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Original Research

Wastewater Evaluation for Multan, Pakistan: Characterization and Agricultural Reuse

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Abstract

Wastewater (WW) volume generated from both domestic and industrial sectors has increased due to rapid industrialization and urbanization. WW is increasingly used on farms because it is cheap and easily available all year, causing various environmental and health implications. In order to evaluate Multan WW, this study characterizes 154 WW samples collected from 11 disposal stations. These samples were analysed for 23 parameters related to organic matter, nutrients, inorganic matter, and pathogens to determine pollution extent distribution, agricultural reuse potential, and WW treatment database. A major contamination concern was found regarding biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total coliform, and E-Coli. The average values of BOD and COD were found to be 2.7 and 3.8 times higher than the permissible limits respectively. The microbiological parameters such as total coliform and E-Coli were found to be 10.6 and 36 times higher than the permissible limits, respectively. However, heavy metals and nutrients were found within the permissible limit except phosphorus. Here, the correlation study on selected WW parameters indicated the direct or indirect relationship among WW constituents and the impact of different sources of pollution on WW characteristics. The present study also presents a critical review of different treatment options according to contamination strength in disposal stations.

Keywords: agriculture, characterization, permissible limit, correlation, wastewater treatment

Introduction

Pakistan is the world's 6th most populous country with more than 190 million, which will exceed 240 million by 2030 [1, 2]. Therefore, the demands for food and water have increased to feed its growing population. On the other hand, the domestic, industrial and agricultural effluents have also increased [3]. At the same time, surface water resources are losing rapidly in Pakistan, including in Multan, due to their mismanagement, increased agricultural activities, and rapid industrialization [1, 4]. Similarly, high population

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growth rates, rapid urbanization, and an inefficient sewerage system are also imparting immense pressure on the quality and quantity of existing water sources. Consequently, the need for water to increase food production has rapidly increased [5-7]. Therefore, the effluents generated from different sources are being used without treatment for agriculture purposes in order to cope with increasing water scarcity in many parts of the country, including in Multan District [8], which is considered to be an influential, political, and agricultural centre of Pakistan covering an area of 304 km^2 with a population of 1.9 million. Its location is at 710 m above mean sea level on the east bank of the Chenab River [9]. Being the most important agricultural district of Pakistan, the water demand for irrigation has increased to boost agricultural produce. In the present situation, it has become necessary for the planners to consider other additional unconventional sources of water to cope with increasing water scarcity that can be used economically and effectively for irrigation, and WW is important for this [10-12].

WW use in agriculture is justified according to economic and agronomic points of view, but precautions and treatment are needed to minimize impacts on health and the environment [13]. In Pakistan, the WW generation of 6.414 billion m^3 (BCM) per year was estimated, which consisted of 4.953 BCM per year from municipalities and 0.395 BCM per year from industry [14], out of which WW of 0.876 BCM per year are being directly used for agriculture. The irrigating land served by WW is about 32500 ha [15]. Vegetables, fodder, cotton, and to some extent rice are the most commonly grown crops irrigated using WW [15]. It has been reported that total daily WW disposal to drainage systems or agricultural land in Pakistan is about 8.80 x 10^6 m^3, and 26% of total vegetables are produced using WW irrigation [6, 16]. Similarly, Multan has effluent potential of 5.17 m^3/sec with total WW production of 66 x 10^6 m^3 per year. The produced WW in Multan is managed by the Multan Water and Sanitation Authority (MWASA) in urban areas and by the Tehsil Municipal Administration (TMAs) in rural and peri-urban areas. Its receiving water bodies are the Chenab, irrigation canals, and farms [17]. MWASA has established a sewerage network that includes sewers of main, sub-main, and lateral types of 1028 km length with six main disposal stations and five intermediate pumping stations collecting domestic, industrial, and storm water. The cumulative pumping capacity of these disposal stations is about 22 m^3/sec. This sewerage network caters to 70% of households and other users [9]. 180 industrial units – mostly of paper, textile, leather, and pesticides – are present in Multan Industrial Estate (MIE) Phase I [9]. The untreated effluents from these industries have created multiple environmental challenges to the district. WW reuse at farms is also preferred due to its consistent year-round availability, high concentration of plant nutrients, and supporting the livelihood of millions of farmers [18-20]. However, the most important risks associated with WW irrigation are related to the impact on environment and human health [21], safety and quality of agricultural products [22], salt accumulation, and water infiltration capacity of soil [23], along with the accumulation of heavy metals and contamination caused by nutrient leaching [24, 25]. Therefore, a characterization study of WW for impact and nutrient assessment is essential. Different characterization studies of WW conducted for impact assessment in different cities of Pakistan such as Lahore [1, 26], Faisalabad [14, 17], Haroonabad [27, 28], Queta [29], Peshawar [30, 31], and Rawalpindi [32] reveal that different physical, biological, and chemical parameters were exceeding their permissible limits; thus the degree of pollution is increasing.

As little or no work is done on characterizing the Multan regional WW, where most of the farmers are using untreated WW for irrigating their farms with rare exceptions, it is essential to characterize it to assess its suitability for agricultural use and to develop baseline data for WW treatment [8]. Due to industrial process variations and poor sanitation, effluent constituents vary commonly and include toxic chemicals that lead to severe problems related to crops, human health, plants, animals, and marine life [1]. For best monitoring of WW quality, treatment, and its reuse, the physical, biological and chemical properties of WW should be properly analysed. Keeping in view the present study, it was accomplished for the physical, biological, and chemical characterization of WW of 11 disposal stations of Multan in order to determine contamination strength being discharged into the receiving environment and assess its potential for agricultural reuse.

Materials and Methods

Study Area

The study was conducted from June 2016 to March 2017 at Multan (30°12′0″North and 71°28′0″East) in southern Punjab, Pakistan on the east bank of the Chenab River, which included 11 disposal stations (six main and five intermediate disposal stations): i. Bahauddin Zakariya University (1-BZU), ii. Bypass (2-Byp), iii. Suraj Miani (3-Sur), iv. Chongi No. 9 (4-Cho), v. Sameejabad (5-Sam), vi. Vehari road (6-Veh), vii. Kirri Jamanda (7-Kirri), viii. Old Shujabad (8-Shuj), ix. Farooqpura (9-Far), x. Waheedabad (10-Wah), and xi. New Shahshams (11-Sha) (Fig. 1).

Experimental Methodology and Procedure

Two composite samples (samples of constant volume at variable durations relative to the WW flow) per day were taken from each disposal station throughout a week in 1.5-L pre-sterilized sampling bottles following the standard sampling procedure for sample integrity and test results validity [33]. To maintain sample integrity, these were analysed immediately or stored in containers at 4˚C with preservatives such as nitric acid and sulphuric acid to retard chemical and biological changes, preservation requirement, and pH adjustment depending upon the parameters to be analysed as shown in Table 1 [1]. The WW samples were analysed for pH, COD, BOD, EC, alkalinity, TDS, TSS, TN, NH_3-N, NO_3-N, Cr, Fe, Cu, Pb, Zn, Ca, Mg, total coliform, and E-Coli according to standard methods of wastewater examination [17, 33].

Heavy Metals Analysis

Atomic absorption spectrometry was used for heavy metals analysis. To get free metal ions and reduce organic matter interference the samples were digested using the standard method [33]. 100 mL of WW sample and 5 mL of nitric acid was poured into digestion tubes. The digestion tubes were placed in a digester until the light color of the sample and clear solution were obtained (3030E Nitric Acid Digestion). Then digested samples were filtered and preserved in sampling bottles for subsequent analysis. Atomic absorption spectrometry (AAS) works based on the amount of energy absorbed in the flame of the characteristic wavelength. This characteristic wavelength is proportional to the element concentration in the sample. Here a light beam is directed toward a monochromator from the flame, and on to a detector that is used to determine the quantity of light absorbed by the atomized element in the flame (Fig. 2.). It also presents high specificity, sensitivity, and selectivity advantages to analyze the heavy metals [35].

Results and Discussion

Physical Parameters

Electrical conductivity (EC) indicates the salinity of water by measuring its current carrying capacity. It was also observed that EC variations are almost stable and its values highly less than the recommended

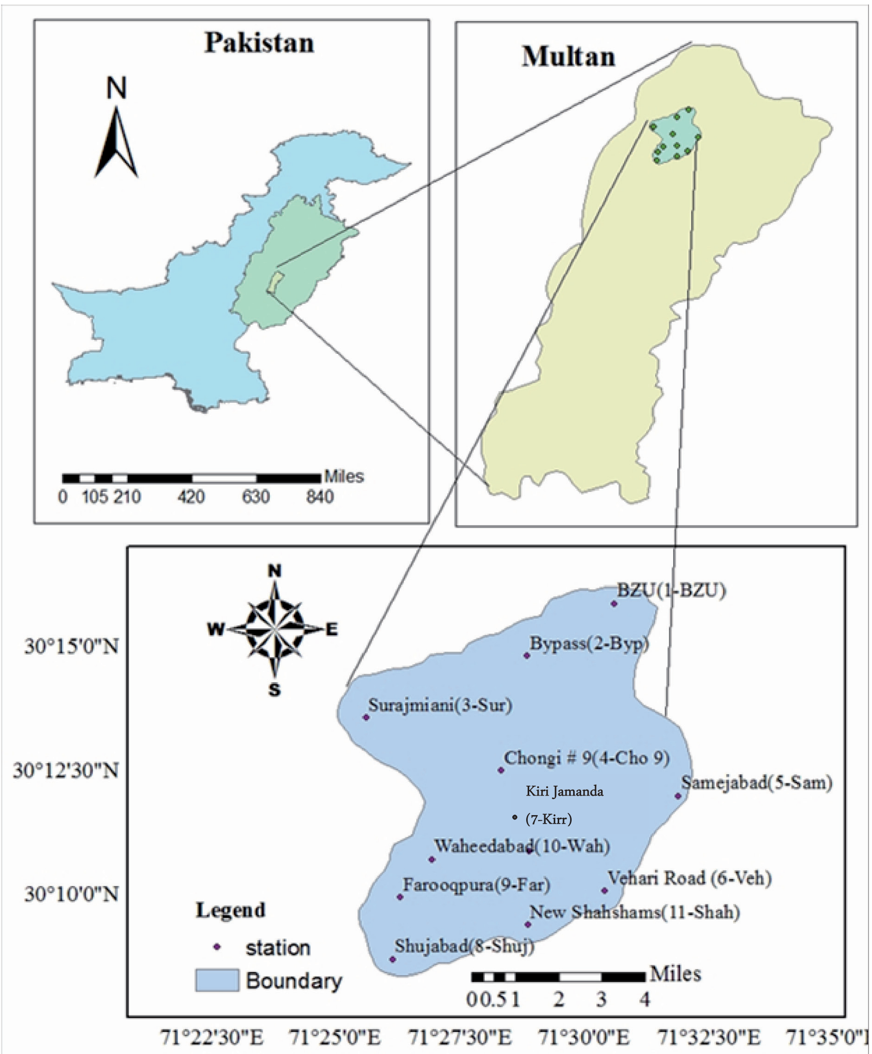

Fig. 1. Location of sampling sites.

Table 1. Preservation techniques and holding times of selected parameters [33].

Parameter	Preservation	Max. Holding Time
Alkalinity	Storage at 4ºC	14 d
BOD	Storage at 4ºC	48 hours
COD	Storage at 4ºC, analyse immediately if possible or for pH <2 add H_2SO_4	28 days
DO	Not required	Analyze immediately
pH	Not required	Analyze immediately
EC	Not required	Analyze immediately
Color	Storage at 4ºC	48 hours
Turbidity	Dark Storage up to 24 h, cool at 4˚C	48 hours
Solids	Storage at 4˚C	7 days
TN, NH_3-N, NO_3-N	Analyse immediately if possible or for pH <2 add H_2SO_4, Storage at 4ºC	48 hours (NO_3-N), 28 days (TN, NH_3-N)
P	Add H_2SO_4 to pH <2 and Storage at 4ºC	28 days
Metals (Cu, Pb, Zn, Cr, Fe, Ca, K)	Add HNO_3 to pH <2 and filter immediately for dissolved metals	6 months

values as described by FAO. So, it is concluded that Multan regional WW found no restriction for agricultural reuse according to EC points of view. The WW having EC<0.7 dS/m has no restriction of agriculture use while the degree of restriction becomes severe for EC>3 dS/m due to its impact on plant growth, crop yield, and quality of produce [13]. Total dissolved solids (TDS) and total suspended solids (TSS) are also important parameters because more solids lead to raised osmotic pressure in soil solution, a carrier of pathogens, specific ion toxicity, viscosity of WW, and affect the aesthetic value of receiving water bodies [36]. The maximum value of TDS was recorded at a disposal station of 4-Cho of 1500 mg/L while the minimum value of TDS of 1-BZU of 510 mg/L was recorded. The TSS varies widely in effluents at all the disposal stations, which is due to variation in industrial manufacturing processes. The most variability was observed at 6-Veh (233 mg/L) and the least at 1-BZU (20 mg/L) (Fig. 3a). In regional WW, the average value of TSS ranged from 76 to 600 mg/L, with standard deviation of 208 mg/L, which indicates the strong need of WW treatment before its use for agriculture due to beyond permissible limits (200 mg/L) [37] (Table 2). The 50 to 70% of TSS can be removed by applying the primary treatment. The high rate of biological treatment processes have the ability to remove 85% of TSS such as activated sludge, trickling filter, and rotating biological

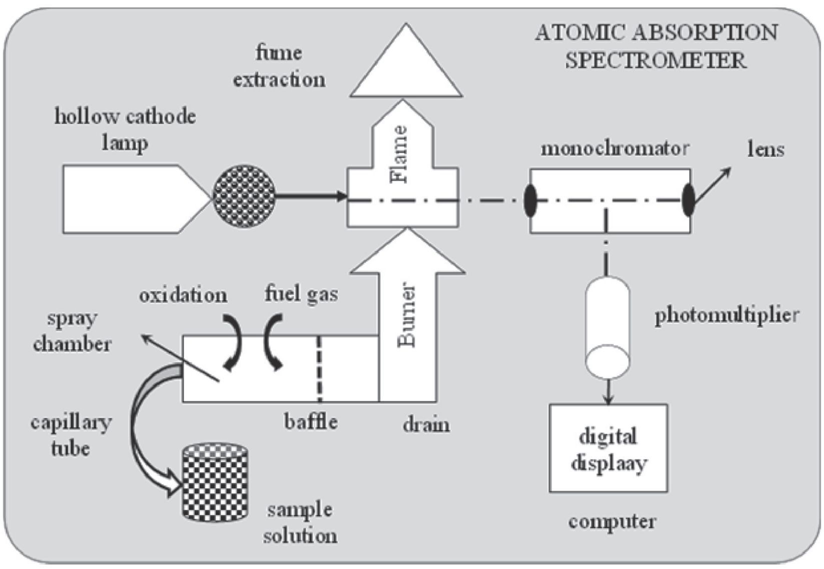

Fig. 2. Schematic diagram of atomic absorption spectrometer.

Table 2. TSS, COD, and BOD trend of regional wastewater.

Parameters	TSS				COD (mg/L)				BOD (mg/L)			
Disposal Stations	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV
1-BZU	79	53	124	20	160	90	195	30	131	75	167	26
2-Byp	132	83	195	42	168	140	190	16	134	117	164	16
3-Sur	203	149	246	39	266	156	406	92	211	137	345	82
4-Cho	510	310	716	203	292	286	300	7.2	236	219	251	16
5-Sam	428	296	520	92	374	303	440	46	298	230	333	35
6-Veh	560	122	784	233	492	262	646	124	400	252	531	94
7-Kirri	299	214	374	45	434	379	512	48	351	309	419	39
8-Shuj	613	279	856	215	359	259	471	86	302	210	398	69
9-Far	401	336	523	71	552	399	868	190	436	311	660	143
10-Wah	418	276	531	100	597	415	908	326	470	270	756	238
11-Sha	434	195	664	212	552	329	998	188	420	301	680	141
Average	370	210	503	115	386	274	539	105	309	221	428	82

contactors [13]. A cascade system integrated with the settler is also a promising technology for TSS removal. Furthermore, the greater removal of TSS values result in better reduction in total coliform and fecal coliform through disinfection of the unit [38].

It was observed that turbidity variability was high in the range of 79-771 FAU, with standard deviation of 274 FAU due to variation in effluent composition. Pritchard et al. [39] found that high turbidity reduces the effect of disinfectants because colloidal particles protect pathogenic organisms. Sehar et al. [40] described that turbidity treatment is essential to avoid pathogenic organism's flourishment and anaesthetic impact on receiving environment. Bakopoulou et al. [38] suggested the application of effective advance treatment for removal of higher values of turbidity prior to the disinfection process. Fixed biofilm reactor (FBR), sand column filter (SCF), and wetlands were found to be effective at turbidity removal of WW [41].

The dissolved oxygen (DO) parameter was used to reflect the physical and biological processes prevailing in water, degree of pollution in water bodies, and growth rate of microorganisms [40]. The water could support the oxygen requirements of the aquatic organisms for higher DO value of 7.1±0.8 mg/L of WW [42]. The range and variation in DO level with time and space is quite narrow and critical (0.1-0.9 mg/L). The results indicate that there is a strong need for treating WW before its disposal in order to receive an environment to control the degraded water quality situation. It has been reported that COD, BOD, TDS, and TSS have an inverse relationship with DO [41, 43]. So it can be increased from conventional WW treatment. The WW colour is a qualitative characteristic that can represent the freshness and general condition of WW and the presence of sight pollutants. The average colour values ranged from 596-3444 pt/co. We observed that WW represents different colours due to decomposition differences in industrial wastes and dissolved organic matter. We also concluded that colour removal of WW is essential in order to avoid unfavourable aesthetic impact on the receiving environment along with its toxicity. Chavez et al. [44] reported the interlinked relationships of COD, colour, turbidity, conductivity, and suspended solids. Khan et al. [41] described the strong logical relationships between the above WW parameters and reported that the removal of one parameter also resulted in the reduction of other parameter values.

Microbiological Parameters

BOD refers to the amount of oxygen consumption by microorganisms for oxidizing organic matter to CO_2, H_2O, and other end products under an aerobic environment [45]. The BOD status in WW was determined at the selected stations and was used for selecting and designing a secondary treatment system. It was also used to indicate the contamination strength of waste and treatment efficiency of the WW treatment system. The average BOD values ranged from 131 to 470 mg/L, with standard deviation of 145 mg/L determined at all disposal stations (Table 2). The results indicated that WW was highly organically contaminated at 6-Veh, 9-Far, 10-Wah, and 11-Sha disposal stations having BOD values > 400 mg/L, whereas moderately organically contaminated WW was found at disposal stations of 3-Sur, 4-Cho, 5-Sam, 7-Kirri, and 8-Shuj with BOD values of > 200 mg/L [46] (based on the permissible limit = 80 mg/L). The WW at 1-BZU and 2-Byp disposals stations was relatively less contaminated because BOD values at these disposal stations were lighter and higher than those of permissible limit as reported by National Environmental Quality Standards (NEQS) [46, 47].

The less organically contaminated WW at 1-BZU and 2-Byp disposal stations was due to less discharge of industrial effluents and high discharge of domestic WW. Overall results indicated that the BOD values were higher than that of permissible limits as described by Pak-NEQS (Fig. 3b). The optimum value of BOD_5 may be attained by primary treatment (25 to 50% of BOD) and by high-rate biological treatment processes such as activated sludge, oxidation ditches, trickling filter, rotating biological contactors (RBCs), or a combination of these processes in series (almost 85% of BOD) with primary treatment. The authors work on indigenously developed maize cobs trickling filter (MCTF) that has BOD removal efficiency of about 79% on average basis [34].

Pathogen removal technologies are evaluated based on fecal contamination indicators (intestinal nematodes, E. coli, faecal coliforms (FC), total coliforms (TC), thermotolerant coliforms) [16, 47]. The coliform group consists predominantly of species of the genera Citrobacter, Escherichia, Enterobacter, Faecal Coliforms and Klebsiella, of which E-coli has a unique importance. In most states, monitoring total coliform and E-Coli is considered essential due to indications of potential pathogens in water resources [48]. Coliform bacteria identification is relatively

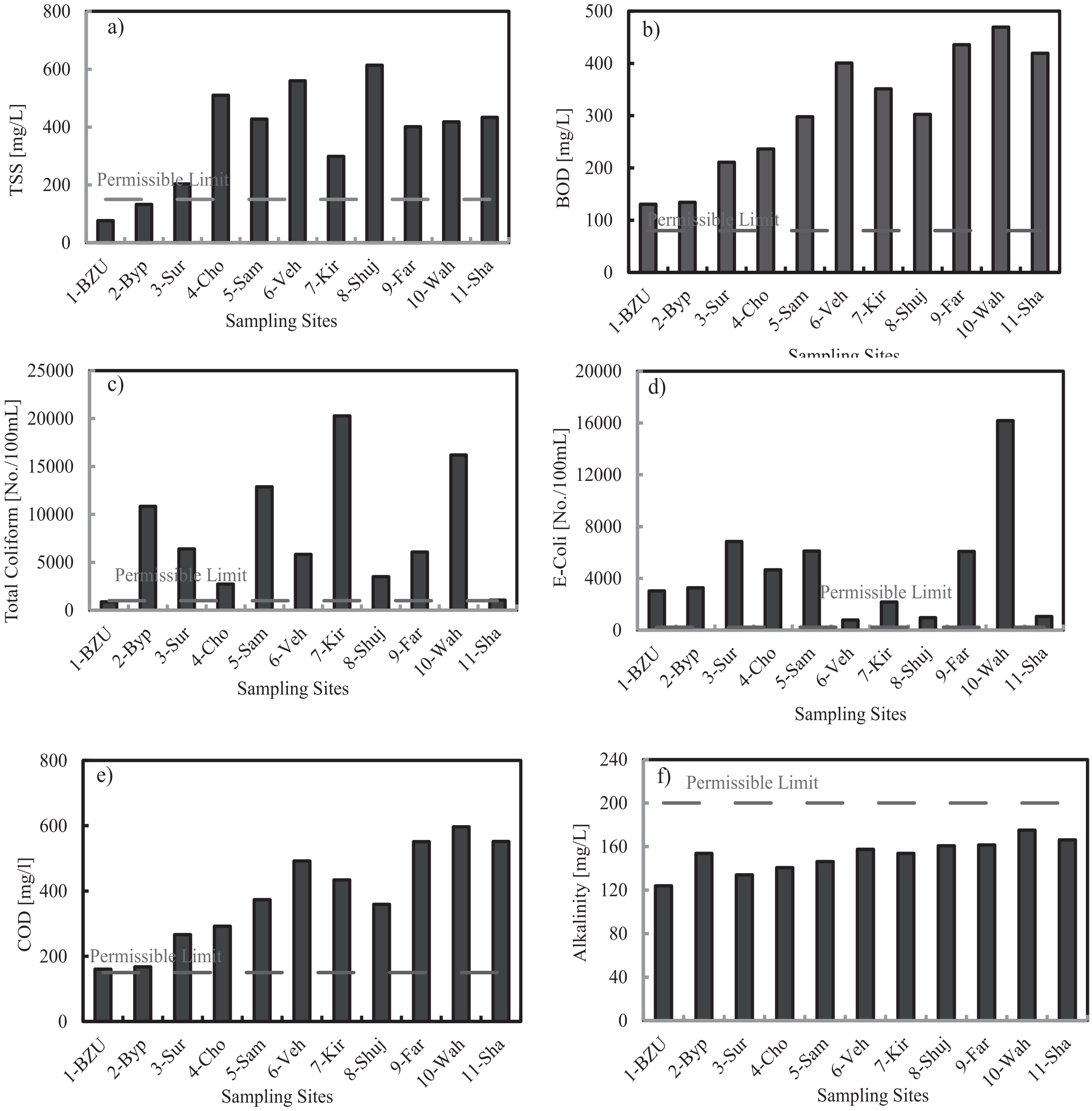

Fig. 3. Variations observed for TSS, BOD, total coliform, E-Coli, COD, and alkalinity.

simple due to its existence in more numbers than other dangerous pathogens. Also, they have the tendency to react with the natural environment and with treatment processes in the same way as other pathogens. Hence by the analysis of coliform bacteria, the level of other pathogens can be estimated [17]. Its value was found beyond the permissible limit specified by the Canadian Council of Ministers of the Environment [49]. The highest value of total coliform observed for 7-Kirri (average value 20275 No. /100ml) and the lowest value for 1-BZU disposal station (average value 870 No. /100ml) (Fig. 3c). E-Coli is the most reliable parameter for WW reuse on farms because the fecal coliform test may contain non-fecal organisms that can breed at 44ºC [13]. Its value was found beyond the permissible limit specified by ambient water quality criteria for bacteria. The highest value of total E-Coli was observed in 10-Wah (average value 16190 No./100ml), and the lowest value was found for 6-Veh station (average value 870 No./100ml) (Fig. 3d). For agricultural reuse, removal of total coliform and E-Coli is essential in order to avoid diseases in the farming community. In a chemical or biochemical disinfection unit, the techniques for removal of pathogenic organisms are based on a microorganism's oxidation through strong oxidants and biological solution, as well as physical separation, including electrochemical treatment and membrane technologies and maturation ponds.

Chemical Parameters

COD indicates the pollution strength of WWs. It is defined as the extent of oxygen required for chemical oxidation of organic matter completely to CO_2, NH_3, and H_2O using a strong oxidizing agent like potassium dichromate under acidic conditions [45]. COD measures oxidation in the presence of sulphuric acid and silver with potassium dichromate, thus it indicates both oxygen equivalents to organic matter and microorganisms in WW. Table 2 shows the variability in concentration of COD. The maximum COD concentration of 998 mg/L was observed from 11-Sha and the lowest concentration of 90 mg/L was recorded from 1-BZU with average standard deviation of 190. The WW at disposal stations of 9-Far, 10-Wah, and 1-Sha was more chemically contaminated as compared to the 1-BZU station. The WWs 1-BZU and 2-Byp disposal stations were not chemically contaminated as criteria developed by NEQS (Fig. 3e). The results also indicated that the high COD values at 10-Wah, 9-Far, and 11-Sha disposal stations indicate the presence of toxic substances in city sewerage water. Thus, there is a strong need for WW treatment at 10-Wah, 9-Far, and 11-Sha, and primary treatments were required at 1-BZU and 2-Byp disposal stations in order to overcome the harmful impact of high content of organic substances. The COD/BOD ratio varies in the range of 1.2-1.3, which indicates a large proportion of organic biodegradable matter [50]. Thus a biological treatment will be effective against WW treatment. It has been reported that the optimum value of COD may be attained by primary treatment (25 to 50% of COD) and by high-rate biological treatment processes such as activated sludge, oxidation ditches trickling filter, rotating biological contactors (RBCs), or a combination of these processes in series (almost 85% of COD) [13].

Minimum pH of 4.78 was analyzed at disposal station 10-Wah and maximum pH of 6.53 was found at disposal station 1-BZU. The results indicate that

Table 3. NH_3-N, NO_3-N, and TN assessment of wastewater.

Parameters	NH_3-N (mg/L)				NO_3-N (mg/L)				TN (mg/L)			
Disposal Stations	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV
1-BZU	6.37	3.56	9.76	1.8	3.88	3.03	4.97	0.6	19.30	75	24.65	3.30
2-Byp	5.00	3.45	6.89	1.3	3.95	2.89	4.87	0.6	15.80	117	17.34	1.30
3-Sur	4.79	2.45	9.08	2.4	4.60	3.65	6.26	1.0	13.10	137	15.35	2.10
4-Cho	4.03	3.19	3.59	1.1	4.52	2.92	6.52	1.8	11.90	219	12.74	1.30
5-Sam	6.95	3.56	9.76	1.4	4.23	2.13	8.13	1.9	17.40	230	24.31	3.40
6-Veh	5.48	3.99	7.21	1.3	2.65	1.63	3.33	0.6	11.08	252	14.57	2.80
7-Kirri	6.03	4.45	7.43	0.9	2.74	2.13	3.67	0.6	13.60	309	23.76	4.60
8-Shuj	6.77	5.67	7.65	0.9	3.59	2.19	4.67	0.9	17.00	210	22.78	3.70
9-Far	6.40	4.67	5.45	1.6	4.00	2.12	5.78	1.6	21.11	311	26.78	4.90
10-Wah	6.13	4.56	8.45	1.5	3.89	3.28	4.67	0.6	3.89	270	20.89	1.70
11-Sha	6.23	4.23	7.56	1.1	3.95	2.67	4.98	0.8	22.56	301	26.34	2.20
Average	5.83	3.98	9.76	1.39	3.82	2.60	5.26	1.0	15.16	221	20.85	2.84

the WW was found to be less acidic at 1-BZU disposal station than that of 10-Wah, which was due to the disposal industrial effluents – especially from the tannery industry. pH is an important parameter that tells the acidity or basicity of WW. Jiménez et al. [51] found that the slightly alkaline WW (7.2-7.6) helps in metal fixing of soil. Bai et al. [52] described that for the existence of most biological life, the pH range is quite narrow and critical, i.e., 6-9. Similarly, the most suitable pH range of 6-9 for macrophyte performance was found by Shah et al. [45]. The optimum pH of WW can be attained by microbial degradation of organic matter and in vegetated treatments due to the release of acidic root exudates from vegetation and carbon dioxide (CO_2) production by root respiration [3, 53-56].

Alkalinity refers to the capacity of water to neutralize acid or absorb hydrogen ions, i.e., buffering capacity [57]. It describes the ability of water to repel the change in pH [17]. It is a major chemical requirement for biological activity and nitrification [54]. The alkaline nature of WW may deteriorate soil structure, thus impeding agricultural productivity. The highest concentration of 179 mg/L was detected from a disposal station of 10-Wah and the lowest concentration 123.9 mg/L was detected from a disposal station of 1-BZU with standard deviation of 9.4 mg/L, which indicates the availability of sufficient alkalinity for biological nitrification (Fig. 3f). Alkalinity variation

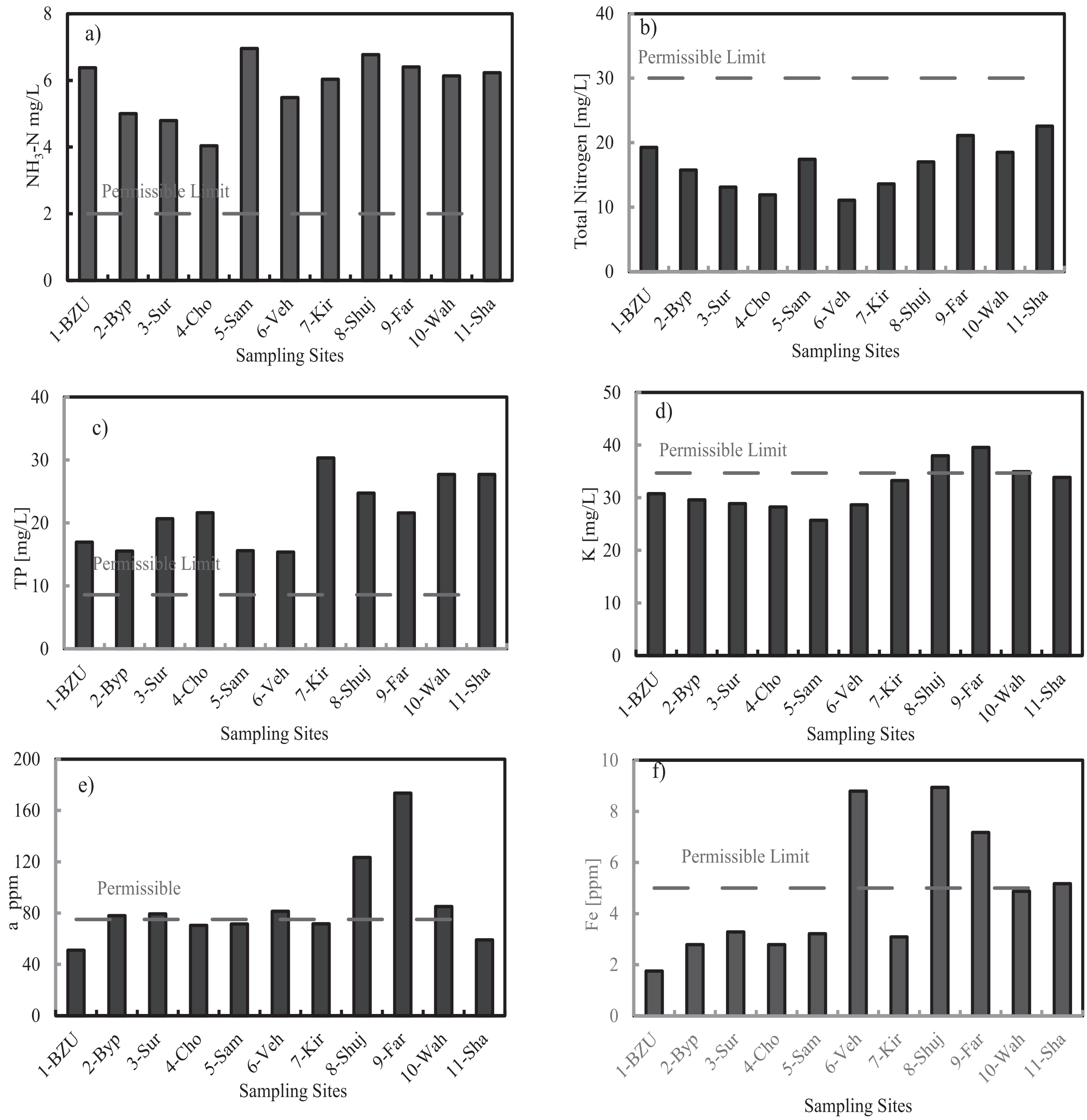

Fig. 4. Nutrients and metals assessment.

Table 4. Alkalinity, total phosphorus, and potassium content in wastewater.

Parameters	Alkalinity (mg/L)				TP (mg/L)				K (mg/L)			
Disposal Stations	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV	Ave	Min	Max	STDEV
1-BZU	123.9	18.6	34.6	19.4	17.00	15.30	30.73	4.60	30.00	18.60	34.60	6.35
2-Byp	153.7	19.0	34.7	17.8	16.00	15.31	15.73	0.19	29.00	19.00	35.00	6.20
3-Sur	134.0	21.0	36.3	7.2	21.00	15.38	21.54	2.30	29.00	21.00	36.30	5.80
4-Cho	140.7	19.0	33.5	4.9	22.00	21.54	21.75	0.12	28.00	19.00	33.50	8.00
5-Sam	146.2	16.0	34.5	9.5	15.00	14.34	19.56	1.50	26.00	16.00	34.70	6.70
6-Veh	157.5	18.8	37.2	8.4	16.00	15.35	15.38	1.50	28.00	18.80	37.20	6.90
7-Kirri	153.7	21.0	35.0	13.1	15.00	26.50	31.20	0.02	33.00	21.00	35.10	5.60
8-Shuj	160.8	35.4	40.0	8.4	30.00	24.60	25.00	1.50	38.00	35.40	40.00	2.03
9-Far	401.0	38.0	41.4	7.2	25.00	21.54	21.58	0.16	39.00	38.00	41.40	1.10
10-Wah	179.0	29.0	38.7	3.9	22.00	27.66	27.69	0.019	40.00	29.00	38.70	3.60
11-Sha	166.0	31.4	35.6	4.1	28.00	27.68	27.70	0.013	34.00	31.40	35.60	2.02
Average	174.2	24.3	36.5	9.4	20.63	20.47	23.44	1.08	32.18	24.29	36.55	4.94

such as average, min, max, and standard deviation is shown in Table 4.

Assessing Nutrients

In addition to other pollutants, WW also contains a high concentration of nutrients due to natural and other anthropogenic sources consisting of atmosphere, intense farming, agricultural runoff, marshlands, and fertilizers [58, 59]. Sources of nitrogen were investigated and ranked as atmospheric deposition (direct) (37%), ~WW (36%), >atmospheric deposition (indirect) (16%) >fertilizer (12%) [60, 61]. Urine fraction of WW contains about 80% nitrogen, and black water (urine, flush water, toilet paper, and faeces) contributes about 90% of nitrogen [59]. Organic waste, urea, animal and human excreta, and other predacious substances in WW contribute NO_2 nitrites, ammonia (NH_3), and NO_3 nitrate concentrations [30, 59]. In regional WW, the average values of NH_3-N, NO_3-N, and total nitrogen are in the range of 4-7 mg/L, 3-5 mg/L, and 12-22 mg/L with standard deviations of 1.6, 1.2, and 4.5, respectively. This indicates the availability of sufficient nitrifiers to exert nitrogenous BOD and the need for denitrification [1, 17, 62] (Figs 4a and 4b). The NH_3-N, NO_3-N, and TN observed at different stations are shown in Table 3. In WW treatment, the processes including ammonification, nitrification, denitrification, and ammonia volatilization are recommended for removing particulate forms of nitrogen. Treatment technologies that are mainly evaluated in terms of nutrient removal for irrigation purposes include media filtration, constructed wetlands, or stabilization ponds [16, 63].

Phosphorus is the macro-nutrient present in WW in small amounts. Its tendency to impact the environment is low even for high applications due to its scarcity in soil [64-66]. Juan and Jiménez [67] found that WW irrigation resulted in the accumulation of phosphorous in the soil due to its stability and low solubility. It also plays an important role in all life processes such as photosynthesis, metabolism, energy transfer, and building of cell walls. The TP variation such as average, min, max, and standard deviation are shown in Table 4. The highest concentration of TP was received from 7-Kirri 31.20 mg/L, while the minimum concentration of 15.30 mg/L and 16.93 mg/L was found at 5-Sam and 1-BZU, respectively (Fig. 4c). The higher concentration of TP than the permissible limit indicated that the WW requires phosphorus removal to avoid eutrophication of the receiving environment. The treatment technologies that have been mainly evaluated in terms of Phosphorus removal for irrigation purposes includes media filtration, constructed wetlands, or stabilization ponds [16, 63]. We also found that potassium content was observed beyond the permissible limit at stations 8-Shuj and 9-Far (Table 4). The lowest concentration of potassium was found in samples collected from disposal station 2-Byp ranging from 19 to 34.7 mg/L, while the highest concentration was foimd for the disposal station of 9-Far 38 to 41.42 mg/L with standard deviation of 6.7 (Fig. 4d). Overall, results indicated that there is no need to treat the WW at all the selected disposal stations (1-BZU to 11-Sha). However, little treatment may be required at disposal stations of 8-Shuj and 9-Far. Potassium is present in the soil in high concentrations (around 3% of the lithosphere), but its bioavailability is impeded due to its chemical form, so it is essential to add potassium to soils via fertilizers [67]. In order to cultivate some crops, 185 kg of potassium is required per hectare [51].

Characterizing Heavy Metals

WW analysis for metals detection is essential before its use for agriculture because of their toxicity, bioaccumulation, persistence, and bio magnifications through food chains causing a potential threat to ecological systems and human health [68-71]. The highest value of magnesium was received for samples collected from 8-Shuj and 9-Far up to 40.0 and 38.75 mg/L, respectively, while the lowest concentration was detected for a sample collected from disposal stations of 2-Byp 24.5 to 25.0 mg/L. Being a micronutrient, it also plays an important role in agricultural productivity. The highest concentration of 173.75 mg/L was detected for the samples collected from disposal station 9-Far and the lowest concentration was detected for the samples collected from disposal station 1-BZU (51.01 mg/L) (Fig. 4e). This parameter has a unique importance of reclamation of sodic soil. Its concentration for most sites was found within safe limits, indicating a strong potential for agriculture. Iron is an important micronutrient for plants – particularly leafy crops that can absorb iron in high amounts and present mostly in association with carbonate fraction [1]. It is among the low risk metals (Mn, Zn, Fe, Se, Cu, and Sb) [72, 73]. In the present study, the highest-value iron was detected for the samples collected from disposal stations 8-Shuj and 6-Veh at up to 9.0 and 8.8 mg/L, respectively, while the lowest concentration was detected at 1-BZU and ranged from 0.49 to 3.23 mg/L (average 1.75 mg/L) (Fig. 4f). Its value is also found to not be challenging for agricultural productivity at most disposal stations. The iron was found at some stations more than standard value due to industrial activities of atmospheric deposition and livestock manure.

Copper plays a significant role in synthesis of hemoglobin, enzymes essential part, and micronutrient for soil and irrigation water [74, 75]. However, high levels of copper can cause mouth, eye, and nose irritation, diarrhea, vomiting, nausea, stomach cramps, and even death [33]. At pH 5.5 copper uptake by plants has been found to be maximum [17]. Copper was detected only for the sample collected from disposal station 11-Sha, ranging from 0.55 to 0.58 mg/L (on average 0.56 mg/L) due to industrial activities, corrosion of plumbing fittings, livestock manure, and atmospheric deposition. A high amount of zinc causes anemia, muscle pain, acute renal failure, and pancreatitis [67]. It possesses low-risk characteristics in irrigation water [70]. The concentration of zinc was detected in samples collected from the disposal stations of 6-Veh, 8-Sha, 9-Far, and 10-Wah up to 0.45, 0.58, 0.28, and 0.55 mg/L. Its value was found below the standard value (5 ppm) [47]. Chromium and lead are among the high-risk characteristic heavy metals in irrigation water [72]. After arsenic, lead is the second most poisonous heavy metal [67]. Chromium and lead were not detected in any of the samples collected from the selected disposal stations because the WW lacked effluents from tanning, metallurgy, ink manufacture, wood preserving, phosphate fertilizers, metal plating, dyes, and ceramic industries. Heavy metal contamination was not found to be severe at most sites in Multan, which indicates a strong potential for WW reuse in agriculture.

WW Parameter Correlations

The Pearson correlation coefficients were determined using Satatixs vs. 10 along with their significance of nine selected parameters [50, 51, 77]. Table 5(a-c) shows the correlation coefficients between the parameters for all the selected disposal stations. Although it was observed that most of the correlation coefficients were insignificant, some important connections were found between various parameters at the sites having similar characteristics of WW. A highly significant ($\alpha = 0.05$) positive relationship seems to exist on BOD and COD at all the stations because BOD represents the quantification of biodegradable carbon while COD indicates an oxidizable amount of carbon (except 4-Cho and 5-Sam stations). These results indicate that disposal stations 1-BZU, 4-Cho, 5-Sam, 6-Veh, 7-Shu, 8-Kirr, 9-Far, 10-Wah, and 11-Sha received organic and inorganic WW from industrial and domestic sources. On the other hand, 4-Sur and 5-Sam received domestic WW and agricultural runoff (Table 5a). Similarly, the positive correlation between BOD and COD for raw WW was reported by Khaled et al. [50]. The significant positive relationships were observed between TSS and Turbidity at 1-BZU and 11-Sha disposal stations (Table 5b-c). Similarly, a significant positive relationship was also found between the TSS and TDS at the same disposal station. The results indicated that suspended particles of WW at 1-BZU disposal station were the main threat for the receiving water bodies. Singh et al. [76] also found the same relationship between TDS and TSS. Similar behavior was found at 2-Byp station for TSS and Turbidity. The significant relationship between the TSS and turbidity indicated that these two parameters may represent each other in determination WW quality. Nkansah [77] found the significant positive relationship between TDS and turbidity and reported that the same parameters represent each other in determining WW quality; however, TDS is not a direct measurement of turbidity. pH also has a significant connection at 2-Byp disposal station (Table 5a). No significant connection was observed at 3-Sur disposal station except among the COD and BOD. A significant relationship between TSS and pH was found at 4-Cho. BOD and DO also have a significant relationship (Table 5a).

The highly positive significant correlations of TSS with BOD and COD were observed, and a negative significant relationship was found among TSS and DO at disposal station 6-Veh (Table 5a). The positive relationships of TSS with BOD and COD at 6-Veh disposal station indicate that the WW was received from food processing and textile industries having both types

Table 5a. Correlation among WW parameters for 5-SAM to 8-Kirr disposal stations.

Station	Parameter	pH mg/L	TDS mg/L	TSS mg/L	Turb FAU	TN mg/L	DO mg/L	BOD mg/L	COD mg/L	TP mg/L
5-Sam	pH	1								
	TDS	0.107	1							
	TSS	-0.044	0.468	1						
	Turb	-0.093	0.311	0.857**	1					
	TN	-0.006	-0.19	-0.582	-0.462	1				
	DO	0.694*	0.191	-0.073	-0.300	-0.337	1			
	BOD	0.071	0.507	0.327	0.205	-0.048	0.328	1		
	COD	0.250	0.374	-0.137	-0.223	0.699*	-0.044	0.103	1	
	TP	0.116	-0.225	-0.384	-0.415	0.354	-0.120	-0.777*	0.482	1
6-Veh	pH	1								
	TDS	-0.273	1							
	TSS	-0.303	0.364	1						
	Turb	0.108	0.590	0.711	1					
	TN	-0.800*	0.268	0.292	-0.285	1				
	DO	0.281	-0.360	-0.898**	-0.794*	-0.035	1			
	BOD	-0.432	0.044	0.874*	0.283	0.548	-0.679	1		
	COD	-0.417	0.185	0.918**	0.383	0.540	-0.732	0.988**	1	
	TP	0.262	-0.757	-0.080	-0.545	0.052	0.221	0.314	0.221	1
7-Shu	pH	1								
	TDS	0.422	1							
	TSS	0.671	0.622	1						
	Turb	0.446	0.359	0.847*	1					
	TN	-0.524	-0.195	-0.700	-0.397	1				
	DO	-0.320	-0.900	-0.750	-0.674	0.171	1			
	BOD	0.498	0.616	0.471	0.575	0.253	-0.712	1		
	COD	0.597	0.702	0.447	0.435	0.203	-0.688	0.974**	1	
	TP	-0.570	-0.419	-0.900	-0.664	0.934**	-0.486	-0.055	0.418	1
8-Kirr	pH	1								
	TDS	0.334	1							
	TSS	-0.174	0.565	1						
	Turb	0.001	0.175	0.708*	1					
	TN	-0.074	0.173	0.280	0.372	1				
	DO	-0.320	0.900	-0.750	-0.674	0.171	1			
	BOD	-0.087	0.368	0.710*	0.635	-0.161	0.043	1		
	COD	-0.280	0.133	0.465	0.486	-0.308	-0.047	0.901**	1	
	TP	-0.493	-0.714*	-0.551	-0.329	0.364	-0.296	-0.620	-0.387	1

**highly significant correlation; *significant correlation at α =0.05

Table 5b. Correlation among WW parameters for 1-BZU to 4-Cho disposal stations.

Station	Parameter	pH	TDS mg/L	TSS mg/L	Turb† FAU	TN mg/L	DO mg/L	BOD mg/L	COD mg/L	TP mg/L
1-BZU	pH	1								
	TDS	0.158	1							
	TSS	-0.051	0.589*	1						
	Turb	0.160	0.556	0.876**	1					
	TN	0.211	-0.359	-0.517	-0.467	1				
	DO	0.320	0.452	0.536	0.522	-0.057	1			
	BOD	-0.258	-0.182	0.279	0.257	-0.128	0.159	1		
	COD	-0.410	-0.357	0.089	-0.038	0.138	0.164	0.902**	1	
	TP	0.221	-0.111	-0.005	-0.241	-0.092	-0.105	-0.451	-0.375	1
2-Byp	pH	1								
	TDS	-0.059	1							
	TSS	0.648*	0.227	1						
	Turb	0.574	0.229	0.990**	1					
	TN	-0.305	0.681	0.256	0.356	1				
	DO	0.128	0.821*	0.190	0.154	0.382	1			
	BOD	0.516	-0.369	-0.175	-0.285	-0.824*	0.102	1		
	COD	0.156	-0.311	-0.222	-0.308	-0.713	0.053	0.760*	1	
	TP	-0.255	0.301	0.018	-0.029	-0.102	0.071	-0.147	0.317	1
3-Sur	pH	1								
	TDS	-0.596	1							
	TSS	-0.583	0.458	1						
	Turb	0.407	-0.574	-0.042	1					
	TN	0.098	-0.020	-0.563	0.211	1				
	DO	-0.376	0.212	0.687	0.282	-0.597	1			
	BOD	0.377	0.036	-0.141	0.456	0.680	-0.360	1		
	COD	0.348	0.241	-0.199	0.081	0.638	-0.553	0.917**	1	
	TP	-0.379	0.284	0.322	-0.373	-0.465	0.383	-0.586	-0.533	1
4-Cho	pH	1								
	TDS	0.593	1							
	TSS	-0.987*	-0.717	1						
	Turb	-0.013	-0.813	0.176	1					
	TN	0.958	0.336	-0.898	0.276	1				
	DO	-0.929	-0.850	0.977	0.383	-0.782	1			
	BOD	-0.945	-0.824	0.986	0.339	-0.811	0.999*	1		
	COD	-0.817	-0.020	0.712	-0.566	-0.948	0.545	0.583	1	
	TP	0.756	0.975	-0.853	-0.664	0.536	-0.945	-0.929	-0.240	1

**highly significant correlation; *significant correlation at α =0.05; †turbidity

Table 5c: Correlation among WW parameters for 9-Far to 11-Sha disposal stations.

Station	Parameter	pH	TDS mg/L	TSS mg/L	Turb FAU	TN mg/L	DO mg/L	BOD mg/L	COD mg/L	TP mg/L
9-Far	pH	1								
	TDS	0.163	1							
	TSS	-0.597	0.839*	1						
	Turb	-0.633	-0.751	0.750*	1					
	TN	-0.320	0.331	-0.307	-0.358	1				
	DO	0.0174	-0.0721	-0.127	-0.216	0.088	1			
	BOD	-0.201	0.735	-0.481	-0.409	0.671	-0.486	1		
	COD	-0.325	0.709	-0.419	-0.350	0.724	-0.406	0.990**	1	
	TP	0.827	-0.049	0.432	0.4741	0.043	-0.096	0.038	-0.428	1
10-Wah	pH	1								
	TDS	-0.331	1							
	TSS	0.165	0.598	1						
	Turb	0.121	0.164	0.729	1					
	TN	0.306	0.307	0.941	0.739	1				
	DO	-0.805	0.571	-0.241	-0.493	-0.485	1			
	BOD	0.299	0.001	0.789	0.820	0.933**	-0.462	1		
	COD	0.343	-0.019	0.782	0.807	0.933**	-0.684	0.999**	1	
	TP	-0.079	-0.036	-0.616	-0.987**	-0.654	0.514	-0.789	-0.775	1
11-Sha	pH	1								
	TDS	-0.042	1							
	TSS	-0.547	0.334	1						
	Turb	-0.555	0.489	0.952**	1					
	TN	-0.067	0.004	0.589	0.527	1				
	DO	0.037	-0.985**	-0.446	-0.591	-0.091	1			
	BOD	-0.302	0.387	0.652	0.649	0.831*	-0.412	1		
	COD	-0.202	0.318	0.597	0.553	0.844*	-0.338	0.981**	1	
	TP	0.795*	-0.148	-0.417	-0.369	0.224	-0.172	-0.144	-0.408	1

**highly significant correlation; *significant correlation at $\alpha = 0.05$

of organic and inorganic constituents. Similarly, Haydar and Bari [78] characterized the textile WW generated from the textile mills in Lahore, Punjab Pakistan and found a significant positive correlation between TSS with COD and BOD. The strong connection of the TP and TN was detected at 7-Shu. The 7-Shu disposal station was present near most of the land used for agriculture (Table 5a). The excessive use of nitrogenous and phosphorus fertilizers washed out by the surface runoff that may dispose in the WW stream of the 7-Shu disposal station. Similarly, Hou et al. [79] investigated that these activities lead to enhanced TP and TN contents of WW. A negative correlation was observed between TP and TDS at 8-Kirr disposal station (Table 5a). The TP and TDS relationship may be due to the use of lime and iron chloride chemicals by the industries located in nearby areas. It has been reported that lime and iron chloride were used for phosphorus removal, which leads to increased TDS of WW. Patoczka and MacDonald [80] found that that addition of chemicals (Alum, Caustic, Lime, Cl_2, SO_2) will almost always increase TDS.

Conclusions

A total of 154 WW samples were collected from 11 disposal stations in Multan District following standard procedures. The collected samples were analyzed in the laboratory for determining pH, COD, BOD, EC, alkalinity, solids (TDS and TSS), TN, NH_3-N, and NO_3-N, chromium, iron, copper, lead and zinc, total phosphorus, calcium, magnesium, total coliforms and E-Coli, and potassium. It was observed that the WW parameters such as BOD, COD, and TSS exceeded the permissible limits of all the disposal stations, which demand urgent need to treat WW before its re-use for agriculture. The heavy metal contamination (Fe, Cr, Pb, Zn, and Cu) was not found to be severe because their values were within permissible limits. Similarly, Chromium and lead were found to be totally absent from WW. Contamination by total coliform and E- Coli was found in WW in almost all the collected samples.

These results provide strong evidence for WW disinfection for its use in agriculture. The WW was found to be acidic in nature with pH ranging from 5.1 to 5.9. Variation in correlation coefficients (R^2) among WW constituents desribe the impact of point and non-point sources of pollution on WW composition. We conclude that the regular monitoring and proper treatment of WW is necessary for its re-use on farms. It is necessary to force all the industries in the study area for implementing environmental laws. Similarly, a detailed study should be conducted to investigate contamination in vegetables, fish, and soil that were irrigated by WW. Research on different treatment technologies should be conducted according to the constituents present in WW, and suitable treatment technologies should be adopted for successful agricultural re-use of WW.

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Conflict of Interest

The authors declare no conflict of interest.

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