

## Effect of Industrial Effluents of Zob-Ahan on Soil, Water and Vegetable Plants

Hamid Reza Rahmani and Mosleheddin Rezaei

Department of Soil and Water, Esfahan Agricultural and Natural Resources Research Center,  
P.O. Box 81785-199, Esfahan, Iran

**Abstract:** Monitoring harmful chemicals especially heavy metals in industrial effluent for prevention and degradation of natural resources are required. The Effluent Water (EW) of Zob-Ahan (steel industrial complex), were seasonally collected, three times during 48 h period. The soils, well-water and vegetable plant samples were collected in land irrigated with EW and soil in adjacent virgin lands. The EW EC, TDS, BOD, COD, sulfate, chloride, bicarbonate, N-NO<sub>3</sub> and Cd, Co and Cr were above permissible limit, for wells water in the down side of evaporation ponds EC, TDS, N-NO<sub>3</sub>, sulfate, chloride, bicarbonate and concentration of Cu, Co, Fe and Cr were above permissible limit and the soils treated with EW Zn, Mn and Cd concentration were in critical range. Soils irrigated with EW had higher OC content and available concentration of Cd, Fe, Cu, Mn, Zn and Pb compared to control sample (adjacent virgin land). In vegetable plants, all measured heavy metals concentration (except Cu content in Taree Irani that was in critical rang) was in normal range. The heavy metals concentration in unwashed plant samples were higher than washed ones. The results showed that Zob-Ahan EW has limitation for application as irrigation water, discharge into surface and subsurface water. Therefore, the EW, should properly be treated before discharging into environment. The heavy metals in soil and well-water affected by EW and irrigated plants with EW should regularly and closely be monitored.

**Key words:** Zob-Ahan, Esfahan, heavy metals, permissible limit, critical limit

### INTRODUCTION

The contamination of water resources in arid region is a serious problem. In such region the irrigation water resources are limited and should be prevented from contamination. In arid and semi-arid area, industrial effluent water utilize as a source of irrigation water. Eventhought, the land application of irrigation water is an easy and least expensive method of disposal however, long-term land application of EW may cause excessive accumulation of heavy metals such as Cr, Ni, Cd, in soil and toxicity in plants (Torabian and Baghuri, 1996).

The accumulation of heavy metals in environmental samples such as plants, sediments, soils, sewage sludges, solid residues, etc. is a potential risk to human health due to their transformation and their uptake by plants and their subsequent introduction into the food chain (Cid *et al.*, 2002).

Cadmium (Cd) and Lead (Pb) accumulation in soil are among the main environmental concerns. Cd is highly toxic to animals and plants (Di Toppi and Gabrielli, 1999). In plants exposure to Cd causes reductions in photosynthesis, water and nutrient uptake (Di Toppi

and Gabrielli, 1999). When Cd concentration exceeds 100 mg kg<sup>-1</sup> the plant growth rate decreases (Malakoti *et al.*, 2000). The soil permissible Cd concentration is about 0.5 mg kg<sup>-1</sup> (Malakoti *et al.*, 2000). The permissible concentration of Cd in soil which does not adversely affect plant growth and quality and EW application to agricultural land is 3 mg kg<sup>-1</sup> (Malakoti *et al.*, 2000).

The application of wastewater and sludge in agricultural lands generates numerous sanitary problems (Abedi and Najafi, 2001). In Taiwan more than 800 ha of land has been contaminated with industrial EW. The mean brown rice concentration of Cd, Cr, Cu, Pb and Zn were 0.07, 0.16, 2.48, 0.43 and 39.2 mg kg<sup>-1</sup>, respectively (Chen, 2000). Study of the 5 regions in Taiwan show that the soils are containing high level of Pb, Cd and other heavy metals. The Cd, Pb and Zn concentrations were ranging from 175 to 378, 252 to 3145 and 100 mg kg<sup>-1</sup>, respectively (Chen, 2000).

Esfahan Province is located in a semi-arid to-arid region in central part of Iran, where the water resources are scare and water quality should be preserved. Due to, establishment and rapid expansion of various industries,

the environmental contamination of region by heavy metals are among main environmental concern. The objectives of this study were to study the properties of Zob-Ahan steel industrial complex EW and effect of application EW on heavy metals concentration on soil, water, vegetable plants.

**MATERIALS AND METHODS**

Zob-Ahan steel industrial complex is located 22 km East of Esfahan City which has gone through several expansion phases. It daily consumes about 86400 m<sup>3</sup> water and produces 14400 m<sup>3</sup> EW. The EW of Zob-Ahan after partial treatment use for irrigation of agricultural land and woody plants. This research did in agricultural lands (around of Zub-Ahan) in 2003. During a one-year period, the EW was seasonally sampled for 48 h (any sample removed in 8 h periods and samples in 48 h mixed and made one complex sample). In 15 locations soil from 0 to 20 cm in agricultural land irrigated with EW and in the virgin land, were sampled in three replicates. Water from four irrigation-wells, adjacent to land irrigated with EW; in the down side of industrial waste evaporation ponds were sampled. The EW and well-water: pH, EC, TDS, TSS, NO<sub>3</sub>-N, cations, anions, BOD, COD and the concentration of heavy metals including Cu, Zn, Mn, Ni, Co, Cd, Fe, Pb, Cr were measured by standard methods (APHA, 1995). The soil samples pH, EC, texture, organic matter, cations, anions and concentration of heavy metals

including Cu, Cd, Zn, Fe, Mn, Pb were measured by standard methods (Page, 1991). The plant samples Basil (*Ocimum basilicum*) and Allium ampeloprasum ssp.persicum (Taree Ilrani) the concentration of heavy metals, including Cu, Cd, Zn, Fe, Mn and Pb were measured by standard methods (Robert, 1990). The results were compared with the standard permissible concentration levels (IEPO, 1994; EPA/ROC, 1989; Allaway, 1990; Pendas and Pendas, 1992).

**RESULTS AND DISCUSSION**

Comparison of the results of analysis of EW (Table 1) with the permissible levels (IEPO, 1994; Ayers and Westcot, 1985), show that for discharge EW into surface and absorption wells, the COD, BOD, TSS, TDS, EC, NO<sub>3</sub>-N, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> and for utilization of EW for irrigation water, the TDS, EC, SAR, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub>-N, Cl<sup>-</sup>, Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> are the limiting factors. The chemical properties of EW from this study are similar to Yazd City textile and industrial EW (Rahmani, 1998). None of the measured concentration of heavy metals exceeded the threshold levels for discharge into surface water and absorption well (IEPO, 1994). Cobalt (Co) concentration is higher than permissible level for utilization of EW for irrigation water. Comparing the results with the United State Environmental Protection Agency (EPA) standards shows concentration of Cr, Co and Cd exceed the permissible level for irrigation water (EPA/ROC, 1989).

Table 1: The chemical properties and range of concentration of heavy metals in EW and Well water compare to permissible limit

Parameters	Well-water	Effluent water	Permissible limit (IEPO, 1994)			
			Discharge to surface water	Discharge to absorption well	Use for irrigation	
					IEPO, 1994	EPA/ROC, 1989
pH	6.8-7.6	7-7.7	6.5-8.5	5-9	6-8.5	6.5-8.5
EC (dS m <sup>-1</sup> )	4.0-25	0.84-26.7	-	-	-	3
NO <sub>3</sub> -N (mg L <sup>-1</sup> )	4.5-67.2	0.18-165.8	50	10	-	-
Hardness (mg L <sup>-1</sup> )	1000-3400	200-2800	-	-	-	-
TDS (mg L <sup>-1</sup> )	2585-12384	537.6-17088	-	-	-	2000
TSS (mg L <sup>-1</sup> )	--	36-62	40	-	100	-
BOD (mg L <sup>-1</sup> )	--	6-55	50	50	100	-
COD (mg L <sup>-1</sup> )	--	44.5-115	100	100	200	-
CO <sub>3</sub> <sup>2-</sup> (meq L <sup>-1</sup> )	--	--	-	-	-	-
HCO <sub>3</sub> <sup>-</sup> (meq L <sup>-1</sup> )	0-4.4	0-2	-	-	-	9.84
Cl <sup>-</sup> (meq L <sup>-1</sup> )	20-1200	3.2-2000	-	-	-	31
SO <sub>4</sub> <sup>2-</sup> (meq L <sup>-1</sup> )	17.9-65	2.3-21	-	-	-	21
Na <sup>+</sup> (meq L <sup>-1</sup> )	21.3-80	4.4-42.9	-	-	-	39
Ca <sup>2+</sup> +Mg <sup>2+</sup> (meq L <sup>-1</sup> )	20-68	4-56	-	-	-	-
SAR	6.7-20.6	2.54-9.85	-	-	-	15
Fe (mg L <sup>-1</sup> )	0.07-19.8	0.08-0.41	3	3	3	5
Cu (mg L <sup>-1</sup> )	0.025-0.125	0.02-0.08	1	1	0.2	0.1
Ni (mg L <sup>-1</sup> )	0.055-0.175	0.0-0.042	2	2	2	-
Cd (mg L <sup>-1</sup> )	LD	0.0-0.02	0.1	0.1	0.05	0.01
Pb (mg L <sup>-1</sup> )	0.06-0.13	0.0-0.06	1	1	1	2
Cr (mg L <sup>-1</sup> )	0.125-0.250	0.0-0.13	0.5	1	1	0.1
Co (mg L <sup>-1</sup> )	0.14-0.20	0.0-0.14	1	1	0.05	0.05
Zn (mg L <sup>-1</sup> )	0.08-0.21	0.02-0.25	2	2	2	-

Table 2: Mean available concentration of heavy metals in polluted soil compare with non polluted soil (virgin land)

Soil samples	Concentration (mg kg <sup>-1</sup> )					
	Fe	Cu	Mn	Zn	Cd	Pb
Polluted soil	22.80	2.67	15.41	5.10	0.42	4.48
Non polluted soil	4.02	1.07	9.90	1.83	0.12	1.76

Table 3: Mean total concentration of heavy metals in soil samples compare with normal and critical range (Allaway, 1990; Pendas and Pendas, 1992)

Samples	Concentration (mg kg <sup>-1</sup> )					
	Fe	Mn	Cu	Zn	Cd	Pb
Soil samples	17267	564	26.9	57.6	5.0	54.0
Normal range	-	100-400	2-25	1-900	0.01-2	2-300
Critical range	-	-	60-125	70-400	3-8	100-400

Table 4: Mean concentration of heavy metals in washed and unwashed plant samples compare to normal and critical range (Allaway, 1990; Pendas and Pendas, 1992)

Plant samples	Concentration (mg kg <sup>-1</sup> )					
	Fe	Zn	Cu	Mn	Cd	Pb
<b>Taree Irani (shoot)</b>						
Washed	163.9	57.5	17.9	49.5	<LD*	<LD
Unwashed	570.7	54.7	34.1	67.3	<LD	<LD
<b>Basil (shoot)</b>						
Washed	189.7	66.6	13.9	41.4	<LD	<LD
Unwashed	214.0	72.4	37.9	48.5	<LD	<LD
Normal range	-	1-400	5-20	15-100	0.1-2.4	0.2-20
Critical range	-	100-400	20-100	-	5-30	30-300

\*: Less than detection level

Heavy metals may accumulate in soil as the result of long-time application of industrial EW within the range of permissible concentration level. Therefore, for EW discharging into surface water, absorption well, or land irrigation monitoring the heavy metals concentrations in soil are required.

The results of well-water properties in the down side of evaporation ponds (Table 1) shows that the well-water limiting chemical properties are: salinity, bicarbonate, TDS, NO<sub>3</sub>-N, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and SAR. The utilization of well water for direct human and animal consumption have serious limitation and requires special treatments for irrigation of agricultural land. The comparison of the result of concentration of heavy metals with the permissible level (IEPO, 1994) shows that Iron concentration is the limiting factor for discharge into surface water or into absorption wells. Investigation of underground water (well-water) in the EW irrigated land in the Yazd City shows that concentration of non of the Cr, Cu, Zn, Cd and Pb exceed permissible level (Rahmani, 2001) while others report contamination of soil, surface and ground water, due to discharge of EW into environment and utilization as irrigation water. The well-water and associated irrigated land should be monitor closely, due to high concentration level of heavy metals. The well-water concentration of Co and Fe for irrigation are higher than permissible levels (IEPO, 1994). The well-water concentration of Fe, Cu, Cr and Co are higher than permissible level for crop lands irrigation (EPA/ROC, 1998).

The available concentration of heavy metals in well-water treated soil is considerably higher than control (Table 2 ), which shows the gradual accumulation of heavy metals with time due to application of well-water. The comparison of the average total concentration of heavy metal in soil irrigated (Table 3) with EW with the permissible level (Allaway, 1990; Pendas and Pendas, 1992) shows that the Pb concentration is in the permissible, the concentration of Zn and Cd is in critical and Zn and Mn is higher than permissible range, respectively.

Considering the results of analysis of heavy metals in soil irrigated with EW and control (the virgin land) and the high concentration level of various heavy metals in land, irrigated with EW, it is concluded that the heavy metal concentration of EW is the limiting factor and significantly (p<0.05) increased heavy metals concentration in soil compare with control. Also, the total content of heavy metal in soil have increased more than permissible levels therefore, has caused soil contamination. Many reports shows that application of untreated EW may increase the concentration of heavy metals more than permissible level (Elliott and Stevenson, 1986). In Taiwan, 800 ha of agricultural land irrigated with industrial EW, the concentration of Cd, Cr, Pb, Zn, Cu were 10, 16, 120, 80 and 100 mg kg<sup>-1</sup>, respectively that are higher than permissible levels according to US. Environmental Protection Agency (USEPA) standards (Frank and Martinez, 1981). Others report no

environmental, hazard has been associated with land disposal of industrial EW (Elliott and Stevenson, 1986). In general, many researchers have reported an increase of heavy metals in soils treated with industrial EW (Elliott and Stevenson, 1986).

The result of heavy metals in Taree Irani (Table 4) shows that the concentration of Cu in Taree Irani (Allaway, 1990; Pendas and Pendas, 1992) is in critical range and other heavy metals are not limiting. The comparison of the of heavy metals concentration in Basil (Table 4) with the permissible and critical levels (Allaway, 1990; Pendas and Pendas, 1992) shows that heavy metals concentration are in the normal range and are not limiting. The heavy metals concentration in unwashed plant samples were higher than washed samples that shows aerosol deposition of heavy metals by industrial pollutant on plants.

### CONCLUSIONS

The EW has not been treated sufficiently and contain higher than permissible concentrations of many hazardous chemicals for discharge into surface water or absorption wells. The soil and water resources and plant treated with EW has been contaminated with and the concentration of heavy metals are higher than permissible levels. The increasing trend of hazardous chemical concentrations of soil, water and plant in EW treated area shows the contamination of environment by EW.

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