reach water bodies through run off. Once they reach water bodies, they get adsorbed onto water sediments from where aquatic plants obtain nutrients. Thus they enter the food chain and biomagnifies as they move to different trophic levels finally ending up in human body where they bioaccumulate to cause various health effects.




Health Effects

- Irritation to stomach, vomiting and diarrhoea - As, Ba, Cd, Hg and Se accumulation.
- Carcinogenic - As, Cr.
- Gets stored in kidneys ultimately leading to kidney damage - Pb, Hg, Cr, Cd accumulation.
- Damage to brain - Pb, Hg, Cr accumulation.
- Improper development of foetus - Pb and Hg accumulation.
- Reduction in sperm production - Pb accumulation.
- Affects the strength of bones - Cd accumulation
- Skin irritation and rashes - As, Hg accumulation.
- Hypertension - As, Pb accumulation.
- Improper development of body - Hg, Pb. Cd accumulation.
- Ultimately leading to Death - all toxic metal accumulation.

**Figure 2.1.** Movement and Fate of Toxic Metals in Environment

# Chapter 3

# MATERIALS AND METHODS

The study has been carried out to estimate the concentration of various heavy metals - Cd, Cr, Cu, Fe, Ni, Pb and Zn in the sediments of River Ganga in the Himalayan region with respect to different particle size. The longitudinal variation in the concentration of heavy metals for each of the metal will be plotted. This will help in understanding any sudden increase in the concentration of any heavy metal thus helping in finding out the source of discharge. The results of the study will also be used to understand the degree of the pollution at each site using various factors like Metal Enrichment Factor, Contamination Factor, Relative Mobility, and indices like Geo-accumulation Index, Sediment Pollution Index and Pollution Load Index. Also the relationship between the concentration of heavy metals and the particle size of sediments and the interrelationship between each of the elements will be studied. The ultimate aim of the study is thus to understand the potential of the sediments to pollute the water column above it.

## 3.1. SAMPLING STATIONS AND SEDIMENT SAMPLING

The study was carried out in collaboration with National Institute of Hydrology (NIH), Roorkee. To analyse the metal content in the sediments of River Ganga, 7 sampling sites were chosen from a flow length of around 300 Km of the river. The stations are tabulated below in Table 3.1. along with their exact location and their distance from the origin i.e. Gomukh. Stations were chosen keeping in mind the activities that have been taking place at that site. The first 3 stations - Gomukh, Bhojwasa and Gangotri represent a more unpolluted sampling stations as the anthropogenic activities in these sites are relatively nil. The last 3 stations - Chinyalisaur, Devaprayag and Rishikesh represent a more polluted sampling stations as these areas have been recently effected by lot of tourist activities, industrial activities, increasing population and many other anthropogenic activities.

**Table 3.1.** Location and Distance of Each Site from Origin

| Sl. No. | Sampling Station | Location | | Distance from Origin (Km) |
|---|---|---|---|---|
| | | Latitude | Longitude | |
| 1 | Gomukh | 30.92678N | 79.08078E | 0 |
| 2 | Bhojwasa | 30.94959N | 79.05058E | 4 |
| 3 | Gangotri | 30.99460N | 78.93985E | 18 |
| 4 | Jhala Bridge | 31.02782N | 78.71473E | 42 |
| 5 | Chinyalisaur | 30.58543N | 78.32538E | 152 |
| 6 | Devaprayag | 30.14572N | 78.59781E | 274 |
| 7 | Rishikesh | 30.08276N | 78.28992E | 291 |


**Figure 3.1.** Location of Sampling Stations in the Study

The sampling was done post the winters, on February 28 and February 29, 2016. The sediment samples were collected from the top 5-10cm of the river bank of each of the 7 sampling station. They were collected using an EKman dredge sampler and then stored in pre-cleaned air tight polythene bags for processing. Sampling tools were washed with water and dried before the next sample was collected. The wet sediment samples were dried by heating in a pre-heated oven at a temperature of 60°C.

## 3.2. EXPERIMENTAL PROCEDURES

### 3.2.1. Granulometric Analysis

After cooling the dried sediments, granulometric analysis was carried out on the sample. Sample from each of the location weighing 30g was passed through sieves to obatin various fractions (0-75, 75-150, 150-200, 200-250, 350-300, 300-450, 450-600 μm. Each of these samples were transferred into plastic vials and properly named. The particle size distribution curve was plotted for all the locations.


**Figure 3.2.** Sediments Stored in Plastic Vials after Sieving

### 3.2.2. Acid Digestion of Sediment Samples

All the sediment sample obtained after sieving were subjected to acid digestion process. 200 mg of sample of each size from each location were taken in conical flask. An acid prepared from concentrated Nitric acid and concentrated Sulphuric acid in the ratio 3:1 was used for digestion. 10 ml of acid was added to each of the conical flasks. These were then heated on a hot plate at 110 - 120°C for hours till the acid dried and formation of fumes stops. If the acid gets dried and more fumes were still coming, additional amount of acid was added. Figure 3.3. shows the experimental set up. Figure 3.4 shows the sediment sample after proper digestion. After digesting the sediments, distilled water was added to the extracts of sediments and they were made up till a volume of 50 ml. These were stored in plastic vials and refrigerated (Figure 3.5.).

**Figure 3.3.** Acid Digestion of Sediments on Hot Plate

**Figure 3.4.** Sediment sample after acid digestion

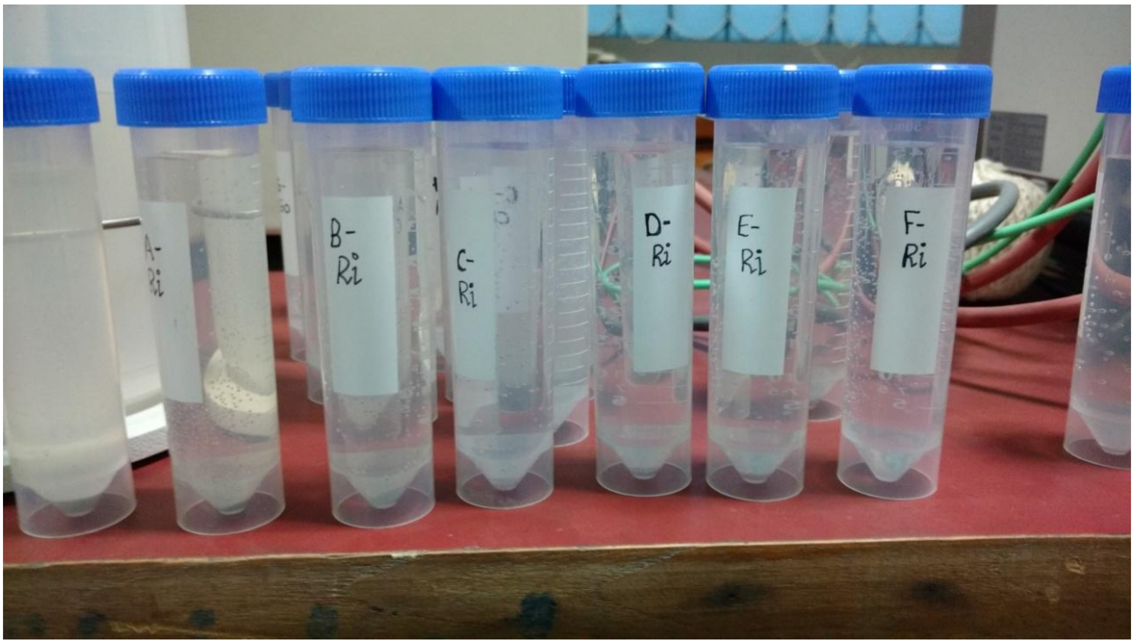



**Figure 3.5.** Extracts of Sediments stored in plastic vials after dilution

### 3.2.3. Standard Preparation for Heavy Metals

The study deals with the measurement of Al, Cd, Cr, Cu, Fe, Ni, Pb and Zn in the sediment samples. A standard solution of 100 ppm was made for all of the above metals. The procedure adopted for preparation was stock solution for each of the metal is explained below:

- 100 ppm standard solution for Al was made by adding 2.407 g of Aluminium Sulphate to 4ml concentrated HCl and 4ml distilled water mixture. This was mixed thoroughly and volume was made up to 1000ml.
- 100 ppm standard solution of Cd was made by adding 0.100g of Cd to 10ml of concentrated $HNO_3$. It was mixed and dissolved thoroughly and volume was made up to 1000ml.
- 100 ppm standard solution of Cr was prepared by adding 0.1923 g of $CrO_3$ to 10 ml $HNO_3$. It was mixed and dissoved and volume was made up to 1000 ml.
- 100 ppm standard solution of Cu was prepared by adding 0.1 g of Cu metal to 10 ml of concentrated $HNO_3$. It was mixed and dissolved thoroughly and volume was made up to 1000ml.
- 100 ppm standard solution of Fe was made by adding 0.1 g of Fe metal to10 ml of concentrated $HNO_3$. It was mixed and dissolved thoroughly and volume was made up to 1000ml.
- 100 ppm standard solution of Ni was prepared by adding 0.1 g of Ni metal to 10 ml of concentrated $HNO_3$. It was mixed and dissolved thoroughly and volume was made up to 1000ml.
- 100 ppm standard solution of Pb was prepared by adding 0.1598 g of Lead Nitrate into a mixture of 1 ml distilled water and 11 ml concentrated $HNO_3$. It was mixed thoroughly and dissolved and the volume was made up to 1000 ml.
- 100 ppm standard solution of Zn was prepared by adding 0.1 g of Zn metal to a mixture of 1ml distilled water and 1ml concentrated HCl. It was mixed thoroughly and dissolved. The volume was made up to 1000 ml.

Figure 3.6. shows the standard solution of 100 ppm prepared for each of the metal in volumetric flasks.


**Figure 3.6.** Stock Solutions for each of the metal

### 3.2.4. Heavy Metal Analysis on AAS (Analytik-jena novAA 350)

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals (excited state) for a short period of time (nanoseconds) by absorbing a defined quantity of energy (radiation of a given wavelength). This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, and the width of an absorption line is only of the order of a few picometers (pm), which gives the technique its elemental selectivity. The radiation flux without a sample and with a sample in the atomizer is measured using a detector, and the ratio between the two values (the absorbance) is converted to analyte concentration or mass using the Beer-Lambert Law.

For analysis, the standard solutions prepared were diluted to the required measure. The standard solutions of Cd, Cr, Cu, Ni, Pb and Zn were diluted to 10ppm solution. The standard solutions of Fe and Al were diluted to 1 ppm. All the 53 samples were analysed for heavy metal concentration in them.


**Figure 3.7.** Heavy Metal Analysis on AAS

The concentration values of each of the metal is used to determine factors such as Metal Enrichment Factor and Contamination Factor. The quality of sediments with respect to each metal is evaluated with respect to each metal by calculating Geo-accumulation Index. The quality of sediments for every location was also assessed by calculating Sediment Pollution Index and Pollution Load Index. The ease with which metals can get solubilised from sediments to water was calculated using Relative Mobility of a metal with respect to a conservative metal. The correlation between different metal was found by carrying out statistical analysis in Microsoft Excel. This was used to identify the common sources of pollution for different heavy metals.

# Chapter 4

# RESULTS AND DISCUSSION

## 4.1. PARTICLE SIZE DISTRIBUTION OF SEDIMENTS

The granulometric analysis of the sediments revealed the particle size distribution of sediments from each of the location. The percentage finer was found out using the formula:

$$Percentage\ Finer = 1 - Cumulative\ Percentage\ of\ particles\ retained \quad \text{Eq. 4.1}$$

**Table 4.1.** Calculation of Percentage Finer for Sediments from Gomukh

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.3374 | 1.1255 | 1.1255 | 98.8744 |
| **450** | 3.5561 | 11.8625 | 12.9880 | 87.0119 |
| **300** | 0.0802 | 0.2675 | 13.2556 | 86.7443 |
| **250** | 5.1076 | 17.0381 | 30.2937 | 69.7062 |
| **200** | 4.0751 | 13.5938 | 43.8875 | 56.1124 |
| **150** | 1.1898 | 3.9689 | 47.8565 | 52.1434 |
| **75** | 6.5800 | 21.9498 | 69.8063 | 30.1936 |
| **0** | 9.0513 | 30.1936 | 100.0000 | 0.0000 |
| **Total Sum** | 29.9775 | | | |

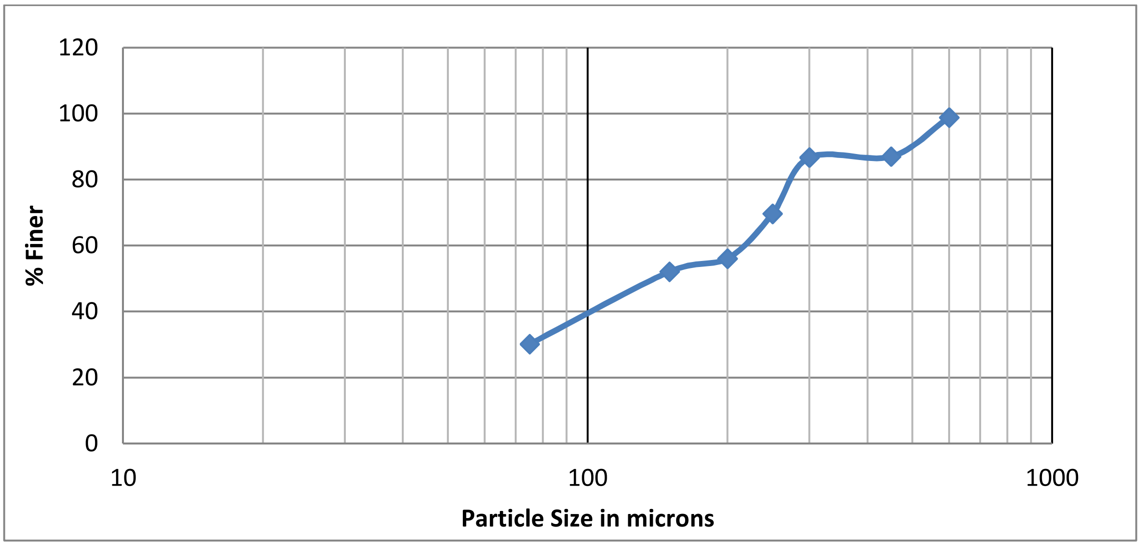



**Figure 4.1.** Particle Size Distribution Curve for Sediments from Gomukh

The calculations for granulometric analysis of sediments from Gomukh is shown in Table 4.1. and the Particle Size Distribution Curve is depicted in Figure 4.1. The sediment particles in Gomukh were really fine, with more than 50% of them getting retained in the sieve with sieve size 75µm. They are mostly clayey and silty particles. This fineness of the sediments can be attributed to glacial weathering which the sediments were subjected to during the winter months.

**Table 4.2.** Calculation of Percentage Finer for Sediments from Bhojwasa

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.0000 | 0.0000 | 0.0000 | 100.0000 |
| **450** | 1.1368 | 3.7994 | 3.7994 | 96.2005 |
| **300** | 0.0189 | 0.0631 | 3.8625 | 96.1374 |
| **250** | 1.9047 | 6.3659 | 10.2285 | 89.7714 |
| **200** | 2.6575 | 8.8819 | 19.1104 | 80.8895 |
| **150** | 1.6092 | 5.3782 | 24.4887 | 75.5112 |
| **75** | 8.0887 | 27.0341 | 51.5228 | 48.4771 |
| **0** | 14.5045 | 48.4771 | 100.0000 | 0.0000 |
| **Sum** | 29.9203 | | | |

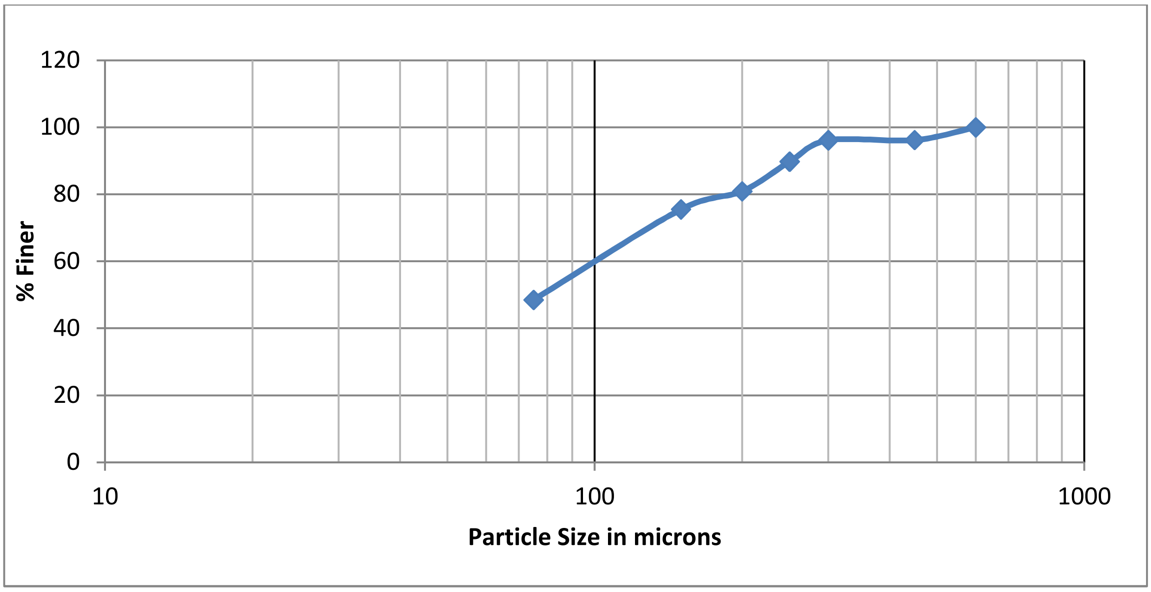



**Figure 4.2.** Particle Size Distribution Curve for Sediments from Bhojwasa

The calculations for granulometric analysis of sediments from Bhojwasa is shown in Table 4.2 and the Particle Size Distribution Curve is depicted in Figure 4.2. The sediments from Bhojwasa had about 50% of the sediment particles passing through

75μm sieve and getting retained on the pan. The sediments in this region was also dominated by silt and clay.

**Table 4.3.** Calculation of Percentage Finer for Particles from Gangotri

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| | | | | |
| **600** | 0.0000 | 0.0000 | 0.0000 | 100.0000 |
| **450** | 0.6896 | 2.3016 | 2.3016 | 97.6983 |
| **300** | 0.0188 | 0.0627 | 2.3643 | 97.6356 |
| **250** | 4.9720 | 16.5948 | 18.9591 | 81.0408 |
| **200** | 7.5132 | 25.0764 | 44.0356 | 55.9643 |
| **150** | 2.4749 | 8.2603 | 52.2959 | 47.7040 |
| **75** | 9.1158 | 30.4253 | 82.7213 | 17.2786 |
| **0** | 5.1769 | 17.2786 | 100.0000 | 0.0000 |
| **SUM** | 29.9612 | | | |

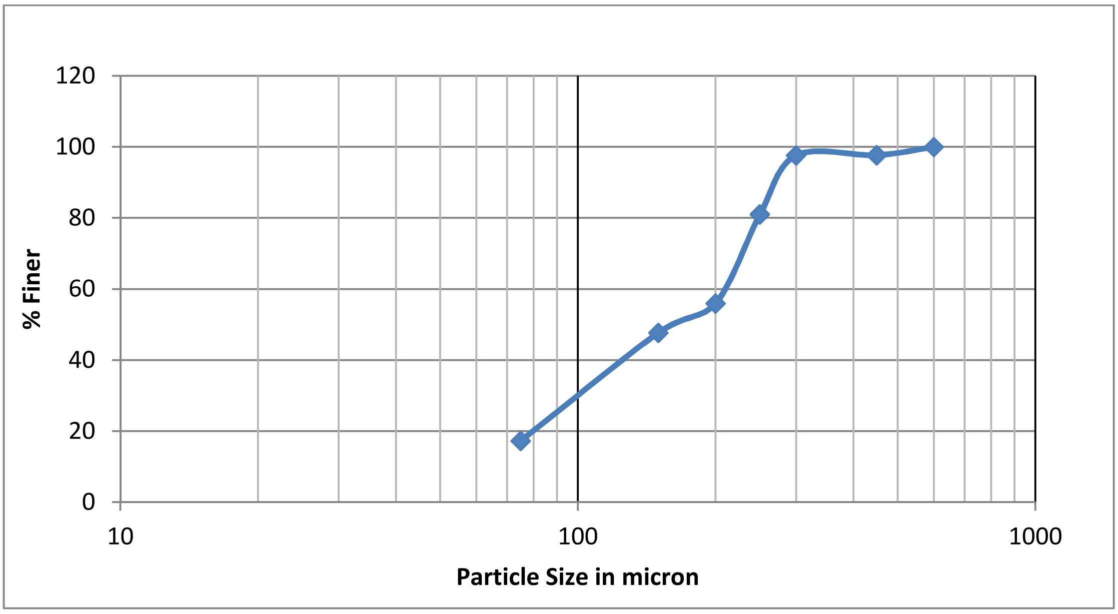



**Figure 4.3.** Particle Size Distribution Curve of Sediments from Gangotri

The calculations for granulometric analysis of sediments from Gangotri is shown in Table 4.3. and the Particle Size Distribution Curve is depicted in Figure 4.3. Around 80% of the particles were found to be finer than 250μm. The sediments mostly composed of sand and silt and they were found to be more coarser than the sediments from Gomukh and Bhojwasa.

**Table 4.4.** Calculation of Percentage Finer for Sediments from Jhala Bridge

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.3632 | 1.2125 | 1.2125 | 98.7874 |
| **450** | 10.3661 | 34.6073 | 35.8198 | 64.1801 |
| **300** | 0.0905 | 0.3021 | 36.1219 | 63.8780 |
| **250** | 9.3269 | 31.1379 | 67.2599 | 32.7400 |
| **200** | 3.4656 | 11.5699 | 78.8298 | 21.1701 |
| **150** | 0.7725 | 2.5789 | 81.4088 | 18.5911 |
| **75** | 3.5746 | 11.9338 | 93.3426 | 6.6573 |
| **0** | 1.9941 | 6.6573 | 100.0000 | 0.0000 |
| **Sum** | 29.9535 | | | |

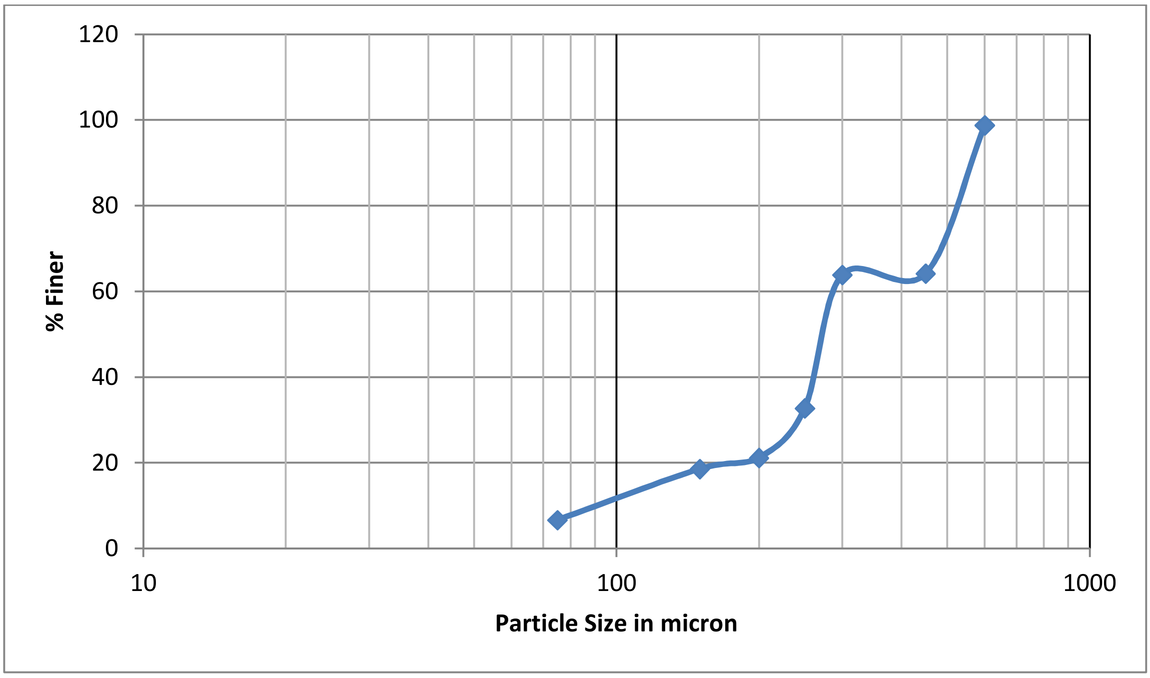



**Figure 4.4.** Particle Size Distribution of Sediments from Jhala Bridge

The calculations for granulometric analysis of sediments from Jhala Bridge is shown in Table 4.4 and the Particle Size Distribution Curve is depicted in Figure 4.4. Maximum sediment particles were observed to be getting retained in the sieve of size 450µm. The sediments were gap graded as around 30% of the particles were retained in the sieve of size 250µm and 450µm, but only 0.3% of the particles got retained in the sieve of size 300µm sieve. The sediment particles were mostly sand particles and were coarser than the sediments from Gomukh, Bhojwasa, Gangotri and Jhala Bridge.

**Table 4.5.** Calculation of Percentage Finer for Sediments from Chinyalisaur

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.1197 | 0.4000 | 0.4000 | 99.5999 |
| **450** | 8.3665 | 27.9603 | 28.3604 | 71.6395 |
| **300** | 0.3673 | 1.2274 | 29.5879 | 70.4121 |
| **250** | 5.0268 | 16.7992 | 46.3871 | 53.6128 |
| **200** | 7.2552 | 24.2464 | 70.6336 | 29.3663 |
| **150** | 4.9453 | 16.5269 | 87.1605 | 12.8394 |
| **75** | 3.0745 | 10.2748 | 97.4353 | 2.5646 |
| **0** | 0.7674 | 2.5646 | 100.0000 | 0.0000 |
| **Sum** | 29.9227 | | | |

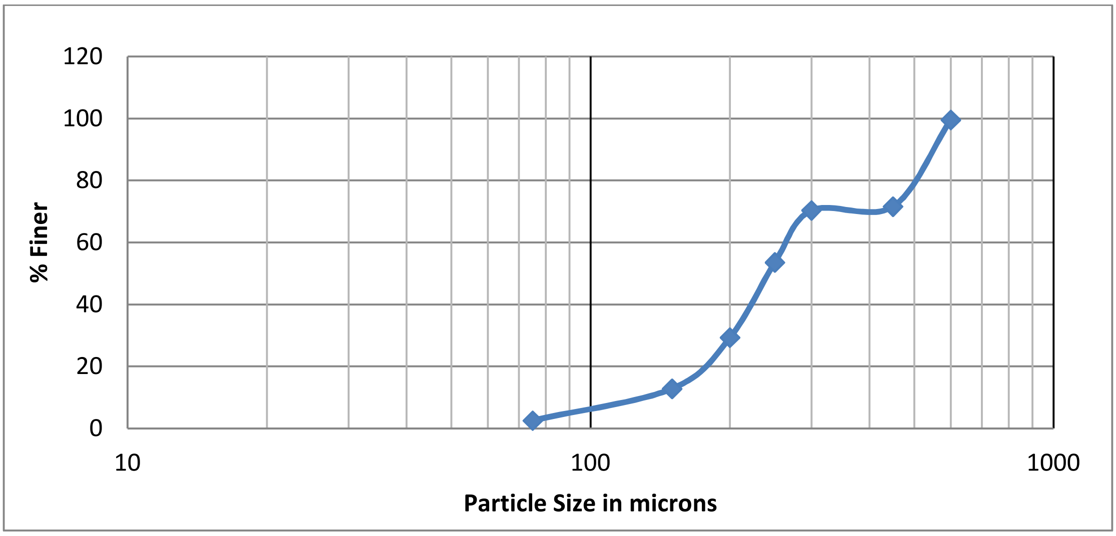



**Figure 4.5.** Particle Size Distribution Curve for Sediments from Chinyalisaur

The calculations for granulometric analysis of sediments from Chinyalisaur is shown in Table 4.5 and the Particle Size Distribution Curve is depicted in Figure 4.5. The sediments were found to be mostly well graded as it had a good representation of particles in various fractions of size. The particles retained in the sieve with sieve size 300µm was found to be less implying that the particles whose size were greater than 450µm and less than 300µm were found to be very less (around 1.2%). Also the particles with size greater than 600µm and less than 75µm were also found to be less in the case of these sediment samples from Chinyalisaur . The sediment particles mostly composed of sand.

**Table 4.6.** Calculation of Percentage Finer for Sediments from Devaprayag

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.0000 | 0.0000 | 0.0000 | 100.0000 |
| **450** | 0.1537 | 0.5137 | 0.5137 | 99.4862 |
| **300** | 0.0126 | 0.0421 | 0.5558 | 99.4441 |
| **250** | 2.7088 | 9.0537 | 9.6096 | 90.3903 |
| **200** | 9.3998 | 31.4174 | 41.0271 | 58.9728 |
| **150** | 3.8595 | 12.8998 | 53.9269 | 46.0730 |
| **75** | 11.3629 | 37.9788 | 91.9058 | 8.0941 |
| **0** | 2.4217 | 8.0941 | 100.0000 | 0.0000 |
| **SUM** | 29.9190 | | | |

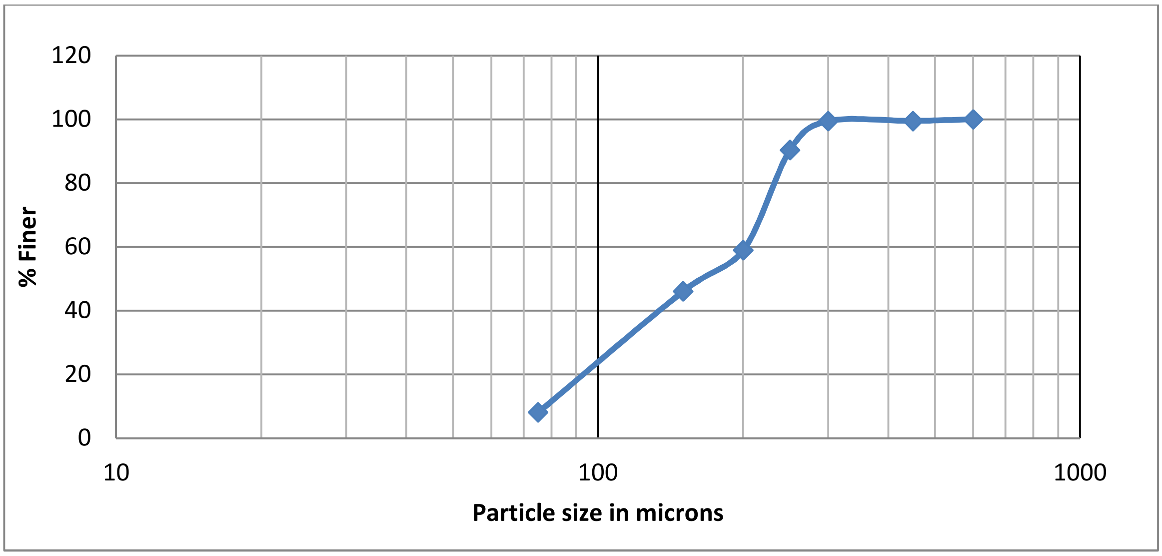



**Figure 4.6.** Particle Size Distribution Curve for Sediments from Devaprayag

The calculations for granulometric analysis of sediments from Devaprayag is shown in Table 4.6 and the Particle Size Distribution Curve is depicted in Figure 4.6. The sediment particles at Devaprayag were found to be finer than the sediments from Jhala Bridge and Chinyalisaur, but not as fine as the sediments from Gomukh and Bhojwasa. Around 99% of the particles were found to be finer than 300µm as they passed through the sieves of size 600, 450 and 300µm. The sediment particles mostly composed of sand and silt.

**Table 4.7.** Calculation of Percentage Finer for Sediments from Rishikesh

| Sieve Size in micron | Weight of particles retained (g) | Percentage of particles retained | Cumulative Percentage of particles retained | Percentage Finer |
|---|---|---|---|---|
| **600** | 0.2735 | 0.9119 | 0.9119 | 99.0880 |
| **450** | 0.7648 | 2.5501 | 3.4620 | 96.5379 |
| **300** | 0.0133 | 0.0443 | 3.5064 | 96.4935 |
| **250** | 9.8006 | 32.6790 | 36.1854 | 63.8145 |
| **200** | 11.2812 | 37.6159 | 73.8013 | 26.1986 |
| **150** | 2.6723 | 8.9104 | 82.7118 | 17.2881 |
| **75** | 4.579 | 15.2681 | 97.9800 | 2.0199 |
| **0** | 0.6058 | 2.0199 | 100.0000 | 0.0000 |
| **SUM** | 29.9905 | | | |

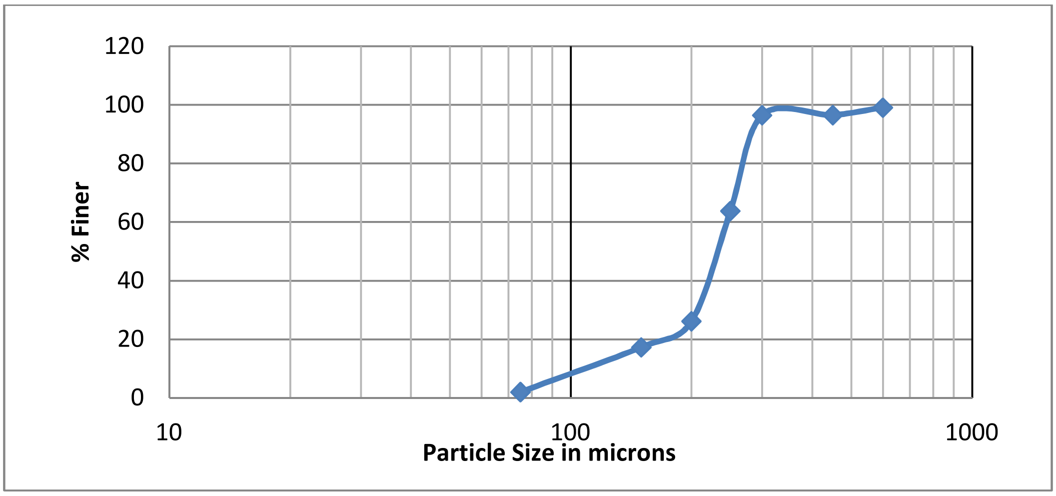



**Figure 4.7.** Particle Size Distribution of Sediments from Rishikesh

The calculations for granulometric analysis of sediments from Rishikesh is shown in Table 4.7 and the Particle Size Distribution Curve is depicted in Figure 4.7. The sediments of Rishikesh was found to be well-graded compared to the sediments from all other locations. More than 65% of the particles were retained in the sieves of size 250 and 200µm. The sediments of Rishikesh was found to be dominated by sand with some amount of silt as well.

## 4.2. CONCENTRATION OF HEAVY METALS IN SEDIMENTS

The concentration of heavy metals in each of the size fractions at all the 7 sampling stations were found out using AAS. The mean concentration was evaluated using the formula:

$$Mean\ Concentration = \frac{\sum(Ci*Wi)}{100} \qquad \text{Eq 4.2}$$

where, $C_i$ is the concentration of the metal in the particles with size range i, and $W_i$ is the percentage weight of sediments that fall in the range i.

The results are tabulated from Table 4.8 to 4.14.

**Table 4.8.** Concentration of Metals in Gomukh

| | **Concentration of Metals** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Size (µm)** | **Al (g/Kg)** | **Fe (g/Kg)** | **Cr (mg/Kg)** | **Zn (mg/Kg)** | **Pb (mg/Kg)** | **Cu (mg/Kg)** | **Ni (mg/Kg)** | **Cd (mg/Kg)** |
| **0-75** | 226.5 | 99.4 | 36.72 | 44.75 | 25.97 | 3.26 | 2.75 | 0.49 |
| **75-150** | 180.3 | 96.2 | 35.42 | 39.25 | 25.62 | 3.22 | 2.72 | 0.34 |
| **150-200** | 162.6 | 92.1 | 35.555 | 36.52 | 23.05 | 3.23 | 2.70 | 0.35 |
| **200-250** | 151.6 | 88.2 | 32.19 | 35.38 | 23.2 | 3.19 | 2.60 | 0.37 |
| **250-300** | 170.5 | 81.9 | 29.16 | 31.11 | 20.37 | 3.05 | 2.59 | 0.39 |
| **300-450** | 157.8 | 80.2 | 24.19 | 29.15 | 14.00 | 2.45 | 2.57 | 0.33 |
| **450-600** | 153.3 | 76.4 | 21.27 | 28.15 | 10.57 | 2.10 | 2.4 | 0.30 |
| **>600** | 117.8 | 74.0 | 18.64 | 26.35 | 10.52 | 1.93 | 2.22 | 0.25 |
| **AVERAGE** | 182.8 | 90.2 | 32.17 | 37.13 | 22.24 | 3.03 | 2.63 | 0.39 |
| **S.D. ±** | 30.8 | 9.4 | 7.010 | 6.28 | 6.50 | 0.55 | 0.18 | 0.07 |

The sediments at Gomukh reported presence of all the metals considered in the present study with average concentration of 182.8 g/Kg for Al, ranging from 117.8 g/Kg (associated with particle size > 600 µm) to 226.5 g/Kg (associated with 0-75 µm sized sediments). Fe concentration varied from 74 g/Kg to 99.4 g/Kg with a mean value of 90.2 g/Kg. Fe and Al were relatively abundant compared to other metals. The concentration of Cr varied from 18.64 mg/Kg (with >600 µm sized sediments) to 36.72 mg/Kg (associated with 0-75 µm sized sediments) with an average of 32.17 mg/Kg. Similar trend was observed for Zn and Pb with mean concentration of 37.13 mg/Kg and 22.24 mg/Kg, respectively. The concentration of Cu and Ni was relatively less with an average of 3.03 mg/Kg and 2.63 mg/Kg, respectively. The deviation in concentration of Cu and Ni was very less with respect to particle size of sediments. Minimum metal concentration was observed for Cd ranging from 0.25 mg/Kg to 0.49 mg/Kg with an average of 0.39 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. Further it was observed that the metal concentration decreased with an increase in particle size of sediments which may be attributed to more surface area and binding sites over the sediments. With respect to relative abundance Al > Fe > Zn > Cr > Pb > Cu> Ni > Cd trend was observed at Gomukh.

**Table 4.9.** Concentration of Metals in Bhojwasa

| | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Size (µm)** | **Al (g/Kg)** | **Fe (g/Kg)** | **Cr (mg/Kg)** | **Zn (mg/Kg)** | **Pb (mg/Kg)** | **Cu (mg/Kg)** | **Ni (mg/Kg)** | **Cd (mg/Kg)** |
| **0-75** | 215.7 | 97.3 | 38.90 | 46.72 | 27.98 | 5.76 | 2.83 | 0.52 |
| **75-100** | 180.0 | 93.1 | 40.23 | 42.91 | 28.92 | 5.82 | 2.90 | 0.48 |
| **150-200** | 154.8 | 91.6 | 37.45 | 40.95 | 28.91 | 5.45 | 2.65 | 0.46 |
| **200-250** | 150.4 | 84.4 | 32.87 | 36.90 | 26.53 | 4.73 | 2.40 | 0.43 |
| **250-300** | 169.0 | 78.6 | 30.55 | 32.89 | 24.91 | 4.28 | 2.30 | 0.41 |
| **300-450** | 140.3 | 77.3 | 26.91 | 29.18 | 23.32 | 3.91 | 2.22 | 0.37 |
| **450-600** | 129.4 | 74.4 | 24.35 | 27.94 | 22.45 | 3.00 | 2.20 | 0.36 |
| **AVERAGE** | 190.6 | 92.7 | 37.55 | 42.90 | 27.75 | 5.47 | 2.75 | 0.48 |
| **S.D. ±** | 28.8 | 8.9 | 6.12 | 7.13 | 2.65 | 1.05 | 0.29 | 0.06 |

The sediments at Bhojwasa reported presence of all the metals considered in the present study with average concentration of 190.6 g/Kg for Al, ranging from 129.4 g/Kg (associated with particle size > 600 µm) to 215.7 g/Kg (associated with 0-75 µm sized sediments). Fe concentration varied from 74.4 g/Kg to 97.3 g/Kg with a mean value of 92.7 g/Kg. Fe and Al were relatively abundant compared to other metals. The concentration of Cr varied from 24.35 mg/Kg (with >600 µm sized sediments) to 40.23 mg/Kg (associated with 75-150 µm sized sediments) with an average of 37.55 mg/Kg. Similar trend was observed for Zn and Pb with mean concentration of 42.90 mg/Kg and 27.75 mg/Kg, respectively. The concentration of Cu and Ni was relatively less with an average of 5.47 mg/Kg and 2.75 mg/Kg, respectively. The deviation in concentration of Cu and Ni was very less with respect to particle size of sediments. Minimum metal concentration was observed for Cd ranging from 0.36 mg/Kg to 0.52 mg/Kg with an average of 0.48 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. In general, it can be said that as the particle size increased, there was a decrease in metal concentration owing to lesser surface area available for binding. With respect to relative abundance Al > Fe > Zn > Cr > Pb > Cu > Ni > Cd trend was seen.

**Table 4.10.** Concentration of Metals in Gangotri

| | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Size (µm) | Al (g/Kg) | Fe (g/Kg) | Cr (mg/Kg) | Zn (mg/Kg) | Pb (mg/Kg) | Cu (mg/Kg) | Ni (mg/Kg) | Cd (mg/Kg) |
| **0-75** | 200.5 | 97.3 | 41.79 | 52.93 | 31.23 | 18.56 | 9.25 | 0.43 |
| **75-150** | 178.9 | 96.2 | 42.80 | 51.79 | 31.02 | 18.22 | 9.42 | 0.39 |
| **150-200** | 156.4 | 80.2 | 40.89 | 49.28 | 30.62 | 17.54 | 9.26 | 0.32 |
| **200-250** | 149.3 | 73.2 | 37.92 | 40.90 | 28.95 | 17.30 | 9.01 | 0.23 |
| **250-300** | 119.0 | 69.4 | 32.80 | 38.97 | 26.32 | 16.91 | 8.32 | 0.21 |
| **300-450** | 108.5 | 66.2 | 31.45 | 36.89 | 24.90 | 16.42 | 7.99 | 0.22 |
| **450-600** | 94.6 | 66.1 | 30.20 | 34.50 | 21.73 | 15.96 | 7.82 | 0.19 |
| **AVERAGE** | 161.4 | 84.1 | 39.29 | 46.51 | 29.51 | 17.72 | 9.05 | 0.32 |
| **S.D. ±** | 38.6 | 13.5 | 5.28 | 7.56 | 3.62 | 0.93 | 0.66 | 0.09 |

The sediments at Gangotri reported presence of all the metals considered in the present study with average concentration of 161.4 g/Kg for Al, ranging from 94.6 g/Kg (associated with particle size 450-600 µm) to 200.5 g/Kg (associated with 0-75 µm sized sediments). Fe concentration varied from 66.1 g/Kg to 97.3 g/Kg with a mean value of 84.1 g/Kg. Fe and Al were relatively abundant compared to other metals. The concentration of Cr varied from 30.20 mg/Kg (with 450-600 µm sized sediments) to 42.80 mg/Kg (associated with 75-150 µm sized sediments) with an average of 39.29 mg/Kg. Similar trend was observed for Zn and Pb with mean concentration of 46.51 mg/Kg and 29.51 mg/Kg, respectively. The concentration of Cu and Ni was relatively less with an average of 17.72 mg/Kg and 9.05 mg/Kg, respectively. The deviation in concentration of Cu and Ni was very less with respect to particle size of sediments. Minimum metal concentration was observed for Cd ranging from 0.19 mg/Kg to 0.43 mg/Kg with an average of 0.32 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. Due to greater surface area available for binding, it was seen that the metal concentration increased with decrease in particle size. With respect to relative abundance of metals, Al > Fe > Zn > Cr > Pb > Cu > Ni > Cd trend was seen.

**Table 4.11.** Concentration of Metals in Jhala Bridge

| Size (μm) | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Al (g/Kg) | Fe (g/Kg) | Cr (mg/Kg) | Zn (mg/Kg) | Pb (mg/Kg) | Cu (mg/Kg) | Ni (mg/Kg) | Cd (mg/Kg) |
| **0-75** | 198.0 | 80.4 | 68.93 | 74.76 | 54.90 | 14.89 | 24.12 | 0.81 |
| **75-150** | 199.6 | 74.3 | 58.92 | 63.86 | 53.05 | 14.10 | 21.35 | 0.80 |
| **150-200** | 175.9 | 65.4 | 47.89 | 58.90 | 47.80 | 12.34 | 18.85 | 0.74 |
| **200-250** | 156.3 | 63.0 | 42.90 | 51.90 | 48.12 | 10.89 | 18.99 | 0.72 |
| **250-300** | 147.8 | 59.3 | 40.56 | 49.70 | 46.54 | 9.53 | 12.45 | 0.62 |
| **300-450** | 134.9 | 50.6 | 39.85 | 46.34 | 45.55 | 9.52 | 11.45 | 0.68 |
| **450-600** | 95.4 | 47.9 | 36.30 | 42.80 | 43.36 | 8.64 | 9.87 | 0.57 |
| **>600** | 85.0 | 43.9 | 30.69 | 39.00 | 40.54 | 8.24 | 7.72 | 0.54 |
| **AVERAGE** | 158.3 | 63.3 | 46.83 | 54.00 | 48.59 | 11.42 | 17.08 | 0.71 |
| **S.D. ±** | 42.9 | 12.8 | 12.54 | 11.84 | 4.73 | 2.51 | 5.97 | 0.10 |

The sediments at Jhala Bridge reported presence of all the metals considered in the present study with average concentration of 158.3 g/Kg for Al, ranging from 85.0 g/Kg (associated with particle size >600 μm) to 199.6 g/Kg (associated with 75-150 μm sized sediments). Fe concentration varied from 80.4 g/Kg to 43.9 g/Kg with a mean value of 63.3 g/Kg. Fe and Al were relatively abundant compared to other metals. The concentration of Cr varied from 30.69 mg/Kg (with >600 μm sized sediments) to 68.93 mg/Kg (associated with 0-75 μm sized sediments) with an average of 46.83 mg/Kg. Similar trend was observed for Zn and Pb with mean concentration of 54 mg/Kg and 48.59 mg/Kg, respectively. The concentration of Cu and Ni was relatively less with an average of 11.42 mg/Kg and 17.08 mg/Kg, respectively. There was a decrease in the Cu concentration from the previous station. The deviation in concentration of Cu was very less with respect to particle size of sediments. Minimum metal concentration was observed for Cd ranging from 0.54 mg/Kg to 0.81 mg/Kg with an average of 0.71 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. With respect to relative abundance, Al > Fe > Zn > Pb > Cr > Ni > Cu > Cd trend was seen. The size of the particles and the metal concentration were seen to have a negative relation.

**Table 4.12.** Concentration of Metals in Chinyalisaur

| Size (μm) | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Al (g/Kg) | Fe (g/Kg) | Cr (mg/Kg) | Zn (mg/Kg) | Pb (mg/Kg) | Cu (mg/Kg) | Ni (mg/Kg) | Cd (mg/Kg) |
| **0-75** | 79.8 | 54.2 | 106.24 | 84.87 | 71.94 | 76.45 | 99.87 | 3.50 |
| **75-150** | 77.6 | 53.3 | 108.92 | 82.10 | 70.93 | 74.09 | 98.93 | 3.50 |
| **150-200** | 72.3 | 52.9 | 105.29 | 75.92 | 69.45 | 73.72 | 93.37 | 3.44 |
| **200-250** | 64.0 | 48.9 | 104.32 | 73.93 | 62.11 | 70.54 | 90.75 | 3.26 |
| **250-300** | 59.8 | 43.9 | 106.93 | 70.25 | 58.80 | 66.45 | 93.09 | 3.10 |
| **300-450** | 52.3 | 41.1 | 102.09 | 66.93 | 52.56 | 63.85 | 92.04 | 2.90 |
| **450-600** | 49.8 | 40.2 | 94.90 | 62.12 | 49.90 | 62.94 | 93.00 | 2.87 |
| **>600** | 43.8 | 39.1 | 91.78 | 56.83 | 48.70 | 60.63 | 91.93 | 2.02 |
| **AVERAGE** | 62.3 | 46.8 | 102.73 | 71.31 | 60.34 | 68.65 | 93.30 | 3.18 |
| **S.D. ±** | 13.4 | 6.4 | 6.07 | 9.57 | 9.56 | 5.91 | 3.37 | 0.50 |

The sediments at Chinyalisaur reported presence of all the metals considered in the present study with average concentration of 62.3 g/Kg for Al, ranging from 43.8 g/Kg (associated with particle size >600 μm) to 79.8 g/Kg (associated with 0-75 μm sized sediments). Fe concentration varied from 39.1 g/Kg to 54.2 g/Kg with a mean value of 46.8 g/Kg. Fe and Al were relatively abundant compared to other metals, although a sudden decrease in the concentration of Al was noted. A sudden increase in the concentration of Cr was noted. The concentration of Cr varied from 91.78 mg/Kg (with >600 μm sized sediments) to 108.92 mg/Kg (associated with 75-150 μm sized sediments) with an average of 102.73 mg/Kg. Zn and Pb had a mean concentration of 71.31 mg/Kg and 60.34 mg/Kg, respectively. The concentration of Cu and Ni also showed a sudden jump with an average of 68.65 mg/Kg and 93.30 mg/Kg, respectively. Minimum metal concentration was observed for Cd ranging from 2.02 mg/Kg to 3.5 mg/Kg with an average of 3.18 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. It was also observed that the concentration of metals decreased with increase in size of sediment particles. With respect to relative abundance, Al > Fe > Cr > Ni > Zn > Cu > Pb > Cd, trend was seen.

**Table 4.13.** Concentration of Metals in Devaprayag

| | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Size (µm)** | **Al (g/Kg)** | **Fe (g/Kg)** | **Cr (mg/Kg)** | **Zn (mg/Kg)** | **Pb (mg/Kg)** | **Cu (mg/Kg)** | **Ni (mg/Kg)** | **Cd (mg/Kg)** |
| **0-75** | 77.5 | 56.8 | 187.78 | 80.54 | 140.54 | 50.67 | 71.90 | 2.72 |
| **75-150** | 70.1 | 55.1 | 174.67 | 80.00 | 138.72 | 49.87 | 70.87 | 2.70 |
| **150-200** | 65.7 | 54.0 | 172.97 | 74.32 | 134.55 | 46.89 | 67.03 | 2.67 |
| **200-250** | 54.4 | 46.5 | 167.45 | 71.69 | 132.11 | 42.11 | 61.06 | 2.63 |
| **250-300** | 52.1 | 44.1 | 163.75 | 66.54 | 130.87 | 41.10 | 59.00 | 2.59 |
| **300-450** | 50.2 | 39.0 | 159.86 | 63.66 | 129.00 | 39.24 | 58.03 | 2.5 |
| **450-600** | 47.8 | 39.9 | 153.32 | 60.56 | 127.11 | 39.01 | 52.03 | 2.42 |
| **AVERAGE** | 63.8 | 51.3 | 172.12 | 75.37 | 135.47 | 46.26 | 66.20 | 2.67 |
| **S.D. ±** | 11.5 | 7.4 | 11.24 | 7.81 | 4.96 | 4.94 | 7.33 | 0.11 |

The sediments at Devaprayag reported presence of all the metals considered in the present study with average concentration of 63.8 g/Kg for Al, ranging from 47.8 g/Kg (associated with particle size 450-600 µm) to 77.5 g/Kg (associated with 0-75 µm sized sediments). Fe concentration varied from 39.9 g/Kg to 56.8 g/Kg with a mean value of 51.3 g/Kg. Fe and Al were relatively abundant compared to other metals. A sudden increase in the concentration of Pb was noted. The concentration of Pb varied from 127.11 mg/Kg (with 450-600 µm sized sediments) to 140.54 mg/Kg (associated with 0-75 µm sized sediments) with an average of 135.47 mg/Kg. Zn and Cr had a mean concentration of 75.37 mg/Kg and 172.12 mg/Kg, respectively. The concentration of Cu and Ni had an average of 46.26 mg/Kg and 66.20 mg/Kg, respectively. Minimum metal concentration was observed for Cd ranging from 2.42 mg/Kg to 2.72 mg/Kg with an average of 2.67 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. In Devaprayag as well, the metal concentration showed an increase with decrease in the particle size of sediments. With respect to relative abundance, Al > Fe > Cr > Pb > Zn > Ni > Cu > Cd trend was seen.

**Table 4.14.** Concentration of Metals in Rishikesh

| | Concentration of Metals | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Size (µm)** | **Al (g/Kg)** | **Fe (g/Kg)** | **Cr (mg/Kg)** | **Zn (mg/Kg)** | **Pb (mg/Kg)** | **Cu (mg/Kg)** | **Ni (mg/Kg)** | **Cd (mg/Kg)** |
| **0-75** | 72.1 | 51.1 | 129.54 | 153.56 | 96.54 | 110.67 | 82.75 | 5.22 |
| **75-150** | 72.3 | 50.2 | 127.43 | 150.55 | 94.23 | 106.67 | 80.11 | 5.01 |
| **150-200** | 72.4 | 45.3 | 126.53 | 143.94 | 89.76 | 103.25 | 75.18 | 5.00 |
| **200-250** | 64.6 | 45.0 | 121.80 | 140.32 | 86.30 | 102.54 | 74.63 | 4.76 |
| **250-300** | 61.1 | 43.2 | 115.75 | 139.05 | 84.00 | 101.75 | 71.00 | 4.32 |
| **300-450** | 54.7 | 39.0 | 101.43 | 136.86 | 81.30 | 99.43 | 64.35 | 3.97 |
| **450-600** | 53.1 | 36.8 | 90.90 | 130.90 | 79.04 | 96.75 | 63.46 | 3.51 |
| **>600** | 49.0 | 36.1 | 85.08 | 127.67 | 73.40 | 95.81 | 58.12 | 3.11 |
| **AVERAGE** | 65.0 | 45.1 | 120.12 | 141.69 | 86.96 | 102.92 | 74.05 | 4.64 |
| **S.D. ±** | 9.4 | 5.7 | 17.52 | 8.90 | 7.79 | 4.95 | 8.60 | 0.77 |

The sediments at Rishikesh reported presence of all the metals considered in the present study with average concentration of 65.0 g/Kg for Al, ranging from 49.0 g/Kg (associated with particle size >600 µm) to 72.4 g/Kg (associated with 150-200 µm sized sediments). Fe concentration varied from 36.1 g/Kg to 51.1 g/Kg with a mean value of 45.1 g/Kg. Fe and Al were relatively abundant compared to other metals. A sudden increase in the concentration of Zn was noted. The concentration of Zn varied from 127.67 mg/Kg (with >600 µm sized sediments) to 153.56 mg/Kg (associated with 0-75 µm sized sediments) with an average of 141.69 mg/Kg. Pb and Cr had a mean concentration of 86.96 mg/Kg and 120.12 mg/Kg, respectively. The concentration of Cu and Ni had an average of 102.92 mg/Kg and 74.05 mg/Kg, respectively. Minimum metal concentration was observed for Cd ranging from 3.11 mg/Kg to 5.22 mg/Kg with an average of 4.64 mg/Kg. The deviation in concentration of Cd with respect to particle size was observed to be minimum. Like all the previous stations, here too there was a decrease in metal concentration with increase in particle size of sediments. With respect to relative abundance, Al > Fe > Zn > Cr > Cu > Pb > Ni > Cd, trend was seen.

Overall it was seen that Al and Fe showed its maximum value at Bhojwasa, Ni concentration was maximum at Chinyalisaur, Cr and Pb had their maximum concentration at Devaprayag and Rishikesh had the maximum values for Zn, Cu and Cd.

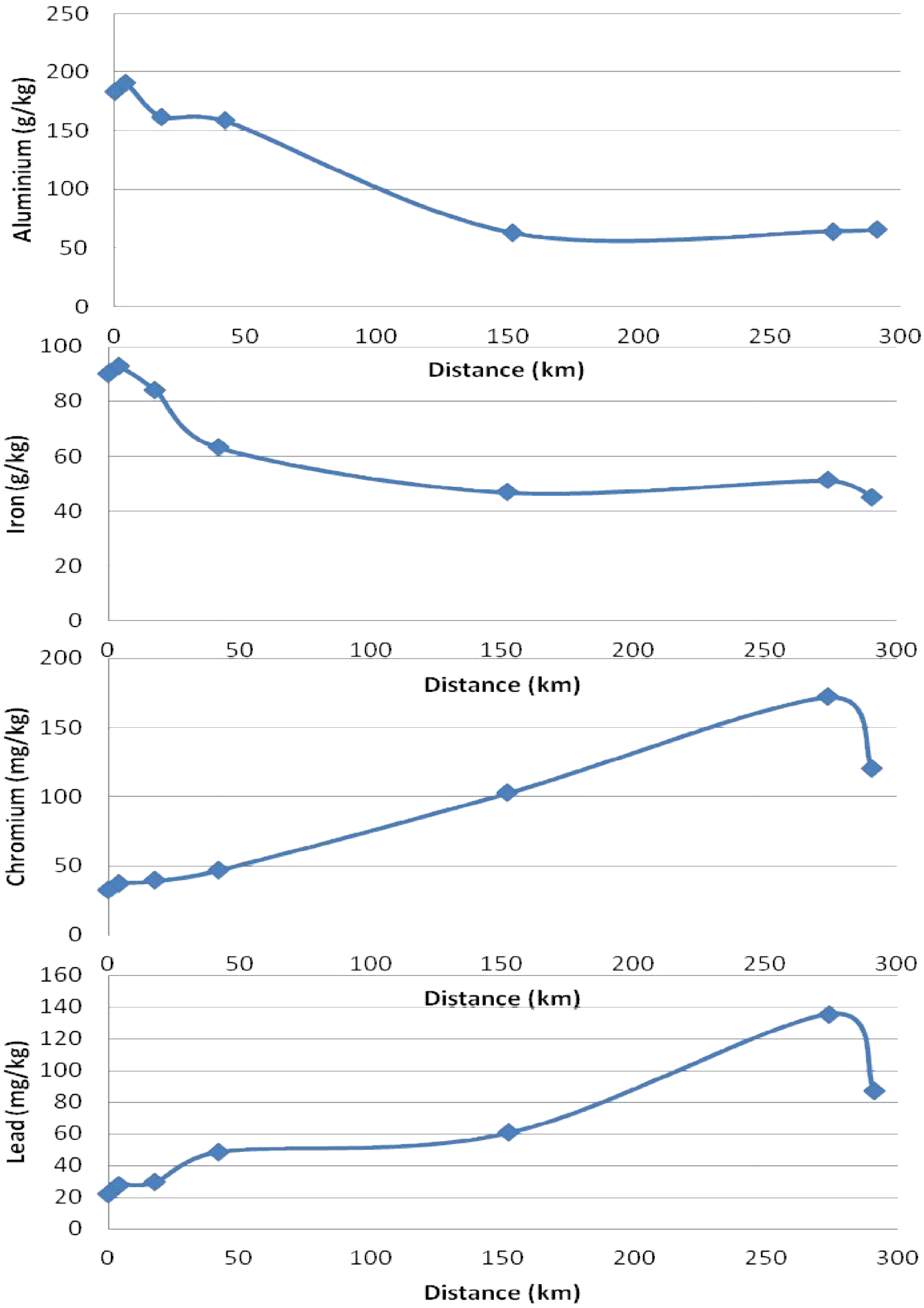



**Figure 4.8.** Longitudinal Profile for Aluminium, Iron, Chromium and Lead

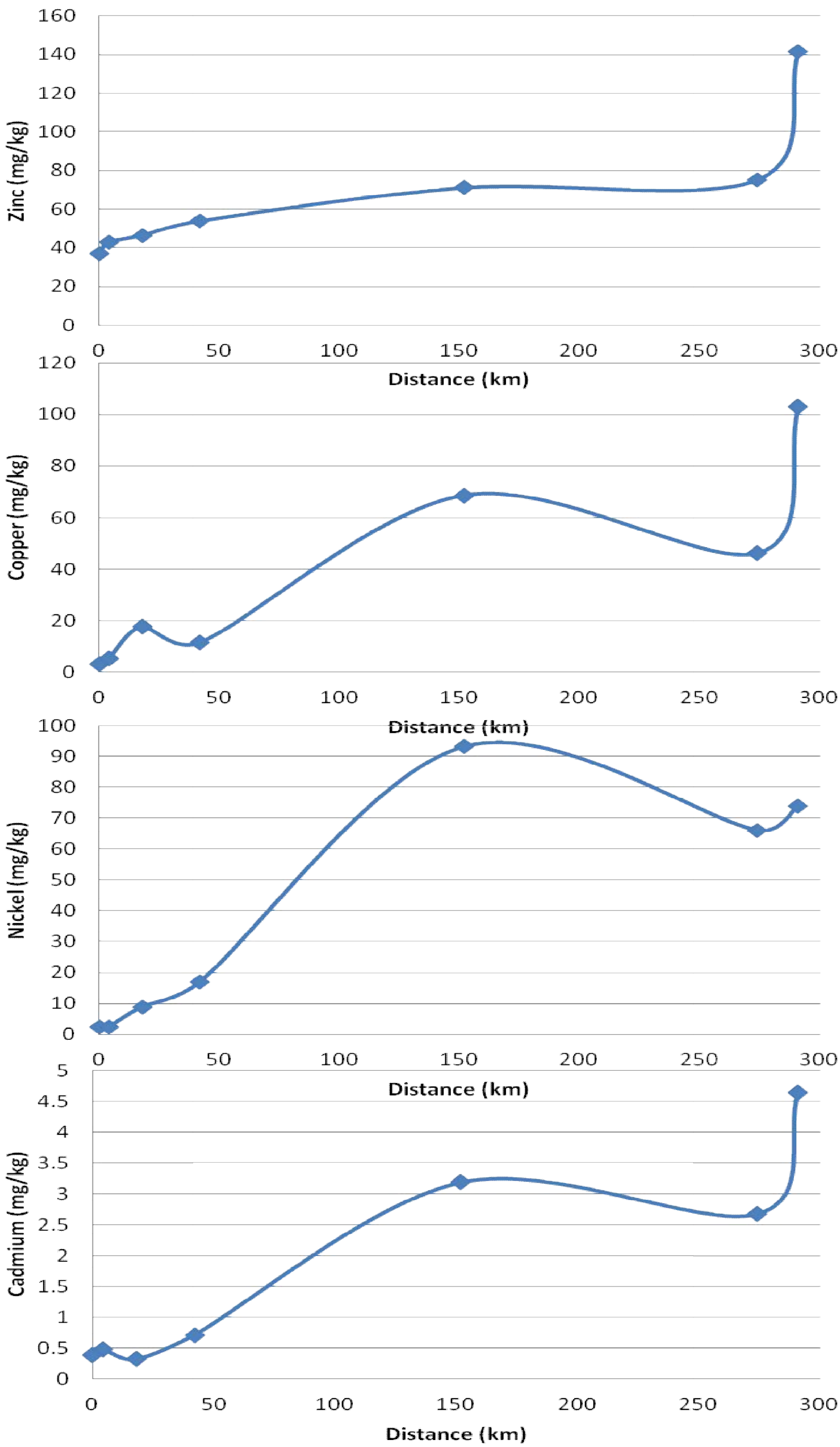



**Figure 4.9.** Longitudinal Profile for Zinc, Copper, Nickel and Cadmium

The mean concentration of Cr increases till Devaprayag, and decreases at Rishikesh. Zn has a sudden increase at Rishikesh. Pb shows a sudden increase at Devaprayag and then decreases at Rishikesh. Cu and Cd increases till Chinyalisaur, decreases at Devaprayag and then increases again at Rishikesh. The sediments seem to be getting affected by various anthropogenic activities like industrial effluents, domestic sewage, tourist activities, agricultural run offs etc especially at locations of Chinyalisaur, Devaprayag and Rishikesh. Sudden increase of Cr and Pb at Chinyalisaur and decrease at Rishikesh suggests that Cr and Pb at Chinyalisaur originate from a common source. Similar trend for Zn, Cu, Ni and Cd suggests another common source for these metals.

### 4.2.1. Correlation Among Metals

The correlation among different metals are shown in the Table 4.15. There exist a very strong positive correlation between Al-Fe, Cr-Pb, Zn-Cu, Zn-Cd, Zn-Cd, Cu-Cd and Ni-Cd. A moderately strong positive correlation also exist between Cr-Ni and Cu-Ni. This is an indication of a common source for all the strongly correlated heavy metals. It can also be noted that Al and Fe have a negative correlation with all other metals. This shows that both these metals originate from a source different from other metals and are mostly crustal. Their addition to river sediments is mainly due to physico-chemical weathering. It is also observed that when the heavy metals are introduced into the system by anthropogenic sources, the sediments show a priority to these metals over Al and Fe thereby decreasing their concentration when there is an increase in the concentration of other metals.

**Table 4.15.** Correlation Among Metals

| | **Al** | **Fe** | **Cr** | **Zn** | **Pb** | **Cu** | **Ni** | **Cd** |
|---|---|---|---|---|---|---|---|---|
| **Al** | 1 | | | | | | | |
| **Fe** | 0.941 | 1 | | | | | | |
| **Cr** | -0.911 | -0.818 | 1 | | | | | |
| **Zn** | -0.759 | -0.768 | 0.653 | 1 | | | | |
| **Pb** | -0.826 | -0.773 | 0.974 | 0.608 | 1 | | | |
| **Cu** | -0.892 | -0.852 | 0.719 | 0.937 | 0.612 | 1 | | |
| **Ni** | -0.975 | -0.926 | 0.831 | 0.715 | 0.713 | 0.889 | 1 | |
| **Cd** | -0.921 | -0.883 | 0.798 | 0.926 | 0.703 | 0.982 | 0.916 | 1 |

### 4.2.2. Relationship between Metal Concentration and Particle Size

The Table 14.16 shows the relationship between size of the particles and the concentration of metals i.e. adsorption capacity of metals. It clearly shows a strong negative correlation. This means that finer the particles size, more will be the chances of metals getting adsorbed onto that. This relationship is seen to be true for all of the metals as each of them show a correlation coefficient greater than the numerical value of 0.900. The strongest negative correlation was shown by Al.

**Table 4.16.** Metal Concentration and Particle Size Relationship

| | Al | Fe | Cr | Zn | Pb | Cu | Ni | Cd |
|---|---|---|---|---|---|---|---|---|
| **SIZE** | -0.982 | -0.958 | -0.941 | -0.975 | -0.917 | -0.959 | -0.963 | -0.951 |

## 4.3. METAL ENRICHMENT FACTOR

One of the most common methods to evaluate the anthropogenic impact on sediments is by calculating the Metal Enrichment Factor. It is given by the formula :

$$Metal\ Enrichment\ Factor = \frac{[\frac{Mean\ Concentration\ of\ the\ Metal}{Mean\ Concentration\ of\ the\ Reference\ Metal}]}{[\frac{Baseline\ Concentration\ of\ the\ Metal}{Baseline\ Concentration\ of\ the\ Reference\ Metal}]} \quad \text{Eq.4.3}$$

Al or Fe are normally considered as the reference metals. It is because these metals are abundantly present in the Earth's crust, so it can be assumed that their concentration gets least effected by human intervention. One of the major problems in quantification of heavy metal enrichment in sediments is to know the baseline concentrations of different heavy metals. Normally average shale concentration is considered as baseline concentration as stated by Turekian and Wedepohl (1961). Recently baseline concentration of sediments in the Ganga River was found by Singh et al., (2002). In the present study, the values provided by Singh et al., 2002 was used as the baseline concentration for each of the metal. They gave the baseline concentration values for Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd in mg/Kg as 150, 1715, 40400, 21, 46, 55, 106, 23 and 0.55. In the present study Fe is taken as the reference metal.

Table 4.17 shows the Metal Enrichment Value for the heavy metals Cr, Zn, Pb, Cu, Ni and Cd. When the Enrichment Factor goes above 1.5, it can be said that there is sufficient disturbance that is coming from the anthropogenic side, which is responsible for the increase in concentration. By using this criteria, it can be seen that the concentration of all the heavy metals in the sediments of Gomukh, Bhojwasa, Gangotri and to some extent in Jhala Bridge as well, are within the limits (<1.5). However there is an enrichment of Pb, Ni and Cd in the sediments of Chinyalisaur, Pb and Cd in the sediments of Devaprayag and Pb, Cu and Cd in the sediments of Rishikesh. These metal enrichment can be attributed to the facts that anthropogenic activities in these areas are much more than the activities in the upper ranges of Himalayas. Hence these stations are polluted because of various human interferences such as discharge of sewage from various households, industrial effluents, waste water from various plants, agricultural run offs etc. The presence of various tourists spot near these areas is also adding to the stress of river pollution.

**Table 4.17.** Metal Enrichment Factors at Different Sampling Stations

| | **Metal Enrichment Factor** | | | | | |
|---|---|---|---|---|---|---|
| **Location** | **Cr** | **Zn** | **Pb** | **Cu** | **Ni** | **Cd** |
| **Gomukh** | 0.096 | 0.156 | 0.433 | 0.024 | 0.025 | 0.317 |
| **Bhojwasa** | 0.109 | 0.176 | 0.525 | 0.043 | 0.026 | 0.380 |
| **Gangotri** | 0.125 | 0.210 | 0.616 | 0.154 | 0.094 | 0.279 |
| **Jhala Bridge** | 0.199 | 0.325 | 1.348 | 0.132 | 0.236 | 0.823 |
| **Chinyalisaur** | 0.591 | 0.580 | 2.264 | 1.077 | 1.750 | 4.991 |
| **Devaprayag** | 0.903 | 0.559 | 4.638 | 0.662 | 1.133 | 3.823 |
| **Rishikesh** | 0.717 | 1.197 | 3.386 | 1.676 | 1.442 | 7.557 |

## 4.4. CLASSIFICATION OF SOURCE

The source for all the metals were classified into natural sources and anthropogenic sources. The contribution of anthropogenic sources to the metals is calculated using:

$$Anthropogenic\ Contribution, A\ (\%) = \frac{(Cs - Cr)}{Cr} \text{X}\,100 \qquad Eq. 4.4$$

where, $C_s$ and $C_r$ are the concentration of metal at that particular site and at the reference site (Gomukh). The contribution of lithogenic sources to the metals was calculated using the formula:

$$Lithogenic\ Contribution, L(\%) = 100 - A \qquad Eq\ 4.5$$

where A is the Anthropogenic concentration in percentage.

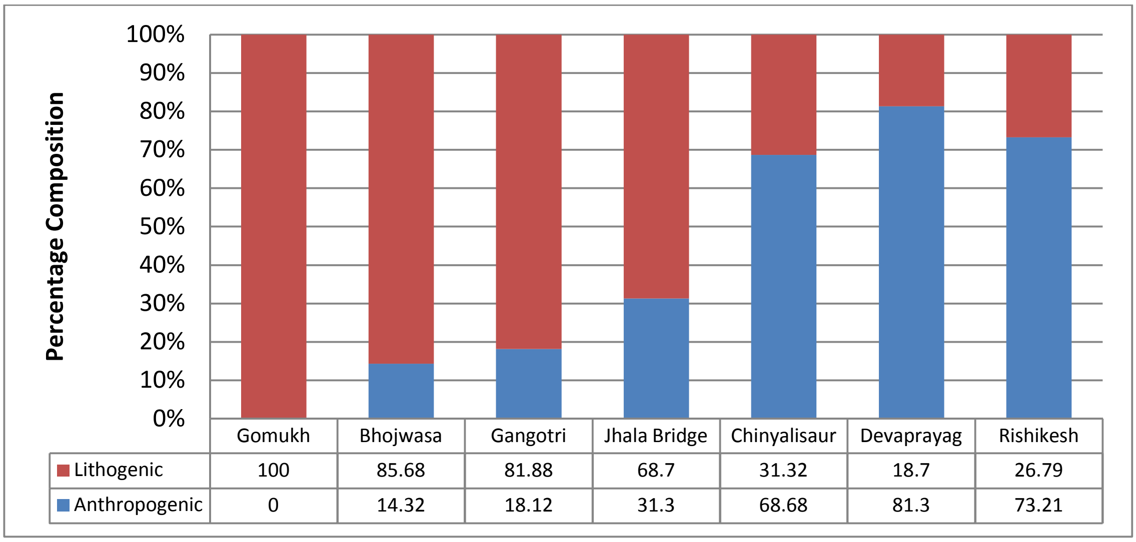



**Figure 4.10.** Percentage Composition of Anthropogenic and Lithogenic Source of Cr

Figure 4.10 shows the contribution of lithogenic and anthropogenic sources to the concentration of Cr. The concentration of Chromium at Gomukh was taken as the reference.  It can be clearly seen that, Gomukh and Bhojwasa, the source of Cr was lithogenic. The Cr concentration due to anthropogenic sources at Bhojwasa, Gangotri, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh were about 14%, 18%, 31%, 69%, 81% and 73% respectively.

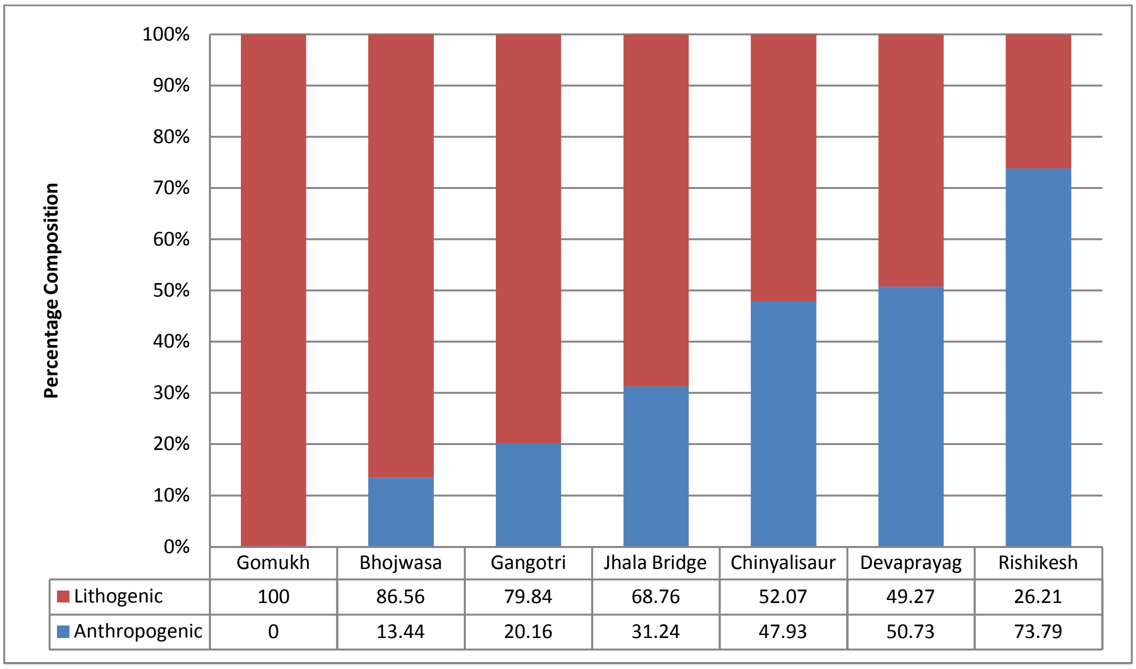
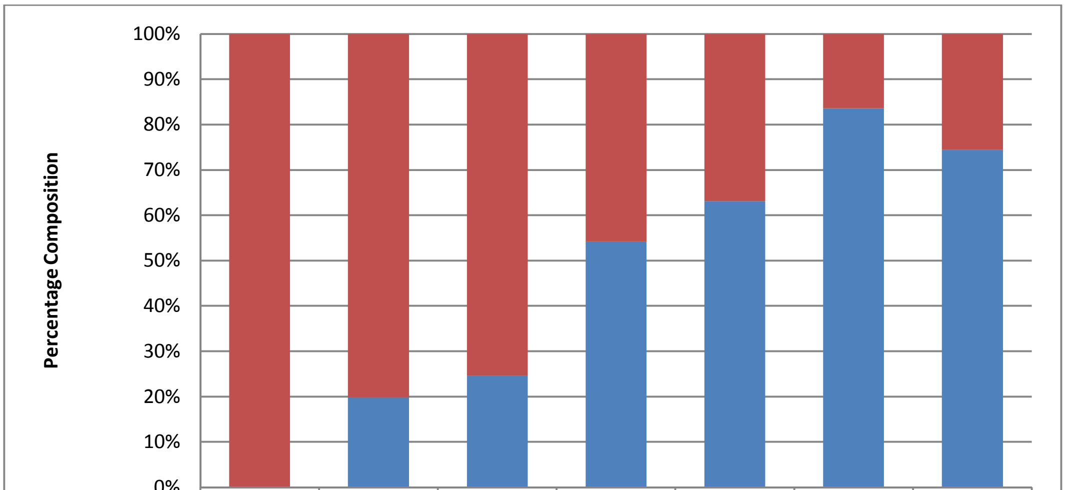



**Figure 4.11.** Percentage Composition of Anthropogenic and Lithogenic Source of Zn

Figure 4.11 shows the contribution of lithogenic and anthropogenic sources to the concentration of Zn. Zn concentration in sediments of Ganga river at Gomukh was taken as reference.  It can be clearly seen that at Gomukh the source of Zn was lithogenic. The Cr concentration due to anthropogenic sources at Gomukh, Gangotri, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh were about 13%, 20%, 31%, 48%, 50% and 74%, respectively.

Figure 4.12 shows the contribution of lithogenic and anthropogenic sources to the concentration of Pb. Pb concentration in sediments of Ganga river at Gomukh was taken as reference. Gomukh is the only station which is completely free of any anthropogenic source of Pb. Bhojwasa, Gangotri, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh has a contribution of around 20%, 25%, 54%, 63%, 83% and 74%, respectively from anthropogenic sources.




| | Gomukh | Bhojwasa | Gangotri | Jhala Bridge | Chinyalisaur | Devaprayag | Rishikesh |
|---|---|---|---|---|---|---|---|
| Lithogenic | 100 | 80.15 | 75.37 | 45.78 | 36.86 | 16.42 | 25.58 |
| Anthropogenic | 0 | 19.85 | 24.63 | 54.22 | 63.14 | 83.58 | 74.42 |

**Figure 4.12.** Percentage Composition of Anthropogenic and Lithogenic Source of Pb

Figure 4.13 shows the contribution of lithogenic and anthropogenic sources to the concentration of Cu. Cu concentration in sediments of Ganga river at Gomukh was taken as refernece.  Gomukh is the only station which is completely free of any anthropogenic source of Cu. Bhojwasa, Gangotri, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh has a contribution of around 44%, 83%, 73%, 96%, 93% and 97%, respectively.

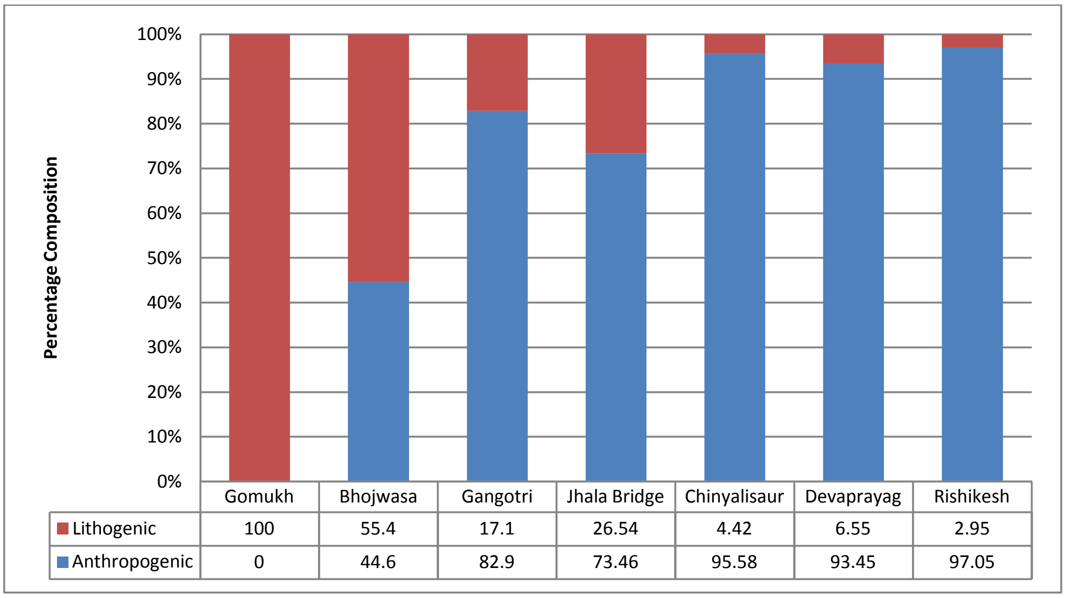



**Figure 4.13.** Percentage Composition of Anthropogenic and Lithogenic Source of Cu

Figure 4.14 shows the contribution of lithogenic and anthropogenic sources to the concentration of Ni. Ni concentration in sediments of Ganga river at Gomukh was taken as reference. The source of Ni at Gomukh was lithogenic. At Bhojwasa, Gangotri, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh, an anthropogenic contribution of about 4%, 71%, 85%, 97%, 96% and 96%, respectively was seen.

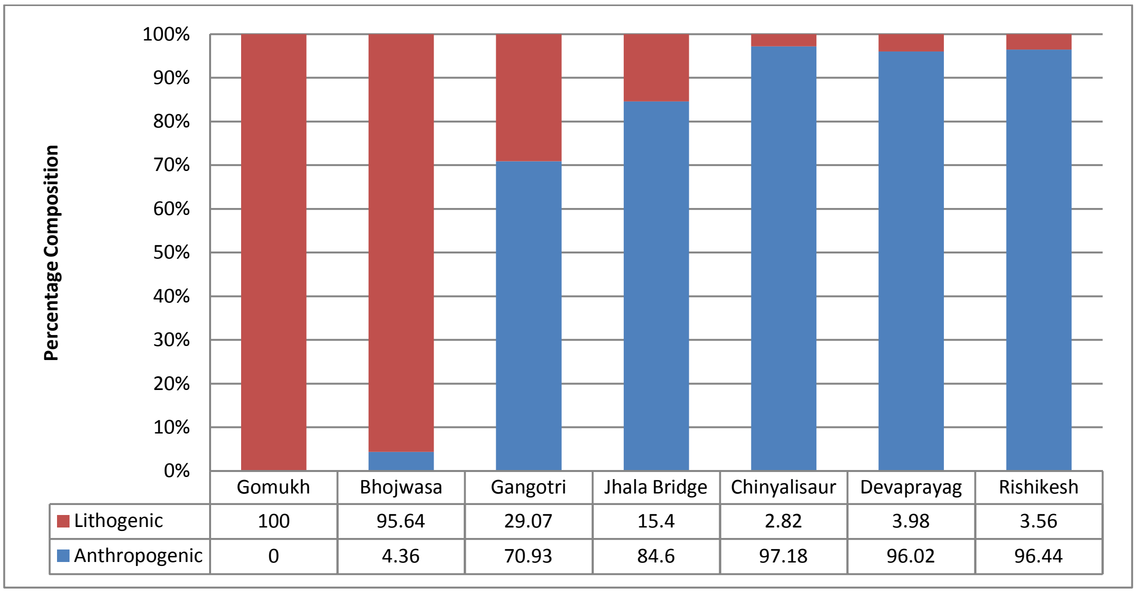
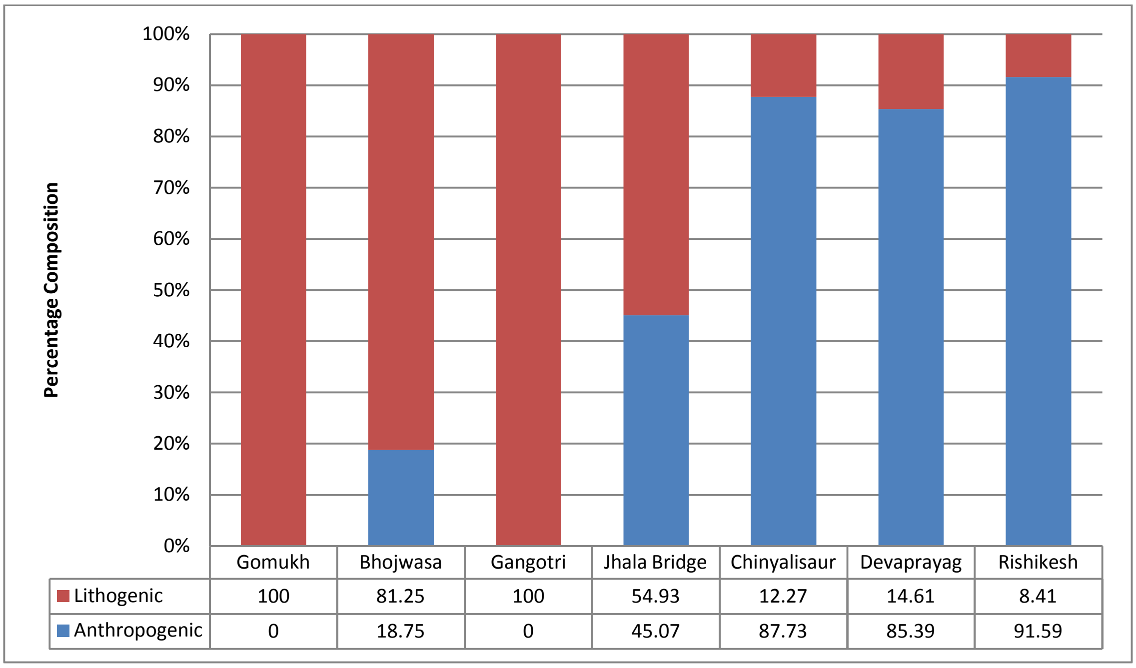



**Figure 4.14.** Percentage Composition of Anthropogenic and Lithogenic Source of Ni

Figure 4.15 shows the contribution of lithogenic and anthropogenic sources to the concentration of Cd. Cd concentration in sediments of Ganga river at Gomukh was taken as reference. The lithogenic composition was found to be 100% at Gomukh and Gangotri. Bhojwasa, Jhala Bridge, Chinyalisaur, Devaprayag and Rishikesh has a contribution of around 18%, 45%, 88%, 85% and 92%, respectively from anthropogenic sources.




| | Gomukh | Bhojwasa | Gangotri | Jhala Bridge | Chinyalisaur | Devaprayag | Rishikesh |
|---|---|---|---|---|---|---|---|
| Lithogenic | 100 | 81.25 | 100 | 54.93 | 12.27 | 14.61 | 8.41 |
| Anthropogenic | 0 | 18.75 | 0 | 45.07 | 87.73 | 85.39 | 91.59 |

**Figure 4.15.** Percentage Composition of Anthropogenic and Lithogenic Source of Cd

## 4.5 SEDIMENT QUALITY ASSESSMENT

The analysis of sediment quality can be done in different ways. In the present study sediment quality assessment was done by calculating 3 indices: Geo-accumulation Index, Sediment Pollution Index and Pollution Load Index.

### 4.5.1 Geo-accumulation Index

Geo-accumulation Index was proposed by Muller (1979). It is a quantitative measure of pollution of sediments due to heavy metals, when the concentration of toxic heavy metals is 1.5 times or more than their lithogenic bacKground values. It is calculated by using the following equation:

$$GAI = \log_2 \frac{C}{1.5B} \quad \text{Eq. 4.6}$$

where, C is the  measured total concentration and B is the bacKground concentration of the element. GAI classification consists of 7 grades i.e. from Class 0 to Class 6. This is depicted in Table 4.18. Table 4.19 shows the GAI for different heavy metals. It can be seen from Table 4.19 that the sediments of Jhala Bridge are uncontaminated to moderately contaminated with Pb. The sediments of Chinyalisaur are uncontaminated to moderately contaminated with Pb and Ni and moderately contaminated with Cd. The sediments of Devaprayag are moderately contaminated with Pb and Cd. The sediments of Rishikesh are uncontaminated to moderately contaminated with Cu and Ni, moderately contaminated with Pb and moderately to strongly contaminated with Cd. The values obtained for GAI, are in accordance with the anthropogenic sources of various metals found for each location.

**Table 4.18.** Classification of Sediment Quality based on GAI (Source : Muller, 1979)

| GAI Values | Class | Sediment Quality |
|---|---|---|
| GAI ≤ 0 | Class 0 | Uncontaminated |
| 0 < GAI < 1 | Class 1 | Uncontaminated to Moderately Contaminated |
| 1 < GAI < 2 | Class 2 | Moderately Contaminated |
| 2 < GAI < 3 | Class 3 | Moderately to Strongly Contaminated |
| 3 < GAI < 4 | Class 4 | Strongly Contaminated |
| 4 < GAI < 5 | Class 5 | Strongly to Extremely Contaminated |
| GAI ≥ 5 | Class 6 | Extremely Contaminated |

**Table 4.19.** GAI values for Different Heavy Metals from Different Stations

| | Geo-accumulation Index | | | | | |
|---|---|---|---|---|---|---|
| Location | Cr | Zn | Pb | Cu | Ni | Cd |
| Gomukh | -2.80 | -2.09 | -0.63 | -4.76 | -4.71 | -1.08 |
| Bhojwasa | -2.58 | -1.88 | -0.31 | -3.91 | -4.64 | -0.78 |
| Gangotri | -2.51 | -1.77 | -0.22 | -2.21 | -2.93 | -1.36 |
| Jhala Bridge | -2.26 | -1.55 | 0.49* | -2.85 | -2.01 | -0.21 |
| Chinyalisaur | -1.13 | -1.15 | 0.80* | -0.26 | 0.43* | 1.94** |
| Devaprayag | -0.38 | -1.07 | 1.97** | -0.83 | -0.05 | 1.69** |
| Rishikesh | -0.90 | -0.16 | 1.33** | 0.31* | 0.10* | 2.49*** |

*-  Class 1 (Uncontaminated to Moderately Contaminated)  **-  Class 2 (Moderately Contaminated)

***- Class 3 (Moderately to Strongly Contaminated)

### 4.5.2. Sediment Pollution Index

GAI is a single metal approach to quantify metal pollution in sediments. A multi-metal method was introduced to make an overall assessment of sediment quality. This index is dependent upon the heavy metal concentration and relative toxicity of metals (Singh et al., 2002). This index is called Sediment Pollution Index and is given by the formula:

$$SPI = \frac{\sum(EFm * Wm)}{\sum Wm} \quad \text{Eq. 4.7}$$

where EF is the Enrichment Factor, W is the toxicity weight (1 for Cr and Zn, 2 for Cu and Ni, 5 for Pb and 300 for Cd). and m is the metal taken into consideration. SPI Classification is shown in Table 4.20. Table 4.21 shows the SPI values for all the locations. The SPI values obtained for each of the location is in accordance with the values of GAI.

**Table 4.20.** Classification of sediment quality based on SPI (Source : Singh *et al.*, 2002)

| SPI | Class | Sediment Quality |
|---|---|---|
| 0 - 2 | SPI 0 | Natural Sediments |
| 2 - 5 | SPI 1 | Low Polluted Sediments |
| 5 - 10 | SPI 2 | Moderately Polluted Sediments |
| 10 - 20 | SPI 3 | Highly Polluted Sediments |
| > 20 | SPI4 | Dangerous Sediments |

**Table 4.21** SPI for each Station

| Location | SPI | Sediment Quality |
|---|---|---|
| Gomukh | 0.314 | Natural Sediments |
| Bhojwasa | 0.376 | Natural Sediments |
| Gangotri | 0.282 | Natural Sediments |
| Jhala Bridge | 0.820 | Natural Sediments |
| Chinyalisaur | 4.872 | Low Polluted Sediments |
| Devaprayag | 3.778 | Low Polluted Sediments |
| Rishikesh | 7.370 | Moderately Polluted Sediments |

### 4.5.3. Pollution Load Index

Another index used to understand the quality of sediments is Pollution Load Index (PLI) given by Tomlinson *et al.* (1980). It is the $n^{th}$ root of n number of multiplied

Contamination Factor (CF) values. CF for a metal is the ratio of concentration of that metal to the bacKground concentration of that metal. A PLI > 1 indicated progressive deterioration of sediment quality (Tomlinson *et al.*, 1980). The PLI for different sampling stations are shown in Table 4.22.

$$CF = \frac{[c]}{[B]} \qquad \text{Eq. 4.8}$$

where [c] and [B] are the observed concentration of the metal and baseline concentration of the metal, respectively.

$$PLI = \sqrt[n]{CF1 \text{ X } CF2 \text{ X} \ldots \text{X CFn}} \qquad \text{Eq. 4.9}$$

where CFn is the Contamination Factor of the $n^{th}$ metal.

**Table 4.22.** CF and PLI for Different Stations

| Contamination Factor | | | | | | | PLI |
|---|---|---|---|---|---|---|---|
| **Location** | **Cr** | **Zn** | **Pb** | **Cu** | **Ni** | **Cd** | |
| **Gomukh** | 0.194 | 0.319 | 0.833 | 0.051 | 0.055 | 0.642 | 0.213 |
| **Bhojwasa** | 0.220 | 0.347 | 1.136 | 0.085 | 0.054 | 0.790 | 0.261 |
| **Gangotri** | 0.245 | 0.411 | 1.209 | 0.314 | 0.189 | 0.522 | 0.394 |
| **Jhala Bridge** | 0.305 | 0.503 | 2.064 | 0.200 | 0.339 | 1.251 | 0.547 |
| **Chinyalisaur** | 0.683 | 0.675 | 2.632 | 1.247 | 2.046 | 5.600 | 1.610 |
| **Devaprayag** | 1.123 | 0.670 | 5.794 | 0.802 | 1.366 | 4.740 | 1.682 |
| **Rishikesh** | 0.748 | 1.324 | 3.720 | 1.856 | 1.547 | 7.937 | 2.092 |

From the Table 4.21 it can be clearly seen that PLI is >1 for Chinyalisaur, Devaprayag and Rishikesh with Rishikesh being the highest. This shows that the sediments at these 3 sampling stations - Chinyalisaur, Devaprayag and Rishikesh are progressively getting deteriorated.

## 4.6 RELATIVE MOBILITY

Relative Mobility of different metals is obtained by studying the Metal/Fe and/or Metal/Al ratio. Fe and Al have been chosen as conservative elements for analysis, because of their relative abundance in Earth's crust. Therefore their tendency to get influenced by human activities is decreased. It is generally assumed that Fe and Al have reached a steady state and is not being accumulated by the soil layer and is only derived by land erosion. The relative mobility of different metals with respect to Al is tabulated in Table 4.23 and represented in Figure 4.16 and 4.17.

**Table 4.23.** Variation of Metal/Al ratio at different sites

| Location | Cr/Al ($x10^{-3}$) | Zn/Al ($x10^{-3}$) | Pb/Al ($x10^{-3}$) | Cu/Al ($x10^{-3}$) | Ni/Al ($x10^{-3}$) | Cd/Al ($x10^{-3}$) |
|---|---|---|---|---|---|---|
| **Gomukh** | 0.1759 | 0.2031 | 0.1216 | 0.0170 | 0.0155 | 0.0021 |
| **Bhojwasa** | 0.1970 | 0.2250 | 0.1455 | 0.0892 | 0.0153 | 0.0026 |
| **Gangotri** | 0.2434 | 0.2881 | 0.1828 | 0.1097 | 0.0606 | 0.0019 |
| **Jhala Bridge** | 0.2958 | 0.3411 | 0.3069 | 0.0738 | 0.1078 | 0.0046 |
| **Chinyalisaur** | 1.6489 | 1.1446 | 0.9685 | 1.1019 | 1.4975 | 0.0493 |
| **Devaprayag** | 2.6978 | 1.1813 | 2.1233 | 0.7250 | 1.0376 | 0.0435 |
| **Rishikesh** | 1.8480 | 2.1798 | 1.3378 | 1.5833 | 1.1392 | 0.0699 |

Relative mobility follows the following trend:

Gomukh Zn > Cr > Pb > Cu > Ni > Cd
Bhojwasa Zn > Cr > Pb > Cu > Ni > Cd
Gangotri Zn > Cr > Pb > Cu > Ni > Cd
Jhala Bridge Zn > Pb > Cr > Ni > Cu > Cd
Chinyalisaur Cr > Ni > Zn > Cu > Pb > Cd
Devaprayag Cr > Pb > Zn > Ni > Cu > Cd
Rishikesh Zn > Cr > Cu > Pb > Ni > Cd

The overall relative mobility of the study area is following the order Zn > Cr > Pb > Ni > Cu > Cd. This shows that Zn has more tendency to solubilise into water from the sediments under favourable conditions, among all heavy metals. Cd has the least tendency to solubilise into sediments.

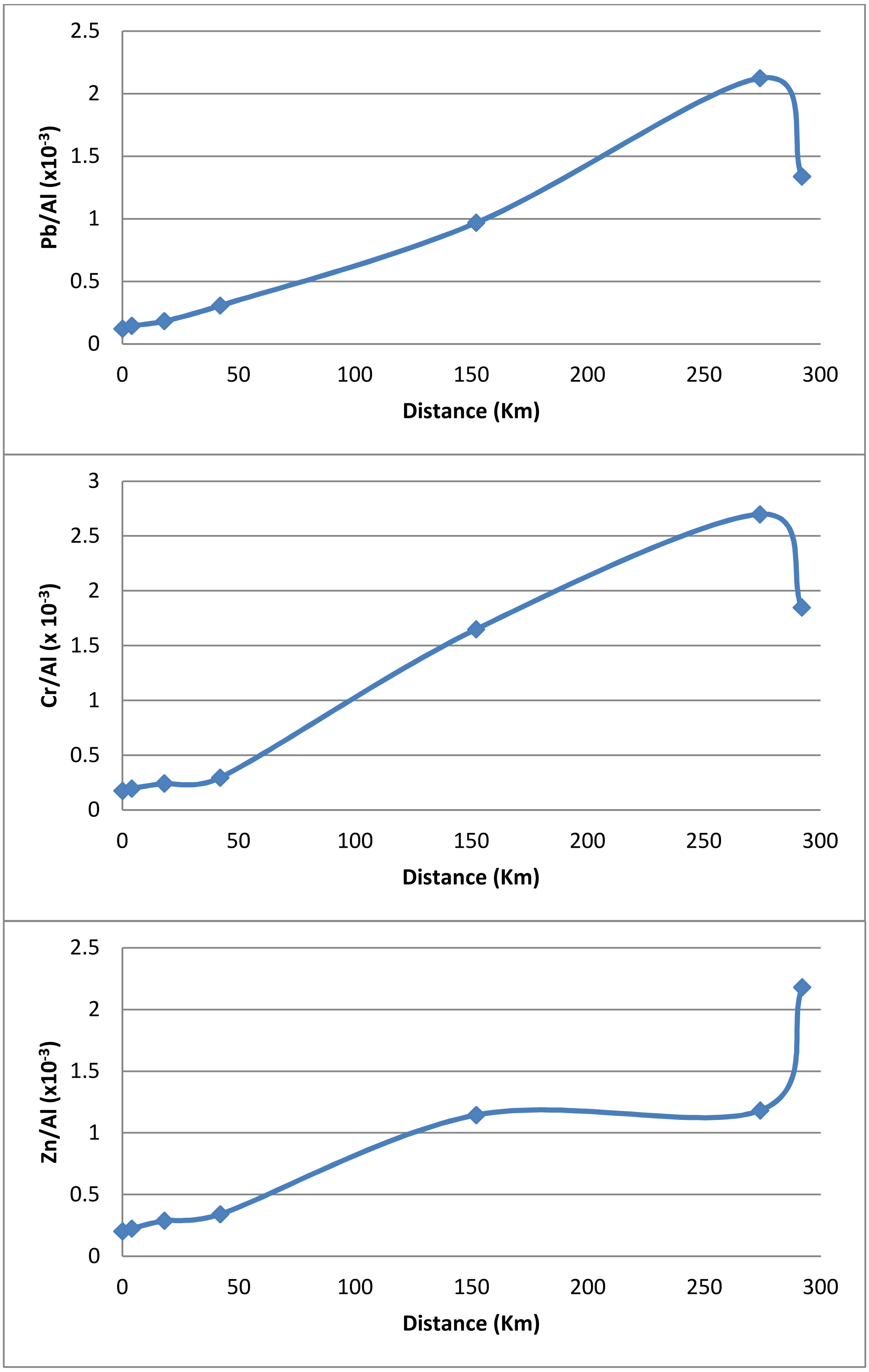



**Figure 4.16.** Variation in M/Al ratio in Lead, Chromium and Zinc

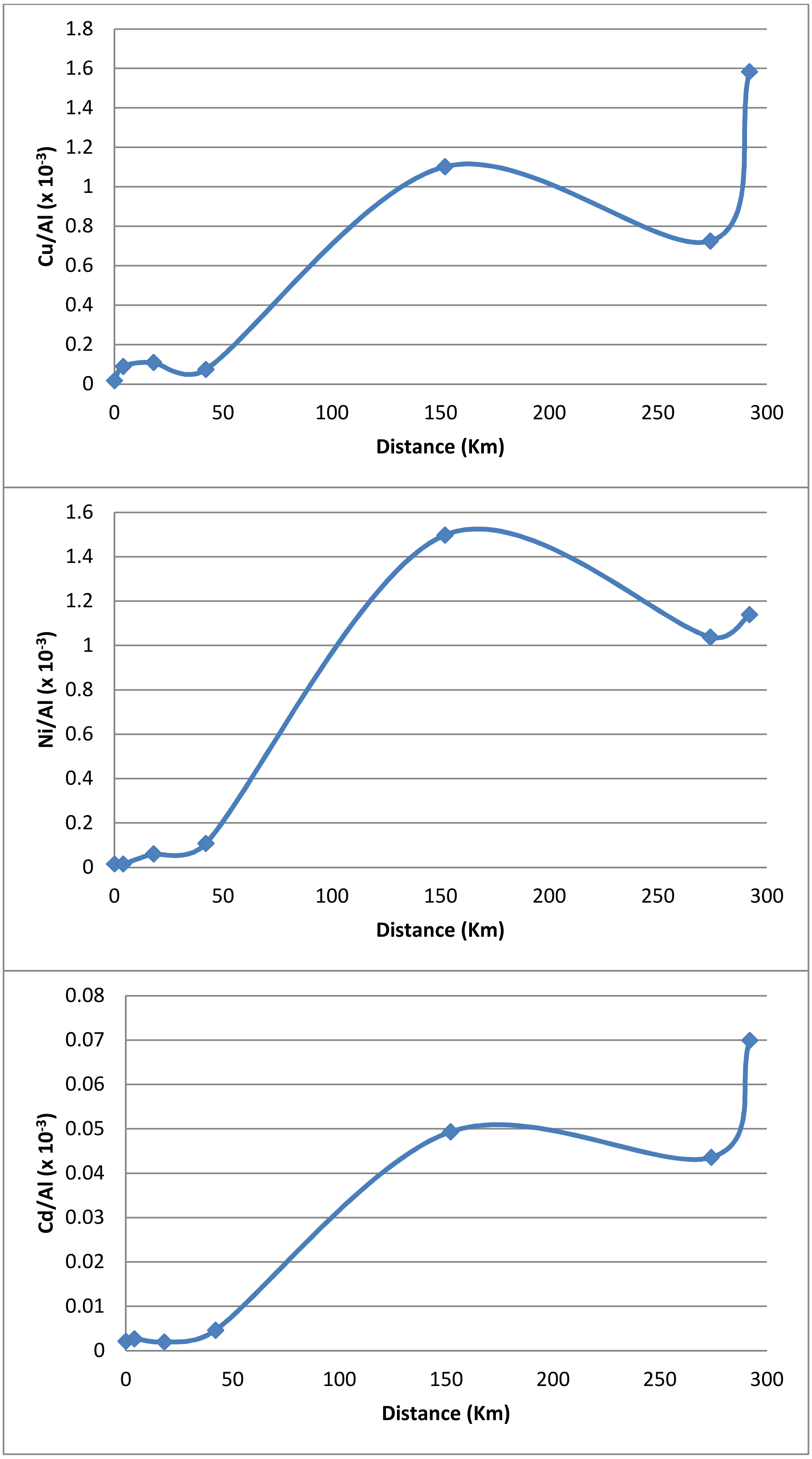



**Figure 4.17.** Variation in M/Al in Copper, Nickel and Cadmium

From the results obtained, it is observed that the study area has the presence of all the metals considered. From the  values of different metals, it was observed that Al and Fe were the most prominent metals and their major source was lithogenic. Other metals like Cr, Zn, Pb, Cu, Ni and Cd had most of their contributions coming from anthropogenic sources. The longitudinal profile indicated a common source for the metals Cr and Pb as they showed a similar pattern. Similarly, it was observed that Zn, Cu, Ni and Cd also had a similar source as they all have shown a sudden increase at Chinyalisaur and then again at Rishikesh. This was confirmed when the correlation between different metals and the sources for different metals were studied. The Metal Enrichment Factor showed that there is an enrichment of Pb, Ni and Cd in the sediments of Chinyalisaur; Pb and Cd in the sediments of Devaprayag; and Pb, Cu and Cd in the sediments of Rishikesh, which can be attributed to the anthropogenic activities being undertaken in this area. The GAI, SPI and PLI further confirmed the inferior quality of sediments at Chinyalisaur, Devaprayag and Rishikesh. As per the GAI, the sediments of Jhala Bridge are uncontaminated to moderately contaminated with Pb, the sediments of Chinyalisaur are uncontaminated to moderately contaminated with Pb and Ni, and moderately contaminated with Cd; the sediments of Devaprayag are moderately contaminated with Pb and Cd; and the sediments of Rishikesh are uncontaminated to moderately contaminated with Cu and Ni, moderately contaminated with Pb and moderately to strongly contaminated with Cd. While PLI indicated that the sediments of Chinyalisaur, Devaprayag and Rishikesh are progressively getting deteriorated. The Relative Mobility values showed that Zn had the highest tendency to solubilise from sediments to water at Gomukh, Bhojwasa, Gangotri, Jhala Bridge and Rishikesh. Whereas at Chinyalisaur and Devaprayag, Cr showed the maximum mobility.

# Chapter 5

# CONCLUSION

From the study, it can be concluded that the downstream locations of Himalayan stretches of River Ganga, i.e., Chinyalisaur, Devaprayag and Rishikesh have deteriorated sediments compared to the upper Himalayan locations. The order of occurrence of metals varied from site to site. Al and Fe were the most abundant metals in the region, their origin being mostly crustal. But, their concentration is significantly reduced with distance from the origin. Cd was the metal with the least concentration. Considering the entire area the concentration of heavy metals varied in the order : Al > Fe > Cr > Zn > Pb > Ni > Cu > Cd. The relative mobility of metals showed the trend Zn > Cr > Pb > Ni > Cu > Cd. The maximum concentration of Al and Fe were mostly found near the origin (Bhojwasa) and this was mainly due to natural weathering. Chinyalisaur showed the maximum concentration for Ni, Devaprayag had the maximum concentration of Cr and Pb and Rishikesh had the highest concentration of Zn, Cu and Cd. A strong negative relationship was found between concentration of heavy metals on the sediments and the particle size of the sediments indicating that finer particles have more tendency to accumulate these toxic compounds. A strong positive correlation existed between various metals like Al-Fe, Cr-Pb, Zn-Cu, Zn-Cd, Cu-Cd and Ni-Cd indicating a common source for these metals. The sediments of Chinyalisaur were found to be enriched with Pb, Ni and Cd; Devaprayag was found to be enriched with Pb and Cd; and Rishikesh was found to be enriched with Pb, Cu and Cd. The GAI revealed that the sediments of Chinyalisaur are uncontaminated to moderately contaminated with Pb and Ni and moderately contaminated with Cd; the sediments of Devaprayag are moderately contaminated with Pb and Cd and the sediments of Rishikesh are uncontaminated to moderately contaminated with Cu and Ni, moderately contaminated with Pb and moderately to strongly contaminated with Cd. SPI revealed that Chinyalisaur and Devaprayag had low polluted sediments and Rishikesh had moderately polluted sediments. A measure of PLI showed that the sediments of Chinyalisaur, Devaprayag and Rishikesh arre progressively getting deteriorated. The major reason for the pollution of the sites at the above said locations are the increase in anthropogenic activities in these area. Human population have started increasing in these region, thus also increasing the waste water coming from households. Various agricultural activities have also been undertaken in these lower Himalayan reaches of River Ganga. Adding to the stress, are the tourists activities, coming up of new industries and chemical plants. All these factors have led to increase in the inclusion of pollutants through anthropogenic sources. The sediments of the lower Himalayan reaches of the River Ganga is thus getting deteriorated and even though the scenario may not be as serious as the condition of River Ganga in the plains, it still needs attention.

## REFERENCES


Abbasi S. A., N. Abbasi and R. Soni (1998). Heavy Metal in the Environment. Mittal Publication 1:234-235.

Abolude D. S., D. O. Augustina and B. Zebedee (2013). Analysis of Heavy Metals in Water and Sediment of Bindare Stream, Chikaji Industrial Area. IJSRES 1(6):115-121.

Ajmal, M., Khan, M. A. and Nomani, (1985). Distribution of Heavy Metals in Water and Sediments of Selected Sites of Yamuna River (India). Environ. Mont. Assess. 5, 205–214.

Akhtar M. W., M. Paramasivam, M. Ganguly, S. Purkait and D. Sengupta (2008). Assessment and occurence of various heavy metals in surface water of Ganga river around Kolkata. Environ Monit Assess 160(1):207-213.

Albretsen J. (2006). The toxicity of iron, an essential element; Veterinary medicine; 2006. pp. 82–90.

Alina M., A. Azrina, A. S. Mohd Yunus, S. Mohd Zakiuddin, H. Mohd Izuan Effendi, and R. Muhammad Rizal (2012). Heavy metals (mercury, arsenic, cadmium, plumbum) in selected marine fish and shellfish along the Straits of Malacca. Int Food Res J. 19(1):135–140.

Al-Yousuf M. H., M. S. El-Shahawi and S. M. Al-Ghais (2000). Trace metals in liver, skin and muscle of Lethrinus lentjan fish species in relation to body length and sex. Sci Total Environ 256:87–94.

Ansari A. A., I. B. Singh and H. J. Tobschall (1998). Status of anthrpogenically induced metal pollution in the Kanpur-Unnao industrial region of the Gang Plain. Environmental Geology 38(1): 25-33.

Apollaro C., L. Marini, T. Critelli, D. Barca, A. Bloise and R. D. Rosa (2011). Investigation of rock to water release and fate of major, minor and trace elements in the metabasalt-sepentinite shallow aquifer of Mt. Reventino by reaction path modelling Carmine. App Geochem 26(1):1722-1740.

Ayyadui K., C. S. Swaminathan and V.S. Krishnaswami (1994). Studies of heavy metal pollution in Fin fish from river Kaveri. Indian Journal of Environmental Health 36(2):99-103.

Azimi S., A. Ludwig, J. L. Colin (2003). Trace metal determination in total atmospheric deposition in rural and urban areas. Sci Total Environ 308(1):247-256.

Balachandran K. K., C. M. Laluraj, G. D. Martin, K. Srinivas and P. Venugopal (2005). Environmental analysis of heavy metal deposition in a flow restricted tropical estuary and its adjacent shelf. Estuar Coast Shelf Sci 65:361-370.

Balls P.W., S. Hall, B.S. Miller, J.M. Pirie and W. Proctor (1997). Trace metals in Scottish estuarine and coastal sediments, Mar. Pollut. Bull. 34:2–50.

Bernard A. (2008) Cadmium & its adverse effects on human health. Indian J Med Res. 128(4):557–64.

Borbely-Kiss I., E. Koltay, G. Y. Szabo, L. Bazo and K. Tar (1999). Composition and sources of urban and rural atmospheric aerosols in Eastern Hungary. J Aerosol Sci 30(1):369-391.

Bragazza L. (2006). Heavy metals in bog waters. Global Planet Changes 53(1):290-298.

Brochin R., S. Leone, D. Phillips , N. Shepard, D. Zisa and A. Angerio (2008) . The cellular effect of lead poisoning and its clinical picture. GUJHS 5(2):1–8.

Bruins M. R., S. Kapil and F. W. Oehme (2000). Microbial resistance to metals in the environment. Ecotox Environ Safe 45:198-207.

Bureau of Indian Standards (BIS) (2012) Indian standard drinking water specification (second revision) BIS 10500:2012, New Delhi.

Calmano W., J. Hong and U. Forstner (1993). Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. Water Sci Technol 28:223-235.

Canli M. and G. Atli (2003). The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. Environ Pollut 121(1):129–136.

CCME (1999). Canadian water quality guidelines for protection of aquatic life, technical report, Canadian environmental quality guidelines, Canadian water quality index 1.0.

Central Pollution Control Board (CPCB) (2008) Guidelines for Water Quality Monitoring, MINARS/27/2007–08, New Delhi.

Chakraborty S., A. R. Dutta, S. Sural, D. Gupta and S. Sen (2013). Ailing bones and failing kidneys: a case of chronic cadmium toxicity. Ann Clin Biochem. 50(5):492–495.

Chen C. W., C. M. Kao, C. F. Chen and C. D. Dong (2007). Distribution and accumulation of metals in sediments of Kaoshiung Harbor, Taiwan. Chemosphere 66:1431–1440.

Chowdhury U. K., B. K. Biswas, T. R. Chowdhury, G. Samanta, B. K. Mondal, G. C. Basu, D. Chakraborti (2000). Groundwater arsenic contamination in Bangladesh and West Bengal, India. Environ Health Perspect.108(5):393–397.

CPCB (2004). Status of water quality in India-2004. New Delhi.

CPCB Report (2012). Water quality of Peninsular rivers by Central Pollution Control Board.

DEFRA Report (2002). Sewage Treatment in the UK: UK Implementation of the EC Urban Waste Water Treatment Directive.

Dhanakumar S., S. Mani, R. C. Murthy, M. Veeramani and R. Mohanraj (2011). Heavy metals and their fractionation profile in surface sediments of upper reaches in the Cauvery. Int J Geol Earth Environ Sci 1:38–47.

Eisenreich S. J. (1980). Atmospheric Input of trace metals to Lake Michigan. Water Air Soil Pollut 13(1)287-301.

Ergin M., C. Saydam, O. Bastwrk, E. Erden and R.Yoruk (1991). Heavy metal concentration in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the North eastern sea of Marmara. Chem. Geol. 91:269–285.

Esen E. , F. Kucuksezgin , E. Uluturhan (2010). Assessment of trace metal pollution in surface sediments of Nemrut Bay, Aegean Sea. Environ Monit Assess 160:257–266.

FAO (1975). Manual methods in aquatic environment research, Food and Agricultural Organisation of United Nations: Part 1.

FAO (1983). Compilation of legal limits for hazardous substances in fish and fishery products. FAO. Fish Circ 464:5–100.

Fernandez - Caliani J. C., C. Barba - Brioso, I. Gonzalez and E. Galan (2009). Heavy metal pollution in soils around the abandoned mine sites of the Iberian pyrite belt (Southwest Spain). Water Air Soil Pollut 200(1):211-226.

Ferner D. J. (2001). Toxicity of heavy metals. eMed J. 2(5):1.

Fine J. S. (2000). Iron poisoning. Curr Probl Pediatr. 30(3):71–90.

Forstner U. and G.Muller (1981). Metal Transfer between Solid and Aqueous Phases, in: Metal Pollution in the Aquatic Environment, Springer, Berlin, pp. 197–269.

Förstner U., and G.T.W Wittmann, (1983), Metal Pollution in the Aquatic Environment, Springer- Verlag, Berlin, Heidelberg, New York, 481 pp.

Gerhardsson L., L. Dahlin, R. Knebel and A.Schütz (2002). Blood lead concentration after a shotgun accident. Environ Health Perspect. 110(1):115–117.

Ghrefat H. A. , Abu-Rukah qnd M. A. Rosen (2011). Application of geo accumulation index and enrichment factor for assessing metal contamination in sediments of Kafrain Dam, Jordan. Environ Monit Assess 178:95–109.

Gibbs R. J. (1973). Mechanisms of trace metal transport in rivers. Science 180:71-73.

Govil P. K., J. E. Sorlie, D. Sujatha, A. K. Krishna, N. N. Murthy, K. Rama Mohan (2011), Assessment of Heavy metal pollution in lake sediments of Katedan Industrial Development Area, Hyderabad. Environ Earth Sci 66:121-128.

Haritash A. K., R. Baskar, N. Sharma and S. Paliwal (2007). Impact of slate quarrying in soil properties in semi-arid in Mahendragarh in India. Environ Geol 51:1439-1445.

Haritash A. K., S. Gaur and S. Garg (2014). Assessment of water quality and suitability analysis of River Ganga in Rishikesh. Applied Water Sci. DOI 10.1007/s13201-014-0235-1

Henson M. C. and P. J. Chedrese (2004). Endocrine disruption by cadmium, a common environmental toxicant with paradoxical effects on reproduction. Exp Biol Med (Maywood) 229(5):383–392.

Hershko C., G. Link and C. Ioav (1998). Pathophysiology of iron overload. Ann N Y Acad Sci. 850:191–201.

Hogstrand C. and C. Haux (1991). Binding and detoxification of heavy metals in lower vertebrates with reference to metallothionein. Comp Biochem Physiol 100(1/2):137–141.

Hoque M. A., W. G. Burgess, M. Shamsudduha and K. M. Ahmed (2011). Delineating low-arsenic groundwater environments in the Bengal Aquifer System, Bangladesh. Appl Geochem. 26(4):614–623.

Horowitz A. J. (1991). A Primer in Sediment. Trace Element Chemistry pp136.

Jain C. K., D. C. Singhal and M. K. Sharma (2004). Metal Pollution of Sediment and Water in the River Hindon, Environmental Monitoring and Assessment 105: 193-207.

Jain C. K., D. C. Singhal and M. K. Sharma (2005). Metal Pollution of Sediment and Water in the River Hindon, Environmental Monitoring and Assessment 105: 193-207.

Jaishankar M., T.Tseten, N. Anbalagan, B.B.Mathew and K.N.Beeregowda (2014), Toxicity, Mechanism and Health effects of some Heavy Metals, Interdiscip Toxicol 7(2):60-72.

Jarup (2003). Hazards of heavy metal contamination. Br Med Bull 68(1):167–182.

Jayaprakash M., M. P. Jonathan, S. Srinivasalu, S. Muthuraj, V. Ram-Mohan and Rajeshwara-Rao (2008). Acid-leachable trace metals in sediments from an industrialized region (Ennore Creek) of Chennai City, SE coast of India: an approach towards regular monitoring. Estuar Coast Shelf Sci 76:692–703.

Jayaraju N., K. R. Reddy and B. C. S. R. Reddy (2011). Anthropogenic metal pollution in surface sediments of the Tambaraparni River Estuary, Chemistry and Ecology 27(4):337-350.

Jha P.K., V. Subramanian, R. Sitasawad and Van Grieken (1990), Heavy metals in sediments of the Yamuna river (a tributary of the Ganges). Sci. Total Environ. 95, 7–27.

Johnson F. M. (1998). The genetic effects of environmental lead. Mutat Res 410:123-140.

Jorgensen E. H., J. E. Killi, N. Alluru and M. M. Vijayan (2006). Toxicokinetics and effects of PCBs in Arctic fish: a review of studies on Arctic charr. J Toxicol Environ Health 69(1-2):37-52.

Joshi D. M., N. S. Bhandari, A. Kumar and N. Agarwal (2009). Statistical Analysis of Physico-chemical parameters of water of Ganga river in Haridwar district. RJC 2(3):579-587.

Kamal J., K. Shareef, M. Nizam and El-Ashghar (2013). Heavy metal concentrations in some commercially important fishes and their contribution to heavy metals exposure in Palestinian people of Gaza Strip (Palestine). Journal of the Association of ArabUniversities for Basic and Applied Science 13(1):44-51.

Kansal A., N. A. Siddiqui and A. Gautam (2012). Assessment of heavy metals and their interrelationships with some physico-chemical parameters in eco-efficient rivers of Himalayan region. Environ Monit Assess 185(1):2553-2563.

Kar D., P. Sur, S. K. Mondal, T. Saha and R. K. Kole (2008). assessment of heavy metal pollution in surface water. Int J Environ Sci Tech 5(1):119-124.

Kaushik A., H. R. Sharma, S. Jain, J. Dawra and C. P. Kaushik (2010). Pesticide pollution of river Ghaggar in Haryana, India. Environ Monit Assess 160(1-4):9-61.

Keshav Krishna A. and K. Rama Mohan (2012). Metal Contamination and Their Distribution in Different Grain Size Fractions of Sediments in an Industrial Development Area. Bull Environ Contam Toxicol 90(1):170-175.

Khan Y. S. A., M. S. Hussain, S. M. G. Hossain and A. H. M. Hallimuzzaman (1998). An environmental assessment of trace metals in Ganges-Brahmaputra-Meghna estuary. J Rem Sens Environ 2(1):103-117.

Koutras G. A., A. S. Schneider, M. Hattori and W. N. Valentine (1965). Studies on chromated erythrocytes. Mechanisms of chromate inhibition of glutathione reductase. Br J Haematol 11(3):360–369.

Kraft C., W. Tumpling and D. W. Zachmann (2006). The effects of mining in Northern Romania on the heavy metal distribution in sediments of the rivers Szamos and Tisza, Hungary. Acta Hydrochim Hydrobiol 34:257-264.

Krishna A. K. and K. R. Mohan (2012). Metal contamination and their distribution in different grain size fractions in an industrial development area. Bull Environ Contam Toxicol 90(2):170-175.

Kumar A. and S. K. Maiti (2014). Translocation and bioaccumulation of metals in Oryza sativa and Zea mays growing in Chromite-asbestos contaminated agricultural fields, Jharkhand, India. Bull Environ Contam Toxicol 93(1):434-441.

Kumar A. and S. K. Maiti (2015). Assessment of potentially toxic heavy metal contamination in agricultural fields, sediment and water from an abandoned chromite-asbestos mine waste of Roro hill. Environ Earth Sci 74(1):2617-2633.

Kumar R. N., R. Solanki and J. N. Kumar (2013). Seasonal variation in heavy metal contamination in water and sediments of river Sabarmati and Kharicut canal at Ahmedabad, Gujrat. Environ Monit Assess 185:359–368.

Kumar R. N., R. Solanki and J.N. Kumar (2013). Seasonal variation in heavy metal contamination in water and sediments of river Sabarmati and Kharicut canal at Ahmedabad, Gujrat. Environ Monit Assess 185:359–368.

Kumar S. (1992). Heavy metal in Ganga river sediments, Uttar Pradesh : a preliminary report. Geology Dept. University of Lucknow pp 59-66.

Li S. and Q. Zhang (2008). Spatial characterisation of dissolved trace metals and heavy metals in the Upper Han River. J Hazardous Material 176(1):579-588.

Li S. and Q. Zhang (2010). Risk assessment and seasonal variations of dissolved trace elements and heavy metals in the Upper Han River. Journal of Hazardous Material 181(1):1051-1058.

Macklin M.G., P. A. Brewer, D. Balteanu, T. J. Coulthard, B. Driga, A. Howard and Sa. Zaharia (2003). The long term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failure in Maramures County, Romania. Appl Geochem 18(2):241-257.

Marathe R., Y. Marathe , C. Sawant and V. Shrivastava (2011). Detection of trace metals in surface sediment of Tapti River: a case study. Arch Appl Sci Res 3(2):472–476.

Markowitz M. (2000). Lead Poisoning. Pediatr Rev. 21(10):327–335

Marschchner H. (1995). Mineral nutrition of higher plants. Academic Press, London.

Martin J., M. Meybeck (1979). Elemental mass-balance of material carried by major world rivers. Mar Chem 7(3):178–206.

Martinand S. and W. Griswold (2009). Human health effects of heavy metals. Environmental Science and Technology Briefs for Citizens (15):1–6.

Matsumoto S. T., M. S. Mantovani, M.I.A. Malaguttii, A. L. Dias, I. C. Fonseca and M. A. Marin-Morales (2006). Genotoxicity and mutagenicity of water contaminated with tannery effluents, as evaluated by the micronucleus test and comet assay using the fish Oreochromis niloticus and chromosome aberrations in onion root-tips. Genet Mol Biol. 29(1):148–158.

McCord J. M. (1998). Iron, free radicals, and oxidative injury. Semin Hematol. 1998;35:5–12.

Melisa, Monica and Jorge (2012). Heavy metals concentrations in zooplankton and suspended particulate matter in a southwestern Atlantic temperate estuary (Argentina). Environmental Monitoring and Assessment 185(2):1495-1513.

Mileusnic M., B. S. Mapani, A. F. Kamona, S. Ruzicic, I. Mapaure and P. M. Chimwamurombe (2014). Assessment of Agricultural soil contamination by potentially toxic metals dispersed from improperly disposed tailings, Kombat mine, Namibia. J Geochem Explor 10(1):1016-1024.

Mohamed B., A. Khidr and N. Dheina (2011). Assessment of heavy metal concentration in water, plankton, and fish of lake Manzala. Turk J Zool 35(2):271-280.

Morais S., F. G. Costa and M. L. Pereira (2012). Heavy metals and human health. In: Oosthuizen J, editor. Environmental health – emerging issues and practice pp. 227–246.

Mosby, Glanze, Anderson, St. Louis; (1996). Mosby Medical Encyclopedia, The Signet 7(2):121-131.

Muller G. (1969). Index of geo-accumulation in the sediments of the Rhine river. Geol J 2:108-118.

Muller G. (1979). Schwermetalle in den Sedimenten des Rheins - Veranderungen seit. Umschau 79:778-783.

NIS (Nigerian Industrial Standard) (2007). Nigerian Standard for Drinking Water Quality. Pg 1-30.

O'Brien T., J. Xu , S. R. Patierno (2001). Effects of glutathione on chromium-induced DNA crosslinking and DNA polymerase arrest; Molecular Mechanisms of Metal Toxicity and Carcinogenesis; US: Springer pp. 173–182.

Oniye, Ega, O. J. Ajanusi, Agbede (2002). Some aspects of Physico-chemical parameters of Zaria Dam, Nigeria. Journal of Agricultural and Environment 3(2): 367-379.

Pandey J. and M. Agarwal (1994). Evaluation of air pollution phytotoxicity in a seasonally dry tropical urban environment using three woody perennials. New Phytol 126(1):53-61.

Pandey J. and R. Singh (2015). Heavy metals in sediments of Ganga river : up- and stream urban influences. Applied Water Science pp 1-10.

Pandey J. and U. Pandey (2009). Accumulation of heavy metals in dietary vegetables and cultivated soil horizon in organic farming system in relation to atmospheric deposition in a seasonally dry tropical region of India. Environ Monit Assess 148(1):61-74.

Pandey J., A. V. Singh and R. Singh R (2013). Impact of changing atmospheric deposition chemistry on nitrogen and phosphorous loading to Ganga River. Bull Environ Contam Toxicol 91:184–190.

Pandey J., A. V. Singh, A. Singh and R. Singh (2013). Impact of changing atmospheric deposition chemistry on nitrogen and phosphorous loading to Ganga River. Bull Environ Contam Toxicol 91:184–190.

Papanikolaou N. C., E. G. Hatzidaki, S. Belivanis, G. N. Tzanakakis and A. M. Tsatsakis (2005). Lead toxicity update-A brief review. Med Sci Monitor 11(10):329-332.

Pote J., L. Haller, J. Loizeau, A.G. Bravo and W. Wilde (2008). Effects of a sewage treatment plant outlet pipe extension on the distribution of contaminants in the sediments of Bay of Vidy, Switzerland. Biosource Technol 99:7122-7131.

Rajeshkumar S., S. Sukumar, N. Munuswamy (2013), Biomarkers of selected heavy metal toxicity and histology of Chanos Chanos from Kaattuppalli Island, Chennai. Environ Earth Sci 72:207-219.

Raju K. V., R. Somashekar and K. Prakash (2012). Heavy metal status of sediment in river Cauvery, Karnataka. Environ Monit Assess 184(1):361–373.

Reilly C. (2007). Pollutants in Food – Metals and Metalloids. In: Szefer P, Nriagu JO, editors. Mineral Components in Foods. Boca Raton, FL: Taylor & Francis Group pp. 363–388.

Ryan T. P. and S. D. Aust (1992). The role of iron in oxygen-mediated toxicities. Crit Rev Toxicol. 22:119–141.

Saeed S., V. D. Marzieh, H. Akbar and K. Toba (2014). Heavy metals in water and sediments of Tembi River. Journal of Environmental and Public Health. 34(1):34-39.

Sakai, Hiromitsu, Y. Kojima and K. Saito (1986). Distribution of heavy metals in water and sieved sediments in the Toyohira river. Water Res 20(5):559-567.

Salah E. A. M., T. A. Zaidan, A. S. Al-Rawi (2012). Assessment of heavy metals pollution in the sediments of Euphrates River, Iraq. J Water Res Prot 4:1009–1023.

Schlatter C. and U. Kissling (1973). Acute fatal bichromate poisoning. Beitrage zur Gerichtlichen Medizin. 30:382–388.

Sharma R. K., M. Agarwal and F. Marshall (2007). Heavy metal contamination of soil and vegetables in suburban areas of Varanasi. Ecotoxicol Environ Safety 66(1):258-266.

Shiklomanov I. (1993). Water in Crisis : A guide to water resources. Oxford University Press, Chapter 2.

Singh H., S. Yadav and D. N. Shukla (2012), Assessment of Geochemical Environment from Study of River Sediments in the Middle Stretch of River Ganga at Ghazipur, Buxar and Ballia area. Proc Natl Acad Sci 83(3):371-384.

Singh M. (1996). The Ganga River : Fluvial geomorphology, sedimentation process and geochemical studies. Band 8, Heidelb Beitr Umwelt-Geol 21:750-761.

Singh M. (1999). Heavy metal polution in freshly deposited sediments of the Yamuna river. Environmental Geology 40(6).

Singh M., A. A. Ansari, G. Muller and I. B. Singh (1997). Heavy metals in freshly deposited sediments of Gomti river. Environ Geol 29:246-252.

Singh M., G. Muller and I. B. Singh (2002). Heavy metals in freshly deposited stream sediments of rivers associated with urbanisation of the Ganga Plain. Water Air Soil Pollut 141:35-54.

Singh R. K. and M. Agarwal (2005). Atmospheric deposition around a heavily industrialised area in a seasonally dry tropical environment of India. Environ Pollut 138(1):142-152.

Singh V. K., K. P. Singh, D. Mohan (2005). Status of heavy metals in water and bed sediments of river Gomti—a tributary of the Ganga River, India. Environ Monit Assess 105:43–67.

Smith A. H., E. O. Lingas , M. Rahman (2000). Contamination of drinking-water by arsenic in Bangladesh: a public health emergency. Bull World Health Organ. 78(9):1093–1103.

Spalding J. (1998). Industrial Discharge into Hudson River, New York. Water Air Soil Pollut 38(1)247-261.

Subramanian V., N.Sitasawad, N. Abbas, and P.K. Jha (1988), Environmental Geology of the Ganga River Basin, Geol. Soc. of India 30(1):335–355.

Subramanian V., V. Grieken and L. Dack (1987). Heavy metals distribution in the sediments distribution in the sediments of Ganges and Brahmaputra rivers. Environ Geol Water Sci 9:93-103.

Swarnalatha K., J. Letha and S. Ayoob (2012), An investigation into heavy metal burden of Akkulam - Veli Lake ion south India, Environ Earth Sci 68: 795-806.

Teo J., K. Goh, A. Ahuja and W. Poon (1997). Intracranial vascular calcifications, glioblastoma multiforme, and lead poisoning. AJNR 18:576–579.

Thornton G. J. B. and N. B. Dise (1998). The influence of catchment characteristics, agricultural activities and atmospheric deposition on the chemistry of small streams in English Lake District. Sci Total Environ 216(1):63-75.

Thornton J. A., A. J. McComb and S. O. Ryding (1975). The role of sediments in eutrophic shallow estuaries and lagoons. CRC Boca Raton pp 205-223.

Tomlinson D.C., J.G. Wilson, C.R. Harris and D.W.Jeffrey, (1980). Problems in the Assessment of HeavyMetal Levels in Estuaries and the Formation of a Pollution Index, Helgel Meeresuntters 33, 566–575.

Turekian K.K. and K.H. Wedepohl (1961). Distribution of Elements in Some Major Units of the Earth's Crust, Bull. Geol. Soc. Am. 72, 175–192.

Udayakumar P., J. Jean Jose, K. Anoop Krishnan, C. S. Ratheesh Kumar, M. N. Manju and P. M. Salas (2014). Heavy Metal accumulation in the surficial sediments along southwest coast of India, Environ Earth Sci 72:1887-1900.

UEPPCB (2007). Status of grossly polluting industries discharging their effluent along the rivers and lakes. Dehradun.

UPJN (2009). Sewage generation from various cities ans status of sewage treatment plants along rivers of Uttarakhand. Dehradun.

US EPA (1991). Sediment quality guidelines Draft report EPA, Chicago.

US EPA (1993). Standard Methods for the Examination of Water and Wastewater; US: American Public Health Assoc.

US EPA (1999) US Environmental Protection Agency: screening level ecological risk assessment protocol for hazardous waste combustion facilities. Appendix E: toxicity reference values.

US EPA (2006), Edition of the drinking water standards and health advisories.

US EPA (2006). Risk Assessment of Guidance for Superfund Volume 1: Human Health Evaluation Manual. Office of Superfund Remediation and Technology Innovation, Washington D. C.

US EPA (2013). Wastewater Treatment Cleans Up Border Waterways in U.S.-Mexico Border.

WHO (1973). World Health Organisation technical report series No. 532. Geneva.

WHO (1993). Guidelines for Drinking-Water Quality Volume 1: Recommendations (2nd edition). WHO, Geneva.

WHO (1998). Guidelines for drinking water quality: recommendations 2nd edition. Geneva.

WHO (2004). Guidelines for drinking water quality. World Health Organization, Geneva, p 515.

WHO (2006). Guidelines for Drinking water quality, Third Edition. Geneva.

WHO Report (2013). Diarrhoeal disease, Fact Sheet Number 330.

WHO. Guidelines for drinking-water quality. Sixty-first meeting; 10–19 June 2003; Rome. 2004.

Wojciech W., J. Gromadzińska and K. Rydzyński (2001). Blood Concentration of essential trace metals and heavy metals in workers exposed to Lead and Cadmium. IJOMEH 14(3):223-229.

Zaherruddin K. S. and U. M. Shabber (1996). Heavy metal pollution in parts of Delhi. Indian Journal Environmnetal Proceedings 16(11):828-830.

Zhang J. and C. L. Liu (2002). Riverine composition and estuarine geochemistry of particulate metals in China - weathering features, anthropogenic impact and chemical fluxes. Est Coast Mar Sci 54:1051-1070.

Zhang J. and C.L. Liu (2002). Riverine composition and estuarine geochemistry of particulate metals in China—weathering features, anthropogenic impact and chemical fluxes. Estuar Coast Shelf Sci 54:1051–1070.

Zhitkovich A. (2005) Importance of chromium-DNA adducts in mutagenicity and toxicity of chromium (VI) Chem Res Toxicol. 18(1):3–11.

Zoumis T., A. Schmidt, L. Grigorova and W. Calmano (2001). Contaminants in sediments: Remobilisation and Demobilisation. Sci Total Environ 266:195-202.