

## Surface and Ground Water Contamination in NWFP and Sindh Provinces With Respect to Trace Elements

MIDRAR-UL-HAQ, RIAZ A. KHATTAK<sup>†</sup>, HAJI KHAN PUNO, M. SALEEM SAIF AND KAZI SULEMAN MEMON

*Department of Soil Science, Sindh Agriculture University, Tandojam-Pakistan*

<sup>†</sup>*Department of Soil and Environmental Sciences, NWFP Agricultural University, Peshawar*

Corresponding author's e-mail: [midrarulhaq59@yahoo.com](mailto:midrarulhaq59@yahoo.com)

### ABSTRACT

This paper presents the contamination of surface and ground water samples with respect to trace elements (Zn, Cu, Fe, Mn, Cd, Cr, Ni and Pb) by industrial and domestic effluents. A total of 16 surface and eight ground water samples were collected from NWFP while eight surface and four ground water samples from Karachi (Sindh) and analyzed for trace elements concentration with the help of atomic absorption spectrophotometer. The reported values of trace elements in surface and ground waters were 0.04 and 0.13, 0.20 and 0.21, 0.19 and 0.16, 0.22 and 1.22, 0.02 and 0.04, 0.04 and 0.14, 0.21 and 0.96, 0.16 and 0.33 mg L<sup>-1</sup> for NWFP province while 0.16 and 0.26, 0.31 and 0.10, 0.78 and 1.22, 0.33 and 0.10, 0.04 and 0.03, 0.10 and 0.03, 0.59 and 1.2, 0.19 and 0.15 mg L<sup>-1</sup> for Sindh province for Zn, Cu, Fe, Mn, Cd, Cr, Ni and Pb, respectively. The observed values in this study were also compared with USEPA and WHO recommended levels as well as with the concentrations reported by other investigators. The comparison showed that the levels of selected trace elements were quite high and were within the range generally reported for contaminated surface and ground waters.

**Key Words:** Ground Water; Contamination; Trace element

### INTRODUCTION

Surface and ground water contamination with respect to trace elements by industrial and domestic effluents has increased in recent years (Nasreen *et al.*, 1995; Lone *et al.*, 1999; Mathrani & Khwaja, 2001; Bashir *et al.*, 2001; Ilyas, 2002). All the water bodies including rivers, canals and the drainage canals are being used by industries, industrial estates and municipalities of towns and cities for the discharge of effluents from industrial, construction, transportation and other activities. The untreated effluents and solid wastes are dumped into rivers and canals considering them as the most easily available 'sink' (Ali, 1997). According to Saleemi (1993), about 9000 million gallons of wastewater is being discharged daily into the water bodies from industrial sector of Pakistan. Therefore, it is expected that surface and ground water may get contaminated widely. The contamination of Amankot and Gaga Canals at Mingora, Swat (NWFP) by industrial and municipal activities was also reported by Ikramullah (2000). Khattak and Rehman (1992) also reported elevated concentrations of trace elements (Zn, Cu, Fe, Mn, Cd, Ni and Pb) in Kabul River and its tributaries in NWFP. The increased levels were mostly linked to industrial and domestic wastewater flow into this river. Discharging untreated industrial effluents in the surface drains contaminate the surface waters and hence could affect agricultural production.

Similarly, the ground water contamination can be associated with different sources, such as seepage of agro-chemicals, sewage and industrial wastewater. Seepage from unlined sewage and industrial wastewater channel cause a great threat to ground water quality (Bashir *et al.*, 2001).

Throughout the world, there is an increasing interest in the ground water quality used for drinking (Olwin, 1977; Meranger *et al.*, 1979). Many elements present in drinking water are reported to be essential for human health. However, their ingestion in excessive amounts may cause severe health problems (Angino *et al.*, 1977; Begum *et al.*, 1998). Therefore, it is highly necessary to study the quality of different industrial effluents thoroughly and suggest remedial measures to be adopted to protect the soil and water resources from contamination. To that end, this study was designed to assess the surface and ground water quality with respect to trace elements at some selected sites of NWFP and Korangi Industrial Area of Karachi in Sindh provinces of Pakistan.

### MATERIALS AND METHODS

This study was conducted during the years 2000 and 2001 in NWFP and Sindh provinces of Pakistan. The surface water samples were collected from Kabul River, Naguman River, Bakhshoo Pul Airab (Drain) and Kalpani Drain in NWFP while Malir River in Karachi, Sindh. The ground water samples were collected from wells in Charsadda and Risalpur in NWFP and in Korangi Industrial Area of Karachi, Sindh province. The selected sites of sampling for surface and ground water in both provinces were linked to industrial units for effluents discharge. The ground water level in the selected areas was observed at 50-60 ft. Therefore, the risk of water contamination from industrial/ municipal source at these sites was assumed to be the maximum. In that context, the samples were collected both in summer and winter seasons. So, a total of 16 surface and eight ground water samples were obtained from NWFP

while eight surface and four ground water samples from Sindh. All the water samples were taken in plastic bottles and then brought to the laboratory. To stop the growth of microbes few drops of toluene were added. The samples were filtered through Whatman 42 filter paper and analysed for trace elements with the help of atomic absorption spectrophotometer (APHA, 1992). The results were compared with USEPA (1976), WHO (1984) and the reported values of different investigators for surface and ground water quality.

## RESULTS AND DISCUSSION

All the surface and ground water samples showed substantial concentrations of trace elements. The description of each element is given below:

**Zinc.** The surface water samples collected from various sites of NWFP contained Zn from 0.003-0.08 mg L<sup>-1</sup> with an average value of 0.04 mg L<sup>-1</sup> (Table I). The highest value of 0.08 mg L<sup>-1</sup> was observed in a sample collected from Kalpani Drain while the lowest value of 0.003 mg L<sup>-1</sup> was recorded in a sample collected from Bakhshoo Pul Airab. Similarly, the concentration of Zn ranged from 0.06 to 0.29 mg L<sup>-1</sup> with an average value of 0.16 mg L<sup>-1</sup> in surface water samples collected from Malir River in Karachi (Sindh).

The concentrations of Zn varied between 0.002-0.27 mg L<sup>-1</sup> with an average value of 0.13 mg L<sup>-1</sup> in ground water samples collected from different sites of NWFP (Table II) while those collected from Korangi Industrial Area, Karachi (Sindh) ranged from 0.04-0.52 mg L<sup>-1</sup> with an average value of 0.26 mg L<sup>-1</sup> (Table II).

**Copper.** The concentration of Cu in surface water samples collected from various sites of NWFP ranged from 0.01-0.77 mg L<sup>-1</sup> with an average value of 0.20 mg L<sup>-1</sup> (Table I). The maximum and minimum values of 0.77 mg L<sup>-1</sup> and 0.01 mg L<sup>-1</sup> were reported in samples collected from Kalpani Drain and Bakhshoo Pul Airab, respectively. Similarly, the concentration of Cu varied between 0.01-0.84 mg L<sup>-1</sup> with an average value of 0.31 mg L<sup>-1</sup> (Table I) in surface water samples collected from Malir River, Karachi (Sindh).

The concentration of Cu in ground water samples collected from various sites of NWFP ranged from 0.004-0.67 mg L<sup>-1</sup> with an average value of 0.21 mg L<sup>-1</sup> (Table II). However, the ground water samples collected from Korangi Industrial Area, Karachi (Sindh) contained Cu concentration, which ranged from 0.01-0.21 mg L<sup>-1</sup> with an average value of 0.10 mg L<sup>-1</sup> (Table II).

**Iron.** The concentration of Fe varied between 0.01-1.29 mg L<sup>-1</sup> with an average value of 0.20 mg L<sup>-1</sup> (Table I) in surface water samples collected from various sites of NWFP. The highest value of 1.29 mg L<sup>-1</sup> was observed in a sample collected from Kabul River while the lowest value of 0.01 mg L<sup>-1</sup> was recorded in a sample collected from Bakhshoo Pul Airab. Similarly, the concentration of Fe in surface water samples collected from Malir River in Karachi, Sindh ranged from 0.13-2.91 mg L<sup>-1</sup> average being of 0.31 mg L<sup>-1</sup>.

The concentration of Fe ranged from 0.01-0.43 mg L<sup>-1</sup> with an average value of 0.16 mg L<sup>-1</sup> (Table II) for ground water samples collected from various sites of NWFP. However, the concentration of Fe varied between 0.51-2.39 mg L<sup>-1</sup> with an average value of 1.22 mg L<sup>-1</sup> (Table II) in ground water samples collected from Korangi Industrial Area, Karachi (Sindh).

**Manganese.** The values of Mn varied from 0.01-1.11 mg L<sup>-1</sup> with an average value of 0.22 mg L<sup>-1</sup> in surface water samples collected from various sites of NWFP (Table I). The maximum value of 1.11 mg L<sup>-1</sup> was recorded in a sample collected from Naguman River while the minimum value of 0.01 mg L<sup>-1</sup> was observed in a sample collected from Bakhshoo Pul Airab. Similarly, the values reported for Mn in samples collected from Malir River, Karachi (Sindh) were in the range of 0.05-0.57 mg L<sup>-1</sup> with an average value of 0.33 mg L<sup>-1</sup> (Table II).

The concentration of Mn in ground water samples collected from various sites of NWFP ranged from 0.08-2.56 mg L<sup>-1</sup> with an average value of 1.22 mg L<sup>-1</sup> (Table II). However, the values observed in ground water samples collected from Korangi Industrial Area, Karachi (Sindh) varied between 0.07 to 0.12 mg L<sup>-1</sup> with an average value of 0.10 mg L<sup>-1</sup> (Table II).

**Cadmium.** The concentration of Cd in surface water samples collected from various sites of NWFP ranged from 0.002-0.09 mg L<sup>-1</sup> with an average value of 0.02 mg L<sup>-1</sup> (Table I). The highest concentration of 0.09 mg L<sup>-1</sup> was reported in a sample collected from Kalpani Drain while the lowest concentration of 0.002 mg L<sup>-1</sup> was observed in a sample collected from Bakhshoo Pul Airab. Similarly, Cd values observed in surface water samples collected from Malir River in Karachi (Sindh) varied between 0.002-0.07 mg L<sup>-1</sup> with an average value of 0.04 mg L<sup>-1</sup> (Table I).

The observed concentration of Cd in ground water samples collected from various sites of NWFP ranged from 0.01-0.07 mg L<sup>-1</sup> with an average value of 0.04 mg L<sup>-1</sup> (Table II). However, the values observed in ground water samples collected from Korangi Industrial Area, Karachi (Sindh) varied from 0.02-0.04 mg L<sup>-1</sup> with an average value of 0.03 mg L<sup>-1</sup> (Table II).

**Chromium.** The concentration of Cr in surface water samples collected from various sites of NWFP ranged from 0.01-0.12 mg L<sup>-1</sup> with an average value of 0.04 mg L<sup>-1</sup> (Table I). The maximum value of 0.12 mg L<sup>-1</sup> was recorded in a sample collected from Kalpani Drain while the minimum value of 0.01 mg L<sup>-1</sup> was observed in a sample collected from the same source. However the values observed for Cr in surface water samples collected from Malir River in Karachi (Sindh) ranged from 0.03-0.29 mg L<sup>-1</sup> with an average value of 0.10 mg L<sup>-1</sup> (Table I).

The values reported for ground water samples collected from various sites of NWFP varied between 0.01-0.30 mg L<sup>-1</sup> with an average value of 0.14 mg L<sup>-1</sup> (Table II). Similarly, the concentrations of Cr ranged from 0.003-0.07 mg L<sup>-1</sup> with an average value of 0.03 mg L<sup>-1</sup> in ground water

samples collected from Korangi Industrial Area, Karachi-Sindh (Table II).

**Nickel.** The concentration of Ni ranged from 0.01-1.52 mg L<sup>-1</sup> with an average value of 0.21 mg L<sup>-1</sup> (Table I). The highest concentration of 1.52 mg L<sup>-1</sup> was recorded in a sample collected from Naguman River while the lowest concentration of 0.01 mg L<sup>-1</sup> was observed in a sample collected from Kabul River. Similarly, the concentration of Ni reported in samples collected from Malir River in Karachi, Sindh ranged from 0.02-1.06 mg L<sup>-1</sup> with an average value of 0.59 mg L<sup>-1</sup> (Table I).

The concentration of Ni varied from 0.002-3.66 mg L<sup>-1</sup> with an average value of 0.96 mg L<sup>-1</sup> (Table II) in ground water samples collected from various sites of NWFP. However, the values reported for Ni in Korangi Industrial Area of Karachi - Sindh varied between 0.01-2.19 mg L<sup>-1</sup> with an average value of 1.2 mg L<sup>-1</sup> (Table II).

**Lead.** The reported concentration of Pb in surface water samples collected from various sites of NWFP ranged from 0.02-0.38 mg L<sup>-1</sup> with an average value of 0.16 mg L<sup>-1</sup> (Table I). The maximum and minimum values were observed in samples collected from Kabul River and Bakhshoo Pul Airab, respectively. Similarly, the values observed for Pb in surface water samples collected from Malir River, Karachi (Sindh) ranged from 0.09 to 0.32 mg

L<sup>-1</sup> with an average value of 0.19 mg L<sup>-1</sup> (Table I).

The concentration of Pb in ground water samples collected from various sites of NWFP varied between 0.02-0.73 mg L<sup>-1</sup> with an average value of 0.33 mg L<sup>-1</sup> (Table II). While, the concentration of Pb varied between 0.1-0.24 mg L<sup>-1</sup> with an average value of 0.15 mg L<sup>-1</sup> in ground water samples collected from Korangi Industrial Area, Karachi, Sindh (Table II).

The results obtained in this study could be compared with those reported by other investigators. Ikramullah (2000) conducted a study in Mingora, Swat, NWFP, the reported values in water samples collected from Amankot canal were 0.3, 2.6, 0.16, 0.03 and 0.5 mg L<sup>-1</sup> for Zn, Cu, Fe, Cd and Ni, respectively. However, Khattak and Rehman (1992) reported the maximum concentration of 0.03, 0.02, 0.34, 0.02, 0.05 and 0.14 mg L<sup>-1</sup> for Zn, Cu, Fe, Cd, Ni and Pb in the Kabul River at Pirsabak NWFP-Pakistan. In the United States of America, the staff of the National Academy of Sciences, NAS (1977) collected 1577 surface water samples and reported the maximum concentration of 1.2, 0.3, 4.6, 0.12, 0.13 and 0.14 mg L<sup>-1</sup> for Zn, Cu, Fe, Cd, Ni and Pb, respectively. While, Procter *et al.* (1973) observed the highest value of 0.14, 0.005 and 0.07 mg L<sup>-1</sup> for Zn, Cd and Pb in the Missouri River, USA. In the Chamber River of India, the maximum values of Zn, Cu and Fe were 0.013,

**Table I. Comparison of trace elements concentration in Surface water samples collected from various sites of NWFP and Sindh provinces with USEPA Standards**

Elements	USEPA* Standards (mg L <sup>-1</sup> )	Range mg L <sup>-1</sup>	Surface water samples used for irrigaton						
			NWFP (n=16)			Sindh (n=8)			
			Mean	USEPA standards violation No. of samples	% of samples	Range mg L <sup>-1</sup>	Mean	USEPA standards violation No. of samples	% of samples
Zn	2.000	0.003-0.080	0.040	-	-	0.060-0.290	0.160	-	-
Cu	0.200	0.010-0.770	0.200	4	25	0.010-0.840	0.310	5	63
Fe	5.000	0.010-1.290	0.190	-	-	0.130-2.910	0.780	-	-
Mn	0.100**	0.010-1.110	0.220	5	31	0.050-0.570	0.330	7	88
Cd	0.010	0.002-0.090	0.020	7	44	0.002-0.070	0.040	6	75
Cr	0.050**	0.010-0.120	0.040	6	38	0.030-0.290	0.100	4	50
Ni	0.200	0.010-1.520	0.210	4	25	0.020-1.060	0.590	6	75
Pb	5.000	0.020-0.380	0.160	-	-	0.090-0.320	0.190	-	-

\* Source: USEPA (1976)

\*\* Drinking water standards (WHO, 1984).

**Table II. Comparison of trace elements concentrations in ground water samples collected from wells at various sites of NWFP and Sindh provinces with WHO health guideline**

Elements	WHO* guidelines (mg L <sup>-1</sup> )	Ground water samples used for drinking								
		Range mg L <sup>-1</sup>	NWFP (n=8)			Range mg L <sup>-1</sup>	Mean	Sindh (n=8)		
			Mean	WHO guideline violation				Mean	WHO guideline violation	
				No. of Samples	% of samples				No. of Samples	% of samples
Zn	5.000	0.002-0.270	0.130	-	-	0.040-0.520	0.260	-	-	
Cu	1.000	0.004-0.670	0.210	-	-	0.010-0.210	0.100	-	-	
Fe	0.300	0.010-0.430	0.160	2	25	0.510-2.390	1.220	4	100	
Mn	0.100	0.080-2.560	1.220	7	88	0.070-0.120	0.100	2	50	
Cd	0.005	0.010-0.070	0.040	8	100	0.020-0.040	0.030	4	100	
Cr	0.050	0.010-0.300	0.140	6	75	0.003-0.070	0.030	1	25	
Ni	0.200**	0.002-3.660	0.960	4	50	0.010-2.190	1.200	3	75	
Pb	0.050	0.020-0.730	0.330	7	88	0.100-0.240	0.150	4	100	

\* Source: WHO (1984)

\*\* Irrigation water standard (USEPA, 1976).

0.009 and 0.3 mg L<sup>-1</sup>. Now it is understood that variations from river to river and other surface water are mainly because of diverse anthropogenic activities (industrial, agricultural and domestic) and different ecological conditions. But the general comparison indicates that the concentration of selected trace elements in this study is quite high and could be considered as contaminated by industrial effluents. Comparing the surface water samples of NWFP and Sindh with USEPA criteria (1976), 25 and 63, 44 and 75, 25 and 75% samples crossed the critical levels of 0.2, 0.1 and 0.2 mg L<sup>-1</sup> for Cu, Cd and Ni, respectively, while the rest of the samples were found within the permissible limits (Table I).

Similarly, the concentration of trace elements in ground water samples could be compared with fresh and polluted ground water of the Netherlands. Matthess (1974) observed < 0.01 mg L<sup>-1</sup> of Zn, Cu, Fe and Pb while 1 mg L<sup>-1</sup> Mn, < 0.007 mg L<sup>-1</sup> Cd, 0.001 mg L<sup>-1</sup> Cr and < 4 mg L<sup>-1</sup> Ni in the fresh ground water, while Brinkman (1974) reported the values of 0.05-0.7 mg L<sup>-1</sup> Zn, 0.008-0.02 mg L<sup>-1</sup> Cu, 0.0002-0.001 mg L<sup>-1</sup> Cd, 0.0005-0.02 mg L<sup>-1</sup> Cr, 0.008-0.02 mg L<sup>-1</sup> Ni and 0.005-0.12 mg L<sup>-1</sup> Pb in the polluted ground water of the Netherlands. Mattrani and Khowaja (2001) observed the values of 0.002-2.9, 0.001-0.4, 1.4-4.6, 0.003-0.44, 0.002-0.41, 0.002-0.12, 0.001-0.16 mg L<sup>-1</sup> for Zn, Cu, Fe, Mn, Cd, Cr and Ni in the ground water of Hyderabad, Sindh. While, Ilyas (2002) reported the range of 0.03-3.62, 0.47-0.82, 0.32-0.37, 0.03-0.32, 0.02-0.14, 0.48-1.45, 0.09-0.77 mg L<sup>-1</sup> for Zn, Cu, Fe, Mn, Cd., Ni and Pb, respectively in the ground water of Peshawar, NWFP. Comparison with other studies indicates that the concentration of trace elements in the ground water of Charsadda and Risalpur in NWFP and Malir in Karachi, Sindh are quite high and all the elements have exceeded the values reported for polluted ground water of the Netherlands, which suggest the high level of ground water contamination. This high level of trace elements depends upon anthropogenic activities, ecological conditions, soil texture and water table depth. Comparing the observed values of trace elements in samples of NWFP and Sindh with WHO guidelines, 25 and 100, 88 and 50, 100 and 100, 75 and 25, 88 and 100% samples crossed the critical levels of Fe, Mn, Cd, Cr and Pb, respectively (Table II), while the rest of the samples were found within the permissible level.

## CONCLUSION

The maximum industrial units in the selected areas discharge their effluents directly into surface water and the seepage taking from the effluents as well as other anthropogenic activities impair the quality of surface and ground water and making them unfit for irrigation and drinking purposes. So, the treatment of the effluents before disposal into surface drains should be practiced in all industrial premises of the country to safeguard better water quality.

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