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Journal of Advances in Environmental Health Research
Kurdistan University of Medical Sciences
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3. Kuczmarski RJ, Ogden CL, Grammer-Strawn LM, Flegal KM, Guo SS, Wei R, et al. CDC growth charts: United States. Advance data from vital and health statistics. No. 314. Hyattsville, Md: National Center for Health Statistics, 2000. (DHHS publication no. (PHS) 2000-1250 0-0431)
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Original Article(s)

Journal of Advances in Environmental Health Research

Healthcare waste management and practices: A case study in Kodagu District, Karnataka, India

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Original Article

Abstract

Inappropriate handling and disposal practices of healthcare waste (HCW) at healthcare centers are significantly increasing health and environmental hazards. This paper summarizes the existing situation of HCW handling and management practices at healthcare facilities in Kodagu district (India). This study was conducted for a period of six months using well-designed checklists along with field observations and personal interviews with healthcare workers. Various HCW management issues like quantitative generation, category-wise handling, source level segregation, existing treatment, and disposal methods were studied. Moreover, drawbacks and practices in segregation, collection, transportation, storage, and final disposal methods of HCW in healthcare centers were investigated. The present study showed that lack of knowledge, guilty attitude, negligence of healthcare workers, and poor infrastructure were the major reasons for failure in the HCW handling and management system in the district. In addition to HCW management and infrastructures, associated health and environmental impacts were also discussed. Based on the existing situation and HCW management practices, suggestions and recommendations were made that may ensure the potential HCW handling and management practices and environmental risks minimization.

KEYWORDS: Healthcare Waste, Health Hazard, Kodagu District, Environmental Risk, Hospital, Waste Handling Persons, Disposal

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Introduction

Healthcare wastes (HCW) refer to all waste generated by the healthcare establishments such as hospitals, research institutions, clinics, laboratories, blood banks, animal houses, and healthcare teaching institutes. It is estimated that 15-20% of HCW is highly infectious, hazardous, and has the potential for creating a variety of health and environmental risks. Major hospitals contribute substantially large quantity of HCW, smaller hospitals, nursing homes, clinics, pathological laboratories, blood banks, and etcetera also contribute to a substantial amount of infectious wastes which are highly hazardous. Healthcare activities lead to production of large amount of HCW that may lead to adverse effects on human health and their surrounding environment. About 15-20% of infectious waste (such as sharp waste, body part waste, chemical or pharmaceutical waste, and radioactive and cytotoxic waste, broken thermometers, and etcetera) are highly injurious to human beings,

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animals, and the environment.[1-6] Approximately 80-85% of HCW (noninfectious wastes) are non-hazardous and as harmless as any other municipal waste. It is important to realize that if both (noninfectious and infectious wastes) of these two types of HCW are mixed together then the whole waste becomes harmful.[7-11] Sharp wastes, including needles, broken glasses, ampoules, and vials, produced in small quantities are highly infectious and their improper management causes health hazards to healthcare workers, waste handlers, and surrounding communities. In special cases, improper management of infected needles and syringes presents a particular threat to the society through them being reused by unauthorized persons which may spread infection.[3,4] Epidemiological studies indicate that a person who has experienced one needle-stick injury from a used needle has a 30, 1.8, and 0.3% risk of becoming infected with HBV, HCV, and HIV, respectively. In 2004, the results of a WHO assessment conducted in 22 developing countries showed improper disposal of HCW generated in major healthcare facilities in India causing nosocomial infection.[1,12-16] The handling, collection, transportation, storage, and proper disposal of HCW has become a significant concern for both healthcare workers and the public. Since the implementation of biomedical waste handling and management rules in India, every concerned healthcare personnel is expected to have correct knowledge, practice, and capacity to guide others for HCW collection, management, and appropriate handling techniques.[17,18]

The present study aims at exploring the current situation, practices, and drawbacks in the HCW management system in Kodagu District, India. An effort was made to explore the particular reasons for failure in the HCW handling and management system at healthcare facilities in the district. The present study has much scope with respect to environmental impact and HCW management, because the Kodagu is identified as one of the most ecologically rich areas in the country.

Materials and Methods

The data concerning HCW handling and management practices in Kodagu district, India, was obtained through the hospital records, field observation, hospital survey, and interaction and interviews with healthcare workers, nonclinical workers, and waste handling persons. Photographic evidences were also made related to generation, storage, collection, transportation, treatment, and disposal of HCW. The data were collected using well designed questionnaires for determination of healthcare workers knowledge, attitude, and behavior on HCW handling and management in terms of collection, segregation, transportation, treatment, and disposal. In addition, a survey was conducted for analysis of the HCW management system; for example, in terms of existing practices and drawbacks. In total, 53 important healthcare facilities were selected for the study, including 39 governmental hospitals [30 primary health centers (PHC) of 5-10 beds, 6 community health centers (CHC) of 30-50 beds, 2 Taluk level hospitals (TGH) of 180-200 beds, and 1 district hospital (DGH) of 400-450 beds] and 14 private nursing homes (PNH) of 10-50 beds. Generally, 120 healthcare workers such as doctors, nurses, lab-technicians, pharmacist, and nonclinical/waste handling persons were randomly selected for the personal interviews and interactions.

Kodagu is one of the smallest districts in Karnataka State (South India) comprising of three Taluks (Madikeri, Somwarpet, and Virajpet). The district has an area of 4102 sq. km and 30% of the district is forest area. Its population as per 2011 census is 554,762. The district has a mountainous configuration, which presents a grand panorama of verdant valleys, ravines, fast flowing streams, lofty peaks, and awe inspiring spurs. The major peaks are Tadiandamol, Brahmagiri, and Pushpagiri Hills. Kodagu is a veritable botanist's paradise with more than 1,300 species. The district has a very moist, rainy monsoon climate and most of the healthcare facilities in the district are located on the river beds or next to the channels which are connected to the river stream. Figure 1 shows the location of healthcare facilities selected for the study in the district.

Results and Discussion

Qualitative and Quantitative Study

All categories of HCW described in the biomedical waste (handling and management) rules (Ministry of Forest and Environment, 1998) were generated in all the healthcare facilities in the district. During the study, it was observed that large healthcare facilities like DGH, TGHs, and a few PNHs were generating large quantities of infectious HCW. Qualitative and quantitative data of HCW generated at different levels of healthcare facilities in the district are given in table 1. The present study showed that Cat-1 (anatomical waste) and Cat-4 (sharp waste including needles, broken glasses, ampoules, vials, blades, and etcetera) were the primary and secondary components of HCW generated, respectively, in the district. Moreover, Cat-6 (soiled waste including infected cotton, dressing cloths, bandages, and swabbing materials), Cat-7 (solid wastes including IV bottles, catheters, syringes, intravenous tubes, and etcetera), and Cat-3 (laboratory wastes such as swabs, culture, and culture media) were observed as other major components of HCW generated in most of the healthcare facilities. Other HCW, such as Cat-5 (discarded medicines and drugs), and Cat-10 (chemical waste including pesticides and

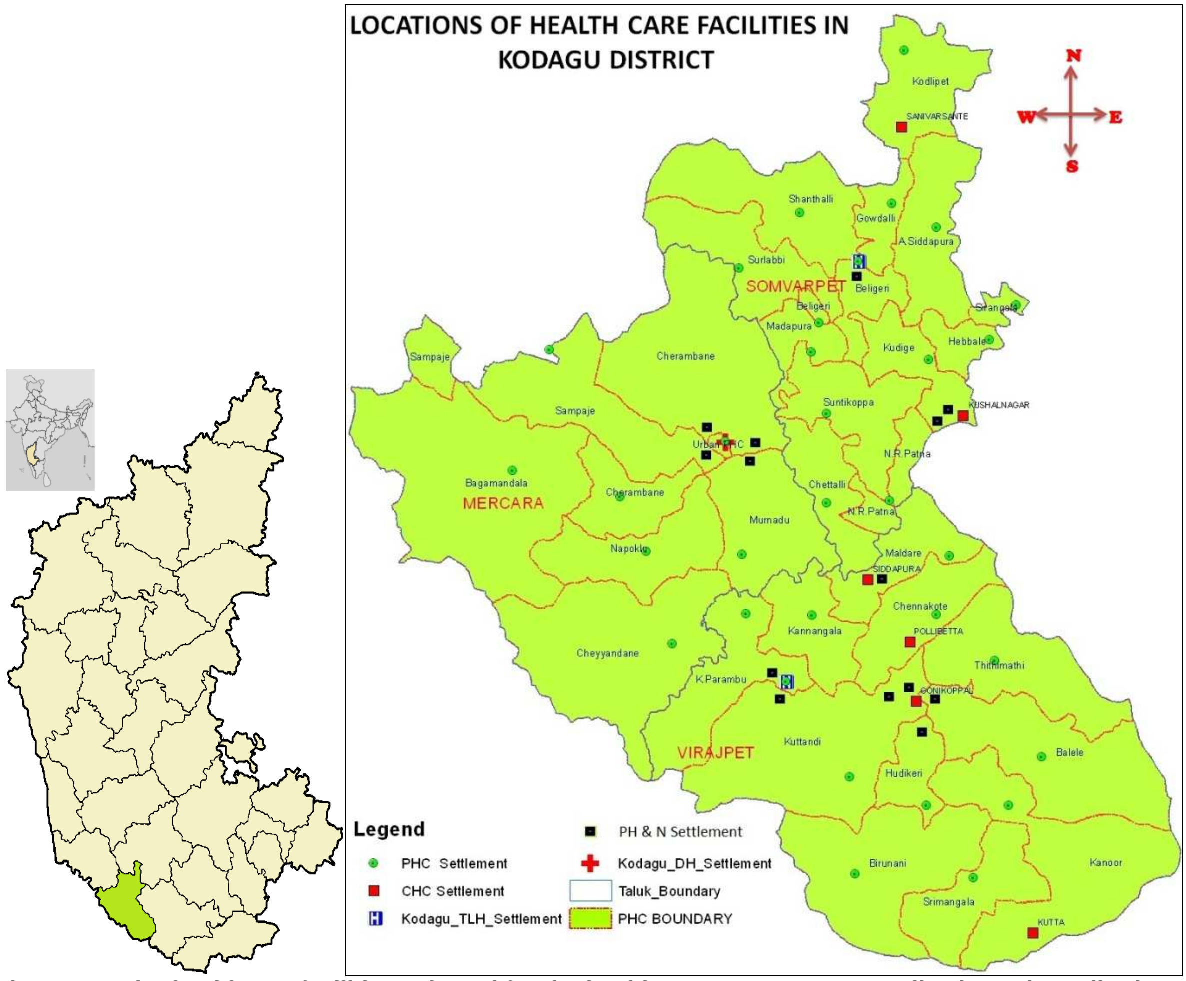

Figure 1. Major healthcare facilities selected for the healthcare management studies in Kodagu district

Table 1. Categories of healthcare wastes (HCW) quantitative generation per day at different level health care facilities in Kodagu district

Average HCW generated at different health care facilities in Kodagu district (in kg/day)				
	DGH (1)	TGH (2)	CHC (6) & PNH (9)	PHC (29) & PNH (5)
Category 1	4.20	2.80	1.45	0.72
Category 2	--	--	--	--
Category 3	1.20	0.82	0.42	0.15
Category 4	3.38	1.20	0.66	0.50
Category 5	0.83	0.40	0.07	0.02
Category 6	1.83	1.41	0.70	0.40
Category 7	1.40	1.03	0.67	0.01
Category 9	--	--	--	--
Category 8	> 2000 L	> 400 L	> 250	> 120 L
Category 10	0.15	0.05	--	--

HCW: Healthcare wastes; DGH: District hospital; TGH: Taluk level hospitals; CHC: Community health centers; PHC: Primary health centers PNH: Private nursing homes

insecticides), were occasionally generated as minor components. Generation of large volume of liquid HCW from laboratories, operation theaters, and the delivery section was observed throughout the study. During the investigation, we did not find generation of any considerable quantities of HCW such as Cat-2 (animal wastes) and Cat-10 (incineration ash) at healthcare facilities in the district. Figure 2 shows the percentage of major components in categories of HCW generated at different level healthcare facilities in the district. The results showed that Cat-4 and Cat-7 were the major components of HCW generated, and recycling of such HCW may reduce the environmental risk by resource utilization and waste reduction at the source.

Handling, Segregation, and Collection

Among the healthcare facilities in the district, about 85.71% (12 PNHs) of private nursing homes and 15.38% (2 CHCS and 4 PHCS) of governmental hospitals were found to have inappropriate practice and management of HCWs. During the study, improper segregation of HCW generated in private nursing homes (12 PNH) and in a few governmental hospitals (2 CHCS and 4 PHCS) in the district was observed. In total, about 33.96% of healthcare facilities in the district had inappropriate segregation and collection of HCW. In such healthcare facilities, all categories of HCWs, including general wastes (noninfectious wastes), were put together using single containers. Due to improper segregation of HCW at the initial stage, 80-85% of noninfectious waste would be converted into infectious waste; this indicates a 4-5 times increased rate of health and environmental risks along with HCW management cost. The study revealed that a few PNHs (57.14%) provided required color coded containers for segregation and collection of HCW, even though waste handling persons were not following standard procedures for segregation and collection of HCW. In the district, two PNHs (14.29%) and 33 governmental hospitals (84.62%) including 1 DGH, 2 TGHs, 4 CHCs, and 25 PHCs appropriately segregated HCWs at initial stages using color coded bins and liners as per the abovementioned standard guidelines. About 25 PHCs (86.20%), located in rural and remote areas in the district, used three color coded containers and liners for segregation and collection of HCW. The placenta (Cat-1) generated, and handed over to the custodian and buried according to the religious rites was reported in 4 PHCs, located in rural areas. At the remaining healthcare facilities (33.96%) in the district, we found inappropriate and inadequate usage of color coded containers for segregation and collection of HCW. Color coding used for segregation and collection of HCW in different healthcare facilities in the district was studied and reported (Table 2). Segregation is an

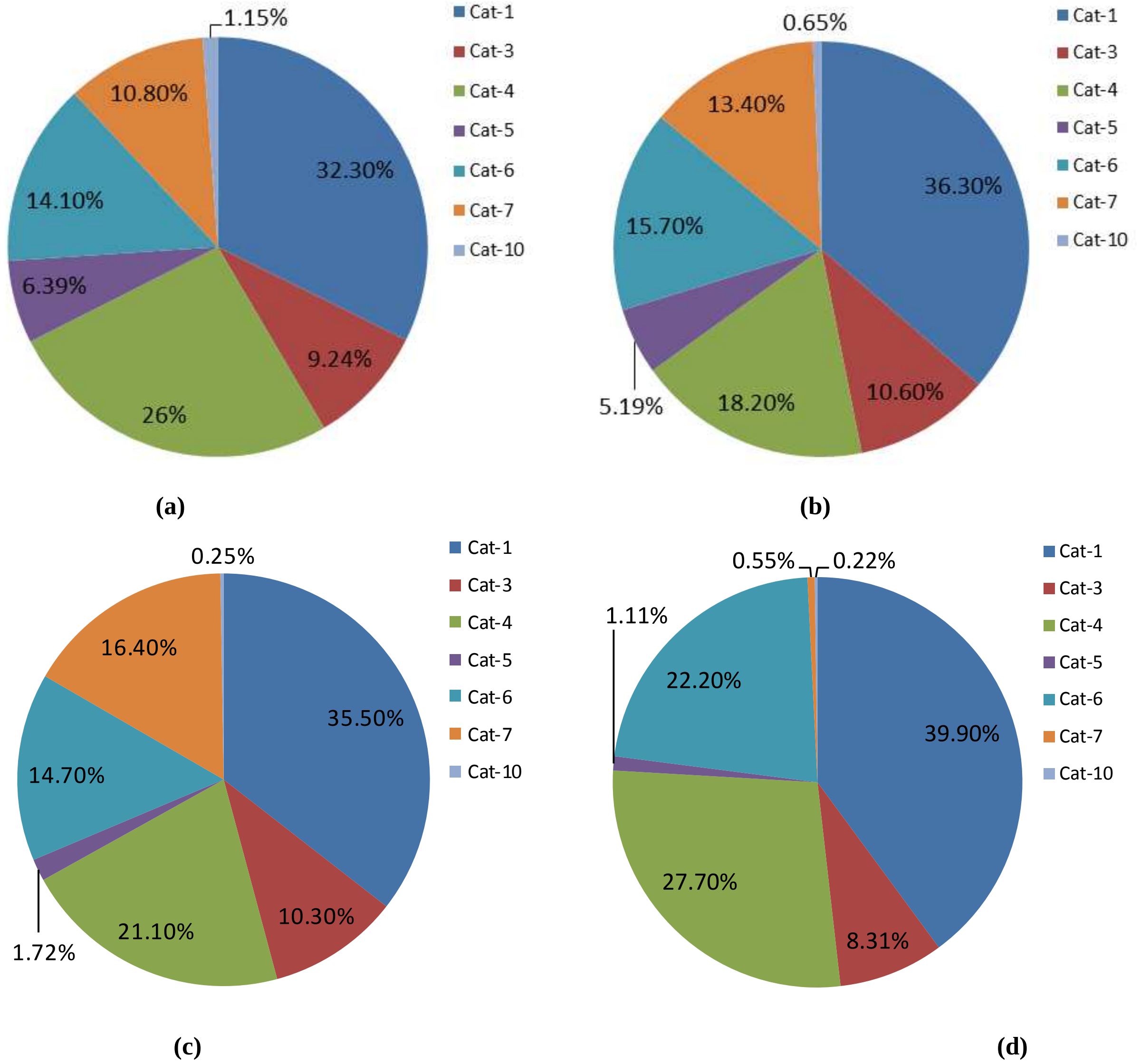

Figure 2. Important categories of healthcare waste components at different level healthcare facilities in Kodagu district: (a) 400-450 bed facility hospitals; (b) 180-200 bed facility hospitals; (c) 30-50 bed facility hospitals; and (b) 5-10 bed facility hospitals

Table 2. Color codes used for segregation and collection of health care wastes generated in different level hospitals in the district

Color codes used	DGH, 2 TGHs, 2 PNHs & 4 CHC	25 PHCs	2 CHCs, & 4 PHCs
Yellow	Category 1	Category 1, 3, and 6	Category 7
Red	Category 3, and 6	-	-
Blue	Category 7	Category 7	Category 1, 3, 4, and 6
Black	Category 5, and 8	-	-
Translucent white	Category 4	Category 4	Category 4, 7, and 3

DGH: District hospital; TGH: Taluk level hospitals; CHC: Community health centers; PHC: Primary health centers
PNH: Private nursing homes

important and appropriate step in HCW management and it is the initial responsibility of each healthcare worker at healthcare facilities during HCW handling and management. Systematic segregation determines the optimal functioning of treatment technology and potential optimized usage, and also increases the longevity of HCW disposal system. Source segregation reduces HCW management cost, amount of infectious waste, and HCW hazards. Moreover, it enables the better recycling and implanting of a system of disinfection, which reduces the overall health and environmental risk in HCW management system.

Transportation and Temporary Storage

In major healthcare facilities such as DGH, TGHs, and PNHs, no utilization of any equipment, like trolleys or moving baskets, for internal and external transportation of HCW was found. The transportation equipment, like trolleys or moving baskets, are basic needs for HCW transportation within or outside the hospitals. In all healthcare facilities internal transportation of HCW was carried out manually by waste handling persons using polythene or ordinary bags without any safety measurement. They did not use any separate path or route for internal transportation of infectious HCW, and in some healthcare facilities (61%) transportation of infectious HCW was carried out at day time (i.e., peak hours of crowding and medical activities). Major healthcare facilities, like DGH and TGH, where large amounts of HCW are generated and more transportation activities are expected, should be provided with basic facilities and requirements such as separate path or route, and high quality and safe equipment for transportation of HCW. HCW, segregated and collected using color coded bins, were transported into a temporary storage room located within the hospital premises without any safety measurement. It was also observed that temporary storage facilities in all major healthcare facilities (DGH, 2 TGHs, 2 CHCs, and 2 PNHs) were easily accessed by the public or unauthorized recycling persons. During the study, no separate temporary storage room was found in healthcare facilities and collected HCW was temporarily stored in an open room within the hospital, where public areas, such as toilets, patient wards, and etcetera were situated. HCW segregated and collected at PHCs, was transported to disposal sites at the end of shift or day using plastic containers. Only recyclable plastic wastes were temporarily stored in a separate room after disinfection and mutilation using polythene bags in all the PHCs. The study confirmed that inappropriate and unsafe practices were taking place during the transportation and temporary storage of HCW in the major healthcare facilities, like DGH, TGHs, CHCs, and a few PNHs in the district. In addition, we found that the storage time of HCW in a temporary storage room was between 1-2 weeks, depending on the common treatment agency contracted for off-site transportation and disposal. This was contrary to the biomedical waste handling and management regulation.

Waste Treatment and Disposal

It was observed that about 64.15% of healthcare facilities including 1 DGH, 2 TGH, 4 CHCs, 2 PNHs, and 25 PHCs, follow the standard treatment procedures such as disinfection, needle burning, and mutilation of solid HCWs. Hypochlorite solution (1%) or bleach solution was used as an effective disinfection reagent in all healthcare facilities in the district. Infected solid wastes like plastics and metal wastes were disinfected and mutilated as per the guidelines, then sent for temporary storage or recycling using plastic containers. Needles generated in the hospitals were burnt using electric burners and disinfected, then sent for temporary storage or recycling using puncture proof translucent white containers. Infected HCW such as anatomical wastes, and soiled wastes were carefully collected using yellow and red colored non-chlorinated polythene bags, respectively, and were sent for disposal. Inappropriate and incomplete disinfection and handling procedures were observed during treatment of HCW in 35.84% of healthcare facilities (12 PNHs and 4 PHCs). The present study revealed that only major healthcare facilities (24.53%) were handing over the collected and temporarily stored HCW to a common treatment private agency called Shree Consultants, Mysore for off-site disposal. On the other hand, among 24.53% of these hospitals only 16.98% followed standard guidelines for mutilation, disinfection, and color coding with appropriate labeling. The remaining 30.77% of hospitals used chlorinated liners for HCW collection, packing with inappropriate segregation, and labeling. The chlorinated liners and plastic wastes along with HCW were directly burned in the incineration chambers at common treatment facilities (CTF). As a result of inadequate and improper maintenance of incineration temperature in the incineration chambers, the chlorinated liners and plastic wastes will produce a large amount of furans, dioxins, chlorinated ions, and other toxic gaseous compounds which further cause health and environmental hazards.[14-16] Disinfected biodegradable infectious HCW (Cat-1, 3, and 6) and sharp wastes were disposed using well designed deep burial pits and sharp pits, respectively. Schematic diagram of deep burial pit and sharp pit are shown in figure 3. During the study we observed unscientific construction and maintenance of deep burial and sharp pits in 9 PHCs and 3 PNHs. In 7 PHCs, deep burial pits had been constructed near or in wet lands, where infectious pathogen could easily spread and there is a potential of groundwater contamination.

Only about 64.15% of healthcare facilities in the district performed on-site treatment of liquid HCW using small liquid treatment units (LTU). Lapse in the construction and maintenance of LTUs, and also improper disinfection of liquid HCW was observed in a few hospitals (2 CHCs, 3 PNHs, and 3 PHCs). Throughout the study we found inattentiveness to the liquid HCW treatment and its improper management in most healthcare facilities, and irregular disinfection of liquid HCW. These issues were attributed to the lack of awareness, interest, and guilty attitudes in healthcare workers. Release of incomplete and untreated liquid HCW into the drainage or ambient environment will cause health and environmental risk.[4-20] There were no effluent treatment plants for mass treatment at healthcare facilities, where a large volume of liquid HCW is expected to be generated in the district. Moreover, no incinerator was observed while frequent open burning of HCW within the hospital premises was observed. Such conditions can cause air pollution and health risks for healthcare workers, and patients and visitors in the hospitals.[16,18,19]

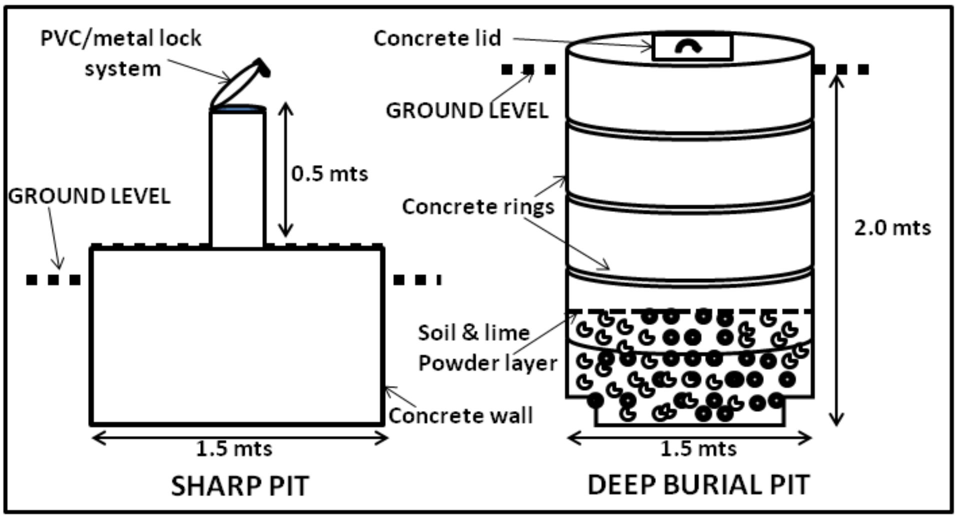

Figure 3. Schematic diagrams of sharp pit and deep burial pit used for disposal of solid healthcare wastes

Storage of infectious HCW for a long duration will cause nosocomial infections to healthcare workers, patients, and the surrounding public.[16-20] The lack of adequate and scientific infrastructure for the external transportation (from hospital to CTF) of HCW in the private agency, may cause the spreading of infection throughout the route and cause health risks.[16-20]

Prophylactic Measures, Knowledge and Awareness

During the study, we found only 2-3% of needle stick injuries were reported in the hospital records. Personal interviews and interactions confirmed that 17.5% (21 persons) of needle stick injuries occurred during HCW handling, but were not reported. The obtained data showed that the proportion of vaccination in healthcare workers was less in the private sectors compared with governmental sectors. Moreover, there were no record of other accidents related to breaking thermometers or overturning of infectious waste containers, splashing of liquid infectious wastes, cross infections, and nosocomial infections by HCW mismanagement in any healthcare facilities in the district, but during our study such accidents were frequently reported by healthcare workers. Moreover, reporting and record keeping related to HCW accidents, needle injuries and nosocomial infections were very poor and not regularly updated. Throughout the study we observed no use of personal protection equipment like utility gloves, protection mask, gum boots, and protection cloth by waste workers during their activities. The study found that handling of sharp and infected wastes in a few PNHs by the nonclinical and waste handling persons was performed with their bare hands. This clearly confirmed the lack of knowledge and awareness on safety measurement and HCW associated risks in low class workers. During the study about 13.33% of doctors were found to have low awareness of HCW management practices, regulations, consequences of HCW on health and environment, and standard regulations to be implemented. About 26.66% of doctors expressed their guilty attitudes and behaviors on HCW management, and also showed the least interest toward systematic management and standard procedure follow-ups during HCW management. About 50 and 66.66% of duty nurses and lab technicians, respectively, had low awareness about and showed low interest in HCW management in their healthcare centers. Among them, 20% and 68% of duty nurses and lab technicians, respectively, showed guilty attitudes and low interest in HCW management. About 80% of nonclinical and waste handling persons regularly involved in cleaning and sanitation works in healthcare centers were found to be completely unaware of HCW management, safety measurement, and HCW associated risks. Only 20% of nonclinical and waste handling persons were moderately aware of HCW and risks associated to it. The least awareness about and interest in HCW management in the district, was observed in the healthcare workers at private hospitals, as compared with the governmental hospitals. About 85 and 8% of healthcare workers (like doctors, nurses, and lab technicians) in governmental and private health sectors, respectively, had joined training and awareness programs on HCW management and regulations.

This study revealed that there were well defined plan or policy, guideline, and definite budget concerning HCW management system in the district, but lack of knowledge, and low awareness and guilty attitudes of healthcare worker might cause inappropriate handling and management practices of HCW.

Suggestions and Recommendations for the Better Management of HCW

Training programs on scientific handling and management practices of HCW generated, standard regulations and policy should be conducted for all healthcare workers; especially for all the low class workers, like nonclinical/waste handling persons, at healthcare centers. Private HCW collection agencies should be trained to improve the knowledge about safe and systematic management of HCW. It is suggested that awareness programs, seminars, and capacity buildings (consultation) be conducted for all healthcare workers including doctors, nurses, and lab technicians for improving attitudes and creating positive behaviors toward HCW management. In all the steps of HCW management a labeling and naming system should be introduced, and the local language is suggested for naming and HCW management guidelines. Establishment of a common treatment facility within the district is suggested to avoid delay of disposal of infectious HCW. All healthcare facilities in the district are strongly recommended to dispose of HCW through CTF instead of on-site disposal for environmental pollution remediation in the district. Constructing or equipping major hospitals with suitable wastewater treatment plants is strongly recommended. Moreover, it is suggested to have appropriate management and continuous monitoring of generated HCW, and frequent environmental impact assessment could be performed for better management of HCW and to avoid associated risks on health and environment.

Conclusion

The current study revealed that there are inappropriate practices in segregation, collection, and transportation in the HCW management system in Kodagu District, Mysore, India. This study explored the major drawbacks in infrastructures and facilities for the collection, transportation, temporary storage, and disposal of HCW. The present study showed that the lack of knowledge, low awareness, and guilty attitudes in healthcare workers on HCW management, and inadequate service provided by private agencies are the drawbacks in HCW management system in the district. The study confirmed the lower knowledge and awareness on HCW and safety measurement in nonclinical/waste handling persons (lower class workers) in healthcare centers when compared with higher class healthcare workers. Qualitative and quantitative generation of HCW at different level healthcare centers were determined and discussed.

Conflict of Interests

Authors have no conflict of interests.

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The effect of incubation time and silk worm cocoon on mobility of zinc and copper in contaminated clay soil

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Original Article

Abstract

Of the problematic agents in the ecosystem, heavy metals have special importance because they are unabsorbable and have physiologic effects on living beings at low concentrations. This study has investigated the effect of silk worm cocoon on reducing mobility of zinc (Zn) and copper (Cu) for the first time. To this end, 5% cocoon adsorbent was added to the studied soil, which had been contaminated with Cu and Zn in separate containers at concentration of 600 mg/l. The experiment was performed in three repeats and two treatments (with and without adsorbent). Samples were incubated at 28°C at constant humidity for 3 hours, 1, 3, 7, 14, 21, and 28 days. Then both treatments were extracted using sequential extraction method and the concentration of Zn and Cu was processed using atomic absorption spectrophotometry. The results showed that there were changes in mobility of the Zn and Cu added to soil; adding silk worm cocoon to soil increased organic phase of Zn and Cu as compared to the soil without adsorbent. Data were analyzed by SPSS software. All comparisons of the means were performed at statistical level of 5% using Student's independent t-test. Student's independent t-test showed that the highest significant difference ($P < 0.05$) was observed in the organic fraction of the Cu-Zn contaminated soil with cocoon, as compared with the Cu-Zn contaminated soil without cocoon.

KEYWORDS: Soil, Zinc - Copper, Decreased mobility, Silk worm cocoon, Incubation

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Introduction

Today, environmental pollution has sharply increased along with industrial and technological growth in human societies. Different parts of the environment such as water, air, and soil are contaminated in different forms.[1] After water and air, soil is the third most important part of the environment for human beings.[2] Distribution of heavy metals in the environment, which accompanies industrial development and increasing population, is a major environmental problem in many countries.[3] Concentration of heavy metals in the soil can contaminate the food chain, and consequently endanger human health.[4] Due to their relative stability and non-biodegradability, heavy metals accumulate in different body organs like kidney, liver, and bones, and cause serious disorders.[5] The toxicity of heavy metals in plants ranges from reducing the product through their effect on the growth of the root and leaves to enzyme preventing activity.[6] Heavy metals are a group of elements that are considered pollutant at concentrations higher than their critical limit. A heavy metal is an element with an atomic mass higher than that of Fe (55.8 g/mol), and with a specific gravity of higher than 4.5 g/cc.[7] Copper (Cu) and zinc (Zn)

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are heavy metals that cause serious disorders in human and plant health at concentrations higher than threshold. As an essential element, Cu plays a role in the metabolism including development of bones, central nervous system, and ligaments. Overdose of Cu causes capillary disorder, liver and kidney complications, nervous system irritability, and depression. According to studies, Zn is more easily dissolved than other heavy metals and almost 60% of the soluble Zn in soil is in the form of soluble organic complex.[8]

These metals are naturally found at low concentrations in soil and rocks, and enter the environment through natural processes (geochemical and weathering), but human activities have increased their release and distribution in the environment.[9] The important human sources of contamination of soil with heavy metal contamination include mining, batteries, electric plating, electrolysis, mine survey, leather, manufacturing of electric appliances, polishing metal surfaces, pharmaceutical uses, atomic energy or aerospace utilities that dispose of their contaminated wastewater directly or indirectly in the environment.[10] Due to the environmental hazards of heavy metals, their removal has been attended to in recent decades. Surface adsorption is one of the most practical methods because of its easy application[11] In this method, heavy metals are adsorbed to the surface pores of adsorbents, which are water insoluble.[12] The use of natural materials as heavy metal adsorbent is more suitable for adsorbing heavy metals than other materials because they are not costly. Agricultural byproducts are suitable because they have hydroxyl, carboxyl, and phenol groups and have a high affinity with heavy metals.[13] These material are mainly the waste products of industrial and agricultural activities, and have cellulose origins.[14] Wastes like, tree bark, orange waste, wool, olive leave, pine needle leaves, cactus leaves, coconut skin, grapes waste, walnut shell, teakwood, apple waste, banana skin, and date stone, have been reported to be good adsorbents for surface metals.[12,15-19] Generally, this study aimed to determine the efficiency of silk worm cocoon in decreasing mobility of Cu and Zn through their effect on fractions of elements in clay soil at different time intervals.

Materials and Methods

Soil sampling was conducted at the depth of 0-30 cm from around the city of Hamedan. The soil was air dried and passed through a 2-mm sieve. Some of the physical and chemical properties of soil were determined in the following ways: texture was measured using hydrometer method and based on Stox law, pH was measured in a 1:5 water/soil solution using a pH meter, electric conductivity was measured in a 1:5 water/soil solution using an EC meter, sodium (Na^+) and potassium (k^+) were measured using film photometer, sulfate, nitrate and phosphorus were measured using spectrophotometer, bicarbonate was measured using neutralization with acid, and Cloride (Cl^-), Calcium (Ca^+), and Maguesium (Mg^{2+}) were measured by titration.[20-22] Some of the physical and chemical properties are shown in table 1.

The concentration of Zn and Cu was measured in 2 treat soils using nitric acid extraction by atomic absorption spectrophotometry.[23] The total concentration of Cu and Zn in silk worm cocoon was measured; silk worm cocoon was chopped into 1cm pieces and analyzed by inductively coupled plasma (ICP) (Verian710-Es).[24]

The studied soil was contaminated with Cu and Zn at the concentration of 600 mg/l in

Table 1. Some physical and chemical properties of the studied soils

Solution cations and anions (mg/l)								%			Soil texture	EC (ds.m$^-$)	pH
Ca^{+2}	K^+	Mg^{+2}	Na^+	PO_4^{3-}	Cl^-	SO_4^{2-}	NO^{3-}	Sand	Silt	Clay	Clay- loam	0.15	7.22
32	45	9.6	26.22	0.63	81.6	13.3	69.4	26	43	31			

EC: Electrical conductivity

separate containers, and mixed with 5% of the adsorbent (silk worm cocoon).[25,26]

Samples of soil with adsorbent and samples without adsorbent were incubated at 28°C.[27] At intervals of 3 hours, and 1, 3, 7, 14, 21, and 28 days, samples were taken from the soil in the incubator. The tests were performed in three repeats and two treatments (with and without adsorbent), and the concentration of Zn and Cu was measured at different fractions including exchangeable, carbonate, Fe-Mn oxide, organic, and residual fractions using sequential extraction and atomic absorption spectrophotometry (GBC-Avante).[23,28]

Heavy metal components of soil were fractionated using sequential extraction method of Salbu and the following components were recognized.[28]

Fraction 1. Exchangeable: extraction with 20 mL of 1 MNH_4OAc at pH 7 for 2 hours at room temperature.

Fraction 2. Specifically sorbed and carbonate-bound: extraction of the residue from F1 with 20 mL of 1 MNH_4OAc at pH 5 for 2 hours at room temperature.

Fraction 3. Fe–Mn oxides occluded: extraction of the residue from F2 with 20 mL of 0.04 MNH_2OH_HCl in 25% HOAc for 6 hours in a water bath at 60°C.

Fraction 4. Organically complexed HM: extraction of the residue from F3 with 15 mL of 30% H2O2 at pH 2 for 5.5 hours in a water bath at 80°C.

Fraction 5. Residual: after cooling, 5 mL of 3.2 MNH_4OAc in 20% HNO_3 was added to the residue of F4. Sample was shaken for 0.5 hours, and finally diluted to 20 mL with distilled water.[29]

The solutions obtained from each fraction were read by atomic absorption spectrophotometer.

Results and Discussion

Characterization of soil

Some physical and chemical properties of the studied soil are presented in table 1. Accordingly, pH was 7.22, EC was 0.15 ds/m, and the texture of the soil was loamy clay. On the basis of the results, the concentration of the whole Cu and Zn in non-contaminated clay and silk work cocoon was not detectable by atomic absorption spectrophotometer.

Changes of Cu in two treatment of soil

Accessible Cu in soils is mainly found as divalent cation on the surface of clay minerals or bound to organic matters of the soil. That is why preserving Cu is increased in clay and organic matters of the soil and its availability is also increased.[29] The results showed that Fe-Mn fraction had the highest adsorption of Cu (Figure 1, Table 2). Luo et al. reported the same results in contaminated paddy fields in China in that the highest concentration of Cu was found in the Fe-Mn fraction of the soil.[30] Bartlet and James found that the surface of iron oxide acts as active adsorbent and adsorbs most of the metal ions dissolved in soil.[31]

The order of increase in different fractions of soil is as follows:

Fe-Mn > exchange > carbonate > residual > organic

On the basis of the results, Cu in the organic fraction has significantly increased in the soil with cocoon compared with that of in the soil without cocoon at all times; it increased from 2.7% to 36.52% at 3 hours, from 0.005% to 37.69% on day 3, from 0.003% to 45.33% on day 7, from 0.003% to 23.14% on day 14, from 0.002% to 32.61% on day 21, and from 0.003% to 24.33% on day 28. Student’s independent t-test showed that the highest significant difference ($P < 0.05$, $P = 0.007$) was observed in Cu in the organic fraction of the Cu contaminated soil with cocoon as compared with the Cu-contaminated soil without cocoon.

As seen in figure 2 and table 3, the amount of organic matters increased relative to the blank soil. This shows that when silk worm cocoon is added, metals in the exchange fraction reduce and those in the organic phase increase, and their mobility reduces. Cu can bind with organic matters easily because it creates highly stable

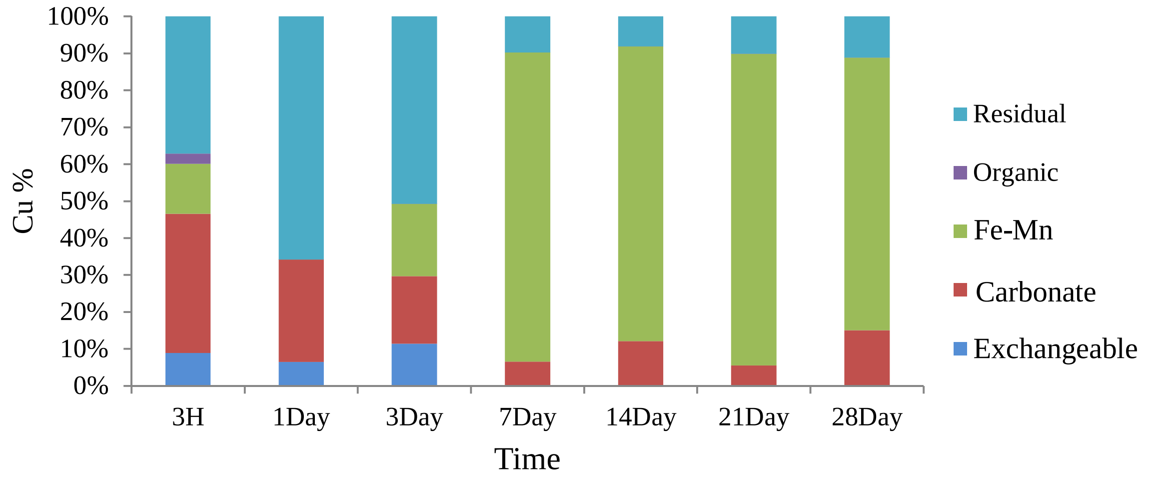

Figure 1. Different fractions of Cu in blank soil (%)

Table 2. Different fractions of Cu in blank soil (mg/kg^{-1})

Time	Exchangeable	Carbonate	Fe-Mn	Organic	Residual
3H	8.58	36.29	13.00	2.68875	35.73
1d	6.62	28.35	0.01	0.00750	67.38
3d	16.05	25.76	27.63	0.00750	71.47
7d	0.01	14.76	189.15	0.00750	22.00
14d	0.01	26.47	175.15	0.00750	17.83
21d	0.01	14.21	216.38	0.00750	25.96
28d	0.01	28.67	141.00	0.00750	21.35

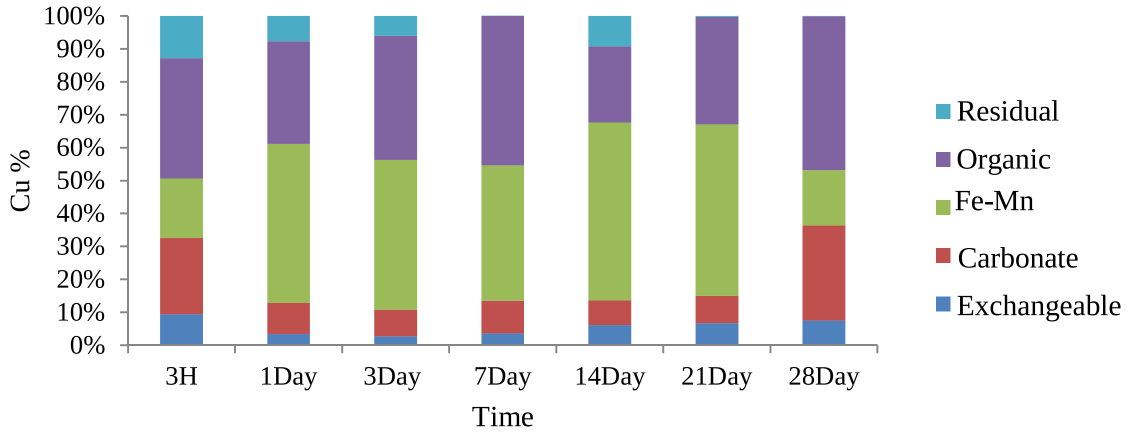

Figure 2. Different fractions of Cu in contaminated soil with silk worm cocoon (%)

Table 3. Different fractions of Cu in contaminated soil with silk worm cocoon (mg/kg^{-1})

Time	Exchangeable	Carbonate	Fe-Mn	Organic	Residual
3H	9.82	23.95	26.86	29.850	13.32
1d	12.00	33.14	243.43	37.250	26.84
3d	10.32	30.63	248.16	69.300	22.99
7d	9.54	26.39	156.92	73.840	0.01
14d	12.93	15.89	162.98	0.007	19.47
21d	13.81	17.12	153.55	21.180	0.54
28d	4.33	30.00	28.89	47.690	0.01

combinations in the soil. This binding stabilizes Cu, reduces Cu washing, and reduces availability of Cu for plants.[32] Furthermore, it was observed that on days 1 and 3, Cu in exchange fractions reduced and in organic fractions increased. On days 7, 14, 21, and 28, Cu in the Fe-Mn fraction reduced and in the organic fraction increased. At all times, except 3 hours, the highest fraction of Cu was reported bound with Fe-Mn. investigated soils of paddy fields in China, showed that the highest percentage of Cu was bound with organic matters.[33] The highest percentage of Cu reduction in residue was observed on day 1; it reached from 7.61% to 65%. Kim et al. reported that heavy metals were fixed using improved treatment of waste with oyster.[26] Lindsay found that organic residue decreased the mobility of Cu in soil, which results from the gradual formation of insoluble Cu complexes.[34] After the organic fraction, Fe-Mn fraction has the highest amount of Cu.

Furthermore, Jalali and khanlari reported that most of the added Cu was distributed in organic and Fe-Mn fractions.[27]

Changes of Zn in two treatment of soil

Solubility of Zn minerals during weathering especially in acidic and oxidative conditions mobilizes Zn. Zinc is found in many minerals in the soil, and because of the proximity of its ionic radius to that of Fe and Mg, it can substitute these ions in different mineral structures.[2] Based on our results, at all times except 3 hours, Fe-Mn fraction had the highest adsorption of Zn (Figure 3, Table 4).

The order of Zn increase in the fractions of soil is as follows:

Fe-Mn > carbonate > residual > exchange > organic

On the basis of the results, organic fraction increased in the soil with cocoon as compared with the soil without cocoon at all times; it

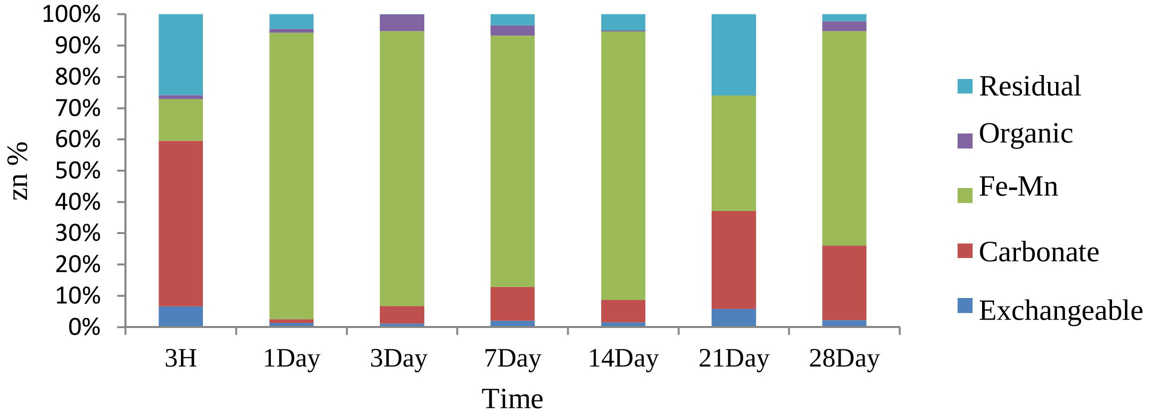

Figure 3. Different fractions of Zn in blank soil (%)

Table 4. Different fractions of Zn in blank soil (mg/kg^{-1})

Time	Exchangeable	Carbonate	Fe-Mn	Organic	Residual
3H	6.42	50.96	12.98	1.120	24.96
1d	5.82	5.98	422.28	5.350	21.58
3d	5.58	27.83	439.62	26.640	0.28
7d	7.24	39.10	289.20	11.940	12.74
14d	6.42	31.83	380.80	1.270	22.82
21d	5.95	32.18	37.87	0.007	26.61
28d	7.62	81.20	234.20	10.960	7.36

increased from 1.16% to 34.34% at 3 hours, from 1.16% to 29% on day 1, from 5.32% to 29.88% on day 3, from 3.31 to 32.15% on day 7, from 0.28% to 30.16% on day 14, from 0.007% to 31.04% on day 21, and from 0.31% to 3.21% on day 28. Student's independent t-test showed a significant difference ($P < 0.005$, $P < 0.001$) between organic fraction in the soil contaminated with Zn with silk worm cocoon, and that in the soil contaminated with Zn without silk worm cocoon. There was no significant difference observed in other fractions.

On the basis of our findings, at 3 hours, and on days 21 and 28, Zn in the carbonate fraction reduced and in the organic fraction increased. On days 1, 3, 7, and 14, Zn in the Fe-Mn fraction decreased and in the organic fraction increased (Figure 4, Table 5). On the basis of past researches, Zn dissolves more easily than other heavy metals, and about 60% of Zn is found as soluble organic complex in soil.[8] Kim et al., using egg shell to investigate the mobility of heavy metals, reported that the amount of heavy metal before using egg shell was 37% bound to organic fraction, but it increased to 52.2% after applying egg shell.[26] Clemente et al. found that using organic soil fixes Pb and Zn.[35] Luo reported similar results.[30]

Conclusion

In order to study the mobility of heavy metals in loamy clay soil, we used Salbu sequential extraction. On the basis of our results, the organic fraction had a significant increase in Zn and Cu at all times. Organic fraction in the soil with adsorbent of Cu increased more than that in the soil with adsorbent of Zn. Zn and Cu were reported to be higher in Fe-Mn fraction than other fractions in the blank soil. The residual fraction reduced in the soil with adsorbent of Zn and Cu. The exchange fraction of Zn had a significant decrease as compared to that of Zn.

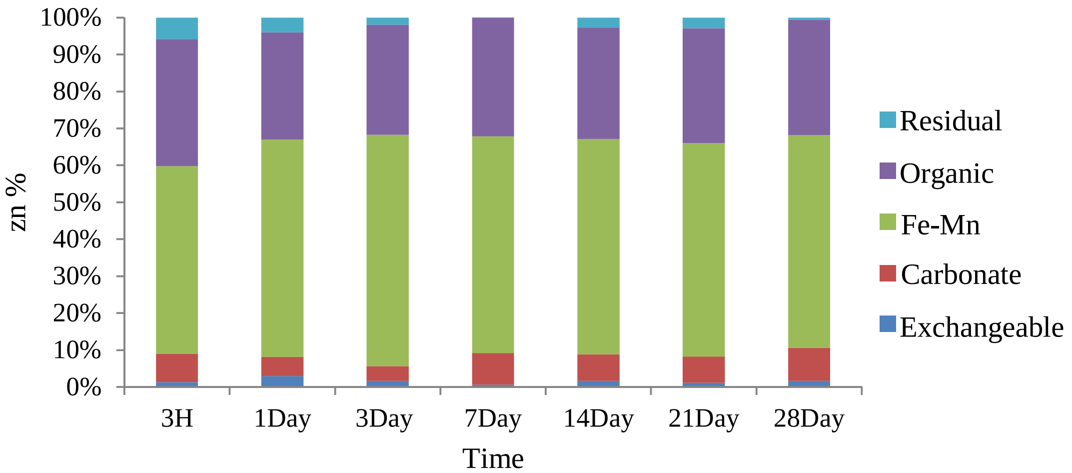

Figure 4. Different fractions of Zn in contaminated soil with silk worm cocoon (%)

Table 5. Different fractions of Zn in contaminated soil with silk worm cocoon (mg/kg)

Time	Exchangeable	Carbonate	Fe-Mn	Organic	Residual
3h	6.42	39.42	369.24	64.15	29.59
1d	12.87	22.62	367.71	16.57	17.42
3d	8.03	20.02	443.70	15.21	9.36
7d	2.67	34.93	343.97	28.76	0.01
14d	7.53	33.41	385.55	24.04	12.57
21d	5.35	32.54	378.18	28.76	13.31
28d	6.77	37.37	343.97	27.35	2.49

Student's independent t-test showed a significant difference ($P < 0.05$) between organic fractions in the Cu contaminated soil with silk worm cocoon and in the blank soil. Furthermore, a significant difference was seen in the organic fraction of Zn contaminated soil with silk worm cocoon as compared with that in the blank soil.

Conflict of Interests

Authors have no conflict of interests.

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Concentration levels of heavy metals in irrigation water and vegetables grown in peri-urban areas of Sanandaj, Iran

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Original Article

Abstract

Concentration and daily intake (DI) of heavy metals [lead (Pb), chromium (Cr), cadmium (Cd) and copper (Cu)] were investigated in four common edible vegetables including coriander, dill, radish root and radish leaf grown at peri-urban sites in Sanandaj, Iran. A total of 120 composite samples of vegetables were taken from ten vegetable farms during six months from May to October 2012. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to estimate the levels of heavy metals. The results showed that Pb and Cr concentrations exceeded the safety limits given by Food and Agriculture Organization (FAO) or the World Health Organization (WHO) for human consumption with the exception of copper and cadmium that were lower than the permissible leveling in all of the samples. Furthermore, the results showed that there was a significant variation in the levels of these metals among the examined vegetables ($P < 0.001$). DI values for Pb, Cu, Cr and Cd could be 0.1, 1.5, 0.94 and 0.004 mg per day, respectively. As respect, DI values for Pb and Cd were also below the international guideline bases. Although Pb level was higher than the permissible standard, it seems that daily intake of these vegetables may not have detrimental health hazards to consumers.

KEYWORDS: Vegetables, Heavy Metals, Daily Intake

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Introduction

In recent years, vegetables consumption was increasing in the world and constituted an important part of the human diet and nutrition. This was due to vegetables contain essential diet components of vitamin, protein, minerals, trace elements and other nutrients. Buffering agent is another and important function of vegetables for acidic and some toxic substances produced during the digestion process. In spite of this fact, nutritional value and consumer acceptance must be taken into consideration when vegetables are being considered as foodstuffs; because vegetables can contain both essential and toxic elements over a wide range of concentrations.[1,2] Therefore, Food safety issues and potential health risk are a major public concern worldwide and make it as one of the most serious environmental concerns.[3]

It is well known that heavy metals are among the major contaminants of foodstuffs and can considered as one of the most

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important problems for human health because they have long biological half-lives, non biodegradable and accumulation potential in different organic bodies.[3] Among the organics, vegetables may become contaminated with heavy metals if they grow on soils contaminated by natural or anthropogenic sources such as industrial and agricultural activities.[4] Therefore, intake of heavy metal-contaminated vegetables may pose a direct threat to the human health and considered as one of the most important aspects of food quality assurance.[2,3,5] International and national regulations on food quality have lowered the maximum permissible levels of toxic metals in food items due to an increased awareness of the risk these metals pose to food chain contamination.[3,5]

Unorganized urbanization and rapid industrial and agricultural developments resulted in an increase of heavy metal metals in the environment.[5] Contamination of soil with heavy metals is common and it can be a major source of metals to crops and finally may be a primary path of human exposure to these potentially toxic metals.[6,7] Several authors have shown heavy metals as important contaminants of the vegetables.[5,8,9] However, bioaccumulation of elements in vegetables is more complicated because their uptake by plants depends upon the climate, soil properties, atmospheric depositions, irrigating water quality and plant physiologic factors.[8]

Kurdistan province is one of the major agriculture areas in the west part of Iran. Sanandaj, the capital of Kurdistan province currently covers more than 100 km^2 peri-urban areas for agricultural activities specially vegetables production. Agricultural activities in this area causes significant alterations in the water resources and increases the toxic metals resulting from fertilizers and metal-based pesticides, industrial emissions, transportation and harvesting process. Since crop irrigation is mostly depend upon groundwater, a concern in Sanandaj agricultural products from urban and peri-urban sites is the transfer of toxic metals from vegetables through the food chain to humans. For example, it has been estimated that vegetables consumption contributes up to 70% of the dietary intake of Cd.[6] Adekunle et al. have reported that Pb in vegetables exceeded the recommended values for three cities in Nigeria.[10] Demirezen and Aksoy have shown high concentrations of [lead (Pb), cadmium (Cd) and copper (Cu)] in Abelmoschus esculentus collected from urban areas of Kayseri, Turkey.[11] Similarly, Maleki and Zarasvand observed high concentrations of Pb, Cd and Cr in sweet basil, parsley, leek and garden cress collected from peri-urban areas of Sanandaj, Iran.[12] Zhuang et al. have reported heavy metal concentration exceed food standards for vegetables grown close to metal smelters.[13] Thus, monitoring and assessment of heavy metals concentrations in the vegetables from the peri-urban sites in developing countries are necessary. However, limited published data are available on heavy metals concentrations in the vegetables and human exposure to contaminants from the peri-urban sites of Iran. Therefore, the present study aimed to determine the concentrations of heavy metals in selected edible vegetables grown at peri-urban sites in Sanandaj and to estimate their contribution to the daily intake of the metals.

Materials and Methods

The present study was carried out since May to October 2012 in the peri-urban areas of Sanandaj, located in the west part of Iran. Six major vegetable farms (from two major agricultural area namely Naysar region and Gharezeh region) were selected to study the level of trace metal contamination in vegetables and irrigation waters. Four common vegetables including coriander (Coriandrum sativum), dill (Aniethum graveolens), radish (Raphanus sativus) and radish leaf were selected for the evaluation. Samples of vegetables were randomly and simultaneously collected monthly from the selected farms, prepared and preserved in the laboratory until analyzed. A total of 120 samples of vegetables were taken as described below.

The vegetable samples were randomly collected in the form of sub-samples from each site at various distances (10 m, 30 m, 50 m, 70 m, 120 m and 140 m) away from the first sub-sample. Then they were thoroughly mixed to give a composite sample as a representative fraction of the vegetables. The vegetable samples were washed with distilled water to remove soil particles. Then they were air-dried for two weeks to remove excess moisture until stable weights were obtained. Samples were then grounded in a porcelain mortar with a pestle, passed through a 10 mesh sieve. For vegetable digestion, 1 g of each sample was taken into a Pyrex beaker and 10 ml of tri-acid mixture [Nitric acid (HNO_3), Perchloric acid ($HClO_4$) and Sulfuric acid (H_2SO_4) in 1:1:1 ratio)] was added. It was kept for 24 hours and then heated on the hot plate at 95° C until its volume was reached to 10 ml. Then 10 ml of tri-acid mixture was added again and heated again until the solution was reduced to 4 ml.[14] Thereafter, it was diluted with 50 ml deionized water. The digest was filtered and the final volume of 100 ml was made with double deionized water. The selected farms were irrigated with ground water. Water samples were collected in a 500 ml washed polypropylene bottle and 1 ml of concentrated acid nitric was added to the samples to avoid microbial activity.

Determination of the heavy metals was achieved by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Model Spectro arcos., SPECTRO Inc., Germany). The main operation parameters including torch type, detector type, nebulizer type, nebulizer flow, plasma power, coolant flow and pump rate were flared end EOP Torch 2.5 mm, CCD, cross flow, 0.85 l/min, 1400 W, 14.5 l/min and 30 RPM, respectively. All used chemical reagents were of analytical grade including standard stock solutions of different heavy metals.

The daily intake (DI) of heavy metals from vegetables consumption was calculated using the following formulas:[14]

$$DI = C_{metal\ in\ vegetable} \times M_{vegetable\ ingested}$$

Analysis of Kruskal-Wallis test were employed to examine the statistical significant of differences in the mean concentration of metals between group of vegetable families using SPSS for Windows (version 16.0, SPSS Inc., Chicago, IL, USA). A probability level of $P < 0.05$ was considered statistically significant.

Results and Discussion

Levels of Heavy Metals in Irrigation Waters

The chemical properties and metal concentrations of water from the six water irrigation sources are given in tables 1-3. As it is illustrated, the pH of the irrigation waters ranged from 7.6 to 8.1, the total dissolved solid (TDS) from 0.479 to 0.732 mg l^{-1}, and the electrical conductivity (EC) measured at 25° C from 0.479 to 0.732 dS/m (Table 1). These values are within the acceptable range recommended for irrigation waters.[15] The concentration of cations in water used for irrigation was highest for Mg, followed by Ca, Na, and K (Table 2). The cations and anions concentrations of the water except for Mg and K were found to be lower than the acceptable range recommended for irrigation waters.[15] According to table 3, the concentrations of heavy metals in the all irrigation water sources were lower than the acceptable range recommended for irrigation waters.[15] The presence of low amounts of these metals in irrigation waters may decrease their levels in soils, which in turn may weaken metal uptake by plants ultimately leading to down concentrations in the vegetables.

Levels of Heavy Metals in Vegetables

The mean concentration and range of heavy metals found in vegetables samples from cultivated sites are summarized in table 4. The heavy metal concentrations were determined based on vegetable dry weight. The results

Table 1. Some properties of irrigation waters of vegetable farms

Farm	pH	EC (dS/m)	TDS (mg l^{-1})	Total hardness (mg l^{-1} $CaCO_3$)	Turbidity (NTU)	Total alkalinity (mgl^{-1} $CaCO_3$)
1	8.1	0.585	379	280	5.0	126
2	7.9	0.479	312	208	3.1	130
3	7.6	0.610	396	312	2.5	140
4	7.6	0.600	388	300	2.4	137
5	7.6	0.732	477	440	1.2	166
6	7.7	0.715	465	432	1.0	170
Recommended Max. Concentration[15]	6.5-8.4	0-3	0-2000	-	-	-

EC: Electrical conductivity; TDS: Total dissolved solid

Table 2. Cations and anions concentrations in the irrigation waters of vegetable farms in terms of mg l^{-1}

Farm	Ca^{+2}	Mg^{+2}	Na^{+}	K^{+}	Cl^{-}	Br^{-}	SO_4^{-2}	NO_3^{-}	SAR
1	8.00	9.88	2.44	0.070	1.56	0.003	1.75	1.03	0.81
2	9.00	10.53	2.39	0.100	1.74	0.003	2.20	1.13	0.76
3	9.60	9.87	2.39	0.102	1.60	0.003	1.93	0.85	0.76
4	10.00	9.00	2.60	0.092	1.46	0.003	1.85	0.80	0.84
5	15.60	10.30	1.39	0.023	1.32	0.003	0.63	2.37	0.38
6	14.45	9.71	1.52	0.025	1.40	0.003	0.73	2.33	0.43
Recommended Max. Concentration[15]	0-20	0-5	0-40	0-0.05	0-30	-	0-20	0-10	0-15

Table 3. Heavy metal concentrations in the irrigation waters of vegetable farms

Element (ppb)	Farm						Recommended Max. Concentration[15]
	1	2	3	4	5	6	
Cd	0.10	0.10	0.10	0.10	0.10	0.10	10
Pb	1.00	1.00	2.00	2.00	1.00	1.00	5000
Cu	0.30	0.30	0.30	0.30	0.30	0.30	200
Cr	5.00	4.00	4.00	5.00	5.00	5.00	100
Zn	0.10	0.10	0.10	0.10	5.00	4.00	2000
Co	2.00	1.00	2.00	2.00	2.00	3.00	50
Fe	8.00	9.00	9.00	5.00	84.00	70.00	5000
Al	0.10	0.10	0.10	0.10	0.10	0.10	5000
Hg	0.10	0.30	0.50	0.30	0.20	0.40	-
As	0.10	0.10	0.10	0.10	0.10	0.10	100
Ni	0.20	0.20	0.20	0.20	0.20	0.20	200
Mo	0.20	0.20	0.20	0.20	0.20	0.20	10
Sn	12.00	9.00	8.00	9.00	8.00	8.00	-
Mn	0.10	0.10	0.10	0.10	0.10	0.10	200
Ba	0.00	0.00	0.00	0.00	0.00	0.00	-
B	33.00	30.00	30.00	29.00	18.00	19.00	700-3000
Li	70.00	80.00	90.00	70.00	90.00	80.00	2500
F	290.00	310.00	350.00	330.00	370.00	390.00	1000
Sr	157.00	140.00	169.00	178.00	172.00	167.00	-
Mg	5157.00	3889.00	4797.00	4710.00	5415.00	5400.00	10000
Be	10.00	9.00	10.00	9.00	10.00	10.00	100
P	17.00	19.00	16.00	17.00	10.00	11.00	-
Sb	0.40	0.40	0.40	0.40	0.40	0.40	-
Se	10.00	10.00	11.00	9.00	8.00	10.00	20
V	0.10	0.10	0.10	0.10	0.10	0.10	100

Table 4. Concentration of heavy metals in vegetables cultivated in main farmland areas of Sanandaj, Iran, in terms of mg Kg^{-1} dry weight

Element	Dill	Coriander	Radish root	Radish leaf	Recommended Max. level for vegetables[16]
Cd	0.006 (0.00-0.01)*	0.006 (0.00-0.01)*	0.011 (0.01-0.015)*	0.04 (0.00-0.10)*	0.20
Cr	3.93 (3.70-4.10)*	4.25 (4.00-4.50)*	4.00 (3.50-4.60)*	5.00 (4.20-5.80)*	2.30
Pb	0.48 (0.40-0.60)*	0.47 (0.40-1.00)*	0.42 (0.30-0.50)*	0.40 (0.20-0.60)*	0.30
Cu	10.70 (8.70-13.30)*	9.10 (7.90-11.00)*	3.15 (2.50-3.80)*	4.46 (4.10-5.00)*	40.00

* Values in the parenthesizes are minimum and maximum concentration of each element respectively.

showed a high level of Pb and Cr in all the vegetables from the cultivated area according to Food and Agriculture Organization (FAO) or the World Health Organization (WHO) guidelines.[16] The results showed that the levels of Pb in all the commodities were between 0.42 mg kg^{-1} in radish root and 0.48 mg kg^{-1} in dill with range of 0.3-0.5 and 0.4-0.6, respectively. Cd contents varied from 0.006 mg kg^{-1} in coriander and dill to 0.04 mg kg^{-1} (0.00-0.1) in radish leaf. In this study, maximum quantity of Cr was detected in radish leaf (5 mg Kg^{-1}) while dill had the lowest concentration (3.93 mg Kg^{-1}). Within the selected vegetables, the highest concentrations of Pb were noticed in dill. Furthermore, the highest concentration of Cu was observed in dill. Good agreement of these data was observed when the levels of Pb and Cd were compared to previously reported data by Fergusson.[17] For instance our values for lead were within the range of 0.05 to 6.7 mg/100 g, and 0.13 to 2.27 mg/100 g, reported for vegetables from Ireland and New York, respectively. For Cd, vegetables from Ireland showed a range of 0.005 to 0.06 mg/100 g, and those from New York had a range of 0.004 to 0.061 mg/100 g which was somewhat higher than our results. Besides, the concentrations of Cd in this study were below the range 0.09 to 0.26 mg/100 g reported for vegetables grown in Metropolitan Boston and Washington DC.[18] Furthermore, according to table 5, the Cd and Pb levels reported in this study were lower than those reported for vegetables in China[1] and India[19] and somewhat higher than those reported for vegetables in Uganda[6] for Cd and China for Pb.[20] The high contamination found in some vegetables might be closely associated to the pollutants in irrigation water, farm soil or due to pollution from the highways traffic.[21] All vegetables had lower levels of Cu than the permissible value (4 mg/100 g) in food provided by FAO/WHO.[16] Apart from its function as a biocatalyst, Cu is necessary for body pigmentation in addition to iron, the maintenance of a healthy central nervous system, prevention of anemia, and is interrelated with the function of zing and iron in the body.[22] Generally, plants contain the amount of Cu, which is inadequate for normal growth of plants. Application of micronutrient fertilizers and Cu-based fungicides may sometimes increase it to the alarming levels. In the present study, the mean levels of Cu were ranged from 3.15 to 10.70 mg kg^{-1}. The highest amount was found in dill and the lowest in radish root. From the results, it can be noted that the levels of Cu obtained in this study were comparatively lower than those reported by Begdeli and Seilsepour.[2]

As shown in table 4, the mean levels of Pb and Cr (0.44 and 4.3mg Kg^{-1}) were 1.46 and 1.87 times over the permissible levels set by FAO and WHO for human consumption. This trend was similar to those reported in previous study for Pb.[23] However, Cu and Cd amounts were within the acceptable levels. This trend was dissimilar to those reported in previous studies for Cd by Gupta et al.[19] and Ahmad and Goni[24] The

Table 5. Concentration ranges and safe limitations of heavy metals in vegetables from Iran and other countries (mg Kg^{-1} dry weight).

	Cu	Cr	Pb	Cd	Reference
Ranges					
Our study	5.8-8.28	3.85-4.75	0.33-0.68	0.003-0.03	
China	13.1-34.8	ND-1.07	6.07-15.6	0.14-4.47	1
China	8.65-317	0.08-15.4	0.18-7.75	0.036-0.18	20
India	8.63-27.94	3.70-9.03	11.97-22.09	2.05-2.91	24
India	15.66-34.49	34.83-96.30	21.59-57.63	10.37-17.79	19
India	10.95-28.58	5.37-27.83	3.09-15.74	0.5-4.36	25
Uganda	8.65-317	0.08-15.4	0.18-7.75	0.036-0.18	6
Iran	4.54-39.99	-	0.74-3.83	0.00-1.86	2
Greece	4.25-258	0.28-43.00	0.19-10.86	0.04-2.71	26
Iran	1.26-33.0	0.19-70.5	0.16-5.69	0.01-1.48	12
Safe limitations					
FAO/WHO (1984)	40	5	5	0.3	27
FAO/WHO (2001)	40	2.3	0.3	0.2	16
China EPA	20	0.5	9	0.2	28

FAO: Food and Agriculture Organization; WHO: World Health Organization; EPA: Environmental Protection Agency

variations of metal contents in these vegetables depend on the physical and chemical nature of soil and absorption capacity of each metal by plant, which is altered by innumerable environmental and human factors and nature of the plant.[25] The results showed that there was significant variations in the levels of these metals among the examined vegetables by Kruskal-Wallis test ($P < 0.001$).

Daily Intake Estimate of Heavy Metals

Exposure of consumers and related health risks are usually expressed as provisional tolerable daily intake (PTDI), a reference value established by Joint FAO/WHO.[27] Table 6 represents the estimation of each heavy metal intake through consumption of the studied foodstuffs.

The National Nutrition and Food Research Institute of Iran have estimated that the average consumption of edible vegetables is 218 g per day for every individual.[12] Results showed that the mean levels of Pb, Cu, Cr and Cd were 0.44, 6.85, 4.3 and 0.016 mg Kg^{-1}, respectively. Therefore, the DI of Pb, Cu, Cr and Cd could be 0.1, 1.5, 0.94 and 0.004 mg per day, respectively. Other studies from various countries have reported that the dietary intake for lead in adult was between 30 µg per day[4] and 427 µg per day.[29] For cadmium and copper, the estimated daily intake was from 4.6 µg to 30 mg per day, and 0.45 to 20 mg per day, respectively.[4,29] It could be concluded that estimation of daily intake for Cr and Cu in the present study was above those reported from other countries whereas the estimation for Cd and Pb are lower than the range.[1] Moreover, the estimated daily intake for the Pb and Cd in this study was below that those reported by FAO/WHO who have set a limitation for heavy metal intake based on body weight for an average adult (60 kg body weight). PTDI for Pb, Cd and Cu are 214 µg, 60 µg and 3 mg, respectively.[16] Thus, the authors believe that daily intake of these vegetables is not to cause a detrimental health hazard to the consumer.

Table 6. Mean heavy metal contents in vegetables and estimated of daily intake through consumption of vegetables in Sanandaj, Iran

	Pb	Cu	Cr	Cd
Mean concentration (mg Kg^{-1} dry weight)	0.44	6.85	4.30	0.016
Estimated daily intake (mg day^{-1})	0.10	1.50	0.94	0.004

Conclusion

The present study provided additional data on heavy metals pollution and also can help in risk assessment of consumer exposure to the expected heavy metal levels. A comparison of the levels of heavy metals in the studied vegetables was done with the permissible levels required for safe food. The results clearly showed a divergence from the permissible levels by FAO and WHO. High Pb contents were found in dill. High levels of Cd were found in radish leaf, and these amounts could be toxic and hazardous if taken in large quantities. However, the results of this study indicated that the daily intake of Cu and Cd through edible vegetables from farmland areas may not constitute a health hazard for consumers because the values are below the recommended daily intake of this metal.

Nonetheless, all these metals have toxic potential, but the detrimental impact becomes apparent only after decades of exposure. Although the concentration of some metals were not excess than permissible levels, the authors strongly recommended that people should not take large quantities of those vegetables so as to avoid large accumulation of the heavy metals in the body. It is therefore suggested that regular monitoring of heavy metals in plant tissues is essential in order to prevent excessive build-up of these metals in the human food chain. Appropriate measures should be put in place by the companies to always treat their waste effluents before discharging them into the immediate environment, since this will control the levels of heavy metals in the soil.

Conflict of Interests

Authors have no conflict of interests.

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Application of artificial neural network (ANN) for the prediction of water treatment plant influent characteristics

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Original Article

Abstract

Application of a reliable forecasting model for any water treatment plant (WTP) is essential in order to provide a tool for predicting influent water quality and to form a basis for controlling the operation of the process. This would minimize the operation and analysis costs, and assess the stability of WTP performances. This paper focuses on applying an artificial neural network (ANN) approach with a feed-forward back-propagation non-linear autoregressive neural network to predict the influent water quality of Sanandaj WTP. Influent water quality data gathered over a 2-year period were used to building the prediction model. The study signifies that the ANN can predict the influent water quality parameters with a correlation coefficient (R) between the observed and predicted output variables reaching up to 0.93. The prediction models developed in this work for Alkalinity, pH, calcium, carbon dioxide, temperature, total hardness, turbidity, total dissolved solids, and electrical conductivity have an acceptable generalization capability and accuracy with coefficient of determination (R^2) ranging from 0.86 for alkalinity to 0.54 for electrical conductivity. The predicting ANN model provides an effective analyzing and diagnosing tool to understand and simulate the non-linear behavior of the influent water characteristics. The developed predicting models can be used by WTP operators and decision makers.

KEYWORDS: Neural Network, Time Series, Influent Water Characteristics, Forecasting

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Introduction

To maintain a stable performance in a water treatment plant (WTP), it is desirable to know in advance the influent water characteristics of the WTP. Water characteristics such as turbidity, total suspended solids, and pH are important water quality parameters. There is a significant relationship between these parameters and the amounts of coagulants and flocculants used in treatment processes. Prediction of the influent water characteristics is helpful in the optimal scheduling of the coagulation and flocculation process. In practice, the influent water characteristics are usually estimated by the operators based on experience and or using online sensors. Such estimations, however, are not accurate enough to manage WTPs, especially for operators that want to manage the WTP performance for the next day. The precipitation may cause large variability of the influent water characteristics, thus reducing the efficiency of WTPs. Moreover, heavy rainfall overwhelms the water treatment system, causing spills and overflows. Thus, prediction models for water

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quality characteristics, based on their registered historical data, can be built by the data mining approach.[1] Data mining is a promising approach for building prediction models. It is the process of finding patterns from data by algorithms versed on the crossroads of statistics and computational intelligence.[2]

Artificial neural networks (ANNs) are one of the most accurate and widely used data mining processes and forecasting models. It has been shown that a network can approximate any continuous function to any desired accuracy. ANNs are nonlinear and non-parametric methods, and unlike traditional approaches, such as the Box–Jenkins or ARIMA, do not assume that the time series under study are generated from linear processes. However, they may be inappropriate if the underlying mechanism is nonlinear. In fact, real world systems are often nonlinear.[3] Artificial neural networks have been found to be a viable contender to various traditional time series models.[4,5] Lapedes has reported the first attempt to model nonlinear time series with artificial neural networks.[6] Imrie et al. have reported the application of ANN for the river flow prediction.[7] Wu and Lo used the ANN to model the nonlinear relationship between accumulated input and output numerical data for the coagulation processes in water treatment.[8] Melessea et al. have presented the application of a multilayer perceptron (MLP) ANN with an error back propagation algorithm for the prediction of suspended sediment load of river systems.[9] An ANN data driven modeling approach was used by Huo et al. to predict the water quality indicators of Lake Fuxian, the deepest lake of southwest China.[10] Patil et al. have presented a study of predicting sea surface temperature with nonlinear autoregressive neural networks.[11]

In this study, we used an ANN approach to predict daily influent water characteristic to Sanandaj water treatment plant. This paper presents a data-mining approach to predict influent water characteristic in a WTP for a short-term period (one day ahead). In this work, the proposed approach is based on the classical nonlinear autoregressive time series using time-lagged feed-forward networks, in which the data from the daily time series are used to forecast the next day. In this study the prediction models are developed for alkalinity (Alk), pH, calcium (Ca), carbon dioxide (CO_2), temperature (T), total hardness (TH), turbidity (Tur), total dissolved solids (TDS), electrical conductivity (EC), and chloride (Cl) as the influent water characteristics. The models output is evaluated using statistical indices and observed water quality data.

Materials and Methods

ANN model was developed to predict the characteristic parameters of influent water of Sanandaj water treatment plant. This plant is one of the oldest water treatment plants in Iran. It is located in the northeast of the city of Sanandaj at an altitude of 1510 meters above sea level and near Nanaleh village road. Nominal design capacity of the treatment plant is 0.7 cubic meters per second, and can increased up to 1.5 cubic meters per second when needed. The raw water is supplied from Gheslagh dam. The water is transferred through a concrete and steel transmission line, with the length of 8 kilometers, by gravity force. The treated water, after disinfection and storage, is pumped by a steel transmission pipeline with the length of 2.2 km to Faizabad storage tank and then the distribution network. Registered daily historical data of the influent water quality parameters including carbon dioxide, total hardness, chloride, total calcium, total dissolved solids, total alkalinity, electrical conductivity, pH, turbidity, and temperature were used to conduct the study. The data was provided by the urban Water and Wastewater Company of Kurdistan and collected over a 2-year period. This period was satisfactory as it covered all probable seasonal variations in the studied variables.

The numbers of data points for plant data used for the training and test data sets together are 707 points. The description of the variables, units of measure, range of the data, together with the mean and standard deviation of the plant's raw data are presented in table 1.

Artificial Neural Network is an information processing tool that is inspired by systems such as biological nervous systems. The objective of a neural network is to compute output values from input values by some internal calculations.[12]

Neural network is trained to construct the specific black box function by adjusting the values of the connections (weights) between layers of elements based on a comparison of the output and the target until the network output matches the target.[13]

Figure 1 illustrates neural network training structure. There are many different types of training algorithms. One of the most common classes of training algorithms for feed forward neural networks (FFNNs) is called back propagation (BP).[14]

The basic component of a neural network is the neuron, also called node. Figure 2 illustrates a single node of a neural network. The inputs are represented by a_1, a_2, and a_n, and the output by O_j. Several signals can be inserted into the node. The node manipulates these inputs in such a way to give a single output signal. The values W_{1j}, W_{2j}, and W_{nj}, are weight factors associated with each of the inputs to the node. The other input to the node, b_j, is the node's internal threshold, also called bias. This is a randomly chosen value that governs the node's net input through the following equation:[15]

Table 1. Raw influent water characteristics data of Sanandaj, Iran water treatment plant (WTP)

	Mean (µ)	SD	Min	Max	µ-4SD	µ+4SD
CO_2	3.24	10.89	0.10	199.00	-40.32	46.80
TH	153.51	11.79	122.00	205.00	106.35	200.66
Cl	9.40	7.63	5.50	160.40	-21.12	39.92
Ca	47.14	7.01	32.40	146.30	19.12	75.17
TDS	209.87	19.16	157.00	252.00	133.22	286.53
Alk	157.95	16.57	0.00	193.00	91.68	224.23
EC	332.56	138.65	0.00	3337.00	-222.03	887.15
pH	8.47	7.18	7.16	175.90	-20.24	37.17
Tur	3.71	5.26	0.50	65.00	-17.33	24.76
T	11.42	6.31	2.00	90.00	-13.81	36.64

SD: Standard deviation; TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity; Tur: Turbidity; T: Temperature

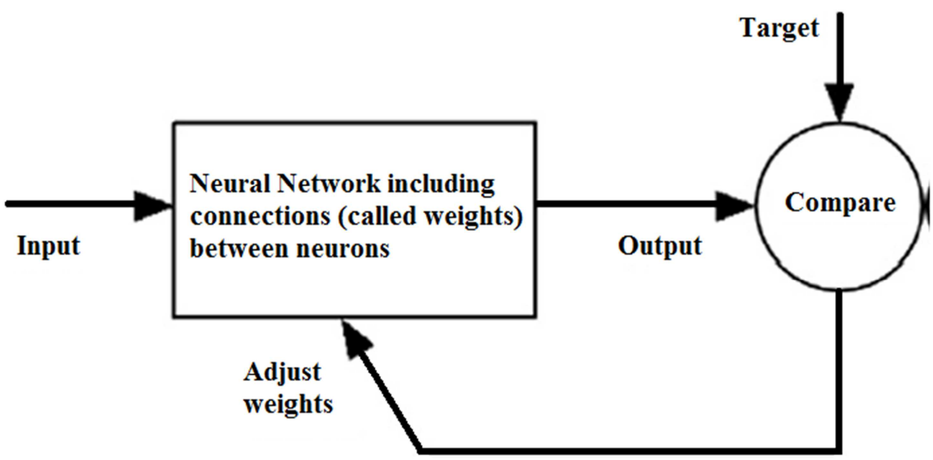


Figure 1. Neural network training structure

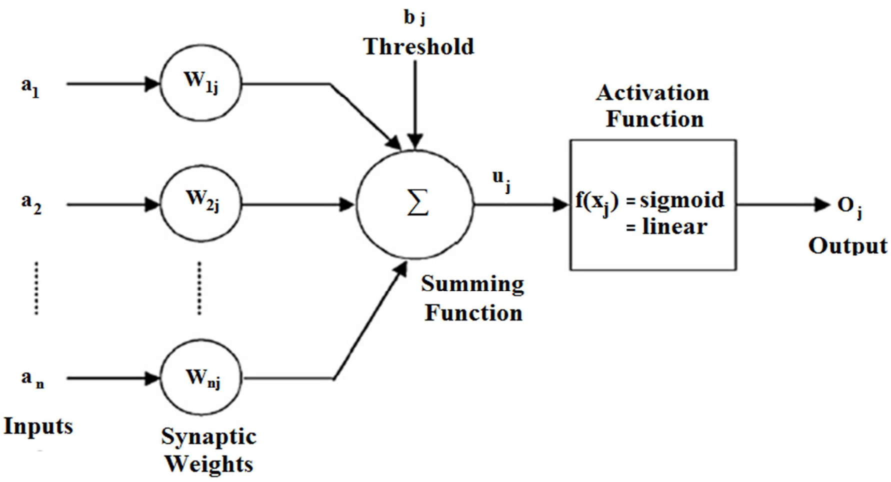


Figure 2. Single node anatomy

$$u_j = \sum_{i=1}^{n} (W_{ij} \times a_i) + b_j$$

The transfer function can transform the node's net input in a linear or non-linear manner. Commonly used transfer functions in hidden layer are sigmoid transfer function and hyperbolic tangent transfer function as follows:[15]

- Sigmoid transfer function

$$f(x) = \frac{1}{1+e^{-x}} \qquad 0 \le f(x) \le 1$$

- Hyperbolic tangent transfer function

$$f(x) = \tanh(x) = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} \qquad -1 \le f(x) \le 1$$

The neuron's output O_j is found by performing linear function on the hidden layer neuron's outputs as follows:[15]

- Linear transfer function

$$f(x) = x \qquad -\infty < f(x) < +\infty$$

Neural networks very rarely operate directly on the raw data, although this is possible. The disadvantage of using raw data values is that the training time for the neural network would be significantly longer as the various variables have very different ranges. Data pre-processing can have a significant effect on the generalization performance of a supervised neural network.[16]

Plant data is, most often, not very reliable and many problems can occur which can affect the reliability or integrity of the data. Missing data is a common problem in statistical analysis.[17]

Tarassenko proposes some strategies to deal with missing data.[18] One method consists of replacing the missing data value by its mean or median across the training set.[19] The other method is to estimate the missing value for an n-dimensional input vector from knowledge of the other n-1 input variables. The last method uses either a linear model or a NN network to predict the n[th] value given the set (n-1)-dimensional vectors as inputs. The approach eventually adopted was to use a linear interpolation method to replace the missing data values in the Sanandaj WTP plant data set. In a few instances, the missing data points were consecutive, but this did not extend to more than 5 consecutive missing points.

Data that appear to be very distant from the normal data distribution may be classified as being outliers. In certain instances however, this outlying value may be correct and is a natural product of the variables distribution.[20] One approach for data rejection is to plot the histogram of the data distribution and then carefully scrutinize the data which appear as outliers. The standard deviation based outlier analysis is also a mechanism for revealing values that are numerically distant from the rest of the data. In this study, we took a normal distribution with cutoff 4 standard deviations from the mean to detect the outliers. Thus, the data that were more extreme than μ ± 4SD were considered as outliers.

Neural networks can be trained by using raw data as inputs, but the training time will be considerably longer. However, if scaled data is presented to the network, the weights can remain in small, similar predictable ranges. Box-cox transforms non-normally distributed data to a set of data that has approximately normal distribution. The Box-Cox transformation is a family of power transformations. The values of λ parameter for studied variables are shown in table 2. These values were not zero for all water characteristic parameters and the transformation of data was performed according to the following relationships:

If λ is not = 0, then $$data(\lambda) = \frac{data^{\lambda} - 1}{\lambda}$$

If λ is = 0, then $$data(\lambda) = \log(data)$$

After pre-processing the raw data, the neural network model was created in MATLAB software (version 7.12; Mathworks Inc., USA) that offers a platform for the simulation application. A nonlinear autoregressive (NAR) time series neural network was used and trained to predict the variable for the next day from that series' past values. The NAR is a network with feedback arrangement as shown in figure 3. In NAR network, there is only one series involved. The future values of a time series y (t) are predicted only from past values of that series. This form of prediction is called nonlinear autoregressive and can be written as follows:

$$y(t+1) = f(y(t), y(t-1), ..., y(t-d))$$

The network was trained using the common algorithm of Levenberg-Marquardt. The network had non-linear sigmoid transfer function for the hidden layer and a linear transfer function for the output layer neurons. The number of feedback delays was determined by depicting partial autocorrelation function (PACF). The numbers of delays in PACF chart with a significant correlation coefficient were considered as the numbers of feedback delays. The numbers of feedback delays are shown in table 2. The other network properties are as follows:

- Network type: Feed-Forward Back-Propagation
- Training function: TRAINLM
- Performance function: MSE
- Number of hidden layers: 1

Hidden layer size: A single hidden layer with different count of neurons (i.e. 1 to 20) has been assessed for this study. As shown in figure 4 the performance of the network decreased almost by increasing the hidden layer size. These decreases are more considerable almost after ten sizes for neurons in all models. Thus, in this study 10 neurons were considered as the maximum possible size for the hidden layer for all models.

Table 2. Pre-processed influent water characteristics data and number of feedback delays

	Description and unit of measure	Min.	Median	Mean	Max.	SD	λ	Feedback Delays*
CO_2	Carbon dioxide (mg/l)	0.10	2.3	2.6	8.2	1.5	0.41	6
TH	Total Hardness (mg/l)	122.00	155.3	154.0	197.2	10.1	1.86	4
Cl	Chloride (mg/l)	5.50	9.0	8.9	12.5	1.2	-0.20	8
Ca	Calcium (mg/l)	32.40	48.0	47.2	59.8	4.0	2.43	6
TDS	Total dissolved solids (mg/l)	157.00	214.0	211.0	252.0	12.6	5.05	7
Alk	Total alkalinity (mg/li)	120.60	160.2	158.2	193.0	14.0	1.76	5
EC	Electrical conductivity (µ.mohs/cm)	260.00	333.5	330.0	393.0	18.5	4.59	11
pH	-	7.16	8.2	8.2	8.9	0.3	-0.02	5
Tur	Turbidity (NTU)	0.50	2.0	3.3	24.0	3.5	-0.20	8
T	Temperature (°C)	2.00	6.0	11.0	11.4	5.3	0.72	6

* Feedback delays: The number of auto-regressive series lags as inputs of the NAR neural network; SD: Standard deviation; TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity; Tur: Turbidity; T: Temperature

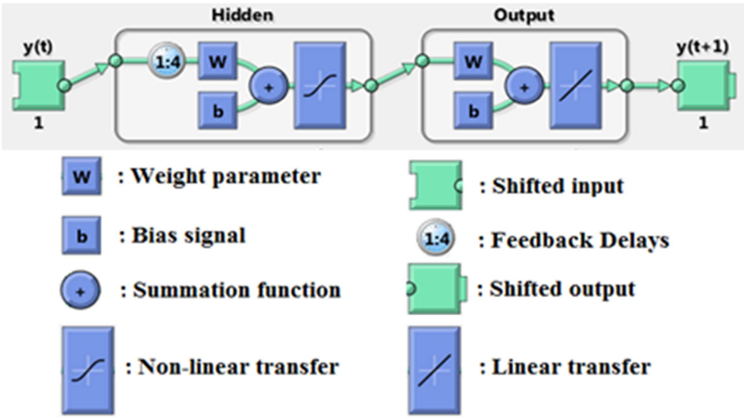


Figure 3. Neural network predicting structure with a hidden layer

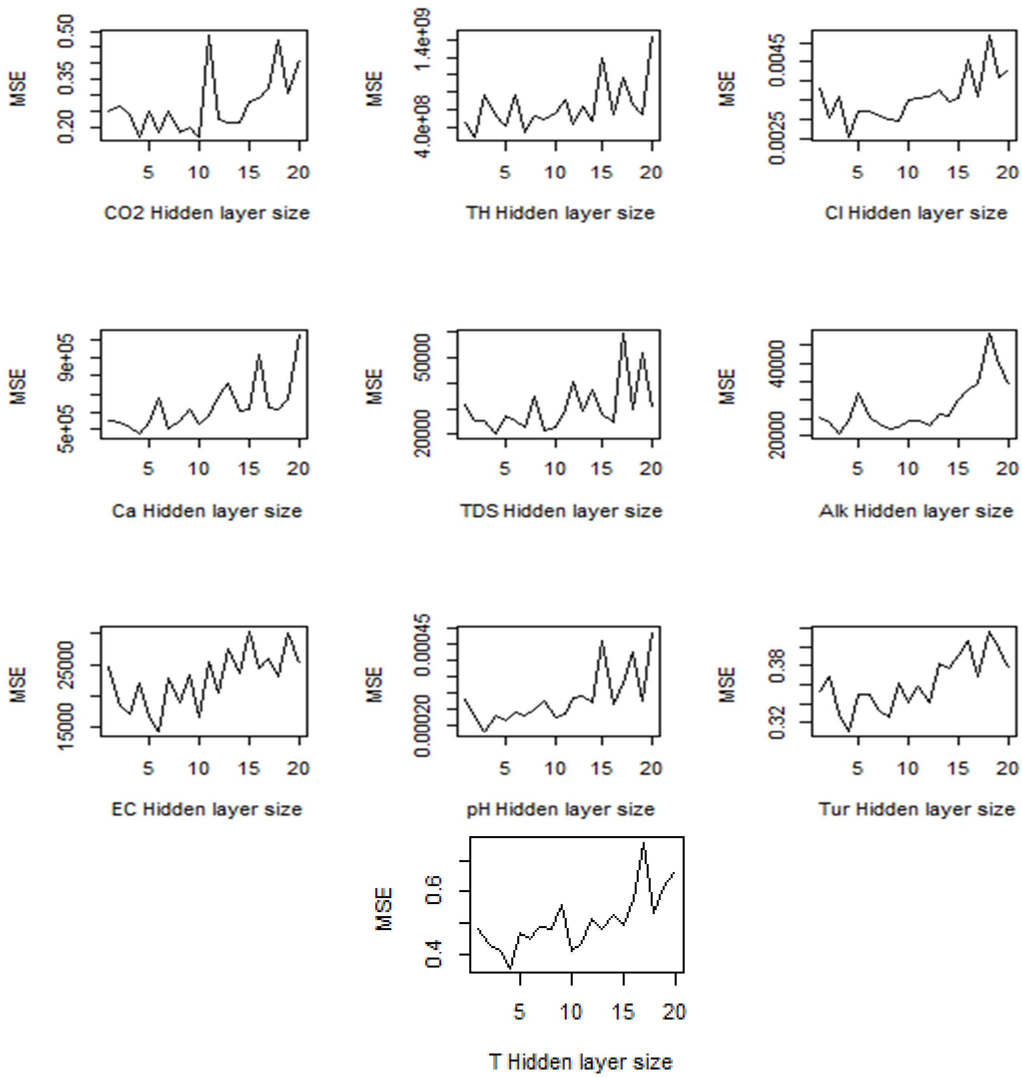


Figure 4. Hidden layer size versus network performance

The MATLAB routine *trainlm* (training with Levenberg-Marquardt algorithem) was used for the optimization. This algorithm attains fast learning speed and high performance relative to other optimization algorithms and the details of this algorithm are reported by Hagan et al.[15] The performance function used for training is based on the mean square errors (MSE) between actual WTP influent water characteristics and network predictions. Based on the selected network structure, the training process was activated to achieve a performance target of 1×10^{-3} for a maximum training of 1000 epochs. The learning rate was chosen to be 0.01. The value of this parameter was obtained after performing several trial and error runs. It was found that this value insures stable fast learning.

In order to study the relative performance of the network, the correlation coefficient (R) and root of mean square error (RMSE) were worked out. The underlying expressions as well as the strengths and weaknesses of these parameters are given as below.[11]

Correlation coefficient (R):

$$R = \frac{\sum_{i=1}^{n}(X-\bar{X})(Y-\bar{Y})}{\sqrt{\sum_{i=1}^{n}(X-\bar{X})^2(Y-\bar{Y})^2}}$$

where X = observed y_t , $\bar{X}$ = mean of X, Y = predicted y_t, $\bar{Y}$ = mean of Y, and n = number of observations.

The correlation coefficient (R) shows the extent of the linear association and similarity of trends between the target and the realized outcome. It is a number between 0 and 1; such that the higher the correlation coefficients the better the model fit. It, however, is heavily affected by the extreme values.

Root of mean square error (RMSE):

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(X-Y)^2}{n}}$$

RMSD is a good measure of accuracy, but only to compare forecasting errors of different models for a particular variable and not between variables, as it is scale-dependent.[21]

Results and Discussion

The most common training algorithm used in the ANN literature is called back propagation (BP). Back propagation was developed and popularized by Rumelhart et al. and it is the most widely implemented of all neural network algorithms.[22] It is based on a multi-layered feed forward topology with supervised learning. The network uses the default Levenberg–Marquardt algorithm for training. The input vectors and target vectors are randomly divided into three sets as follows: 70% are used for training, 10% are used to validate that the network is generalizing and to stop training before over-fitting, the last 20% are used as a completely independent test of network generalization. The number of networks to fit with different random starting weights was 20 times. These are then averaged when producing predicts.

Figure 4 shows the results of regression between network outputs and data sets of validation, and training and test targets. It is observed that the output tracks the targets well. Data from table 3 shows R and RMSE of each ANN for validation, training, and test steps. The correlation coefficient (R) measure the correlation between outputs and targets. An R value of 1 means a close relationship and 0 a random relationship while the RMSE is the root of mean squared difference between outputs and targets. The lower the values are the better.

The coefficient R for the validation phase upon application of the test set, ranges from 0.61 for Cl to 0.93 for Alk, and the coefficient of determination R^2 ranges from 0.37 for Cl to 0.86 for Alk. These figures indicate that 37% of the variation in the Cl variable can be explained by the variable time delays. The remaining 64% can be attributed to unknown, lurking variables, or inherent variability. Neural network model for Cl may, therefore, not able to solve this particular input-output mapping problem well.

The results for Alk in table 3 are interesting as the R correlation coefficient is 0.93 (R^2 = 0.86) for the validation phase. This indicates that this

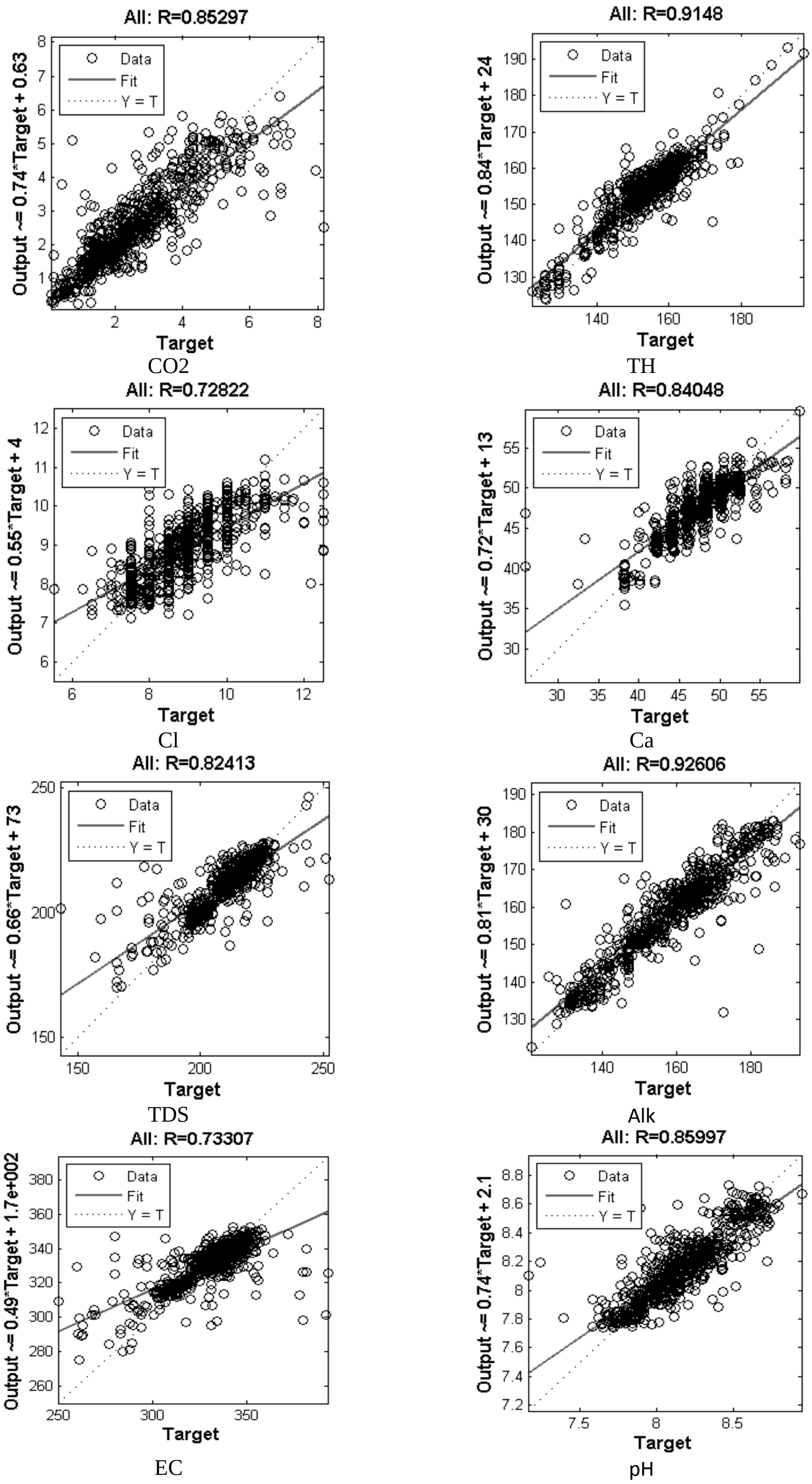


Figure 4. Measured and predicted output variables

TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity model has the best result throughout. However, all other results are also acceptable. The regression coefficient ranges from 0.74 for EC (R^2 = 0.54) to 0.89 (R^2 = 0.79) for pH. Thus, for these variables more than 50% of the variation in them can be explained by their time delays. Time series models for these variables, therefore, are able to solve the input-output mapping problem well.

For all studied water influent characteristics, the simulation results of influent parameters are presented in figure 5 by plotting the measured and predicted output variables. The network response is satisfactory, and simulation can be used for entering new inputs. Given the above, it can be conclude that a feed-forward neural network based nonlinear autoregressive (NAR) model can be used for forecasting time series values well. The results of this study indicated high correlation coefficient between the measured and predicted output variables, reaching up to 0.93. Therefore, the prediction models developed in this work for Alk, pH, Ca, CO_2, T, TH, Tur, TDS, and EC have an acceptable generalization capability and accuracy with coefficient of determination ranging from 0.86 for Alk to 0.54 for EC. As a result, the neural network modeling could effectively simulate and predict these influent water quality parameters of Sanandaj WTP. In the case of Cl, neural network modeling may not able to predict this influent water characteristic well, at least in this study. Thus, it is necessary to conduct more studies to make its behavior clear. The testing step of the models also provided similar results to validation step results. The correlation coefficient ranges from 0.65 (R^2 = 0.42) for Cl to 0.88 (R^2 = 0.77) for TH and T. for Alkalinity, the test phase R is 0.85 (R^2 = 0.72). Thus, these results confirm the validation step.

The application of predictive models for wastewater influent characteristics has been reported in several studies.[23-25] Neural network modeling has rarely been used in water treatment plant influent forecasting. Zhang and Stanley, in their two studies, used ANN models to predict treated water turbidity and color at the Rossdale water treatment plant in Edmonton, Alberta, Canada.[26,27] Lamrini et al. adapted the Levenberg–Marquardt method in ANN to predict the coagulant dosage for the raw water with high turbidity.[28]

Conclusion

This study presented a detailed methodology for developing successful ANN models for modeling influent water characteristics. The utility and applicability of this methodology is demonstrated through a case study in which some successful NAR models to predict influent water characteristics were developed. It is concluded that nonlinear autoregressive or NAR neural network provides an effective analyzing and diagnosing tool to understand and simulate the non-linear behavior of influent water characteristics of the water treatment plant. Moreover, it is a valuable predicting tool for

Table 3. Performance of MLP networks

Parameter	Training phase		Validation phase		All phases		Testing phase	
	RMSE	R	RMSE	R	RMSE	R	RMSE	R
Cl	0.68	0.59	0.89	0.37	0.74	0.53	0.87	0.42
EC	12.81	0.55	12.41	0.55	12.69	0.53	12.43	0.49
TDS	6.70	0.72	6.96	0.61	7.20	0.67	9.34	0.55
Tur	1.76	0.72	1.97	0.69	1.91	0.71	2.41	0.69
TH	3.61	0.86	4.77	0.71	4.07	0.83	5.19	0.77
T	1.20	0.86	2.19	0.71	1.53	0.83	2.01	0.77
CO_2	0.72	0.76	0.77	0.71	0.76	0.72	0.92	0.64
Ca	2.27	0.71	2.03	0.72	2.18	0.71	1.87	0.74
pH	0.14	0.76	0.14	0.79	0.14	0.74	0.17	0.62
Alk	4.79	0.88	4.75	0.86	5.33	0.86	7.74	0.72

RMSE: Root of mean square error; TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity; Tur: Turbidity; T: Temperature

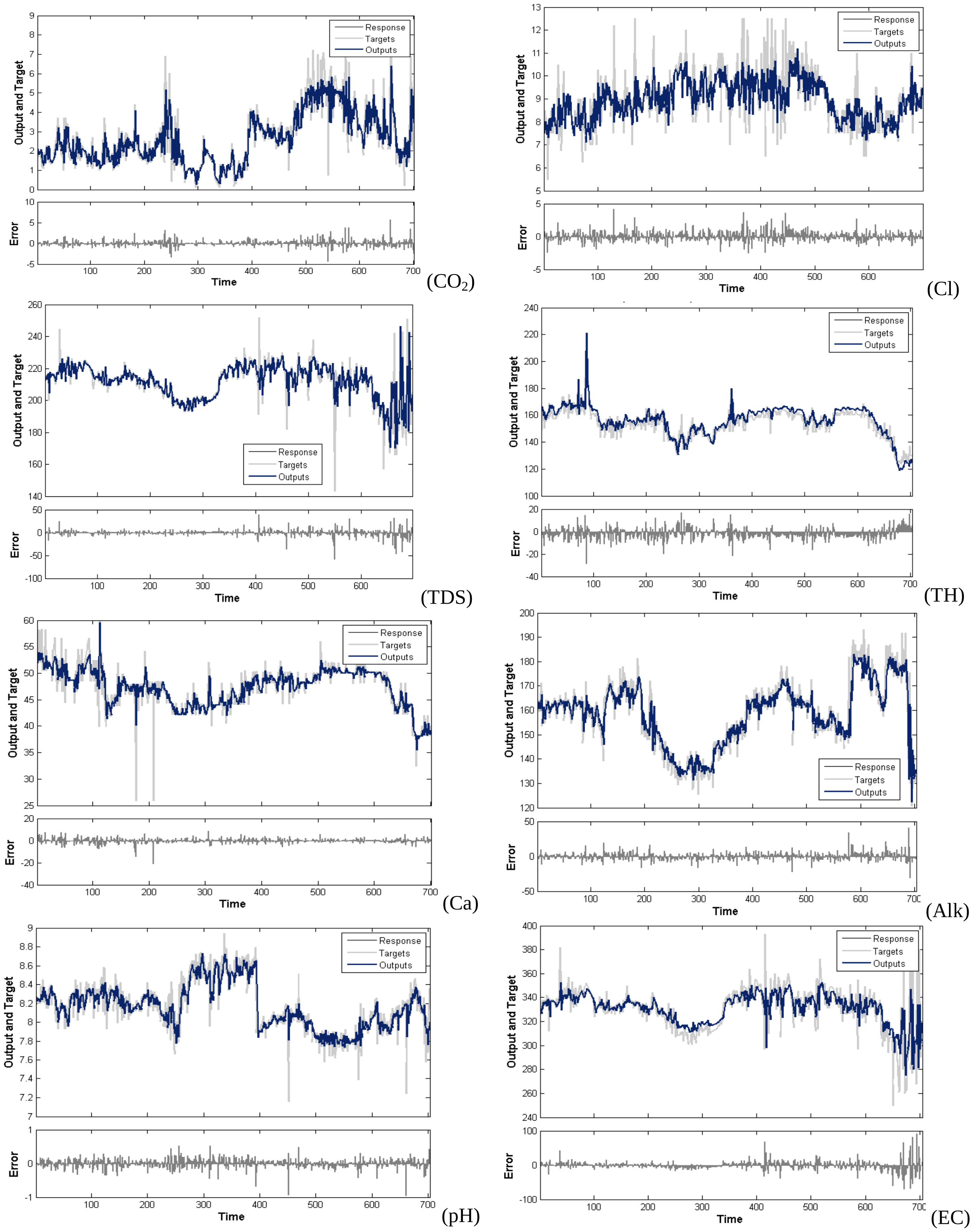
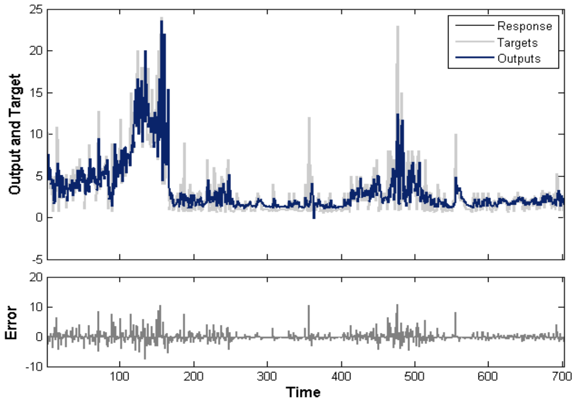
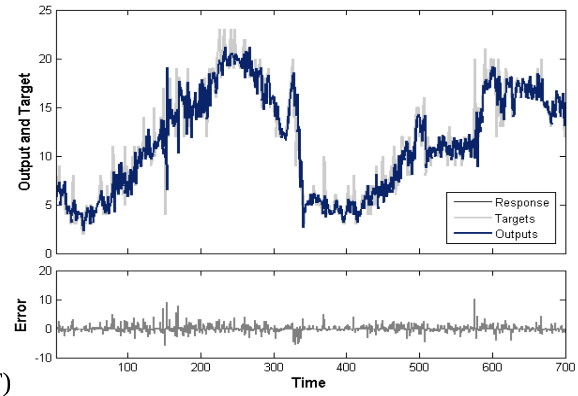


Figure 5. Networks responses and errors

TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity; Tur: Turbidity; T: Temperature



(Tur)



(T)

Figure 5. Networks responses and errors (Continue)
TH: Total hardness; TDS: Total dissolved solids; Alk: Alkalinity; EC: Electrical conductivity; Tur: Turbidity; T: Temperature

plant operators and decision makers. The NAR models are robust artificial intelligence models that can be proposed as a useful tool to understand the complex and dynamic nature of influent water characteristic.

Conflict of Interests

Authors have no conflict of interests.

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Assessment of Birjand flood plain water quality by physico-chemical parameters analysis in Iran

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Original Article

Abstract

We assessed the physico-chemical status of twelve surface water samples from the Birjand flood plain (east of Iran) during fall 2010. The sampling points were selected on the basis of their importance. The physico-chemical parameters such as pH, temperature (T), electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulphtate (SO_4^{2-}), bicarbonate (HCO_3^{-}), carbonate (CO_3^{2-}), nitrite (NO_2^{-}), nitrate (NO_3^{-}), dissolved oxygen (DO), biochemical oxygen demand (BOD_5), and chemical oxygen demand (COD) of surface water were determined. The results showed that there were a statistical significant positive correlation between the pH and DO. pH and temperature indicated negative association with most of the parameters. Furthermore, EC showed highly significant positive association with TDS, TH, Ca^{2+}, Na^{+}, and Cl^{-}. Results showed that the quality of surface water was not suitable for drinking, with references to the concentrations of EC, TDS, TH, Na^{+}, HCO^{3-}, and BOD_5 which were more than the prescribed limits, in most sites.

KEYWORDS: Water Quality, Hardness, Biochemical Oxygen Demand, Birjand Flood Plain

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Introduction

Today, the competition for scarce water resources is intense both in Iran and in many places all around the world; because water is the most essential commodity for human consumption and is one of the most important renewable resources, which must be prevented from deterioration in quality. The eastern part of Iran has a semi-arid climate with average annual rainfall of 171 mm. Therefore, communities must share freshwater sources from aquifer natural resources. Water source is one of the most important limiting factors in arid and semi-arid regions that can exhibit the development of sustainable population growth.[1] Many people around the world enjoy the benefits of technological and economic developments and

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high standards of living; however, many scientists are aware that these developments cause lots of issues such as bioenvironmental problems specially water resources pollution.

Human activities can have direct or indirect contaminating effect on drinking water resources such as streams, rivers, lakes, dams, reservoirs, and groundwater.[2] The main sources of water pollution are discharge of domestic sewage and industrial effluents -which contain organic pollutants-chemicals and heavy metals, and run-off from land-based activities.[3] Increasing water pollution causes not only the deterioration of water quality but also threatens human health and the balance of aquatic ecosystems, economic development, and social prosperity.[4] Given the effects of human activities on water quality, it is necessary to notice the quality of water resources.[5] Monitoring can be the first and the most important step toward applying an appropriate quality management plan in order to eliminate water pollution.[6] A large number of physico-chemical parameters can fluctuate the quality of water resources, and monitoring these parameters can strongly be affected by magnitude and source of pollution.[7] Assessment of water resource quality in any region is an important aspect of its developmental activities, because rivers, lakes and man-made reservoirs are water supplies for domestic, industrial, and agricultural applications.[8] Hence, the objective of this article was to investigate the physico-chemical parameters (pH, temperature (T), electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{2-}, NO_2^{-}, NO_3^{-}, dissolved oxygen (DO), biochemical oxygen demand (BOD5), and chemical oxygen demand (COD) and Wilcox and Schoeller diagrams of surface water in Birjand flood plain, east of Iran. The analyzed data were compared with standard values recommended by the World Health Organization (WHO) for drinking purposes.[9]

Materials and Methods

The studied site was located in Birjand, east of Iran, and is the capital city of Southern Khorasan province. It is situated at latitude of 32˚ 86' N and longitude of 59˚ 21' E and is about 1490 m above the sea level (Figure 1). The climate of the city is semi-arid with cold winter and approximately 8 months dry season (from middle of April to December). Its average rainfall is 171 mm and unevenly distributed throughout the year. The average annual temperature is 16.5° C with the warmest month in July (average 28.5° C) and the coldest in January (average 3.5° C). The sunlight duration in a year is 255 days.

Water samples were collected from 12 stations, three samples from each of them in the Birjand flood plain during fall 2010. Water samples were collected in acid washed 250-ml plastic bottles. The samples were kept in refrigerator at 4° C. The water samples were filtered using a 0.45 µm nitrocellulose membrane filter. Prior to any analysis, all the equipment and containers were soaked in 10% HNO_3 and rinsed thoroughly with deionized distilled water before use. Water temperature was measured during sampling using an ordinary thermometer. The physico-chemical parameters such as pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, CO_3^{2-}, NO_2^{-}, NO_3^{-}, DO, BOD, and COD were determined using standard methods[10] (Table 1). Finally, the resulted data were compared with the WHO standards specified for the maximum rate of physicochemical parameters allowed in drinking water. Statistical analyses were carried out using Excel and SPSS for Windows (version 16.0, SPSS, Inc., Chicago, IL, USA) and the Pearson correlation (*r*) was used to test correlations. All the concentrations were reported in mg/l except for pH, EC (in micromhos/ cm), and temperature (in ° C).

Results and Discussion

pH and water temperature

Measurement of pH is one of the most important and frequently used tests in water chemistry. pH is an important factor in determining the chemical and biochemical properties of water. It

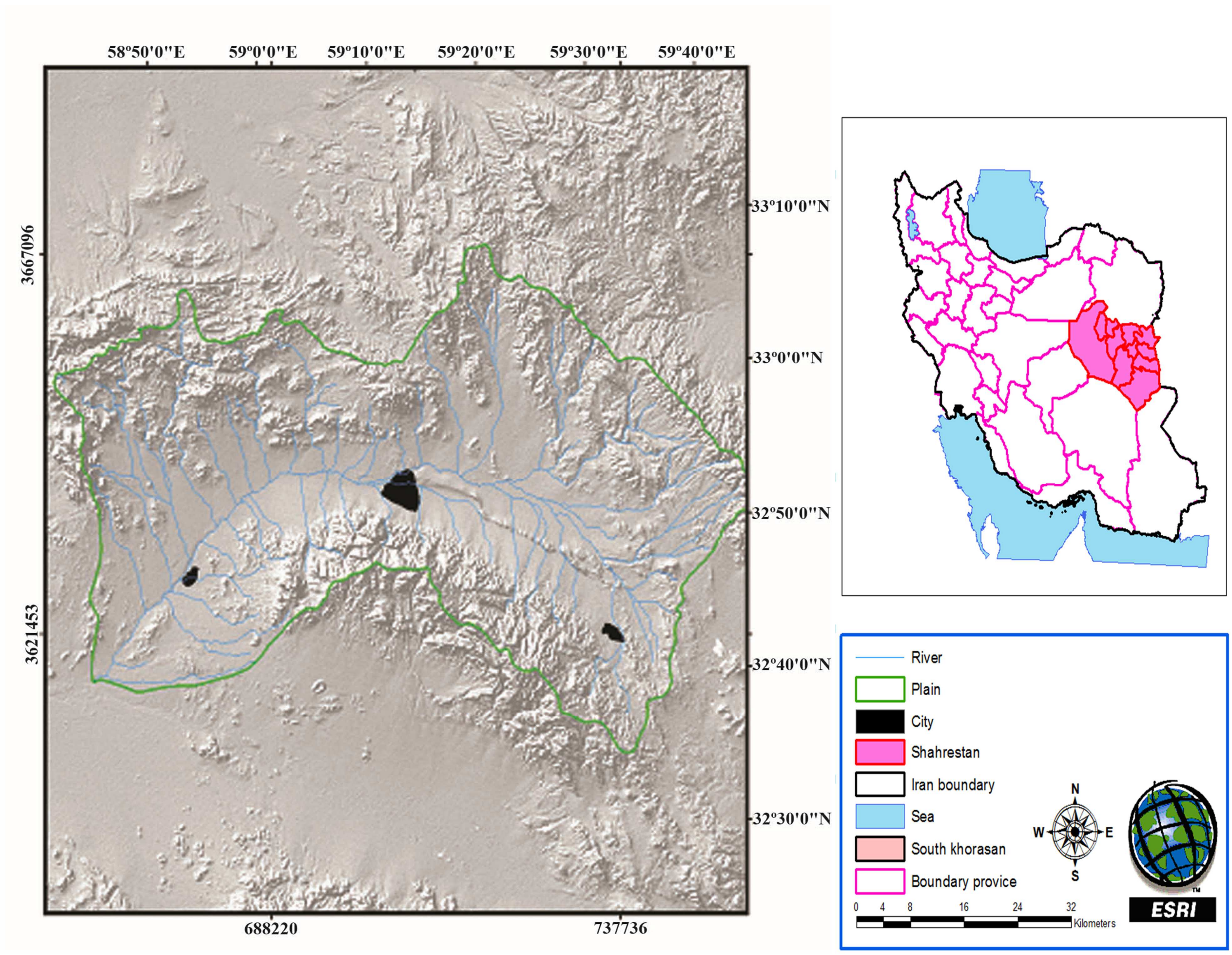

Figure 1. Map of the study area (Birjand, Iran flood plain)

Table 1. Methods used for estimation of physicochemical parameters

Parameters	Test methods
pH	Multi Parameter Analyzer (Consort, Model: C534T & Istek, Model: pdc815)
EC	Multi Parameter Analyzer (Consort, Model: C534T & Istek, Model: pdc815)
TDS	Multi Parameter Analyzer (Consort, Model: C534T & Istek, Model: pdc815)
TH	Titration method
Ca^{2+}	Titration
Mg^{2+}	Titration
Na^{+}	Flame Photometric method
K^{+}	Flame Photometric method
Cl^{-}	Argentometric titration
SO_4^{2-}	Photometer
HCO_3^{-}	Titration
CO_3^{2-}	Titration
NO_2^{-}	Photometer
NO_3^{-}	Photometer
DO	Multi Parameter Analyzer
BOD_5	5 days incubation at 20 °C and titration of initial and final DO
COD	Open reflux method

EC: Electrical conductivity; TDS: Total dissolved solids; TH: Total hardness; DO: Dissolved oxygen; BOD_5: Biochemical oxygen demand; COD: Chemical oxygen demand can almost have chemical effects on most water substances.[11] pH of surface water was alkaline, with an average value of 8.3 (Table 2). They were (total of stations) within the WHO standard values for pH in drinking water (6.5-9.5).

Temperature is another important factor and all life processes are accelerated or slowed down by temperature changes in the environment. It influences the solubility of gases and salts in water. Most chemical equilibrium is temperature dependent. Important environmental examples are the equilibrium between ionized and unionized forms of ammonia, hydrogen cyanide, and hydrogen sulfide.[11] The water temperature recorded from surface water Birjand flood plain showed only slight variations. Average water temperature of surface water varied from 25.4° to 27.8° C (Table 2).

TDS

TDS indicate the general trend of the surface quality or salinity of the surface water bodies. In natural waters, the major contributors to TDS are carbonate, bicarbonate, chloride, sulfate, phosphate, and nitrate salts.[11] During the present study, minimum and maximum values of TDS were recorded at stations 9 (1145 mg/l) and 8 (2960 mg/l), respectively. This may be due to natural sources and urban runoff from the sampling stations.[12] Water with a TDS < 1200 mg/l generally had an acceptable taste. Higher TDS could adversely influence the taste of drinking water and may have a laxative effect.[11]

Total hardness, calcium and magnesium (Ca^{2+}, Mg^{2+})

Total hardness ranged from 339-893 mg/l as $CaCO_3$. The highest and lowest values were recorded at stations 8 and 9, respectively (Table 2). It might be due to the dissolution of land derived carbonates and bicarbonate in the water. The concentrations of Ca^{2+} and Mg^{2+} observed from the studied area varied from 30-200 mg/l as $CaCO_3$ and 42-148 mg/l as $CaCO_3$, which are below the standard limits of 200 and 150 mg/l as $CaCO_3$ in the surface water samples respectively. Ca^{2+} is an important ion to develop proper bone growth. Although Mg^{2+} is an essential ion for functioning of cells in enzyme activation, it is considered as laxative agent at higher concentration.[13]

Sodium (Na^+)

Sodium varied from 91 to 651 mg/l, the amount which exceed the maximum permissible limit i.e. 200 mg/l for drinking water prescribed by WHO (Table 2). It makes the water unsuitable for drinking, because it causes severe health problems e.g. hypertension.[14] Surface water in most of the study area comes under the non-safe zone for drinking, with reference to the concentration of Na^+. Therefore, sodium restricted diet is suggested to the patients suffering from heart diseases and kidney problems.[13]

Potassium (K^+) and Chloride (Cl^-)

Potassium in collected water samples lies in the range from 1.1 to 1.8 mg/l. It maintains the fluid balance in the body. High potassium values may cause nerviness and digestive disorder. Chloride varied from 266 to 923 mg/l. The amount presented do exceed the maximum permissible limit i.e. 600 mg/l for drinking water prescribed by WHO. On the other hands, the chloride levels in unpolluted waters are often below 10 mg/l[15], but mean concentrations observed in this study ranged from 266 to 923 mg/l. In high concentrations, chlorides in urban areas are indicators of large amounts of non-point pollution; pesticides, grease and oil, metals, and other toxic materials with high levels of chloride.

Bicarbonate (HCO_3^-)

The results showed that the concentration of HCO_3^- (336 to 671 mg/l) was 1.12 to 2.23 times higher than that of the desirable limit (300 mg/l) in the surface water (Table 2). HCO_3^- has no known adverse health effects on human health, if it exceeds 300 mg/l in the drinking water.[16] However, it should not exceed 300 mg/l in the potable water, as it may lead to kidney stones in the presence of higher concentration of Ca^{2+}, especially in dry climatic regions.[13]

Table 2. Levels of the physico-chemical parameters (mean ± SD*) in surface water samples

	Station												Mean ± SD	WHO 2008
	1	2	3	4	5	6	7	8	9	10	11	12		
pH	8.5 ± 0.2	8 ± 0.2	8 ± 0.1	8.6 ± 0.4	8.1 ± 0.3	8.9 ± 0.2	8.7 ± 0.2	8.2 ± 0.1	8.4 ± 0.1	8.1 ± 0.4	8.5 ± 0.4	8.7 ± 0.3	8.3 ± 0.2	6.5-9.5
T	15 ± 0.7	17 ± 0.5	16 ± 1.2	16 ± 01.4	15 ± 0.5	15 ± 0.4	16 ± 0.8	15 ± 0.5	16 ± 0.6	16 ± 01.1	15 ± 01.3	17 ± 0.5	15.7 ± 0.7	-
EC	3820 ± 40	1983 ± 37	2710 ± 15	1848 ± 12	1798 ± 23	2650 ± 35	2350 ± 18	4640 ± 44	1794 ± 25	4000 ± 38	3820 ± 50	1948 ± 18	2780 ± 29	1400
TDS	2440 ± 41	1267 ± 33	1731 ± 31	1180 ± 27	1150 ± 25	1690 ± 29	1500 ± 37	2960 ± 46	1145 ± 23	2552 ± 48	2440 ± 34	1383 ± 31	1786 ± 34	1000
TH	594 ± 16	394 ± 17	542 ± 13	342 ± 11	694 ± 15	346 ± 13	741 ± 21	893 ± 16	339 ± 13	642 ± 17	594 ± 24	370 ± 14	541 ± 217	500
Ca^{2+}	110 ± 10	90 ± 7	110 ± 8.4	50 ± 6	80 ± 6	30 ± 3	30 ± 5	200 ± 11	50 ± 6	120 ± 13	110 ± 8	70 ± 7	86 ± 8	200
Mg^{2+}	78 ± 6.1	42 ± 4	66 ± 5.9	54 ± 3.1	120 ± 7	66 ± 3	148 ± 7	72 ± 5	54 ± 6	84 ± 5	78 ± 6	54 ± 3	75 ± 5	150
Na^{+}	602 ± 28	270 ± 24	370 ± 31	262 ± 27	91 ± 15	447 ± 21	194 ± 11	651 ± 30	250 ± 17	620 ± 25	602 ± 20	270 ± 16	385 ± 23	200
K^{+}	1.3 ± 0.2	1.4 ± 0.3	1.3 ± 0.1	1.2 ± 0.4	1.1 ± 0.4	1.5 ± 0.1	1.7 ± 0.1	1.8 ± 0.2	1.6 ± 0.2	1.1 ± 0.1	1.3 ± 0.1	1.3 ± 0.2	1.3 ± 0.2	10
Cl^{-}	834 ± 27	301 ± 21	639 ± 31	266 ± 26	372 ± 34	532 ± 28	408 ± 32	674 ± 29	301 ± 20	923 ± 37	834 ± 29	286 ± 19	530 ± 28	600
SO_4^{2-}	321 ± 30	144 ± 15	124 ± 17	240 ± 14	43 ± 6	168 ± 7	240 ± 13	100 ± 8	117 ± 9	264 ± 9	321 ± 15	230 ± 18	192 ± 013	400
HCO_3^{-}	488 ± 21	671 ± 33	396 ± 18	366 ± 27	337 ± 19	487 ± 31	427 ± 24	427 ± 17	427 ± 29	518 ± 21	488 ± 34	377 ± 25	454 ± 25	300
NO_2^{-}	0.01	0.02	0.02	0.01	0.02	0.08	0.07	0.01	0.06	0.01	0.01	0.01	0.02	< 0.1
NO_3^{-}	11.7 ± 0.5	19.9 ± 0.8	5.1 ± 0.5	2.8 ± 0.2	2.7 ± 0.2	8.2 ± 0.6	10.1 ± 0.3	11.6 ± 0.4	11.7 ± 0.2	2.8 ± 0.1	11.7 ± 0.4	3.8 ± 0.3	8.5 ± 0.4	45
DO	9.4 ± 0.4	3.7 ± 0.5	6.9 ± 0.2	15.5 ± 0.4	2.5 ± 0.1	10.3 ± 0.5	7.1 ± 0.4	1.9 ± 0.1	2.4 ± 0.1	8.5 ± 0.2	9.4 ± 0.2	13.5 ± 0.4	7.5 ± 0.3	-
BOD_5	15 ± 01.1	9.5 ± 0.7	15.6 ± 0.7	7 ± 0.3	9 ± 0.5	14 ± 0.9	14 ± 0.6	10 ± 0.8	10 ± 0.8	11 ± 0.7	15 ± 01.2	8 ± 0.4	11.5 ± 0.7	-
COD	9.9 ± 0.5	18 ± 0.8	16.9 ± 0.6	11 ± 0.4	15 ± 0.2	18 ± 0.7	24 ± 1.2	15 ± 1.1	15 ± 0.8	33 ± 3.2	9.9 ± 1.2	13 ± 1.2	16.5 ± 0.6	-

(All parameters are in mg/l except pH, T and EC in micromhos/cm, Temperature in ^{o}C; *Standard deviation); T: Temperature EC: Electrical conductivity; TDS: Total dissolved solids; TH: Total hardness; DO: Dissolved oxygen; BOD_5: Biochemical oxygen demand; COD: Chemical oxygen demand

Nitrate (NO_3^-) and nitrite (NO_2^-)

Maximum concentration of NO_3^- was observed at station 2 and minimum was at station 5 (Table 2). Presence of NO_3^- ion could be due to the anthropogenic sources, namely; domestic sewage, agricultural wash off and other waste effluents containing nitrogenous compounds.[17] A high NO_3^- concentration in water not only induces environmental eutrophication under certain conditions, but also is a causative factor in methemoglobinemia and cancers.[18,19]

Dissolved oxygen (DO)

The value of DO in our samples fluctuated from 1.9 mg/l to 15.5 mg/l (Table 2). The maximum values were recorded at station 4 and minimum values were at station 8. The high DO is due to increase in temperature and duration of bright sunlight influence on the percentage of soluble gases (O_2 and CO_2).[20]. Oxygen is one of the most important gases in any living ecosystem. The amount of dissolved oxygen in water depends on temperature. Dissolved oxygen is an important factor in assessing water quality. Dissolved oxygen is consumed by the degradation (oxidation) of organic matters in water.[21]

Biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD)

The biochemical oxygen demand ranged from 7 to 15.6 mg/l and chemical oxygen demand was between 9.9 and 33 mg/l (Table 2). Measurement of BOD has long been the basic means of determining the degree of organic pollution in aquatic systems, and a river is said to be unpolluted if its water has a BOD_5 of 2 mg/l or less.[22] BOD is an indicator of the potential for a water body to become depleted in oxygen and possibly become anaerobic because of biodegradation. Water with a high BOD may not support aquatic life, unless there is a means for rapidly replenishing dissolved oxygen.[11]

Wilcox and Schoeller diagram

Wilcox diagram is based on the relationship between the EC and SAR of irrigation water on agricultural land. This diagram is classified into different categories (SAR: S1 to S4 and EC: C1 to C4) based on the water conation in soil.[22] The result of this study showed that the water quality of surface water was suitable for irrigation (except station 7 and 8; Figure. 2). These two sources are located in the region of Birjand plain output, so the concentrations of solutes in these two sources were higher than the other stations.[23] High level of these elements would cause leaf blight, reduce production efficiency and product quality.[24] These two sources of water (according to the amount of salt and sodium in water) need essential actions in agriculture section including irrigation reduction, increased leaching, using drip irrigation system with proper filtration.[25]

Schoeller diagram which is based on the concentration of the major cations and anions with water hardness play an important role in the situation of drinking water in a region.[26-27] These parameters are set according to WHO standards and it can be used to establish a relationship between the lines to identify areas suitable for drinking. Station 7 was found unsuitable for drinking purpose because of high concentration of sulfate (Figure 3). Therefore, it is recommended to apply chemical treatment to meet the drinking water standard.

In order to quantitatively analyze and confirm the association among physico-chemical parameters of surface water samples, Pearson's correlation analysis was applied to the data (Table 3). Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of other parameter.[28] A significant positive association was found between pH and DO. pH and temperature showed negative correlation with most of the parameters. EC showed highly significant positive correlation with TDS, TH, Ca^{2+}, Na^+, and Cl^-. This suggests that electrical conductivity depends on dissolved solids which depend on salts compound[29,] such as NaCl, $CaCl_2$. The strong positive correlation (r = 0.89)

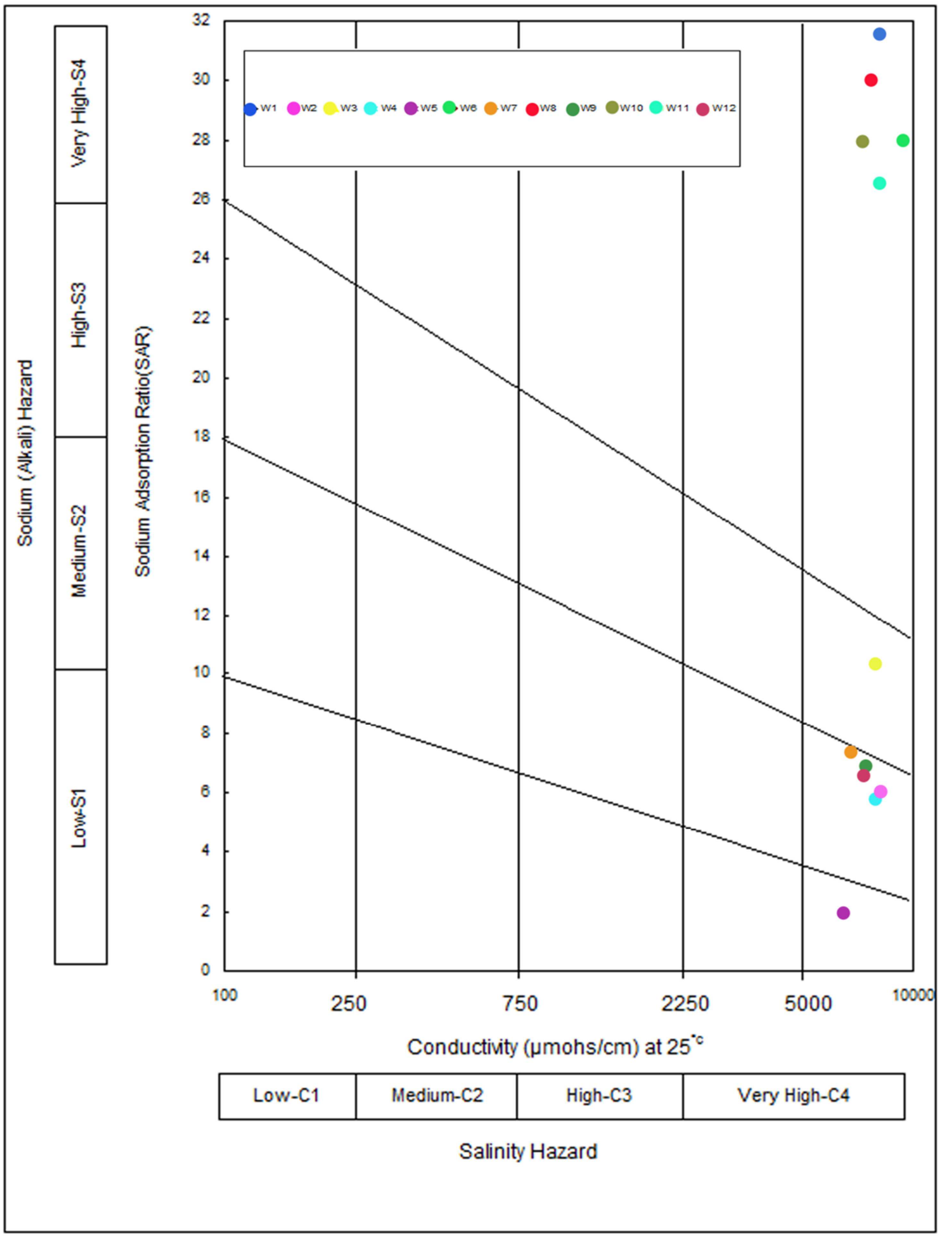

Figure 2. Wilcox diagram of Birjand, Iran f1ood plain

between electrical conductivity, TDS and chloride reflects the fact that chloride increases the electrical conductivity of water, and thus its state of being corrosive.[9] TDS showed significant association with TH, Ca^{2+}, Na^{+}, and Cl^{-}. The significant association between TDS and chloride reflects the fact that chloride is one of the principal anionic constituents of dissolved solids. Moderately positive correlations were found between hardness and Ca^{2+}, and Na^{+}. Therefore, it may be suggested that total hardness of the experimented water samples might be due to presence of salts of these ions.[30] There was a moderately positive association between Ca^{2+} and Na^{+} and Cl^{-} ($P < 0.05$), and, between Cl^{-} and BOD_5 ($P < 0.05$). Moreover, there was a moderately positive association between SO_4^{2-} and DO ($P < 0.05$). Highly positive correlations were found between Na^{+} and Cl^{-} ($P < 0.01$), and, between HCO_3^{-} and NO_3^{-} ($P < 0.01$).

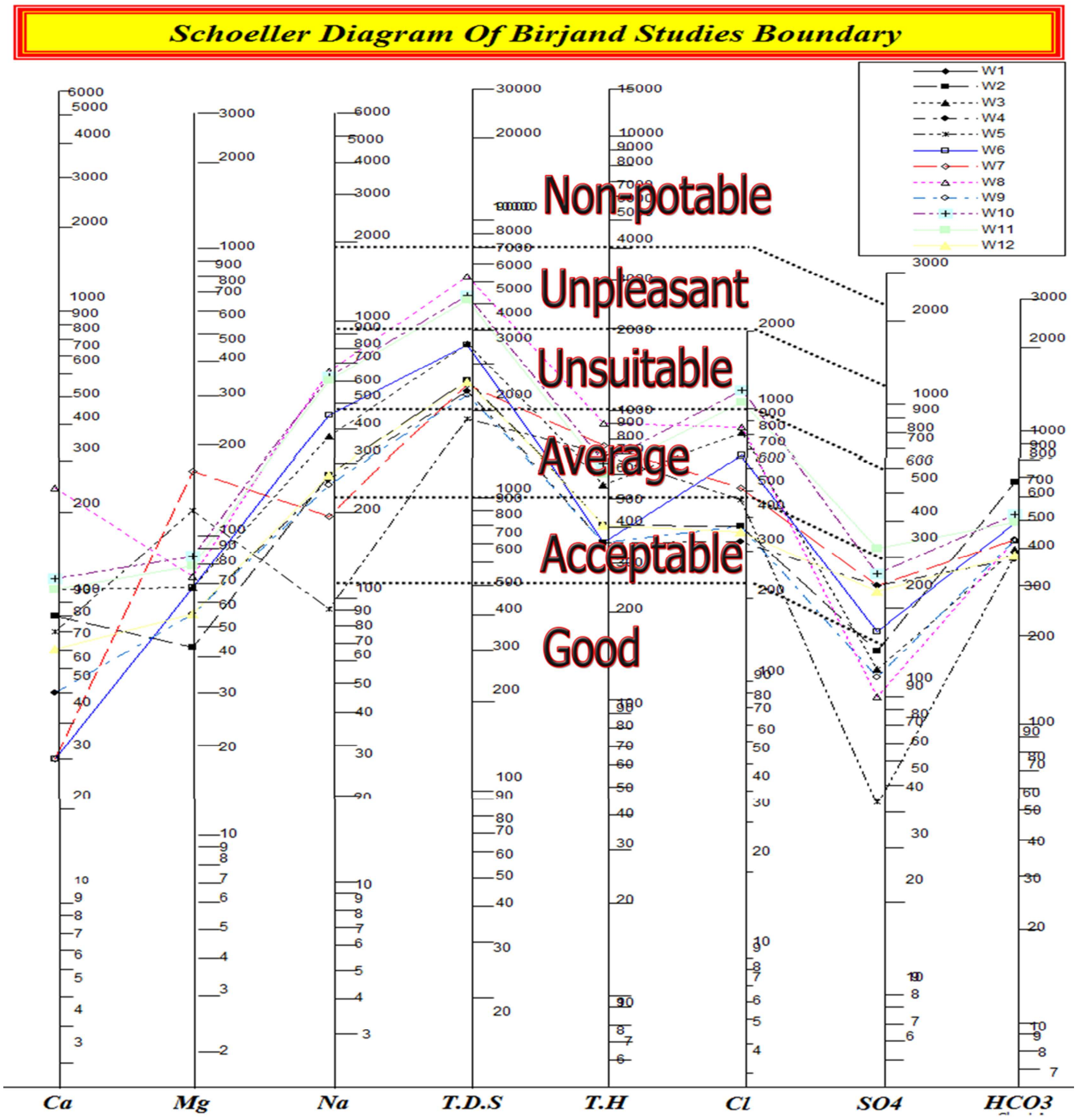

Figure 3. Schoeller diagram of Birjand, Iran f1ood plain
TDS: Total dissolved solids; TH: Total hardness

Conclusion

The results of Wilcox diagram showed that the water quality of surface water (except the station 7 and 8) was appropriate for agriculture. Moreover, the results indicated that the concentrations of EC, TDS, TH, Na^+, HCO^{3-} and BOD_5 in the surface water samples were above the recommended limits prescribed by the WHO guideline values for drinking water in many stations. In conclusion, the results of physico-chemical analysis of the surface water showed that water of the Birjand flood plain was suitable for agricultural irrigation.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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Table 3. Pearson's correlation coefficients of parameters surface water in Birjand, Iran flood plain

	pH	T	EC	TDS	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	NO_2^{-}	NO_3^{-}	DO	BOD_5	COD	pH
pH	1																	
T	-0.12	1																
EC	-0.15	-0.52	1															
TDS	-0.13	-0.50	0.99**	1														
TH	-0.33	-0.48	0.63*	0.63*	1													
Ca^{2+}	-0.53	-0 29	0.77**	0.77**	0.68*	1												
Mg^{2+}	0.17	-0.31	0.04	0.02	0.63*	-0.15	1											
Na^{+}	-0.03	-0.43	0.94**	0.94**	0.34	0.65*	-0.22	1										
K^{+}	0.24	-0.08	0.15	0.15	0.24	0.18	0.13	0.08	1									
Cl^{-}	-0.18	-0.53	0.89**	0.88**	0.50	0.53	0.10	0.87**	-0.14	1								
SO_4^{2-}	0.45	-0.01	0.35	0.36	-0.07	-0.13	0.04	0.46	-0.22	0.46	1							
HCO_3^{-}	-0.27	0.20	0.19	0.17	-0.11	0.08	-0.25	0.28	0.03	0.1	0.16	1						
NO_2^{-}	0.49	-0.08	0.34	-0.6	-0.21	-0.60*	0.31	-0.32	0.5	0.30	-0.21	0.1	1					
NO_3^{-}	-0.11	0.07	0.13	0.15	-0.0	0.16	-0.18	0.16	0.54	0.01	0.0	0.73**	0.16	1				
DO	0.68*	0.17	-0.09	-0.07	-0.46	-0.39	-0.19	0.08	-0.40	-0.01	0.68*	-0.23	-0.15	-0.45	1			
BOD_5	0.11	-0.44	43	0.4	0.4	0.01	0.30	0.42	0.15	0.63*	0.3	0.16	0.27	0.1	-0.02	1		
COD	-0.24	0.23	0.13	0.12	0.24	-0.04	0.35	0.05	-0.0	0.22	-0.3	0.27	0.24	-0.16	-0.17	0.0	1	1

*Correlation is significant at P value 0.05;**Correlation is significant at P value 0.01; T: Temperature EC: Electrical conductivity; TDS: Total dissolved solids; TH: Total hardness; DO: Dissolved oxygen; BOD_5: Biochemical oxygen demand; COD: Chemical oxygen demand

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Journal of Advances in Environmental Health Research

Characteristics and disposal options of sludge from a steel mill wastewater treatment plant

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Original Article

Abstract

In the present study, sludge from a steel wastewater treatment plant (SWWTP) was analyzed regarding its physicochemical characteristics and metal contents, and disposal options. For these purposes, grab sampling was used to collect 18 slurry and 18 cake sludge samples in 6 mouth (May-October 2012). Mann-Whitney U test, one sample T-test and Wilcoxon signed rank test were applied to analyze the obtained data. Canadian Soil Quality Guidelines (CSQG) and Florida Department of Environmental Protection Soil Cleanup Target Levels (FDEPSCTLs) were used to discuss the disposal fate of the generated sludge. The results showed that the order of the studied metals in the sludge was as: Fe>Al>Ca>Mg>Zn>Na>Pb>Mn>Cu>Cr>Ni>Co>Cd. It was found that due to higher concentration of Cu, Pb, Zn and Fe in the generated sludge, compared with CSQG and FDEPSCTLs, it is not suitable for residential and non-residential applications.

KEYWORDS: Industrial Wastewater Sludge, Physicochemical Characteristics, Steel Mill, Disposal

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Introduction

Waste management has become a serious issue in many parts of the world. Management options need some extensive waste characterization operations, because many of them may contain dangerous compounds for the environment, such as heavy metals.[1] Heavy metals are part of many industrial sludge and they are considered as hazardous waste.[2] They are non-biodegradable and have tendency toward bioaccumulation in living organisms. Therefore, they can negatively affect human and animals, and also environment.[3,4]

There are different methods for sludge management. It can be used in agricultural lands,[5,6] manufacturing construction materials,[2,7] wastewater treatment reagents,[8] sludge dewatering[9] or land filling. Such methods in addition to their advantages, including economic savings on over all treatment plant operation costs and environmental sustainability, have some limitations such as complexity of the method and problems that can be caused by pollutants presented in the sludge and can be extracted from it. Thus, having knowledge of sludge properties is crucial in selecting the suitable disposal option.

This investigation tries to determine the physicochemical characteristics and heavy metals of the slurry and cake sludge from a steel

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wastewater treatment plant in Ahvaz, southwestern Iran. The heavy metal concentrations were compared with Canadian Soil Quality Guidelines (CSQG) for the Protection of Environmental and Human Health[10] and Florida Department of Environmental Protection Soil Cleanup Target Levels (FDEPSCTLs).[11] Finally, some of sludge disposal methods were discussed.

Materials and Methods

The studied steel wastewater treatment plant, located in the south west of Iran, has a capacity of 3000 m^3/h. Figure 1 shows the WWT procedure in the studied steel wastewater treatment plant (SWWTP). Alum [$Al_2(SO_4)_3$], and polyelectrolyte (anionic polymer) are used as coagulant and coagulant aid, respectively. The sludge from DAF and Clarifier is dewatered by passing a filter press and cake sludge is produced. Cake sludge is dumped every day somewhere out of the studied site, without any analysis on its component and any consideration of public health and environmental sustenance.

In this study, that is a spatial cross-sectional analysis of sludge from a steel mill wastewater treatment plant, 36 samples, including 18 slurry sludge and 18 cake sludge samples were collected in 6 months, May-October 2012. Slurry and cake samples were collected before and after dewatering operation, respectively, both in grab sampling manner. Samples transportation and storage were according to Standard Methods for the Examination of Water and Waste Water.[12]

Total solids (TS), total suspended solids (TSS), total dissolved solids (TDS) (oven Heraeus, Germany), fixed and volatile solids (FSS and VSS) (Furnace Vecstar Ltd., England), pH (pH meter Mettler-Toledo, Switzerland) and electrical conductivity (EC) (conductivity meter WTW, Germany) were determined. Metal content (Al, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, Zn) were measured by an ICP-OES HORIBA JobinYvon-ULTIMA 2 Cin the cake sludge samples. Chemical components (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, MnO, P and S) were also determined using a XRF MDX1000, England.

Metals content and chemical components were determined using ASTM[13] and other parameters were measured according to Standard Methods for the Examination of Water and Waste water.[12] All chemicals used in this study were of analytical grade. Heavy metals standards for ICP were Assurance Company production (France).

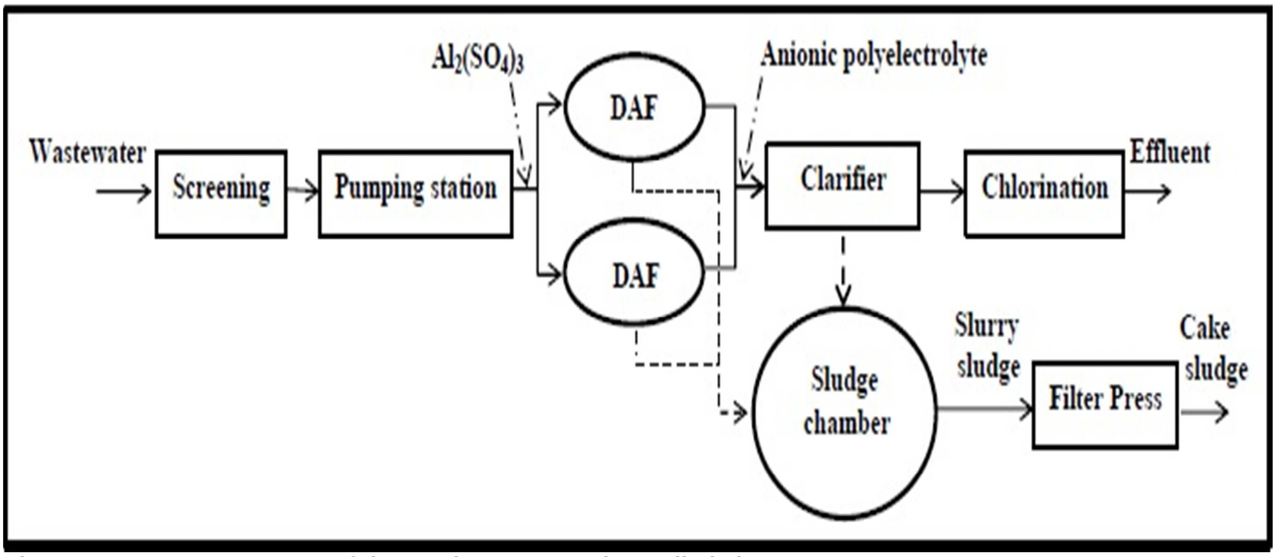

Figure 1. Treatment process of the steel wastewater in studied site

At first, samples were dried and sieved to obtain same sized particles. Then proper amount of these particles was digested with a mixture of concentrated HCl and concentrated HNO_3 on a hot plate. After being cooled, the samples were filtered through an ashless filter paper and the filtrate was diluted to a volume of 100 ml with deionized water.

In order to analyze the data, first of all explorer command and stem and leaf graph were used to exclude outlier data. Then, to assess the normality of the data, Kolmogorov-Smirnov Z analysis was performed. Mann-Whitney U test was used to compare non-normal distributed data. One sample t-test (for normal distributed data) and Wilcoxon signed rank test (for non-normal distributed data) were applied to compare metals concentration with the standard values. Since, there are no standards, regulations, or legal restrictions available for soil clean-up levels in Iran, CSQG and FDEPSCTLs were used for this purpose.

Results and Discussion

Characteristics of the steel sludge waste

Table 1 represents some physicochemical characteristics of both slurry and cake sludge in studied SWWTP. The number of samples for some parameters is less than 18, which is due to omission of outlier data. The results of Kolmogorov-Smirnov Z test introduced distributions of sludge's physicochemical parameters as non-normal. So, Mann-Whitney U test was used for them (Table 1).

As table 1 shows, and according to Mann-Whitney U test results, TS, VSS, FSS and TSS in cake sludge is significantly higher than those of slurry sludge ($P < 0.0001$). It was expected because after dewatering using filter press, solid content of the sludge is concentrated. Ahmadi et al. in their study on sludge from a petrochemical wastewater treatment plant reported a similar TSS but higher TDS for their studied sludge than that of this study.[14]

EC of the studied sludge was lower than that of reported by Bahremand et al. and Kassray and Saedi and Dashti et al. for their studied sludge.[6,15,16] Higher EC means higher salinity, which makes the studied sludge unsuitable for land application. pH has an important role in metals behavior in soil and their uptake by organisms.[3] pH of the studied sludge was slightly alkaline.

Table 2 represents the metal content of the studied cake sludge. As mentioned before, omitting outlier data, the number of samples for some metals is less than 18. Considering table 2, the order of the studied metals in the sludge is as follows:

Fe>Al>Ca>Mg>Zn>Na>Pb>Mn>Cu>Cr>Ni>Co>Cd

As it has been expected, Fe had the highest

Table 1. Physicochemical characteristics and statistical results of slurry and cake sludge

Parameter/unit	Sludge	Number of samples	Mean ± SD	Median	P
TS (%W)	Slurry	16	1.74 ± 0.47	1.72	< 0.0001
	Cake	18	34.540 ± 8.720	21.760	
VSS (%W)	Slurry	14	0.609 ± 0.086	0.630	< 0.0001
	Cake	18	11.45 ± 4.276	10.94	
FSS(%W)	Slurry	16	1.00 ± 0.31	0.98	< 0.0001
	Cake	18	23.090 ± 7.178	34.065	
TSS (mg/l)	Slurry	15	13873.53 ± 3069.03	13728	< 0.0001
	Cake	18	318481.11 ± 97110.631	329550	
TDS (mg/l)	Slurry	16	3081.09 ± 405.65	3147.5	-
EC (µs/cm)	Slurry	18	4866.780 ± 633.289	4920	-
pH	Slurry	18	7.680 ± 0.223	7.7	-

TS: Total solids; VSS: Volatile solids; FSS: Fixed solids; TSS: Total suspended solids; TDS: Total dissolved solids; EC: Electrical conductivity

Table 2. Metal content of the cake sludge

Metal	Unit	Number of samples	Mean ± SD	Median
Al	mg/kg dry solid	18	41432.43 ± 39131.09	34744.00
Ca	mg/kg dry solid	16	31268.75 ± 27796.29	14275.00
Cd	mg/kg dry solid	16	2.36 ± 2.82	0.70
Co	mg/kg dry solid	16	8.03 ± 8.17	2.60
Cr	mg/kg dry solid	18	57.16 ± 34.70	59.14
Cu	mg/kg dry solid	18	295.47 ± 317.56	296.32
Fe	mg/kg dry solid	16	306131.44 ± 35268.03	306048.74
Mg	mg/kg dry solid	16	11424.06 ± 10474.43	5280.00
Mn	mg/kg dry solid	17	378.47 ± 313.21	306.76
Na	mg/kg dry solid	15	3940.16 ± 2908.66	2262.66
Ni	mg/kg dry solid	13	35.54 ± 32.10	38.30
Pb	mg/kg dry solid	18	393.21 ± 306.83	357.96
Zn	mg/kg dry solid	15	6491.88 ± 3841.05	6327.00

concentration amongst the studied metals. Since $Al_2(SO_4)_3$has been used as the coagulant, Al had the second rank. Zn had the third and first ranks amongst the metal contents and heavy metals, respectively. Comparing our results with those of Silva et al.,[2] it was observed that Cu, Ni, Pb and Zn in our studied sludge were higher than those in their studied metal-mechanics, textile and automotive sludge. Considering the differences in the nature of sludge, such dissimilarity in the results can be expected.

XRF results for chemical composition of the studied sludge introduced Fe_2O_3asthe main composite (30.15%) and Al_2O_3 as the second composite with the highest percentage (30.15 and 11.02%, respectively). As mentioned before, Fe and Al are two metals with the highest concentration in the studied sludge (See table 2). Then, such result was expectable. CaO, SiO_2, MgO, P, S, Na_2O and MnO with 8.70, 4.06, 1.89, 1.65, 0.6, 0.456 and 0.018%, respectively, were also found in the studied sludge. Comparing our results with those of Vieira et al.[7] from fine steel sludge showed that CaO, Fe_2O_3 and MgO in our studied sludge were lower, and Al_2O_3, Na_2O and SiO_2were higher than theirs.

SWWTP Sludge disposal

Sludge quality requirements need considering sludge management methods, disposal and reuse practices.[1] In our study, a comparison of studied heavy metals with the standards determined by CSQG and FDEPSCTLs showed that according to CSQG, Cu, Pb and Zn concentrations in the studied sludge were significantly beyond the permitted values for residential/ parkland, agricultural and commercial applications (see table 3). Cu and Zn concentrations are also significantly higher than CSQG standards for industrial applications. Table 3 also represents that compared to FDEPSCTLs, Fe and Zn concentrations in the studied steel sludge are significantly high for residential, and both residential and nonresidential applications, respectively, which restricts sludge's use for such applications.

Land use

One of the methods for wastes managing is to use upper soil zone, which is defined as land use. Hazardous or toxic wastes are not advisable to use in this method. It is necessary to consider the amounts of pollutants in the sludge and the loading rate of a pollutant applying to the land to prevent their accumulation in the soil. Only sludge with pollutants within the recommended concentrations should be used on land. A relatively simple and cost effective method, land use uses natural processes for waste recycling and soil structure improving.[17]

In this study, as mentioned before, compared with CSQG standard for park land and agricultural use, Cu, Pb and Zn concentrations in the studied sludge were higher, which make it unsuitable for land application. There are researchers that have reported the exceeding of heavy metals in their studied sludge from

Table 3. Statistical results of comparing the investigated heavy metals with the standards determined by CSQG and FDEPSCTLs

Heavy metal	CSQG								FDEPSCTLs			
									soil direct exposure			
	Residential/ parkland		Agricultural		Commercial		Industrial		Residential		Non Residential	
	Standard (mg kg^{-1})	P^*	Standard (mg kg^{-1})	P^*	Standard (mg kg^{-1})	P^*	Standard (mg kg^{-1})	P^*	Standard (mg kg^{-1})	P^*	Standard (mg kg^{-1})	P^*
Al	-	-	-	-	-	-	-	-	80000	$0.001^{\downarrow O}$	-	-
Cd	10	$< 0.0001^{\downarrow W}$	1.4	$0.234^{\uparrow W}$	22	$< 0.0001^{\downarrow W}$	22	$< 0.0001^{\downarrow W}$	82	$< 0.0001^{\downarrow W}$	1700	$< 0.0001^{\downarrow W}$
Cr	64	$0.472^{\downarrow W}$	64	$0.472^{\downarrow W}$	87	$0.004^{\downarrow W}$	87	$0.004^{\downarrow W}$	210	$< 0.0001^{\downarrow W}$	470	$< 0.0001^{\downarrow W}$
Cu	63	$0.078^{\uparrow W}$	63	$0.078^{\uparrow W}$	91	$0.078^{\uparrow W}$	91	$0.078^{\uparrow W}$	150	$0.085^{\downarrow W}$	89000	$< 0.0001^{\downarrow W}$
Fe	-	-	-	-	-	-	-	-	53000	$< 0.0001^{\uparrow O}$	-	-
Mn	-	-	-	-	-	-	-	-	3500	$< 0.0001^{\downarrow W}$	43000	$<0.0001^{\downarrow W}$
Ni	50	$0.130^{\downarrow O}$	50	$0.130^{\downarrow O}$	50	$0.130^{\downarrow O}$	50	$0.130^{\downarrow O}$	340	$< 0.0001^{\downarrow O}$	35000	$< 0.0001^{\downarrow O}$
Pb	140	$0.003^{\uparrow O}$	70	$< 0.0001^{\uparrow O}$	260	$0.083^{\uparrow O}$	600	$0.011^{\downarrow O}$	400	$0.926^{\downarrow O}$	1400	$< 0.0001^{\downarrow O}$
Zn	200	$< 0.0001^{\uparrow O}$	200	$< 0.0001^{\uparrow O}$	360	$< 0.0001^{\uparrow O}$	360	$< 0.0001^{\uparrow O}$	440	$< 0.0001^{\uparrow O}$	11000	$< 0.0001^{\uparrow O}$

* P-value < 0.05 is considered as a significant level.
$^{\uparrow}$ and $^{\downarrow}$ indicate that measured amounts are higher and lower than standards, respectively.
O and W are p-values from One sample t-test and Wilcoxon signed rank test, respectively.
- shows that no standard value has been set.
CSQG: Canadian Soil Quality Guidelines
FDEPSCTLs: Department of Environmental Protection Soil Cleanup Target Levels

standards for land application.[5]

Residential, commercial and Industrial uses

Table 3 shows that Zn concentrations in the studied sludge were significantly higher than CSQG and FDEPSCTLs for all types of applications. Cu and Pb both have restrictions to be used for residential and commercial uses. Cu also was significantly higher than CSQG for industrial uses. On the other hand, Fe concentration in the studied sludge was beyond the FDEPSCTLs for residential applications. Some residential and non-residential applications of sludge have been discussed.

Using as building and construction materials

Incinerated sludge ash contains predominantly amount of Fe, Al, Ca and Si. Thus, it can be used as a raw material for manufacturing of construction materials such as bricks, tiles, blocks.[18] The results of XRF showed that these elements have the first to forth rank in the studied sludge. So that, studied sludge has a good potential for using as a raw material for manufacturing of construction materials. However, heavy metals content, which was above the standards, can restrict its application for this purpose. Although, according to FDEP guidance, sludge can be blend with uncontaminated soil to reduce the potential health threats from exposure to the sludge, provided that the resulting mixture be still appropriate for beneficial use. To determine the appropriate blend ratio (ratio of blend material to sludge) for lowering the contaminants contained in the sludge FDEP recommends the following equation:[11]

$$\text{Blend Ratio} = \frac{(A-B)}{(B-C)} \qquad (1)$$

where, A = concentration of contaminant in the sludge, mg/kg, B = target concentration of the blended material, mg/kg, C = concentration of contaminant in the material used for blending, mg/kg.

In a similar study, Vieira et al., found that using 5 w.t% of the fine steel sludge is beneficial to the ceramic building. But, they did not consider the heavy metal contents of the sludge.[7] In another study, Silva et al. used stabilized/solidification technology to treat sludge from an electroplating industry and the resultant product was used as a raw material to build concrete block. They found that the metal leachability and solubility of the resultant block is very low, indicating a low environmental impact.[2]

Using in wastewater treatment

Sludge can be used in waste water treatment process. For example, the leaching solution of a textile sludge incineration residue was studied for its coagulant effect on textile wastewater treatment. The results showed that it can be a coagulant agent for textile wastewater treatment.[8] Results of another study, revealed that pretreating the tannery sludge with a combination of tannery sludge incineration slag and cationic polyacrylamide can improve sludge dewaterability over cationic polyacrylamide conditioning alone.[9]

Other uses of sludge

As another reuse practice, pyrolysis process can be used to convert sludge with a high concentration of heavy metals or toxic chemicals to oil. The disadvantage of this method is its high capital and running costs.[19]

Land filling

The final option for disposal of the sludge that cannot be reused is their land filling. Since such sludge usually contain toxic materials, which can cause groundwater contamination, it is necessary to line the landfill with the proper lining materials, such as clay or plastic liner.[19]

Current management of the studied steel wastewater sludge is to discharge it, in the form of cake sludge, in an unlined dumping site. In such disposal method, sludge can contribute to landfill leachate, cause groundwater pollution, enter the food chain and cause health problem. Al Yaqout, recommended that lined evaporation ponds can be used as an economic and safe method for the industrial liquid and sludge disposal in arid climates.[20]

Conclusion

In this study, different physicochemical characteristics, heavy metal contents and chemical composition of a steel wastewater treatment plant were investigated. The measured heavy metals compared with international standards and according to the obtained results compared with CSQG, the investigated sludge was polluted for residential/parkland, agricultural, commercial and industrial use because of its high Cu, Pb and Zn concentrations. It was also observed that according to FDEPSCTLs, the studied sludge was not suitable for residential and non-residential applications due to its high Fe and Zn contents. said it also should be mentioned that there are some other parameters, including different organic and inorganic compounds, in CSQG and FDEPSCTLs than those investigated in this study and it would be better that these parameters be considered in future studies.

Conflict of Interests

Authors have no conflict of interests.

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Journal of Advances in Environmental Health Research

The evaluation of heavy metals concentration related to PM_{10} in ambient air of Ahvaz city, Iran

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Original Article

Abstract

Airborne particulate matter along with volatile organic compounds, heavy metals, and other compounds have raised many concerns to many countries including Iran. In this study, the concentrations of seven heavy metals (Cd, Cr, Co, Ni, Pb, Zn, and Al) associated with PM_{10} have been investigated during normal and dusty days from September to February 2012. The mean PM_{10} concentrations on the normal days in the winter and autumn were 189.4109 and 116.5087 μgm^{-3}, respectively. PM_{10} concentrations during dusty days for the winter and autumn were 741.6467 and 410 μgm^{-3}, respectively. The heavy metals concentrations are vary in different days of a month. Enrichment factors (EF) are used to determine and assess the source type of released heavy metals in particulate matter. The results of EFs analysis showed that Al metal had low enrichment suggesting crustal origin, whereas Zn (zinc) and Pb (lead) metals were appeared to result from non-crustal sources such as vehicular and industrial emissions because of their high enrichment factors. Results of the present study revealed that the concentrations of PM_{10} were higher than the reliable standards for the two studied seasons.

KEYWORDS: Air Pollution, Heavy Metals, PM_{10}, Enrichment Factor, Ahvaz

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Introduction

Air pollution due to metals, is a product of urbanization and other factors related to population density, industrialization, and mechanization, which are providing human beings requirements. In most of the developing and developed countries, the growing

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population and uncontrolled urban area, along with increasing number of vehicles and industries, improper maintenance of vehicles, and the lack of strategy and implementation of stringent emission standards are the main causes of air pollution problems.[1]

Today, the concentrations of pollutants released from natural and anthropogenic sources have reached to a point that leads to adverse effects on human health and the environment, so that according to the World Health Organization (WHO) report, approximately 4-8% of deaths occurring annually in the world are related to air pollution.[2,3] The size of airborne particulate matter typically ranges from a few nanometers in diameter to 100 micrometers. The respirable suspended particulate matter (RSPM) is considered globally as a major concern because of high probability of deposition in the respiratory tract and the presence of toxic elements in its composition. Moreover, in the recent decades, the characterization of particulate matter (PM), for identifying its sources and also to study the atmospheric chemical phenomena that favor its transport and removal, has gained important attention of many researchers.[4,5] Total suspended particulate (TSP) matter can be classified into two categories: coarse fraction and fine fraction (PM_{10} and $PM_{\leq 2.5}$). The finer fraction (especially $PM_{\leq 2.5}$), has the potential to penetrate into the lungs and may even reach to the alveolar region of the respiratory system, and can translocate in other parts of the human body. Therefore, short- and long-term effects such as premature death, increased respiratory symptoms and disease, decreased lung functions, and alterations in lung tissues are more likely associated with these particles.[6] In addition, heavy metals (such as lead, chromium, cadmium and arsenic) cations and anions which are transported by particles can cause significant cardiovascular effects. Among these, the heavy metals associated with PM_{10} plays an important role in air pollution.

Heavy metals are metals and metalloids having atomic density of 4 grams per cubic centimeters or five times greater than water. In the atmosphere, heavy metals are formed in the fine and light compounds and suspended in the air. A part of these metals is removed by precipitations and the other part remains in the atmosphere as suspended particles. Natural (minerals, volcanic dust and so forth) and anthropogenic (dyeing industries, metal planting and batteries) sources released various chemical forms of heavy metals into the environment via different routes.[7,8] The presence of heavy metals in the air breathing not only threatens human health but also affects the ecosystem structure. In addition, high concentrations of such metals affect on absorption and transport of essential elements, disrupt metabolism and have sever impacts on growth and reproduction ability, as well as causing diseases such as Saturnism, Mercurialism, Alzheimer's disease, carcinogenic and affect the central nervous system, kidney, bone, liver and skin.[9,10]

In recent years, many studies have been performed to determine the concentrations of heavy metals in respirable particulate matter. For example, Chelani et al.[10] investigated the concentrations of heavy metals in the ambient air of Mumbai, India, from 1993-1998. Their results showed that RSPM and lead (Pb) were major air pollution problems in Mumbai. The authors reported that the main contributors of air pollution in the city were transport sector followed by power plants, industrial units and burning of garbage. The highest concentrations of studied metals were observed in winter. Pike and Moran[11] reported that during the normal days, there was a higher association between TSP and heavy metal concentrations than on misty days at both urban-residential and industrial areas.

According to complex composition of particulate matter, determination of which characteristic of particulate matter causing negative health effect is extremely difficult, and also there is no enough information in this field. If the composition and characteristics of particulate matter link to the negative health effects, the relationship between such effects and pollution sources can be found out because this information is very valuable for control and reduction strategies. In addition to adverse effects of heavy metals associated with PM_{10} on human health, due to the presence of rich oil and gas resources, large petrochemical, metal and non-metal industries, power plants as well as hot and humid weather condition in most seasons of the year, Ahvaz has experienced air pollution. Therefore, the present study aimed to investigate concentrations of PM_{10} and associated heavy metals in the ambient air of Ahvaz city during September to February 2012.

Materials and Methods

Ahvaz, the capital city of Khuzestan province, is one of the major cities of Iran, and located in an arid area in the south-western of Iran near Iraq, Saudi Arabia, and Kuwait, which are the major sources of dust events in the Middle East. In addition, low vegetation cover, strong surface winds, high temperatures, and humidity are other characteristics of this city, all of which are known as the major causes of dust storm. For example, the mean values of temperature during the autumn and winter seasons were 24.6° C and 16.4° C, respectively. The mean, maximum and minimum values for relative humidity (%) during the autumn season were 58, 78, and 38, respectively, the corresponding values for the winter season were 63, 86, and 41, respectively.[12] The geographical location of Ahvaz is 31° 20 N, 48° 40 E and 18 meters above sea level. The presence of large industrials plants, South Oil-rich Zones Company, National Iranian Drilling Company, official and industrial facilities, has turned Ahvaz into one of the most important industrial centers of Iran, it in turn, has caused many immigrants to Ahvaz.[13] Figure 1 presents the location of the sampling point, and indicates Khuzestan province in the Middle East and in relation to the previously mentioned sources of dust events. As shown in the figure, Khuzestan province attached to the Persian Gulf and Iraq from the south and west, respectively.

The sampling was carried out according to Environmental Protection Agency (EPA) method on 6 days intervals during the study period. Additional sampling was also done in the case of dust storms occurrence. The sampling station was located at an urban background area in the city. PM_{10} samples were collected using a high volume air sampler (Model: Anderson) fitted with a fiberglass filter. The sampler was placed on the roof top of the Health Research Center at the height of 4 m above the ground level and away from any obstruction to minimize the potential effects of natural and anthropogenic features on the air flow, and therefore, particle concentrations. The sampler operating with a flow rate of 1.1-1.7 m^3/min (and finally the average flow rate was calculated) for 24 h. Filter conditioning before and after the sampling was performed according to the procedure presented by Shahsavani et al.[14] and Zhang et al.[15]

After sampling, one-fourth of the exposed fiberglass filter, was cut and put in a Teflon container, then a mixture of Nitric acid, Hydrochloric acid, and Hydrofluoric acid was added to it, and the filter was digested in a hot oven at 170 degrees Celsius for 4 hours. After that time elapsed, we opened the cap of the Teflon container on a heater at 95-100° C to evaporate all the remaining acids inside it. After cooling, in the next stage, concentrated Nitric acid and distilled water (ratio 1:9 V%) were added and shaken for 15 minutes. The obtained solution was filtered through a Whatman-42 filter paper. The resultant solution was then diluted to 25 mL with distilled water and stored in a clean, sterile, and plastic bottle at 4° C until further analyses.[5,13] The digested samples were analyzed for target heavy metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES; model: ARCOUS, Germany).

Results and Discussion

PM_{10} levels

The results of the study are presented in table 1. As shown in the table, the mean PM_{10}

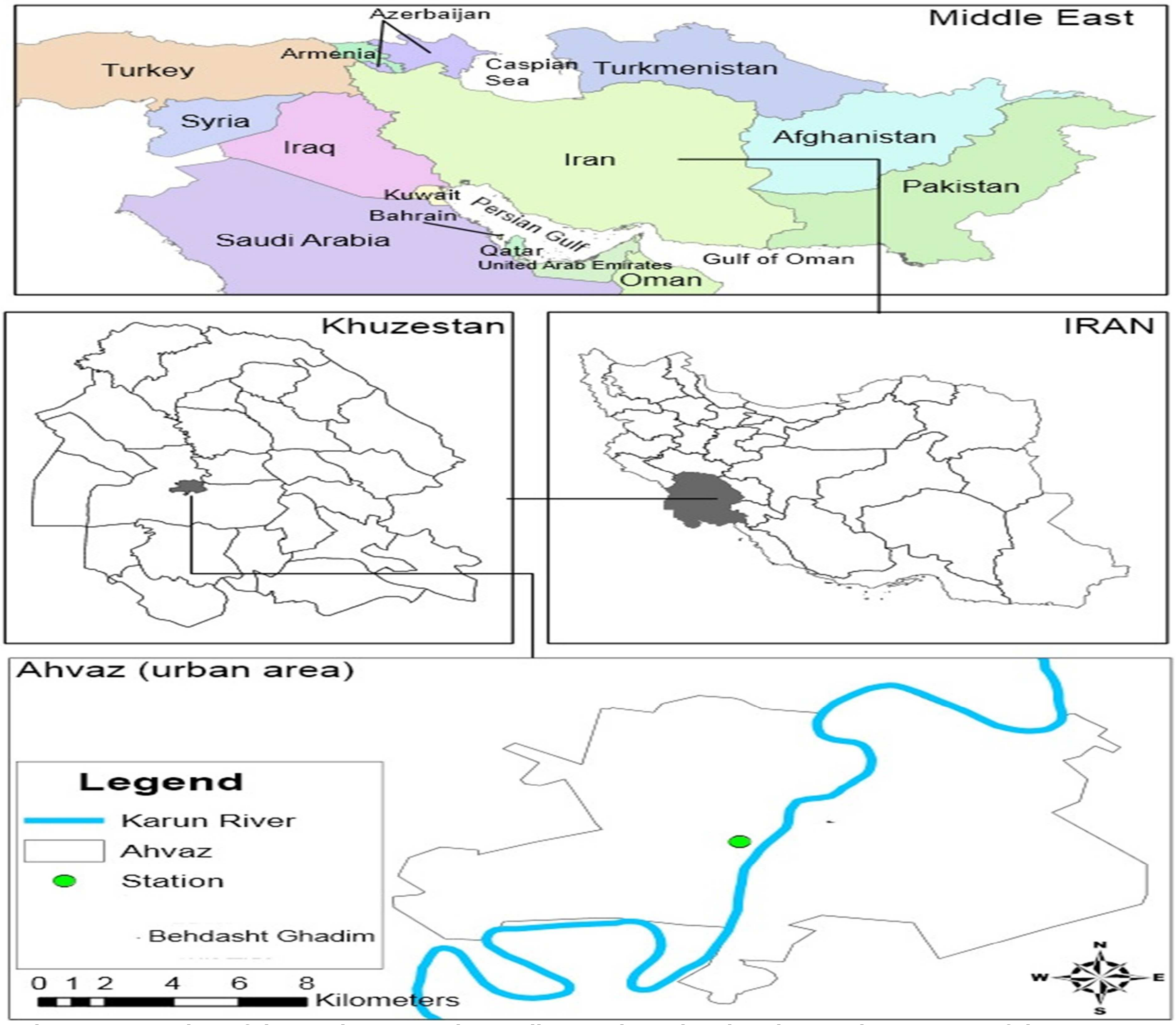

Figure 1. Location of the study area and sampling station, showing the nearby sources of dust storms

Table 1. The mean concentrations of PM_{10} and the associated heavy metals in the ambient air of Ahvaz, Iran during dusty and normal days in the two seasons

Pollutant (μg/m^3)	Autumn (normal day)	Autumn (dust day)	Winter (normal day)	Winter (dust day)
PM_{10}	116.508	410	189.410	741.646
Cd	0.190	0.517	0.225	0.876
Co	0.298	1.446	0.849	1.582
Cr	0.394	1.548	1.051	1.814
Ni	0.609	1.781	1.583	2.353
Pb	2.848	3.671	5.718	5.782
Zn	2.810	4.026	7.950	8.231
Al	11.339	21.307	16.316	34.324

concentrations on the normal days in the winter and autumn were 189.4 and 116.5 μgm^{-3}, respectively. For the winter, this value was greater than 24-h standard of National Ambient Air Quality (NAAQS) (150 μgm^{-3}). Furthermore, this value was greater in contrast with the industrialized countries such as Japan (Tokyo: 38 μgm^{-3}), England (London: 28 μgm^{-3}), and the other East-Asian and European countries (100 µgm^{-3})[16]. In addition, PM_{10} concentrations of dusty days for the two studied seasons were evaluated (Table 1). The results showed that PM_{10} concentrations during the dusty days in the winter and autumn seasons were 741.6 and 410 µgm^{-3}, respectively. These values were 3.5 to 4 times greater than those for normal ones in the autumn and winter, respectively. Furthermore, mean PM_{10} concentration on dusty days during the autumn was 2.7 times higher than the daily maximum acceptable limit of 150 µgm^{-3}. The corresponding value for dusty days in the winter was about 5 times higher than 150 µgm^{-3}. These high PM_{10} concentrations are attributed to the large deserts located at the west of the city, which are known as the major sources of dust storms in this region. Similar results were found by Shahsavani et al;[13] the authors investigated air pollution of Ahvaz, and reported that the higher particulate matter concentration, was due to the lack of precipitation and neighboring with the large arid deserts at the west of the city.

In the study conducted by Draxler et al.[17] in Iraq, Kuwait, and Saudi Arabia, regions located near our study area, PM_{10} concentrations greater than 1000 µgm^{-3} were observed.

Heavy metals concentrations

The heavy metals concentrations on dusty and normal days are shown in table 1. The heavy metals concentrations were vary in different days of a month. In some days in the autumn and winter reached to the minimum values, and in some days especially dusty ones reached to the highest values. For example, in the autumn, the mean concentrations for Zn, Pb, and Cd during dusty days were 1.43, 1.3, and 2.7 times higher than normal ones, respectively. The results of this study also showed that the heavy metals concentrations in the winter were higher than the autumn. This could be due to the combined effects of high activities of releasing sources such as vehicles, meteorological conditions (low temperature, low wind speed and mixing height), and regular temperature inversion which cause the pollutants accumulation by limiting the dilutions and dispersions.

Cao et al.[18] observed that the concentrations of most of the heavy metals were higher in the winter compared to those in the other seasons. Such high concentrations were attributed to more vehicular activities and the presence of temperature inversion during the winter season.

Singh and Sharma[16] also reported that the heavy metals concentration were higher during the winter season. They indicated that these high concentrations were due to high fossil fuels and biomass consumption, low mixing, and the presence of inversion in this city.

Lee and Park[19] investigated heavy metals in airborne particulate matter on misty and normal days at both urban-residential and an industrial areas, reported that average concentrations of TSP and heavy metals in TSP on misty days, were significantly higher than those on normal ones. These high concentrations were attributed to the differences between relative humidity and ambient ventilation indices on misty days and normal days.

Haritash and Kaushik[1] also observed that meteorological factors played an important role in the concentrations of the heavy metals in RSPM during two different seasons. Based on that study, low wind speed, low temperature, and high relative humidity favor low concentration of the pollutants, whereas, turbulent conditions result in higher concentration. Table 2 compares the concentrations of evaluated heavy metals in this study with the other studies. According to the table, the measured concentrations of heavy metals in this study are lower than the results of similar ones at industrial and urban areas. Various factors such as industrial operations, old facilities, adjacent to arid deserts, meteorological conditions such as humidity and precipitation, and vehicular density can be some reasons for these differences in heavy metals concentrations at these locations.

Enrichment factors

Heavy metals in aerosols are derived from various natural and anthropogenic sources. Enrichment factors (EF) are used to determine

Table 2. The heavy metals mean concentration (ng/m3) in PM_{10} samples in comparison with other Asian cities

Location		Type of PM	Pb	Cd	Cr	Ni	Zn	Co	Reference
			Parameter						
Ahvaz (Iran)		PM_{10}	4.5395	0.3445	1	1.3991	5.8901	0.8374	Present study
Kuala Lumpur (Malaysia)		TSP	181	-	-	27.9	87	-	20
Beijing (China)		TSP	430	7	19	22	770	4.6	21
Ho Chi Minh (Vietnam)		PM_{2-10}	73	-	7	-	326	1.80	22
Taichung (Taiwan)		$PM_{2.5-10}$	90.6	3.8	9.0	4.3	40.3	-	23
Islamabad (Pakistan)		TSP	163	3	36	8	567	14	24
Guangzhou (China)	Huizhou	PM_{10}	466	19	69	52	1685	-	25
	Baiyun		324	10	46	38	906	-	
	Tianhe		342	12	79	39	901	-	
	Liwan		425	15	62	36	803	-	
Isfahan (Iran)		PM_{10}	117	4.4	12.3	13	348	-	26
Chongqing	Guanyinqiao	PM_{10}	64.8	-	-	11.7	159.4	3.2	27
	Jiulongpo		108. l	-	-	10.6	243.7	14	
	Jinyunshan		10.2	-	-	6.4	67.1	1.2	

PM: Particulate matter; TSP: Total suspended particulate

and assess the source type of released heavy metals in particulate matter. Al is normally used as the source indicator element for natural sources or earth's crust; Pb and Zn are used as indicator elements for industrial sources and vehicles. EF can be calculated using the following equation [5]:

$$EF = \frac{C_{xp}/C_P}{C_{xc}/C_C}$$

where C_{xp} and C_p are the concentration of a trace metal x and Al in the particulate, respectively, and C_{xc} and C_c are their concentrations in crustal material. According to this equation, the EF value less than 10 is taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEE). In contrast, if the EF value is greater than 10 indicating that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE). The distribution of EF_s for the individual heavy metals is shown in figure 2. The results of this section of the study show that Al metal exhibited low enrichment suggesting crustal origin, whereas Zn and Pb metals are appeared to result from non-crustal sources such as vehicular and industrial emissions because of their high enrichment factors. Mohd et al.[5] determined trace metals in airborne particulate matter of Kuala Terengganu, Malaysia, found that Pb, Cd and Zn metals originate from vehicular emission with enrichment factor > 10, and Al, Fe, Mn and Cr group that appears to have crustal origin with enrichment factor < 10.

Haritash and Kaushik[1] by calculating EF_S reported that Pb, Cu, Ni, and As were chiefly emitted from anthropogenic sources, and Fe, Mn, and Mg in RSPM were observed as crustal in origin.

Correlations

Correlation calculations are a convenient and tested method to describe sources of the particulate aerosol and associated heavy metals. We utilized SPSS for Windows (version 18.0, SPSS Inc., Chicago, IL, USA) to determine the correlations among PM_{10} concentrations and the heavy metals in PM_{10} collected on normal days and dusty ones for the study period. The Pearson linear correlation coefficients with significant values (p) are summarized in table 3. From the table, it can apparently be seen that a lot of the component pairs show significantly positive correlations at levels of 0.01 or 0.05. For instance, there are a strong positive correlation

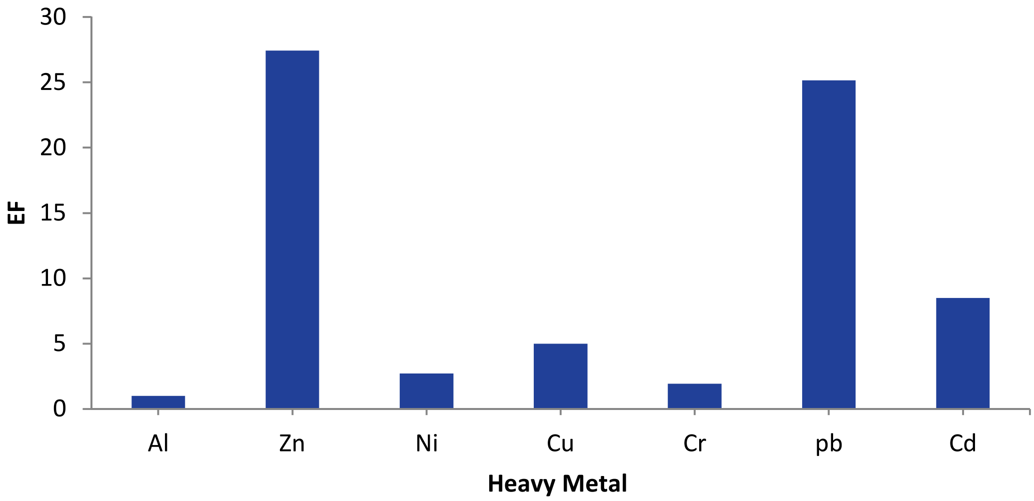

Figure 2. Enrichment factors (EFS) distribution for the heavy metals in the ambient air of Ahvaz city, Iran

among PM_{10} and all the associated heavy metals during normal days for the entire study period. Among the heavy metals themselves, in particular, Al- Zn, Al- Pb, Al- Co, Al-Ni, and Al-Cr pairs show high positive correlations ($P < 0.01$) on normal days, Al-Cd pairs also show a fairly high positive correlation during normal days, representing common sources such as anthropogenic. There was no correlation between Zn and Pb with Cd. On the whole, for normal days, Cd also not well correlated with the other heavy metals in spite of having p-value less than 0.05 owing to its low R values. On dusty days, all the heavy metals have correlations with PM_{10} except Zn. Among the heavy metals themselves, there are very strong correlations between Pb-Cd, Pb-Cr, Pb-Ni, and Pb-Co pairs ($P < 0.01$), indicating that these elements can be derived from similar source. There are also high correlations between Zn-Pb and Zn-Al. However, there are no correlations among Zn with the other evaluated heavy metals on dusty days.

Conclusion

Given the importance of measurement of pollutants in Ahvaz city, PM_{10} and the associated heavy metals were measured and evaluated in this paper. Results of the present study revealed that the concentrations of PM_{10} were higher than the reliable standards (WHO and NAAQS) for the two studied seasons. It can be harmful to inhabitants of the city in long-term periods. Besides, enrichment factor analysis indicate that most of the heavy metals resulting from anthropogenic activities.

Therefore, based on the obtained results, it is suggested that given the importance and effects of PM_{10} and related heavy metals, further studies are needed on concentrations, effects, and their relationship to emerging diseases during pollution periods in the coming years. Control methods such as mulching, removal of old devices in industries, removal of leaded gasoline should be considered and implemented.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

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Table 3. Correlation coefficients between concentrations of PM10 and the heavy metals in PM_{10} on normal and dusty days in the ambient air of Ahvaz, Iran

(a) Normal days								
n = 29	PM_{10}	Cd	Cr	Ni	Co	Pb	Zn	AL
PM_{10}	1							
Cd p	0.780 < 0.01	1						
Cr p	0.707 < 0.01	0.414 < 0.01	1					
Ni p	0.650 < 0.01	0.344 < 0.05	0.995 < 0.01	1				
Co p	0.690 < 0.01	0.431 < 0.05	0.974 < 0.01	0.966 < 0.01	1			
Pb p	0.539 < 0.05	0.252	0.957 < 0.01	0.971 < 0.01	0.939 < 0.01	1		
Zn p	0.515 < 0.05	0.210	0.937 < 0.01	0.958 < 0.01	0.889 < 0.01	0.953 < 0.01	1	
Al p	0.785 < 0.01	0.463 < 0.05	0.976 < 0.01	0.963 < 0.01	0.936 < 0.01	0.913 < 0.01	0.906 < 0.01	1

Table 3. Correlation coefficients between concentrations of PM10 and the heavy metals in PM_{10} on normal and dusty days in the ambient air of Ahvaz, Iran (Continue)

(b) Dusty days								
n = 11	PM_{10}	Cd	Cr	Ni	Co	Pb	Zn	AL
PM_{10}	1							
Cd p	0.994 < 0.01	1						
Cr p	0.962 < 0.01	0.979 < 0.01	1					
Ni p	0.972 < 0.01	0.977 < 0.01	0.974 < 0.01	1				
Co p	0.950 < 0.01	0.965 < 0.01	0.982 < 0.01	0.935 < 0.01	1			
Pb p	0.858 < 0.01	0.834 < 0.01	0.768 < 0.01	0.877 < 0.01	0.717 < 0.05	1		
Zn p	0.493	0.459	0.395	0.575	0.277	0.837 < 0.01	1	
Al p	0.617 < 0.05	0.587	0.536	0.673 < 0.05	0.467	0.912 < 0.01	0.925 < 0.01	1

Note: P represents p-values less than 0.01 or 0.05; PM: Particulate matter

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Failures analysis of water distribution network during 2006-2008 in Ahvaz, Iran

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Original Article

Abstract

Failures in the water distribution network are some most important factors in water losses, water shortage and dissatisfaction of users and secondary pollutions as well. This research aimed to analyze failure in water distribution networks during 2006-2008, for better water management. Daily failure reports in Ahvaz, Iran distribution network during 2006-2008, were collected from emergency department of Ahvaz water and Wastewater Company; thereafter, they were entered into an Excel database, also failures were defined by pipes type, pipe diameter, and cause of the failure, and finally the data were analyzed. Results indicated that asbestos and polyethylene pipes show maximum failures; maximum failure and fracture has occurred in pipes with 100 and 150 mm diameters. The most important factors affecting on failure were corrosion, traffic load and landslide. In addition, simultaneous influence of type and the diameter of the pipe on the failures were statistically significant. The depth of pipes establishment, corrosion and obsolescence of pipes as well as improper type of pipes were the most important causes of failures in Ahvaz Water Distribution Network. In this regard, upgrading pipe material setting standards and renewing water pipe network are the main strategies for failures minimization.

KEYWORDS: Failures Analysis, Water Distribution Network, Ahvaz

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Introduction

Optimum operation of water distribution networks is one of the priorities of sustainable development of water resources.[1] In recent years, water loss reduction has been raised as one of the most strategic and most economical ways of coping with drought in Iran.[2,3] The protection and maintenance of existing water networks is one of the projects that should be considered by water and wastewater companies.[4,5] Failure at the distribution level can be extremely critical because it is closest to the point of delivery and there are virtually no safety barriers before the consumption.[6]

Several parameters affect pipes and fittings failure. For example, numerous factors can cause the pipe failures such as, high water pressure, poor quality of pipe material, soil surrounding the pipes, age, diameter, corrosion, operational conditions, climatic conditions, traffic contribute to accidents and mechanical failure of pipes.[7-14]

In general, the mechanical failure of pipe under normal conditions (normal corrosion)

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occurs when the tensions resulting from environmental and operational conditions exceed pipe elasticity limit.[13]

Ahvaz is the center of Khuzestan province; located in the south west of Iran; with a population over 970,000 people; longitude of 49.68° North and latitude of 31.32° East; over 17,000 hectares; with an average height of 16 m from sea level.[15,16] Ahvaz has a total of three water treatment plants and a large water storage tank. Karun River is the main source of drinking water of Ahvaz,[17] with a minimum and maximum water flow of 90 m^3/s and 5,000 m^3/s in the low-water season and the flood season, respectively, and with an average flow rate of 2,500 m^3/s. The length of the water distribution network is about 2260 km.[18,19] Ahvaz water distribution network has a total of 254,888 subscribers.

Several studies have shown that most of the incidents have occurred in the iron and asbestos materials, respectively; most failures have occurred in diameters of 150 and 200 mm. The most important factors in pipes fracture incidence were corrosion, the physical pressure and the traffic; and numbers of fractures have been reduced by increasing the diameter.[20-31]

Due to lack of proper information about the failures in Ahvaz water distribution network, the importance of recognizing factors influencing it, this study was designed and performed using failures data during 2006-2008.

The main objective of this paper was to offer Ahvaz Water and Wastewater Company network modification and determination of the pipe material standards to reduce leakage and losses in Ahvaz water distribution network and have an appropriate distribution network for citizens.

Materials and Methods

Daily failure reports of Ahvaz Water Distribution Network were collected from emergency department of Water and Wastewater Company, Ahvaz, Iran, during 2006-2008. Therefore, they were entered into a Microsoft Excel database. Descriptive statistics including the maximum and minimum number of failures in distribution network were calculated and reported. All the statistical analyses were performed using Microsoft Excel program and SPSS for Windows (version 19.0, SPSS Inc., Chicago, IL, USA) with chi-square test. The P-value less than 0.05 set as a statistically significant level in all the statistical analyses. After collecting the required data i.e. pipe diameter and pipe materials, cause of the failure in the distribution network and in the divisions; and the values for every failure factors were defined. The results were compared to the standard values issued by The USEPA. Figure 1 shows the components Ahvaz Water and Wastewater Network, included (water pipes, pumps, valves, fittings, reservoir, waste pipes and manholes) and also pavements, parcels, river and rail.[21]

Results and Discussion

In this study, it was tried to analyze the failure and fracture in water distribution network of Ahvaz, Iran.

Number of failures based on the pipes materials

Figure 2 shows the frequency of failures in Ahvaz water distribution network in the different materials during 2006 to 2008.

According to figure 2, the highest number of incidents in Ahvaz water distribution network during the 2006-2008 has occurred in the type of asbestos (86.35%) and polyethylene (8.9%); and the lowest number of accidents has occurred in the ferrous type (0.0232%). The data analyzed using chi-square test also showed a statistical significant effect of type on fracture rates ($P = 0.0001$).

According to a study performed by Kettler and Goulter, failure rates for cast-iron pipe were found to decrease with increase in diameter. They found that failure rate of asbestos-cement and cast-iron pipes increased with time, but for different reasons. Analysis of the modes of failure showed that joint failure was predominant for cast-iron pipe systems with bolted and universal joints whereas the predominant mode of failure for asbestos-cement pipe systems was circumferential cracking.[32]

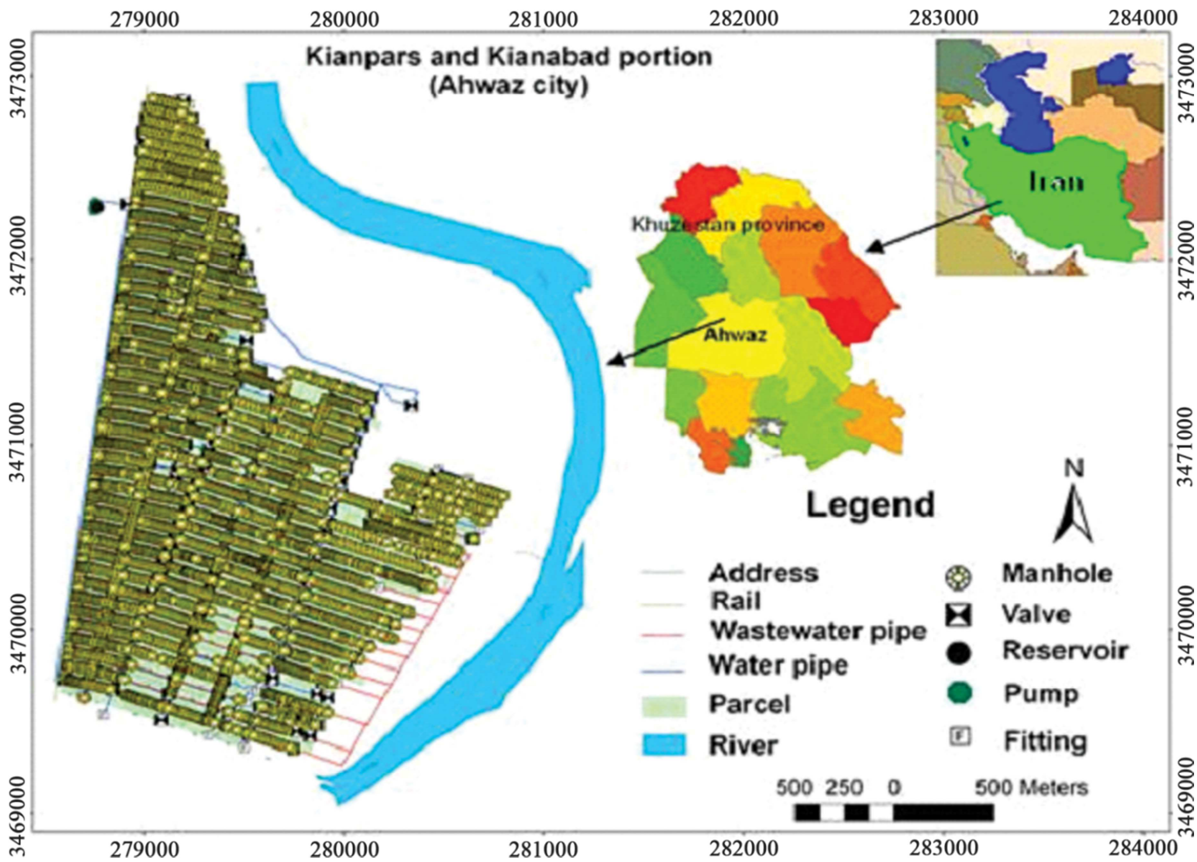

Figure 1. Study site location in the Ahvaz Water Distribution Network, in the south west of Iran21

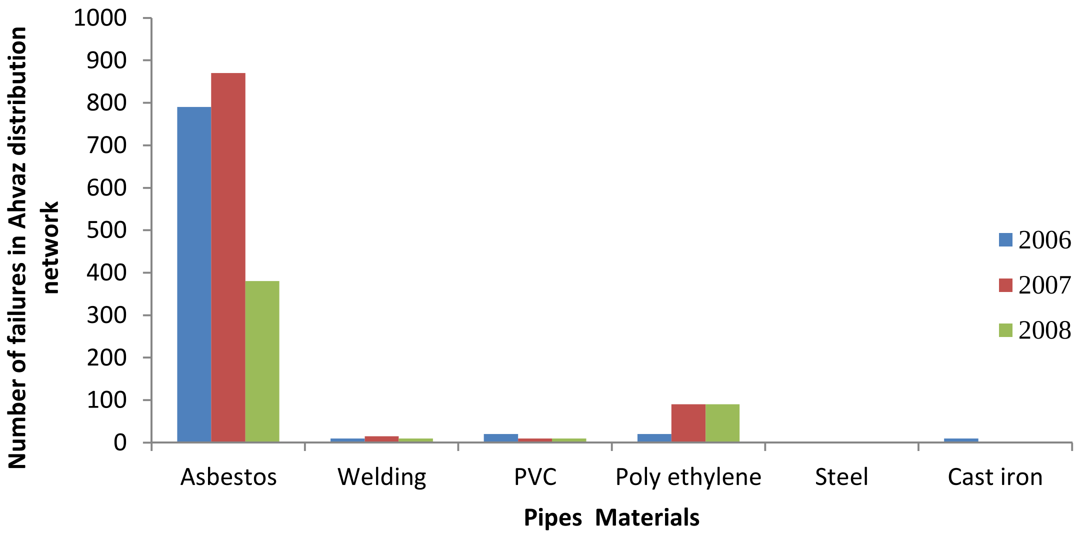

Figure 2. Number of failures in Ahvaz, Iran distribution network based on type of the pipe during 2006-2008
PVC: Polyvinyl chloride

Studies in Gorgan, Iran showed that over 50% of the failures have happened on polyvinyl chloride (PVC) pipes.[20]

Studies conducted in 21 cities in Canada, showed that more than 50% of the failures have happened in the ferrous pipes and the lowest amount of accidents and fractures in the PVC pipes (10%).[21]

According to a study conducted by Schuster (2008) in Toronto, the greatest failures and incidents happened in ferrous pipes.[23]

Number of failures based on the pipes diameter

Figure 3 shows the frequency of failures in different diameters in Ahvaz Water Distribution Network from 2006 to 2008. As the figures show, the greatest number of failures have occurred in diameter of 100 (39.78%) and 150 mm (18.39%) and lowest in diameters of 400 and 1500 (0.0424%)

The data were analyzed using chi-square test also shows a statistical significant effect of diameter on fracture rates (P = 0.0001).

The combined effects of type and diameter in the number of fractures in various years were evaluated using chi-square test. The diameter of the pipes was categorized in three 80-200 mm, 200-500mm and 500 mm > groups, and pipe type was divided into six groups: asbestos, welded, PVC, polyethylene, iron and cast iron; and the impact of both type and diameter was evaluated; and results showed that the type of fracture has a significant effect on the fracture rate.

Based on studies conducted, most of the failures have happened in diameters less than 200 mm.[24]

According to a study conducted by Schuster and McBean in Toronto, the most accidents and incidents had happened in diameters of 150 (50%) and 300 mm (30%).[23]

According to a study conducted by O'Day et al., the greatest failures and accidents had happened in diameters 150-200 mm.[25]

The results show that in the diameters less than 200 mm during 2006, 92% , 4.4%, 3%, 0.2%, and 0.4%, of the failures had occurred in the asbestos, PVC, polyethylene, ferrous, and cast iron types, respectively. In diameters of 200-500, 100% of the accidents happened in the asbestos type, and in diameters more than 500, 96.7%, and 3.3% of the failures had happened in the fusion, and in the ferrous types, respectively.

In this year, the simultaneous impact of type and diameter on fracture was statically significant, so that increase in diameter causes to decrease in frequency of fractures (the Pearson chi-square = 0.0001).

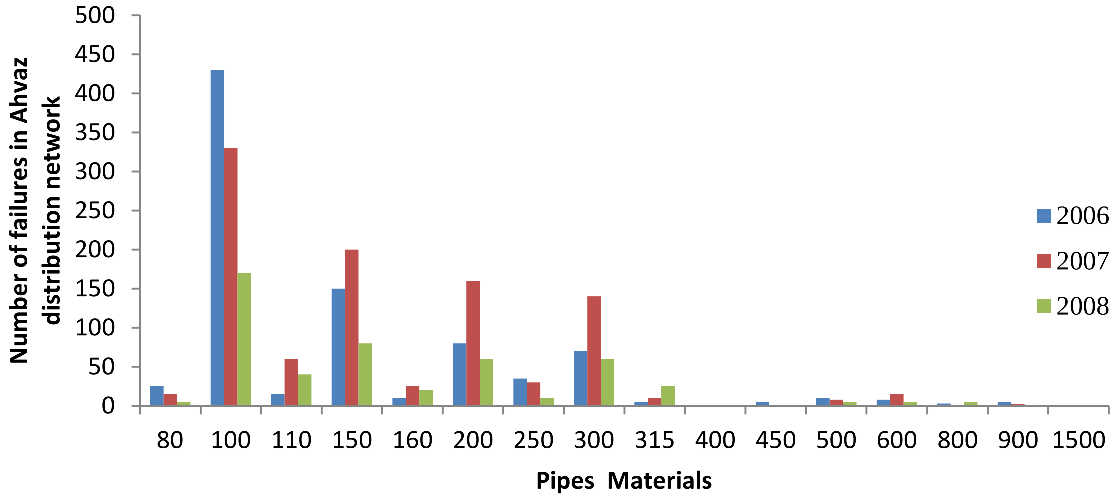

Figure 3. Number of failures in Ahvaz, Iran distribution network based on the pipes diameter during 2006-2008

In diameters less than 200 mm during 2007, 84.7%, 2.2%, and 13.1% of failures happened in the asbestos, PVC, and polyethylene types, respectively. In diameters 200-500mm, 95.9%, and 4.1% of failures happened in the asbestos and polyethylene types, respectively. In diameters more than 500 mm, 100% of the accidents happened in the fusion type. In this year, the simultaneous impact of type and diameter on fracture was statically significant, so that increase in diameter causes to decrease in frequency of fractures (the Pearson chi-square = 0.0001).

In diameter less than 200 mm during 2008, 77.3%, 2.8%, and 19.9% of failures happened in the asbestos, PVC, and polyethylene types, respectively. In diameters 200-500 mm, 84.8% and 15.2% of failures and accidents happened in the asbestos and polyethylene types, respectively. In diameters more than 500 mm, 100% of the accidents happened in the fusion type. In this year, the simultaneous impact of type and diameter on fracture was statically significant, so that, increase in diameter cause to decrease in frequency of fractures (the Pearson chi-square = 0.0001).

The results of the statistical analysis using chi-square test indicated that the impact of simultaneous number of failures in the type and diameter had been significant in the water distribution network during 2006-2008, also shows that with increasing the diameter, number of fractures reduces. Different studies have shown such result.[22-25]

Factors and number of failures in distribution network and connection network

Table 1 and 2 respectively show incidence factors in the distribution network and divisions network during 2006-2008.

The ratio of failure to total length of Ahvaz distribution network during 2006, 2007 and 2008 are 0.37, 0.509 and 1.089 cases per kilometer, respectively and from 2006 to 2008, this value was 0.211 cases per kilometer.

In the United States, (USEPA Standards; US Environmental Protection Agency) there are an estimated 237600 pipe breaks in 1,408,000 km, length of the water supply network, per year (The ratio of failure was 0.168).[33,34] Table 1 shows that average number of failures in Ahvaz distribution network was 845 in 2,349 km, length of the water supply network, during 2006-2008 (The ratio of failure was 0.359), which was higher than USEPA standards.

Table 1. Factors and number of failures in Ahvaz, Iran distribution network during 2006-2008 (Ahvaz Water and Wastewater Company)

Failure factors	Mean 2006		Mean 2007		Mean 2008		Mean 2006-2008	
	Number of failures	Percent	Number of failures	Percent	Number of failures	Percent	Number of failures	Percent
Corrosion	310	36.0465	594	50.1689	278	56.6192	1182	46.6272
Improper context	78	9.0698	94	7.9392	11	2.2403	183	7.2190
Improper quality of pipes and fittings	69	8.0233	23	1.9426	17	3.4623	109	4.2998
Scissors on (in a landslide)	140	16.2791	65	5.4899	53	10.7943	258	10.1775
Department of Gas	35	4.0698	13	1.0980	10	2.0367	58	2.2880
Department of Telecommunications	10	1.1628	10	0.8446	2	0.4073	22	0.8678
Department of electrical	4	0.4651	14	1.1824	2	0.4073	20	0.7890
Municipal	46	5.3488	74	6.2500	34	6.9246	154	6.0750
Sewage unit	77	8.9535	62	5.2365	29	5.9063	168	6.6272
Customer affairs	2	0.2326	21	1.7736	1	0.2037	24	0.9467
Car transportation	69	8.0233	179	15.1182	42	8.5540	290	11.4398
Oil company	3	0.3488	7	0.5912	0	0.0000	10	0.3945
Unauthorized connections	17	1.9767	11	0.9291	0	0.0000	28	1.1045
Water contractor	0	0.0000	10	0.8446	9	1.8330	19	0.7495
Subway contractor	0	0.0000	7	0.5912	3	0.6110	10	0.3945
Total	860	100	1184	100	491	100	2535	100

Table 2. Factors and number of failures in Ahvaz, Iran connection network during 2006-2008 (Ahvaz Water and Wastewater Company)

Failure factors	Mean 2006		Mean 2007		Mean 2008		Mean 2006-2008	
	Number of failures	Percent	Number of failures	Percent	Number of failures	Percent	Number of failures	Percent
Corrosion	6630	40.2599	10388	43.2761	4171	46.1751	21189	42.8017
Air entering the network	586	3.5584	250	1.0415	0	0.0000	836	1.6887
Context inappropriate	649	4.0017	407	1.6956	11	0.1218	1067	2.1553
Traffic load	450	2.7933	261	1.0873	3	0.0332	714	1.4423
Unsuitable quality of pipes and fittings	400	2.4897	360	1.4998	124	1.3727	884	1.7857
Department of Gas	226	1.3724	549	2.2871	176	1.9484	951	1.9210
Department of Telecommunications	206	1.2995	471	1.9622	109	1.2067	786	1.5877
Department of electrical	31	0.1882	187	0.7790	23	0.2546	241	0.4868
Municipal	272	1.6517	633	2.6371	267	2.9558	1172	2.3674
Sewage unit	312	1.8946	528	2.1996	193	2.1366	1033	2.0867
Eclipse (low pressure and water cut)	1298	8.4892	2178	9.0735	636	7.0409	4112	8.3062
Customer affairs (water cut accidents and fractures)	107	0.6497	255	1.0623	35	0.3875	397	0.8019
Destructive	110	0.6680	375	1.5622	108	1.1956	593	1.1979
Car transportation	795	4.8275	1459	6.0782	823	9.1110	3077	6.2155
Repair groups the network	71	0.4311	212	0.8832	43	0.4760	326	0.6585
End of the useful life of the pipe	2262	14.0393	3003	12.5104	1434	15.8751	6699	13.5319
Events by the water contractor	21	0.1275	198	0.8249	11	0.1218	230	0.4646
Adhesive outwear	772	4.6879	514	2.1413	127	1.4060	1413	2.8543
By common	275	1.6699	559	2.3288	168	1.8598	1002	2.0240
Unknown	807	4.9004	1217	5.0700	571	6.3213	2595	5.2419
Total	16468	100	24004	100	9033	100	49505	100

As shown in table 1, the most important factors in the occurrence of failures in the distribution network in 2006-2008 were corrosion (46.62%), car transportation (11. 43%) and landslide (10.17%), respectively; and weakest factors were occurrence of accidents in the metro contractors and Oil Company (0.3945).

According to a study conducted by Kleiner and Rajani in Australia, the most important factors in occurrence of failures in pipes were corrosion and high age of pipes.[26] Leaks often occur through a buildup of corrosion that causes structural failures in aging pipes, particularly at joints.[35]

As shown in table 2, the most important factors in occurrence of the failures on the divisions during 2006-2008 were corrosion (42.8%), eclipse (8.3%) and car transportation (6.2%), and weakest factor was contractor (0.4646).

The ratio of the failures in the distribution network to the total length of pipes of the water distribution network in Ahvaz in 2006, 2007 and 2008 was 0.37, 0.509, 1.089 cases per kilometer, respectively and in 2006-2008, this value was 0.211 cases per kilometer. According to a study conducted by Agbenowosi, the rate of accidents and fractures in the water distribution network in Europe was 311 cases per kilometer.[27]

According to a study conducted by Agbenowosi, the rate of accidents and fractures in the United States water distribution network was the 0.137 cases per kilometer.[27]

In the United States, The ratio of the failures of division to the total length of the pipes in water distribution network was 5.92 cases per kilometer.[34] The ratio of the failures of division to the total length of the pipes in Ahvaz city water distribution network in 2006, 2007 and 2008 was respectively 7.08, 10.32, 3.88 cases per kilometer, and in 2006-2007, this value was 21.28 cases per kilometer which is higher than USEPA standards.

Based on studies conducted by Beigi in 1999, the number of failures in divisions in the water distribution network in 1998 was 9.48 kilometers of the distribution network.[24]

In the United States, an estimated 7,000 km of pipe requires replacement each year at a cost of around USD 2.7 billion while water losses (estimated to be 10%) cost around USD 4.3 billion per year.[33]

Given the most of the failures were due to corrosion and obsolescence of pipes in the distribution network, the necessary measures should be taken for replacing them. Since the failure rates on the pipe of the asbestos has the upper value, so replacing this type of pipes with some other high quality pipes, particularly polyethylene pipes for divisions is necessary. Considering the rate of 95.1% of the failures in the divisions, paying attention to the standardization of the divisions is necessary. Another cause for failures is low depth of pipes in the network due to the pressure created by vehicles traffic. With the increasing growth of urbanization, redesign and modification of the network and creation of more pressure zones with a right amount of pressure is necessary, which would reduce leaks, pipe breaks and water losses.

Conclusion

According to results, most of failures in Ahvaz water distribution network are resulted from corrosion and amortized pipes. Therefore, it is necessary to replace damaged pipes with new ones. With regard to results, failures in Ahvaz water distribution network are frequent, and consequently lead to cost wasting in water supply operation. In order to reduce failures in water distribution network, structural amendment in network is critical. According to the increasing population and development of urbanization it considers redesigning and modification of water distribution network is essential. Furthermore, creating additional pressure zones with appropriate pressure is necessary. This can be reduced leaks and failures in the piping distribution network.

Conflict of Interests

Authors have no conflict of interests.

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