CURRENT STATUS OF HEAVY METAL POLLUTION NEAR SELECTED INDUSTRIAL SITES IN DELHI

A dissertation submitted in the fulfillment of the
requirement for award of the degree of

MASTER OF TECHNOLOGY
IN
Environmental Engineering
BY

DINESH KUMAR
(Roll No. 2K15/ENE/03)

Under Guidance of

DR. ASHOK KUMAR GUPTA
(Professor& HEAD)

Department of Environmental Engineering

Delhi Technological University

(Formerly Delhi College of Engineering)

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दिल्ली प्रौद्योगिकी विश्वविद्यालय
DELHI TECHNOLOGICAL UNIVERSITY
(Formerly Delhi College of Engineering)
DTU
Delhi Technological
UNIVERSITY

CERTIFICATE

*This is to certify that Mr. Dinesh Kumar, M. Tech. student in the Department of Environmental Engineering has submitted a project report "**CURRENT STATUS OF HEAVY METAL POLLUTION NEAR SELECTED INDUSTRIAL SITES IN DELHI**" in partial fulfillment of the requirement for award of degree of Master of Technology in Environmental Engineering, during the academic year 2016-17.*

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

Dr.A.K.Gupta
Head of Department
Dept of Env.Engg.
DTU, New Delhi

Declaration of Originality

I hereby undertake that Dinesh Kumar, 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/our report, including all revisions, as approved by my supervisor, and that this report has not been submitted for any other degree to any other University or Institution.

DINESH KUMAR

M.Tech (ENE)

Roll No. 2K15/ENE/03

PREFACE

It is the requirement of the M.Tech (Environmental Engg.) degree that a student has to undergo project training at the forth semester of two year course. In this time period he has to acquire the work experience in any organization in public sector, private sector or government departments. Along with working exposure the student has to develop an application or model of it.

I underwent my project training at Environment laboratory (Dept. of Env. Engg.) in DTU campus. During project training I have analyzed the heavy metal contamination levels under project named "*CURRENT STATUS OF HEAVY METAL POLLUTION NEAR SELECTED INDUSTRIAL SITES IN DELHI*" at Env. Lab. This project is developed for scientific analysis. This report briefly describes the systematic approach taken to develop this project. The project development report contains information about objective, material & methods required, analysis and result discussion.

Acknowledgement

Any accomplishment requires the efforts of many people and this work is no exception. I appreciate the contribution and support which various individuals have provided for the successful completion of this study. It may not be possible to mention all by name but the following were singled out for their exceptional help.

First and foremost, I would like to express my deepest gratitude to my project supervisor ***Dr.A.K.Gupta****, Department of Environmental Engineering, Delhi Technological University, for his valuable guidance, support, motivation and encouragement during the project work, without which the completion of the work would have been impossible.*

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I would like to thank my family members for supporting and helping me at every step of life. Their sincere blessings and wishes have enabled me to complete my work successfully. I am also thankful to all my friends for their unconditional support and motivation during this work.Above all thanks to the God, for the blessings that has been bestowed upon me in all my endeavors.

DINESH KUMAR

ABSTRACT

Our National Capital 'Delhi' is situated along the Yamuna river, a major contributory of the river Ganges. It has a population of 18.98 million people, and it supports one of the largest bunch of small-scale industries in India, producing waste of varying characteristics. It is figured out that the city generates 2370 million liters of sewage water and 6600 tones of solid waste daily. This waste stream is often discharged into open nalas, which further sum-up with others before vacuuming their contents into the Yamuna river, thus, finally resulting in the overall degradation of the overall water quality. In this study,sewagewater samples were collected from selected industrial sites (Jhilmil, Mondoli, Narela and Mayapuri) within the NCT of Delhi representing the longitudinal spread of the industrial belt on both of the sides of the Yamuna river. Cumulative estimation of heavy metals (Ni, Cd, Co, Mn, Fe,Cu, Zn, Pb, Cr, and Hg) was calculated out using Advance Single Beam UV-VIS Spectrophotometer Model LT-290.

The results extracted by this represent that the pH of the sewage water were moderately basic in nature. Sewage water samples having basic pH levels had relatively high heavy metal contents in it. Clearly we can assure that Jhilmil industrial site had very high levels of Ni, Pb, Mn, Cd, Co,Cu, Zn, and Fe in the sewage compared with the other industrial sites. Also, the spatial distribution of heavy metals in liquid waste water showed that Jhilmil had large amount of Cu and Hg, while Narela had Co, Pb, Ni, Cr, and Fe compared with the other industrial sites. These high levels were the clear indicator of heavy anthropogenic input from industrial, urban, domestic and agricultural sources.

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WQ	Water Quality
Hg	Mercury
Co	Cobalt
Pb	Lead
As	Arsenic
Cd	Cadmium
Cr	Chromium
Mn	Manganese
Cu	Copper
Fe	Iron
Ni	Nickel
Zn	Zinc
EC	Electric Conductance
µg/dL	Microgram per Deciliter
PPM	Parts Per Million
BIS	Bureau of Indian Standard
AAS	Atomic Absorption Spectrophotometer
FNB	Food and Nutrition Board
WHO	World Health Organization
IUPAC	International Union of Pure and Applied Chemistry
US EPA	Environmental Protection Agency (USA)
APHA	American Public Health Association

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CHAPTER 1.0 INTRODUCTION

1.1 URBANISATION TREND IN RECENT YEARS

The whole world population has continued to grown up from an approx 3 billion in 1960 to 7 billion in 2011 and it is estimated to reach the 10 billion digit by the year 2050 (Moore,1991). Along this, while 14% of the total world's population was only urban in 1920, this increased to 19% and 25% in 1940 and 1960. It has been assumed that 44% of the total world population will be in urban nature by the year 2000 (Metcalf and Pitts, 1969).

Given below Tables 1 and 2 shows the growth of the major urban cities and the current urbanization trends in India. These tables clearly show that there has been a drastic increase in the total urban population of India ,particularly after the country's independence period in 1947. Table 1 shows that before 1941(i.e. prior to independence) there were only two cities in whole India with a population of over 1 million people mark, representing about 12% of the total urban population. This scenario however, changed very quickly from 2 to 5 cities soon after independence in 1951, and after this 1991 there were almost 23 cities in this category with approx. 32.5% of the total urban population in India (Central StatisticalOrganization,2011). In same way, the urbanization trend in growing India (Table 2) has shown a steady increase from a small 11 % in 1901 to about 26% by 1991. It is currently can be estimated that the urban population contributes almost 29% of the whole population in India. The National Capital Territory (NCT) of Delhi like other Indian cities in the whole developing world has explained a steady increase in population, from a small 0.304 millions in 1921 to 9.37 million people by 1991. It was clear that the Delhi total population hit the 13.5 million mark by early 2000 (Table 3) .

This drastic rapid increase in the Delhi urban population in India is similar to other developing countries, which continuously subjected to considerable rural to urban migration in its major time period. This is mainly due to more job opportunities in urban cities, lack of basic service and poverty in the most of the rural areas. For example, Zambia a country like India is a developing country with a major problem of rural to urban migration, mainly into the country's capital (Kalapula, 1989). Just before the time when Zambia attained its independence from British rule in 1964, the estimated urban population was be 20.5% of the total country's population. This again, drastically increased to 29% within six years. Again later in 1969 and by 1980, 40% of the population of Zambia was urban in nature(Kalapula 1989). Obviously, such drastic increase in urban population leads to various and environmental , social and economic related problems.

Urbanization in the economically developed countries experienced same type trends in their initial years of development phase as the current developing countries of the world. For example, it has been shown that 95% of the population of the USA was of rural nature based in 1790.

Table 1: Growth of Urban Cities in India with a Population of over 1 million Peop1e (Central Statistical Organization, 2011)

Year	No. of Urban cities	Population(millions)	% of Urban Population
1901	1	1.51	5.84
1911	2	2.76	10.65
1921	2	3.13	11.14
1931	2	3.41	10.18
1941	2	5.31	12.02
1951	5	11.75	18.81
1961	7	18.10	22.93
1971	9	27.83	25.51
1981	12	42.12	26.41
1991	23	70.66	32.54
2001	35	107.88	39.82
2011	53	160.70	48.27

This has however, changed in following years, and while the rate of change might have slowed down considerably, it is estimated that 85% of the USA total population will have become urban-natured by the year 2000. It shows the urbanization trend in the United states between the year 1790 and 2000 (Metcalfe and Pitts 1969).

Thus, in order to increase and maintain the life standards, man's activities have resulted in small scaled urban cities growing into major cities, thereby changing small to large industrial cities that are generally involved in a large number of activities. These have also resulted into large number of migrant workers & their dependants. The major consequences of this large scale economic and socio ecological change are more clear and resulted into the urban air and water pollution problems . This large economic boom, especially in the last 35 years, has brought both increased recognition of the industrial and urban and domestic waste disposal problems.

While developing countries, mainly industrial sludge, hazardous and domestic waste, are usually dumped into low lying areas, or in areas previously considered as a unhygienic place. Towards the end of the 1970s, the main problem of managing dumping landfill sites became more serious due to the contamination of both soil and groundwater (with e.g., heavy metals, chromium, pesticides, halogenated organic compounds and detergents) and the resultant potential risk to exposed populations(Bourassa and Van Impel 1998).

Table 2: Urbanization Trends in India (Central Statistical Organization, 2011)

Year	**Urban Population(millions)**	**% of total Population as urban**
1961	85.72	14.84
1971	109.11	19.91
1981	159.46	23.34
1991	217.18	25.72
2001	277.20	28.63
2011	384.78	31.80

In general, the pollution of groundwater contamination has often resulted in abandoning the use of some major drinking water sources, or affected the future use of groundwater for drinking. It must be noted that recognition of the increased potential human health and environmental risks has also increased the efforts on national and international level on the magnitude of this problem.

Following Table 4 shows the waste production amount generated in some of the major industrialized countries. It is generalized that while the amount of total waste produced varies considerably according to the country geographical belts, these industrialized countries still produce large quantities of waste of varying characteristics in nature.

The European region for example produces an estimated 2.6 billion tones of all type of waste per year. This includes approx 220 tones of its municipal solid waste, 980 million tones of its industrial waste, 01 billion tones of its agricultural wasteland and about 450 million tones of other waste forms that include mainly mining, sewage sludge and demolition wastes (World Health Organization, 1995).

Table 5 shows the total produced waste load in some of the major cities of India. It is estimated that total solid waste generated in mainly small, medium and large cities and towns is approx to 0.1,0.3-0.4 and 0.5 Kgs. per capita per day.

Table 3: Population Trends in the National Capital Territory of Delhi (Central Statistical Organization, 2011)

Census	Population	Growth rate (in %)
1901	405,819	-
1911	413,851	2.0
1921	488,452	18.0
1931	636,246	30.3
1941	917,939	44.3
1951	1,744,071	90.0
1961	2,658,612	52.4
1971	4,065,698	52.9
1981	6,220,406	53.0
1991	9,420,644	51.4
2001	13,782,976	46.3
2011	16,735,235	21.6

The waste produced may be solid, liquid, or gaseous in nature, and they may contain inerter hazardous constituents. Liquid, as well as gaseous wastes, originate from point sources, such as from different commercial processes, dredging and through de-watering of pits

Table 4: Waste Production (x 10^6 tones) in some selected Industrialized Countries (Source: Come, 1994.)

Country	Year	Domestic Waste	Industrial Waste	Demolition Waste	Mining Waste
Germany	1989	19.5	61.4	11.8	9.5
France	1989	17	50	-	100
France	1993	20.5	-	-	-
Italy	1989	17.3	40	34.3	57
UK	1989	20	50	25	230
USA	1989	208.9	760	31.3	1400
Canada	1989	16.4	61	1.5	10.5
Japan	1988	48.3	312	57.8	26

On the other hand, Delhi with a overall population of about 11 million people only generates waste of the order of 4600 tons of solid phase and 1480 million liters of liquid phase waste per day. The solid waste often consists of approx 0.64% and 41.8% of metal and other mineral materials .The remaining waste is composed of organic and other miscellaneous substances (Central Pollution Control Board, 1997).

Table 5: Quantity of Solid and Liquid Waste Generated in Major Cities in India (Ministry of Environment and Forests-2006)

City	**Solid waste(Tones/day)**	**Liquid waste(Tones/day)**
Mumbai	5000	1714.40
Calcutta	3500	780.90
Delhi	4600	1480.00
Chennai	3500	200.00
Banglore	1800	348.00
Kanpur	1314	325.00
Ahmedabad	1600	381.60
Jaipur	1021	134.40
Pune	1527	161.80
Surat	1000	138.02
Nagpur	1100	192.00
Hyderabad	2800	522.00
Lucknow	1043	221.60

Often, the waste may contain heavy metals such as mercury, lead, copper, zinc, nickel ranging from 0 to 100 mg Kg^{-1} in domestic liquid waste, and 100 to 10000 mg Kg-1 in solid and liquid sewage sludge, various industrial wastes (Bonanza and Van Impel, 1998). These have also resulted into large number of migrant workers & their dependants. The major consequences of this large scale economic and socio ecological change are more clear and resulted into the urban air and water pollution problems . This large economic boom, especially in the last 35 years, has brought both increased recognition of the industrial and urban and domestic waste disposal problems.

The generated liquid waste materials can generally be classified into domestic, industrial, hazardous and radioactive categories. Of these, domestic and industrial wastes are mostly most voluminous, while hazardous and radioactive wastes are the most dangerous for humans. As well as, domestic solid waste is known to be more homogeneous than industrial waste. Below Table 6 shows the waste components of different part of the world. It clearly shows that organic waste has the largest share as a percentage of the total waste generated. It is also interesting to note that each individual city has an different waste stream composition, as this is an important factor in the waste processing and management strategy of the local authorities.

Table 6:Waste Components as Weight Percentage for Some Selected World Cities*(Bouazza et al, 2012)

Component→ City^{+} ↓	**Metals**	**Paper, Cardboard**	**Plastics Wood, Rubber**	**Leather,**	**Textiles materials**	**Putrescible**	**Glass**	**Others**
1	1	25	-	7	3	44	1	19
2	1	5	1	1	-	45	1	46
3	3	14	13	-	-	61	2	5
4	3	12	5	-	-	74	4	2
5	5	30	10	-	-	48	-	7
6	1.5	8	6.5	1	1	79	2	1
7	-	14	-	-	-	56	-	30
8	5	22	-	3	-	20	6	46
9	1	9	8	-	4	72	1	5
10	1	20	11	4	4	23	7	30
11	3	22	8	2	-	52	4	9
12	2	10	3	6	3	61	1	14
l3	5	24	4	-	4	50	5	8
14	2.5	31	9.5	4	5	28	9	11
15	3	9	4	-	5	45	1	33
16	4	19	7	4	-	59	2	5
17	1	2	3	1	-	71	1	21
18	-	12	-	-	-	59	-	-
19	7	18	-	10	-	50	10	5

*Note: I-Bangkok (Thailand); 2-Peking (China); 3-Sao Paulo (Brazil); 4-Nairobi (Kenya); 5-Kuala Lumpur (Malaysia); 6-Bandun City (Indonesia); 7-Madras (India); 8-New York (USA); 9-Algiers (Algeria); IO-Zagreb (Croatia); ll-Meruelo (Spain); 12-Istanbul (Turkey); 13-Beymouth (Lebanon); 14-Geneva (Switzerland); 15- Dakar (Senegal); 16-Athens (Greece); 17-Cochabamba (Bolivia); 18-Moscow (Russia); 19-Darwin (Australia).

1.2 LITERATURE REVIEW

It is acknowledged that, metals and their metal compounds are critical to the safety and economy of most of the countries, and have played grand roles in the liberation of modern civilization from disease ,hunger and discomfort. Since the century passes down, the continuously expanding economical, technological development has resulted in the form of increased consumption of large quantities of heavy metals. Indeed, there are few, if any, of the trace metals known to man which have not found any application in the industry, and the number of commercial uses of these continued to grow with the development of science and technology.

The term "heavy metal" often refers to the elements having densities generally greater than 5.0. For all practical purposes, it is considered as a synonymous with other terms such as micronutrients, microelements, minor elements ,trace elements, and trace inorganic (Adriano 1986).However, in a more specific way, trace metals generally refers to elements that occur in natural and enclosed systems in small amounts and that when also present in very much concentrations is toxic to all living organisms as well as abiotic components. While iron has been included in this study, it is assumed that it can’t strictly fall under this definition.

Table 7 shows below estimated global annual discharges of trace metals into the open environment (Nriagu, 1988). It should be noted that heavy metals are present in the environment, present in varying concentrations in soil, water, air, bedrock and also in all biological matter (Bowen 1979). In pre-technological times, the natural cycling of each metal was basically at stagnant phase, and a tight control was maintained on its percentage distribution in any ecosystem y the nature itself. Now the anthropogenic inputs have overwhelmed this natural biogeochemical cycles of heavy metals in many ecosystem. This has resulted into mainly by increased circulation of toxic metals in water, soil, air and build-up of such toxins in the human food chain and thus in whole food chain. As well, it should be noted that some of the toxic metals such as Hg, Tl, Pb, Cd and Ag have no any kind of beneficial effects in humans, and there is no any known mechanism for them (Nriagu 1988). Thus the continuous accumulation of metals due to the long-term exposure may progressively lead to more and more complicated and severe disturbances in the normal functioning of the organic systems. It has been known scientifically from ancient times that the symptoms of heavy metal toxicity are usually non-specific and random in nature, rather than early warning. Alterations in the basic signs become clear only after the major intoxication process has gone advanced to the next higher stage where the basic homeostatic mechanisms can sustain no longer to maintain the normal body functions within their accepted normal range.

It is estimated that the toxicity of all heavy metals which are released annually into the open environment far exceeds the combined total toxicity of all type of radioactive and organic wastes as measured by the total quantity of water needed to dilute such liquid wastes to the drinking water standards as per the study (Nriaguand Pacyna, 1988).

Table 7: Global Discharges of Trace Metals (xl000 tones per year) (Nriagu, 2005)

Metals	Water	Air	Soil
Arsenic	41	19	82
Cadmium	9.4	7.6	22
Chromium	142	30	896
Copper	112	35	954
Lead	138	332	796
Mercury	4.6	3.6	8.3
Nickel	11	56	325
Selenium	41	3.8	41
Tin	-	6.4	-
Zinc	226	132	1372

It is also has been recognized that heavy metals are non-degradable and they grow a continuous build up of such toxins in man's overall life-support systems, constitutes a serious hazard to human health.

Toxicity of heavy metals can be well understood (Wood 1971,Tyler 1972, Purves 1978, Luoma 1983, Oehme 1985, Nriagu 1988, WHO 1989, Moore 1991, Banerji and Martin 1997, Carpenter 1998). For example, arsenic metal was used for a long time as an heavy metal instrument of murder and suicide. As well as other metals like arsenic, antimony, lead, cadmium, and beryllium have also been associated with the accidental deaths in industry works. Indeed, it is estimated that lead poisoning may have gone affected more than 1% of the world's urban children (Giddings and Monroe 1972).

The toxicity of heavy metals is best exampled by the well known accidents like Minimata, ltai-ltai disasters. The Minimata disease first reported in 1956 badly affected peoples who had consumed mercury-contaminated small fish and other marine products directly taken from the contaminated Minimata Bay in Kumamoto in Japan. This disastrous mercury element was shown to have originated from a nearby local chemical manufacturing company, which used amounts of mercury compounds used as a catalyst. Company’s production wastes were dumped directly untreated into the Minimata Bay resulting in the consistent bioaccumulation of mercury, which further resulted into the increased numbers of dead fishes in the water and a subsequent decline in fish production.

Similarly, the cadmium induced ltai-ltai (Ouch-Ouch) disease was firstly reported in 1968 in Juntsu river in Japan, caused extreme pain in the bones, apart from this, making them shrivel and become more and more brittle. Cadmium, even at lower levels, is also has been associated with various types of cardiovascular, respiratory, and tumor problems, especially in heavily populated urban cities (Van Loon et al 1973). Along this, the public health from the disposal of the hazardous chemical wastes in the water bodies has been a well known example and highlighted by the histories of the Valley of the Drums ,the Love Canal. It has been concluded that toxic metals in the environment are a far more serious problem than the pollution caused by most of the pesticides, SO_2 , NO_x CO and other gaseous contaminants (Giddings and Monroe1972).

Heavy metals are generally released into the environment from a wide variety of natural and anthropogenic sources (Nriagu 1988, Ramamoorthy 1994). While most of metal pollution in soils is derived from urban refuse, atmospheric gravity fall out, coal, fly and bottom ash, animal waste and agricultural and food waste, the principal sources of pollutant metals in natural waters are the discharge of domestic and industrial waste water and the dumping of sewage sludge produced (Nriagu 1988). Below table 7 shows the approx global (annual) discharges of heavy metals into the ecosystem.

Most of the waste of city population enters into water bodies through the all over discharge of wastewater. Thus, the water mostly used by the urban population for their drinking needs, washing or by industrial process for cooling, washing is discharged carrying with unwanted substances (Welch 1992). The waste products of civilization can enter water bodies through point and non-point type of sources. The waste water contains a complex mixture of waste materials, including all those from urban run-off, agricultural lands and from remote watersheds, which receives their waste products from the atmosphere also. Thus, water is used as a major conveying medium for most of the waste materials generated. Such type of wastes often contains toxic chemicals and heavy metals in it, which are more hazardous to all forms of life. As well as, when this materials do not degrade into innocuous substances, they become more liable to accumulate in the overall food chain, there by causing a serious environmental and health hazard (Bradshaw 1992). Similarly, a of these trace metals are completed with aero particulate matter and may not be in the form normally considered as toxic. However, environmental changes in most of the water bodies often may lead to the release of these trace metals into the water body, thus altering their toxicity levels considerably. While most of metal pollution in soils is derived from urban refuse, atmospheric gravity fall out, coal, fly and bottom ash, animal waste and agricultural and food waste, the principal sources of pollutant metals in natural waters are the discharge of domestic and industrial waste water and the dumping of sewage sludge produced (Nriagu 1988).

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Table 8: Historical Changes in Primary Production of Metals (x 1000 tones yr) (Nriagu, 2005)

Element	1930	1940	1950	1960	1970	1980	1985
Aluminium	120	831	1500	4520	9660	15396	13690
Antimony	23.6	33.0	48.5	55.4	70.0	63.3	55.0
Arsenic(white)	71.0	47.0	47.0	49.6	45.0	-	-
Bismuth	1.4	1.4	2.4	3.7	6.6	8.3	-
Cadmium	1.3	4.8	6.0	11	17	15	19
Chromium	560	1300	2270	4421	6057	11248	9940
Cobalt	0.73	5.0	7.2	14	24	31	36
Copper	1611	2050	2650	4212	6026	7660	8114
Gold	1.3	1.0	1.4	1.5	1.2	1.5	
Iron(steel only)	80180	107880	189000	346000	594600	714490	715440
Lead	1696	1730	1670	2378	3395	3096	3077
Magnesium	45	41	93	220	316	327	-
Manganese(Ore concentrates)	491	5170	5800	13640	18240	26720	-
Mercury	3.8	5.5	4.9	8.3	9.8	7.1	6.8
Molybdenum	17	15	41	82	110	98	
Nickel	22	133	144	326	629	759	778
Platinum metals	0.003	0.014	0.019	0.04	0.13	0.21	0.25
Silver	8.6	6.2	7.5	9.4	11	13	
Tin	179	240	172	183	232	251	194
Tungsten(Ore concentrates)	17	40	39	30	32	51	47
Vanadium	3.1	1.8	6.4	18	35	34	-
Zinc	1394	1640	1970	3286	5465	5229	6042
Zirconium	399	679	775	-	-	-	-

1.2.1 TOXICITY OF SOME METALS

Among the metals present in higher concentration, the most problematic are Mercury (Hg), Lead (Pb), Arsenic (As), Cadmium (Cd), Copper (Cu), Zinc (Zn), Chromium (Cr), Iron (Fe) and Nickel (Ni). Sometimes a very small concentration of a minor constituent may be of great hazard / benefit to human health and to plant nutrition. After it was discovered in the 1930s that fluoride in drinking water could be useful in preventing tooth decay, fluoride determination became routine in analyses to water for the public supply. It is interesting that although trace elements are essential, just a little more than the required amount of some elements is toxic, inhibiting growth or in extreme cases even causing death. Zinc in trace amounts stimulates growth in many plants, but in large amounts it poisons the soil to such an extent that plants won't grow at all. Boron is an essential trace element for all plants, but its presence as little as 1 ppm in irrigation water; inhibits the formation of fruits such as orange and lemon. Similar example could be cited for other essential elements.

Lithium is an element seldom determined in routine irrigation water analyses, but as per a research study conducted in California, as little as 0.05-0.10 ppm of lithium in irrigation water can be toxic to citrus & avocado trees and to red kidney beans.

High concentration of the inorganic trace elements in the irrigated soils and shallow ground water bodies poses a major threat to the agricultural productions and to the human & animal health. The modes of action are three, as follows:

- Trace elements can accumulate in plants to levels that cause phyto-toxicity
- Trace elements in plants can adversely affect the human body and animals who consume to these plants; and
- Trace elements can also migrate with seepage through plant's root zone and into the groundwater, possibly re-emerging with the subsurface drainage in surface waters, thus affecting the major wildlife, or within ground water pumped for the domestic use, thus ultimately threatening the human health.

Many trace elements are biologically beneficial at very low concentrations, but become toxic or otherwise detrimental to the health of organisms and plants at low to moderate concentrations. Long term exposure at sub-lethal concentrations to certain trace elements may result in chronic biological effects. Some trace elements can accumulate to potentially harmful levels in soils and sediment through chemical immobilization, in plants through bioconcentration, or via a food chain through the biomagnifications.

In present time, heavy metals are the most widespread causes of the pollution, both in water bodies and in the soil medium. Their presence of increasing levels of metals in the open environment is continuously causing a serious concern in public opinion owing to the extreme toxicity shown by most of them. Most heavy metals are generally defined as metals with high atomic no. atomic weight and a density which is greater than 5.0 gcm^{-3} , but it is possible to find many different definitions. Just in time, International Union of Pure and Applied Chemistry (IUPAC) defined term as "heavy metal" as a diplomatic and misleading one. Truly speaking, metals are the natural component of the Earth's crust and many of them are at higher concentrations, they can have toxic effects. Many other metals (ex., mercury, cadmium, lead, etc.) have their direct toxic effects on human health. Due to chemical characteristics, most of the metals remain in the environment, in many cases only changing from one chemical phases to another one and finally bioaccumulation in food chain. These pollutants can easily enter the open environment through a wide variety of the human activities, like refining, mining, electroplating industries.

The effluents produced by such industrial activities contain a lot of variety of heavy metals like copper, chromium, lead, cadmium, nickel and zinc, and thus slowly release in the water bodies may significantly contribute to the overall increased presence of toxic heavy metals in the aquatic environments. Due to their high level of water solubility, these toxic metals can be most easily absorbed by all the living organisms and due to their high level mobility in natural water ecosystems and the high valued toxicity to living forms, have been ranked as one of the major inorganic contaminants in the surface as well as ground waters. Even if they can be present in very much diluted, almost undetectable quantities, their resistance to the degradation and further persistence in the water bodies finally imply that, through the natural processes like bio-magnification, the concentration may become elevated to the extent that they even may begin disastrous toxic effects.

Of the total 30 metals considered dangerous for the human health, 19 had been defined as the heavy metals: arsenic, bismuth, cadmium, cobalt, mercury, nickel, copper, gallium, gold, iron, platinum, silver, tellurium, thallium, tin, antimony, cerium, chromium, lead, manganese, uranium, vanadium, and zinc. However, one of the major threats to the human health from metals are linked with wide exposure to arsenic, mercury, lead, cadmium (this element is a metalloid but it is generally defined as a toxic metal). Large amounts of the metals can cause severe or may be chronic toxicity which may resulting in the damaged or decreased mental and other central nervous functions, or may even modify blood composition or the damage the lung, liver, kidney and other vital organs.

Long-term exposure to the above described heavy metals may even result in the slowed progressing like physical, muscular, and mostly neurological degenerative processes that can excrete Alzheimer's disease, muscular dystrophy, Parkinson's disease and even multiple sclerosis. Heavy metals can enter the human body throughout water, food, and air or even may be absorbed by the open skin when they enter into the contact directly with the humans in agriculture or in the residential, manufacturing, industrial, pharmaceutical settings. Although many adverse health effects of the heavy metals had been known since a long time such type of exposure to these metals is continuing increasing. Thus, the strict control of heavy metal dumplings and the wide removal of the toxic heavy metals from waters has become a major challenge for the twenty-first century.

1.2.2. STUDY OBJECTIVE & STUDY AREA

Delhi as national capital supports a population of about 12 million people. It is one of the top 20 largest cities of the world. It supports one of the largest cluster of small-scale and medium scale industries in India, generating mostly solid and liquid waste of large variety in characteristics and quantities. It is now estimated that 6600 tones of solid waste and 2300 million liters of liquid waste water are generated discharged on a daily basis. The solid waste is often disposed-off mainly by the roadsides, or in landfill sites, which are mostly not properly and scientifically engineered. The liquid waste i.e. sewage on the other hand is discharged mostly via open drains directly into the Yamuna River, which also serves as the main water source of drinking water for Delhi region. It should be noted that the Yamuna River as a major tributary of the River Ganges also supports the livelihood of millions of people at the down stream of it.

The objectives of the present study was:
To estimate CURRENT STATUS OF HEAVY METAL POLLUTION NEAR SELECTED INDUSTRIAL SITES IN DELHI i.e. Jhilmil (JL), Mondoli (MON), Narela (NAR) and Mayapuri (MAY) representing the all round regional spread of the major industrial belt of Delhi. In this, heavy metal levels were estimated as follows:

1. Cadmium
2. Chromium
3. Cobalt
4. Copper
5. Mercury
6. Iron
7. Lead
8. Nickel
9. Zinc

Below given as Figure 3 clearly shows up the map of Delhi, indicating the industrial areas used in this study

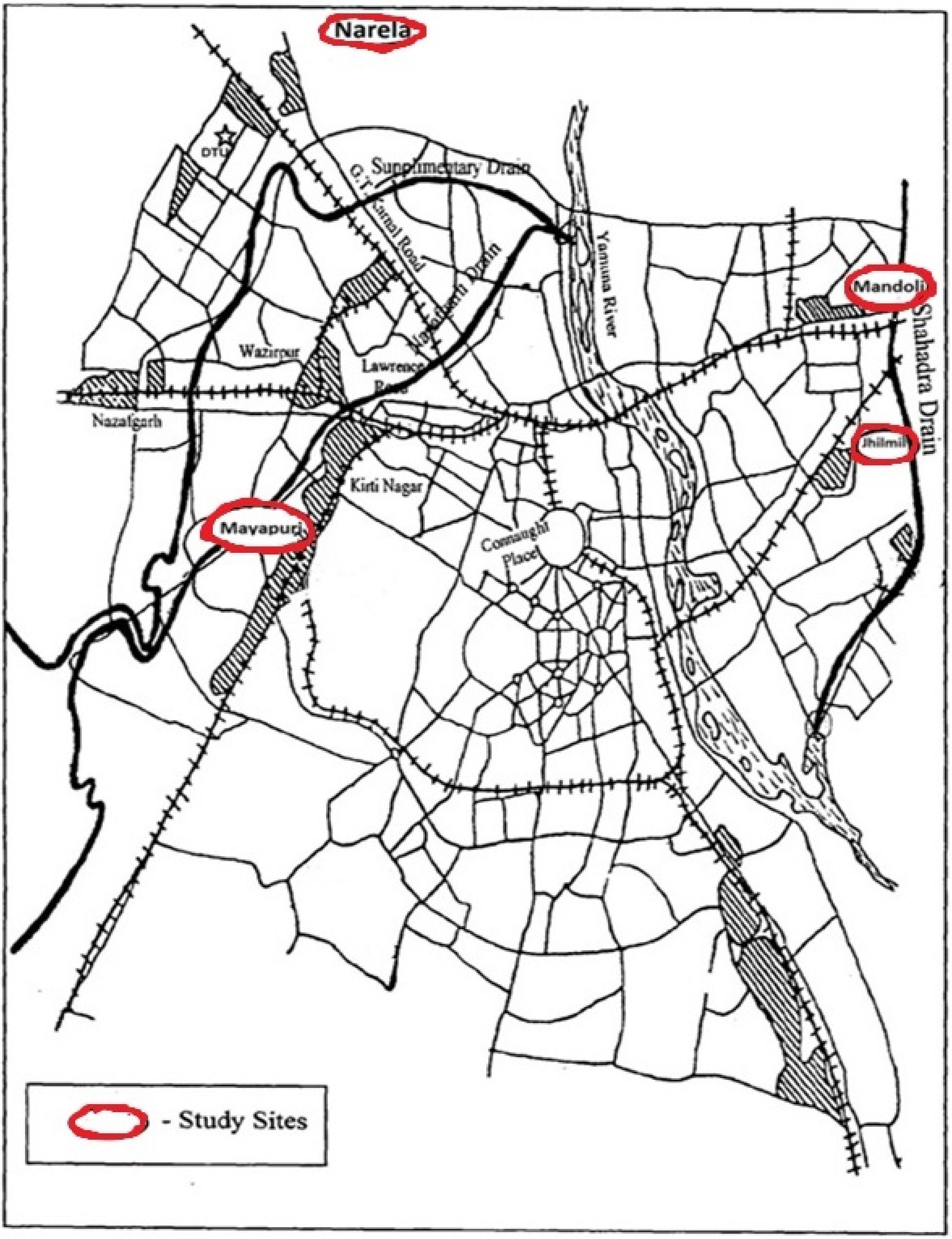


Figure 3: Map showing the Study Sites in the NCT of Delhi

CHAPTER 2.0 THE NATIONAL CAPITAL TERRITORY

The National Capital Territory (NCT) is situated at approx 170 Kms. south of the Himalayas range at an attitude of 28° 25'N and a longitude of 76° 50' E, along with an altitude of ranging from 213 to 305mtrs. above sea level. This city with a population size of about 12 million peoples extends over an area of approx 1483 Km^2, and experiences mostly sub-tropical climate, with some hot summers and moderately cold autumns.

Delhi ,the national capital, unlike the other big metropolitan cities in India (e.g. Mumbai, Chennai and Calcutta) which starts their origins to the major outposts of the British East India Company, known as a ancient city which again dates back to the 11th century (United Nations, 1998). It was thus designated as the capital of British ruled India in 1912, which not only put it into other political focus, but also increased its overall growth. The partition of the India subcontinent brought a refugee movement on a massive scale at that time , and special rehabilitation measures were adopted, such as construction of housing and other facilities, which started the economy and provided a large no. of employment for a bigger section of the residents at that time.

Traditionally, Delhi is well known as a commercial and bureaucratic city, which had gradually industrialized in its last few decades. In 1951, there was approx 15% of the labor force in Delhi were employed only in the industrial manufacturing sector. However, at the end of 1981, about 29% (approx.569000) of the overall labor force was only engaged in small-scale industrial units.

Delhi has itself one of the largest clusters of small-scale industries in India, and experienced unbelievable growth during the time period 1968 to 1996. This comparative growth of the industrial sector in Delhi is beautifully summarized in Figures 1 and 2 below. They clearly compare the overall growth trends with respect to the number of most of the industrial units and employment over time (Figure 1), and also, with major industrial investment and production over time (Figure 2). It is shown clearly that there is a sharp increase in the establishment of new industrial units over the period, thus resulting in a subsequent rise in employment opportunities and production. However It should be noted, that major part of industrial units are located in a well planned way, many other units are found in densely populated residential areas.

In general, we can say, the Industrial establishments in the NCT of Delhi are situated in 28 industrial zones spread across the entire city. The wide nature of the industrial activities, vary from through fabrication of garments and electrical appliances, printing and publishing, consumer electronics, electroplating and steel processes etc to the food processing (Commissioner of Industries,1996). These no. of industries generate waste of varying characteristics in nature and in varying quantities which depends upon the nature of the industrial process. It can be estimated that the total municipal solid waste generated in NCT of Delhi is of the order of 7000 metric tones per day of the city. In addition, Delhi also generates 2300 million liters per day of liquid waste as sewage (CPCB 1997).

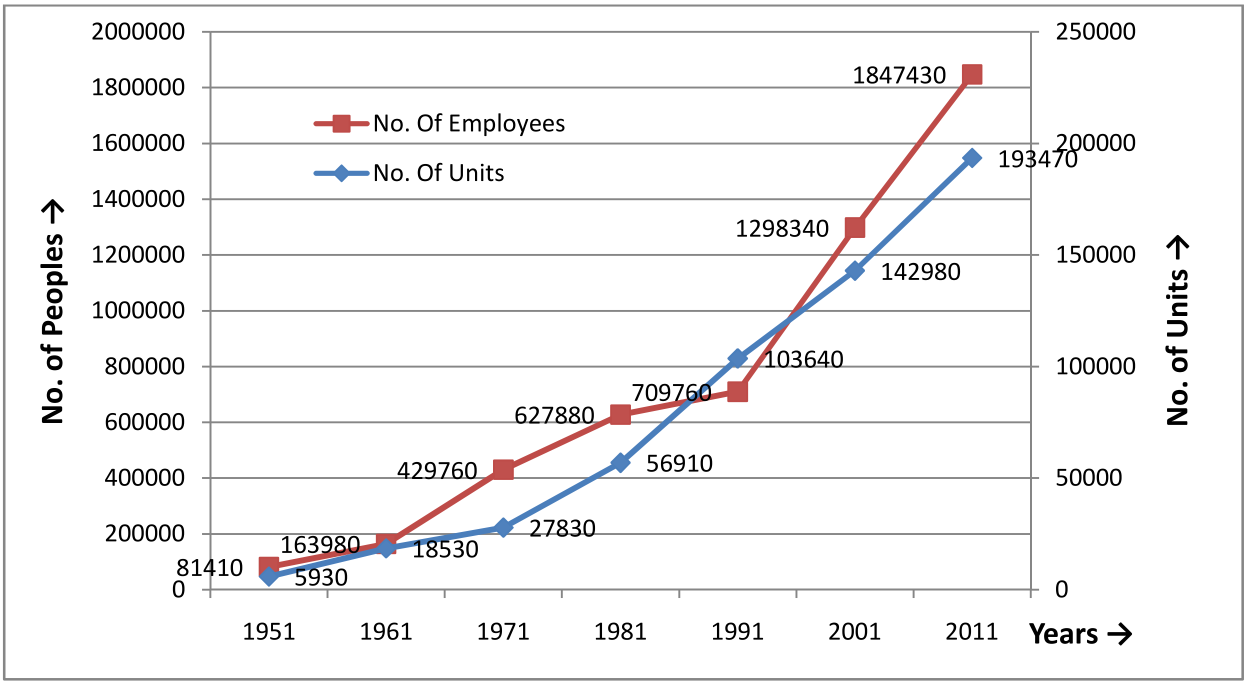


Figure 1: Growth Trends in the Industrial Units and Employment in Delhi, 1951-2011

The supply of drinking water in Delhi doesn’t meet the city's demand and about 70% of the city population does not have any type of access to sewage carrying system. The wastewater generated from the domestic and industrial process in Delhi is generally discharged directly by the municipal authorities into the municipal sewage carrying system. However, these waste-sewers often suffer from day to day blockages, thus, resulting in the wastewater being discharged directly into open big storm drains, which further link-up with other drains, before eventually emptying their contents into the holy Yamuna river which flows along the city from the north end to the south-east direction. It is now estimated that over 2000 million of liters of untreated sewage water and industrial effluents are directly discharged into the holy Yamuna river daily (Banerji and Martin 1997), resulting in the consistent deterioration of its water quality.

The solid waste also dumped on the road-sides within the industrial areas, from where it is again collected by the local municipal bodies and tipped-off at low lying areas which acts as dump sites for them. It should be noted that the waste may also be swept directly into the open storm drains, specially, during the major monsoon rains, when it is also susceptible to leaching.

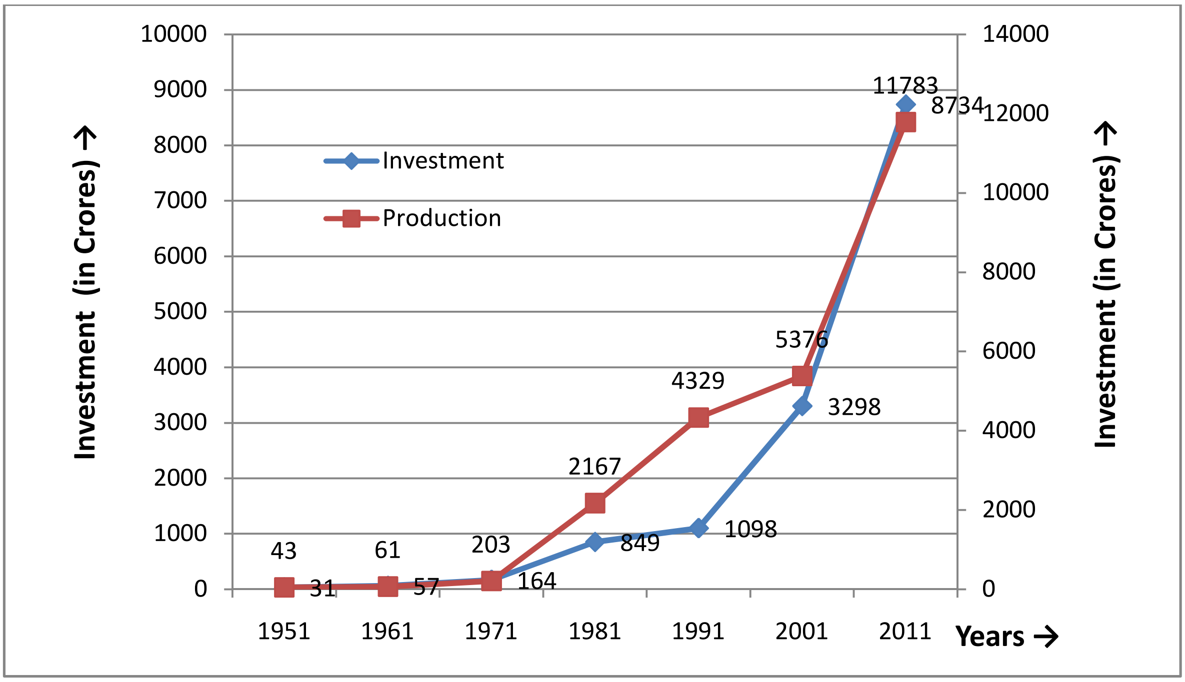


Figure 2: Growth Trends in the Industrial Investment and Production in Delhi, 1951-2011

The wastewater generated from the domestic and industrial process in Delhi is generally discharged directly by the municipal authorities into the municipal sewage carrying system. However, these waste-sewers often suffer from day to day blockages, thus, resulting in the wastewater being discharged directly into open big storm drains, which further link-up with other drains, before eventually emptying their contents into the holy Yamuna river which flows along the city from the north end to the south-east direction.

CHAPTER 3.0 METAL TOXICITY

Important issues related to selected toxic metals like occurrences in nature, sources of water pollution, toxic effects etc. are described here under:

3.1. TOXICITY OF ARSENIC

Arsenic is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust, 14th in the seawater, and 12th in the human body (Mandal and Suzuki, 2002). Arsenic occurs in the environment in rocks, soil, water, air, and in biota.

The element occurs in the environment in different oxidation states e.g., As as As^{+5}, As^{+3}, As^{0} and As^{-3}. The chemical forms and oxidation states of arsenic are more important as regards to toxicity. Generally, inorganic forms are more toxic and mobile than organ arsenic species, while arsenate is considered to be more toxic than arsenate. It has been reported that As^{+3} is 4 to 10 times more soluble in water than As^{+5} (Squibb and Fowler 1983; Xu et al. 1988; Lambe and Hill 1996; US EPA, 2002). Moreover, it has been found that As^{+3} is 10 times more toxic than As^{+5} and 70 times more toxic then Mono Methyl Arsenate {MMA^{+5}} and Di Methyl Arsinate {DMA^{+5}}. However, the trivalent mentholated arsenic species, i.e., MMA^{+3} and DMA^{+3} have been found to be more toxic than inorganic arsenic because they are more efficient at causing DNA breakdown (Styblo et al. 2000; Dopp et al. 2004). Arsenic enters the human body through ingestion, inhalation, or skin absorption. Most ingested and inhalator arsenic is well absorbed through the gastrointestinal tract and lung into the bloodstream.

People drinking arsenic contaminated water generally show arsenical skin lesions, which are a late manifestation of arsenic toxicity. Long term exposure to arsenic contaminated water may lead to various diseases such as conjunctivitis, hyperkeratosis, hyper pigmentation, cardiovascular diseases, disturbance in the peripheral vascular and nervous systems, skin cancer, gangrene, leucomelonisis, non pitting swelling, hepatomegaly and splenomegaly (Kiping, 1977; WHO, 2001; Pershagen, 1983). Chronic symptoms caused by a long exposure to As are unspecific (weight loss, chronic weakness) but a long exposure provokes arsenicosis, cardiovascular diseases, skin lesions among other organ function disorders (Bissen and Frimmel 2003). Arsenicosis is a chronic illness resulting from drinking water with high As level over a long period of time (Kapaj et al. 2006). The effects on the lungs, uterus, genitourinary tract and other parts of the body have been detected in the advance stages of arsenic toxicity. Besides, high concentrations of arsenic in drinking water also result in an increase in stillbirths and spontaneous abortions (Csanady and Straub, 1995).

3*.2. TOXICITY OF CADMIUM*

Cadmium is an element that occurs naturally in the earth's crust. It is uniformly distributed in the Earth's crust, where it is generally estimated to be present at an average concentration of between 0.10 and 0.50 µg/g. Cadmium occurs in nature in the form of various inorganic compounds and as complexes with naturally occurring chelating agents; oregano-cadmium compounds are extremely unstable and have not been detected in the natural environment. Cadmium is produced during extraction of zinc and is used in plating industry, pigments, in manufacture of plastic material, batteries and alloys. The water is contaminated with cadmium by industrial discharge, leaches from land filled area. Drinking water is generally contaminated with galvanized iron pipe, plated plumbing fitting of the water distribution pipes

Cadmium ranks next to mercury in its toxicity. Exposure at low levels usually does not produce immediate health effects, but may cause severe health problems over long periods. The gastrointestinal tract is the major route of Cd uptake in both humans and animals. Cadmium is toxic to humans, animals, micro-organisms and plants, however only a small amount of cadmium intake is absorbed by the body and will be stored mainly in bones, liver and, in case of chronic exposure, in kidneys. In the last few years there have been some evidences that relatively low cadmium exposure may give rise to skeletal damage due to low bone mineral density (osteoporosis) and fractures. The toxicity of the metal lies in that, after absorption, it accumulates in soft tissues. Animal tests have shown that cadmium may be a risk factor for cardiovascular disease (Jarup, 2003). For acute exposure, absorbed cadmium can cause symptoms such as salivation, difficulty in breathing, nausea, vomiting, a pain, anemia, kidney failure, and diarrhea. Inhalation of cadmium dust or smoke may cause dryness of the throat, headache, chest pain, coughing, increased uneasiness and bronchial complications (Lu et al., 2007). The adverse health effects caused by ingestion or inhalation of Cd include renal tubular dysfunction due to high urinary Cd excretion, high blood pressure, lung damage, and lung cancer.

Furthermore, cadmium accumulation in animals and humans occurs throughout their life spans. The sites of greatest cadmium accumulation are the liver and kidney. After inhalation or absorption from the gastrointestinal, cadmium is concentrated in the kidney, where its half-life may exceed 10 to 20 years. One of the most widely known toxic effects manifested by Cd poisoning is nephrotoxicity. Adverse renal effects are more commonly seen with exposure to low levels of Cd. The effects are manifested by excretion of low-molecular weight plasma proteins, such as 2-microglobulin and retinol-binding protein (RBP). The widely reported Cd poisoning itai-itai-byo episode occurred in Japan after World War II. In Japan cadmium from mining and refinery factories polluted Jinzo River water which was used for irrigation to raise the paddy crop. The rice grown on such irrigated fields absorbed cadmium which the humans consumed through water and food chain and caused ostomolacia and skeletal deformation. There was sever pain in body and joints and the people cried ITAI –ITAI (Ouch-Ouch).

3.3. TOXICITY OF CHROMIUM

Chromium can exist in valances from -2 to 6 but is present in the environment mainly in the trivalent or hexavalent state. Trivalent chromium (Cr^{+3}) is the most common naturally occurring state; most soils and rocks contain small amounts of chromic oxide (Cr_2O_3). Hexavalent chromium (Cr^{+6}) occurs infrequently in nature, and chromates (CrO_4^{-2}) and dichromate's ($Cr_2O_7^{-2}$) present in the environment are generally the result of industrial and domestic emissions. Chromium is considered an essential nutrient and a health hazard because Cr exists in more than one oxidation state. Specifically, Cr in oxidation state +6, written as Cr^{+6}, is considered harmful even in small intake quantity (dose) whereas Cr in oxidation state +3, written as Cr^{+3} is considered essential for good health in moderate intake. Chromium Cr^{+3} is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. Trivalent chromium is necessary for the synthesis of fat from glucose and also for the oxidation of fat to carbon dioxide. But the uptake of too much chromium Cr^{+3} can cause health effects as well, for instance skin rashes.

Chromium (Cr^{+6}) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium. Chromium Cr^{+6} is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing in, chromium Cr^{+6} can cause nose irritations and nosebleeds. Other health problems that are caused by chromium Cr^{+6} are:

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material
- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Hexavalent chromium is toxic to plants and animals. It causes yellowing of leaves of wheat and paddy. Maximum permissible limit of chromium in drinking water as recommended by WHO is 0.05 mg/l.

3.4. TOXICITY OF COPPER

Copper is an essential micronutrient (Underwood 1977; Goyer 1991). The Food and Nutrition Board (FNB) recommends dietary copper intake for adults of 1.53 mg/day (NRC 1989). Three major valence states: copper metal (Cu^o), Cu^{+1} and Cu^{+2}. Copper is commonly found in ores. Copper occurs in nature as the metal and in minerals, most commonly cuprite (Cu_2O) and malachite ($Cu_2CO_3(OH)_2$). The principal copper ores are sulphides, oxides, and carbonates

Copper is both essential and toxic to living systems. As an essential metal, copper is required for adequate growth, cardiovascular integrity, lung elasticity, revascularization, neuroendocrine functions, and iron metabolism. An average adult human ingests about 1 mg of copper per day in the diet; about half of which is absorbed (Harris 1997). Copper is obligatory for enzymes involved in aerobic metabolism, such as cytochrome oxidase in the mitochondria, lysyl oxidase in connective tissue, dopamine monooxygenase in brain, and ceruloplasmin. As a cofactor for apo-copper-zinc superoxide dismutase, copper protects against free-radical damage to proteins, membrane lipids, and nucleic acids in a wide range of cells and organs. Severe copper deficiencies, either gene defects due to mutations or low dietary copper intakes, although relatively rare in humans, have been linked to mental retardation, anemia, hypothermia, neutropenia, diarrhea, cardiac hypertrophy, bone fragility, impaired immune function, weak connective tissue, impaired central-nervous-system (CNS) functions, peripheral neuropathy, and loss of skin, fur (in animals), or hair color (Linder and Goode 1991; Uauy et al. 1998; Cordano 1998; Percival 1998).

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of concern is a topic for further investigation. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea.

Excess amount of copper sulphate also shows detrimental effect on botanical environment. Copper in ionic form is very toxic to the photosynthesis of the green algae, Chlorella pyrenoidosa and the diatom, Natchez plea in concentrations of copper normally found in natural waters. Copper accumulates progressively in soils where copper fungicides are used, particularly in vineyards and orchards, which are spread repeatedly. Thus, it is seen that though copper is essential of life and health, its deficiency or excesses both cause adverse effects.

3.5. TOXICITY OF IRON

Iron is essential to almost all living things, from micro-organisms to humans. Iron is the fourth most abundant element in the earth's crust and the most abundant heavy metal; it is present in the environment mainly as Fe^{+2} or Fe^{+3}. Iron is generally present in surface waters as salts containing Fe^{+3} when the pH is above 7. Most of those salts are insoluble and settle out or are adsorbed onto surfaces; therefore, the concentration of iron in well aerated waters is seldom high. Under reducing conditions, which may exist in groundwater, some lakes or reservoirs, and in the absence of sulphide and carbonate, high concentrations of soluble Fe^{+2} may be found. The presence of iron in natural waters can be attributed to the weathering of rocks and minerals, acidic mine water drainage, landfill leachates, sewage effluents and iron-related industries.

Iron, an essential element in human nutrition, is an integral component of cytochromes, porphyrins and metallo enzymes. Dietary iron requirements vary according to sex and age; older infants, children and women of menstrual age are most vulnerable to iron deficiency. Iron is an essential constituent in plant metabolism. It is indispensable for the synthesis of chlorophyll in green plants, although it does not enter in the constituent of the chlorophyll molecules. Most of the iron in plants is present as a constituent of organic molecules, enzymes and carries cataloes, peroxide and cyto-chromes which play important role in cellular metabolism. Iron is indispensable for the synthesis of chlorophyll molecules. Deficiency of iron in plants causes chlorosis. It is one of the most immobile elements in plants.

Iron is also widely distributed in human body where it exists in the ionic (loosely bound, inorganic iron) and nonionic (tightly bound organic form) state. It is also a constituent of hemoglobin molecule. It is more often suggested that iron deficiency predispose children to lead poisoning. Deficiency of iron with other trace elements is the cause of pica (a morbid appetite for unusual or unfit food, as clay, chalk, ashes, bricks etc., showing itself especially in hysteria, pregnancy and chlorosis). Iron deficiency also affects the transport of lead to the tissue. According to Dr. Ronald Hoffman, depending upon the age, sex and body weight, minimum daily requirement of iron varies from 6 mg/day to 30 mg/day.

While normal amount of iron is essential, the normally large amount adversely affects the human system, which may result in haemo chromatosis. Iron absorption is enhanced by hemi, ascorbic acid, amino acids and inhibited by tannins, calcium, phosphate, phytic acid and fibers. Although the human body contains only about 0.004% iron, this element plays a central role in the life processes. As a constituent of the respiratory pigment hemoglobin, iron is essential for the functioning of every organ and tissue of the human body. Over half of the iron is present in the form of hemoglobin; the remaining iron is stored mainly in the liver. Nutritional anemia is one of the most prevalent deficiency diseases throughout the world. Although anemia may result from many different causes, the form most frequently encountered is iron deficiency anemia (Tsai, 1975). Anemia is a major health problem in India, with over half of ever-married woman having the condition. The problem clearly requires immediate attention and intervention

Iron usually exists in natural water both in ferric and ferrous form. The form of iron however may be altered as a result of oxidation or reduction due to the growth of bacteria in the water during storage, usually the ferric form is predominant in the most of the natural waters. Iron in water may be either in true solution or in a colloidal state or in the form of relatively coarse suspended particles. The iron determination is helpful in assessing the extent of corrosion and aiding in the solution of these problems. Research on corrosion and methods of corrosion control requires the use of many types of tests to evaluate the extent of metal loss. The most important one of them is the iron determination (Sawyer, 1978). In drinking water 0.3 mg/l is the highest desirable limit and 1mg/l the maximum permissible limit of iron in absence of alternative sources.

3.6. TOXICITY OF LEAD

Lead is the most common of the heavy elements. Several stable isotopes exist in nature, lead being the most abundant. Lead is used principally in the production of lead-acid batteries, solder and alloys. The oregano-lead compounds tetraethyl and tetra methyl lead have also been used extensively as antiknock and lubricating agents in petrol, although their use for these purposes in many countries is being phased out. Owing to the decreasing use of lead containing additives in petrol and of lead-containing solder in the food processing industry, concentrations in air and food are declining, and intake from drinking-water constitutes a greater proportion of total intake.

Lead toxicity has been known for over two thousand years. The early Greeks used Pb as a glazing for ceramic pottery and became aware of its harmful effects when it was used in the presence of acidic foods. Researchers suggest that some Roman emperors became ill, and even died, as a result of Pb poisoning from drinking wines contaminated with high levels of Pb.

Lead is found in all human tissues and organs, though it is not needed nutritionally. It is known as one of the systemic poisons because, once absorbed into the circulation, Pb is distributed throughout the body, where it affects various organs and tissues. It inhibits haematopoiesis (formation of blood or blood cells) because it interferes with hemi synthesis, and Pb poisoning may cause anemia. Pb also affects the kidneys by inducing renal tubular dysfunction. This, in turn, may lead to secondary effects. Effects of Pb on the gastrointestinal tract include nausea, anorexia, and severe abdominal cramps (lead colic) associated with constipation. Pb poisoning is also manifested by muscle aches and joint pain, lung damage, difficulty in breathing, and diseases such as asthma, bronchitis, and pneumonia. Pb poisoning can also damage the immune system, interfering with cell maturation and skeletal growth. Pb can pass the placental barrier and may reach the fetus, causing miscarriage, abortions and stillbirths.

Lead poisoning is the most common and serious environmental disease affecting young children. Children are much more vulnerable to Pb exposure than adults because of their more rapid growth rate and metabolism. Pb absorption from the gastrointestinal tract in children is also higher than in adults (25% vs. 8%), and ingested Pb is distributed to a smaller tissue mass. Children also tend to play and breathe closer to the ground, where Pb dust concentrates. One particular problem has been the Pb poisoning of children who ingest flakes of lead-based paint. This type of exposure accounts for as much as 90% of childhood Pb poisoning. The main health concern in children is retardation and brain damage. High exposure may be fatal.

Plants grown in lead mining area are known to accumulate high levels of lead. Plants near highways accumulate atmospheric dust containing Pb as foliar deposits, from the combustion of petrol as well as absorb if from soil.

3.7. TOXICITY OF MERCURY

Mercury (Hg) is the only common metal that is liquid at room temperature. Mercury occurs naturally in the earth's crust. Although it may be found in air, water and soil, mercury is mostly present in the atmosphere as a gaseous element. Mercury's major natural source results from the degassing of the earth's crust, emissions from volcanoes and evaporation from natural bodies of water. Mining of metals also causes indirect mercury discharges to the atmosphere. Due to its long lifetime of approximately of 1 year in the atmosphere, mercury's dispersion, transport and deposition in the environment will cause harmful effects on ecosystems and human health. Mercury may be present in the environment in several forms: elemental or metallic mercury, inorganic mercury compounds and organic mercury compounds. Pure mercury is a volatile liquid metal. It has traditionally been used in products like thermometers, switches, barometers and instruments for measuring blood pressure. Mercury is naturally present in many rocks including coal. When coal is burned, mercury is released into the environment. For this reason, coal-burning power plants are one of the largest anthropogenic sources of mercury emissions to the air, in addition to all domestic human-caused mercury emissions. Burning hazardous wastes, producing chlorine, breaking mercury products, and spilling mercury, as well as the improper treatment and disposal of products or wastes containing mercury, can also contribute to its release into the environment (EPA, 2009).

Mercury compounds are produced in small quantities for chemical and pharmaceutical applications. In ancient Greece mercury was used as a cosmetic to lighten the skin (Jarup, 2003): in some sub-Saharan African countries the use of cosmetic products to bleach or to lighten the skin is still frequent. The long term use of some pharmacologic compounds (hydroquinone, glucocorticoids and mercury) can cause severe health adverse effects (Jarup, 2003). Large quantities of mercury compounds are still used for amalgamation in illegal gold mining, in some developing countries. Anthropogenic sources of mercury and its compounds may result basically from the same sources as enunciated for Cadmium. In addition, underground mining, mining quarrying, opencast and, production of phytopharmaceutical products and biocides, pharmaceutical industry, landfills, urban waste treatment plants, industrial waste-water treatment plants, etc. (E-PRTR, 2010) also add to the list of sources of mercury.

Exposure to mercury may mainly occur as a consequence of the deposition from air into water or into soil. By natural biological processes certain microorganisms can change mercury into methyl mercury, a highly toxic and stable form that builds up in fish, shellfish and animals that eat fish, accumulating in the food chain. General population is exposed to methyl mercury through the food chain; fish and shellfish are the main source of exposure through the ingestion pathway (EPA, 2009). Breathing mercury vapor is another possible exposure pathway. This can occur when elemental mercury or products that contain elemental mercury break and release mercury into air, in especial in indoor spaces without enough ventilation. Nevertheless, the main exposure pathway is through food chain and not by inhalation (EPA, 2009).

High level of mercury can cause harmful effects, such as nerve, brain and kidney damage, lung irritation, eye irritation, skin rashes, vomiting and diarrhea. Mercury has a number of effects on humans that can be simplified into the following main effects:

- Disruption of the nervous system
- Damage to brain functions

- DNA damage and chromosomal damage
- Allergic reactions, resulting in skin rashes, tiredness and headaches
- Negative reproductive effects, such as sperm damage, birth defects and miscarriages

Damaged brain functions can cause degradation of learning abilities, personality changes, tremors, vision changes, deafness, muscle in coordination and memory loss. High levels of methyl mercury in the bloodstream of little children may affect nervous system, affecting the normal thinking and learning (EPA, 2009). Chromosomal damage is known to cause mongolism.

In Japan, human illness and death occurred in the 1950's among fisherman who ingested fish, crabs and shellfish contaminated with a simple alkali mercury compound from Japanese coastal industries. This mercury poisoning produced a crippling and often fatal disease known as "Minamata" disease. In minamata episode, crabs contained as much as 24 ppm, while kidney's from human victims contained 144 ppm. Chloro-alkali plants and primary mercury processing plants are known to emit mercury into the atmosphere in sufficient quantities to create a public health problem. Poisoning of mercury may cause anxiety, insomnia, muscular tremor and other psychological disturbances.

3.8. TOXICITY OF NICKEL

Nickel is the 24th most abundant element (twice as Cu) and comprises approximately 0.008% of the content of the earth's crust; hence, it is a natural component of soil (parent material) and water (Alloway 1995; Hostynek and Maibach 2002; Hedfi et al. 2007). It is the 5th most abundant element in the biosphere, Ni was only discovered through the mining of other metals. Its principal ores are nickelite (NiAs), millerite (NiS), and pentlandite ([Ni, Fe]S).

Nickel is released into the environment from a variety of natural and anthropogenic sources. Among industrial sources, a considerable amount of environmental Ni derives from the combustion of coal, oil, and other fossil fuels. Other industrial sources that contribute to nickel emissions are mining and refining processes, nickel alloy manufacturing (steel), electroplating, and incineration of municipal wastes (Sharma 2005; Ensink et al. 2007). Wastewater from municipal sewage treatment plants also contributes to environmental metal accumulation (vander Hoek et al. 2002).

In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health. Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. The most common type of Ni exposure for the public is through direct skin contact with Ni plating. $Ni(CO)_4$ gas, the most toxic of the Ni compounds, was the first to cause deaths in refineries. The immediate symptoms included headaches, nausea, weakness, dizziness, vomiting, and epigastria pain.

There was a latency period of 1 to 5 days, followed by secondary symptoms, which included chest constriction, chills and sweating, shortness of breath, coughing, muscle pains, fatigue, gastrointestinal discomfort, and, in severe cases, convulsions and delirium.

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of a dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity, once acquired, appears to persist indefinitely. High level occupational exposure has been associated with renal problems, vertigo and dyspnoea (Commission of European Communities, 1976). Nickel and certain nickel compounds have been listed by the National Toxicology Program (NTP) as being reasonably anticipated to be carcinogens. The International Agency for Research on Cancer (IARC) has listed nickel compounds within group 1 (there is sufficient evidence for carcinogenicity in humans) and nickel within group 2B (agents which are possibly carcinogenic to humans).

3.9. TOXICITY OF ZINC

Zinc is the twenty-fifth most abundant element. It is widely found in nature and makes up 0.02% by weight of the earth’s crust (Budavari, 1989). Zinc normally appears dull grey owing to coating with an oxide or basic carbonate. It is extremely rare to find zinc metal free in nature (Beliles, 1994). The major source of zinc is sphalerite, smithsonite, hemimorphite and franklinite. The largest natural emission of zinc to water results from erosion. Natural inputs to air are mainly due to igneous emissions and forest fires. Anthropogenic and natural sources are of a similar magnitude. The main anthropogenic sources of zinc are mining, zinc production facilities, iron and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and incineration, and the use of zinc-containing fertilizers and pesticide

Zinc is an essential element for both animals and man and is necessary for the functioning of various enzyme systems. Nutritional zinc deficiency in humans has been reported in a number of countries. In Egypt endemic zinc deficiency syndrome among young men has been reported (Prasad, et al., 1961; Halsted et al., 1972). This syndrome having characters of retarded growth, signs of immaturity and anemia is probably caused by low intestinal absorption of zinc. Its complete cure was observed by administration of large doses of zinc sulfate.

Acute toxicity arises from the ingestion of excessive amounts of zinc salts, either accidentally or deliberately as an emetic or dietary supplement. Vomiting usually occurs after the consumption of more than 500 mg of zinc sulfate. Mass poisoning has been reported following the drinking of acidic beverages kept in galvanized containers; fever, nausea, vomiting, stomach cramps, and diarrhea occurred 3–12 h after ingestion. Food poisoning attributable to the use of galvanized zinc containers in food preparation has also been reported; symptoms occurred within 24 h and included nausea, vomiting, and diarrhea, sometimes accompanied by bleeding and abdominal cramps.

Symptoms of zinc toxicity in humans include vomiting dehydration, electrolyte imbalance, abdominal pain, nausea lethargies, dizziness and lack of muscular co-ordination (Prasad and Oberleas, 1976). Acute renal failure caused by zinc chloride has also been reported (Csata, 1968). Zinc unlike Hg, Pb or Cd is an essential trace element for organism and plays a vital role in the physiological and metabolic processes of many organisms. However, in high concentration, zinc can be toxic to the organisms.

Zinc is an essential trace element for plants and animals including human begins and it plays vital role in metabolic processes. The most common effect of zinc poisoning in human are non fatal ‘metal fume’ fever, caused by inhalation of zinc oxide fumes and illness arising from the ingestion of acidic foods prepared in zinc galvanized containers. Zinc salts, particularly zinc chloride produce dermatitis upon contact with the skin.

CHAPTER 4.0.GENERAL EFFLUENT STANDARDS

4.1.Standards for General Effluent

These standards in India are laid down by CPCB as mentioned in following table:

Table 9: General Standards for Discharge of Environmental Pollutants as Effluents (CPCB manual for waste water standards)

S.No.	**Parameter**	**Standards**			
		Inland surface water	**Public Sewers**	**Land for irrigation**	**Marine coastal areas**
1	Suspended solids mg/l, Max.	100	600	200	100
2	pH Value	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0	5.5 to 9.0
3	Temperature	shall not exceed 5oC above the receiving water temperature	-	-	shall not exceed 5oC above the receiving water temperature
4	BOD_5 (at 20 ˚*C)*mg/l, Max.	30	350	100	100
5	COD mg/l, Max.	250	-	-	250
6	Arsenic	0.2	0.2	0.2	0.2
7	Cadmium	2.0	1.0	-	2.0
8	Chromium(Cr^{+6})	0.1	2.0	-	1.0
9	Total Chromium(Cr)	2.0	2.0	-	2.0
10	Copper	3.0	3.0	-	3.0
11	Nickel	3.0	3.0	-	5.0
12	Lead	0.1	1.0	-	2.0
13	Mercury	0.01	0.01	-	0.01
14	Zinc	5.0	15.0	-	15.0
15	Iron	3.0	3.0	-	3.0

In India, to maintain the minimum quality standard for wide effluent has led to the formulation of the waste water quality criteria and standards. These waste water quality standards can be considered as the general requirements on which a judgment or decision to support a particular case will be based.

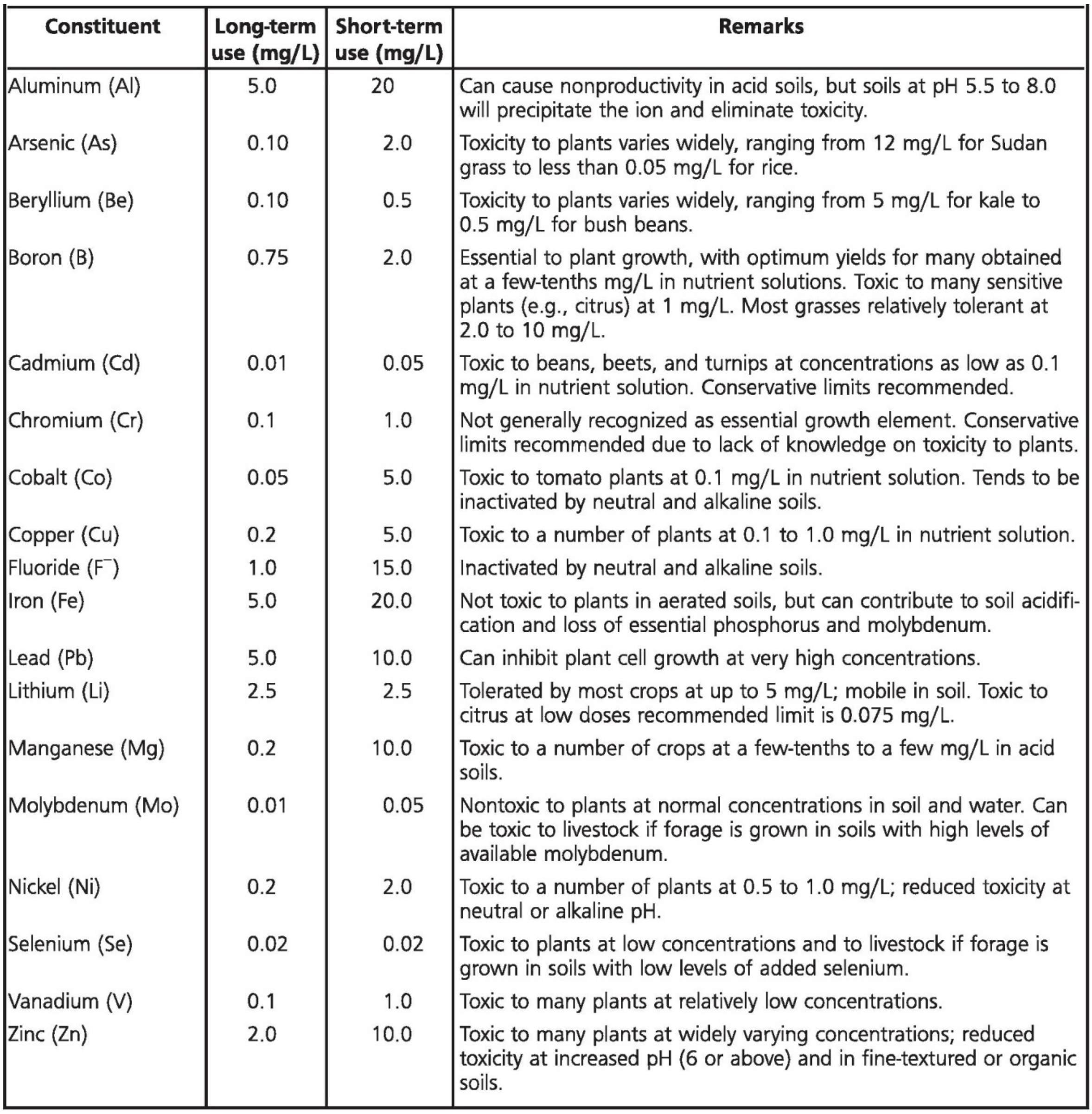
The general criteria for many uses are developed based on the experimental data and our current knowledge about health, ecology and other type issues and continuously and continuously assessing over and over its overall economical effect because these are not such a set of fixed and stable values, but consistently subject to further modification as the scientific data get updated time to time because more and more knowledge is gathered. This term “standard” applies here to any definite principle or any other measure established by the authority by keep limiting concentration of the different constituents in the water to ensure the safe use of water and also safeguard the environment.

4.2.WATER QUALITY FOR IRRIGATION

Nearly all type water bodies contain a few dissolved salts and toxic elements, which can be a result of the natural weathering over the earth’s surface. In most of general irrigation situations, the main water quality concern is the suddenly increased salinity levels, since the salts can affect both the soil structure and also crop yield. However, a no. of heavy metals are found in the water bodies which can also limit its water use for irrigation purpose. The general criteria for many uses are developed based on the experimental data and our current knowledge about health, ecology and other type issues and continuously and continuously assessing over and over its overall economical effect because these are not such a set of fixed and stable values, but consistently subject to further modification as the scientific data get updated time to time because more and more knowledge is gathered.

The required quality of the irrigation water can vary substantially, mainly depending upon the salinity and soil permeability, toxicity and some other miscellaneous concerns like excessive nitrogen loading on soil or unusual pH levels of water. Some elements in the irrigation water may be directly toxic to most of the crops. When an element is added to the concerned soil medium from irrigation, it may be inactivated just by chemical reactions or it can build up in the soil until it can reaches to a toxic level. Any element at a given concentration in the water may be immediately much toxic to a weather crop because of the foliar effects if sprinkler irrigation system is used. If furrow irrigation is used, then it may require a no. of years for the element to more and more accumulate to toxic levels, or it can be immobilized in the infected soil and never can reach to toxic levels. The recommended standard water quality for irrigation water is shown in Table -10.

Table 10: Recommended limits for constituents in reclaimed water for irrigation((CPCB manual for irriagtion water standards)



Constituent	Long-term use (mg/L)	Short-term use (mg/L)	Remarks
Aluminum (Al)	5.0	20	Can cause nonproductivity in acid soils, but soils at pH 5.5 to 8.0 will precipitate the ion and eliminate toxicity.
Arsenic (As)	0.10	2.0	Toxicity to plants varies widely, ranging from 12 mg/L for Sudan grass to less than 0.05 mg/L for rice.
Beryllium (Be)	0.10	0.5	Toxicity to plants varies widely, ranging from 5 mg/L for kale to 0.5 mg/L for bush beans.
Boron (B)	0.75	2.0	Essential to plant growth, with optimum yields for many obtained at a few-tenths mg/L in nutrient solutions. Toxic to many sensitive plants (e.g., citrus) at 1 mg/L. Most grasses relatively tolerant at 2.0 to 10 mg/L.
Cadmium (Cd)	0.01	0.05	Toxic to beans, beets, and turnips at concentrations as low as 0.1 mg/L in nutrient solution. Conservative limits recommended.
Chromium (Cr)	0.1	1.0	Not generally recognized as essential growth element. Conservative limits recommended due to lack of knowledge on toxicity to plants.
Cobalt (Co)	0.05	5.0	Toxic to tomato plants at 0.1 mg/L in nutrient solution. Tends to be inactivated by neutral and alkaline soils.
Copper (Cu)	0.2	5.0	Toxic to a number of plants at 0.1 to 1.0 mg/L in nutrient solution.
Fluoride (F^-)	1.0	15.0	Inactivated by neutral and alkaline soils.
Iron (Fe)	5.0	20.0	Not toxic to plants in aerated soils, but can contribute to soil acidification and loss of essential phosphorus and molybdenum.
Lead (Pb)	5.0	10.0	Can inhibit plant cell growth at very high concentrations.
Lithium (Li)	2.5	2.5	Tolerated by most crops at up to 5 mg/L; mobile in soil. Toxic to citrus at low doses recommended limit is 0.075 mg/L.
Manganese (Mg)	0.2	10.0	Toxic to a number of crops at a few-tenths to a few mg/L in acid soils.
Molybdenum (Mo)	0.01	0.05	Nontoxic to plants at normal concentrations in soil and water. Can be toxic to livestock if forage is grown in soils with high levels of available molybdenum.
Nickel (Ni)	0.2	2.0	Toxic to a number of plants at 0.5 to 1.0 mg/L; reduced toxicity at neutral or alkaline pH.
Selenium (Se)	0.02	0.02	Toxic to plants at low concentrations and to livestock if forage is grown in soils with low levels of added selenium.
Vanadium (V)	0.1	1.0	Toxic to many plants at relatively low concentrations.
Zinc (Zn)	2.0	10.0	Toxic to many plants at widely varying concentrations; reduced toxicity at increased pH (6 or above) and in fine-textured or organic soils.

CHAPTER 5.0 MATERIALS AND METHODS

The raw samples used in this study reported herein were obtained from four industrial sites i.e. Jhilmil (JL),mandoli (MAN), Mayapuri (MAY) and Narela (NAR) in the National Capital Territory of Delhi. Here it should be noted down that, while all these industrial belts were established several years ago, Mandoli; on the other hand is relatively a new industrial zone. The sites here represent the Overall lateral spread of the industrial areas on both side of the Yamuna River, as it passes through Delhi region.Below given as Figure 3 clearly shows up the map of Delhi, indicating the industrial areas used in this study.

Sampling was carried out between 15th March 2017 and 20th March 2017, representing the major autumn seasons in Delhi. Wastewater samples were obtained from waste drainage points within the industrial zones itself. Total three (3) samples were then collected in acid pre-washed polyethylene bottles of 250 ml each, tightly closed and kept at 4°C in the freezer until required for further processing and analysis.

The combined suspended matter was separated by filtering wastewater through a 0.2µm polycarbonate filter membrane with the use of a suction pump.

5.1 pH & Electrical Conductivity

Here all pH measurements were taken using the Rachho Scientifiques meter combined with glass electrodes. First of all calibration of instrument was done by using standard pure water at pH 7. Then allow the pH value to stabilize down before the setting by letting it simply sit for approx 1-2 minutes. Once we get a stable reading, set the pH meter to the value of the buffer's pH by pressing the measure button a second time. Setting pH meter once the final reading has stabilized will also allow for more and more accurate and accurate readings. Now the glass electrode is placed in the sample, again we press the measure button and leave the electrode in the sample for approximately 1-2 minutes. After it, we note down the corresponding pH readings for each sample.

On the other hand , Electrical conductance (EC) gives semi-quantitative estimation of the salt content of the samples. It has been shown by experiments (Jackson 1973) that conductance measurements may be affected by the dilution ratios, since the sample to water ratio influences the amount and composition of the salts extracted. Conductance measurements were made using conductivity meter, model 306. The conductivity of the wastewater was measured following the given procedure described in as Standard Methods for the Examination of Water and Wastewater.

5.2. Determination of Nitrates (NO_3^-)

The detennination of nitrates (NO_3^- anions) was carried out as per the Coming Scientific (1981) manual guide to the selective electrode analysis. The main reagent used for NO_3^- analysis was prepared as follows:

- 2M standard Ammonium sulphate as the Ionic Strength Adjustment Buffer.

- Nitrate standard stock solution (1000 mg/ltr) was prepared by dissolving 1.630 gm. of AR grade KNO_3 powder in demonized and distilled water and made up to 1 liter by proper dilution. Working standards of 100, 10 and 0.1 mg/ltr. NO_3^- was prepared by proper dilution of the stock solution.

- Also standard Ammonium sulphate (0.1M) was prepared as the outer filling solution of the standard electrode. The solution was prepared by dissolving properly 2.650 gm. of its pure salt in deionized and distilled water before diluting to a 100 mL in a volumetric flask. As well as, 4M KCl solution was used as the inner filling solution.

Now Standard solution (50 mL) and ISAB (1 mL) both were transferred into a beaker and a nitrate ion sensitive and reference electrodes were immersed into the solution. The mV reading was properly noted down on a Consort Ion Meter model P602. Again a standard plot of mV response with the concentration of the standard solution was plotted on a logarithmic scale of these variables.

Again in the same way, equal amounts of both samples and ISAB were transferred into a beaker, and then corresponding mV response of the nitrate ion sensitive electrode was noted down. The nitrate concentration in the sample was computed from the standard calibration plot of these variables.

5.3 Determination of Chlorides (Cl^-)

The main reagents required for the estimation of chlorides (Cl^-) in the sample were prepared as follows:

First ISAB was prepared by dissolving l5.00 gm. of reagent grade sodium bromate in 800 mL of deionized and distilled water and then adding 75 mL of concentrated HNO3 again stirred well, before diluting to l litre solution. It should be noted down that the preparation of ISAB was only carried out in the fume hood, since we know sodium bromate is also a strong oxidant.

Chloride standard solution (1000 mg/L) was also prepared by dissolving 1.641 gm. Of NaCl (dried for 1 hour at 650°C) in deionized and distilled water before diluting to 1 liter in a standard flask.

Standard sample of 100, 10 and 0.1 mg/L Cl^- were prepared by proper dilution of the Chloride standard stock solution.

Equal volumes of 20 mL each standard sample and ISAB were placed in a dry beaker .The reference. and Chloride sensitive electrodes were immersed into the given solution. Then mV response was read out on Consort Ion Meter model P602. Again standard curve of mV response with the standard concentrations of sample was plotted on a logarithmic scale graph. The sewage samples were treated in the same way as the standards, and their Chloride concentrations were directly computed from the standard calibration plot of these variables.

5.4.Determination of Heavy Metals

In the current sample study, samples were collected only in polyethylene bottles. These water samples were prepared for the determination of nine selected heavy metals, viz., arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel and zinc by UV-VIS spectrophotometer.

5.4.1.Metal Detection Technique

The instrument used here was ultraviolet-visible spectroscopy also called as UV-VIS spectrophotometer. It mainly measures the intensity of light passing down inside a sample, and then compares it to the intensity of light that it before passes through the sample. This ratio is called as the transmittance of sample and it is generally expressed as percentage (%T). This absorbance is based on the transmittance.

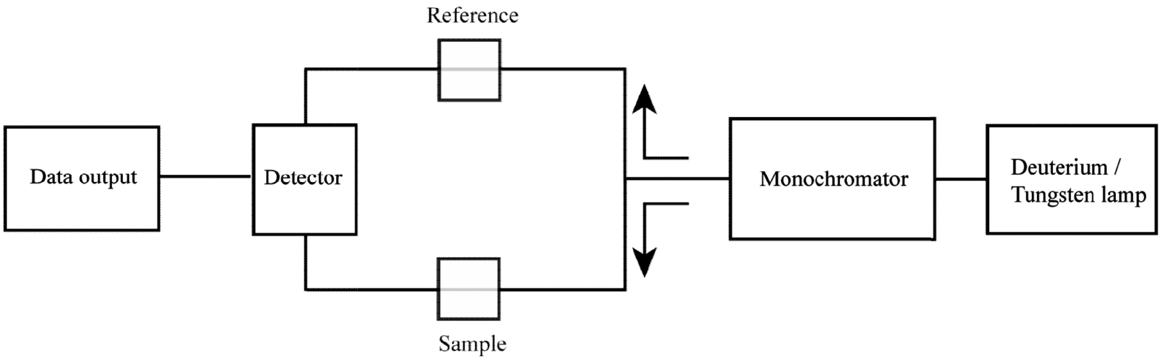


Figure 4: Flow Diagram of UV-VIS Spectrophotometer

The UV-visible spectrophotometer can be configured to measure reflectance. In present case, spectrophotometer measures the intensity of the light that is reflected from the sample, and then compares it to the reflected intensity of light from a reference material (like a white tile). This ratio is called as the reflectance, and it is usually expressed as a percentage (%R).

The most basic parts of a spectrophotometer are a light source and a holder to hold the sample, also a diffraction grating in a monochromatic used to separate out the different wavelengths of the light, and a detector. The main radiation source is generally a Tungsten filament (300-2600 nm)m and a deuterium arc lamp, which intensity of the light reflected from the reference material which is continuous over the UV region (180-400 nm). Xenon arc lamp can also be used, which is continuous from 170-2,000 nm and more recent, LED for the visible wavelengths lights. The only one detector is commonly a photodiode.

A spectrophotometer can be categorized either by single beam or double beam. In the single beam instrument, all of the light wavelengths passes through the sample column must be measured by just removing the sample. UV-visible spectrophotometer may also be configured to measure the reflectance. In the case, the spectrophotometer measures only the intensity of the light reflected from the sample and compares it to the intensity of the light reflected from the reference material. This ratio is called as the reflectance, and it is generally expressed as a percentage. This one was the earliest design of it and it is still in general use both in teaching and industrial laboratories.

The 2nd one is double-beam instrument, in which the light is split mainly into two beams just before, it reaches to the sample. As one beam is used as reference and the other one beam passes through sample. The reference beam intensity is generally taken as 100% Transmission (or 0% Absorbance) and measurement displayed is ratio of two beam intensities. But some double-beam instruments can have two detectors as photodiodes, and the sample and reference beam are quickly measured at the same time.

5.4.2. CHEMICALS AND REAGENTS

All chemicals and reagents used in the chemical analysis during the study were of analytical reagent grade (Merck). Standard solutions of metals ions were procured from Merck, Germany. De-ionized water was used throughout the study. All the glass wares and bottles that are used were thoroughly cleaned by just soaking in detergent and then followed by soaking in 12% nitric acid for 48 hrs and then finally rinsed with the de-ionized water by several times prior to use.

5.4.3.Method

Trace and toxic metals were analyzed by using Single Beam UV-VIS Spectrophotometer Model LT-290. The wave length, current, slit and method employed using atomic absorption spectrophotometer is given in Table-11.

Table11: The wavelength & slit used for chemical analysis by UV-VIS spectrophotometer(APHA manual)

Sr.	Parameter	Wavelength(nm)	Slit(nm)
1	Cadmium	228.8	1.0
2	Chromium	357.9	1.0
3	Cobalt	240.7	1.0
4	Copper	324.7	1.0
5	Mercury	253.7	1.0
6	Iron	248.3	1.0
7	Lead	283.3	1.0
8	Nickel	232.0	1.0
9	Zinc	213.9	1.0

5.4.4.Instrument Specifications

Technical specifications are As per following table-12

Table 12: Advance Single Beam UV-VIS Spectrophotometer Model LT-290(Lab Manual)

Optical System	Single Beam, Grating 1200 lines/mm
Wavelength Range	200-1000nm
Band Width	1 nm
Wavelength Accuracy	±0.5 nm
Wavelength Repeatability	+0.1nm
Wavelength Setting	Automatic
Photometric Accuracy	±0.1 %T
Photometric Repeatability	+0.3 %T
Photometric Display Range	-0.3-3.0A,0-200%T, 0-9999C
Stability	+0.002A/h @ 500nm
Stray Light	≤0.3%T @220nm, 360nm
Data Output Port	USB
Printer Port	Parallel Port
Display	128*64 Dots LCD
Lamps	Deuterium Lamp & Tungsten Halogen Lamp
Detector	Silicon Photodiode
Power Requirement	AC220V/50 Hz

CHAPTER 6.0 RESULTS AND DISCUSSION

Here ,In this study, it was concluded that the composition of the waste water was quite rich in heavy metal concentration. Consequently, all discussions in this thesis will refer to this one. In addition to this, all detailed results obtained during this study were placed in the Appendices section, whereas the computed mean values were properly tabulated and placed in the following main text.

6.1. Physic-chemical Parameters

6.1.1 pH, EC, Cl^- and $N0_3^-$

Below given table 13 and Appendix 4 shows some general physic-chemical parameters of waste water sample from the industrial zones used in this study. It shows clearly that the pH of the waste sample water ranges in between medium basic in nature. Mandoli area had more and more basic samples compared with others from the different industrial areas. In general, we can say that most of the waste samples were in the neutral to basic pH range. Again as expected, there was proportionality between pH and electrical conductivity (EC) of the waste water sample. The basic impact of high pH on the dissolution of metals has been discussed earlier in the thesis. Indeed, high pH levels are generally associated with high dissolution and further mobilization, resulting in high metal ion activity.

While electric conductivity measurements are used to serve many purposes, generally these are used to establish the amount of mineralization and to assess the overall effect of total concentration of metal ions on chemical equilibrium also physiological effect on both plants and animals. It should be clearly noted that electric conductivity is dependent only upon the presence of ions, mobility , their total concentration and valiancy and on the temperature at the time of measurement. Consequently, most of the solutions of inorganic compounds are generally good conductors while molecules of most of the organic compounds are not (APHA 1995). Again the conductivity of domestic wastewater is generally near that of potable water (50 to 1500 µm/cm), also some industrial wastes has shown up the conductivity above 10 000 µm/cm. In the study, the mean conductivity range in the sample (Table 13) was from 2.35 to 6.17 mS/cm, and also the highest value (6.17 mS/cm) was reported in Mandoli industrial area during the autumn sampling season. It was shown that Mandoli showed up higher EC levels and along this relatively higher metal concentration compared with all the other industrial sites. In general we can say, conductivity levels were well above the limits for those found in potable water.

In the same way, the mean Cl^- and NO_3^- levels show same distribution range. The autumn distribution indicated a significantly larger concentration of Chlorides and nitrates during the seasons. Generally a high Chloride content tends to lead to higher corrosion of metallic pipes and water structures as well as harming growing plants (APHA, 1995). It was already expected that there was a positive relationship between Electric Conductivity and chlorides in the waste water from all the industrial sites. It is considered as an essential nutrient for many of the photosynthetic autotrophs segment and in some cases it has been identified also for the growth-limiting nutrient. Generally fresh domestic wastewater contains low amounts of nitrate. Although effluents released from nitrifying biological treatment plants may show up considerably higher concentrations of nitrates. The results tabulated in Table 13 shows up that the concentrations of nitrates ranging. It is now significant to note that in most of the cases, the concentrations were quite above the levels generally reported in fresh domestic wastewater. Really, the waste water discharge in the NCT of Delhi (CBPCWP 1979, Sitasawad 1984), was 50.29 mg/L.

Table 13: Mean Distribution of Some Physic-Chemical Parameters in Wastewater

Serial No.	**Site**	**pH**	**EC(mS/cm)**	**Cl^{-1} (mg L^{-1})**	**NO_3^{-1} (mg L^{-1})**
1	JIL	7.87	3.94	879.0	260.0
2	MAN	8.57	6.17	1668.0	674.0
3	MAY	7.77	4.52	1527.0	588.0
4	NAR	7.56	2.35	*353.0*	*249.0*

6.2 DISTRIBUTION OF HEAVY METALS

Concentrations and distributions in surface and near the earth surface and in the atmosphere are the result of continuous mobility and precipitation of the free ions, anionic complexes and ionic compounds. These may be in the form of gases or vapors that evaporate or may be sublime from liquids or solids also as solid metal or as dust or fumes or metal oxides that particulate and condense from vapors, and also in aqueous combination or in the form of solids (Siegel,1998).

Whether the metal ions or anionic complexes are precipitated or mobilized and then perhaps re-mobilized is produced by some changes in physical and chemical conditions in source areas. In soils and its associated sediments, food animals, and aquifer waters, food crops, the major controlling parameters that mostly influence the mobility and deposition of potential toxic metals includes as :

pH, redox potential, chemical gradients, cation exchange capacity, concentrations, adsorption/desorption, clay minerals and bioaccumulation (Barcellos 1988, Siegel 1998).

Many metal species in aquatic systems derived from their indigenous or anthropogenic sources maybe transported either in dissolved or any particulate forms. Still investigations on transport and distribution of heavy metals in these three phases are therefore more important in evaluating their overall mobility distribution and fate in the environment. In the present study, attempts are made to evaluate the overall distribution of heavy metals in water samples only. In addition to this , comparisons based upon the seasonal and spatial heavy metal distribution are also made. Again, heavy metal composition in the liquid waste were estimated. As well as, chemical analysis was carried out in order to assess the mobility and bioavailability of these heavy metals.

Table 14: Mean Heavy Metals concentration (mg/L) in Wastewater

Sr.	**Site-sample**	**Cd**	**Cr**	**Co**	**Cu**	**Fe**	**Hg**	**Ni**	**Pb**	**Zn**
1	**JIL**	**4.06**	**155.65**	**8.52**	**84.13**	**113.23**	**0.84**	**39.98**	**33.25**	**73.94**
2	**MAN**	**4.38**	**65.67**	**7.69**	**84.61**	**170.81**	**0.16**	**10.92**	**14.69**	**63.25**
3	**MAY**	**2.06**	**35.54**	**2.54**	**26.47**	**144**	**0.28**	**66.59**	**31.93**	**122.42**
4	**NAR**	**5.33**	**119.07**	**3.31**	**106.00**	**180.52**	**0.22**	**89.14**	**55.60**	**92.87**

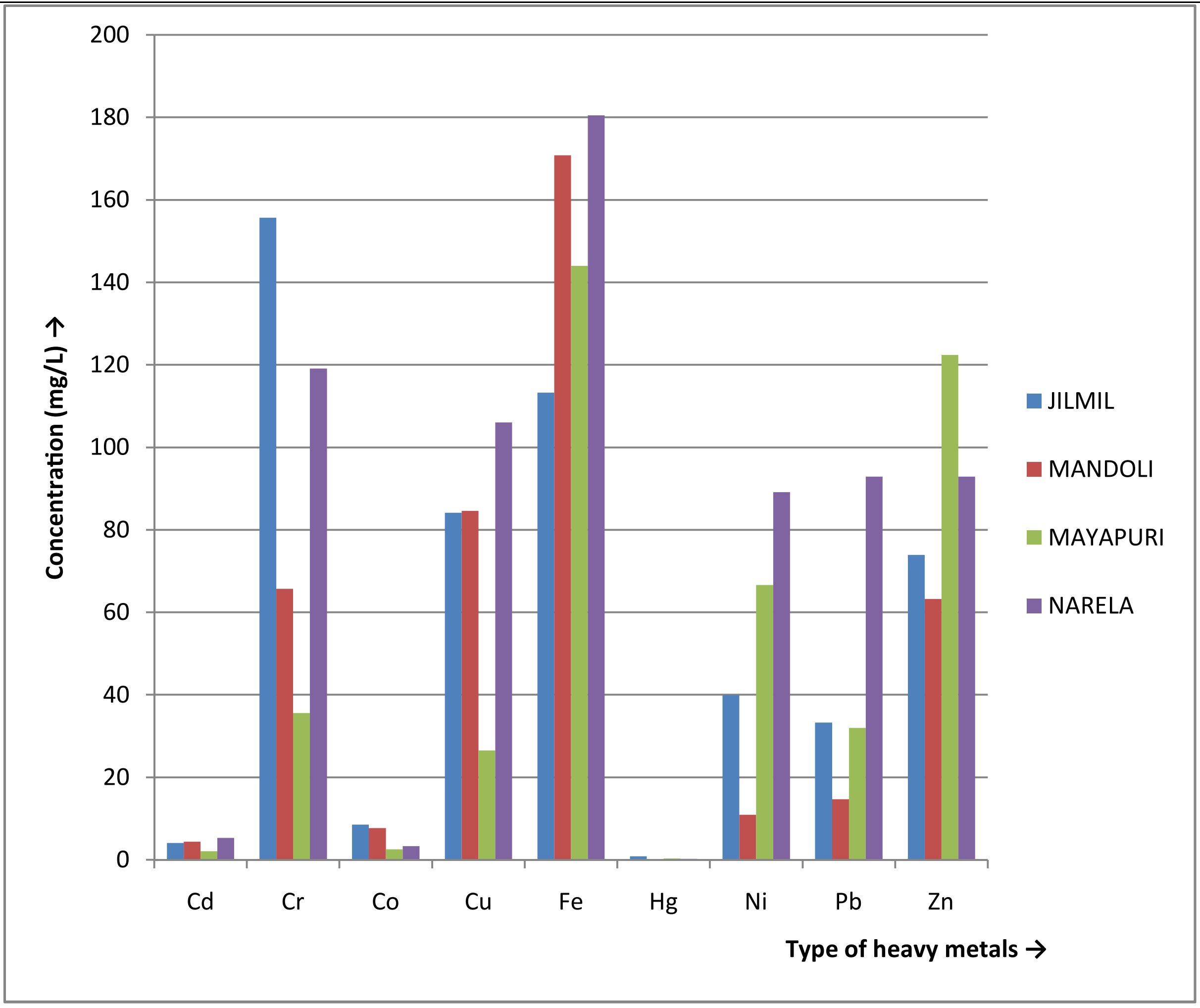


Figure 5: Mean Distribution of Heavy Metals (mg/l) in Wastewater

In most of the developing countries, the disposal of waste water and industrial waste water is often conducted without critical analysis of the impact upon the receiving water-bodies (Shivkumar, 1999). It has been now demonstrated that the domestic and industrial effluents generally lead to the continuous heavy metal enrichment of water body. Studies show that the effect of sewage effluent on the concentration of dissolved metals in major coastal sea-water in the nearby of Los Angeles country Out-fall at Whites Point. Also urban storm-water contains enough metal concentrations, which varies extremely with regard to the locality and time of sampling. As well as, increased domestic use of the detergents has been shown to the significantly contribute to the metal contamination in aquatic systems. Recent investigations carried out in Ottawa and Rideau rivers indicated that the source of most of the metallic contamination was from industrial and municipal wastewater (Oliver and Kindrade, 1972).

In our study, the concentrations of heavy metals in waste water samples are tabulated in following Table 14, Figures and Appendices. It can be also observed that the pH of wastewater generally varied enough and ranged from 2.6 to 8.2(Jhilmil), 2.3 to 8.3 (Mandoli), 7.0 to 7.8 (Narela) and 3.6 to 9.4 (Mayapuri). While this range of wide values were not reflected in all the sampling sites, there was significantly low pH values obtained in Jhilmil, Mandoli and Mayapuri (PH 2.25-3.62) during autumn.

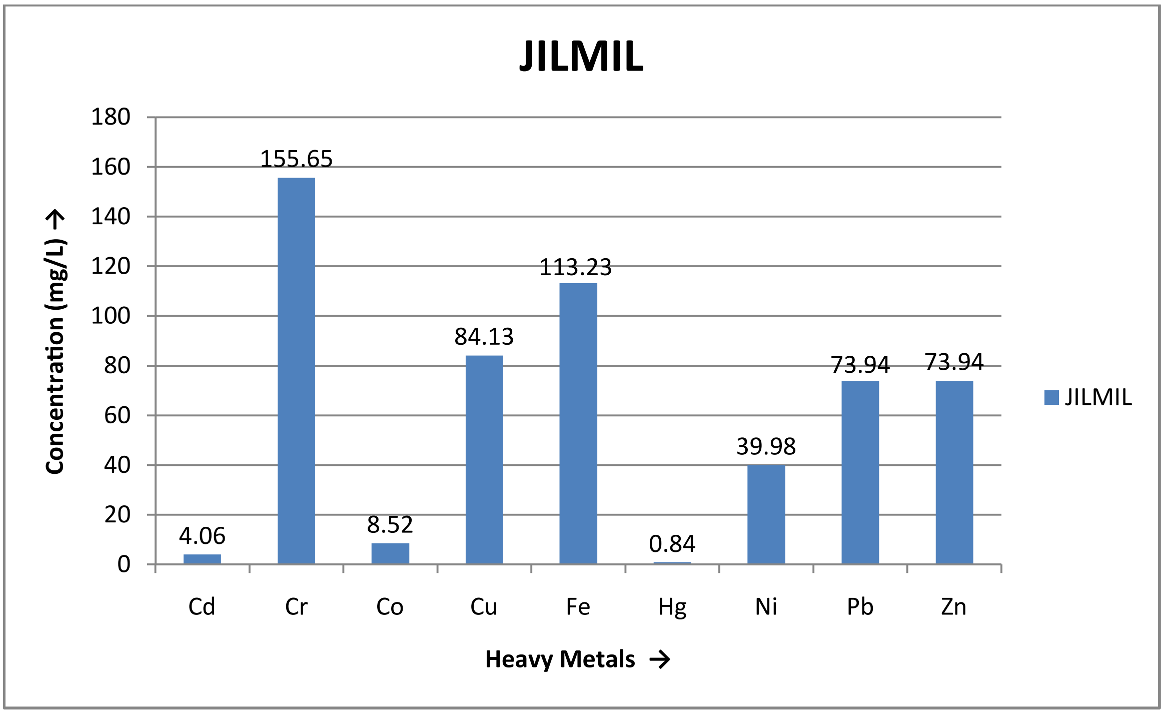


Figure 6: Mean Variation of Heavy Metals (mg/l) in Wastewater at Jhilmil

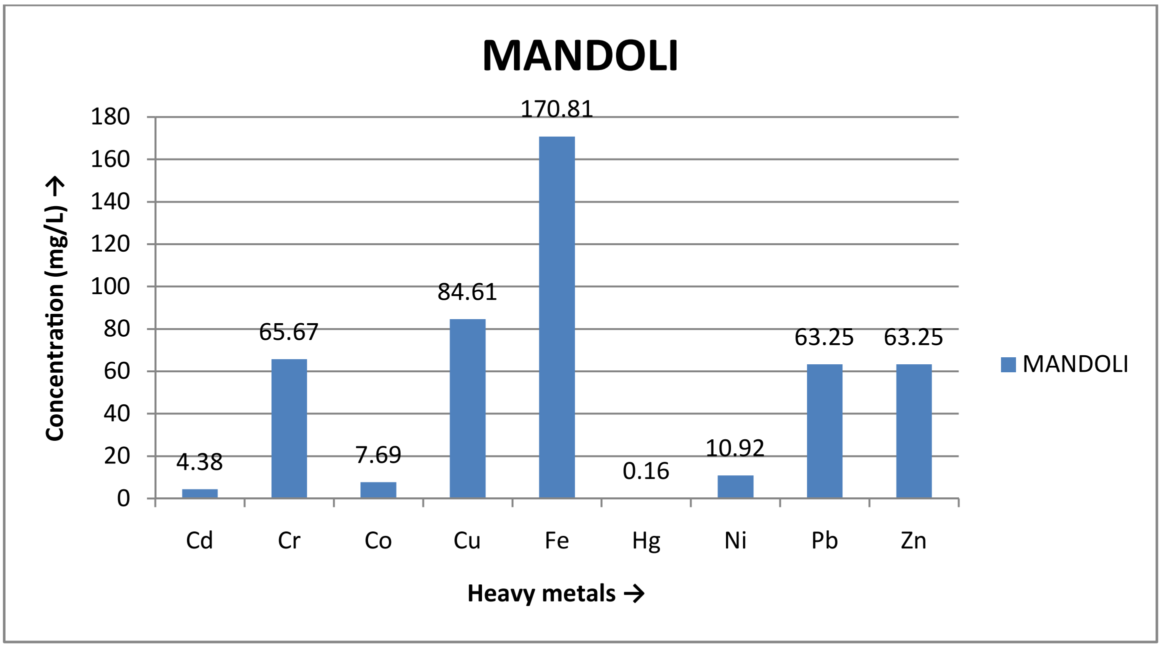


Figure 7: Mean Variation of Heavy Metals (mg/l) in Wastewater at Mandoli

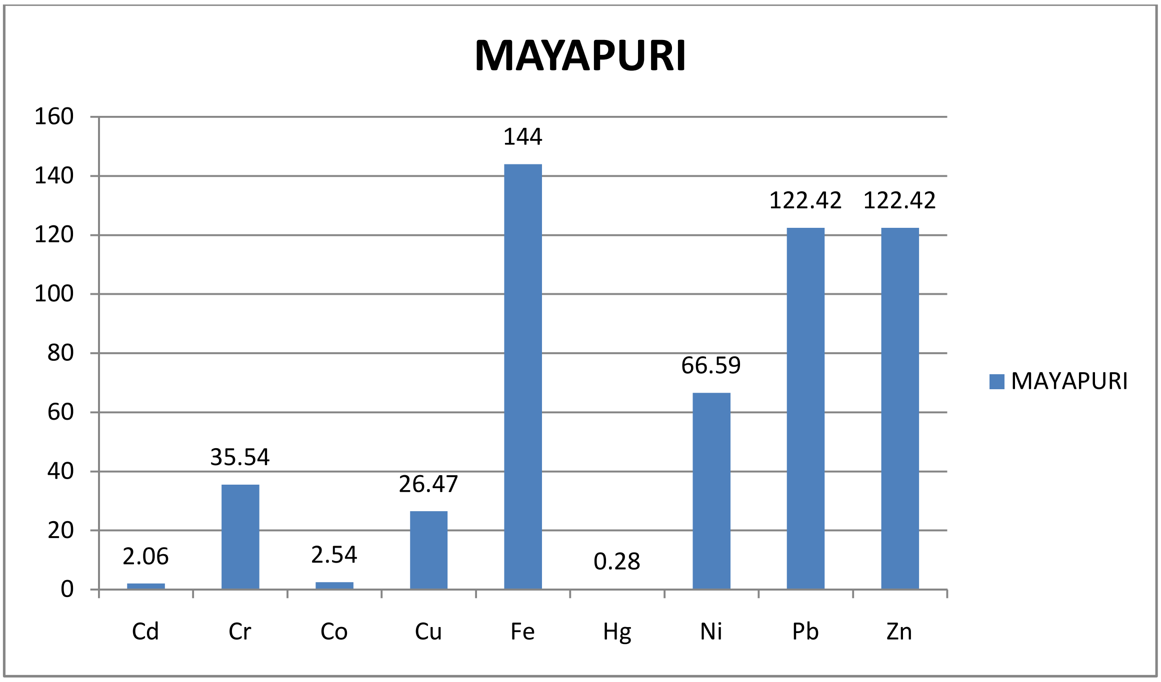


Figure 8: Mean Variation of Heavy Metals (mg/l) in Wastewater at Mayapuri

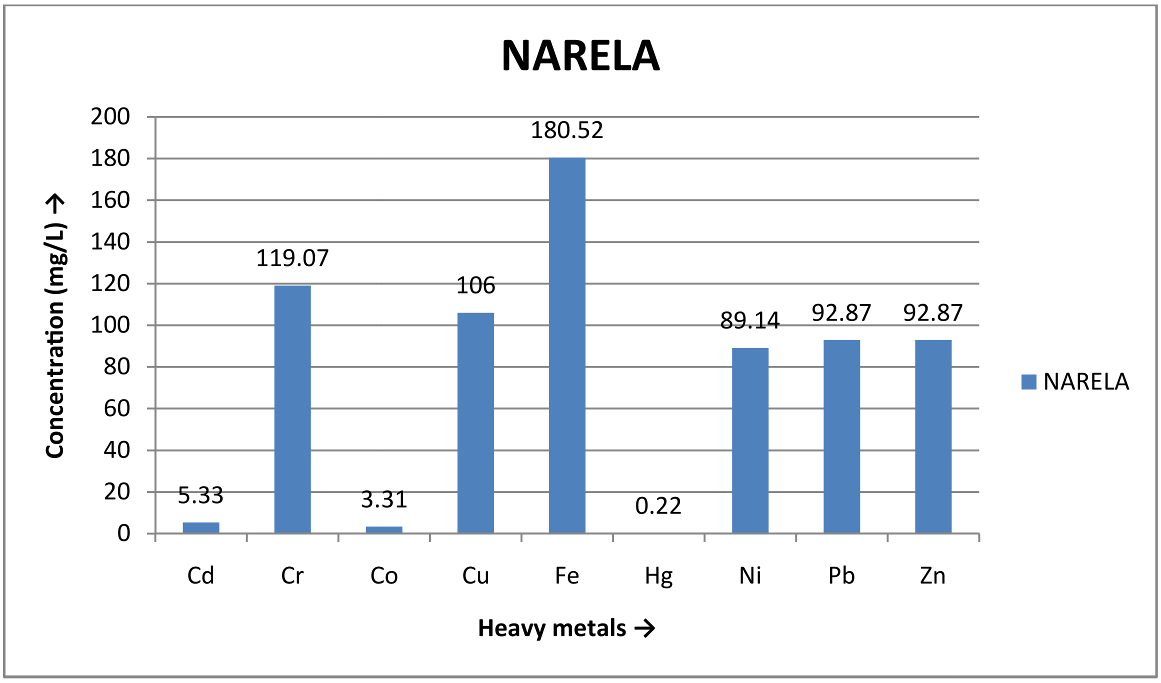


Figure 9: Mean Variation of Heavy Metals (mg/l) in Wastewater at Narela

It is generally observed that the availability of heavy metals in the aquatic systems often depends upon the pH among others.

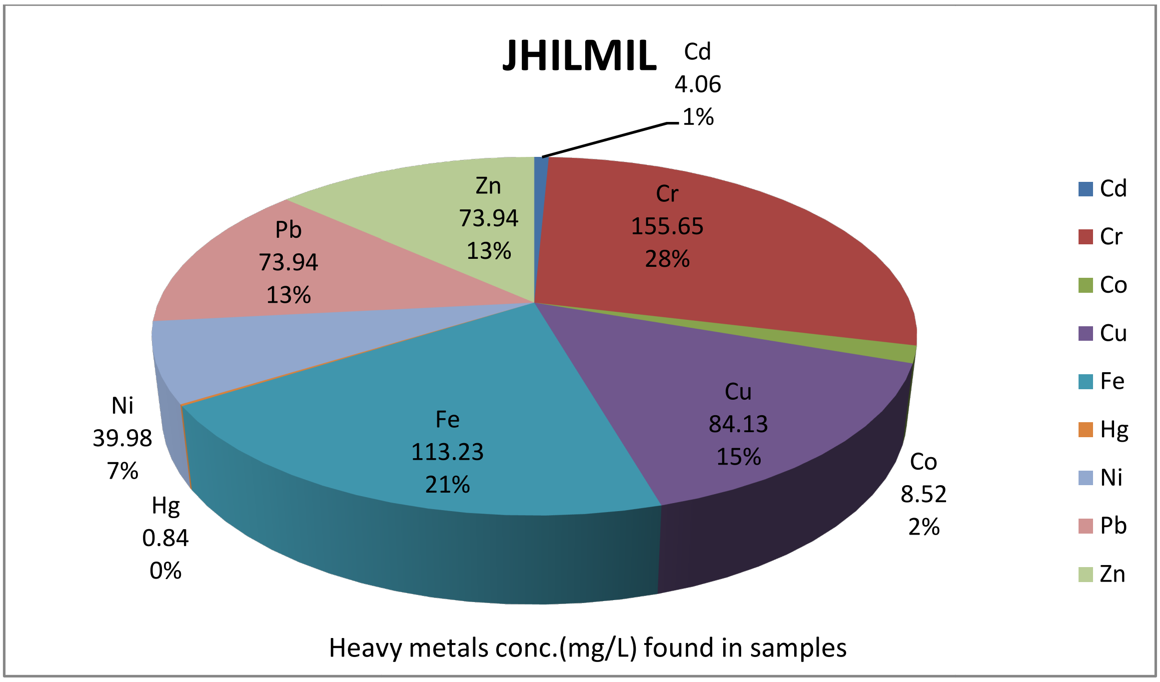


Figure 10: Order of higher occurrence of toxic metals at Jhilmil

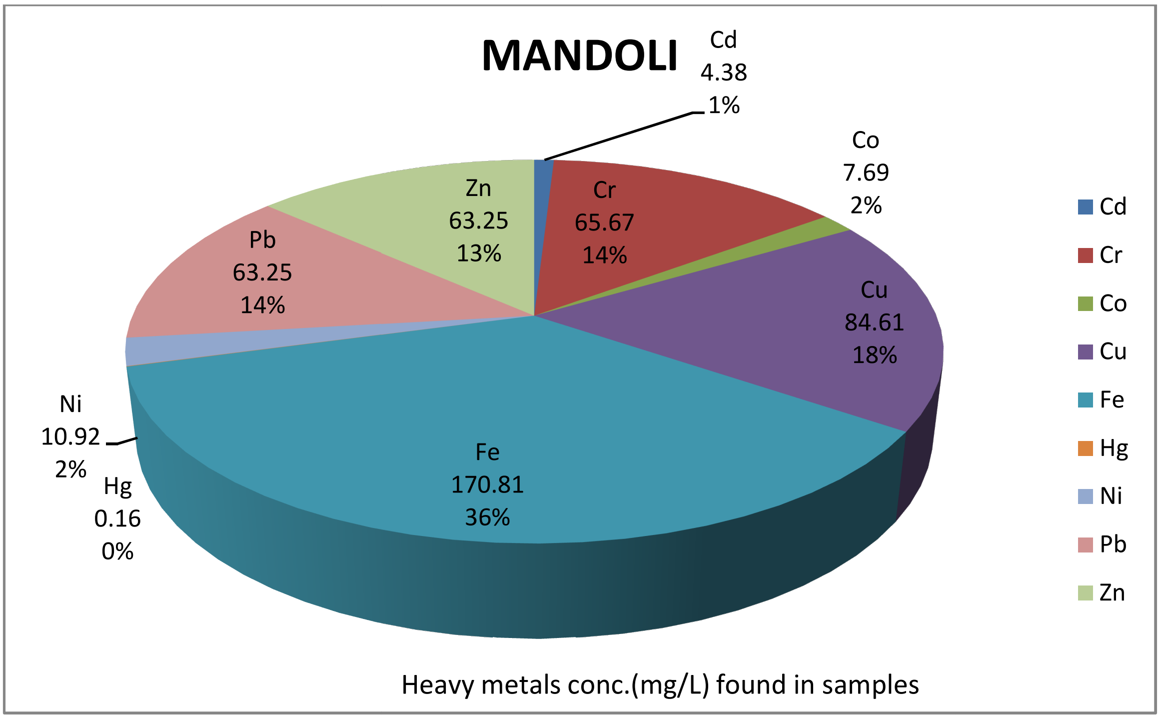


Figure 11: Order of higher occurrence of toxic metals at Mandoli

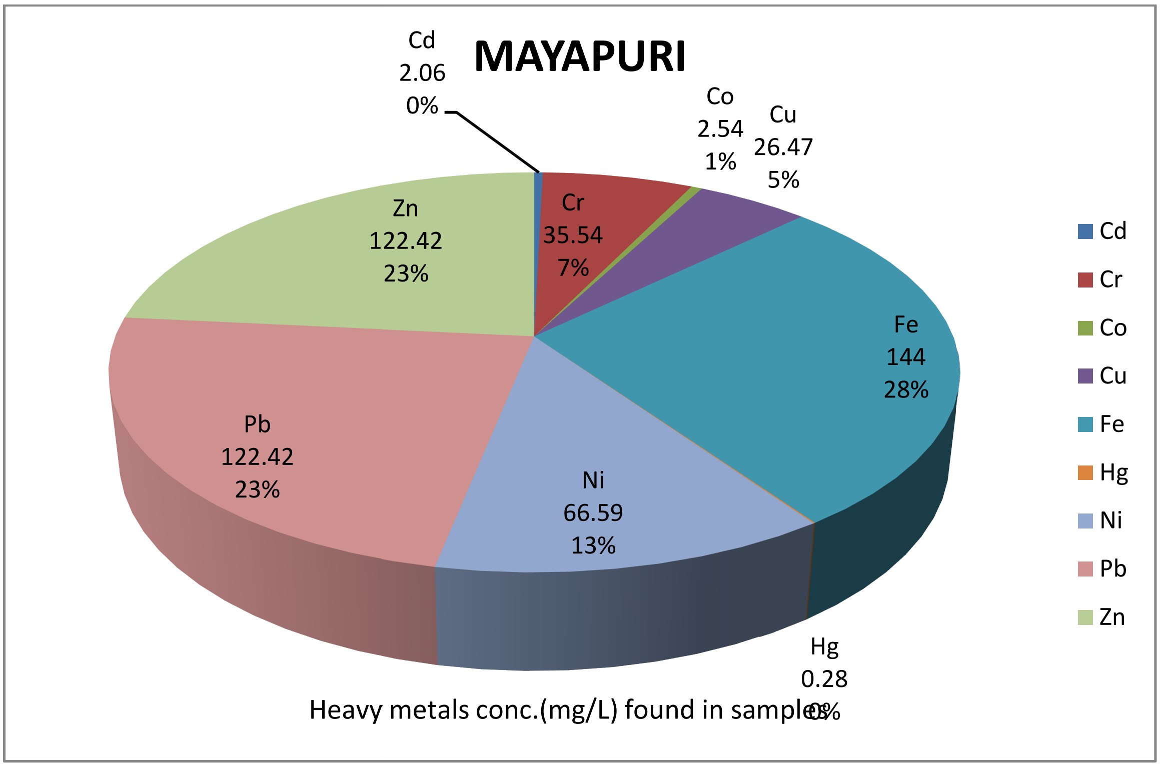


Figure 12: Order of higher occurrence of toxic metals at Mayapuri

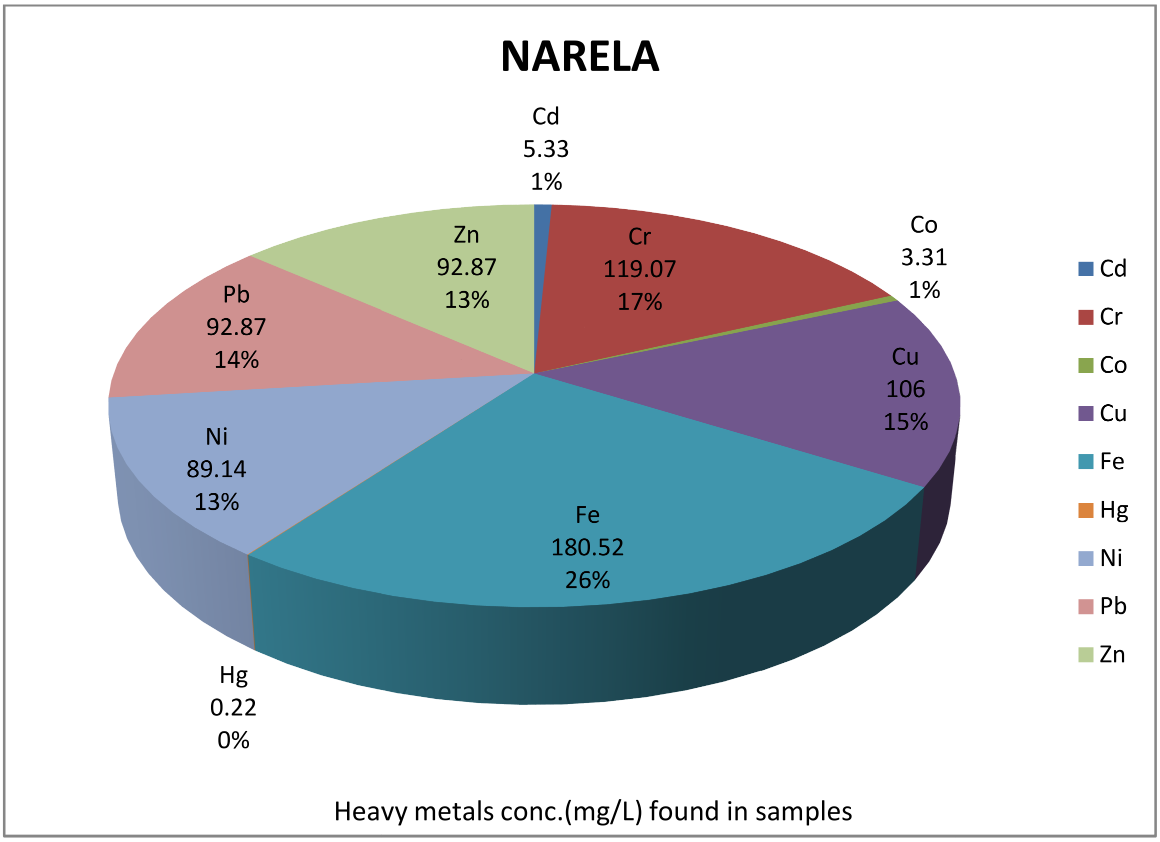


Figure 13: Order of higher occurrence of toxic metals at Narela

In general, the mean concentration of trace metals in the wastewater was higher in the samples from the Jhilmil as compared with those from the other industrial sites of Mandoli, Narela and Mayapuri .This trend was consistent throughout the season of autumn. Similarly, it was also observed that most samples with high metal concentrations had a low to neutral pH (3.3 - 7.0) range. This was shown also to be the case with samples taken in autumn season, from all the industrial zones under this study. Waste water samples taken during the autumn season were found to have higher contents of Metals especially those from Jhilmil industrial area. It may be noted that while low pH generally leads to high dissolution and hence more mobility of heavy metals, also the amount of metal mobilized also depends upon the waste material. Initial low metal contents in the liquid waste discharge would yield in lowered metal concentrations in the samples, irrelevant of the pH of the sample was acidic in nature.

Thus, ultimately depending on the amount of heavy metal ions present in the ecosystem, also low pH values tend to lead to the greater dissolution of metals, leading to the higher bioavailability in the aquatic system. This was best collaborated with the results obtained in Appendix 7a. For instance, samples from the Jhilmil with a pH range of 2.6-3.9, showed much higher metal concentrations in comparison with those samples with the neutral or basic pH ranges. This trend was already duplicated in the other sampling sites in all the industrial areas. Similarly, there was no so much significant variation in the total concentrations of the heavy metals during the autumn seasons.

6.3. General discussion

Contamination of all type of heavy metals in the environment is now of high concern because of their toxic nature and threat to human life and the environment (Mac and Rao 1997). The intensity to which a metal becomes more toxic depends upon the amounts already present as well as the other forms in which they generally occur. The chemical complex determine the metal behavior in the ecosystem as well as its re-mobilization ability. Thus, the use of the concentration can give an indication on potential mobility and bioavailability.

Also, in most of the time ,a significant proportion of the metals was associated with the non-residual phase. That was suggestive of significant anthropogenic inputs, especially as indicated by the high levels in the potentially mobile complexes associated with the exchangeable, carbonate-bound , water-soluble, and oxides. In general, the waste from Jhilmil industrial site had relatively high. However, there was substantial proportions of the elements in the exchangeable as well as carbonate-bound forms in the waste water from Jhilmil and Narela industrial sites. As well as ,while Cobalt toxicity to plants and animals is relatively low, the environmental threat of Cadmium is well known. Thus, the level of Cadmium in the relatively mobile and available forms far exceeds than 0.6-1.1 mg/ Kg levels in the itai-itai case in Japan.

CHAPTER 7.0 GENERAL DISCUSSION & CONCLUSION

The most importance of undertaking trace or toxic heavy metal studies has been underlined by the Nriagu(1988), who clearly observed that mostly developing countries (including India) have become the major producers of non-ferrous metals i.e. heavy metals, with many industries tending to be more dirtier, and employing less stringent environmental control measures like compared with the majority of developed countries. He also argued that major part of population in developing countries are likely to be more and more susceptible to the environmental metal pollutants as a planned result of:

(i) The high population density with poor hygienic conditions in mostly in crowded cities,
(ii) The preponderance of the major groups considered to be most at risk, specially children and pregnant women
(iii) Poor nutritional & health status
(iv) Consumption of major proportion of foods grown locally in the already metal contaminated areas. It may also observed that other endemic health problems can also make an influence the severity of the metal toxicity in the developing countries.

The aim of this present study was only to investigate the distribution of heavy metals in the liquid waste water released from the selected industrial sites in the NCT of Delhi. In addition to this, since effluent standards are also laid by CPCB, so the overall comparison of these metal parameters are also shown.

In general, we found that there was a little variation of pH in the wastewater was in moderately basic (PH 8.57). The majority of the wastewater samples however, had pH near above the neutral range. High pH was in many cases associated with higher levels of heavy metals. This was to be expected, since high pH often leads to higher dissolution and hence higher mobility and bioavailability of metals. Overall, Jhilmil had higher concentrations of Cr, Co, Hg in wastewater compared with the other industrial areas in the study. This was suggestive of the presence of both ferrous and non-ferrous based industries, including Cr and Zn plating and battery manufacturing activities. There was no significant variation of heavy metals in wastewater within the individual industrial areas.

The mean annual fluxes of heavy metals showed that Mayapuri discharges the highest proportions of Cr, while Jhilmil generates more Cr, Co, Hg, with Narela having a somewhat higher levels of Cd, Cu, Fe, Ni, Pb in the wastewater. In addition, it was observed that there was anomalously high Ni fluxes in the wastewater of the major canals draining the industrial sites and the Yamuna river water. In view of the comparatively lower levels of Ni in the wastewater and suspended matter within the industrial sites, it was speculated that additional Ni discharge from other industrial sites might be responsible for the high fluxes.

Table 15: Some Hazardous Materials in Industrial Waste Stream (USEPA 1979)

	As	Cd	Cl-H*[1]	Cr	Cu	CN	Pb	Hg	Other Organics*[2]	Se	Zn
Mining & Metallurgy	X	X		X	X	X	X	X		X	X
Paints & Dyes	X	X	X	X	X	X	X	X	X	X	
Pesticides	X		X			X	X	X	X		X
Electrical & Electronic			X		X	X	X	X		X	
Printing & Duplicating	X		X	X	X		X		X	X	
Electroplating & Metal Finishing				X	X	X				X	
Chemical Manufacturing			X	X	X			X	X		
Explosives	X				X		X	X	X		
Rubber & Plastics			X			X		X	X		X
Batteries		X					X	X			X
Phannaceuticals	X							X	X		
Textile				X	X				X		
Petroleum & Coal	X		X				X				
Pulp & Paper								X	X		
Leather				X					X		

*1 = Chlorinated hydrocarbon

*2 = Aerolein,chloropicerin,dimethyl sulphate,dinitrobenzene,dinitrophenol,nitroanaline and pentachlorophenol

While the suspended matter from Jhilmil had higher mean concentrations of Cu and Zn, Mayapuri had higher levels of Cr, Mn and Fe and Patparganj had Cd and Ni. This to a large extent reflects on the industrial activities taking place in these areas. Also, there was no significant seasonal variation of heavy metal levels in all the industrial areas. However, Jhilmil exhibited higher metal levels during monsoon and autumn compared with the summer. This was not duplicated in the other industrial areas.

The environmental effects and toxicity of heavy metals and metalloids to plants and animals is well documented. The mean concentration range of most of the metals in the solid waste was between 10mg Kg-I and 10000 mg Kg-I, with a few going beyond this mark. There are often no standards that are universally applicable to all situations in all countries, however, the high levels of metals observed in the waste from these industrial areas suggest that there is a real potential threat to the environment. This was compounded by the sometimes low pH levels observed in some of the waste, which may lead to the dissolution of the metals, thus enhancing their mobility and bioavailability. Haphazard disposal of the solid waste. On road sides and in some cases, low lying areas and unscientifically engineered landfill sites may result in the leaching of these metals, thus threatening both plant and animal life.

The spatial distribution of heavy metals in the solid waste showed that Jhilmil had higher mean levels of Cu and Hg, while Narela had Cd and Zn, and Mayapuri had Pb, Ni, Cr, Fe and Co compared with the other sites. There was however, no significant seasonal variation of heavy metals in all the industrial areas under this study. This was to be expected since the industrial processes within the industrial units are often carried out independent of the seasonal changes. Thus, while the type of waste generated from different industrial units reflect on their individual activities, the nature and quality of the waste may remain basically the same throughout all seasons.

The heavy metals in the solid waste and bed residues from selected sites in the NCT of Delhi were sequentially extracted in order to estimate the forms in which they were present. The study demonstrated that these metals were mostly associated with the residual phase, which possibly consisted of detritus silicates and perhaps resistant synthetic materials from the industrial processes. It was also noted that in general, the residual fraction in the solid waste was comparatively higher than in the bed residues.

There was however, evidence of substantial anthropogenic fluxes indicated by the relatively high mean levels and proportions of the potentially mobile forms associated with the water- .soluble, exchangeable, carbonate-bound and Fe-Mn oxide fractions. The solid waste from Jhilmil and Mayapuri had a significant proportion of Cu in the carbonate bound fraction respectively. On the other hand, there was a substantial amount of exchangeable carbonate and Fe-Mn oxides of Zn in solid waste from Mayapuri. High levels in these fractions pose a serious threat to plants and animal life in the aquatic and other systems.

In order to estimate the impact of phosphorus, it was necessary to obtain information about the magnitude of flux and its geochemical reactivity within different chemical composition. Thus, five pools of phosphorus were isolated. The mean levels of phosphorus were. It was also noted that the antigenic carbonate fluoro apatite fraction was the most dominant fraction both in the solid waste and in the bed residues. This fraction consists of the active phosphorus pool that often acts both as asource and sink of phosphate. It has also been reported (Subramanian 1999) to be dominating the Yamuna river sediments which receives large quantities of urban and industrial effluents from the NCT of Delhi.

In the same way, it has been well recognized that suspended sediments incorporate metals, attaining 3 to 5 orders of magnitude (Bryan and Langston 1992) compared with the overlaying water column. With such high concentrations, the bioavailability of even a small fraction of the total sediment metal assumes considerable importance, especially in some filter feeding and burrowing organisms. Also, several metals, including Hg and Pb may be transformed in sediments to organ metallic compounds having increased bioavailability and toxicity. The results of the present study indicate that the mean concentration of heavy metals in suspended matter was high compared with the levels in the bed residues. This was to be expected, since suspended matter has a much larger surface area and are therefore more reactive compared with the bed residues.

These levels were significantly high and may be indicative of high anthropogenic input from urban, industrial and agricultural sources. Balchand and Nair (1994) also reported similarly high phosphorus levels in recently deposited sediments of a tropical estuary. Fractions associated with Fe and organics in both solid waste and bed residues were comparatively lower than all other phosphorus phases.

In conclusion, the results presented in this thesis exhibited low pH, high metal levels in waste water, suspended matter, bed residues and solid waste. This was indicative of high anthropogenic input of heavy metals from ferrous and non-ferrous metal based industries among others. It was also reflection of the inefficient technologies and processes employed in these industrial sites, giving rise to high waste generation.

Similarly, sequential extraction showed that there were significantly high levels of heavy metals in the potentially mobile and bio-available non-residual phases that would seriously threaten the aquatic environment and the livelihood of millions of people down stream. It was also observed that there were elevated annual heavy metal fluxes in the wastewater and suspended matter from the selected industrial sites and a few major canals draining the industrial belt of the NCT of Delhi. Indeed, high Ni levels in wastewater and suspended matter, and the anomalously high annual fluxes from these canals suggest that there may be other sources of discharge apart from those used in the present study. It should also be noted that the study covered 4 sites out of over 28 industrial areas. Thus, in order to build a database, on the heavy metal discharge from the industrial belt of the NCT of Delhi, it would be necessary to critically carry out a systematic study of the remaining sites. This will be useful in the overall assessment of the quantities and the potential threat posed by toxic heavy metals discharged on to the terrestrial and aquatic systems in and around the NCT of Delhi.

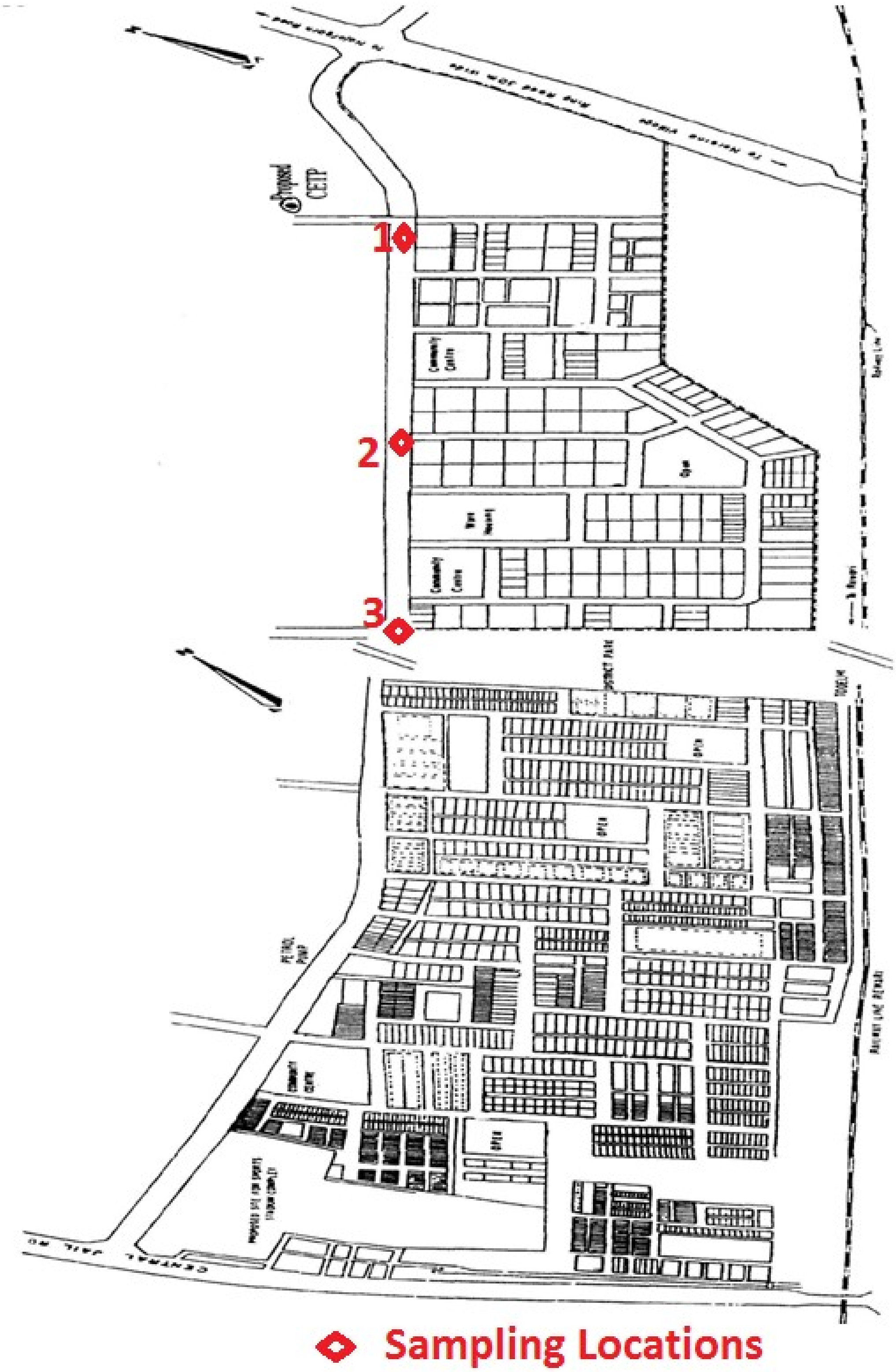
CHAPTER 8.0 RECOMMENDATIONS & FUTURE SCOPE

Based on the evaluation of the results extracted from the comprehensive analysis of the waste water samples, it is highly recommended that the heavy metals in the waste water samples can be monitored at least three or four times during the year for example one in the periods of pre-monsoon and second one in monsoon and then in post monsoon for continuously at least 10 years at all the major industrial water discharge points which are identified as **CONTAMINATED** in this report. Only long term monitoring can help in ascertaining the exact reason for the pollution and in suggesting suitable remedial measures.

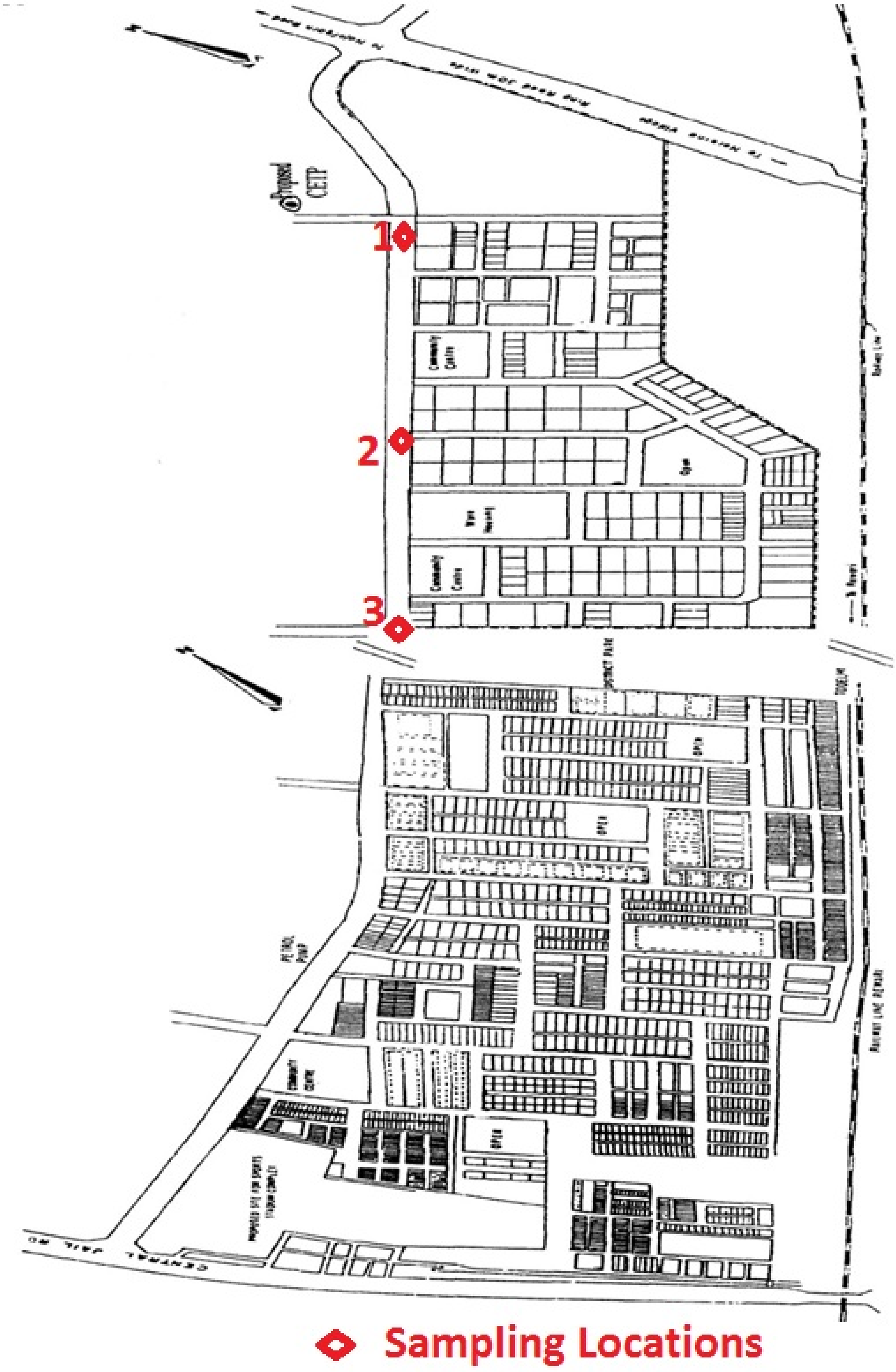
Special studies for the particular stretches of the industrial sewage receiving water body may also be undertaken mostly suitable by the concerned organization. The number of the parameters and also the frequencies of sampling can be further increased for more better observations, interpretation and modeling purposes also, for the other important parameters such as some biological parameters.

APPENDICES

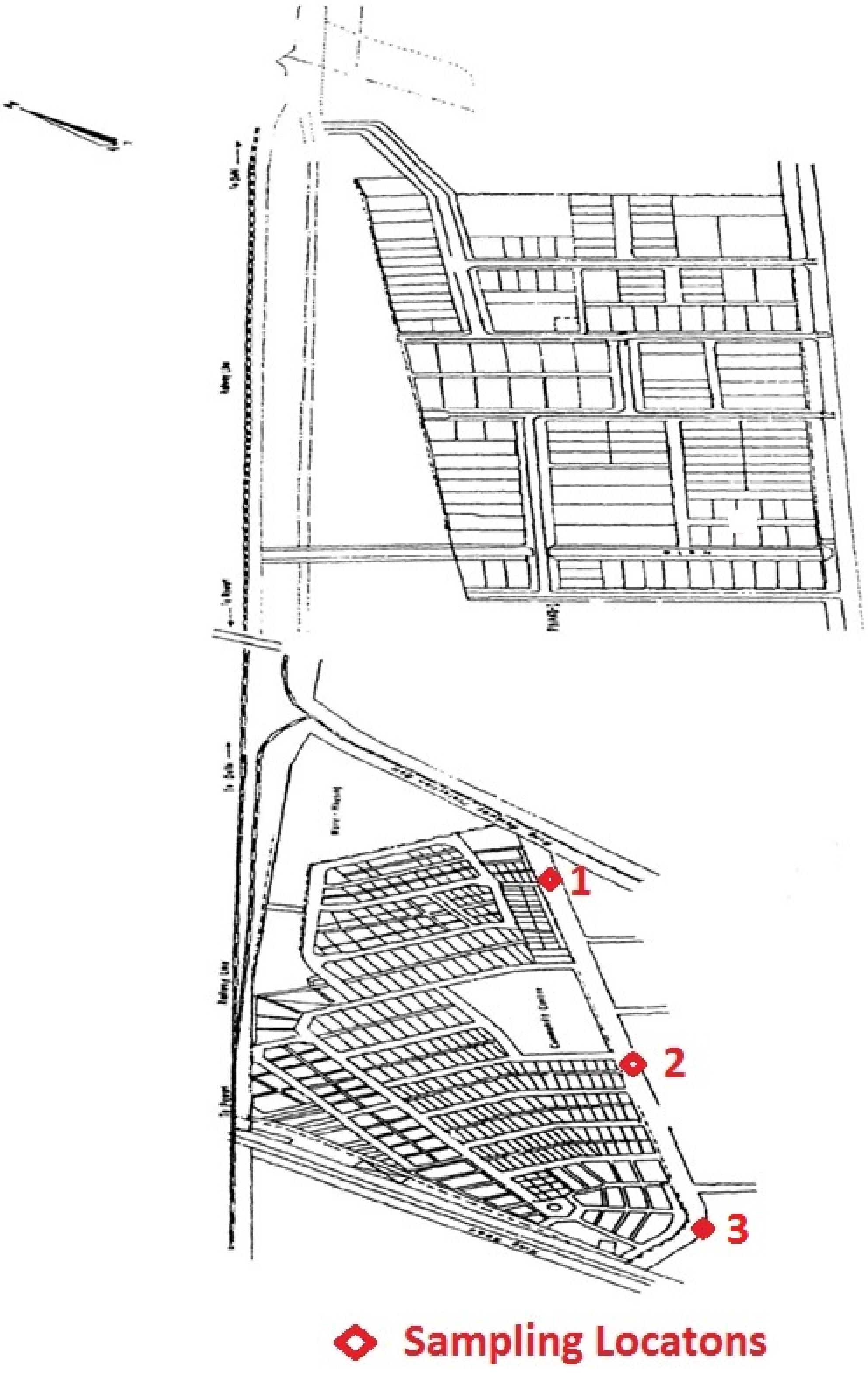
Appendix 1: Ground Map of Jhilmi1 Industrial Site



Appendix 2: Ground Map of Mayapuri Industrial Site



Appendix 3: Ground Map of Mandoli Industrial Site



Appendix 4: Distribution of Some Physico-Chemical Parameters in Wastewater

Serial No.	Site Ref:	pH	EC(mS/cm)	Cl^{-1} (mg L^{-1})	NO_3^{-1} (mg L^{-1})
1	JIL-1	7.95	3.53	728.0	238.0
2	JIL-2	7.52	3.89	848.0	314.0
3	JIL-3	8.15	4.41	1062.0	227.0
	Mean	**7.87**	**3.94**	**879.0**	**260.0**
1	MAY-1	8.60	6.38	1662.0	634.0
2	MAY-2	8.17	5.95	1597.0	745.0
3	MAY-3	8.94	6.19	1745.0	643.0
	Mean	**8.57**	**6.17**	**1668.0**	**674.0**
1	NAR-1	7.42	4.52	1553.0	539.0
2	NAR-2	8.05	4.19	1482.0	632.0
3	NAR-3	7.85	4.84	1545.0	593.0
	Mean	**7.77**	**4.52**	**1527.0**	**588.0**
1	MON-1	7.11	2.71	362.0	263.0
2	MON-2	7.96	1.95	319.0	232.0
3	MON-3	7.62	2.39	378.0	254.0
	Mean	**7.56**	**2.35**	***353.0***	***249.0***

Appendix 5: The wavelength & slit used for quantitative analysis by AAS

Sr.	Parameter	Wavelength(nm)	Slit(nm)
1	Cadmium	228.8	1.0
2	Chromium	357.9	1.0
3	Cobalt	240.7	1.0
4	Copper	324.7	1.0
5	Mercury	253.7	1.0
6	Iron	248.3	1.0
7	Lead	283.3	1.0
8	Nickel	232.0	1.0
9	Zinc	213.9	1.0

Appendix 6: Heavy Metal Concentration (mg/L) in waste water samples

Site-sample	Co	Cd	Cr	Cu	Ni	Pb	Hg	Zn	Fe
JIL-1	9.48	3.81	152.43	87.10	37.68	29.83	0.89	74.86	113.68
JIL-2	7.56	4.62	141.67	72.67	43.54	33.53	0.79	69.63	126.33
JIL-3	8.53	3.76	172.85	92.63	38.73	36.39	0.84	77.32	99.67
Mean	**8.52**	**4.06**	**155.65**	**84.13**	**39.98**	**33.25**	**0.84**	**73.94**	**113.23**
MAN-1	7.82	3.94	61.03	91.72	8.69	15.32	0.13	60.38	180.43
MAN-2	6.62	4.87	76.63	83.76	10.63	19.43	0.19	56.65	172.64
MAN-3	8.63	4.32	59.34	78.34	13.43	9.32	0.16	72.73	159.36
Mean	**7.69**	**4.38**	**65.67**	**84.61**	**10.92**	**14.69**	**0.16**	**63.25**	**170.81**
MAY-1	2.63	1.67	26.40	24.04	75.25	21.73	0.39	114.86	122.81
MAY-2	1.27	2.89	38.56	36.72	56.79	36.73	0.25	132.63	152.76
MAY-3	3.72	1.63	41.65	18.65	67.73	37.34	0.19	119.76	156.43
Mean	**2.54**	**2.06**	**35.54**	**26.47**	**66.59**	**31.93**	**0.28**	**122.42**	**144.00**
NAR-1	4.07	5.21	99.10	105.46	80.51	48.92	0.23	91.42	195.37
NAR-2	2.53	4.34	123.43	92.87	98.34	63.24	0.09	82.54	167.25
NAR-3	3.34	6.45	134.67	121.48	88.56	54.65	0.34	104.65	178.94
Mean	**3.31**	**5.33**	**119.07**	**106.60**	**89.14**	**55.60**	**0.22**	**92.87**	**180.52**

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