

Palwasha Akram^{1*}, Ghulam Shabir Solangi², Farrukh Rahim Shehzad³, Aftab Ahmed Kandhro¹, Sadaf sadia Arain⁴, Muhammad Afzal Kamboh⁴

¹Dr. M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan

²U.S. –Pakistan center for Advanced Studies in Water (USPCAS-W), Mehran University of Engineering & Technology, Jamshoro, Pakistan

³School of Environmental Studies, China University of Geosciences, Wuhan 430074, Hubei, PR China

⁴Department of Chemistry, Shaheed Benazir Bhutto University, Shaheed Benazirabad, Sindh, Pakistan

*Corresponding Authors: Palwasha Akram, Dr. M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan

Abstract: The impact of water quality degradation on human welfare and the environment is currently a major global challenge. Change in physical and chemical attributes of water occurred due to the contamination of several inorganic and organic chemicals. Present studies aim to investigate the ground-water quality status of nine urban & industrial cities of Sindh province, Pakistan through the determination of physicochemical parameters along with the water quality index (WQI) method. Water samples were analyzed for pH, Chlorides (Cl^-), Electrical Conductivity (EC), Total dissolved solids (TDS), Dissolved oxygen (DO), Chemical oxygen demand (COD), Alkalinity, Salinity & Total hardness (TH) to check their suitability for domestic and commercial usage. The determined results for physicochemical parameters are compared with the standard values recommended by WHO. The WQI model revealed that, three cities with WQI value 28.9, 49.8 & 50 fall in the category of excellent water quality. Three sampling sites possess normal WQI value i.e. 55.8, 60.9 & 72.7 and their water quality status is good. Water samples from remaining three cities are found contaminated as their WQI value is very high i.e. 100.6, 106.6 & 164.2 so the water is found unfit for drinking and commercial usage.

Keywords: Groundwater, physicochemical, contamination, WQI, water quality

1. INTRODUCTION

Water quality is considered as an important factor to detect the environmental changes which are associated with social and economic development [1]. The recent global crisis of surface water, population growth and rapid industrialization has ultimately resulted in relying on groundwater consumption. Hence groundwater becomes an indispensable source for the drinking, household doings, livestock needs, irrigation, industrial and many more commercial activities [2, 3]. The quality of groundwater depends upon its physical characteristics, the concentration of chemical constituents and the geology of the area. Different natural and anthropogenic activities tend to change the physicochemical characteristics of ground-water and deteriorate its quality [4, 5].

Groundwater contamination has caused adverse health issues especially in developing countries where the groundwater is a conventional source for domestic use due to ease of availability. The modern urbanization, industrialization and agricultural practices are primary factors in the degradation of water quality [6, 7]. Inappropriate disposal of agro-industrial, municipal and animal farming waste into the soil results in transportation of hazardous constituents into the aquifer system via leaching process [8-10]. Contaminated water possesses a high concentration of toxic elements and chemical substances which can induce serious health effects and chemical intoxication. Furthermore it also has negative impacts on the economy as it is unable to use directly for commercial activities due to change in its color and odor [11]. The treatment process of contaminated water is difficult and costly therefore it is better to do regular monitoring and protect the water sources before getting polluted [12].

Pakistan is one of those developing countries which are facing alarming health problems [13, 14]. nearly half of its all identified illness cases are due to consumption of unhealthy groundwater. It contains a number of harmful viral, bacterial, and protozoan agents. According to the studies, about 40% of deaths occur in Pakistan due to water-borne diseases such as gastroenteritis, diarrhea, typhoid and hepatitis [15-17]. Generally the water quality is crossing the limit above WHO standards in nearly all provinces and the situation is getting worst especially in Sindh province [18]. Sindh is recognized as a populated province and the economical backbone of Pakistan. It controls most of country's industrial and manufacturing activities, ultimately contributes a huge amount of hazardous waste into the environment. Several analysis studies have indicated continues degradation of water quality and presence of bacteria, arsenic, nitrate and fluorides in various cities of Sindh province [19, 20]. Karachi, Hyderabad, Sanghar, Umerkot, Naushehro Feroz, Tando Muhammad Khan, Mirpurkhas, Tando Allahyar, and Jamshoro are some of the major urban cities which are either partially or fully dependent on groundwater. The problem of water quality degradation is much more acute in these cities because of being surrounded by many textiles, pharmaceutical, sugar and manufacturing industries. The direct release of industrial waste into water bodies and unorganized dumping of municipal waste to vacant areas has caused the pollution of groundwater exceeding WHO standards. Therefore it is an urge to determine the physico-chemical parameters of groundwater and to calculate the WOI [21] for these cities to assess their water quality level.

Our present study includes qualitative analysis along with the determination of physicochemical contents of groundwater used by inhabitants of above mentioned cities via the standard analysis methods. The results obtained are then compared with quality standards of WHO (Table 1). Hence WQI is also calculated based on data from groundwater sampling. This research is a profound source for understanding the current climate conditions and water quality in different nine cities of Sindh province. Moreover, based on presented report a standard legal framework may be designed to prevent the water pollution for the greater cause of public health safety and economic growth.

| Sr. No | Parameters | Units | WHO Standard |
|--------|-------------------------|-------|--------------|
| 1 | pH | - | 6.5–8.5 |
| 2 | Chlorides | mg/l | 250 |
| 3 | Electrical conductivity | μS/cm | 1000 |
| 4 | Total dissolved solids | mg/l | 500 |
| 5 | Dissolved oxygen | mg/l | 4-6 |
| 6 | Chemical oxygen demand | mg/l | <45 |
| 7 | Alkalinity | mg/l | 200–600 |
| 8 | Salinity | g/l | _ |
| 9 | Acidity | g/l | _ |
| 10 | Total Hardness | mg/l | mg/l |

 Table1.Standard values/Guidelines of WHO

2. MATERIALS AND METHODS

Sample collection:

The research group physically visited and collected water samples from selected groundwater sources of Karachi, Hyderabad, Sanghar, Umerkot, Naushehro Feroz, Mirpurkhas, Tando Allahyar, Tando Muhammad Khan and Jamshoro cities. The geographical locations of the cities are shown in Fig 1. We used very clean, pre-washed and dried plastic jars for sampling to decrease the possibility of contamination in water from the jar. The collection of samples was done after running the water pumps for 10 minutes and then sealed tight in jars. Further, samples were transported to the laboratory in a dark colored ice box to avoid the unusual change in quality. The samples were stored in the refrigerator before analysis.

Sample Analysis:

We selected ten physicochemical parameters to analyze the quality level of groundwater. Physical features like Odor and color were noted at the time of sampling where the further chemical analysis was conducted at the inorganic research laboratory. The determination of pH was done by pH meter, Electrical conductivity by conductivity meter and Total dissolved solids (TDS) by using TDS meter. The Hardness was calculated by EDTA method using Eriochrome black T (EBT) as an indicator.

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Chloride estimation was carried out by Argent metric titration method using Standard silver nitrate $AgNO_3$ as a chemical and Potassium chromate (K_2CrO_4) as indicator respectively. Alkalinity, Chemical oxygen demand (COD) and Acidity levels of water were determined by titration methods. The electrode method was applied to calculate the Salinity level whereas Dissolved oxygen (DO) value was calculated by the iodometric method.

Figures

Kashmore Shikarpur Shahdacket Dadu Nawabshah Matari Iando Allahyar KARACHI KARACHI KARACHI Matari Badin Mithin

Fig1.*The map of study area showing Sindh province, Pakistan. The red circles indicate selected cities for analysis of ground water quality.*

WQI Estimation:

In this work, weighted arithmetic index method following three steps is applied to determine the WQI of groundwater from selected locations [22]. Eight physico-chemical parameters *i.e.* pH, EC, TDS, Alkalinity, TH, Cl^- , DO and COD were used to calculate WQI. The formula to calculate the WQI is given as

$$WQI = \sum_{i=1}^{n} SI_i \tag{1}$$

Where SI_i represents the sub-indices

$$SI_i = W_i \times Q_i \tag{2}$$

Firstly each parameter is assigned a weightage (wi) in numbers from 1-5 according to its importance and impact on human health. Then relative weight (Wi) of each parameter is calculated by dividing its weightage with a total weightage of all parameters (Table 2). The formula for calculation of relative weight is as under

Table2. Physico-chemical parameters, their assigned weight and relative weights

| Parameters | Assigned Weight (wi) | Relative weight (Wi) |
|-------------------------|----------------------|----------------------|
| pH | 3 | 0.103 |
| Electrical conductivity | 5 | 0.172 |
| Total dissolved solids | 5 | 0.172 |
| Chlorides | 3 | 0.103 |
| Alkalinity | 1 | 0.034 |
| Salinity | 3 | 0.103 |
| Acidity | 3 | 0.103 |
| Total hardness | 2 | 0.068 |
| Dissolved oxygen | 2 | 0.068 |
| Chemical oxygen demand | 2 | 0.068 |
| Total | Σ wi= 29 | Σ Wi= 0.994 |

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$$W_i = \frac{w_i}{\sum_{i=1}^n w_i}$$
 (3)After that, Q_i value of each parameter is calculated by dividing the observed resulted value with the standard value of WHO [23] and their

calculated by dividing the observed resulted value with the standard value of WHO [23] and their result then multiplied by 100.

$$Q_I = \frac{V_O}{V_S} \times 100 \tag{4}$$

Finally, WQI of each sample is found by putting all resulted values from equation (3) and equation (4) into the equation (2) and then taking the sum of the individual SI_i values. Based on resulted WQI values the water is divided into five categories (Table 3) such as excellent, good, poor very poor and not fit for drinking [24-27].

| Sr. No | WQI Range | Classification |
|--------|-----------|----------------------|
| 1 | 0-50 | Excellent water |
| 2 | 50-100 | Good water |
| 3 | 100-200 | Poor water |
| 4 | 200-300 | Very poor water |
| 5 | >300 | Not fit for drinking |

Table3. Quality criteria of ground water with respect to its WQI value

3. RESULTS AND DISCUSSION

The groundwater samples from the selected cities were analyzed for physical and chemical parameters such as pH, Cl⁻, EC, TDS, DO, COD, Alkalinity, Salinity, Acidity & TH. The results show the quality level and contamination of groundwater due to the leaching process (Fig 2).



Fig2. Pictorial demonstration of the water contamination causes. Various types of wastes containing hazardous constituents are dumped into surface water and open area which reaches aquifer through leaching process.

pH:

pH is the quantitative measurement of acidity or basicity of liquids. It plays an important role in maintaining the physicochemical balance of water. If pH value exceeds the standard range (6.5-8.5) prescribed by WHO, it can affect the palatability of water. The high pH level can stimulate demineralization which leads to muscle atrophy and some types of kidney stones. The results of pH analysis for present study are given in Fig 3. According to results, the water sample of Tando Allahyar city possesses high pH value *i.e.* 7.7 where the Hyderabad sample has low pH *i.e.* 7.1. The pH level of all examined samples is normal and has no threat to health.

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Fig3. The Water sample analysis for pH and Chlorides

Chlorides:

Chlorides are inorganic ions and the presence of the excessive amount of chlorides indicates the contamination of water due to municipal and industrial waste. The extreme amount of chlorides in water beyond a certain value (*i.e.* 250 mg/l) advised by WHO could lead to various side effects on human health. The high concentration of chlorides in water used for irrigation purpose can pose toxic effects on plants. It can affect plant function, reduce the production and growth. As given in Fig 3, the water of samples of Tando Muhammad Khan and Tando Allahyar city exhibits maximum concentration of chlorides *i.e.* 1659 mg/l & 475 mg/l respectively. The minimum concentration of chlorides *i.e.* 35.4 mg/l is observed in the Jamshoro sample.

Electrical Conductivity (EC):

Electrical conductivity is a parameter to check the purity of water and quantity of minerals present in the water. It serves as an indicator showing the presence of various pollutants in the water. The conductivity of water is higher if it contains a high amount of dissolved salts. According to the results (Table 4), all the examined water samples possesses conductivity values ranges from 303 to 1794 μ S/cm while the WHO recommended standard limit is 1000 μ S/cm. The highest conductivity value (*i.e.* 1794 μ S/cm) is shown by Tando Allahyar sample which could be attributed to the presence of a large number of ions or minerals in it. On the other hand, water sample of Jamshoro city has shown the lowest conductivity value *i.e.* 303 μ S/cm which could be due to the low quantity of ions or minerals.

| Sr. | Sample locations | EC | TDS | DO | COD |
|-----|------------------------|------------|----------|----------|---------|
| No | - | | | | |
| 1 | Jamshoro | 303 | 143 | 3.68 | 16 |
| 2 | Hyderabad | 319 | 400 | 5.5 | 64 |
| 3 | Sanghar | 364 | 179 | 6.4 | 128 |
| 4 | Karachi | 592 | 298 | 3.1 | 112 |
| 5 | Mirpurkhas | 526 | 250 | 3.4 | 160 |
| 6 | Naushehro feroz | 774 | 370 | 2.64 | 192 |
| 7 | Umerkot | 1641 | 792 | 2.56 | 144 |
| 8 | Tando Allahyar | 1794 | 859 | 9.6 | 16 |
| 9 | Tando Muhammad Khan | 1405 | 685 | 1.79 | 240 |
| | WHO permissible limits | 1000 µS/cm | 500 mg/l | 4-6 mg/l | <45mg/l |

Table4. The calculated results of EC, TDS, DO and COD for various sample locations

Total Dissolved Solids (TDS):

Amount of Total dissolved solids (TDS) and Electrical conductivity are proportional to each other. The exceeding TDS value from standard value also indicates addition of pollutants to the water. The results for TDS analysis presented in Table 4 shows that all the cities are found to contain normal TDS value in water as approved by WHO except Tando Allahyar, Umerkot and Tando Muhammad khan which is may be due to higher level of salinity. The maximum TDS value (*i.e.* 859 mg/l) is

observed in Tando Allahyar city sample. The samples of Sanghar and Jamshoro cities hold low TDS values (*i.e.* 179, 143 mg/l) due to continues recharging of groundwater through rain and surrounding canals.

Dissolved Oxygen (DO):

The existence of dissolved oxygen in water is necessary to keep water sources healthy and maintain the appropriate level of numerous pollutions. It is one of the significant parameters which indicate the extent of municipal and industrial effluence to water. As per guidelines of WHO, the oxygen level in water about 4-6 mg/l represents healthy state of aquifer while the DO level below 3 mg/l is considered as hazardous. Extremely low concentration of DO causes growth of anaerobic microorganism in the water. The sampling locations of Tando Muhammad Khan, Naushehro Feroz and Umerkot cities exhibit low DO values which indicate heavy contamination. The minimum DO value (*i.e.* 1.79 mg/l) is found in Tando Muhammad Khan city sample while the maximum value (*i.e.* 9.6 mg/l) is recorded in Tando Allahyar sample.

Chemical Oxygen Demand (COD):

High COD level in water leads to the depletion of oxygen reaches a harmful level (<45mg/l) through microbes decomposition. Our calculated results for Chemical oxygen demand (COD) in water samples are given in Table 4. According to results the highest amount of COD was observed in Tando Muhammad khan sample *i.e.* 240 mg/l and the lowest value (*i.e.*16 mg/l) were detected in samples of Jamshoro and Tando Allahyar cities.

Alkalinity:

Alkalinity is a tendency of water to neutralize the acids; it is mainly caused by carbonates and bicarbonates. Extreme alkalinity level can pose serious effects on industrial activities because consumption of alkaline water could cause precipitation of slush in the boilers and caustic embrittlement. In present study, the alkalinity level was observed under the range from 140 mg/l to 666 mg/l. Among the analyzed samples, the highest value (*i.e.* 666 mg/l) was found in Tando Allahyar sample and the lowest value (*i.e.* 140 mg/l) was observed in Tando Muhammad Khan sample. However for the analyzed samples, there are no major adverse effects of alkalinity on health.

Salinity:

Salinity is referred as concentration of salts in the water. Salts are soluble in water and can be transported to groundwater aquifer systems. Consumption of saline water can originate serious health problems such as hypertension, diarrhea and abdominal pain. It also has adverse effects on agriculture as saline water cause dehydration in plants which leads to yield reduction. Salinity assessment results (Fig 4) has validated that the salinity level in all examined samples is under the permissible limit of WHO. The groundwater of Tando Allahyar city is comparatively more saline (*i.e.* 0.9 g/l) than other cities due to high concentration of dissolved salts. Jamshoro sample is found less saline (0.1 g/l) due to deficiency of dissolved salts in water. Higher Salinity trend is observed in agricultural dry zones due to reasons of repeated salting process. The precipitation of salt from irrigated water or rain water due to the evaporation results in leaching of salt to the underground.



Fig4.Results obtained for Alkalinity, Salinity, Acidity and Total hardness

Acidity:

Acidity is the number of reactive ions present in the water. It is the capacity of water to neutralize the bases. The consumption of acidic water for drinking purpose can lead to vomiting, diarrhea, stomach cramps, nausea and liver diseases .The resulted acidic values obtained for analyzed samples are between the range 600 g/l-1143 g/l. Results given in Fig 4 revealed that only 30% of samples lie within the normal acidic range where the rest of 70% samples are found to be highly acidic. The highest value of acidity (*i.e.* 1143 g/l) was found in Naushehro Feroz sample and the lowest value (*i.e.* 600 g/l) was observed in Jamshoro sample.

Total Hardness:

Generally, the hardness represents the concentration of calcium and magnesium in water. The hardness level of water is mainly caused by bicarbonates, carbonates, polyvalent metallic ions, calcium cations & magnesium cations. Therefore hardness is a very important factor to measure in the aspect of water consumption for different household and industrial activities. The use of hard water for irrigation purpose can increase the pH of the soil and could result in leaving acidic effects in plants. In the present research it is observed that, compare to other cities the groundwater of Umerkot city possesses high hardness level *i.e.* 1.98 mg/l. the lowest value of hardness (*i.e.* 0.02 mg/l) is found in Tando Allahyar sample.

Water Quality Index (WQI):

The WQI was proposed by Horton [28, 29], it is a rating given to the water sample on the basis of calculated physico-chemical parameters. WQI is a simple way of understanding and expressing the quality level of water to the public and concerned authorities [30]. The WQI value of water samples ranges from 0-50 indicates excellent quality of water. Water samples with resulted WQI value ranges in between 50-100 are supposed to be of good quality. If the WQI value exceeds then 100, water is considered as poor in quality and not healthy for drinking. According to WQI calculation results presented in Table 5, the groundwater of Jamshoro, Hyderabad and Sanghar cities fall in the category of excellent water quality. Karachi, Mirpurkhas and Naushehro Feroz city are found to contain water of good category. The groundwater of Umerkot, Tando Allahyar and Tando Muhammad Khan is observed as poor in quality.

| Sr. No | Sample location | WQI value | Water quality status |
|--------|---------------------|-----------|----------------------|
| 1 | Jamshoro | 28.9 | Excellent water |
| 2 | Hyderabad | 49.8 | Excellent water |
| 3 | Sanghar | 50.0 | Excellent water |
| 4 | Karachi | 55.8 | Good water |
| 5 | Mirpurkhas | 60.9 | Good water |
| 6 | Naushehro feroz | 72.7 | Good water |
| 7 | Umerkot | 100.6 | Poor quality water |
| 8 | Tando Allahyar | 106.6 | Poor quality water |
| 9 | Tando Muhammad Khan | 164.2 | Poor quality water |

Table5. Resulted WQI values of each ground water sample and its quality status



Fig5.Results obtained for Acidity and Total hardness

4. CONCLUSION AND RECOMMENDATIONS

Groundwater samples collected from major residential and industrial cities of Sindh province are investigated for different physical and chemical parameters along with WQI calculation. In view of obtained results, it is concluded that the WQI values of Tando Muhammad Khan, Tando Allahyar and Umerkot cities are found to be 164.2, 106.6 & 100.6 respectively. Hence the water in these cities is not healthy for drinking without treatment and the inhabitants are at great risk of catching water-borne diseases. The groundwater of Tando Allahyar city possesses higher Alkalinity *i.e.* 666 mg/l, so it is not suitable for industrial use. Furthermore the Umerkot city sample is found to possess the high value of hardness *i.e.* 1.98 mg/l, so it is not adequate for irrigation purpose. The groundwater samples of Naushehro feroz, Mirpurkhas and Karachi cities with WQI values 72.7, 60.9 & 55.8 respectively are observed average in quality. In comparison with other cities, the groundwater samples of Sanghar, Hyderabad and Jamshoro cities with WQI values 50, 49.8 & 28.9 are found very fit for drinking and commercial use. It is recommended that an environmental protection program should be launched for public awareness. There should also make a comprehensive policy to control the disposal and treatment of industrial & municipal waste. Henceforth water should be treated well before domestic and commercial usage.

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