



Distribution and potential ecological risk assessment of trace elements in the stream water and sediments from Lanmuchang area, southwest Guizhou, China

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Abstract

Trace elements contamination in sediment is regarded as the global crisis with a large share in developing countries like China. Water and sediment samples were collected during (2016) from Qingshui Stream and analyzed for major physicochemical properties and trace elements by using ICP-MS. Our result of sediments showed that studied trace elements (except Pb, Cd, Co) had a concentration higher than Chinese sediment guideline as well as stream water data for studied trace elements (except Cr, Pb, Cd, Cu, and Zn) had a higher concentration than the maximum permissible safe limit of WHO. Contamination factor (CF) confirmed a moderate to high contamination in the sediment samples due to As and Tl, respectively. The values of pollution load index (PLI) were found above one (> 1), describing the progressive sediment quality decline. Pearson correlation showed that there was a significant positive association between Tl and As ($r = 0.725, p < 0.05$) in sediment samples. Results revealed that water-rock interaction, weathering of Tl sulfide mineralization, and hydrogeological conditions were major sources of stream water and sediments contamination in the study area. This experimental study contributes to a better understanding of the geochemistry and prevention of trace element contamination in sediments from Lanmuchang area.

Keywords Stream water · Sediments · Contamination · Trace elements · Pollution indices · Southwest Guizhou

Highlights

- Availability of trace elements in stream water and sediment samples were assessed.
- Smelting and mining discharges constituted the primary anthropogenic sources of trace elements in the study area.
- Tl, As, and Co enrichment was more in sediment studied samples.

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Introduction

Sediment contamination with the trace elements is a global issue (Fernandes et al. 2008; Kucuksezgin et al. 2008; Dou et al. 2013; Sungur 2016; Long and Luo 2017). In present years, the toxic element of pollution in the aquatic environment has worldwide concern because of its natural lethality, abundance, and perseverance (Yuan et al. 2011; Armitage et al. 2007). Huge amounts of hazardous elements have been discharged into rivers worldwide because of fast population growth and agricultural and industrial activities (Islam et al. 2014; Su et al. 2013; Srebotnjak et al. 2012). Mining and smelting activities are observed as the primary source of trace elements in the environment (Razo et al. 2004; Sun et al. 2010). The mining waste impact on the environment is considered as the most significant threat to the aquatic system and sediment ecological immovability due to their high content of trace elements causing from ore processing (Silva et al. 2009). The overall behavior of trace elements in the environment is strongly influenced by the relationship of metals with various geochemical levels in stream water and sediments (Morillo et al. 2004; Singh et al. 2005).

Geochemical speciation and the distribution of trace elements in the sediments were predicting the potential pollution, bioavailability and versatility in the aquatic biota and even various living microorganisms all through the stream (Pekey et al. 2004; Caeiro et al. 2005). The distribution of trace elements in stream sediments and water can be utilized to investigate anthropogenic and geogenic impacts on biological systems and furthermore evaluate the natural hazard (Zheng et al. 2008; Kwon and Lee 2001). The ecological risk evaluation is performed to determine the possibility of a strong ecological impact because of exposure to the environment (Posthuma et al. 2010). The geo-accumulation and potential ecological risk indices are the most conventional techniques, which are used to evaluate the ecological risk of trace elements in sediments (Chen et al. 2007).

Trace elements pollution of drinking water sources happened near Pearl River, China, in rapid sequence in the year 2013 and further provoked public alarms regarding metal pollution in China (Xiao et al. 2012). Conversely, it was well known that metals could be entering into the natural water from human activity and weathering of sulfide mineralized rocks (Chen et al. 2007; Gutierrez et al. 2009). Quaternary alluvium and Permo-Triassic age sediments overlain and underlain the Lanmuchang Tl-As deposit study area, respectively. Lime-stones, coal seams, and argillites are included as the most exposed (Xiao et al. 2003). Moreover, river sediment contamination has lightly been investigated in China in general, but no information is available for the Qingshui Stream sediments of Lanmuchang study area. The Qingshui stream is a main feeding tributary of the Lanmuchang area which was the reasonable source of drinking water for local population (Xiao et al. 2003) and is suffering from everyday anthropogenic impacts due to the pressure of serve mining plus ore covering and smelting activities midstream, the metal associated production downstream, and heavily inhabited areas in the entire stream. The previous research work, which dealt out Tl, focused on rocks, soil, minerals, water, and vegetation (Xiao et al. 2003; Jia et al. 2013), Tl poisoning issues (Zhang et al. 1997; Xiao et al. 2007), among others. The research work on stream water allied metals assignment into sediments is limited. Also, the scope and impact of hydrogeochemical transfer processes from irrigational and natural on the ecosystem is not well understood. According to the best of our knowledge, no research work has been done on trace element contaminations in steam water and sediments of the study area.

Therefore, the current study is designed (1) to determine the distribution, occurrence, and concentration of the trace elements in water and sediments, (2) to observe the potential ecological risk of the trace elements in sediments, (3) to evaluate the stream water quality using different approach, and (4) to identify possible sources of trace element pollutions using multivariate statistical tools. The findings of this study provide the baseline data highlighting the exposure-levels of trace

element contamination in the local groundwater and river sediment at Lanmuchang and associated pollution risk both locally and globally.

Materials and methods

Reagents

High purity ultra-pure water (18.2 M Ω cm) obtained from a Milli-Q50 system (Millipore, USA), ethanol 96% ($d = 0.808 \text{ g L}^{-1}$) pure pro analysis (Poch, www.poch.com.pl), HNO₃ 68% ($d = 1.42 \text{ g mL}^{-1}$) ultranal (Chemana, www.ciechtrading.com), nitric and hydrochloric acids (Merck, Darmstadt, Germany), hydrogen peroxide (H₂O₂, 30% v/v) GR grade (Sinopharm Chemical Reagent Co., Ltd., Beijing, China), and hydrofluoric acid (CNW Corporation, Shanghai, China). All the flasks, dish sets, and plastic were cleaned by retentive debilitate with the nitric acid ratio (1:9) and were cleaned with distilled water before used.

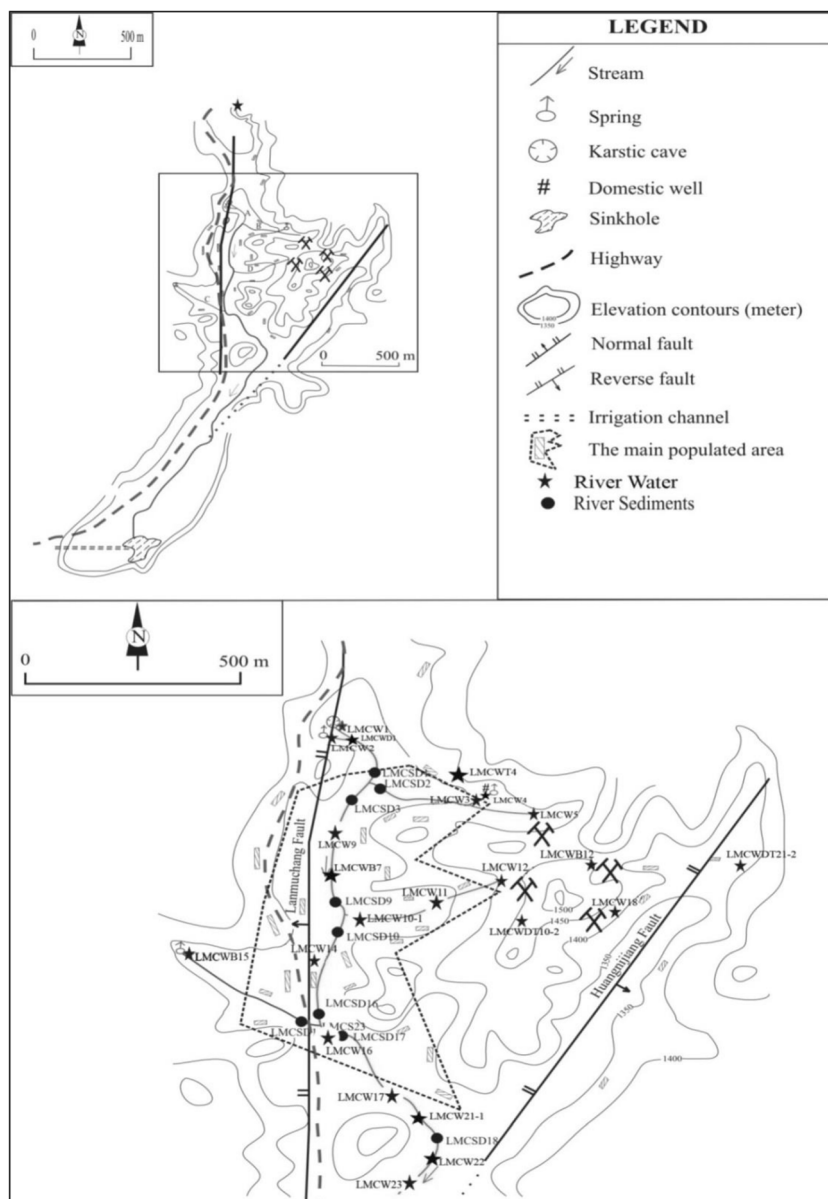
Study area

The study area (105° 30' 23" E, 25° 31' 28" N) is a small town (population ~1000), located in Lanmuchang in southwest Guizhou Province, China (Fig. 1). It is widely developed for agricultural and residential purposes. The latitude of the study area is between 1000 and 1600 m (asl) with a relative relief 200–600 m. The topography is characterized by valleys, depressions, peaks, sinkholes, karstic caves, and underground rivers. The local stream (Qingshui) runs through the Tl mineralized zone, into a natural wetland downstream (Xiao et al. 2003). Sulfide mineralization and local geology are well described in previous work (Xiao et al. 2003; Sun et al. 2012; Rasool and Xiao 2018). Briefly, the natural weathering of Tl-rich minerals (lorandite, realgar, orpiment, cinnabar, etc.) and past indigenous mining for cinnabar and agricultural activities have introduced high amounts of Tl into local soil, water, sediment, and crops, which brought about health risk on local residents (Xiao et al. 2007, 2012; Sun et al. 2012). The local residents are suffering from hair loss, muscle and joint pain, weakness, vision disturbance, etc., which are the symptoms of chronic Tl poisoning (Xiao et al. 2004).

Sample collection

Thirteen samples of sediments and 24 samples of water were collected at upstream and downstream of the Qingshui, respectively, during May 2016 from Lanmuchang area southwest Guizhou (Fig. 1). All the samples were filtered on site using Millipore Strives syringe capsules, which contain 0.45- μm cellulose acetate filters. The filtered water was collected in pre-cleaned 60 ml Nalgene bottles (twin samples),

Fig. 1 Sampling location map of Lanmuchang study area, southwest Guizhou



one of them for anion and the other for cation determination (secured using 0.4% ultra-pure HNO_3 , which acidify samples at $\text{pH} = 2.0$). The parameters of water, for example, temperature, pH, electrical conductivity (EC), and TDS, were estimated in situ by using pH/EC meter (AISI pHB9901, Taiwan, China). The pH meter was calibrated with buffer solutions ($\text{pH} = 4, 7, \text{ and } 10$) to adjust the pH electrode. During sampling, the duplicate samples were collected at every 10th sites. From every sampling site, the water replicates 500 ml was collected into a Nalgene polythene bottle. The sediment samples at the depth 0–10 cm (approximately 500 g) were collected at the same point as water samples using portable Ekman grab sampler, repeated three times, and stored in polythene bags. All the samples were sealed, stored in coolers at 4°C , then transferred to the laboratory and kept at the same

temperature. Sediments samples were air-dried, standardized, and sieved (2-mm mesh) before analysis. The sieved samples were ground in Bico ceramic disc grinder and ceramic ball mill to ensure the reduction to 80-mesh powder. Since soil is comprised of three soil separates, i.e., sand, silt, and clay, sediments were passed through 2-mm sieve to reflect soil conditions (Deng et al. 2017). In addition, several researchers have already published the metal association with 2 mm sediments (Sun et al. 2012; Louhi et al. 2012; Wu et al. 2014; Rasool and Xiao 2018).

Sample preparation and analysis

To measure pH, and electrical conductivity (EC), 10 g dry ground samples and 25 ml Milli-Q water were put into a

100-ml Erlenmeyer flask. The mixtures were shaken for 1 h and then measured using a calibrated HACH HQ30d pH meter (HACH, Loveland, USA) after equilibrating by standing 30 min. For sulfate and nitrate measurement, 10 g of dry ground samples were mixed with 50 ml Milli-Q water in a 100-ml Erlenmeyer flask. The mixture was shaken for 5 min, then standing for 4 h for equilibration. The supernatant was filtered using a 0.45-mm filter membrane after centrifuged at 3500 rpm. The anions of filtrate were determined by ion chromatography (DIONEXICS-40, Sunnyvale, CA, USA). Sediment organic matter (OM) was determined by the $K_2Cr_2O_7-H_2SO_4$ oxidation method. Total organic carbon (TOC) was measured by an elemental analyzer (Vario MACRO cube Elementar, Hanau, Germany), (Schumacher 2002; Xiao et al. 2016). Trace elements and major cations were measured by ICP-MS (Agilent, 7700x, California, USA) and ICP-OES (iCAP6500, Thermo Scientific, Germany), (Qi et al. 2000) after digesting 50 mg sediment samples in a Teflon tube with HNO_3 and HF (5:1, v/v), (Edgell 1989; Xiao et al. 2016). All of the experiment and analysis in this study were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Science.

Quality assurance/quality control

The analytical precision determined based on the standard quality control procedures using internationally certified reference materials (CRM stream sediment GBW07302a, US NIST), internal standards (Rh at 500 $\mu g/L$), reagents blanks, and duplicates were better than $\pm 10\%$. The recoveries of samples spiked with standards ranged from 95 to 106%, and the relative standard deviation (RSD) was within 5%. The concentration of toxic elements in blank always gave values less than 3% of the measured content in samples.

Sediment pollution indices

The magnitude of contamination can be evaluated using Enrichment factor (EF), which is considered as an effective tool for this purpose (Franco-Uria et al. 2009; Salati and Moore 2010). The EFs was calculated using the equation (Pereira et al. 2007; Zhang and Shan 2008; Selvaraj et al. 2004) for each element.

$$EF = [C_x/C_i]_{Sample} / [C_x/C_i]_{Background} \tag{1}$$

where (C_x/C_i) is the concentration ratio of the targeted element (C_x) to normalized elements (C_i , usually from natural sources and exhibiting traditional behavior) in the samples and their corresponding background values. The reference element is conservative, and the most commonly used elements are Al, Fe, and Ti (Hernandez et al. 2003; Abraham and Parker 2008).

Al is one of the important components of the Earth crust and was used as the reference element (Amin et al. 2009; Benhaddyya and Hadjel 2014). The geochemical abundances of the Guizhou sediment (Cr, Co, Cu, Zn, As, Cd, Tl, and Pb at 133.3, 0.612, 38.6, 135.9, 28.5, 1.244, 0.33, and 33.1 mg/kg, respectively) were selected as reference background values. $EF = 1.5$ is considered a critical value for distinguishing the anthropogenic input and natural input (Wang et al. 2015). The EF values could be classified as no (< 1.5), moderate (1.5–5), significant (5–20), very high (20–40), and extreme enrichment (> 40) (Sutherland 2000).

The geo-accumulation index (I_{geo}) (Muller 1979) can be used to assess the degree of contamination from trace elements. I_{geo} had widely been used in heavy metal studies of sediments (Santos Bermejo et al. 2003; Singh et al. 2005; Amin et al. 2009). To characterize the level of contamination in the sediment (Banat et al. 2005), I_{geo} values were calculated using the following equation:

$$I_{geo} = \log_2 [C_n / (1.5B_n)] \tag{2}$$

where C_n is the measured concentration of the metal in the sediment, and B_n is the geochemical background value of the element in the background sample (Yu et al. 2011; Islam et al. 2015a). To compensate for variations in background values and anthropogenic influences, factor 1.5 was used, respectively.

In river sediment, the level of metal contamination was expressed by the parameter of CF using the following equation:

$$CF = C_i / C_{bi} \tag{3}$$

where C_i is the measured concentration of the metal in the samples and C_{bi} is the corresponding background values.

For each site, the procedure of Tomlinson et al. was adopted to evaluate the pollution load index as follows:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n} \tag{4}$$

where n is the number of metals. The value of PLI, which is an effective tool to evaluate heavy metal pollution, higher or less than one indicates the samples are polluted or not, respectively.

Hakanson 1980 invented the method to assess the potential ecological risk which is widely used to assess the soil and sediment pollution. The potential ecological risk index is derived from integrating ecological toxicity and concentration of different pollutants as

$$Ri = \sum_{n=1}^n Ei = \sum_{n=1}^n Ti \times Ci \tag{5}$$

where Ei is the potential ecological contamination hazard factor, while Ti is lethal reaction factor and Ci is the proportion of trace component concentration in the samples of sediment

comparing background level. According to Hakanson 1980, the sediments can be divided into five classes. Chen and Xu et al. described this method in detail (Chen et al. 1989; Xu et al. 2008). The toxicity coefficients of As, Cu, Zn, Pb, and Cr have been determined, but the toxicity coefficient of common environmental pollutants, such as Tl, has not been determined in the environmental impact assessment, so RI method seldom is used for assessment of its pollution. Thus, the toxicity coefficient of Tl was calculated according to the calculation principle proposed by Hakanson. The researcher showed that the toxicity of Tl was similar to As (Lv 2014). In summary, Tl toxicity coefficient was determined as 10 in this study, and calculated values were, As=Tl = 10, Cd = 30, Pb=Cu = 5, Cr = 2, and Zn = 1, respectively (Hakanson 1980; Lv 2014; Liu et al. 2018). There are four levels of RI; low (RI < 150), moderate (150 < RI < 300), considerable (300 < RI < 600), and very high ecological risk (RI > 600).

Statistical analysis

Microsoft Excel (v.2010) and SPSS (v.17) were used to perform statistical analysis including Cluster Analysis (CA), Principle Component Analysis (PCA), and Correlation Matrix (CM). Gibbs and Chadha diagrams (Gibbs 1970; Chadha and Ray 1999) and Piper diagram (Piper 1994) were used to determine major ion chemistry of stream water and hydrochemical facies, respectively. ArcGIS (v.10.2) and CorelDraw (v.12) were used for mapping.

Results and discussion

Physicochemical characteristics

All the physicochemical parameters of stream water and sediment samples are summarized in (Table 1 and Table 2). One of the most significant parameters of water quality is pH. The pH was observed slightly alkaline between 7.62 and 8.3, except for deep mine water sample LMCW9, which is acidic with pH value 2.62, whereas in sediment was acidic in the range 3.65 to 6.89, respectively. The pH values were mostly within the permissible limits, as described by WHO (6.5–8.5) (WHO 1993; Rasool et al. 2016b). Water's taste was bitter because of higher pH, which was due to water-rock interaction and presence of HCO_3^- as a result of weathering of carbonate rocks (Shyamala et al. 2008; Lopez-Pazos et al. 2010). Relatively acidic pH of river sediment samples might be due to the weathering of sulfide mineralization and deep mine activity in the study area (Xiao et al. 2004; Adomako et al. 2008). The EC values ranged from 26.4 to 153.5 $\mu\text{S}/\text{cm}$ in water samples, whereas in sediment ranged from 283 to 2840 $\mu\text{S}/\text{cm}$, respectively. Sediment sample LMCS16 of

downstream near mine shows higher EC value. All water samples were within the permissible limits of WHO 500 $\mu\text{S}/\text{cm}$ for EC (WHO 1993; Rasool et al. 2016b). The water quality from different aquifers can easily be determined using EC (Arain et al. 2008; Adhikary et al. 2010). In the current study, higher dissolved salts and mine waste resulted in higher EC of stream water sediments (Xiao et al. 2007; Abbas et al. 2014). The TDS values ranged from 17.68 to 102.85 mg/L in water samples. All water samples were within the permissible limits of WHO for TDS (WHO 1993; Rasool et al. 2016b). The TDS in stream water originate from natural sources, domestic waste, and chemicals used in the water treatment process (Pradeep 1998; Rasool et al. 2016a). The concentration of major ions like calcium (Ca^{2+}) ranged from 34.94 to 128.2 mg/L in water, whereas 709.46 to 75,746 mg/kg in sediment samples. All samples of water were below WHO limits 100 and 200 mg/L of Mg^{2+} and Ca^{2+} (WHO 1993; Rasool et al. 2016b), but in sediments, all samples exceeded the SEPA permissible limit (SEPA 1995). Higher Mg^{2+} and Ca^{2+} concentrations in river sediment samples were resulted due to weathering of silicate minerals and accumulation of these ions in river water through interactions between water and rocks (Ashraf and Foolad 2007; Xiao et al. 2004). Nitrate (NO_3^-) concentration was found between 0.15 to 37.97 mg/L and 0 to 1.77 mg/kg in water and river sediment samples of the study area. The highest NO_3^- concentration (37.97 mg/L) was noted in midstream sampling location LMCWDT10-2 study site. WHO maximum permissible limit for NO_3^- in water is 10 mg/L, 83% samples exceed the WHO limit (WHO 1993; Rasool et al. 2016b), as well as all sediment samples below permissible limit SEPA (SEPA 1995). Agricultural activities and higher sewage discharge were the main reasons for higher concentrations of NO_3^- in samples (Ahmed et al. 2004; Kahlowan et al. 2006). Similarly, sulfate (SO_4^{2-}) concentrations ranged from 8.18 to 1283.26 mg/kg in water and 27.56 to 1501.69 mg/kg in sediment samples of site Lanmuchang area. Ninety-six percent of the water samples exhibited lowers the WHO permissible limits (250 mg/L) (WHO 1993; Rasool et al. 2016b), while 54% sediment samples crossed SEPA safe limit (SEPA 1995). Natural erosion and weathering contributed to higher values of sulfate in sediment samples. Among these parameters were likely higher organic matter (OM) content at LMCS10-2 (106.1 g/kg), while higher total organic carbon (TOC) content at LMCS10-2 (61.75 g/kg) in sediment samples from midstream of study area (Rasool and Xiao 2018). Solubility and mobility of trace elements are controlled by higher TOC in sediment samples (Carrillo-Gonzalez et al. 2006). The higher organic matter is due to an organic waste influx in midstream by surface runoff during monsoon season, the influx of organic wastes by surface runoff during monsoon season (Abilio et al. 2012).

Table 1 Concentrations of major ions and trace elements of stream water in Lannuchang study area ($n = 24$)

Samples ID	pH	EC	TDS	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	HCO ₃	K ⁺	Mg ²⁺	Na ⁺	Cr	Co	Cu	Zn	As	Cd	Tl	Pb
LMCW1	7.93	44.21	29.62	2.36	14.21	57.13	68.53	260	1.24	9.95	3.68	0.71	0.28	0.76	15.18	0.61	0.06	0.17	0.64
LMCWD1	7.91	44.1	29.54	2.28	14.53	56.76	62.05	270	1.55	9.97	3.29	0.89	0.19	0.26	11.97	0.3	0.04	0.12	0.17
LMCW2	8.08	38	25.46	1.9	11.63	97.3	77.32	280	1.83	11.54	3.13	0.14	0.06	0.22	35.03	1.16	0.03	1.29	0.26
LMCW3	8.3	26.4	17.68	1.99	22.83	14.69	34.97	250	1.72	3.58	1.75	2.81	0.03	0.32	7.15	0.35	0.01	0.01	0.19
LMCW4	8.08	31.1	20.87	2.57	25.48	30.78	62.57	270	0.83	3.58	1.59	2.19	0.05	0.4	8.27	0.39	0.01	0.01	0.33
LMCW5	7.57	41.7	27.99	3.21	16.18	74.42	77.58	280	3.63	7.71	3.69	1.49	0.45	0.62	9.44	4.71	0.01	2.01	0.31
LMCW9	2.62	153.5	102.85	0.86	0.14	1283	115.66	320	6.02	12.03	1.04	27.81	64.42	128.1	408.9	2.17	0.96	75.65	1.25
LMCW10-1	6.7	44.7	29.99	6.5	12.37	78.31	77.85	310	5.35	7.45	6.76	0.63	0.46	0.28	10.26	7.33	0.01	0.72	0.18
LMCW11	7.85	35.4	23.78	3.86	23.55	24.62	62.79	350	1.94	5.05	2.76	0.52	0.51	0.26	7.745	8.84	0.01	0.90	0.16
LMCW12	7.87	49.6	33.22	7.87	3.69	83.88	85.98	310	7.07	7.36	9.01	0.49	0.55	0.25	10.39	15.62	0.02	1.61	0.19
LMCW14	7.77	40.8	27.36	5.25	14.88	49.43	75.59	320	3.58	5.79	5.83	0.41	0.41	0.32	10.07	9.99	0.01	1.34	0.06
LMCW16	7.57	28.1	18.87	5.68	11.95	49.27	72.97	340	3.64	5.71	5.79	0.71	0.53	0.56	25.16	18.02	0.04	2.12	0.37
LMCW17	7.75	29.3	19.61	5.41	10.31	46.87	76.41	310	4.72	5.69	4.83	1.94	0.12	0.42	10.09	1.44	0.08	0.06	0.13
LMCW18	8.01	30.1	20.17	4.63	16.74	43.86	72.43	320	4.91	5.23	3.87	0.39	0.81	0.69	22.07	18	0.06	1.91	0.39
LMCW20	8.29	32.7	21.99	1.62	18.57	8.18	62.01	200	1.43	4.59	1.56	2.42	0.05	0.39	1822	0.23	0.27	0.07	2.97
LMCW21-1	8.02	30.1	20.67	1.9	24.71	8.17	128.2	250	1.46	3.52	1.65	3.49	0.03	0.36	12.02	3.42	0.08	0.37	0.17
LMCW22	7.77	47.7	31.59	3.59	30.64	13.5	65.85	310	0.62	3.34	1.08	2.45	0.04	0.33	37.07	0.08	0.04	0.07	0.18
LMCW23	6.69	57.11	38.27	10.91	0.36	149.68	78.99	220	5.66	8.31	5.56	0.51	1.09	0.17	16.24	642	0.09	2.04	0.12
LMCWDT4	8.18	31.4	21.38	2.69	26.29	31.39	57.45	280	0.89	3.42	1.57	2.14	0.05	0.45	7.89	0.51	0.06	0.04	0.32
LMCWDT10-2	6.8	44.8	30.16	12.75	37.97	81.15	118.79	320	5.98	4.16	8.07	0.38	0.05	0.45	31.2	1.96	0.02	1.02	0.12
LMCWDT21-2	8.12	30.4	20.68	1.52	18.45	8.25	66.59	260	1.35	4.69	1.61	2.45	0.05	0.37	182	0.26	0.24	0.05	2.91
LMCW87	7.62	48.5	32.95	5.23	16.36	48.49	68.98	310	4.17	5.65	5.01	0.27	0.12	0.65	83.01	12.77	0.04	1.73	0.38
LMCW812	7.97	51.6	34.52	7.87	3.55	84.46	85.84	300	7.25	7.45	9.26	1.17	0.79	0.87	25.53	17.84	0.03	2.03	0.36
LMCW815	7.67	29.1	19.47	2.34	14.54	57.56	59.37	320	1.14	10.05	3.31	0.46	0.12	0.08	14.99	0.46	0.07	0.18	0.05
WHO			1000	250	10	250	100	500	12	50	200	50	10	2000	3000	10	3	2	10

The abbreviation LMCW express Lannuchang water and LMCWDT represent the drinking water samples of Lannuchang. TDS express in mg/L. All cations and anions with WHO values are expressed in mg/L, while all trace elements with WHO are in µg/L, and EC in (µS/cm), n number of samples

Table 2 Concentrations of major ions and trace elements of stream sediments in Lanmunchang study area ($n = 13$)

Samples ID	pH	EC	TOC	OM	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Cr	Co	Ni	Cu	Zn	As	Cd	Tl	Pb
LMCSD1	5.88	345	20.05	35.26	1.778	70.72	21556	1356	92.84	28.55	69.25	74.72	130.1	196.36	0.47	16.31	18.41
LMCSD2	6.49	966	53.04	91.23	0	189.2	36,148	1214	103.57	27.69	53.93	89.73	129.67	330.48	0.68	36.44	30.33
LMCSD3	6.6	283	24.12	41.49	0.548	27.56	23,492	1959	480.8	49.83	163.28	108.27	167.28	139.44	0.53	0.72	18.88
LMCSD9	3.65	948	55.54	95.53	0.539	504.1	709.46	147.6	103.28	6.27	22.66	69.90	62.64	383.23	0.64	72.34	49.36
LMCSD10	5.8	1443	38.01	65.38	0	346.2	22,880	1296	210.78	31.715	76.76	103.29	271.3	309.49	0.68	13.75	28.07
LMCSD10-2	5.74	2750	61.75	106.1	0	1501	34,064	2001	184.73	31.41	67.67	104.27	349.8	254.3	0.84	16.35	29.98
LMCSD11	6.43	1079	58.72	100.9	0	237	75,746	3750	118.45	32.72	68.96	84.52	239.8	123.06	0.61	4.337	24.06
LMCSD12	6.07	2420	53.39	91.83	0	1432	49,408	2940	176.67	32.02	76.58	117.49	330.8	258.16	0.94	22.29	32.87
LMCSD14	6.14	2380	50.93	87.59	0	1059	48,518	6011	209.49	34.7	74.69	97.75	236.9	204.7	0.88	14.64	30.13
LMCSD15	6.68	544	32.86	56.52	0.732	111	26,554	1042	208.95	39.704	78.29	108.88	182	291.92	0.51	16.49	28.25
LMCSD16	6.09	2840	55.78	95.94	0	643	38,196	6254	222.27	37.96	84.22	109.48	278.7	230.75	0.77	15.24	26.01
LMCSD17	6.04	1000	38.69	66.54	0	250	24,866	4836	279.94	42.35	102.41	102.55	210.2	306.64	0.72	7.23	24.51
LMCSD18	6.89	962	28	48.16	1.193	310	11,376	2049	226.5	41.95	93.66	109.21	190.7	230.95	0.7	5.78	25.18
SEPA (mg/kg)									250	50	60	100	300	5	10	1	350

The abbreviation LMCSD represents Lanmunchang river sediment. All major ions and trace elements values are expressed in mg/kg while TOC and OM are expressed in g/kg and EC in ($\mu\text{S}/\text{cm}$); n number of samples

Hydrogeochemical assessment of water

The interaction between rock chemistry and percolated water chemistry in the study area is well indicated by Gibbs plot (Gibbs 1970), which stress that weathering influenced the local water quality more as compared to evaporation because of rock dominance presence in the study area (Figure S1). The water-rock interactions, including secondary carbonates dissolution due to precipitation, water-clay minerals ion exchange, and rock-forming minerals' chemical weathering, increase the major ion concentrations in water samples (Moghaddam and Fijani 2008). The hydrogeochemical evolution of water of an area is mostly controlled by various cationic and anionic reactions occurring in an aquifer system, the residence time of groundwater, rock-groundwater interaction, and chemical compositions of recharging water (Mukherjee et al. 2009).

The chemical compositions of water were identified by plotting a figure as proposed by (Chadha and Ray 1999), (Figure S2). The figure showed that all water samples of Lanmunchang study area lie in Ca²⁺ HCO₃⁻ type. Chadha diagram of the present study (Figure S2) showed 100% of samples Ca–HCO₃ type of water in Lanmunchang study area which displays due to the rock-water interaction on overall water chemistry (Nabila et al. 2014). Classification of geochemical facies and interpretation of chemical data of water can be classified by dominant ions using the weathering plot (Figure S3). Weathering plot show SO₄²⁻ and HCO₃⁻ are dominant ion in study area water. In Figure S3, results show that the samples highlighted in the circle of the Lanmunchang study area groundwater indicating the highest ratios of

calcium plus magnesium versus sulfate plus bicarbonates which are associated silicate weathering that influences on overall groundwater quality of study area (Navoni et al. 2014). Four types of hydrogeochemical processes result as shown by Piper diagram (Fig. 2). Water quality characterization of the study area was done through the use of a Piper plot. These water types show hydrochemical diversity among the water samples. The results revealed that water displayed Na–Cl, Na–Ca–HCO₃, Ca–HCO₃, Ca–Mg–Cl types of water. About 25% had Ca–HCO₃ types of water chemistry, while 13% of samples had the Ca–Mg–Cl type of water chemistry.

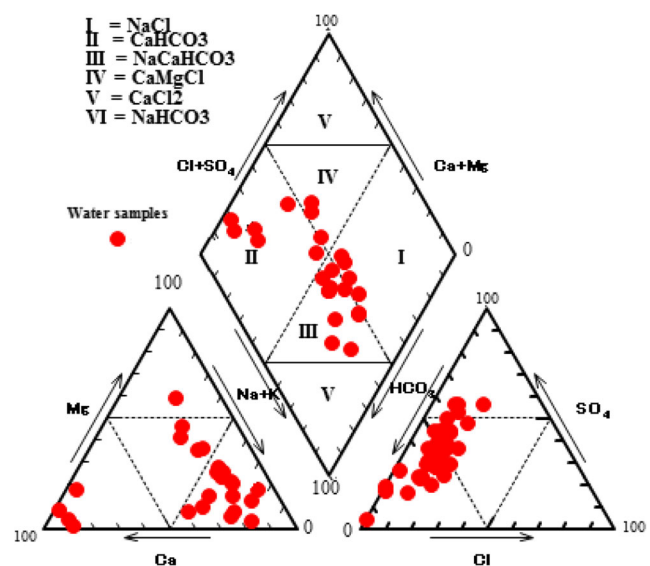


Fig. 2 Classification of groundwater of the study area according to Piper's plot

Likewise, 17% samples had the Na–Cl type of water, and 33% had dominant type Na–Ca–HCO₃⁻ water chemistry of study area (Fig. 2). Water quality characterization of the study area was done through the use of Piper plot at different depth of aquifers. These water types show hydrochemical diversity between the water samples displayed Na–Ca–HCO₃ types of water in Lanmuchang (SunBaek and Xiao Guang 2004). The different types of weathering process and cations-anions exchange reactions occur in aquifer system and responsible for to control concentrations of ions in water such as evaporate dissolution, silicate weathering, and carbonate dissolution (Mukherjee et al. 2009; Navoni et al. 2014).

Distribution of trace elements in stream water and sediments

The trace element results of water were listed in (Table 1). Thallium (Tl) concentrations ranged from 0.004 to 75.65 µg/L in water samples of Lanmuchang study area. Only 21% of samples crossed WHO permissible limit 2 µg/L (Xiao et al. 2003, 2004). Chromium (Cr) concentrations were 0.14–27.8 µg/L in water samples, respectively. The Cr in all the samples were found below the permissible limit (WHO) at 50 µg/L. Lead (Pb) was observed between 0.05 and 2.97 µg/L (below the WHO limit of 10 µg/L) in Lanmuchang study area water samples (WHO 1993; Rasool et al. 2016b). As ranged from 0.08 to 642.08 µg/L in water samples, respectively (Table 1), and about 25% samples crossed WHO safe limit 10 µg/L (WHO 1993; Rasool et al. 2016b). Cobalt (Co) concentrations ranged from 0.03 to 64.42 µg/L in water (Table 1), only 4% above 10 µg/L (WHO permissible limit) (WHO 1993; Rasool et al. 2016b). Other metals like Cu and Zn (Table 1) had low concentrations in local water which were below the relative safety limits regulated by WHO (WHO 1993; Rasool et al. 2016b). The concentrations of all trace elements in sediment samples are provided in (Table 2). All trace elements' concentrations were compared with the permissible limits (State Environmental Protection Administration, China) (SEPA 1995). The concentration of As was ranged from 123.06 to 383.23 mg/kg, while Tl was ranged from 0.72 to 72.34 mg/kg in sediment samples, respectively. About 92% of Tl samples were found beyond the permissible limits (1 mg/kg; SEPA 1995) for all the sediment samples. The concentration of Cu ranged from 69.90–117.49 mg/kg, and 62% samples crossed permissible limit 100 mg/kg of Cu set by (SEPA 1995). The Zn concentration ranged from 62.64 to 349.81 mg/kg, as well as 85% of sediment samples lie within the permissible limit of SEPA (300 mg/kg) for Zn (SEPA 1995). The value of Cr was within the safe limits (250 mg/kg) set by SEPA (1995) in all of the river sediment samples except one and value of Cr recorded was 92.84–480.8 mg/kg. The range value of Pb was found from 18.4 to 49.36 mg/kg; however, all values of samples lies within the

safe permissible limit (350 mg/kg; SEPA 1995). All other trace elements such as Cd and Co were within the safe limit of SEPA (Table 2). The results of the analysis of water and sediment samples in the Qingshui stream revealed that the average concentration of Cu, Co, As, and Tl in the midstream was higher than that in the downstream and upstream (Tables 1 and 2). This indicates the effect of the entry of sewage wastewater, smelting, and mining activity around the stream. In similar, research investigated in the Warri River in Nigeria with trace metals showed the concentration of trace elements in the river was higher than the standard level due to the influence of agricultural activity, sewage waste, and mining activity near the river (Wogu and Okaka 2011). The average concentrations of metals (Cr, Co, Pb, Cd, and Zn) in the stream water and sediment samples were comparatively lower (Tables 1 and 2). These may be due to a decrease in the order of mine activity near stream or movement, and deposition of suspended sediments containing the elements was minor but showing a spatial dispersion similar to Tl and As.

The spatial distribution patterns of As and Tl in water and sediment samples of the Lanmuchang study area are shown in Fig. 3. The deep mine east-west sections of midstream water and north-south units of sediment samples showed higher concentrations for As. Spatial distribution of Tl in water and sediment samples show different patterns; near acid mine samples (LMCW9, LMCS9) had the highest enrichment of Tl in midstream, somewhat away from Tl mineralized area minor enrichment of Tl in downstream samples and belonged to a first group in the clustering analysis (Figure S4). Identification of concentration of desired elements and evaluation of possible sources of contamination can be achieved by spatial distribution (Li et al. 2014). In water and sediment samples, hydrological conditions, Tl mineralization, and water-rock interactions constrained the distribution of Tl. The water-rock interactions were driven by Tl-bearing sulfides weathering and dissolution of limestone. The shallow groundwater had less Tl concentrations as compared to stream water. Concentrations of Tl in sediment are higher due to dilution effects, Tl-rich soil water seepage, and acid mine drainage (AMD). In the present study, the spatial distribution of higher As concentrations were mainly held in the east-west area. Among all the trace elements analyzed, As concentration was exceeding in all the sediment samples of Lanmuchang study area. For sediments, at site LMCS9, the highest value of As was found while the lowest one was found at point LMCS11. Similarly, in water samples, the highest value was observed at point LMCW23 while the lowest one was found at point LMCW9. The As level was much higher in sediments as compared to water due to weather of sulfide mineralization and rock-water interaction in Lanmuchang study area (Ghrefat et al. 2011; Kansal et al. 2013). Anthropogenic activities are the cause of about 90% As release into the environment (Abraham and Parker 2008). The

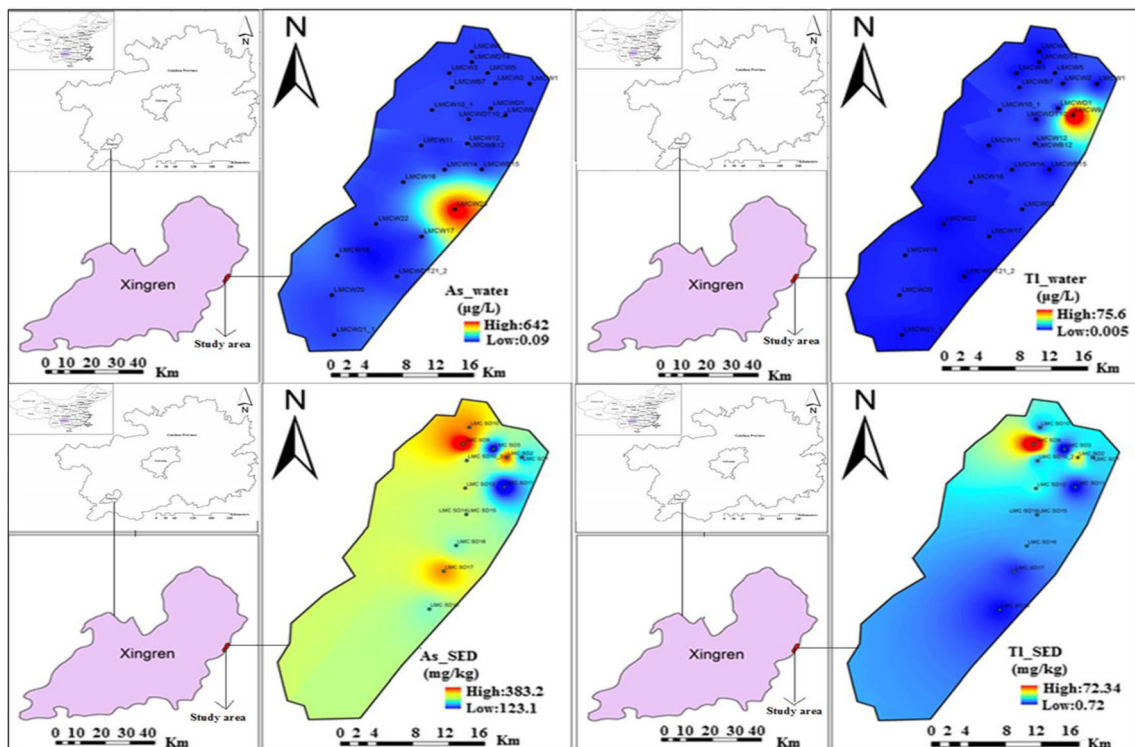


Fig. 3 Spatial distribution of selected elements such as Tl and As in water and river sediment samples of Lanmunchang study area

results of the study are supported by previous work which concluded that As and trace element contaminations in water and sediments posed a severe health risk to residents (Muhammad et al. 2011; Shah et al. 2012; Xiao et al. 2012; Khan et al. 2013). Tl and As showed similar spatial distribution pattern as well as a strong positive correlation (Table 6) in stream sediment (Li et al. 2014). The inflow of the stream water distributed the Tl and As to north-west zones, as the limits of the coefficient of variation exceeded by 60% for both types of the samples. Overall results of this study stressed that Tl concentration is higher near the acid mine drainage and mining activities than other trace elements. The results are in line with the previous studies (Zheng et al. 2008; Shah et al. 2012; Li et al. 2014) which represented similar patterns.

Evaluation of sediment pollution indices

Pollution indices are used to classify and assess trace elements contamination in sediment samples concerning reference elements are shown in Table 3. The enrichment factor (EF) is commonly used to separate trace elements connection with anthropogenic activities from natural sources (Amin et al. 2009; Gao and Chen 2012). Generally, the value of EF around one indicates that a given element originated from natural weathering processes or parent material, while values of greater than 1.5 suggest that anthropogenic and natural activities may be the important source (Zhang et al. 2002; Feng et al. 2004; Islam et al. 2015). The EF value of Cr in all sediment

samples show no enrichment, while 54% Co samples exhibit moderately serve enrichment, as well as 46%, serve enrichment, when compared with EF classes (Table S2), indicating these trace elements originated natural weathering process of rocks (Table 3). Similarly, Cu, Zn, Pb, and Cd show no enrichment, as compared with classes of EF less than one (Table S2). Furthermore, 8% sediment samples As show severe enrichment exceeded value 10 when compared with EF classes (Table S2). Tl, only one sample LMCS D3 show no enrichment because of EF less than 1, whereas 46% samples show moderately severe enrichment of Tl due to EF value greater than 5; furthermore, 15% samples show severe enrichment of Tl (EF > 10), and LMCS D9 exhibit extremely severe enrichment (EF = 239.5) in midstream sediment sample, when compared with EF classes (Table S2). Natural and anthropogenic sources for trace elements (Selvaraj et al. 2004; Birch and Olmos 2008) can be differentiated by alleviated enrichment factor (Salati and Moore 2010). The enrichment calculation and reduction in variability of trace elements under mineralogy of sediments can be achieved by geochemical parameter (Zhang and Shan 2008). Enrichment of trace elements (Table 3), concerning their background typical values in our study designated that metal amassing was influenced by Tl-bearing sulfide mineralization, and mining activity in Lanmunchang (Sayadi et al. 2010; Masoud 2014). The results suggested that values of EF for Tl, Co, and As in sediment are higher than permissible limits due to mining activities, natural erosion, and weathering of Tl–Hg–As sulfide mineralization,

Table 3 Enrichment factor of trace elements in the stream sediments from Lanmunchang study area

Samples ID	EF Cr	EF Co	EF Cu	EF Zn	EF As	EF Cd	EF Tl	EF Pb
LMC SD1	0.15	10.07	0.42	0.21	1.48	0.08	10.66	0.12
LMC SD2	0.11	6.07	0.31	0.13	1.55	0.07	14.82	0.12
LMC SD3	0.65	14.76	0.51	0.22	0.88	0.08	0.39	0.10
LMC SD9	0.84	11.19	1.97	0.50	14.69	0.56	239.5	1.62
LMC SD10	0.27	8.99	0.46	0.35	1.88	0.09	7.2	0.14
LMC SD10-2	0.19	7.20	0.38	0.36	1.25	0.09	6.95	0.12
LMC SD11	0.13	8.02	0.32	0.26	0.64	0.07	1.97	0.11
LMC SD12	0.13	5.24	0.30	0.24	0.91	0.07	6.75	0.09
LMC SD14	0.15	5.51	0.24	0.16	0.69	0.07	4.31	0.08
LMC SD15	0.25	10.48	0.45	0.22	1.64	0.06	8.03	0.13
LMC SD16	0.19	7.29	0.33	0.24	0.95	0.07	5.43	0.09
LMC SD17	0.31	10.4	0.04	0.23	1.61	0.09	3.29	0.11
LMC SD18	0.48	19.71	0.81	0.40	2.32	0.16	5.03	0.22
Background value	133.3	0.612	38.6	135.9	28.5	1.24	0.33	33.1

farming activities, and domestic coal use in the study area (Zhang and Shan 2008; Birch and Olmos 2008).

The determination of sediment in Lanmunchang study area was done by categorizing the I_{geo} values into various classes (Table S1, Fig. 4). The pollution quality of stream sediment samples was achieved by calculating the I_{geo} (Muller and Suess 1979; Abraham and Parker 2008). No pollution was detected by the I_{geo} values of Cu, Cd, Zn, and Pb in sediment samples (Table S1, Fig. 4). Among metals, Tl showed the highest I_{geo} value in sample LMCS9 of sediment. Tl I_{geo} ranged from 0.54 to 7.19, which belongs to class 5 and class 6 of highly to very highly polluted and very highly polluted sediment samples, respectively. Greater I_{geo} value of Tl recorded 7.19 in midstream of Lanmunchang study area (Table S1, Fig. 4). Cr pronounced the sediment is unpolluted to moderately polluted when compared with I_{geo} classes (Table S2). Co appeared as a high to very high pollutant of downstream sediment sample LMCS17 was 5.52 belonging to class 6. The mean I_{geo} values of As for study area site

LMCS9 was 3.16, so the sediments of this position were moderate to highly pollute (Table S2). Cr showed more enrichment in sediment as compared to elements that had higher I_{geo} values in the study area due to sulfide-bearing rocks and mining activity naturally (Suthar et al. 2009). Co appeared as a strongly pollutant of the sediment samples because Co is one of the most important metals and found in small quantity in water and soil. I_{geo} values of Tl had higher pollution enrichment in sediment samples of Lanmunchang area over Tl-bearing mineralization, and mining activity; smelting and the hydrogeological regime may be main sources in the mid-stream (Duman et al. 2007; Zahra et al. 2014).

Table 4 shows CF values for all trace elements. The concentration of each metal in the sediment was divided by the CF values to get CF ratio as suggested by Hakanson 1980; moreover, CF less than one indicates low contamination, CF less than three shows moderate contamination, CF value < 6 represents considerable contamination, and CF value > 6 indicates very high contamination (Table S2). CF of As ranged from 6.89 to 13.45 of sediment samples, which belong to class level CF > 6, which show high pollution (Table S2). The metals that showed the most extensive contamination are Tl (ranges from 2.18 to 219.2) and Co (ranges from 10.24 to 81.42). Likewise, Cr and Pb show no contamination factor in sediment samples.

The potential load index (PLI) for trace elements of Lanmunchang study area were listed in (Table 4). PLI was obtained as CF was done, shown in Table 4. The PLI value of greater than 1 shows pollution, whereas less than one represents no pollution (Harikumar et al. 2009; Shorabi et al. 2010). Potential contamination indices (PLI) showed that trace metals Cd and Pb were indicated no pollution occurred in sediment samples as well as other metals were displayed pollution (PLI > 1) in sediment samples of the study area

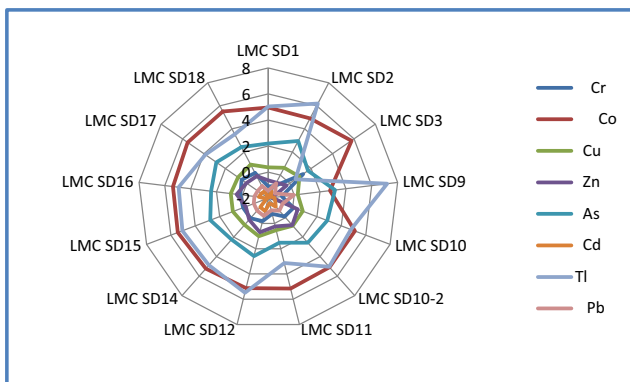


Fig. 4 Geo-accumulation index (I_{geo}) of different elements in stream sediment samples of the study area Lanmunchang

Table 4 Contaminated factor values of trace elements in Lanmuchang study area

Samples ID	CF values							
	Cr	Co	Cu	Zn	As	Cd	Tl	Pb
LMC SD1	0.69	46.66	1.93	0.95	6.89	0.38	49.43	0.55
LMC SD2	0.77	45.25	2.32	0.95	11.59	0.55	110.44	0.91
LMC SD3	3.66	81.42	2.80	1.23	4.89	0.43	2.18	0.57
LMC SD9	0.77	10.24	1.81	0.46	13.44	0.51	219.21	1.49
LMC SD10	1.58	51.82	2.67	1.99	10.85	0.55	41.67	0.84
LMC SD10-2	1.38	51.33	2.70	2.57	8.92	0.68	49.55	0.90
LMC SD11	0.88	53.46	2.18	1.76	4.31	0.49	13.14	0.72
LMC SD12	1.32	52.32	3.04	2.43	9.05	0.75	67.55	0.99
LMC SD14	1.57	56.7	2.53	1.74	7.18	0.711	44.36	0.91
LMC SD15	1.56	64.87	2.82	1.33	10.24	0.41	49.98	0.85
LMC SD16	1.66	62.03	2.83	2.05	8.09	0.62	46.19	0.78
LMC SD17	2.1	69.21	2.65	1.54	10.75	0.58	21.93	0.74
LMC SD18	1.69	68.55	2.82	1.40	8.10	0.56	17.51	0.76
PLI	1.36	50.58	2.52	1.44	8.4	0.55	36.28	0.82
ERF	39		158	21	1143	217	332	55

(Table 4). Ecological risk factor (ERF) values for trace elements are given in Table 4. An ecological risk factor can be evaluated on behalf of risk index (RI) four level classes which are shown in Table S2. ERF of Tl was found 7332, which belong to $RI > 600$, very high ecological risk as well as As value was 1143, which belong to high ecological risk. Similarly, Cd and Cu have a moderate ecological risk ($RI < 300$). Cr, Ni, and Pb have a low ecological risk ($RI < 150$), respectively. The Pollution Load Index (PLI) is obtained as concentration factors, and it was higher in trace elements of sediment such as Tl, Co, and As. PLI of As and Co is highly polluted, furthermore Tl also extremely polluted due to weathering of Tl-related minerals and natural mining activity in Lanmuchang study area (Suthar et al. 2009; Harikumar et al. 2009). Ecological risk factor (ERF) values for selected trace elements such as Cr, Cu, Zn, As, Cd, Pb, and Tl of the study area were calculated on based on risk index (Abraham and Parker 2008).

Identification of pollution sources

Various multivariate techniques such as cluster analysis (CA), Pearson correlation analysis, and Principle component analysis (PCA) are useful to identify sources of trace elements, interpret spatial variations, and complex environmental data matrices, and assess the ecological status of studied systems (Buttafuoco et al. 2010; Guagliardi et al. 2013). Correlation between trace elements might reflect the migration and origin of these elements (Suresh et al. 2011; Wang et al. 2012). High positive correlations between selected trace elements in the

stream water and sediments may reflect alike levels of contamination which have the same pollution sources (Li et al. 2009; Rasool et al. 2016b). The correlation of selected trace elements in stream water samples was listed in (Table 5). The Pearson's correlation coefficients were obtained at $P \leq 0.05$ levels. Significant positive correlations were found between several parameters such as EC–Co ($r = 0.940$), EC–Cu ($r = 0.937$), EC–Tl ($r = 0.944$), Cr–Co ($r = 0.982$), Cr–Cu ($r = 0.984$), Cr–Co ($r = 0.982$), Co–Cd ($r = 0.953$), Cr–Tl ($r = 0.999$), and Cd–Tl ($r = 0.949$) as shown by the correlation matrix. The results of the Pearson correlation analysis of sediment samples are shown in Table 6. Significant positive correlations were found between Co–pH ($r = 0.850$), Cd–EC ($r = 0.881$), As–Tl ($r = 0.725$), and Tl–Pb ($r = 0.980$), at $P \leq 0.05$ levels in sediment studied samples. Furthermore, the co-relationship of trace elements was supported by cluster analysis (CA) in water samples (Figure S3a). Pearson correlation analysis provides an effective way to reveal the relationships between trace elements in stream water and sediments (Tables 5 and 6) and have been helpful for understanding the influencing factors (Mico et al. 2006). The sources of water contamination are geogenic and anthropogenic in the study area as shown by above correlations (Bhowmik et al. 2015). Tl show highly positive correlation with Cr, Cd, Pb, Cu, and As, which may be caused due to the hydrological setting, water-rock interaction, and weathering Tl mineralization in Lanmuchang study area water samples (Alamdard et al. 2016). Significant positive correlations were observed between different elements such as Tl–As, indicating common originating sources related to Tl–As bearing sulfide mineralization, smelting, and mining activity in Lanmuchang (Fu et al. 2014). Furthermore, domestic coal use and carbonate minerals enriched with black sand deposits are responsible for the positive correlation between Cr and Tl (Zhou et al. 2007; Magesh et al. 2011). Domestic waste, smelting, and farming activities caused a positive correlation between Tl and Pb (Ryu et al. 2011). Previous studies (Adomako et al. 2008; Zahra et al. 2014) also concluded similar contamination sources.

The similarity and difference among the elements to be clustered can be measured by CA method (Singh et al. 2004; Chen et al. 2007, Ali et al. 2016). The cluster analysis showed the similar groups of elements in the water and sediment samples of the Qingshui stream (Figure S4a, b). These trace elements would be clustered into three groups, and their correlation coefficients were given in Tables 5 and 6. Three groups of sites with similar characteristic features and the same source of contamination were generated using the clustering procedure. Group 1 (G1) includes pH, Cr, Cd, and Pb, group 2 (G2) includes Co, Tl, and Cu, while group 3 (G3) includes EC, Zn, and As shown in (Figure 43a). Likewise, three statistically significant groups were found in sediment samples of Lanmuchang study area. G1 consists of pH, Tl, Cd, and Co, whereas G2 include Pb and Cu and G3 contain EC, Cr, Zn,

Table 5 Pearson correlation coefficient matrix of selected trace elements and physicochemical parameters in water of the study area

Parameters	pH	EC	Cr	Co	Cu	Zn	As	Cd	Tl	Pb
pH	1									
EC	<i>-0.935</i>	1								
Cr	<i>-0.872</i>	<i>0.894</i>	1							
Co	<i>-0.923</i>	<i>0.94</i>	<i>0.982</i>	1						
Cu	<i>-0.919</i>	<i>0.937</i>	<i>0.984</i>	1	1					
Zn	0.032	0.005	0.155	0.087	0.092	1				
As	<i>-0.157</i>	0.115	<i>-0.081</i>	<i>-0.035</i>	<i>-0.051</i>	<i>-0.084</i>	1			
Cd	<i>-0.842</i>	<i>0.875</i>	<i>0.953</i>	<i>0.953</i>	<i>0.955</i>	0.377	<i>-0.078</i>	1		
Tl	<i>-0.926</i>	<i>0.944</i>	<i>0.977</i>	<i>0.999</i>	<i>0.999</i>	0.077	<i>-0.03</i>	<i>0.949</i>	1	
Pb	<i>-0.049</i>	0.109	0.26	0.196	0.202	0.982	<i>-0.114</i>	0.48	0.186	1

Italic correlation is significant at the 0.05 level. *n* number of samples

and As are shown in (Figure 43b). The first group of Cd, Pb, pH, and Cr possibly originated from parent rock material, agricultural and human activity, and hydrogeological setting in stream water (Nafees et al. 2009; Strachan 2010; Shah et al. 2010). The second group of Co, Cu, and Tl indicated the same sources, such as mining activities, agricultural activities, water-rock interaction, and weathering of mafic and ultramafic rocks in water samples of Lanmuchang study area (Shah et al. 2010; Rasool et al. 2016b). Higher Tl pollution level suggested the coal combustion, weathering of local mafic and ultramafic rocks, weathering of Tl sulfide mineralization, and acid rain in the study area (Xiao et al. 2004; Khan et al. 2012). The third group of EC and As contamination was due to the influence of sewerage waste, rock-water interaction, and weathering of parent rock material in stream water (Nickson et al. 2005; Bai et al. 2012; Khan et al. 2012).

Similarly, contamination of trace elements in sediment samples was influenced by mining and farming activities, weathering of sulfide mineralization, and coal combustion in Lanmuchang (Simeonov et al. 2003; Xiao et al. 2007; Khan et al. 2010). The first group including pH, Co, Cd, and Tl

might be coming from weathering and erosion of thallium related rocks and mining activity in sediments of the study area (Wenning et al. 2002; Xiao et al. 2012; Abilio et al. 2012). The second group including Pb and Cu could be coming from natural and anthropogenic activity (Nazeer et al. 2014; Ali et al. 2016). Moreover, the third group including Cr, Zn, and As came from similar sources which influenced by mining and processing activities and sulfides rock weathering into the sediment of Lanmuchang study area (Demirak et al. 2006).

The principal component analysis (PCA) assists the reduction of data and description of a given multidimensional classification using a small number of new variables. The present data were exposed from PCA to explore the possible similarities in the behavior of various forms of the trace elements contamination in stream water and sediments samples (Facchinelli et al. 2001; Zhou et al. 2007). The results of PCA for trace elements concentration of stream water samples are listed in (Table 7). Three factors (eigenvalue > 1) were extracted from PCA to explain approximately 98% of the total variance. The first factor contributes 67.3% of the variance

Table 6 Pearson correlation coefficient matrix of selected trace elements and physicochemical parameters in stream sediments of the study area

Parameters	Cr	Co	Cu	Zn	As	Cd	Tl	Pb	pH	EC
Cr	1									
Co	<i>0.753</i>	1								
Cu	0.593	<i>0.725</i>	1							
Zn	0.127	0.349	0.67	1						
As	<i>-0.348</i>	<i>-0.562</i>	<i>-0.138</i>	<i>-0.257</i>	1					
Cd	<i>-0.067</i>	<i>-0.046</i>	0.441	<i>0.686</i>	0.138	1				
Tl	<i>-0.532</i>	<i>-0.901</i>	<i>-0.565</i>	<i>-0.494</i>	<i>0.725</i>	0.031	1			
Pb	<i>-0.429</i>	<i>-0.801</i>	<i>-0.297</i>	<i>-0.193</i>	<i>0.715</i>	0.326	<i>0.89</i>	1		
pH	0.37	<i>0.85</i>	0.589	0.297	<i>-0.551</i>	<i>-0.063</i>	<i>-0.824</i>	<i>-0.781</i>	1	
EC	<i>-0.129</i>	<i>-0.065</i>	0.397	<i>0.778</i>	0.025	<i>0.881</i>	<i>-0.006</i>	0.242	<i>-0.096</i>	1

Italic correlation is significant at the 0.05 level. *n* number of samples

Table 7 Factor loading for selected trace elements in stream water of Lanmuchang

Parameters	Factor 1	Factor 2	Factor 3
pH	-0.927	0.241	-0.128
EC	<i>0.947</i>	-0.188	0.094
Cr	<i>0.979</i>	-0.003	-0.085
Co	<i>0.993</i>	-0.083	-0.050
Cu	<i>0.993</i>	-0.075	-0.065
Zn	0.179	<i>0.966</i>	0.162
As	-0.011	-0.243	<i>0.967</i>
Cd	<i>0.974</i>	0.216	-0.018
Tl	<i>0.992</i>	-0.094	-0.047
Pb	0.284	<i>0.948</i>	0.124
Eigen value	6.730	2.050	1.019
Variance %	67.300	20.520	10.200
Cumulative %	67.300	87.800	98.010

Value of dominant element of each factor are reported in italic

and has positive loading on EC ($r = 0.947$), Cr ($r = 0.979$), Co ($r = 0.993$), Cu ($r = 0.993$), Cd ($r = 0.974$), and Tl ($r = 0.992$), respectively. The second factor contributes 20.5% of the variance and has positive loading with high values of Zn ($r = 0.966$) and Pb ($r = 0.948$), respectively. In the third component factor, third contribution rate of the variance is 10.2% with high positive loading As ($r = 0.967$). Similarly, in the case of sediments, three factors were extracted to explain approximately 89% of the total variance (Table 8). Factor 1 has contributed by 50.89% of the variance with high loading on pH ($r = 0.818$), Cr ($r = 0.751$), Co ($r = 0.969$), Ni ($r = 0.882$), and Cu ($r = 0.774$), respectively (Table 8). Factor 2 has positive

Table 8 Factor loading for trace elements in sediment samples of Lanmuchang

Parameters	Factor 1	Factor 2	Factor 3
pH	<i>0.818</i>	-0.130	-0.278
EC	0.084	<i>0.956</i>	-0.065
Cr	<i>0.751</i>	-0.220	0.539
Co	<i>0.969</i>	-0.145	0.056
Ni	<i>0.882</i>	-0.314	0.262
Cu	<i>0.774</i>	0.418	0.342
Zn	0.510	<i>0.783</i>	-0.168
As	-0.648	0.197	<i>0.573</i>
Cd	0.087	<i>0.931</i>	0.095
Tl	-0.920	0.073	<i>0.298</i>
Eigen value	5.100	2.790	1.010
Variance %	50.890	27.970	10.140
Cumulative %	50.890	70.14	89.01

Value of dominant element of each factor are reported in italic

loading with variance of 27.97% of the elements with EC ($r = 0.956$), Zn ($r = 0.783$), and Cd ($r = 0.931$), respectively. Factor 3 has contributed by 10.14% of the variance with high loading value of As (0.573) and Tl ($r = 0.298$), respectively (Table 8). Factor loading analyses including principal component analysis (PCA) were used to explain the sources of selected trace elements in sediments and stream water (Tables 7 and 8). The first factor contributes high loading variables such as EC, Cr, Co, Cu, Cd, and Tl in stream water, which is an indicator of natural activities in thallium sulfide mineralized study area Lanmuchang (Jones et al. 2009). The second factor including elements Zn and Pb indicates the contribution of smelting and mining activities in the study area water sample (Chen et al. 2007). In the factor, high loading variance element As comes from weathering of Tl–As mineralized rock into the stream (Shridhar et al. 2010). Likewise, in sediment samples, the sources of Cr, Co, pH, Ni, and Cu in factor loading first could be geogenic due to weathering of minerals, smelting of rocks, and anthropogenic due to agricultural activities (Yang et al. 2009). Factor second contributes to Zn, EC, and Cd, which stresses the involvement of both anthropogenic and geogenic source (Shridhar et al. 2010; Ahmad et al. 2016). Factor 3 shows As and Tl contribute in midstream sediment contamination due to weathering Tl–As rich sulfide mineralized rock and mining activities in the study area (Zhou et al. 2007; Rodriguez et al. 2008).

Conclusions

The current study demonstrates that Tl and As concentrations were higher in stream water samples than their respective permissible limits of water set by WHO, likewise Tl and As concentrations were higher in stream sediments than their limits set by SEPA. The dominant water type Na–Ca–HCO₃ in the present study due to the weathering of rocks. Sediments of site LMCS9 from midstream had the highest potential ecological risk factor (ERF) and required greater attention. Tl and As concentrations were above the ERF classes values, whereas Tl was the only trace element having exceeded RI value representing its potential toxicity to the ecosystem. The overall conclusion is that the Qingshui stream needs environmental remediation to reduce the ecological risk and to protect human health. PCA and CA results revealed the natural source prominent for contamination of trace elements in stream water and sediment of the Lanmuchang. Examination of the data reveals that midstream is more polluted than upstream and downstream. Finally, it is recommended that stringent steps must be taken to check the contamination level in the existing Qingshui stream, which is being used for both drinking and agricultural.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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