PROBABILISTIC RISK ASSESSMENT APPROACH IN METAL CONTAMINATED SOIL AND GROUNDWATER

Ph.D. THESIS

by

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
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A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree

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by

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled "**PROBABILISTIC RISK ASSESSMENT APPROACH IN METAL CONTAMINATED SOIL AND GROUNDWATER**" in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the Department of Paper Technology of the Indian Institute of Technology Roorkee, Saharanpur Campus is an authentic record of my own work carried out during a period from January, 2013 to February, 2019 under the supervision of Dr. Chhaya Sharma, Associate Professor, Department of Paper Technology, Indian Institute of Technology Roorkee, Saharanpur Campus, Saharanpur.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institution.

(VIVEK KUMAR GAURAV)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(Chhaya Sharma)
Supervisor

Date:

I dedicate this thesis to my parents for making me who I am

ABSTRACT

Rapid industrial expansion along with urbanization and intensive agriculture without adequate environmental management strategies leads to a significant enrichment of contaminants in the ecological system. Heavy metal contamination in natural matrixes (soil or groundwater), whether through natural weathering, anthropogenic activities, or both, had been the concern of many researchers because of their potential toxicity, persistence, and high bio-accumulative tendency. The soil is the ultimate and the crucial sink of trace elements in the terrestrial environment. Soil has a great capacity for absorbing, decomposing and remediating wastes and pollutants of different kinds.

Unmanaged disposal of industrial and domestic wastes, long span wastewater irrigation, atmospheric decompositions, leaching from landfills etc. leads to a substantially high buildup of heavy metal concentration in the soil and further percolation in the groundwater plume. Plants are the major carriers of heavy metal from soil to human. Therefore, the presence of metals in the soil is important in the chemistry of plants and in human health as well. High buildup of heavy metals in environmental system has important repercussions for the environment and human health, thus it is essential to identify the potential of a source to introduce risk associated with metal contamination into the environment, estimated amount of risk agents that have come to contact with the human-environmental boundaries and quantifies the health impact of the exposure.

Heavy metal distribution was analyzed in the soil of three industrial zones of Saharanpur district of India, viz. Pilakhni, Nanauta and Railway Road. The mean concentration ($mgkg^{-1}$) of As, Cu, and Pb were observed to be maximum (22.10±9.68, 88.4±21.68 and 40.50±14.90 respectively) in Pilakhni industrial area; Cd (1.98±0.79), Cr (92.10±42.39) and Zn (97.04±33.07) in Nanauta; whereas, Ni (95.38±48.13) was observed maximum at Railway Road industrial area. Geo-accumulation index (I_{geo}) reflects moderate to high contamination of Cu, Pb, Cr, Ni, and Zn, whereas, high enrichment and contamination factor were observed in As and Cd in all three industrial areas. Health risk due to exposure of metal was potentially high in the children in comparison to adults in the study area.

High metal contamination was observed in the groundwater sample collected from Pilakhni followed by Nanauta and Railway Road industrial zones. Maximum groundwater contamination of As (84.4 μgL^{-1}), Cr (123.3 μgL^{-1}), Mn (703.5 μgL^{-1}), Pb (44.1 μgL^{-1}), Zn (288.8 μgL^{-1}) were observed in Pilakhni; Cd (7.2 μgL^{-1}) and Cu (88.7 μgL^{-1}) in Nanauta and Ni

(88.2 μgL^{-1}) was observed in the Railway Road area. Health risk via oral pathway was assessed in both adult and children population. Non-carcinogenic risk (HQ) value was observed to be > 1.00E+00 for As and Cr contamination in both adult and children population in Pilakhni and Nanauta area indicating high non-carcinogenic risk. Cancer risk associated As contamination observed to be potentially high (> 1.00E-03) in all three industrial zones in both adult and children population in the study area.

The present study also indicates the status of metal contamination in the vegetables/crops grown in the uppermost Ganga-Yamuna doab region of India and associated health risk. Commonly grown vegetables and crops were sampled and analyzed for metal contamination. Maximum concentration (mg/kg) of Cd and Cr, was observed in Radish (7.6) and Cabbage (56.24) respectively, whereas the maximum concentration of Pb, Ni and Zn were observed in the edible parts of Mustard plant (95.4, 58.6, 756.43 respectively). Bio-concentration factor (BCF) value indicated the transfer level of metal from soil to crop; indicated high transfer value of Cd in Radish followed by cabbage and spinach. Considerably high BCF value was observed in the Mustard (8.13), Cabbage (4.18) and radish (3.07) for Zn contamination. Estimated daily intake (EDI) and Hazard quotient (HQ) or Non-carcinogenic health risk was calculated using the USEPA method. The result revealed that the metal intake and associated health risk was considerably high in the children population in comparison to the adult population. The fuzzy-based aggregate risk assessment revealed a high risk of cadmium and arsenic toxicity in the study area with the risk score of 0.751 and 0.698, respectively. The fuzzy-based risk assessment is a conceptual methodology that restricts the vagueness in the estimation of risk for better decision-making approach. Probabilistic risk estimation by Monte Carlo simulation on iterating the Risk assessment expression for 10,000 trials inferred high risk in children population for Cr and As contamination.

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(**VIVEK KUMAR GAURAV**)

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LIST OF ABBREVIATIONS

USEPA	United States Environmental Protection Agency
ICP	Inductively Coupled Plasma
OES	Optical Emission Spectroscopy
SRM	Standard Reference Material
OM	Organic Matter
TN	Total Nitrogen
EC	Electrical Conductivity
WHO	World Health Organization
BIS	Bureau of Indian Standards
Min	Minimum
Max	Maximum
SD	Standard Deviation
dS/m	deci Siemens per metre
NTU	Nephelometric Turbidity Unit
DO	Dissolved Oxygen
COD	Chemical Oxygen Demand
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
PCA	Principal Component Analysis
PC	Principal Component
I_{geo}	Geo-accumulation Index
EF	Enrichment Factor
PERi	Potential Ecological Risk Index
C_f^i	Contamination Factor
C_{deg}	Contamination Degree

HQ	Hazard Quotient
UCL	Upper Confidence Limit
HCA	Hierarchical Cluster Analysis
BCF	Bio-Concentration Factor
ADI	Average Daily Intake
MSME	Ministry of Micro, Small & Medium Enterprises
DI	Daily Intake
EF	Exposure Frequency
ED	Exposure Duration
RfD	Reference Dose
AT	Average Time
FAO	Food and Agricultural Organization
BGL	Below Ground Level
T_r^i	Toxic Response
C_{deg}	Contamination Degree
MCS	Monte Carlo Simulation
PDF	Probability Density Function
PAHs	Poly Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
POPs	Persistent Organic Pollutants

LIST OF PUBLICATIONS/CONFERENCE PRESENTATIONS

- **Gaurav, Vivek Kumar**, and Chhaya Sharma. "Estimating health risks in metal contaminated land for sustainable agriculture in peri-urban industrial areas using Monte Carlo probabilistic approach." ***Sustainable Computing: Informatics and Systems* (2019)**. DOI: https://doi.org/10.1016/j.suscom.2019.01.012

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Other Publications:

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- **Gaurav, VK**, and Chhaya Sharma, "Heavy metal contamination and related risk in private and government installed handpumps. A comparative study in industrial area of Saharanpur district, India". International Conference on Water and Environmental Engineering (iCWEE-2017). Western Sydney University (Parramatta Campus), Sydney, Australia (2017).

- **Gaurav et al.,** "Fuzzy based probabilistic ecological risk assessment"**,** International conference on Soft Computing: Theories and Applications **(**SoCTA-2016), Jaipur, India, 2016.

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CHAPTER I

INTRODUCTION

1.1. OVERVIEW OF HEAVY METAL

Heavy metals are the group of metals with the atomic weight ranges from 63.5 and 200.6 $gmol^{-1}$, low density, highly toxic and having specific gravity more than 5g cm^{-3}. Heavy metals are biodegradable and ubiquitous in nature and thus lead to the severe risk to human health and the environment, when available beyond the permissible limit. On the basis of toxicity evaluation of the heavy metals by the global agencies including United State Environmental Protection Agency (US-EPA), World Health Organization (WHO), Food and Agriculture Organization (FAO) etc., Cd, Pb, As, Cr and Hg metals are ranked in top 10 lists of the toxicity. Through alimentary chain, these heavy metals get accumulated in the biosphere and thus enters in the biological system.

Bioavailability of metal in soil exerts a critical impact on soil quality and resulting food production so it is important to assess metal contamination in industrial areas [1]–[4]. However, the sources of heavy metals in soil can be both geogenic and anthropogenic [5], [6] but the fraction of anthropogenic contamination is much higher than geogenic or natural contamination [7]. Several investigations were made in order to monitor and access both ecological and health related risks by toxic metal contamination in the terrestrial environment [8], [9]. Intensive use of chemical fertilizers has also been reported to contribute to metal contamination [10], [11].

Long term wastewater irrigation contributes to high metal enrichment in the soil which ultimately percolates and contaminate groundwater plume [12], [13]. The long-term impact of wastewater irrigation can be observed clearly in the study area in terms of health-related issues where the population is directly consuming groundwater through wells, tube wells, hand-pumps etc.

Metals can concentrate in algae and other lower plants which form the first level of food chains, leading to the risk that metals might pass through a food chain and end up in large organisms potentially including humans. They impact the biochemical life cycle by attaching with the thiol group of the protein. While some of these toxic metals (e.g. Cd, Hg, Pb) are nonessential in most organisms, some metals (e.g. Zn, Cu, Mn) are essentially required in micro-scale quantities as trace nutrients in plants and animals. These essential metals are involved in a broad range of biochemical pathways and play significant roles in cellular activities like enzyme catalysis, nutrition and osmotic regulation [14]–[16]. Trace metals also perform vital biological functioning of the cell including transportation and cell signaling. Nevertheless, toxicity is experienced when all of these metals are present at high concentration.

The acute or chronic exposure devoid metal ions to follow the mechanistic pathway, that results in the binding of metal ions with the regular protein and thus promoting toxicity to different live forms. The mechanisms involved in the proliferating toxicity include oxidative stress, enzymatic inhibition, and impairment of antioxidant metabolism. The free radicals generated by these mechanisms promote lipid peroxidation, DNA damage and protein sulfhydryl depletion [17].

1.2. OCCURRENCE, EXPOSURE, AND DOSE OF HEAVY METALS

1.2.1. Arsenic

Arsenic being a ubiquitous element, present in low concentration virtually in all matrices of the environmental system. Arsenic in inorganic state enters into the environment through varieties of anthropogenic activities including combustion of fossil fuel and coal, pharmaceuticals manufacturing and waste disposal, wood preservatives, and the use of pesticides [18], [19]. Arsenic-based pesticides like lead hydrogen arsenate, Calcium arsenate were extensively used in the past few decades, due to high persistent behavior of As, its bioavailability and impact is still a matter of concern. Exposure of As to the human is subjected to the ingestion and inhalation via contaminated soil. Accumulation of As in the food crop is not very frequent as the level of soil acidity require for the As mobility would not be suitable for the growth of the majority of food crops. Health-related problems associated with As exposure include skin lesions, multiple organ failure, and cancer. Skin lesions are the most prominent characteristics and a sign of As toxicity, skin undergoes pigmentation which is also called melanosis followed by keratosis of skin [20]. Organs which get affected on a cellular level include heart, lung, liver, kidney, and brain as well. As toxicity facilitate the release of reactive oxygen resulting in lipid peroxidation of a cell leading to cell death. The process of Lipid peroxidation induces oxidative deterioration of polyunsaturated fatty acids majorly required for the functioning of the cell. As toxicity also affect DNA repair mechanism which also results in inducing malignancy [19], [21], [22].

1.2.2. Cadmium

Cadmium is one of the highly toxic heavy metal that is found naturally in earth crust as cadmium sulfide (CdS). Cadmium shows limited abundance, comparing other heavy metals, ranging from 0.1 to 1 ppm of the earth's crust [23].

Cadmium is found associated commonly with metal ores such as Cu and Zn, and it enters in the urban environment through emission from smelting [24], [25]. The other anthropogenic sources include e-waste scraps, batteries, fertilizers and pesticides, combustion of fossil fuels, sludge from sewage or industries etc. [20], [26]. Use of Cd for the manufacturing of batteries increased drastically from 1970 to 2000. Because illegal dumping is a large issue in many urban areas, improper Cd battery disposal adds to the Cd soil accumulation [27]. A human can be exposed to the Cd via ingestion of soil particle, contaminated dust inhalation and intake of crops grown in contaminated soil. Cd possesses high bioaccumulation ability and research inferred that food is the major pathway [28]. Bio-concentration factor is affected by Cd mobility and bioavailability, thus soil with low pH may facilitate to high Cd toxicity in the surrounding population. Exposure of Cd to the human is pernicious in both chronic and acute exposure. Metabolization of Cd is not possible in the human body so it accumulates in organs like kidney, brain, lungs, liver and nervous system. Cd accumulation leads to organ failure by affecting cellular mechanism. Cd ions replace essential metal ions and enter into the cell and disrupt the cell functioning. Cd competes and replace Fe and Cu in cytoplasmic membrane and induces oxidative stress in a cell leading to cell death and organ failure. Chronic exposure leads to malignancy [20].

1.2.3. Copper

Copper (II) ions mainly present in the wastewater generated by metallurgical and mining industries. It is one of the essential nutrients required in trace amount for the growth and development of higher plants and animal. Reactive oxygen species (superoxide, hydrogen peroxide, the hydroxyl radicals) are generated by free cupric ions, that induces lipid, proteins and DNA damage. Symptoms of acute copper (II) ingestion include low blood pressure, nausea, gastrointestinal problem etc. Toxicity of copper at a chronic level in human is not common due to absorption and excretion regulated by the transport mechanism of the body. However, on chronic exposure, liver and kidney may get severely affected. Prolong exposure may lead to autosomal recessive mutation, also called Wilson's disease associated with copper bioaccumulation and liver cirrhosis in persons inherited with two defective genes [29].

1.2.4. Chromium

The two stable oxidation state in which Chromium exists in the environment are Cr (III) and Cr (VI). Chromates and di-chromates oxy-anionic species forms of Cr (VI) is readily soluble, resulting in mobility and bioavailability under alkaline to slightly acidic condition ensuing high toxicity. Among, different industries Leather tanning industries are known for contributing Chromium in the environmental system. The process involves in the tanning of leather requires Chromium sulfate salt ($Cr_2(SO_4)_3$), in this process 20-40% of chromium goes into the wastewater. In mammals, Cr (III) contributes to maintaining effective glucose, metabolism associated with lipid and protein. On the other hand, whereas, Cr (VI) is noxious for the biological systems [30]–[33].

Chromium is hydrophilic and possesses oxidizing potential and biological membrane permeability, thus it is highly toxic and shows irritative behavior on human skin [20]. Chronic exposure cause kidney and liver failure, chromate dust is a well-known carcinogen.

1.2.5. Lead

Lead is cationic, naturally occurring metal, found associated with different metals like oxygen, sulfur etc. Pb is used in a variety of industries including mining, battery, leaded paint, leaded gasoline, ammunition production etc. that makes Pb fifth most industrially produced metal. The past overuse of leaded paint and leaded gasoline emissions are the major sources of topsoil contamination [34]. Extensive usage of Pb paint for additional paint pigmentation and enhanced paint flexibility and durability, use of Pb in the form of tetraethyl-Pb, an anti-knock agent in gasoline severely impacted the overall enrichment of Pb in the environment. there is no metabolic use of Pb so once exposed it accumulates in the human body. Chronic exposure may lead to a high level of lead in blood. Pb accumulation in body severely impacts the brain and kidneys leading to the organ failure, other known negative impact includes cardiovascular, renal, and hepatic systems disorders, increase bone deterioration, and diminished IQ [35]. Likewise, other heavy metals, Pb induces oxidative stress that damages cellular components by forming Reactive Oxygen Species (ROS) and reduces the cell's pool of antioxidants. Pb suppress the enzyme glutathione reductase (GR) activity which facilitates the production of antioxidants as well responsible for inhibiting ∂-aminolaevulinic acid dehydrogenase (ALAD). The absorption rate of Pb in adults is less than 5% comparing 50% in children, thus making children more sensitive toward Pb exposure. Pb toxicity in children promotes severe mental problems including a low IQ and attention deficit disorder [17], [34], [36].

1.2.6. Nickel

Nickel is the fifth most abundant element by weight, constituting about 3% of the earth's total composition. Natural sources of Ni include mass forest fires, volcanic emissions and windblown dust, whereas, the anthropogenic activities include fossil fuel combustion, the incineration of waste and sludge, excessive use of phosphate fertilizer etc. [37]. Industrial emission of Ni has observed to be more than 100 folds than that of geogenic sources [38].

1.2.7. Zinc

Zinc in trace concentration is essential for the growth and development of plants and animals. However, potentially harmful when present in excessive concentrations or beyond the threshold limits. The major anthropogenic sources include industries and the application of liquid manure, composted materials, chemical pesticides and fertilizers in the agriculture. Zinc mobility in the soil is quite high in the soil [39], [40]. And the other factors that affect the Zinc enrichment in the soil are weathering of the matrix, atmospheric precipitation, decomposition of living matter and wastewater irrigation. Importance of zinc (Zn (II)) in the human body can be can be understood from the fact that more than twenty metalloenzymes, including many that are active in nucleic acid metabolism. Excess oral exposure of Zn (II) may lead to acute gastrointestinal distress followed by nausea [41].

1.3. STATUS OF SOIL HEAVY METAL CONTAMINATION IN DIFFERENT PARTS OF INDIA

Industrial expansion in developing countries like India without adequate environmental management strategies is a serious concern. In the past 10 years, many new sites which are highly contaminated and were not previously reported came into the picture. This may support the fact that with the time there has been a considerable increase in the metal contaminated sites apart from the extensive research in this field. According to the literature available, most of the reported sites for metal contamination observed in the Uttar Pradesh state of India. Uttar Pradesh being one of the biggest and highly populated states comprises plenty of large, medium and small-scale industries. Cities like Kanpur, Varanasi, Ghaziabad, and nearby outskirt areas are well reported for industrial expansion and soil and groundwater contamination related issues. Agriculture is a major sector contributes around 17.4% of the total GDP of the Indian economy [42]. Availability of freshwater resources for irrigation and other agricultural related activities is quite limited in India, to counter this issue utilization of industrial wastewater, sewage and domestic wastewater are quiet popular alternatives. It has been observed that wastewater contains a substantial quantity of nutrients and organic matters that add to the overall N, P and other essential plant growth components [43], [44]. Apart from the nutrient enrichment, wastewater also contributes to the significant amount of organic and inorganic toxic entities from the industries and domestic wastes into the soil, which consequently leads to severe deterioration of soil and groundwater quality [12], [16], [45]–[49]. Some empirical analyses also indicated the translocation of heavy metal in the food chain via contaminated soil system[50], [51]. High enrichment of metal concentration in agriculture land leads to the transfer and accumulation of metal in food items like vegetables, crops, fruits, and fodders [12], [48], [52]–[55]. This soil-crop-food pathway is a major channel of metal exposure to human and thus crops grown in metal enriched land lead to the potential risk to human health [56]–[58]. Metal exposure more than chronic level via dietary intake or by any other pathways leads to severe health-related issues like gastrointestinal cancer, retardation, disability, immunological disorders, malnutrition etc [53], [59], [60]. The adverse impact of metal exposure on human health apparent after certain years, thus it's important to keep track on the sources, concentration and risk associated with the metal concentration [53], [61].

The recent literature survey based on the metal contamination in different parts of India infers that studies have been mostly conducted in the industrial area, wastewater irrigated area, mining fields, and dumpsites. Details related to the location, number of samples, depth, digestion method and analytical instrument used is briefly shown in Table 1.1.

The analyzed level of metal contamination in most of the samples was observed to be higher than the international threshold values. The status of heavy metal contamination in some mining areas of India has also been studied and the result revealed that most of the mining areas are highly contaminated. The heavy metal contamination in the agricultural soil around Singhbhum copper belt was observed to be higher than the world average value. High concentration of Pb, Zn, and Cr in the area has been subjected to activities related to copper mining and vehicular influences[8]. Another study in Jharia coalfield in the Jharkhand state of India inferred high enrichment of toxic heavy metals due to mining activities, fossil fuel burning and atmospheric depositions in nearby areas of coalfield [62]. The study carried out in the Naggihalli (Karnataka) around chromite mining areas, the detected level of toxic heavy metals was observed to be exceeding the international threshold limits [63]. In another study in a copper mining area in Khetri, Rajasthan; exceptionally high Cu enrichment was observed in the nearby soil, whereas the concentration levels of As, Pb, Ni, and Zn were observed around the copper mining area [15].

Many studies have also been conducted in different industrial areas of India in order to determine the level of heavy metal contamination. The study conducted in Kazipalli industrial area of Hyderabad revealed that due to unmonitored and unmanaged disposal of solid waste and wastewater metals, high enrichment of As, Cr, Cu, and Pb were observed in the soils of Kazipalli [64]. In one of the studies performed in the Ghaziabad district of Uttar Pradesh showed that overall mean concentration of Cu, Cr, Pb, Zn, and Ni was several folds higher than the prescribed international guidelines. Statistical analysis revealed that the concentration of Cd, Cr, and Ni in soil was due to anthropogenic influences whereas Cu, Pb and Zn have been subjected to the mixed origin [65]–[67]. The study conducted in Mandoli industrial area of Delhi evaluated the heavy metal contamination in the area. The unmanaged informal e-waste recycling and disposal contributed severely to the elevated levels of As, Cu and Pb contamination. The consumption of coal-based energy in thermal power plants are considerably high, a study based on the heavy metal analysis in the surrounding areas of Singrauli thermal power plant revealed that the mean concentration of As, Cd, Ni, and Pb was found to be maximum in post-monsoon season in comparison to the pre-monsoon season. The mean concentration of these potentially toxic metals was found higher than the prescribed international limits [68]. The Gangetic plain is the most fertile and densely populated region in Northern India, the leather industry situated in this area is considered as one of the most potential polluting sources. A large quantity of chromium based chemicals are used in tannery industries, thus high enrichment of Cr, along with other potentially toxic metals from vivid sources has been observed in the nearby areas [69].

Use of contaminated water or industrial wastewater for irrigation purpose results in substantial building up of metal heavy metals in the soil system. Continuous input of tannery industry wastewater in the agricultural field resulted in heavy enrichment of Cr in the industrial areas nearby Kanpur district [70]. The paper mill generates an enormous amount of wastewater and due to limited availability of fresh water for irrigation, use of industrial water as a primary water source for irrigation is quite common in the local farmers. Studies showed a high concentration of Cr, Cu, and Pb in the paper mill wastewater irrigated agricultural field. Paper industry involves multiple processes including pulping, screening, washing, bleaching de-inking etc., such processes involve substantial involvement of metals like Cr, Cu, Pb, and Zn [48], [71]. The study conducted in Umariya industrial area of Vadodara district revealed the influence of repeated wastewater irrigation from different types of industries including chemical, petrochemical, pesticide, pharmaceutical, agrochemical industries etc. the result showed substantial enrichment of As, Cd, Cr, Cu, Pb, Ni and Zn [52]. Multiple studies have been conducted in the nearby areas of Varanasi city and the impact of wastewater treatment on the soil quality and its uptake in crops was briefly discussed. The major input of heavy metal in the irrigation water stream was subjected to the sewage treatment plant, burning of fossil fuel, waste from local industries, atmospheric depositions etc. [21], [45], [72]–[75].

Table 1.1: Brief literature survey on soil heavy metal contamination in India and involved methodology

State	City/ Location	Type of Area	No. of Samples	Depth (cm)	Digestion	Instrument	Reference
Jharkhand	Singhbhum	Mining	48	0-15	USEPA 3052	ICP-MS	[8]
UP	Kanpur	WWI	17	0-15	Aqua regia	ICP-OES	[46]
UK	Lalkuan	WWI	24	0-15	Boric Acid	EDXRF	[71]
UK	Udham Singh Nagar	WWI	30	0-35	HNO_3+ HClO4	AAS	[48]
Maharashtra	Thane- Belapur	Industrial	15	0-15	HNO_3+ HF	ICP-AES	[76]
Andhra Pradesh	Kazipalli, Hyderabad	Industrial	45	10-15	Boric Acid	XRF	[64]
Jharkhand	Jharia, Dhanbad	Mining	75	0-15	HNO_3+ $HClO_4$	AAS	[62]
UP	Ghaziabad	Industrial	45	0-20	HNO_3 + H_2SO_4 + $HClO_4$	AAS	[66]
Delhi	Mandoli	Industrial	20	0-15	USEPA 3050B	AAS	[27]
Gujrat	Surat	Industrial	12		USEPA 3052	AAS	[77]
Haryana	Panipat	Industrial	9	15	HNO_3+ $HClO_4$	AAS	[78]
Karnataka	Nuggihalli	Mining	57	15	Boric Acid	XRF	[63]
UP	Ghaziabad	Industrial	42	0-20	HNO_3 + H_2SO_4 + $HClO_4$	AAS	[65]
UP	Varanasi	WWI	27	0-10	HNO_3 + H_2SO_4 + $HClO_4$	AAS	[75]
UP	Ghaziabad	Industrial	41		USEPA 3050 B	AAS	[67]
UP	Varanasi	WWI	49	22.5	HNO_3+ $HClO_4$	AAS	[16]
AP	Hyderabad	Dumpsite	45	35-40	Boric Acid	XRF	[5]
Gujrat	Umariya, Vadodara	WWI	30	0-20	$HClO_4$ + HNO_3	ICP	[52]
Maharashtra	Thane	Industrial	12	0-91.4	Aqua regia	ICP-AES	[79]

AP	Balanagar, Hyderabd	Industrial	16	10-50	Boric Acid	XRF	[80]
MP+ UP	Singraul + Sonbhadra	Industrial	256	0-30	HNO_3+ $HClO_4$	AAS	[68]
Rajasthan	Khetri	Mining	6	3-10	HNO_3+ $HClO_4$ + HF	INNA & AAS	[15]
UP	Jajmau + Unnao	Industrial	53	5-15	Boric Acid	XRF	[69]
UP	Dinapur, Varanasi	WWI	15	15	HNO_3 + H_2SO_4 + $HClO_4$	AAS	[2]
UP	Lohta, Varanasi	WWI		15	HNO_3 + H_2SO_4 + $HClO_4$	ICP-AES + MS	[45]
Punjab	Ludhiana	WWI	37	0-15	HNO_3 + $HClO_4$ + HCl	AAS	[81]
UP	Lohta, Varanasi	WWI	173	0-15	HNO_3 + H_2SO_4 + $HClO_4$	AAS	[82]

*UP= Uttar Pradesh; UK=Uttarakhand; MP= Madhya Pradesh; AP= Andhra Pradesh; WWI= Wastewater irrigation.

1.4. STATUS OF GROUNDWATER HEAVY METAL CONTAMINATION IN DIFFERENT PARTS OF INDIA

Groundwater is an irreplaceable resource for mankind as well as for all biotic components of the earth. The dependency on the groundwater is just not restricted to the drinking but also for innumerable applications. With the increasing pace of industrialization and urbanization, the severe impact has been observed in both quantity and quality of the groundwater. Unmanaged disposal of both industrial and domestic waste, agricultural runoffs has led the infiltration or percolation of contaminants to the plume of aquifers. Soil system act as geochemical sink and control transport of chemical entities in the aquatic environment; high enrichment of metal contamination in the soil substantially influence the quality of the groundwater. The deteriorating quality of groundwater in many cities of India is a matter of serious concern. It is evident from the previous researches, conducted in different parts of India that various anthropogenic activities severely impacting the quality of groundwater. The groundwater samples procured from the sources nearby tannery industries in Kanpur in a study showed significant contamination of Cr, while other metals were potentially close to the permissible limit [70]. The study conducted in industrial clusters of Jaipur city observed metal contamination in groundwater under permissible limits [83]. The groundwater sample taken from industrial areas nearby Haridwar district in a study revealed that Co, Cr, Ni, and Zn were observed in 94%, 98%, 90% and 99% of the samples respectively. The concentration of Co was reported higher than the prescribed permissible limit. The groundwater samples collected from goa mining areas from 45 locations, inferred that most of the samples were observed within the acceptable range except the elevated values of Fe indicating that groundwater is not critically contaminated in the mining areas of Goa [84]. Ghaziabad city is located in the vicinity to capital city Delhi, tremendous growth in industrialization and urbanization has been seen in the past few decades. The quality of groundwater was analyzed in a study that revealed all the samples were contaminated with As, Cd, Cr, Pb, and Ni and were well above the permissible limits, indicating potentially harmful for the consumption [85]. In another separate study conducted in Barpeta and Kamrup district of Assam showed the elevated concentration of Pb, Cd, Mn, and Fe; attributed to the excessive use of chemical-based fertilizers, local industries and geogenic characteristics [86], [87].

1.5. METAL BIOAVAILABILITY IN PLANTS

Plants are very crucial ecosystem component, that facilitates the transfer of elements from abiotic to the biotic environment. Soil being the ultimate sink, act as the most fundamental source of metals to the plant followed by air, water, and other geogenic and anthropogenic activities [88]. Plant absorb various elements including both essential and non-essential elements. Essential elements are the group of elements which are required by the plants in a trace concentration for vital biochemical activities to complete the life cycle; whereas, the non-essential elements are not required by the plants and may be toxic even at low concentrations. However, the essential elements may also become toxic when uptake concentration is above the required threshold value. Several factors influence the bioavailability of elements to the plant system including geographical conditions, soil quality, the genotype of the plant, agronomic management etc. [22].

The various anthropogenic activities including rapid urbanization and industrialization, wastewater irrigation, unmanaged landfills, atmospheric depositions etc. are responsible for high bioavailability of metals in the plant system. Mining fields are one of the major sources of heavy metal enrichment in the environment. Various studies showed the excessive bioavailability of heavy metals in the edible plants grown in the agricultural soil around mining fields globally [8], [89]–[94]. Limited availability of fresh water sources for agricultural activities leads to the incorporation of the sustainable step of using treated industrial wastewater for irrigation purposes. Wastewater irrigation is quite popular around the globe in the countries were the availability of fresh water is limited, but the quality of treated wastewater is questionable subjected to the utility for irrigation purposes. Long term application of sewage and industrial wastewater in the agricultural land leads to a substantial build-up of heavy metal concentration in the top soil. Edible crops are grown in metal enriched soil, on consumption results in inducing severe clinical issues in living organisms. Heavy metals have a tendency to bioaccumulate and persist for a longer time, metals like lead (Pd), Cadmium (Cd), Arsenic (As), Chromium (Cr) etc are listed in USEPA's priority chemicals. Metal accumulation also depends on the type of the plant for e.g. leafy and tuberous vegetables tend to accumulate comparatively more metals in comparison to the other vegetables [95]. The basis of estimation of soil to plant transfer factor is a total metal concentration of soil, however, this transfer factor solely doesn't represent all the other factors that influence overall bioavailability [12]. Heavy metals from vehicular and industrial emissions may also be deposited on the edible plant surface during the complete process of production to marketing [74]. Studies also reported the influence of atmospheric depositions on the elevated concentration of heavy metals in the common vegetables sold in the market [47], [82], [96].

1.6. RISK ASSESSMENT STRATEGIES

Arising concern toward the environmental conditions and risks subjected to the anthropogenic activities have developed a significant interest in risk assessment studies. The estimation of risk is a multi-step process broadly divided in identifying the problem, assessment of magnitude associated with the event and management and mitigation of risk. For overall risk assessment, a significantly large amount of data is required. Statistical outputs also contribute to asperity and frequency of probabilistic risk. The environmental risk assessment serves as the scientific basis to frame ecological policy and management.

The prominent lacunae in risk assessment studies are vagueness and impreciseness of the results which is subjected to the randomness and incompleteness of the environmental data set. In order to deal with the uncertainties associated with the risk assessment results, the probabilistic and fuzzy based approach has been used in the available literature. The probability theory uses probability function through which random variables of environmental parameters are described. Whereas; in fuzzy logic, membership function and linguistic parameters are used for expressing vagueness associated with environmental data. Studies on uncertainties associated with environmental risk assessment classified uncertainties in two broad categories viz. stochastic and cognitive. Different rationales are involved in these two approaches. The use of probabilistic approach comes into the role when substantial information is available in order to estimate probability distributions of parameters which are uncertain by nature; whereas, when there is limited information available fuzzy-set method is used to deal with the associated uncertainties.

The widely popular probabilistic approach to quantify uncertainties is the Monte Carlo simulation technique. This simulation technique simulates various probability distributions associated with the risk assessment equation for several iterations. The expression assumes model parameters as random variables corresponding to relative density functions. The availability of substantial information regarding environmental data and statistics ensure the efficiency of this tool to assess risk and quantify uncertainty.

For cognitive uncertainties, fuzzy logic is widely used; the membership function of the fuzzy set approach characterizes vagueness of human judgment. The fuzzy approach is capable of processing “partial truth” to quantification of uncertainty assorted to linguistic variables. The fuzzy approach has been substantially used in various environmental applications in the past few years [97]–[100]. Advances in risk estimation uncertainties have been minimized by various hybrid approaches as well, that can assess both cognitive and stochastic uncertainties along with the environmental guideline prospects related to the condition of the site and associated health risk [99], [101]–[103].

1.7. MOTIVATION AND OBJECTIVES

The above discussion indicated the status of heavy metal contamination in the industrial areas of different cities in India. An extensive literature survey, no significant information regarding metal contamination and associated health risk assessment was observed. The geographical location of Saharanpur district has been a foremost factor for such rapid industrialization and urbanization. Alluvium rich soil contributes to the high fertility soil in this area and thus the major economy of Saharanpur district is based on agriculture. It's vicinity to the capital city of India and other commercial cities including Chandigarh, Ambala, Dehradun etc., availability of natural resources and cheap labor has led to significant industrializations in this area. Unmanaged disposal of domestic, urban and industrial waste, extensive and long-term wastewater irrigation has significantly impacted the soil and groundwater quality of Saharanpur district. Certain villages nearby the industrial areas have been severely affected with serious health-related issues including gastrointestinal disorder, mental retardation, cancer etc. The reports from local bodies and media are the primary sources of information regarding the prevailing issues due to the pollution. In order to render and explore the scientific basis to the problems related to the heavy metal contamination and fill the gaps in the literature following objectives are required to be addressed.

1. Since the availability of information related to the soil and groundwater metal contamination is very limited in the industrial areas of Saharanpur district, the current status of metal contamination in soil and groundwater needs to be examined thoroughly.
2. To estimate the risk to the ecological system by accumulation or enrichment of heavy metal in the soil due to long term application of wastewater for irrigation, inappropriate disposals, landfills etc., ecological risk assessment required to be evaluated.
3. The potency of heavy metal contamination in soil and groundwater to impart carcinogenic and non-carcinogenic impacts on the population exposed to the contamination, need to be estimated using Health risk assessment models.
4. The mobility of metals from contaminated soil to edible plant parts required to be estimated in order to determine the bioavailability or Bio-concentration factor of metals, average daily intake through the edible plant parts and health risk associated with it.

5. In order to deal with the vagueness and randomness associated with the risk assessment studies, the application of soft computing tool in risk assessment analysis may meliorate the precision of the results.

1.8. THESIS OUTLINE

The thesis is organized in six chapters as discussed below

- ***Chapter-I***

The introductory chapter briefs about the details of the distribution of heavy metal contamination, the methodology adopted for analysis of heavy metals and the level of risk in different industrial areas as per the available literature. This chapter also highlights the brief industrial profile of the study area and signifies the importance of the study, further followed by the motivation and objectives of the thesis.

- ***Chapter-II***

In this chapter experimental methodology, used in the present work has been explained. The description of site selection, sampling strategies, and sample preservation till analysis has been extensively discussed, followed by the technical description of analytical instruments (Microwave digester, ICP-OES etc.) used in the present work. This chapter also deals with the different types of Risk assessment tools and methods prescribed by USEPA along with the use and importance of soft computing simulation tools for probabilistic risk analysis approach.

- ***Chapter-III***

The distribution of heavy metal in the top soil and groundwater quality in terms of physio-chemical characteristics and heavy metal contamination have been analyzed in the study area of three industrial areas of the Saharanpur district. Multivariate statistical analysis has been applied and discussed in this chapter for the possible source apportionment of heavy metal contamination in the region. Both ecological and human risk assessment has been analyzed and discussed in brief. Health risk assessment has intensively been discussed in terms of Non-cancerous Risk and Cancerous risk in both adult and children population. The present chapter also signifies the geogenic influences of metal contamination in the groundwater plume.

- ***Chapter-IV***

The transfer of metal from contaminated soil to the plant tissue has been estimated in eight different edible plants. The physiochemical characteristics of soil along with the heavy metal analysis in both soil and plant samples have been determined. Accumulation of heavy metal in edible plants with respect to its concentration in soil substrate is analyzed by Bio-concentration factor (BCF) and non-cancerous risk associated with the intake of plants growing in contaminated soil had been analyzed in both children and adult population.

- ***Chapter-V***

The application of soft computing programs (Fuzzy logic and Monte Carlo simulation) are used to reduce the uncertainty and vagueness associated with the environmental data and reaching up-to-the best possible conclusion, are briefly discussed in this chapter. Fuzzy logic is applied to the indices of ecological risk assessment, whereas, Monte Carlo simulation has been applied in the human health risk assessment.

- ***Chapter-VI***

The conclusion of the present work and some major future recommendations have been briefly discussed in this chapter.

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CHAPTER II

EXPERIMENTAL METHODOLOGY

2.1. ABSTRACT

This chapter contains the methodology involved in the sampling, physiochemical analysis, heavy metal estimation, and risk assessment analysis. Detail information about the study area has also been discussed along with the justification of sampling strategies applied.

2.2. STUDY AREA

2.2.1. Topography and General Characteristics of the Study Area

Saharanpur is one of the major commercial city located at 29.97°N 77.55°E in the northernmost part of Uttar Pradesh state of India. It covers the northern position of the Doab land which lies in between two major rivers of India, viz. The Ganges and the Yamuna. The northern frontier is surrounded by Shivalik hills. In Northeast of the city the Dehradun district, the capital city of Uttarakhand state is separated by Shivalik hills and separates it from. In the west river, the Yamuna separate the district from Yamunanagar and Karnal district of Haryana state.

The forest cover of the district is around 3.32 Lac hectares which is around 9.13% of total land cover of Saharanpur district. Common trees found in Shivalik forest reserve are *Shorea robusta* (Sal), *Dalbergia sissoo* (Sheesham). The features and characteristics of the district are quite different from the general features of other regions of *Doab* and Gangetic plain. Majorly the area belongs to the upland Bangar, that stretches up to Allahabad district.

The main characteristics of the district can be divided into four parts.

1. Shivalik Hill Tract
2. The Bhabar Land
3. Bangar Land
4. Khadar Land (Yamuna, Hindon).

The Yamuna along with its tributaries like Hindon, Solani, Nagdev etc. constitutes the physical characteristics of the district. Rivers of the districts are tributaries of either Ganga or Yamuna. Saharanpur is majorly agriculturally based district. Near about 70% of the land is used for agricultural purposes use still the region is of little importance from the point of view of pastures. Agriculture plays a vital role in the economy with the surprising fact that even though the agricultural land cover has declined in the past few years but still food production has increased significantly. The major commercial crop of the region is sugarcane; whereas, important food crops include Wheat, Maize, Oilseeds, Rice, Bajra etc.

2.2.2. Soil

Saharanpur lies in the western Indo-Gangetic plain, which is rich in alluvial deposits, brought down by the water bodies from the Himalayan region. The study area lies in the significant and complex of Gangetic plain i.e., Sub-montane belt running along the feet of Shivaliks, comprises of two parallel strips known as Bhabar and Tarai. Details of the type of soil are briefly discussed in Chapter II as well.

2.2.3. Climate and Rainfall

Saharanpur experiences moderate sub-tropical monsoon type climate. Temperature varies from 3°C to 45°C, the maximum temperature drop is observed in the month of December and January, whereas May and June are the hottest months. It receives rainfall from the month of June to September due to the influence of South -West monsoon, July and August receive maximum rainfall. North- East monsoon also results in some rainfall during January and February. The annual rainfall recorded from 498 to 1566 mm with an average rainfall value of 1027 mm. A falling trend was found during the years 2000 to 2011 with an exception in 2001 and 2010. The recent decline in the annual rainfall yield is predominantly as a result of the substantial decline in July to October rainfall. The decline in rainfall in the months of July to October might have serious agricultural implications because most agricultural activities of Kharif and Rabi seasons in this area rely on rainfall of this period. The decline in the annual rainfall yield also led to the lowering of the water table in some parts of the study area. This has an implication in the digging of wells, construction of boreholes, and other water resource development projects that depend on water from groundwater sources.

2.2.4. Groundwater table

The data from a geo-hydrological study of the area confirms three aquifer system in the study area

(a) Shallow aquifer plume (60 Feet BGL)
(b) Intermediate aquifer plume (70-150 Feet BGL)
(c) Deep aquifer plume (300- 500 Feet BGL)

The average fluctuation in the groundwater table for pre-monsoon and post-monsoon groundwater table has been recorded around 1.6 m in the study area.

2.2.5. Industrial Profile of the Study Area

Saharanpur is a growing industrial city, According to MSME; Saharanpur is divided into 5 industrial zones viz. Pilakhni, Mini I/e Ambehtapeer, Mini I/e Titron, Railway Road and Delhi Road.

Table 2.1: Industrial areas of Saharanpur district

S. No.	Name of industrial area	Land acquired (In acre)
1.	Pilakhni	95.45
2.	Mini I/e Ambehtapeer	NA
3.	Mini I/e Titron	NA
4.	Railway Road	30
5.	Delhi Road	30

Table 2.2: Details of Industries and the number of existing units

S. No.	Name of the Industry	No. of units	Type of industry
1.	ITC Ltd. (Cigarette Mfg.)	1	Large
2.	Star Paper Mill Ltd.	1	Large
3.	Sugar Mills	8	Medium
4.	Skimmed Milk Powder	4	Medium
5.	Maida Mill	2	Medium
6.	Solvent Extraction	1	Medium
7.	Cotton Textile	2	Medium
8.	Printing paper	2	Medium
9.	Industrial Alcohol (Distillery)	3	Medium
10.	Calcium carbonate	5	Medium
11.	Alloy steel	1	Medium
12.	Vanaspati Ghee	1	Medium
13.	Medicine	1	Medium
14.	Agri based	777	Micro & small
15.	Soda water	27	Micro & small
16.	Cotton Textile	271	Micro & small

17.	Woollen, Silk & artificial thread-based clothes.	76	Micro & small
18.	Jute & jute based	110	Micro & small
19.	Readymade garment and embroidery	931	Micro & small
20.	Wooden furniture	2160	Micro & small
21.	Paper and paper products	353	Micro & small
22.	Leather-based	656	Micro & small
23.	Rubber, Plastic & Petro based	297	Micro & small
24.	Chemical/Chemical based	358	Micro & small
25.	Mineral based	391	Micro & small
26.	Steel/ metal Fabrication	270	Micro & small
27.	Machinery & part	712	Micro & small
28.	Engineering units	429	Micro & small
29.	Electrical machinery	564	Micro & small
30.	Transport equipment & parts	36	Micro & small
31.	Miscellaneous manufacturing	2587	Micro & small
32.	Repairing and services	6085	Micro & small

2.3. SAMPLING STRATEGIES

2.3.1. Selection of Sampling Site

Selection of sampling sites can be selected using the following approach

(a) Haphazard sampling,
(b) Judgment sampling, or
(c) Probability sampling.

Table 2.3: Strategies for selection of sampling sites

Haphazard sampling	Judgment sampling	Probability sampling
• Also known as accessibility, or convenience sampling. • Comprises of nonreproducible, idiosyncratic decisions	• Also, refer to purposive sampling [2]. • Selection of sampling points	• Selection of random sampling points based on specific sample layouts.

made by the sampler [1]. • Lacks a systematic approach to ensure that samples procured are a true representative of the population. • Contrary to the scientific sampling approaches.	solely dependent on the best knowledge acquired by the researcher. • Results inaccurate estimation of population parameters but it fails in measuring the accuracy of these estimates. • The reliability of the estimate is only as good as the judgment of the researcher.	• Results in accurate estimation of population parameters as well as in measuring the accuracy of these estimates [3]. • The scope of statistical analyses based on the estimates of variability about the mean. • The most popular and frequently used sampling approach in soil science [1].

2.3.2. Sampling Methods

Among the various prevalent sampling designs, random and systematic sampling approach is most frequently used in soil and earth science.

In simple random sampling, all samples of the defined size are probably to be the one selected for the sampling. In stratified random sampling, points are attributed to determined groups or strata and a simple random sample taken from each stratum. The probability of being picked out can be weighted proportionately to the stratum size or the fraction of points sampled can vary from class to class in disproportionate sampling.

The systematic sampling is most popular and frequently used sampling design for field studies using either transects or grids. Systematic sampling is often criticized by the statistician globally; however, the ease and efficiency impart by this sampling design make this approach quite popular in the area of earth science. Random selection of initial point of transect grid or its orientation is an ideal approach. The important precaution in the application of systematic sampling approach with a perpetual spacing is that the target to be sampled must avoid arrangement in an orderly manner; otherwise, it might correspond to the spacing along the transect or the grid.

2.4. HEAVY METAL ANALYSIS

2.4.1. Inductive Coupled Plasma- Optical Emission Spectrometry

Inductive coupled plasma atomic spectrometry (ICP) is the popular and an advanced technique for the analysis of all metal ions. The plasma generated by argon gas compatible with aqueous aerosols render energy enough for drying, dissociation, atomization, and ionization of the analytes. The pure form of Helium and Nitrogen can also be used for the plasma generation. Plasma sources exhibit multiple advantages over the flame and electrothermal methods. The high degree of excitation and ionization contributes to highly sensitive results. High frequency electric current when passes through cooled induction coil it generates a magnetic field which results in coupling. This inductor generates a speedily oscillating magnetic field oriented in the vertical plane of the coil. A spark from the Tesla coil inducts the ionization of argon gas. The ions generated and their associated electrons from the Tesla coil, interact with the fluctuating magnetic field. This process generates sufficient energy to ionize furthermore argon atoms by collision excitation. The electrons generated in the magnetic field are accelerated perpendicularly to the torch. At high speeds, cations and electrons collides with argon atoms to generate further ionization which causes a significant increase in the temperature. In 2 ms, a steady state is created with a high electron density. A plasma is generated in the top of the torch. The temperature range of plasma reaches up to 5500–6500 K which is sufficient to destroy the molecular bonding and ionizes several elements to a high extent. A long, elongated tail emerges from the top of the high-temperature plasma on the top of the torch. This torch is the spectroscopic source. It constitutes all the analyte atoms and ions that have been excited by the heat of the plasma. The standard configuration of an ICP includes a pneumatic nebulizer for the formation of the aerosols and a spray chamber acts as a filter selecting droplets with a maximum cut off the diameter. The light emitted by the atoms on their return from the excited to a lower energetic state is resolved into a line spectrum by either a polychromator or a monochromator, depending on the equipment. The wavelength is specific for the atom and the intensity for its concentration.

On the basis of the type of sample and the level of detection, there are two common types of the detector of ICP i.e., Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also known as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS)

ICP-OES is mainly used for samples with high total dissolved solids (TDS) or suspended solids and is, therefore, more robust for analyzing groundwater, wastewater, soil, and solid waste. It can be used for drinking water analysis as well. But in general, ICP-OES is used to measure contaminants for environmental safety assessment and elements with a higher regulatory limit. ICP-MS, on the other hand, is especially useful for analyzing samples with low regulatory limits. In addition, ICP-OES has a much higher tolerance for TDS (up to 30%). ICP-MS has a much lower tolerance for TDS (about 0.2%) although there are ways to increase the tolerance. Although both ICP-OES and ICP-MS can be used for high matrix samples, sample dilution is often necessary for use on ICP-MS. In addition, if a sample contains analytes of the great difference in concentration, ICP-MS has a wider dynamic linear range so the sample may not be diluted to detect these elements at the same time.

2.4.2. Microwave digestion

Prior to analytical analysis in many analytical instruments or technique including ICP, solid samples are required to be converted into liquid form. This process involves certain digestion processes, which include classical techniques of wet digestion, dry ashing, and fusion techniques. These digestion techniques are often time and acid consuming, prone to contamination, chances of analyte loss are high as well. Microwave digestion has become an increasingly popular method to dissolve metals as the digestion process can be completed in minutes, rather than the hours it takes with hot plate digestion. The success of this method is due to the high temperatures and pressures created by using microwaves. Also, the complete sample is captive in the vessel so micro levels can be measured later in the analysis.

2.4.2.1. USEPA 3052 Digestion method

USEPA 3052 digestion method is used for siliceous and organically based matrices. This is a total digestion method with different combinations of acids applicable to most matrices. 1g of the sample was taken in inert polymeric microwave vessels. Double-distilled water (0.5 ml) was added to improve the solubility of the minerals and avoid temperature spikes due to exothermic reactions. Subsequently, 4.5 ml of HNO_3, 2ml of HF, 1 ml of HCl, and 0.5 ml of HF were added. The vessels were sealed and then heated in a microwave system (MarsXpress). The samples were filtered through Qualitative Whatman filter paper (no. 1; pore size 11 mm) after cooling and the volume was made up to 50 ml by adding 2% (v/v) HNO_3 [6].

2.4.2.2. USEPA 3015-A Digestion method

USEPA 3015A digestion method is used for aqueous samples including drinking water. 45 ml of sample was taken in inert polymeric microwave vessels. Subsequently, 4 ml of HNO_3

and 1 ml of HCl were added. The vessels were sealed and then heated in a microwave system (MarsXpress). The samples were filtered through Qualitative Whatman filter paper (no. 1; pore size 11 mm) after cooling and the volume was made up to 50 ml by adding 2% (v/v) HNO_3 [7]

2.5. RISK ASSESSMENT

2.5.1. Ecological Risk Assessment

The presence of heavy metal in the soil in elevated concentrations exert a critical impact on the quality of the soil and on its productivity. Thus, assessment of the metal concentration in the soil is of major importance in the agricultural soil. In the present work level of soil contamination was assessed using indices Index of Geoaccumulation (I_{geo}), Enrichment Factor (EF), Contamination Factor (C_f^i), Contamination degree (C_{deg}) and Potential Ecological Risk Index (PER_i).

2.5.1.1. Index of Geo-accumulation (I_{geo})

The index of geo-accumulation (I_{geo}) access the contamination by comparing the current concentration of heavy metal with pre-industrial concentration originally used with bottom sediments [8]. It is calculated by the given equation:

$$I_{geo} = log_2 \frac{C_n}{1.5\,B_n} \tag{2.1}$$

where C_n is the total concentration of element 'n' in the surface layer of soil examined, and B_n is the geochemical background value of the element 'n' in the Earth's crust [9]. A factor of 1.5 corresponds to the possible natural fluctuation in the base level of the metal estimation in the environment and as a correction factor for any small anthropogenic influences. The study was to focus on the comparison between the concentration observed and concentrations of elements in earth's crust, as the soil is the part of the layer of Earth's crust and its chemical composition is related to one of the crusts. Total six classes of the geo-accumulation index have been distinguished [10]–[12].

Table 2.4: Classes of Geo-accumulation index *(I_{geo})*

Class	Value	Soil Quality
0	$I \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Class 6 is an open class and represent all geo-accumulation value index higher than class 5.

2.5.1.2. Enrichment factor (EF)

Enrichment factor for soil is based on standardization of an examined element against a reference one. The reference soil can be any soil without contamination and the reference element can be characterized by low occurrence variability. Some common reference materials are Sc, Mn, Ti, Al, St, and Fe [13], [14]. In the present study, Al was taken as the reference element. The enrichment factor was calculated using the modified formula based on the equation used by [15].

$$EF = \left[\frac{C_{n\ (Sample)}}{C_{ref\ (Sample)}}\right] \Big/ \left[\frac{B_{n\ (Background)}}{B_{ref\ (Background)}}\right] \quad (2.2)$$

where C_n *(Sample)* refers to the content of the examined element in the study area, C_{ref} *(Sample)* is the content of the reference element in the study area, B_n *(Sample)* is the content of examined element in the reference environment and B_{ref} *(Sample)* is the content of the reference element in the reference environment. On the basis of the value of enrichment factor, five contamination categories were recognized [10], [16], [17] Table 2.

Table 2.5: Classes of contamination categories of Enrichment Factor (EF)

Class	Value	Soil Quality
0	<2	Deficiency to minimal enrichment
1	2-5	Moderate enrichment
2	5-20	Significant enrichment
3	20-40	Very high enrichment
4	>40	Extremely high enrichment

2.5.1.3. Contamination factor and degree of contamination

Soil contamination is also assessed by the contamination factor (C_f^i) and contamination degree (C_{deg}). Contamination factor is a single element index whereas, contamination degree is the sum of all contamination factors for all examined elements. The contamination factor was calculated using equation 2.3 [18].

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \quad (2.3)$$

where C_{0-1}^i refer to the mean content of individual metals from at least five sampling sites and C_n^i is pre-industrial concentration of individual metals. As per modification of this factor, in the present study concentration of elements in the earth crust was considered as a reference value. Four classes of Contamination factor and contamination degree are recognized for the assessment [18].

Table. 2.6: Classes of Contamination factor (C_f^i) and Contamination degree(C_{deg})

Contamination factor (C_f^i)	**Category**	**Contamination degree (C_{deg})**
$C_f^i < 1$	Low contamination factor	$C_{deg} < 8$
$1 \leq C_f^i \leq 3$	Moderate contamination factor	$8 \leq C_{deg} \leq 16$
$3 \leq C_f^i \leq 6$	Considerable contamination factor	$16 \leq C_{deg} \leq 32$
$6 \leq C_f^i$	Very high contamination factor	$32 \leq C_{deg}$

Table. 2.7: Classes of Potential Ecological Risk Index (PERi)

Class	**Value**	**Soil Quality**
0	$E_r^i < 30$; $R_i < 100$	Low Risk
1	$30 \leq E_r^i < 50$; $100 \leq R_i < 150$	Moderate Risk
2	$50 \leq E_r^i < 100$; $150 \leq R_i < 200$	Considerable Risk
3	$100 \leq E_r^i < 150$; $200 \leq R_i < 300$	Very High Risk
4	$E_r^i \geq 150$; $R_i \geq 300$	Disastrous Risk

2.5.1.4. Potential Ecological Risk Index (PERi)

Potential ecological risk index *(PERi)* assess the environmental impact by the presence of multiple metals in the soil, the approach of Ecological Risk assessment was adopted. The method used was proposed by [18] and Risk Index (RI) was introduced to assess the degree of heavy metal pollution in soil or sediments, according to the toxicity of heavy metals and the response of the environment. Potential Ecological Risk Index (*Ri*) was used to determine the degree of contamination associated with heavy metal concentration in soil and sediment. E_r^i in the expression represents a monomial potential ecological risk factor, whereas T_r^i is toxic response factor for As, Cd, Cu, Pb, Ni, Cr, Zn are 10, 50, 2, 5, 5, 5 and 1 respectively [19], [20]. R_i is defined according to Eq. (2.4) as the summation of E_i

$$E_r^i = T_r^i \times C_f^i \tag{2.4}$$

$$R_i = \sum E_r^i \tag{2.5}$$

2.5.2. Health Risk Assessment

There are three major pathways via human can get exposed to the heavy metal

(a) Oral ingestion

(b) Inhalation through mouth and nose

(c) Dermal adsorption through the skin.

Average daily intake of metal via oral, inhalation and dermal pathways were calculated using equation no. 2.6, 2.7 and 2.8 respectively

$$ADI_{ing} = C_{soil} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad (2.6)$$

$$ADI_{inh} = C_{soil} \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \qquad (2.7)$$

$$ADI_{dermal} = C_{soil} \times \frac{SAF \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad (2.8)$$

2.5.3. Bioconcentration Factor (BCF)

To evaluate the bioaccumulation of hazardous pollutants with the assumption that organisms achieve a chemical equilibrium subjected to the particular medium or exposure pathway [28]. This approach involves bioconcentration or bioaccumulation factors (BCFs or BAFs) to analyse the pollutant residues in plants from appraised concentrations in the suitable reference media. Normalization of soil metal concentrations with metal values of upper continental crust of earth is an important step. [9]. The bioconcentration factor is represented as

$$BCF = C_{biota}/C_{soil} \qquad (2.9)$$

where, C_{biota} and C_{soil} represents the total metal concentrations (mg/g) in the biota or plant tissue and soil, respectively. The same formula was adopted to calculate BCF for all the collected samples of biota with the assumption that the distribution of a contaminant (e.g. metal) in the environment is controlled by a continuous exchange among phases such as air, water, soil/ sediment, and biota.

Table 2.8: Input parameter for Health risk assessment calculation

Input Parameter	Description	Value	References
IngR	Ingestion Rate (mg/day)	100*, 200**	[21], [22]
InhR	Inhalation rate (m^3/day)	20*; 7.6**	[22], [23]
EF	Exposure Frequency (days/year)	350	[6], [24]
ED	Exposure Duration (year)	24 years*; 6 years**	[6], [21]

LT	Life Time (year)	65	[25]
BW	Body weight (Kg)	60^{*}; 15^{**}	[22], [24]
SA	Skin surface area available (cm^2)	5700*; 2800**	[6], [26]
SAF	Skin adherence factor for soil	0.07mg/cm^2/h* 0.2 mg/ cm^2/h**	[26], [27]
PEF	Particle emission factor (m^3/day)	1.36 x 10^9	[6], [22]
ABS_{dermal}	Dermal absorption factor	0.001 (all metal)	[22], [23]
AT	Average time (Days)	Noncarcinogenic ED x 350 Carcinogenic- LT x 365	[22], [24]

2.6. PROBABILISTIC RISK ASSESSMENT TOOLS

2.6.1. Fuzzy Logic

The Fuzzy logic and the fuzzy set theory were introduced by Lotfi A. Zadeh, a mathematician in 1965. The fuzzy approach explicitly intromits the uncertainty of truth and can efficiently act on information served in linguistic form. To determine the percentage of soil heavy metal contaminate of a sampling site, the application of fuzzy logic has been introduced in this work. It is a mathematical structure having the capability to operate with linguistic terms. This concept is totally different from traditional Boolean logic as it assigns a given statement an intermediary level of truth rather than either false or true. This provides a better resemblance to the human way of thinking. The final result of fuzzy logic provides an analytical-deductive process which is automatically consistent with a priori set of principles, unlike standard human reasoning which often affected by various consideration and is neither consistent nor realistic. A fuzzy set can be seen as an extension of a classical set. If U is a functional set and its elements are denoted by x, then we can define a fuzzy set A as a set of ordered pairs

$$A = \{x, \mu_A(x) \mid x \in U\} \tag{2.10}$$

where μA(x) is the membership function of x in A. This membership function provides a mapping of each element of U to a membership value between 0 and 1.

The fuzzy logic was performed through implementation of a fuzzy interference system, in which we have defined the process of connection, usually made from the data collected on the field, with a consequence, namely a deduction or a result. The main steps in the fuzzy approach include (**Fig. 2.1**): defining membership functions, fuzzification, inference system, and fuzzy output.

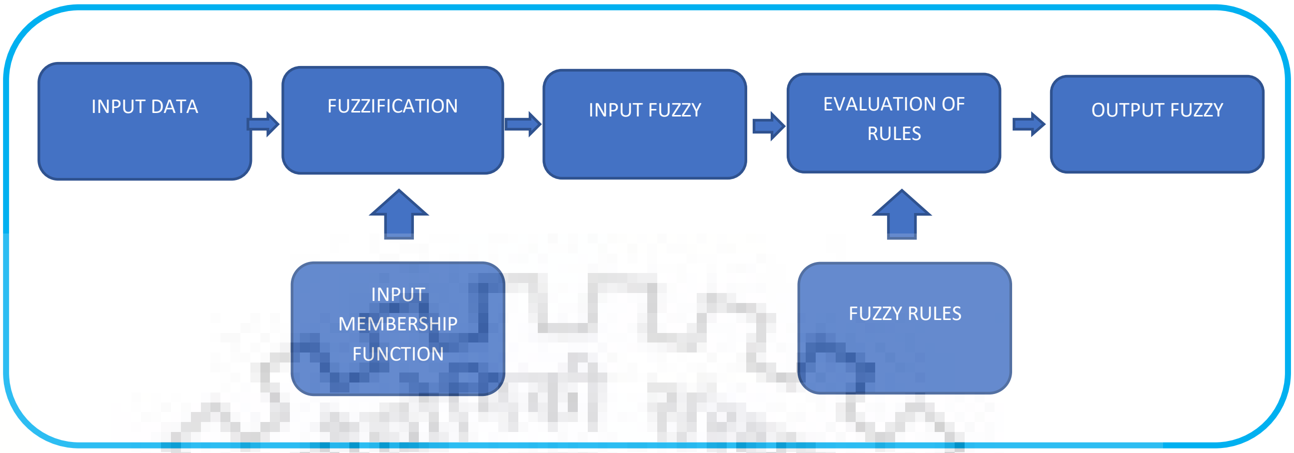

Fig. 2.1: *Basic Steps in Fuzzy Logic System*

The defining of the membership function is the most important step on which all other subsequent operations are based. These functions represent the fuzzy sets, can have different shapes (triangular, Gaussian, trapezoidal, etc.) according to the situations and can take values between and 1.

The second step is fuzzification, in which a given input parameter is attributed to a level of membership to the different fuzzy sets in which the parameter dominance is subdivided. In this, we normalize all the data within the interval [0, 1], in order to make a comparison between quantities different from each other and measured in different scales. In the next step, the inference we apply the rules of combination between fuzzy sets, from which it is possible to deduce the results. These rules are the linguistic expressions, turned into mathematic formalism by using the expression 'if and then' of the logic itself.

The fuzzy output also represents the value of membership which can be both 'pure' signifying a qualitative property and 'defuzzified' which signify a real number which is compatible with non-fuzzy approaches.

2.6.1.1. Fuzzification

In fuzzification, the input variables are converted into a fuzzy measure of their membership to given classes. Such conversion is performed through the membership function pre-set for those classes. A membership function can be defined as a function which relates a value (mostly numerical) with the level of membership to the set.

The real number representing the level the membership [$\mu(x)$], have a 0 value when the element doesn't belong to the fuzzy set, and a value 1 when it belongs completely to it. The membership functions of fuzzy sets can have different types. The simplest one is straight lines and the most used are trapezoidal and triangular. The triangular membership function can be defined with three scalar parameters a, b and c and is given by the following expression:

$$F(x;a,b,c) = \max\left(\min\left(\frac{x-a}{b-a},\frac{c-x}{c-b}\right),0\right) \tag{2.11}$$

while, the trapezoidal membership function depends on four scalar parameters a, b, c and d and given by the following expression:

$$F(x;a,b,c,d) = \max\left(\min\left(\frac{x-a}{b-a},1,\frac{d-x}{d-c}\right),0\right) \tag{2.12}$$

Similar to these functions there are more complex functions such as Gaussian function, Gaussian2 function, bell membership function, Sigmoid Membership function, Design Membership function, P-sig Membership function, Z Membership function, Pi Membership function, S Membership function.

2.6.1.2. Fuzzy inference system

The inference provides the decisional engine i.e. the rules referring to the fuzzy output. These rules constitute if-then-else structure, which represents antecedent, defining the conditions; and resultant of which defines the action. For every single input variable, in the antecedent, there is a clause of the type (x is L) where L represents linguistic label which reveals a fuzzy set. In this way, the antecedent facilitates the characterization of the system conditions required to be modeled.

Generally, the antecedent consists of clause conjunction, having one for every single observed variable, whereas, the consequent determines the output conditions. Therefore, we can also state in conclusion that a fuzzy system is a non-linear function which has the potential of transforming certain input variables into the output with the implementation of fuzzy rules.

After fuzzy inference system, it is required to transform the incoming data from the evaluation of defined rules into real numerical data, this step is completely antagonistic to fuzzification, so it is referred as output fuzzification or defuzzification.

2.6.1.3. Defuzzification

This represents output values evaluated through the fuzzy model. It can either be linguistic, when the output defines a level of membership associated, or numerical, of “crisp” type (non-fuzzy).

Some of the frequently applied defuzzification methodologies are:

- Centroid method: the output value is evaluated as the center of mass of fuzzy sets
- Bisector method: the output value is the abscissa of the bisector of the area delimited to the fuzzy data set.
- Middle of the maximum method (Mom): the output value represents the set average of maximum values
- Largest of the maximum method (Lom): the output value is calculated as the maximum of maximum
- Smallest of the maximum method (Som): the output value represents the minimum value.

2.6.2. Monte Carlo Simulation

Monte Carlo simulation is a type of simulation that relies on repeated random sampling and statistical analysis to compute the results. This method of simulation is very closely related to random experiments, experiments for which the specific result is not known in advance. In this context, Monte Carlo simulation can be considered as a methodical way of doing so-called what-if analysis. We will emphasise this view throughout this tutorial, as this is one of the easiest ways to grasp the basics of Monte Carlo simulation. These models typically depend on a number of input parameters, which when processed through the mathematical formulas in the model, results in one or more outputs.

The utility of Monte Carlo simulation is in quantitively characterizing uncertainty and variability in estimates of exposure or risk and in identifying key sources of variability and uncertainty and to quantify the relative contribution of these sources to the overall variance and range of model results. MCS is a computer-based simulation technique that combines multiple probability distributions associated with risk assessment equation. Iterations or repeated executions of the risk assessment model using probability theory to quantify model parameter uncertainty relies on the statistical representation of available information. It assumes that the model parameters are random variables that can be represented by probability density functions (PDFs). However, a serious shortcoming of this method is that it is not capable of coming to grips with the pervasive fuzziness of information in the knowledge base, and, as a result, is mostly ad hoc in nature.

Exposure assessment was conducted by means of Monte Carlo simulation, which was carried out using a software platform (Crystal Ball, Oracle). The simulation was performed using the presented parameters, and the model was run for 10,000 iterations. Then, the mean value, and the 50th and 90th percentiles of the intake dose distribution were obtained from the simulation.

Table. 2.9: Monte Carlo simulation parameter distribution for exposure risk assessment.

Input Parameter	Description	Value
Ing R	Ingestion Rate (mg/day)	Triangular[a], Log-normal [b]
EF	Exposure Frequency (days/year)	Triangular [a, b]
ED	Exposure Duration (year)	Point [a, b]
BW	Body weight (Kg)	Log-normal [a, b]
SA	Skin surface area available (cm^2)	Triangular [a, b]
SAF	Skin adherence factor for soil	Log-normal [a, b]
ABS_{dermal}	Dermal absorption factor	Point [a, b]

*a= adult; b= children

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CHAPTER III

DISTRIBUTION AND RISK ANALYSIS OF SOIL AND GROUNDWATER HEAVY METAL CONTAMINATION IN THE INDUSTRIAL AREAS OF "*THE UPPERMOST DOAB LAND OF GANGA AND YAMUNA*" SAHARANPUR, INDIA*

* *The research work described in this chapter is under review in "Bulletin of Environmental Contamination, Springer" and "Applied Geochemistry, Elsevier".*

3.1. ABSTRACT

The distribution of heavy metal in the topsoil and groundwater quality in terms of physio-chemical characteristics and heavy metal contamination have been analyzed in the study area of three industrial areas of the Saharanpur district. Multivariate statistical analysis has been applied and discussed in this chapter for the possible source apportionment of heavy metal contamination in the region. Both ecological and human risk assessment has been analyzed and discussed in the brief. Health risk assessment has intensively been discussed in terms of Non-cancerous Risk and Cancerous risk in both adult and children population.

3.2. INTRODUCTION

Heavy metal contamination in soil leads to the deterioration of overall soil quality, productivity and water quality through percolation. Some metals (Cu, Fe, Mn, Ni and Zn) serve as micronutrient and regulate physiological activities, however long-term exposure of metals like As, Cd, Cr and Pb even in low concentration induces carcinogenic effect and other health related issues including mental disorders, neurological, cardiovascular, kidney and bone diseases [1]. The major pathway of heavy metal exposure to the human being includes soil to crop transfer of heavy metals. Excessive use of chemical fertilizers, pesticides, long term irrigation through industrial wastewater in order to meet the food supply with increasing population are some of the major sources of metal contamination in soil. Food crops grown in the metal contaminated soil uptake metals and get bioaccumulated through food chain resulting in adverse impact on both ecological system and human health [2].

The other cities which form the part of Upper Doab are Muzaffarnagar, Saharanpur, Meerut, Ghaziabad, Gautam Budh Nagar, Baghpat & Bulandshahr. Out of these cities. Ghaziabad is one of the rapidly growing industrial cities of India and have been extensively studied in terms of heavy metal contamination and related health risk. The overall mean concentrations of Cu, Cr, Pb, Zn and Ni were found to be higher than the many other cities in the world. Non-carcinogenic health risk in children was found to be higher than adults and cancer risk was found to be in acceptable range for the metals like Cr, Cd, Pb and Ni [3]. Heavy metals were also estimated in the sediments of Hindon river which originates from Saharanpur district flows through Muzaffarnagar, Meerut, Baghpat, Ghaziabad and Gautambudh Nagar till its confluence with river Yamuna. Hindon receives hundreds of liters of urban and industrial wastewater per day throughout its length (280 kms) before its confluence in Yamuna. The sediment samples were found to be highly contaminated with Cd, moderately contaminated by Cu, Cr and Fe [4]. On the basis of limited information so available in terms of heavy metal contamination in Saharanpur district, high contamination of As and Cd was observed followed by moderate contamination of Pb in one of the industrial areas of the city [5].

The present work aims at determining the status of heavy metal contamination in soil as well as groundwater and associated health risks, as there is no comprehensive study available on heavy metal pollution and related health risk in Saharanpur district.

3.3. MATERIAL AND METHOD

3.3.1. Study area

For the present study, a probabilistic sampling approach has been implied and detail description of the sampling sites in three industrial areas is given in ***Table 3.1*** and depicted in the map ***Fig. 3.1***.

Major parts of Saharanpur are mostly plains except in the northern part of the district due to the presence of Shivalik mountains. The district is surrounded by the river Yamuna in the west, Muzaffarnagar and Haridwar districts in south and east respectively.

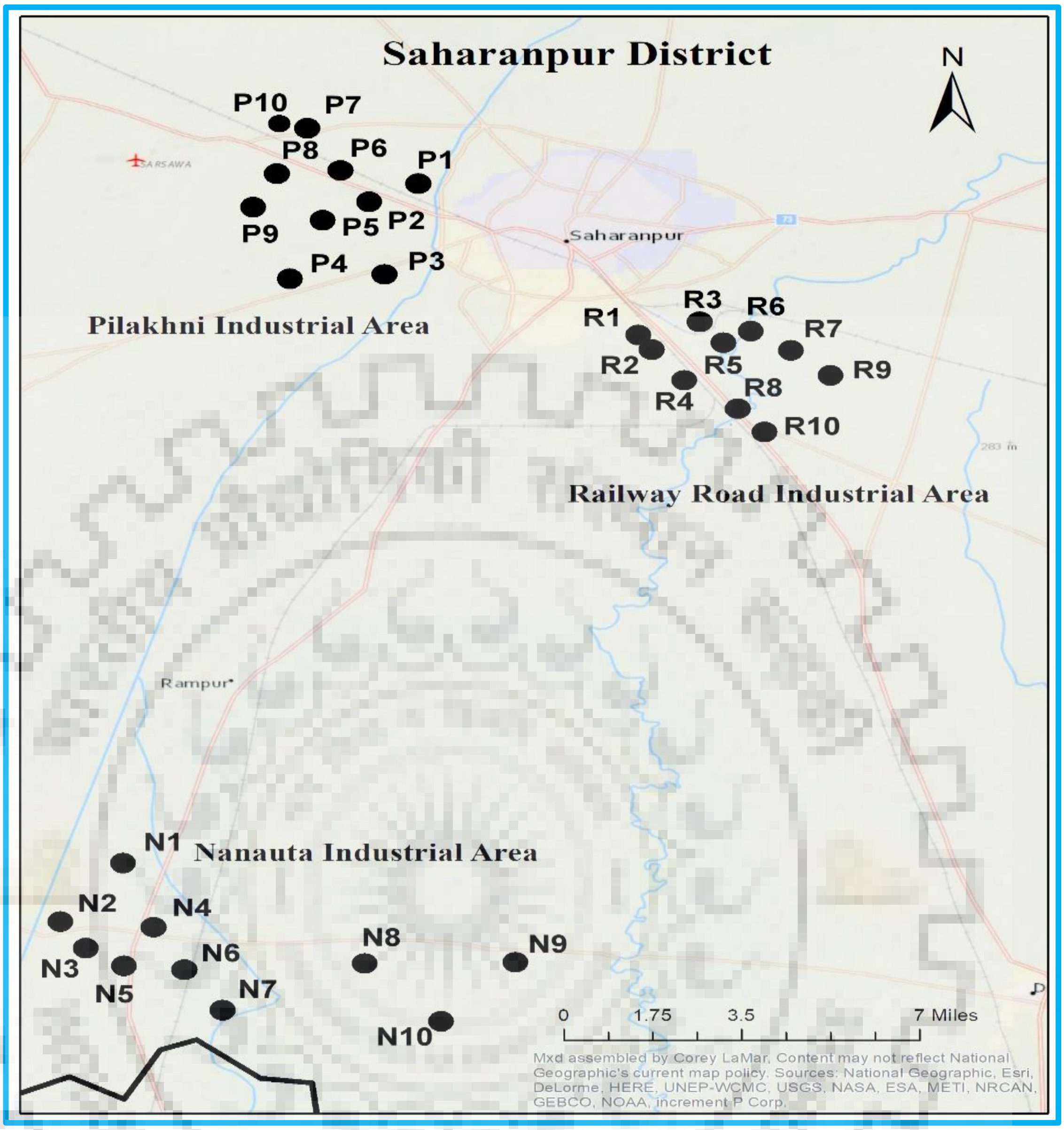


Fig. 3.1: *Sampling sites in the study area*

Rivers and nallahs like Hindon, Krishni, Kali, Maskara, Dhamola, Katha Nallah etc. drain the study area throughout the year. A major source of the natural drain in the study area is the Hindon river. The major source of shallow aquifer recharge in adjoining areas is the eastern Yamuna canal and Deoband branch of upper Ganga canal which flow across the study area. The alluvium stretches of Doab land between river Ganga and Yamuna, are highly fertile and has a considerable contribution in the agriculture-based economy in this region. Wastewater irrigation is quite prevalent in some of the industrial areas; as pulp and paper industry, distillery, sugar mill industries etc. are high water-intensive industries and it generates a high volume of industrial wastewater. Long term wastewater irrigation contributes to high metal enrichment in the soil which ultimately percolates and contaminate groundwater plume.

Table 3.1: List of sampling sites with geographical coordinates.

Code	Area	Sampling site	Longitude	Latitude
P1	Pilakhni	Pilakhni-1	77.4609	30.0036
P2	Pilakhni	Bani Kheda	77.4692	30.0024
P3	Pilakhni	Brahman Khera	77.4605	29.9859
P4	Pilakhni	Nalheda Bakkal	77.4786	29.987
P5	Pilakhni	Alipura	77.4538	29.9737
P6	Pilakhni	Pilakhni-2	77.4736	29.9689
P7	Pilakhni	Jairampur	77.4869	29.9757
P8	Pilakhni	Adampur	77.5009	29.9822
P9	Pilakhni	Kumhar Hera	77.4643	29.9478
P10	Pilakhni	Mukhlispur	77.4913	29.9493
N1	Nanauta	Badgaon	77.5285	29.7003
N2	Nanauta	Jhabiran	77.4857	29.6999
N3	Nanauta	Umahi	77.5088	29.6803
N4	Nanauta	Bhanhera Khemchand	77.445	29.683
N5	Nanauta	Brahman Mazra	77.4182	29.7377
N6	Nanauta	Pando Kheri	77.4342	29.6977
N7	Nanauta	Nanauta	77.4254	29.713
N8	Nanauta	Nanauta-1	77.4171	29.699
N9	Nanauta	Nanauta Dehat	77.4061	29.7055
N10	Nanauta	Nanauta Dehat-1	77.399	29.7151
R1	Rly Rd	Dabki	77.5843	29.9356
R2	Rly Rd	Sheikhpura-1	77.5673	29.9222
R3	Rly Rd	Shaikhpura-2	77.5711	29.9303
R4	Rly Rd	Paragpur Aht	77.581	29.9323
R5	Rly Rd	Paragpur Must	77.5803	29.9208
R6	Rly Rd	Tapari	77.5856	29.9159
R7	Rly Rd	Kapasa	77.5956	29.9289
R8	Rly Rd	Lakhnaur-1	77.5919	29.9008
R9	Rly Rd	Lakhnaur-2	77.6032	29.9047
R10	Rly Rd	Kapasi	77.6216	29.9162

3.3.2. Soil sampling and pre-treatment

Total of 60 top-soils (0-15 cm) was procured from thirty sampling sites using stratified random sampling approach from three industrial areas (Pilakhni, Delhi Road and Railway Road) of Saharanpur city (29.9671° N, 77.5510° E). Samples were zipped packed in a polyethylene bag, transferred to the laboratory within three hours from sampling and stored at 4°C till complete analysis. Before analytical step samples were dried (at 50°C), pulverized and sieved with 70-mesh plastic sieve [6]. The heavy metal was analyzed by digesting the soil samples using USEPA 3052 method [7] in the microwave oven (MarsXpress). Digested transparent solution was cooled, filtered through Whatman no. 42 filter paper and diluted up to 50 mL with 1% nitric acid. The metal concentration in the filtrate of digested soil samples was analyzed by ICP- OES. Certified reference soil (SRM 1646a- Estuarine sediment) was used to ensure the validation of analytical procedure and was observed in the good agreement with respect to the certified values with recovery percentage 82.43% to 108.09%.

3.3.3. Groundwater sampling

Simple randomization technique was used for sampling groundwater from different sources (tube-well, well and hand pump) used for drinking purpose from 30 different sampling locations within three industrial areas. Before taking any sample standing water was pumped out for at least 5 minutes in order to avoid any external interference. Samples were acidified (pH <2) with 65% (v/v) HNO_3 in order to check the adsorption to the container wall, crystallization, and microbial degradation and stored in 4°C till complete analysis. For heavy metal estimation, 50 ml of groundwater samples were digested with 10 ml of HNO_3 at 80°C, till it turns transparent and was filtered (Whatman No. 2) and diluted to 50 ml with double distilled water. The metal analysis was carried out by Inductive coupled plasma - optical emission spectrometry (ICP-OES).

3.3.4. Risk Assessment studies

Risk assessment studies have been performed to analyze risk associated with both soil and groundwater contamination. Estimating this risk involves identifying the events that imply hazards and assessing the magnitude of their consequences and frequency. Environmental risk assessment is an essential element in any decision-making process in order to minimize the effects of human activities on the environment. Both ecological and health risk assessment has been evaluated. The health risk has been assessed in both adult and children population. The methodology involved in the risk assessment studies is briefly described in **Chapter II**.

3.4. RESULT AND DISCUSSION

3.4A. ANALYSIS OF HEAVY METAL CONTAMINATION IN THE SOIL

3.4A.1. Physiochemical characteristics of the soil sample

The basic physiochemical characteristics of the agriculture soil are shown in table 3.2. The soil pH was observed to be near neutral to slightly alkaline with 56.10% and 5.36% of mean moisture content and organic matter respectively. High phosphate and chloride content in the soil may result due to long-term wastewater irrigation. The mean conductivity was observed to be 2.49 $mScm^{-1}$ considering the fact that the presence of ions and metals enhances the overall soil conductivity of the soil.

Table 3.2: Physiochemical characteristics of the agriculture soil in the study area

pH	7.5 ± 0.5
Sand (%)	52.0 ± 11.4
Silt (%)	35.22 ± 7.56
Clay (%)	12.8 ± 1.82
Moisture (%)	56.10 ± 3.81
OM (%)	5.36 ± 1.02
TN ($mgkg^{-1}$)	103.53 ± 6.14
Sulfate ($mgkg^{-1}$)	157.24 ± 7.58
Phosphate ($mgkg^{-1}$)	701.04 ± 16.58
Potassium ($mgkg^{-1}$)	153.0 ± 8.6
Chloride ($mgkg^{-1}$)	1014.0 ± 36.65
EC ($mScm^{-1}$)	2.49 0.02

3.4A.2. Heavy metal concentration in soil

The heavy metal distribution in the study area is shown briefly in table 3.3. Arsenic content with mean concentrations of 22.10 and 14.16 mg/kg in Pilakhni and Railway road industrial area respectively indicates high toxic level of As content in the area followed by Nanauta industrial area (10.03 mg/kg). Metal extraction units, emissions from the burning of crude oil or fossil fuels in small scale industries including brick baking industries, jaggery making industries etc., which are quite common in the study area may contribute to the contamination of As in the soil. Other sources may include the use of arsenical fungicides, herbicides, and insecticides in agriculture. Use of timber preservatives which contain a significant amount of

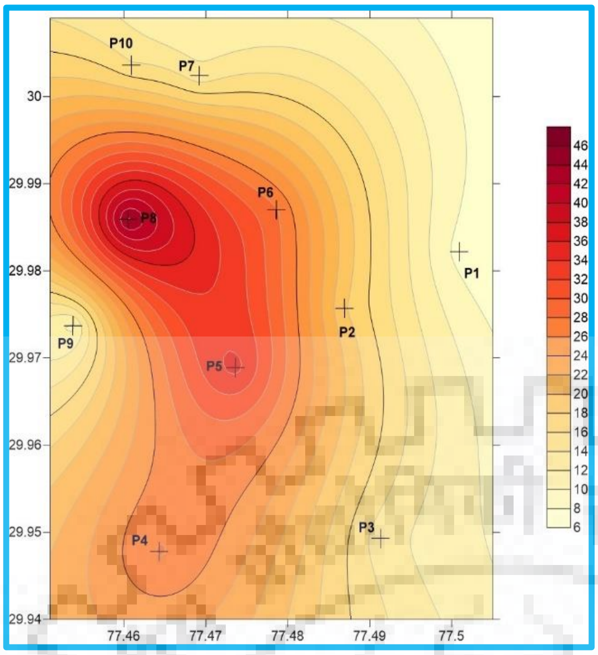
Arsenic may also be anticipated for the contribution in enhanced As content in the Railway road industrial area.

Moreover, the probability of geogenic influences on overall As contamination cannot be neglected due to the presence of Pleistocene sediments in the study area [8], [9]. The mean Cd concentration was observed to be highest in the Nanauta (1.98 mg/kg) industrial area followed by Pilakhni and Railway road industrial area. The sources of Cd may include inappropriate disposal of e-waste, application of Cd-based fertilizers or pesticides along with, the discharge from metallurgical industries and other urban activities. Elevated concentration of Cu (88.48 mg/kg) in Pilakhni industrial area may be majorly associated with the activities and disposal related to the sugar mill industry [10]. The maximum concentration of Cr (178.20 mg/kg) was observed in the Nanauta industrial area followed by the railway road industrial area. Unmanaged disposal of waste generated by the distillery paper industry, textile dyeing, and chrome plating units may be responsible for the enhanced level of Cr concentration in the study area [10], [11]. High Ni concentration in Railway road (95.38 mg/kg) and Nanauta (83.59 mg/kg) industrial area may be attributed to the waste generated by many small to medium scale industries including electroplating industry, paint industry, cement manufacturing units, chemical and catalyst industries etc [12].

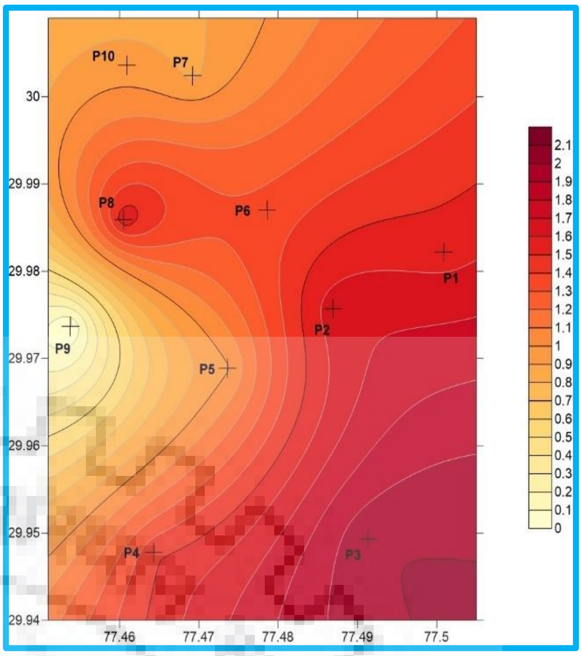
The spatial distribution of soil heavy metal contamination is shown in fig 3.2(a-g), 3.3(a-g), and 3.4 (a-g) in Pilakhni, Nanauta and Railway road industrial area respectively.

Table 3.3: Mean concentration ($mgkg^{-1}$) of metal contamination in the soil of three industrial areas and the background value of the metals

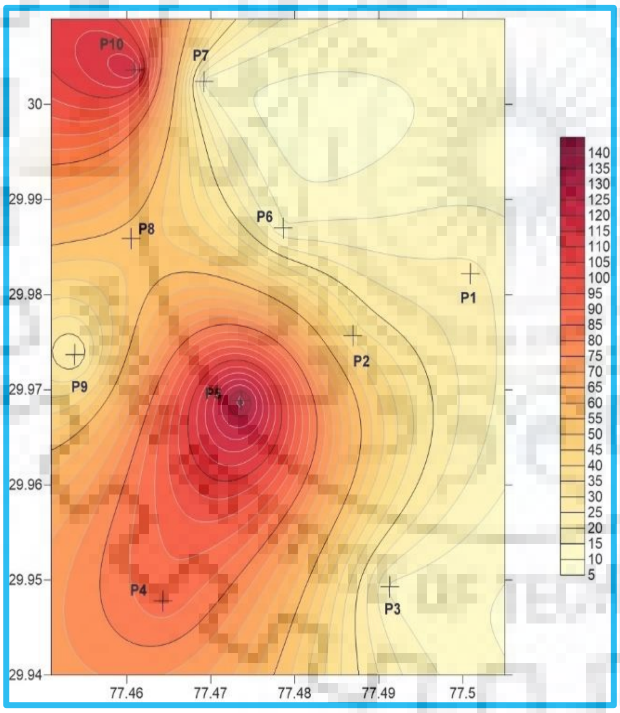
Metal	Pilakhni ($mgkg^{-1}$)			Nanauta ($mgkg^{-1}$)			Railway Road ($mgkg^{-1}$)			Reference Value ($mgkg^{-1}$)
	Mean	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	
As	22.10 ± 9.68	7.25	44.40	10.03 ± 4.70	1.82	18.54	14.16 ± 10.51	2.38	46.42	1.60
Cd	1.35 ± 0.40	0.77	2.10	1.98± 0.79	0.45	3.02	1.07 ± 0.35	0.45	1.92	0.10
Cu	88.48 ± 21.68	11.82	98.88	47.41 ± 25.21	18.24	108.20	35.70 ± 16.64	12.84	78.28	39.00
Pb	40.50 ± 14.90	22.10	77.30	34.07 ± 15.99	13.70	77.30	31.50 ± 13.01	12.34	55.20	17.00
Cr	68.99 ± 39.51	13.52	138.36	92.10 ± 42.39	14.13	178.20	89.28 ± 28.02	23.60	118.24	69.00
Ni	67.95 ± 43.87	33.20	198.08	83.59 ± 32.88	17.24	168.79	95.38 ± 48.13	40.75	205.08	55.00
Zn	91.07 ± 29.14	35.30	135.23	97.04 ± 33.07	48.60	182.45	85.31 ± 33.69	35.30	166.76	67.00



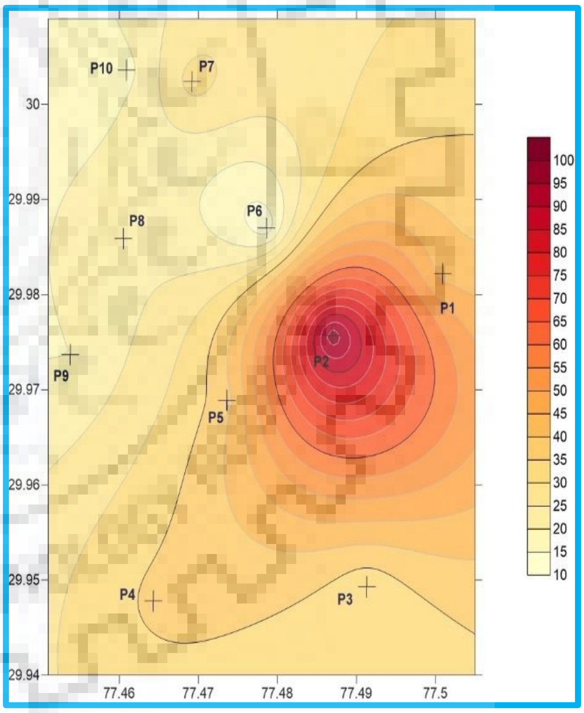
(a) As



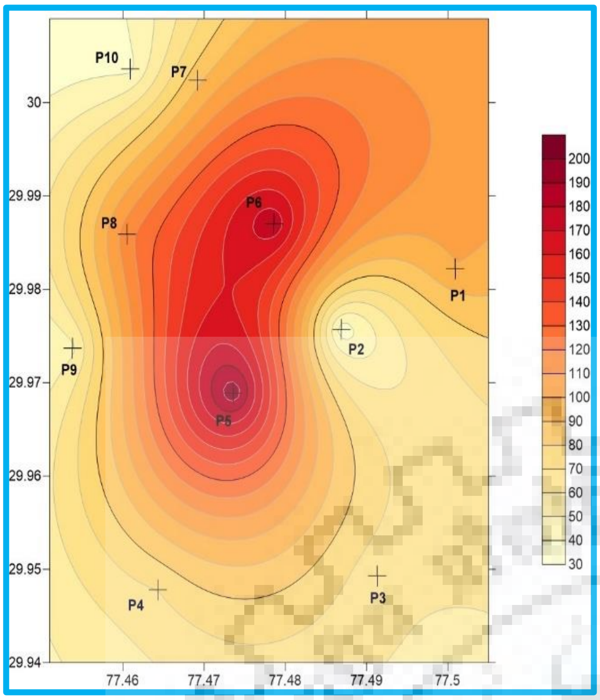
(b) Cd



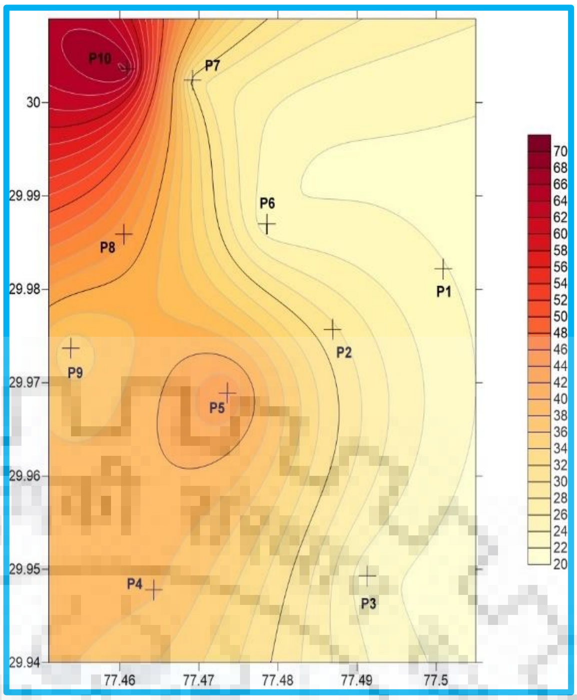
(c) Cr



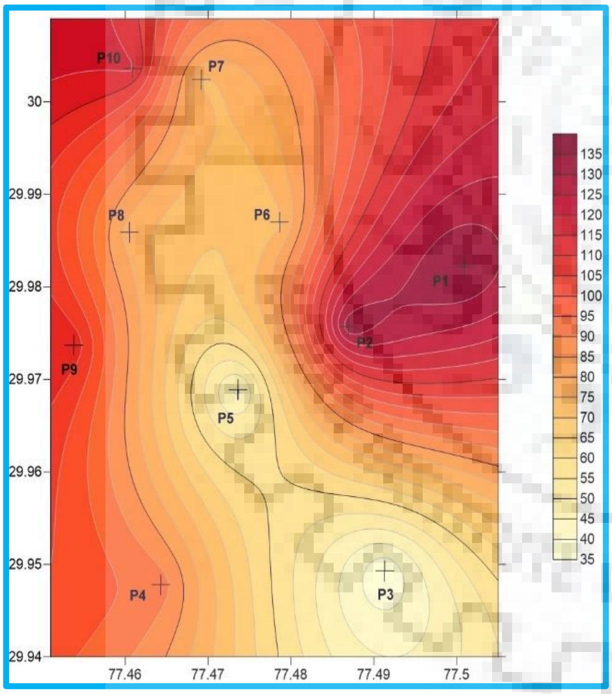
(d) Cu



(e) Ni

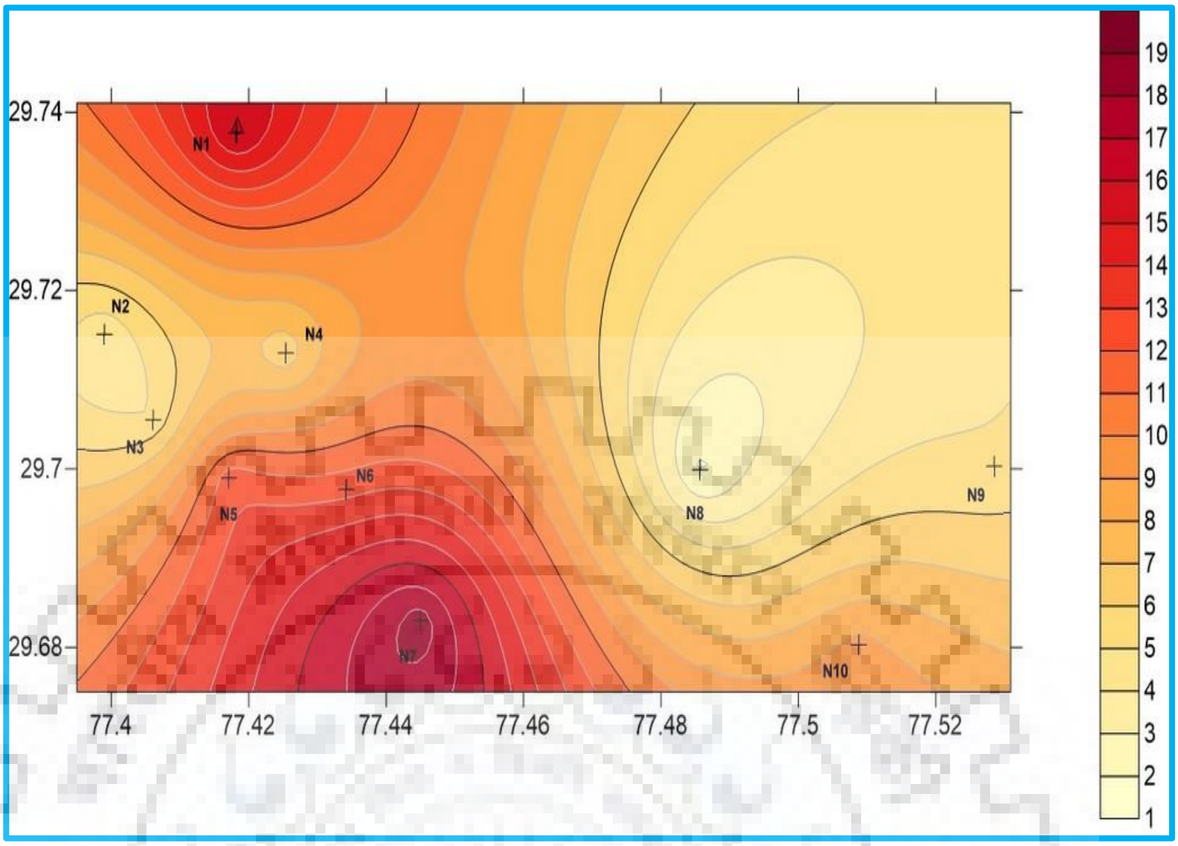


(f) Pb



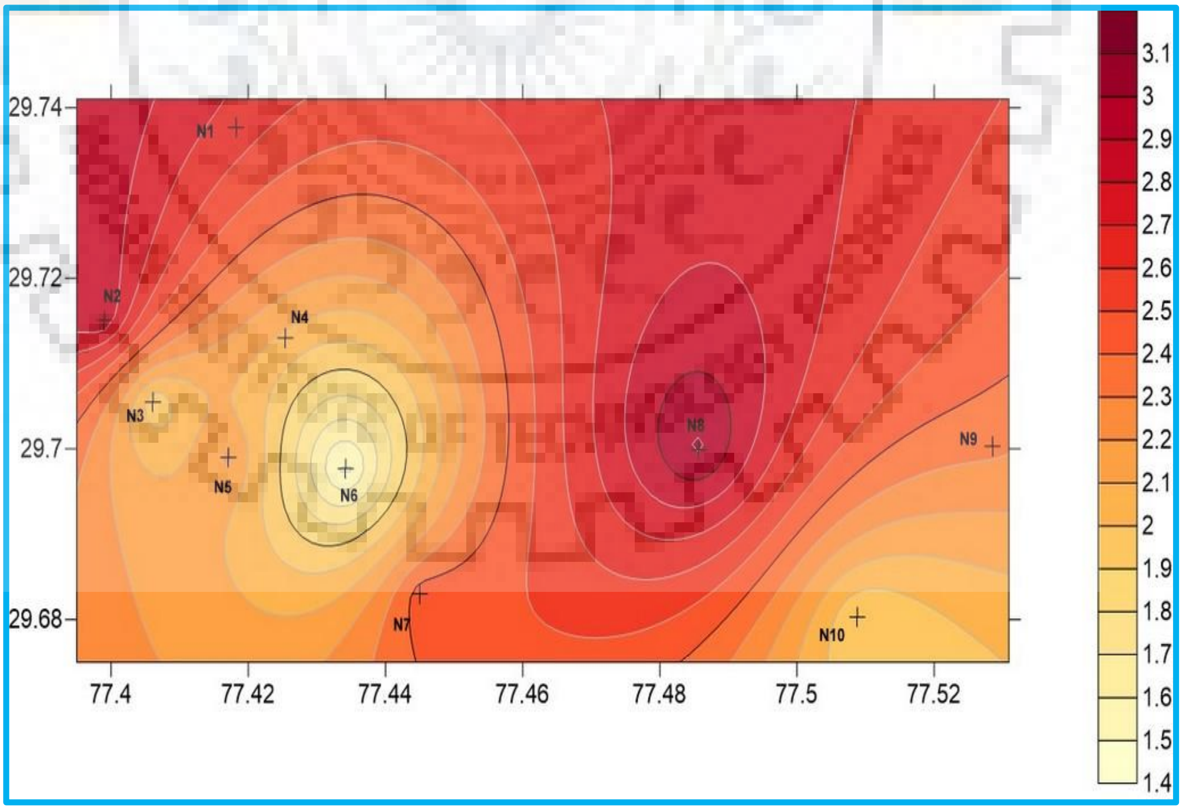
(g) Zn

Figure 3.2: *(a-g) Spatial distribution of heavy metal contamination in Pilakhni industrial area*



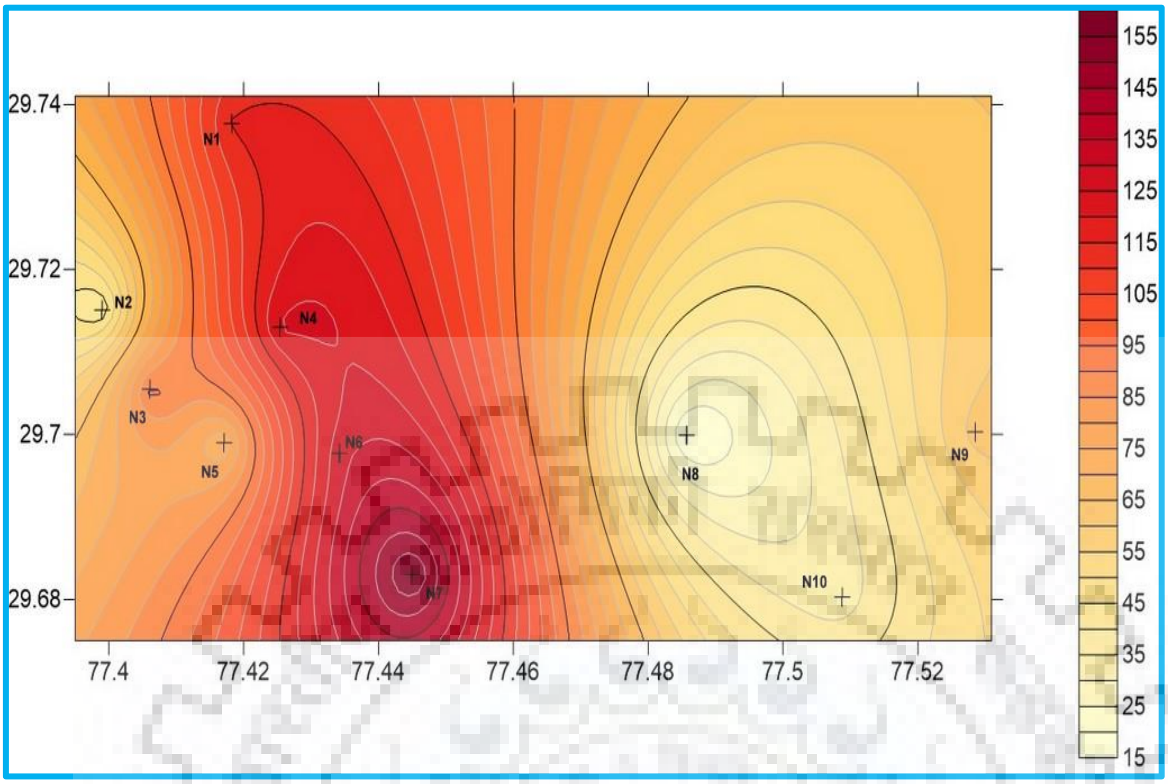
29.74
29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1

(a) As



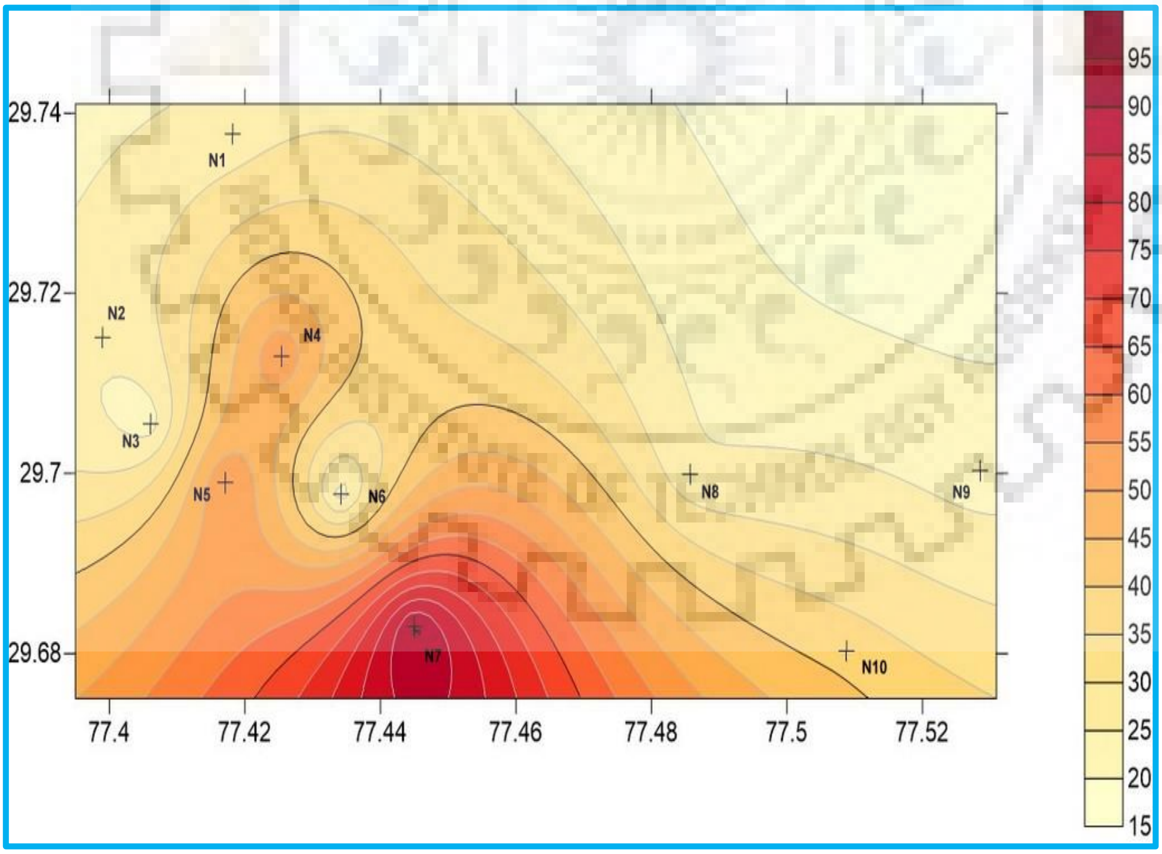
29.74
29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
3.1
3
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4

(b) Cd



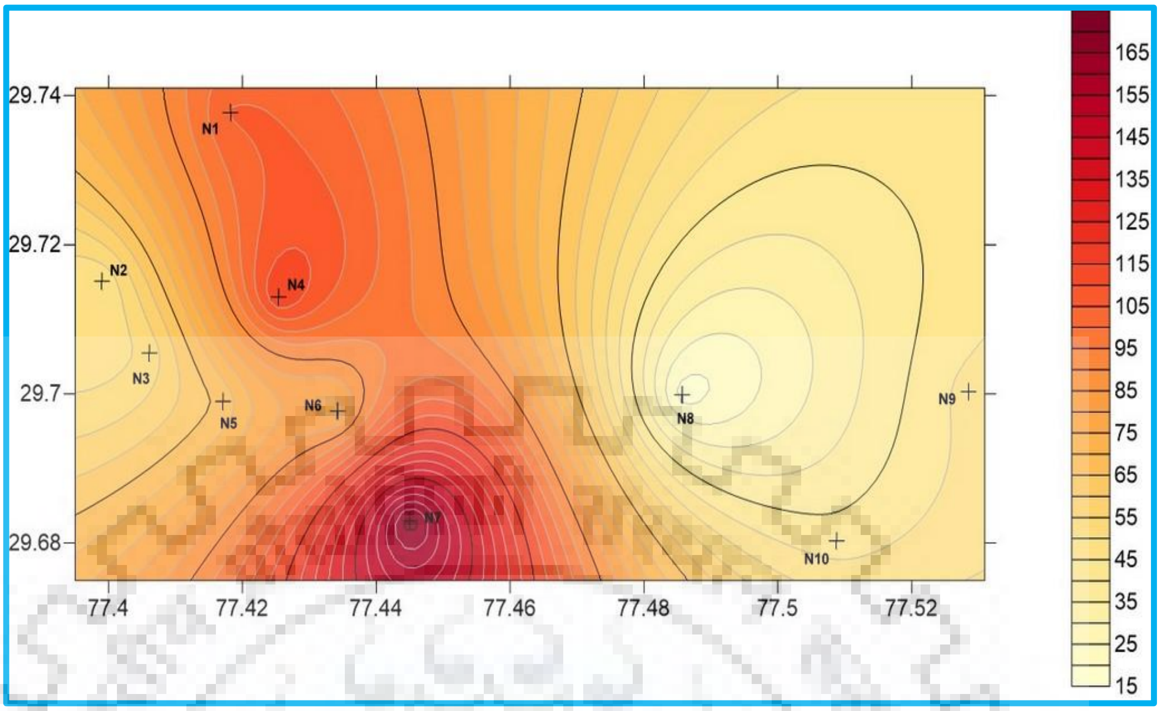
29.74
29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
155
145
135
125
115
105
95
85
75
65
55
45
35
25
15

(c) Cr



29.74
29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

(d) Cu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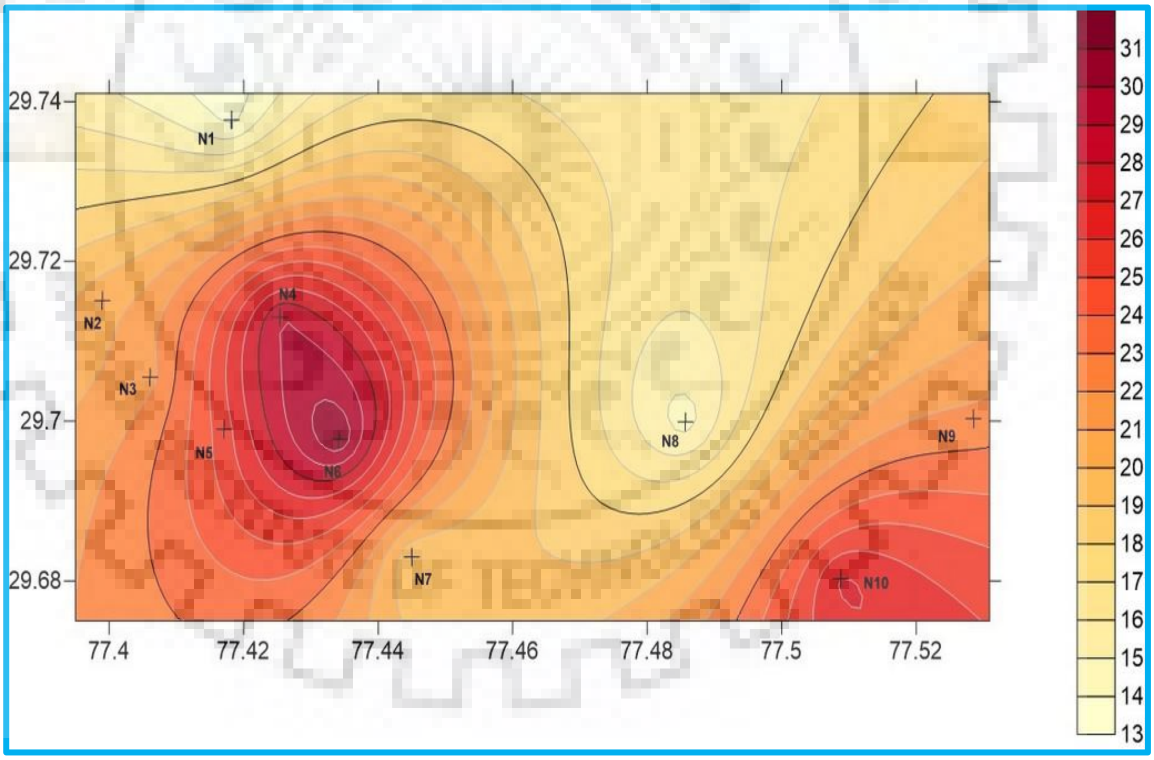
29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
165
155
145
135
125
115
105
95
85
75
65
55
45
35
25
15

(e) Ni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29.72
29.7
29.68
77.4
77.42
77.44
77.46
77.48
77.5
77.52
N1
N2
N3
N4
N5
N6
N7
N8
N9
N10
31
30
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27
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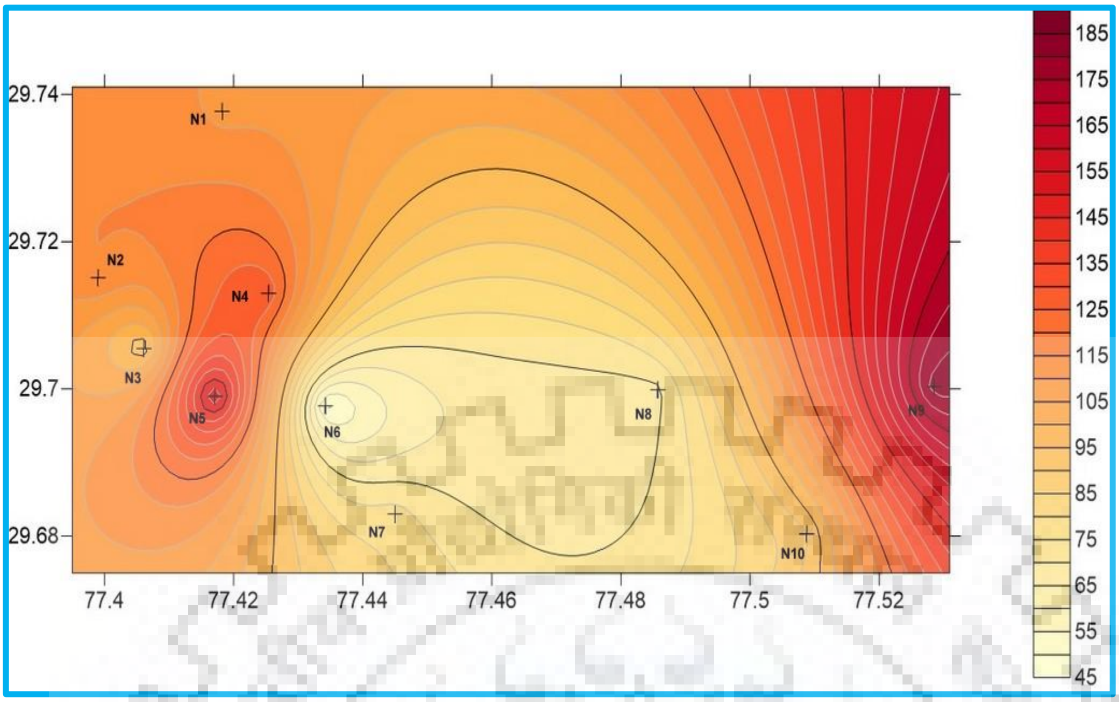
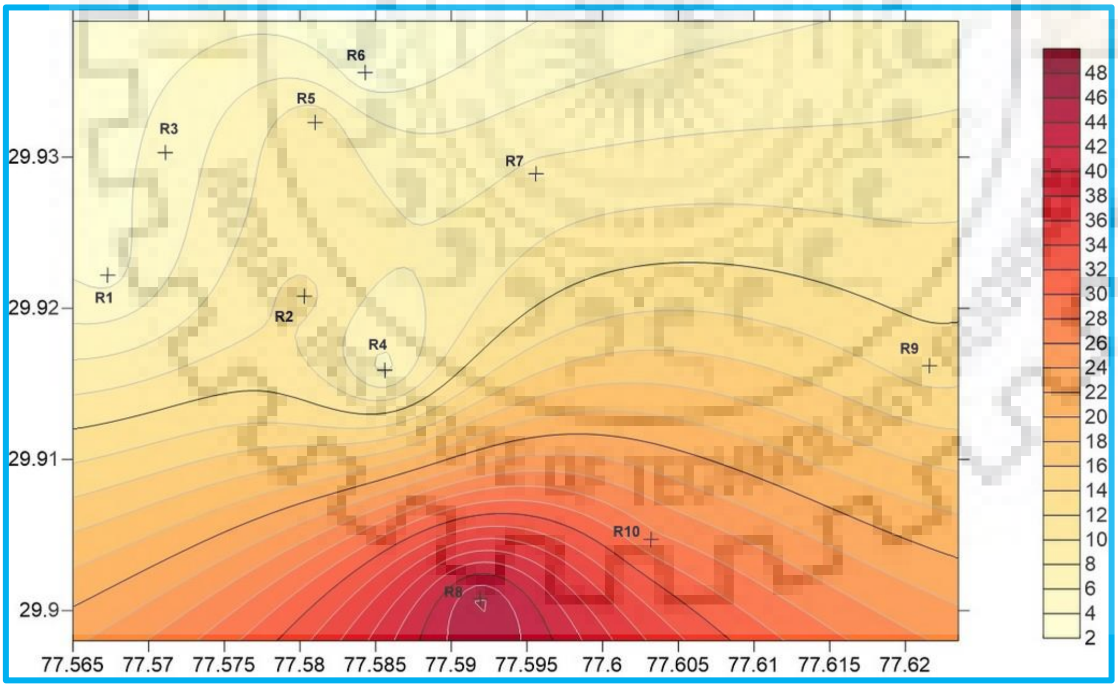
14
13

(f) Pb

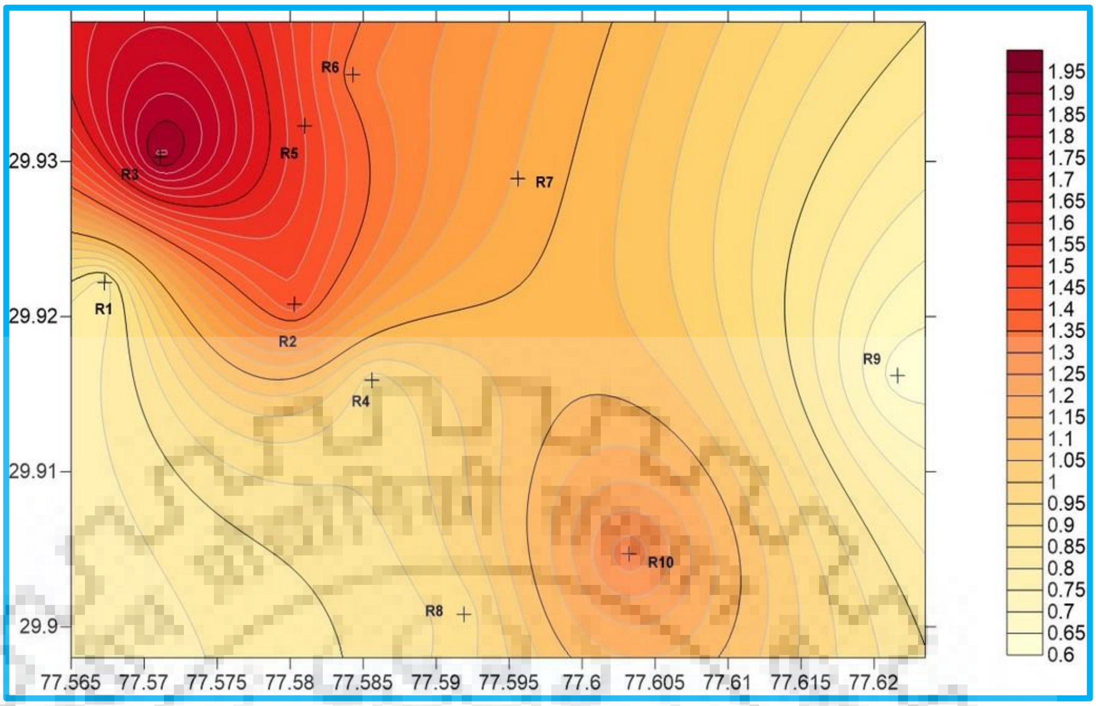


(g) Zn

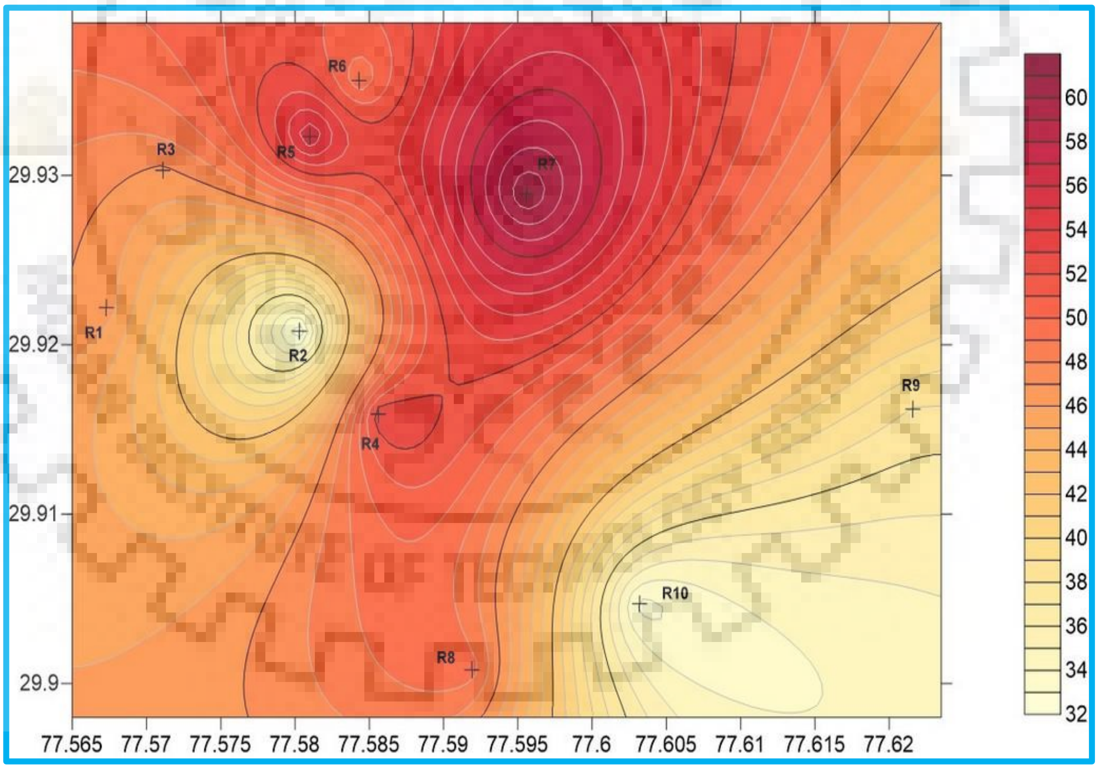
Fig 3.3 (a-g): *Spatial variation of heavy metal contamination in Nanauta industrial area*



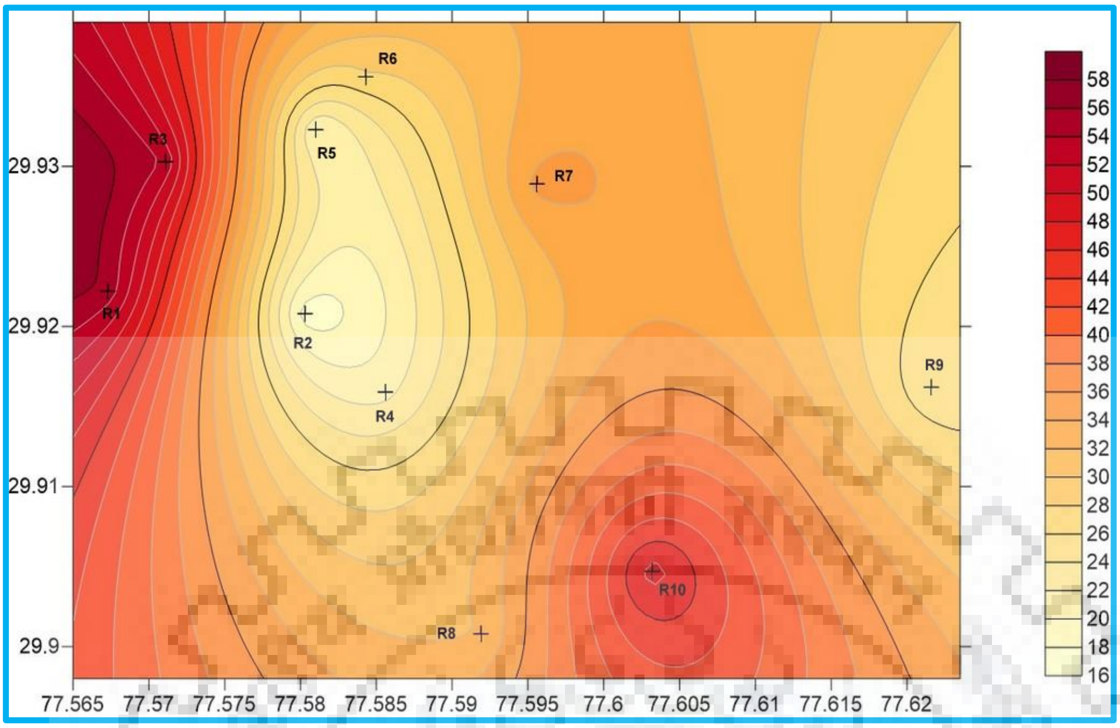
(a) As


R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
77.565
77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
1.95
1.9
1.85
1.8
1.75
1.7
1.65
1.6
1.55
1.5
1.45
1.4
1.35
1.3
1.25
1.2
1.15
1.1
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6

(b) Cd


R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
77.565
77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
60
58
56
54
52
50
48
46
44
42
40
38
36
34
32

(c) Cr



R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
77.565
77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
58
56
54
52
50
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44
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26
24
22
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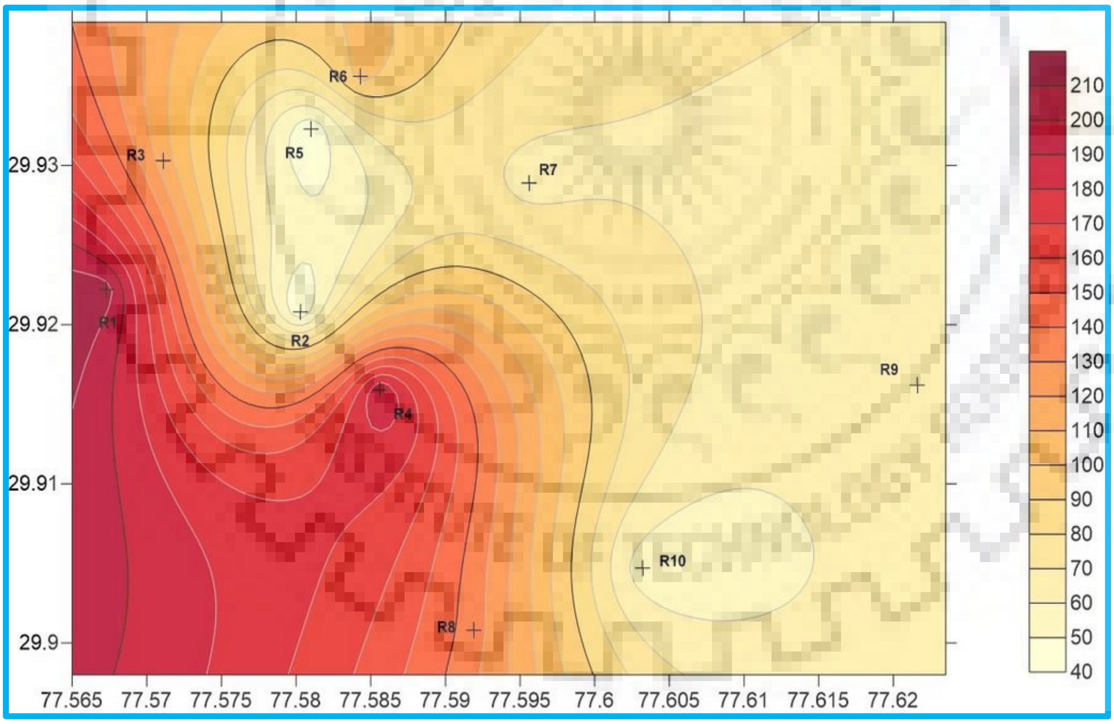
18
16

(d) Cu



R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
77.565
77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
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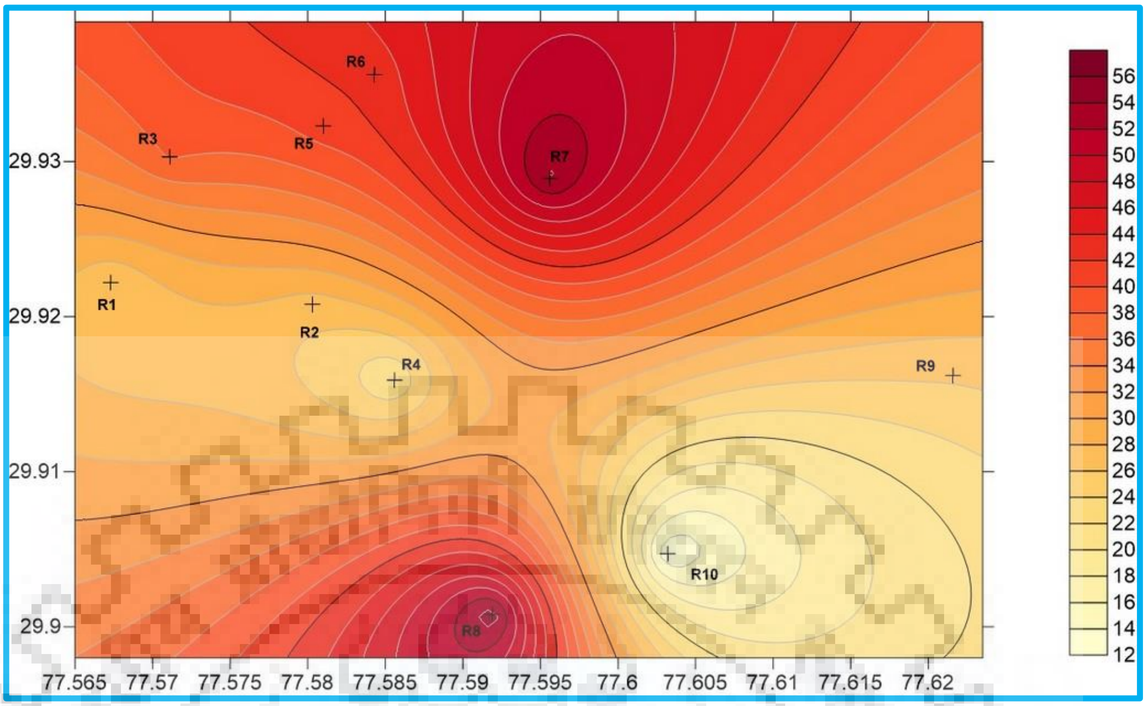
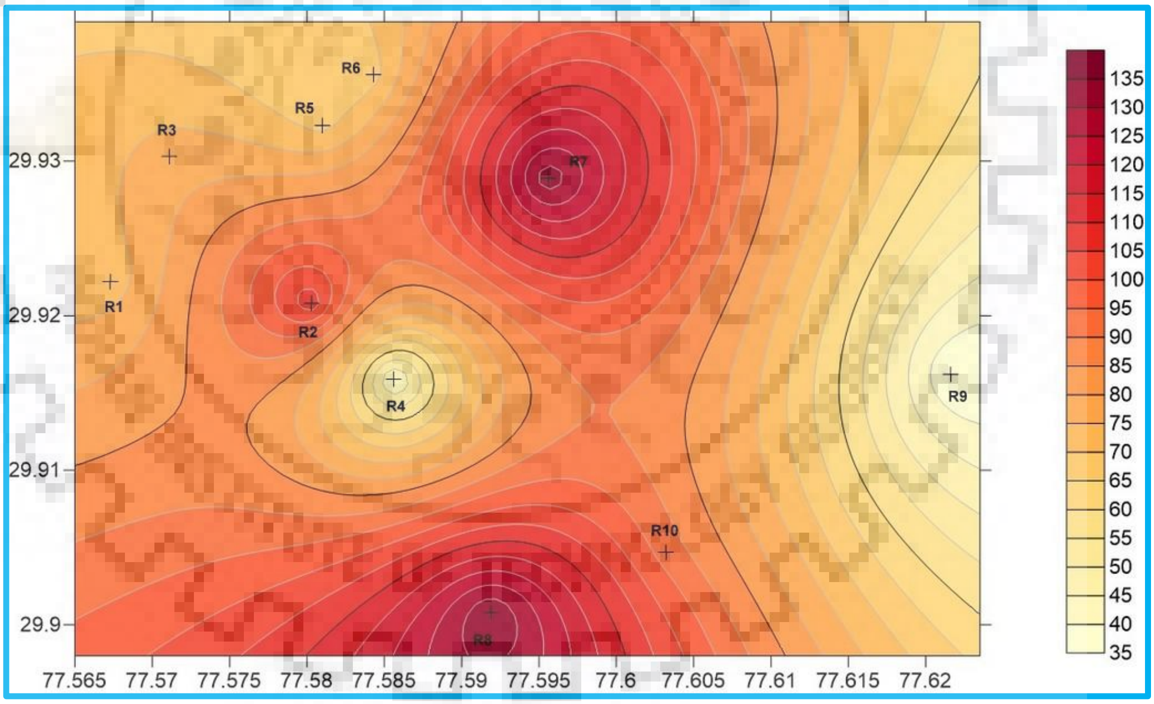
60
50
40

(e) Ni



(f) Pb



(g) Zn

Fig 3.4 (a-g): *Spatial variation of heavy metal contamination in Railway Road industrial area.*

3.4A.3. Statistical analysis for metal contamination in soil

Principal component analysis (PCA) was performed on heavy metal concentration analyzed at different sampling sites in order to interpret their multivariate relationships and to explore the reduction of the experimental variables. The purpose of PCA is to reduce the dimensionality of the dataset since a few of the new components explain the major part of the variation of the data. PCA has been used as a major application in the source identification of heavy metal [13], [14]. The factor score for the PC loading is presented in table 4. The two-factor components were accounted for 88.75%, 87.15% and 91.3% of the variance in Pilakhni, Nanauta and Railway road industrial area respectively.

Table 3.4: Factor loadings, eigenvalue, variance (%) and cumulative (%) analyzed from principal component analysis

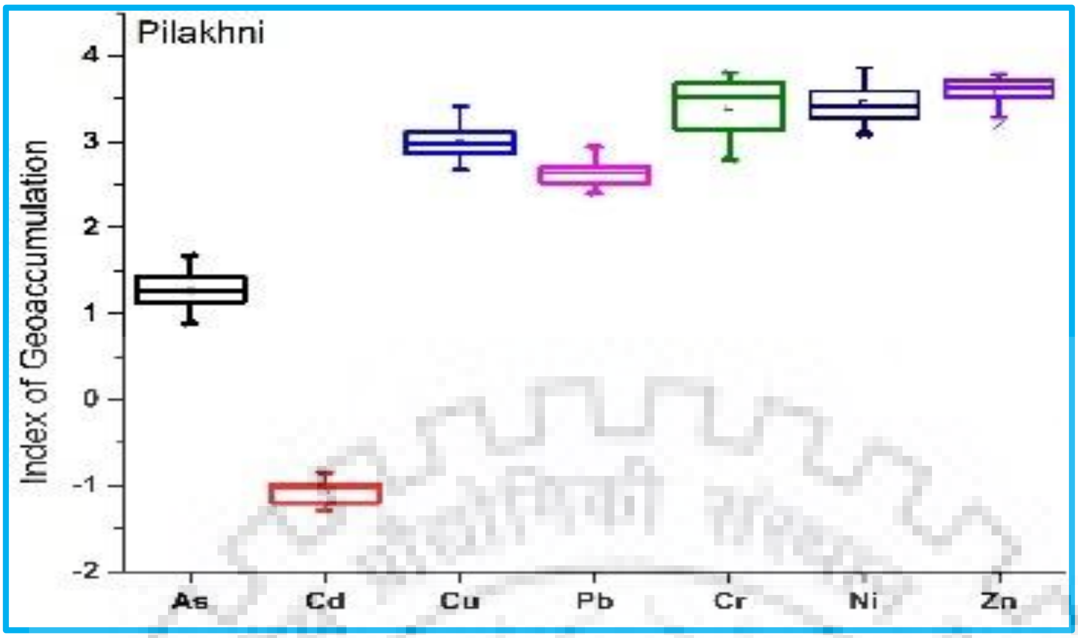
	Pilakhni		**Nanauta**		**Railway road**	
Metal	**PC 1**	**PC 2**	**PC 1**	**PC 2**	**PC 1**	**PC 2**
As	0.77	0.21	0.52	0.34	0.79	0.10
Cd	0.48	-0.65	0.90	0.17	0.65	0.45
Cu	0.83	0.22	0.68	0.33	0.12	0.84
Pb	0.70	0.27	0.82	-0.12	0.72	-0.08
Cr	0.65	0.05	0.70	-0.02	0.92	-0.09
Ni	0.67	0.05	0.83	0.15	0.97	0.19
Zn	0.59	0.45	0.81	0.20	0.23	0.86
Eigenvalues	5.40	1.08	5.88	1.89	4.80	3.30
Variance (%)	60.03	28.72	61.98	25.17	52.8	38.55

The value of factor loadings >0.75, 0.75–0.5 and 0.5–0.3 represents ‘strong’, ‘moderate’ and ‘weak’ loading respectively. The PC1 loading in Pilakhni industrial area As and Cu showing strong loading whereas moderate loading was observed for Pb, Cr, Ni, and Zn. The factor PC1 elucidate 60.03% of variance in the data and has significant loading of As, Cu, Pb, Cr, Ni and Zn in Pilakhni industrial area and can be related to the impact of Sugar mill industry, and other medium to small-scale industries including steel fabrication, brick baking industries etc., which are quite common in this area. The strong positive loading of Cd, Pb, Ni, and Zn was observed in PC1 of Nanauta industrial indicating the influence of industries like a distillery, textile dyeing, pesticide formulations, induction/foundries etc. The major large-scale industry in the railway road industrial area is the paper mill industry, which generates a large volume of industrial wastewater. the paper industry is globally well-apprehended industry for generating a considerable amount of pollution. The significant loading of Cr, Ni and Pb may indicate the influence of unmanaged paper mill wastewater disposal and long-term wastewater irrigation in the study area. The significant loading of As and Cd may also indicate the impact of vehicular emissions and excessive incorporation of chemical fertilizers and pesticides in the area. The strong loading of Cu and Zn in PC2 of Railway road industrial area may attribute to the geogenic sources.

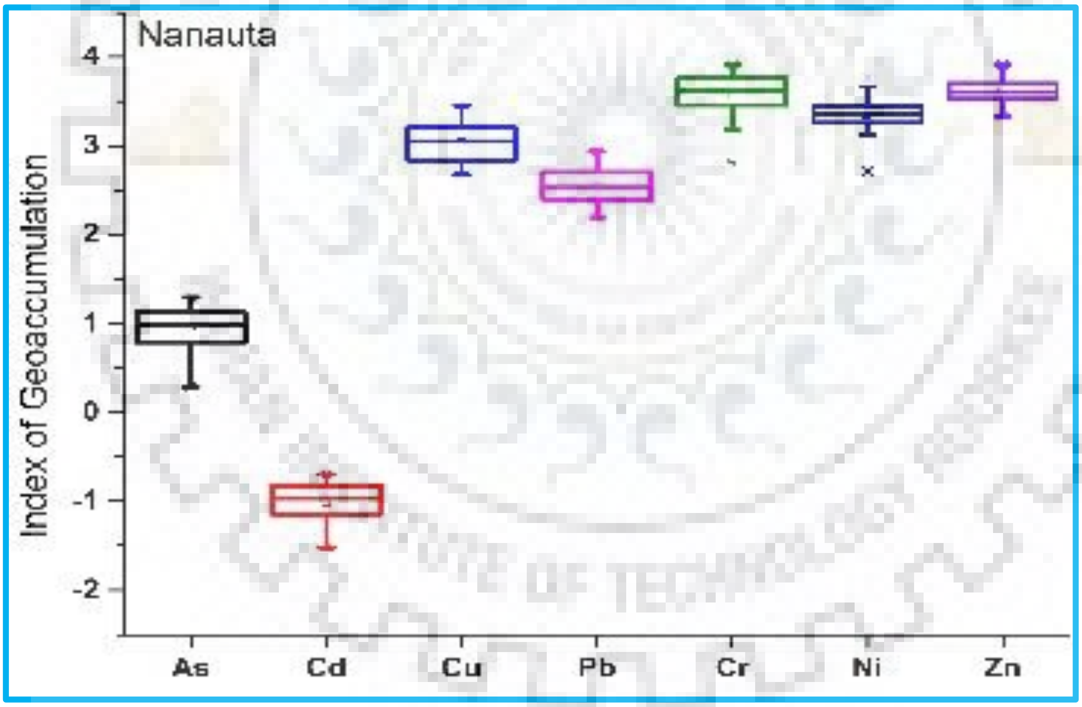
3.4A.4. Ecological risk assessment analysis

Geo-accumulation index (I_{geo}), Enrichment Factor (EF) and contamination factor represented in the box-plot graph in fig. 3.5 (a-c) and 3.6 (a-c) indicating moderate to high Index of geo-accumulation and enrichment factor of As throughout the study area as well. Cd can also have geogenic sources including underlying bedrock or transported parent material such as glacial till and alluvium [9], [15] apart from anthropogenic inputs including atmospheric deposition, sewage sludge, manure and phosphate fertilizers [16].

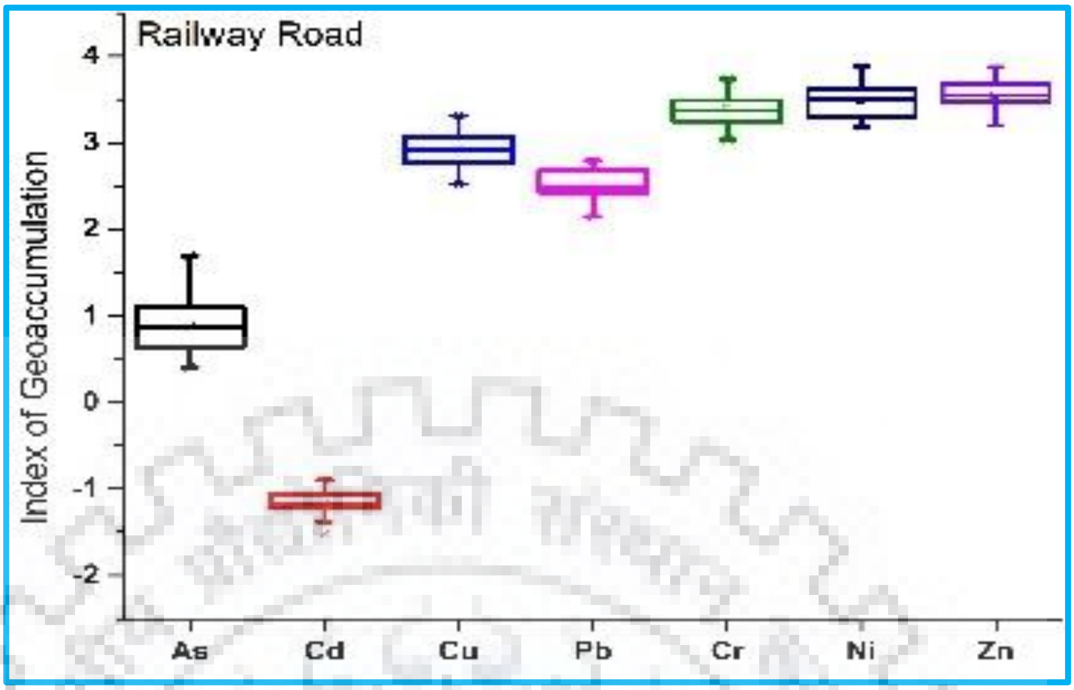
Comparatively, high Cd enrichment was observed in Nanauta followed by Pilakhni and railway Road industrial area. Fly ash from large scale industries to small scale industries including jaggery making unit, brick baking etc. can also be anticipated for the contribution in the overall metal contamination of Cr, Cu, Pb and Ni in the study area. Low or negligible contamination factor was observed for Cu, moderate contamination factor was observed for the metals Pb, Cr, Ni and Zn, and extremely high contamination factor was found associated with As and Cd in all three industrial areas. The Potential ecological risk index (PERi) inferring significantly high risk is associated with the As and Cd contamination, the risk associated with other metals was found to be low in all three industrial areas (Table 3.5).


Pilakhni
Index of Geoaccumulation
4
3
2
1
0
-1
-2
As
Cd
Cu
Pb
Cr
Ni
Zn

(a)

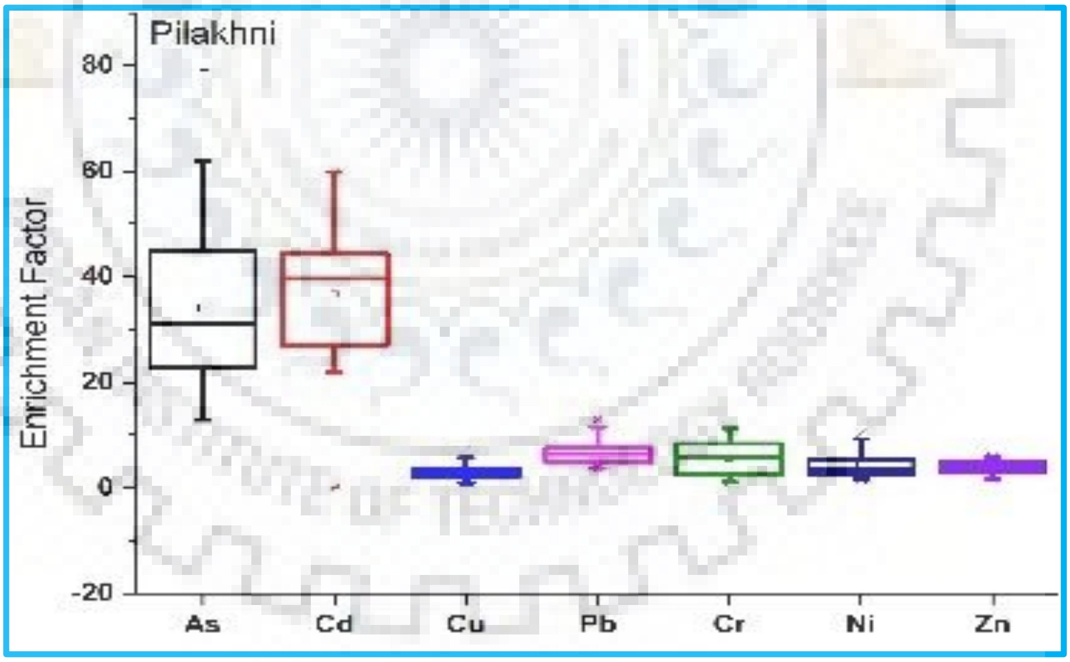

Nanauta
Index of Geoaccumulation
4
3
2
1
0
-1
-2
As
Cd
Cu
Pb
Cr
Ni
Zn

(b)

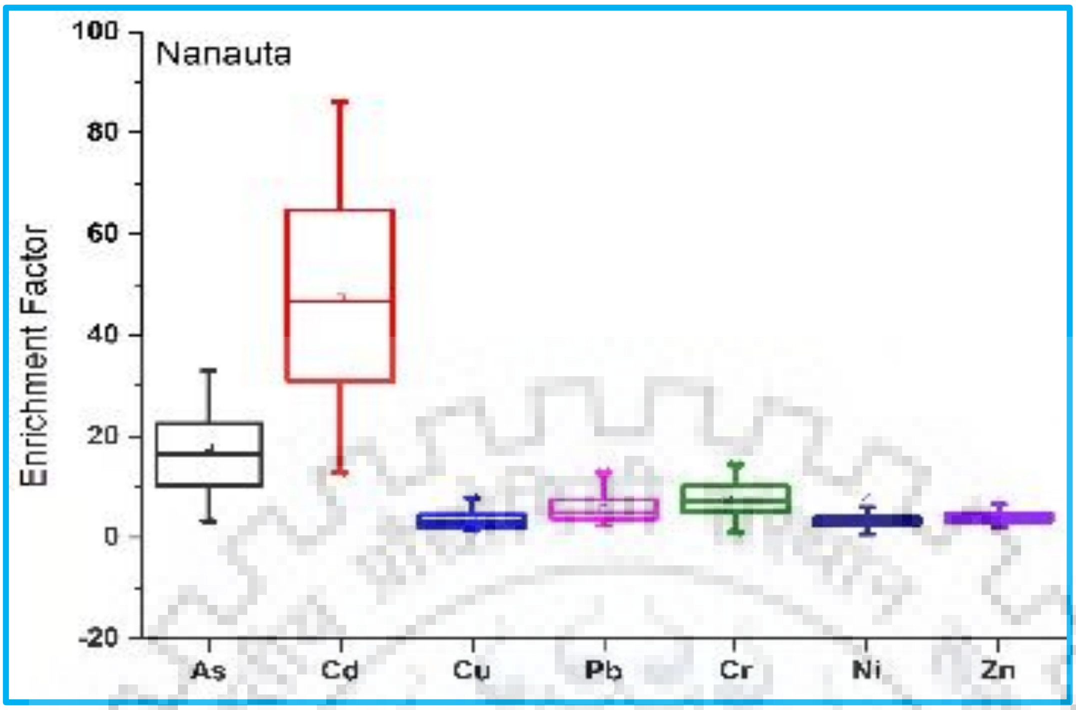


(c)

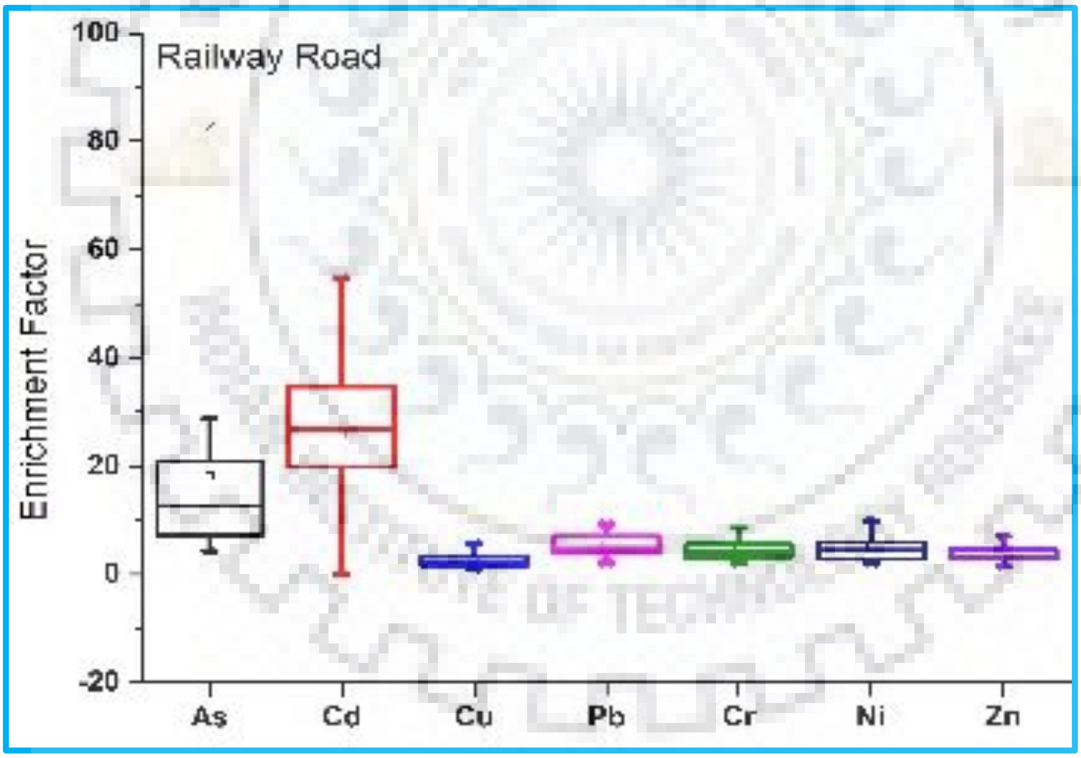
Fig. 3.5 (a-c): *Index of Geo-accumulation in the study area*



(a)



(b)



(c)

Fig. 3.6 (a-c): *Enrichment factor in the study area*

Table 3.5: Heavy metal geo-accumulation, enrichment, contamination factor and risk assessment in the study area

	Contamination factor			PERi		
Metal	**P**	**N**	**R**	**P**	**N**	**R**
As	11.94	6.27	6.35	2387.00	1253.25	1269.69
Cd	12.84	16.65	9.09	12837.70	16653.10	9088.00
Cu	1.06	1.22	0.92	106.35	121.58	91.53
Pb	2.38	2.00	1.85	238.16	200.40	185.27
Cr	1.97	2.63	1.69	78.85	105.26	67.75
Ni	1.52	1.24	1.73	151.98	123.54	173.42
Zn	1.36	1.45	1.27	27.19	28.97	25.47

*P= Pilakhni; N= Nanauta; R= Railway road.

3.4A.5. Health risk assessment analysis

The estimation of both non-carcinogenic and carcinogenic health risk (95% UCL) via ingestion pathway is presented in the table.6, briefly represents the average daily intake (ADI) for both non-carcinogenic and carcinogenic risk estimation along with hazard quotient (HQ) and Carcinogenic Risk (CR).

The results indicate that both non-carcinogenic and carcinogenic risks due to the exposure of metal contaminated soil are comparatively higher in children than adult population in all three industrial zones. HQ value <1 and Cancer Risk in between the range 1E-06 to 1E-04 typically considered to be under acceptable range [3]. The risk associated with As contamination was observed to be comparatively high in Pilakhni industrial zone followed by Railway road and Nanauta industrial zone. The value of HQ estimated for As indicating a considerable risk to the children population in comparison to the adult population. Four sampling sites from Pilakhni and two from Railway road industrial area were observed with high As chronic risk in children population, whereas, risk in adult population were in the acceptable range in all three industrial zones.

Potential non -carcinogenic risk can be anticipated with the exposure of Pb, Cr and Ni as HQ values in both adult and children population were observed approaching the safe value (HQ = 1). The negligible risk was observed for Cu and Zn contamination in all three industrial zones.

Significant Cr carcinogenic risk was observed in all three industrial areas, considerably high risk was observed in children population.

The carcinogenic risk associated with As, Pb and Ni were observed to be within the acceptable range (1E-06 to 1E-04), whereas the negligible risk was observed for Cd contamination.

The toxicity of heavy metal is well apprehended, but pernicious impacts become evident on long-term exposure. Severe health impacts related to kidney, bones, nervous, cardiovascular system along with disruption of other biochemical mechanisms may occur due to the accumulation of heavy metals at the chronic level due to prolong exposure via different pathways. The profound attention is required to the increasing level of heavy metals in the study area particularly considering the high risk to the children population. There is a high risk of transfer of metals from soil to the food chain, as the study area comprises of a considerable fraction of agricultural land. Furthermore, leaching of heavy metals from highly contaminated sites in the shallow water plume can be anticipated for the metal contamination in the groundwater as well. Appropriate measures and intervention in policy are required to safeguard the deteriorating quality soil system. Social awareness regarding environmental contamination and its consequences may also check the mass exposure and health-related hazards.

Table 3.6: Hazard quotient and cancer risk (95% UCL) associated with metal contamination in both adult and children in the study area

	As	Cd	Cu	Pb	Cr	Ni	Zn
P (A)[a]	1.06E-01	2.24E-03	1.72E-03	1.92E-02	3.82E-02	6.94E-03	5.04E-04
P (C)[a]	8.49E-01	1.80E-02	1.38E-02	1.54E-01	3.07E-01	5.58E-02	4.05E-03
N (A)[a]	5.55E-02	2.76E-03	1.97E-03	1.62E-02	5.10E-02	5.64E-03	5.37E-04
N (C)[a]	4.46E-01	2.22E-02	1.58E-02	1.30E-01	4.10E-01	4.53E-02	4.32E-03
R (A)[a]	5.62E-02	1.77E-03	1.48E-03	1.49E-02	3.28E-02	7.92E-03	4.72E-04
R (C)[a]	4.52E-01	1.43E-02	1.19E-02	1.20E-01	2.64E-01	6.36E-02	3.79E-03
P (A)[b]	1.69E-05	5.02E-07		1.03E-06	1.00E-03	3.42E-05	
P (C)[b]	1.27E+00	1.14E-02		5.81E-04	6.48E+00	2.58E-01	
N (A)[b]	8.32E-02	1.74E-03		8.26E-05	6.79E-01	4.28E-02	
N (C)[b]	6.69E-01	1.40E-02		6.64E-04	5.45E+00	3.44E-01	
R (A)[b]	8.43E-02	1.12E-03		6.22E-05	6.27E-01	2.76E-02	
R (C)[b]	6.78E-01	8.99E-03		5.00E-04	5.04E+00	2.21E-01	

*a and b represent non-carcinogenic and carcinogenic respectively

3.4B. ANALYSIS OF METAL CONTAMINATION IN GROUNDWATER SAMPLES

3.4B.1. Physiochemical characteristics of groundwater

The physio-chemical analysis of groundwater sample from the study area is summarized in Table 3.2. The pH of the groundwater sample ranged from slightly acidic to slightly alkaline; most of the samples analyzed were within the WHO and BIS permissible limits. Low pH value (< 6.5) may lead to the corrosion of metal pipes or fixtures on direct contact and result in the release of toxic metals. Health-related issues including gastrointestinal, neurological and reproductive disorders may also result from regular consumption of low pH drinking water [17], [18].

The conductivity of water corresponds to the presence of ions in the water. The range observed in the samples (0.62 to 5.82 dS/m) were higher than the permissible limits. The direct impact of conductivity on the human health is not significant whereas, for industrial and agricultural activity it is essential to monitor electrical conductivity as high conductivity results in the deposition of minerals which may alter variables associated with corrosive properties and plant growth.

The aquatic health and metabolic activities of aquatic flora and fauna significantly depend on the Dissolved oxygen (DO) concentration in the aquatic system. High DO level (> 8 mg/l) induces the corrosive ability whereas low DO concentration make water unfit for drinking and induces stress to the aquatic life.

Table 3.7: Physiochemical characteristics of the groundwater in the study area

Parameters	Unit	Min	Max	Mean	SD	WHO	BIS
pH		6.04	8.05	7.25	0.33	7.0-8.0	6.5-8.5
EC	dS/m	0.62	5.82	3.65	0.88	0.7	0.3
DO	mg/l	0.89	6.25	3.05	0.92		8
COD	mg/l	4.2	34.45	14.2	5.35	10	10
Turbidity	NTU	0.44	14.5	4.32	1.74	5	5
TDS	mg/l	411.5	3155	1245	660	500	500
TSS	mg/l	125	1876	634.12	245.5	500	

The DO concentration in the samples was observed to be in the permissible limit but extremely low DO indicates the poor quality of the drinking water in the study area. The mean COD value observed to be higher than the permissible limit indicating the presence of chemical constituents in the samples. The COD value ranged from 4.2 to 34.35 mg/l in the study area. the mean value of TDS and TSS were observed higher than the permissible limit, whereas, the mean value of turbidity was observed within the permissible limit.

3.4B.2. Heavy metal concentration in the Groundwater

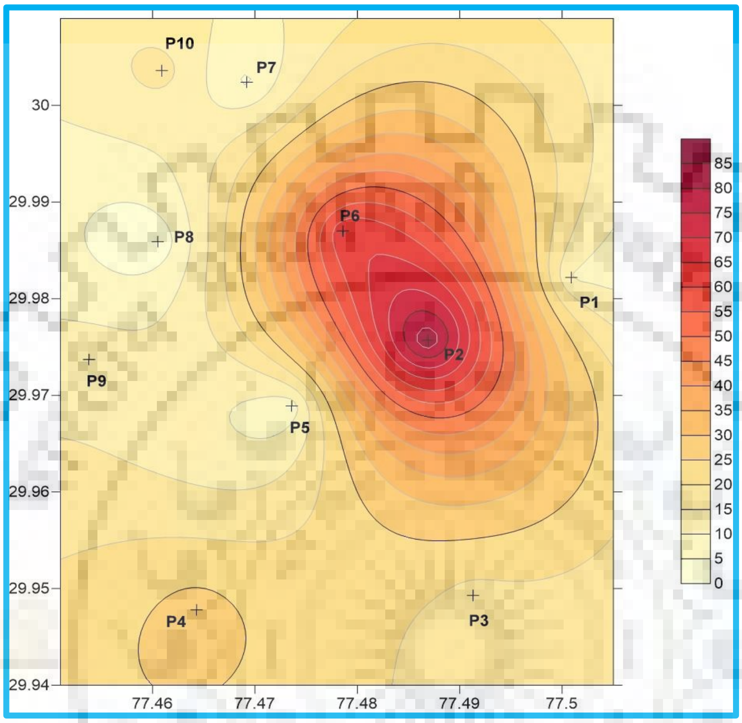
The heavy metal analysis revealed that Pilakhni is severely contaminated with metal constituents in the groundwater followed by Nanauta and Railway road industrial area. The mean concentration of As, Cr, Mn, Pb an Zn were observed to higher in the Pilakhni industrial area, whereas, high mean concentration of Cd and Cu was observed in Nanauta industrial area.

Table 3.8: Descriptive statistics of groundwater metal concentration in three industrial zones of Saharanpur district

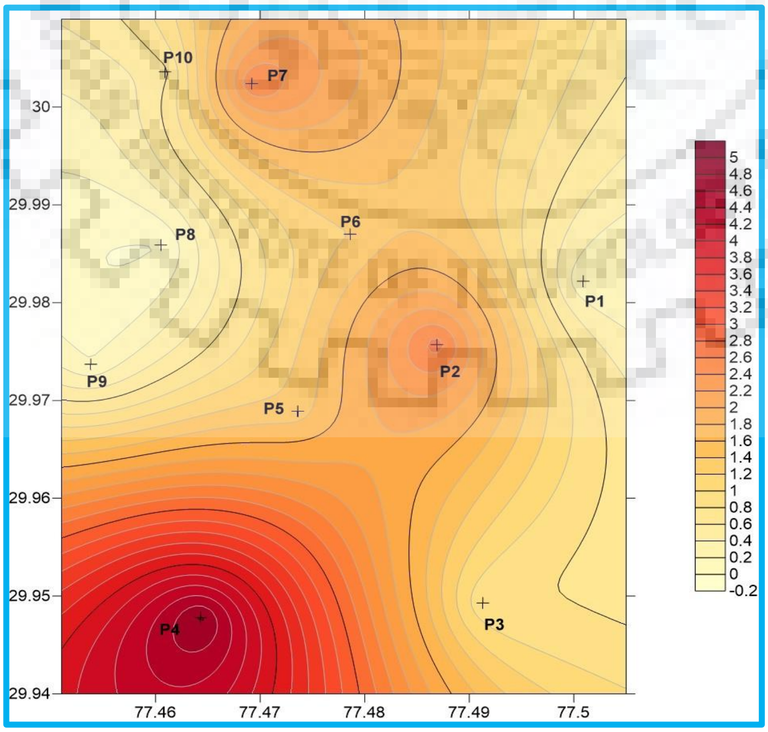
Metal (μgL^{-1})	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
P (n=20)								
Mean	24.70	1.67	85.70	34.06	297.96	31.48	21.275	104.78
S.D.	27.58	1.49	16.21	21.56	179.64	17.99	10.64	92.79
Min	1.3	ND	69.47	9.23	56.3	4.6	8.3	12.9
Max	84.4	4.83	123.3	66.2	703.5	50.5	44.1	288.8
Variance	760.95	2.23	262.99	465.06	3227.04	323.92	113.42	8610.94
Kurtosis	1.60	1.50	2.50	-1.59	2.21	-1.77	1.14	0.49
Skewness	1.60	1.26	1.46	0.40	1.21	-0.47	1.09	1.20
N (n=20)								
Mean	8.72	2.66	17.94	46.84	47.49	25.35	8.64	67.78
S.D.	7.26	2.54	13.91	20.08	38.03	11.07	10.31	31.69
Min.	0.56	ND	2.8	22.5	6.23	9.34	0.67	24.9
Max.	23.2	7.2	44.2	88.7	120.2	42.98	34.2	125.6
Variance	52.83	6.47	193.61	403.28	1446.76	122.73	106.39	1004.61
Kurtosis	0.23	-0.48	-0.42	0.96	-0.11	-0.91	4.16	-0.37
Skewness	0.91	1.10	0.80	1.08	0.95	0.06	1.93	0.53
R (n=20)								
Mean	3.71	0.33	9.25	28.57	83.93	38.92	3.22	35.15
S.D.	3.75	0.23	4.14	11.95	34.23	27.21	2.26	15.61
Min.	ND	ND	4.27	8.22	41.6	11.6	0.44	12.88
Max.	12.5	0.62	16.3	44.5	155.2	88.24	7.82	65.45
Variance	14.08	0.06	17.17	143.04	1172.05	740.43	5.13	243.92
Kurtosis	3.86	-2.75	-1.14	-1.00	0.82	-0.89	0.64	0.09
Skewness	1.79	0.37	0.26	-0.36	0.97	0.84	0.86	0.53
Standard Limits								
WHO (2011)	10	3	50	2000	400	70	10	NA
USEPA (2012)	10	5	100	1300	300	NA	15	5000

P= Pilakhni; N: Nanauta; R: Railway Road.

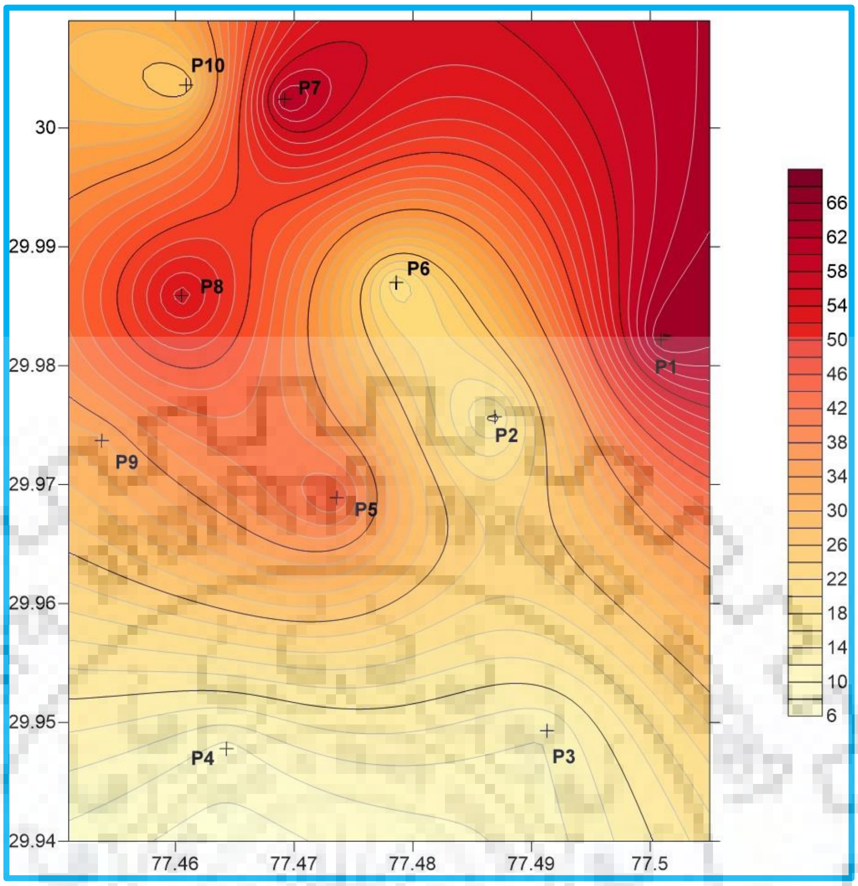
The mean concentration of As, Cr, and Pb were found to be 2.47 times, 1.714 times and 2.12 times respectively more than the permissible limit set by the [19]. Overall other metals mean concentrations were under or close to the prescribed standard WHO (2011) and [20] limits. The spatial distribution of groundwater contamination is shown in fig 3.7(a-h), 3.8(a-h), and 3.9 (a-h) in Pilakhni, Nanauta and Railway road industrial area respectively.



(a) As



(b) Cd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P3
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29.96
29.95
29.94
77.46
77.47
77.48
77.49
77.5
66
62
58
54
50
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42
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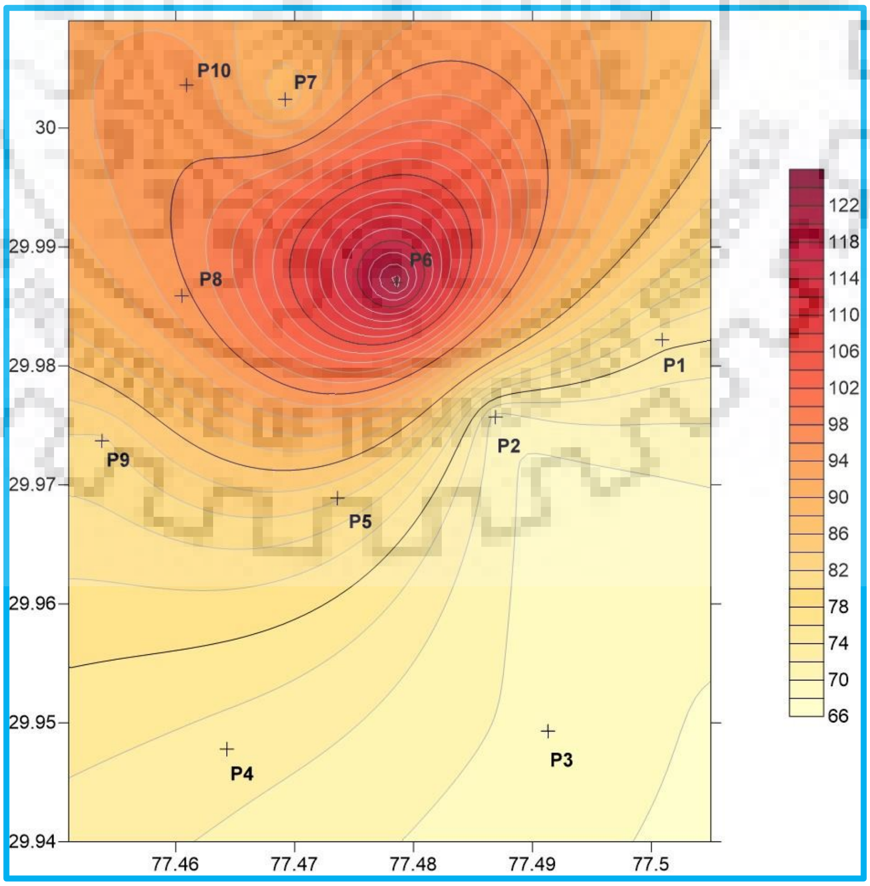
14
10
6

(c) Cu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P3
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29.95
29.94
77.46
77.47
77.48
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102
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94
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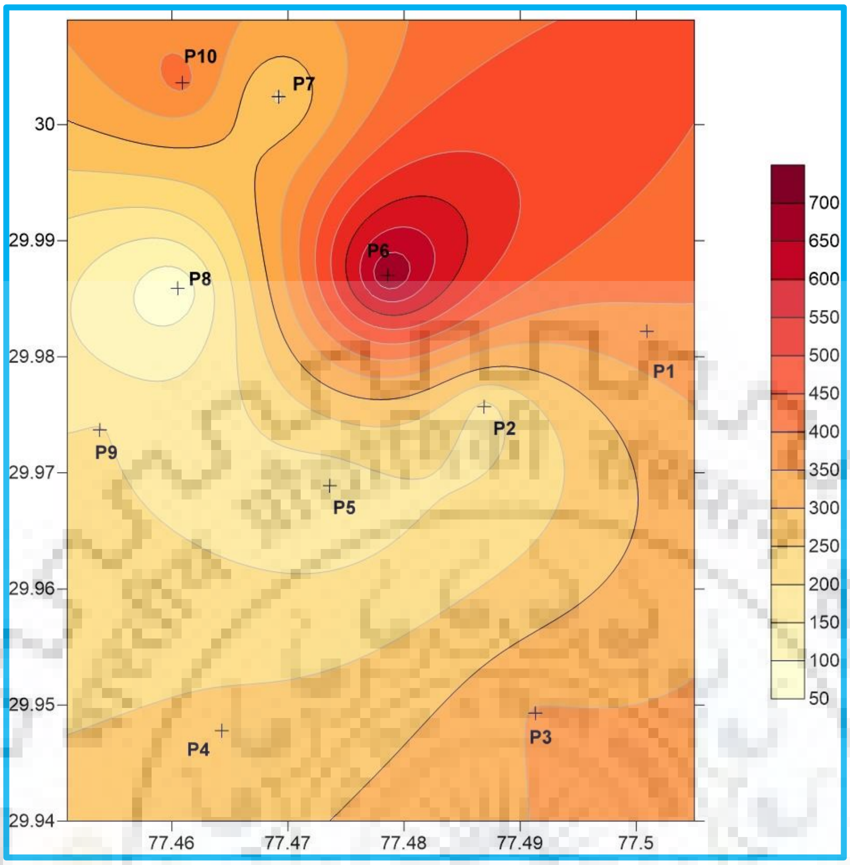
74
70
66

(d) Cr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P3
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29.95
29.94
77.46
77.47
77.48
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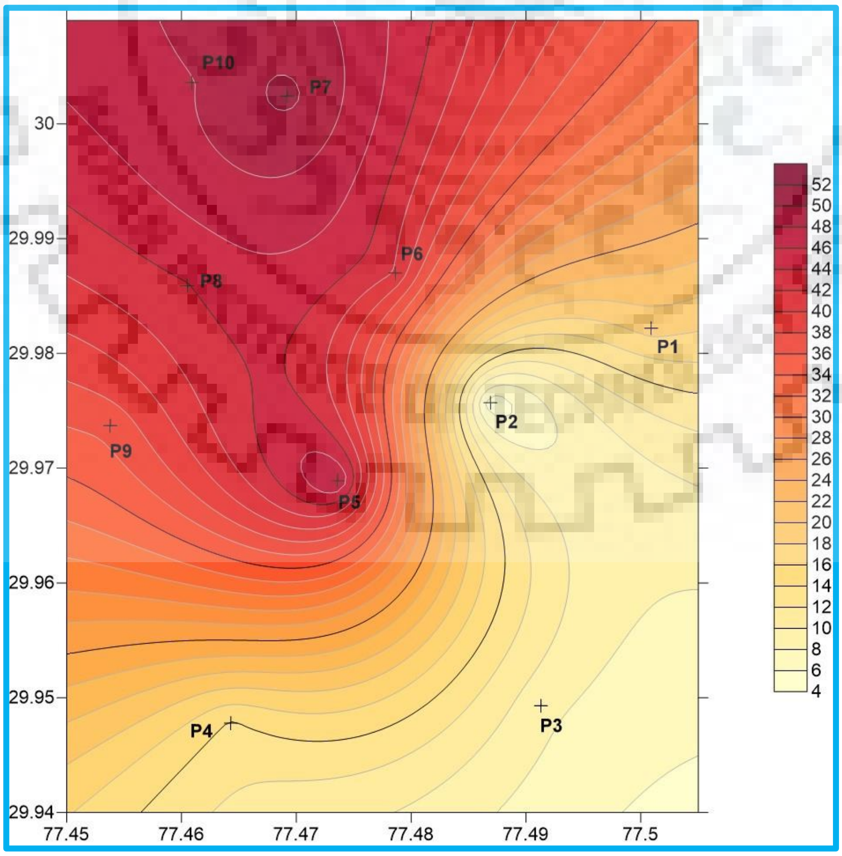
77.5
700
650
600
550
500
450
400
350
300
250
200
150
100
50

(e) Mn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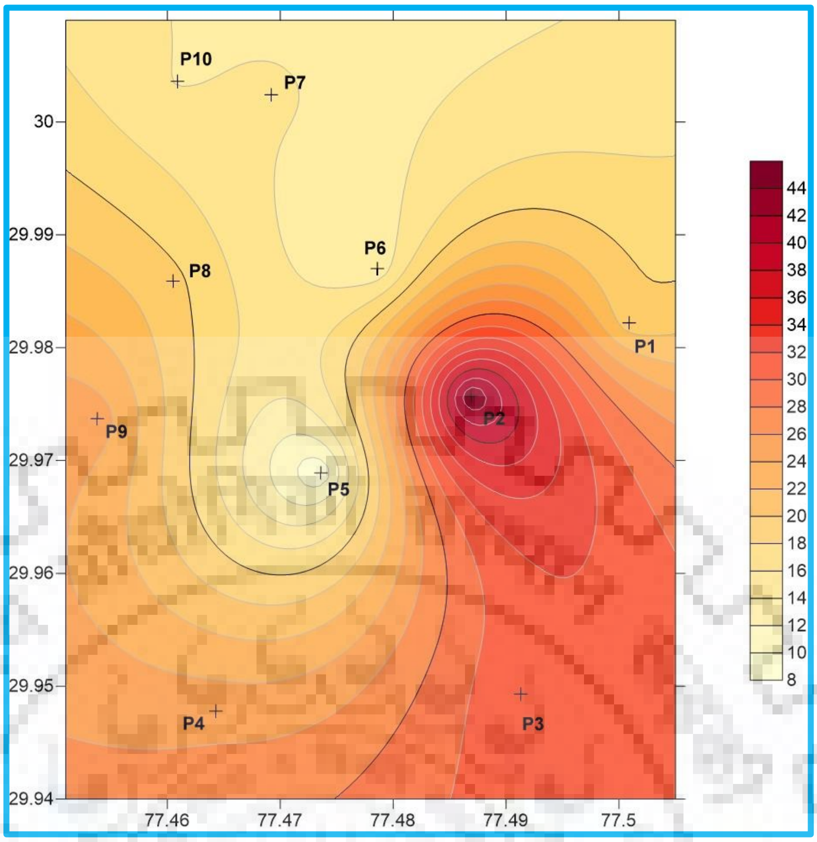
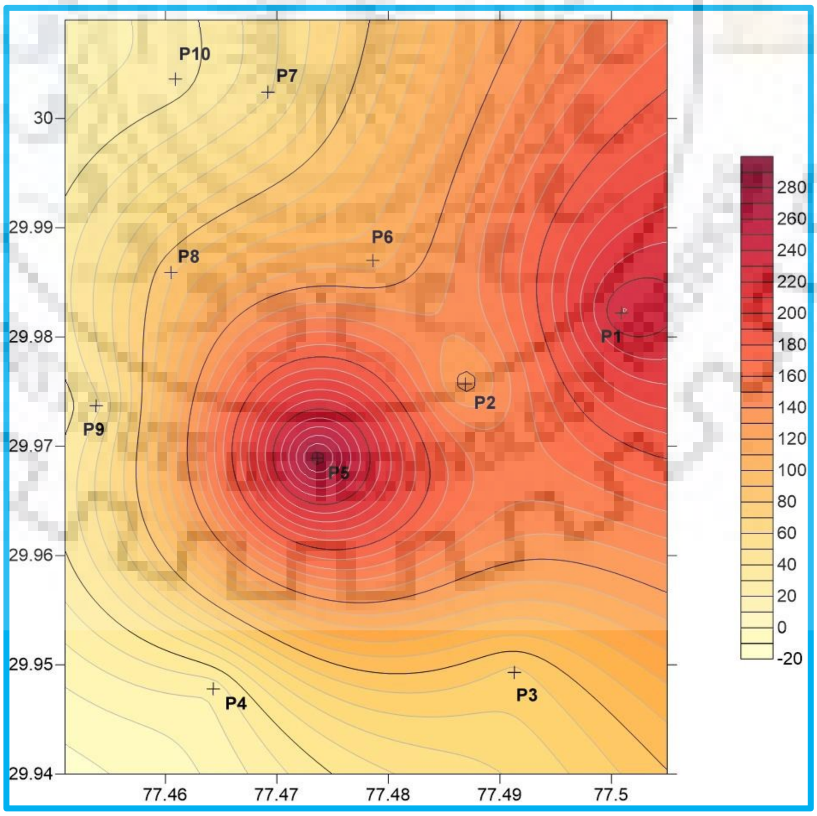
6
4

(f) Ni

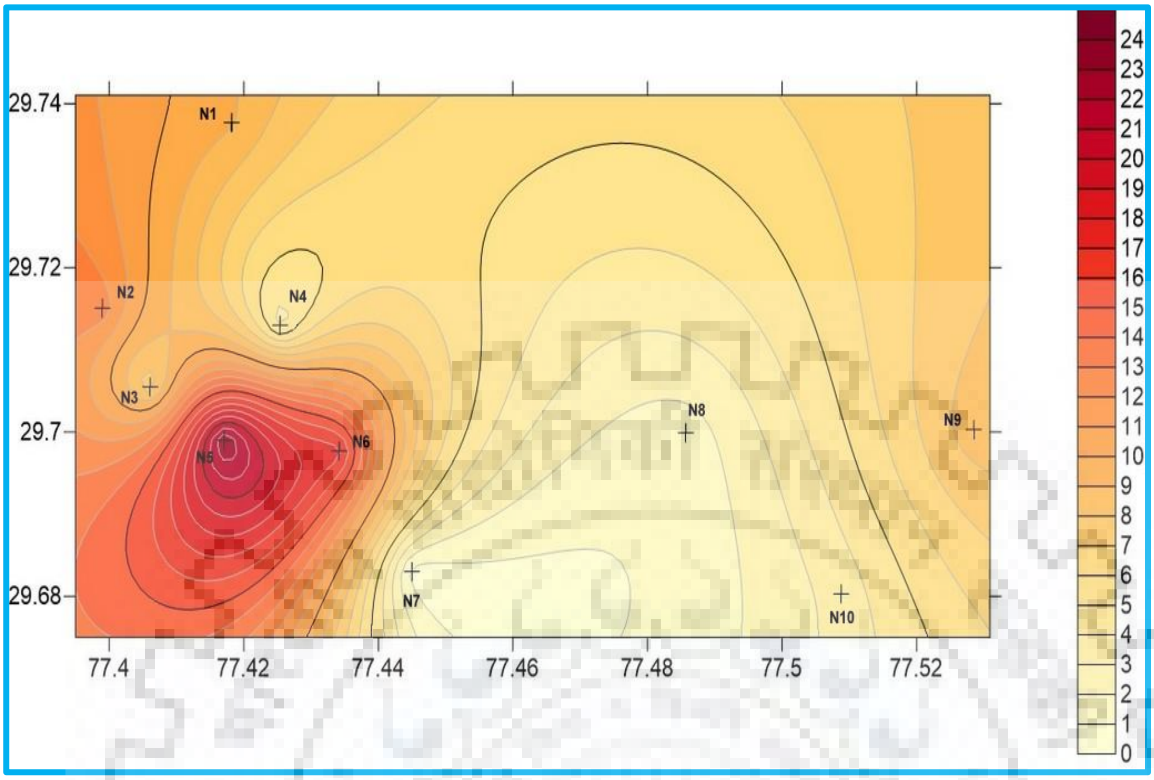


(g) Pb



(h) Zn

Fig. 3.7 (a-h): *Spatial distribution of groundwater metal contamination in Pilakhni industrial area*



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77.42
77.44
77.46
77.48
77.5
77.52
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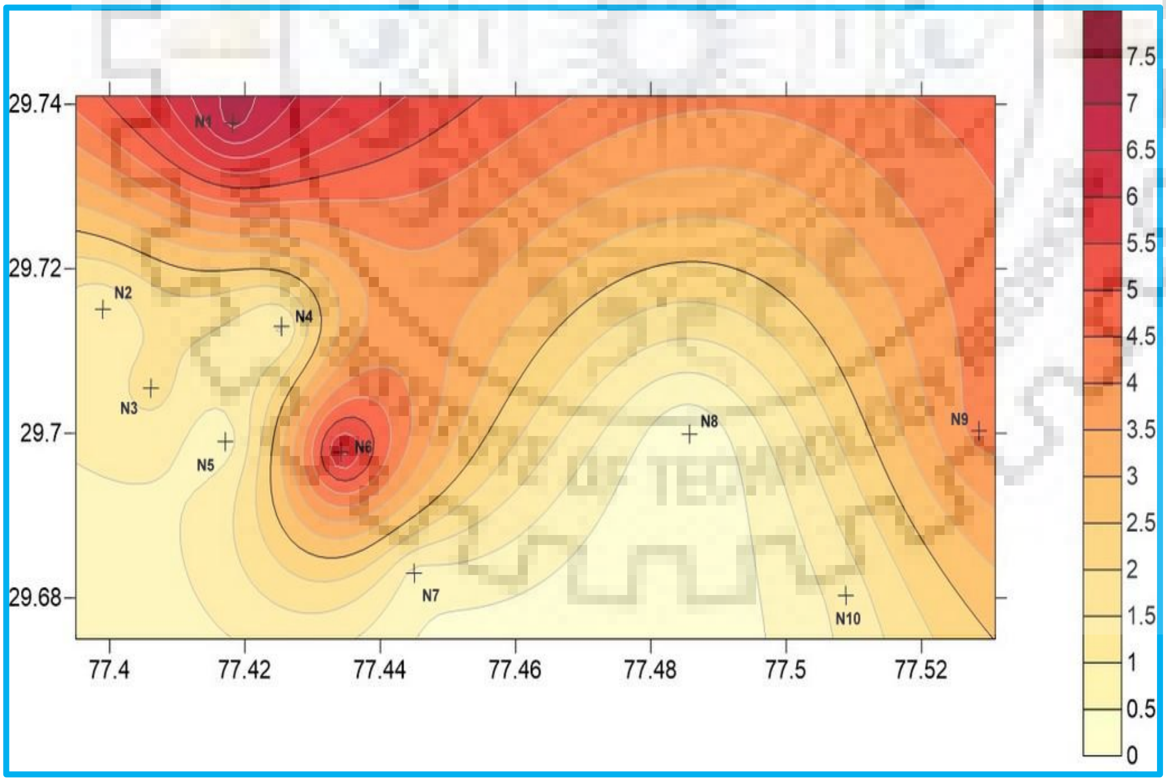
7
6
5
4
3
2
1
0

(a) As



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77.46
77.48
77.5
77.52
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N5
N6
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N9
N10
7.5
7
6.5
6
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5
4.5
4
3.5
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2
1.5
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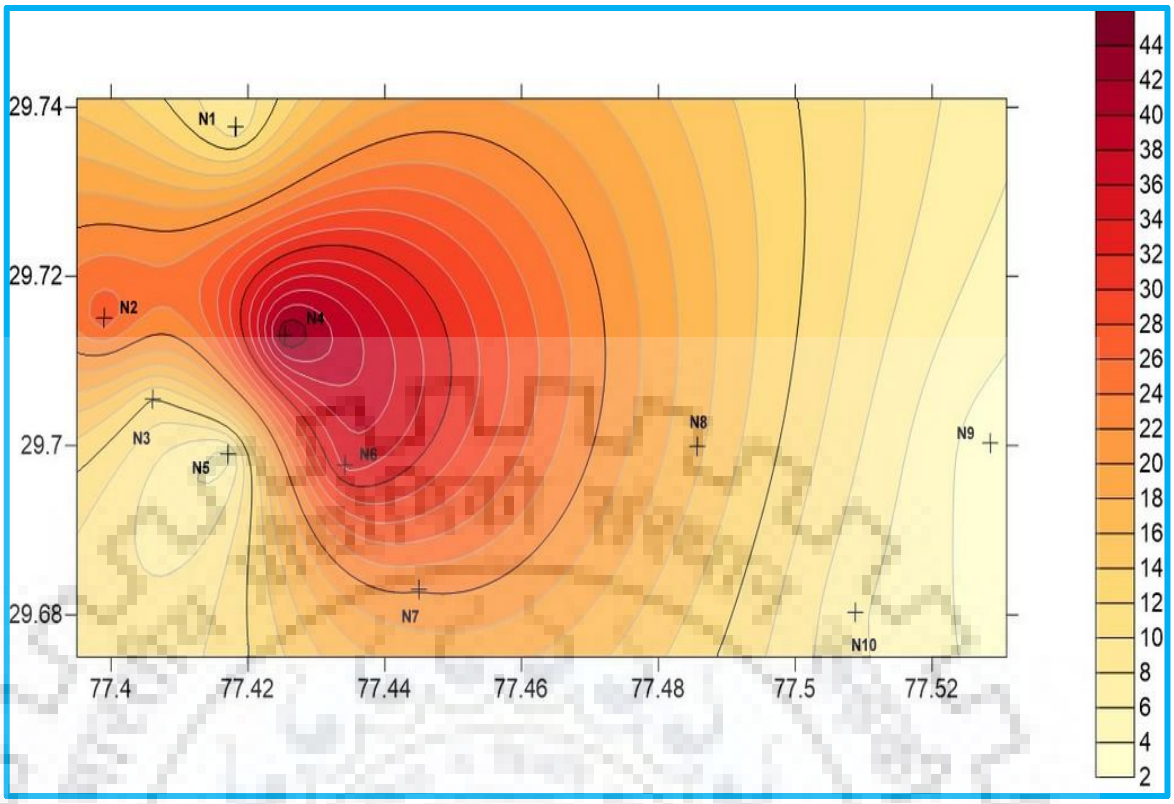
0

(b) Cd



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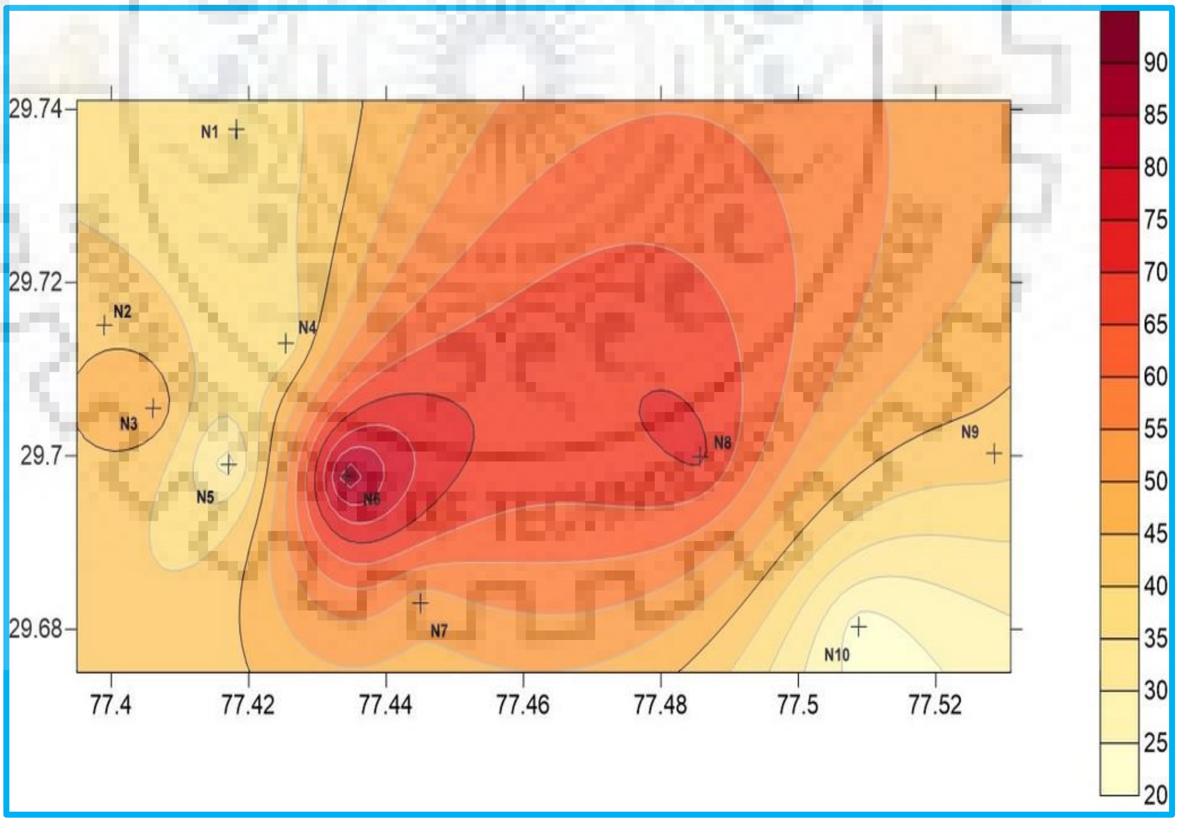
6
4
2

(c) Cr



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29.72
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77.4
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77.44
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77.48
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77.52
N1
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N6
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85
80
75
70
65
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55
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45
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35
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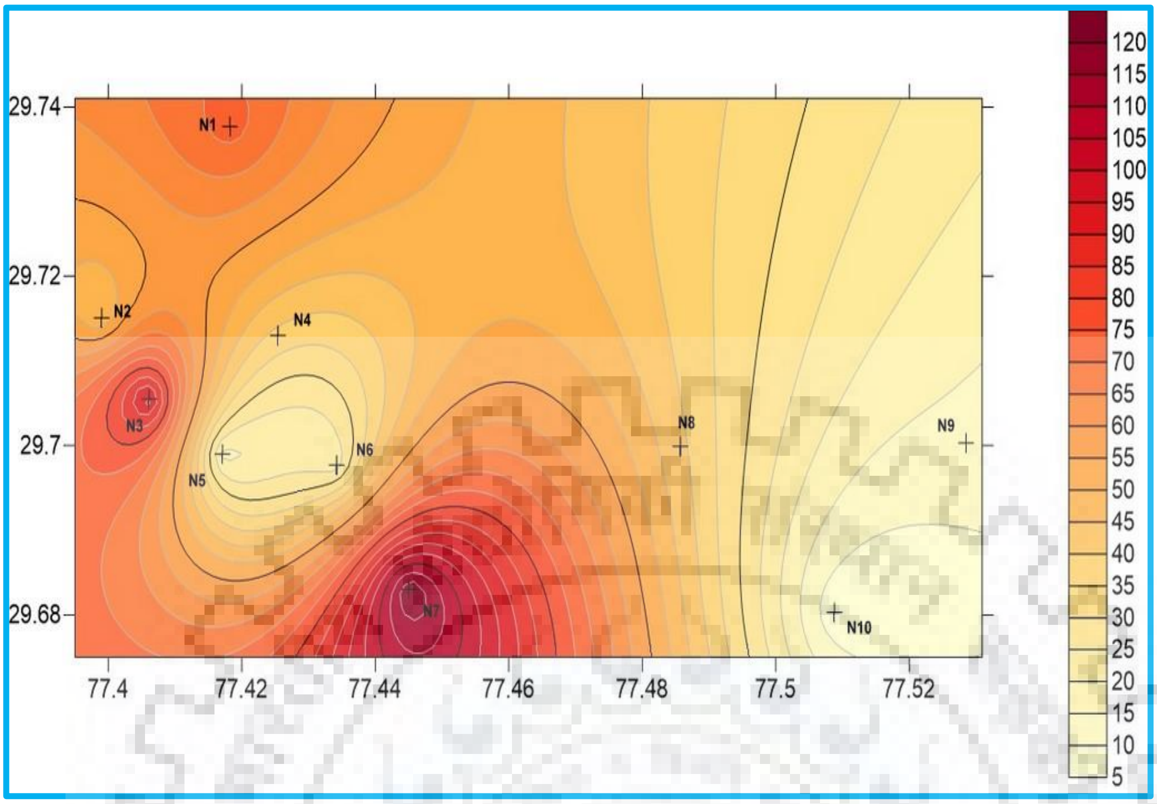
25
20

(d) Cu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N8
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77.42
77.44
77.46
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77.5
77.52
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115
110
105
100
95
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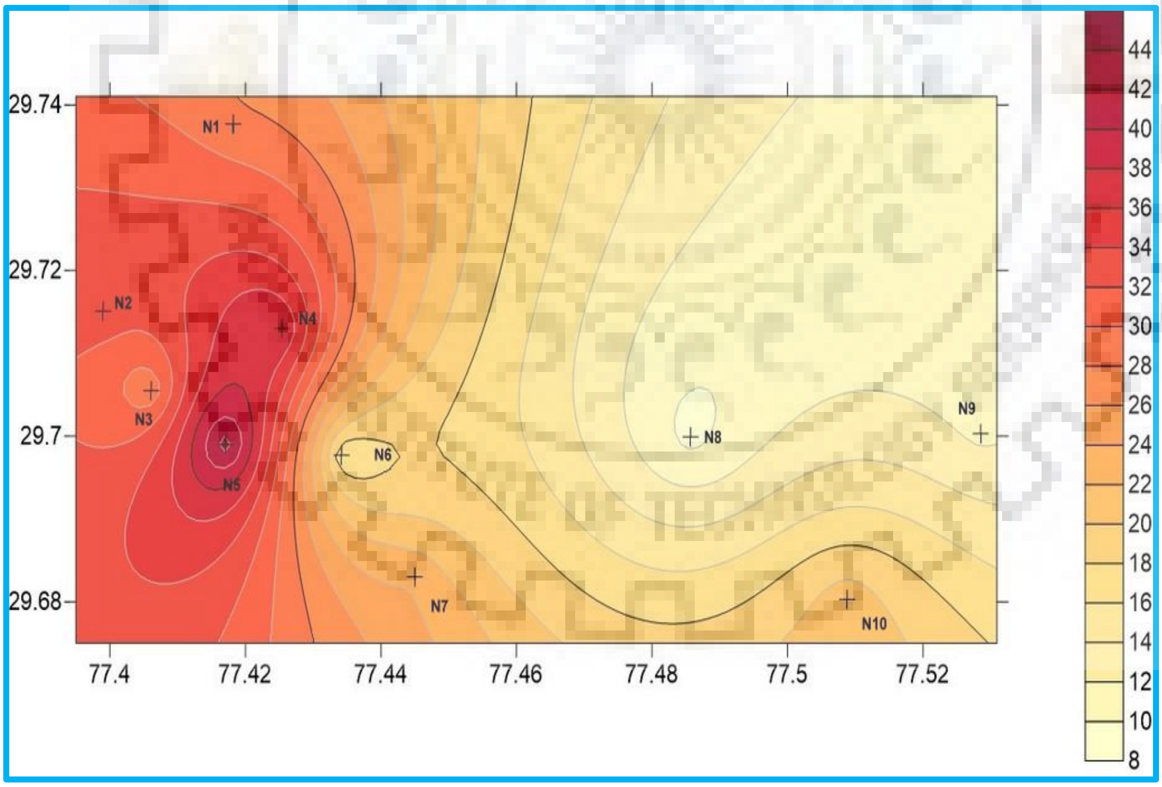
20
15
10
5

(e) Mn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N6
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N8
N9
N10
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77.4
77.42
77.44
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77.48
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77.52
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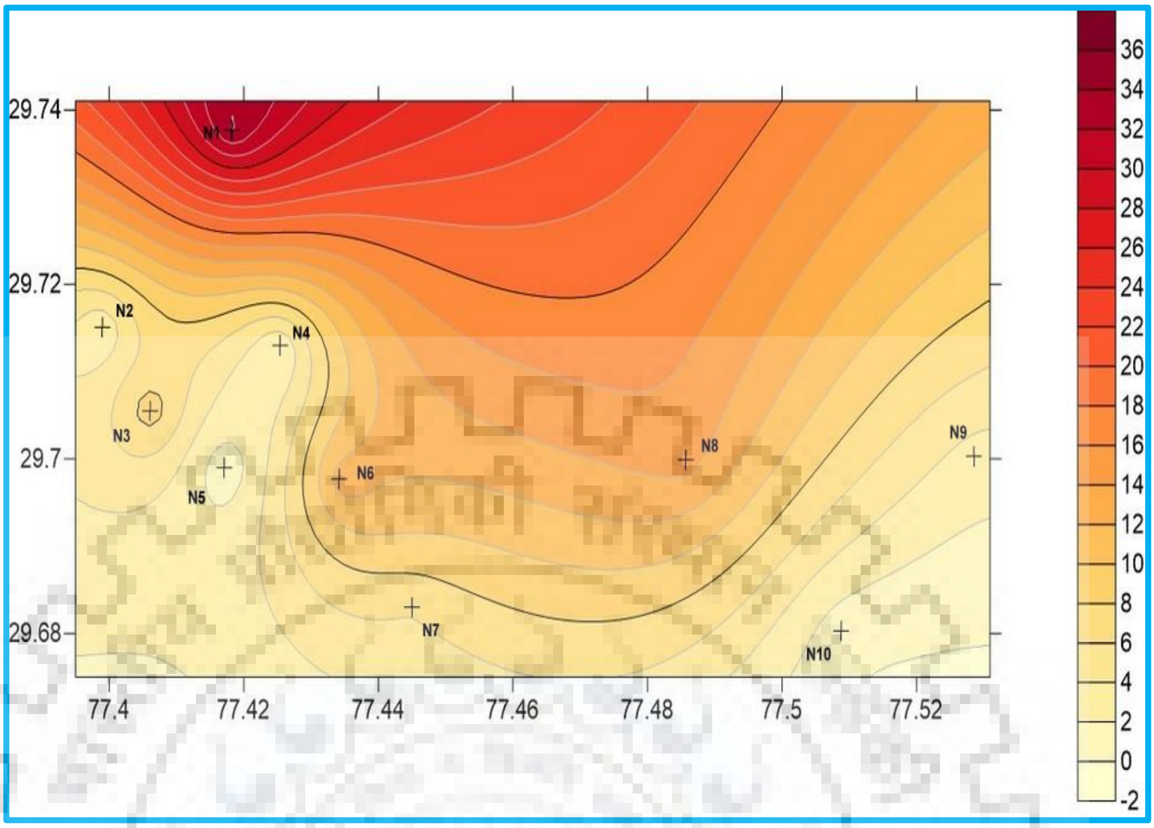
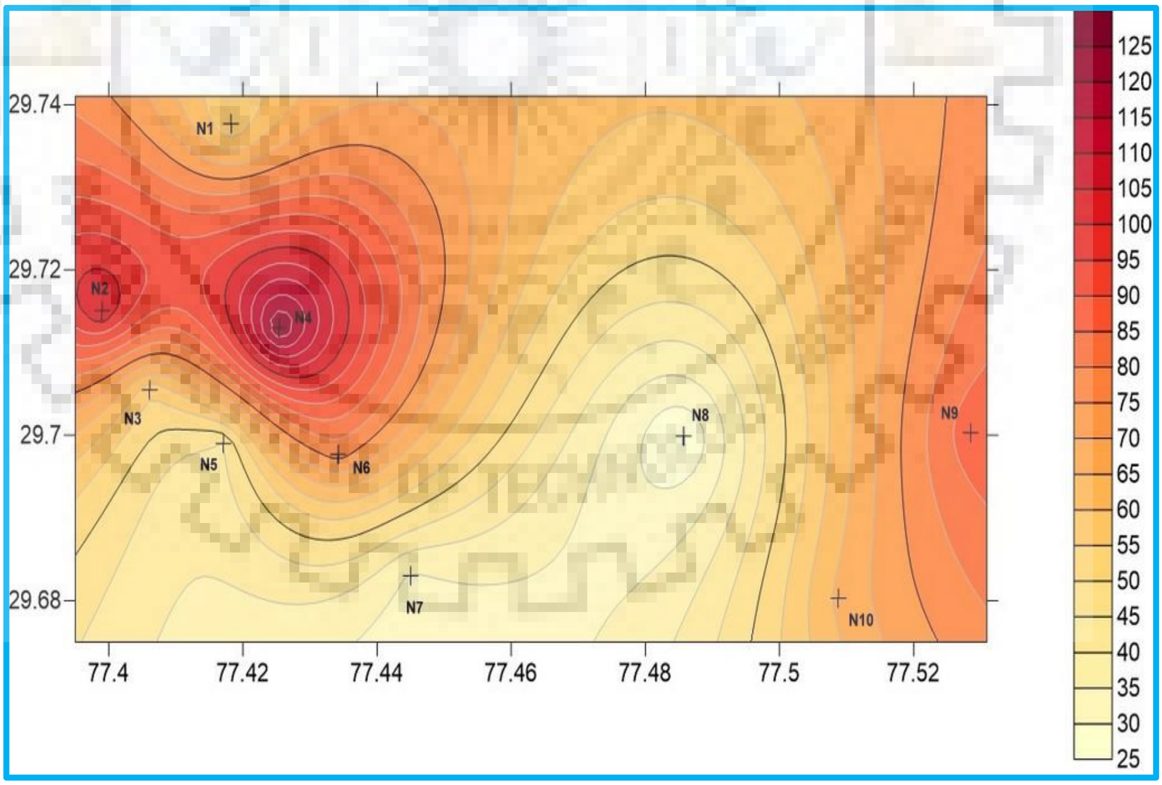
(f) Ni

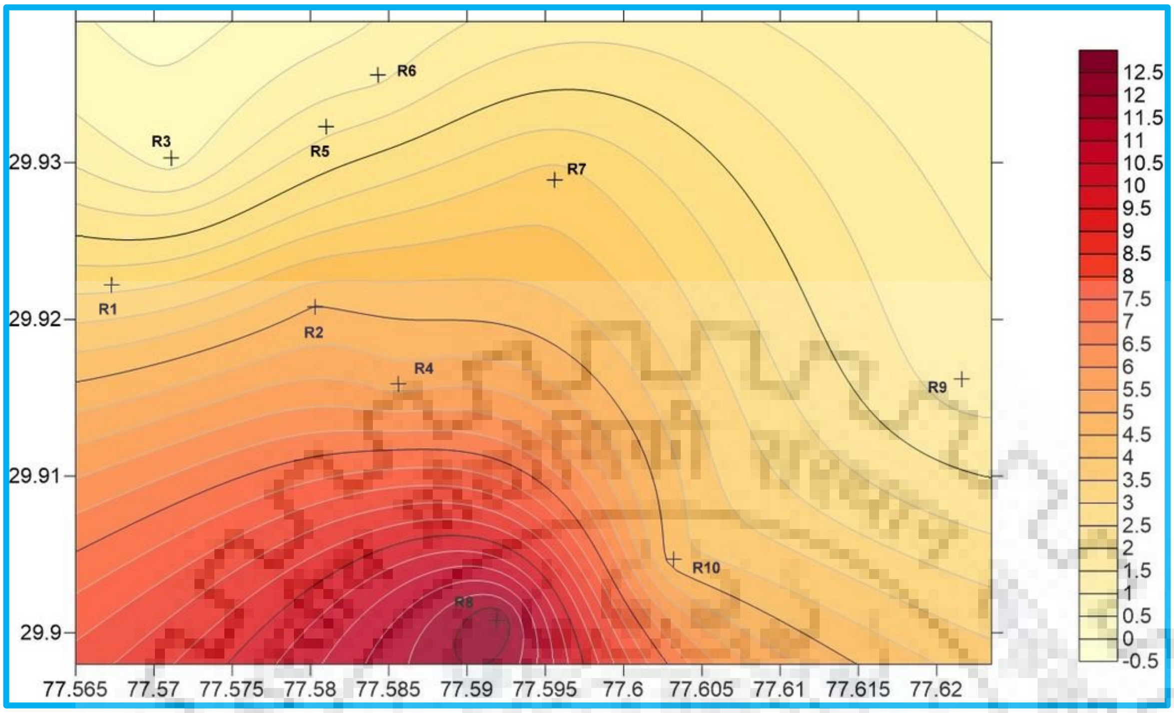


(g) Pb



(h) Zn

Fig. 3.8 (a-h) *Spatial analysis of metal groundwater contamination in Nanauta industrial area*



R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
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29.92
29.91
29.9
77.565
77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
12.5
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
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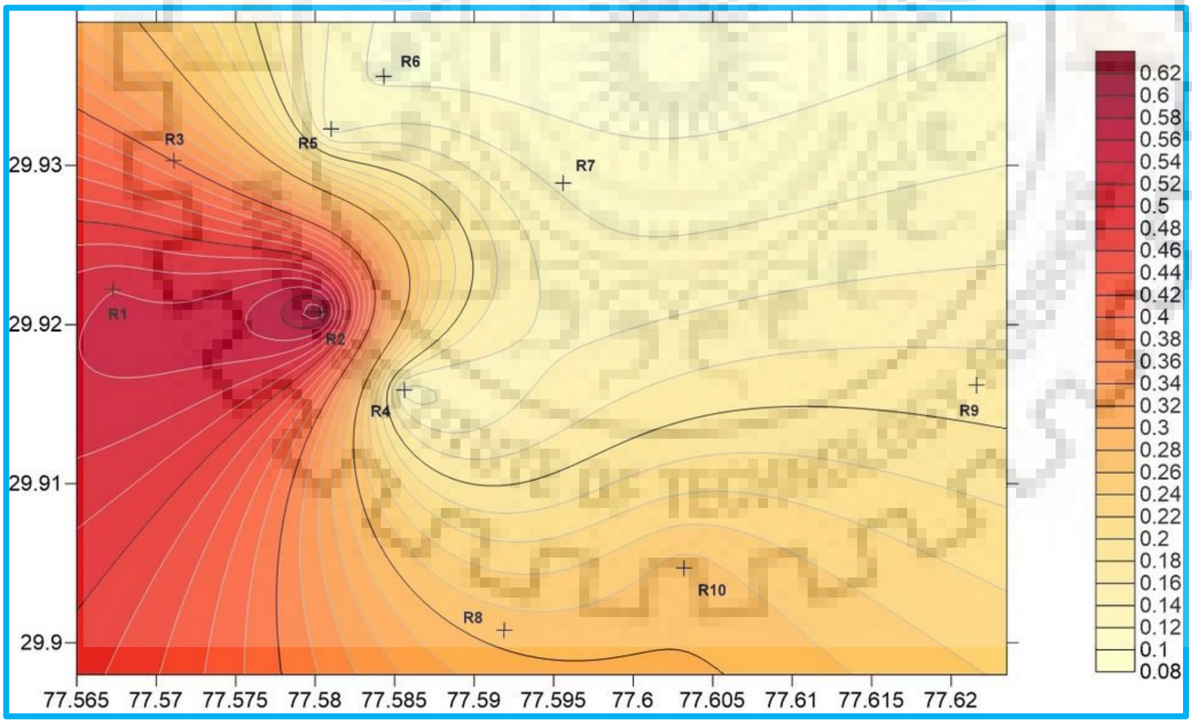
2.5
2
1.5
1
0.5
0
-0.5

(a) As



R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
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77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
0.62
0.6
0.58
0.56
0.54
0.52
0.5
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0.28
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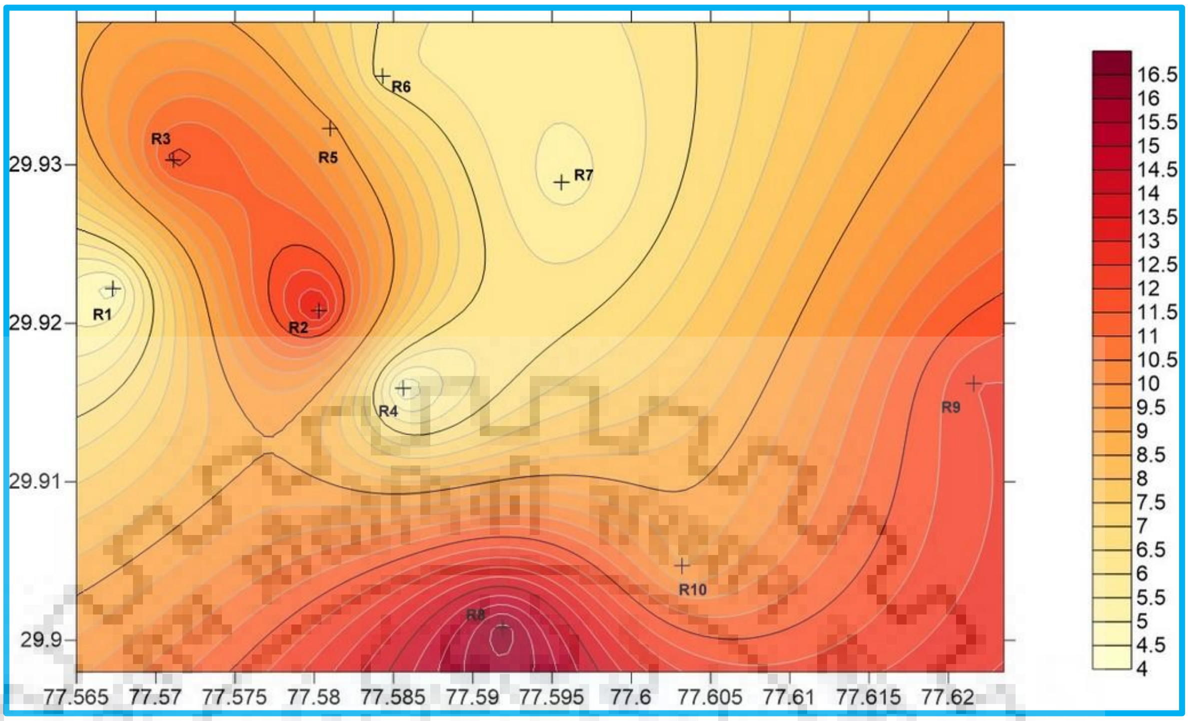
0.2
0.18
0.16
0.14
0.12
0.1
0.08

(b) Cd


R1
R2
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R6
R7
R8
R9
R10
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29.92
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77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
16.5
16
15.5
15
14.5
14
13.5
13
12.5
12
11.5
11
10.5
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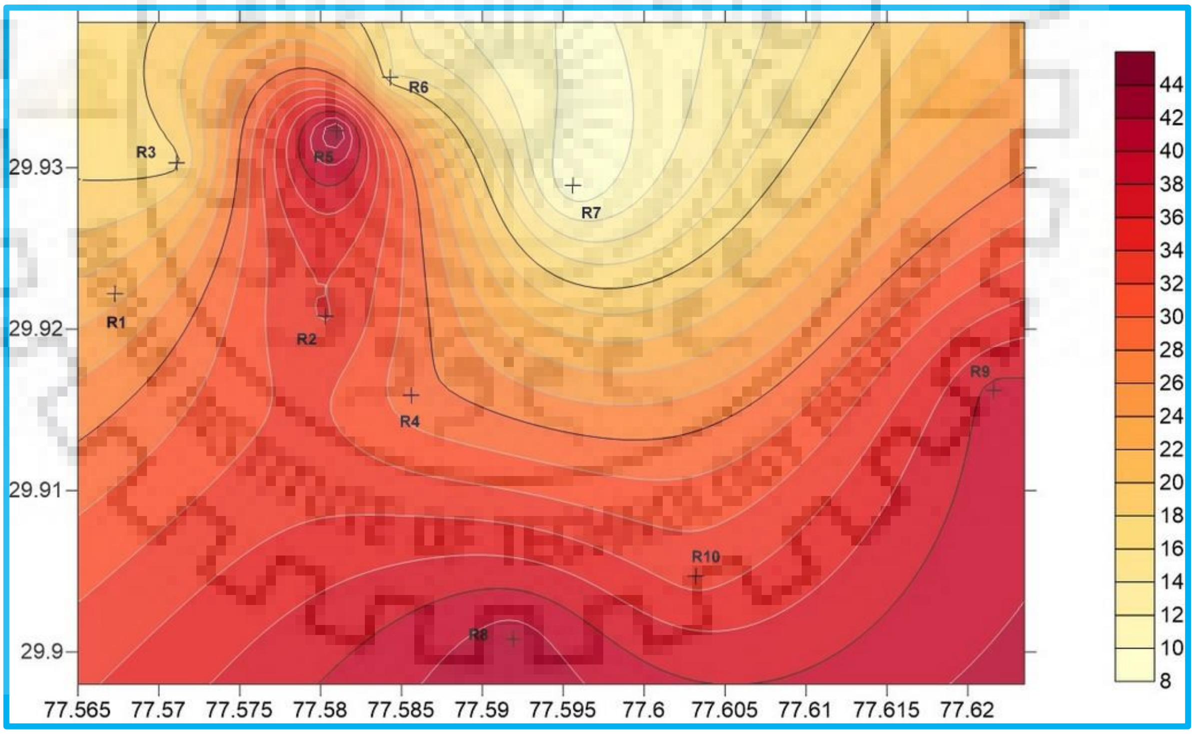
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4

(c) Cr


R1
R2
R3
R4
R5
R6
R7
R8
R9
R10
29.93
29.92
29.91
29.9
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77.57
77.575
77.58
77.585
77.59
77.595
77.6
77.605
77.61
77.615
77.62
44
42
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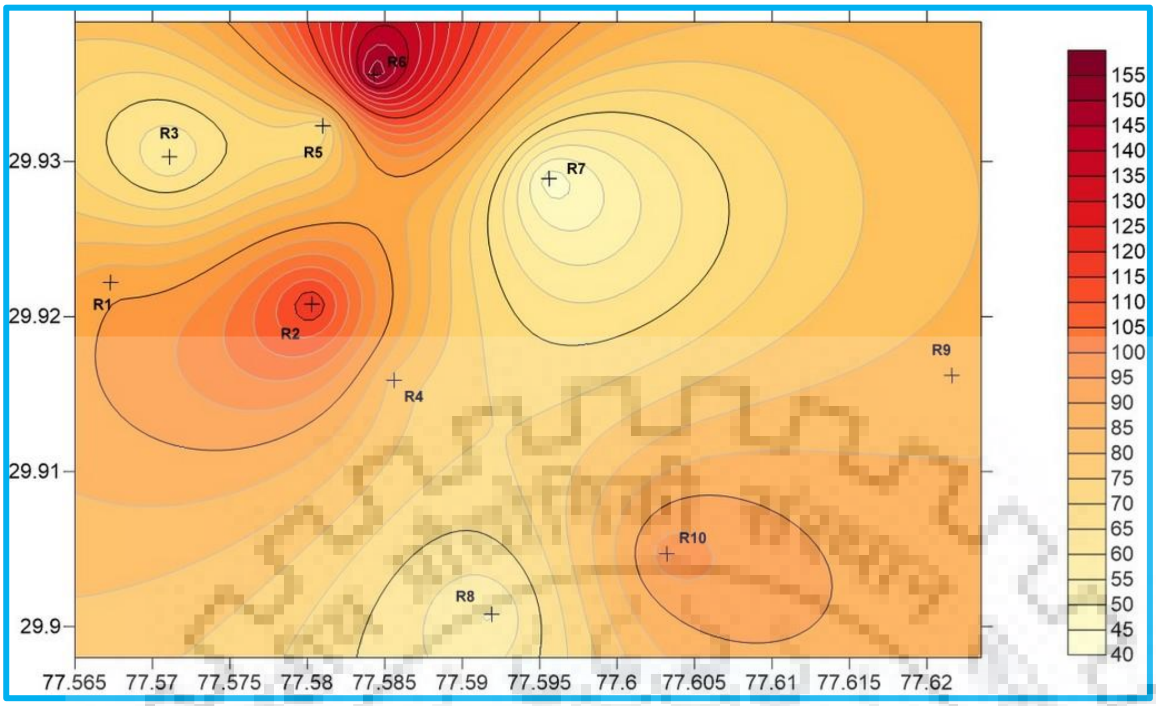
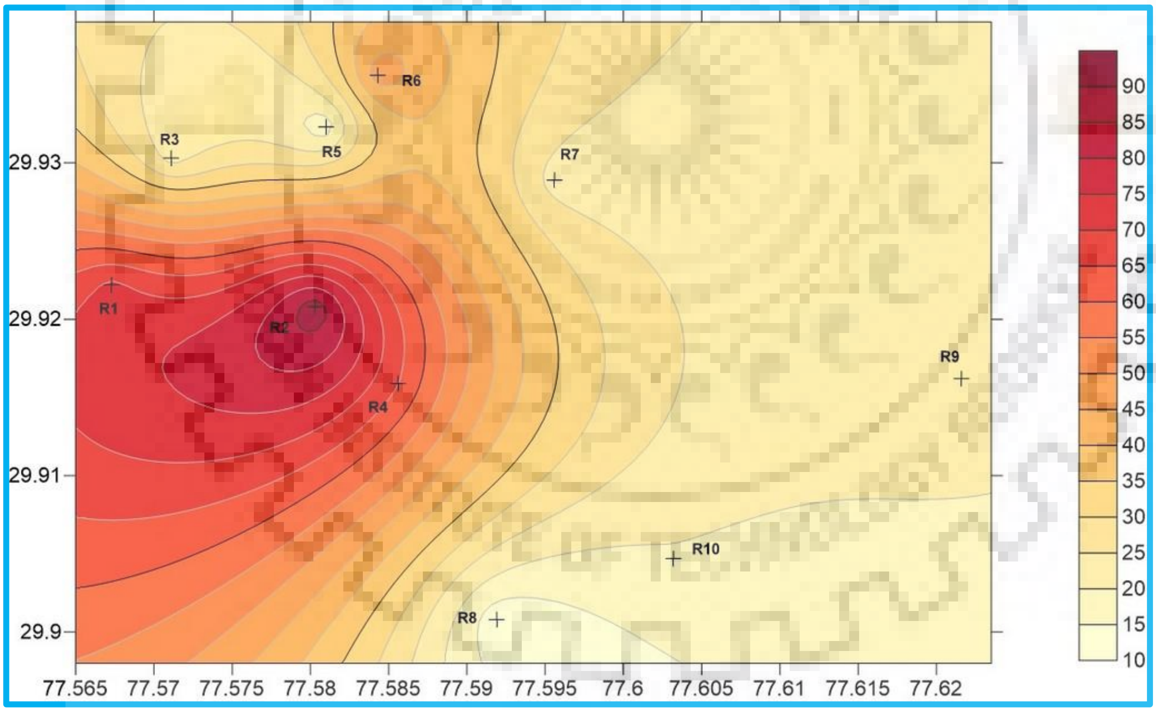
8

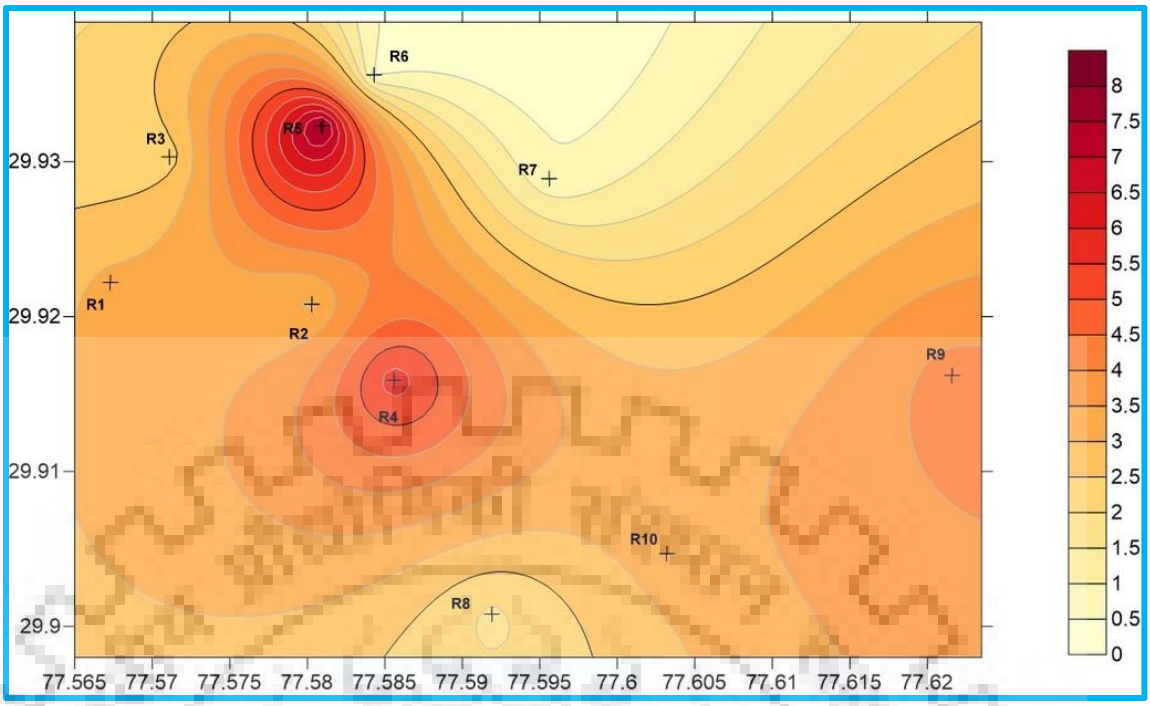
(d) Cu


R3
R5
R6
R7
R1
R2
R4
R9
R10
R8
29.93
29.92
29.91
29.9
77.565 77.57 77.575 77.58 77.585 77.59 77.595 77.6 77.605 77.61 77.615 77.62
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40

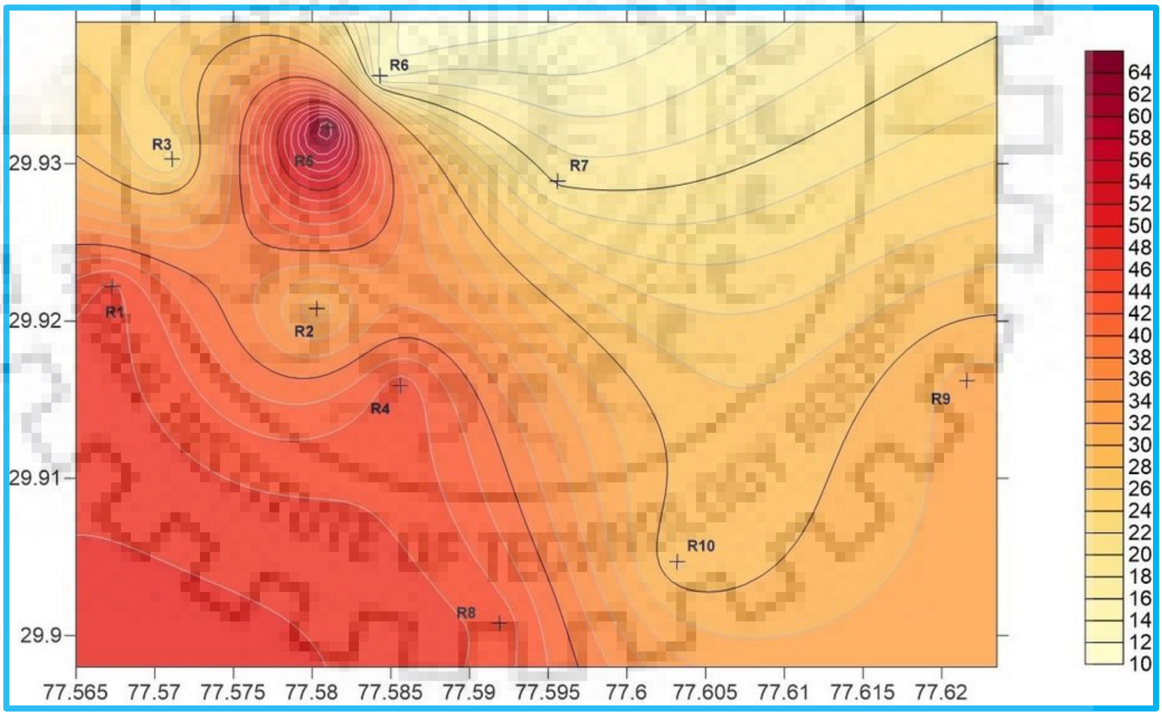
(e) Mn


R6
R3
R5
R7
R1
R2
R4
R9
R10
R8
29.93
29.92
29.91
29.9
77.565 77.57 77.575 77.58 77.585 77.59 77.595 77.6 77.605 77.61 77.615 77.62
90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10

(f) Ni



(g) Pb



(h) Zn

Fig.3.9 (a-h): *Spatial analysis of metal groundwater contamination in Railway Road industrial area*

Table 3.9: Pearson correlation matrix of groundwater metal concentration in the study area.

Pilakhni

Metal	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
As	1.00							
Cd	0.28	1.00						
Cr	**0.72**	-0.19	1.00					
Cu	-0.62	-0.34	0.07	1.00				
Mn	0.37	-0.25	**0.58**	-0.32	1.00			
Ni	-0.46	-0.26	**0.67**	0.48	0.02	1.00		
Pb	**0.54**	0.23	-0.61	-0.49	-0.26	-0.85	1.00	
Zn	-0.03	-0.30	-0.06	0.43	-0.03	0.03	-0.27	1.00

Nanauta

Metal	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
As	1.00							
Cd	0.21	1.00						
Cr	-0.10	-0.10	1.00					
Cu	0.02	0.44	0.43	1.00				
Mn	-0.40	-0.08	0.09	0.12	1.00			
Ni	0.40	-0.50	0.19	-0.57	0.11	1.00		
Pb	-0.06	**0.81**	-0.12	0.26	0.33	-0.22	1.00	
Zn	0.09	-0.06	**0.54**	-0.18	-0.36	0.30	-0.35	1.00

Railway Road

Metal	As	Cd	Cr	Cu	Mn	Ni	Pb	Zn
As	1.00							
Cd	0.33	1.00						
Cr	0.43	0.32	1.00					
Cu	0.37	-0.44	**0.59**	1.00				
Mn	-0.24	**0.81**	-0.15	-0.03	1.00			
Ni	-0.05	**0.69**	-0.34	-0.15	**0.55**	1.00		
Pb	-0.12	-0.82	-0.03	**0.67**	-0.19	-0.01	1.00	
Zn	0.30	-0.50	0.08	**0.72**	-0.34	-0.01	**0.83**	1.00

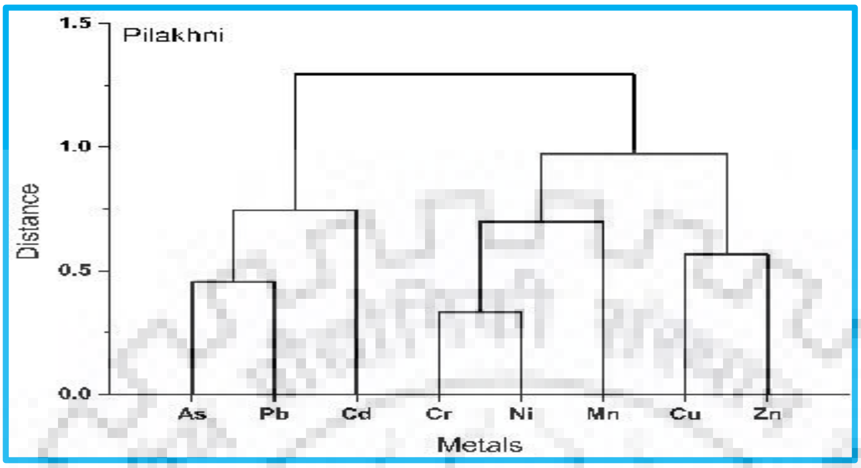
*Bold values are showing a significant positive correlation.

3.4B.3. Statistical analysis for metal contamination in groundwater

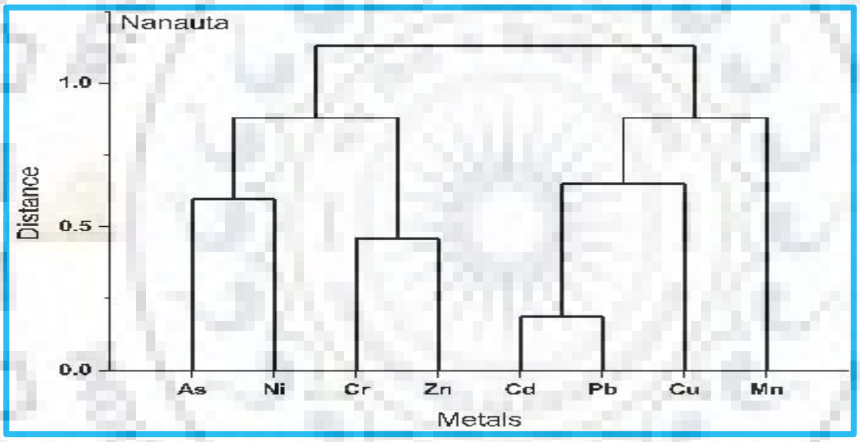
Pearson correlation analysis was performed to analyze the relationship among the metal concentrations in all three industrial clusters (Table 3.9). A significant positive correlation was observed among Cr-As (0.72), Pb-As (0.54), Ni-Cr (0.67) and Mn-Pb (0.86) in the Pilakhni industrial zone; indicating the source of contamination may be due to the distillery plant and other industrial activities [21], [22]. Most of the area in Pilakhni industrial zone has highly contaminated groundwater, physically characterized as yellow to dark brown color groundwater with the unpleasant smell as vicinity to the distillery unit approaches. The above correlation matrix analysis supports the fact that there is a significant contribution of distillery unit in groundwater contamination in Pilakhni industrial zone due to the unmanaged disposal of wastewater generated from the distillery. In Nanauta industrial zone moderate positive correlation was observed among Cd-As (0.21), Cu-Cd (0.44), Cu-Cr (0.43), Ni-As (0.40), Pb-Cu (0.26), Pb-Mn (0.33) and Zn-Ni (0.30) and strong positive correlation was observed between Pb-Cd (0.81) and Zn-Cr (0.54). The association of Cu-Cd-Cr, As-Cd-Ni, Pb-Cu-Mn, and Zn-Cr-Ni indicates the contamination source must be of anthropogenic origin. Following metal associations were suppose to be associated with Sugar mill wastewater [23], [24], as this industrial cluster (Nanauta) majorly comprises of sugar industries and its processing units. In Railway road industrial zone Cr-As, Cu- Cr, Mn-Cd, Ni-Cd, Ni-Mn, Pb-Cu, Zn-Cu and Zn-Pb associations were found to be in strong positive correlation (>0.5). Wastewater irrigation using Paper mill wastewater is quite a common practice in the railway road industrial zone, long-term implication of paper mill wastewater resulted in high enrichment of metals in the soil system. The association of metals in railway road industrial zone may also be supposed to be influenced by traffic, atmospheric depositions and other industrial activities.

HCA (Hierarchical Cluster Analysis) contributes to the classification of variables into discrete clusters on the basis of interrelating characteristics of variables and reducing into small homogenous clusters. Wards method and squared Euclidean distance approach was used in performing HCA clustering for the present data set Fig. 3.10 (a-c). Total three major clusters were observed in each industrial area.; As-Pb, Cr-Ni and Cu-Zn in Pilakhni; As-Ni, Cr-Zn, and Cd-Pb in Nanauta and As-Cr, Pb-Zn and Cd-Mn in Railway roads industrial area. HCA result for metal is complimenting the results of correlation and PCA analysis.

Principal component analysis (PCA) was performed on heavy metal concentration analyzed at different sampling sites in order to interpret their multivariate relationships and to explore the reduction of the experimental variables. The purpose of PCA is to reduce the dimensionality of the dataset since a few of the new components explain the major part of the variation of the data. PCA has been used as a major application in the source identification of heavy metal [13], [14], [25]–[27].



(a)



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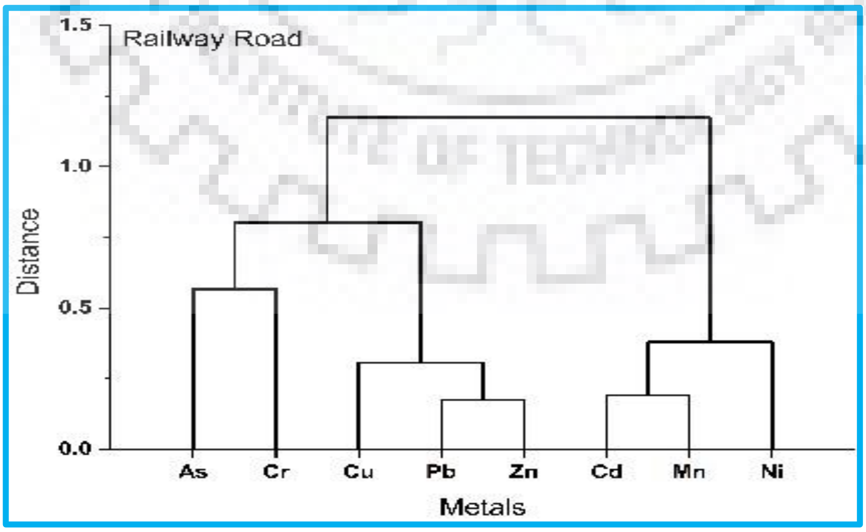


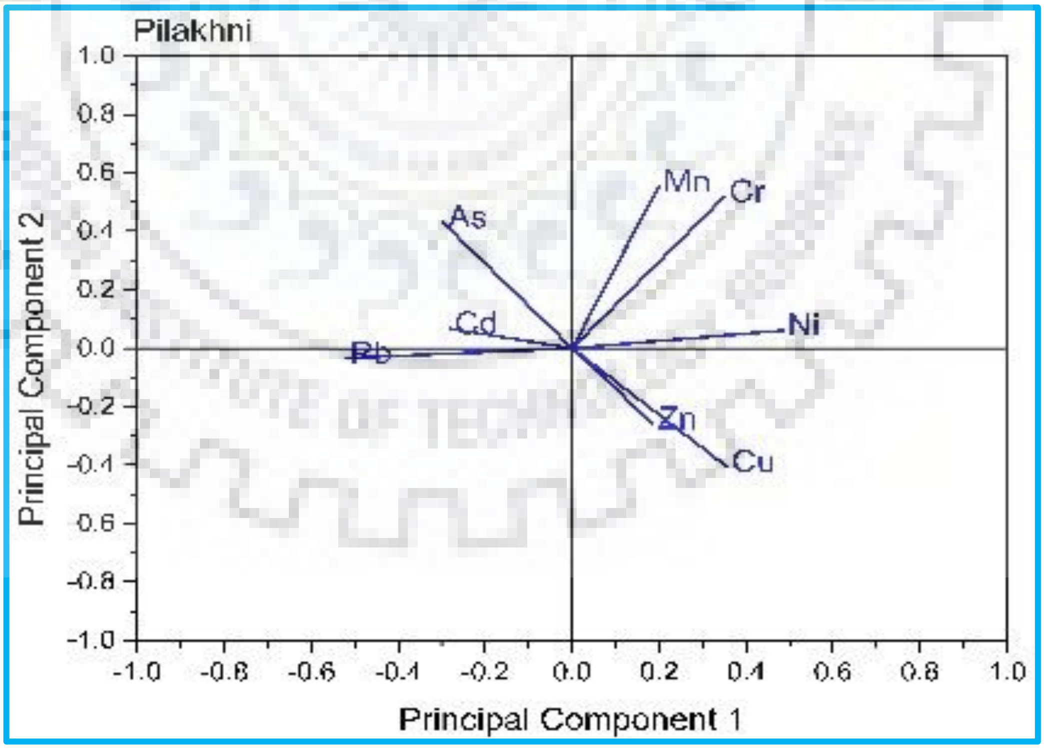
(c)

Fig. 3.10 (a-c): *Dendrogram showing clustering of metals in three industrial areas*

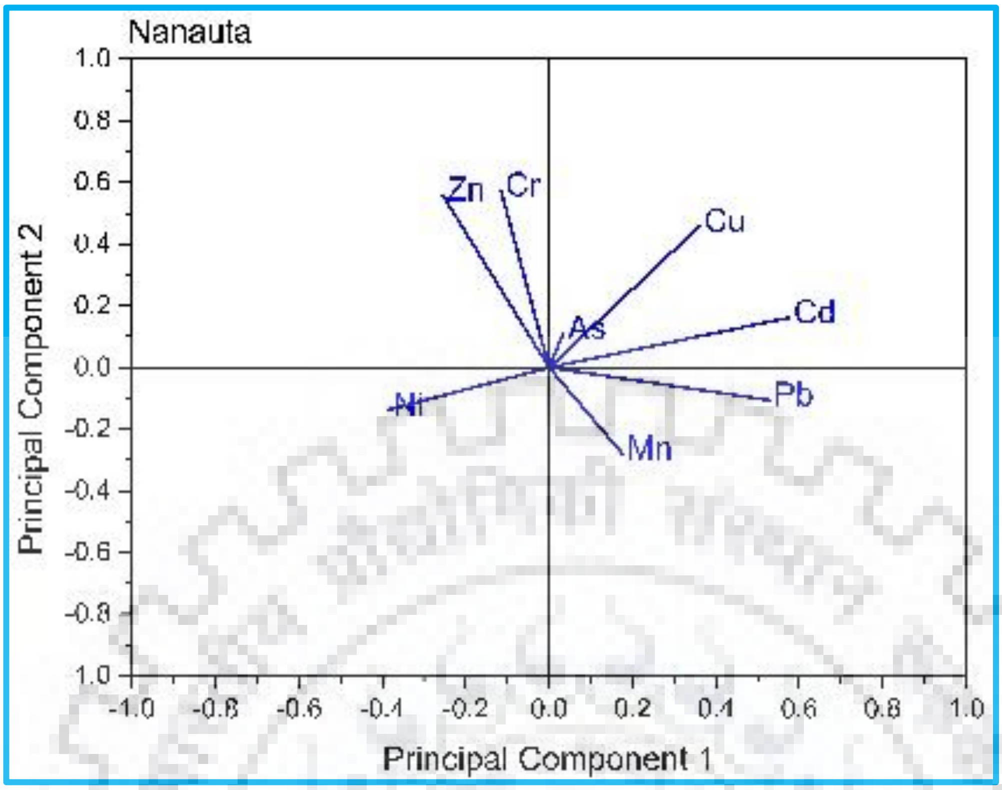
Table 3.10: Principal component analysis of groundwater metal concentration in industrial zones of Saharanpur

Metal	Components		
	PC1	PC2	PC3
As	**0.48**	-0.10	-0.13
Cd	0.07	**-0.61**	0.12
Cr	**0.49**	0.26	0.23
Cu	-0.25	-0.12	**0.66**
Mn	**0.47**	0.32	0.05
Ni	-0.16	**0.53**	-0.11
Pb	**0.44**	-0.35	-0.05
Zn	0.14	0.15	**0.69**
Eigen Value	2.87	1.70	1.34
Variance (%)	35.91%	21.26%	16.77%
Cumulative (%)	35.91%	57.17%	73.94%

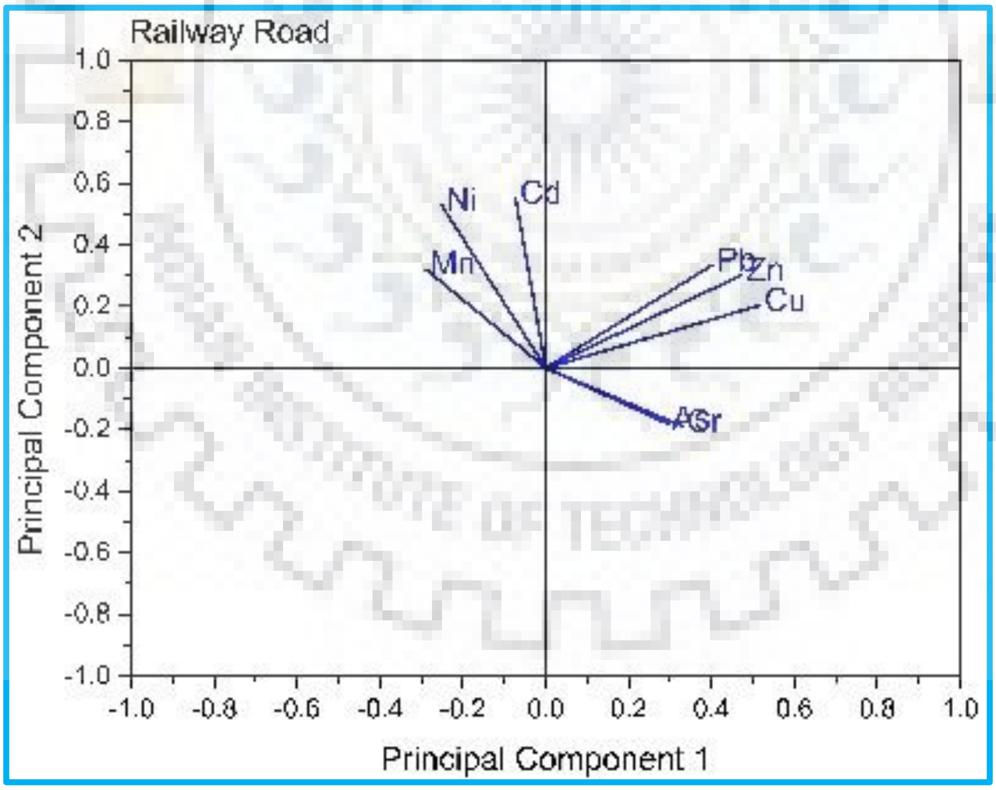
*p>0.4 is shown in bold



3(a)



3(b)



3(c)

Fig. 3.11 (a-c): *PCA loading of metals in the study area*

The PCA results are summarized in Table 3.10 and loading is shown in fig. 3.11 (a-c). The PC1 inferred that 35.91% of total variance is dominated by As, Cr, Mn, and Pb. This indicates the anthropogenic influence on the contamination of groundwater in the study areas. High loading of Mn can also be accountable for the geogenic origin [28] so it can be anticipated that there are mixed probabilities of anthropogenic and geogenic origins. Whereas PC2 showed 21.26% of the variance with the moderate loading of Ni, which may indicate the lithogenic origin [29]. 16.77% of total variance was inferred by the PC3, with the strong positive loading of Cu and Zn. Major anthropogenic sources of these heavy metal can be the unmanaged disposal of industrial waste and wastewater, in addition to its numerous point and non-point sources discharging urban and domestic wastes.

3.4B.4. Non-carcinogenic (HQ) and Carcinogenic risk

The Health quotient (HQ) represents the non-carcinogenic risk and its value > 1.00 can be anticipated as the potential risk to human health. The table 3.11 shows the non-carcinogenic risk both in adult and children population in the study area through the oral pathway. Out of the studied metals, the risk associated with As contamination was observed to have maximum non-cancerous health risk in both Adult and children population. Non-cancerous risk due to As found to be severely distributed in Pilakhni followed by Nanauta and Railway road industrial area. Level of health risk was found to be similar for the contamination associated with the metals Cd, Cr, Mn, and Pb; approaching to the severe risk. Nanauta industrial area was found to be on the higher risk associated with Cd contamination followed by Pilakhni and Railway road. No significant risk was observed with the contamination associated with Cu, Ni, and Zn.

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Table 3.11: Non-carcinogenic and carcinogenic risk for adult and children (95% UCL)

	95 % UCL					
	HRA (Adult)			**HRA (Children)**		
Metal	**P**	**N**	**R**	**P**	**N**	**R**
As	3.84E+00	1.01E+00	4.35E-01	4.39E+00	1.16E+00	6.41E-01
As*	1.20E-03	4.89E-04	1.96E-04	1.37E-03	5.60E-04	2.24E-04
Cd	1.34E-01	2.28E-01	3.46E-02	1.53E-01	2.61E-01	3.96E-02
Cr	2.26E-01	1.94E-01	5.76E-02	2.58E-01	2.21E-01	6.59E-02
Cu	2.25E-02	2.09E-02	1.25E-02	2.57E-02	2.40E-02	1.43E-02
Mn	1.63E-01	3.45E-02	3.11E-02	1.86E-01	3.95E-02	3.55E-02
Ni	3.75E-02	2.31E-02	5.68E-02	4.29E-02	2.64E-02	6.49E-02
Pb	1.27E-01	1.23E-01	2.70E-02	1.45E-01	1.41E-01	3.09E-02
Zn	1.29E-02	4.41E-03	2.17E-03	1.48E-02	5.04E-03	2.48E-03

As* = As (cancer)

A similar trend was observed in the HQ in both adult and children population but the overall high risk was estimated in children population. Non-carcinogenic risk related to As and Cr was found to be potentially high in Pilakhni and Nanauta region in both adult and children population, whereas risk estimated in Railway Road industrial zone was found to be relatively lower than other two industrial zones. Risk related to Pb can be significant in the near future in the study areas as some of the sites are in or approaching closer to the high non-carcinogenic risk index. Cancer risk associated with the As contamination in the three industrial zones is shown in table 6. According to the index formulated by USEPA [30], considerably high cancer risk was observed in the Pilakhni industrial area followed by Nanauta and Railway road in both adult and children population. While performing face to face interview in the study area problems related to skin, respiratory system, diabetes, obstetric etc. were quite prominent. Moreover, cancer associated with skin, bladder, lungs etc were observed in the areas directly dependent on the groundwater without any further effective purification, which indicates the strong probability of As toxicity in the study area.

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CHAPTER IV

ASSESSMENT OF METAL ACCUMULATION IN THE VEGETABLES AND ASSOCIATED HEALTH RISK IN THE UPPER-MOST GANGA-YAMUNA DOAB REGION, INDIA *

* *The research work described in this chapter has been published in* ***American Journal of Plant Sciences*** *(doi: 10.4236/ajps.2018.912170)*

4.1. ABSTRACT

The present study indicates the status of metal contamination in the vegetables/crops grown in the uppermost Ganga-Yamuna doab region of India and associated health risk. Commonly grown vegetables and crops were sampled and analyzed for metal contamination. Maximum concentration (mg/kg) of Cd and Cr, was observed in Radish (7.6) and Cabbage (56.24) respectively, whereas the maximum concentration of Pb, Ni and Zn were observed in the edible parts of Mustard plant (95.4, 58.6, 756.43 respectively). Bio-concentration factor (BCF) value indicated the transfer level of metal from soil to crop; indicated high transfer value of Cd in Radish followed by cabbage and spinach. Considerably high BCF value was observed in the Mustard (8.13), Cabbage (4.18) and radish (3.07) for Zn contamination. Estimated daily intake (EDI) and Hazard quotient (HQ) or Non-carcinogenic health risk was calculated using the USEPA method. The result revealed that the metal intake and associated health risk was considerably high in the children population in comparison to the adult population.

4.2. INTRODUCTION

The toxicity, ubiquitous nature, and persistence characteristics of heavy metal has raised considerable apprehension globally [1], [2]. Heavy metal contamination in soil deteriorates overall soil quality, productivity, and water quality through percolation. Heavy metal contamination in agricultural soils is a crucial issue as it can pose long-term environmental problems [3]. Transfer of metals from Soil-to-crop is one of the major sources of metal exposure to the human. Unmanaged disposal of waste, runoffs, landfills along with rapid industrialization has severely enriched the soil with metals [4], [5]. Moreover, excessive use of chemical-based pesticides, fertilizers, and manures in order to counter the demand for food supply has triggered the excessive accumulation of metals in the soil. Vegetables grown in such soil accumulate a high concentration of toxic metals. Consumption of metal accumulated vegetables/crops may lead to severe health hazards. Due to the scarcity of available freshwater use of industrial wastewater for irrigation is a common practice in India. Wastewater contains toxic metals and long-term wastewater irrigation results in accumulation of substantially high concentration of heavy metals. Atmospheric deposition has now been identified as one of the principal sources of heavy metal contamination to crops and vegetables grown in urban and industrial areas [6].

In the present study Saharanpur which lies in the most uppermost part of Doab land which stretches between the river Ganges and Yamuna, India has been taken into consideration. Primarily Saharanpur is an agricultural district but also comprises of many medium and small scale industries including some highly water intensive large scale industries like Paper Industry, Sugar mill and distilleries [7]. Unmanaged disposal of industrial wastes, long-term wastewater irrigation practices along with other anthropogenic activities has severely affected the soil quality of the study area. This study aims at determining the level of metal contamination in the soil and vegetables growing in the metal contaminated areas, bio-concentration factor or transfer factor, and the health risk associated with the level of metal exposure to the adult and children population.

4.3. MATERIAL METHOD

4.3.1. Sampling and analytical analysis

The study area is located in the Saharanpur district (29.8361° N, 77.4702° E) which is located in the uppermost Ganga-Yamuna doab region (Fig.1). The soil samples were collected from three different areas of Saharanpur district, designated as industrial areas by Ministry of Micro, Small & Medium Enterprises, Govt. of India (MSME) [7]. The top-soil (0-15 cm) were procured randomly from thirty sampling sites from three industrial areas (Pilakhni, Delhi Road and Railway Road) of Saharanpur city. Samples were zipped packed in a polyethylene bag, transferred to the laboratory within three hours from sampling and stored at 4°C till complete analysis. Before analytical step samples were dried (at 50°C), pulverized and sieved with 70-mesh plastic sieve [8]. The heavy metal was analyzed by digesting the soil samples using USEPA 3052 method [9] in the microwave oven (MarsXpress). Digested transparent solution was cooled, filtered through Whatman no. 42 filter paper and diluted up to 50 mL with 1% nitric acid. The metal concentration in the filtrate of digested soil samples was analyzed by ICP- OES.

The edible part of plant samples Spinach (*Spinacia oleracea*), mustard (*Brassica nigra*), cabbage (*Brassica oleracea*), radish (*Raphanus sativus*), carrot (*Daucus carota*), sugarcane (*Saccharum officinarum*), rice grain (*Oryza sativa*), tomato (*Solanum lycopersicum*) were collected and washed and dried at 70–80°C for 24 h to a constant weight. Dried samples were crushed and powdered for homogenization of the sample. Powdered plant samples were digested with concentrated HNO_3, H_2SO_4, and $HClO_4$ in 5:1:1 ratio (total 15 ml) using USEPA 3052 method. The digested sample further analyzed in ICP-OES for the heavy metal estimation.

4.3.2. Bio-concentration factor (BCF)

BCF index is an approach to determine the accumulation of particular metal in the vegetable with respect to its concentration in a soil substrate. It was calculated using the formula

$$\mathrm{BCF} = \frac{C_{\mathrm{plant}}}{C_{\mathrm{soil}}} \tag{4.1}$$

where C_{plant} and C_{soil} represent the heavy metal concentration in the edible part of vegetables and soils, respectively. [10]

4.3.3. Health Risk Assessment

Health risk assessment was performed using the USEPA model [11], it estimates risk related to the exposure of heavy metal contamination via ingestion pathway in both adult and children. Hazard quotient (HQ) is the ratio of the estimated concentration of a pollutant to the reference dose, it also indicates the non-carcinogenic. If the value of HQ <1, it is supposed there is no significant risk of non-carcinogenic effects. If the HQ >1 considerable health risk can be anticipated.

$$ADI = C \times DI/BW \tag{4.2}$$

$$HQ = EDI \times EF \times ED/ RfD \times AT \tag{4.3}$$

in this study, Daily intake (DI) for adult is 0.345 kg/person/day and for children is 0.232 kg/person/day [12] 15kg for children and 70kg for adults, HQ is the Hazard Quotient, EF is the Exposure Frequency (350 days), ED is the Exposure Duration (70 years), RfD values of different metals were taken from the USEPA guidelines [13] and AT is the Average Time (70×365 years) [10]

4.4. RESULT AND DISCUSSION

4.4.1. Physiochemical characteristics and heavy metal status in the soil

The basic physiochemical characteristics of the agriculture soil are shown in **Table 3.2** The soil pH was observed to be near neutral to slightly alkaline with 56.10% and 5.36% of mean moisture content and organic matter respectively. High phosphate and chloride content in the soil may result due to long-term wastewater irrigation. The mean conductivity was observed to be 2.49 mScm^{-1} considering the fact that the presence of ions and metals enhances the overall soil conductivity of the soil. The mean concentration of Cd, Cu, Cr, Pb, Ni, and Zn were observed to be 1.65 ± 0.65, 35.82 ± 20.18, 60.70 ± 40.91, 30.76 ± 13.05, 89.63 ± 53.62 and 90.02 ± 36.65 mg/kg respectively.

4.4.2. Metal concentration in plant

The mean metal concentration in the edible parts of samples vegetables is shown in the fig. 2 (a-f). The metal concentrations were compared with the permissible safe limits prescribed by the Indian Standard [14] and the World Health Organization (WHO)/ Food and Agricultural Organization (FAO) [15]. Permissible limits of metals in food (mg/kg) as per Indian Standards are: Cd (1.5), Cu (30.0), Cr (20.0), Pb (2.5), Ni (1.5), Zn (50.0), and while WHO/FAO (2007) safe limits are: Cd (0.2), Cu (40.0), Cr (0.1) Pb (5.0), and Zn (60.0). There is a considerable difference in both the permissible limits; the concentration of Cd in Spinach, cabbage, and radish were observed to be higher than the Indian permissible limit whereas, only Carrot (0.01) and Rice grain (0.01) samples were found to be under the permissible limit of WHO/FAO. Cu concentration in the sampled vegetables was high in Spinach (42.6), mustard (95.4) and cabbage (42.5), rest of the samples were in the permissible range. Cr concentration was observed highest in the cabbage (56.24) followed by sugarcane, mustard, and radish. Pb concentration in mustard (56.24) was observed several folds higher than both Indian and WHO/FAO permissible limit followed by spinach, tomato, and radish. Ni and Zn concentration were found highest in the mustard (114.6 and 756.43 respectively). Ni concentration in all the sampled vegetables was above the permissible limit.

Elevated concentrations of Cd, Cr, and Pb more than the permissible limit is a serious concern in the study area as these metals are potent carcinogens and may lead to several diseases including cardiovascular, blood, kidney, and nervous system as well as diseases related with bone and muscles [2], [15].

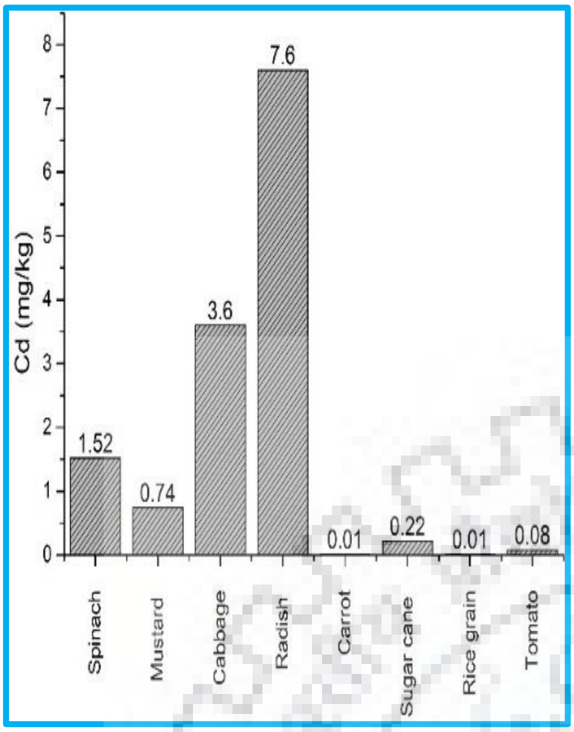
The sources of these metals are mainly anthropogenic in origin which may include industrial and domestic waste, atmospheric deposition, vehicular emission etc. The study area comprises of large-scale industries including paper industry, distillery, and sugar mill which is supposed to contribute significantly in the overall metal contamination in the study area. Paper mill generated wastewater contain a significant concentration of Cr due to extensive use of Chromium-based chemicals for the different process involved in the manufacturing of paper [10], [16], [17]. The bioaccumulation potential of Ni is still under the study but Ni has a significant toxic impact on the human being and considered as a potent carcinogen. Zinc is an essential trace element for the growth of plants and animals, but excessive concentration may reduce the beneficial microbial activity and cause toxic effect [18].

Table 4.1: The concentration of heavy metal (mg/kg) in the plant sample and permissible limit

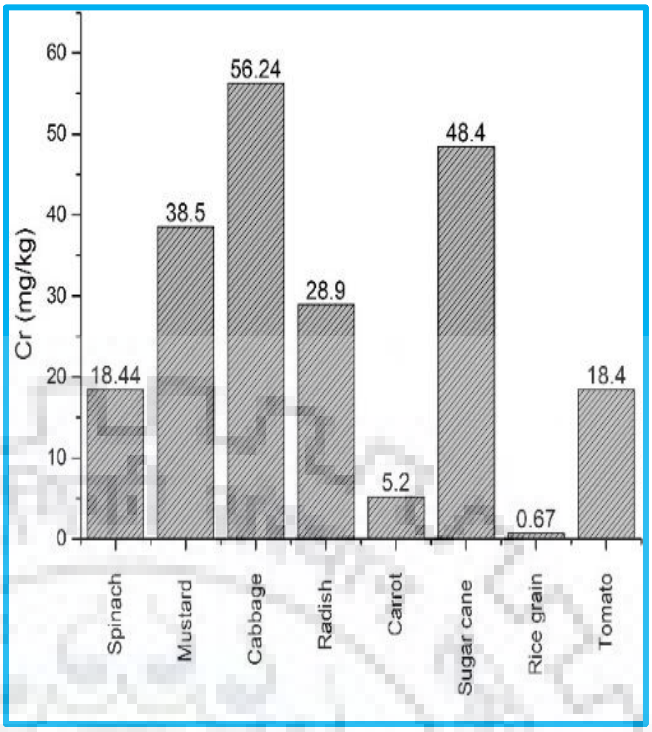
Vegetable	Cd	Cu	Cr	Pb	Ni	Zn
Spinach	1.52	42.6	18.44	32.4	88.2	178.94
Mustard	0.74	95.4	38.5	58.6	114.6	756.43
Cabbage	3.6	42.6	56.24	5.34	62.4	388.6
Radish	7.6	35.6	28.9	11.45	58.4	285.6
Carrot	0.01	18.4	5.2	8.4	12.8	120.5
Sugar cane	0.22	32.5	48.4	2.2	3.57	67.8
Rice grain	0.01	1.8	0.67	0.72	2.45	2.6
Tomato	0.08	4.2	18.4	14.22	25.5	48.4
Indian Standard	1.5	30.0	20.0	2.5	1.5	50.0
WHO/FAO	0.2	40.0	0.1	5.0	--	60.0

4.4.3. Estimation of Bio-concentration factor and Average Daily Intake (ADI)

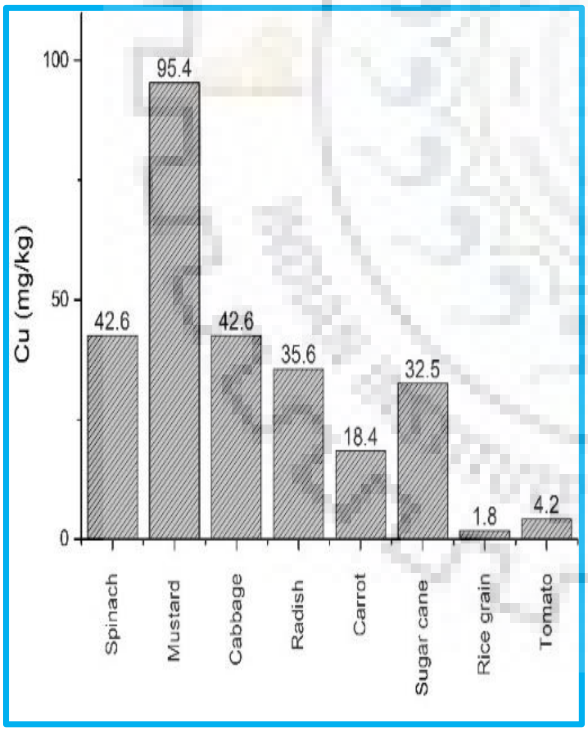
The soil-plant transfer factor was estimated and a wide range of transfer values has been observed. High transfer factor was observed in spinach for all the metals except Cr (Fig. 3 (a-f)). BCF of Cd was significantly high in the Radish and cabbage. Mustard is an important crop, both leaves and oilseeds are used by the people; a very high BCF value of Zn (8.13) followed by Cu (2.66), Pb (1.91) and Ni (1.28) was observed in the mustard plant. Leafy structure of cabbage may lead to accumulate metals significantly thus found to have considerably high BCF values for all the metals except Pb. the minimum transfer factor value was observed in the Rice grains followed by tomato and carrot.


Cd (mg/kg)
0
1
2
3
4
5
6
7
8
1.52
0.74
3.6
7.6
0.01
0.22
0.01
0.08
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

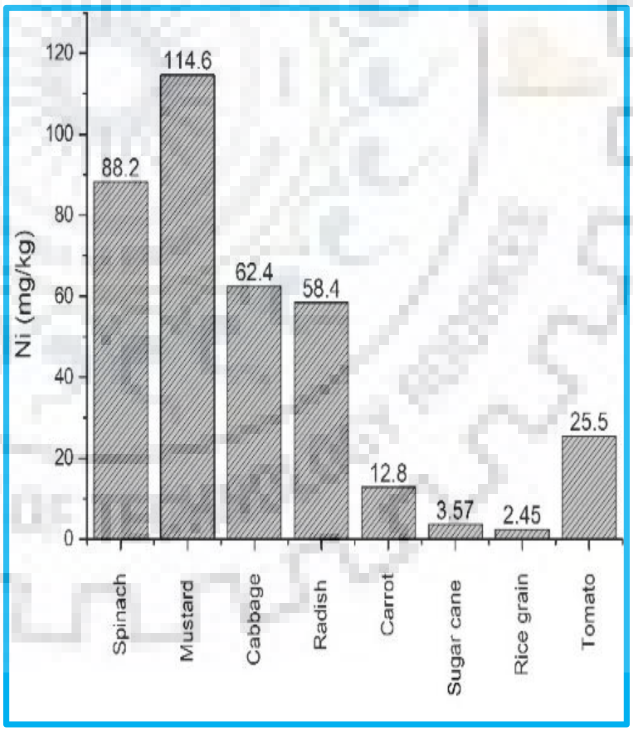
(a)


Cr (mg/kg)
0
10
20
30
40
50
60
18.44
38.5
56.24
28.9
5.2
48.4
0.67
18.4
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

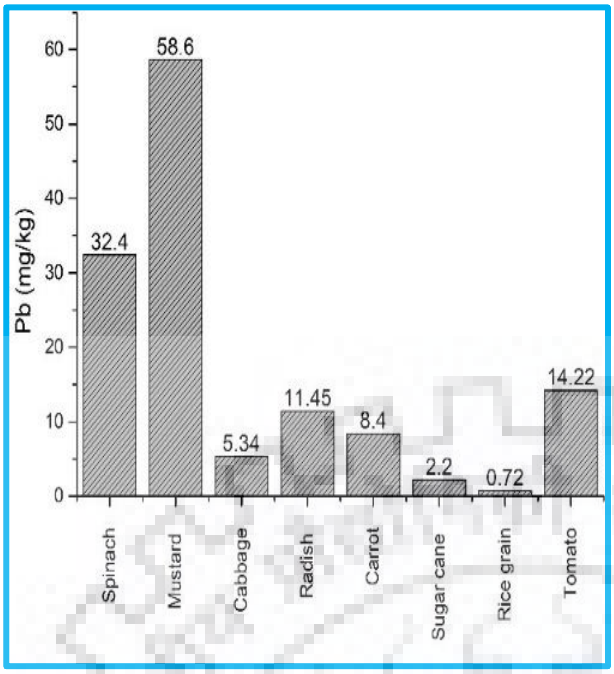
(b)


Cu (mg/kg)
0
50
100
42.6
95.4
42.6
35.6
18.4
32.5
1.8
4.2
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

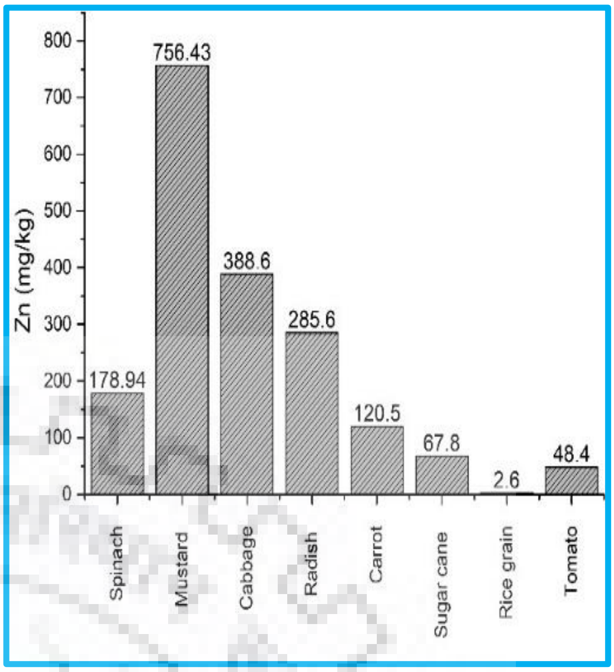
(c)


Ni (mg/kg)
0
20
40
60
80
100
120
88.2
114.6
62.4
58.4
12.8
3.57
2.45
25.5
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

(d)

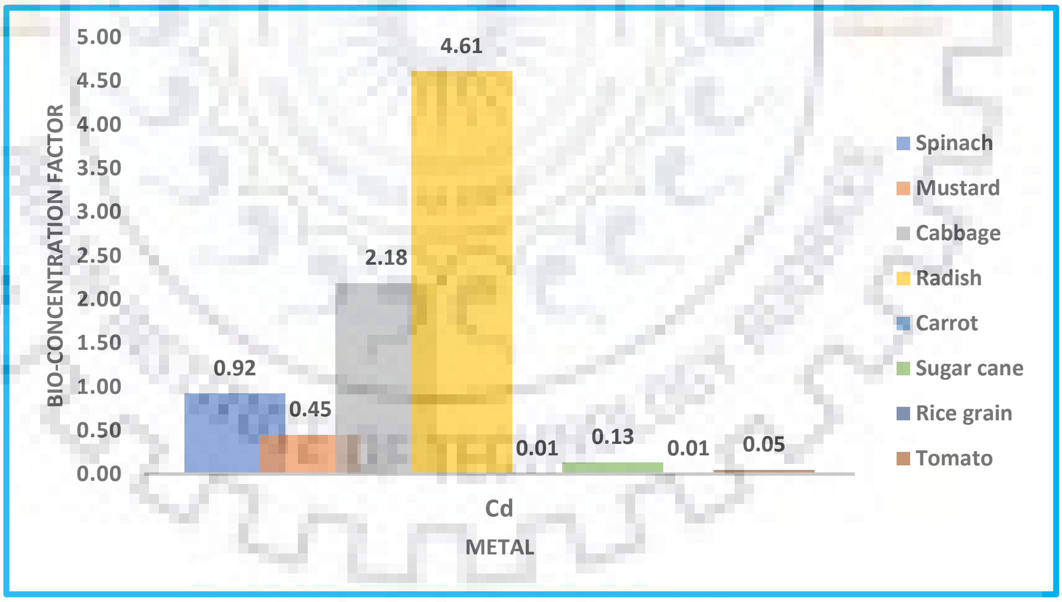


(e)

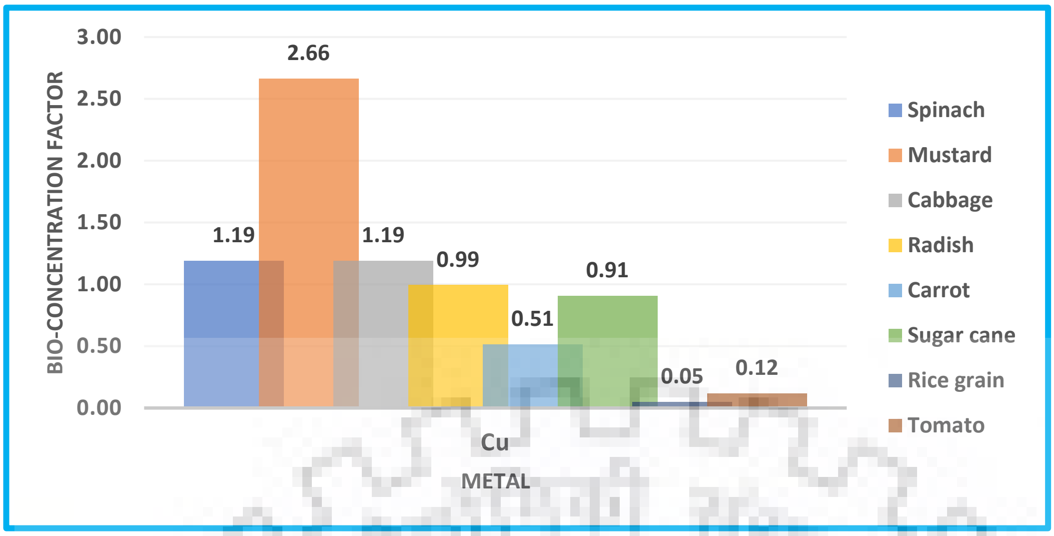


(f)

Fig. 4.1 (a-f) *Metal concentrations in the vegetable samples procured from the study area*

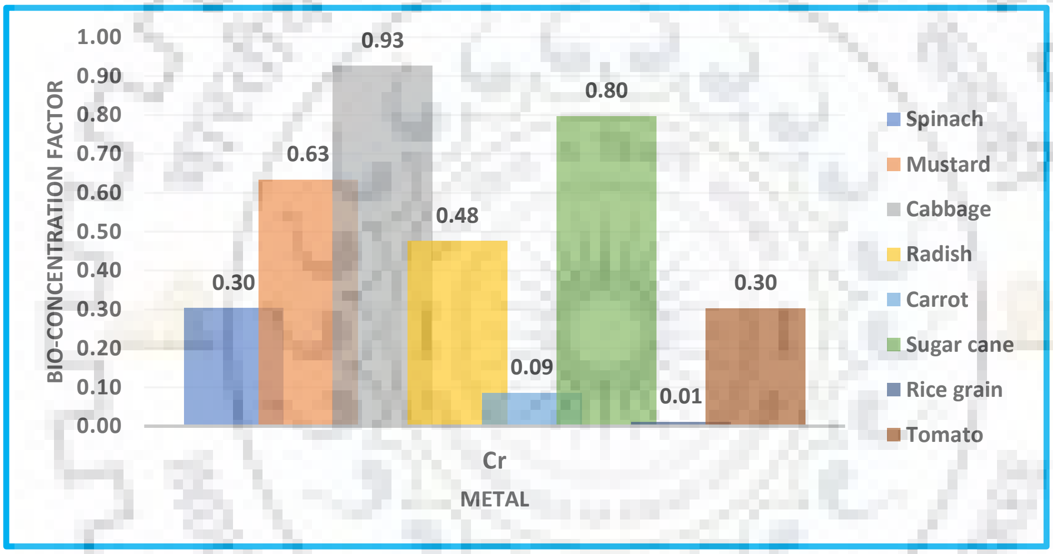


(a)



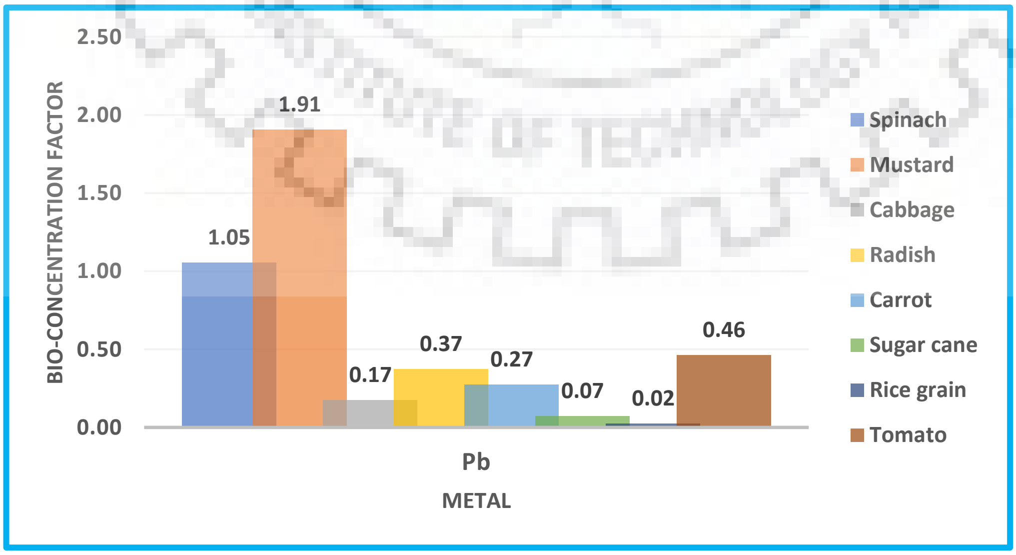
3.00
2.50
2.00
1.50
1.00
0.50
0.00
BIO-CONCENTRATION FACTOR
2.66
1.19
1.19
0.99
0.91
0.51
0.05
0.12
Cu
METAL
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

(b)



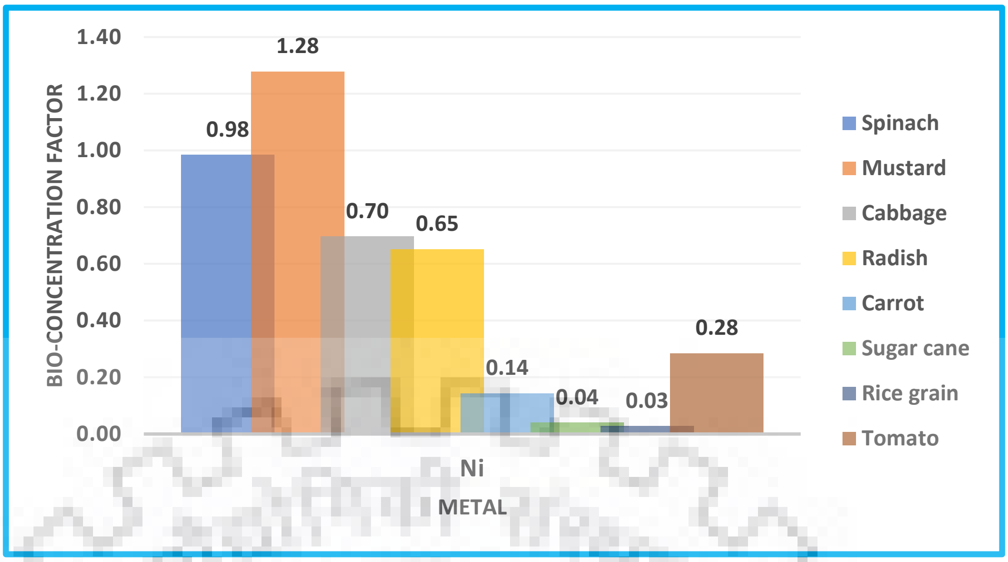
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
BIO-CONCENTRATION FACTOR
0.93
0.80
0.63
0.48
0.30
0.30
0.09
0.01
Cr
METAL
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

(c)

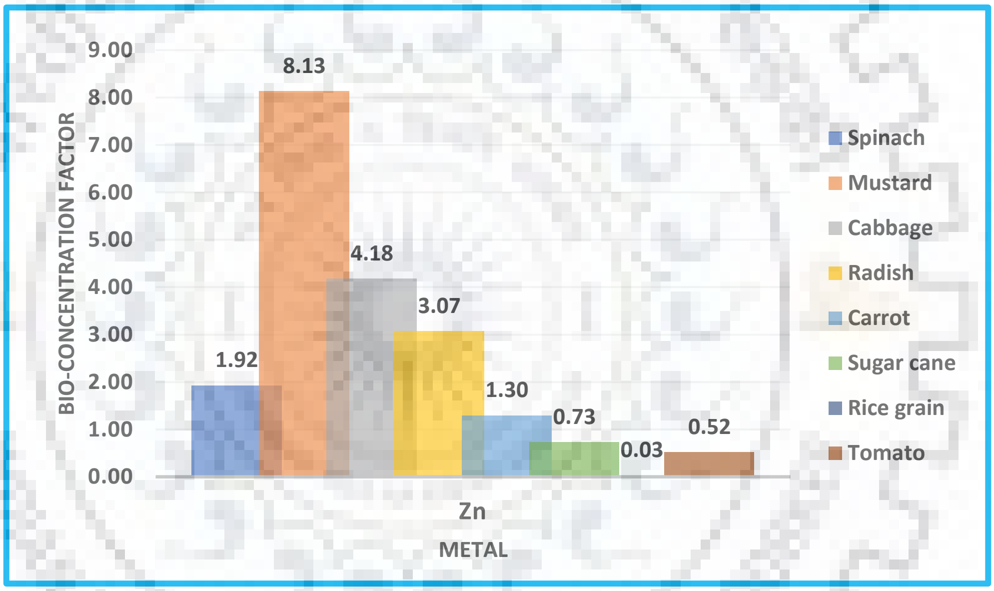


2.50
2.00
1.50
1.00
0.50
0.00
BIO-CONCENTRATION FACTOR
1.91
1.05
0.17
0.37
0.27
0.07
0.02
0.46
Pb
METAL
Spinach
Mustard
Cabbage
Radish
Carrot
Sugar cane
Rice grain
Tomato

(d)



(e)



(f)

Fig. 4.2(a-f) *Estimation of Bio-concentration Factor in different vegetables*

4.4.4. Health Risk Assessment in adult and children population

The maximum daily intake of Cd was observed to be higher through the consumption of radish (3.05E-03) and cabbage (1.45E-03) followed by spinach and mustard. Among all the sampled vegetables maximum intake of Cu, Pb, and Ni was observed through the intake of mustard. Both leaf and oil seed of mustard is extensively consumed in India, that may lead to the high exposure of these metals via food. The detailed data of ADI both in adult and children population is shown in ***Table 4.3 (a-b).***

Table 4.2 (a): ADI (mg/kg/day) of metal through vegetables in adult population

VEGETABLE	ADULT					
	Cd	Cu	Cr	Pb	Ni	Zn
Spinach	6.11E-04	1.71E-02	7.41E-03	1.30E-02	3.54E-02	7.19E-02
Mustard	2.97E-04	3.83E-02	1.55E-02	2.35E-02	4.60E-02	3.04E-01
Cabbage	1.45E-03	1.71E-02	2.26E-02	2.15E-03	2.51E-02	1.56E-01
Radish	3.05E-03	1.43E-02	1.16E-02	4.60E-03	2.35E-02	1.15E-01
Carrot	4.02E-06	7.39E-03	2.09E-03	3.37E-03	5.14E-03	4.84E-02
Sugar cane stem	8.84E-05	1.31E-02	1.94E-02	8.84E-04	1.43E-03	2.72E-02
Rice grain	4.02E-06	7.23E-04	2.69E-04	2.89E-04	9.84E-04	1.04E-03
Tomato	3.21E-05	1.69E-03	7.39E-03	5.71E-03	1.02E-02	1.94E-02

Table. 4.2 (b): ADI (mg/kg/day) of metal through vegetables in children population

VEGETABLE	CHILDREN					
	Cd	Cu	Cr	Pb	Ni	Zn
Spinach	1.82E-03	5.11E-02	2.21E-02	3.89E-02	1.06E-01	2.15E-01
Mustard	8.88E-04	1.14E-01	4.62E-02	7.03E-02	1.38E-01	9.08E-01
Cabbage	4.32E-03	5.11E-02	6.75E-02	6.41E-03	7.49E-02	4.66E-01
Radish	9.12E-03	4.27E-02	3.47E-02	1.37E-02	7.01E-02	3.43E-01
Carrot	1.20E-05	2.21E-02	6.24E-03	1.01E-02	1.54E-02	1.45E-01
Sugar cane stem	2.64E-04	3.90E-02	5.81E-02	2.64E-03	4.28E-03	8.14E-02
Rice grain	1.20E-05	2.16E-03	8.04E-04	8.64E-04	2.94E-03	3.12E-03
Tomato	9.60E-05	5.04E-03	2.21E-02	1.71E-02	3.06E-02	5.81E-02

The Hazard quotient also referred to as the non-carcinogenic risk was estimated in both adult and children population and depicted in the ***Table. 4.4 (a) & (b).*** Children population were observed to be more susceptible to the risk associated with metal exposure through the intake of vegetables. The risk associated with Cd was found to be maximum via consumption of Radish cabbage and spinach in both adult and children population. The leafy vegetables including spinach, cabbage, mustard leaves showing high health risk probability of metal exposure through consumption as they receive high amount of atmospheric depositions, vehicular and industrial dust when grown in peri-urban areas and could absorb heavy metals due to their large foliar surface area [19]. For the reason, health risk associated with consumption of Spinach, cabbage, Mustard along with root or tuberous vegetable were observed to be considerably high in comparison to the tomato, sugarcane, and rice grains. Health risk index associated with Ni exposure through consumption of spinach, mustard, cabbage, and radish were observed to be higher than the threshold value (HQ>1) signifying considerable health risk in both adult and children population. Sugarcane is the extensively grown throughout the study area; the exposure of metal through sugarcane consumption was found to be under the permissible range for the adult population but was observed to be closer to the threshold value in children population. Rice is the staple food crop in India, although the concentration of metal and risk associated with it was observed to be low but daily consumption may lead to pronounced dietary intake of metal.

Table. 4.3 (a): Health risk or Hazard quotient (HQ) in the adult population in the study area

VEGETABLE	ADULT					
	Cd	**Cu**	**Cr**	**Pb**	**Ni**	**Zn**
Spinach	6.11E-01	4.28E-01	4.94E-03	3.25E+00	1.77E+00	2.40E-01
Mustard	2.97E-01	9.58E-01	1.03E-02	5.88E+00	2.30E+00	1.01E+00
Cabbage	1.45E+00	4.28E-01	1.51E-02	5.36E-01	1.25E+00	5.20E-01
Radish	3.05E+00	3.58E-01	7.74E-03	1.15E+00	1.17E+00	3.82E-01
Carrot	4.02E-03	1.85E-01	1.39E-03	8.44E-01	2.57E-01	1.61E-01
Sugar cane stem	8.84E-02	3.26E-01	1.30E-02	2.21E-01	7.17E-02	9.08E-02
Rice grain	4.02E-03	1.81E-02	1.79E-04	7.23E-02	4.92E-02	3.48E-03
Tomato	3.21E-02	4.22E-02	4.93E-03	1.43E+00	5.12E-01	6.48E-02

Table. 4.3 (b): Health risk or Hazard quotient (HQ) in the children population in the study area

VEGETABLE	CHILDREN					
	Cd	**Cu**	**Cr**	**Pb**	**Ni**	**Zn**
Spinach	1.82E+00	1.28E+00	1.48E-02	9.72E+00	5.29E+00	7.16E-01
Mustard	8.88E-01	2.86E+00	3.08E-02	1.76E+01	6.88E+00	3.03E+00
Cabbage	4.32E+00	1.28E+00	4.50E-02	1.60E+00	3.74E+00	1.55E+00
Radish	9.12E+00	1.07E+00	2.31E-02	3.44E+00	3.50E+00	1.14E+00
Carrot	1.20E-02	5.52E-01	4.16E-03	2.52E+00	7.68E-01	4.82E-01
Sugar cane stem	2.64E-01	9.75E-01	3.87E-02	6.60E-01	2.14E-01	2.71E-01

Rice grain	1.20E-02	5.40E-02	1.44E-03	2.16E-01	1.47E-01	1.04E-02
Tomato	9.60E-02	1.26E-01	3.36E-03	4.27E+00	1.53E+00	1.94E-01

4.5. CONCLUSION

The present study revealed the status of metal contamination in the vegetables grown in the uppermost Ganga-Yamuna doab region of India and associated health risk. Metals concentration in leafy/tuberous vegetables were observed higher than other vegetables. The metal concentration in almost all plant samples was found to be beyond or close to the permissible limit. The overall bio-concentration factor or transfer factor from soil to plant was observed in the trend Zn> Cd> Cu> Pb> Ni >Cu. Health risk assessment revealed considerable health risk for Cd, Pb and Ni metals. HQ index for Cu and Zn was observed to be close or beyond the safe limit but has to considerably low toxic impact in comparison to other studied metals. The results of the present work suggest precise monitoring of metals contamination in agricultural soils and in vegetables as well. So that excessive input of metals in human food chain system can be checked.

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CHAPTER V

PROBABILISTIC RISK ASSESSMENT

PART-A: FUZZY-BASED PROBABILISTIC ECOLOGICAL RISK ASSESSMENT APPROACH: A CASE STUDY OF HEAVY METAL CONTAMINATED SOIL *

* *The research work described in this chapter has been published in* ***Soft Computing: Theories and Applications*** *(https://doi.org/10.1007/978-981-10-5699-4_39)*

5A.1. ABSTRACT

The ecological risk assessment tools viz. Index of Geo-accumulation (I_{geo}), Enrichment Factor (EF) etc. are the classical models for the assessment of risk related to the soil and sediment contamination. These models are well classified into several classes for the assessment of contamination risk. The vagueness in the estimation of risk associated with these models creates voids for computational approaches. In the present study, Fuzzy based probabilistic model was developed to restrict the vagueness of risk estimation. Both I_{geo} and EF were taken as input variables for aggregate risk determination. The linguistic attributes were assigned for risk estimation and qualitative scale presented as a trapezoidal fuzzy number. For the validation of methodology, a case study was taken into account for risk determination. The fuzzy based aggregate risk assessment revealed a high risk of Cadmium and Arsenic toxicity in the study area with the risk score of 0.751 and 0.698 respectively. The fuzzy based risk assessment is a conceptual methodology that restricts the vagueness in the estimation of risk for better decision-making approach.

5A.2. INTRODUCTION

The fuzzy set theory can be viewed as a qualitative assessment approach that can be used to develop and evaluate a hierarchical model for assessment of soil health risk based on parameters such as organic content, heavy metal deposition, enzymatic activity, etc. [1], [2]. The concept of fuzzy logic had been introduced by Zadeh in 1965, is used today in several fields. Initially, this concept applied the human way of thinking to modify the concept of binary logic and abandoning the probabilistic approach of either true or false.

Fuzzy logic is a computational approach which is based on the 'degree of truth', rather than the probabilistic approach of true or false. The truth value in fuzzy logic varies extremely from 0 to 1.

The concept of fuzzy logic was mainly used to control the means of transport, electrical appliances, and industrial processes. But today with the advancement of computing technologies it has broadened the involvement of fuzzy logic in the environment, analysis and diagnosis of HTR nuclear power plant, phosphoric acid production, selecting layered manufacturing techniques, ophthalmology, machine monitoring, and diagnostics, hazard identification connected to oil drilling waste, hydraulics or water management, the transportation of hazardous materials on roads, ducts, hydrogeology and for identification of the vulnerability of aquifers [3]–[9].

Over the past decade, Japan, USA and Europe have achieved numerous applications of the fuzzy system in the areas of pattern recognition, robotics, image/signal processing, medicine/biomedical, data mining, healthcare, drug administration, banking and financial decision system, household electronic appliances such as washing machines and televisions, nuclear power stations and handwriting recognition, photocopy machines and elevators.

Today, fuzzy sets have transformed into a number of concepts, models and techniques in order to deal with complex mechanisms which otherwise hard to dissect with classical methods of probability theory. The Industrial and atmospheric electrostatics have successfully applied the concept of fuzzy logic in fuzzy automated diagnosis, fuzzy fault tree analysis and fuzzy risk evaluation [10].

Agricultural and food system have also successfully introduced the concept of fuzzy models in their analytical approaches [11]. In Industrial work environment, there is always involvement of exposing workers to high-risk associated tasks. Therefore, a decisional instrument to assess the risk has been designed with the help of fuzzy logic as it allows treating uncertain and qualitative data [12].

Fuzzy logic has also been implemented in determining the environmental impact assessment. This system helps in the evaluation of expected change in the physical, social, biological and economic systems due to the implementation of an activity or project [13].

Further application of fuzzy logic can be introduced in the area of soil contamination[14]. Soil contamination is among the world fastest growing global environmental problem. This indeed poses a great threat to human health and environmental quality. Over the last few decades, heavy metals soil pollutant has received larger attention. The accumulation of heavy metals in soil can directly affect its physical and chemical properties, reducing its biological activity and nutrient availability. Along with these, it can also pose indirect effects to the soil in terms of environmental, human and animal health [15]. Increased level of heavy metals in soil can threaten food safety via plant uptake [16].

The major challenge is to accurately predict the risk associated with the exposure of heavy metal contamination [17] due to a complex spatial pattern of heavy metals and high coefficient of variation. Therefore, there is need for innovative scientific methodology to precisely predict the percentage of heavy metal contaminated soil from the non-contaminated soil areas.

Therefore, the approach of fuzzy logic has been introduced in this work to determine the percentage of heavy metal contaminated soil, which is cost-effective, quickly and precisely identifies the most serious threat to the environment.

The parameters used for defining the soil health in terms of heavy metals are Geo-accumulation index (I_{geo}) [18] and Enrichment factor (EF) [19]. For each parameter, membership function has been defined in the fuzzy system, thus performing the fuzzification. Further this fuzzy rule has been defined in order to identify the soil health of each site in terms of the ecological risk index. Thus, the fuzzy analysis has been applied to determine the soil health index, which is then further used to define the soil health level based on the basic data obtained from the sampling site.

5A.3. METHODOLOGY

5A.3.1. The Fuzzy based approach to determine aggregate ecological risk

The conceptual model depicted in Fig. 5A.1 illustrate the model structure used for determining aggregate ecological risk for the heavy metal contamination in the soil.

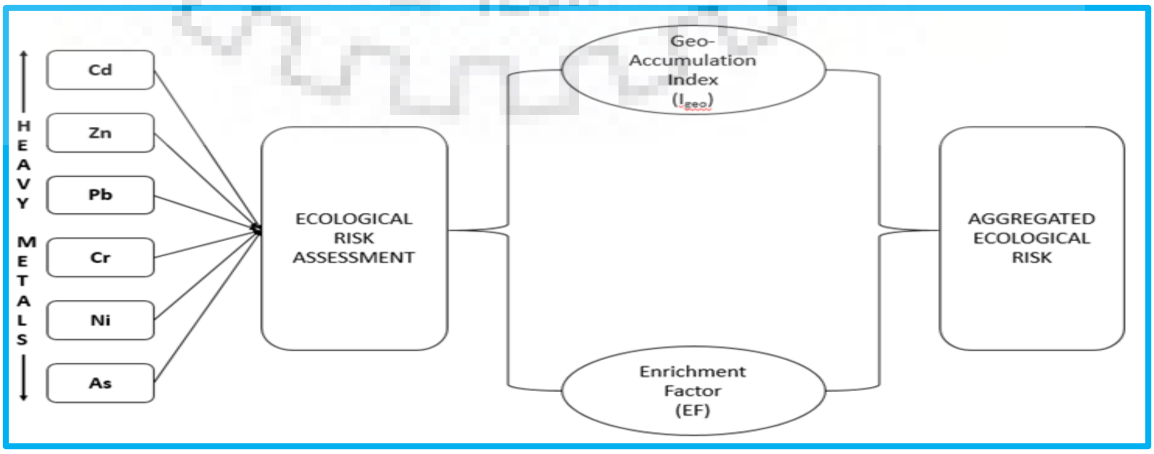

Fig. 5A.1: *Conceptual diagram of the implemented fuzzy logic model*

The conceptual model involves the analysis of heavy metal from the collected soil sample, assessment of ecological risk and evaluation of aggregate risk using fuzzy logic approach. This three-step process has been briefly discussed.

5A.3.2. Analysis of heavy metal concentration

Soil samples from suburban areas of Saharanpur district (India) were collected and heavy metal concentrations were analyzed for the metals viz. Cd, Zn, Cu, Pb and As. The location of sampling areas with their geographical coordinates are mentioned in Table 5A.1. The samples were taken randomly from each area in the month of March, 2016; using post hole soil auger from the upper horizon (0-20 cm). Samples were kept in a polyethylene bag and transferred to the laboratory within 3 hrs from sampling. All the samples were stored at 4°C till complete analysis. For heavy metal analysis, firstly soil samples were digested using microwave digestion oven (MarsXpress) using USEPA 3052 (USEPA 1996) methodology. Further digested solutions were diluted as per the recommended method and heavy metal concentration was analyzed using ICP-OES.

Table 5A.1: Sampling areas with their geographical coordinates

S. No.	Area	Coordinates
1	Sheikhpura Quadeem	29°55'30"N 77°34'21"E
2	Tapri	29°55'19"N 77°35'40"E
3	Lakhnaur	29°53'45"N 77°36'50"E
4	Paragpur	29°55'43"N 77°35'20"E
5	Kapasa	29°55'0"N 77°36'28"E

5A.3.3. Ecological Risk assessment

Geo-accumulation and Enrichment factor of metals in the study area were assessed on the basis of equation and classification proposed by Muller (1981) and Buat et al. (1979) respectively [20], [21]. The brief description of both the ecological risk assessment indices has been discussed in chapter II.

5A.3.4. Steps for fuzzy based analysis

The study is focused on the development of the fuzzy based methodology for the aggregate ecological risk assessment of heavy metal contaminated sites. In order to apply the fuzzy logic, classes of I_{geo} and EF have been modified and represented in table 5A.2. The input data as defined in the form of membership functions for each of them and the defuzzification method chosen for obtaining the Fuzzy output, which in the present case is an aggregate ecological risk at contaminated sites. The sensitivity analysis was performed by using the fuzzy approach to overcome the problem of uncertainty associated with the input data and the implemented fuzzy model. A fuzzy inference process has been deployed for facilitating the kind of aggregated risk quantification, by using fuzzy membership functions and fuzzy rules (Table. 5A.3).

Table 5A.2: Classification and representation of class according to the soil quality

Class	I_{geo}	EF	Soil Quality
0	I_0	EF_0	Deficiency to minimal enrichment
1	I_1	EF_1	Moderate enrichment
2	I_2	EF_2	Significant enrichment
3	I_3	EF_3	Very high enrichment
4	I_4	EF_4	Extremely high enrichment

Table.5A.3: Fuzzy rules for determination of Soil risk assessment

Index of Geo-accumulation	Enrichment Factor	Risk Characteristics
I_0	EF_0	No Risk
I_0	EF_1	Low Risk
I_0	EF_2	Medium Risk
I_0	EF_3	Medium Risk
I_0	EF_4	High Risk
I_1	EF_0	No Risk
I_1	EF_1	Low Risk
I_1	EF_2	Medium Risk
I_1	EF_3	Medium Risk
I_1	EF_4	High Risk
I_2	EF_0	No Risk
I_2	EF_1	Low Risk
I_2	EF_2	Medium Risk
I_2	EF_3	Medium Risk

I_2	EF_4	High Risk
I_3	EF_0	No Risk
I_3	EF_1	Low Risk
I_3	EF_2	Medium Risk
I_3	EF_3	Medium Risk
I_3	EF_4	High Risk
I_4	EF_0	No Risk
I_4	EF_1	Low Risk
I_4	EF_2	Medium Risk
I_4	EF_3	Medium Risk
I_4	EF_4	High Risk
I_5	EF_0	No Risk
I_5	EF_1	Low Risk
I_5	EF_2	Medium Risk
I_5	EF_3	Medium Risk
I_5	EF_4	High Risk

The aggregation waste determines the contaminants depending on the heavy metal content. Therefore, with the increase of geo-accumulation index or enrichment factor, the aggregation risk will increase. The procedure to determine the aggregated risk combines the results obtained by two fuzzy diagrams (Fig. 5A.3 & 5A.4).

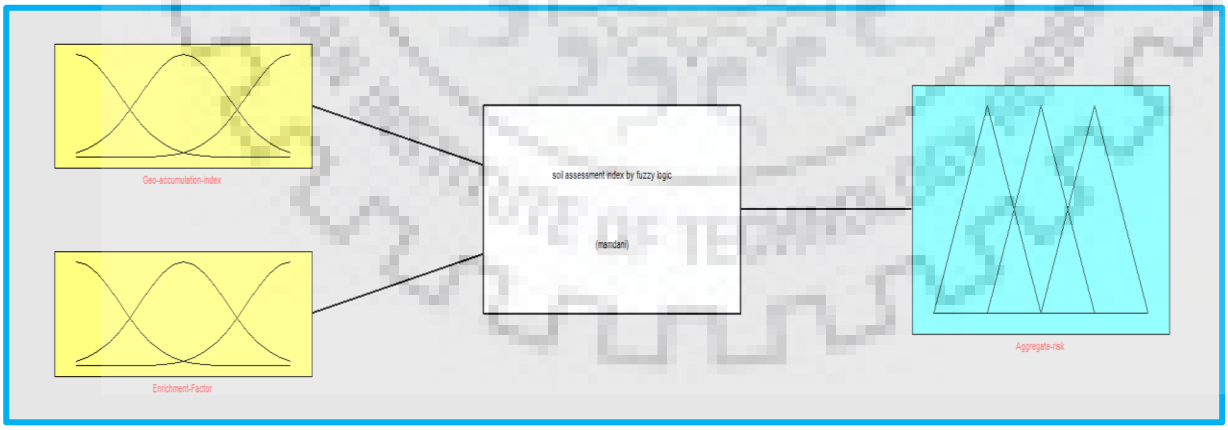

Fig. 5A.2. *Fuzzy inference engine*

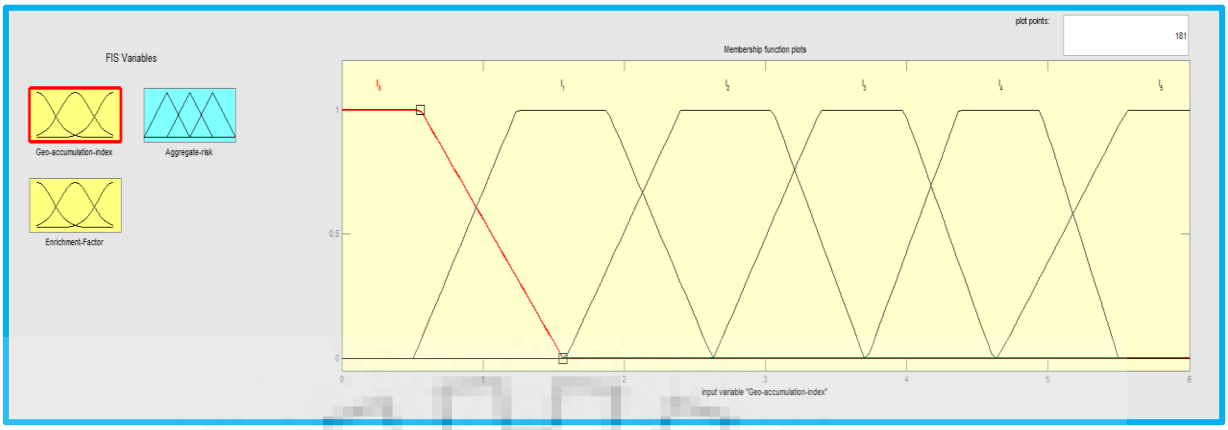

Fig. 5A.3. *Fuzzy rule-based input variable of geo-accumulation index*

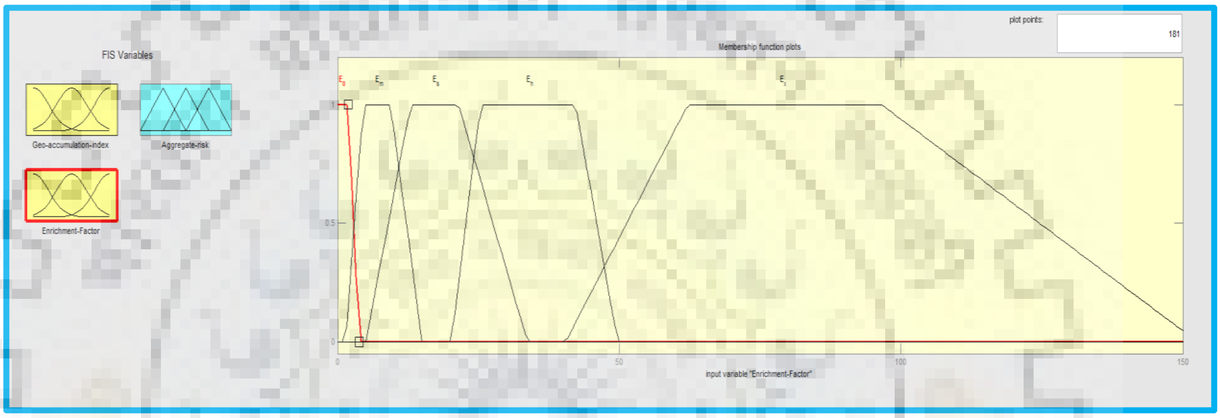

Fig. 5A.4 *Fuzzy rule-based input variable of enrichment factor*

The final result of the process was obtained through defuzzification (Fig. 5.5) by providing a numerical value between 0 and 1 and represents the risk index.

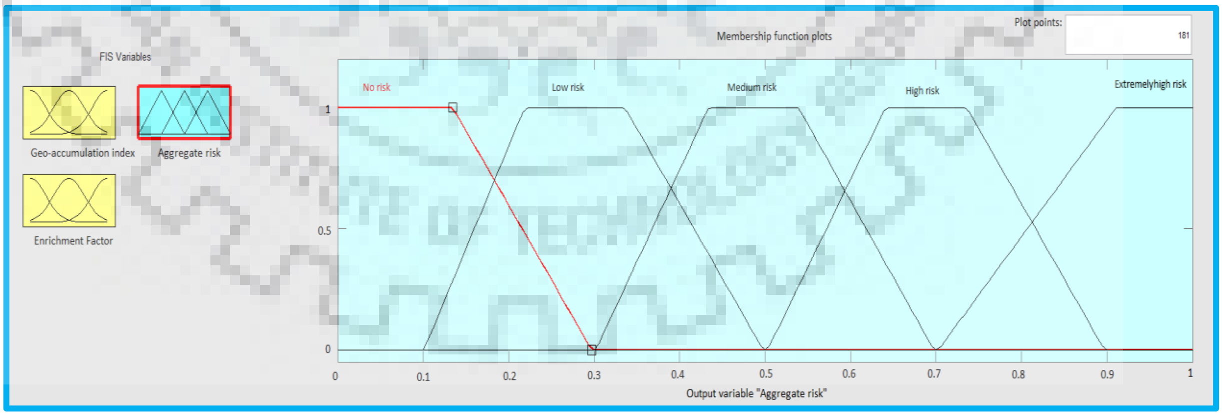

Fig. 5A.5 Fuzzy rule-based output variable of aggregate risk

In order to ease the methodology, we used the MATLAB® software passing through the graphical interface by means of creating three different graphical interfaces to describe the three planned variable sets. Our attention focused on the aggregation-based risk assessment.

5A.4. RESULT AND DISCUSSION

5A.4.1. Fuzzy based analysis of aggregated ecological risk assessment

The work described dealt with the study of ecological risk assessment of heavy metal contamination. High risk of heavy metal accumulation was observed in suburban areas of Saharanpur district. The geometric mean of heavy metals observed in the study areas is depicted in Table 5A.4.

Table 5A.4: Geometric mean of heavy metal concentration in study areas

Metal	Cd	Zn	Pb	Cr	Ni	As
Geometric mean of metal concentration (mg/kg)	2.24± 0.48	99.58± 40.62	22.45± 5.74	84.34± 46.28	256.88± 46.24	9.38± 4.23

The fuzzy inferences have been shown in the conceptual diagram in Fig. 5A so as to manage the algorithm easily. High geo-accumulation of Cadmium (Cd) was observed in the study area followed by the Arsenic (As) contamination. Samples were moderately contaminated by Lead (Pb) and Nickel (Ni), whereas Zinc (Zn) has practically uncontaminated status in the study area. Extremely high enrichment of Cadmium (Cd) and Arsenic (As) were observed in the study area whereas Lead (Pb), Chromium (Cr) and Nickel (Ni) has moderate enrichment in the study area. Moderate enrichment of Zinc (Zn) was observed in the study area.

Fuzzy logic uses the linguistic type of variables which are defined by a continuous range of truth values or FMFs in the interval [0, 1] instead of the strict binary (true or false) decisions. The linguistic input and output associations when combined with an inference procedure, constitutes the fuzzy-based system. The membership functions represent the degrees to which the specified concentration belongs to the fuzzy sets. The trapezoidal membership function was used to perform the simulations which are in the agreement with the input data trend.

Table 5A.5. Fuzzy inference of aggregate risk assessment

Metal	I_{geo}	EF	Aggregate Risk
Cd	3.92	128.49	0.71
Zn	-0.23	7.17	0.499
Pb	1.9	17.14	0.499
Cr	0.68	13.55	0.499
Ni	0.98	16.66	0.497
As	2.5	47.98	0.701

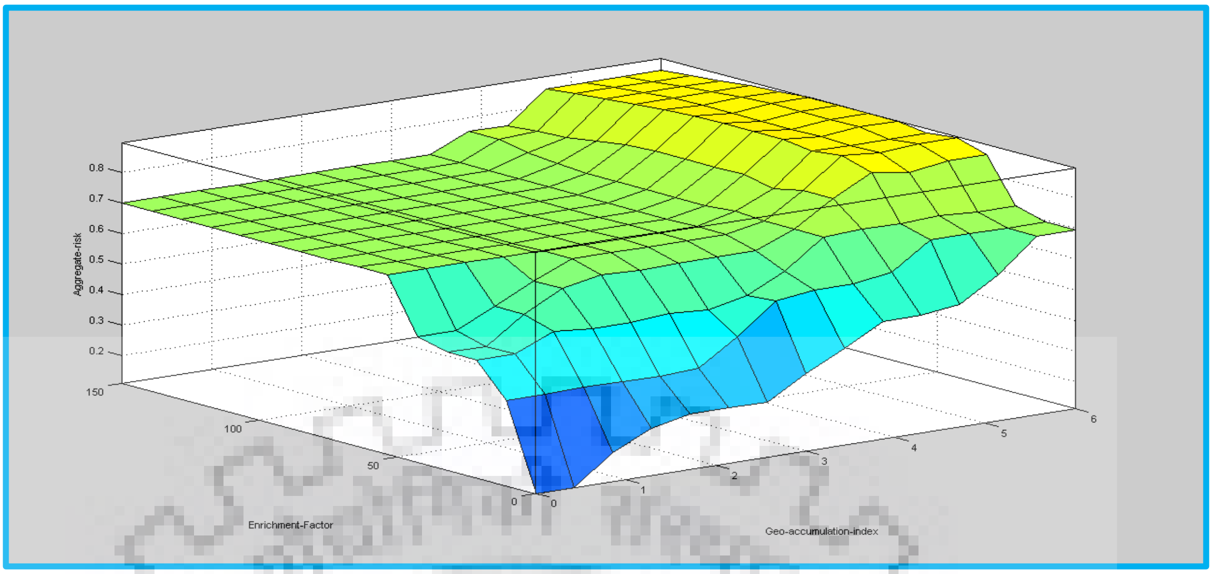

Fig. 5A.6 *Fuzzy Risk assessment index represented three-dimensionally with enrichment factor and geo-accumulation index*

A surface diagram (Fig. 5A.6) approach is presented for the identification of aggregation risk concentration (Table. 5A.5) feature based on a set of rules by considering the methodology variables such as geo-accumulation index and enrichment factor. A fuzzy rule system approach is used because of the imprecise, insufficient, ambiguous and uncertain data available. In this manner, without mathematical formulations, expert maximum risk assessment system is identified.

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CHAPTER V

PROBABILISTIC RISK ASSESSMENT

PART-B: ESTIMATING HEALTH RISKS IN METAL CONTAMINATED LAND FOR SUSTAINABLE AGRICULTURE IN PERI-URBAN INDUSTRIAL AREAS USING MONTE CARLO PROBABILISTIC APPROACH *

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5B.1. ABSTRACT

Health risks associated with heavy metal contamination were characterized in the agriculture soil procured from the peri-urban areas of Saharanpur, India. The mean concentration of As, Cd, Cu, Pb, Cr, and Ni were observed to be 14.50, 1.65, 35.82, 30.76, 60.70 and 89.63 mg/kg respectively. Statistical analysis was performed for the source apportionment of the metal in the study area. The health risk to adult and children population was estimated using the expression derived by USEPA. Non-carcinogenic health risk via ingestion, inhalation, and dermal pathways was estimated by hazard quotient (HQ) and hazard index (HI), whereas Carcinogenic risk was estimated via the inhalation pathway. HI combined (ingestion, dermal and inhalation) for both adult and children population exceeded the safe level (HI ≥1) for Cr (2.21). Cancer risk were observed within the admissible range (1E-06 to 1E-04). Monte Carlo simulation approach was applied for uncertainty analysis of estimated non-carcinogenic and carcinogenic risks by simulating the variables associated with risk estimation for 10,000 iterations.

5B.2. INTRODUCTION

The anthropogenic activities including industrialization, unmanaged disposals of waste, excessive input of chemical fertilizers etc are severely impacting the quality of the soil. Heavy metal accumulation is a serious concern for both human and soil health[1], [2]. Use of industrial wastewater is a sustainable agriculture approach against the depleting fresh water resources but on long term applications the efficiency of soil to retain heavy metals get reduced leading to excessive accumulation of metals like Cd, Cr, Pb, Ni and Zn in the topsoil [3]–[5]. High input and accumulation of heavy metals in agricultural soil may enhance the metal uptake by the crops

and thus contaminating the food chain, which is the major pathway of heavy metal exposure to the human body [2], [6], [7]. With the increasing toxic level of metals in topsoil, it is important to monitor the health risk in the population directly exposed to the metal toxicity. The important steps include identification of the potential source of contamination, amount of the pollutant that interacting with the human body from different exposure pathways and quantifying the consequences of exposure to the human health [2], [8].
The expression for the estimation of health risk assessment was developed by USEPA [9]–[11]. To estimate exposure to an average individual (i.e., a central tendency), the 95% upper confidence limit (UCL) on the arithmetic mean has been considered for the exposure point concentration, and central estimates (i.e., arithmetic average, 50^{th} percentile, median) are chosen for all other exposure parameters [10]. Uncertainty in risk assessment is pervasive and it arises due to randomness and incompleteness in the environmental data. Monte-Carlo simulations technique is the approach to estimate the uncertainty distributions of risk by taking account of simultaneous consideration of variables associated with the exposure routes [12]. Monte Carlo simulation has been widely used probabilistic approach to reduce associated uncertainties. Probability distributions in risk assessment equations are simulated using repeated executions of the numerical model. The probabilistic distribution of carcinogenic and non-carcinogenic risk in the population has been determined in previous studies [12]–[16] via different exposure mediums. Schumacher et al. [16] assessed incremental lifetime risk using Monte-Carlo simulation techniques, in the population residing nearby municipal solid-waste incinerator (MSWI). Water quality modelling has also been performed by Monte Carlo analysis in some studies [14] .

In the present study, the agricultural soil from peri-urban areas of Saharanpur district is analyzed for the heavy metal concentration and related health risk was estimated. The Saharanpur district lies in the *doab* (a water-rich tract of land lying between two converging, or confluent, rivers) land between the holy river Ganga and Yamuna is characterized as highly fertile and alluvium rich area agriculture land; Agricultural practices contribute considerable fraction in the economy of the city. With the course of time, rapid industrialization and urbanization without implementation of adequate environmental management approach have severely impacted the quality of soil, water, food, and human health as well [17]. This study aims at determining the level of metal contamination and related risk to the adult and children population exposed to the metals via ingestion, inhalation and dermal contact pathways. Monte Carlo simulation approach was used to estimate the probabilistic health risk in the study area.

5B.3. MATERIAL AND METHODS

5B.3.1. Study area

Saharanpur (29.9671° N, 77.5510° E) district lies in the northernmost doab land stretch formed by two major rivers of India i.e., The Ganga and Yamuna. Due to this fertile alluvium rich stretch agriculture plays a crucial role in the economy of the district. Wheat, Rice, Maize, Sorghum, millets, sugarcane are the major crops grown in this region. Saharanpur district is one of the major industrial city of Uttar Pradesh state so the agriculture areas are majorly distributed in peri-urban areas of the city. In the present study, agriculture soils were analyzed for heavy metal contamination and associated health risk in male, female and children populations in three peri-urban areas viz. Pilakhni, Nanuta and Railway road.

5B.3.2. Sampling and analytical technique

The soil samples were procured from thirty sampling sites distributed in three peri-urban areas. The map in Fig. 1 is showing the sampling points distributed in the study areas. Detail description of sampling sites is provided as supplementary material. Total of 60 top-soils (0-15 cm) was procured from thirty sampling sites from three industrial areas (Pilakhni, Delhi Road and Railway Road) of Saharanpur city (29.9671° N, 77.5510° E). Triplicate samples were composited and zipped packed in a polyethylene bag, transferred to the laboratory within three hours from sampling and stored at 4°C till complete analysis. Before analytical step samples were dried (at 50°C), pulverized and sieved through 2 mm mesh plastic sieve [18]. The heavy metal was analyzed by digesting the soil samples using USEPA 3052 method [19] in the microwave digester (MarsXpress). Digested transparent solution was cooled, filtered through Whatman no. 42 filter paper and diluted up to 50 mL with 1% nitric acid. The metal concentration in the filtrate of digested soil samples was analyzed by ICP- OES.

5B.3.3. Quality assurance and control

Certified reference soil (SRM 1646a- Estuarine sediment) was used to ensure the validation of analytical procedure and was observed in the good agreement with respect to the certified values with recovery percentage 82.43 % to 108.09 %.

5B.3.4. Risk Assessment analysis

Ingestion, Inhalation, and dermal contact are three major pathways via which an individual get exposed to soil metal contamination. The expression which estimates the risk to the population due to metal exposure was developed United State Environmental Protection

Agency [9], [10], [20]. The Average Daily Intake (ADI) via all three exposure pathways can be estimated by the following expressions:

$$ADI_{ing} = C_{soil} \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5B.1)$$

$$ADI_{inh} = C_{soil} \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \quad (5B.2)$$

$$ADI_{dermal} = C_{soil} \times \frac{SAF \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (5B.3)$$

ADI_{ing}, ADI_{inh}, ADI_{dermal} stands for Average daily intake (mg/kg-day) via ingestion, inhalation and dermal pathways respectively. C_{soil} = metal concentration in soil(mg/kg), IngR= ingestion rate of soil (100 for adults and 200 for children); InhR= inhalation rate of soil (20 for adult and 7.3 for children; mg/day, m^3/day), EF is the exposure frequency (350 days/year), ED is the exposure duration (24 years for adults and 6 years for children), BW is the body weight (60 for adults and 15 for children) of the exposed individual (kg), AT is the time period over which the dose is averaged (day) for Non-carcinogenic (ED x 365 days) and for Carcinogenic (Lifetime x 365 days) , PEF is the particle emission factor (1.36e+09 m^3/kg), SAF is the skin adherence factor (0.07 and 0.2 mg/cm^2/h for adult and children respectively), and ABS is the dermal absorption factor (0.001 for all metals) [12].

The ADI for each metal and exposure pathway are subsequently divided by respective reference dose (RfD, mg/kg-day) to estimate non-carcinogenic hazard quotient (HQ), whereas for carcinogenic risk estimation ADI for each metal was multiplied with slope factor. On the basis of the assumption that inhaled particle bound toxic entities show a similar impact on being ingested, values of oral reference doses were used for the inhalation as well [12], [21]. The values of RfD and Slope Factor (SF) is mentioned in the Table. 5B.1

5B.4. RESULT AND DISCUSSION

5B.4.1. Metal contamination in Agricultural Soil

The heavy metal contamination for the analyzed metals is summarized in Table 5B.2. Throughout the study area, a wide range of heavy metal was observed which indicate considerable anthropogenic influences in the area. Long term wastewater irrigation severely impacts the soil quality and metal enrichment in the area [3], [4], [17], [22]. The mean concentration of As, Cd, Cu, Pb, Cr, and Ni were observed to be 14.50, 1.65, 35.82, 30.76, 60.70 and 89.63 respectively.

Table 5B.1: Reference dose for Ingestion, inhalation and dermal exposure and slope factor (Inhalation)

Metal	RfD(ing)	RfD(Inh)	RfD(derm)	SF (Inh)
As	3.00E-04	4.30E-03	8.00E-04	1.51E+01
Cd	1.00E-03	1.80E-03	1.00E-05	6.30E+00
Cu	4.00E-02	4.00E-02	1.20E-02	------------
Cr	3.00E-03	1.20E-02	6.00E-05	4.20E+01
Pb	3.50E-03	3.50E-03	5.25E-04	-------------
Ni	2.00E-02	2.00E-02	5.40E-03	8.40E-01

*Inh =Inhalation; Ing=Ingestion; Derm= Dermal

Most of the metal concentration analyzed were under the safe limits but metals like As, Cd, Pb Cr, and Ni could be potentially harmful in the near future, as the higher range of these metals were found close or above the safe limit prescribed by the Indian standards. The peri-urban areas of Saharanpur district comprise of several large and small-scale industries which can be anticipated for the considerably high metal contamination in the study area.

Table 5B.2: Concentration metal analyzed in the agricultural soils of the study area

Metal	Mean (ppm)	Median (ppm)	Range (ppm)	Safe Limit* (ppm)
As	14.50 ± 11.87	11.65	1.82 – 46.42	--
Cd	1.65 ± 0.65	1.55	0.62-3.02	3-6
Cu	35.82 ± 20.18	29.36	11.82 – 98.88	135- 270
Pb	30.76 ± 13.05	27.15	12.34 – 68.45	250-500
Cr	60.70 ± 40.91	49.33	13.52 – 155.79	--
Ni	89.63 ± 53.62	70.22	14.13 – 205.07	75-150

*Indian standard guideline for the safe limit [23]

5B.4.2. Statistical analysis

Principal component analysis (PCA) has been applied to the heavy metal concentration analyzed at different sampling sites in order to interpret their multivariate relationships. The purpose of PCA is to reduce the dimensionality of the dataset since a few of the new components explain the major part of the variation of the data. The components of PCA i.e., eigenvalues, variance (%) and cumulative (%) and PCA factor loading are shown in table.5B.3 and Fig. 5B.2 respectively. The PC1 inferred 34.51% of total variance dominated by As, Cu, and Pb, which indicate anthropogenic influences may be vehicular emissions, atmospheric depositions etc. Whereas, PC2 and PC3 showed a total variance of 22.23 % and 15.36% respectively indicating both anthropogenic and geogenic influences. As the study area is alluvium rich land, Cd contamination due to geogenic sources including underlying bedrock or transported parent material such as glacial till and alluvium could be anticipated [24], [25]

Hierarchical Cluster Analysis (HCA) was performed using Wards method and squared Euclidean distance approach. HCA contributes to the classification of variables into discrete clusters on the basis of interrelating characteristics of variables and reducing into small homogenous clusters. Two major clusters As-Pb and Cu-Cr-Ni were obtained. Fly ash from large scale industries to small scale industries including jaggery making unit, brick baking etc. can be anticipated for the contribution in the overall metal contamination of Cr, Cu, and Ni in the study area.

Table 5B.3: Principle component analysis of agriculture soil samples procured from the study area

Metal	**Components**		
	PC1	**PC2**	**PC3**
As	**0.48**	0.03	0.06
Cd	-0.53	0.31	0.32
Cr	-0.06	**0.66**	-0.23
Cu	**0.52**	-0.14	**0.50**
Ni	0.23	**0.61**	**0.49**
Pb	**0.41**	0.30	-0.59
Eigen Value	2.07	1.33	0.92
Variance (%)	34.51%	22.23%	15.36%
Cumulative (%)	34.51%	56.75%	72.11%

*p>0.4 is shown in bold

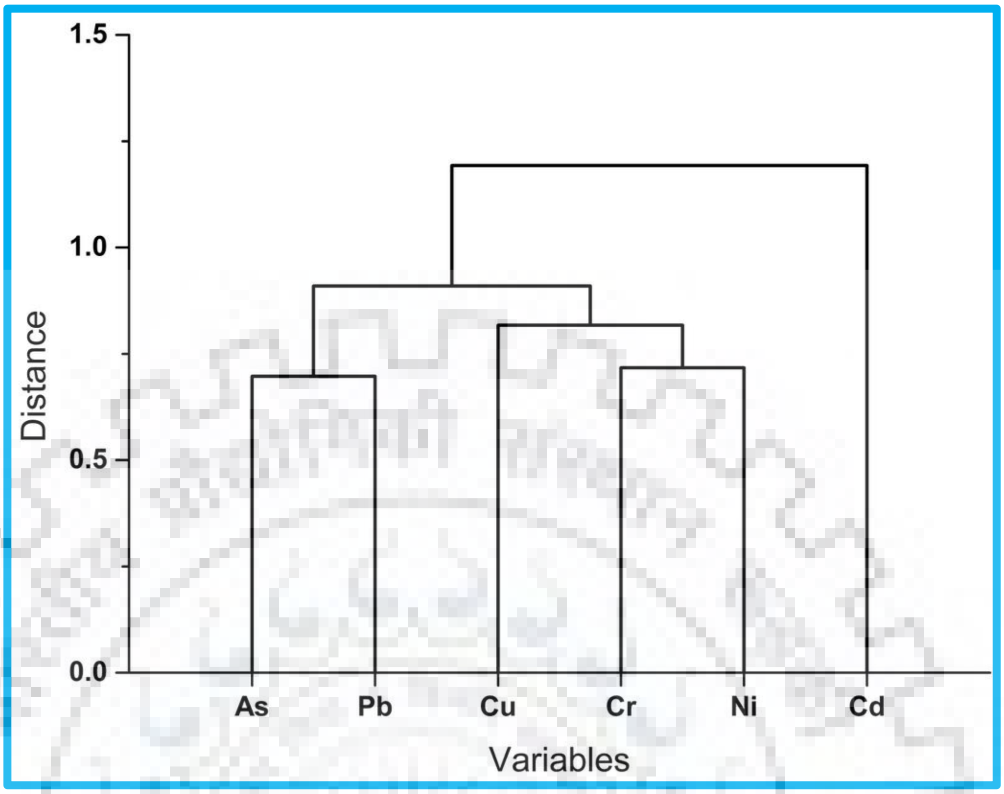


Fig. 5B.1: Hierarchical Cluster Analysis of metals

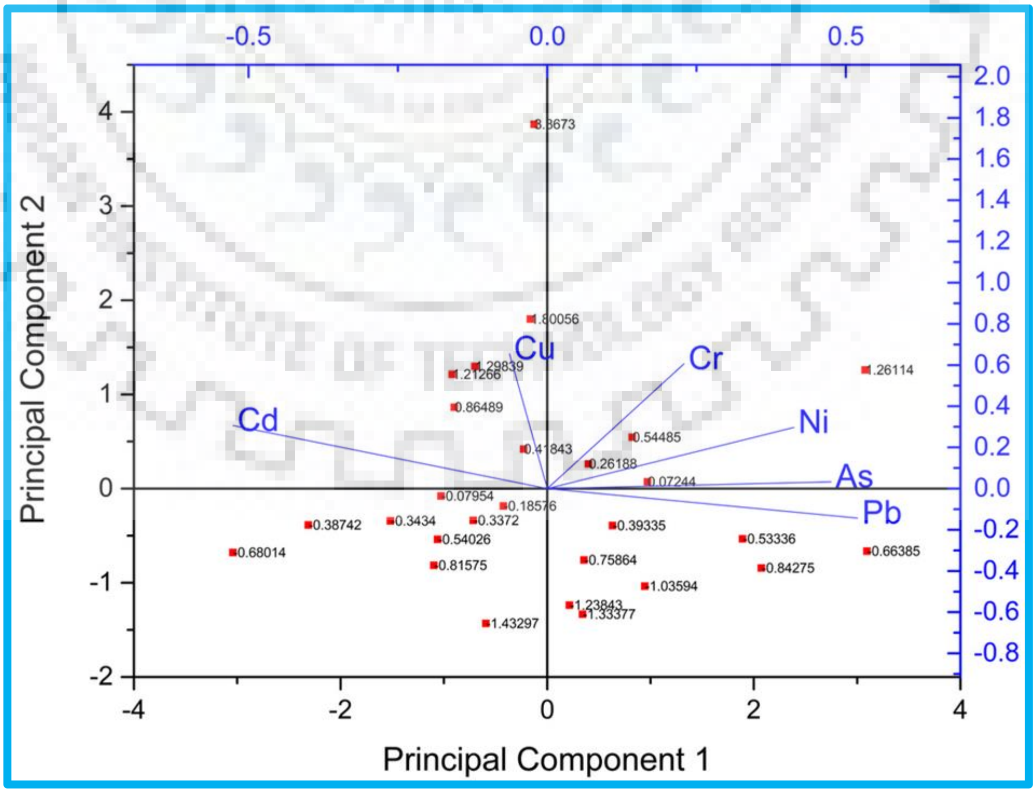


Fig. 5B.2: *PCA factor loading of metals*

5B.4.3. Analysis of Health Risk

Health risk due to soil metal exposure via three pathways (ingestion, inhalation and dermal) was analyzed and summarized in table 4. The exposure through the ingestion pathway was observed to be the most potential exposure pathway followed by dermal and inhalation. Both mean and 95% UCL were estimated in order to understand the level of risk associated with the particular metal. A similar trend of health risk was observed in both the adult and children population. Out of the metals analyzed in the present work, the non-carcinogenic risk associated with Cr (3.63) was found to be the maximum followed by Cd, As and Pb. No significant risk was observed by Cu and Ni contamination. HI for Cd (0.4), As (0.3) and Pb (0.21) is below the threshold value of risk but could be potentially harmful if exposed to the excessive average daily dose. Exposure of these metals to human populations to via different exposure pathways may have fatal effects on the organs such as the kidneys, cardiovascular system, liver, lungs, reproductive system, and overall immune system can be affected. Considerably high dose of Pd may lead to developmental and neurological disorders as well [12].

Table 5B.4: Non-Carcinogenic risk ($HI = \Sigma HQ_{(ing+ inh + dermal)}$) for adult and children population

Metal	Adult			Children		
	Mean	**S. D**	**95% UCL**	**Mean**	**S. D**	**95% UCL**
As	1.11E-01	9.25E-02	3.07E-01	8.92E-01	7.31E-01	2.46E+00
Cd	2.40E-01	1.29E-01	4.49E-01	1.93E+00	1.04E+00	3.61E+00
Cu	7.59E-03	4.33E-03	1.59E-02	6.10E-02	3.44E-02	1.28E-01
Pb	1.21E-01	5.22E-02	2.16E-01	9.74E-01	4.13E-01	1.73E+00
Cr	1.65E+00	1.12E+00	3.63E+00	1.33E+01	8.93E+00	2.92E+01
Ni	4.06E-02	2.47E-02	8.82E-02	3.27E-01	1.95E-01	7.09E-01

Table 5B.5: Carcinogenic risk estimation (inhalation pathway) for both adult and children population

Metals	Adult			Children		
	Mean	**SD**	**95%UCL**	**Mean**	**SD**	**95%UCL**
As	1.88E-08	1.54E-08	5.2E-08	7.2E-09	5.9E-09	1.99E-08
Cd	8.05E-10	4.33E-10	1.51E-09	3.08E-10	1.66E-10	5.76E-10
Cr	2.19E-07	1.48E-07	4.83E-07	8.39E-08	5.65E-08	1.85E-07
Ni	6.47E-09	3.87E-09	1.4E-08	2.48E-09	1.48E-09	5.37E-09

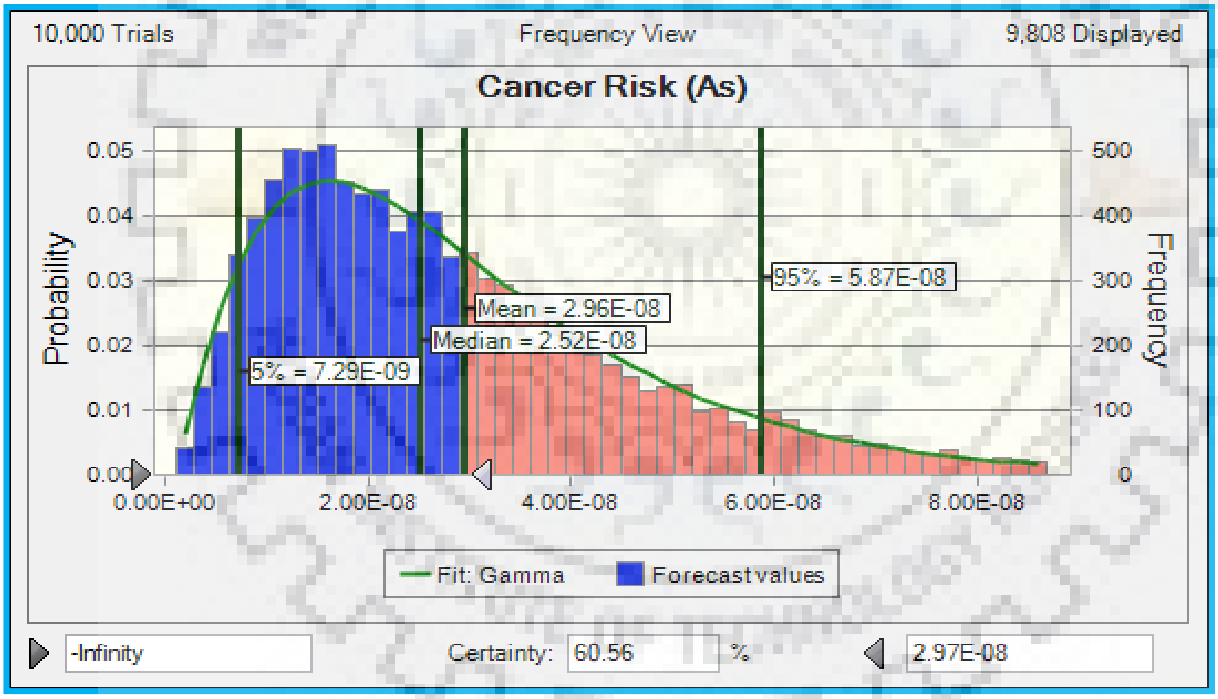
Table 5B.6. The range of non-carcinogenic risk estimated by Monte-Carlo Simulation analysis

Metal	Adult				Children			
	Mean	5th Percentile	95th Percentile	Certainty (%)	Mean	5th Percentile	95th Percentile	Certainty (%)
As	4.57E-01	2.52E-01	6.29E-01	84.02	3.45E-01	4.97E-02	9.95E-01	86.35
Cd	2.21E-02	5.83E-03	4.74E-02	87.5	9.09E-03	1.74E-03	2.48E-02	80.31
Cu	5.99E-03	1.36E-03	1.40E-02	86.03	6.17E-03	1.04E-03	1.76E-02	90.07
Pb	4.59E-02	1.15E-02	1.02E-01	91.52	5.46E-02	9.61E-03	1.51E-01	89.15
Cr	9.29E-01	1.97E-01	2.18E+00	87.7	1.27E+00	6.05E-01	3.58E+00	88.24
Ni	1.87E-02	3.86E-03	4.43E-02	84.32	2.54E-02	3.96E-03	7.29E-02	81.71

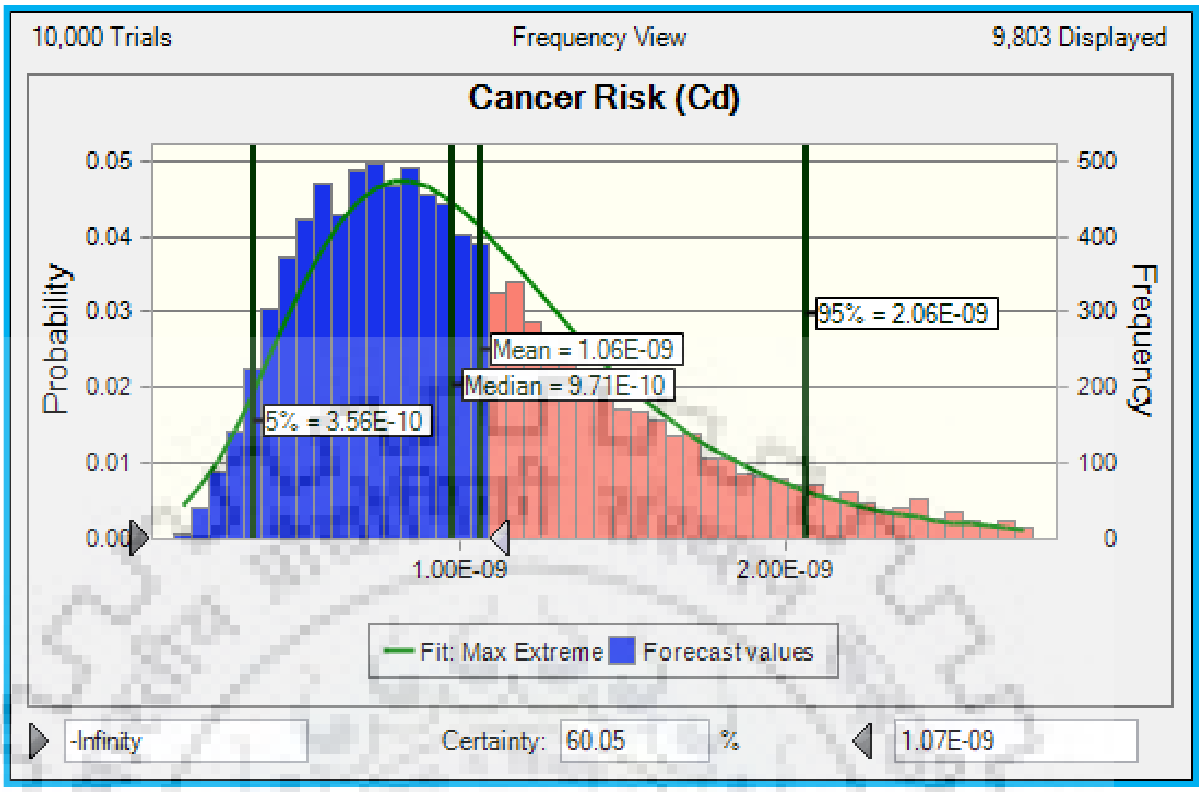
Table 5B.7. The range of carcinogenic risk estimated by Monte-Carlo Simulation analysis

Metal	Adult				Children			
	Mean	5th Percentile	95th Percentile	Certainty (%)	Mean	5th Percentile	95th Percentile	Certainty (%)
As	2.96E-08	7.29E-09	5.87E-08	60.56	1.64E-08	1.60E-09	4.06E-08	67.04
Cd	1.06E-09	3.56E-10	2.06E-09	60.05	5.60E-10	3.82E-11	1.31E-09	64.06
Cr	3.02E-07	8.68E-08	6.81E-07	62.94	2.51E-08	3.05E-09	5.95E-08	65.84
Ni	8.00E-09	2.31E-09	1.51E-08	60.85	4.42E-09	5.35E-10	1.04E-08	66.76

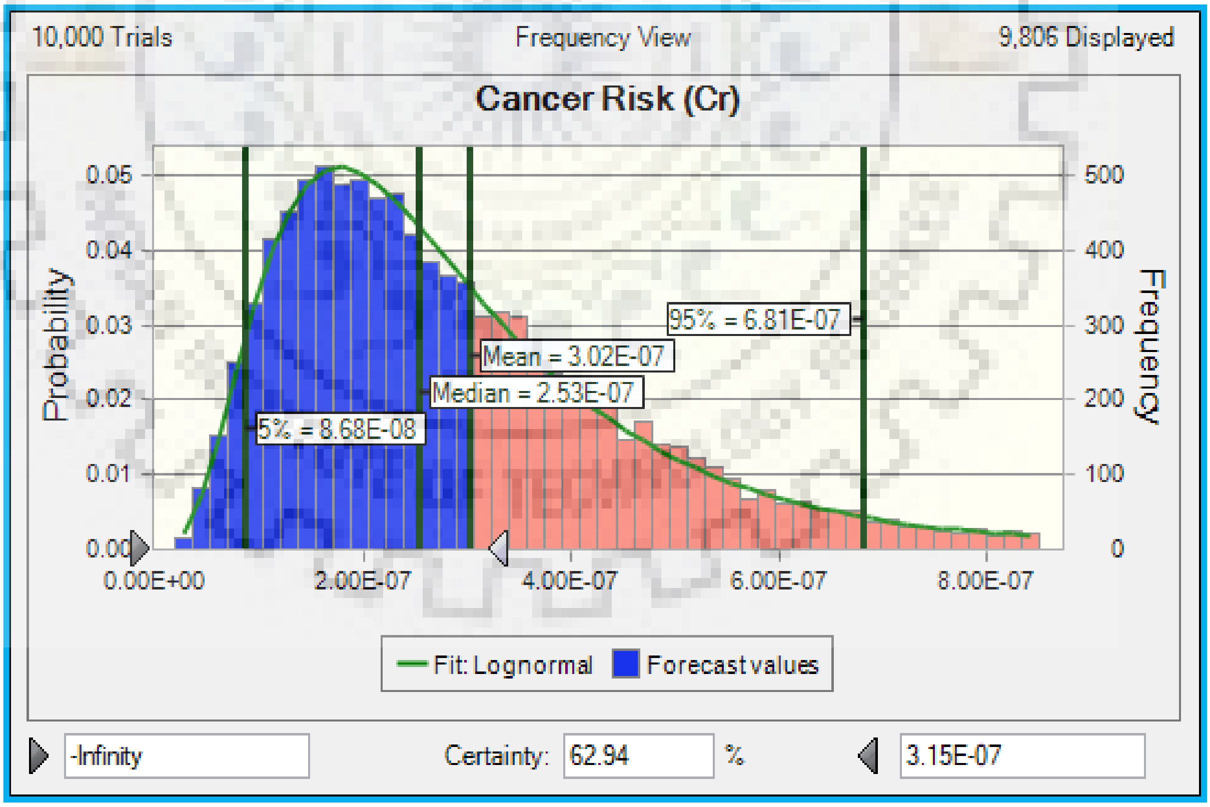
Probabilistic non-carcinogenic risk (via all three exposure pathways) and carcinogenic risk (via inhalation pathways) were estimated using the Monte Carlo simulation approach. The observation in terms of mean, 5th percentile, 95th percentile and certainty have been mentioned in the table. 6 (a-b). According to the probabilistic risk estimation maximum non-carcinogenic risk can be anticipated form the Cr contamination followed by As and Pb. The risk estimated for Cr at 95th percentile for adult and children population were 2.18 and 3.58 respectively which is quite high than the acceptable range. Whereas, the risk associated with As was observed to be 6.29E-01 and 9.95E-01 in adult and children population respectively approaching toward high-risk index. Moderate risk can be anticipated from the Pb contamination in the study area. Other metals (Cd, Cu, and Ni) were observed to be in the admissible limit according to the simulation performed for 10,000 iterations. Monte Carlo simulation result for carcinogenic risk was observed to be under the acceptable limit for all the analyzed heavy metals (As, Cd, Cr, and Ni). But potential cancer risk can be anticipated from As and Cr contamination.



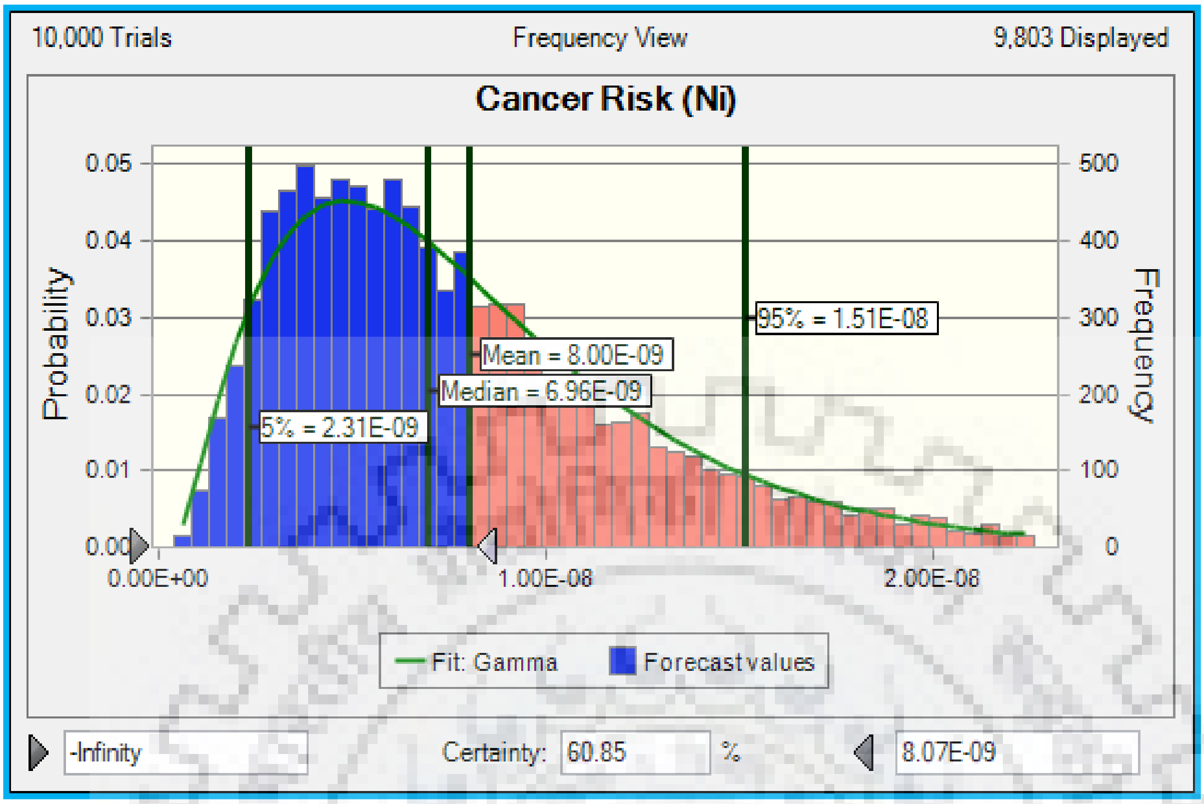
(a) As


10,000 Trials
Frequency View
9,803 Displayed
Cancer Risk (Cd)
Probability
Frequency
95% = 2.06E-09
Mean = 1.06E-09
Median = 9.71E-10
5% = 3.56E-10
1.00E-09
2.00E-09
Fit: Max Extreme
Forecast values
-Infinity
Certainty: 60.05 %
1.07E-09

(b) Cd

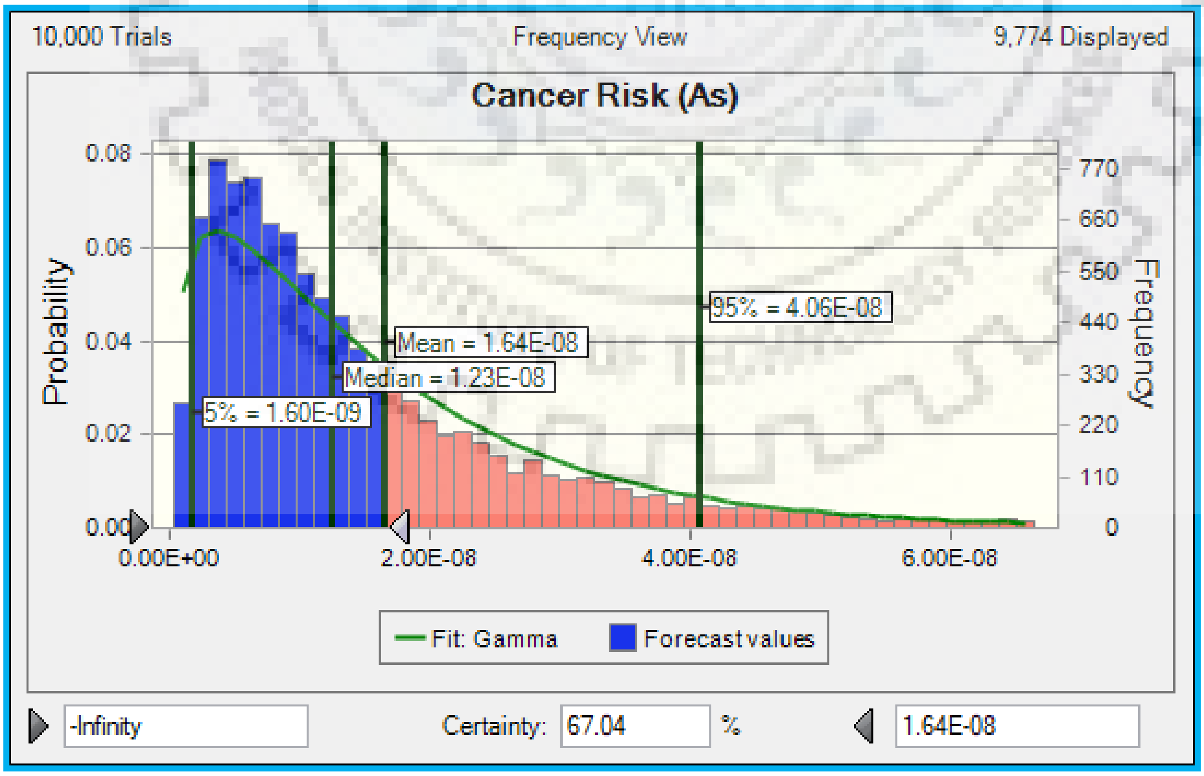

10,000 Trials
Frequency View
9,806 Displayed
Cancer Risk (Cr)
Probability
Frequency
95% = 6.81E-07
Mean = 3.02E-07
Median = 2.53E-07
5% = 8.68E-08
0.00E+00
2.00E-07
4.00E-07
6.00E-07
8.00E-07
Fit: Lognormal
Forecast values
-Infinity
Certainty: 62.94 %
3.15E-07

(c) Cr

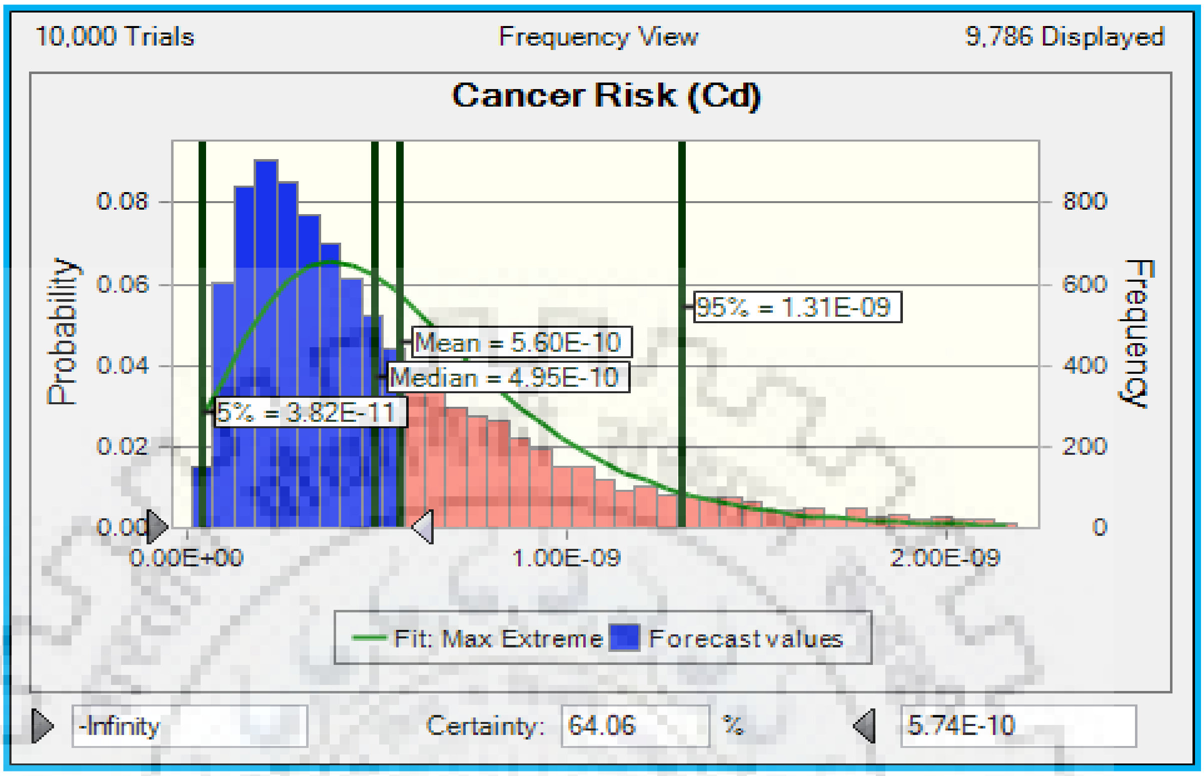


(d) Ni

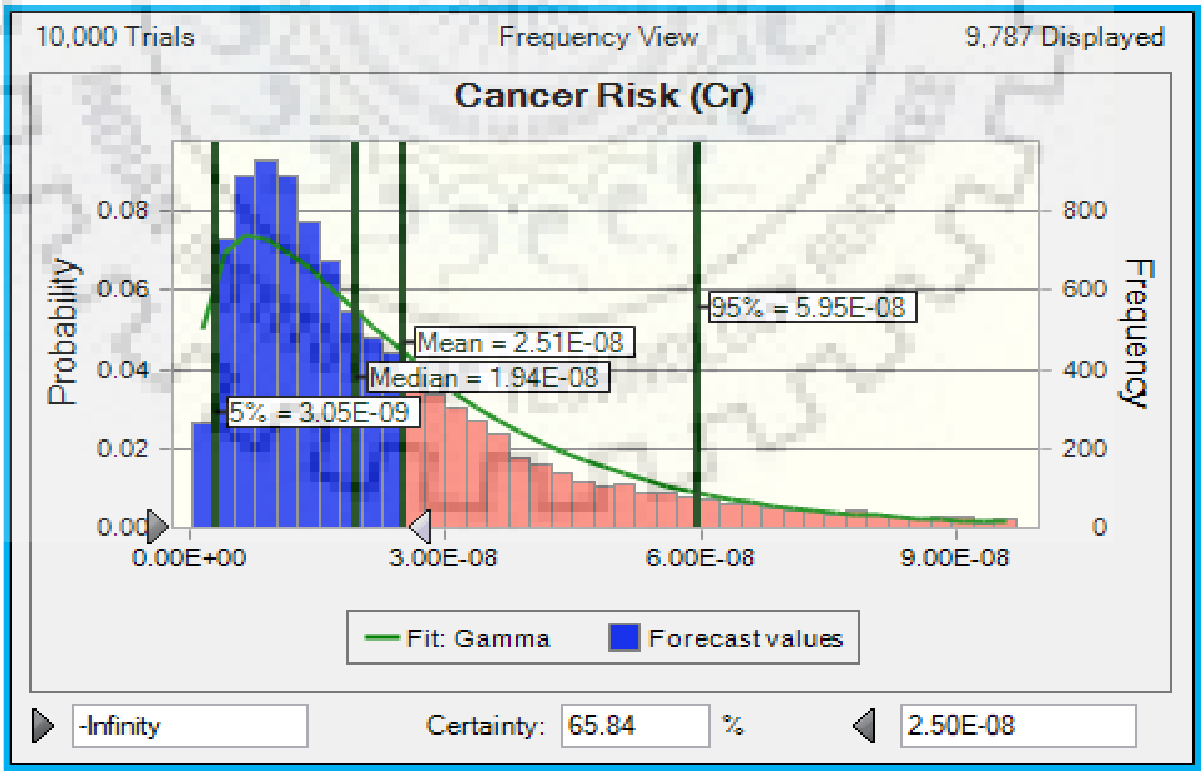
Fig. 5B.3 (a-d): *Monte Carlo simulation for cancer risk estimation in adult population*



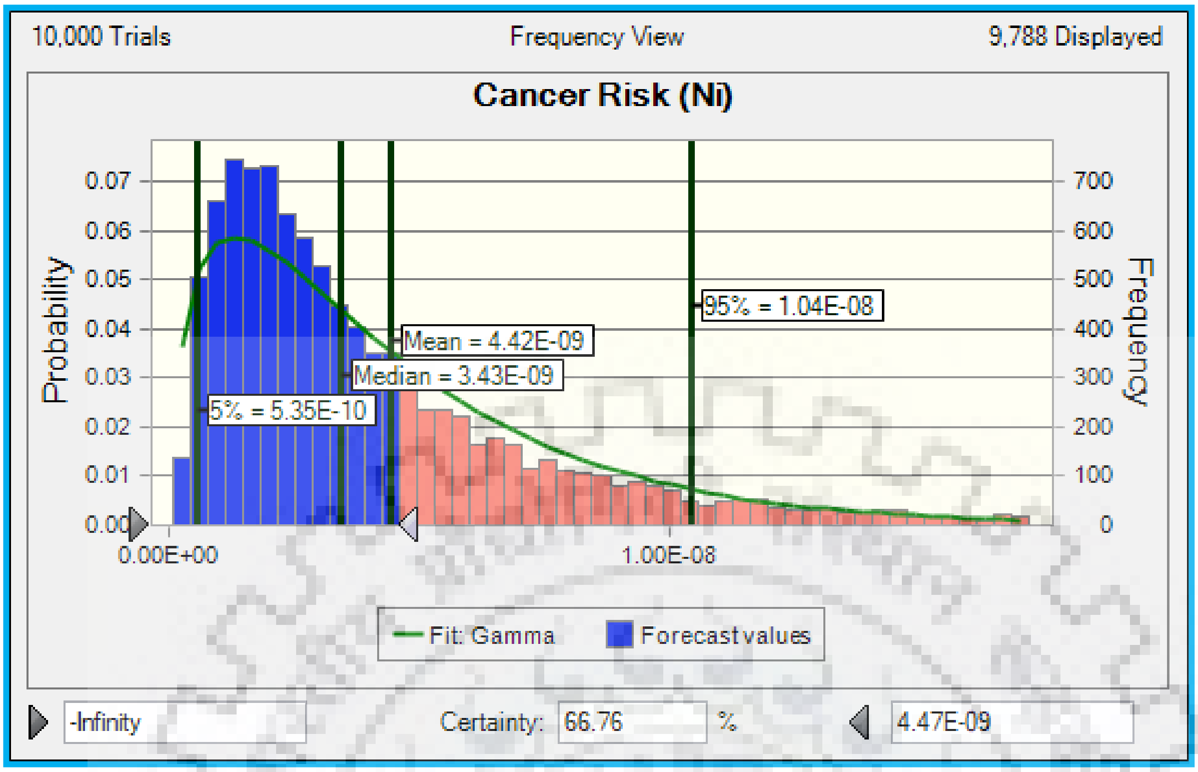
(a) As


10,000 Trials
Frequency View
9,786 Displayed
Cancer Risk (Cd)
Probability
Frequency
95% = 1.31E-09
Mean = 5.60E-10
Median = 4.95E-10
5% = 3.82E-11
0.00E+00
1.00E-09
2.00E-09
Fit: Max Extreme
Forecast values
-Infinity
Certainty: 64.06 %
5.74E-10

(b) Cd


10,000 Trials
Frequency View
9,787 Displayed
Cancer Risk (Cr)
Probability
Frequency
95% = 5.95E-08
Mean = 2.51E-08
Median = 1.94E-08
5% = 3.05E-09
0.00E+00
3.00E-08
6.00E-08
9.00E-08
Fit: Gamma
Forecast values
-Infinity
Certainty: 65.84 %
2.50E-08

(c) Cr



(d) Ni

Fig. 5B.4 (a-d): *Monte Carlo simulation for cancer risk estimation in children population*

5B.5. CONCLUSION

The present study analyzed the metal concentration in the agricultural soil procured from peri-urban areas of Saharanpur district, India. The mean concentrations of analyzed metals were under the respective permissible limit, but the non-carcinogenic and carcinogenic risk associated with the metals (Cr, As, Cd and Pb) were observed to be more or close to the threshold risk values. Cr contamination in soil is the major concern in the study area followed by As contamination. Non-carcinogenic health risk in both adult and children population via all exposure pathway revealed that the maximum exposure of metals was through ingestion or oral pathway followed by dermal contact. The probability of risk in children population was observed to be higher than the adult population. Carcinogenic risk found associated with the Cr was observed to be close to the acceptable limit. Probabilistic risk estimation by Monte Carlo simulation on iterating the Risk assessment expression for 10,000 trials inferred high risk in children population for Cr and As contamination. Social awareness regarding environmental contamination and its consequences may also check the mass exposure to the contaminated soil up to a certain extent. Appropriate measures and intervention in policy are required to safeguard the deteriorating quality of soil for sustainable agriculture in the future.

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CHAPTER VI

CONCLUSION AND FUTURE RECOMMENDATIONS

6.1. CONCLUSIONS

The present thesis work deals with the analysis of heavy metal contamination and associated probabilistic ecological and human risk assessment in three industrial areas of Saharanpur district. The heavy metal analysis has been performed in the soil sample, groundwater sample and in some edible plant parts. Both ecological and health risk assessment has been estimated in all three industrial zones. Health risk has been estimated in both adult and children population using the standard methodology of USEPA. Metal accumulation due to the transfer of metals from contaminated soil to edible plant tissue has also been estimated. Probabilistic risk assessment methods (Monte Carlo Simulation) and Fuzzy logic have been incorporated in order to accommodate uncertainties associated with risk assessment outcomes. The results have been summarized in the following paragraphs.

The heavy metal analysis was performed in total of thirty sampling sites within three industrial areas of Saharanpur district. Elevated concentration of As has been observed in the Pilakhni industrial zone followed by Nanauta and Railway Road industrial area. High Cd, Cr, and Zn concentration were observed in Nanauta study area indicating the unmanaged disposal of e-waste, irrigation with highly contaminated wastewater from the sugar industry, excessive application of chemical-based fertilizers or pesticides etc. High concentration of Ni in Railway road indicates the anthropogenic influences including fossil fuel burning, vehicular emission and waste generated by local industries. Statistical analysis was applied for source apportionment of metal is the study area, the result indicated significant influence of the sugar industry, distillery and paper industry in Pilakhni, Nanauta, and Railway road industrial area respectively. Ecological risk assessment indices collectively indicated substantial metal contamination in the study area. High enrichment of toxic metals including As, Cd, Pb and Cr in the study area is a matter of concern and need to be monitored regularly. Assessment of both non-carcinogenic and carcinogenic risk in adult and children population revealed; high risk to the children population. Substantial non-carcinogenic health risk due to As exposure have been observed, whereas, potential non-carcinogenic risk can also be anticipated with the exposure of Pb, Cr and Ni in the study area. Estimated carcinogenic risk observed for As, Pb, and Ni were in acceptable range.

In terms of overall groundwater contamination level in the study area, high contamination was observed in Pilakhni industrial area followed by Nanauta and Railway road industrial area. Elevated concentration of heavy metal in the nearby area is a serious concern for both adult and children population in terms of health-related issues. The non-carcinogenic risk associated with Cr, As and Ni contamination and cancer risk associated with As were observed to be potentially high in the study area.

The study on estimation of bioconcentration factor in the edible parts of vegetables grown in the study area revealed the trend Zn> Cd> Cu> Pb> Ni >Cu. Substantial metal uptake has been observed in the plants having leafy or tuberous edible parts like cabbage, spinach, radish etc. Most of the samples were observed with metal concentration beyond the permissible limits prescribed by WHO/FAO. health risk has been estimated due to exposure of Cd, Pb and Ni metals. High HQ index for Cu and Zn was also observed but has a considerably low hazardous impact on human health.

In order to deal with the vagueness of classical ecological risk models, the fuzzy based methodology was developed for aggregate ecological risk analysis. The trapezoidal fuzzy membership function has been applied to the linguistic attributes of risk estimation. The high aggregate risk was observed for As and Cd contamination in the study area (in Railway road industrial area); whereas, moderate ecological risk has been assessed for Pb and Zn contamination.

Probabilistic health risk approach has been estimated and discussed briefly using Monte Carlo risk assessment approach. The health risk assessment model was iterated for 10,000 trials for both adult and children population. The overall result revealed that maximum exposure was through ingestion/oral pathway followed by dermal exposure. Potential non-carcinogenic and carcinogenic risk were found associated with As and Cr exposure in children population followed by adult population in the study area.

6.2. FUTURE RECOMMENDATIONS

- Estimation of organic pollutant including Poly Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs) and other persistent organic pollutants (POPs) with the application of GC-MS may be useful research in terms of decision making and policy framing.

- There is considerable scope in studies related to the fate estimation and leaching studies of organic pollutants and xenobiotics in the soil and groundwater to analyze the movement of water in the soil using water tracers.
- Study related to *In-vitro* gastrointestinal studies for estimating the bio-accessibility of soil contaminants would be significant research in this field of research.
- Application of Remote Sensing coupled with Fuzzy logic, Monte-Carlo Simulation or Artificial Neural Network (ANN) in the spatial and temporal monitoring of contaminants in the study area will be a significant approach toward the risk assessment analysis.
- Other soft computing tools can be extensively explored for the developing more precise risk assessment tool.