Occurrence and spatial distribution of selected heavy metals and plastic fractions in surface soils irrigated with urban wastewater of Okara City, Pakistan

Master of Philosophy

in

Environmental Sciences

by

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DEPARTMENT OF ENVIRONMENTAL SCIENCES

FACULTY OF BIOLOGICAL SCIENCES

QUAID-I-AZAM UNIVERSITY

ISLAMABAD, PAKISTAN

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A Dissertation Submitted in the Partial Fulfillment of the
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Sana Rubab

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Abbreviations	Words
Cd	Cadmium
CF	Contamination Factor
Cu	Copper
E_r^i	Ecological risk factor
EC	Electrical Conductivity
EF	Enrichment Factor
Igeo	Geo accumulation index
HI	Hazard Index
HQ	Hazard Quotient
HMs	Heavy Metals
Fe	Iron
Pb	Lead
Mn	Manganese
MPs	Microplastics
NDS	North Disposal Station
OM	Organic Matter
I_{POLL}	Pollution Index
PLI	Pollution Load Index
RI	Risk Index
SSL	South Sewage Line
WHC	Water Holding Capacity
Zn	Zinc

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ABSTRACT

Background: The use of wastewater for irrigation has been suggested as an alternative to the use of freshwater. Several studies have reported heavy metals (HMs) and microplastics (MPs) accumulation in wastewater irrigated surface soils and their related health outcomes. In Okara city, agricultural soils have been irrigated with wastewater.

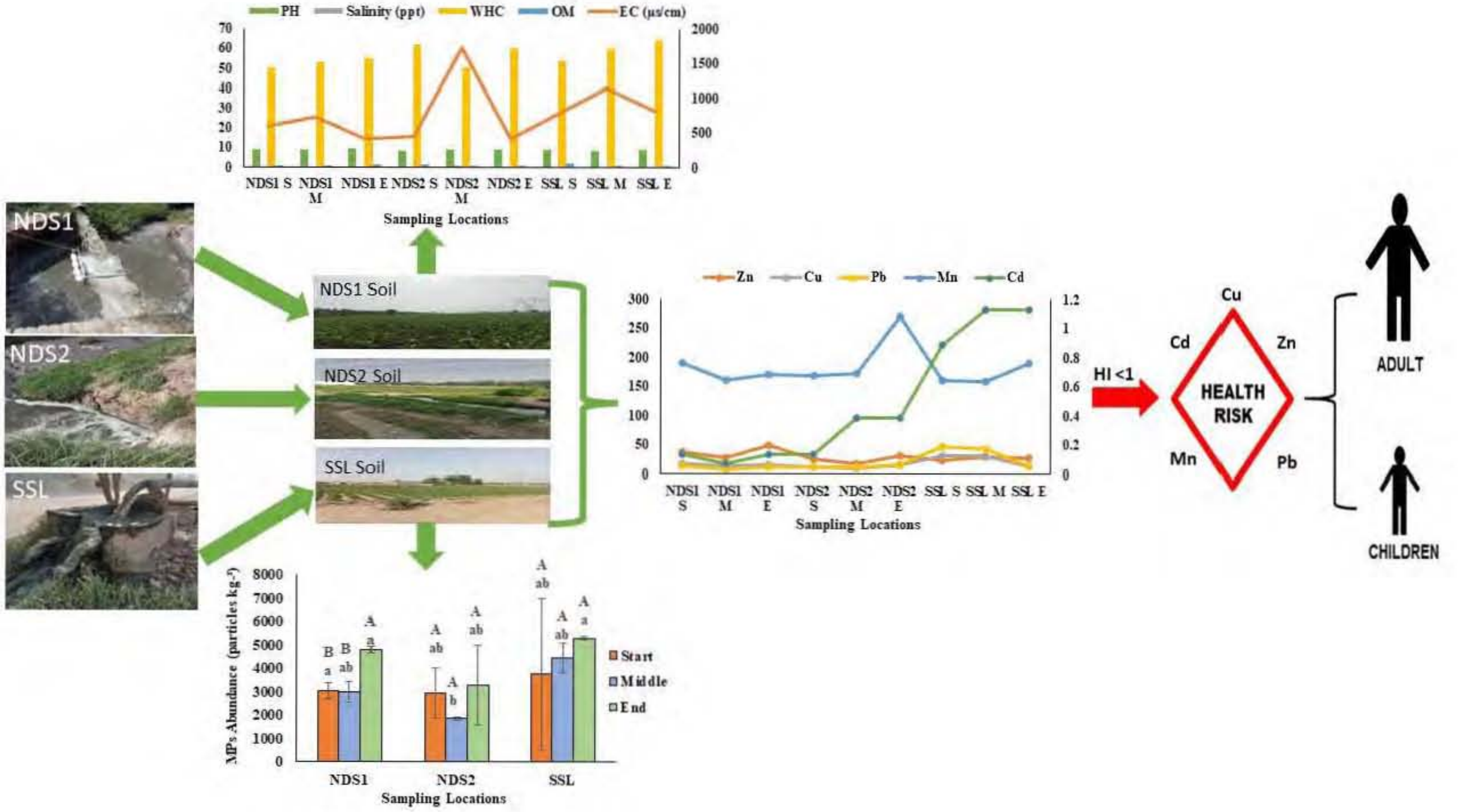
Objectives: The present study was aimed to investigate the HMs and MPs concentration level and their spatial distribution in wastewater irrigated surface soils of Okara, Pakistan. Furthermore, ecological, and human health risks associated with wastewater irrigated surface soils contaminated with HMs were evaluated.

Methodology: Three wastewater disposal facilities North disposal station 1 (NDS1), North disposal station 2 (NDS2), South sewage line (SSL) were selected in Okara city. A total of 27 surface soil samples irrigated with three wastewater disposal facilities from nine locations on the basis of distance (Start, Middle, End) were collected and further examined the soil for physicochemical properties such as pH, EC, salinity, OM, WHC and HMs (Cd, Cu, Zn, Pb, Fe, Mn) via Atomic Absorption Spectrophotometer-AAS (Agilent 55AA). Furthermore, MPs in soil were characterized by binocular microscopy. Pollution indices for ecological risk and non-carcinogenic health risks were calculated for HMs in contaminated soil.

Results: The results revealed that wastewater irrigated surface soils were contaminated with HMs having mean concentrations (Cd: 0.48 mg kg^{-1}, Cu: 17.99 mg kg^{-1}, Zn: 29.73 mg kg^{-1}, Pb: 19.65 mg kg^{-1}, Fe: 8559.5 mg kg^{-1}, Mn: 182.94 mg kg^{-1}) were in permissible limits recommended by WHO/FAO and EU, except Mn. Moreover, high HMs contents (Cd, Cu, Pb) were recorded in soil samples of SSL attributed to statistically significant variations from soil samples of NDS1 and NDS2 while Zn, Fe, Mn showed non-significant difference. The results depicted MPs abundance in wastewater irrigated surface soils was ranged between 1850-5300 particles kg^{-1} and depicted non-significant variations among soil samples of three disposal facilities. The small sized MPs <500µm showed greater portion (31%) in wastewater irrigated surface soil samples. Soil physicochemical properties such as pH affected HMs mobility. EC and salinity showed negative correlation with HMs and MPs while OM and WHC showed positive correlation. On the basis of pollution indices CF, I_{POLL}, Igeo, EF HMs pollution in soil was in the range of low pollution to considerable pollution and Risk index (RI) for all HMs was <150 attributed to low ecological risk. In the present study, negligible non-carcinogenic human health risk via three pathways (oral, inhalation, dermal) to both adults and children was detected. However, high vulnerability and susceptibility for children was investigated via HMs contamination in soil.

Conclusion: The study revealed high level of Mn and <500µm MPs in wastewater irrigated surface soils. However, HMs contamination presented low ecological risks and negligible non-carcinogenic human health risks. But, monitoring of HMs and MPs level in the soil of particular area and their remediation plans are suggested for future management approaches.

GRAPHICAL ABSTRACT



Chapter 1 INTRODUCTION AND LITERATURE REVIEW

Soils form the basis of human life, with 95% of global food being produced directly or indirectly in soils. Soil is an important environmental matrix, integrated into many ecological services. The intensive use of soils worldwide makes it vulnerable towards human utilization and the input of pollutants (Weber et al., 2021).

1.1. Pakistan—an agricultural country and water scarcity

Pakistan is an agricultural country with 60% of its pollution directly or indirectly dependent on agriculture. Almost 19% share of the country's GDP is from the agriculture sector and from the laborer's society 38.5% of the population is connected to the agriculture sector. Thus, agriculture is the backbone of the country. Annual water usage in the 21st century has increased 6.3-fold compared to the usage of water in the 20th century. 70% of fresh water consumed in irrigation practices (Seufert, 2013). Excessive use of fresh water caused the scarcity of water in streams and underground water. According to a WHO report there are possible chances that within 50 years 40% of the population face water shortage. There is dire need to take preventive measures to manage water resources in sustainable manners. The demand for water increased by increasing population, high lifestyles, natural calamities, economic progress and pollution. Water usage is expanding more quickly than population expansion in some areas of the universe.

In 1947, Pakistan had large resources of water with 5650 m^3 of water available annually per person, but now Pakistan is a water deficient country. In 1960 the Indus treaty formulated, the water flow into the river decreased, the population growth increased, and all these factors directly hit water scarcity. At present, Pakistan's annual water accessibility is 964 m^3, and due to inadequate management, poor nations like Pakistan are losing their freshwater reservoirs and going to be a water scarce country. Pakistan is moving towards extreme water shortage. In Pakistan groundwater is a common source of irrigation. Water scarcity and aquifer contamination problems are increasing as a result of reliance on groundwater (Razzaq et al., 2018).

1.2. Existing irrigation status in Pakistan

Pakistan's climate varies dramatically across the country. Due to the country's semi-arid to arid environment, freshwater is infrequent in areas of Sindh and some cities of Southern Punjab. Groundwater and canal water are the most common sources of water used for irrigation. As Pakistan is facing an energy crisis, the use of groundwater can be costly and unpredictable. In some areas of Pakistan groundwater is being contaminated due to percolation of waste disposal. Wastewater utilization in irrigation practices is common there.

Flood irrigation is the most commonly used method in Pakistan but it’s not an effective irrigation method. It is demonstrated that the agricultural water output of Pakistan is just 0.13 kg m^{-3}, that is just one-sixth as productive as China and one-third as productive as India declared by GOP.

Sprinkle irrigation methods, and drip irrigation are common irrigation methods used nowadays. Due to the rising need for irrigation water, the use of these methods is quite expensive but important. Drip irrigation is considered a more flexible method as compared to sprinkle irrigation. A unique irrigation technique is sprinkler irrigation. It's affordable, saves water, and installed easily (Razzaq et al., 2018).

1.3. Impacts of water scarcity on agricultural productivity

Water scarcity is the condition in which the demands for water in agriculture and other economic sectors cannot be fulfilled. Population expansion, industrial advancement and cropland expansion, have led to more water extractions and ultimately many regions of the world become water scarce. According to WSIʙᴡ estimation, central and southwestern parts of the United States, North Africa, Mexico, Middle East, Northwest India, North China and Pakistan facing water scarcity (Hou et al., 2019). Water is vital component of planet's life support system, hence a lack of it creates an insecurity that must be resolved in order for socioeconomic development to proceed. The economy of many countries based on agricultural activities and due to scarcity of clean water these agricultural practices are affecting. For the past few years, Pakistan has been facing a similar situation. Some factors like, small farm size, inadequate resources for modern technology, water scarcity, natural disasters, and declining land proficiency limited the agricultural sector competences. Population growth on one hand, requires more food supplies, and on the other hand, when coupled with mismanagement has produced water scarcity in Pakistan. The country's GDP rate has been steadily reducing since the 1960s.

1.4. Wastewater irrigation: a viable solution for water scarcity

Usage of treated water is important in water pollution reduction because discharge of wastewater in rivers, streams and other freshwater reservoirs declines. That’s why wastewater is considered a valuable source rather than a waste product. The root cause of wastewater use for agricultural activities is the presence of organic and inorganic substances. In some developing countries of the world, wastewater usage by agricultural groups of urban and some peri urban areas is an attractive source of revenue, wastewater use is beneficial due to its high accumulation of nutrients. Globally about 8% of agriculture lands are irrigated with wastewater and among these, 66% of this lands are from Asia (Ma et al., 2023). About 32500 hectares of land in Pakistan is irrigated using wastewater, accounting for approximately 30% of the total wastewater produced in the country (Sarwar et al., 2020). In some cities, municipal water collection system exists which contain <50% of domestic waste produced in urban areas. Wastewater usage in crop production is increasing rapidly, data related to wastewater usage has been reported both at national and international scale. On a worldwide scale, Pakistan, Iran, China, Mexico and India, five biggest nations where wastewater utilization in agriculture without proper treatment is common in semiarid to arid climates.

Wastewater irrigation is not new, and it is in practice for centuries (Kanwal et al., 2020). About 1700 BC, brick-conduits were utilized for wastewater carrying from farming fields to irrigate crops in Crete. Several reports of wastewater irrigation globally are also reported in literature (Table 1.1). During last decades, the amount of wastewater generation has increased in municipalities due to the rapid population increase and change in industrialization patterns. The increases in wastewater production for China, Cuba, Egypt, Columbia, Belarus, and India were 158%, 68%, 97%, 15%, 18%, and 215%. During the same period, Tunisia, Israel, Nicaragua, Switzerland, Netherlands, and Indonesia have reported 50%, 72%, 353%, 11%, 17% and 285% rises in municipal wastewater production. Wastewater utilization in agricultural areas is considered an efficient and beneficial approach. As Pakistan is facing water scarcity issues, wastewater utilization in irrigation practices can be helpful. About 11% of all agricultural land on the planet is cultivated with unprocessed wastewater. Wastewater usage is so common that approximately 10% of the population of the whole world consumes yields grown in wastewater. Due to unregulated urbanization, industrial and urban development, climate variation, and rising lifestyle, this percentage is anticipated to climb in the future. Approximately 88 percent of water consumed in the metropolitan area in Pakistan is released by means of wastewater, amounting 330 km^3 per year (Sarwar et al., 2020). Approximately 40 M hectare terrestrial land can be irrigated by this water, it accounts for nearly 15 percent of all cultivated land. This estimation proved a large number of food crops grow in wastewater.

In Pakistan, domestic garbage discharges directly into water reservoirs due to the absence of a proper management system. Although municipal water assemblage structures are working in some cities of Pakistan, they often run into adjacent water bodies. Almost half of the total waste is collected by these systems in most urban areas. Different technologies' usage assessed that over 10% of the country's sewage is under hazard. As Pakistan is not a developed country, wastewater is only treated at primary level, no secondary and tertiary water collection or treatment systems are existing (Kanwal et al., 2020).

1.5. Wastewater discharge in clean water bodies

Organization for Economic Co-operation and Development (OECD) nations have highlighted agricultural water quality as one of their top environmental concerns. Developed countries discharge 70% of wastewater after treatment. In underdeveloped countries, the equivalent ratio lowers to only 8% of total wastewater generated. Due to absence of proper wastewater treatment infrastructure, approximately 80% of wastewater discharge into the environment without proper treatment. Due to the absence of a proper disposal system for waste generated by industrial units in major cities of the country, these waste disposals are directly released into water tributaries, or dumped into cultivated land. The Ravi River stands Pakistan's utmost dirty river. Lahore's wastewater is said to be dumped at a rate of around 18 $m^3 s^{-1}$ in Ravi waterway. The amount of dumped waste has risen up to 28 $m^3 s^{-1}$ (Razzaq et al., 2018). Pakistan has diverse companies that are estimated to emit roughly 40 x 109 L of waste run-offs daily into water bodies. Tanning industries, crude oil industries, natural gas reservoirs, food handling factories, fabric industries, processing plants, paper and sugar productions, among others, remain foremost causes of Pakistan's water contamination. These industrial units release thousands of gallons of wastewater including a massive number of pollutants like cation, anions, nitrates, nitrites and some toxic HMs. Only 2% of cities in Pakistan have wastewater treatment facilities, according to a national assessment, whereas 80 percent cities having a population of 10,000 individuals utilize unprocessed wastewater to irrigate their land (Natasha et al., 2018).

1.6. Wastewater effects on soil physicochemical properties

Wastewater has detrimental influences on soil health. Excessive use of wastewater affects soil by changing its physicochemical characteristics like pH, organic matter (OM), cation exchange capacity, and some biological states of soil. The alteration in soil characteristics significantly regulate the fate of contaminated substances of soil (Natasha et al., 2022). It depends on the composition of wastewater and type of soil that either the soil is negatively or positively impacted by nutrients supply. Excessive usage of wastewater can critically alter the pH of soil and Phyto availability of toxic metallic elements and nutrients influenced. Wastewater application in different vegetable fields increased soil pH. Soil pH greatly impacts on the bioavailability and mobilization of HMs and change in soil pH relates to wastewater application.

The amount of soil OM also alters the contaminant retention time in soil and impact on the transfer of contaminant from soil towards plant. Soil of Pakistan is not rich in OM, its average amount is 1%. It has been reported that use of wastewater enhances the amount of OM in soil as compared to the background history. Shahid et al. (2017) stated in a study of Vehari, Pakistan that the soil was rich in OM content when vegetables were cultivated in wastewater and OM content was low in soil which was treated through fresh water. But OM content depends on wastewater composition and its availability. Soil salinity increases due to excessive use of wastewater which cause structural changes in soil and ultimately crop yield decreases.

1.7. Heavy Metals contamination in soil

Wastewater generated from different sources is used for agricultural practices. Wastewater usage for irrigation practices is increasing with time and it is continuously monitoring. According to an estimate, the bulk of research on wastewater practices with related ecological and well-being outcomes were conducted in the provinces of Punjab and Khyber Pakhtunkhwa (KP). Pb, Co, Cd, Cr, Ni, Cu, and Zn were considered the most toxic metallic element existing in wastewater. Even if the wastewater is treated, HMs concentration is not removed and stored in soil which cause HMs pollution. Wastewater first flows into water channels then is used for crop production. But some toxic chemicals are also part of wastewater (Barakat et al., 2020). HMs are produced due to some natural factors like bedrock erosion, deposition of ores, and weathering phenomena. Some anthropogenic activities like industrialization, mining activities, poor agricultural practices and improper disposal of waste are the causes of HMs production. HMs produced from the outcomes of nature and man-made actions eventually made a portion of wastewater.

1.8. Microplastics contamination in soil

Plastic utilization has been increased for a few decades due to its outstanding properties such as its low cost and its versatile nature. Excessive use of plastic can cause plastic pollution after their disposal into the environment. These plastic fragments convert into MPs with time (Bajt, 2021). Sewage sludge and plastic mulches are considered the basic source of MPs pollution in soil. Several types of irrigation and use of fertilizers can cause MPs pollution in soil. MPs have ability to alter the soil physicochemical properties such as soil WHC, bulk density and soil texture. Soil nutrients availability affect in presence of MPs (Ding et al., 2020). MPs contaminated soil can affect plants growth by producing significant stress. MPs can affect plant biomass production and act as vector for different types of HMs and pollutants which affect plant health (Zhou et al., 2019). MPs have ability to persist in soil environment and their accumulation can affect the growth and reproduction abilities of soil microorganisms.

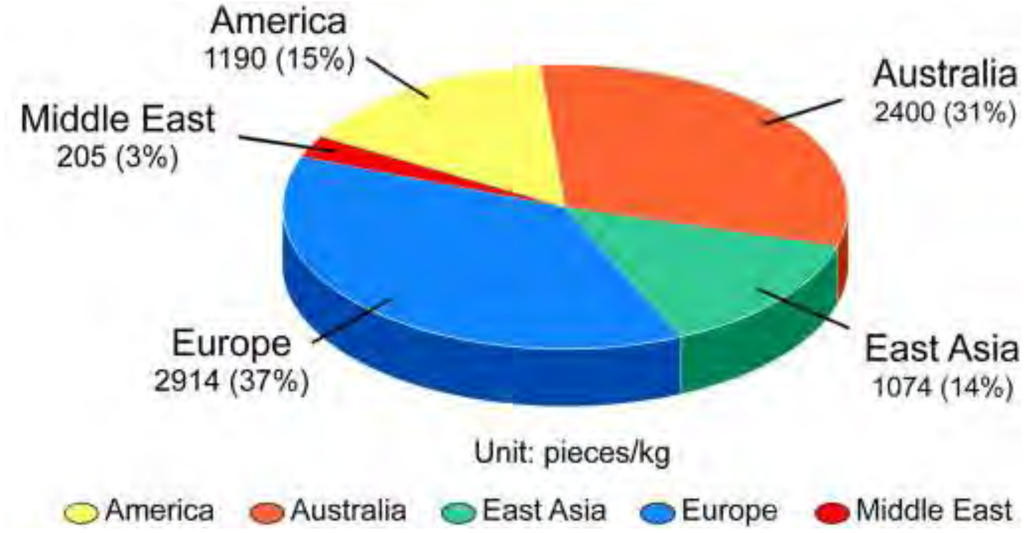


Fig. 1.1: Global percentage of soil MPs concentration (Chia et al.,2021)

Table 1.1: HMs concentration in agricultural soils

Location	Source	Samples/ Depth (cm)	Cd	Zn	Fe	Mn	Cu	Pb	Reference
Okara, Pakistan	Urban wastewater	27 (0-15)	0.48	29.73	8559	182.87	18	19.63	Present study
Beni-Mellal city (Morocco)	Peri urban wastewater	13 (0-15)	2.20	154.63	3.37%	N/A	37.24	31.45	Barakat et al., 2020
Northeast Cairo (Egypt)	Sewage wastewater	33 (0-30)	0.20	N/A	N/A	N/A	35.1	15.0	Abd-Elwahed, 2018
Bhopal (India)	Sewage wastewater	6 (------)	0.04–0.06	0.63–2.59	N/A	N/A	2.7–7.59	1.29–2.05	Dotaniya et al., 2018
El-Fayoum (Egypt)	Raw urban wastewater	12 (0-90)	0.59 to 0.98	9.11-11.19	N/A	N/A	N/A	3.32 -5.44	Alnaimy et al., 2021
Huizhou (China)	Industrial wastewater	94 (0-20)	0.85	143	N/A	N/A	36.8	73.2	Xiao et al., 2019
Erbil (Iraq)	Municipal wastewater	10 (0-30)	21.72	189.09	N/A	N/A	28.58	41.85	Tariq, 2021
Marrakech (Morocco)	Sewage wastewater	15 (0-20)	11.22	112.71	N/A	N/A	17.70	57.36	Chaoua et al., 2019
Vehari	Municipal wastewater	106 (0-15)	1.6	102	8598	268	40	3	Natasha et al., 2022
Multan	Untreated urban wastewater	30 (0- 15)	0.28	N/A	N/A	135.5	17.67	5.61	Iqbal et al., 2022

Multan	Industrial wastewater	30 (0- 15)	5.65	N/A	N/A	66.55	20.15	63.95	Iqbal et al., 2022
Vehari	Untreated city wastewater	108 (0- 15)	1.6	102.2	8598	268	40.3	31	Sarwar et al., 2020
Sialkot	Industrial wastewater	36 (3-15)	N/A	92	N/A	N/A	21.36	118.5	Jadoon & Malik, 2019
D.I Khan	Untreated urban wastewater	7 (------)	0.022	N/A	65.41	N/A	0.598	2.313	M. Iqbal et al., 2020
Kasur, Pakistan	Municipal wastewater	48 (0-30)	4.21–4.54	91.36–94.56	51.32–56.28	33.41–129.32	21.24–24.36	32.12–33.48	Ashraf et al., 2021
WHO/FAO 2007			3.0	300	N/A	N/A	100	250	Tariq, 2021

Cd (cadmium), Zn (Zinc), Cu (copper), Pb (lead), Fe (iron), Mn (Manganese), WHO (World Health Organization), FAO (Food and Agriculture Organization) (United Nations), N/A (not available)

Table 1.2 MPs contamination in agricultural soil of different regions

Study Area	MPs Abundance	MPs Color	MPs Shape	MPs Size	MPs Type	Reference
Okara, Pakistan	1850 to 5300 particles kg^{-1}	Black, blue, green, red, multi, transparent and others	Fiber, fragment and film	<500 µm- 5mm	N/A	Present study
Chai River valley, China	7100 to 42,960 particles kg$^{−1}$	N/A	Fiber, fragment and film	1- 0.05mm	N/A	G. S. Zhang & Liu, 2018
Qinghai province, China	240 to 3660 particles kg^{-1}	N/A	Fiber, fragment film, and pallet	<0.5mm- 5mm	N/A	Lang et al., 2022
Xianjiang, China	288 to 1452 particles kg-^{1}	White, black and multicolor	Lump, fiber, film and foam	<0.5mm- 5mm	PE, PP, PS and PVC	Li et al., 2022
Valencia, Spain	930 to 1100 particles kg^{-1}	N/A	Fiber, fragment and film	50 µm- > 1mm	PP and PVC	van den Berg et al., 2020
Schleswig-Holstein, Northern Germany	0 to 217.8 particles kg^{-1}	Black, white, brown, red, green, gray, transparent, yellow, blue	Fragment, fiber, foil, platelet	1- 5mm	PE, PP, PA, nylon, PVDF, PDAP, PMMA, PET, PVF, PVA, PVS	Harms et al., 2021

Korea	195 to 306 particles kg^{-1}	N/A	N/A	20-2000 µm	PE, PP and PET	Park & Kim, 2022
Wuhan, China	4.3×10^4 to 6.2×10^5 particles kg^{-1}	N/A	Fragment, bead ball and fiber	50- > 500µm	PE, PA, PP, PS and PVC	Zhou et al., 2019
Tunisian	13.21 to 852.42 particles kg^{-1}	Black, blue, red, yellow and gray	Fiber and fragment	300µm- 5mm	PE, PP, PBAT, PEVA and PLA	Boughattas et al., 2021
Mauritius	73.3 to 433.3 particles kg^{-1}	transparent, black, white, blue and red	fiber, fragment, flakes, film, sphere, and foam	0.25- 4.9mm	PP, PE, PA, PS and EVA	Ragoobur et al., 2021
Xiamen, China	280 to 2360 items kg^{-1}	White, blue, red, black, yellow and green	Fiber, fragment and particles	0.05 -2mm	PE, PS, PP and PET	Liu et al., 2022
South East, Germany	0.34 to 0.36 items kg^{-1}	N/A	Fiber, fragment and film	1- 5mm	PE, PP and PS	Piehl et al., 2018

PE (polyethylene), PA (polyamide), PP (polypropylene), PS (Polystyrene), PVC (poly vinyl chloride), PIB (polyisobutylene), PVDF (poly vinylidene fluoride), PVA (polyvinyl acetate), PVS (polyvinyl stearate), PBAT (polybutylene adipate terephthalate), PEVA (polyethylene vinyl acetate), PLA (polylactic acid), EVA (ethylene vinyl acetate), N/A (not available)

1.9. Interaction between HMs and MPs in soils

Multiple anthropogenic activities like domestic waste, commercial and industrial waste are the producers of wastewater. Urban wastewater composition is solely related to residents' lifestyle, domestic and industrial discharge, and the infrastructure of sewerage systems. Organic and inorganic substances are the major constituents of wastewater composition. Some bacteria and pathogens are also present in treated wastewater. Although wastewater has been treated but some toxic materials like HMs, man-made contaminants and semi synthetic composites remain known as micro contaminant. To determine the quality of treated wastewater, different biological and chemical characterizations are done but it's hard to entirely visualize its consequences to its reuse.

MPs aid in the absorption or desorption of HMs on their surface and also increase the bioavailability of HMs in the environment. MPs and HMs generally coincide in same surroundings because both are originated as a result of anthropogenic activities. A monitoring report has reported the coincidence of MPs and HMs such as Ni, Al, Zn, Sb, Mo, Cd, Mn, Co, Hg, Pb, and Cu in street dust of Bushehr city, Iran (Abbasi et al., 2017). MPs toxicity increases several times in the environment when they act as synergetic anthropogenic stressors by making associations with toxic HMs.

1.10. Wastewater irrigation effects on plants/crops

The accumulation of contaminated substances in plants/crops correlates with the presence of toxic metals in soil. When wastewater is applied on soil the concentration of HMs in edible crops increases. In some situations, uptake of HMs in crops exceeds than threshold level. Several reports are present related to the threshold level of toxic metals in crops. For example, radish have high levels of toxic metals like Cu, Ni, Pb, Cd when they are cultivated in wastewater (Natasha et al., 2022). Pb levels were found to be high in three vegetables, spinach, cauliflower, and radish. Different plants have different capacities to accumulate toxic metals in their organs. Toxic metals move towards aerial parts of the body after wastewater irrigation. Some plant species have 100 times more capacity to accumulate toxic metals than other plant species. The accumulation rate of toxic metals in leafy vegetables is higher as compared to other vegetables (S. Khalid et al., 2017).

Generally, lethal metals are mostly accumulated in root tissues of plants. Major portion of HMs (90%) accumulate in plant roots. Several transporter proteins help in accumulation of toxic metals and in their transfer to aerial parts of plants. Numerous transporter families elaborate metal transfer to shoots have been revealed via genetic and cellular research. Metal and plant species determine the expression of these metal transporter proteins, along with their potency within the plant tissues. Various metals may significantly differ in how different plant species allocate their root-shoots during wastewater irrigation.

1.11. Food chain transfer of contaminants and risks to human well-being

Developing countries have not enough resources to use fresh water for irrigation purposes, so in urban and peri urban areas, people are compelled to use wastewater to irrigate their crops. Undiluted wastewater use is more common than other wastewater due to its cheap source and availability of more nutrients. The main reason to use wastewater for irrigation purposes in some countries is that farmers, citizens, and government agencies are not well aware of hazardous health impacts that a person can face after the usage of contaminated food. Many HMs and pathogens are present in wastewater and due to irrigation, HMs present in soil once entered in the food chain can cause several human disorders like anemia, cancer, circulatory and gastrointestinal disorders etc.

Wastewater irrigation practices firstly impact farmers and then the consumer who consumes the contaminated food, also exposed to pathogens, and suffer from infections (Tariq, 2021). Different kinds of viruses, bacteria, parasitic worms, and protozoa are part of wastewater, farmers and their families who exposed this wastewater daily are at high health risk. Many poor farmers even cannot afford treatment of their infections and diseases which are due to usage of wastewater. It is observed that farmers who use wastewater are suffering more from helminth infection as compared to farmers who use fresh water for their irrigation practices. Nails and skin diseases are common in agronomists who are exposed to wastewater. Many studies are reported related to human health risk assessment via ingestion, inhalation and dermal contact (Mohammadi et al., 2020). Numerous techniques are being used to identify the pollution sources, and pollution indices are tools to measure the human health risk via HMs intake and to make the strategy plans for pollution prevention. Geo accumulation index (Igeo), Pollution load index (PLI), Contamination factor (CF) and Risk index (RI) are important soil pollution indices tools but carcinogenic and non-carcinogenic risks are calculated to assess the HMs impacts on human health (Jadoon & Malik, 2019).

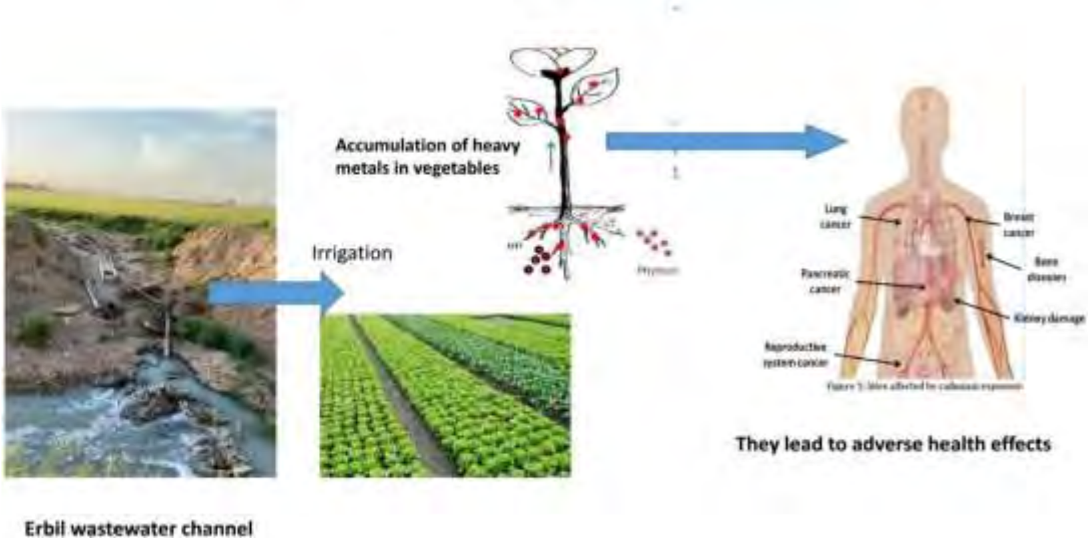


Fig. 1.2: Food chain transfer of HMs in humans (Tariq, 2021)

1.12. Untreated wastewater irrigation: a common practice in Pakistan

Climate of Pakistan fluctuate in different areas and fresh water is scarce in many areas of Punjab and Sindh from semiarid to arid areas. Canal water and groundwater are commonly used for irrigation practices but use of pumping motor for groundwater irrigation is costly method. Groundwater has also been contaminated due to excessive accumulation of salts and HMs (Natasha et al., 2022). So, wastewater is more feasible solution of all these problems to irrigate the agricultural fields. About ¼ part of wastewater generated by different sources is use for irrigation purpose. Wastewater is reliable and cheap source of irrigation for farmers. Nutrients are available in wastewater although their threshold level is still unknown. People of municipality controlling system are well aware of importance of wastewater for farmers, so they sell it to farmers for income to maintain the proper functioning of disposal stations machinery. Wastewater usage decrease the demand of fertilizers and ultimately crops prices decrease. Although wastewater is cost effective approach for irrigation purpose, but it can be dangerous for human health. Farmers do not consider the health consequences on their income. Groundwater is also being contaminated due to excessive use of wastewater because HMs and other contaminants present in wastewater leach down during irrigation process. Toxic pollutants persist in soil and damage soil structure and also bioaccumulate in plants and affect food chain. Use of toxic pollutants is common in household items and different industrial activities and which ultimately became the part of wastewater (Kanwal et al., 2020).

1.13. Research gaps

Organic and inorganic contaminants are harmful to human health were present in untreated industrial and urban wastewater (Sarwar et al., 2020). Non-biodegradable and inorganic pollutants, such as HMs and MPs, can have negative impacts on organisms. The five largest nations in the world where untreated wastewater is utilized in agriculture, particularly in semi-arid to dry climates, are India, Pakistan, China, Iran, and Mexico (Shahid et al., 2017). In Pakistan, many studies have reported the occurrence of HMs in wastewater irrigated surface soil and crops, and their associated human health risks (M. Iqbal et al., 2020; Sarwar et al., 2020). In Faisalabad, agricultural soil irrigated with wastewater have been reported to be contaminated with MPs and HMs but their relationship was not discussed (Ahmad et al., 2022). In Okara city, presence of HMs (Cd, Ni, Pb, Mn, As, Cu and Zn) have been reported in cotton/wheat fields, and relationship between HMs occurrence and fertilizer usage but MPs accumulation was not recorded (Rafique & Tariq, 2016). In Pakistan, no study has evaluated wastewater irrigation as a source of HMs and MPs pollution, considered the influence of wastewater on soil physicochemical characteristics, and assessed possible human health risks. Developing countries like Pakistan lack proper wastewater treatment system hence leads to groundwater, soil pollution and poses public health risk. This study will be useful in filling these research gaps and provide knowledge for future studies in similar agricultural regions in the country.

1.14. Problem statement

Pakistan is predominantly an arid to semi-arid country, which coupled with climate change and increasing population has led to a significant decline in freshwater availability. Consequently, farmers in this region have been compelled to resort to the use of wastewater for crop irrigation. Okara city, located in Punjab, (Pakistan) is one of the key agricultural hub for the cultivation of crops such as potatoes and wheat for export purposes. Notably, the use of urban wastewater for irrigation has been a common practice in the region for the past 30-35 years. However, this practice may have potentially negative implications on the agricultural soil quality due to the presence of heavy metals (HMs) and microplastics (MPs) in the wastewater, as already reported across different regions. Hence, the following study is designed to assess the levels of contamination in the agricultural soil of Okara and to evaluate the imposed impacts.

1.15. Objectives

- To investigate the physiochemical parameters and HMs in agricultural soils irrigated with urban wastewater coming from three wastewater facilities of Okara city.
- To evaluate the abundance, physical characteristics of MPs in wastewater irrigated surface soil of Okara city
- To assess Ecological and human health risks associated with wastewater irrigated surface soils contaminated with HMs.

Chapter 2 MATERIALS AND METHODS

2.1. Description of study area

Okara is district of Punjab, Pakistan. It lies in between north latitudes from 30º48'30.6000" N 49ºand east longitudes from 73º 27' 33.8256" E. Okara is divided by railway line in two parts namely northern and southern sides. The mean maximum and minimum temperature are about 44ºC and 2ºC respectively. The average rainfall is 200 mm per year. Moreover, the nature of soil is loamy, alkaline and non-saline. The main crops cultivated in this region are sugar cane, wheat, potatoes, rice, maize and cotton. Okara is considered an agricultural hub of Punjab, Pakistan and its agricultural fields were irrigated with urban wastewater from previous 30-35 years. Therefore, to investigate the impact of wastewater irrigation practices on soil Okara is selected as study area. The well-developed and commercialized portion of the city's north side is split into A, B, C, D, E, and F blocks using a block system. In 2016, 154121 people were deemed to reside there. On this side, there are the majority of businesses. The south side of the city is underdeveloped, has comparatively inferior living conditions, and has limited access to sources of fresh water and food. The population density in the south side of the city, which was estimated at 226850 in 2016, is higher since it covers a large number of chaks.

2.2. Northern side sewage system

The city's disposal station is connected to 9 to 48 inch-diameter sewer pipelines that make up the northern side's sewer system. There are two disposal facilities on the city's northern edge named as NDS1 located at 30º49'50.6"N, 73º26'32.5"E and NDS2 located at 30º52'56.2"N, 73º28'08.7"E. These specially constructed disposal facilities have a screening chamber, two collection chambers, and a pumping chamber. The discharge pump receives the urban wastewater collected in the stations and throws it into the Katcha sullage carrier, each of which has a length of 10,000 Rft. In order to get the main disposal, drain, the sullage carrier passes across agricultural areas where it is used for irrigation purpose by the framers.

2.3. Southern side sewage system

A rather poor and under privileged area located at 30º47'13.7"N, 73º27'09.0"E is the southern part of the city. Because it is at lower elevation than rest of the city, a pumping and distribution station was not present. Due to the difference in elevation, the wastewater flows via the sullage carrier under the influence of gravity after being collected from the city's sewage in the main sewage line. Due to lack of resources, the majority of farmers irrigate their farms using sewage water. The sullage transporter runs along the agricultural lands.

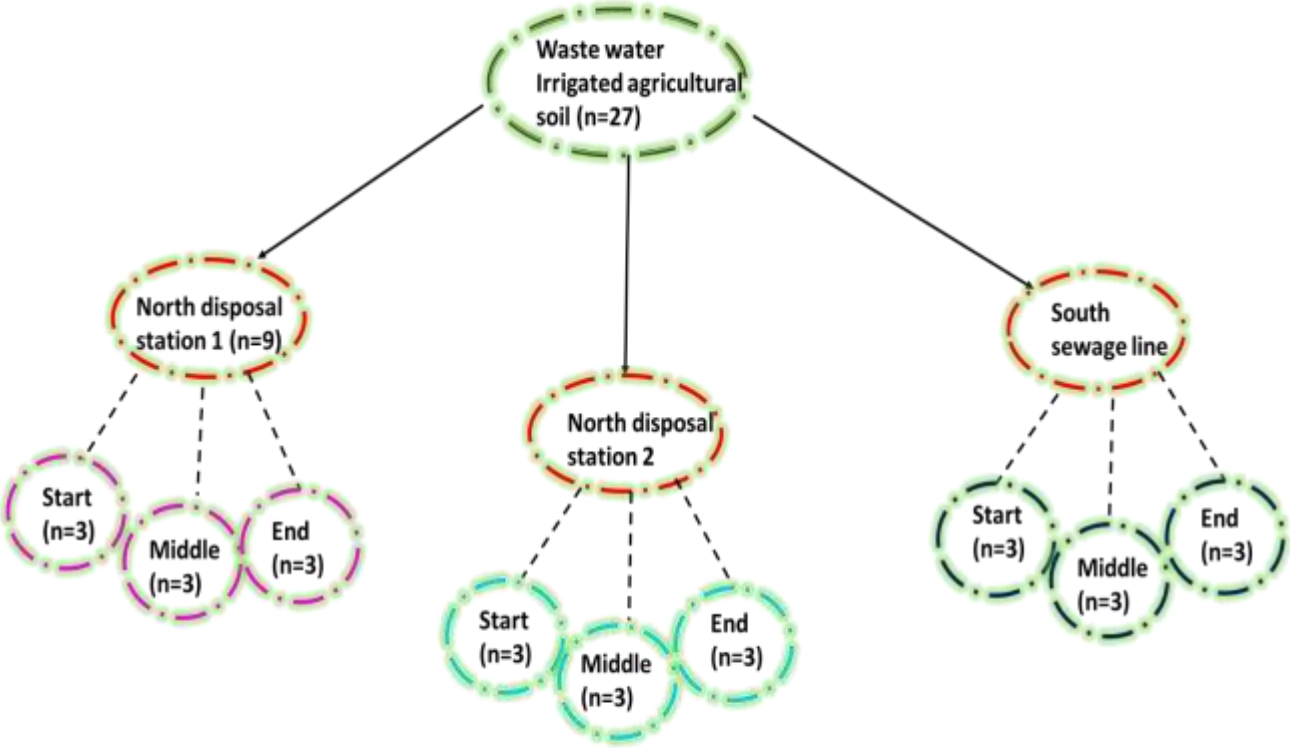


Fig. 2.1: Sampling strategy of wastewater irrigated surface soils

2.4. Study design and selection of sites

The sampling locations are shown in Fig. 2.2. A total of 27 composite wastewater irrigated surface soils samples were collected from nine locations (n=3) at 0-5cm depth on the basis of distance (Start (S), Middle (M), End (E). Wastewater irrigated surface soils were collected using steel auger and then packed into polyethylene zipper bags. The wastewater irrigated surface soil's locations were recorded by using GPS.

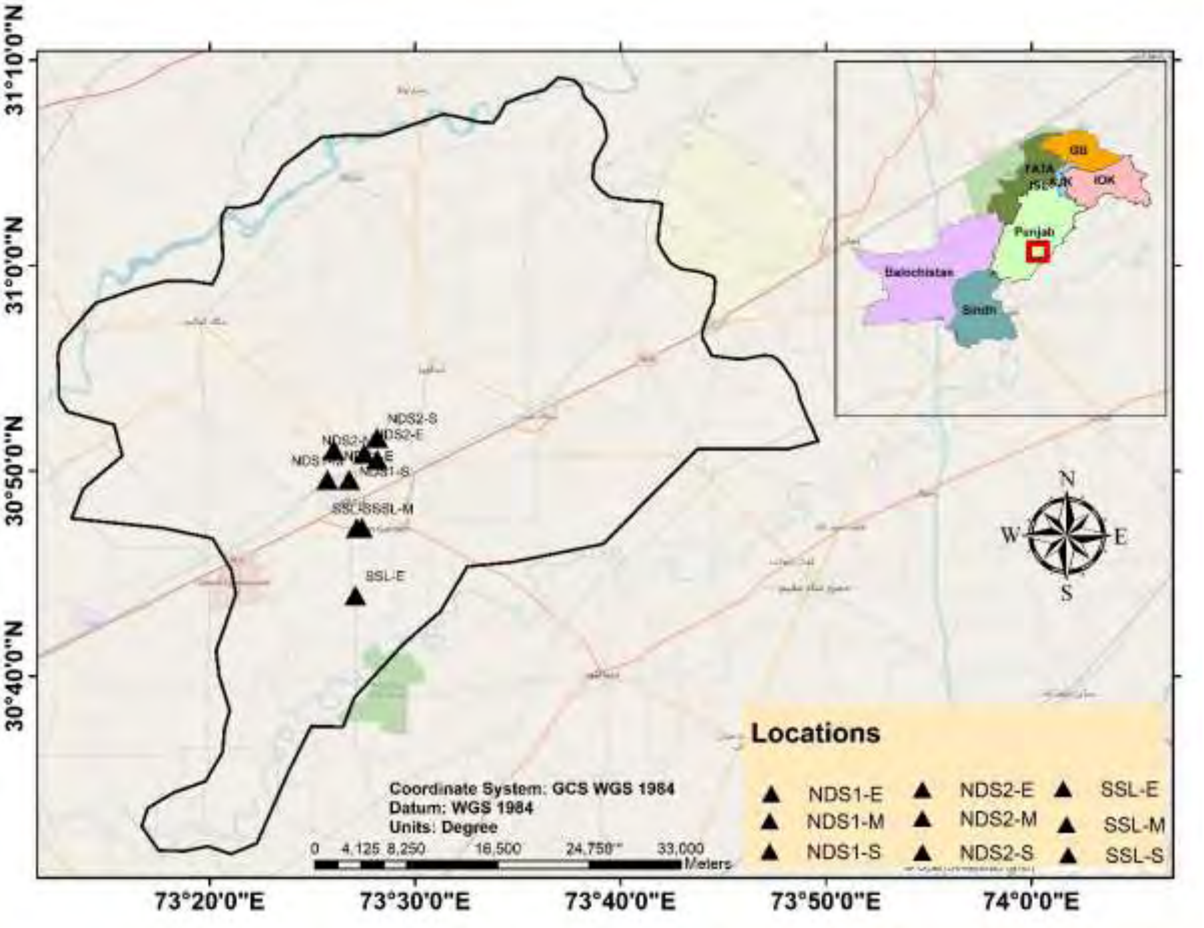


Fig. 2.2: Map of Okara city

2.5. Physicochemical parameters of wastewater irrigated surface soils

Oven-dried wastewater irrigated surface soil samples were grounded and passed through a 2 mm sieve. Physiochemical parameters including pH, EC and salinity of soil samples were measured in 1:5 (w/v) H_2O suspension using a portable electrode meter (OAKTON) (Ma et al., 2023). WHC was measured 1:1 (w/v) in soil and H_2O mixture (Sun et al., 2012). Sieve method was used to determine the texture of wastewater irrigated surface soils. The wastewater irrigated surface soils (100g) were fractioned as gravel, sand and silt by using 2mm and 53µm sieve. The obtained fractions were weighed, and values were plotted on textural triangle to obtain the soil type.

Wet digestion method by Walkley-Black was employed for determining the soil OM (Jadoon & Malik, 2019). Wastewater irrigated surface soils were digested with 10 ml of 1 N solution of K2Cr2O7 and 20 ml of concentrated H2SO4 for 30 mins. The digested wastewater irrigated surface soils were diluted up to 200 ml with deionized water and 10 ml H3PO4 and 10- 15 drops of diphenylamine indicator were added to the solution. Each sample was titrated against 0.5M (NH4) 2SO4.FeSO4.6H2O solution, until color changed from violet to green. Black oxidizable organic carbon (BOC) was calculated as following:

$$Organic\ Matter(\%) = 1.724 \times Total\ Organic\ Carbon\ (\%) \qquad (1)$$

2.6. HMs analyses of wastewater irrigated surface soils

For HMs analyses, soil samples (1g) were digested with 10 ml aqua regia 1:3 (v/v) at 110ºC for 45 minutes. After cooling 20 ml of 1.2% HNO3 added and again heated for 30 minutes at 80º C then filtered through Whatman filter paper no 42. The filtrate was diluted to 50 ml with deionized water and analyzed on atomic absorption Spectrophotometer -AAS (Agilent 55 AA) (Ahmadpour et al., 2015).

2.7. MPs analyses of wastewater irrigated surface soils

MPs present in wastewater irrigated surface soils were separated through density separationmethod by National Oceanic and Atmospheric Administration (NOAA) (Pagter et al., 2018). The oven-dried wastewater irrigated surface soil samples (10g) were treated with 100 ml $ZnCl_2$ for overnight. Furthermore, the MPs floated on the surface of supernatant. The supernatant was separated in a flask and digested with Fenton's reagent. After digestion, solution was filtered through filter papers (0.2µm) via using vacuum assembly. However, the filter papers transferred into petri plates for microscopic observation. Moreover, for an identification and counting of MPs, a binocular microscope (CX41; Olympus Co. Ltd., Japan), magnification power up to 100X equipped with digital camera (ISH500; U-TV0.5XC-3, Co. Ltd, Japan) was used. Filter papers were observed under the magnification power of 4X. The identification of MPs was confirmed according to the protocol (Hidalgo-ruz et al., 2012).

2.8. Quality control and quality assurance

All chemicals and reagents used in experimental procedure were of analytical grade. All glassware were rinsed with 10% HNO3 and coated with aluminum foil. All HMs analyses were carried out using Atomic Absorption Spectrophotometer-AAS (Agilent 55AA). Each sample was analyzed in triplicate; however, mean value of triplicate samples was used for results interpretation to remove procedural errors. To analyze the cross contamination during digestion process, blank samples (n=6) were prepared in the same way as soil samples were prepared for digestion, but original soil sample was not added. Blank samples were run after every five samples. HMs standards were made from 1000 ppm stock solution of respective HMs salt for their accurate dilution. For checking of instrumental efficiency and accuracy, calibration curves were run for every HM. The procedural blanks and calibration standards were run after every five sample for quality control and assurance.

2.9. Pollution load assessment of HMs in wastewater irrigated surface soil

Pollution indices are tools that are used for the assessment of anthropogenic contamination in soil. Pollution indices such as contamination factor (CF), pollution index (Ipoll). geo-accumulation index (Igeo), enrichment factor (EF), pollution load index(PLI) and risk index were used to compute the concentrations of HMs in soil (Jadoon & Malik, 2019; Mohammadi et al., 2020).

2.9.1. Contamination Factor (CF)

CF tool is used to determine the rate of HMs contamination in soil. CF estimate the level of pollution in soil. CF was computed by using the formula purposed by Hakanson: (Mohammadi et al., 2020)

$$CF = \frac{C_n}{C_b} \tag{2}$$

Here, C_n represented the concentration of HMs in sample and C_b is the background concentration of the metal.

2.9.2. Pollution Index (I_{POLL})

I_{POLL} was used to calculate the intensity of metal contamination insamples. Pollution index was calculated by using the formula:

$$I_{POLL} = log_2\left(\frac{C_n}{B_n}\right) \tag{3}$$

Here Cn is the concentration of HMs in soil sample and Bn represented the lithogenous portion of metal.

2.9.3. Geo-accumulation Index(I_{geo})

I_{geo} was used to computed the degree of HMs pollution in soil samples by using following equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) \tag{4}$$

Here, n represented HMs concentration in soil samples and Bn represented geochemical background concentration of HMs in shale (Turekian et al., 1961) and factor 1.5 was used to interpret the possible variations in background concentrations of HMs.

2.9.4. Enrichment Factor (EF)

HMs pollution and their possible emission source is calculated through EF. Following equation was used to calculate the EF:

$$EF = \frac{\left({}^{C_i}/_{C_M}\right) sample}{\left({}^{C_i}/_{C_M}\right) background} \tag{5}$$

Here, (Ci/CM) sample represented the value of target metal and value of reference metal, and (Ci/CM) background showed the background concentration of target metal and value of reference metal respectively. Fe was used as a reference metal.

2.9.5. Pollution Load Index (PLI)

PLI is used for multi metal contamination assessment in soil along with proper consideration to metal toxicity. The equation used to calculate pollution index is:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_n} \tag{6}$$

CF represented the concentration factor and n represented the number of targeted elements.

2.9.6. Potential Ecological Risk Index (RI)

RI is used to determine the potential ecological risk from targeted metal. RI is used to assess the sensitivity of area from HMs and possible potential ecological risk. RI is calculated by using equation:

$$RI = \sum E_r^i \tag{7}$$

$$E_r^i = (T_i \times f_i); f_i = \left(\frac{C_i}{B_i}\right) \tag{8}$$

Here, fi is metal contamination, Ci depicted the metal concentration in wastewater irrigated surface soil sample, Bi showed background concentration of target metal in uncontaminated soil, E_r^i is the potential ecological risk factor of individual metal, Ti is toxic response factor, and its value is suggested by Hakanson.

2.10. Daily intake of HMs and human health risk assessment for wastewater irrigated surface soil

Human health risk assessment for wastewater irrigated surface soil was calculated through three pathways via oral, inhalation, and dermal pathway. In this study, Health risk assessment was calculated according to the protocol given by United States Environmental protection Agency. Residents categorized on the basis of children and adults. The chronic daily intake in mgkg^{-1} for HMs such as Cd, Zn, Cu, Pb and Mn through oral, inhalation, and dermal pathways was calculated by using equation; (Mohammadi et al., 2020)

$$ADD_{ing} = C \times \frac{IngR \times EF \times ED}{BW \times AT} \times 10^{-6}$$

(09)

$$ADD_{inh} = C \times \frac{InhR \times EF \times ED}{PEF \times BW \times AT} \tag{10}$$

$$ADD_{dermal} = C \times \frac{SA \times AF \times ABF \times EF \times ED}{BW \times AT} \times 10^{-6} \tag{11}$$

Here IngR, InhR represented the ingestion and inhalation rates respectively. EF represented exposure frequency value (365days/year) and ED represented the exposure duration (6 years for children and 24 years for adults). SA represented the exposed skin surface area, ABF showed the value of absorption factor, BW is body weight (15kg for children and 55.9kg for adult) and AT represented average time.

In this study non carcinogenic risk (HQ, HI) was calculated. Hazard quotient (HQ) is the ratio of ADD and reference dose of each metal for every pathway. Hazard index (HI) is the sum of all HQ through all three pathways. HQ and HI were calculated using equation.

$$HQ = \frac{ADD_n}{RFD} \tag{12}$$

$$HI = \sum HQI \tag{13}$$

2.11. Statistical analysis

Statistical Package for Social Sciences IBM SPSS Version 22 was applied to determine basic descriptive statistics including mean, standard deviation, Pearson correlation and one way analysis of variance (ANOVA). However, ANOVA applied to determine difference among different locations for HMs concentration in soil at $p<0.05$ using Tukey test after assessing the normality of data via normality test. Pearson correlation was used to predict positive and negative association among HMs, MPs and physicochemical properties of soil at $p< 0.01$ and $p<0.05$. All these probabilities were used to analyze the significance of results among different locations. The Arc Geographic Information System (ArcGIS) 10.8 software was used for the preparation of study area location map.

Chapter 3 RESULTS AND DISCUSSION

3.1. Physicochemical properties of wastewater irrigated surface soils

The basic descriptive statistics for physicochemical properties in wastewater irrigated surface soils are presented in table 3.1. The physicochemical properties in wastewater irrigated surface soils were ranged between 8.6 (SSL M) to 9.4 (NDS1 E), 410 μScm^{-1} (NDS1 E) to 1724 μScm^{-1} (NDS2 M), 0.1 ppt (NDS1 E) to 0.9 ppt (NDS2 M), 0.9% (NDS1 S and SSL E) to 1.8% (SSL S), 50% (NDS1 S) to 64% (SSL E) for pH, EC, salinity OM and WHC, respectively.

The studied results showed that pH was alkaline in nature in all wastewater irrigated surface soils, while EC ranges from marginally saline to extremely saline in wastewater irrigated surface soils. The basic pH occurrence in studied soil related to the presence of higher accumulation of Ca, Mg, Na and K and they are reported to be the main constituent of most detergents for washing clothes at homes. The high EC values attributed to the presence of high salts contents in upper soil layer after wastewater irrigation. Soil OM, WHC and soil texture have great role in soil fertility and quality. Pakistani soil contains <1% OM (Natasha et al., 2022) but current studied wastewater irrigated surface soil samples were >1% OM that are within the range of organic rich soils. These soils showed high WHC and sandy loam texture in nature are resulted from the subsequent use of urban wastewater irrigation that have mainly their composition such as detergents, food remains (fruits and vegetables peels) and medicinal products etc. Lipids, proteins, sugars, trace organic chemicals were responsible for the increase in soil OM contents and WHC. Libohova et al. (2018) stated that increase in OM outcome in increase of WHC of soil.

Among the investigated three disposal facilities (NDS1, NDS2 and SSL) it was revealed that no significant variations were recorded for pH, EC, salinity, OM and WHC in the wastewater irrigated surface soils. The reason was clearly mentioning that three disposal facilities have similar wastewater composition that generally contains high amount of lipids, proteins, sugars, trace organic chemicals etc. But on the other hand, the nine-location comparison and on the basis of distance from wastewater facilities i.e. (S, M, E) showed significant difference at $p<0.05$ for EC, salinity, OM and WHC. The variations in EC and salinity at different localities are due to fertilizers application especially in the case of nitrogen-based fertilizers that decrease soil pH and increase soil EC (Han et al., 2015). But OM and WHC variation in soil could be due to existence of MPs (Chia et al., 2022). Most of the studies have evidenced that prolong wastewater irrigation resulted in deposition and increase of various physiochemical properties like pH, EC, salinity, OM and WHC in the soil (Dotaniya et al., 2018; Natasha et al., 2022; Libohova et al., 2018).

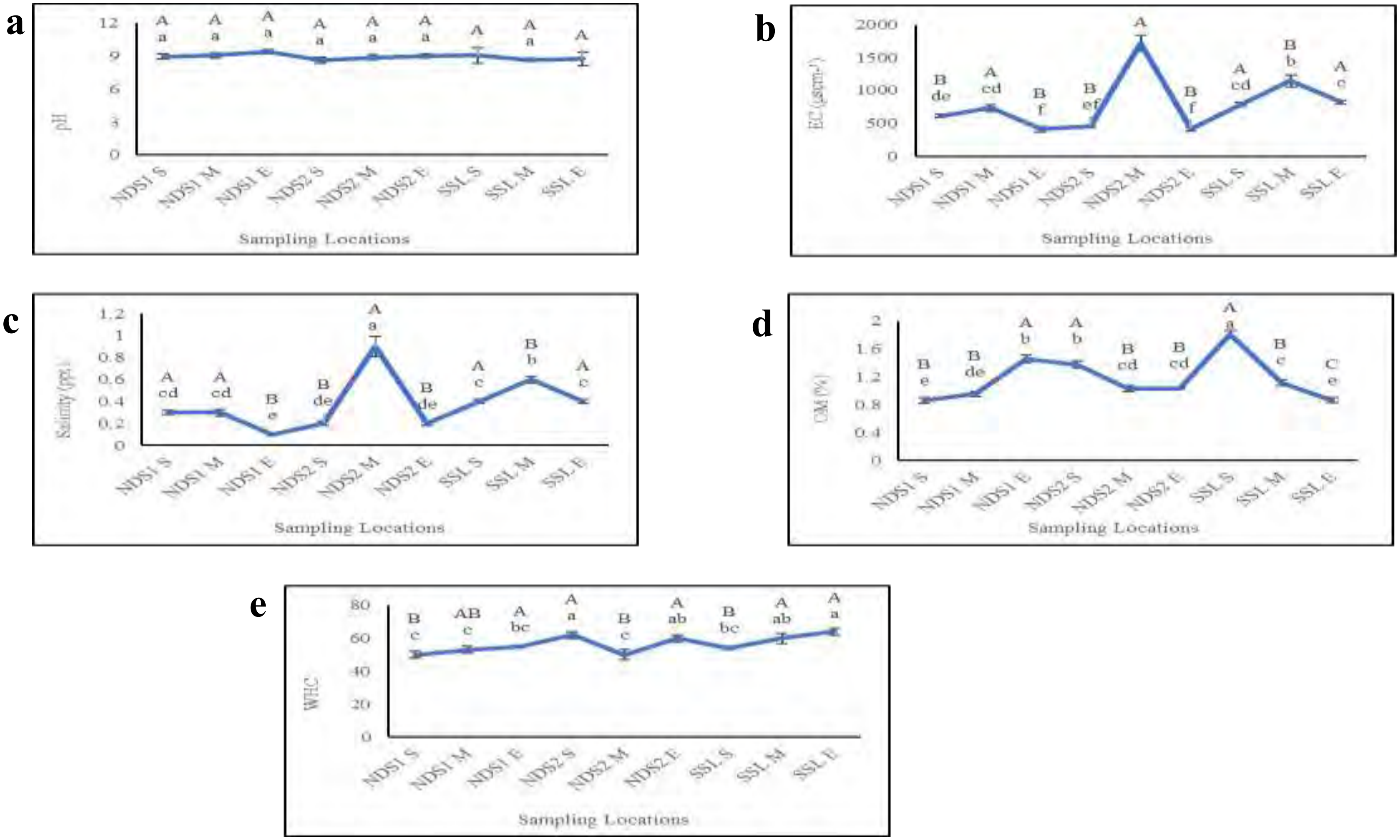


Fig. 3.1: Physichochemical parameters of wastewater irrigated surface soils. Capital letter denote ANOVA between intra sites of same disposal stations (start, middle, end) and small letters denote ANOVA among all nine site of three disposal stations (*p* <0.05; Tukey test)

Table 3.1: Depicting Physicochemical properties and HMs concentration in the wastewater irrigated surface soils of Okara City, Pakistan

Groups	**Locations**	**pH**	**EC**	**Salinity**	**OM**	**WHC**	**Cd**	**Zn**	**Cu**	**Pb**	**Fe**	**Mn**
North disposal station 1	NDS1 S	8.9±0.2^{a}	604±24de	0.3±0.02^{cd}	0.9±0.05^{e}	50±2^{c}	0.1±0^{c}	36.5±7.1^{a}	18.3±2.9^{b}	13.2±3.6^{b}	9520.6±2666.5^{a}	190.4±15.9^{b}
	NDS1 M	9.1±0.2^{a}	731±49^{cd}	0.3±0.03^{cd}	0.9±0.04^{de}	53±2^{c}	0.1±0^{c}	28.2±5.9^{bc}	14.0±2.7^{ab}	8.7±4.1^{b}	8245.6±341.5^{a}	161.1±28.3^{b}
	NDS1 E	9.4±0.2^{a}	410±40^{f}	0.1±0.01^{e}	1.5±0.06^{b}	55±1^{bc}	0.1±0^{c}	48.5±5.1^{a}	15.0±0.2^{ab}	12.5±1.9^{b}	11395.6±1716.5^{a}	171.6±29.8^{b}
	Total NDS1	9.2±0.3^{a}	581.7±161.6^{a}	0.2±0.1^{a}	1.1±0.3^{a}	52.7±2.5^{a}	0.1±0.1^{b}	37.7±11.3^{a}	15.8±3.2^{ab}	11.5±4.2^{b}	9720.6±2465.3^{a}	174.4±30.9^{a}
North disposal station 2	NDS2 S	8.7±0.3^{a}	454±20^{ef}	0.2±0.02^{de}	1.4±0.05^{b}	62±2^{a}	0.1±0^{c}	24.9±3.6^{bc}	12.3±0.9^{c}	10.9±2.4^{b}	8345.6±1716.5^{a}	168.6±13.7^{b}
	NDS2 M	8.8±0.2^{a}	1722±122^{a}	0.9±0.1^{a}	1.0±0.04^{cd}	50±3^{c}	0.4±0.3^{bc}	17.7±6.1^{c}	10.3±2.6^{c}	11.9±2.7^{b}	7558.1±1196.0^{a}	172.4±33.9^{b}
	NDS2 E	9±0.2^{a}	416±34^{f}	0.2±0.02^{de}	1.0±0.01^{cd}	60±2^{ab}	0.4±0.3^{bc}	31.7±0.6^{bc}	16.0±0.7^{ab}	11.9±2.7^{b}	8795.6±1191.5^{a}	270.6±10.7^{a}
	Total NDS2	8.8±0.2^{a}	864±743.2^{a}	0.4±0.4^{a}	1.2±0.2^{a}	57.3±6.4^{a}	0.3±0.3^{b}	24.8±7.8^{a}	12.9±3.2^{a}	12.9±3.4^{b}	8233.1±1622.5^{a}	203.6±57.1^{a}
South sewage line	SSL S	9.1±0.7^{a}	783±33^{cd}	0.4±0.02^{c}	1.8±0.05^{a}	54±1b^{c}	0.9±0.3^{ab}	22.9±8.9^{bc}	32.0±1.8^{a}	46.9±0.7^{a}	8733.1±1628.9^{a}	161.1±22.7^{b}
	SSL M	8.6±0.2^{a}	1143±93^{b}	0.6±0.03^{b}	1.1±0.04^{c}	60±3^{ab}	1.1±0^{a}	28.9±4.1^{bc}	30.5±3.3^{a}	43.7±3.1^{a}	7045.6±2866.5^{a}	159.6±3.2^{b}
	SSL E	8.8±0.6^{a}	822±28^{c}	0.4±0.02^{c}	0.9±0.04^{e}	64±2^{a}	1.1±0.5^{a}	28.2±0.1^{bc}	13.3±0.1^{ab}	12.9±1.9^{b}	7395.6±1166.5^{a}	191.1±30.2^{b}
	Total SSL	8.8±0.2^{a}	916±197.6^{a}	0.5±0.1^{a}	1.3±0.5^{a}	59.3±5^{a}	1.1±0.4^{a}	26.7±6.9^{a}	25.3±9.7^{b}	34.5±16.9^{a}	7724.8±2350.9^{a}	170.6±28.8^{a}
	Anova	**0.317**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	**0.000**	0.178	**0.000**

WHC (Water Holding Capacity); EC (Electrical Conductivity); OM (Organic Matter); Cd (Cadmium); Cu (Copper); Zn (Zinc); Pb (Lead); Fe (Iron); Mn (Manganese); NDS S (North Disposal Station Start); NDS M (North Disposal Station Middle); NDS E (North Disposal Station End); SSL (South Sewage Line)

WHO/FAO (2007) / USEPA permissible limits of HMs (mgkg^{-1}): Cd (3.0 mgkg^{-1}), Cu (100 mgkg^{-1}), Zn (300 mgkg^{-1}), Pb (250 mgkg^{-1}), Fe (50000 mgkg^{-1}), Mn (72 mgkg^{-1}) (Chaoua et al., 2019; Omran, 2016)

3.2. Concentration and distribution patterns of HMs in wastewater irrigated surface soils

The statistical summary (mean ± SD) for selected HMs viz., Cd, Zn, Cu, Pb, Fe and Mn in wastewater irrigated surface soils of Okara are presented (Table 3.1). HMs concentration in wastewater irrigated surface soils were ranged between 0.07 $mgkg^{-1}$ (NDS1 M) to 1.13 $mgkg^{-1}$ (SSL M and SSL E), 17.7 $mgkg^{-1}$ (NDS2 M) to 48.4 $mgkg^{-1}$ (NDS1 E), 10.3 $mgkg^{-1}$ (NDS2 M) to 32.0 $mgkg^{-1}$ (SSL S), 8.7 $mgkg^{-1}$ (NDS1 M) to 47.0 $mgkg^{-1}$ (SSL S), 7045.6 $mgkg^{-1}$ (SSL M) to 11395.6 $mgkg^{-1}$ (NDS1 E), 161.2 $mgkg^{-1}$ (NDS1 M and SSL S) to 270.6 $mgkg^{-1}$ (NDS2 E) for Cd, Zn, Cu, Pb, Fe, and Mn, respectively. The highest mean concentration in the wastewater irrigated surface soil of Okara were recorded for Fe (8559 $mgkg^{-1}$) followed by Mn (182.87 $mgkg^{-1}$) > Zn (29.73 $mgkg^{-1}$) > Pb (19.63 $mgkg^{-1}$) > Cu (18 $mgkg^{-1}$) > Cd (0.48 $mgkg^{-1}$). The current results revealed that all the studied HMs in wastewater irrigated surface soils were within the permissible limit of WHO/FAO (2007) and USEPA (2010) that relates to their background concentration and continuous absorption by plants. But the Mn concentration in wastewater irrigated surface soils exceeded the WHO/FAO (2007)/USEPA (2010) limits due to the reason of its high concentration in wastewater used for irrigation purposes. The other key sources for its origin are available anthropogenic activities such as application of maneb and mancozeb pesticides with Mn composition; and beside that animal manure in wastewater irrigated surface soils. Drozdova et al. (2019) have stated that urban wastewater is accompanied with different wastes and food items like nuts, grains, vegetables remain, tea leaves and feces that are then ultimate responsible for Mn pollution.

Among the studied three (3) disposal facilities (NDS1, NDS2 and SSL), it was found that no significant variation (p<0.05) was depicted for Zn, Fe and Mn, and that clearly indicating that the disposal facilities have similar wastewater origin and composition that mainly contains high contents of laundry detergents, personal care products, pigments, food items and medicinal products etc (Drozdova et al., 2019). But however, in the case of Cd, Cu and Pb significant variations were observed in the wastewater irrigated surface soils that reflected that those soils had receive more Pb and Cd concentration due to traffic pollution in areas nearby roads while significant difference in Cu concentration could be attributed to the corrosion of sewage pipelines. The distance wise variation for HMs from wastewater facilities i.e. (S, M, E) depicted significant difference at $p< 0.05$ for Cu, Zn, Pb and Mn while non-significant variations for Cd and Fe. Such signification variation at S, M and E attributed to the different anthropogenic activities at different location such as application of agrochemicals, pesticides, herbicides, animal manure.

The overall distribution trends for selected HMs in wastewater irrigated surface soils on the basis of distance from wastewater facilities are shown. In present scenario, the concentration of Cd and Zn increased with respect to the distance of wastewater facilities that reflects showed same behavior. Their high concentration depicted the use of Zn containing fertilizers such as zinc sulfate, chelate, zinc EDTA and Cd deposition in soils due to the accumulation of phosphates through detergents and several types of dishwash bars. High Cd concentration at some locations attributed to high OM and high mineral availability there (Rezapour et al., 2019). But on the other hand, Cu and Pb depicted higher concentration at the start of wastewater facilities and decrease towards end of the wastewater facilities. Higher concentration of Cu attributed to usage of Cu based fertilizers such as copper sulfate and due to corrosion of Cu based pipelines while high concentration of Pb at start locations attributed to major contribution of traffic pollution. Agricultural fields near road side showed higher concentration of Pb. Jadoon & Malik, (2019) reported that pb deposition in atmosphere could occur in soil near to the roads and urban areas with considerable traffic. Mn showed increasing trend from start to end for NDS2 and SSL and decreasing trend from start to end for NDS1. The high concentration of Mn attributed to Mn pesticides application such as Maneb and Mancozeb.

The HMs concentration of present study in wastewater irrigated surface soil was compared with similar studies results that were conducted globally (Table 1.1). The current study results showed lower concentration for HMs as compared to other study results conducted in Morocco, Iran and Pakistan by different researchers (Barakat et al., 2020; Tariq, 2021; Natasha et al., 2022). But on the other hand, higher concentration for studied HMs in current study was also depicted when compared to other study conducted by (Dotaniya et al., 2018). Such high concentrations of HMs revealed that different anthropogenic activities such as animal manure, sewage sludge, pesticides (containing Fe, Mn, Zn, Pb) and metal-based fertilizers applications in respective study areas. Some natural sources such as weathering of minerals, volcanic activities and parent material erosion also enhanced HMs concentrations in those study areas.

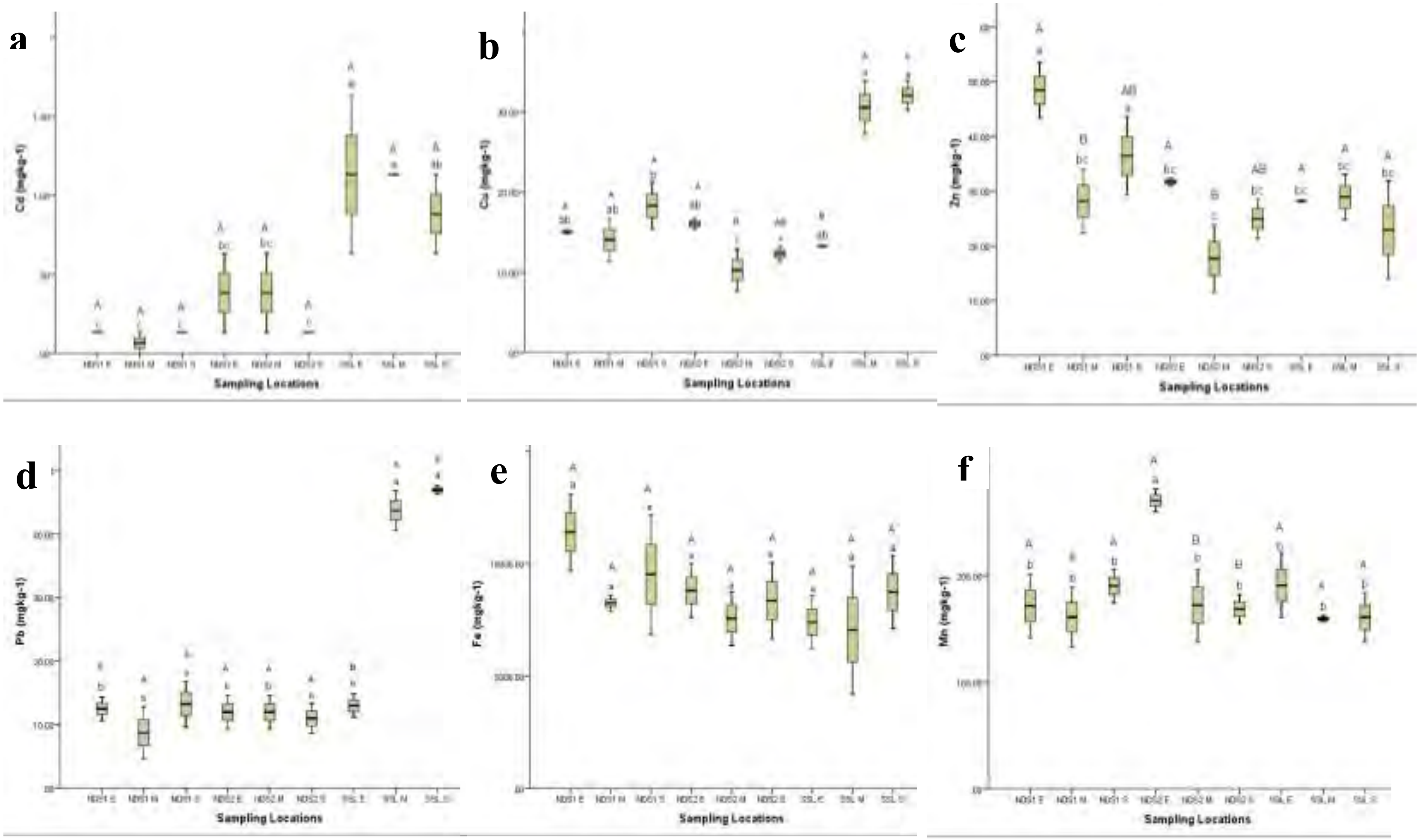


Fig. 3.2: HM concentration in wastewater irrigated surface soils (a) Cd, (b) Cu, (c) Zn, (d) Pb, (e) Fe, (f) Mn. Capital letter denote ANOVA between intra sites of same disposal stations (start, middle, end) and small letters denote ANOVA among all nine site of three disposal stations (p <0.05; Tukey test)

3.3. MPs abundance and its physical properties in wastewater irrigated surface soils

3.3.1. MPs abundance in wastewater irrigated surface soils

The average abundance of MPs varied from 1850 particles kg^{-1}(NDS2 M) to 5300 particles kg^{-1} (SSL E) particles kg^{-1} at different sampling locations in wastewater irrigated surface soils (fig.3.3a). Among the studied three disposal facilities MPs abundance in wastewater irrigated surface soils depicted the following trends: SSL (3750-5300 particles kg^{-1}) > NDS1 (3050-4800 particles kg^{-1}) > NDS2 (1850-3300 particles kg^{-1}) but on other hand, there was found no significant differences (p<0.05) among three disposal facilities. It was clearly attributing to their similar source origin of wastewater that was purely urban wastewater contaminated with domestic wastes such as detergents, personal care products, laundry residues, medicinal products, plastic particles through urban runoff, and most probably soils behaved similarly in nature and similar activities were performed at all locations. However, on the basis of distance among three wastewater disposal facilities, the highest abundance for MPs was recorded at E followed by S and M of the NDS1 and NDS2. But the trends for SSL were followed as: E > M > E but no statistically significant variations were observed. The MPs abundance trend on the basis of distance was attributed to several factors such as population size, plastic waste dumping, use of plastic films in agricultural soils, soil texture and agricultural fields nearby roads. Several other studies conducted globally that recorded higher MPs abundance as compared to MPs abundance (1850- 5300 particles kg^{-1}) in current study (Zhang & Liu, 2018; Zhou et al., 2019; Lang et al., 2022). The high abundance of MPs in those study areas attributed to the application of sewage sludge, nearby industrial activities, street runoffs and weathering depositions. While in present study no industrial activity was present. Many studies recorded low abundance of MPs in comparison with current study (Li et al., 2022; Harms et al., 2021; Ragoobur et al., 2021).

3.3.2. Physical properties of MPs in wastewater irrigated surface soils

The Fig. 3.3b depicted three different shapes of MPs such as fibers, fragments and films in wastewater irrigated surface soils of Okara. Overall, fragment (49.6%) revealed the most predominant shape followed by fibers (38.8%) and films (11.5%). The highest number of fragments recorded in wastewater irrigated surface soil samples of SSL E (31.5%), fibers in NDS1 E (17.2%) and films in NDS1 E (22.7%). The ultimate source of fibers in agricultural soil are residues of clothes during washing process while fragments originated from the decomposition of agricultural plastic wastes, such as agricultural tools, plastic woven bags, plastic seed bags and plastic packaging materials. The higher fragments proportions in the soils relates to its presence of high proportion of PP and PE plastic particles. Rodrigues et al. (2018) also reported that higher numbers of fragments are closely related to PP and PE plastic types. Furthermore, the fragments attributed to the application of wastewater sources without segregation of large plastic particles, and it takes time in degradation and number of plastic fragments increase. Relative similar studies to current study conducted globally which showed fragments and fibers were the dominant shapes in agricultural soils (Zhou et al., 2019; Ragoobur et al., 2021; Li et al., 2022; Zhang & Liu, 2018).

The black (40.1%) color MP percentage was dominated in wastewater irrigated surface soils followed by transparent (18%) > red (16.3%) > blue (9%) > others (6.3%) > multi (5.2%) and green (4.2%) colors represented in (Fig. 3.3c). In current study, black MPs showed dominancy as a result of wastewater application containing synthetic textiles, plastic pellets and in highly traffic areas due to the presence of tire dust, road paint and probably associated with disposable plastics and mulching/vinyl films (Rodrigues et al., 2018). Transparent MPs may be originated from the use of plastic bags, plastic packaging materials, plastic films, etc. Many studies conducted globally to record MPs colors on the basis of different natural and anthropogenic activities (Li et al., 2022; Harms et al., 2021; Ragoobur et al., 2021). The size distribution of MPs in wastewater irrigated surface soils were classified into 5 categories as presented in fig. 3.3d. The MPs size ranges of <500µm, 0.5mm- 1mm, 1mm-1.5mm, 1.5mm-2mm, and 2mm-5mm that is accounted by 31%, 26%, 8%, 7% and 28%, respectively in wastewater irrigated surface soils dominating by small sizes particles. The results depicted that wastewater irrigated surface soils contained highest number of MPs in size range of <500 µm in NDS1 M attributed to MPs degradation via physical abrasion, weathering, ageing and soil erosion. Zhou et al. (2019) conducted a study and reported that high concentration of small sized particles was attributed to the biodegradation of large sizes of MPs. Many other studies reported size classification of MPs is in accordance with current study (Lang et al., 2022; Li et al., 2022).

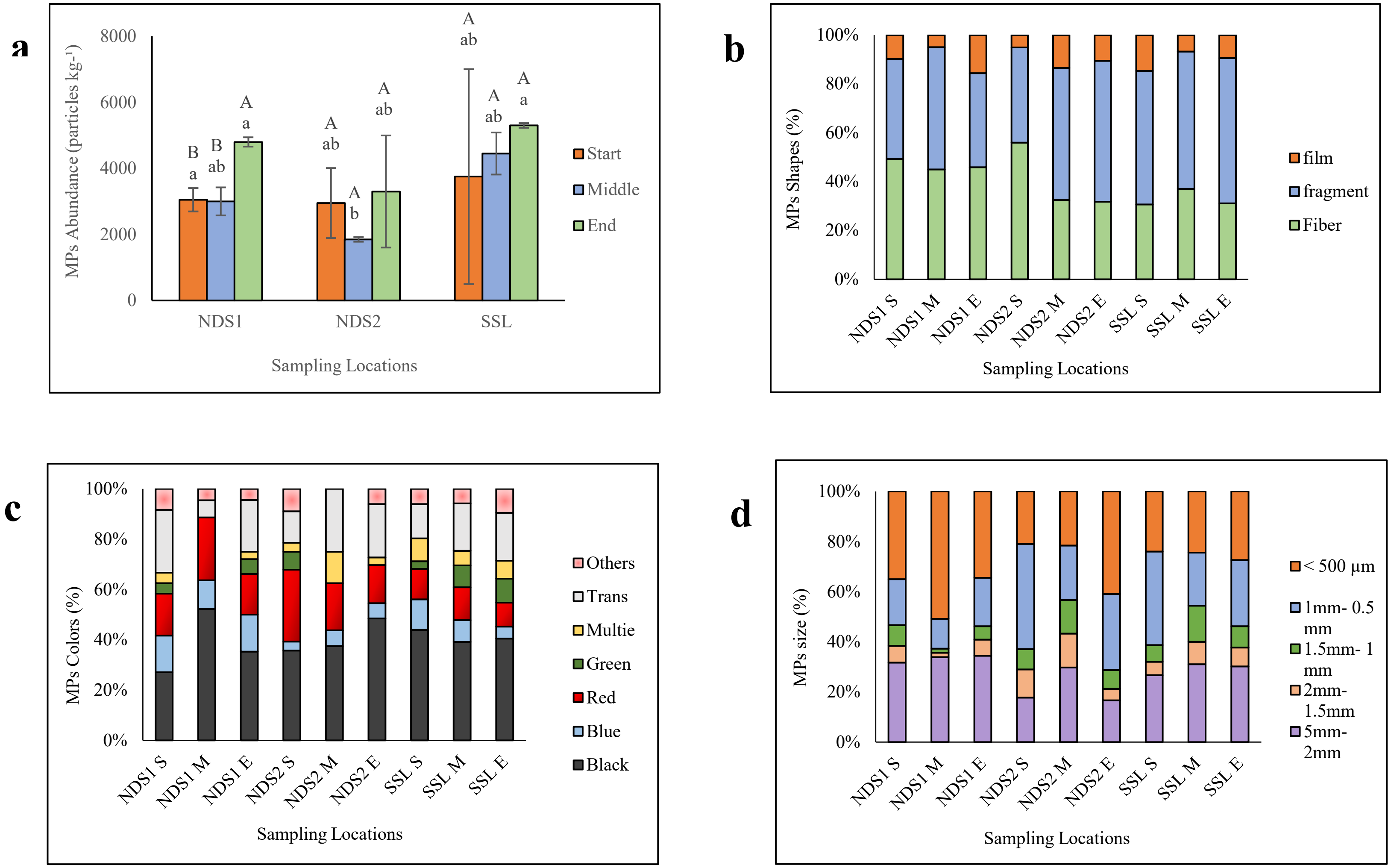


Fig. 3.3: MPs contamination in wastewater irrigated surface soils
(a) MPs abundance, (b) MPs shapes, (c) MPs colors, (d) MPs sizes

3.4. Governing role of physicochemical properties in distribution of HMs and MPs in wastewater irrigated surface soils

The Pearson correlation at $p<0.05$ and $p<0.01$ for physicochemical viz., pH, EC, salinity, OM and WHC with HMs and MPs at the wastewater irrigated surface soils are given in Table 3.2. The strong positive correlation for pH with HMs (Zn and Fe) and MPs (2mm-5mm and <500 µm) in wastewater irrigated surface soils are presented. While irrespectively, a negatively correlation with Cd, EC and salinity were recorded. Alkaline soils have the ability to retain HMs and reduces their mobility (Jadoon & Malik, 2019). Moreover, the variation (decrease or increase) of pH in soil depends on MPs type and its shape (Chia et al., 2022). Such elevated trend for pH in soil form different complexes that affect the HMs mobility and solubility. Mainly, the wastewater had its origin from three disposal facilities accompanied with different sizes of MPs where they were expected to be released from clothes after washing and from other consumer and non-consumer products into the streams. Soil EC showed strong positive correlation with salinity ($p<0.01$) while EC and salinity recorded negative correlation with HMs (Zn and Fe) and MPs (1mm-0.5mm and <500 µm). The possible reason of negative correlation between EC and HMs can be the inverse relationship of soils pH with soils EC and salinity. Decrease in pH indicates large number of hydrogen ion which ultimately increase soils EC. The change in soil EC and salinity depends on quantity and type of MPs in soil (Chia et al., 2022). OM showed positive correlation with HMs (Cu, Pb) and MPs (2mm-5mm and 1.5mm-2mm). Association of Cu with OM is important due to its ability to form complexes with OM present in soils. Soils OM plays a vital role in reducing the HMs mobility in soils by stable complexes formation which explained the Cu and Pb correlation with OM in soils (Jadoon & Malik, 2019). When plastic particles enter into soil, they breakdown into MPs with ageing and due to their degradation OM content in soil increases. WHC showed positive correlation with Cd and MPs (1mm- 0.5mm) while negatively correlated were observed with pH. Soil pH affects the amount of nutrients and chemicals that are soluble in soil water, and therefore the amount of nutrients available to plants. Some nutrients are more available under acid conditions while others are more available under alkaline condition.

Correlation between WHC and MPs depends on the type of MPs. Polyester MPs increase the WHC of soil (Chia et al., 2022).

3.5. Role of MPs sizes on the HMs distribution in wastewater irrigated surface soils

Table 3.2 summarized the Pearson correlation at $p<0.05$ and $p<0.01$ among HMs (Cd, Cu, Zn, Pb, Fe and Mn) and MPs (5mm-2mm, 2mm-1.5mm, 1.5mm-1mm, 1mm-0.5mm, <500µm) in wastewater irrigated surface soils. The strong positive correlation at $p<0.01$ was recorded among HMs (Cu and Cd; Pb and Cd; Pb and Cu; Fe and Zn). Such strong positive correlation between HMs attributed to their common source of origin such as wastewater application, use of agrochemicals and traffic pollution in road side agricultural fields.

Cu enters into wastewater through corrosion of pipelines while Cd contaminate water as a result of detergents, dishwashers, washing powders usage in homes. Their source of origin is similar which attributed to their strong positive correlation. While Cd and Pb correlation attributed to agricultural practices in agricultural fields and nearby traffic activities. A study conducted by Jadoon & Malik, (2019) which revealed agricultural soils near roads showed high concentration of Pb. Another study conducted by Wang et al. (2018) reported HMs correlation (Cd and Pb) and (Cd and Zn) due to their similar source of origin. Pb was mainly accumulated through vehicular emissions and Cd accumulated as a result of fertilizers application. The strong correlation between Pb and Cu attributed to common source of origin such as road dust. Cu is commonly associated with car components, lubricants and tire abrasions while vehicular emission is common source of Pb deposition in nearby agricultural soils. Zn showed positive correlation with Fe which attributed to similar discharge or contamination level and similar behavior during transport in soil system. Zn and Fe made part of wastewater as a result of domestic discharge such as food contents, health and diet supplements, personal care products and detergents etc. Other important source of Zn and Fe in agricultural soil was application of fertilizers containing Zn and Fe constituents such as zinc sulphate, iron sulphates.

Different size of MPs showed positive and negative correlation with HMs. MPs (2mm-5mm) showed positive correlation at $p<0.01$ with HMs (Cu and Pb) and negatively corelated at $p<0.05$ with Mn. MPs (1.5mm-2mm) positively corelated at $p<0.05$ and $p<0.01$ with Cu and Pb. MPs (1mm- 1.5mm) depicted positive correlation with HMs (Cd and Pb) at $p<0.01$ while MPs (0.5mm- 1mm) at $p <0.05$ positively corelated with Cd. PE MPs increased the mobility and exchangeability of Cu in soil and thus its availability increased. Therefore, this phenomenon attributed to strong positive correlation between Cu and MPs and small size MPs had large surface area to adsorb HMs on their surface. It has been reported that Cd toxicity in soil increased due to addition of plastic mulch films in agricultural ecosystem that attributed to positive correlation between MPs and Cd. Another reason of Cd concentration increases in soil with increase in MPs increase attributed to usage of Cd in plastic products as stabilizer and pigments (Cao et al., 2021). Pb is most commonly detected HM in PVC MPs products. Due to degradation of MPs in soil Pb released into the soil environment and they both positively correlate to each other. The negative correlation between MPs and Mn showed that Mn mobility and toxicity decreased in soil in the presence of MPs. PP and PVC MPs adsorb Mn on their surface and ultimately decrease Mn mobility in soil that attributed negative correlation between MPs and Mn content (N. Khalid et al., 2021).

Table 3.2: Correlation among physicochemical parameters, HMs and MPs in wastewater irrigated surface soils

	WHC	**pH**	**EC**	**Salinity**	**OM**	**Cd**	**Cu**	**Zn**	**Pb**	**Fe**	**Mn**	**5mm-2mm**	**2mm-1.5mm**	**1.5mm - 1 mm**	**1mm-0.5 µm**	**500 µm**
WHC	1															
pH	-0.5*	1														
EC (µs/cm)	-0.3	-0.4*	1													
Salinity	-0.4	-0.4*	0.9**	1												
OM	-0.01	0.3	-0.2	-0.2	1											
Cd	0.4*	-0.4*	0.3	0.2	0.1	1										
Cu	0.0	-0.02	0.04	0.1	0.5*	0.5**	1									
Zn	0.02	0.6**	-0.6**	-0.6**	0.01	-0.3	0.02	1								
Pb	0.1	-0.1	0.2	0.2	0.5**	0.6**	0.9**	-0.1	1							
Fe	-0.02	0.5**	-0.4*	-0.7**	0.2	-0.3	-0.1	0.6**	-0.1	1						
Mn	0.2	0.1	-0.3	-0.2	-0.3	-0.1	-0.2	0.2	-0.3	-0.0	1					
5mm-2mm	-0.1	0.5*	-0.1	-0.2	0.5**	0.4	0.6**	0.3	0.6**	0.2	-0.5*	1				
2mm-1.5mm	0.2	-0.2	0.1	0.0	0.5*	0.3	0.4*	-0.1	0.5**	0.2	-0.3	0.3	1			
1.5mm- 1 mm	0.3	-0.3	0.2	0.02	0.3	0.5**	0.5**	-0.1	0.7**	0.1	-0.2	0.4*	0.5*	1		
1mm- 0.5 mm	0.7**	-0.2	-0.3	-0.5*	0.4	0.4*	0.2	-0.1	0.3	0.3	-0.1	0.3	0.4*	0.5**	1	
<500 µm	-0.1	0.5**	-0.4*	-0.3	0.2	-0.1	0.3	0.2	0.1	0.2	-0.04	0.5*	0.3	-0.1	0.1	1

3.6. Pollution status level and ecological risk of HMs in wastewater irrigated surface soils

The summary of pollution level and ecological risk viz., pollution index (I_{POLL}), geo accumulation index (I_{geo}), Contamination factor (CF), Enrichment factor (EF), pollution load index (PLI), Ecological risk factor (E_r^i) and risk index (RI) for selected HMs in wastewater irrigated surface soils are presented (Table 3.3).

The I_{POLL} index for HMs viz., Cu, Zn and Pb fall in category 1 that attributed to the low pollution risk in wastewater irrigated soil. I_{POLL} value for Cd at some locations (SSL M and SSL E) and for Mn at all locations was >1 (category-2) that showed low to moderate pollution in the soils. The current study depicted relative similar I_{POLL} value for HMs in wastewater irrigated soil samples as compared to other studies conducted globally (Mohammadi et al., 2020) and relatively higher I_{POLL} values were recorded by other studies (Stevanović et al., 2018; Adimalla et al., 2019). Moreover, the Igeo indexes indicates the HMs intensity in wastewater irrigated surface soils that have shown unpolluted to moderately pollution for Cd, Cu, Zn, Pb at different locations, while moderately pollution for Mn at NDS2 E was declared. Relative high value for Igeo in agricultural soils were recorded in studies conducted by (Jadoon & Malik, 2019; Mohammadi et al., 2020) but other studies having measured comparative similar Igeo values (Adimalla et al., 2019; Stevanović et al., 2018).

The CF values have shown considerable Mn contamination; considerable to moderately contamination for Cd; and moderately contamination for Pb at different sites. However, low CF values were recorded for Cu and Zn in all wastewater irrigated surface soils samples. Such comparable CF results for Pb were measured in the study of Mohammadi et al. (2020) that have shown moderately contamination but they have recorded high CF values for Cd. Other studies conducted globally showed relative similar results for CF values in soil samples (Ghouma et al., 2022; Karimi et al., 2020). The minimal EF value for Zn and Mn; moderate EF for Cu; significant enrichment for Cd and Pb; were recorded in the wastewater irrigated surface soils at different site. It was also deduced that no site of the study has shown extreme enrichment (EF >40) for selected

HMs. The present study declared high EF value for HMs in wastewater irrigated soil samples in comparison with the EF value of other studies conducted globally (Adimalla et al., 2019; Karimi et al., 2020; Jadoon & Malik, 2019) and relative similar EF values were recorded as compared to study conducted by Jadoon & Malik, (2019).

The locations of wastewater irrigated surface soils (NDS1 and NDS2) were considered as unpolluted because the PLI values recorded were <1, but for the location (SSL), the PLI values were ranged between 1 to 2 that are declared as unpolluted to moderately polluted sites. The higher mean PLI values were reported in different studies carried out word widely in comparison to the present study results (Karimi et al., 2020; Jadoon & Malik, 2019; Stevanović et al., 2018) .

The HMs (Cu, Zn, Pb, Mn) showed E_r^i value <40 that predicts low potential ecological risk but irrespective of that E_r^i (<80) for Cd in wastewater irrigated surface soils was reported that showed moderate ecological risk. The E_r^i values for Cd at SSL depicted considerable potential ecological risk (E_r^i <160). A study conducted by Ihedioha et al. (2017) showed similar results to our current study results and they had recorded moderate to very high E_r^i value for Cd while all other HMs had E_r^i <40 that showed low potential ecological risk. The mean E_r^i values of current study results were lower than other study conducted (Jadoon & Malik, 2019). All the sampling locations of the wastewater irrigated soil samples showed that the RI values were recorded in the range of 14.0 to 131.2 for all the studied HMs that showed low ecological risks. A study conducted by Ghouma et al. (2022) showed high RI value of 652.9 to 1054.6 in comparison to the current study results for RI values. Although the RI results in wastewater irrigated surface soil of current study showed low potential ecological risks, but regular monitoring is necessary for soil protection and future benefits.

Table 3.3: Pollution level and ecological risk scenarios for HMs in different wastewater irrigated surface soils of Okara, Pakistan

Location	HMs	I_{POLL}	Igeo	CF	EF	PLI	E_r^i	RI	Risk grade
NDS1 S	Cd	0.1	0.1	0.5	2.2	-	13.4	-	
	Zn	0.1	0.1	0.4	1.9	-	0.4	-	
	Cu	0.1	0.1	0.4	2.0	-	2.0	-	
	Pb	0.2	0.1	0.7	3.3	-	3.3	-	
	Mn	1.2	0.8	3.8	1.1	-	3.8	-	
	Total					0.7		22.9	Low ecological risk
NDS1 M	Cd	0.1	0.0	0.2	1.3	-	6.7	-	
	Zn	0.1	0.1	0.3	1.7	-	0.3	-	
	Cu	0.1	0.1	0.3	1.8	-	1.6	-	
	Pb	0.1	0.1	0.4	2.5	-	2.2	-	
	Mn	1.0	0.7	3.2	1.1	-	3.2	-	
	Total					0.5		14.0	Low ecological risk
NDS1 E	Cd	0.1	0.1	0.5	1.9	-	13.4	-	
	Zn	0.2	0.1	0.5	2.1	-	0.5	-	
	Cu	0.1	0.1	0.3	1.4	-	1.7	-	
	Pb	0.2	0.1	0.6	2.6	-	3.1	-	
	Mn	1.0	0.7	3.4	0.8	-	3.4	-	
	Total					0.7		22.1	Low ecological risk
NDS2 S	Cd	0.1	0.1	0.5	2.5	-	13.4	-	
	Zn	0.1	0.1	0.3	1.5	-	0.3	-	
	Cu	0.1	0.1	0.3	1.5	-	1.4	-	
	Pb	0.2	0.1	0.6	3.1	-	2.7	-	
	Mn	1.0	0.7	3.4	1.1	-	3.4	-	

	Total					0.6		21.1	Low ecological risk
NDS2 M	Cd	0.4	0.3	1.3	8.0	-	38.4	-	
	Zn	0.1	0.0	0.2	1.2	-	0.2	-	
	Cu	0.1	0.1	0.2	1.4	-	1.1	-	
	Pb	0.2	0.1	0.6	3.7	-	3.0	-	
	Mn	1.0	0.7	3.5	1.3	-	3.5	-	
	Total					0.7		46.2	Low ecological risk
NDS2 E	Cd	0.4	0.3	1.3	6.9	-	38.4	-	
	Zn	0.1	0.1	0.3	1.8	-	0.3	-	
	Cu	0.1	0.1	0.4	1.9	-	1.8	-	
	Pb	0.2	0.2	0.8	4.3	-	4.0	-	
	Mn	1.6	1.1	5.4	1.7	-	5.4	-	
	Total					0.9		49.9	Low ecological risk
SSL S	Cd	0.9	0.6	3.0	15.9	-	88.4	-	
	Zn	0.1	0.1	0.2	1.3	-	0.2	-	
	Cu	0.2	0.1	0.7	3.8	-	3.6	-	
	Pb	0.7	0.5	2.4	12.7	-	11.7	-	
	Mn	1.0	0.7	3.2	1.0	-	3.2	-	
	Total					1.3		107.2	Low ecological risk
SSL M	Cd	1.1	0.8	3.8	25.3	-	113.4	-	
	Zn	0.1	0.1	0.3	2.0	-	0.3	-	
	Cu	0.2	0.1	0.7	4.5	-	3.4	-	
	Pb	0.7	0.4	2.2	14.6	-	10.9	-	
	Mn	1.0	0.6	3.2	1.3	-	3.2	-	
	Total					1.4		131.2	Low ecological risk
SSL E	Cd	1.1	0.8	3.8	24.1	-	113.4	-	
	Zn	0.1	0.1	0.3	1.9	-	0.3	-	

	Cu	0.1	0.1	0.3	1.9	-	1.5	-	
	Pb	0.2	0.1	0.7	4.1	-	3.2	-	
	Mn	1.2	0.8	3.8	1.4	-	3.8	-	
	Total					1.0		122.2	Low ecological risk
Total	Cd	0.5	0.3	1.6	9.9	-	48.8	-	
	Zn	0.1	0.1	0.3	1.7	-	0.3	-	
	Cu	0.1	0.1	0.4	2.3	-	2.0	-	
	Pb	0.3	0.2	1.0	5.7	-	4.9	-	
	Mn	1.1	0.7	3.7	1.2	-	3.7	-	
	Total					0.9		59.6	Low ecological risk

I_{POLL} (Pollution load Index); Igeo (geo accumulation index); CF (Contamination factor); EF (Enrichment factor); PLI (Pollution load index); $\boldsymbol{E_r^i}$ (Potential ecological risk index); RI (Risk index)

3.7. Human health risk assessment from wastewater irrigated surface soils intake

HMs pollution in agricultural soils by wastewater irrigation practices is key issue of concern when consumed via dietary and non-dietary pathways because soil has directly or indirectly relation to human health. Therefore, for this purpose the wastewater irrigated surface soils intake accompanied with HMs and its exposure to the local children's and adults are presented in Table 3.4. The mean ADD, HQ and HI for both adults and children via ingestion, inhalation and dermal contact with HMs (Cd, Zn, Cu, Pb and Mn) at different wastewater irrigated surface soils are presented (Table 4). The non-carcinogenic risk HQ in both children and adults for the studied HM at different wastewater facilities were portrayed in following order: ingestion>dermal>inhalation. Human health risk assessment via ingestion was higher as compared to other routes of HMs entry in human body. Children are more susceptible to HMs pollution as compared to adults due to their outdoor activities like playing, physiology, developmental growth etc.

However, the overall, HI values for HMs via soil intake at different sites for children were Pb (1.80E-01)>Mn (5.30E-02)>Cd (7.20E-03)>Cu (5.80E-03)>Zn (1.30E-03); but on other for adults were: Pb (2.60E-02)>Mn (1.20E-02)>Cd (3.40E-03)>Cu (8.50E-04)>Zn (2.00E-04), respectively. The HI value for both children and adults were less than 1 which indicated that there is no health risk from soil intake accompanied with HMs. On the basis of three wastewater disposal facilities the highest value of HI value of (Cd, Cu, Pb) for both child and adults were recorded in soil samples irrigated with wastewater of SSL while HI value for Zn was highest in soil samples at NDS1 and HI value for Mn recorded highest at NDS2 sites. Several studies in comparison with current study were conducted globally whose results depicted negligible non carcinogenic risk to children and adults via soil intake through ingestion, inhalation and dermal contact (Ihedioha et al., 2017; Mohammadi et al., 2020).

Table 3.4: Health risk assessment scenarios for selected HMs via intake of wastewater irrigated surface soils via non-dietary pathways by Children's and adult's resident of Okara, Pakistan

Group	Location	HMs	ADDing	ADDinh	ADDder	HQ ing	HQ inh	HQ der	HI	interpretation
Child	NDS1 S	Cd	1.7E-06	4.8E-11	2.7E-09	1.7E-03	4.8E-08	2.7E-04	2.0E-03	Negligible risk
		Zn	4.7E-04	1.3E-08	7.5E-07	1.6E-03	4.3E-08	1.2E-05	1.6E-03	Negligible risk
		Cu	2.3E-04	6.5E-09	3.7E-07	5.9E-03	1.6E-07	3.1E-05	5.9E-03	Negligible risk
		Pb	1.7E-04	4.7E-09	2.7E-07	1.2E-01	1.3E-06	5.2E-04	1.2E-01	Negligible risk
		Mn	2.4E-03	6.8E-08	3.9E-06	5.3E-02	1.5E-06	2.1E-03	5.5E-02	Negligible risk
	NDS1 M	Cd	8.6E-07	2.4E-11	1.4E-09	8.6E-04	2.4E-08	1.4E-04	9.9E-04	Negligible risk
		Zn	3.6E-04	1.0E-08	5.8E-07	1.2E-03	3.4E-08	9.6E-06	1.2E-03	Negligible risk
		Cu	1.8E-04	5.0E-09	2.9E-07	4.5E-03	1.3E-07	2.4E-05	4.5E-03	Negligible risk
		Pb	1.1E-04	3.1E-09	1.8E-07	8.0E-02	8.8E-07	3.4E-04	8.0E-02	Negligible risk
		Mn	2.1E-03	5.8E-08	3.3E-06	4.5E-02	1.3E-06	1.8E-03	4.7E-02	Negligible risk
	NDS1 E	Cd	1.7E-06	4.8E-11	2.7E-09	1.7E-03	4.8E-08	2.7E-04	2.0E-03	Negligible risk
		Zn	6.2E-04	1.7E-08	9.9E-07	2.1E-03	5.8E-08	1.7E-05	2.1E-03	Negligible risk
		Cu	1.9E-04	5.4E-09	3.1E-07	4.8E-03	1.3E-07	2.6E-05	4.8E-03	Negligible risk
		Pb	1.6E-04	4.5E-09	2.6E-07	1.1E-01	1.3E-06	4.9E-04	1.1E-01	Negligible risk
		Mn	2.2E-03	6.1E-08	3.5E-06	4.8E-02	1.3E-06	1.9E-03	5.0E-02	Negligible risk
	NDS2 S	Cd	1.7E-06	4.8E-11	2.7E-09	1.7E-03	4.8E-08	2.7E-04	2.0E-03	Negligible risk
		Zn	3.2E-04	8.9E-09	5.1E-07	1.1E-03	3.0E-08	8.5E-06	1.1E-03	Negligible risk
		Cu	1.6E-04	4.4E-09	2.5E-07	3.9E-03	1.1E-07	2.1E-05	4.0E-03	Negligible risk
		Pb	1.4E-04	3.9E-09	2.2E-07	1.0E-01	1.1E-06	4.3E-04	1.0E-01	Negligible risk
		Mn	2.2E-03	6.0E-08	3.5E-06	4.7E-02	1.3E-06	1.9E-03	4.9E-02	Negligible risk
	NDS2 M	Cd	4.9E-06	1.4E-10	7.9E-09	4.9E-03	1.4E-07	7.9E-04	5.7E-03	Negligible risk
		Zn	2.3E-04	6.3E-09	3.6E-07	7.5E-04	2.1E-08	6.0E-06	7.6E-04	Negligible risk
		Cu	1.3E-04	3.7E-09	2.1E-07	3.3E-03	9.2E-08	1.8E-05	3.3E-03	Negligible risk
		Pb	1.5E-04	4.3E-09	2.5E-07	1.1E-01	1.2E-06	4.7E-04	1.1E-01	Negligible risk
		Mn	2.2E-03	6.2E-08	3.5E-06	4.8E-02	1.3E-06	1.9E-03	5.0E-02	Negligible risk

	NDS2 E	Cd	4.9E-06	1.4E-10	7.9E-09	4.9E-03	1.4E-07	7.9E-04	5.7E-03	Negligible risk
		Zn	4.1E-04	1.1E-08	6.5E-07	1.4E-03	3.8E-08	1.1E-05	1.4E-03	Negligible risk
		Cu	2.1E-04	5.7E-09	3.3E-07	5.1E-03	1.4E-07	2.7E-05	5.2E-03	Negligible risk
		Pb	2.0E-04	5.7E-09	3.3E-07	1.5E-01	1.6E-06	6.2E-04	1.5E-01	Negligible risk
		Mn	3.5E-03	9.7E-08	5.5E-06	7.5E-02	2.1E-06	3.0E-03	7.8E-02	Negligible risk
	SSL S	Cd	1.1E-05	3.2E-10	1.8E-08	1.1E-02	3.2E-07	1.8E-03	1.3E-02	Negligible risk
		Zn	2.9E-04	8.2E-09	4.7E-07	9.8E-04	2.7E-08	7.8E-06	9.9E-04	Negligible risk
		Cu	4.1E-04	1.1E-08	6.6E-07	1.0E-02	2.9E-07	5.5E-05	1.0E-02	Negligible risk
		Pb	6.0E-04	1.7E-08	9.6E-07	4.3E-01	4.8E-06	1.8E-03	4.3E-01	Negligible risk
		Mn	2.1E-03	5.8E-08	3.3E-06	4.5E-02	1.3E-06	1.8E-03	4.7E-02	Negligible risk
	SSL M	Cd	1.5E-05	4.1E-10	2.3E-08	1.5E-02	4.1E-07	2.3E-03	1.7E-02	Negligible risk
		Zn	3.7E-04	1.0E-08	5.9E-07	1.2E-03	3.5E-08	9.9E-06	1.2E-03	Negligible risk
		Cu	3.9E-04	1.1E-08	6.3E-07	9.8E-03	2.7E-07	5.2E-05	9.8E-03	Negligible risk
		Pb	5.6E-04	1.6E-08	8.9E-07	4.0E-01	4.4E-06	1.7E-03	4.0E-01	Negligible risk
		Mn	2.0E-03	5.7E-08	3.3E-06	4.4E-02	1.2E-06	1.8E-03	4.6E-02	Negligible risk
	SSL E	Cd	1.5E-05	4.1E-10	2.3E-08	1.5E-02	4.1E-07	2.3E-03	1.7E-02	Negligible risk
		Zn	3.6E-04	1.0E-08	5.8E-07	1.2E-03	3.4E-08	9.6E-06	1.2E-03	Negligible risk
		Cu	1.7E-04	4.8E-09	2.7E-07	4.3E-03	1.2E-07	2.3E-05	4.3E-03	Negligible risk
		Pb	1.7E-04	4.6E-09	2.7E-07	1.2E-01	1.3E-06	5.1E-04	1.2E-01	Negligible risk
		Mn	2.4E-03	6.8E-08	3.9E-06	5.3E-02	1.5E-06	2.1E-03	5.5E-02	Negligible risk
	Total	Cd	6.2E-06	1.7E-10	1.0E-08	6.2E-03	1.7E-07	1.0E-03	7.2E-03	Negligible risk
		Zn	3.8E-04	1.1E-08	6.1E-07	1.3E-03	3.5E-08	1.0E-05	1.3E-03	Negligible risk
		Cu	2.3E-04	6.4E-09	3.7E-07	5.8E-03	1.6E-07	3.1E-05	5.8E-03	Negligible risk
		Pb	2.5E-04	7.0E-09	4.0E-07	1.8E-01	2.0E-06	7.7E-04	1.8E-01	Negligible risk
		Mn	2.3E-03	6.5E-08	3.7E-06	5.1E-02	1.4E-06	2.0E-03	5.3E-02	Negligible risk
Adult	NDS1 S	Cd	2.3E-07	3.4E-11	7.0E-09	2.3E-04	3.4E-08	7.0E-04	9.3E-04	Negligible risk
		Zn	6.3E-05	9.2E-09	1.9E-06	2.1E-04	3.1E-08	3.2E-05	2.4E-04	Negligible risk
		Cu	3.1E-05	4.6E-09	9.6E-07	7.8E-04	1.2E-07	8.0E-05	8.6E-04	Negligible risk
		Pb	2.3E-05	3.3E-09	6.9E-07	1.6E-02	9.5E-07	1.3E-03	1.8E-02	Negligible risk

	Mn	3.3E-04	4.8E-08	9.9E-06	7.1E-03	1.0E-06	5.4E-03	1.3E-02	Negligible risk
NDS1 M	Cd	1.2E-07	1.7E-11	3.5E-09	1.2E-04	1.7E-08	3.5E-04	4.7E-04	Negligible risk
	Zn	4.8E-05	7.1E-09	1.5E-06	1.6E-04	2.4E-08	2.5E-05	1.9E-04	Negligible risk
	Cu	2.4E-05	3.5E-09	7.3E-07	6.0E-04	8.9E-08	6.1E-05	6.6E-04	Negligible risk
	Pb	1.5E-05	2.2E-09	4.6E-07	1.1E-02	6.2E-07	8.7E-04	1.2E-02	Negligible risk
	Mn	2.8E-04	4.1E-08	8.4E-06	6.0E-03	8.8E-07	4.6E-03	1.1E-02	Negligible risk
NDS1 E	Cd	2.3E-07	3.4E-11	7.0E-09	2.3E-04	3.4E-08	7.0E-04	9.3E-04	Negligible risk
	Zn	8.3E-05	1.2E-08	2.5E-06	2.8E-04	4.1E-08	4.2E-05	3.2E-04	Negligible risk
	Cu	2.6E-05	3.8E-09	7.9E-07	6.5E-04	9.5E-08	6.6E-05	7.1E-04	Negligible risk
	Pb	2.1E-05	3.1E-09	6.5E-07	1.5E-02	8.9E-07	1.2E-03	1.7E-02	Negligible risk
	Mn	2.9E-04	4.3E-08	9.0E-06	6.4E-03	9.4E-07	4.9E-03	1.1E-02	Negligible risk
NDS2 S	Cd	2.3E-07	3.4E-11	7.0E-09	2.3E-04	3.4E-08	7.0E-04	9.3E-04	Negligible risk
	Zn	4.3E-05	6.3E-09	1.3E-06	1.4E-04	2.1E-08	2.2E-05	1.6E-04	Negligible risk
	Cu	2.1E-05	3.1E-09	6.4E-07	5.3E-04	7.8E-08	5.4E-05	5.8E-04	Negligible risk
	Pb	1.9E-05	2.8E-09	5.7E-07	1.3E-02	7.9E-07	1.1E-03	1.5E-02	Negligible risk
	Mn	2.9E-04	4.3E-08	8.8E-06	6.3E-03	9.3E-07	4.8E-03	1.1E-02	Negligible risk
NDS2 M	Cd	6.6E-07	9.7E-11	2.0E-08	6.6E-04	9.7E-08	2.0E-03	2.7E-03	Negligible risk
	Zn	3.0E-05	4.5E-09	9.2E-07	1.0E-04	1.5E-08	1.5E-05	1.2E-04	Negligible risk
	Cu	1.8E-05	2.6E-09	5.4E-07	4.4E-04	6.5E-08	4.5E-05	4.9E-04	Negligible risk
	Pb	2.1E-05	3.0E-09	6.2E-07	1.5E-02	8.6E-07	1.2E-03	1.6E-02	Negligible risk
	Mn	3.0E-04	4.4E-08	9.0E-06	6.4E-03	9.5E-07	4.9E-03	1.1E-02	Negligible risk
NDS2 E	Cd	6.6E-07	9.7E-11	2.0E-08	6.6E-04	9.7E-08	2.0E-03	2.7E-03	Negligible risk
	Zn	5.4E-05	8.0E-09	1.7E-06	1.8E-04	2.7E-08	2.8E-05	2.1E-04	Negligible risk
	Cu	2.8E-05	4.1E-09	8.4E-07	6.9E-04	1.0E-07	7.0E-05	7.6E-04	Negligible risk
	Pb	2.7E-05	4.0E-09	8.3E-07	2.0E-02	1.1E-06	1.6E-03	2.1E-02	Negligible risk
	Mn	4.6E-04	6.8E-08	1.4E-05	1.0E-02	1.5E-06	7.7E-03	1.8E-02	Negligible risk
SSL S	Cd	1.5E-06	2.2E-10	4.6E-08	1.5E-03	2.2E-07	4.6E-03	6.1E-03	Negligible risk
	Zn	3.9E-05	5.8E-09	1.2E-06	1.3E-04	1.9E-08	2.0E-05	1.5E-04	Negligible risk
	Cu	5.5E-05	8.1E-09	1.7E-06	1.4E-03	2.0E-07	1.4E-04	1.5E-03	Negligible risk

	Pb	8.1E-05	1.2E-08	2.5E-06	5.8E-02	3.4E-06	4.7E-03	6.2E-02	Negligible risk
	Mn	2.8E-04	4.1E-08	8.4E-06	6.0E-03	8.8E-07	4.6E-03	1.1E-02	Negligible risk
SSL M	Cd	2.0E-06	2.9E-10	5.9E-08	2.0E-03	2.9E-07	5.9E-03	7.9E-03	Negligible risk
	Zn	5.0E-05	7.3E-09	1.5E-06	1.7E-04	2.4E-08	2.5E-05	1.9E-04	Negligible risk
	Cu	5.2E-05	7.7E-09	1.6E-06	1.3E-03	1.9E-07	1.3E-04	1.4E-03	Negligible risk
	Pb	7.5E-05	1.1E-08	2.3E-06	5.4E-02	3.1E-06	4.4E-03	5.8E-02	Negligible risk
	Mn	2.7E-04	4.0E-08	8.3E-06	6.0E-03	8.8E-07	4.5E-03	1.1E-02	Negligible risk
SSL E	Cd	2.0E-06	2.9E-10	5.9E-08	2.0E-03	2.9E-07	5.9E-03	7.9E-03	Negligible risk
	Zn	4.8E-05	7.1E-09	1.5E-06	1.6E-04	2.4E-08	2.5E-05	1.9E-04	Negligible risk
	Cu	2.3E-05	3.4E-09	6.9E-07	5.7E-04	8.4E-08	5.8E-05	6.3E-04	Negligible risk
	Pb	2.2E-05	3.3E-09	6.8E-07	1.6E-02	9.3E-07	1.3E-03	1.7E-02	Negligible risk
	Mn	3.3E-04	4.8E-08	1.0E-05	7.1E-03	1.1E-06	5.4E-03	1.3E-02	Negligible risk
Total	Cd	8.4E-07	1.2E-10	2.6E-08	8.4E-04	1.2E-07	2.6E-03	3.4E-03	Negligible risk
	Zn	5.1E-05	7.5E-09	1.6E-06	1.7E-04	2.5E-08	2.6E-05	2.0E-04	Negligible risk
	Cu	3.1E-05	4.5E-09	9.4E-07	7.7E-04	1.1E-07	7.8E-05	8.5E-04	Negligible risk
	Pb	3.4E-05	5.0E-09	1.0E-06	2.4E-02	1.4E-06	2.0E-03	2.6E-02	Negligible risk
	Mn	3.1E-04	4.6E-08	9.6E-06	6.8E-03	1.0E-06	5.2E-03	1.2E-02	Negligible risk

ADDing (Chronic daily intake by ingestion); ADDinh (Chronic daily intake by inhalation); ADDderm (Chronic daily intake by dermal contact); HQ (Hazard quotient); HI (Hazard Index)

3.8. Conclusion

- This is the first study done on the occurrence and distribution of HMs and MPs in agricultural soils irrigated with wastewater in Okara City.
- The current study experienced various degree of HMs contamination in following order: Fe > Mn > Zn > Pb > Cu > Cd. Accumulation and distribution of HMs in wastewater irrigated surface soils were affected by soil physicochemical properties such as soil pH, EC, WHC, OM and soil texture.
- The abundance of MPs (5mm - <500 µm) in wastewater irrigated surface soils ranged from 1850- 5300 particles kg^{-1}. The MPs <500µm accounted 31% suggested their dominant role. The most prevalent shape of MPs was fragments accounted 49.6% followed by fibers 38.8% and films 11.5%. MPs abundance in agricultural soil irrigated with SSL was higher than the wastewater irrigated soil from other disposal stations but without any statistically significant variation.
- MPs showed correlation with HMs content in the wastewater irrigated surface soils. Positive correlation between HMs and MPs attributed to their common source of contamination and MPs ability to adsorb organic molecules to enhance HMs concentration in soil while negative correlation between HMs and MPs revealed MPs ability to adsorb HMs on their surface and decrease their bioavailability.
- In present study pollution indices and human health risk assessment via non-dietary intake for HMs contamination was calculated and results indicated low ecological and negligible health risks for both adults and children. However, children showed more vulnerability and susceptibility via HMs contamination in wastewater irrigated surface soils.

3.9. Recommendations

- The co-occurrence of HMs and MPs might present ecological risks and pose potential adverse impacts on soil organisms. Monitoring of HMs levels and MPs contamination in the soil profile of the region and remediation programs are recommended for future management strategies.

- There is need to include other sources like agricultural products (maize, sugarcane, wheat, vegetables) grown in similar conditions to predict human health risks.

References

Abbasi, S., Keshavarzi, B., Moore, F., Delshab, H., Soltani, N., & Sorooshian, A. (2017). Investigation of microrubbers , microplastics and heavy metals in street dust : a study in Bushehr city , Iran. *Environmental Earth Sciences*, *76*(23), 1–19. https://doi.org/10.1007/s12665-017-7137-0

Abd-Elwahed, M. S. (2018). Influence of long-term wastewater irrigation on soil quality and its spatial distribution. *Annals of Agricultural Sciences*, *63*(2), 191–199. https://doi.org/10.1016/j.aoas.2018.11.004

Adimalla, N., Qian, H., & Wang, H. (2019). Assessment of heavy metal (HM) contamination in agricultural soil lands in northern Telangana, India: an approach of spatial distribution and multivariate statistical analysis. *Environmental Monitoring and Assessment*, *191*(4). https://doi.org/10.1007/s10661-019-7408-1

Ahmad, T., Amjad, M., Iqbal, Q., Batool, A., Noor, A., Jafir, M., Hussain, H., & Irfan, M. (2022). Occurrence of Microplastics and Heavy Metals in Aquatic and Agroecosystem: A Case Study. *Bulletin of Environmental Contamination and Toxicology*, *109*(2), 266–271. https://doi.org/10.1007/s00128-022-03523-5

Ahmadpour, P., Ahmadpour, F., & Sadeghi, S. (2015). Evaluation of Four Plant Species for Phytoremediation of Copper-Contaminated Soil. In *Soil Remediation and Plants*. Elsevier Inc. https://doi.org/10.1016/B978-0-12-799937-1.00007-3

Aiman, U., Mahmood, A., Waheed, S., & Malik, R. N. (2016). Enrichment, geo-accumulation and risk surveillance of toxic metals for different environmental compartments from Mehmood Booti dumping site, Lahore city, Pakistan. *Chemosphere*, *144*, 2229–2237. https://doi.org/10.1016/j.chemosphere.2015.10.077

Alnaimy, M. A., Shahin, S. A., Vranayova, Z., Zelenakova, M., & Abdel-Hamed, E. M. W. (2021). Long-term impact of wastewater irrigation on soil pollution and degradation: A case study from Egypt. *Water (Switzerland)*, *13*(16), 1–15.

https://doi.org/10.3390/w13162245

Ashraf, I., Ahmad, F., Sharif, A., Altaf, A. R., & Teng, H. (2021). Heavy metals assessment in water, soil, vegetables and their associated health risks via consumption of vegetables, District Kasur, Pakistan. *SN Applied Sciences*, *3*(5), 1–16. https://doi.org/10.1007/s42452-021-04547-y

Bajt, O. (2021). From plastics to microplastics and organisms. *FEBS Open Bio*, *11*(4), 954–966. https://doi.org/10.1002/2211-5463.13120

Barakat, A., Ennaji, W., Krimissa, S., & Bouzaid, M. (2020). Heavy metal contamination and ecological-health risk evaluation in peri-urban wastewater-irrigated soils of Beni-Mellal city (Morocco). *International Journal of Environmental Health Research*, *30*(4), 372–387. https://doi.org/10.1080/09603123.2019.1595540

Boughattas, I., Hattab, S., Zitouni, N., Mkhinini, M., Missawi, O., Bousserrhine, N., & Banni, M. (2021). Assessing the presence of microplastic particles in Tunisian agriculture soils and their potential toxicity effects using Eisenia andrei as bioindicator. *Science of the Total Environment*, *796*, 148959. https://doi.org/10.1016/j.scitotenv.2021.148959

Cao, Y., Zhao, M., Ma, X., Song, Y., Zuo, S., Li, H., & Deng, W. (2021). A critical review on the interactions of microplastics with heavy metals: Mechanism and their combined effect on organisms and humans. *Science of the Total Environment*, *788*, 147620. https://doi.org/10.1016/j.scitotenv.2021.147620

Chaoua, S., Boussaa, S., El Gharmali, A., & Boumezzough, A. (2019). Impact of irrigation with wastewater on accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco. *Journal of the Saudi Society of Agricultural Sciences*, *18*(4), 429–436. https://doi.org/10.1016/j.jssas.2018.02.003

Chia, R. W., Lee, J. Y., Jang, J., Kim, H., & Kwon, K. D. (2022). Soil health and microplastics: a review of the impacts of microplastic contamination on soil properties. *Journal of Soils and Sediments*, *22*(10), 2690–2705. https://doi.org/10.1007/s11368-022-03254-4

Ding, L., Zhang, S., Wang, X., Yang, X., Zhang, C., Qi, Y., & Guo, X. (2020). The occurrence and distribution characteristics of microplastics in the agricultural soils of Shaanxi Province, in north-western China. *Science of the Total Environment*, *720*, 137525. https://doi.org/10.1016/j.scitotenv.2020.137525

Dotaniya, M. L., Rajendiran, S., Meena, V. D., Coumar, M. V., Saha, J. K., Kundu, S., & Patra, A. K. (2018). Impact of Long-Term Application of Sewage on Soil and Crop Quality in Vertisols of Central India. *Bulletin of Environmental Contamination and Toxicology*, *101*(6), 779–786. https://doi.org/10.1007/s00128-018-2458-6

Drozdova, J., Raclavska, H., Raclavsky, K., & Skrobankova, H. (2019). Heavy metals in domestic wastewater with respect to urban population in Ostrava, Czech Republic. *Water and Environment Journal*, *33*(1), 77–85. https://doi.org/10.1111/wej.12371

Ghouma, A., Aydi, A., Martin, J. A. R., & Gasmi, M. (2022). Health risk assessment associated to heavy metal pollution levels in Mediterranean environment soils: a case study in the watershed of Sebkhet Ariana, Tunisia. *Arabian Journal of Geosciences*, *15*(8). https://doi.org/10.1007/s12517-022-09877-8

Han, J., Shi, J., Zeng, L., Xu, J., & Wu, L. (2015). Effects of nitrogen fertilization on the acidity and salinity of greenhouse soils. *Environmental Science and Pollution Research*, *22*(4), 2976–2986. https://doi.org/10.1007/s11356-014-3542-z

Harms, I. K., Diekötter, T., Troegel, S., & Lenz, M. (2021). Amount, distribution and composition of large microplastics in typical agricultural soils in Northern Germany. *Science of the Total Environment*, *758*, 143615. https://doi.org/10.1016/j.scitotenv.2020.143615

Hidalgo-ruz, V., Gutow, L., Thompson, R. C., & Thiel, M. (2012). *Microplastics in the Marine Environment: A Review of the Methods Used for Identification and Quantification*.

Hou, S., Zheng, N., Tang, L., Ji, X., & Li, Y. (2019). Effect of soil pH and organic matter content on heavy metals availability in maize (Zea mays L.) rhizospheric soil of non-ferrous metals smelting area. *Environmental Monitoring and Assessment*, *191*(10).

https://doi.org/10.1007/s10661-019-7793-5

Ihedioha, J. N., Ukoha, P. O., & Ekere, N. R. (2017). Ecological and human health risk assessment of heavy metal contamination in soil of a municipal solid waste dump in Uyo, Nigeria. *Environmental Geochemistry and Health*, *39*(3), 497–515. https://doi.org/10.1007/s10653-016-9830-4

Iqbal, M., Ahmed, S., Rehman, W., Menaa, F., & Ullah, M. A. (2020). Heavy metal levels in vegetables cultivated in Pakistan soil irrigated with untreated wastewater: Preliminary results. *Sustainability (Switzerland)*, *12*(21), 1–19. https://doi.org/10.3390/su12218891

Iqbal, Z., Abbas, F., Ibrahim, A. M. M., Yamin, M. G. M., & Imtiaz, B. A. M. (2022). Human health risk of heavy metal contamination in groundwater and source apportionment. *International Journal of Environmental Science and Technology*, *19*(8), 7251–7260. https://doi.org/10.1007/s13762-021-03611-9

Jadoon, W. A., & Malik, R. N. (2019). Geochemical approach for heavy metals in suburban agricultural soils of Sialkot, Pakistan. *SN Applied Sciences*, *1*(2), 1–11. https://doi.org/10.1007/s42452-019-0167-3

Kanwal, S., Sajjad, M., Farooq, H., & Hussain, E. (2020). Towards sustainable wastewater management : A spatial multi-criteria framework to site the Land-FILTER system in a complex urban environment. *Journal of Cleaner Production*, *266*, 121987. https://doi.org/10.1016/j.jclepro.2020.121987

Karimi, A., Naghizadeh, A., Biglari, H., Peirovi, R., Ghasemi, A., & Zarei, A. (2020). Assessment of human health risks and pollution index for heavy metals in farmlands irrigated by effluents of stabilization ponds. *Environmental Science and Pollution Research*, *27*(10), 10317–10327. https://doi.org/10.1007/s11356-020-07642-6

Khalid, N., Aqeel, M., Noman, A., Khan, S. M., & Akhter, N. (2021). Interactions and effects of microplastics with heavy metals in aquatic and terrestrial environments. *Environmental Pollution*, *290*(September), 118104. https://doi.org/10.1016/j.envpol.2021.118104

Khalid, S., Shahid, M., Khan, N., Murtaza, B., Bibi, I., & Dumat, C. (2017). A comparison of technologies for remediation of heavy metal contaminated soils. *Journal of Geochemical Exploration*, *182*, 247–268. https://doi.org/10.1016/j.gexplo.2016.11.021

Lang, M., Wang, G., Yang, Y., Zhu, W., Zhang, Y., Ouyang, Z., & Guo, X. (2022). The occurrence and effect of altitude on microplastics distribution in agricultural soils of Qinghai Province, northwest China. *Science of the Total Environment*, *810*, 152174. https://doi.org/10.1016/j.scitotenv.2021.152174

Li, J., Peng, D., Ouyang, Z., Liu, P., Fang, L., & Guo, X. (2022). Occurrence status of microplastics in main agricultural areas of Xinjiang Uygur Autonomous Region, China. *Science of the Total Environment*, *828*, 154259. https://doi.org/10.1016/j.scitotenv.2022.154259

Libohova, Z., Seybold, C., Wysocki, D., Wills, S., Schoeneberger, P., Williams, C., Lindbo, D., Stott, D., & Owens, P. R. (2018). Reevaluating the effects of soil organic matter and other properties on available water-holding capacity using the National Cooperative Soil Survey Characterization Database. *Journal of Soil and Water Conservation*, *73*(4), 411–421. https://doi.org/10.2489/jswc.73.4.411

Liu, X., Lin, H., Xu, S., Yan, Y., Yu, R., & Hu, G. (2022). Occurrence, distribution, and characteristics of microplastics in agricultural soil around a solid waste treatment center in southeast China. *Journal of Soils and Sediments*, *2019*. https://doi.org/10.1007/s11368-022-03341-6

Ma, S., Hu, Y., Wang, W., Zhang, Q., Wang, R., & Nan, Z. (2023). Exploring the safe utilization strategy of calcareous agricultural land irrigated with wastewater for over 50 years. *Science of the Total Environment*, *863*(December 2022), 160994. https://doi.org/10.1016/j.scitotenv.2022.160994

Mohammadi, A. A., Zarei, A., Esmaeilzadeh, M., Taghavi, M., Yousefi, M., Yousefi, Z., Sedighi, F., & Javan, S. (2020). Assessment of Heavy Metal Pollution and Human Health Risks Assessment in Soils Around an Industrial Zone in Neyshabur, Iran.

Biological Trace Element Research, *195*(1), 343–352. https://doi.org/10.1007/s12011-019-01816-1

Muhammad, N., Sana, S., Behzad, K., Anwar, H., Haidar, A., Aneeza, S., & Zunaira, S. (2020). A critical analysis of wastewater use in agriculture and associated health risks in Pakistan. *Environmental Geochemistry and Health*, *3*. https://doi.org/10.1007/s10653-020-00702-3

Natasha, N., Shahid, M., Murtaza, B., Bibi, I., Khalid, S., Al-Kahtani, A. A., Naz, R., Ali, E. F., Niazi, N. K., Rinklebe, J., & Shaheen, S. M. (2022). Accumulation pattern and risk assessment of potentially toxic elements in selected wastewater-irrigated soils and plants in Vehari, Pakistan. *Environmental Research*, *214*(July). https://doi.org/10.1016/j.envres.2022.114033

Natasha, Shahid, M., Niazi, N. K., Khalid, S., Murtaza, B., Bibi, I., & Rashid, M. I. (2018). A critical review of selenium biogeochemical behavior in soil-plant system with an inference to human health. *Environmental Pollution*, *234*, 915–934. https://doi.org/10.1016/j.envpol.2017.12.019

Omran, E. S. E. (2016). Environmental modelling of heavy metals using pollution indices and multivariate techniques in the soils of Bahr El Baqar, Egypt. *Modeling Earth Systems and Environment*, *2*(3), 1–17. https://doi.org/10.1007/s40808-016-0178-7

Pagter, E., Nash, R., & Connor, I. O. (2018). *Standardised protocol for monitoring microplastics in sediments*. *May*. https://doi.org/10.13140/RG.2.2.36256.89601/1

Park, S. Y., & Kim, C. G. (2022). A comparative study on the distribution behavior of microplastics through FT-IR analysis on different land uses in agricultural soils. *Environmental Research*, *215*(P2), 114404. https://doi.org/10.1016/j.envres.2022.114404

Pérez-Reverón, R., González-Sálamo, J., Hernández-Sánchez, C., González-Pleiter, M., Hernández-Borges, J., & Díaz-Peña, F. J. (2022). Recycled wastewater as a potential source of microplastics in irrigated soils from an arid-insular territory (Fuerteventura, Spain). *Science of the Total Environment*, *817*.

https://doi.org/10.1016/j.scitotenv.2021.152830

Piehl, S., Leibner, A., Löder, M. G. J., Laforsch, C., & Bogner, C. (2018). *Identification and quantification of macro- and microplastics on an agricultural farmland*. 1–9. https://doi.org/10.1038/s41598-018-36172-y

Rafique, N., & Tariq, S. R. (2016). Distribution and source apportionment studies of heavy metals in soil of cotton/wheat fields. *Environmental Monitoring and Assessment*, *188*(5). https://doi.org/10.1007/s10661-016-5309-0

Ragoobur, D., Huerta-lwanga, E., & Devi, G. (2021). Science of the Total Environment Microplastics in agricultural soils , wastewater ef fl uents and sewage sludge in Mauritius. *Science of the Total Environment*, *798*, 149326. https://doi.org/10.1016/j.scitotenv.2021.149326

Razzaq, A., Rehman, A., Qureshi, A. H., Javed, I., Saqib, R., & Iqbal, M. N. (2018). An economic analysis of high efficiency irrigation systems in Punjab, Pakistan. *Sarhad Journal of Agriculture*, *34*(4), 818–826. https://doi.org/10.17582/journal.sja/2018/34.4.818.826

Rezapour, S., Atashpaz, B., Moghaddam, S. S., Kalavrouziotis, I. K., & Damalas, C. A. (2019). Cadmium accumulation, translocation factor, and health risk potential in a wastewater-irrigated soil-wheat (Triticum aestivum L.) system. *Chemosphere*, *231*, 579–587. https://doi.org/10.1016/j.chemosphere.2019.05.095

Rodrigues, M. O., Abrantes, N., Gonçalves, F. J. M., Nogueira, H., Marques, J. C., & Gonçalves, A. M. M. (2018). Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). *Science of the Total Environment*, *633*, 1549–1559. https://doi.org/10.1016/j.scitotenv.2018.03.233

Sarwar, T., Shahid, M., Natasha, Khalid, S., Shah, A. H., Ahmad, N., Naeem, M. A., ul Haq, Z., Murtaza, B., & Bakhat, H. F. (2020). Quantification and risk assessment of heavy metal build-up in soil–plant system after irrigation with untreated city wastewater in Vehari, Pakistan. *Environmental Geochemistry and Health*, *42*(12), 4281–4297. https://doi.org/10.1007/s10653-019-00358-8

Seufert, P. (2013). *The FAO Voluntary Guidelines on the Responsible Governance of Tenure of Land , Fisheries and Forests The FAO Voluntary Guidelines on the Responsible*. *7731*. https://doi.org/10.1080/14747731.2013.764157

Shahid, M., Dumat, C., Khalid, S., Schreck, E., Xiong, T., & Niazi, N. K. (2017). Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *Journal of Hazardous Materials*, *325*, 36–58. https://doi.org/10.1016/j.jhazmat.2016.11.063

Stevanović, V., Gulan, L., Milenković, B., Valjarević, A., Zeremski, T., & Penjišević, I. (2018). Environmental risk assessment of radioactivity and heavy metals in soil of Toplica region, South Serbia. *Environmental Geochemistry and Health*, *40*(5), 2101–2118. https://doi.org/10.1007/s10653-018-0085-0

Sun, J. T., Shi, S. C., Wang, D., Zhang, F., Chen, H., Liu, Y., & Liu, H. (2012). Methods of Soil, Plant, and Water Analysis: A manual for the West Asia and North Africa region. *Huanan Ligong Daxue Xuebao/Journal of South China University of Technology (Natural Science)*, *40*(7), 83–89. https://doi.org/10.3969/j.issn.1000-565X.2012.07.015

Tariq, F. S. (2021). Heavy metals concentration in vegetables irrigated with municipal wastewater and their human daily intake in Erbil city. *Environmental Nanotechnology, Monitoring and Management*, *16*(March), 100475. https://doi.org/10.1016/j.enmm.2021.100475

Turekian, K. K., Haven, N., Hans, K., & Universitat, W. M. Der. (1961). KARL K. TUREKIAN Dept. Geology, Yale University, New Haven, Conn. KARL HANS WEDEPOHL Mineralogische-Institut der Universitat, Gottingen, Germany Distribution of the Elements in Some Major Units of the Earth's Crust. *America*, *February*, 175–192.

van den Berg, P., Huerta-Lwanga, E., Corradini, F., & Geissen, V. (2020). Sewage sludge application as a vehicle for microplastics in eastern Spanish agricultural soils. *Environmental Pollution*, *261*, 114198. https://doi.org/10.1016/j.envpol.2020.114198

Wang, Y., Li, F., Song, J., Xiao, R., Luo, L., Yang, Z., & Chai, L. (2018). Stabilization of Cd-, Pb-, Cu- and Zn-contaminated calcareous agricultural soil using red mud: a field experiment. *Environmental Geochemistry and Health*, *40*(5), 2143–2153. https://doi.org/10.1007/s10653-018-0089-9

Weber, C. J., Weihrauch, C., Opp, C., & Chifflard, P. (2021). Investigating microplastic dynamics in soils: Orientation for sampling strategies and sample pre-procession. *Land Degradation and Development*, *32*(1), 270–284. https://doi.org/10.1002/ldr.3676

Xiao, H., Shahab, A., Li, J., Xi, B., Sun, X., He, H., & Yu, G. (2019). Ecotoxicology and Environmental Safety Distribution , ecological risk assessment and source identification of heavy metals in surface sediments of Huixian karst wetland , China. *Ecotoxicology and Environmental Safety*, *185*(May), 109700. https://doi.org/10.1016/j.ecoenv.2019.109700

Yu, L., Zhang, J. Di, Liu, Y., Chen, L. Y., Tao, S., & Liu, W. X. (2021). Distribution characteristics of microplastics in agricultural soils from the largest vegetable production base in China. *Science of the Total Environment*, *756*, 1–9. https://doi.org/10.1016/j.scitotenv.2020.143860

Zhang, G. S., & Liu, Y. F. (2018). The distribution of microplastics in soil aggregate fractions in southwestern China. *Science of the Total Environment*, *642*, 12–20. https://doi.org/10.1016/j.scitotenv.2018.06.004

Zhou, Y., Liu, X., & Wang, J. (2019). Characterization of microplastics and the association of heavy metals with microplastics in suburban soil of central China. *Science of the Total Environment*, *694*, 133798. https://doi.org/10.1016/j.scitotenv.2019.133798

Annexure

Annexure 1.1: Depicting MPs abundance, shapes and colors in wastewater irrigated surface soils of Okara, Pakistan

Locations	**Statistics**	**MPs abundance**	**MPs shapes**			**MPs Color**						
			Fiber	**Fragment**	**Film**	**Black**	**Blue**	**Red**	**Green**	**Multi**	**Transparent**	**Others**
NDS1 S	Mean±SD	3050±354	1500±3	1250±8	300±1	650±4	350±1	400±4	50±1	50±1	600±7	100±1
NDS1 M	Mean±SD	3000±424	1350±1	1500±1	150±2	1150±4	250±2	550±1	0±0	0±0	150±1	50±1
NDS1 E	Mean±SD	4800±141	2200±1	1850±1	750±1	1200±3	500±3	550±5	100±1	50±1	700±3	150±1
NDS2 S	Mean±SD	2950±1061	1650±2	1150±13	150±1	1000±6	100±0	800±3	100±1	100±0	350±1	250±1
NDS2 M	Mean±SD	1850±71	600±1	1000±4	250±2	600±3	50±1	300±1	0±0	100±1	400±3	0±0
NDS2 E	Mean±SD	3300±1697	1050±4	1900±8	350±5	1600±8	200±0	500±1	0±0	50±1	350±5	200±1
SSL S	Mean±SD	3750±71	1150±2	2050±30	550±4	1450±6	400±4	400±1	100±0	150±2	450±2	200±0
SSL M	Mean±SD	4450±636	1650±5	2500±10	300±1	1350±1	300±3	450±1	150±2	100±1	650±4	200±0
SSL E	Mean±SD	5300±3253	1650±9	3150±12	500±0	1700±11	200±0	400±4	400±4	150±2	800±6	400±4

Annexure 1.2: Classes of Contamination Factor

CF	Category
CF < 1	Low contamination
1 ≥ CF ≥ 3	Moderate contamination
3 ≥ CF ≥ 6	Considerable
CF ≥ 6	Very high

Annexure 1.3: Igeo classes with respect to soil quality

Classes	Value	Soil quality
0	<0	Practically uncontaminated
1	0–1	Uncontaminated to moderately uncontaminated
2	1–2	Moderately contaminated
3	2–3	Moderately to heavily contaminated
4	3–4	Heavily contaminated
5	4–5	Heavily to extremely contaminated
6	> 5	Extremely contaminated