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Geochemical Contamination in Seyab River, Islam Shahr, Iran

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Abstract
Seyab River, which crosses Southwest of Tehran to Islam Shahr (10km), is an extremely important river that is in contact with a population of about one million. Freshly deposited seasonal sediments were collected from depths of 0–20 cm at 4 locations (1 to 4) along the 10-km long channel length, in the spring season of the year 2008. There is no water during the summer to the autumn seasons, with the lowest content in winter and the highest content in spring. Hence, the sampling was carried out during spring. In this research, 12 sediment samples, 9 plant samples and 8 water samples were collected from Seyab River and its periphery. The samples were analyzed by AAS for Co, Ni, Cr, Cu, Pb, Zn, Mg, Na, K, Ca, Cd, Se and $HCO3^-$, $CO3^{-2}$, Cl^-, $SO4^{-2}$. The concentrations of Ag, Hg, As, were less than the detection limit for all samples. Data processing shows the average concentrations of Cu, Cr, Zn, Mg and Ca were higher than the upper continental crust background levels. Se was at 174 times and Cd at 220 times the said level. Islam Shahr has been newly developed during the past 15 years, thus such high contaminations during such a short period are a cause for concern. Anthropogenic impacts, industrialization, farming activities, transport, urbanization, animal and human excrement and domestic wastes have affected the river, contaminating it and its sediments with heavy metals especially Se and Cd.

Keywords: water, plants and sediment pollution, seyab river, islam shahr, iran.

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آلودگی های ژئوشیمیایی در رودخانه سیاب اسلام شهر، جنوب تهران

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چکیده
اسلام شهر درجنوب شهر تهران قرار دارد که از شمال به تهران، از شرق به شهرستان ری، از ناحیه جنوب به رباط کریم و از غرب به شهرستان شهریار محدود می‌گردد. مهم‌ترین رودخانه‌ای که از کرانه غربی شهر عبور می‌کند، رودخانه کرج نام دارد که پر آب ترین رودخانه‌های دامنه جنوبی البرز است که در ۴۰ کیلومتری غرب تهران از خرسنگ کوه سرچشمه می‌گیرد و در مسیر خود در دشت اسلام شهر به نام‌های سیاه آب یا سیاب، شاطره و سالور نیز خوانده می‌شود. به منظور تعیین میزان آلودگی آب این رودخانه و زمین‌های اطراف تعداد ۲۹ نمونه از آب رودخانه، خاک و گیاهان کنار آن در ۴ نقطه اوایل، داخل و خارج شهرک چهاردانگه در مجاورات اسلام‌شهر در اواخر فصل بهار که آب رودخانه بیشترین آلودگی را دارد، برداشت گردید. نمونه‌ها در آزمایشگاه مرکز تحقیقات شیمی دانشگاه شهید بهشتی بوسیله دستگاه جذب اتمی برای عناصر Co, Ni, Cr, Cu, Pb, Zn, Mg, Na, K, Ca, Cd, Se و ترکیبات $HCO3^-$, $CO3^{-2}$, Cl^-, $SO4^{-2}$ اندازه‌گیری شدند. مقادیر عناصر Ag, Hg, As کمتر از حد حساسیت دستگاه بود و اندازه‌گیری نشد. بررسی نتایج حاصل از تجزیه شیمیایی این نمونه‌ها نشان می‌دهد که میزان آلودگی حاصل از تاثیر فعالیت‌های مختلف خانگی، صنعتی و کشاورزی در مسیر رودخانه باعث آلودگی آن از نظر عناصر فلزات سنگین و عنصر خطرناک سلنیوم و کادمیوم شده است. میزان آلودگی رسوبات حاشیه رودخانه برای سلنیوم ۱۷۴ برابر و برای کادمیوم ۲۲۰ برابر میانگین پوسته بالائی زمین است. چنین آلودگی برای رودخانه مجاور اسلام شهر با ۱۵ سال سابقه توسعه شهری بسیار خطرناک به نظر می‌رسد.

کلیدواژه‌ها: آب، گیاه، رسوب، آلودگی، رودخانه سیاب، اسلام شهر.

Introduction

Sediment and soil are usually considered as sinks for trace metals. From there trace metals are able to move towards the water column or accumulate in plants and, consequently, contaminate the food chain. The overall objective of this study is to understand better the nature of sediment, water and plant contamination in the Seyab River area, and includes three aspects nearly: (1) to investigating the main sources of heavy metal contamination in the area; (2) determining contamination trends and pollutant types in the area; and (3) finding a proper evaluation approach to metal contamination the area. Such information should be useful for enhancing safe farming areas around Seyab River while minimizing the adverse effects of sediment and soil contamination on human health.

Seyab River, which crosses the Southwest of Tehran to Islam Shahr (10 km), is one of the most important rivers in contact with a population of about one million inhabitants (Fig.1). Anthropogenic activities, industrialization, farming activities, transport, urbanization, animal and human excrement and domestic wastes have affected the river, contaminating it and its sediments with heavy metals. The area is situated in the subtropical region, with hot summers (April–September) and relatively cool and dry winters (October–March). The annual mean temperature is 17°C. The annual total rainfall amounts to approximately 231 mm, most of which falls between September and April.

Seyab River is located in the metropolitan region of Islam Shahr, to the South of Tehran. It is a relatively highly contaminated river, and is becoming gradually polluted due to high urban growth, and it is thus more probable for the soil to interact with the population that lives in the city. However, no systematic study has been made on this river to assess the distribution of the heavy metals in water, soil and plants of the area. The present results provide a general view of metal concentration and distribution in water, sediments and plants of Seyab River area.

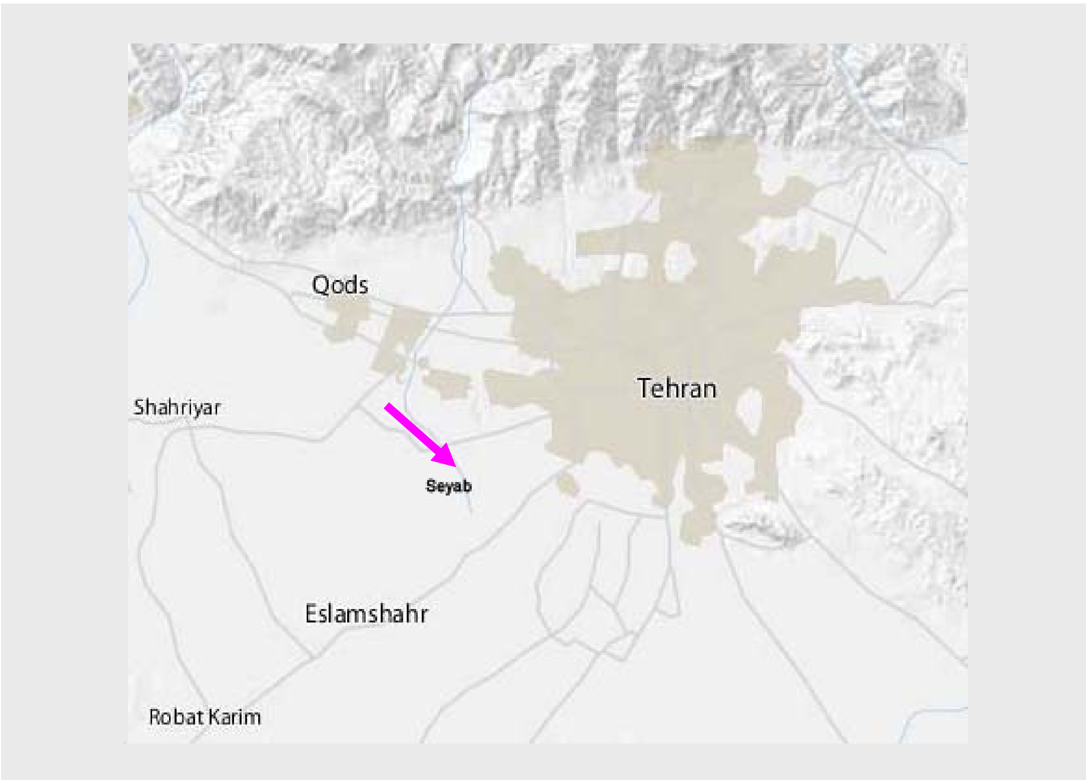

Figure 1. Location photo of Islam Shahr city and Seyab River

Analytical Methods

In this research, 12 sediment samples, 9 plants sample and 8 water samples were collected from Seyab River and its surroundings. Surface sediment (0 to 20 cm depth), water and plants were collected from the river in the season of spring. Samples were collected with plastic collectors, returned to the laboratory in polyethylene bottles, and stored at 4°C. The pH in the water and sediment samples varied between 7 and 8. Prior to analysis, the sediment samples were dried at 105 °C for 48 hours and then sieved (<2 mm) using stainless steel sieves to remove large debris, gravel sized materials and plant roots. Ten gr of the sample were taken in 50 mL distilled water and agitated for 10 minutes. The solution was left undisturbed for 1 hour with occasional shaking before measuring the pH. A combined glass electrode connected to a pH-meter was used for pH measurements. The sieved samples were homogenized and ground with a pestle and a mortar and kept in desiccators prior to chemical digestion. A strong acid digestion method was applied to dissolve the samples and their inorganic contents in solution. All reagents were obtained from the analytical grade of Merck (Darmstadt, Germany). Hydrochloric acid, fluoric acid and nitric acid for solution acidification were of ultra pure quality. Calibration standards of elements were prepared by appropriate dilution of the 1000 mg L−1 stock solutions (Merck). All solutions were prepared with ultra pure water. All glassware and polyethylene bottles were cleaned by soaking in 10% (v/v) HNO3 (Merck) followed by three rinses with deionized water. Sediment, water and plant reference material (Iranian Internal standard) were used for validation of the methodology for carbonates and total concentrations of these elements.

Digestion was by a standard procedure (APHA, 1992). In brief, the tertiary acid mixes HNO3–HClO4–HF and HNO3–H2SO4–HClO4 were used for the digestion of soil or similar materials and vegetation. Standard analytical methods were used for all types of sample analysis: pH and Eh were measured using a single electrode pH and mV meter, respectively; conductivity using a conductivity meter; chloride by the silver nitrate method; sulphate with a turbidity meter. Atomic absorption spectrometry (ASS, Perkin-Elmer) was used to determine strong-acid extractable elemental concentrations of the samples in the Chemical Laboratory of Shahid Beheshti University. The samples were analyzed by ASS for Co, Ni, Cr, Cu, Pb, Zn, Mg, Na, K, Ca, Cd, Se and $HCO3^{-}$, $CO3^{-2}$, Cl^{-}, $SO4^{-2}$ (Tables 1-3). The concentrations of Ag, Hg, As, were less than the detection limit in all samples. Metal quantification was based on calibration curves which were determined several times during the period of analysis. The statistical analyses were conducted using the SPSS software package.

Table 1- Elemental concentrations of sediment in the Seyab River area (ppm).

Sample	K%	Na%	Ca%	Mg%	Se $_{ppm}$	Cu $_{ppm}$	Zn $_{ppm}$	Cr $_{ppm}$	d $_{ppm}$
1-1	0.17	0.17	2.42	1.22	12.4	61	110	-	-
1-2	0.29	0.08	1.74	0.93	11.9	44.9	190	-	9.6
2-1	0.16	0.11	2.44	1.07	8.87	78.4	89	86	-
2-2	0.53	0.38	3.17	1.29	17.2	54	180	33	35
2-3	0.22	0.13	1.87	0.78	17.2	54	112	19	-
3-1	0.43	0.19	4.3	1.33	21	45	290	19	-
3-2	0.77	0.76	4.3	1.32	20.3	54	110	33	-
3-3	0.10	0.08	2.68	1.97	13.2	69.9	106.4	32.5	-
3-4	0.42	0.72	4.46	1.02	18.6	54	150	19	-
4-1	0.22	0.07	2.19	0.80	14.2	45	92	-	22
4-2	0.38	0.72	2.68	0.94	16.6	54	310	33	-
4-3	0.19	0.12	1.71	0.68	16.2	28	108	-	-

The concentration of Ni, Co, Pb was less than detection limit in all samples.

Table 2- Elemental concentrations of **water** in seyab river (ppm)

Sample	K	Na	Ca	Mg	Se	Cl^-	$CO3^{-2}$	$HCO3^{-2}$
1-1	3.58	68.5	74.9	36.2	0.010	165.66	30	366
1-2	2.17	77	102.9	41.2	0.086	177.5	30	335.5
1-3	2.94	68.5	97.8	44.4	0.083	142	15	396.5
1-4	7.43	72.7	80	9.4	0.075	177.5	-	396.5
1-5	5.8	72.7	74.9	28.3	0.083	230.75	45	305
2-1	4.3	72.7	102.9	18.7	0.048	159.75	30	335.5
4-1	8.2	128	69.8	9.48	0.024	177.5	40	427
4-2	5.12	68.5	64.73	5.17	.027	142	15	305

The concentration of Cr, Cd, Co, Cu, Zn, Ni, Pb, $SO4^{-2}$ was less than detection limit in all samples.

Table 3- Elemental concentrations of **plant** in seyab river area (ppm)

Sample	K	Na	Ca	Mg	Se	Zn	Cl^-	$HCO3^{-2}$
2-1	2.22	0.42	0.40	0.21	30.7	0.32	248	366
2-2	1.99	0.16	0.22	0.12	59.8	59.8	249	183
2-3	3.40	2.39	0.54	0.59	37.6	59.4	355	244
3-1	2.78	0.13	0.46	0.18	15.9	53.7	391	275
3-2	3.17	0.19	0.52	0.29	59.7	77.3	160	275
3-3	4.77	0.83	1.16	0.65	42	14	249	336
4-1	2.78	0.10	0.49	0.58	59	52	355	153
4-2	2.89	0.35	0.34	0.11	39	59	497	214
4-3	4.47	0.16	0.97	0.20	100	0.37	266	397

The concentration of Cr, Cd, Co, Cu, Ni, Pb, $CO3^{-2}$, $SO4^{-2}$ was less than detection limit in all samples.

Results and Discussions

The appearance of trace metals in the surface horizon of river sediments originates from the vegetation, atmospheric deposition and adsorption by soil organic matter. The sediments in the Seyab River environment were accumulated by flood activity. In such sediments the metal content varied greatly between sampling sites and was independent of sediment depth due to mixing, moving and back filling of sediment masses, as well as clean sediment having been mixed with polluted sediment. High spatial variation was also found in a study on urban soil metal contents in several sites (Ljung *et al.*, 2006). River sediments close to the city commonly receive a higher load of metals than corresponding rural soils because metals are rather immobile once they reach the sediment, from hazardous elements derived from industrial activities with the addition of industrial, farming and domestic effluent and sewage. The long-term input of metals to the water and sediment has a negative effects on plants, farming and human health. For these reasons, the subject of metal contaminants in plants, sediment and water of Seyab River has received much attention in this research. Results from this research can be used in city planning to identify pollution sources and locate polluted areas. Seyab River and the Islam Shahr urban area are today subject to contamination due to high local pollution of industrial activities close to giant city of Tehran (Yazdi and

Behzad, 2008). Information gathered from a geological map of Tehran shows that the area is located within the Recent Alluvium Formation of Tehran alluvial. This formation is associated with heterogeneous to poorly sorted clays and silts. The lack of depth distribution for many parameters also indicates that the original sediments in Seyab area have been disturbed and mixed by flood soils.

The accuracy of the results, minimum, maximum and median contents of the metals measured in the samples are presented in Tables 1-6. Among the 12 sediment (soil) samples, the highest concentrations of Zn (310ppm), Cu (78ppm), Cr (86ppm), Se (20ppm) and Cd (35ppm) are found in the river close to urban area, where the urban, farming and industrial pollution is high, and is industrialized side of the Islam Shahr city. Urbanization and the associated industrial and agricultural activities result in the release and the subsequent deposition of pollutants and other persistent toxic substances, thereby leading to degradation of the environmental conditions in these parts of the river. Correlation analysis was carried out on the plant, water and sediments (soil) samples of the area. Table 7-10 contains the Pearson correlation coefficients among the measured elements. The heavy metals of Cd, Cr, Cu and Se displayed significant linear correlations. This correlation is chemically plausible and points to genetic similarities between the groups of metals, industrials and agricultural pollutions.

Background levels and guideline values have been established in many countries indicating the concentration of metals of natural origin and a maximum tolerable metal level, respectively. The Iranian Environmental Protection Agency has yet to define yet urban background levels of natural soil metal contents. For these reasons, average upper continental crust values (Wedepohl, 1995) were used as references to compare our data (Table 7). Se and Cd are highly enriched in the studied samples compared to the upper continental crust values. Islam Shahr has been newly developed during the past 15 years, thus such contaminations are extremely high for this short period. In particular, the levels of Cd and Se contaminations on the sediments, water and plants of Seyab River in Islam Shahr city are causing concenrn. This study concludes that the contaminant contents of Cd and Se were mainly derived from urbanization, agricultural and industrial activities sources.

Sediment analysis of the area presents a remarkable contamination picture. Sediment Se and Cd levels are high. This analysis revealed a situation of metal enrichment in the sediment with a mean Se concentration of 15.64 ppm and Cd concentration of 22.2 ppm (Table 7). Correlation analysis of the sediments shows a significant positive correlation of Se with all of the other elements like Cr (0.83), K(0.72), Ca(0.50) and Cu (0.48) (Table 8). This correlation is chemically plausible and points to genetic similarities between the groups of metals. A similar correlation is shown in a cluster with elements of mainly industrial origin (Mg, K, Se, Ca, Zn) and one cluster with metals of mainly farming origin (Na, Cr, Cu, Cd) (Fig2). This is again indicative of a non-geological genesis of the contaminants.

Surface water contains some inorganic contaminants, but the presence of inorganic Se and Cd in the drinking water is now recognized in many parts of the world as having the potential to be a very serious environmental hazard and to cause significant health problems. Se has been classified as a Group A and Category 1 human carcinogen like by the U.S. Environmental and Protection Agency (USEPA, 1997) and the International Association for Research on Cancer (IARC, 1987), respectively. The tests run on the water quality parameters of Seyab River samples revealed that the water is hard with a consistent presence of sulphate, bicarboante and chloride at moderate to low values and that the alkalinity of the water is mostly the same as that of nature. But most of the contaminated sites are located in Chahar Dongeh area in the northern part of Islam Shahr in Seyab River. The correlation study revealed that Se has a positive correlation (0.57) with carbonates (Table 9).

Similarity is seen in a cluster with elements of mainly non-natural origin (Cl, CO_3, K, Na, HCO_3, SO_4, Pb) and one cluster with metals of mainly anthropogenic origin (Ca, Se, Mg) (Fig.3). This is indicative of a non-geological genesis of the contaminants.

In view of the soil enrichment by Se and Cd, the various vegetation forms commonly found in the area were analyzed to determine their levels. Results from nine samples analyzed (Table 3) shows a mean level of Se of 44.70 ppm and a maximum value of 100 ppm. This value attests to a consistent presence of Se in river water and its sediments. The correlation study revealed that Se has a positive correlation with Ca (0.50) and K (0.61) (Table 10). Similarity is seen in cluster with elements of mainly anthropogenic origin (Na, Mg, K, Ca, Se, HCO_3) and one cluster with metals of mainly natural origin (Zn, Cl) (Fig4). This is indicative of non-geological genesis of the contaminants.

Table 4- Minimum, mean, maximum and standard deviation of elemental concentrations of **s**ediments in Seyab River area (n=12 for average pH of 7-8).

	Minimum	Mean	Maximum	Standard deviation
K	0.098	0.323	0.766	0.192
Na	0.0652	0.294	0.766	0.280
Ca	1.707	2.83	4.46	1.006
Mg	0.68	1.11	1.97	0.347
$Se*10^{-4}$	8.87	15.64	20.3	3.61
$Cu*10^{-4}$	28	53.52	78.4	12.84
$Zn*10^{-4}$	89	153.9	310	18.37
$Cr*10^{-4}$	19	34.31	86	21.98
$Cd*10^{-4}$	9.6	22.2	35	12.70

Table 5- Minimum, mean, maximum and standard deviation of elemental concentrations of water in Seyab River (n=8 for average pH of 7-8).

	Minimum	Mean	Maximum	Standard deviation
K	2.17	4.94	8.2	2.12
Na	68.5	78.56	128	20.19
Ca	64.7	83.5	102.9	15.39
Mg	9.4	24.11	44.4	15.52
Se	0.01	0.055	0.086	0.031
Cl^-	142	171.58	230.75	28.11
$CO3^{-2}$	15	29.28	45	11.34
$HCO3^{-2}$	305	358.38	427	254.48

Table 6-Minimum, mean, maximum and standard deviation of elemental concentrations of plants in Seyab River area (n=9).

	Minimum	Mean	Maximum	Standard deviation
K	1.99	3.17	4.77	0.934
Na	0.10	0.52	2.39	0.733
Ca	0.22	0.57	1.16	0.30
Mg	0.11	0.32	0.65	0.22
Se	15.9	44.70	100	25.73
Zn	0.317	41.76	77.3	29.15
Cl^-	159.75	307.6	497	87.74
$HCO3^{-2}$	152.5	271.1	396.5	82.74

Table 7- Enrichment Factors (EF) for the elemental concentrations of sediments in Seyab River. The EF is calculated as the ratio of the average abundance of an element in these samples to its average content in the upper continental crust (Wedepohl, 1995).

Element	Zn	Se	Cu	Cr	Cd	K	Na	Ca	Mg
Seyab River Soils	153.4	15.64	53.52	34.31	22.2	0.32	0.29	2.83	1.11
Upper continental crust	52	0.09	14.3	35	0.1	1.61	1.32	2.15	1.49
Enrichment Factors	2.95	174	3.74	0.98	222	0.29	0.22	1.32	0.74

Table 8- Pearson correlation coefficients of elemental concentrations of sediments in Seyab River

Correlation	K	Na	Ca	Mg	Se	Cu	Zn	Cr	Cd
K	1	0.58	0.24	0.09	0.72	-.18	0.33	-.31	0.04
Na	0.58	1	-.11	0.09	0.37	0.09	0.25	-.31	-.26
Ca	0.24	-.11	1	0.24	0.50	-.17	0.57	-.30	-.21
Mg	0.09	0.09	0.24	1	0.02	0.55	0.09	-.02	0.17
Se	0.72	0.37	0.50	0.02	1	-.48	0.42	-.83	-.36
Cu	-.18	0.09	-.17	0.55	-.48	1	-.23	0.83	0.12
Zn	0.33	0.25	0.57	0.01	0.42	-.23	1	-.36	-.15
Cr	-.31	-.31	-.30	-.02	-.83	0.83	-.36	1	0.45
Cd	0.04	-.26	-.21	0.17	-.36	0.12	-.15	0.45	1

Table 9- Pearson correlation coefficients of elemental concentrations of water in Seyab River

Correlation	K	Ca	Na	Mg	Se	Cl	CO_3	HCO_3
K	1	-.64	0.61	-.81	-.24	0.33	0.52	0.38
Ca	-.64	1	-.29	0.59	0.57	-.20	-.18	-.01
Na	0.24	-.29	1	-.36	-.31	0.16	-.48	0.58
Mg	-.80	0.59	-.36	1	0.42	0.05	-.09	-.04
Se	-.24	0.57	-.31	0.42	1	0.35	0.04	-.12
Cl	0.33	-.20	0.16	0.05	0.35	1	0.88	-.21
CO_3	0.52	-.18	0.48	-.09	0.42	0.88	1	0.03
HCO_3	0.38	-.01	0.58	-.04	-.12	-.21	0.03	1

Table 10- Pearson correlation coefficients of elemental concentrations of plants in Seyab River

Correlation	K	Na	Ca	Mg	Se	Zn	Cl	HCO_3
K	1	0.25	0.96	0.48	0.61	-.42	-.15	0.54
Na	0.25	1	0.15	0.56	-.14	0.08	0.13	0.01
Ca	0.96	0.15	1	0.52	0.56	-.58	-.29	0.63
Mg	0.48	0.56	0.52	1	0.13	-.05	-.11	-.02
Se	0.61	-.14	0.50	0.13	1	-.34	-.24	0.38
Zn	-.42	0.09	-.17	-.05	-.34	1	0.22	-.79
Cl	-.15	0.13	0.57	-.11	-.24	0.22	1	-.41
HCO_3	0.54	0.01	0.63	-.02	0.38	-.79	-.41	1

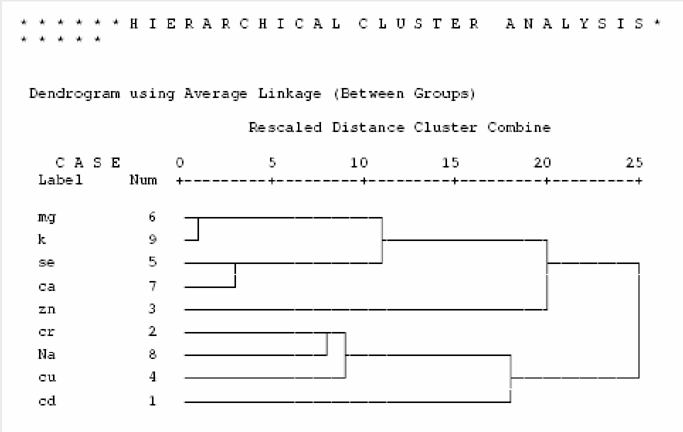

Figure 2. Dendrogram of correlation coefficients for sediment samples of Seyab River

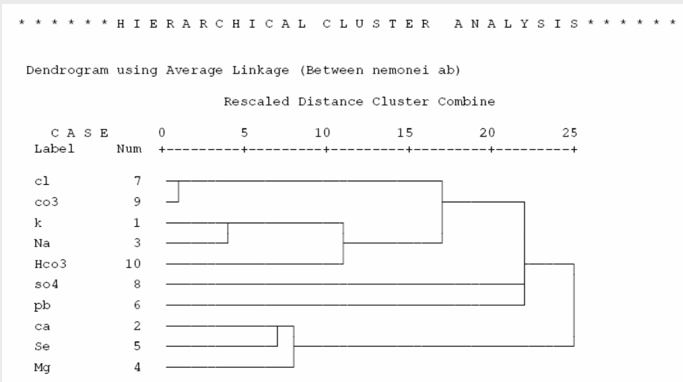

Figure 3. Dendrogram of correlation coefficients for water samples of Seyab River.

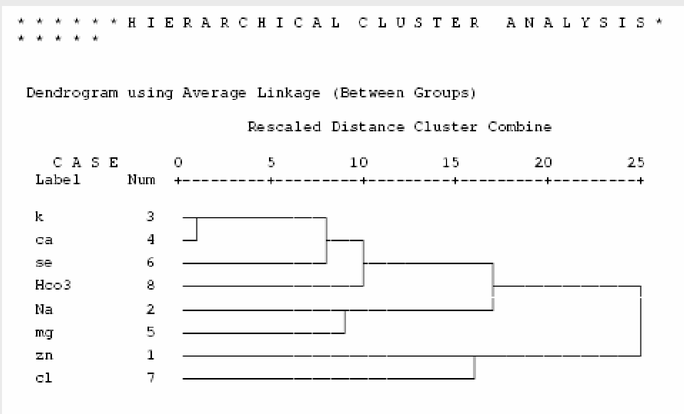

Figure 4. Dendrogram of correlation coefficients for plant samples in Seyab River.

Conclusions

The present study provides a general overview of metal concentrations and their distribution in the water, sediments and plants of Seyab River. Seyab River is a highly contaminated river, and is gradually getting smaller due to urban growth, and it is thus more feasible for the sediments to interact with the population that lives in its vicinity. However, no systematic study has been made on this river to assess the distribution of the heavy metals in the water and sediments. The long-term addition of metals to water and sediment has negative effects on plants, farming and human health. For these reasons, the subject of metal contents in plants, sediment and water of Seyab River has received much attention in this research. The results can be used in city planning to identify pollution sources and relocate polluted areas. Seyab River and Islam Shahr urban area is today subject to the impacts of high local pollutant industrial activities close to the giant city of Tehran (Yazdi and Behzad, 2008).

The results from this study show that Se and Cd are highly enriched in the studied samples compared to the upper continental crust values. Most of the contaminated sites are located in the Chahar Dongeh area in the northern part of Islam Shahr in Seyab River, where urbanization, heavy traffic, agricultural and industrial activities are high. Islam Shahr has developed recently during the past 15 years and, so, such contaminations are extremely high for this short period. In particular, the levels of Cd and Se contaminations in the sediments, water and plants of Seyab River in Islam Shahr city are a cause for concern. The correlation study reveals that the contamination contents of Cd and Se were mainly derived from urbanization, agricultural and industrial activities sources.

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