

Metal speciation and pollution assessment across a small-scale mining creek system tributary

Elmer S Austria, Jr

University of the Philippines Diliman College of Science

Ericho Jeanne M. Fuentes

University of the Philippines Diliman College of Science

Rheo Baguio Lamorena-Lim (✉ rheolamorena9@yahoo.com)

University of the Philippines Diliman <https://orcid.org/0000-0002-7082-5011>

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Abstract

Sediment and water samples along Acupan creek were examined to assess the degree of toxic metal pollution due to anthropogenic wastes from small-scale gold mining activity in the area. Samples were collected from five different locations representing the upstream, midstream and downstream areas of the creek. The total concentration of As, Cd, Cu and Pb in the sediment and aqueous matrix were determined. Chemical speciation of the target metals in the creek system was performed using geochemical software PHREEQC. The metal concentrations in the sediments of midstream and downstream were higher compared to the average shale value (ASV) and toxicological reference values (TRV). Similarly, the total metal concentrations of As and Cu in creek water exceeded the local guidelines set for effluent waters. Speciation results identified HAsO_4^{2-} , Cd^{2+} , CuOH^+ and PbOH^+ as the major species of the target metals. Metal supersaturation in sediment and low solubility in the aqueous matrix point out to re-suspension and transport of metals as colloidal suspensions. The enrichment factor and geo-accumulation index values indicate significant levels of enrichment and pollution in the midstream and downstream area. The pollution load index confirmed the progressive deterioration of the sediment quality along the creek. Speciation and environmental index results confirmed that anthropogenic sources in the midstream were transported to the downstream catchment.

1. Introduction

Toxic metal contamination in aqueous and sediment matrices has attracted significant attention in the scientific community because of its increasing abundance and the numerous hazards it imposes to the whole ecosystem (Shikazano et al. 2012; Song et al. 2017). Aside from naturally-occurring point sources, the bulk of the generated metal pollution originate from anthropogenic processes like agricultural discharges, wastewater effluents, industrial productions, smelting and mining operations (Alloway 2013; Manta et al. 2013). Sediment can act as an environmental sink for both organic and inorganic forms of these metals (Brady et al. 2014). Thus, sediments provide a valuable platform to monitor and identify the amount and types of the metal pollutants that exists in such systems. The level of metal contamination is usually assessed using a combination of various environmental pollution indices like enrichment factor (EF), geo-accumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI) (Goher et al. 2014; Islam et al. 2015).

Deposition in sediments represents a possible transport route of metals in aquatic systems. Nonetheless, these deposited metals can be remobilized back into the water upon reaching specific physicochemical parameter levels such as pH, total concentration, redox potential, and salinity (Zhao et al. 2013; Zhang et al. 2014). Metal behavior and concentration in sediments are both relevant in identifying the point sources, degrees of contamination and distribution mechanisms in aquatic systems (Li et al. 2012). However, the assessment of the full impact of contamination in aqueous and sediment systems requires more than the total metal concentration because of the differences in the behavior and property of each species. Chemical speciation is essential in supplying information regarding the bioavailability, reactivity and transport processes of toxic metals (Capangpangan et al. 2016). The majority of speciation studies in aquatic systems are usually carried out using multi-step sequential extraction techniques (Tessier et al. 1979; Gu et al. 2015; Capangpangan et al. 2016). In recent years, geochemical modeling programs such as Visual MINTEQ and

PHREEQC were used to generate chemical speciation results based on metal concentration, mineral content, pH and redox potential (da Silva et al. 2016; Thorslund et al. 2016).

During the past decades, the small-scale gold mining sector in the Philippines has been gradually expanding (Verbrugge 2017). Apart from artisanal panning methods, small-scale miners have utilized liquid metallic mercury and cyanide in order to extract the gold from its ores (Corpus et al. 2010). Mine tailings and chemicals used by small-scale miners in the amalgamation process, and anthropogenic inputs coming from the domestic activities and agricultural production contribute to the wastes released in streams and creeks. The lack of technical knowledge has caused some of the small-scale mining communities to overlook the health hazards involved with their mining practices. Previous literatures within the same region have separately identified the prevalence of highly toxic methylmercury and metallic Hg in the Acupan region (Clemente et al. 2004; Corpus et al. 2011). In addition, four other sub-basins of the Ambalanga River, including Acupan, were revealed to contain significant concentrations of methylmercury (Corpus et al. 2011). However, aside from Hg, no extensive studies on other metal contaminants were documented for the Acupan mining region. The main objectives of this study are (1) to compare the concentrations of As, Cd, Cu and Pb in the sediment and water matrices with various reference and threshold values in literature; (2) to identify the major forms of the metal chemical speciation with PHREEQC in the creek system; and (3) to assess the degree of enrichment and pollution in the Acupan creek using established environmental indices such as EF, I_{geo} and PLI values.

2. Methodology

2.1. Study Area

The Acupan creek system is located at Sitio Acupan, Brgy. Virac, municipality of Itogon, province of Benguet, Philippines (Fig. 1). The creek flows from the mountains of Acupan and drains down into the Acupan sub-basin. The creek system is a tributary of the larger Ambalanga River which connects multiple sub-basins of Itogon. The municipality of Itogon has been operating as a mining town since 1903 when American colonizers established Benguet Consolidated Mining Corporation, the first large-scale mining operation in the Philippines. Currently, four major mining companies, along with a number of artisanal and small-scale miners, still operate in the municipality.

The upstream area of the Acupan creek is generally unaffected by the mining activities. The creek flows directly along the Acupan mines where numerous small-scale gold mining operations are present. Tailings from the mining activity, along with other anthropogenic wastes from the households situated in the midstream area, are disposed regularly along the creek. All tributary waters from the Acupan creek drain into the downstream area which serves as its catch-basin.

2.2. Sample Collection

Five different stations along the natural creek were selected as sampling sites. Sediment and creek water samples were obtained and labeled as AC 1, AC 2.1, AC 2.2, AC 2.3, and AC 3 (Fig. 1). Description and geographic coordinates of the location of the sampling stations were summarized in Table 1.

Sediment samples were collected in clusters within the vicinity of each sampling site and were homogenized through mixing. The samples were taken from the top 10 cm of the creek sediment bed and were stored into airtight polyethylene bags after sampling. Creek water samples were also collected at the same sites and stored into pre-rinsed high density polyethylene (HDPE) bottle containers. Collection was done around November in order to avoid the rainfall and typhoon season in the Philippines which would cause higher water flow, as well as the summer season which would cause lower stream flow. Water parameters (temperature, pH and dissolved oxygen) were tested in situ using a portable water analyzer (D-55, Horiba, Japan). The collected water samples were acidified using 10% HNO₃ (v/v). All samples were stored and kept at 4°C until analyses.

Table 1. Location of the sampling sites along the Acupan Creek.

Site	Description	GPS position
AC 1	Upstream area of the creek system, background area where household and mining activity are absent	N 16°20'15.9"; E 120°39'12.5"
AC 2.1	Main tributary section of the creek in midstream; majority of the mining activities are located in this site	N 16°21' 25.3"; E 120°39'22.1"
AC 2.2	Secondary tributary section of the creek in midstream; household communities and mining activities are located in this site	N 16°21' 25.6"; E 120°39'21.9"
AC 2.3	Confluence of the primary and secondary tributary section of the creek in midstream	N 16°21' 25.9"; E 120°39'22.5"
AC 3	Downstream area of the entire Acupan sub-basin	N 16°21'47.7"; E 120°39'57.9"

2.3. Analysis of sediments and creek water samples

Sediment samples were sent to a service laboratory for the analysis of the four target toxic metals (Cu, Cd, Pb, and As). The samples were initially dried at 50°C, and were sieved using a 67 µm nylon mesh. The prepared samples were digested in a hot HNO₃-HCl mixture for 4 hours, and were filtered prior to analysis. The sediment samples were analyzed by ICP-OES (Agilent 720 Series, Agilent, CA, USA). The detection limit for Cu, Cd, Pb and As were 0.1, 0.5, 5 and 10 ppm, respectively. The acidified water samples were filtered through a 0.45 µm membrane filter paper using a vacuum filtration set-up. Quantitative analysis of the target metals (Cu, Pb, Cd and As) in water was performed by AAS (AA-6501 Shimadzu, Japan).

The identification of the mineral content of the sediment samples was done by XRD analysis (Shimadzu XRD-700, Maxima, Japan). The Cu K α radiation was set to 40 kV and 30 mA. The scan range used for each spectrum was from 3 to 90° with 2° per minute scan speed.

2.4. PHREEQC simulation

Chemical speciation of the metals in solution was carried out using PHREEQC software with the Minteq.v4.dat database (Parkhurst et al. 2013). The PHREEQC program developed by the USGS has become a standard in the chemical equilibrium calculations in groundwater. The software is based on the equilibrium relationship between the minerals, gases and other parameters present in the aqueous solution. The program calculates the equations from a chemical database (.dat) and an input file (.pgi). In this study, PHREEQC version 3.2.0 was used to generate the identity and concentration of each species of the four metal analyte in the solution. Input parameters for the speciation modeling were temperature, pH, dissolved oxygen, metal concentration in sediment and aqueous phase, and minerals identified from XRD analysis.

2.4. Pollution index calculations

2.4.1. Enrichment factor (EF)

The enrichment factor, or EF, is an established pollution index to classify anthropogenic pollution and contamination levels based on enrichment ratios (Shikazano et al. 2012). The corresponding EF was calculated using Eq. 1:

$$EF = \frac{(C_{HM}/C_{Fe})_{sample}}{(C_{HM}/C_{Fe})_{background}} \quad (1)$$

where $(C_{HM}/C_{Fe})_{sample}$ is the ratio of the metal concentration and Fe in the sediment samples, and $(C_{HM}/C_{Fe})_{background}$ is the similar ratio for the background. The equation was normalized with Fe because of its abundance in the sample and its tendency to be immobile. The background concentration values used for this study listed in Table 2 were acquired from the ASV in previous literature (Turekian et al. 1961).

2.4.2. Index of geo-accumulation (I_{geo})

The geo-accumulation index, or I_{geo} , is another widely used pollution index used in literature to compare the sediments with a non-polluted background sample. The I_{geo} values were calculated using the following

equation (Eq. 2) introduced by Muller (Muller 1981),

$$I_{geo} = \log_2 \left(\frac{C_{sample}}{1.5 * C_{BG}} \right) \quad (2)$$

where C_{sample} and C_{BG} were the concentration of the metals in the sediment samples and background, respectively. The factor 1.5 was included to account for the minor anthropogenic and lithogenic variations experienced by the background sample (Goher et al. 2014). Similar with the EF, the background concentrations used for the calculating I_{geo} were from the ASV listed in established literature (Turekian et al. 1961).

2.4.3. Pollution load index

The pollution load index, or PLI, was used to assess the total level of pollution in a certain location. The PLI, which was proposed by Tomlinson (Tomlinson et al. 1980), gives a comparative value that can be used for evaluating the quality of an area. In addition, the PLI provides a simple means for the public, as well as policy and decision makers, to understand the trends regarding the pollution level in an environmental system. The PLI was calculated via Eq. 3,

$$PLI = \sqrt[n]{CF_1 * CF_2 * \dots * CF_n} \quad (3)$$

where CF is the contamination factor which is evaluated by dividing the metal concentration in the sediment with the background and n is the total number of metals evaluated.

3. Results And Discussion

3.1. Metal analysis of sediment and aqueous matrices

The total concentration of each metal analyte in the sediment samples is presented in Table 2. Due to the absence of stringent local guidelines for toxic metal levels in the Philippines, the sediment samples in this study were compared with average reference and toxicological reference values. Average shale value (ASV) reported by Turekian has been widely used for comparing the samples with the background levels of the element in standard earth materials like shale (Turekian et al. 1961). The toxicity reference values (TRV) are estimated threshold value set by USEPA (1999) where wildlife species are adversely affected because of metal exposure. The values of copper and lead in the upstream (AC 1) are higher compared to their corresponding ASV and TRV. The concentration of all metals dramatically increased in the midstream area (AC 2.1, AC 2.2, AC 2.3) where the small-scale mining activity along the creek starts. Increased metal concentration towards the downstream (AC 3) was also observed. Moreover, all target analyte in the midstream and downstream samples were higher compared to their corresponding ASV and TRV suggesting metal contamination in these areas.

Table 2. Comparison of toxic metal concentration (mg kg^{-1}) in creek sediment samples with various reference values.

Analyte	Upstream	Midstream			Downstream	Standard Values	
	AC 1	AC 2.1	AC 2.2	AC 2.3	AC 3	ASV	TRV
As	10	200	21	162	231	13	60
Cd	< MDL	1.0	3.0	2.0	2.0	0.3	0.6
Cu	104	147	200	165	156	45	16
Pb	55	216	640	293	195	20	31

MDL - Method detection limit (Cd - 0.5 mg kg^{-1})

X-ray diffraction analysis was carried out to qualitatively check the minerals present in the sediment. For the midstream, AC 2.3 was used as the representative sample since it is the confluence of the main creek from the upstream (AC 2.1) and the tributary creek from a secondary point source (AC 2.2). XRD results (SD Fig. 1, found in Supplementary Data section) show that quartz is the major mineral content in all three samples as indicated by the major peaks.

The metal concentration of the aqueous matrix were compared with the Average Metals in River (AMR) values, which are the average elemental composition of river water in the world, proposed by Martin (Martin et al. 1983). The TRV for freshwater samples suggested by the USEPA (1999) was also used for comparison. Lastly, the obtained values from the aqueous phase were compared with the Water Quality Guidelines (WQG) set by the Department of Environment and Natural Resources (DENR) of the Philippines for Class SD marine water (i.e. navigable waters).

Table 3. Comparison of toxic metal concentration (mg L^{-1}) in creek water samples with various reference values.

Analyte	Upstream	Midstream			Downstream	Standard Values		
	AC 1	AC 2.1	AC 2.2	AC 2.3	AC 3	AMR	TRV	DENR WQG
As	< MDL	0.2000	0.0200	0.0140	0.0500	0.0170	0.1500	0.0400
Cd	0.0072	0.0089	0.0071	0.006	0.0071	0.0200	0.0022	0.0100
Cu	0.0224	0.9049	0.4636	0.4562	0.0591	1.5000	0.0090	0.0400
Pb	0.0437	0.0554	0.0427	0.057	0.0356	0.0001	0.0025	0.1000

MDL = Method detection limit (As - 0.001 mg L^{-1})

Based on the results (Table 3), the metal levels in the upstream were lower compared to the AMR values except for Pb. The Cu and Pb levels in the midstream and downstream samples were higher than the AMR. Some of the As and Cu levels in the midstream and downstream samples were also higher than the local guidelines. Moreover, all values of Cu, Pb and Cd exceeded the TRV for freshwater samples. Similar with the observed trend for sediments, the concentration levels of the target metals increases as the water flows from the upstream towards the downstream.

3.2. Chemical Speciation

The total metal concentration only provides partial information in predicting the effects of toxic metals in environmental systems. Since it does not include the bioavailable and dominant forms of each analyte, metal speciation was necessary to provide information crucial for better risk assessment strategies and environmental management procedures (Magu et al. 2016). In this study, inorganic chemical speciation was done to identify the prevalent chemical species of each metal present in the different parts of the creek system using the PHREEQC software and Minteq.v4 database. The results from total metal analyses in sediment and water samples, XRD analysis, and physicochemical parameters such as pH and dissolved oxygen (SD Table 1, found in Supplementary Data section), were used as input values for the PHREEQC simulation.

3.3.2. Index of geo-accumulation (I_{geo})

Based on the I_{geo} classification proposed by Muller (Muller et al. 1981), the upstream was within the unpolluted to moderately polluted range (Fig. 4) for all metals indicating that the background was relatively free from contaminants. The I_{geo} for As (0.11 to 3.57), Cd (1.15 to 2.74) and Pb (2.70 to 4.41) were all in the highly polluted range for the midstream and downstream sections which correlated well with the EF results. The I_{geo} of Pb (4.41) in the AC 2.2 even reached the extremely polluted range which reflected the results from anthropogenic point sources (i.e. mining activity) within the area.

3.3.3. Pollution load index

All sediment samples were over the PLI threshold (PLI = 0.0 indicates no pollution, 1.0 indicates baseline level, and > 1.0 indicates progressive pollution in the site) as illustrated in Fig. 5. The upstream AC 1 sample, which was the background, was near the baseline limit (PLI = 1.7) indicating minor pollution in the area. This elevated value can be attributed to the high concentration of naturally-occurring metal analyte such as copper and lead which were supported by the moderate EF values shown in Fig. 3. On the other hand, the PLI values are remarkably higher in the midstream (PLI = 6.5 to 8.2) and downstream (PLI = 7.9) samples which indicate that these parts of the creek are progressively deteriorating. It should be noted that the downstream does not have any mining activities present in the vicinity. Thus, the PLI results provided clear evidence that the anthropogenic inputs from the midstream leaches out to the downstream (approx. 1.5 km) of creek through dissolution and transport in the aqueous media. Effluents from the household communities and small-scale artisanal mining activities were identified as possible point sources of these metal contaminations.

3.3.4. Implications

The three pollution indices show the presence of toxic metal pollution in the Acupan creek. Significant levels of contamination were seen in the midstream and downstream area which is alarming since these are where the local miners and their families are situated. The results from this study, in conjunction with the reported elevated levels of mercury in the Acupan area (Clemente et al. 2004; Corpus et al. 2011), points out to the outdated and hazardous practices of the small-scale and artisanal gold miners. In addition, this study was limited only to the Acupan sub-basin. According to Corpus (Corpus et al. 2011), the contamination were also prominent in the other five sub-basins in the area which meant that the case was not isolated. Implementation of better mining safety procedures and regulatory practices are recommended.

4. Conclusion

The extent of toxic metal contamination along different locations across the Acupan creek system was investigated in this study. The total metal concentrations of As, Cd, Cu and Pb in both sediment and creek water were above their corresponding ASV, AMR, TRV and DENR WQG, especially in the midstream and downstream. Inert quartz was found to be the predominant mineral present across all sites. Sediment posing as a secondary metal source was also unlikely because the composition of the minerals present does not involve the target metal analyte. Chemical speciation identified cations CuOH^+ , PbOH^+ and Cd^{2+} as the prevalent forms of Cu, Pb and Cd while anionic HAsO_4^{2-} was the main species of As. Supersaturation of analyte in sediment and creek water points out to the re-suspension and transport of toxic metals as colloidal particles as the possible fate and transport mechanism. The relative neutrality of the pH and the lack of electrostatic interaction between the chemical species and quartz contributed to the re-suspension of metals in the water. Proximal pH values in all sites did not caused drastic changes in the solution which were highlighted by the recurring major metal species observed.

Pollution indices calculated from toxic metal concentrations further showed the contamination of the natural creek. EF and I_{geo} values indicated significant to extreme levels of enrichment and pollution of As, Cd and Pb especially in the midstream and downstream sites. Moreover, the same locations suffered from progressive deterioration based on PLI values. Lastly, the three environmental indices confirmed that the combined anthropogenic sources originating from domestic, agricultural and small-scale mining effluents present in the midstream can be transported down to the other parts of the creek system. This extensive deterioration of midstream and downstream in the creek tributary might possibly influence the other sub-basins and catchments connected to the Ambalanga river. Though the specific fractions of the metals were not validated through the use of analytical techniques, the results of the study may contribute in understanding the extent of stability and mobility of trace metals in the environment. The results may also contribute to the development of better waste management practices in small-scale mining sectors.

Declarations

Author's Contribution

The authors

E.S. Austria Jr.: Methodology, formal analysis, validation, investigation, data curation, and writing-original draft

E.M. Fuentes: Methodology, formal analysis, validation, and investigation

R. B. Lamorena: Supervision, project administration, funding acquisition, conceptualization, review and editing,

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Declaration of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

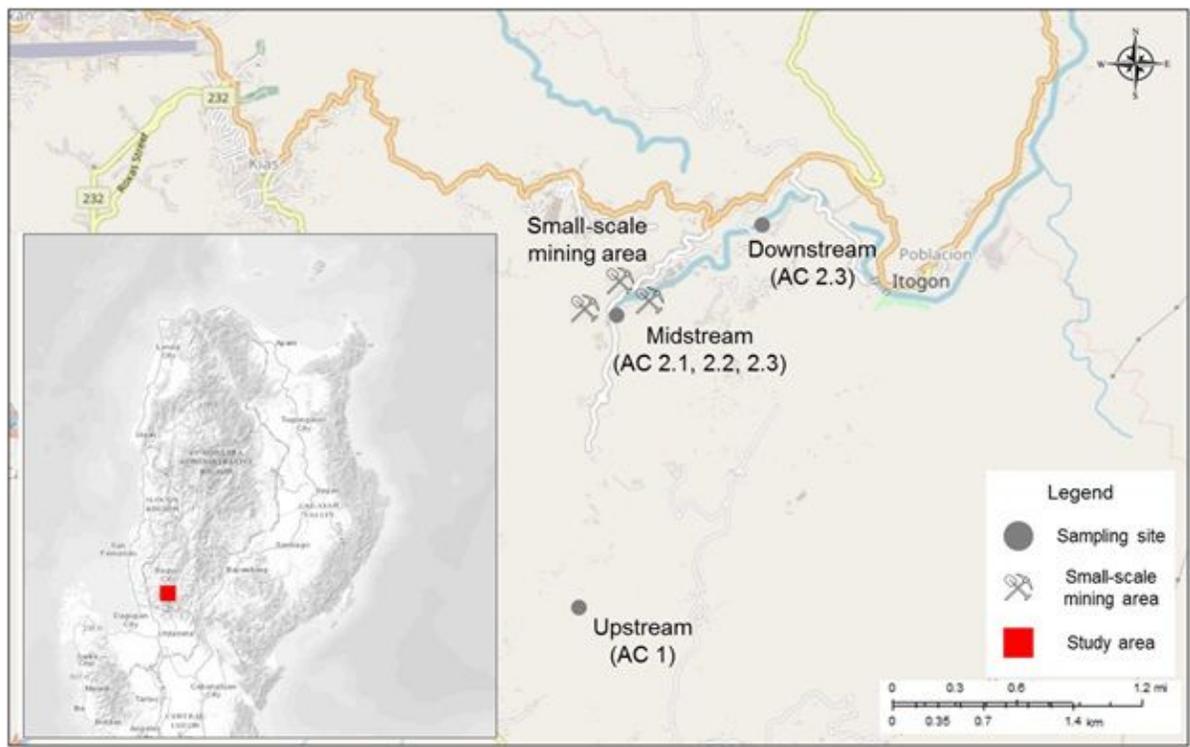


Figure 1

Location of the sampling sites and small-scale mining areas along the Acupan creek.

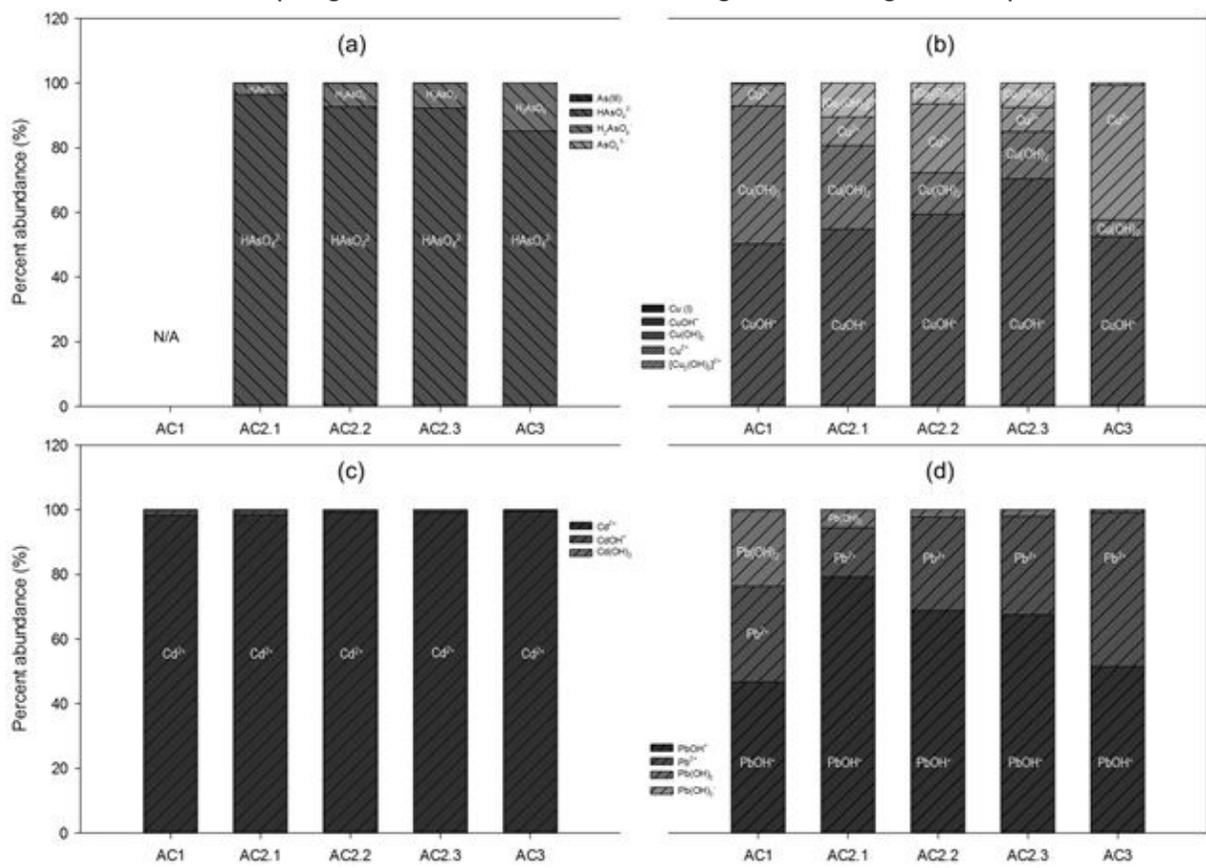


Figure 2

Chemical speciation of (a) arsenic, (b) copper, (c) cadmium and (d) lead in the creek system.

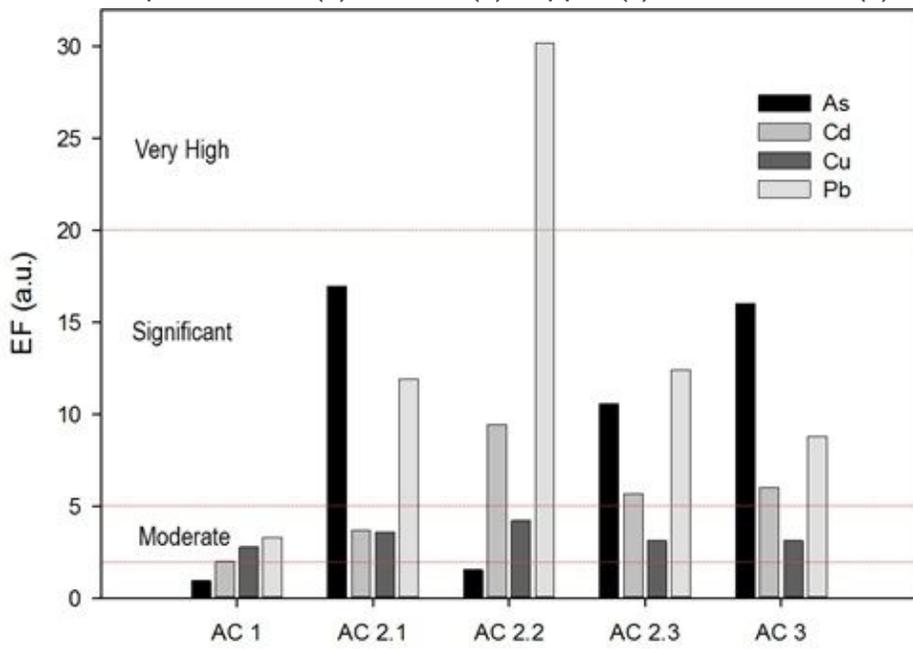


Figure 3

Enrichment factor of each metal in the creek sediments.

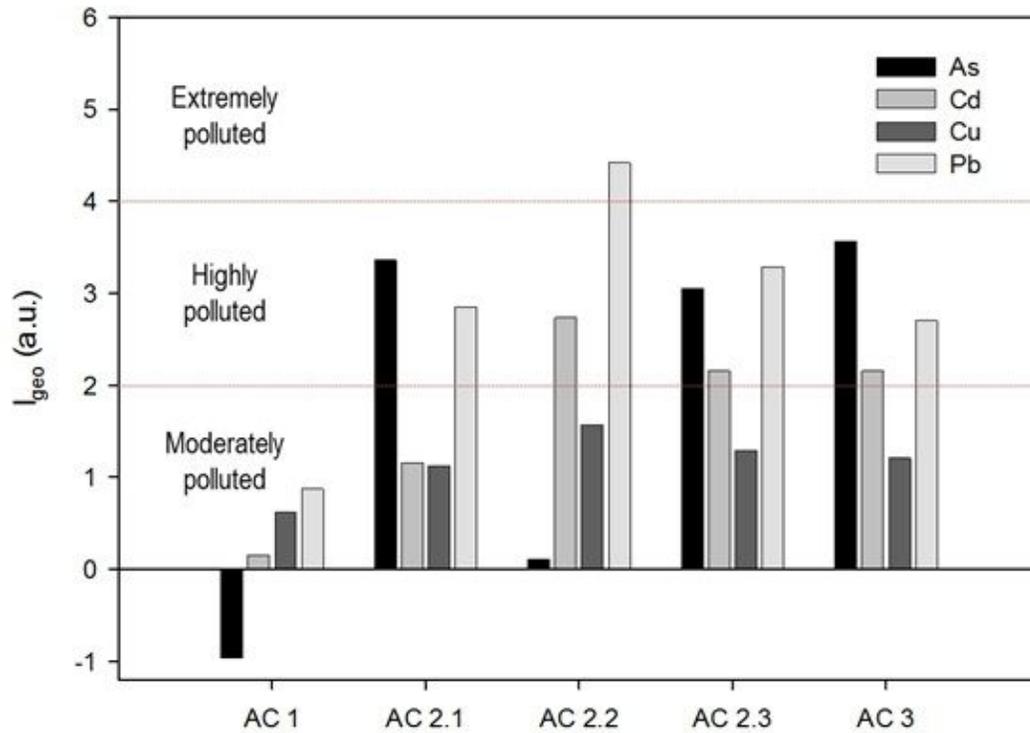


Figure 4

Geo-accumulation index of each metal in the creek sediment samples.

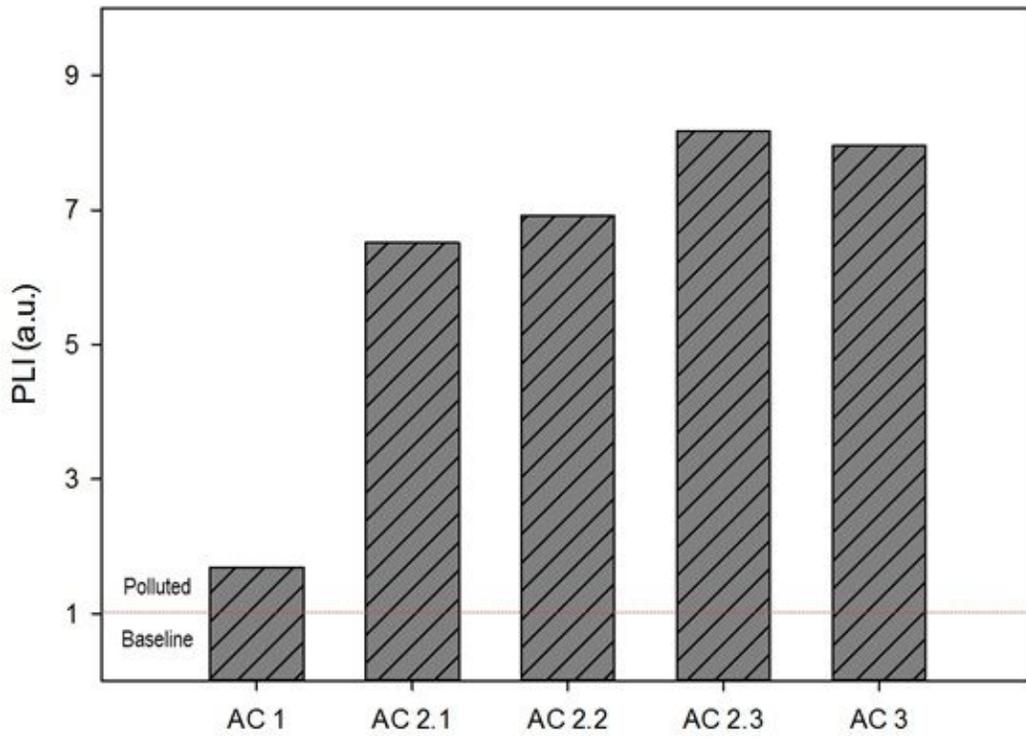


Figure 5

Pollution load index across the five different sampling sites in creek.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [EES2021MetalSpeciationSupplementaryDataAustriaJr.docx](#)