Geochemical Evaluation of Toxic Trace Elements in Recent Wind Driven Sediments of Zahedan Catchment Area

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Abstract: - Toxic trace elements were analyzed in recent wind driven sediment samples collected from 40 various sites in the Zahedan catchment area, east of Iran, as part of the National Water/Soil Quality Assessment program. Sites sampled represented mining, agricultural, residential/recreation, and mixed land uses and background conditions. The results for 8 toxic trace elements in wind driven sediment samples are presented in this report. Six of the selected trace elements were detected in wind driven sediment samples collected at all sites. The median cadmium concentration was lowest in wind driven sediment samples. Median concentrations of lead, nickel, and chromium were highest in sediment samples from the Zahedan physiographic region. Lead and arsenic were selected for a more detailed analysis. Lead and arsenic concentrations in wind driven sediment were highest at mining land use sites in the Zahedan Catchment Area. The concentration of trace elements in wind driven sediment generally increased as particle size decreased. Although the samples are all collected one year ago, and element content may have changed during storage, we discovered that the concentrations vary among samples, and As tends to be more abundant in sediments from mining sites, major roads and urban/rural areas. Comparison of wind driven sediment to three other similar studies in Iran and U.S generally indicated relatively similar patterns in relation to land use for wind driven sediment. Lead and arsenic concentrations in wind driven sediment were highest at sites affected by mining in three of the study units, Zahedan Catchment Area, Upper Colorado River Basin, and South Platte NAWQA. The median frequency of sediment samples for lead and arsenic in the study area was higher than the analyzed sediment samples of Upper Colorado River Basin and Southern Caspian Sea study basins. Recently, the expansion of Zahedan urban areas has led to large changes in human mediated inputs of trace elements, both intentional and inadvertent, that are introduced and dissipated into this physiographic zone. Investigating the spatial distribution of toxic trace elements in study sediments can reveal human influences on this terrestrial ecological system, and may influence other aspects of urban ecology as well as decision making. At present, the distribution of dust particles containing trace elements and volcanic gases in the lower atmosphere of study area includes the most important environmental and climatic problem.

Key-words: geochemical evaluation; toxic trace elements; wind driven sediments; catchment area; background conditions; human mediated inputs; spatial distribution; ecological system

1 Introduction

An urban ecological system differs from other ecological systems in that it is dominated by the activity of humans. Studying the processes and patterns of an ecological system that integrates both social and ecological variables requires careful constraint of complex models, especially in the case of fluxes of trace elements and materials in an urban desert system[1]. Desertification is one of the greatest global environmental concerns which that transform productive, or marginally productive land to deteriorated land and soil unable to support plants and animals[2]. This process specially occurs as a sequence of events: (1) Exposure and excessive stress dries out the soil; (2) Native plant species decline, resulting in less production of organic matter[3]; (3) During rainstorms, water runs off the landscape rather than infiltrating, scouring the soil so that rilling, gullying, and widespread erosion occur. Material fluxes are critical links between seasonal aquatic and desert ecosystem components. Sediment is the largest recipient system of toxic trace elements in most terrestrial ecosystems, and is also the foundation of all plant, animal, and human activities[4]. Trace element composition is a relatively new tool for provenancing wind driven sediments. However, because of the general homogeneity of upper crustal chemistry[5] coupled with homogenization during transport, chemical fingerprints of source areas can quickly become blurred[6].

The National Water/Soil Quality Assessment(NIWSQA) program is a new program of the Iranian Department of the Environment(DOE) designed to describe the status and trends in the quality of the Nation's water and soil resources and to provide an understanding of the natural and human factors that can affect the quality of these resources. The program is interdisciplinary and integrates chemical, physical, and biological data to assess the Nation's water/soil quality at local, regional, and national levels[7]. One components of this integrative assessment is to examine the occurrence and distribution of selected toxic trace elements in recent sediment samples on a watershed scale. The NIWSQA program emphasizes the use of consistent protocol methods for a nationwide approach. Characterizing the geographic distribution of trace element constituents with regard to background conditions and sources is one goal of the assessment. The use of sediment analyses provides an understanding of the fate, distribution, and potential effects of these constituents[8]. Measuring concentrations of toxic trace elements in wind driven sediments offers a complete description of the occurrence and distribution of trace elements in a catchment area. Trace elements in desert system may be attributed to natural geologic sources or to past and present land uses[9]. Although some toxic trace elements originate from restricted natural sources, human activities such as mining, agriculture, and urbanization can intensively affect their concentration and distribution[10].

The Zahedan Catchment Area(ZCA) is 1 of 10 study units selected for the national assessment. A study to determine the occurrence and distribution of toxic trace elements in wind driven sediment was conducted in the ZCA between April and June 2005. This report presents results of toxic trace elements analyses for recent wind driven sediments.

It (1)identifies the geochemical occurrence and distribution of selected toxic trace elements in wind driven sediments at sampled sites; (2)determines the relation of trace elements in sediment samples to natural and anthropogenic factors; (3)compares the results with some similar studies in Iran and U.S.

1.1 Description of Study Unit

The Zahedan catchment area, in Sistan and Balouchestan province(east of Iran), comprises 313km^2 and extends from the Lar mountain in the north, through the

Piedmont zone, to the Mohammad Abad Plain in the southern half of the catchment area(Fig.1).Predominant land use in the ZCA is sparse vegetation land and piedmont plain. Within the sparse vegetation and piedmont setting, other major land use sites are mining, urban/rural, recreation, and agriculture. The physiographic unit also has two background sites. Past and present mining activities have included the extraction of metals(copper, lead, molybdenum, nickel, and zinc) and construction rock. Urban/rural is one of the bigger land uses in the study unit. A number of urban/recreation areas are associated with growth resulting from energy development in the 1980's.Zahedan is one of the fastest developing cities, and is located in a broad piedmont plain surrounded by vast acreage of deserts. The Quaternary and Neogene sediments of piedmont plain, derived from the uplift of the mountain ranges on the east, consist of coarse conglomerates and sandstones[11]. In 1996, the Islamic Republic of Iran was introducing large-scale changes in the management of Zahedan city along with urban geology consideration and this was expected to continue into 2000s[12]. Almost all of urban area growth and expansion has occurred in the second half of the twentieth century.

2 Methods of study

2.1 Sample Collection

The distribution of various toxic trace elements in wind driven sediments can be determined by analyzing samples collected from locations randomly distributed across the whole of area. Collection and field processing of sediment samples for analysis of toxic trace elements followed established NAWQA protocols[13,14]. Wind driven sediment samples were collected at 40 sites throughout the Zahedan study unit(Fig.1 ; table1). Sediments were collected from undisturbed, depositional zones in the aeolian environment. Depositional zones were selected to represent running wind effects and various flow regimes. Sampling was confined to the upper three-fourths inch of desert sediment to insure that the most recent deposition was being sampled. Each depositional zone at a sampling site was subsampled at several locations, and the subsamples were composited. In the field, each composited sample was sieved through a 2-mm(10 mesh) stainless-steel screen, and the minus-2-mm fraction retained; the larger size fraction was discarded.

2.2 Sample Preparation and Analyses

Wind driven sediment samples were dried at ambient room temperature(25^{o}C) and sieved to minus-80-mesh(<0.18mm) prior to laboratory analyses. The sediment samples were digested with a mixed-acid solution consisting of HCl, HNO_3, $HClO_4$, and HF. This procedure(total digestion) is effective in dissolving most minerals, including silicates, oxides and sulfides; resistant or refractory minerals such as zircon, chromite, and some tin oxides are only partially dissolved. Previous investigations using a variety of materials support the completeness of the digestion[15,16]. Sediment samples were analyzed for toxic trace elements at the Islamic Azad University of Tehran(Science and Research Campus),Laboratory Complex, Geochemistry Analytical Services Group. Results are reported for 8 trace elements analyzed by ICP-AES(High Resolution Inductively coupled plasma - atomic emission spectroscopy ; table 2). Limits of determination for the total digestion method as well as a statistical summary of mean values, standard deviations, and median values for four National Institute of Standards and Technology(NIST) standard reference materials(SRM-2704, SRM-2709, SRM-2710, and SRM-2711) are given by Fey *et al.*(1999b)[17]. Comparisons with certified values for these standards[18] are also given by Fey *et al.*(1999b)[17]. Both analytical precision and accuracy are well within acceptable ranges. ICP-

AES analysis permits very low detection limits for trace elements in wind driven sediment samples. Replicate samples were collected for sediment for quality assurance/quality control. The difference between field replicate samples for wind driven sediment ranged from 10 to 15 percent.

3 Analytical results

Trace elements are unevenly distributed in the terrestrial environment and, by the process of adsorption, tend to be associated with fine grained sediment. Some trace elements, such as arsenic, cadmium, lead, silver, mercury, chromium, bismuth, nickel, and selenium, can be toxic to terrestrial biota[19]. The concentration of trace elements in sediment is strongly affected by the particle size distribution of the sample. Six of the 8 selected toxic trace elements were detected in sediment at all sites(table 2). Cadmium and mercury were the only toxic trace elements that were not detected at all sites. Among trace elements, the median cadmium concentration was lowest in wind driven sediment samples. Low median concentration of cadmium in sediment samples is the consequence of agricultural poisons and drainage water of marginal farms entering from the northern boundary of the study unit. Median concentrations of lead, nickel, and chromium were highest in sediment samples from the Zahedan physiographic region. Weathering of rocks and soils provides a pathway for the natural release these trace elements into the study desert system. Concentrations of mercury and bismuth in sediments are generally lower and show a smaller range than those of other toxic trace elements. Fairly high median concentration of mercury in selected sites may be a combination of agriculture activities and natural processes(continuous weathering of volcanic rocks, south of basin). In other side, urban effluents containing trace elements can deliver mercury and bismuth in the receiving waters of the study unit. Elevated concentrations of bismuth at some sites also could be a combination of natural and human factors. The agricultural sediment samples had the highest concentrations of selenium. Irrigation practices near agricultural land use sites may be mobilizing and redistributing selenium. The highest concentrations of arsenic show mining land use sites. Because of their concentrations in the study unit and their toxicity to terrestrial biota, Lead and arsenic were selected for detailed analysis. Lead and arsenic are potent poisons and already widely contaminate ecosystems. Lead is harmful in very low quantities. Short term exposure to high doses of lead can make human seriously ill. Lead is present naturally in the shale bedrock of the middle and lower reaches of the unit and in the ground water. Arsenic is toxic to human of all ages through ingestion and inhalation. Children are more susceptible because they still have developing nervous systems and are often exposed during normal play activities. One approach to evaluate elevated concentrations is by comparison to reliable studies in Iran and other countries. To determine the extent of contamination in a land system by means of the trace elements in recent sediments, the natural level(or the background concentration)needs to be established. A catchment area-specific background concentration for lead and arsenic was determined by plotting cumulative frequency curves[20] for the study unit for data from 40 wind driven sediment samples(Fig.2). The concentration at the first break point(change in slope) was designated as the background concentration. Lead and arsenic had determined background concentrations of 430 and 54ppm. Trace element concentrations greater than the background concentration were considered elevated and may have been affected by natural or human activities. Sites 3 and 18(sites chosen to represent background conditions; table1) had lower concentrations of lead and arsenic than the background concentrations for the catchment area. Because of the extent of mineralized zones in the Zahedan study unit, the concentrations of lead and arsenic could represent natural conditions at some sites. Twenty five sites exceeded background concentrations for the Zahedan study unit for lead, and eleven sites exceeded background concentrations for the study unit for arsenic(table 2). Elevated arsenic concentrations from sites 20, 21, and 40 may be results of human factors include sparse mining. Although site 38 represents mining land use, it also had past urban activities in the lower part of the area. Site 9 represents a mixed land use site and receives water from a mining affected zone just upward from the sampling site. The weathering of the rocks in the Southern Mountains of physiographic region produces large amounts of small particulates(silt/clay). Higher percentages of silt/clay particles in combination with mining land use at sites 20, 21, and 40 may be a factor for higher concentrations of lead and arsenic. Surprisingly, the sediment samples from some residential sites show relatively high concentrations of lead. Site 38, a mining land use site, with the highest concentration of lead, had one of the highest percentages of silt/clay particles of the sites in the ZCA.

4 Discussion

Although the samples are all collected one year ago, and element content may have changed during storage, we discovered that the concentrations vary among samples, and As tends to be more abundant in sediments from mining sites, major roads and urban/rural areas. Once we collected data on many samples, we found that the high concentrations of particular toxic elements such as Ni and Hg in agricultural areas other than mining and transportation areas are just exceptional results for individual samples. Long term using of pesticides in agricultural areas is result in high median Ni concentration in the study sites. Plants may absorb Cr, Cd and Bi from contaminated sediments and decrease concentrations in agricultural land use sites, which may result in damage to the plant systems or DNA, or may in turn harm the health of humans and animals that depend upon these plants as food. Lead and arsenic concentrations in sediment samples collected from the ZCA were compared to concentrations from three other study units(table3). Comparison of background concentrations for the four study units indicated significant differences for lead and arsenic between Zahedan Catchment Area and two basins, Upper Colorado River Basin(UCOL) and Southern Caspian Basin(SCB), and indicated that lead and arsenic were significantly different among these study units. Regional similarities in sediment concentrations occurred more often than regional differences among the study units. More relations were observed between two study units, Zahedan Catchment Area and South Platte NAWQA(SPLT), rather than among all four study units. All four study units have agricultural, mining, urban/rural, and recreation land use. The median frequency of sediment samples for lead and arsenic in the study area was higher than the analyzed sediment samples of Upper Colorado River Basin and Southern Caspian Sea study units. The highest concentrations for lead and arsenic in sediment for three study units, ZCA, UCOL, and SPLT were at sites affected by mining whereas the highest concentrations for SCB were at sites affected by urban effluents. Human disturbances at the mining land use sites of ZCA may have contributed to the larger percentages of silt/clay particles. Overall, sites in the ZCA contained larger percentages of silt/clay particles than sites in the SCB and UCOL study units(fig.3). Weathering of the metamorphic and sedimentary rocks in the ZCA is one contributing factor to large percentages of silt/clay particles at these sites. In recent, the expansion of Zahedan urban areas has led to large changes in human mediated inputs of trace elements, both intentional and inadvertent, that are introduced and dissipated into this physiographic region. The spatial distribution of various toxic trace elements in sediments can be mapped by analyzing samples collected from deeper surface zones(4-12 inchs interval). Investigating the geochemical distribution of toxic trace elements in study sediments can reveal human influences on this terrestrial ecological system, and may influence other aspects of urban ecology as well as decision making. At present, the distribution of dust particles containing trace elements in the lower atmosphere of study area includes the most important environmental and climatic problem. Many marginal lands have steep slopes, are prone to high rates of wind erosion, and are more fragile than other lands, which may result in widespread degradation and deterioration of soil and trace elements resource base. The atmospheric pollution by volcanic gases is also a potential hazard. The carbon dioxide and sulfur dioxide gases seeping from Taftan volcano(south of Zahedan city), accumulated at the bottom of shallow ponds, create ionic complex which may contaminate ground water.

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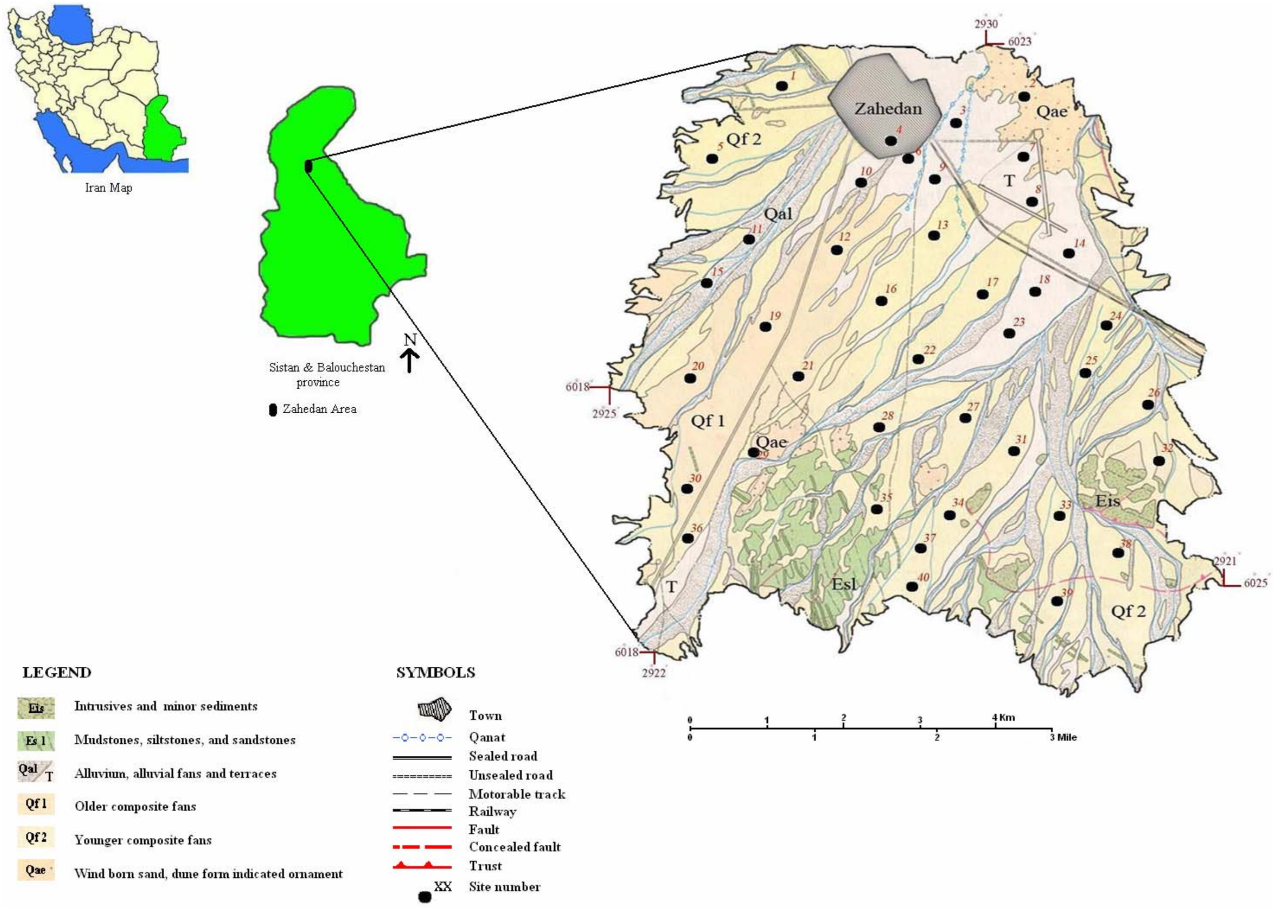

Figure 1. Location of sites for collection of wind driven sediment samples in the Zahedan study catchment area.

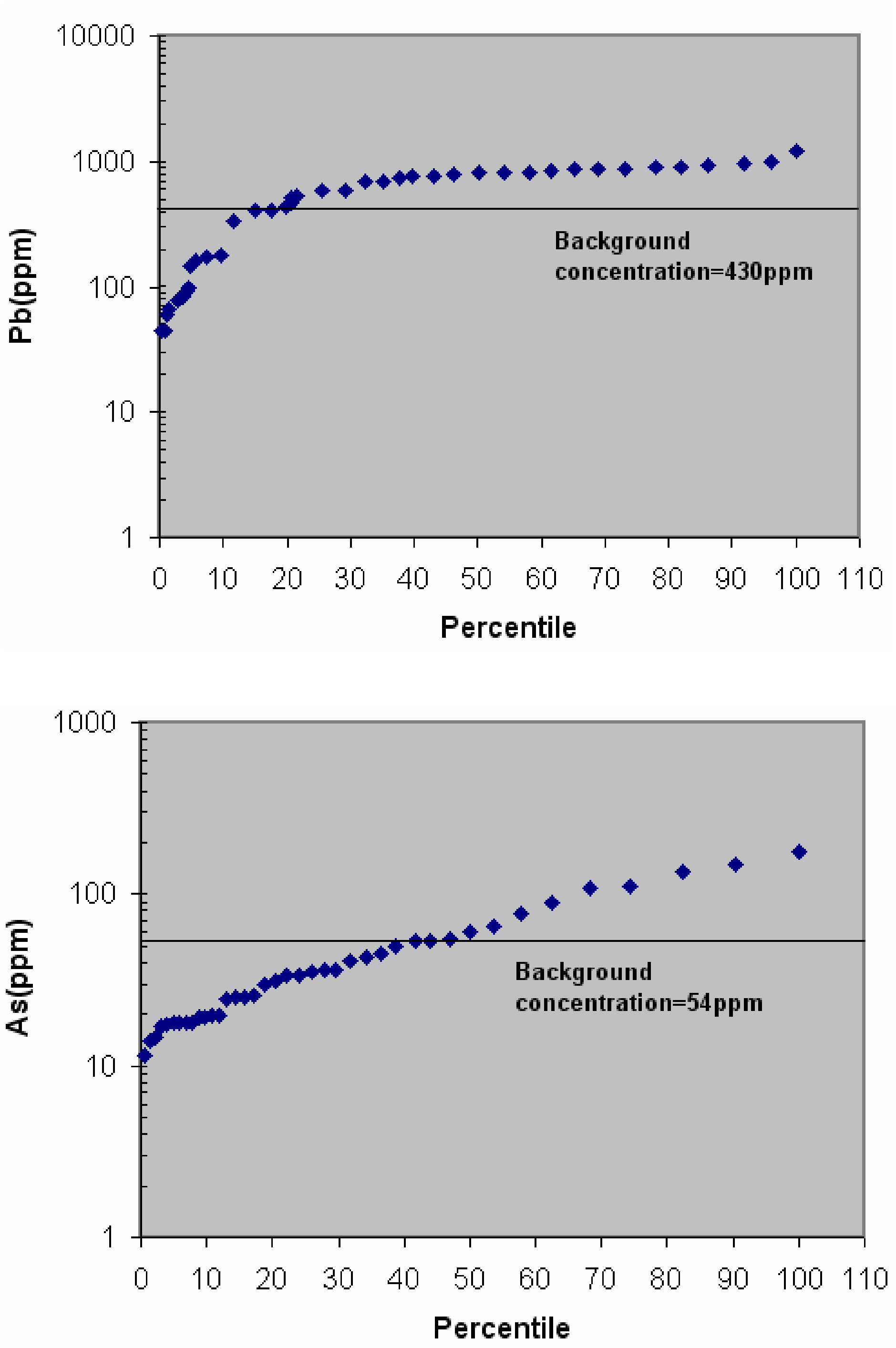

Figure 2. Cumulative frequency curves used to determine the background concentration of lead and arsenic.

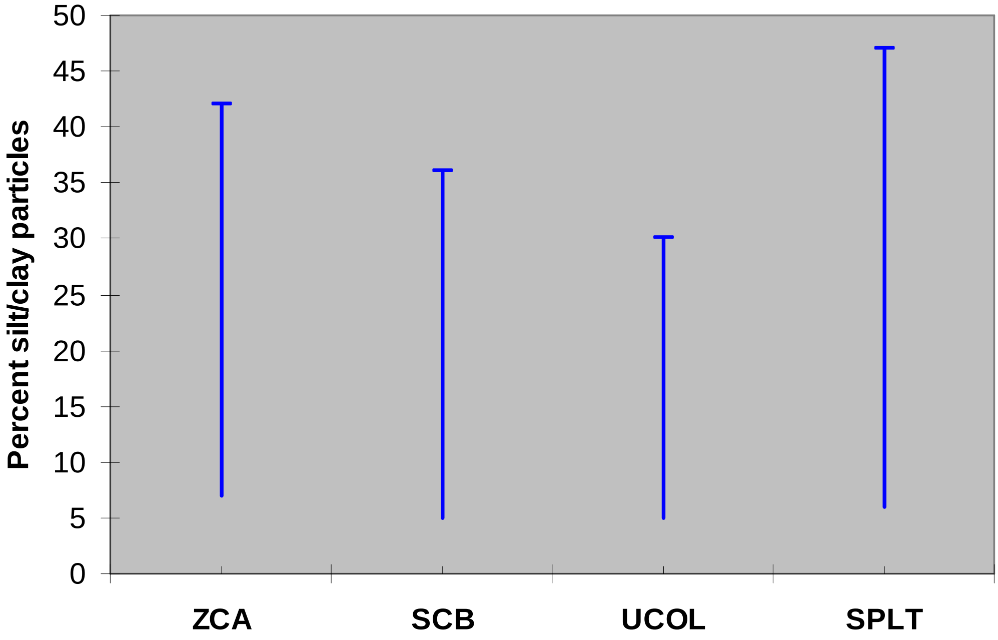

Figure 3. Comparison of particle size percentages between sites in the Zahedan Catchment Area(ZCA), Southern Caspian Basin(SCB), Upper Colorado River Basin (UCOL), and South Platte NAWQA(SPLT) physiographic units.

Table 1. Description of sampling sites in the Zahedan Catchment Area.

Site number	Site name	Site type	Elevation(feet)
Sp_1	Cheshmeh Ziarat	Rural	4596
Sp_2	Zahedan Airport	Urban	4593
Sp_3	Zahedan Airport	Background	4593
Sp_4	Khash Gate	Mixed	4593
Sp_5	Cheshmeh Ziarat	Major Road	4596
Sp_6	Khash Gate	Urban	4593
Sp_7	Zahedan Airport	Urban	4593
Sp_8	Zahedan Airport	Urban	4593
Sp_9	Zahedan Airport	Mixed	4593
Sp_{10}	Zahedan Payam-E-Noor	Major Road	4593
Sp_{11}	Cheshmeh Ziarat	Agriculture	4596
Sp_{12}	Zahedan Payam-E-Noor	Major Road	4593
Sp_{13}	Zahedan Payam-E-Noor	Urban	4593
Sp_{14}	Zahedan Airport	Agriculture	4593
Sp_{15}	Zahedan Jahad	Agriculture	4593
Sp_{16}	Zahedan Payam-E-Noor	Major Road	4593
Sp_{17}	Ziba Shahr	Urban	4593
Sp_{18}	Ziba Shahr	Background	4593
Sp_{19}	Zahedan Jahad	Recreation	4593
Sp_{20}	Zahedan Jahad	Mining	4593
Sp_{21}	Zahedan Payam-E-Noor	Mining	4593
Sp_{22}	Zahedan Payam-E-Noor	Mining	4593
Sp_{23}	Ziba Shahr	Urban	4593
Sp_{24}	Ziba Shahr	Urban	4593
Sp_{25}	Ziba Shahr	Urban	4593
Sp_{26}	Imam Ali	Urban	4593
Sp_{27}	Imam Ali	Urban	4593
Sp_{28}	Zahedan Payam-E-Noor	Major Road	4593
Sp_{29}	Zahedan Payam-E-Noor	Major Road	4593
Sp_{30}	Kalat-E-Razaqzadeh	Recreation	4594
Sp_{31}	Imam Ali	Urban	4593
Sp_{32}	Imam Ali	Urban	4593
Sp_{33}	Padagi Mountain	Rural	4595
Sp_{34}	Kalat-E-Razaqzadeh	Recreation	4594
Sp_{35}	Kalat-E-Razaqzadeh	Recreation	4594
Sp_{36}	Kalat-E-Razaqzadeh	Recreation	4594
Sp_{37}	Kalat-E-Razaqzadeh	Recreation	4594
Sp_{38}	Padagi Mountain	Mining	4595
Sp_{39}	Padagi Mountain	Mining	4595
Sp_{40}	Padagi Mountain	Mining	4595

Table 2. Concentrations of selected trace elements in wind driven sediment samples collected from sites in the Zahedan study unit[Values in ppm].

Sample No.	As	Bi	Cd	Cr	Hg	Ni	Pb	Se
Sp 1	14.5	2.1	0.25	39.6	0.43	54	84	29.5
Sp 2	25	2	0.25	46	0.43	50	100	40
Sp 3	41	2	0.25	32.7	0.38	41.2	45	31.8
Sp 4	54	2.2	0.35	44	0.35	45	66.5	35
Sp 5	36	1	-	15	1.31	106	334	23.1
Sp 6	45.3	1.8	0.35	23.5	1.1	98	176	60
Sp 7	50	2.1	0.35	57	0.69	70	91	41.5
Sp 8	61	2.1	0.3	49.5	0.42	34	60	37
Sp 9	54.1	2	0.3	41	0.44	32	77.5	36.5
Sp 10	90.2	3.1	0.4	118	0.55	65	171	57.7
Sp 11	108.2	3.5	0.35	97.4	0.5	46	413.5	65
Sp 12	77	2.1	0.35	67	0.39	40	464	64.3
Sp 13	26	1.5	0.15	14	1.2	213	436	80.1
Sp 14	18	1.5	0.2	12.6	0.85	103	742	82
Sp 15	19	2.1	-	14.5	0.65	87	537	69.6
Sp 16	34	1.8	0.3	49	0.42	32	512.5	54
Sp 17	42.9	1.8	0.25	55.7	0.4	37.3	162.5	48
Sp 18	18	1.6	0.25	16	0.4	34	45	51
Sp 19	18	1.5	0.2	13.6	0.55	45	144	65.5
Sp 20	136	3	0.35	107	0.36	29	877	43
Sp 21	175.4	1.8	-	35	0.35	34.5	812	25.6
Sp 22	54.3	1.8	0.35	42.5	-	30	684	31
Sp 23	36	2	0.3	29	0.55	37	575.5	28
Sp 24	19.5	1	0.25	13.4	-	22.6	586	23.7
Sp 25	17.2	1.2	-	13	0.68	138	403	41.9
Sp 26	24.6	1.5	0.25	18	0.7	176	769	28
Sp 27	30	2	0.35	43.8	0.6	56	689	33
Sp 28	33.7	2.1	0.35	45.3	0.55	43	810	30.4
Sp 29	19	1	-	11.1	0.75	121	871	19.5
Sp 30	18	1.5	0.3	54	0.5	35	866	25
Sp 31	11.6	1.5	0.25	19	0.65	31	754	22.4
Sp 32	14	1	0.25	14.9	0.5	25.9	813	19
Sp 33	19.5	1	-	15.5	0.65	33	780	18
Sp 34	17	1.5	0.35	22.4	0.6	42.2	934	18
Sp 35	24.8	1.8	-	19.5	0.55	36	1006	19.5
Sp 36	35.5	1.8	0.15	18.8	0.6	69	912.5	46
Sp 37	31	2.1	0.25	45	1	119	895.5	35
Sp 38	65.5	2.1	0.25	42	1.52	388	1210	32.1
Sp 39	112.5	3	0.4	143	0.68	35.5	944	43
Sp 40	150	1	-	12.4	0.8	40	842	57.5

Table 3. Background concentrations for selected trace elements in sediment samples[All values in ppm.40 sediment samples were analyzed and used to compute background concentrations for this study].

Element	Shaham (1999) [1]	Deacon (1995-96) [2]	Heiny & Tate (1997) [3]	Zahedan study Area	Range of Concentration from this study
Lead	70	12	465	430	45-1210
Arsenic	42	8.9	60	54	11.6-175.4

[1]Background concentrations established for Southern Caspian Basin sediment samples(SCB)[21].
[2]Geochemical data for sediment samples in the Upper Colorado River Basin,Colorado(UCOL)[8].
[3]Background concentrations established for the South Platte NAWQA study(SPLT)[22].