

## Groundwater Contamination by Heavy Metals in Water Resources of Shiraz Area

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**ABSTRACT.** Lack of sewage collection systems, percolation of surface waters, and seepage of wells have raised the groundwater table in Shiraz area in the south of Iran. The growing population generates environmental pollution resulting in the degradation of the quality of surface and groundwaters used for agriculture. Inorganic and organic pollutants have been traced in Shiraz water resources. Heavy metals,  $As^{+2}$ ,  $Cd^{2+}$ ,  $Cr^{2+}$ ,  $Fe^{2+}$ ,  $Hg^{2+}$ , and  $Pb^{2+}$  have been reported as potential pollutants of both surface and groundwaters. The safety of groundwater supplies in Shiraz was studied with respect to heavy metal concentrations. From 50 semi deep wells, which supply water for agricultural production, three water samples per well were examined to determine the physical and chemical characteristics of the water. The results of the study indicated that the concentration of  $Cd^{2+}$ ,  $Cr^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ , and  $Pb^{2+}$  exceed permissible values for crop production. A network of gallery systems was proposed for wastewater collection and the disposal of Shiraz groundwater, to increase the water table depth in urban areas. It is estimated that about 100M m<sup>3</sup> wastewater could be drained annually through the proposed gallery system which could be used for agricultural production. It is believed that mixing the drained waters from the proposed network of galleries with the agricultural water supplies will help control concentrations of heavy metals so they do not have serious acute impacts on agricultural production. The chronic effects of the impacts of water quality on agricultural production should be monitored temporarily.

**Keywords:** Deep wells, Groundwater, Heavy metals, Iran, Shiraz, Semi-deep wells

### INTRODUCTION

The presence of heavy metals in surface and groundwaters is usually related to man's industrial activities. Vertical displacement and leaching of trace metals may occur in the soil profile and contaminate the groundwater (1, 15, 19 and 11). Urban runoff may contain significant concentrations of iron, lead, zinc, and copper, and to a lesser extent, cadmium, chromium, mercury and nickel (4, 12 and 8). Thus, concentrations of metals in water may be significant, particularly in the groundwater (6). Obviously, because of the possible influence on the human food chain, environmental contamination by heavy metals is a global concern nowadays. Therefore, it is worthwhile to estimate the spatial distribution of the heavy metal concentration in the water supply wells of a given region (e.g. Shiraz area). To evaluate natural concentration variations of heavy metals and to assess their contamination in

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groundwater, it is necessary to survey trace metal background levels to understand their distribution and effects on the quality of irrigation water and agricultural crop production (13 and 7). The objective of the present work was to study various heavy metals' ions concentrations in the deep and semi- deep water wells of Shiraz region, Fars province, south of Iran.

## MATERIALS AND METHODS

The 1009 km<sup>2</sup> Shiraz basin partly comprises of the watershed of the Khoshk (“dry”) seasonal river, which runs to Maharloo salt lake located to the south of the city. Shiraz has a population of about 1,500,000 and is the fifth major city of the country. The land gradient of the city slopes from the northeast ending with a very mild slope near Maharloo Salt Lake. Figure, 1 shows the location of Shiraz. Almost half of the water used for domestic and industrial purposes is supplied from deep and semi-deep wells scattered in the region. Due to the lack of a sewage collection system in the city, about 80-85% of the municipal water used (250 L per cap. per day) drains into the groundwater, mostly reaching Maharloo Salt Lake. The area is waterlogged during wet years when the runoff water in the Khoshk River is high. In the southwest and south of Shiraz where small and medium size industrial plants dealing with melting zinc, lead, and cast iron are located, traces of Cd<sup>2+</sup>, Cr<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, etc. leach through the soil profile and contaminate the groundwater, resulting in the worst water quality in the Shiraz area (see G4 on city map, fig.2).

Due to the topographic situation and land use of different parts of Shiraz, the Shiraz basin is divided into 5 sections. Each part contains a number of wells that are referred to as Group 1, through Group 5 as follows.

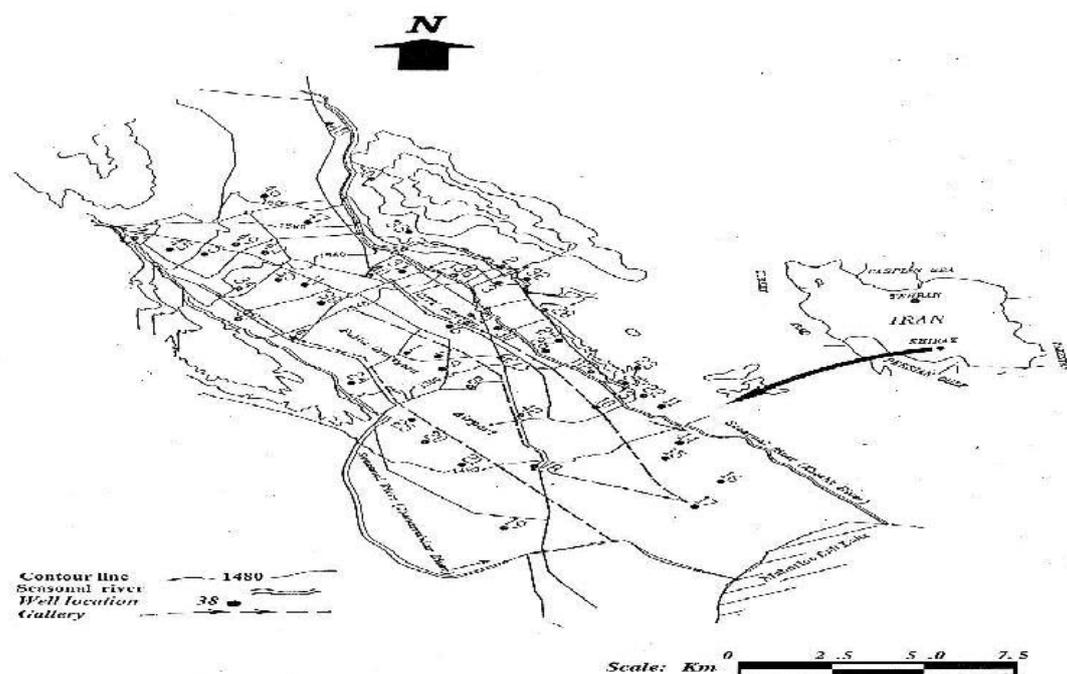


Fig. 1. Location of the water sampling wells and purposed gallery routes of Shiraz

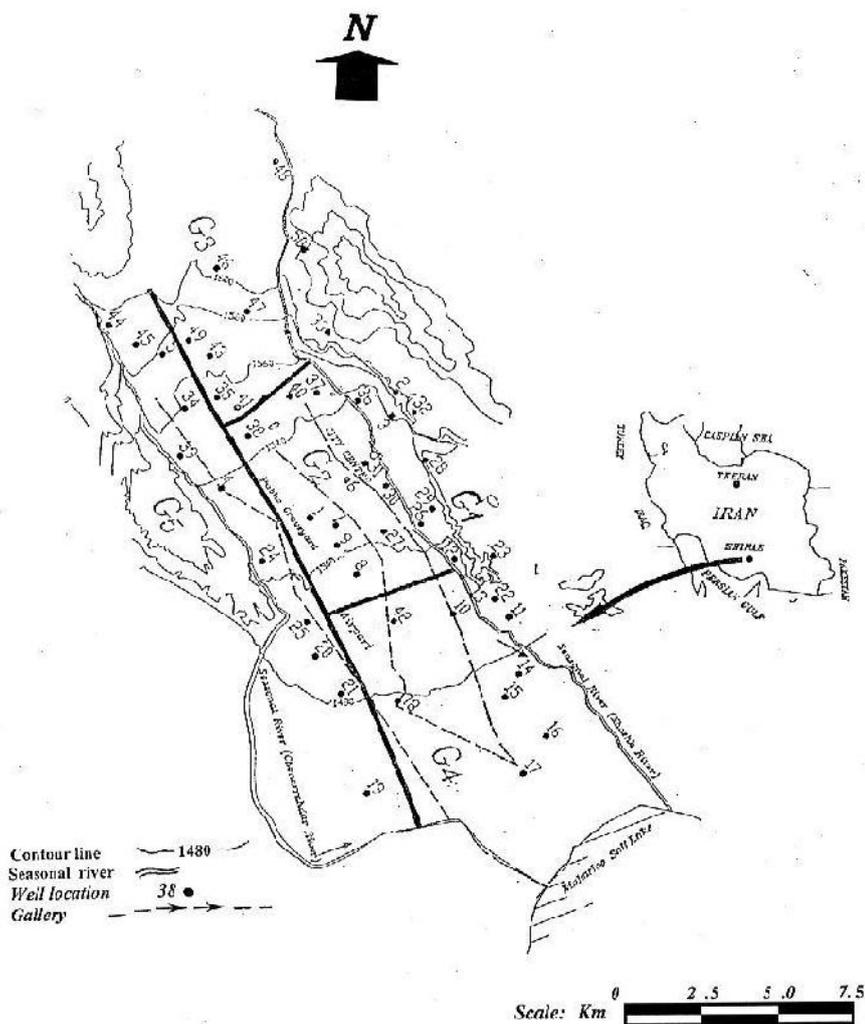


Fig. 2. Partitioning of Shiraz basin and sampling water wells groups

**Group 1**

contains 14 wells (2, 3, 11, 12, 13, 22, 23, 26, 28, 29, 32, 33, 36, and 50). These wells are located in the upper part of the Khoshk river (Fig. 1). This part of the city is mostly urban and due to the slope steepness all the wastewater from the cesspools, drains rapidly to the south, causing water logging in the flat portion of the basin lands near Maharloo Salt Lake. The Carstic geological formation of this area coupled with the rapid natural drainage of the percolation water due to high slope steepness, results in the best quality of groundwater in the area.

**Group 2**

consists 11 wells (1, 6, 7, 8, 9, 27, 30, 31, 37, 38, and 40). These wells are located in the center of the city. Specially, wells 1, 7, and 9 are situated near the Shiraz public graveyard. Accordingly, these wells are expected to show more deterioration in quality than the wells of Group1.

**Group 3**

has 7 wells (35, 41, 43, 46, 47, 48, and 49). Located in the west and the north the city basin. It is expected that the water from these wells will be best for all-purpose.

#### **Group 4**

contains 7 wells (10, 14, 15, 16, 17, 18, and 42) scattered in the flat and waterlogged part of the basin (Fig. 2). Due to the lack of a system for sewage collection and drainage in this area, the worst water quality is expected here.

#### **Group 5**

contains 11 wells (4, 5, 19, 20, 21, 24, 25, 34, 39, 44, and 45), scattered in the marginal part of the west of the city basin. Some are located in areas that are waterlogged during wet years. Some of the groundwater at the north of the city is drained to this area before finally reaching the lands around wells 21 and 19. Water quality in this area (both surface and groundwater) are not expected to be useful for agricultural purposes.

The total annual runoff from the Khoshk River to Maharloo Salt Lake has an average of about 52.9 Mm<sup>3</sup>, of which 26.4 Mm<sup>3</sup> is the base flow of the river (5). Because of the shortage of river groundwater, almost 50% of the water for agriculture is pumped from these semi-deep and deep groundwater wells.

These 50 wells were selected randomly to investigate whether the occurrence of heavy metals was affecting groundwater quality. Three sets of 2-liter water samples were collected from each well in polyethylene bottles. The first water sample was taken immediately at the start of pumping, and the second one was collected 15 minutes after pumping, and the third was taken after an hour and a half. The total concentration of heavy metals in the water samples was checked using Atomic absorption (14 and 3) (designed by G. B. C. 903, Australia). Chlorine, sulfate ions and PO<sub>4</sub><sup>3-</sup> were detected by Mohr and gravimetric methods, as described by the Standard Methods of the American Public Health Association (2), using a spectrophotometer (designed by G. B. C. 911, Australia). Other ions were also measured according to the Standard Methods of the American Public Health Association (2). The average concentrations of the three water samples per well formed the basis of the interpretation of the water quality of the wells under study.

## **RESULTS AND DISCUSSION**

Table 1 shows that concentrations of heavy metals, chlorine and sulfate of the specified study wells are almost at hazardous levels. In the table, zero or non-significant levels of the specified ions are indicated as blanks.

Chemical analysis of the water samples showed that Ba<sup>2+</sup> concentration exceeded permissible values only in wells 24 and 25 (1.30 and 1.02 mgL<sup>-1</sup>, respectively, see Table 1). These wells belong to Group 5 wells that are located in the low land areas.

Cadmium ions exceeded permissible concentrations in 28 water wells with a range of 0.01 mgL<sup>-1</sup> to 0.06 mgL<sup>-1</sup>. Well 26 had the highest concentration (0.06 mgL<sup>-1</sup>) Well 17 from Group 4 had a cadmium concentration of 0.04 mgL<sup>-1</sup>. This is considered normal for this part of the basin. Isoconcentration contours of Cd<sup>2+</sup> ions are shown in Figure 3.

Chromium was traced in only three samples from wells 17, 24, and 25, with 0.04, 0.05, and 0.07 mgL<sup>-1</sup>, respectively. These wells are situated in flat and lower land areas, identified as Group 4 and Group 5 wells. The accumulation of seepage

water from the whole basin area to this part is the cause of elevated concentration here.

Table 1. Concentrations of heavy metal ions and Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in Shiraz water wells<sup>†</sup>

Well No.	Well group	Ba <sup>2+</sup>	Cd <sup>2+</sup>	Cr <sup>2+</sup>	Fe <sup>2+</sup>	Mn <sup>2+</sup>	Pb <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
1	2		0.01			0.01 <sup>‡</sup>	0.04	234	668
2	1				0.20	0.01			
3	1		0.01		4.80	0.01		402	328
4	5		0.013		0.30	0.55		776	1947
5	3						0.04		499
6	2		0.01						239
7	2				2.20				592
8	2		0.01			0.015		304	964
9	2		0.01			0.03	0.06	480	2072
10	4		0.01			0.01	0.04	383	1461
11	1								226
12	1					0.01			
13	1		0.01			0.02		285	483
14	4								
15	4		0.01						
16	4							400	243
17	4		0.04	0.04		0.01		1564	355
18	4		0.01		2.70	0.03		262	1300
19	5					0.01		813	615
20	5				0.40	0.02		453	1784
21	5		0.01		0.20	0.04		296	1530
22	1					0.01			
23	1				1.30	0.08			296
24	5	1.30	0.01			0.06	0.04	556	2606
25	5	1.02	0.012	0.05		0.02	0.06	667	2593
26	1		0.06	0.07		0.01	0.02	462	784
27	2		0.01			0.01		248	618
28	1								
29	1								257
30	2		0.01			0.01		398	844
31	2		0.01			0.01		343	864
32	1								
33	1		0.01						
34	5		0.01			0.01			1031
35	3					0.01		305	1307
36	1					0.01			225
37	2					0.01			317
38	2					0.01		396	1187
39	5		0.01		2.50	0.05		277	1316
40	2		0.01						251
41	3		0.01		0.20	0.01		323	763
42	4		0.01			0.03		227	987
43	3				1.20	0.06		440	1245
44	5		0.01						1216
45	5		0.01		0.70			267	944
46	3								355
47	3		0.01			0.01			409
48	3		0.01						
49	3								428
50	1					0.01			

<sup>†</sup> Only the concentrations which are significant are shown

<sup>‡</sup> The water was not potable with Mn<sup>2+</sup> concentration ≥ 0.01 mgL<sup>-1</sup> (10)



The manganese ion concentration range was  $0.01 \text{ mgL}^{-1}$  to  $0.55 \text{ mgL}^{-1}$ , with the highest concentration detected in well 4. However, in 33 wells,  $\text{Mn}^{2+}$  was more than the permissible concentrations (for portable water). It should be noted that well 4 belonged to the Group 5 wells, in which high concentrations of heavy metals are expected. Isoconcentration contours of  $\text{Mn}^{2+}$  ions are shown in Figure 5.

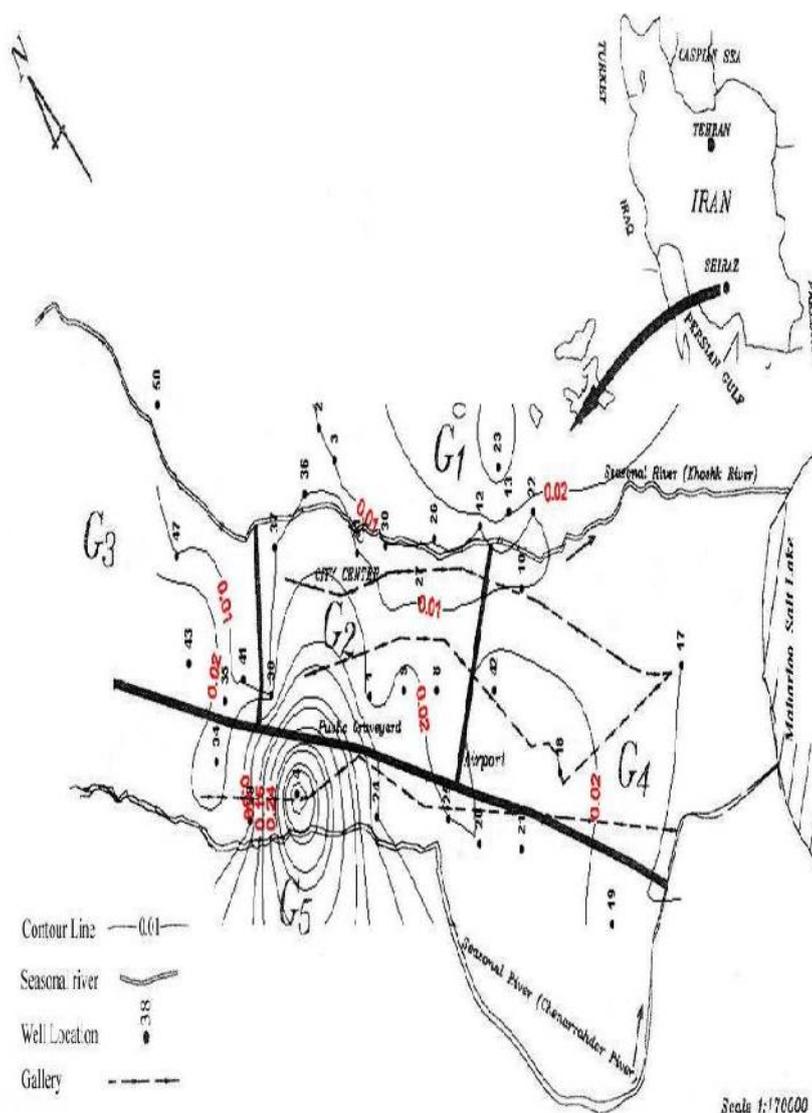


Fig. 5. Isoconcentration contours of  $\text{Mn}^{++}$  ion for Shiraz basin

The range of the detected  $\text{Pb}^{2+}$  concentrations was between  $0.02 \text{ mgL}^{-1}$  and  $0.06 \text{ mgL}^{-1}$ , in wells 26 and 9, respectively. Permissible lead concentration (for domestic use) was exceeded in only 7 wells (1, 5, 9, 10, 24, 25, and 26). Isoconcentration contours of  $\text{Pb}^{2+}$  ions are shown in Figure 6.

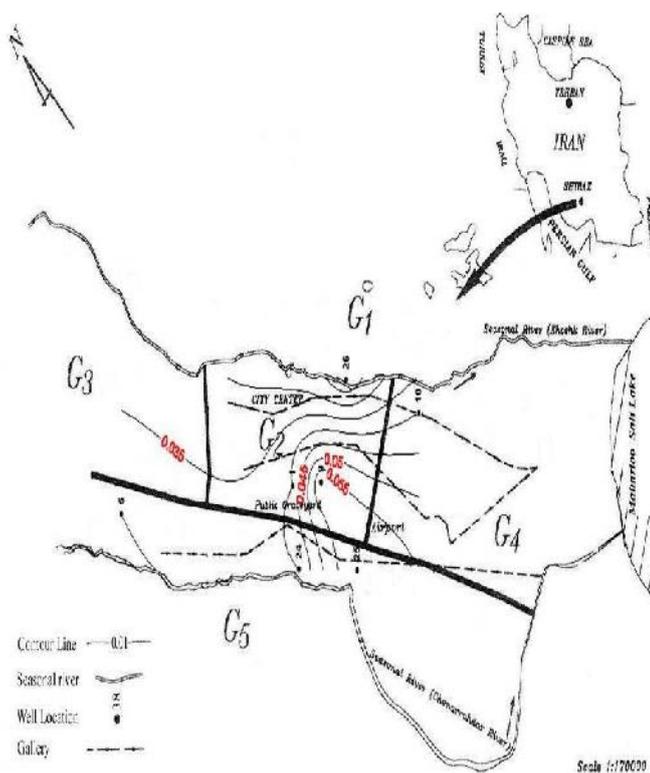


Fig. 6. Isoconcentration contours of  $Pb^{++}$  ion for Shiraz basin

Higher than permissible values for domestic and agricultural usage of chlorine ions ( $250 \text{ mgL}^{-1}$ , FAO, 1985) were seen in 27 wells. The range was  $227 \text{ mgL}^{-1}$  to  $1564 \text{ mgL}^{-1}$ , in wells 39 and 17 respectively. Isoconcentration contours of  $Cl^{-}$  ions are shown in Figure 7.

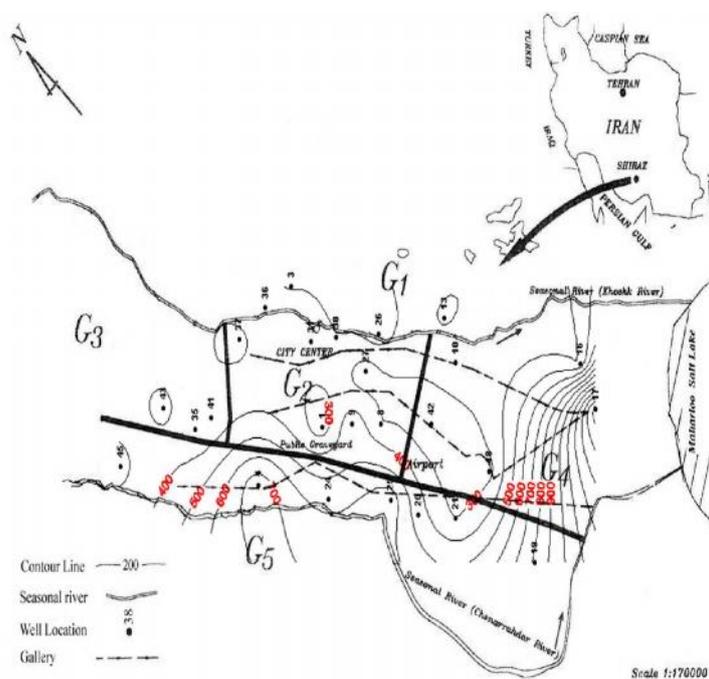


Fig. 7. Isoconcentration contours of  $Cl^{-}$  ion for Shiraz basin

Sulfate ion concentration ranged from 225 mgL<sup>-1</sup> to 2606 mgL<sup>-1</sup> in wells 36 and 24, respectively. These concentrations show that the water from these wells should not be permitted for drinking, industrial use, or even irrigation of agricultural lands. The highest concentration was reported for the water sample of well 24 which belonged to group 5 wells. Isoconcentration contours of  $\text{SO}_4^{2-}$  ions are shown in Figure 8.

Taken together, these results indicate that well water in Shiraz area is not safe. The water from the wells is heavily contaminated with more than permissible levels of Chlorine, Sulfate and certain amounts of heavy metals. To resolve the problem, a wastewater collection system needs to be established. Such a system would: (1) help lower groundwater-table levels in urban areas, (2) free the groundwater from contamination, and (3) direct the water to areas under cultivation. Figure 1 illustrates the proposed network of the gallery system. It involves three separate galleries, each about 8 kilometers long. The depth of each gallery would be about 35 m at the starting point, reduced to ground elevation near the contour line of 1480, where the collected water can be transferred by pumping or gravity to other parts of Fars Province rather than being drained to the salty Lake of Maharloo. It is estimated that about 100 Mm<sup>3</sup> yr<sup>-1</sup> of water will be transferred through this network system to irrigate about 10,000 ha of agricultural land if the quality can meet the permissible levels of different ions. Building a sewage water collection system and a wastewater plant for Shiraz city is also suggested. After construction of the proposed plant the treated wastewater will be reused for irrigation of the above mentioned agricultural lands.

## CONCLUSIONS

To investigate the quality of deep and semi-deep water supply wells for agricultural and industrial use in the Shiraz region, three samples were collected from each of the 50 wells under study and the concentrations of the anions and cations were measured in the laboratory. The results showed that six wells (1, 4, 9, 10, 24, and 25) had the richest concentration of  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . Wells 1, 9, and 10 had trace concentrations of  $\text{Cr}^{2+}$  and  $\text{Fe}^{2+}$ , lower than the recommended level for domestic usage. Chlorine was detected in 27 wells while sulfate was found in 40 wells at more than the permissible concentration levels. Manganese and Cadmium were detected in 33 and 28 water wells, respectively. Iron ions were traced in 12 wells while Chromium and Barium were only seen in 3 and 2 wells respectively. Lead was detected in seven wells, the concentration exceeding permissible levels for domestic use.

A collection gallery system is proposed to drain seepage water and to convey surface water to a seasonal river other than Maharloo Salt Lake. Due to high concentrations of chlorine and sulfate in Group 5 wells, the collected water of this part needs to be drained to a seasonal river, such as the Chenarrahdar So that the discharge water of upper and middle galleries can be mixed together. In an average year (with 350 mm precipitation) almost 90 Mm<sup>3</sup> yr<sup>-1</sup> of water will be collected, which could be conveyed for agricultural use. Therefore, the groundwater quality of the Shiraz basin will permit agricultural use. The water quality should be regularly

checked for chlorine and sulfate. With proper irrigation management, the water could be used for irrigation. It is expected that the proposed gallery system will help alleviate groundwater depth in the Shiraz basin and shift the disposal of polluted water to the east rather than the local water table, as occurring currently. It is anticipated that the heavy metal concentrations of the groundwater in the end of the upper and middle galleries' mixing points can be reduced to meet the permissible level for agricultural use. Recently, a wastewater treatment plant was proposed to be constructed in the south of Shiraz to prevent and regulate the contamination of groundwater level and pollution.

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## آلودگی آب زیر زمینی به فلزات سنگین در منابع آب منطقه شیراز

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**چکیده** - نبود سیستم جمع آوری فاضلاب، نفوذ آبهای سطحی و نشت از دیواره چاه های فاضلاب خانگی سبب بالا آمدن سطح آب زیر زمینی منطقه شیراز شده است. افزایش جمعیت، موجب آلودگی محیط شده که منجر به زوال کیفیت آبهای سطحی و زیر زمینی مورد استفاده در کشاورزی می گردد. آلوده کننده های آلی و غیر آلی در منابع آب شیراز مشاهده شده است از جمله فلزات سنگین مانند آرسنیک، کادمیم، کروم، آهن، جیوه و سرب به عنوان عمده ترین آلوده کننده های آب زیر زمینی و سطحی گزارش شده اند. در این تحقیق سلامت ذخایر آب زیر زمینی شیراز از نظر غلظت فلزات سنگین مطالعه گردید. از ۵۰ چاه نیمه عمیق تامین کننده نیاز آبی بخش کشاورزی سه نمونه گرفته و خصوصیات فیزیکی و شیمیایی آب آنها بررسی گردید. نتایج این تحقیق نشان می دهد که غلظت یون های کادمیم، کروم، آهن، منگنز و سرب بیش از حد مجاز برای تولیدات گیاهی می باشد. شبکه جمع آوری فاضلاب و دفع آب زیر زمینی شیراز برای افزایش عمق سطح ایستابی در مناطق شهری پیشنهاد شده است. تخمین زده می شود در حدود ۱۰۰ میلیون متر مکعب فاضلاب که سالانه توسط این سیستم زهکشی دفع می شود می تواند برای تولیدات کشاورزی استفاده شود. مطمئناً ترکیب آب زهکش شده از سیستم زهکشی با آب منابع آب کشاورزی غلظت فلزات سنگین را کنترل خواهد کرد. در نتیجه اثرات جدی در کوتاه مدت روی تولیدات کشاورزی نخواهد داشت. بررسی کنترلی در مورد اثرات بلند مدت آن لازم است.

واژه های کلیدی: آب زیرزمینی، ایران، شیراز، چاه های عمیق، چاه های نیمه عمیق، فلزات سنگین

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