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Evaluating stream sediment chemistry within an agricultural catchment of Lebanon, Northeastern USA

Oluyinka Oyewumi · Jonathan Feldman · Jonathan R. Gourley

Abstract Recent arsenic pollution of drinking-water wells across Lebanon, northeastern USA has led to a growing concern about possible impact of agricultural activities on the hydrologic system. This study assessed the concentrations and distributions of arsenic and ten other elements (Al, Cd, Cr, Cu, Fe, K, Mn, P, Pb, and Zn) in stream sediments. The overall goal is to determine the extent of these elements within the fluvial systems, as well as overall sediment quality. A total of 65 stream sediments samples were collected, and analyzed for particle size distributions, organic matter contents, trace, and major elements concentrations. Results showed spatial variability in the concentrations of trace elements due to variation in sediments grain sizes, organic matter content, as well as land use activities within the study area. Calculation of sediment enrichment with respect to As, Cd, Cr, Cu, Mn, Pb, and Zn showed that about 48–52% of all the sampling locations are not enriched, nevertheless, approximately 2–11% of all the sampling locations are significantly enriched, an indication of anthropogenic input. However, results of ecological risk assessment showed no connection with sediment enrichment as most sampling locations have concentrations below the threshold probable effect concentration (PEC) value. Statistical analysis using principal component analysis (PCA) extracted three significant components explaining over 72% of total variance covering elements having origin in both natural and anthropogenic sources, thus suggesting that the concentrations and distribution of these elements within stream sediments are related to a combination of weathering processes on the bedrock geology, and anthropogenic activities.

Keywords Stream sediments · Enrichments · Trace elements · Fluvial system · Agricultural watershed

Introduction

The input of trace elements into drainage systems could be through natural sources relating to rock weathering and soil formation processes (Robinson and Ayotte 2006; Sharma and Rajamani 2000) or anthropogenic sources relating to human activities. For example, the use of organoarsenicals (roxarsone) as poultry feed additives has been known as a major source of arsenic within predominantly agricultural regions (Oyewumi et al. 2014; Rutherford et al. 2003). Roxarsone is often added to poultry feed at concentrations between 27 and 45 g per ton in order to boost growth, and prevent survival of cossidia intestinal parasites (O'Connor et al. 2005). However, roxarsone uptake in poultry tissue is low (Anderson and Chamblee 2001), as most of the roxarsone is excreted resulting in elevated concentration (15–77 mg/kg) of roxarsone in poultry litter

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(Anderson and Chamblee 2001; Garbarino et al. 2003). Studies have shown application of poultry litter containing roxarsone as fertilizer have led to the release of arsenic to agricultural farmlands (Codling et al. 2008), soil water (Brown et al. 2005; Kibet et al. 2013; Oyewumi and Schreiber 2012), drainages ditches (Church et al. 2010), and air from nearby poultry farms (O'Connor et al. 2005; Taupe et al. 2016). Other potential sources of trace and major elements include the use of biosolids, pesticides, and soil fumigations (Böhlke 2002; Gray et al. 1999), mining activities (Garcia-Sanchez and Alvarez-Ayuso 2003), gasoline traffic emission (Won et al. 2007), urbanization (Sutherland 2000; Wong et al. 2006), landfills (Looser et al. 1999), coal and oil combustion, manufacturing, and refuse incineration (Nriagu and Pacyna 1988).

The contamination of soils, sediments, water resources and biota by trace elements is of major concern because of their toxicity, and persistency in the environment (Ikem et al. 2003). Over the last decade, the geochemistry of stream sediments and soil within predominantly agricultural area, such as North Dakota, USA (Holmgren et al. 1993), northern Bangladesh (Bhuiyan et al. 2010), Gascogne region, France (N'Guessan et al. 2009), Algeria (Maas et al. 2010), Berlin, Germany (Säumel et al. 2012), China (Tang et al. 2010; Yu et al. 2012) have been studied for spatial and temporal assessment of the impact of human activities (Rubio et al. 2000; Zhao et al. 2014). Stream sediments are important environmental sinks and play critical roles in controlling the mobility of trace elements within fluvial systems (Ikem et al. 2003; Pekey 2006; Rubio et al. 2000; Segura et al. 2006; Semrod and Gourley 2014). However, the overall concentration of trace elements in stream sediments do not only depend on the pollution sources, but on the general character of solutes being transported as well as the physical composition of the sediments itself, such as grain size, surface area, surface charge (Presley et al. 1980; Viers et al. 2009). Incorporation of these solutes in sediments is further influenced by the pH, dissolved oxygen, geomorphologic, and hydrologic factors of the fluvial system (Emmerson et al. 1997; Pekey 2006; Semrod and Gourley 2014).

Lebanon, Connecticut is a predominantly agricultural community within the Northeastern USA (Fig. 1). It remains one of Connecticut's largest agricultural community despite residential growth pressure (Lebanon 2010), and home to one of the largest egg and broiler poultry farm (Kofkoff), with over 1.2 million yearly chickens production. Manure from Kofkoff poultry farm is often used throughout Lebanon to fertilize corn and hay fields, nurseries and greenhouses, orchards, and Christmas tree farms. Routine testing of drinking water in 2013 at the Lebanon Elementary School revealed traces of arsenic (As) in drinking fountains. In addition, various drinking wells in Lebanon showed elevated concentration of As above EPA standard of 10 μg/L (Metcalf 2015). While various studies on trace elements chemistry in groundwater and topsoil have been conducted within Lebanon area (Kim et al. 2015), the source(s) of arsenic to Lebanon water wells is yet to be fully understood. In order to understand the impact of agricultural activities in Lebanon, CT, it is necessary to elucidate the distribution, concentration and overall fate and transport of trace and major elements in various environments. This study examined the geochemical signature and spatial distribution patterns of arsenic and ten other elements of interest (Al, Cd, Cr, Cu, Fe, K, Mn, P, Pb, and Zn) within stream sediments of a predominantly agricultural watershed in Lebanon, CT.

Materials and method

Sample collection and analyses

A total of 65 stream sediment samples were collected from the Lebanon fluvial system between June 2014 and July 2015 (Fig. 1). Sampling locations were based on the distribution of land use activities as well as accessibility. Each sampling location was marked with the aid of Garmin GPS unit for creation of location map with GIS software. The sampling method employed at all sites were consistent: stream sediment samples were collected using a sterile stainless hand trowel and shovel, which were cleaned with alconox between locations. Samples were collected from the exposed and submerged edges of both sides and bottom of rivers/streams; with samplings depth ranges from the surface to about 10 cm below the surface. In locations where bridges cross river, we made every attempt to sample

Fig. 1 Location of the study area showing streams, sediment sampling sites, transfer station, and Trumbull cemetery in Lebanon, Connecticut, Northeastern USA (*inset*). Gray region is the boundary of Lebanon town
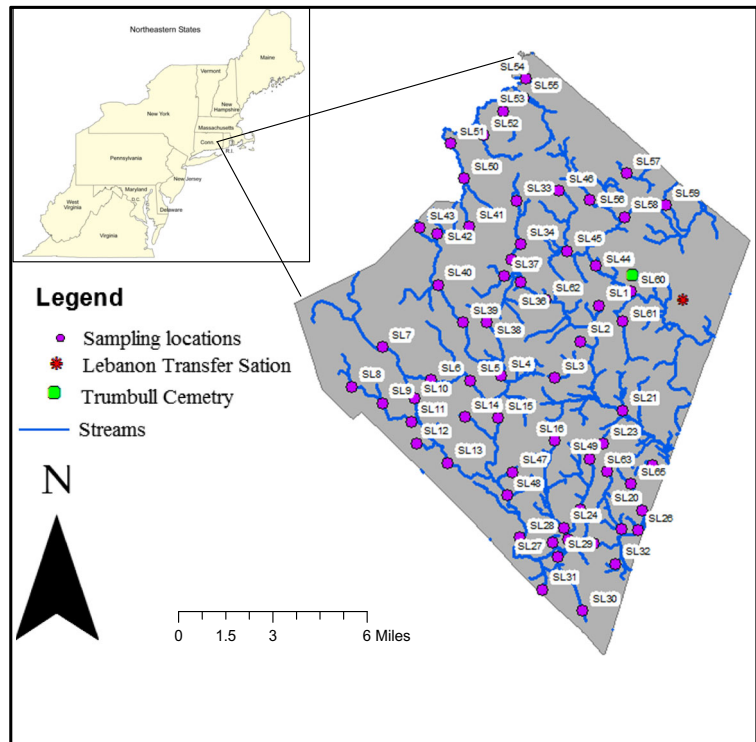
upstream from the bridge. The samples were later thoroughly mixed in a bowl to get a representative sample. During this process, twigs, leaves and other large debris were removed from the samples before packaging them into a labeled ziploc bags for further laboratory analysis.

In the laboratory, sediment samples were air dried, thoroughly homogenized, and sifted through a 2-mm sieve size. Fractions of the dried samples were analyzed for organic atter (OM) fraction using loss on ignition (Dean 1974; Konen et al. 2002). Particle size analysis (PSA) was also carried out using the ASTM 152H hydrometer method after dispersion of the soil with sodium hexametaphosphate (Calgon) for 24 hours (After Dane and Topp 2002). In addition, portion of those sample already sifted through 2 mm sieves were acid-digested using aqua regia based on EPA 3052 method (After Agazzi and Pirola 2000) in a CEM Mars 6 Express microwave. The acids used were not aggressive enough to dissolve the silicate lattice of the samples, only the adsorbed ions by clays, OM, and oxides were extracted into solution. The digested solution was analyzed for arsenic and ten other chemical elements (Al, As, Cd, Cr, Cu, Fe,

K, Mn, P, Pb, and Zn) using inductively coupled plasma-atomic absorption spectrometry (ICP-AES) at Virginia Tech Soil Testing Laboratory, Blacksburg, Virginia. For each individual sample, triplicate measurements were recorded by the ICP-AES detector and any sample that showed poor precision were repeated. In addition, initial, and continuing verification of calibration curve was performed for every 10 samples analyzed. Certified standard reference soil (Ref 2587) obtained from National Institute of Standards and Technology (NIST, Gaithersburg MD 20899) was also extracted with the batch using the same method to determine the degree of recovery of the method.

Assessment of sediment chemistry

Sediment enrichment factors

A number of approaches have been used to assess anthropogenic contributions to stream sediments in many related studies (Caeiro et al. 2005; Chabukdhara and Nema 2012; Loska 2004; Oyewumi et al. 2014;

Sutherland 2000). One such approach is the estimation of enrichment factor (EF) defined as the ratio of the concentration of a particular element in stream sediment samples to its natural background concentrations or concentrations from pristine unpolluted areas as shown in the equation below.

$$EF = \frac{C_m}{B_m}$$

where C_m is the measured concentration of elements in sediment, while B_m is the background reference concentration of the same element. The world average shale concentration is often used as background values, while some studies have also used average concentrations from uncontaminated area (Bhuiyan et al. 2010; Lee 1994; Oyewumi et al. 2014). In this study we used the average concentrations of trace elements at the headwater of streams located within forested area (of the same watershed) as our background reference concentrations.

Another important aspect of EF calculation involves compensation for a possible influence of grain size distribution and provenance on the trace element concentrations in the sediment. This is often done by normalization with a reference conservative element. Previously used reference elements for normalization include Mn (Yongming et al. 2006), Al (Oyewumi et al. 2014; Pokrovsky et al. 2006; Sutherland 2000), Ca (Loska 2004), Fe (Bhuiyan et al. 2010; Schiff and Weisberg 1999), Sc (Lee 1994; N'Guessan et al. 2009) and Li (Loring 1990). For this study we estimated EF by normalizing all chemical elements' concentration to Al concentration in stream sediments to compensate for the effect of grain size and mineralogy variation. Thus the EF takes the simple form (After Oyewumi et al. 2014; Sutherland 2000)

$$EF = \frac{C_{n\_sample} / C_{Al\_sample}}{C_{n-background} / C_{Al\_background}}$$

where C_{n_sample} is the element concentration in the sediment sample, C_{Al_sample} is the Al concentration in the sample, $C_{n-background}$ is the average concentration of element in the reference samples, and $C_{Al\_background}$ is the average concentration of Al in the reference samples.

Various studies have recognized different descriptive classes of enrichment; however, Oyewumi et al. (2014) pointed out an issue with absolute scale of enrichment due to difficulty in determining the actual threshold of enrichment because of the natural variability of elements from one region to another. In this study, we used population percentile values from frequency distribution plots of enrichment factors to operationally define three enrichment categories (After Oyewumi et al. 2014). The EF values that fall between zero and 50th population percentiles (EF $\leq 50^{th}_{percentile}$) are classified as not enriched (which indicates no/to low enrichment), while EF values within $50^{th}_{percentile} < EF < 90^{th}_{percentile}$ are classified as moderately enriched, and EF values greater than EF $\geq 90^{th}_{percentile}$ are considered as significantly enriched.

Evaluation of consensus–based sediment quality

We determined the impact of trace element concentrations on benthic (bottom dwelling) organisms by comparing trace element concentrations to consensus sediment quality guidelines (SQG), based on consensus threshold effect concentrations (TEC), and threshold probable effect concentrations (PEC). The TEC is the level of concentration of elements in sediment below which no effect on the benthic organisms is expected, while the PEC is the sediment concentration above which negative effects are expected frequently (After MacDonald et al. 2000). Locations with concentrations below TEC values do not require any attention, while locations with concentrations above PEC values indicate significant contamination, and thus requires monitoring due to a possible impact on benthic ecosystem within such streams.

Statistical analyses

All statistical analyses were carried out using SAS 9.2 with significant level of $\alpha = 0.05$ (JMP®, Version 12), and statistical package for social sciences (SPSS, Version 22). Geochemical data were tested for normality using Shapiro-Wilk W test ($p < 0.05$). Non-normal data were log-transformed to obtain a more symmetrical distribution that meet assumption of normality and variance homogeneity of a parametric statistics. Descriptive data analyses such as mean, median,

standard deviation, minimum and maximum concentrations were determined.

Correlation and cluster analyses were used to determine strength of geochemical association or relationship among different chemical elements and various components of the sediments such as organic matter (OM), clay, and silt fractions. Understanding such relationship is very important to determining possible partitioning of these elements within the fluvial system. In addition, principal component analysis (PCA) was applied to geochemical data in order to explore possible similarities in behavior of the metals(After de Andrade Passos et al. 2010; Song et al. 2011), and to reduce dimensionality of the geochemical data, and possible sources (Borůvka et al. 2005; de Andrade Passos et al. 2010). Significant principal components (PC) were selected using the scree plot generated from the PCA as well as eigen values greater than 1 (>1) as suggested by the Kaiser criterion (Kaiser 1974). The components were further examined using varimax rotation, and loading weight of elements greater than 0.50 were further considered significant and relevant to each component selected.

Table 1 Descriptive statistics of sediment components and acid extractable concentrations (mg/kg) from 65 stream sediment sampling locations within Lebanon fluvial system, Connecticut, Northeastern USA

Variable	Mean	Minimum	Maximum	Standard deviation
Clay %	2.91	0.04	17.3	3.54
Silt %	3.44	0.14	9.01	1.86
Sand %	93.65	76.97	98.99	4.31
OM %	2.35	0.40	12.72	2.26
Elements	Concentrations (mg/kg)			
Al(0.96)	5500	16,400	21,700	3097
As(0.6)	4.07	bdl	7.32	0.71
Cd(0.24)	0.28	bdl	0.96	0.13
Cr(0.96)	65	3.60	1400	172
Cu(0.72)	7.32	1.68	25	4.32
Fe(1.92)	7900	3326	18,400	3640
K(46)	700	177	1998	413
Mn(0.72)	171	39.17	594.48	103
P(6.48)	450	129	1190	234
Pb(3.6)	10	bdl	59.76	13
Zn(0.96)	23	9	91	15

Detection limits are listed in parenthesis after each element

bdl below detection limit

Results and discussions

Stream sediment characteristics and concentrations

Table 1 presents summary of geochemical data in stream sediments for eleven chemical elements (Al, As, Cd, Cr, Cu, Fe, K, Mn, P, Pb, and Zn) in mean values, standard deviation, minimum and maximum concentrations. All sediment concentrations were reported on a dry weight basis. Results showed Fe has the highest mean concentrations of 7900 mg/kg followed by Al with an average concentration of 5500 mg/kg, respectively. Concentrations of P and K are widespread with over 95% of the sampling locations having P and K concentrations well above 200 mg/kg. The observed distribution of P and K concentrations are likely due to input from agricultural activities within the study area due to the use of inorganic (phosphate) and organic (poultry and animal manure) fertilizer. Studies have shown poultry litter contain about 1700 to 24,900 mg/kg P concentration (Jackson et al. 2003; Oyewumi and Schreiber 2012; Rutherford et al. 2003), and variable concentrations of K ranging from about 8792 to 59,940 mg/kg (Jackson et al. 2003).

Trace elements such as As, Cd, Cr, Cu, Mn, Pb, and Zn have generally low mean concentrations of 4.1, 0.3, 65, 7.3, 171, 10, 23 mg/kg respectively. Concentrations of trace elements have been attributed to a number of factors such as the presence of polluting sources (Förstner and Salomons 1980; Pekey 2006) like agricultural activities, and sewage disposal facilities. Other factors include the type and relative abundance of organic matter content in soil and sediments (Lair et al. 2007), type and abundance of clay minerals (Shaheen et al. 2013), and metal oxides (Hering et al. 2014; Stollenwerk 2003), which influence the quantity of available binding sites (Tyler and McBride 1982) for sorption. Also, basic physicochemical properties of the soil like the pH (Lukman et al. 2013), redox conditions (Pant and Reddy 2001), as well as overall concentrations and speciation of specific elements within the sediments could influence their competition for available binding sites (Alloway 2013).

Arsenic concentrations are generally low (average: 4 mg/kg), with many locations showing concentrations

values below the instrument detection limit of 0.6 mg/kg and. We expected As concentration in stream sediment to be higher due to high concentration determined in top soil (Kim et al. 2015), as well as elevated concentrations (above EPA drinking standard of 10 μg/L) detected in many dug and drilled wells across Lebanon (Metcalf 2015). Also, it was expected that high Fe concentration in fluvial sediments (Average: 7900 mg/kg) would enhance high As adsorption due to well reported affinity between arsenic and iron oxyhydroxides in soil and sediment (Chen et al. 2007; Giménez et al. 2007; Stollenwerk 2003). The low As concentration could be attributed to a possible periodical dissolution of trace elements transported within agricultural runoff, or dilution from transported bed load derived from upper uncontaminated drainage areas, similar to the finding of Chen et al. (2004), or competitive adsorption between As and P, which has been shown to influence their overall concentrations in soils and sediments (Liu et al. 2001; Smith et al. 2002; Zhang and Selim 2008).

Chromium was detected from all sampling locations with a range of 3.6 to 1400 mg/kg. The highest Cr concentration value (1400 mg/kg) was determined at a downgradient side of a cemetery (SL 60). High Cr concentration in soil and sediments have been related to leachate discharge from cemeteries (Amuno 2013; Spongberg and Becks 2000), wastewater discharge (Singh et al. 2004), and abandoned landfill sites (Kemerich et al. 2012; Yusmartini and Setiabudidaya 2013).

The average concentrations of trace elements analyzed in this study are comparable to the background concentration values in shale (Turiekian and Wedepohl 1961) and other studies as shown in Table 2. The overall order of abundance of trace elements of interest in this study are Cr > Zn > Pb > Cu > As > Cd.

Grain size distribution in stream sediments varies across the study area. Information about grain size distribution is very important because it has been shown to influence sediment concentrations in many estuary systems (Miller and Miller 2007; Oyewumi and Schreiber 2012). As expected within stream sediments, 92% of the sampling locations are mostly sand, while clay contents are generally low with the exception of few locations: SL12 (16%), SL13 (17%), and SL23 (8%), respectively. Locations with reasonably high clay content also contained high concentration of various elements as follows: Cu (SL12: 25 mg/kg), Cd (SL13: 0.96 mg/

Table 2 Comparison of average stream sediment concentrations with other studies, and background values in standard world shale. All values are in either mg/kg or μg/g dry weight unless noted as percent (%)

	Background values in shale[a]	Montana, USA[b]	Hawaii, USA[c]	Gascogne, France[d]	Ganga plain, India[e]	Delaware, USA[f]	This study
Elements	Mg/kg	mg/kg	mg/kg	mg/g	μg/g	mg/kg	mg/kg
Al	80,000	8670	8.69(%)	52.99	–	6602.9	5500
As	1.6	72	–	15.14	–	3.47	4.07
Cd	0.3	3.5	–	0.3	2.16	–	0.28
Cr	90	–	107	52.98	20.89	–	65
Cu	45	848	49	18.86	43.48	5.73	7.32
Fe	47,000	3630	4.97(%)	28.59	6547.4	4208.86	7900
Mn	850	982	970	1.05	260.4	57.20	171
P	700	–	1330	0.5	–	208.12	450
Pb	20	15.3	63	24.9	32.88	–	10
Zn	95	557	240	81.73	63.65	39.24	23

[a] Turiekian and Wedepohl 1961

[b] Moore et al. 1989

[c] Sutherland 2000

[d] N' guessan et al. 2009

[e] Singh et al. 2004

[f] Oyewumi et al. 2014

kg), and Zn (SL13: 91 mg/kg). This is not surprising because clay fractions have been known to control abundance and distribution of trace element concentrations due to the presence of suitable binding sites (Shaheen et al. 2013). However, two notable locations (SL60 and SL62) with low clay contents (0.14 and 0.2%) contained high concentration of Cr (1400 mg/kg) and Cu (23 mg/kg), respectively. This unusual high concentration reflects possible anthropogenic point source of these elements at these locations.

Organic matter (OM) content varies from a low value of 0.4% at location SL56 to a high value of 13% at location SL13. Most locations with high clay content also have relatively high OM content such as locations SL8 (OM 6%, clay 7%), SL12 (OM 11%, clay 16%), SL13 (OM 13%, clay 17%), SL23 (OM 8%, clay 8%). As observed, there is a somewhat linear relationship between OM and clay fractions in sediments ($R^2 = 0.6$). Overall, results of this study showed that the distribution of trace and major elements are related to the abundance of OM contents, and fine grain sediment sizes.

Trace elements enrichment and ecological assessments

Table 3 presents result of enrichment factor (EF) for trace elements of interest. Approximately 48–52% of all the sampling locations have no to low enrichment with respect to As, Cd, Cr, Cu, Mn, Pb, P, and Zn. In addition, 40–43% of the sampling locations are moderately enriched, while only 1.5 to 11% of sampling locations are significantly enriched. Sediments with low enrichment suggest a possible reflection of natural source (Yongming et al. 2006) or natural variability in mineralogical composition of the crustal material (N'Guessan et al. 2009; Sutherland 2000), while sediments with moderate and significant enrichment suggest possible influence of anthropogenic input (Oyewumi et al. 2014). From the data, it is apparent that Cu has the most significantly enriched (EF ≥ 90th percentile) sites with 11% of sampling locations compared to 9% of sampling locations for As, Cd, Mn, P, Pb, and Zn, and 1.5% of the sampling locations for Cr. Spatial distribution of enriched locations for As, Cr, P and Pb are presented in Fig. 2. As shown, there is a wide distribution of enriched locations within and outside agricultural area. This might be due to conversion of many agricultural farmland areas due to residential pressure. Sediment enrichment within agricultural area may reflect physical remobilization of trace elements through

Table 3 Summary of calculated stream sediment enrichment from Lebanon fluvial system

Element	No/low Enrichment[1]% (n)	Moderate Enrichment[2]% (n)	Significant Enrichment[3]% (n)
As	51% (33)	40% (26)	9% (6)
Cd	52% (34)	41% (27)	9% (6)
Cr	49% (32)	41% (32)	1.5% (1)
Cu	49% (32)	40% (26)	11% (7)
Mn	48% (31)	43% (28)	9% (6)
Pb	51% (33)	40% (26)	9% (6)
P	51% (33)	40% (26)	9% (6)
Zn	48% (31)	43% (28)	9% (6)

Values under each category represent percentage number of sampling locations while those in parenthesis represent actual number of samples out of 65 samples. The EF values are defined by population percentile with: EF ≤ 50th percentile) considered "no/low enrichment", while 50th percentile < EF < 90th percentile classified as "moderate enrichment", and EF ≥ 90th percentile considered "significant enrichment"

erosion and transport from agricultural farmland to fluvial systems, and possible adsorption to sediments; while those outside agricultural area might be due to contribution from bedrock geology, or transport of fine grain sediment and associated trace elements during river flow from agricultural areas. However, other potential sources of sediment enrichment cannot be ruled out, though they are much less likely at this study area.

Table 4 presents result of ecological assessment of sediment chemistry. This is based on numerical sediment quality guidelines which are often used to evaluate the degree to which sediment concentrations might adversely affect aquatic organisms. Stream sediments quality were determined by comparing the level of sediment concentrations with the consensus–based sediment quality (CBSQ) guidelines using TEC and PEC values for As, Cd, Cr, Cu, Pb, and Zn (After Caeiro et al. 2005; MacDonald et al. 2000). Despite the widespread number of sampling locations with moderately enriched sediments, results of ecological assessment showed that all sampling locations were below the threshold PEC levels for As, Cd, Cu, Pb, and Zn except one location for Cr. Also, only four locations have concentrations above the TEC values for As and Pb. Overall, about 94% of all sampling locations have tolerable concentrations (below TEC levels) of As and Pb, 100% for Cd and Zn, and about 98.5% for Cr, respectively.
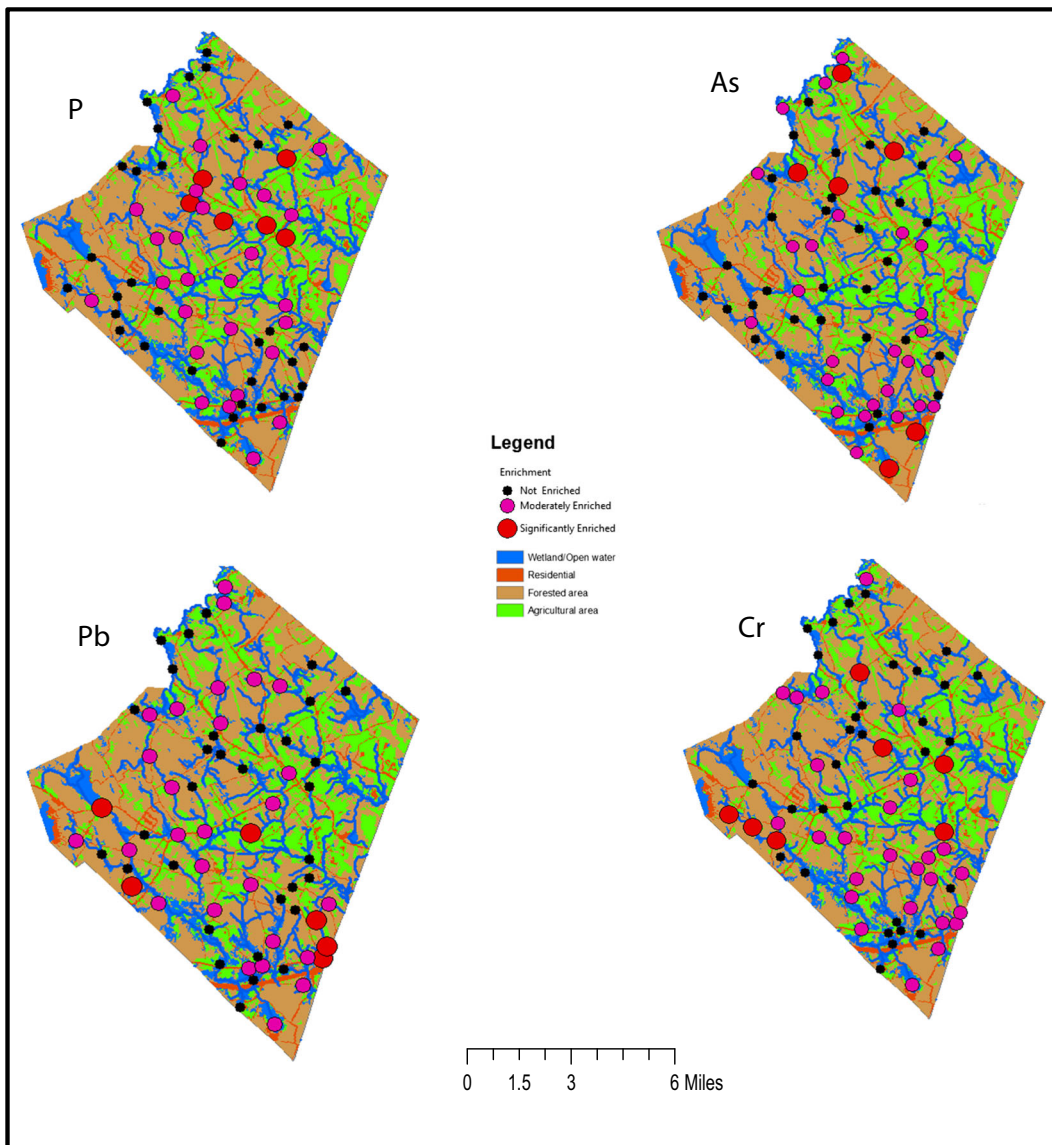
Fig. 2 Spatial distribution of sediment enrichment factor for As, Cr, P and Pb within Lebanon fluvial system. Sampling locations are shown in Fig. 1

Source apportionment

Table 5 showed correlation analysis on all geochemical data and soil constituents (OM, clay, and silt fractions). Geochemical data were initially log transformed before statistical analysis in order to ensure reliability of statistical results (After Oyewumi et al. 2014); however, soil constituents such as OM and sediment grain sizes were not log transformed. Positive significant $(r > 0.5, p < 0.05)$ correlation between Al with seven elements were observed such as Cd(0.71), Cr(0.52), Cu(0.59),

Fe(0.83), K(0.54), P(0.71), and Zn(0.80). This possibly confirms association of these elements with fine fraction in sediments, since Al is a well-known proxy element for clay minerals (Hanson et al. 1993; Pekey 2006). Similar to Al, there is a significant positive correlation between Fe and most elements such as Al(0.83), Cd (0.58), Cr (0.59), Cu (0.58), K(0.64), Mn (0.57), P (0.64), and Zn (0.77). This also possibly confirms association with iron oxide minerals within the sediments (Cornel and Schwertmann 1996; Li and Thornton 2001; McBride 1994). In addition, there is

Table 4 Ecological assessment of stream sediment concentrations showing the TEC and PEC values within Lebanon fluvial system

Concentrations in mg/kg

Element	MacDonald et al. (2000)		Results from this study				
	TEC	PEC	GM	Min	Max	Exceed TEC n (%)	Exceed PEC n (%)
As	6	33	6.70	bdl	7.32	4(6.2)	0
Cd	0.99	4.98	0.52	bdl	0.96	0	0
Cr	43.4	111	10.76	3.6	1400	1(1.5)	1(1.5)
Cu	31.6	149	6.90	1.68	25	0	0
Pb	35.8	128	6.70	bdl	59.76	4(6.2)	0
Zn	121	459	23.04	9.12	91.20	0	0

GM geometric mean concentration, *TEC* Consensus threshold effect concentration, *PEC* threshold probable effect concentration

a significant positive correlation among elements such as Pb and Cu (0.51), P and Cr (0.50), P and Cu (0.58), Zn and Cd (0.65), Zn and Cu (0.67), Zn and P(0.63).

High positive significant correlation also exist between soil components and most elements such as positive significant correlation between OM fraction and Al(0.57), As(0.51), Cd(0.62), Pb(0.54), and Zn(0.59). Also, between clay and Al(0.53), Cd(0.62), and Zn(0.49). Overall, high correlation among various elements might be due to their similar ionic radii (Chen et al. 1999), or possible affinity between these elements by virtue of similar source (Ghrefat et al. 2011), similar adsorptive characteristics between elements and minerals within the sediment (Eggleton and Thomas 2004), or similar biogeochemical processes that are active in influencing their mobility. Similar affinity of elements have been observed in many studies such as As, Cd, Cu, Mn and Zn affinity with the oxides and hydroxides of Fe and Mn (Prego and Cobelo-García 2003; Smedley and Kinniburgh 2002; Stollenwerk 2003); also, affinity between Cu, Zn and Pb to humic substances within sediments (Sekhar et al. 2004). The observed interelatioship between these elements is further illustrated with the cluster analysis (Fig. 3) using Ward linkage and Euclidean distance coefficient. The dendrogram clearly showed association between these elements and soil constituents similar to the observed relationship with correlation analysis.

Table 5 Correlation analysis on log transformed sediment geochemical data

	Al	As	Cd	Cr	Cu	Fe	K	Mn	P	Pb	Zn	OM	Clay	Silt
Al	1													
As	0.36	1												
Cd	0.71	0.44	1											
Cr	0.52	0.17	0.35	1										
Cu	0.59	0.21	0.35	0.58	1									
Fe	0.83	0.27	0.58	0.59	0.58	1								
K	0.54	0.22	0.29	0.38	0.64	0.64	1							
Mn	0.34	0.08	0.34	0.29	-0.02	0.57	0.18	1						
P	0.71	0.22	0.39	0.50	0.58	0.64	0.37	0.29	1					
Pb	0.48	0.12	0.43	0.23	0.51	0.35	0.36	0.02	0.24	1				
Zn	0.80	0.26	0.65	0.56	0.67	0.77	0.56	0.36	0.63	0.68	1			
OM	0.57	0.51	0.64	0.24	0.45	0.28	0.16	0.00	0.36	0.54	0.59	1		
Clay	0.53	0.36	0.62	0.21	0.32	0.20	0.08	-0.15	0.19	0.45	0.49	0.75	1	
Silt	0.05	-0.01	0.15	0.00	0.11	0.00	-0.05	0.00	0.04	0.09	0.08	0.14	0.20	1

Fig. 3 Dendrogram derived from cluster analysis of sediment geochemical data. The cluster analysis is based on Ward's algorithm and Euclidean distance coefficient
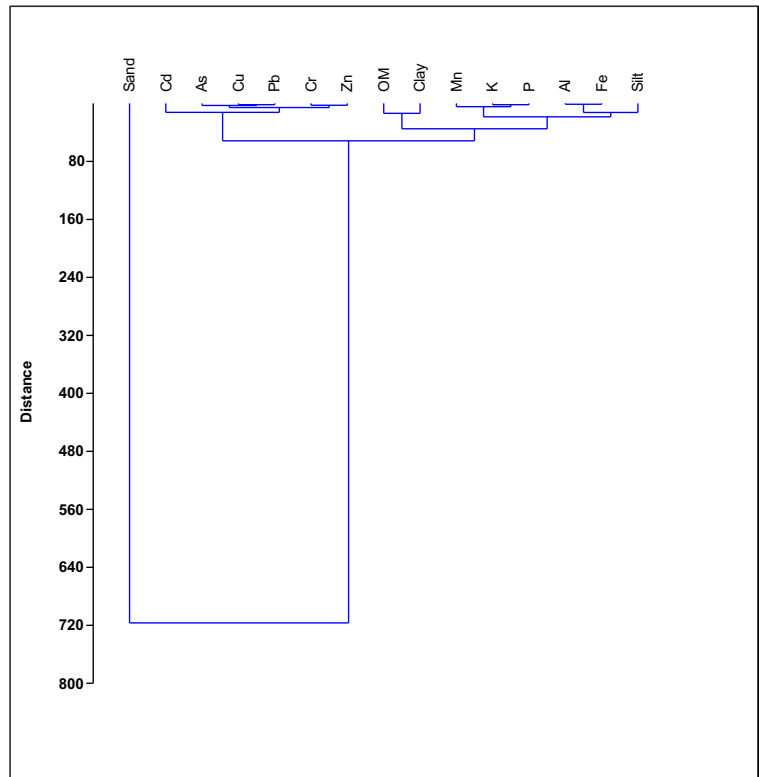
Geochemical data were further examined using multivariate method of principal component analysis (PCA) shown in Table 6. Three principal components (PC) were extracted based on eigenvalue greater than one (using Kaiser Criterion: Kaiser 1974). All the three selected components account for 72.49% of the total variance in the sediment data (Table 6). Elements with rotated component matrix (eigenvector weight)

Table 6 Varimax rotated principal component and eigen values of trace and major elements within stream sediments

	Rotated components matrix			
Elements	PC1	PC2	PC3	Communality
Al	*0.67*	0.41	0.48	0.85
As	0.04	*0.03*	*0.81*	0.64
Cd	0.33	0.31	*0.76*	0.78
Cr	*0.62*	0.43	0.003	0.53
Cu	*0.91*	−0.03	0.09	0.82
Fe	*0.64*	*0.63*	0.27	0.89
Mn	−0.003	*0.89*	0.13	0.79
K	*0.73*	0.13	0.09	0.59
P	*0.62*	0.44	0.13	0.61
Pb	*0.65*	−0.24	0.38	063
Zn	*0.78*	0.30	0.39	0.83
Eigenvalues	6.48	1.26	1.07	
Cumulative % of variation	51.44	62.89	72.49	

Elements influential to the component are italicized in bold (>0.5)

Fig. 4 Component plot in rotated space (components 1, 2, and 3) of major and trace elements within stream sediment of Lebanon fluvial system. The variance percentage of each component is shown in Table 6
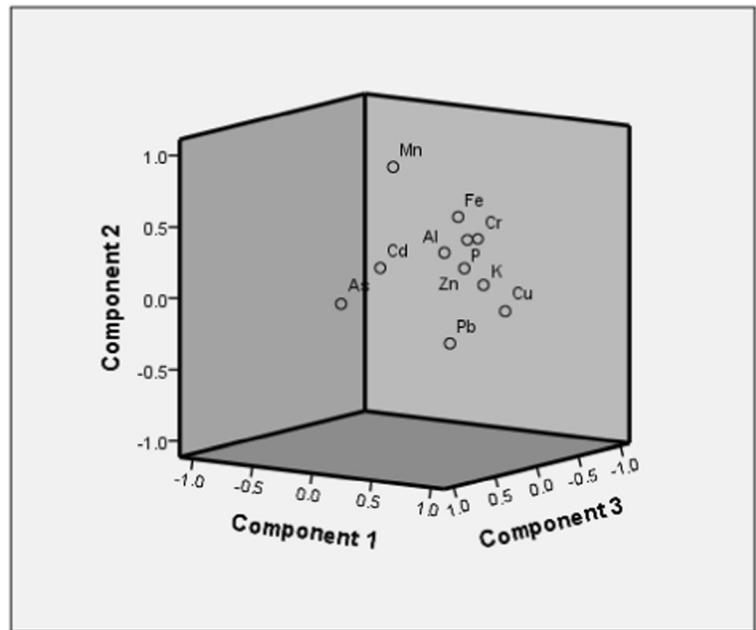
greater than 0.50 were further selected as influential to each component. The first component (PC 1) accounts for 51.44% of total variance in the data set. Eigenvector weight were positive (>0.50) for Al, Cr, Cu, Fe, K, P, Pb, and Zn; while only As, Cd, and Mn were below the threshold value of 0.50 in PC1. The second component (PC II) accounts for 11.45% of the total variance in the data set and eigenvector weight are positive (>0.50) for only Fe (0.63), and Mn(0.89). The third component (PC III) accounts for 9.60% of variance in data sets and eigenvector weight were positive for As(0.81), and Cd(0.76). Analysis of regional concentrations of most elements in PCI showed high concentrations of Fe and Al outside of agricultural area, while other elements have high concentrations within agricultural area of Lebanon. Previous petrographic and XRF analyses on Lebanon rock formations showed significant amount of Al and Fe (Kim et al. 2015) as the main component of various metaigneous rock formations at the study area. However, significant loading of trace elements such as As, Cd, and Mn in components (PCII and III) other than PCI is an indication of alternative sources of these elements within the study area. Spatial representation of the three rotated components is shown in Fig. 4. The wide distribution of element positions further illustrate different alternative sources within the study area.

Conclusion

Trace and major elements chemistry from Lebanon fluvial systems are shown to be due to a combined influence of bedrock geology and anthropogenic activities across the area. This is illustrated by the distribution of elements as well as calculation of sediment enrichment factors (EF), which showed that about 48 to 52% of the sampling locations have low enrichment with respect to As, Cd, Cr, Cu, Mn, P, Pb and Zn; while about 40 to 43% of the sampling locations are moderately enriched, and only 1.5 to 11% are significantly enriched. The low enrichment in sediment is a possible reflection of natural variability in mineralogical composition of the crustal material. Despite elevated arsenic concentrations detected in many drinking-water wells, and topsoil across Lebanon, our results showed low sparsely distributed concentrations of arsenic in stream sediments across Lebanon. Analysis of potential ecological risk of sediments showed that only one site (1.5%) exceeded PEC value for Cr, while four locations (6.2%) exceeded TEC values for both As, and Pb. Our results did not identify connection between sediment enrichment and ecological risks possibly due to low number of sites with significant enrichment. The reason for this is not fully understood; there is a possibility of preferential adsorption of trace elements to stream particulate, and dissolution in water column as they are

transported downstream. Overall, there is no general ecological risk for benthic organisms within the study area. It is imperative to note that geochemical assessment of agricultural landscape could be complicated by many factors such as changes in the land use pattern over time due to residential pressure; changes in weather pattern such as the effect of heavy rainfall and hurricane on stream sediment transport and enrichment. Thus, result from this study might not fully reflect overall impact of agricultural activities; it is therefore necessary for continuous monitoring of stream sediments concentrations so that safe threshold limits are not exceeded over time. Also, further study is warranted to examine geochemistry of trace elements associated with stream particulates, runoff from farmland, and agricultural soils in order to aid complete assessment of the impact of agricultural activities on Lebanon fluvial systems.

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