Spatial distribution and level of contamination of potentially toxic elements in sediments and soils of a biological reserve wetland, northern Amazon region of Ecuador

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Abstract

This study quantifies the degree of pollution and assess the ecological risk of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn in sediments and soils of the Limoncocha Biological Reserve (Ecuador), identified as a Ramsar site with high ecological and socioeconomic value. The hydrologic system of the Reserve is mainly formed by two rivers that drain into the Limoncocha lagoon, which occupies only five percent of the protected area but support a high anthropic influence. Local statistical baseline of studied potentially toxic elements is established using cumulative frequency method, and Al is selected as reference element due to the good correlation with the studied elements. The grade of pollution and the potential ecological risk are evaluated applying three individual (Contamination Factor, Geo-accumulation Index and Enrichment Factor) and six integrated (Degree and modified degree of contamination, Pollution Load Index, Nemerow and modified Nemerow pollution indexes and potential ecological risk index) indices. Results analysis are based on the combined application of traditional statistics, multivariate data analysis and self organizing maps. Outcomes suggest to classify sediments and soils as "moderate contamination and enrichment" due mainly to the concentrations of Cu (66.4 – 110 mg/kg) and Cd (0.0262 – 0.808 mg/kg), derived from domestic wastewaters and agricultural activities, and in a lesser extent due to Mo (0.822 – 4.37 mg/kg), Ni (10.3 – 25.8 mg/kg), Co (7.27 – 24.8 mg/kg) and V (60.3 – 178 mg/kg), derived from oil field drilling activities. The distributions of As (0.328 – 8.83 mg/kg), Ba (143 – 1100 mg/kg), Pb (7.20 – 26.5 mg/kg), Zn (60.1 – 276 mg/kg) and Cr (10.1 – 48.6 mg/kg) are heterogeneous in the studied sampling sites. Sediments located next to the pier and at the central area of the Limoncocha lagoon, show moderate potential risk and according to sediment quality guidelines, the calculated mean Effect Range Median quotient (mERMq) classify the sites as medium-low priority risk level. A three-level classification of a mean quotient based on soil quality and soil potential uses is proposed. Soil sites with high anthropogenic activities show low to moderate potential ecological risk being classified as poor soil quality sites but with all potential soil uses allowed according to the legal limits for land uses in Ecuador.

Keywords: Limoncocha; Biological Reserve; sediment; soil; potentially toxic elements; individual and integral indices; PCA and SOM analysis

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.

1. Introduction

The sediment and soil environmental compartments are heterogeneous natural matrix of materials that can act as sinks, carriers and sometimes as important secondary source of pollutants in the environment, since some pollutants can be mobilized to the water column through physical-chemical and biological processes. Therefore, sediments and soils, which require appropriate protection, are sensitive indicators for monitoring contaminants and management due to their high ecological and socioeconomic value, being able to reflect the current quality of the entire ecosystem (Chapman, 2018).

Among the various contaminants, metals in sediments and soils is of major concern because of their possible toxicity, persistence, bioavailability, bioaccumulation and biomagnification nature and may be transferred to the overlying water and thereby entering into the food chain (Ivanina and Sokolova, 2015); (Chapman, 2008). The environmental behaviour of potentially toxic elements in soil and sediments is critically dependent on several factors as their content, distribution and speciation, the organic matter and clay content of the solid matrix, as well as the changing environmental conditions (e.g., pH, redox potential, organic ligand levels). All of them affect processes that can take place in soil and sediment as adsorption–desorption, redox, precipitation, solubilisation, flocculation, chelation, which finally influences their mobility and potential effects to organisms (Cáceres et al., 2013; Ke et al., 2017; Mazurek et al., 2017). Fine-grained sediments represent a major repository for potentially toxic elements because of their large adsorption capabilities, with variable distribution profiles of metal concentrations in layers.

Particularly wetlands, known as kidneys of the earth, play a vital role in food supply, climate regulation, flood control, aquifers loading and unloading, biodiversity and environmental quality maintenance, providing significant ecosystem services (Gambrell, 1994); (Hernandez Gonzalez et al., 2019); (Xu et al., 2019). At the same time, wetland ecosystems are highly vulnerable to climate change and anthropogenic impacts. Wetlands act as important sinks for metals, allowing the accumulation, migration and transformation of metals between waterbodies, sediments, soils and biota (Engin et al., 2017). In this sense, potentially toxic elements pollution control capabilities of wetlands have received increasing research attention in the last years (Fural et al., 2020); (Kalita et al., 2019), (Hernandez Gonzalez et al., 2019). Protecting these important sites for biodiversity is vital for ensuring long-term and sustainable use of terrestrial and freshwater natural resources as stablished by the Sustainable Development Goal 15 of United Nations (Gardner and Finlayson, 2018).

Pollution indices are widely considered as explicit enforcement tools to quantify the degree of total metal pollution and assess the ecological risk of metals in sediments and soils, as well as in the environmental protection regulatory process (Alvarez-Guerra et al., 2007); (Dung et al., 2013). Pollution indices can be divided into different number of groups taking into consideration: i) the number of metals considered (individual or integrated); ii) the method of calculation (based on geochemical backgrounds (GB) values, based on data other than GB given in the literature or based on metal content in the analysed sediment and soil profile but not in parent material); iii) the different purposes of calculation (individual levels of pollution from each of the analysed metals, the scale of total pollution, the source of metals, the potential ecological risk, the area with the highest potential risk of metal accumulation and the ability of the surface horizon to accumulate metals) (Zhuang et al., 2019); (Kowalska et al., 2018).

Calculation of sediment and soil pollution indices requires the assessment of the geochemical background or geochemical baseline. Geochemical background is understood mainly as a natural value for a given medium not impacted by anthropogenic activities and geochemical baseline is defined as the level of potentially toxic elements in soils that are not under the direct influence of humans. Therefore, the geochemical baseline would be the sum of the geochemical background plus a small quantity due to diffuse contamination (Teng et al., 2009; Matschullat et al., 2000). Different methods usually classified into direct (empirical or geochemical), indirect (statistical or theoretical) and integrated methods (combination of both) (Wang et al., 2019); (Karim et al., 2015); (Wei and Wen, 2012) have been used to determine the geochemical background and baseline. The direct methods use the mean or median values obtained in the study of samples representing pre-industrial period (deep core samples) or collected in pristine areas at a certain distance from anthropogenic pollution sources. The indirect methods use graphical and computational techniques to eliminate the outliers from the distribution of chemical analysis results (Dung et al., 2013); (Gałuszka and Migaszewski, 2011). An important number of authors establish geochemical baseline of elements in soil and sediments using statistical methods (Zhou et al., 2019; Wang W et al., 2019; Karim et al., 2015; Ramos-Miras et al., 2019; Xu at al., 2019), using normalization procedures (Xu at al., 2019) and using combined normalization and statistical procedures (Teng et al., 2009).

The selection of an appropriate background of potentially toxic elements in sediments and soils can be essential for assessing the pollution level and avoid misestimation of the pollution status. A large number of authors (e.g., (Varol et al., 2020) (Kalita et al., 2019); (Shaheen et al., 2019); (Zaaboub et al., 2015) select global reference values as background values for their studies, such as the upper crust averages composition, the bulk crust composition, the world average composition and the sediment concentrations before global industrialization. These values represent hypothetical reference concentrations regardless of natural variability and are part of the geochemical methods (Matschullat et al., 2000). Not only background but also geochemical baseline values have also been recommended for the assessment of sediment metal pollution (Xu et al., 2019); (Wang et al., 2019). Several authors recommend using local and regional background or baseline content, instead global background data, to quantify potential toxic elements contamination in sediments and soils. Not only local and regional references are site and region dependent but they can be more useful to answer problems at these scales (Matschullat et al., 2000); (Sakan et al., 2015); (Kowalska et al., 2018). Two different geochemical backgrounds are specified in the present study, a reference geochemical background that provides a universal character, and a local statistical geochemical baseline obtained by analysis of soil and sediment samples.

Some geographic areas with different bodies of water that are under different protection figures such as Parks and Reserves can be directly or indirectly affected by anthropogenic and natural sources of contamination of potentially toxic elements in sediments and in adjacent soils. Particularly, in Latin American preserved areas are not protected from either the occurrence or the deleterious effects of chemical pollution (Rodríguez-Jorquera et al., 2017). Nonetheless, there is an important lack of information relative to the estimation of the contamination of sediments and soils and its relative impact, resulting in both challenges and opportunities to conserve biodiversity and ecosystems.

Ecuador has 19 Ramsar Sites (i.e., wetland sites designated to be of international importance under the Ramsar Convention), with 1,064,483 hectares of the country inscribed on the list of wetlands of international importance in terms of ecology, botany, zoology, limnology or hydrology. The Limoncocha Biological Reserve (LBR) was identified as the Ramsar site number 956 since 1998 (Ramsar, 2020). LBR is one of the smallest protected areas in Ecuador with a hydrologic system formed by the Pishira and Playayacu small rivers and the Limoncocha lagoon. It has abundant biodiversity and is a source of recreational and agricultural activities and human food base. This area is influenced by oil well drilling and exploitation activities and is under pressure from a population that is constantly growing with increasing human activities as ecotourism, fisheries and agriculture which has brought about great pressure in this protected environment (Valdiviezo-Rivera et al., 2018). In addition, the storm rainfall events might lead to rising water level of the nearby Napo river causing floods events with degradation of the landscape, being a long-term secondary source of sediment and soil pollution that could result in a series of environmental disturbances (Ciszewski and Grygar, 2016).

As far as the authors know, currently the application of pollution indices for the assessing of contamination have not been studied in Limoncocha Biological Reserve so far. Hence, the objectives of this work are (1) to determine the levels, associations and spatial distribution of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn, in sediments and soils of the LBR during rainy and dry seasons; (2) estimate the local geochemical baseline of potentially toxic elements concentrations; and (3) select the conservative reference element and evaluate ecological risk using single and integrated pollution indices in the studied area based on several criteria as the local baseline and reference geochemical backgrounds, the conservative element, the toxic responses, the sediment quality guidelines and the legal Ecuadorian framework for soil uses.

2.- Materials and methods

2.1.- Study area: Limoncocha Biological Reserve

Limoncocha Biological Reserve (LBR), is a Ramsar site of 4613.3 hectares located on the northeastern side of the Ecuadorian Amazon, in the southwestern region of the province of Sucumbíos at a height of 220 meters above sea level (Figure 1). The reserve is characterized by its abundant biodiversity with several ecosystems such as permanent wetlands, flooded forest, dryland forest, and aquatic habitats. The hydrologic system of LBR is formed by the Pishira and Playayacu rivers, that drain into the Limoncocha lagoon, and by the Yanacocha body of water; the area is currently a “dead arm” of the Napo River located 2 km south of the lagoon (Armas and Lasso, 2011).

There is a community of indigenous Kichwas people with the use of natural resources, mainly from the Limoncocha lagoon which is very rich in fish stocks, and a subsistence farming, mostly with banana and yucca cultivations. The Limoncocha village, is located at the east corner of the lagoon with 7146 inhabitants at 2016 that depends mainly on biodiversity to live (Neira et al., 2013). In this village the elimination of excreta is carried out through latrines and in the open air and the community collection of urban waste only reaches 30%. The Reserve is located within Block 15 corresponding to Petroamazonas, with three oil fields extraction and a Center Production Facility (CPF) connected by road inside the Reserve (Figure 1).

Limoncocha lagoon is the main tourism attraction in the LBR and facilities are being developed for ecotourism as well as for research, education and environmental interpretation attracting increasing numbers of visitors. Contrary, the Yanacocha lagoon with a very difficult access, is rarely visited due to myths of the Kichwa communities, about which the area is haunted or occupied by a mystical creature (Armas and Lasso, 2011). The region around the lagoon has experienced a very rapid and constant growth of population, agriculture (particularly palm), aquaculture and ecotourism since 2010, which has brought about great pressure in this protected environment (Cerda, 2015).

The Napo basin in the Limoncocha lagoon area is a Transitional Environment characterized by sediment deposited at 0.49 mm/yr rate in tidal channels influenced by high stand and estuarine settings with lithic arenite sands from the Andean cordillera with abundant chlorite and kaolinite in deposits (Franzinelli and Potter, 1983)(Wittmann et al., 2011).

LBR is a climatic subregion where the weather is characterized by a very rainy season from September to May, with mean precipitation rates above 120 mm/month, and a drier season with only 3 months (June, July and August) in which the monthly precipitation rates drop to about 70 mm/month (Moquet et al., 2011)

2.2.- Sample collection and analysis

The location of the sampling sites was influenced by the requirements of accessibility, which is limited to less than 50% of the reserve, geographical homogeneity, the mouth and the head of the lagoon tributaries, as well as places with different degree of anthropic influence (urban, industrial, agricultural, fishing and tourist activities). The proposed sampling strategy provides a broad spatial coverage of the Reserve and allows a general assessment of sediment and soil quality throughout the lagoon, rivers and soil. Seven sediment samples and six soil samples were collected during dry and rainy season with a density of 3.5 km^2 in the Limoncocha reserve and a density of 0.46 km^2 in the Limoncocha lagoon.The seven sediment sampling points (SE1 – SE7) and six soil sampling point (SO1 – SO6) are shown in Figure 1. Stations SE1, SE3, SE4 and SE5 located along the banks of the Limoncocha lagoon coincident with the mouth of the rivers Playayacu and Pishira. SE2 is located in the lagoon center, and SE6, SE7 are located at the headwater of Playayacu and Pishira rivers respectively, and close to the CPF. SO4 and SO6 are located close to the oil wells, SO1, SO2 and SO3 close to the urbanized area and SO5 in the forest. A portable global positioning system (GPS) was used to locate sediment and soils collection sites which detailed description is shown in Table S1.

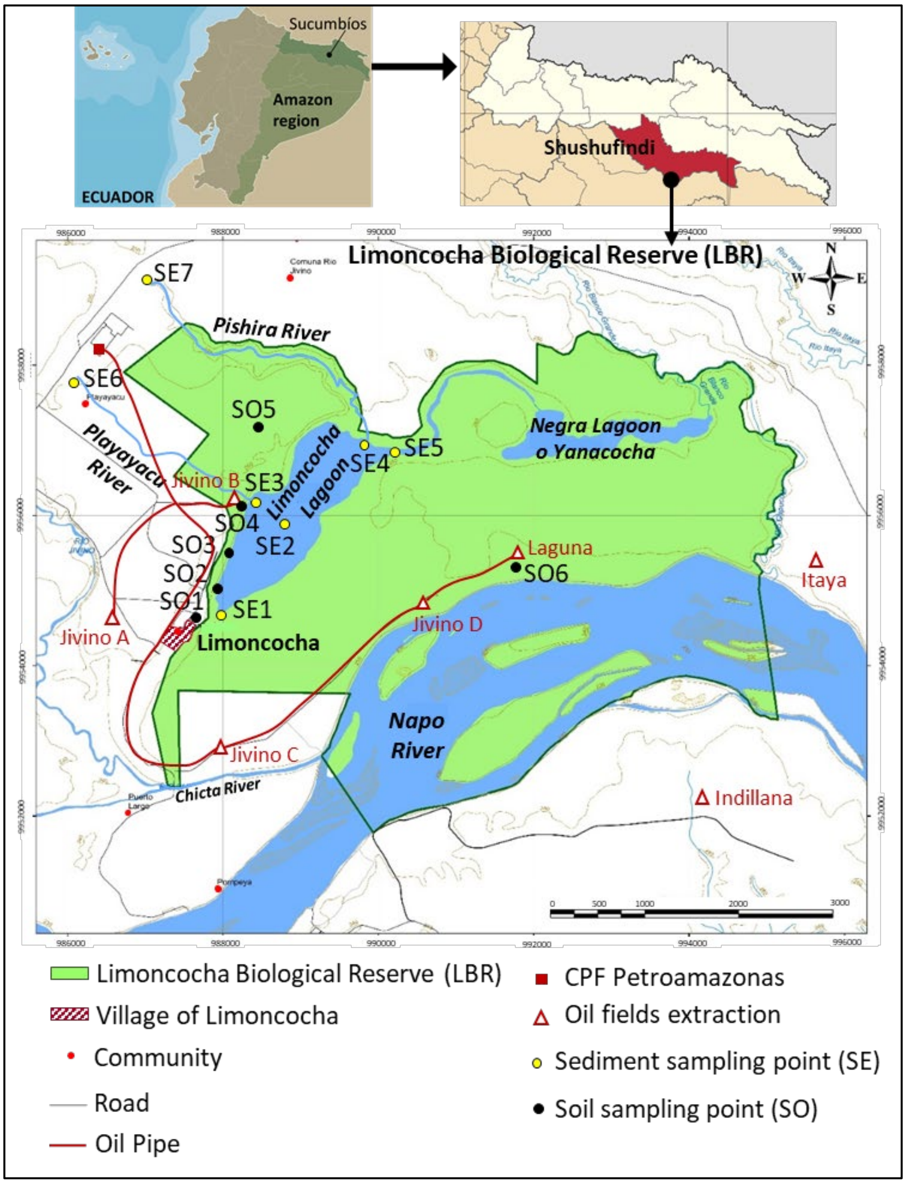


Figure 1. Study area with locations of sediment and soil sampling sites

Two replicate surface (5 cm depth) soil and sediment samples from each selected sampling station (Fig. 1) were collected in the form of mixed composite samples within a square of 1 m^2 by using a plastic spatula. Two additional samples were taken from SO1 site in opposite places around the closed oil extraction well due to his high anthropic activity. Sediments were collected from the lagoon and rivers banks except sample of the central area of the lagoon (SE2) that was gathered by a plastic core sampler using the surface layer (5 cm) for analysis. Sampling was carried out during both of the climatic seasons of the region, rainy season (December 2018) and dry season (July 2019) in order to investigate the seasonal variations in concentration and distribution of studied elements. The total available samples were 28 sediments and 26 soils. Samples were stored in closed plastic vessels previously washed with 1:1 HNO_3 and rinsed with distilled water. The samples were kept on ice until arrival at the laboratory. Once in the laboratory, the samples were dried at room temperature, then they were ground and passed through a 270-mesh sieve. Grain size fraction (<63 μm) was homogenized and stored in polyethylene plastic bags. The sediment texture was determined by the international pipette method (Maiti, 2011). The Organic Carbon (OC) was determined by the Walkley-Black chromic acid wet oxidation method (FAO, 2019)

The analysis of the major elements Al, Fe, Mn and Ti, was carried out at Activation Laboratories Ltd, in Canada using the Major Elements Fusion ICP package (Code WRA/ICPOES-4B). The lithium metaborate/tetraborate fusion technique was employed. The resulting molten bead was rapidly digested in a weak nitric acid solution and the analysis was carried out by ICP and ICPMS. Certified reference material NIST 694, DNC-1, W-2a, SY4 and BIR-1a were used obtaining recoveries from 86.2% to 104.3%.

The rest of metals (Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn) and metalloids (As) concentrations were determined by ICP-MS (Thermo iCAP-Q) in our laboratories. Metals were extracted with a microwave acid digestion system (CEM model Mars 5) according to the SW-846 EPA Method 3051A (US EPA 1987), which involved the digestion of 0.1 g of sediment sample with a mix of 9 mL of nitric acid (65%, Suprapur quality) and 3 mL of hydrochloric acid (30%, Suprapur quality) in Teflon vessels. After the digestions, the samples were diluted to 50 ml using Milli-Q water and then analysed. The accuracy of the analysis was checked with the certified reference materials for marine (PACS2 and MESS 4) and fresh water (FWS-3) sediments. Best recoveries for As, Cd, Cr, Mo, Ni, Pb and V were obtained with PASCS-2 (97%, 96%, 97% 97%, 90% and 99%, respectively), whilst better recoveries for Ba (101%) and Zn (98%) were obtained with FWS-3 and with MESS-4 for Co (88%) and Cu (94%).

2.3.- Statistical analysis and Self-Organizing Maps (SOM)

Data were tested for normality and homogeneity by using the Kolgomorov-Smirnov and Levene tests, respectively. One-way analysis of variance (ANOVA) with Tukey's posthoc test (with Bonferroni correction) was performed to test for significant differences (α =0.006) variations in concentration of potentially toxic elements in terms of seasons and stations. When normality and homogeneity assumptions to satisfy ANOVA requirements were not met, data were logarithm-transformed ($\log_{10}$). In order to provide a description of the structure and distribution of the data obtained with the minimum loss of information, a multivariate analysis was applied using principal component analysis (PCA) as the extraction procedure. The use of PCA allows identify possible sources of contaminants or groups of contaminants and determine the distribution of contamination or types of contamination in sediment and soil. In addition, hierarchical cluster analysis (HCA) was used to identify groups of sediment and soil samples, which were represented visually as dendograms of sampling stations using the Euclidean distance as distance measure and the Ward's method as linkage method. Statistical analyses were performed with the aid of the statistical software SPSS 18.00.

The Self-Organizing Maps (SOM) methodology is applied in the present work to classify sediments and soils sites in relation to the six integrated pollution indices obtained. SOM tool applied to the environmental classification of sediments has been previously used by the authors (Alvarez-Guerra et al., 2008); (Muñoz et al., 2015). Details about the methodology background and use of the SOM are described in these previous articles. Briefly, a SOM is a statistical tool based on a neural network with the SOM considered a map that consists of units (neurons) organized usually on a two-dimensional hexagonal grid. Each neuron is represented by a weighted vector whose dimension is equal to the dimension of the input space. The quality of the SOMs obtained under different normalization method is evaluated using the quantization error (QE) and the topographic error (TE). The optimum map size is chosen based on the minimum QE and TE. To interpret the results, SOM visualization process starts with the map of neurons with a specific weight, allowing to cluster the original information. The map can also be divided into so many component planes as data variables, representing the influence of each variable to the neurons in the map. The SOM Toolbox 2.0 for MATLAB (v. R2014a) is used to carry out the analysis, which is based on unsupervised learning and is trained using the Kohonen algorithm. Detailed information about SOM is included in the Supplementary Information.

2.4.- Local geochemical background establishment

Due to the lack of regional background values for potentially toxic elements in the studied area, two approaches have been proposed. The first approach of the present study has been the use of the average composition of the upper continental crust (UCC) proposed by (Rudnick and Gao, 2014), as direct geochemical background. UCC constitutes a reference geochemical background that represents the lithogenic content of potentially toxic elements that are not under the influence of pedogenic processes (Kowalska et al., 2018). In a second approach, local geochemical values for sediment and soil in Limoncocha reserve were established using statistical methods consisting of the cumulative frequency curves and the iterative 2σ-technique. Results from these methods can present rather realistic data for the geochemical background in different data sets (Matschullat et al., 2000).

2.4.1. Relative cumulative frequency method

The relative cumulative frequency method is based on the different slopes of the relative cumulative frequency–content of elements fitting curves of the sampling points (Wang et al., 2019); (Wei and Wen, 2012). Zero, one, or two inflections appeared in the fitting curves of all of the sampling points to separate the unpolluted and polluted samples. If the cumulative frequency curve approximated a straight line and no inflection point existed, the background value is calculated from the average value of all of the data. If only a higher inflection point is found, then the baseline is obtained from the data below the inflexion value. If two inflections occurred, the lower inflexion point represents the upper limit of natural origin concentrations, and the higher inflexion point represents the lower limit of abnormal concentrations (Zhou et al., 2019). The Kolmogorov–Smirnov test was apply to check the concentrations (or the logarithm of the concentrations) normal distributions (Karim et al., 2015); (Tian et al., 2017). In the present study, the criterion to determine the inflection points is to select those values of the curve that followed a linear model. For this, the upper and lower extreme values of the coordinate data were omitted until the remaining data met this linearity criterion. The average element concentrations of these remaining data were selected as the local geochemical background.

2.4.2 Iterative 2σ -technique

Mean and standard deviation are calculated for the original data set. All values beyond the mean-2σ interval are omitted. This procedure is repeated until all remaining values lie within this range. The mean-2σ calculated from the resulting sub-collective is considered to reflect the local geogenic background. This technique set up an approximated normal distribution around the mode value of the original data set (Matschullat et al., 2000).

2.5.- Contamination assessment methodology

Table S2 shows the indices considered to estimate the contamination level and the potential ecological risk of studied potentially toxic elements in sediments and soils of LBR. From the numerous available indices for the classification of sediments and soils samples (j) as to potentially toxic elements pollution (i), a combination of single and integrated risk assessment indices were used in the present study, to determine the state of contamination in the Limoncocha Biological Reserve. The contamination factor ($\mathrm{Cf}_{i,j}$), the geoaccumulation index ($\mathrm{Igeo}_{i,j}$) and the enrichment factor ($\mathrm{EF}_{i,j}$) are used as individual indices to calculate the degree of contamination of each potentially toxic element at a given site. However, these sediment quality indicators either define a qualitative threshold or focus on ecological risk assessment of a single element. Potentially toxic elements pollution in the environment generally occurs in the form of complex mixtures. Therefore, the degree of contamination (Cd_j), modified degree of contamination (mCd_j), pollutant load index (PLI_j), the Nemerow Pollution Index (NPI_j), the modified Nemerow Pollution Index (mPLI_j), and the potential ecological risk index (RI_j), are used as integrated indices to determine the degree of contamination of the set of pollutants at a given site.

The evaluation of the sediment quality with respect to potentially toxic elements is determined using the sediment quality reference values ($\mathrm{SQG}_{i,j}$) as a mean $\mathrm{SQG}_{i,j}$ quotients (mSQGq_j). According to (Alvarez-Guerra et al., 2007), the main advantage of this approach is that the mSQGq_j values provide a simple, easily understandable numerical index and estimates the probability that a sample is toxic to the recipient organisms. The widely used mean Effect Range Median quotient –mERMq_j-, (Zhuang et al., 2019); (Pejman et al., 2015) is proposed to use in the present work. In the case of soils, the Ecuadorian national regulatory requirements for soil uses (Ecuador, 2015) is applied to determine a mean Maximum Permissible Value quotient (mMPVq_j).

3.- Results and Discussion

3.1.- Seasonal and spatial distribution of contaminants in sediments and soils

The potentially toxic elements concentration in sediments and soils at Limoncocha Biological Reserve are of the same order than other wetland protected areas worldwide (Table S3). The potentially toxic elements concentration in sediments and soils during dry and rainy season are showed in Tables S4 and S5. Table S6 shows the grain size fractions (%) and OC (%) obtained values. Regarding the influence of the seasonal variability on levels of potentially toxic elements in sediment and soil, no significant variations ($\alpha=0.05$) are exhibited by the studied elements content in sediments and soils between the seasons. Only As at SO3 and V at SE7 are significantly higher in rainy season and Cr at SO2 and Cd at SE4 significantly higher in dry season. With the obtained results and the available data, no reason is observed for such elements behaviour at these sampling points. However, the environmental significance of these results will require a longer series of seasonally analysis to determine potential trends. Similar results with not seasonal variability or irregular fluctuations between dry and wet season depending on studied element and location have been previously reported (Satapathy et al., 2019); (Nargis et al., 2019); (Ibanga et al., 2019). Therefore, the average element concentrations of both the seasons are taken into account.

Figure 2 shows the score plot of the sediment and soil samples formed by the PCs as well as the studied elements contribution in each location. The PCA of the potentially toxic elements concentrations in sediments explained 75.01% of the total variance of the data and two principal components (PCs) are defined (Table S7). The principal component 1 (PC1) accounted for 43.7% of the total variance and the elements associated with PC1 are mainly driven by V, Ba, Cr, Co, Ni and Zn. Principal Component 2 (PC2) explained 31.3 % of the total variance and are mainly associated with Mo, Cd, As and Cu.

The HCA showed that sediment sampling sites are grouped into three statistically significant cluster with similar characteristics in the elements content (Fig. 2): Cluster 1 includes SE1 and SE2 samples located in the dock and in the central area of the lagoon respectively, with high concentrations of Mo, Cd, As and Cu. Cluster 2 consist of site SE5 located in the northern zone of very difficult access which is characterized by low concentration of studied elements. Cluster 3 grouped the SE3, SE4, SE6 and SE7 samples located in the headwater and in the mouth of the rivers with high concentrations of V, Ba, Co, Cr, Ni and Zn particularly in site SE6 located in the buffer area of the CPF installations. The low percentages of OC in the sediments (0.100% -0.930% showed in Table S6) do not contribute significantly not PC1 with 0.128 nor PC2 with -0.355, (Table S7). Furthermore, the linear correlations of the elements with OC are very low except for Zn. However, the clay contribution in PC2 is 0.868 because it correlates well with As, Cd and Mo, the main associated elements of PC2 (Table S7).

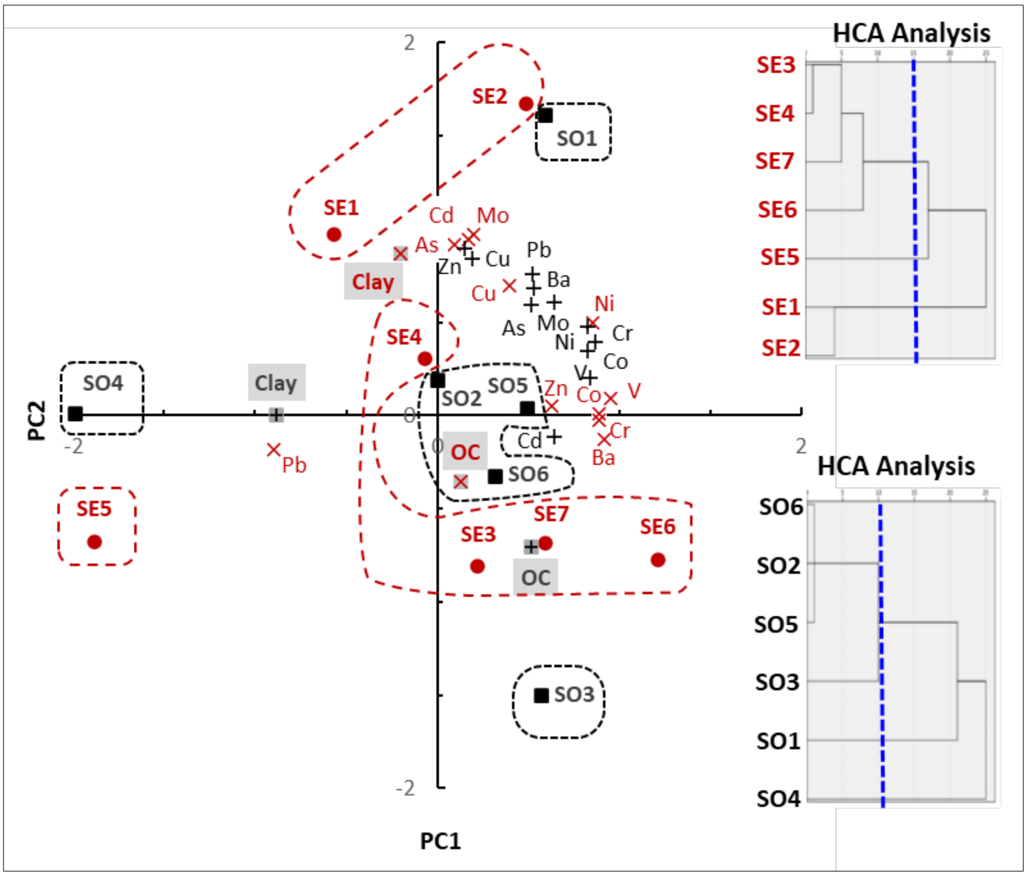


Figure 2: Distribution of the elements and sediment and soils sites in the space defined by two principal components resulting from PCA: (×) represents the elements of the sediments, (☒) OC and Clay of the sediments, (+) elements of soils, (⊞) OC and Clay of soils, (■) sediment site and (●) soil site. Cluster from HCA are grouped with red (sediments) or black (soils) boundaries.

The PCA of the potentially toxic elements concentrations in soils (Fig. 2) revealed that two principal components (PCs) accounted for 71.2% of the total variance (40.7% and 30.4% of the total variance explained by PC1 and PC2, respectively) (Table S8). The contaminants associated with PC1 are mainly driven by Cr, V, Co and Ni. PC2 is mainly associated with Zn, Cu and Pb. The elements Mo, Ba and As contribute in a similar way to PC1 and PC2. The soil sampling sites are grouped by the HCA into four statistically significant cluster with similar characteristics in the elements content. Cluster 1 consist of site SO4 located outside the enclosure of the Pozo Jivino B oil well, which is characterized by low concentration of studied elements. Cluster 2 consist of site SO1, located in an highly anthropic area which is characterized by high concentration of studied elements. Cluster 3 consist in site SO3 with high concentrations on Organic Carbon and Cd located in the left bank of the lagoon. Cluster 4 grouped the SO2, SO5 and SO6 sites, with high concentrations of a high number of elements in SO5 and SO6 located in low anthropogenic activity areas. SO2 site shows low concentration of contaminants except for Zn and V. Soil OC values are an order of magnitude higher than in sediments (Table S6) and show an important contribution in both PC1 (0.516) and PC2 (-0.706) (Table S8). The high contribution of OC in PC2 could be associate with the relative higher linear correlations observed between the Zn, Cu and Pb elements which are mainly associated with PC2 (Table S8). On the other hand, V (associated with PC1) shows the second best linear correlation with OC, which could explain the not negligible contribution value of OC to PC1 (Table S8). The high clay contribution to PC1 (-0.882) may be due to the relatively good linear correlation of Cr and V with the clay content since these elements are the main contributors to PC1 (Table S8).

Both, in sediments and soils, PC1 associates metals V and Ni that have been reported previously as indicators of contamination by oil spillage (Sadeghi et al., 2019); (Ogunlaja et al., 2019). In addition, the exploitation and drilling processes in oil fields might results in metals contamination by Cr, Cu, Co and Zn (Hu et al., 2016); (Ghanavati et al., 2019); (Pratte et al., 2019). In the present work Cr and Co are associated to PC1 in both sediments and soil which could be due to the same contamination source. Cu is associated with PC2 in sediments and soils, and Cd is associated in PC2 in sediments and PC1 in soils. Oil spills (Agah et al., 2012); (Davoodi et al., 2017) and agricultural activities (Dai et al., 2019); (Marrugo-Negrete et al., 2017) have been reported as potential pollution sources of Cd and Cu. On the other hand, Ba is associate in PC1 (sediments) and PC1/PC2 (soils) probably related to the use of barite in drilling muds (Sharma et al., 1999) (Chatterjee et al., 2007). The highest values of Ba correspond to SE6 and SE7 headwaters of the rivers in sediments and SO1and SO5 corresponding to soils in old well and Caiman trail but nevertheless not in SO4 and SO6 that are wells in operation.

PC1 potentially toxic elements may reflect similar anthropic origin from oil fields processes and PC2 potentially toxic elements may reflect mixed anthropic origins (oil field, agricultural, domestic wastewaters) together natural sources in both cases. To elucidate the natural or anthropic origin as well as the meaning of the potentially toxic elements concentrations obtained, we will apply individual and integrated pollution indices, so it will be necessary to determine previously the elements background and the reference element.

3.2.- Determination of background: local statistical baseline and reference geochemical background of studied elements in sediments and soils

Several authors recommend the use of local background content in calculation contamination factors and pollution indices (Sakan et al., 2015) (Kowalska et al., 2018); (Saddik et al., 2019). Table 1 shows the local statistical baseline (LSB) values obtained by the two statistical methods considered in this study: relative cumulative frequency method and Iterative 2σ -technique. In the supplementary material (Fig. S1) the concentration curves (mg/kg) or logarithm of concentration versus cumulative frequency distribution are shown for all the contaminants studied. Both the Table 1 and Figure S1 indicate the LSB average values and the concentration ranges for each LSB. Both LSBs obtained are observed to be similar with coefficient of variance (CV) between the two LSB values that are less than 10% for all pollutants except for Zn in sediments (14.0%) and for As in both soils (11.9%) and sediments (17.0%).

Statistical tests are useful for removing so-called outliers, and therefore for reducing the original dataset to a "clean" data set. From this clean, undisturbed dataset, the essential statistical parameters can be calculated, which describe the local statistical baseline.

The statistical methods applied in the present work propose different strategies to detect and eliminate anomalies. The Iterative 2σ -technique removes outliers, repeatedly excluding those values outside of mean ± 2σ. The relative cumulative frequency method eliminates as outliers, those data that are below or above the inflections of the cumulative frequency curves. It considers that the inflections in the cumulative frequency curves indicate anomalous anthropogenic and natural concentration limits. The concentration ranges shown in Table 1 correspond to the clean collective data (eliminating outliers). It is observed that the range of values of the Iterative 2σ -technique is equal (Co and Mo in sediments) or wider than the range of relative cumulative frequency method. In the Iterative 2σ -technique, the range of As and Cu in sediments includes all the original data. For other elements, only one of the data (highest or lowest) is removed: Ba (sediment), Cr (sediment and soil), Cd, Cu, Ni and V (soil). The highest CV values of iterative 2σ – technique in front of relative cumulative frequency method are due to the largest number of data considered in the former method.

In order to clarify the LSB selection method, the case of As which shows high discrepancies between sediments and soils, is discussed in Supporting Information (Figure S2) as an example applicable to all the studied elements. In the present work, the relative cumulative frequency method is used to determine the LSB because of better distinguishes abnormal processes. Furthermore, the method limits the original data set to a clean one, outside of anthropogenic influence and abnormal natural values (Matschullat et al., 2000).

Table 1. Local statistical baseline (LSB) values obtained by relative cumulative frequency method and Iterative 2σ -technique.

		Local Statistical Baseline (LSB)					
		Relative cumulative frequency method			Iterative 2σ -technique		
		Mean ± σ (mg/kg)	CV (%)	Range (mg/kg)	Mean ± σ (mg/kg)	CV (%)	Range (mg/kg)
Sediments	As	3.46 ± 0.738	21.3	2.56 - 4.76	4.41 ± 2.47	56.0	1.32 - 8.83
	Ba	319 ± 29.7	9.29	277 - 399	328 ± 93.2	28.4	143 - 491
	Cd	0.373 ± 0.100	26.8	0.209 - 0.515	0.338 ± 0.174	51.6	0.000 - 0.626
	Co	19.5 ± 1.48	7.58	16.0 - 21.9	19.8 ± 1.40	7.07	17.3 - 22.6
	Cr	35.5 ± 4.40	12.4	29.1 - 42.5	36.7 ± 8.09	22.0	20.7 - 48.6
	Cu	87.8 ± 7.29	8.30	75.6 - 99.1	88.0 ± 19.1	21.7	54.6 - 123
	Mo	2.40 ± 0.275	11.5	2.06 - 2.95	2.24 ± 0.205	9.17	1.94 - 2.60
	Ni	21.9 ± 2.00	9.12	18.4 - 24.6	22.8 ± 2.52	11.0	18.4 - 27.0
	Pb	13.9 ± 2.41	17.3	10.5 - 18.8	13.8 ± 4.32	31.3	5.98 - 22.4
	V	135 ± 8.06	5.96	117 - 147	136 ± 11.3	8.29	114 - 159
	Zn	110 ± 24.3	22.0	78.5 - 152	90 ± 22.8	25.2	58.6 - 131
Soils	As	1.91 ± 0.563	29.4	1.21 - 3.05	1.62 ± 0.746	46.1	0.328 - 3.05
	Ba	255 ± 35.5	13.9	209 - 318	240 ± 40.9	17.1	182 - 318
	Cd	0.389 ± 0.0741	19.0	0.252 - 0.510	0.344 ± 0.188	54.8	0.00853 - 0.700
	Co	14.5 ± 1.54	10.6	12.1 - 17.0	15.0 ±2.02	13.4	12.1 - 18.9
	Cr	32.8 ± 4.30	13.1	25.1 - 39.1	32.5 ± 8.93	27.5	18.0 - 47.7
	Cu	63.5 ± 8.18	12.9	54.0 - 80.3	65.9 ± 14.5	22.0	42.6 - 93.6
	Mo	1.72 ±0.475	27.6	1.10 - 2.57	1.58 ± 0.598	37.7	0.707 - 2.77
	Ni	18.8 ± 1.99	10.6	16.3 - 21.3	19.6 ±4.43	22.6	11.9 - 27.4
	Pb	14.7 ± 3.37	23.0	9.77 - 20.1	13.4 ± 4.43	33.1	6.96 - 20.6
	V	126 ± 17.4	13.8	103 - 157	133 ± 26.2	19.7	82.5 - 180
	Zn	98 ± 19.7	20.1	73.0 - 131	90.3 ± 22.8	25.2	58.6 - 131

In the present work, despite the reduced number of sites (13), the number of analysis samples (28 soils and 26 sediments) with 0.46 km^2/sample and 3.5 km^2/sample lagoon and wetland sampling density respectively, are considered statistically relevant to obtain LSB and into the range of data number used in previous scientific works (Wei and Wen, 2012; Karim et al., 2015). This has made possible apply different statistics and analysis to obtain a preliminary assessment of the studied area although the incorporation of a higher set of data can improve the pollution time series analysis.

In addition to the local background, several authors provide reference geochemical soil and sediment backgrounds suggesting the applicability of the upper continental crust (UCC) values to obtain pollution indices. Table S9 shows the reference geochemical background (RGB) for the 11 pollutants considered in this study based on UCC values from different authors. (Rudnick and Gao, 2014) propose an estimate for the chemical composition of the upper continental crust, in which the values of the main elements represent averages of the different surface exposure studies.

For both soils and sediments, the range of concentrations of Ba proposed as RGB is above the obtained local statistical baseline. On the contrary, for Cd, Cu, V and Zn (and for Mo in sediments) the range of RGB values is below the LSB range. The RGB and LSB ranges are overlapping for the rest of the elements.

The cumulative frequency method and the reference geochemical background of (Rudnick and Gao, 2014) based on UCC values, will be considered in the present work to obtain pollution indices. Both methods will allow, respectively, on the one hand, a local characterization and monitoring of interest in management programs in the area, and on the other hand, a global comparison of contaminants concentrations with sediment and soil quality backgrounds acknowledged worldwide. In addition to these references, the maximum permissible values (MPV) for soil uses in Ecuador (Ecuador, 2015) and the widely used ERM from (Long et al., 1995) will be used to calculate quotients that allow to quantify in an overall approach the magnitude by which MPV and ERM are exceeded at each soil and sediment sampling site respectively (Table S9).

3.3.- Contamination and ecological risk assessment of potentially toxic elements

3.3.1.-Selection of the reference element

The individual indices $Cf_{i,j}$, $Igeo_{i,j}$ and $EF_{i,j}$ are determined to calculate the degree of contamination of each contaminant at a given site, using the backgrounds RGB and LSB. The determination of $EF_{i,j}$ implies normalization against a conservative reference element. The use of geochemical normalization to obtain enrichment factors (EF) allows to calculate the relative importance of anthropogenic contributions to the sediments and soils being studied (Aloupi and Angelidis, 2001). In the present work, two different criteria are considered for the selection of the reference element:

Variability of reference elements distribution

The variability of reference elements distribution is measured by the robust coefficient of variation, CV^*, as follows:

$$\mathrm{CV}^*(\%) = \frac{\mathrm{MAD}}{\mathrm{Median}}\,100 \qquad \text{Eq. 1}$$

where MAD, or median absolute deviation, is $\mathrm{Median}[|x_i - \mathrm{median}\ (x_i)|]$ that is the median value of the deviations of all individual x_i values (concentrations) from the median value (concentration). This is a robust, nonparametric estimate that it is not affected by the presence of outliers (Reimann and De Caritat, 2005).

In sediments, the CV^* values of the potentially toxic elements are (Table S10) between 7.4 % of Co and 35.7 % of Cd and in soils between 12.1 % of Cu and 34.1 % of As. The CV^* values for Fe are 12.8 % in sediments and 13.6 % in soils. For Mn is 23.6 % in sediments and 24.3 % in soils and for Ti is 27.4 % in sediments and 9.13% in soils. These CV^* values for reference elements (Fe, Mn and Ti) are in the range of CV^* values for potentially toxic elements. However, the CV^* values for Al are 6.75 % in sediments and 1.96 % in soils. These values are lower than the CV^* of the potentially toxic elements and lower than 10% as mean low anthropogenic contributions, thereby Al has less variability and can be considered a conservative element.

Relationship between $Cf_{i,j}$ and $EF_{i,j}$ indices

The main assumption for the application of a geochemical normalization to conservative elements is the existence of a linear relationship between the normalizer and other elements (Sakan et al., 2009); (Aloupi and Angelidis, 2001).

The difference between $Cf_{i,j}$ and $EF_{i,j}$ is the normalization to the reference element (R). Therefore, there should be a linear relationship between both indices, since the reference element must be a conservative element:

$$EF_{i,j} = \frac{Cf_{i,j}}{Cf_{R,j}} = \frac{C_{i,j}/C_{R,j}}{Cb_i/Cb_R} \qquad \text{Eq. 2}$$

In Figure S3, $EF_{i,j}$ is plotted against $Cf_{i,j}$ of all the elements studied using the two geochemical backgrounds (RGB and LSB) and considering Al as conservative element. It is observed that the results fit well to a straight line ($R^2 = 0.991$ for RGB and $R^2 = 0.971$ for LSB in sediments and $R^2 = 0.994$ for RGB and $R^2 = 0.983$ for LSB in soils) with deviations lower than 15 %. The elements Ni, V, Co and Cu show the lowest correlations to Al both in sediments and soils, which may imply an anthropogenic input of these elements (Elkady et al., 2015). When Fe, Mn and Ti are considered as reference elements, much larger deviations (CV in %) and lower values of R^2 are obtained (see Table S11). Consequently, Al is used as a reference element in the calculation of the enrichment factor.

3.3.2.- Sediments and soils contamination assessment based on individual pollution indices

The values $Cf_{i,j}$, $Igeo_{i,j}$ and $EF_{i,j}$ of the studied potentially toxic elements in the sediments and soils of Limoncocha Biological Reserve are presented in Figure S4, using both background values, Reference Geochemical Background (RGB) and Local Statistical Baseline (LSB). Both background references, in accordance with $Cf_{i,j}$, and $EF_{i,j}$, classify all soil and sediment sites except SE6 with some degree of contamination with respect to some of the studied elements. The $Igeo_{i,j}$ values classify sites with the lowest degree of contamination. Cd, Cu, Mo and Zn are the elements on special concern with the highest levels observed for Cd in SE2 using RGB ($Cf_{i,j} = 7.05; Igeo_{i,j} = 2.17; EF_{i,j} = 5.77$).

Using LSB as a background reference, the three individual indicators for all pollutants classify the sediment and soil sites studied in the same way, between “uncontaminated” and “non-enrichment" to "moderate contamination” and “minor enrichment”. $Cf_{i,j}$ and $EF_{i,j}$ determine the same potentially toxic elements as responsible for the categorization of contamination in each site, obtaining however, a very high variability between sediment sites and soil sites of the elements responsible for each classification. Two extreme situations are observed: in SO1 where all the pollutants show values of $Cf_{i,j}$ and $EF_{i,j}$ greater than 1. Contrary, SE6 show $Cf_{i,j}$and $EF_{i,j}$ values less than 1 to all elements. $Igeo_{i,j}$ is the least restrictive indicator, classifying fewer potentially toxic elements as Class 1 “uncontaminated to moderately contaminated” than other individual indicators. Four soil and four sediment sites are classified as Class 0 “uncontaminated”. SO6 due to As, SO1 due to As, Ba, Pb and Mo, SE1 due to As and Cd, SE2 due to As, Cd, Mo, Pb and Zn and SE6 due to Ba and Zn are Class 1 “uncontaminated to moderately contaminated”.

When RGB is used as a reference background (Fig. S4), the three individual indicators classify the studied sediments and soils in the same category. RGB classify in general with one more degree of contamination than using LSB as a background, from "uncontaminated" and "non-enrichment" to "very high contamination" and "moderately severe enrichment". However, the highest contamination or enrichment values correspond to different contaminants. All soil and sediment sites show $Cf_{i,j}$ and $EF_{i,j}$values greater than 1 due to several of the pollutants studied, varying the degree of contamination and enrichment of each other. The highest values of $Cf_{i,j}$ and $EF_{i,j}$ are generally obtained for Cd, that classifies sediments and soils from "very high contamination" and “moderate severely enrichment” to "moderate contamination" and "minor enrichment". Cu, Zn and Mo are responsible of the high values of individual pollution indices in sediments. Igeo follows a behaviour more similar to $Cf_{i,j}$ than to $EF_{i,j}$ in sediments and soils with also fewer elements than other individual indices, classifying the sediment sites from Class 0 "uncontaminated" to Class 3 "moderately contaminated to strongly contaminated". Cd (except in SO2) and Cu in all stations are the primary potentially toxic elements under Igeo.

Generally, the value of $EF_{i,j}$ 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 and Liu, 2002);(Islam et al., 2015). Cd and Cu show EF values > 1.5 in all studied sediment and soils sites when RGB is considered as background. However, the use of LSB background lead $EF_{i,j}$> 1.5 only in SE1 site (due to As and Cd), SE2 site (due to As, Cd, Zn, Pb, Mo), SE6 site (due to Zn and Ba), SO1 site (As, Pb, Mo and Ba) and SO6 site (due to As).

The results of the individual indices $Cf_{i,j}$, $Igeo_{i,j}$ and $EF_{i,j}$ shown that the arrangement of studied potentially toxic elements at the area of Limoncocha Biological Reserve is widely varied and strongly dependent of the considered background. However, results suggested high contamination levels of Cu and Cd in sediment and soil samples using both backgrounds (RGB and LSB). These elements (Cu and Cd) are grouped in PC2 (Tables S7 and S8) suggesting a common origin. In relation to the use of the local background, Ni and Co should be taken into especial consideration in sediments and V, Mo in soils in the studied area. All these elements (Ni, Co, V and Mo) are grouped in PC1 (Tables S7 and S8) suggesting a common origin differentiated from the former.

High concentrations of Cd in agricultural soils of Ecuador have been reported previously due to the anthropogenic activities related mainly to the application of phosphate fertilizers (Chavez et al., 2015)(Chavez et al., 2016). In the same way, Cu is a well-known marker element of agricultural activities, specifically related to application of fertilisers and pesticides (Dai et al., 2019); (Marrugo-Negrete et al., 2017). The use of agrochemicals and the fertilizer practices to improve palm crop yields on the soils of the Limoncocha region (Jarrín et al., 2017) may have contributed to the Cd and Cu contamination. In addition, domestic wastewater from settlements with no sewage infrastructure and aquaculture activities in the LBR area could have been sources of Cd and Cu pollutants in the lagoon. Among other metals, Ni and V have been referenced as indicator of oil spill pollution (Sadeghi et al., 2019); (Pratte et al., 2019); (Ogunlaja et al., 2019). The elevated index obtained for these metals in soil and sediments can be related to the oil field activities on the Limoncocha Biological Reserve.

3.3.3.- Sediments and soils contamination and ecological risk assessment based on integrated indices

The study of individual potentially toxic elements concentrations in sediments and soils, compared to different geochemical background values, is not sufficient to assess the pollution status. The obtained information about pollution status depends mainly on the geochemical background value and on the chosen contamination index (Kowalska et al., 2016); (Saddik et al., 2019). In this study, multi-element indices including, i) the based on the background values, as the degree of contamination (Cd-index), modified degree of contamination (mCd), pollutant load index (PLI) and the Nemerow Pollution Index (NPI), ii) based on the background and reference element values, as the modified Nemerow Pollution Index (mNPI), iii) based on background concentration and toxic response factors, as the potential ecological risk index (RI), are used as integrated indices to assess the degree of contamination and the ecological risk of the studied pollutants at the Limoncocha Biological Reserve. Additionally, mERMq and mMPVq indices obtained without the use of background values, can provided a more proper and accurate description of element pollution in sediments and soils respectively.

Tables S12 and S13 shows the values of the different integrated indices considered in the present study obtained using two different geochemical background (RGB and LSB) at each sampling site. All the obtained integrated indices are higher when RGB is used (Case 1) than when LSB is used (Case 2) except with the PLI index in which PLI2> PL1 in all the soil sites studied. The combination of the mathematical expression (nth root of a product of Cfi,j versus sums or averages of Cfi,j, see Table S2), the concentration values analysed in soils and the background values selected makes PLI2> PLI1 on soils.

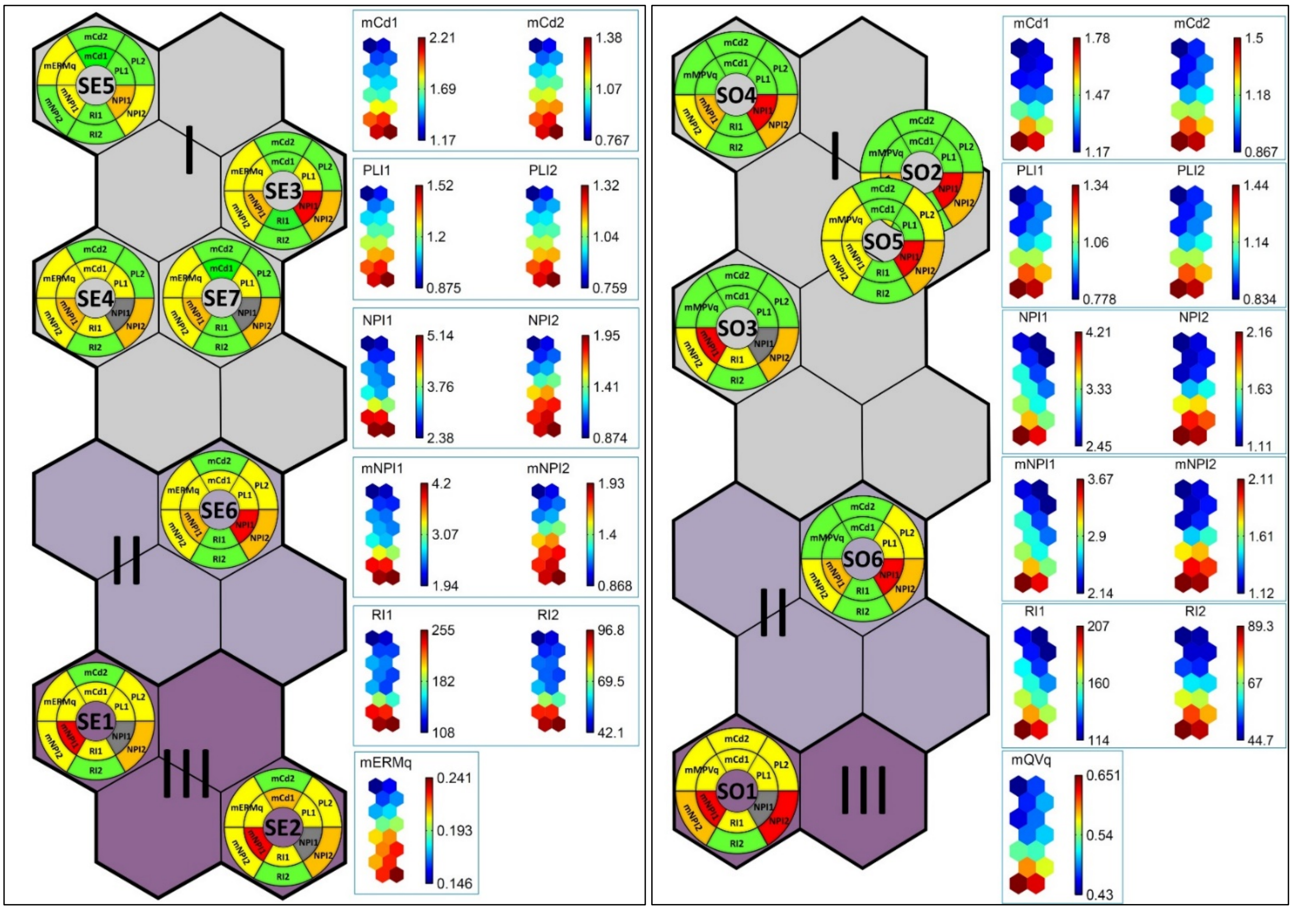
The Self Organizing Maps (SOM) tool is applied to analyse the contamination and ecological risk assessment of potentially toxic elements in sediments and soils using the integrated indices jointly (Fig. 3). Cd-index has not been included in the SOM analysis as it is a linear relation of mCd. The trained map for sediments (Fig. 3a) based onto "range" normalization of data resulted in a 2x8 (16 neurons) map with QE=0.222 and TE=0. K-means clustering method classified the indices into three clusters (clusters I-III). The right side of the Figure 3a shows the component planes of the SOM for the mCd, PLI, NPI, RI and mNPI indices obtained with the RGB and LSB background values as well as mERMq. Each sediment site in its corresponding neuron is surrounded by a double circular crown that indicates the classification provided by each integrated index used (see colour code in Tables S12-13). It is observed that the RGB classifies the stations in a similar way in 32% of the cases, with a higher level of contamination (57% of the cases and especially in SE4) or with two higher levels of contamination (11% of the cases corresponding to the NPI index of SE1, SE2, SE4 and SE7) than the classification using LSB. Cluster I grouped SE3, SE4, SE5 and SE7 sediment sites that showed the lower values of all indices under the two backgrounds used. The SE5 site shows the minimum value of all indices. Cluster II grouped only the SE6 site with intermediate values of all indices. Cluster III grouped SE1 and SE2 sites, showing the latest the highest values of the studied indices and indicating elevated multielement contamination.

The indicators based on backgrounds (Cd-index, mCd, PLI, NPI) and the indicator mNPI based on backgrounds and reference element, classify sediment sites between "moderately polluted" and "heavily polluted" depending on the index and background used. The PLI values are all close to or greater than 1 meaning that pollution exists, except SE5 sediment site with values of 0.64 and 0.74 that is significantly less polluted. The index mNPI that includes the Al as reference element classify the sediment sites in a lower pollution class than the NPI index and in a similar way that other index as Cd-index that use only the background value (Table S12).

All the sediment sites have an index of $RI < 150$ using LSB background, indicating a low ecological risk. Contrary, SE1, SE2 and SE4 sites are classified as moderate potential risk sites using RGB background. The monomial ecological risk factor Eji indicated that the severity of pollution of the studied potentially toxic elements decreases in the following sequence considering both backgrounds: $Cd >> Cu > As > Pb > Ni \approx Zn > Cr$, highlighting the risk posed to the ecosystem mainly by Cd and Cu, and by Cr in a minor extent. RI index, that take into account the toxicity of elements in assessing the risk, mainly matches with the background-based mCd and PLI indices; this coincidence is greater when using the LSB background.

The mERMq value is used to judge the potential biological effects of the composite potentially toxic elements As, Cd, Cr, Cu, Ni, Pb and Zn on sediments, through calculating the mean quotient of each element (MacDonald et al., 2000). According to the classification established for mERMq, all the samples have an index between 0.13 and 0.25 being in the lower part of the range ($0.1 < mERMq \leq 0.5$) that classifies them as "medium-low priority risk level". The highest values are obtained in SE1, SE2 and SE6 sites. All studied elements are below the individual ERM value. The ecological risk decreases in the following sequence Ni > Cu ≈ Zn >> Cr > Pb ≈ As ≈ Cd as common behaviour in all sediment sites. This leads to a sediment risk assessment of high risk level for Ni and Cu. mERMq classification agrees with PLI (9 cases), mNPI (7 cases) and mCd (5 cases) classification. This agreement is higher in sediment sites SE1 and SE2 with the highest pollution (Table S12).

The classifications of sediment sites, both based on the use of integrated indicators through SOM analysis and the groupings based on the content of potentially toxic elements through HCA, offer complementary results (Fig. 2 and Fig. 3a). SE1, next to the pier of the Limoncocha lagoon, and SE2, located at the central area of the lagoon, are the most polluted sediment sites, grouped in cluster III of the SOM analysis and showing high values of the elements of PC2. Cu and Cd from aquaculture activities and domestic wastewater could be responsible of this grouping. These sites are classified as moderate to high degree of contamination showing a moderate potential ecological risk. Special attention should be taken to the center of the lagoon that collects all the pollution contributions of the area through runoff. SE4 and SE7 are the mouth and head of the Pishira river respectively, showing low to slight degree of contamination and low to moderate ecological risk, with the main influence of the potentially toxic elements of PC2. The mouth of the Playayacu river (SE3), is classified in the same SOM cluster I than SE4 and SE7. The head of Playayacu river (SE6), is grouped in the SOM cluster II of integrated indices showing slightly values of elements (Fig. 3a) due to the Principal Component 1 (PC1). This sediment site is classified as medium-low priority probably due to the human activities around the Center Production Facility (Fig. 1). SE5 site in the Northern zone of the lagoon with difficult access, shows low degree of contamination and low potential ecological risk. SE5 is grouped in Cluster I of SOM analysis and shows low values of PC1 and PC2 potentially toxic elements.



a) Sediments **b) Soils**

Figure 3. Clustered map with labels added to the hexagons of the map that indicate the BMU corresponding to each site, a) sediment (SE) and b) Soil (SO). Concentric ring chart in each hexagon represent the site classification obtained using both of the backgrounds (RGB and LSB) according to the colour criteria defined in Tables S12-S13. Component planes of the SOM for the 11 input indices are showed. Each map corresponding to one variable (pollutant index) should be compared to the clustered map representing the distribution of the sediment and soil sites. The colours indicate the value of the component in the weight vector of each unit of the map according to the colour bars on the right.

In the same way that sediment, the SOM tool is applied to analyse the contamination and ecological risk assessment of potentially toxic elements in soil using the integrated indices jointly. The trained map (Fig. 3b) based onto "range" normalization of data resulted in a 2x7 (14 neurons) map with QE=0.274 and TE=0. K-means clustering method classified the indices into three clusters (clusters I-III). The right side of the Figure 3b shows the component planes of the SOM for the mCd, PLI, NPI, RI and mNPI obtained with the RGB and LSB background values as well as mMPVq. It is observed that the use of RGB background classifies the soil sites in a similar way in 55% of the cases, with a higher level of contamination (38% of the cases) or with two higher levels of contamination (7% of the cases related to the NPI and mNPI indices of SO3) than the classification using LSB. Integrated indices classify the contamination degree and the potential ecological risk of soils more uniformly than sediments. Cluster I grouped SO2, SO3, SO4 and SO5 soil sites that showed low values of all indices under the two backgrounds used. The SO4 site shows the minimum value of all indices. SO3 site shows moderate values of NPI1, mNPI1 and RI1 indices. The SO2 and SO5 sites that exhibit similar values of the indices are assigned to the same neuron. Cluster II grouped only the SO6 site with intermediate values of all indices. Cluster III grouped SO1 site showing the highest values of the studied indices and indicating elevated multielement contamination.

The indicators based on backgrounds (Cd-index, mCd, PLI, NPI) and the indicator mNPI based on backgrounds and reference element, classify soil sites between "slight and moderately" for SO2, SO4, SO5 and SO6 sites and "moderately-heavily polluted" for SO1 and SO3 depending on the index and background used. The PLI values are all close to or greater than 1 meaning that pollution exists, except SO4 soil site with values of 0.69 and 0.74 that is significantly less polluted.

The index mNPI that includes the Al as normalization element classify the soil sites in a lower pollution class than the NPI index and in a similar way that other index as Cd-index that use only the background value (Table S12).

All the soil sites have an index of RI < 150 indicating a low ecological risk except SO1 and SO3 that shows moderate potential risk using RGB. The monomial ecological risk factor Eji indicated that the severity of pollution of the studied potentially toxic elements decreases in the following sequence: Cd >>> Cu > As ≈ Pb ≈ Ni ≈ Zn > Cr considering both of the backgrounds (RGB and LSB), highlighting the risk posed by Cd and Cu to the ecosystem. RI index that take into account the toxicity of metals in assessing the risk, mainly matches with the background-based mCd and PL indices

A complementary approach including Ecuadorian standard soil criteria (Ecuador, 2015) should be considered to provide a more accurate and comprehensive assessment of the risk from potentially toxic elements to the soil. All the soil samples have a mMPVq index between 0.4 and 0.7 but Cu in SO1, SO4 and SO5 as well as Ba in SO1 show enrichment as their values are higher than their individual limits ($MPV_{i,j}>1$). The Vanadium element shows $MPV_{i,j}$ values around the unit (1.002 – 1.06) in all soils sites except in the less contaminated soil SO4. There are no classification criteria for sites j based on the mMPVqj indicator. If $mMPVqj> 1$ the maximum legal limits for land uses in Ecuador are exceeded. However, in the present work a three-level classification of the mMPVqj indicator is proposed, which would give how far are the results from both the soil quality limits and the soil use limits of the studied sites. Taking into account the legal limits of soil quality in Ecuador (Soil Quality Threshold, SQT) and the maximum values allowed for different land uses (MPV) in Ecuador (Table S9), the mean of the individual SQT/MPV ratios for the studied potentially toxic elements is 0.52. Thus $mQVqj\leq0.52$ would indicate good soil quality and all soil uses allowed, if $1<mMPVqj<0.52$ it would indicate that all soil uses allowed but poor soil quality. If $mMPVqj>1$ it would indicate that poor soil quality and the maximum permissible values of Ecuadorian soil uses are exceeded (Table S13). The sites SO1 and SO5 with values in the range $1<mMPVqj<0.52$ are of special concern in terms of quality and land uses.

SO1, old well site, shows the highest degree of pollution with high PC1 and PC2 potentially toxic elements contribution, grouped in SOM cluster III and classified as “moderate to heavy pollution” and showing “low to moderate” potential ecological risk. This site is characterized by a high human activity related to aquaculture exploitation and a high degree of urbanization. SO6 is grouped in SOM cluster II, classified from very low (mCd and PLI indices) to heavy degree (NPI and mNPI indices) of contamination with low potential ecological risk. This soil site shows high values of elements of Principal Component 1 (PC1). SO4, SO2, SO5 and SO3 soil sites located on the same bank of the lagoon are grouped in SOM cluster I. All these soil sites show similar classifications that vary according to the index and the background used for its calculation. Despite this, the classification is always from very low (mCd and PLI indices) to heavy degree (NPI and mNPI indices) of contamination, with low potential ecological risk (except RI1 index in SO3 that

4.- Conclusions

In this work, levels and spatial distribution of As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn, in sediments and soils of the Limoncocha Biological Reserve (LBR), a wetland of International importance, have been determined. The data analysis no exhibit significant variations of potentially toxic elements content in sediments and soils between the dry and wet seasons.

Local geochemical baseline of the studied potentially toxic elements has been estimated by two statistical approaches, obtaining the better performance by the relative cumulative frequency method. The aluminium has been selected as reference element considering both its lower variability of distribution against other potential reference elements and the good linear correlation between Contamination Factor and Enrichment Factor indices when Al is considered. The local geochemical baseline and Al as reference element, have been apply to obtain different pollution indices and potential ecological risk assessment indices.

The results of the individual indices $\mathrm{Cf}_{\mathrm{i,j}}$, $\mathrm{Igeo}_{\mathrm{i,j}}$ and $\mathrm{EF}_{\mathrm{i,j}}$ shown that the arrangement of studied potentially toxic elements at the area of LBR is widely varied and strongly dependent of the considered background. In the same way, the eight integrated indices applied classify sediment and soil sites in different categories depending on the index and background used. However, the groupings based on the content of potentially toxic elements through PCA/HCA, on the individual indices as well as on the integrated indices analysis by SOM methodology show complementary results. Cu and Cd from agricultural activities and domestic wastewater discharges and Ni, Co, V and Mo from oil field activities classify sediments and soils as “moderate contamination and enrichment” with SE1, SE2 sediments and SO1 soil as priority sites. SE1 site, next to the pier of the Limoncocha lagoon, and SE2 site, located at the central area of the lagoon, show moderate potential risk and ERM medium-low priority risk level. The highly anthropized soil site SO1 show low to moderate potential ecological risk being on special concern in terms of quality and land uses.

To the best of our knowledge, there are not previous reports about levels and distribution in sediment and soils of potentially toxic elements in the Limoncocha Biological Reserve. In this sense, the present work can constitute the basis for an assessment and monitoring program of sediments and soils quality in the studied area, providing timely reference information to the stakeholders for the wetland protection and restoration in the context of wider planning and sustainable development of the Reserve. The use of different approaches to establish a geochemical background, as analysis of deep sediment cores, as well as an increasingly number of samples have to be assessed in further campaigns to know the contamination evolution in the area.

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