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Lead in Karvandar River Basin Sediment, Sistan and Balouchestan, IRAN

Javad Shahraki*, Mohammad Javad Javdan, Seyed Mahmood Pahlavan Hashemi, Mohsen Jami, Mahdiyeh Nastooh, Seyed Mohammad Kalvandi

Department of Geology, Zahedan Branch, Islamic Azad University, Zahedan, Iran
Email: *Javad_sh1536@yahoo.com

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Abstract

Streambed-sediment samples were collected in the Karvandar River Basin in the Sistan and Balouchestan province to determine the occurrence and distribution of lead in urban/rural and nonurban/rural areas of the basin. During fall 2012 and fall 2013, streambed sediment was collected at 30 sites, and the samples were analyzed for lead. The ranges in concentrations of lead in streambed sediments at urban/rural sites were orders of magnitude higher than the ranges of concentrations at nonurban/rural sites. Concentrations of lead at sites with different geologic settings were considered to be not statistically significant ($t = 0.079$, $p = 0.93$); however, concentrations of lead at these sites can be compared without substantial effects of natural geologic characteristics. Lead in streambed sediment was at concentrations that can adversely affect the aquatic biota in 48 percent of the urban/rural sites in the basin for both particle-size fractions. Lead concentrations in the <43 µm fraction were higher than the total particle-size fraction. Distribution patterns for lead indicate that grossly contamination (>SEL) does not exist throughout the entire drainage basin. A comparison between the sites close to the source and sites downstream indicated that the pattern of increasing concentrations was observed for lead with increasing distance from the source.

Keywords

Lead, Streambed Sediments, Karvandar River Basin, IRAN, Concentration, Urban/Rural Sites, Nonurban/Rural Sites, Particle-Size Fractions

1. Introduction

Many of the common anthropogenic pollution problems are focused in urban settings. Studying the processes

*Corresponding author.

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and patterns of an urban system that integrates both social and environmental variables requires careful constraint of complex models, especially in the case of anthropogenic fluxes of trace element and material. A population shift from urban/rural settings to the suburban environment, however, has caused sources of contaminants to aquatic systems to be contributed by larger geographic areas [1]-[3]. At present, because of the increasing pollution of waterways by trace elements from industrial and municipal sources, we must manage our water resources carefully [4]. There is an urgent need for maintaining water quality.

Lead has been used by humans for a variety of purposes throughout the 19^{th} and 20^{th} centuries. Point-source inputs of lead to aquatic systems include industrial effluents, municipal wastewater effluents, and stack emissions from smelting operations and fossil-fuel combustion [5]-[7]. Today, most of the new anthropogenic lead additions to the environment are derived from material sources. Evidence shows that man is chronically exposed through ingestion of water to lead and related chemical compounds than we were able to identify originally. Even though the exposures are at extremely low levels, it is possible that an increase of detrimental biological effects may be reported in the future. Anyway, further conclusive toxicologic and epidemiologic evidence is needed before many suspected compounds can be proven hazardous to man at the levels presently encountered. These data are urgently needed for the appropriate regulatory actions.

Analyzing Sediment Lead

First, fine-grained particles are natural accumulators of lead in streams, which is highly sorptive and associated with particulate matter in almost all natural surface-water regimes [8]. A large fraction of the total mass of this constituent is usually associated with fine-grained sediments, including clay/silt particles and particulate organic carbon. Consequently, even though the water may contain only small quantities of trace element, suspended sediment and bed sediment may contain relatively large concentrations [9]. Second, nonpoint-source contributions of trace element may be intermittent or storm related; as a result, lead may not be detected in single or periodic water samples. Bed sediments in depositional environments of streams provide a time-integrated sample of particulate matter transported by a stream. Third, when combined with biological tissue analysis, bed sediment concentrations provide a useful measure of the potential bioaccumulation of trace element at a particular site [3].

This paper presents results of lead analysis in streambed sediment in human-mediated sites as well as other sites affected by different sources in the Karvandar River Basin (KRB) study area in Sistan and Balouchestan province (**Figure 1**). Again, it focuses on the effects of anthropogenic activities on low-gradient streams of the Karavandar Morphology county and describes the occurrence and distribution of lead in urban/rural and nonurban/rural areas of the basin. Comparisons were made between lead concentrations on fine-grained sediment and

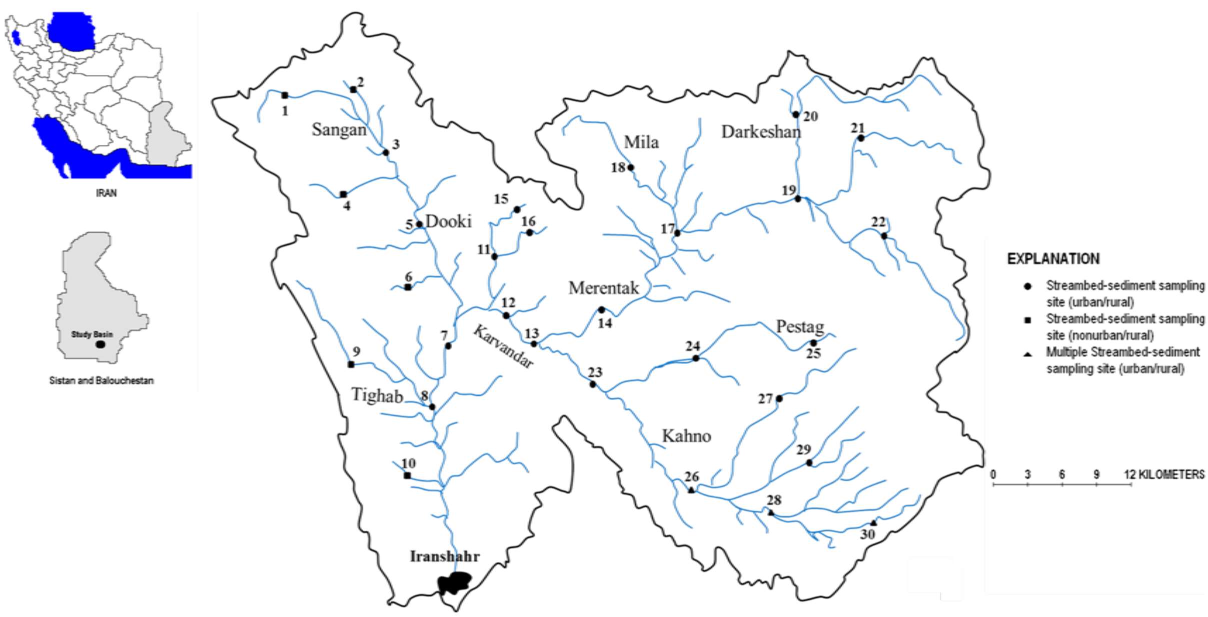

Figure 1. Location of sites for collection of streambed-sediment samples in the Karvandar River Basin.

the total particle-size fraction [10] to determine relations between lead concentrations and particle size. Lead concentrations related to distance from an urban/rural source were compared among some study-basin sites to determine changes in lead concentrations.

2. Materials and Methods

2.1. Basin Description

The study zone includes catchment of Karvandar River which is located in north of Irandegan plain and un the vicinity of Sibe-Sooran, Khash and Poshtkooh plains in Sistan and Balouchestan. This zone is in 27˚34'28" latitude and in 60˚35'61" longitudes. The surface area of this catchment is 2128 km^2 that 1789 km^2 of it is covered by altitudes. The basin includes thinly urbanized to lightly industrialized areas, low-density desert-residential neighborhoods, and small-scale agriculture. The narrow east-west tributaries of stronger north-south flowing streams form reticulations or trellis patterns in basin. In the Sangan valley, drainage in the southeastern part is southeastward to join the three principal stream systems (Tighab, Dooki, and Kahno). These three brackish streams contribute about 70% of the total input to the basin. After the junction point of dooki and Kahno, the channel is named the Karvandar River, the major river of Iranshahr quadrangle, a permanent consequent stream flowing southeast across the entire quadrangle. A series of relatively short, branching streams flows northwestward from the main northwestern waterway (Dooki) to the Karvandar depression, where they debouch and quickly taper out northwestward across the marginal fans into the dunlands of the desert basin.

Although there is a low-steep rainfall gradient between the crest of the mountains and the coast, high-suspended sediment loads are released in the basin during rainstorms. The suspended sediment carries a variety of anthropogenic substances introduced largely in the urban portion of the basin.

The KRB has become a saline, contaminated and eutrophic water body. Water velocity decreases upon entering the KRB because it is much wider and deeper than its tributary streams, leading to deposition of suspended-sediment loads. Thus, the basin serves as a sedimentation basin where accumulation rates are on the order of 0.5 - 1 cm/a. Vegetation is sparse throughout the basin: scattered thorn bush and low scrub grow on the Quaternary terraces, but the hills are stony and bare, with only very sparse development of small bushes. Cultivation in the area is restricted to the main river valleys and patches around villages, where there are small-irrigated plantations of date palm, citrus, and cereal. The increased contamination in the KRB is driven by inputs of organic matter and trace elements from urban and rural sewages, scattered industrial wastes, and storm drain near the head of the main channel. The accumulation of organic matter in the streambed sediments and the high biological O_2 demand leads to anoxia in the lower water column and sediment [11]. Because anoxic sediments minimize bioturbation, preservation of sedimentary layering is enhanced [12]-[14] and Karvandar River sediments generally provide well record of trace elements and organic-compound pollution in urban/rural sites.

2.2. Sample Collection and Processing

Streambed sediments were collected in two time ranges respectively, in the beginning of fall 2012 and beginning of fall 2013 (low-flow conditions) by the author of paper during the field program of sedimentology course. Thirty sites were sampled for trace elements in streambed sediment to assess the effects of anthropogenic activities in the KRB (**Table 1**) (**Figure 1**). Ten sites were sampled in October 2012 (7 urban/rural; 3 nonurban/rural). Twenty additional sites were sampled in October 2013 (15 urban/rural; 5 nonurban/rural). One representative sample was collected at each site, for a total of 30 samples used in the analysis. Replicate samples were collected at 3 of the 30 sites to determine environmental and sampling-technique variability.

Bed-sediment samples were collected using the procedures described by [15]. Environmental representative sample was obtained by collecting and compositing fine-grained surficial sediments from numerous depositional zones at a site. Holes of about 30 × 30 cm surface area were dug using a plastic scoop to depths of 10 to 40 cm. Samples were placed in zip-lock bags. Bed sediments were collected from streams with a plastic scoop and also stored in plastic bags. All stream sediments were also wet sieved into two fractions (2000 to 43 µm and <43 µm). The mass in the two grain-size fractions was determined to a precision of 0.001 g. All samples were oven dried at 60˚C to remove moisture and were homogenized.

2.3. Sample Preparation and Analysis

Subsamples of streambed sediments (200 mg) were dissolved in a microwave oven with a mixture of HNO_3,

Table 1. Name, number, and type of sites and year sample collected.

Stream	Site number	Site type	Sampling year	Fractional uncertainty	Lead concn. (ppm, dry-weight basis)
Sangan	1	nonurban/rural	2012	0/35	58
Sangan	2	nonurban/rural	2012	0/33	60
Sangan	3	urban/rural	2012	0/24	70
Dooki	4	nonurban/rural	2012	0/27	66
Dooki	5	urban/rural	2013	0/03	90
Dooki	6	nonurban/rural	2013	0/36	57
Tighab	7	urban/rural	2013	0/17	77
Tighab	8	urban/rural	2013	0/01	93
Tighab	9	nonurban/rural	2013	0/13	80
Tighab	10	nonurban/rural	2013	0/12	82
Karvandar	11	urban/rural	2013	0/02	93
Karvandar	12	urban/rural	2013	0/20	115
Karvandar	13	urban/rural	2012	0/14	110
Merentak	14	urban/rural	2012	0/25	121
Karvandar	15	nonurban/rural	2013	0/28	65
Karvandar	16	nonurban/rural	2013	0/05	90
Mila	17	urban/rural	2013	0/28	123
Mila	18	urban/rural	2013	0/65	160
Darkeshan	19	urban/rural	2012	0/85	178
Darkeshan	20	urban/rural	2013	0/80	175
Darkeshan	21	urban/rural	2013	0/17	75
Darkeshan	22	urban/rural	2013	0/04	100
Karvandar	23	urban/rural	2013	0/01	96
Pestag	24	urban/rural	2013	0/12	108
Pestag	25	urban/rural	2013	0/30	125
Kahno	26	urban/rural	2013	0/75	170
Kahno	27	urban/rural	2012	0/02	93
Kahno	28	urban/rural	2012	1/45	230
Kahno	29	urban/rural	2013	0/95	186
Kahno	30	urban/rural	2012	1/02	193

HCl, and HF, using the method described by [15]. Procedural blanks and duplicate digestions were performed approximately every tenth sample. Elemental analysis of streambed sediments was performed by atomic absorption spectrophotometry (AAS). Instrument was calibrated with a series of aqueous multi-element solutions of known concentrations prepared from dilution of commercially purchased, NIST-traceable stock standard solutions. Calibration standards were prepared daily prior to analysis.

Quality-control procedures for all samples included analyses of a reference material GXR-2 (enriched soil) and an analytical replicate for each batch of samples analyzed. Values for lead in GXR-2 reference material were within quality-assurance guidelines of ±3 standard deviations. The difference between lab replicates was less than 10% for lead. The precision and bias generally were less than 10% difference between replicate analyses and similar to that reported in [10]. Field replicates were collected in the same depositional zone at the same time as the environmental sample to define the variability in the sampling technique and in the depositional zone. The difference between field replicates of streambed-sediment samples for lead ranged from 0% to 30%. Field replicates were collected at urban/rural-affected sites that have high concentrations of lead and may account for larger variability than expected for lead.

2.4. Data Analysis

Concentrations for fine grain-size fraction of the 30 environmental samples are presented in the **Appendix 1** for lead trace element. Lead was analyzed and discussed on the basis of occurrence and distribution in urban/rural areas, concentration variability among sites, and high concentrations and toxicity concerns. A t-test was used to determine significant statistical differences between the means of two groups of data (urban/rural and nonurban/rural sites) [10]. The statistical method of variation coefficient was used to interpretation the lead-contaminated streambed sediments at urban/rural sites as well as comparison between these sediments to background concentration for lead.

3. Results and Discussion

3.1. Trend

Generally, trace-element concentrations that have been corrected for their background contribution correlate better with measures of human activity or impact such as population density, land use, and toxic-release inventory than uncorrected trace-element concentrations [16]. The term "background concentration" is defined in this document as the concentration of trace element found in sediments surrounding a waste site, but which are not influenced by site activities or releases. A "background site" should be a site that is geologically similar and has similar physical, chemical, and biological characteristics (e.g., particle size, pH, content of organic carbon) as the contaminated site [1] but also should be upstream or up gradient of the site. Samples taken from a site to determine background concentrations will be referred to as background samples. A basin-specific background concentration for lead was determined by plotting cumulative-frequency curves for the KRB study unit for data from 30 streambed-sediment samples (**Figure 2**). The concentration at the first break point (change in slope) was designated as the background concentration [17]. Because of its concentrations in the study unit and its potential toxicity to aquatic biota, lead was analyzed as detailed. Lead had a determined background concentration of 133 ppm (**Figure 2**). Concentrations of lead were high at sites affected by anthropogenic activities in areas of the KRB. Differences in the magnitude of last anthropogenic activities may affect concentrations of lead. Lead trace element can be naturally present in all streambed-sediment samples. Concentrations of lead at some nonurban/rural sites were higher than the suggested background concentrations for US study basins [10] [18] [19],

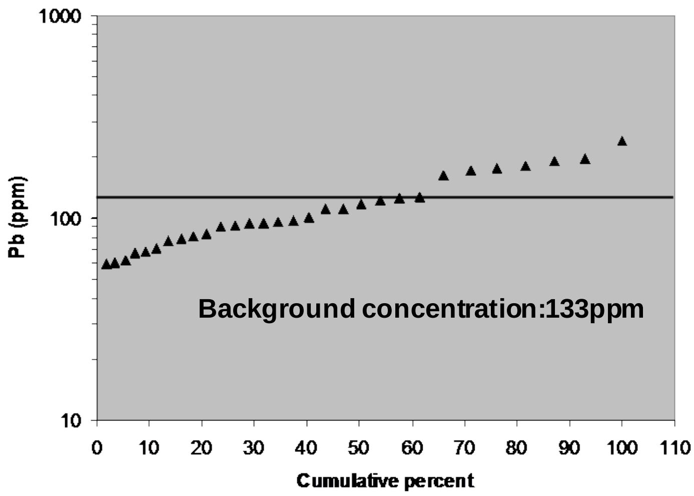

Figure 2. Cumulative-frequency curve used to determine the background concentration of lead.

(**Table 1**). The ranges in concentrations at nonurban/rural sites in this study reflect mineralized areas of the basin. Nonurban/rural sites, used as background conditions (sites 9, 10, and 16) (**Table 1**) (**Figure 1**), are heavily mineralized and therefore have high naturally occurring concentrations of lead. These sites have the highest concentrations in the range of data for nonurban/rural sites for lead (**Table 2**). The ranges in concentrations of lead in streambed sediments at urban/rural sites were generally orders of magnitude higher than the ranges of concentrations at nonurban/rural sites (**Figure 3**). According to Welch t-test, the concentrations of lead at urban/rural sites were not significantly more different than nonurban/rural sites ($t = 0.1330$, $p = 0.8955$). To determine if sites could be analyzed together without major effects from urban/rural and nonurban/rural sources, sites with different geologic settings and highly to lightly affected by anthropogenic activities were compared using an unpaired t-test. Concentrations of lead at sites with different geologic settings were considered to be not statistically significant ($t = 0.079$, $p = 0.93$); however, concentrations of lead at these sites can be compared without substantial effects of natural geologic characteristics. Although adequate data were not available for a statistical test, concentrations of lead were not as high at sites located in anoxic-pit areas compared to the sites located in the natural geologic settings. Therefore, all sites have been grouped for analysis regardless of geologic settings.

National guidelines for trace elements in streambed sediment do not presently exist. However, there are some Interim Sediment-Quality Guidelines for trace elements considered most toxic to aquatic life. These guidelines are based on the total concentration of a chemical in bulk (total particle-size fraction) sediment [10], whereas most of the samples in the basin KRB were the <43 µm fraction. Therefore, comparing the <43 µm fraction lead concentrations in this study with these guidelines may overestimate concentrations that seriously affect aquatic life. However, lead concentrations were analyzed on 30 environmental samples for both the <43 µm fraction and the total particle-size fraction to determine relations between the two fractions and to compare the two fractions to the guidelines.

The chemical quality of sediment is generally assessed by looking at its toxicity to benthic organisms. Elevated concentrations of lead in streambed sediment can seriously affect the biota in the stream. The median concentrations for lead at nonurban/rural sites in the KRB were above the threshold effect level (TEL) develo-

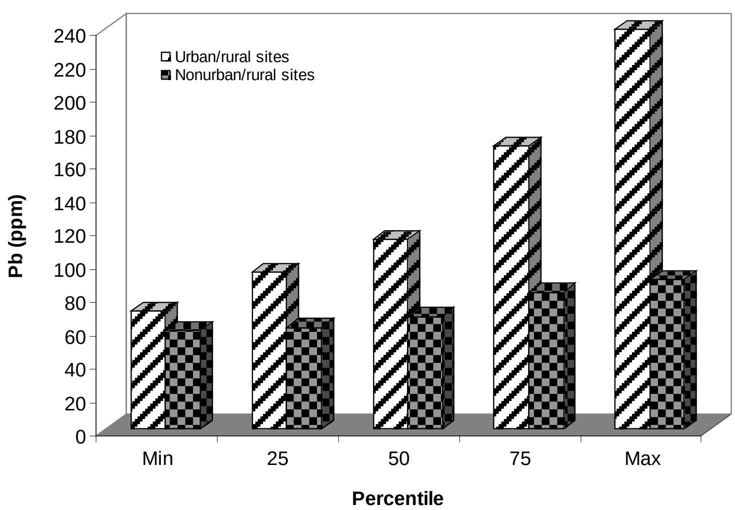

Figure 3. Range of concentrations for lead in streambed sediment for urban/rural and nonurban/rural sites in the Karvandar River Basin.

Table 2. Background concentrations for lead in soil and streambed sediment (All values are in ppm).

Threshold effect level (TEL) (Grimwood and Dixon, 1997)	Probable effect level (PEL) (Grimwood and Dixon, 1997)	Severe effect level (SEL) (Persaud *et al.*, 1993)	Percent of sites with concentrations above the PEL for the total particle-size fraction	Percent of sites with concentrations above the PEL for the <43 µm fraction
30.2	112	250	45.4	50

ped in the Interim Sediment-Quality Guidelines [20] [21]. TEL was established by the Canadian Council of Ministers of the Environment (CCME) and is routinely used by the different stakeholders involved in sediment-management activities. The TEL represents the concentration below which harmful effects to aquatic biota are rarely expected to occur. None of the concentrations for lead at nonurban/rural sites exceeded the probable effect level (PEL). The PEL is defined as a concentration that probably produces harmful effects in organisms. Concentrations of lead in streambed sediment exceeded the PEL for 50 percent of urban/rural sites in the study basin (**Table 3**). Although the <43 µm fraction is not as comparable to the guidelines as the total particle-size fraction, 48 percent of all samples for both particle-size fractions exceeded the PEL for lead. Lead concentrations are higher in the <43 µm fraction; however, within this type of geologic and urban/rural conditions, concentrations in the total particle-size fraction also exceeded the PEL at more than 45 percent ofurban/rural sites for lead. Concentrations of lead generally were highest and exceeded the PEL at sites 28 - 30, located on Karvandar River. Sites 6, 9, and 17, located on Dooki, Tighab, and Mila waterways respectively, are above urban/rural activities and have concentrations below the PEL for lead, indicating that the geologic conditions can produce relatively high trace-element concentrations at some sites. A combination of natural geologic conditions and anthropogenic activities are associated with elevated lead concentrations in streambed sediment at a limited number of sites.

Variation coefficient (V.C) is one of the most appropriate criteria for interpretation the relative variation of lead-contaminated streambed sediments at urban/rural sites. This coefficient has specific applications that there are not in variance and standard deviation. The comparison between two groups of streambed sediments with lead concentrations upper (a) and lower (b) than the background concentration is one important application of variation coefficient. Streambed sediment samples of KRB at urban/rural sites did show homogeneity ($V.C_a$ = 1.009, $V.C_b$ = 1.005). Lead in streambed sediments at urban/rural sites lower than background concentration indicates less relative variation. As lead concentration decreases, the number of depositional sites does not decrease. There is no relation between lead concentrations in streambed sediments and distribution frequency for samples. Maximum content of lead in streambed-sediment samples with concentrations lower than the background concentration was due to secondary agents such as urban sewages mixed with waterways, and dilution by flood that affected on decreasing the anthropogenic concentrations. Negligible difference in variation coefficients for two groups of streambed sediments confirms similar urban/rural activities ($\Delta V.C = 0.004$). The presence of lead in urban/rural streambed sediments of KRB was caused by homogeneous anthropogenic activities. These include direct discharge of urban/rural sewages to basin's surface water but the weakest water from fireproof brick and earthenware factories should be considered.

Distribution patterns for lead indicate that grossly contamination (>SEL, **Table 3**) does not exist throughout the entire drainage network and persists in samples not only for all peripheral waterways but also for main channel, Karvandar River (**Figure 4**) AlthoughKarvandar River lies south and southeast of the upper areas of lead contamination, marginally to significantly contaminated samples (>TEL) were detected throughout the peripheral drainages. Among channels sampled here the Karvandar River shows the most marginally to significantly lead contamination.

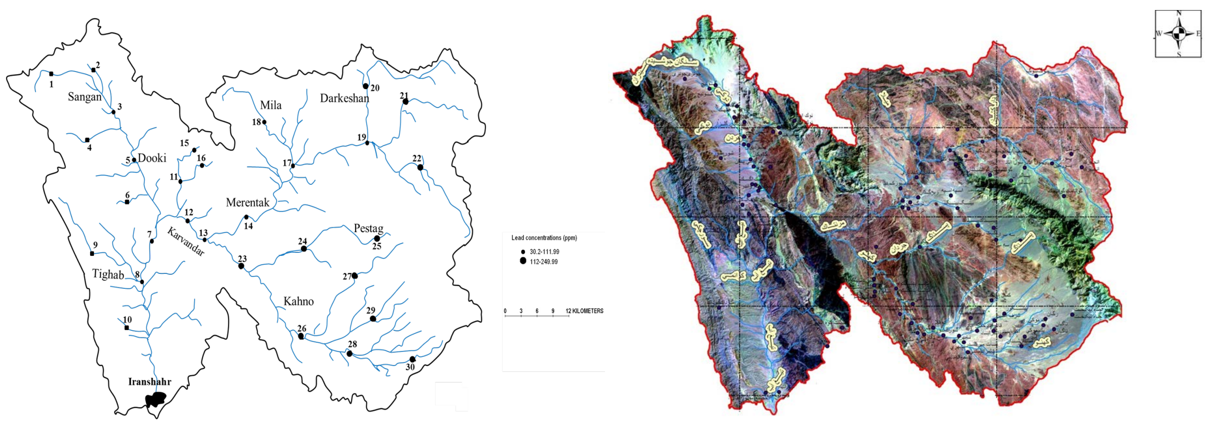

Figure 4. Geochemical map showing location of marginally polluted streambed-sediment samples (small solid circles) and significantly polluted samples (large solid circles) in the Karvandar River Basin.

Table 3. Comparison between Interim sediment-quality guidelines and lead concentrations (in ppm) in streambed sediment at urban/rural sites in this study.

Deacon and Driver (1999)[a]	Salomons and Forstner (1984)[b]	Jenkins (1981)[b]	Range in concentrations for background sites from this study[c] (<43 µm fraction)	Median concentrations for background sites from this study[c] (<43 µm fraction)
23 - 380	29.2	10 - 40	59 - 90	68

[a]Concentrations established for Streambed Sediments at background sites in the Upper Colorado River Basin. [b]Concentrations established at background sites for western US soils. [c]Concentrations from nonurban/rural sites (background conditions) in this study.

3.2. Role of Particle Size on Lead Concentration in Streambed Sediments

All 30 environmental samples were determined particle-size percentages of the depositional zones that were sampled. The particles in the <43 µm fraction in streambed-sediment samples ranged from approximately 35% to 92% at urban/rural sites and from 13% to 75% at nonurban/rural sites. Although percentages of the <43 µm particles differed among nonurban/rural sites, concentrations of lead generally did not largely increase with reduction in particle size. However, lead concentrations generally were higher at urban/rural sites rather than nonurban/rural sites for similar particle-size distribution (**Figure 5**) Anthropogenic activities were the most likely factor for higher percentages of <43 µm particles at urban/rural-affected sites. The concentration of lead on streamed material is strongly affected by the particle-size distribution of the sample [22]-[24]. As particle size decreases, lead concentration increases. Lead occurred at higher concentrations in the <43 µm fraction. (**Figure 6**) shows the relation between the <43 µm and total particle-size fractions for lead. The linear relation between the <43 µm fraction and total particle-size fraction indicates that the data sets are comparable. The smaller particles have more surface area to which the trace element can adsorb. These particles also have flatter surfaces, therefore their ability for adsorbing trace element increases [10]. The total particle-size fraction has less surface area than the <43 µm fraction due to many particles adhering together. Less area is available to which the trace element can adsorb due to the spherical and oddly shaped surfaces of the larger-size particles. However, studies of environmental effects of trace-element contamination need to consider the total particle-size fraction for total content of trace element in different systems.

3.3. Longitudinal Scattering

To evaluate the extent of downstream changes in lead concentrations of the streambed sediment, sites along Karvandar River (sites 13 - 14, 19 - 20, 26, and 28 - 30) were chosen to compare streambed-sediment lead concentrations in a downstream direction (**Figures 1-7**). The sampled sites of Karvandar River are located in an urban/rural area; therefore, lead concentrations at these sites are affected by the anthropogenic activities. Lead concentrations at about 90 percent of these sites were well above the median concentrations for lead at all urban/rural sites. The three sites on the Karvandar River (sites 20, 26, and 29) indicated a decrease in lead concentrations with increasing downstream distance. The headwater area of the Karvandar River is not intensely mineralized; therefore, background conditions may not provide for naturally occurringhigh concentrations of lead. The Spekar Stream (**Figure 1**) has a diluting effect on the Karvandar River drainage because site 27 is an order of magnitude lower in lead concentration than site 28 at near to the outlet point of Karvandar Basin.

To evaluate downstream conditions, sites were categorized into two groups [10] to determine differences in streambed-sediment concentrations between sites close to the anthropogenic source (sites 13 - 14), and sites downstream from the source (sites 19 - 20, 26, and 28 - 30). Comparing lead concentrations among sites indicated obvious differences between two groups. Concentrations of lead were lower at sites close to the source when compared to sites downstream from the source. An increase in concentrations was observed at sites downstream from the source. When comparing sites close to the source and sites downstream from the source as a whole, a pattern of increasing concentrations was observed for lead with increasing distance from the source (**Figure 7**). The increase in concentrations at sites downstream from the source was a result of suspended-sediment deposition on the downstream. Lead concentrations of streambed sediments being deposited at sites just upstream were not at a concentration level that can harmfully affect aquatic biota.

4. Conclusions

Streambed sediments provide an important archive for examining trace element and identifying anthropogenic

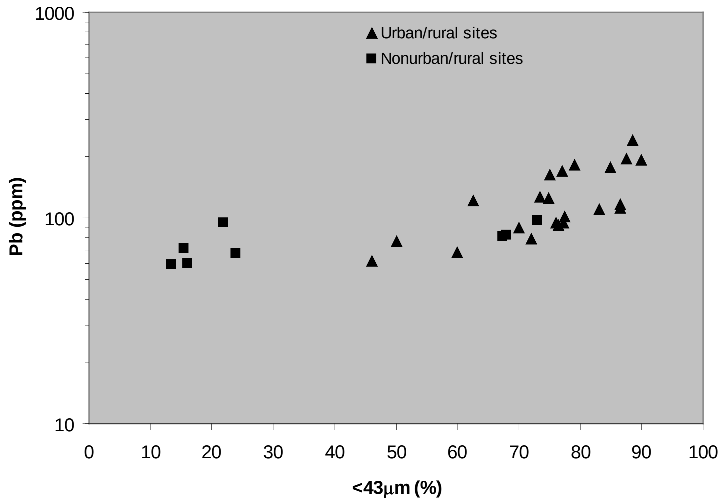

Figure 5. Comparison between trace-element concentrations and percent <43 µm particles for lead.

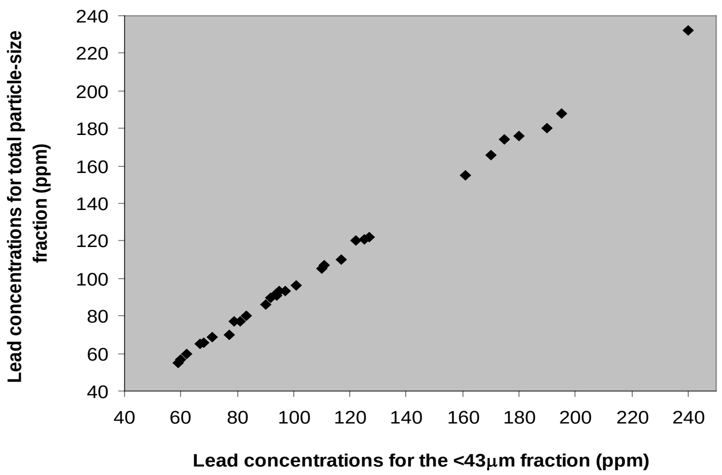

Figure 6. Comparison between the total particle-size fraction and the <43 µm fraction for lead.

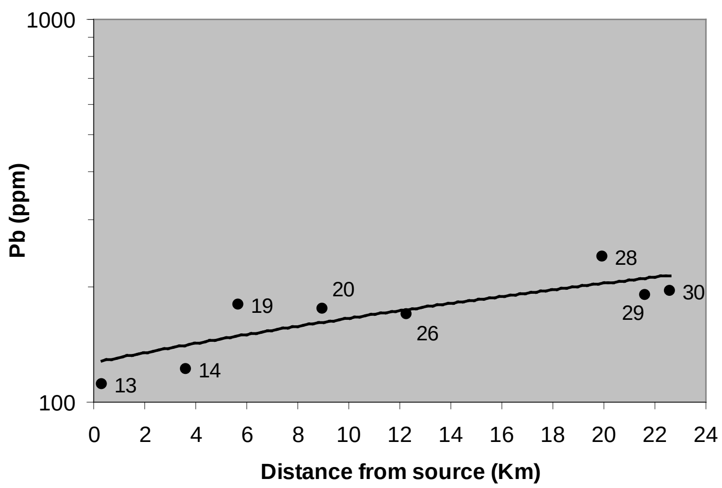

Figure 7. Relation of lead concentrations to distance from source.

pollution signals when detailed investigations are conducted. Lead concentrations need to be measured in streambed sediment for a more complete picture of the relation between geologic setting, element composition in streambed sediment, and land use. The ranges in lead concentrations at nonurban/rural sites in the study reflect mineralized areas of the basin. Because of the statistically insignificant influences from bedrock geology, comparison between sites with different geologic settings can be made without major effects of natural geologic characteristics. Median concentrations of lead from nonurban/rural sites as determined for the study basin were all above the threshold effect level (TEL). None of the concentrations were above the probable effect level (PEL). The range in concentrations of lead at urban/rural sites was generally orders of magnitude higher than the range of concentrations at nonurban/rural sites. Streambed sediment proved to be a useful indicator in defining stream reaches affected by anthropogenic activities. Lead in streambed sediment was at concentrations that can harmfully affect the aquatic biota in 48 percent of the urban/rural sites in the basin for both the <43 µm and total particle-size fractions. Although the study did not address effects on stream biota, other studies have shown that harmful effects on the aquatic biota occur at sites located below the urban/rural areas.

Comparison between lead concentrations at sampled sites in the KRB and the Ontario aquatic-sediment quality guidelines [25] indicates that grossly contamination (>SEL) does not exist throughout the basin.

Particle-size determination of streambed sediment samples indicated that urban/rural land use sites in the KRB contained a larger percentage of fine-grained particles than nonurban/rural sites located in the KRB. As particle size decreases, concentrations of lead increase.

Streambed sediments with the highest lead concentrations were located in the lower zone of the basin and associated with suspended-sediment deposition on the downstream.

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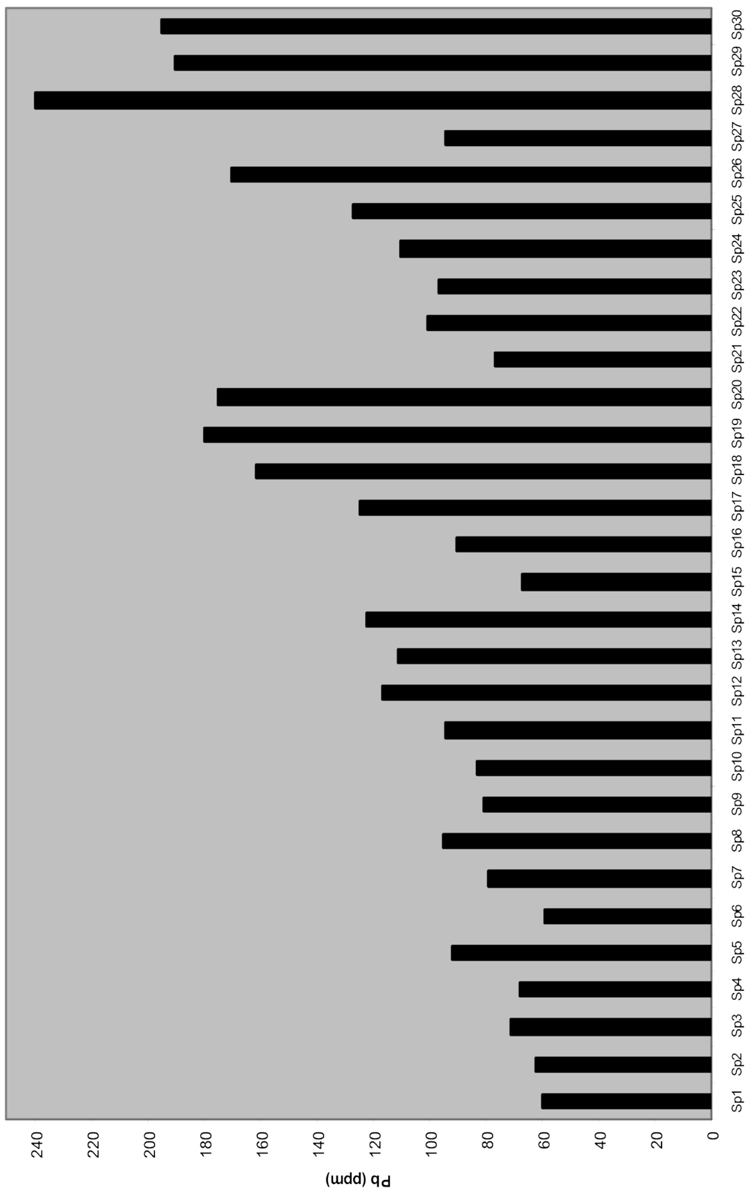
Appendix 1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