THE ANALYSIS OF WATER AND SOIL IN ZARGHAN PLAIN IN TERMS OF CONTAMINATION BY HEAVY METALS

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Abstract

The developments of industries produce wastewaters containing hazardous chemicals and heavy-metallic elements. These wastewaters may be harmful if they are used as drinking water for watering plants. Zarghan plain is situated near Shiraz, Iran, and devoted to agriculture and horticulture. The water that is used for irrigation of this land is extracted from deep and semi-deep wells, where treated wastewater from 135 factories and industrial workshops exists. In this study, some of water shafts have been selected for testing of contamination by heavy metallic elements, and 140 samples were extracted from them in four seasons of a year. Every sample was tested two times for heavy metals such as mercury, arsenic, lead, and nickel. The given tests have indicated that the content of the existing heavy metals in the waters of these wells are at normal levels, and their rate did not exceed the permitted level.

Keywords: *heavy metals, wastewaters, water Well (Shaft), Zarghan plain*

Introduction

Human pressure on the environment is an increasing problem throughout the world. Agriculture, industry, transport, domestic activities, etc. produce a high pollution level in the environment with consequent hazard for animals, plants and also for humans (Ferronato, 2013). Metals with a specific weight equal to or greater than iron or with a nucleus containing 23 neutrons or more are called heavy metals. By this standard, cadmium and arsenic are not in this group; however, due to the creation of environmental hazards and toxicity, they are placed in the group of heavy metals. Some of these metals are especially important in the subject of pollution, and their sediments in plant organs, their tracing in water, and their entrance in the nutrient chain are highly addressed. It is widely accepted that heavy metal contamination in sediment, soil and groundwater is one of the largest threats to environmental and human health. Sediments are the principle sinks for heavy

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metals in aquatic environments and can result in a secondary contamination source affecting the ecosystem (Vaidotas & et al, 2014).

Unlike the organic pollutants, metallic ions are not synthesized in ambience. Hence, they can exist permanently in the environment. Nevertheless, rarefaction and formation of sediment or accumulation of them in plant tissues and animal bodies may reduce their concentration in water. They may also be composed with the sediment or be absorbed and become inactive(engineers, 2000).

Some of these elements accumulate; namely, when they enter into living organisms, they may be accumulated in certain tissues, such as adipose tissue and bone. The heavy metals are used in many big and small size industries for agriculture dependent operations and protection against pests. In chemical fertilizer industries, great amounts of phosphor compounds are consumed in producing superphosphates containing cadmium impurities(engineers,2000). Copper and phosphor compounds as well as arsenic are used in the production of farming insecticides and herbicides. Some fungicides and materials used for wood protection contain arsenic(WaldRon, 1991, Chino, 1991, Duker Schein, 1992).

Heavy metals like mercury, lead, cadmium, and arsenic may be stabilized on enzymatic proteins and inhibit them because of their affinity to composition with thiol agent. The heavy metals, with their carcinogenic roles verified, may affect nucleic acids and create fixed and stable compounds, which leads to accumulation (Abernathy, 1984, Ross, 1998). Some tissues have the property of preserving toxins. Also, in the blood stream, some toxins are combined with plasma proteins and some others are seen as stable on the globules; for example, mercury or copper ions, which are accumulated in plasma and vinegar, are collected in globules. In aquatic ambiences, toxicity of these elements becomes more intensified and more abnormal under physical and chemical conditions. If several metals are placed in the same environment, the final effect caused by the sum of them will be much greater than the effects of each of them. Thus, this has drawn more attention to the presence of heavy metals in water and soil(W.H.O, 1989, Schintu, 1991, Ramelow, 1992). The aforesaid study is also carried out in order to determine the risk to human health in consuming crops containing more than the allowed level of these elements. At the same time, the study seeks to evaluate techniques of preservation of ground and underground waters where farming occurs and also at several places on the Zarghan plain where this water is consumed (Lasheen, 1992).

Materials and methods

Study area

The Zarghan plain is situated 2 km from Shiraz city, where 135 industrial plants have been constructed. Of those, about 64 units are located in an industrial park, well-known as Ab-Barik, and the other 71 plants are placed at other points on the plane (Safavi, 2001). Out of the 120km² in this plane, 4,000 hectares are specified to agriculture and horticulture, out of which approximately 1,850 hectares are allocated to the cultivation of wheat, barley, maize, potato, onion, and alfalfa (Safavi, 2001; Census and Information of Fars Agricultural Jehad Organization, 2009). There is a mountainous area at the westward and southwestern side of this plane where the preservation zone of the Environmental Protection Organization is located, and it is assumed to be one of the most important preservation zones in the country (Fig 1).

Figure 1
The study area of Zarghan plain

All factories, including oil refineries, chemical and food industries, and the local industries, frequently consume raw materials and occasionally produce refined products. The wastewater of these industrial plants and also of the Ab-Barik industrial estate are treated collectively and the runoff passes from the middle of the plane through a channel and is poured into the Kor River.

With respect to a variety of raw materials, the runoff of these units contains heavy metals, according to studies conducted on many occasions, and the produced wastewater in these industries certainly includes these elements. If the content of these materials is more than the allowed level in their treated wastewater, they will have some adverse effects on the subterranean waters and soil and they will threaten the health of the plane in the long run. The experiments have been done on water and soil, so in this investigation, several tests are considered which were conducted on water wells in this zone. Since all the extracted farming crops are irrigated by water from the tested wells, if the content of heavy-metal elements is high, they will directly affect the cultivated plants and cause hazards for consumers (Reporting of technical features and Drilling Logue of wells, 1999, The climate of rainfall, 2012, water balance and water supply, 2003*).*

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Sampling and its circumstance

Before sampling from each well, the pump would be lit about half an hour and it was well –drained from the well for almost 300 minutes, and then the sampling was done from the tube that was mounted on the pipe by 1 meter of the well. The sampling containers were selected from plastic according to the standards and the preparation for sampling containers before taking a sample from the lab was made. (the containers were rinsed with distilled water and Nitric Acid before sampling)
All considerations and principles were carried out to prevent errors mode during the sampling. Since the metal concentration analysis of the samples was measured by Mg/L the necessary considerations become common. -maintenance at samples
Immediately after the sampling, the examples were preserved by HNO_3 (pH<2). The samples were centrifuged for metals before maintenance. - measurement of metals in example of water.

Requirements and materials

1. The atomic absorption device
2. Scale with the precision of 0.00001
3. Centrifuge
4. pH
5. Heater
6. Chemical hood with a strong fan
7. Glass accessories (watch glass, funnel, pipettes, mixer, conglomerate)
8. Sampler in different sizes and head sampler
9.Container in various volumes (Volumetric flash, falcon, beaker)

Chemical ingredients

1. Standard solutions of multi metals with density at 10, 100, 1000 PPM
2, Nitric Acid with high purity (HNO3) (Super Aperio)
3. Sulfuric Acid with high purity (H2so4) (Super Aperio) 4. deionized water

Description at the test

Containers preparation (Washing). Containers are soaked in plastic one) including solution of water and soap or detergent within 24 hours - At first they are rinsed with city network water and then log distilled water -Containers were placed in HNO3 10% in room temperature for at least 6 days - They were by deionized water completely (at least four times) - they were dried and preserved in appropriate location and away from pollution. Attention: this method is used for all plastic and glass containers such as cap, sampler, volumetric flask, which are utilized in lab.
Digestion Method: in order to prepare water samples are used for measuring metal ions by atomic absorption. In the first step, acid digestion act has been utilized by using the common methods. In this research digestion method is cone by Nitric acid – sulfuric acid - put a certain amount of acid sample which is completely mixed into the beaker - Add 5 milliliter of Nitric acid and conglomerate. A clock

was placed on the beaker - Heat the specimen to the boiling point slowly. Continue the evaporation procedure until the sample volume reaches 20 ml - Add 5 ml of Nitric acid and 10 ml of sulfuric acid - Continue the evaporation procedure until the white smoke (so_2) clears - If the sample is not clear, we will add 10 ml of Nitric acid and continue the heating until the release of white smoke (SO_2) and complete deletion of HNO_3 - Where all the brown vapors come out, the sample becomes clear and colorless. (In all the working stages, the sample should be avoided from drying) - Cool the sample and wash the container with 50 ml of distilled water, and heat it till its boiling point - After the dissolution of all salts, the sample was cleared and centrifuged to reach the desired volume.

Making standard solutions for drawing calibration curves. Calibration Standard Solutions are prepared by deionized water from the original multi – metal standards. At least three standards are needed to draw calibration curve. In a way that the concentration at unknown sample and reference samples are in the concentration range at these standards.

Analysis of metals with atomic absorption. Before analyzing, the device conditions for each element should be adjusted, the device conditions for each element should be adjusted according to the device instructions (Cook book) - Use deuterium lamp for complete theme absorption. - Use acetylene – air flame to work with the flame system - Use of incandescent light bulbs for any metal.
Resetting the device with deionized water - Optimizing the device - Infusing metal standards to draw calibration curve - At least one blank sample, one reference sample and one intermediate standard are measured for checking the device before analyzing the sample - Analyzing the samples by the device.

Calculations and preparation of reports. Regarding the water samples, the final concentration of the metal is calculated in the above samples as ppm and ppb. The results from the sample analysis and calibration curve for each metal are stored in each sample. (Moopam 2010, Standard method 2005 (3010B. 3010C))

Data Analysis

There were about 450 wells, mainly semi-deep types (15-50m in depth), located in the Zarghan plain within the studied zone. Some were subjected to drought, and among them, 35 wells meeting the needed qualifications in terms of closeness to factories or nearness to a place of discharge were selected.
The experiment was done with ten agents: mercury, nickel, iron, lead, copper, chrome, zinc, cobalt, barium, and cadmium. Every attempt was made to conduct these tests accurately, and every selected sample was tested twice a season; each test was repeated in order to achieve more precise results. Thirty-five samples were extracted each season, so with respect to the given 10 agents of heavy metals, 140 experiments were carried out on wells in the Zarghan plain throughout a year, and

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every test was repeated once more to achieve high precision and accuracy for the test. 280 tests were done regularly within a year, and the given heavy metals were tested 2,800 times for 10 agents of heavy metals in order to acquire significant results. All of the selected water wells are used for farming purposes, and some of them are also utilized for workshop industries rather than agricultural use. The given wells were mainly selected from shallow types in order to better identify if the industrial wastewaters affected the water.

Results and Discussion

The statistical figures derived from the samples are given separately for each well in Tables 1-4. Few wells were very far from the channel through which treated wastewater of factories was passed. All wells were located in the Zarghan plain, and some of them were placed within 200-500m of the channel. The channel is 2m deep, and the tests indicate that the contents of the channel did not significantly affect the water in the wells in terms of heavy metals, but other chemicals and microbial contaminations affected the water. The findings show that the content of existing heavy metals in the water of the tested wells was not greater than the permitted level.

Table 1. *The average of heavy metals concentration in the water shafts in Zarghan Plain (μgL^{-1}) (Spring 2012) (Agr = agriculture – Ind = Industrial)*

Identification No	Shaft location	Type of application	Cd	Ba	Co	Zn	Cr	Cu	Pb	Fe	Ni	Hg
4217	Bash-plain	Agr	.0	6	.07	10	.01	6	5	2	1	.01
4218	Zarghan plain	Agr	.0	3	.05	.01	7	4	4	3	7	.02
4219	Zarghan plain	Agr	. 2	4	.06	27	. 02	5	1.2	17	3	.01
4253	Ahochar	Agr	.1	6	.2	50	.3	3.5	9.2	55	1	.10
4255	Ahochar	Agr	.1	7	.1	60	.5	3	8.5	60	1	.60
4263	Ahochar	Agr	.0	6	.03	120	.07	4	1	70	2	.01
4264	Zarghan plain	Agr	.1	5	.4	41	.2	6	3	110	5	.60
4273	Zarghan Hose	Ind	.01	7	.05	37	.03	9	2	40	4	.02
4276	Zarghan Hose	Ind	.2	6	. 3	52	.4	8	2	.16	3	.50
4287	Zarghan Hose	Ind	.1	8	.9	27	.2	8	4.1	50	1	.3
4303	Zarghan Hose	Ind-Agr	.2	7	.1	35	.1	6	1.9	60	1.5	.2
4305	Zarghan plain	Ind	.1	4	.1	19	.2	7	.22	80	3	.1
4308	Hossian Abad	Ind-Agr	.1	.5	. 3	67	.3	8	2.3	40	5	.3
4314	Zarghan Hose	Ind-Agr	.2	6	.2	6.2	.2	5	2.1	50	5	.5
4330	Dudaj	Agr	.3	6	.8	176	1.5	8	6	.051	.2	.5
4344	Zarghan plain	Agr	.0	7	.4	15	. 03	8	1.5	10	1	.04
4348	Zarghan plain	Agr	.3	7	.3	75	.3	5	.21	110	4	.3
4352	Zarghan plain	Ind-Agr	.1	4	.2	29	.4	5	.27	70	4	.1
4356	Zarghan plain	Agr	.2	3	.2	92	.5	6	.51	50	1	.2
4380	Zarghan plain	Ind	.3	6	.3	78	.2	8	.27	150	2	.1
4382	Zarghan plain	Ind	.2	6	.4	79	.2	4	.81	120	3	.3
4383	Zarghan Hose	Ind-Agr	.1	7	.8	16	. 3	7	1.7	4	1	.4
4419	Zarghan Hose	Ind-Agr	.2	9	.7	17	4	5	.15	3	2	.33
4519	Dudaj	Agr	.3	8	.8	700	.4	8	.62	200	6	.5
4520	Dudaj	Agr	.2	6	.8	800	.6	7	7.3	700	2	.4
4521	Dudaj	Agr	.3	5	.4	690	.4	70	.63	.36	4	.1
4543	Dudaj	Agr	.2	9	.6	77	.7	50	.45	.86	7	.5
4545	Dudaj	Agr	.2	8	.5	82	.6	60	.56	.85	6	.3
4574	Dudaj	Agr	.0	1	.7	19	.1	1	7	.032	.2	.4
4577	Dudaj	Agr	.3	9	.7	75	.7	60	.68	.47	5	.6
4584	Dudaj	Agr	.1	1	.2	70	.9	1.6	3	.052	.1	.5
4608	Dudaj	Agr	.2	5	.9	195	2.1	7.1	4	.563	.3	.6
4638	Dudaj	Agr	.2	4	.5	300	.3	9	.67	300	5	.1
4650	Bash-plain	Agr	.0	1	.3	2	0	2	1	7.2	.11	.1
4658	Dudaj	Agr	.0	2	.6	27	.9	1.5	8	.11	.1	.4

Table 2. *The average of heavy metals concentration in the water shafts in Zarghan Plain (µgL^{-1}) (Summer 2012) (Agr = agriculture – Ind = Industrial)*

Identifi-cation No	Shaft location	Type of application	Cd	Ba	Co	Zn	Cr	Cu	Pb	Fe	Ni	Hg
4217	Bash-plain	Agr	.0	6.2	.60	10	.19	6.2	4.9	30	1.5	.11
4218	Zarghan plain	Agr	.0	3.1	.50	30	.12	6.9	5.0	30	2.3	.10
4219	Zarghan plain	Agr	.0	3.5	.50	28	.20	4.5	1.5	170	1.9	.27
4253	Ahochar	Agr	.1	3.1	.19	30	.41	5.1	3.0	80	1.9	.27
4255	Ahochar	Agr	.1	5.2	1.9	59	.29	.0	8.9	60	1.7	.30
4263	Ahochar	Agr	.1	6.9	.12	65	.52	3.0	8.2	70	1.6	.20
4264	Zarghan plain	Agr	.0	5.9	.20	17	.69	4.0	2.0	70	1.5	.80
4273	Zarghan Hose	Ind	.0	4.8	3.7	45	1.5	5.2	2.7	12	6.4	.18
4276	Zarghan Hose	Ind	.1	8.0	.51	40	3.5	7.9	1.9	45	2.5	.82
4287	Zarghan Hose	Ind	.2	6.2	.29	49	3.1	7.2	2.1	21	3.1	.75
4303	Zarghan Hose	Ind-Agr	.1	.008	.90	30	.21	7.5	1.5	52	4.3	.63
4305	Zarghan plain	Ind	.21	6.7	.10	37	.10	5.5	.20	65	5.1	.45
4308	Hossian Abad	Ind-Agr	.1	3.9	.10	20	.30	8.1	.24	82	1.8	.19
4314	Zarghan Hose	Ind-Agr	.1	5,0	.30	70	.20	7.1	2.0	45	6.1	.36
4330	Dudaj	Agr	.2	7.0	.21	71	.17	5.1	2.2	59	6.1	.29
4344	Zarghan plain	Agr	.1	5.9	.80	180	2.5	7.0	1.2	510	6.2	.59
4348	Zarghan plain	Agr	.0	.10	.29	67	.0	2.5	2.1	10	1.9	.40
4352	Zarghan plain	Ind-Agr	.2	6.1	.44	81	.70	.30	2.0	150	2.8	.17
4356	Zarghan plain	Agr	.1	3.1	.15	93	.60	5.2	1.6	56	2.1	.24
4380	Zarghan plain	Ind	.3	59	2.9	72	1.9	7.5	2.5	150	1.7	.30
4382	Zarghan plain	Ind	.2	32	2.7	80	1.9	3.7	1.9	140	2.2	.20
4383	Zarghan Hose	Ind-Agr	.1	7.1	.70	61	.21	7.0	1.6	46	4.5	.41
4419	Zarghan Hose	Ind-Agr	.2	9.1	.60	18	.31	6.1	1.7	38	3.5	.39
4519	Dudaj	Agr	.1	7.5	.80	72	3.9	7.0	6.0	250	5.8	.53
4520	Dudaj	Agr	.1	5.7	7.5	82	5.5	6.9	7.7	680	5.1	.61
4521	Dudaj	Agr	.2	4.9	3.9	70	3.9	65	6.5	410	6.2	.69
4543	Dudaj	Agr	.1	8.9	.16	780	7.1	49	5.7	830	1.9	.61
4545	Dudaj	Agr	.1	8.1	.40	850	5.7	57	4.5	810	1.8	.47
4574	Dudaj	Agr	.0	5.0	.65	25	.1	2	7.1	410	4.7	.47
4577	Dudaj	Agr	.21	9.1	.80	81	.71	61	7	490	5.1	.48
4584	Dudaj	Agr	.0	1.2	.20	750	8.9	1.7	2.9	600	5.8	.52
4608	Dudaj	Agr	.2	4.9	.89	210	.3	6.9	3.9	65	.30	.71
4638	Dudaj	Agr	.19	3.9	.59	350	.29	8.9	6.9	300	.60	.59
4650	Bash-plain	Agr	.0	.60	.50	20	.4	7	1.1	70	2.1	.10
4658	Dudaj	Agr	.1	2.0	.59	310	6.9	2	8.1	31	.10	.51

Based on the comparison of conducted experiments with the maximum allowed rate of heavy metals in groundwater, in this irrigation zone, the valid standards were not higher than the determined level in terms of these standards. Tables of experiments in 35 tested wells and also a table of maximum allowed content (µg L^{-1}) of heavy metals for drinking purposes, surface (ground) waters, irrigation, and life of the related aquatic organisms presented by WHO, US Environmental Protection Agency (USEPA), Adriano from Canada, and the current Iranian standard are as follows (Table 5). Given that the studied zone is currently passing through a drought period and the rate of annual precipitations is low in this region, some of these wells contained very little water, and in some others, the daily water discharge did not exceed two hours per day. If the treated wastewaters from these factories included heavy-metal content more than the allowed level, it is possible these heavy metals are stored in the soil and these elements can further penetrate into deeper areas of the soil at times when the rate of annual precipitation is high. Thus, the contents will be increased in subterranean waters.

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Table 3. *The average of heavy metals concentration in the water shafts in Zarghan Plain (μgL^{-1}) (Full 2012) (Agr = agriculture – Ind = Industrial)*

Identification No	Shaft location	Type of application	Cd	Ba	Co	Zn	Cr	Cu	Pb	Fe	Ni	Hg
4217	Bash-plain	Agr	.0	7.1	.7	20	.17	6.7	5	37	1.1	.13
4218	Zarghan plain	Agr	.0	3.5	.5	350	.11	7.1	5	35	.25	.17
4219	Zarghan plain	Agr	.0	4.1	.49	30	.1	4.9	3.1	190	2.5	.25
4253	Ahochar	Agr	.1	5.6	.2	59	.27	4.2	8.7	71	.27	.41
4255	Ahochar	Agr	.1	3.7	.2	41	.37	5.2	2.3	91	1.8	.26
4263	Ahochar	Agr	.1	7.1	.1	67	.5	3.1	8.2	82	2.1	.31
4264	Zarghan plain	Agr	.0	.6	.15	21	.6	3.9	2.2	81	.75	.82
4273	Zarghan Hose	Ind	.0	4.9	.4	47	.16	5.1	6.2	17	1.6	.16
4276	Zarghan Hose	Ind	.1	8.2	.5	42	.3	7.7	2.5	53	8	.77
4287	Zarghan Hose	Ind	.2	6.7	.3	51	.25	6.9	2.2	32	2.5	.73
4303	Zarghan Hose	Ind-Agr	.1	7.1	.8	32	.19	7.4	2.6	65	4.7	.67
4305	Zarghan plain	Ind	.21	7.2	.1	38	.0	4.9	.2	76	5.6	.52
4308	Hossian Abad	Ind-Agr	.1	4.1	.1	24	.27	7.9	1.9	85	2.1	.18
4314	Zarghan Hose	Ind-Agr	.1	4.9	.9	72	.11	6.9	2.2	52	5.9	.38
4330	Dudaj	Agr	.2	7.2	.25	75	.15	5.2	1.7	62	6.2	.32
4344	Zarghan plain	Agr	.13	6.1	.81	210	2.7	7.2	5.2	560	6.1	.58
4348	Zarghan plain	Agr	.0	2.5	.51	71	.1	2.6	2.5	18	.17	.35
4352	Zarghan plain	Ind-Agr	.17	6.3	.37	83	.8	3	2.5	160	1.6	.19
4356	Zarghan plain	Agr	.1	3.4	.16	95	.52	5.3	.2	61	2.7	.22
4380	Zarghan plain	Ind	.27	6.1	.3	72	1.9	7.6	1.9	170	3.3	.28
4382	Zarghan plain	Ind	.19	3.7	.3	69	1.8	3.9	1.4	150	2.1	.19
4383	Zarghan Hose	Ind-Agr	.1	6.9	.71	66	.16	6.7	1.6	49	4.6	.39
4419	Zarghan Hose	Ind-Agr	.15	9.5	.59	19	.3	6	2.8	41	3.3	.29
4519	Dudaj	Agr	.15	8.1	.79	75	3.9	6.1	7.5	290	5.3	.51
4520	Dudaj	Agr	.16	6.1	.8	85	5.5	7.1	6.4	720	4.9	.57
4521	Dudaj	Agr	.18	5.2	.4	73	3.9	6.8	5.9	470	6	.61
4543	Dudaj	Agr	.1	9.1	.65	780	8	5.1	4.7	910	1.5	.59
4545	Dudaj	Agr	.1	8.5	.5	830	6.1	5.8	3.1	920	1.9	.43
4574	Dudaj	Agr	.0	5.6	.7	31	.1	2.6	6.5	520	4.2	.43
4577	Dudaj	Agr	.19	9.3	.53	83	.69	6.2	8	480	.17	.45
4584	Dudaj	Agr	.0	1.5	.2	720	9	1.9	1.2	750	5.7	.51
4608	Dudaj	Agr	.17	5.3	.73	250	.68	6.3	6.8	.67	.27	.69
4638	Dudaj	Agr	.18	4.1	.61	370	.3	8.7	6.7	.39	.59	.54
4650	Bash-plain	Agr	.0	6.5	.4	21	.3	8.1	1.3	76	.19	.21
4658	Dudaj	Agr	.13	2.5	.82	37	.65	2	4.1	510	.12	.56

In this drought period, the Palmer-Bowlus (flume) technique has been adapted to measure the runoff stream in open-mouth channels to determine the rate, quantity, and size of the produced wastewater by factories and the workshop locating in Zarghan plain after treatment of wastewater. Likewise, the flow-meter (main stream) technique was employed as an accurate device for measuring runoff stream, and it determines the pressure, speed, and cross-section of the channel or tube and the amount of passing wastewater (Hosseinian, 1990; Nemerow, 1978). The total wastewater passed daily from this channel is 2,950 m^3, so this is a noticeable quantity during the current drought period, and there is also a possibility for pollution with this amount of runoff during years with a great amount of precipitation. Therefore, the transference of these elements into deeper areas is related to the penetration of water into the soil, and this is exclusively possible by means of surface water or continuous and plentiful precipitation.

On the other hand, the rate of inadvertent usage of chemical fertilizers in farmlands in this region may change properties of the soil and reduce oil permeability toward weather and water and typically harden the soils. Its excessive usage can also affect ground salinity.

Table 4. *The average of heavy metals concentration in the water shafts in Zarghan Plain (µgL^{-1}) (Winter 2012) (Agr = agriculture – Ind = Industrial)*

Identification No	Shaft location	Type of application	Cd	Ba	Co	Zn	Cr	Cu	Pb	Fe	Ni	Hg
4217	Bash-plain	Agr	.0	7	.60	25	.13	5.9	4.1	39	1.2	.1
4218	Zarghan plain	Agr	.0	3.2	.49	36	.15	6.5	5	41	2.8	.19
4219	Zarghan plain	Agr	.0	3.8	.46	29	.1	4.4	2.9	170	2.5	.22
4253	Ahochar	Agr	.0	5.1	.19	61	.25	3.9	8.1	81	2.1	.39
4255	Ahochar	Agr	.12	3.2	.19	43	.31	5.1	2.1	93	1.5	.24
4263	Ahochar	Agr	.0	6.7	.10	68	.49	3.6	6.9	85	2	.28
4264	Zarghan plain	Agr	.0	5.6	.16	21	.55	4.1	2.1	78	7.1	.18
4273	Zarghan Hose	Ind	.0	4.5	.37	46	.14	4.6	6.1	210	1.1	.14
4276	Zarghan Hose	Ind	.10	7.9	.41	43	.28	7.1	2.2	62	7.7	.72
4287	Zarghan Hose	Ind	.15	6.5	.27	50	.25	6.3	1.9	36	2.1	.69
4303	Zarghan Hose	Ind-Agr	.1	7.0	.78	31	.21	7.4	1.7	69	4.2	.63
4305	Zarghan plain	Ind	.15	7.1	.10	37	.1	5.3	1.9	79	5.2	.51
4308	Hossian Abad	Ind-Agr	.15	3.9	.10	24	.24	7.6	2	88	1.9	.15
4314	Zarghan Hose	Ind-Agr	.17	4.7	.28	73	.13	6.6	2	58	5.7	.41
4330	Dudaj	Agr	.19	7.0	.24	74	.14	4.9	1.6	65	6.1	.3
4344	Zarghan plain	Agr	.16	5.7	.79	25	.21	7	5.1	610	6	.60
4348	Zarghan plain	Agr	.0	2.3	.50	73	.1	2.3	3.1	19	1.5	.31
4352	Zarghan plain	Ind-Agr	.12	6.1	.35	82	.78	3.1	2.3	190	1.4	.18
4356	Zarghan plain	Agr	.16	3.4	.17	91	.49	5.2	1.9	64	2.5	.20
4380	Zarghan plain	Ind	.17	5.9	.27	70	.2	7.2	1.9	170	3.0	.19
4382	Zarghan plain	Ind	.12	3.6	.29	65	.17	3.5	1.8	160	2.2	.17
4383	Zarghan Hose	Ind-Agr	.18	6.6	.69	61	.15	6.2	1.4	52	4.3	.32
4419	Zarghan Hose	Ind-Agr	.12	9.1	.58	21	.27	5.7	2.5	45	2.9	.28
4519	Dudaj	Agr	.11	7.9	.76	71	.33	5.9	7	19	4.9	.47
4520	Dudaj	Agr	.13	5.7	.75	82	.51	6.8	6.2	310	4.7	.53
4521	Dudaj	Agr	.0	4.9	.41	7	.31	6.4	5.6	730	6.1	.59
4543	Dudaj	Agr	.0	8.8	.65	79	.75	5.3	5	510	2.0	.60
4545	Dudaj	Agr	0	8.1	.47	85	.56	5.6	3.2	930	2.1	.45
4574	Dudaj	Agr	.0	5.4	.60	31	.15	2.5	6.4	510	.37	.40
4577	Dudaj	Agr	.17	9.1	.51	82	.68	6	7.9	480	.16	.42
4584	Dudaj	Agr	.0	1.3	.18	73	.8	1.8	1.5	810	5.8	.62
4608	Dudaj	Agr	.12	2.3	.80	36	.64	2.1	3.9	320	.12	.51
4638	Dudaj	Agr	.15	5.1	.71	230	.68	6.5	6.7	660	.26	.62
4650	Bash-plain	Agr	.0	5.9	.39	22	.2	7.4	1.7	81	1.7	.20
4658	Dudaj	Agr	.16	3.9	.58	230	.29	8.6	6	370	.56	.53

Table 5
Heavy metals maximum permissible levels for drinking purposes surface and water-irrigation-aquatic life.

No	Metal	Aquatic life	Long termination	Surface water	Drinking water
1	Ag	-	-	0.05	1
2	Al	-	1	-	0.2
3	As	0.05	1	0.05	0.05
4	Ba	-	-	1	2
5	Cd	0.00006	0.005	0.01	0.005
6	Co	-	0.2	-	-
7	Cr	0.002	5	0.05	0.1
8	Cu	0.004	0.2	1	1
9	Fe	-	-	-	0.3
10	Hg	0.0001	-	0.0015	0.002
11	Mn	-	2	0.05	0.05
12	Mo	-	0.005	-	-
13	Ni	0.150	0.5	-	0.1
14	Pb	0.007	5	0.05	0.015
15	Sb	-	-	-	0.006
16	Se	0.001	0.05	0.01	0.05
17	Zn	0.030	5	5	5

However, according to studies conducted on the soil in 2010 and 2009, most of the soil with an EC factor higher than the standard level signified salinity in some of these lands (Radojevic & Baskin, 1999).

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Nitrate, phosphate, and urea fertilizers include some amount of heavy metals such as mercury, arsenic, and nickel, which may pollute the soil if they are used inadvertently. Phosphate fertilizers and atmospheric residues are assumed to be the major ways of polluting soil and transferring agents of this pollution to humans through the consumption plants and the smoking of tobacco (Emami, 2003;Radojevic & Baskin, 1999; Manahan , 1999). The quantity of heavy metals in chemical fertilizers is given according to Table 6.

Table 6 *Heavy metals in the chemical fertilizers*

No	Cd	Mo	Mn	Zn	Cu	Type consumption chemical fertilizer
			(ppm)			
1	187	3.3	65-70	59-165	26	(SSP) Simple Super Phosphate
2	1	0.2	0.5	0.5	0.36	UREA
3	14	0.2	8.0	3.0	3.0	(KCl) Potassium Chloride
4	-	0.1	70	0.5	0.5	Aluminium Sulfate
5	6.0	-	11	6	0.2	Calcium Ammonium Nitrate
6	-	0.1	165-245	53-100	2-12	Triple Super Phosphate
7	0.6	2.0	115-200	80	2-4	Aluminium Phosphate

The use of chemical fertilizers has only long-term effects on the soil ecosystem. However, these effects are supposed to be due to their advertent use in the first place. This issue has not been ignored: the long-term usage of basic fertilizers is not ineffective in soil, and studies conducted in India may be the reason for this issue. India has restricted long-term and inadvertent consumption of chemical fertilizers to the following cases:
The effect of zinc on soil internal reactions
Toxicity due to increase of fluorine ions
Toxicity due to increase of chlorine ions in soil
Toxicity due to increase of cadmium ions in soil
Toxicity due to increase of heavy-metallic ions

Other agents and problems (W.H.O, 1989; Chino, 1991; FAO, 1992; Radojevic & Baskin, 1999; Skoog, 1985; Manahan , 1999; WaldRon, 1991). Long-term usage of various types of chemical fertilizers such as urea, ammonium sulfate, ammonium chloride, and waterless ammoniac (anhydride) under adverse conditions may reduce pH in soil and make the soil extremely acidic (soil pH should be close to neutral). Accumulation of chlorine ions due to the use of some fertilizers such as ammonium chloride and potassium chloride may cause some allergies and sensitivities in crops like bean, potato, lettuce, citrus, and grape. This accumulation restricts absorption of other needed fertilizers by the root; therefore, the plant suffers from lack of vital elements.
Thus, in addition to industrial runoff and treated wastewaters from factories, which have not been perfectly treated and include heavy metals, inadvertent usage of chemical fertilizers and pesticides, herbicides, and fungicides may contaminate surface and underground waters with heavy metals.

Conclusion

The results of this study and survey indicate that the 450 water wells in this region will be threatened during years with plentiful precipitation if heavy metals are stored in the soil. Similarly, inadvertent use of chemical fertilizers may change the soil, and these changes will affect cultivated crops there. If these crops are consumed by humans, they will endanger their health.

Element	Season	Minimun	Maximum	Mean	Standard Deviation
Ba	spring	0.10	9.00	5.52	2.27
	summer	0.32	59.0	6.75	9.40
	fall	0.60	9.50	5.50	2.35
	winter	1.30	9.10	5.55	2.,00
Cd	spring	0.00	0.30	0.13	0.11
	summer	0.00	0.31	0.10	0.08
	fall	0.00	1.00	0.13	0.17
	winter	0.00	0.19	0.09	0.07
Co	spring	0.001	0.900	0.405	0.265
	summer	0.006	7.500	1.164	1.547
	fall	0.10	700.0	20.5	118.2
	winter	0.001	0.900	0.405	0.265
Cr	spring	0.00	35.0	1.43	5.86
	summer	0.00	8.90	1.79	2.42
	fall	0.00	37.0	2.69	6.43
	winter	0.10	0.80	0.35	0.22
Cu	spring	0.10	70.0	11.8	17.9
	summer	0.30	65.0	10.7	15.8
	fall	1.90	8.70	5.60	1.84
	winter	1.80	8.60	5.38	1.72
Hg	spring	0.001	0.50	0.64	1.201
	summer	0.001	0.82	0.38	0.241
	fall	0.13	0.82	0.42	0.19
	winter	0.10	0.81	0.40	0.19
Fe	spring	0.07	860.0	143.3	232.1
	summer	0.31	830.0	230.0	244.6
	fall	17.0	920.0	238.3	270.5
	winter	19.0	930.0	237.0	255.8
Ni	spring	0.02	60.0	4.32	9.92
	summer	0.10	105.0	6.15	17.31
	fall	0.12	8.00	2.86	2.25
	winter	0.12	7.70	3.01	2.19
Pb	spring	1.00	9.20	3.90	2.50
	summer	0.20	8.90	3.51	2.57
	fall	0.20	8.70	3.80	2.46
	winter	0.70	8.10	3.58	2.14
Zn	spring	2	800	121	199
	summer	10	850	188	277
	fall	19	830	158	216
	winter	2	800	121	199

Table 7 *Statistical descriptors related to Ba, Cd, Co, Cr, Cu, Hg, Fe, Ni and Zn in Zarghan zone'water wells in the different seasonal periods (values expressed in µg/L on 35 samples)*

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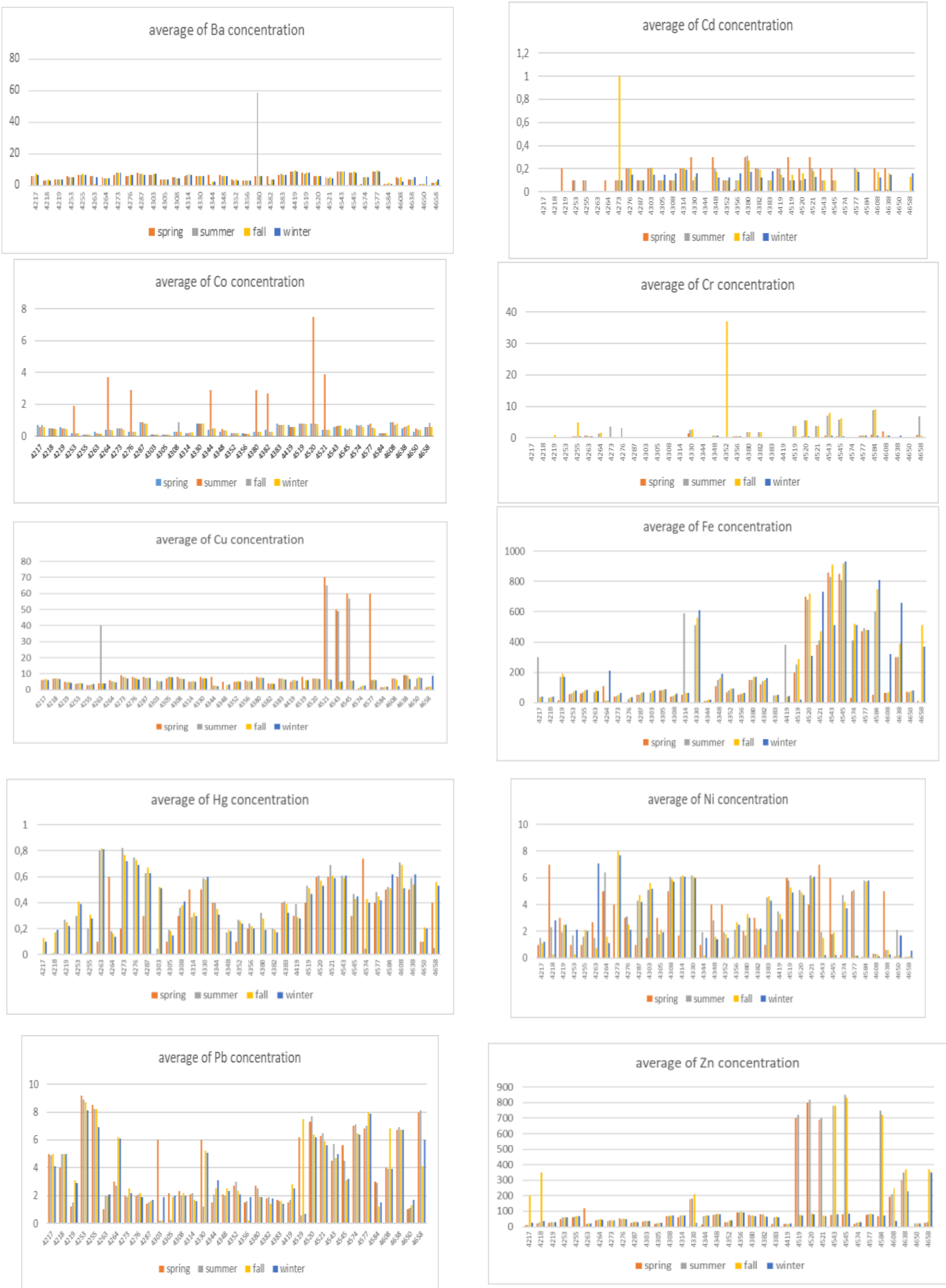

Figure 2. *Comparison of Ba, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Zn in Zarghan zone's water wells in four seasons (values expressed in µg/L).*

On the other hand, pesticides used in farmlands on the plane, are not synthesized and will remain in the soil for many years. They are sublimated without chemical changes, and at the same time, they absorb particles at the surface of the soil. They are also subjected to optical, chemical, and biochemical synthesis reactions. As a result, all three aforesaid factors including heavy metals, inadvertent usage of chemical fertilizers, and excessive use of pesticides can affect water and soil in this zone and make the crops hazardous for the consumers.

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