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Pb, Cr, Ni and Cd contamination in Hand pump and Tap water of Mardan District.

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Abstract

This study was conducted in order to ascertain the present status of heavy metals in Hand pumps and tap water of Mardan District. A total of eight heavy metals (Fe, Zn, Cu, Mn, Pb, Cr, Cd, and Ni) were investigated in hand pump and tap water samples collected in the study area. Atomic Absorption Spectrometry was used to determine the heavy metals. Fe, Zn and Cu levels were within the permissible limits, while Pb, Cr, Cd and Ni levels in the study area exceeded the WHO permissible limits. The high concentration of heavy metals in the drinking water can be attributed to the corrosiveness and aggressiveness of the water in the study area.

Key words: Mardan City, Drinking Water, Contamination, Stability Index, Plumbosolvency.

Introduction

Being excellent solvent water can incorporate a myriad of contaminants. Drinking water is linked with various water borne diseases like cholera, Typhoid, Botulism, Dysentery, Schistosomiasis, dental and skeletal flourosis etc. In the last few decades the levels of trace elements in drinking water have gained much importance in scientific community because of concern for public health, leading to a number of scientific studies being conducted all over the world (1-6). Human activities have resulted in elevated levels of Heavy metals in the environment. Drinking water is one of the most important sources of potential human exposure to heavy metals.

Several metal ions are essential to the health of organisms in low concentration but exceeded levels of these metals are potentially toxic especially to children as they do not have a fully developed detoxification system (7). Others like Pb and Cd have no biological role to play in our bodies but they mimic other essential elements in our body and disrupt biological activities. For example, Cd ions are approximately the same size as Zn ion and can replace Zn in many molecules (8). Heavy metals are also known to bio accumulate in the bones and tissues of living organisms. Elevated levels of these elements in blood and other tissues may cause health problems like cancer and plumbism (9).

Trace metals can be added to drinking water from a wide variety of sources like agricultural activities i.e. use of micronutrient fertilizers and other chemical fertilizers like urea, ammonium sulphate, ammonium phosphate, the dissolution of primary minerals in water, solid waste sites, corrosion of metal pipes (10-13). Iron, Copper, Lead, Zinc, Chromium, Cadmium and Tin can be added to potable water from pipelines through leaching (14). Jaleel et al. (15) reported that in the drinking water sampl6) concluded that contamination of water with cadmium in plumbing is significant, independent of the site type and period. This contamination should be considered as a factor in public health protection programs with special attention to children.

Mardan district lies from 34° 05' to 34° 32' north latitudes and 71^{o} 48' to 72° 25' east longitudes. The total area of the district is 1632 square miles (16). Most of the land is used for agricultural purposes and has one of the best irrigation systems in the world established by the British. Mardan city is the largest city of District Mardan and the second largest in NWFP.

Groundwater obtained as tap water and from Hand pumps is used extensively for drinking and other domestic purposes in Mardan city and adjacent villages. The objectives of this study were to determine the present status of Heavy metals in the Tap and hand pump water of District Mardan and to evaluate its Health risk to the local population. Another objective of the study was to evaluate the degree of corrosiveness of water and its contribution to the heavy metals content in the drinking water.

Results and Discussions

Physico chemical parameters

The results are summarized in Table 1. pH in the study area ranges from 6.88-7.04, EC in the study area shows great spatial variation (range = 289-1468 µS/cm, ave. 805.46) with the lowest value at Sowarian (M-7) and the highest value was recorded at village Toru (M-5). Turbidity values range from 1.1-127.5 NTU with the lowest recorded at village Mayar (M-8) and the highest being recorded at Toru (M-5). Only six samples show values above the permissible limit of 5 NTU (17). At these sampling points locals complained about bad taste and reported that nausea and diarrhea were more common than usual. Turbidity has been linked positively with gastrointestinal diseases in different age groups (18-21).

DO levels were the lowest (2.96 mg/l) at village Toru (M-5) and the highest (3.99 mg/l) at the sampling point near Hoti Bridge in Mardan city (M-9). DO does not show much spatial variation in the study area.

High levels of TDS were found in the study area (range =152 to 783 mg/l, ave. 430.93). In natural waters, TDS consists mainly of inorganic salts such as carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates of calcium, magnesium, sodium, potassium, iron, etc. and small amount of organic matter and dissolved gases. The desirable limit for TDS is 500 mg/l; about 8 samples in the study area exceed this limit.

Total Hardness

Based on the results for Total Hardness test, water in the study area can be classified in to four classes. As it is clear from Table 2. about 53 % of water samples lie in the very hard category and about 16 % in the Moderately hard category and hard water category. Only 10 % samples are classified as soft water. An inverse relationship has been reported between hardness and cardiovascular diseases however the available data is insignificant to indicate a causal relationship. Hence, World Health Organization holds no health based guideline value for hardness (17). Very hard water may cause scale deposition and over consumption of soap, while, soft water is generally believed to increase the corrosion of metal pipes. However, the results of the studies conducted in this regard (corrosion of metal pipes due to soft water) are not in agreement (22-23). In this study no relation could be established between water hardness and the corrosion capacity of water in the study area.

Heavy Metals

A total of eight Heavy metals (Fe, Mn, Cu, Pb, Zn, Cr, Cd and Ni) were determined during the study their values and statistical parameters are given in Table 2. Pb, Cr, Cd, Ni values in the study area exceeded the WHO permissible limits, while Fe, Cu and Zn were found well below the permissible limits recommended by World Health Organization. Fe concentration in groundwater samples varies from 0.105-0.224 mg/l. Fe is found in natural fresh waters at levels ranging from 0.5 to 50 mg/liter. Iron may also be present in drinking-water as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during water distribution. Iron stains laundry and plumbing fixtures at levels above 0.3 mg/l; there is usually no noticeable taste at iron concentrations below 0.3 mg/l, and concentrations of 1–3 mg/liter can be acceptable for people drinking anaerobic well water (17). There is no health based guideline for Fe, both WHO (17) and USEPA (24) have recommended 0.3 mg/l for aesthetic reasons.

Lowest and highest Mn (range=0.015-0.458 mg/l, ave.0.058 mg/l) and Cu (range=0.01-0.049, ave.0.022) concentrations were determined in water samples from Sowarian (M-7) and Toru (M-5) respectively. Cu concentration in all the samples is within the permissible limits while Mn concentration in all but 2 samples Toru (M-5) and Toru (M-6) is within the permissible limits. Zn concentration varied from 0.034 mg/l- 0.32 mg/l and is within the permissible limits.

Pb levels in all drinking water samples were found to be above the permissible limit of 0.01 mg/l (17). The highest concentration of Pb (1.043 mg/l) was recorded in sample from Mardan city (M-15). Usually the source of Pb in drinking water is service connections and plumbing in buildings (17). In urban areas Pb contamination can be caused by tetra alkyl lead in gasoline, lead arsenate as fungicides, plasters, paints, house dusts and waste water (25). Pb can bio-accumulate in bones and tissues. The accumulation of Pb can lead to plumbism (9) and irreversible damage to brain (encephalopathy) (25). Lead absorption also increases in iron deficiency and inhibits enzymatic activities which cause hemoposis. Other toxic effects include anemia, headache, irritability and renal damage (26). Pb is also considered as carcinogenic (27) and is associated with miscarriages, sperm and reproductive abnormalities (9).

Cr concentration in 16 water samples collected from the study area was above the permissible limit of 0.05 mg/l (17). Cr is also considered as carcinogenic (27,28). Excessive in take of Cr may cause irritation of respiratory tract, ulceration, perforation of nasal septum, and skin ulcer (25).

Ni concentration in the study area varies from 0.157-0.283 mg/l. Ni in drinking water may arise from pipes and fittings; water is a minor contributor to the total daily oral intake (17). Ni compounds may be carcinogenic when inhaled (28). Excessive intake of Ni causes allergy, bronchial asthma, dermatitis, eczema, myocardial infarction, larynx, kidney, prostate and stomach cancers (29).

Cd concentration varies from 0.084-0.362 mg/l. Both Ni and Cd concentration in all the samples exceeds the WHO permissible limits of 0.02 mg/l and 0.003 mg/l respectively. Cd is widely used in steel industry, batteries and plastics; waste waters and fertilizers are also major contributors of cadmium in environment. Cd even in low concentration is quite toxic to health (29); it is nephrotoxic, osteotoxic (7) and a known human carcinogen (30) it may cause itai itai disease leading to the weakening of bones (8). Cd is a non essential metal known to accumulate in human kidney, liver, lungs and pancreas. Studies have suggested that Cd may be carcinogenic in human lungs, prostate, kidney and cause human pancreatic cancer (32-34).

Water aggresivity and corrosivity

In this study Ryznar stability index and Langelier Index were used as an indicator of water aggressiveness and corrosiveness. The water samples were classified according to Ryznar (35) and Carrier (36). The Ryznar Stability index in the study area ranged from 11-13 (Table 3) indicating that water is very aggressive with intolerable corrosion capacities. The Langelier Index ranged from -2.98 to – 1.88 (ave: -2.4), indicating that water in the study area has lower tendency to precipitate $CaCO_3$ (Table 5). Corrosion indices provide only an indication about the tendency of Calcium Carbonate to dissolve or precipitate and were traditionally used to understand whether the water is aggressive towards metals or not. Precipitated $CaCO_3$ usually forms a protective layer commonly known as "egg shell" on the inner surfaces of the plumbing systems which helps in the reduction of the dissolution of heavy metals in water. Lower tendency of water to precipitate $CaCO_3$ implies that this protective layer is not formed making the plumbing systems vulnerable to corrosion by water. This assumption is substantiated by field observations, where corrosion could be visibly identified in the plumbing fixtures .As both indices have indicated that the water in the study area is very aggressive towards metals it is probable that the high amounts of the heavy metals concentration in the water samples of the study area can, therefore, be attributed to the high corrosiveness and aggressiveness of the water.

Experimental

Sampling

The drinking water samples were collected in clean 1 liter polyethylene bottles from the major settlements of the study area including Mardan city. The bottles were thouroghly rinsed with the water to be collected. Samples were preserved according to standard methods as recommended by APHA (37). Both tap water and hand pump water samples were obtained directly from the hand pumps and taps early in the morning without flushing them.

Analytical Procedures

Physical parameters like pH, EC and TDS of drinking water samples were determined using Consort electrochemical analyzer (Model C931T). DO and Turbidity of the samples were determined by using Jenco DO meter (Model 9173) and Jenway Turbidimeter (Model 6035) respectively. All these instruments were calibrated prior to examination. Total Hardness and Alkalinity was determined using Hach DR 2000 spectrophotometer. Ca, Mg and a total of eight heavy metals (Fe, Mn, Pb, Cu, Cr, Ni, Cd, and Zn) were determined by using Perkinelmer AAnalyst 700, atomic absorption spectrometer. Ca Hardness was calculated by multiplying the Ca ions concentration by 2.5 and Mg hardness was calculated by subtracting the resultant value from total hardness.

Aggressiveness and Corrosion capacity of Water

In this study both Langelier and Ryznar indices were used in order to determine the aggressiveness and corrosivity of the water in the study area.

The Ryznar Stability Index (34) is calculated by equation No. 1 and Langelier index is expressed by equation No. 2:

$$RSI = 2 \, . \, pHs - pH \qquad (1)$$

$$LSI = pH - pHs \qquad (2)$$

Where pHs is the pH of saturation for $CaCo_3$. It can be calculated by the following equation as given by Edstrom (38):

$pHs = (9.3 + A + B) - (C + D)$

where $A = (\log(TDS) - 1)/10$

$B = (-13.12 \log(C^o + 273)) + 34.55$

$C = (\log(\text{calcium hardness})) - 0.4$

D = log (M Alkalinity)

Conclusions

The drinking water samples of the study area are highly contaminated with Pb, Cr, Ni and Cd. Pb, Ni and Cd in all the samples while Cr in 53.33 % of the samples have concentrations above the permissible limits recommended by World Health Organization. Among all the metals the average Pb concentration is the highest in the study area which is 56 times higher than the WHO permissible limit of 0.01 mg/l. Ryznar Stability index and Langelier Index indicates that the water is very aggressive and corrosive and is contributing to the leaching and dissolution of heavy metals from the plumbing fixtures. High levels of Pb, Cr, Ni and Cd pose a serious threat to the health of local population. Proper treatment and flushing of the taps and hand pumps for 10-15 minutes is recommended before use.

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References

1. M. Soylak, A. Aydin, S. Saracoglu, L . Elci and M. Dogan, Pol. J. Environ. Stud., **11(2)**, 151-156 (2002).
2. J. Nouri, A. H. Mahvi, A. A. Babaei, G. R. Jahed and E. Ahmadpur, Pak. J. of Bio. Sci., **9(3)**, 377-384 (2006).
3. S. Danishwar, M. T. Shah and A. Leghari, Geological Bulletin, University of Peshawar., **28**, 39-47 (1995).
4. A. Ikem, N. O. Egiebor and K. Nyavor, Water. Air. Soil. Pol., **149**, 51-75 (2003).
5. A. Kelepertsis, D. Alexakis and K. Skordas, Environ. Geol., **50**, 76–84 (2006).
6. H. Zhang, D. Ma, Q. Xie and X. Chen, Environ. Geol., **38 (3)**, 223-228 (1999).
7. H. Barton, Food. Addit. Contam., **22**, 816-828 (2005).
8. L. Ritter, K. Solomon, P. Sibley, K. Hall, P. Keen, G. Mattu and B. Linton, J. Toxicol. Env. Health., **65**, 1-142 (2002).
9. K. K Prasad, Analysis of heavy metals in Ground water from coal mining Area in Jamtara District, Jamtara, Jharkand, in A. Kumar and G. Tripathi (Ed.) Water Pollution, Assessment and Management, Daya Publishing House Delhi (2004), p. 283-288.

10. W. M. Edmunds, D. G. Kinniburgh and P. D. Moss, Enviro. Poll., **77**, 129–141 (1992).
11. S. M. Khan, A. Qureshi and J. B. Singh, Indian J. Environ. Health., **38(1)**, 1–6. (1996).
12. R. K. Trivedi and P. K. Goel, Chemical and biological methods for water pollution studies, Environmental Publications, Karad (1986), p 36-38.
13. T. Viraraghavan, K. S. Subramanian and B. V. Rao, Intern. J. Environ. Stud., **56**, 717-743 (1999).
14. U. Förstner, G. T. W. Wittmann, F. Prosi, J.H. Van Lierde, Metal Pollution in the Aquatic Environment, Springer-Verlag (1979), p 337-339.
15. M. A Jaleel, R. Noreen and A. Baseer, J. Ayub Medical College Abbottabad, 13(4), 12-15 (2001).
16. Anonymous. District Census Report, Beruea of Statistics, Government of Pakistan (1998).
17. WHO (World Helth Organization), Guidelines for Drinking water quality, Recommendations. Vol. 1, 3rd ed. (2004).
18. J. Schwartz, R. Levin and R. Goldstein, J. Epidem. Community Health, **54**, 45-51 (2000).
19. J. Schwartz, R. Levin and K. Hodge, Epidemiology, **8(6)**, 615-620 (1997).
20. Egorov., Andrey., Naumova., Elena., Tereschenko., Andrey, Kislitsin, Victor, Ford and Timothy, Intern. J. Environ. Health Research, 1**3 (1)**, 81 – 94 (2003).
21. R. D. Morris, E. N Naumova, R. Levin and R. L. Munasinghe, Amer. J. Public Health, **86(2)**, 237–239 (1996).
22. C. ONG, S. IBRAHIM and B. S. GUPTA, Urban Water J, **4**, 29-41 (2007).
23. C. Y. Yang, Bull. Environ. Contam. Toxicol, **63**, 59-64 (1999).
24. USEPA (United States Environmental Protection Agency), Maximum Contaminant Levels, USEPA website http://www.epa.gov/safewater/contaminants/index.html#inorganic , retrieved on 20th December, 2008.
25. J.S. Khurshid and H.Q. Iqbal, The Nucleus, **21**, 3-23 (1984).
26. M. H. Khan and N. Yasmin, Pakistan J. Biol. Sci., **6 (14)**, 1276-1281 (2003).
27. NAS (National Academy of Sciences), In Chromium, Washington D.C (1974).
28. IARC, Monographs on the Evaluation of Carcinogenic Risks to Humans: Chromium, Nickel and Welding, Vol. 49. Lyon, France (1990).

29. C.R.K. Murti and P. Viswanathan, Toxic Metals in Indian Environment, Wiley Eastern Ltd, New Delhi (1989).
30. N. K Verma, O.P. Jai and P.K. Shrivastava, Proc. Acad. Environ. Biol., **4**, 123-126 (1995).
31. IARC, Monographs on the Evaluation of Carcinogenic Risks to Humans: Beryllium, Cadmium, Mercury and Exposures in the Glass Manufacturing Industry, Vol. 58. Lyon, France (1993).
32. C. L. Potts, Cadmium Proteinurea: The health of battery workers exposed to cadmium oxide dust, Ann. Occup. Hyg, **8**, 55–61 (1965).
33. L. N. Kolonel, Cancer (Phila.), **37**, 1782–1787 (1976).
34. G.G. Schwartz and M.I. Reis, Epidem. Biomarkers and Preven., **9**, 139-145 (2000).
35. J.W. Ryznar, J.Amer. Water Work Assoc., **36**, 47 (1944).
36. Carrier Air Conditioning Company, Handbook of Air Conditioning System Design. McGraw- Hills Books, New York (1965).
37. APHA (American Public Health Association), Standard Methods for the Examination of Water and Waste Water, 17th ed, Washington, D.C (1985).
38. Edstrom Industries., 1998. Scale forming Tendency of Water. www.edstrom.com/lab/bulletins/mi4710.thm

Table 1: Descriptive Statistics Of The Physico-Chemical Parameters In Drinking Water Of Mardan District.

Parameters	Temp	pH	EC	Turbidity	TDS	TH	M Alkalinity	DO	LI	RSI	Ca	Ca-Hardness	Mg-Hardness
Units	C^o		µs/cm	NTU	mg/l	mg/l	mg/l	mg/l	NA	NA	mg/l	mg/l	mg/l
St.Dev	1.24	0.052	342.27	32.27	182.74	139.95	120.33	0.382	NA	NA	1.73	3.44	123.4
Max	26	7.04	1468	127.5	783	535	128	3.99	-2.98	14	7.136	17.84	521.1
Min	21	6.88	289	1.1	152	19.8	66.63	2.96	-2.40	11	1.104	2.76	14.25
Mean	23.4	6.97	805.46	11.04	430.93	227.5	76	3.53	-1.88	11.9	2.78	8.56	293.4

LI = Langelier Index

RSI =Ryznar Stability Index

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Table 2: Classification of water based on Total Hardness

Concentration as $CaCO_3$	Indication	No. Of Samples (%)
0 to 60 mg/L	Soft water	**10**
60 to 120 mg/L	Moderately hard water	**16.66**
120 to 180 mg/L	Hard water	**20**
>180 mg/L	Very hard water	**53.33**

Table 3: Descriptive statistics of heavy metals in the drinking water of Mardan District

Heavy Metals	Fe	Mn	Cu	Pb	Zn	Cr	Cd	Ni
Units	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
St Dev	0.04	0.112	0.010	0.21	0.0857	0.059	0.079	0.037
Max	0.224	0.458	0.049	1.043	0.32	0.162	0.362	0.283
Min	0.105	0.015	0.01	0.37	0.034	0.016	0.084	0.157
Mean	0.164	0.058	0.022	0.561	0.121	0.083	0.194	0.212

Table 4: Classification according to Ryznar (1944) and Carrier (1965)

RI	**Indication (Ryznar 1944)**	**Indication (Carrier 1965)**
RI<5.5	Heavy scale will form	Heavy scale
5.5 < RI < 6.2	Scale will form	Light scale
6.2 < RI < 6.8	No difficulties	Light scale or corrosion
6.8 < RI < 8.5	Water is aggressive	Corrosion significant
RI > 8.5	Water is very aggressive	Corrosion intolerable

Table 5: Interpretation of Langelier Index (Carrier, 1965)

LI Value	Indication
2.0	Scale forming but non corrosive
0.5	Slightly scale forming and corrosive
0.02	Balanced but pitting corrosion possible
- 0.05	Slightly corrosive but non – scale forming
- 2.0	Serious corrosion