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Industrial effluents and environmental contamination of sludge water heavy metals in Warangal District of Telangana (INDIA)

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Abstract

Present study aimed to investigate the Heavy metals in industrial effluent waste water of Warangal City. The samples were collected seasonally in the month of September 2019 to March 2022. These samples were subjected to analysis for six elements like Cd, Cr, Cu, Ni, Pb and Zn. Samples were acid digested using HNO_3, HCL and DH_2O for Hot plate digestion. The samples analyzed in PPM (parts per million) by SHIMADZU AA-6300 Atomic Absorption Spectroscopy. Concentration level of toxic metals fallowed in three seasons Cu>Cr>Zn>Pb>Cd>Ni. Then samples were compared with WHO for drinking water guidelines.

Keywords: industrial waste water, Heavy metals, AAS, Warangal district.

1. Introduction

Warangal is the second largest and heritage city in the newly formed Telangana state. There are no of Leather industrial units and plenty of skin hides are located in the city. Leather tanning industries in the Deshaipet, Chinnawadepally and Enumamula is the biggest and most famous. The existing leather units in the Warangal city do not have modern technically advanced state of art processing unit leads environmental contamination and health problems in the current city (CDP-WMC). Leather tanning refers to the process where raw hides of animals are converted into leather, here after called tanning industry. There are many small scale industrial units such a beedi making factory, dairy product, granite slab polishing, rice mills, oil mills, cotton ginning mills etc. There are number of textile industries in the region which fallows, handlooms, power looms, wool, garment manufacturing and yarn seizing corporate societies. Effluents from the tanneries are discharged in to streams which drain into ponds, thereby polluting the water sources and cultivable land.

In case of leather tanning industry, untreated tannery effluents contain large variety of heavy metals. Once tannery effluents are discharged into water, these metals rapidly partition as dissolved, suspended particulate and sediment metals and contaminate soil[12]. Persistent pollutants from effluents get accumulated in the soil. The buffering capacity of soil is exhausted and detrimental effects on the quality of groundwater starts setting in over time. Studies show that when agricultural land is irrigated by the groundwater or surface water contaminated with tannery effluent, the productivity of soil decreases even when tannery wastage were applied on the field under control conditions[21].

Occupational exposure to elevated levels of heavy metals, associated oxidative stress, and health risks in exposed workers have been reported previously in leather industries worldwide [7]. Exposure to heavy metals in the leather industries has been implicated as the causative agent for many health hazards as documented by many authors in the past. For example, a cross-sectional survey from Kanpur, India have demonstrated the higher prevalence of medical complaints in the form of hand dermatitis, asthma, and low back trouble in the workers[5].

Industrialization and unplanned urbanization have greatly transformed the natural environment. In recent times, the environment has become hostile, posing threat to health and welfare due to release of pollutants from industries and urban sewage[18]. The effluents discharged from industries and urban sewage may find their way into surface water bodies via canals and surface run-off. These water bodies, such as lagoons, ponds, and lakes, thus receive pollutants and become vulnerable. The tannery industry, which uses a variety of chemicals in the tanning process, is recognized as a major contributor of heavy metals to the environment and poses serious environmental threats worldwide. The effluents discharged from tannery industry contain a bulk amount of liquid and solid wastes with substantial quantities of toxic chemicals (sodium sulfate, sodium hydroxide, sodium hydrosulfate, arsenic sulfide, calcium hydrosulfate, dimethyle amine, sodium sulphydrate, and chromium sulfate; Banglapedia. 2006) and other heavy toxic trace metals, organic matter, lime, and sulfide[22]. In addition, several footwear, animal glue, and paint industries, which are commonly clustered with tannery industries, also release some amount of toxic chemicals from their operations. According to Landgrave (1995), about 40,000 tons of basic chemicals and 15,000 tons of chromium salt (as chromium sulfate) are used every year in the world. The general practice in most developing countries is that the untreated effluents discharged from the tanning units is stored in large lagoons or released into open canal[20]. The environmental issues due to globalization and rapid industrialization are becoming more and more nuisance for human being. Therefore efficient and effective methods are needed especially for chemical industries. Most of the elements falls into this category are highly water soluble, well-known toxics and carcinogenic agents. Heavy metals are considered to be the following elements: Copper, Silver, Zinc, Cadmium, Gold, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Molybdenum, Cobalt, Manganese, and Aluminium. They represent serious threats to the human population and the fauna and flora of the receiving water bodies[3].

Contamination of soils by heavy metals, such as Cd, Ni, Zn, Pb, and Cu, has increased dramatically during the last few decades[6] due to mining, smelting, manufacturing, use of agricultural fertilizers and pesticides, municipal waste, traffic emissions, and industrial effluents[6,7]. Although heavy metals widely exist in natural environments, heavy metal pollution is undoubtedly accelerated by anthropogenic activities. In addition, the food chain, which serves as the main intake of pollutants by humans, can cause severe long-term health problems at both local scales, such as enclosed water systems and global scales[9,10,14,23]. Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others[15].

Industrial effluents urban runoffs direct various disposals of wastes into the water bodies' agricultural fertilizer and animal wastes remain the major water contaminants. Pollutants are directly discharged through industrial plants and municipal sewage treatment plants, others come from polluted runoff in urban and agricultural areas, and some are the result of historical contamination.In the environment, Heavy metals are toxic and resist to biodegradation which are discharging pollutants from industrial wastewater. Disposal of effluents from the industries has resulted in serious contamination of numerous sites. Numerous metals such as Pb, Cr, Cu, Zn, Hg, Cd etc. have toxic effects on human's health and also non-renewable resources. Contamination of lakes and streams by the presence of heavy metals from the natural ecosystem, as pollutants adsorption on to the soil and then to lakes etc. has cause the serious problem to human health[25].Long-term disposal of tannery wastes has resulted in extensive contamination of agricultural land and water sources in many parts of India. The tannery industry mushrooming in North India has converted the Ganga River into a dumping ground. Pollution becomes acute when tanneries areconcentrated in clusters in small area like Kanpur[8]. Chromium (Cr), a toxic heavy metal, is a major contaminant in tannery wastes, and its accumulation in soil and water is an environmental issue of increasing public concern in India.

2. Materials and methods

2.1. Sample collection

The samples are collected from different time intervals like Monsoon, Post monsoon and pre monsoon seasons in throughout the year from month of September 2019 to March 2022 at two different sites in and around Warangal Metropolitan City, are followed by 1. Chinnawadepally pond industrial site,
2. Deshaipet drainage industrial site. Shown in Fig.1.

All chemicals and reagents used in this study were of analytical and trace metal grades. Trace metal grades 65 % HNO_3 (Nitric acid), 37 % HCL (Hydrochloric acid) and Double deionised water (pH 6.5±7.0) obtain from zeal chemicals & Co., hanamkonda, Warangal.

Water Samples of industrial sites were collected in 1litre polyethylene bottles during these seasons of the year from adjoining areas of Warangal City. The samples are properly labelled before collecting and kept in 1 litre polyethylene bottles. Which have been washed two times with sewage water before collecting of sample. The sample bottles were tightly covered immediately. After collection samples brought into laboratory for further investigation.

2.2. Method A (nitric acid-hydrochloric acid digestion)

Out of 1Litre, we had taken 100 mL of water sample was placed in 250 mL beaker add 10 mL of freshly prepared acid mixture of 65 % HNO_3 and 10 mL of 37 % HCL was added. Then, the mixture was heated gently over a Hot plate (95 °C ± 5 ^{o}C) for 1-2 h or (until the sample had completely dissolved)[1].Then cool at room temperature the sample volume is reduced up to 20-30 mL. During the digestion procedures, the inner walls of the beakers were washed with 2 mL of deionized water to prevent the loss of the sample, and at the last part of the digestion processes, the samples were filtered with Whatman 42 (pore sized) filter paper. Then, a sufficient amount of deionized water was added to make the final volume up to 100 mL. Method was performed in triplicate for each sample. Keep samples at -4 ^{o}C until analysis.

2.3. Atomic Absorption Analysis of samples

The digested samples were analyzed for heavy metals using SHIMADZOO-6300 Model Atomic Absorption Spectrophotometer (WizAArd software), at Team Labs & Consultants (Environmental pollution control centre), Ameerpet, Hyderabad and CPCB Sanathnagar, Hyderabad.

2. Results and discussion

In the present investigation a total of six heavy metals were recorded in two industrial sites which include Cadmium, Chromium, Copper, Nickel, Lead and Zink. The data collected on these trace heavy metals were analyzed during September 2019 to march 2022, is shown in Figure 2 and 3. Results of evaluated heavy metal parameters of the wastewater effluents were compared against WHO for effluent discharge seasonally (Monsoon, Post Monsoon and Pre Monsoon seasons). The profiles of the heavy metal analysis of the industrial effluent water samples obtained at the Chinnawadepally and Deshaipet are depicted in Table 1and 2.

3.1. Cadmium (Cd):

The main sources of cadmium pollution in these industrial sites are plastic wastes, car repairing exhaust and other sewage domestic wastes. During study period Cadmium concentration at Chinnawadepally industrial site water sample was from monsoon of 2019 to pre monsoon 2022 the highest Cadmium was found in pre monsoon season of March 2022 (0.101 Mg/L) and Cadmium concentration at Deshaipet industrial site highest Cadmium was found in monsoon season of July 2021 (8.7 Mg/L). The WHO limit of Cadmium was 0.01Mg/L. Compare with Control sample and WHO both sites are more concentrated due industrial and domestic sewage effluents. Exposure of Cd leads to abdominal pain, choking, tenesmus, nephritis and wrong bone metabolism.

3.2. Chromium (Cr):

The toxicity and pollution of Chromium in Warangal is due to leather industries. Exceeding Chromium levels of Chinnawadepally site especially in Monsoon season due to painted idols and Ganesh immersion. The Chromium concentration at Chinnawadepally industrial site water sample the more level of Chromium was found in monsoon season of September 2020 (21 Mg/L) and highest Chromium concentration in Deshaipet industrial site was monsoon season of September 2020 (5.7 Mg/L). Both sites are highly compared to control sample and WHO. The WHO limit of Chromium was 0.05Mg/L. Chinnawadepally site was more concentrated compare with Deshapet site. Intake excess levels of chromium leads severe health hazards like kidney, liver and gastric related problems. Reported that the chronic exposure in the leather industries caused pulmonary disorders, such as asthma, chronic bronchitis, and pulmonary tuberculosis[19].

3.3. Copper (Cu):

In this city, Copper is most properly emitted from paper, printing, electronics, house hold wastes and textile industries etc. In Chinnawadepally industrial site water sample the highest amount of Copper was found in post monsoon season of December 2020 (36.02 Mg/L) and highest Copper concentration in Deshaipet industrial site was post monsoon season of September 2021 (16.55 Mg/L). Both sites are highly compared to WHO. The WHO limit of Copper was 2.0 Mg/L. Chinnawadepally site was two times more concentrated compare with Deshaipetsite. Lack of Copper may cause anaemia and osteoporosis. A rare inherited disorder Wilson's disease causes due to deposits of Copper in the liver brain and other organs.

Nickel (Ni): 3.4.

Nickel is used in stainless steel. Ni is highly distributed in the nature. It is an essential element. It may be potentially carcinogenic and toxic at higher levels. In Chinnawadepally industrial site water sample the more concentration of Nickel was found in pre monsoon season of March 2022 (1.921 Mg/L) and more concentration of Nickel in Deshaipet industrial site was pre monsoon season of March 2022 (2.006 Mg/L). It is slightly increased in both sites compare with WHO limits. The WHO limit of Nickel was 0.07 Mg/L. Exposure of Ni compounds causes irreversible damage to the central nervous system, cardiovascular system, lungs and gastro intestinal tract[2].

3.5. Lead (Pb):

Source of lead pollution is due to paints, lead coated pipes, storage batteries, cosmetics, house hold dust and industrial discharge. The painted idol immersion and automobile exhausts are main source to increase level of lead in sample sites. In Chinnawadepally industrial site water sample the more concentration of Lead was found in pre monsoon season of April 2020 (2.398 Mg/L) and more concentration of Lead in Deshaipet industrial site was monsoon season of September 2019 (8.5 Mg/L). It is greatly increased in both sites compare with WHO limits. The WHO limit of Lead was 0.01 Mg/L. The enormous accumulation of Lead causes anaemia, encephalitis, multiple sclerosis and neurological problems.

3.6. Zink (Zn):

Zink is naturally found in air, water and soil. The main pollution of Zink through waste combustion and fertilizers from industries. In Chinnawadepally industrial site water sample the more concentration of

Zink was found in monsoon season of September 2021 (17.78 Mg/L) and more concentration of Zink in Deshaipet industrial site was pre monsoon season of May 2021 (20.08 Mg/L). It is greatly increased in both sites compare with WHO limits. The WHO limit of Lead was 5.0 Mg/L. Presence of Zink raises the acidity of water. It may danger to many flora and fauna.

4. CONCLUSION

In conclusion present study devotes that the presence of toxic metals in industrial water samples. Concentration level of toxic metals sequence fallowed in three seasons Cu>Cr>Zn>Pb>Cd>Ni. Seasonally Cu is more abundant compare those of Cr, Pb and Zn. Cr also more increased due to leather effluents. One and all the Pb and Zn also more because ganesh and painted idol immersion in monsoon season compare with WHO for drinking water guidelines. Cd and Ni are found very less compare with above toxic elements. This study reveals that the effect of aquatic species presence of toxic metals injected through food chain. The surrounding population are also more dangerous to asthma, chronic bronchitis, abdominal pain, chocking, tenesmus and pulmonary tuberculosis.

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Table 1: Seasonal variation of heavy metals concentration at Chinnawadepally pond industrial site

Year			**2019-20**			**2020-21**			**2021-22**		
Parameter	**Control sample**	**WHO Limits**	**Monsoon**	**Post monsoon**	**Pre monsoon**	**Monsoon**	**Post monsoon**	**Pre monsoon**	**Monsoon**	**Post monsoon**	**Pre monsoon**
Cd	**0.15**	**0.01**	**0.21**	**0.29**	**0.076**	**0.36**	**0.45**	**0.05**	**0.24**	**0.30**	**0.101**
Cr	**3.50**	**0.05**	**5.01**	**10.89**	**0.412**	**21**	**10.69**	**0.40**	**14**	**10.9**	**0.822**
Cu	**3.01**	**2.0**	**1.19**	**31.20**	**3.119**	**0.96**	**36.02**	**3.12**	**1.17**	**33.05**	**5.347**
Ni	**0.078**	**0.07**	**0.12**	**0.146**	**1.709**	**ND**	**0.456**	**1.80**	**ND**	**0.046**	**1.921**
Pb	**1.01**	**0.01**	**1.82**	**0.012**	**2.398**	**2.93**	**0.122**	**2.33**	**1.92**	**ND**	**2.123**
Zn	**5.24**	**5.0**	**15.82**	**3.561**	**13.008**	**15.48**	**8.541**	**11.00**	**17.78**	**2.962**	**15.21**

ND=Not detected WHO (World Health Organization) Limits for drinking water quality (2011) Mg/L.

Table 2: Seasonal variation of heavy metals concentration at Deshaipet industrial site

ND= Not detected WHO (World Health Organization) Limits for drinking water quality (2011) Mg/L

Year			2019-20			2020-21			2021-22		
Parameter	Control sample	WHO Limits	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	Pre monsoon
Cd	1.15	0.01	8.01	1.36	0.319	6.98	1.65	0.21	8.7	1.56	0.225
Cr	2.12	0.05	3.41	4.56	1.132	5.21	4.23	1.14	3.34	3.24	1.332
Cu	5.73	2.0	6.56	14.02	9.176	7.02	11.11	8.97	6.16	16.55	8.124
Ni	0.510	0.07	ND	0.865	1.029	ND	0.954	1.07	ND	0.365	2.006
Pb	2.01	0.01	8.5	ND	3.95	2.5	0.321	3.90	3.5	ND	3.054
Zn	6.08	5.0	11.13	4.259	20.061	15.88	5.621	20.08	11.17	3.075	20.12

Fig: 1. Showing sample collection sites

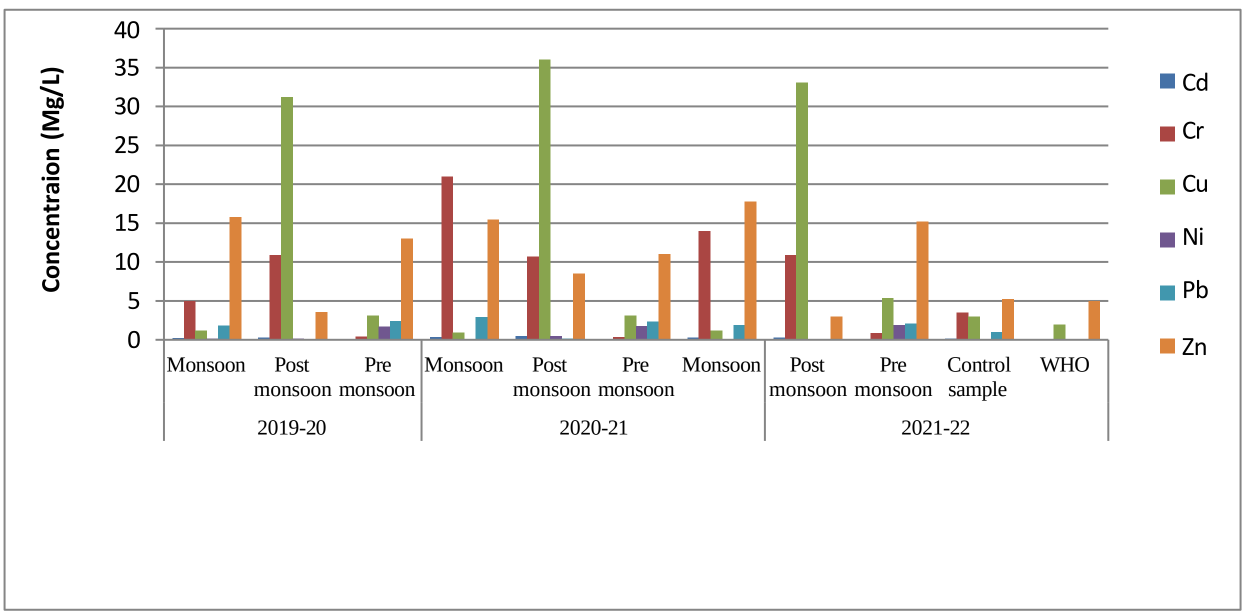

Fig: 2. Seasonal comparison of heavy metals concentration at Chinnawadepally industrial site

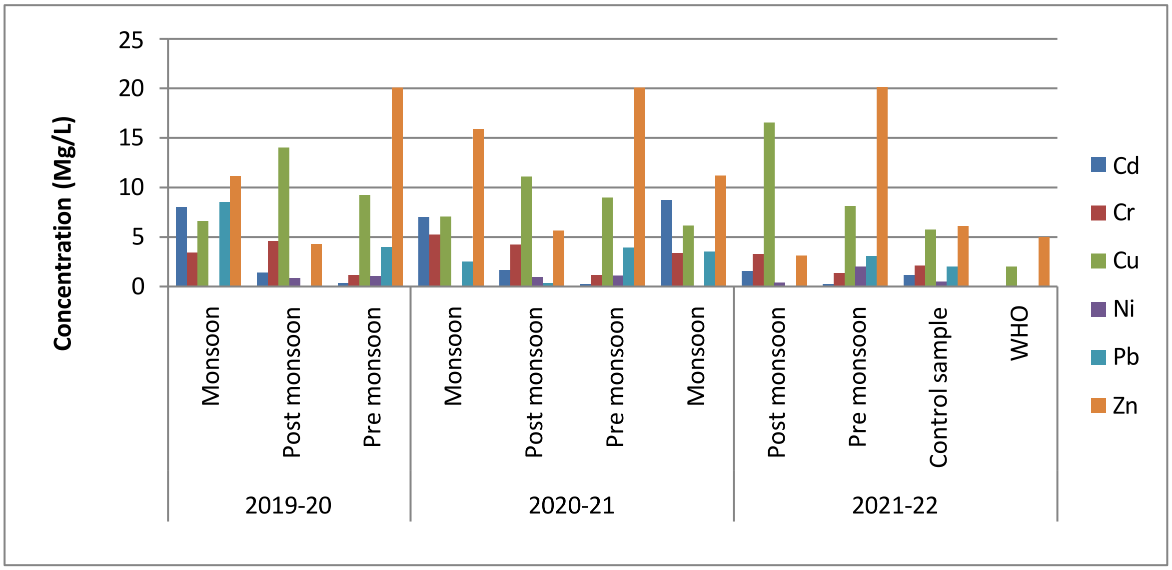

Fig: 3. Seasonal comparison of heavy metals concentration at Deshaipet industrial site