

Effect of Industrial Effluent of Zob-Ahan on soil, water and vegetable plants

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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 meal industrial complex), were seasonally collected, three times during 48 hours period. The soils, well-water and vegetable plants samples were collected in land irrigated with EW and soil in adjacent virgin lands. The EW EC, TDS, BOD, COD, sulfate, chloride, bicarbonate, and N-NO₃ concentration of Cd, Co and Cr were above permissible limit, wells-water in the down side of evaporation ponds EC, TDS, N-NO₃, 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 vegetables 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 was 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.

Keywords: 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^{-1} the plant growth rate decreases (Malakoti et. al., 2000). The soil permissible Cd concentration is about 0.5 mg kg^{-1} (Malakoti et. al., 2000). The permissible concentration of Cd in soil which doesn't adversely affect plant growth and quality and EW application to agricultural land is 3 mg kg^{-1} (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^{-1} , 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^{-1} , respectively (Chen, 2000).

Esfahan Province is located in a semi-arid to -arid region in central part of Iran, where the water resources are scarce 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 application EW effects 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^3 water and produces 14400 m^3 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 hours (any sample removed in 8-hours periods and samples in 48 hours 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, $\text{NO}_3\text{-N}$, 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 standard the permissible concentration levels (IEPO, 1994; EPA/ROC,1989; Allaway, 1990; Pendias and Pendias, 1992).

Results and Discussions:

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, $\text{NO}_3\text{-N}$, Cl^- , and SO_4^{2-} and for utilization of EW for irrigation water, the TDS, EC, SAR, HCO_3^- , $\text{NO}_3\text{-N}$, Cl^- , Na^+ and SO_4^{2-} 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 concentration level for irrigation water (EPA/ROC, 1989).

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, $\text{NO}_3\text{-N}$, Cl^- , SO_4^{2-} 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 for discharge into surface water or into absorption wells are limited by Iron concentration. 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; Pendias and Pendias, 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. Similar results have been reported by various researchers. 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⁻¹, respectively that are higher than permissible levels according to U.S. 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 plants (Allaway, 1990; Pendias and Pendias, 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; Pendias and Pendias, 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.

Conclusion:

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.

Table 1- The chemical properties and range of concentration of heavy metals in EW and Well water compare to permit limit.

Parameter	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)	4.0 – 25	0.84 - 26.7	-	-	-	3
NO ₃ -N (mg l ⁻¹)	4.5 - 67.2	0.18 - 165.8	50	10	-	-
Hardness (mg l ⁻¹)	1000 - 3400	200 - 2800	-	-	-	-
TDS (mg l ⁻¹)	2585 - 12384	537.6 - 17088	-	-	-	2000
TSS (mg l ⁻¹)	--	36 - 62	40	-	100	-
BOD (mg l ⁻¹)	--	6 – 55	50	50	100	-
COD (mg l ⁻¹)	--	44.5 - 115	100	100	200	-
CO ₃ ²⁻ (meq l ⁻¹)	---	--	-	-	-	-
HCO ₃ ⁻ (meq l ⁻¹)	0 - 4.4	0 – 2	-	-	-	9.84
Cl ⁻ (meq l ⁻¹)	20 – 1200	3.2 – 2000	-	-	-	31
SO ₄ ²⁻ (meq l ⁻¹)	17.9-65	2.3 – 21	-	-	-	21
Na ⁺ (meq l ⁻¹)	21.3 - 80	4.4 - 42.9	-	-	-	39
Ca ²⁺ +Mg ²⁺ (meq l ⁻¹)	20 - 68	4 – 56	-	-	-	-
SAR	6.7 - 20.6	2.54 -9.85	-	-	-	15
Fe(mg l ⁻¹)	0.07 – 19.8	0.08 – 0.41	3	3	3	5
Cu(mg l ⁻¹)	0.025 – 0.125	0.02 – 0.08	1	1	0.2	0.1
Ni(mg l ⁻¹)	0.055 – 0.175	0.0 – 0.042	2	2	2	-
Cd(mg l ⁻¹)	LD	0.0 – 0.02	0.1	0.1	0.05	0.01
Pb(mg l ⁻¹)	0.06 – 0.13	0.0 – 0.06	1	1	1	2
Cr(mg l ⁻¹)	0.125 – 0.250	0.0 – 0.13	0.5	1	1	0.1
Co(mg l ⁻¹)	0.14 – 0.20	0.0 – 0.14	1	1	0.05	0.05
Zn(mg l ⁻¹)	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 ⁻¹)					
	Fe	Cu	Mn	Zn	Cd	Pb
soil polluted	22.8	2.67	15.41	5.1	0.42	4.48
non soil polluted	4.02	1.07	9.9	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)

	Concentration (mg kg ⁻¹)					
	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)

		Concentration (mg kg ⁻¹)					
		Fe	Zn	Cu	Mn	Cd	Pb
Taree Irani (shoot)	washed	163.9	57.5	17.9	49.5	<LD*	<LD
	unwashed	570.7	54.7	34.1	67.3	<LD	<LD
Basil (shoot)	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

References:

- [1] - Abedi, M. and P. Najafi. (2001) Use of treated wastewater for irrigation, Iranian National Committee on irrigation and drainage press, No.47,248p.
- [2] - Allaway B.J. (1990) Heavy metals in soils, Blackie and Son Ltd. Glasgow, London, pp .177-196.
- [3] - APHA. (1995) Standard methods for the examination of water and wastewater, prepared and published by APHA , AUWA and WEF , 19th Ed .
- [4] - Ayers. R.S and D.W. Westcot. (1985) Water quality for agriculture, F.A.O. Paper. No.29.
- [5] - Chen. Z.S. (2000) Relationship between heavy metal concentrations in soils of Taiwan and uptake by crops, Department of Agricultural Chemistry, National Taiwan University, Taipei 106, Taiwan, Roc.
- [6] - Cid, B.P., M. de J. Gonzalez and E.F. Gomez. (2002) Analyst, 126, 1304-1311.
- [7] - Di Toppi, L.S., and R. Gabrielli. (1999) Response to Cd in higher plants, Environmental and Experimental Botany, Vol.41, Issue.2, pp.105-130.
- [8] - Elliott L.F., and F.J. Stevenson (1986) Soils for management of organic waste and waste-water. Second printing, Soil. Sci. Am. Madison. Wisconsin, USA. pp. 650.
- [9] - EPA/ROC. (1998) Environmental information of Taiwan, ROC, Environmental Protection Agency (EPA), Taipei, Taiwan, ROC.
- [10] - EPA/ROC. (1989) Final reports of heavy metals contents in Taiwan Agricultural soils, 4 vols. Taiwan, ROC.
- [11] - Frank M.D. and J.A. Martinez. (1981) Municipal waste-water irrigation agriculture. Academic press. pp. 358-362

- [12] - IEPO(Iranian Environmental Protection Organization). (1994) The Standards for discharging effluent water ,The Research deputy of Iranian Environmental Protection Organization.
- [13] - Malakoti M.J., M. Torabi, and H. Tabatabaei (2000) The hazardous effect of Cd and the methods of reducing Cd concentrations in agricultural products. First part. The Technical bulletin 87. Ministry of Agriculture. Soil and water Research Institute.
- [14] - Page .A.L.(1991) Methods of soil analysis (2nd ed.),Asa and SSSA,Madison,WS,USA.
- [15] - Pendias. A.K, and H. Pendias (1992) Trace elements in soils and plants: V. Lead. 2nd ed. Boca Raton Arbor, London, PP:187-198.
- [16] - Rahmani, H.R. (1998) The chemical characteristics and the concentration of Pb, Cd, Ni heavy metals in the effluent water of industrial factories of Yazd City. The Journal of Environmental Studies of Iran. No.31:31-36.
- [17] - Rahmani, H.R.(2001) The pollutant sources of soil, water and plant in Yazd Province. The final report of approved National Scientific board. Yazd University, Iran.
- [18] - Robert . I. A.(1990), Methods of plant analysis , official methods of analysis of the A.O.A.C.
- [19] - Torabian A. and A. Baghuri (1996) Investigation of contamination by application of Industrial and municipal Effluent water in agricultural land in the southern part of Tehran. The Journal of Environmental Studies of Iran.No.18:31-36.



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