Geochemical Behaviour of Heavy Metals in the Sondong Region of Bacgiang, Vietnam: A Comprehensive Case Study

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Abstracts: Characterizing geochemistry is crucial for identifying pollutant sources and providing a scientific basis for environmental control and management. This study aimed to determine the geochemistry of stream water and sediment and metal sources for environmental management of the Luc Nam River basin in the Son Dong area, Bac Giang province, Vietnam. The results revealed geochemical background (GB) and minimum anomalies (MA) of Cu, Pb, Zn, Hg, and pH in water and Cd, Hg, and Cu in sediment. The highest anomalies in stream water were pH (4.2), Zn (63.7MA), Cu (5.7MA), Mo (3.7MA), Hg (3.4MA), Sb (2.0MA), Pb (1.2MA) and As (1.6MA). The highest anomalies in sediment were Pb (1.6MA), Cd (1.2MA), Cu (1.1MA), Ni (1.6MA), Hg (1.9MA) and Co (1.1MA). Based on the geochemistry of water and sediment, three zones were characterized: (1) Zone I: a natural source with recognized copper mines (Lang Lan, Giao Liem, An Lap, and Yen Dinh) and possible unrecognized mines; (2) Zone II: natural and anthropogenic sources from exploited mines (i.e. Khuon Muoi, Dong Bua, and Bien Dong) and deposits that have not been exploited (Phu Nhuan and Tan Thanh copper deposits, Lang Vai gold deposit); and (3) Zone III: natural source with possible unrecognized mines. These findings contribute to understanding the behavior of elements in response to governance changes in the environmental composition of water and sediments, which can affect ecosystems and communities beyond just the environmental standards and regulations of the government.

Keywords: Geochemistry, Heavy Metals, Governance, Sediment, Source, Water.

1. INTRODUCTION

Heavy metals are non-essential elements in human, animal, and plant metabolism [1]. Contamination of heavy metals is one of the most challenging environmental issues due to their existence, nonbiodegradability, bioaccumulation and biomagnification, and toxicities to humans and ecosystems [2]. Identifying pollutant sources is crucial for prevention and management [3]. Geochemical background and minimal anomalies provide an important basis for identifying metal sources and ensuring sustainable environmental management [4-6]. Understanding the geochemical behavior of heavy metals is particularly important in agricultural areas due to its implications for crop development and food safety [7]. Furthermore, the geochemical background is the primary basis for environmental monitoring [8] that offers insights into natural processes (eg mineralization, geological formations, and related changes) and anthropogenic impacts [9]. Stream water and sediment geochemistry are effective tools for identifying the origins of contaminants [10-13]. Of particular concern, pollutants that can disperse heavy metals into tributaries and main rivers from high-elevation areas highlight an urgent need for sustainable management of river basins [4].

The Luc Nam River basin in Son Dong area (Bac Giang) is a crucial water resource for the socioeconomic development of Son Dong district and neighboring areas. The quality in the basin is influenced by various factors including i) Natural processes (e.g., soil formation, leaching and deposition of geological formations, especially mineral deposits, landscape geochemistry); ii) anthropogenic activities, particularly mining, industrial zones, and agriculture. Exploration and exploration of copper, coal, and gold mines may release heavy metals into the surrounding environment. Consequently, the water environment is significantly and comprehensively affected by these processes and factors. Characterizing the geochemistry of water and sediments in the basin in different environments provides information to identify potential pollution sources and environmental changes in the Luc Nam River basin. Reports on the environmental impacts of copper mining activities in the Son Dong area highlight the importance of source identification and environmental management based on geochemical characterization. For example, the surface water of the Cam Dan River at Khe Kinh was polluted with Fe, COD; the wastewater flotation tank exceeds the allowed standards (QCVV40:20/BTNMT - Colum B) for Cu, Mn (baotainguyenmoitruong.vn; Thanhnien.net). Additionally, both natural geological formations (rocks, soils, and mineral deposits) and anthropogenic activities (anomalies related to recognized or unrecognized ore) can directly impact the basin. Understanding the interactions among environmental components (water, sediment, soil, rocks, ores, and weathering crust) through stream water and veins is crucial for clarifying the natural and/or anthropogenic sources and composition changes in the Luc Nam River basin. Furthermore, controlling, monitoring, or assessing environmental impacts based on geochemical background will provide more appropriate, long-term, and spatial information for socio-economic development. Elements without standards can also be monitored for changes in background concentrations during long-term monitoring. For example, before mining activities, the concentrations of certain elements may be higher than the allowable threshold due to the natural conditions of the area (geochemical background).

This study aims to (1) characterize the geochemistry of stream water and sediment and (2) identify sources of heavy metals for environmental management in the Son Dong area, Bac Giang Province, Vietnam. The use of geochemical background in this context identifies elemental anomalies potentially related to mineralization while characterizing the natural geological environment of the study area, independently of the ore formation process or the impact of technical operations. Therefore, the geochemical background is significant in defining the sources of pollution, including sources from hidden ore mineralization. The change in initial properties will be assessed based on the background content, compared to the geochemical anomaly thresholds, serving as a basis for long-term monitoring, socio-economic development planning, and sustainable management of the Luc Nam River basin.

2. MATERIEL AND METHODS

2.1. Description of the study area

The study area is located in Son Dong district, Bac Giang province, Vietnam. Son Dong is a highland district, located 80 km northeast of the provincial center, with a natural area of 860.56 km2 (accounting for 22% of the whole province). It borders the Loc Binh and Dinh Lap districts of Lang Son Province to the north; Ba Che district, Ha Long City, and Uong Bi City of Quang Ninh Province to the east and the south; and Luc Nam and Luc Ngan districts of Bac Giang province to the west.

The district is rich in mineral resources, including copper ore in the Giao Liem and Cam Dan communes (Khuon Muoi and Dong Bua copper mines; Lang Lan deposit: Cu = 0,9-3,56%) [14]; tin ore in Van Son commune and Dong Ri coal mine with reserves of approximately 100 million tons, which supplies coal for the Son Dong Thermal Power Plant with a capacity of 220MW. However, the exploitation and production activities of these resources are also sources of elemental anomalies, potentially causing changes in the water environment of the Luc Nam River basin and leading to pollution. Additionally, nearby copper minerals such as the Dien Dong copper mine (Cu =1.18%; Zn = 3%; Pb = 0.3%, Cd = 0.1%; Ag = 0.01%; Mn = 0.3%; Co = 0.3%; Mo = 0.3%), Phu Nhuan, Tan Thanh copper deposits (Cu = 0,2%), Lang Vai gold deposit in Luc Ngan district [14] can also affect the Luc Nam River basin in Son Dong.

Many high-level stream systems and water exposure points on both sides of the Cam Dan tributary and the Luc Nam River can leach and dissolve the minerals mentioned above and disperse metals into the environment. Undiscovered hidden mineralization in the area could also impact these flows.

2.2. Water, Sediment and ore sampling

Water samples were collected along the stream and the water outcrops (13) and tributary of the Luc Nam River (2) to determine the composition of elements related to the water exchange process with natural geological formations, including mineral deposits. A higher density of sampling sites in streams compared to the tributaries was designed to characterize natural geochemistry in the study area. A total of 15 sediment samples were collected at the water sampling points. The results demonstrated three anomalies of Zn and Sb, two anomalies of Cu and Cd, and one anomaly each of As, Pb, Ni, Sr, and Mo (Table 1). Metal anomalies were often found near the copper mines (Khuon Muoi, Dong Bua, Bien Dong, Lang Lan, and Tan Thanh) and the Lang Vai gold deposit.

An ore sample was also collected by homogeneously mixing 15 subsamples to interpret heavy metal sources. Sample collection was carried out at the end of the dry season in May 2023. The samples were collected according to the Vietnam Geochemistry Standard [15]. Sediment samples were dried at 40 °C, ground into fine powder, and digested according to EPA Method 200.8 [16].

2.3. Sample Analysis

The pH values of water were measured at 59 points in the study area during the field survey using portable equipment (Hanna HI9813-61, Romania). Heavy metal concentrations in water and soils were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, PlasmaQuant MS, Analytik Jena, Germany). The analysis was performed at the Institute for Nuclear Science and Technology. The detectable limits of Cr, Co, Ni, Cu, Zn, As, Sr, Mo, Cd, Sb, and Pb were 1.25, 0.02, 0.16, 0.22, 1.02, 0.33, 0.02, 0.01, 0.01, 0.09, and 0.04 µg/L, respectively.

Internal standards, duplicate analyses, and certified reference materials (CRM016-50G, Sigma-Aldrich) were utilized for quality control of analysis.

2.4. Calculation of Geochemical Parameters

Geochemical background (GB) was calculated as follows [17]:

$$GB = Median \pm 2MAD \quad (1)$$

The method used to process geochemical data in this study includes the Median ± 2MAD method and geometric statistics (Boxplot) to establish geochemical background content and minimum anomalies and the median to assess anomaly contrasts. The Median ± 2MAD method is a statistical approach used to identify geochemical anomalies. 'Median' is a term coined from 'mean' and 'median,' while '2MAD' stands for two times the Median Absolute Deviation, a measure of variability in a dataset. Boxplots, on the other hand, offer a graphical representation of the distribution of data based on a five-number summary (minimum, first quartile (Q1), median, third quartile (Q3), and maximum). They help visualize the central tendency, dispersion, and skewness of the data, aiding in the identification of outliers.

The minimum anomaly (MA) or upper inner fence was calculated using the following equation [17]:

$$MA = Q3 + 1.5\ IQR \quad (2)$$

where Q3 represents the upper hinge of the data set, IQR is the interquartile range (i.e., Q3–Q1 (75th–25th percentile).

The anomaly contrast (CMA) was calculated by the ratio of the metal anomaly concentration to the minimum anomaly (MA).

3. RESULTS AND DISCUSSIONS

3.1. Geochemistry of Stream Water and Sediments

The geochemical background value (GB) of pH water was 7.8, indicating a weak alkaline environment. The GB values of heavy metals (µg/L) of water within the study area were as follows: Cr (3.992), Co (0.309), Ni (2.323), Cu (0772), Zn (0.123), As (1.495), Sr (125.6), Mo (0.325), Cd (0.269), Sb (0.692) and Pb (0.932) (Table 1). The GB values of Cr, Ni, Cu, As, Cd, Sb, and Pb in water were lower than the allowable limits for surface water in Vietnam [18] (Table 1).

Anomalies of heavy metals in water were found: Zn (3), Sb (3), Cu (2), Cd (2), Ni (1) As (1), Sr (1), Mo (1), and Pb (1) (Table 1). These anomalies in water were possibly due to the impacts of mineral ores containing high concentrations of heavy metals such as Cu (1.6%), Zn (1.62%), Pb (2.25%), Mo (0.727%), Sb (886,45 mg/kg), Mn (0.124%) and Li (819.756 mg/kg). Arsenic can be released from sulfide minerals due to the similar chemistry of As and sulphur [19].

MA (+) values (µg/L) were Cr (6.227), Co (0.902), Ni (3.107), Cu (1.645), Zn (0.153), As (2.302), Sr (191.8), Mo (0.514), Cd (0.292), Sb (0.776), and Pb (2.437). Variation values > 100% of Cu, Zn, Sr, and Mo demonstrated the highly uneven distribution of these metals in water in the study area.

The concentrations of heavy metals in stream water were correlated with those of tributary water ($r = 0.57$, $p < 0.05$), showing the elements that are positively correlated with each other include Cu, Cd, As, and Pb. pH has a negative or very weak correlation with this association but showed a positive correlation with Mo (Table 2). This result highlights the importance of understanding the geochemical behavior of elements and managing pollution sources to reduce environmental and health impacts in downstream areas.

Table 1. Geochemistry of the stream water in Son Dong area (µg/L)

Geochemical parameters	pH	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sb	Pb	Hg
GB	7.8	3.992	0.309	2.323	0.772	0.123	1.495	125.6	0.325	0.269	0.692	0.932	0.081
Max	8.1	4.832	0.760	3.469	9.396	9.766	3.645	329.1	1.903	0.606	1.575	2.908	0.400
Min	4.2	0.624	0.097	0.518	0.109	-	0.166	4.34	0.080	0.249	0.480	0.292	0.038
Median	7.2	2.257	0.182	1.508	0.330	0.103	0.837	52.3	0.169	0.258	0.580	0.505	0.054
Mean	6.99	2.267	0.315	1.559	1.238	1.442	1.059	68.8	0.291	0.287	0.709	0.961	0.085
S	0,6796	1.374	0.232	0.766	2.346	3.329	0.822	82.16	0.456	0.090	0.312	0.818	0.093
V (%)	9,7159	60.6	73.7	49.1	190	231	77.6	119	157	31.5	44.1	85.1	109.496
MA(+)	8,18	6.227	0.902	3.107	1.645	0.153	2.302	191.8	0.514	0.292	0.776	2.437	0.116
MA(-)	5,98												
Number of anomalies	3	0	0	1	2	3	1	1	1	2	3	1	2
C_{MAmax}	1.4			1.1	5.7	63.7	1.6	1.7	3.7	2.1	2.0	1.2	3.4
QCVN08: 2023/BTNMT	6.5-8.5 (A) 6. 0-8.5 (B)	50		100	100	500	10			5	20	20	0,001
													0,001

Note: C_{MAmax} – maximum anomaly contrast level

The GB values of the heavy metals were as follows (mg/kg): Cr (0.119), Co (0.015), Ni (0.061), Cu (0.047), Zn (0.176), As (0.011), Sr (0.052), Mo (0.004), Cd (0.016), Sb (0.097) and Pb (0.032) (Table 3). The variation (V) values of heavy metals were lower than 100%, indicating that the content of these elements in samples is quite uniform. The MA values were Cr (0.140), Co (0.019), Ni (0.097), Zn (0.261), As (0.035), Sr (0.063), Mo (0.005), Cd (0.029), Sb (0.159), Hg (0.00016) and Pb (0.041) (Table 3). Heavy metal anomalies were also found in the study area. Specifically, we found two anomalies of Pb in Tay Yen Tu (0.066) and Van Son – Son Dong (0.046), one anomaly of Cu (0.065 in Giao Liem – Son Dong), Cd (0.034 in Tay Yen Tu), Co (0.022 in Tay Yen Tu), and Ni (0.151 in Giao Liem), and three anomalies of Hg (0.00031 in An Lac, 0.000164 in Yen Dinh, 0.000195 in Duong Huu). As is rich in mud at small springs in Tuan Dao (S8: 0.0262 to B2003: 0.0292)

Heavy metal concentrations in stream sediments were correlated with those in tributary sediments ($r = 0.49$, $p < 0.05$), reflecting the importance of the geochemical behavior of elements. Elements that are positively correlated with each other include Cr-Pb-Mo-As-Sb; Pb-Mo-As-Sb-Cd; Cr-Ni; Cr-Zn; Hg has a negative or very weak correlation with these element associations; Zn weakly correlates with Pb. Cu is negatively correlated with Pb, Sb, and Cd (Table 4). During the formation of endogenous sulfide ore, Zn can be closely correlated with Pb, but in the epigenesis process, they exhibit opposite behaviors.

3.2. Anomaly Zoning and Metal Sources

Three main zones were identified based on the geochemistry of water and sediments, geomorphological and geological characteristics of the basin, and natural factors (mineral deposits, mining activities, factories, etc.) in the study area: (1) Zone I (natural source with recognised and possible unrecognized mines): This zone includes copper mines on the left side of the Cam Dan tributary, such as Lang Lan, Giao Liem, An Lap, and Yen Dinh; (2) Zone II (natural and anthropogeni sources): This zone is around the Cam Dan tributary and is characterised by exploited mines (e.g., Khuon Muoi, Dong Bua, and Bien Dong) and unexploited mines such as Phu Nhuan and Tan Thanh copper mines and Lang Vai gold mine; and (3) Zone III (natural source with possible unrecognised mines in Tuan Dao): This zone includes areas with no mining activities nor recognized mines. Outside of these three zones, there are very few elemental geochemical anomalies. This is typical for geochemical background areas (outside Zones I, II, III) of elements such as Cu, Pb, Zn, Mo, Co, Ni and Cd, except for areas near coal mines, which are not enough representative samples).

Zone I (natural source with recognised and possible unrecognized mines):

This zone is located on the mountain slope flowing into the Cam Dan tributary. It is characterised by lower pH values than those in other zones (< 6.6, except W2), with an anomalous pH of 4.94 (W26) (Figure 1). These pH environmental characteristics are consistent with the possibility of mineralization, leaching, and dissolution of sulphide by water. pH shows a negative or very weak correlation with the complex of symbiotic elements Cu-Cd-As-Pb (Table 2), indicating appearance of anomalies of Cu, Pb, As in stream waters in Zone I is related to mineral deposits. On the contrary, the pH values of the streams on the opposite mountain slope (An Lap) were > 7, which may not be related to natural sulphide mineralisation. The weak alkali (pH = 8.1) is possibly due to anthropogenic activities or mineralisation of molybdenum (pH is correlated with Mo, Table 2).

Anomalies of Cu, Mo, Sb, As, and Sr in stream water were found in the Lang Lan copper mine and Pb in Yen Dinh. Cu (0.065µg/L, sample S1) in sediment in sediment were found in Giao Liem. All these locations are on the left side of the Cam Dan tributary. With the pH of the water in Zone I being weakly acidic, many metal elements are highly mobile and can decrease their depositional ability in sediment, especially Zn, Cu, As, and Pb. Therefore, Zone I rarely has these metal anomalies in sediments (Figure 1). The distribution characteristics of elements in stream water and sediment in this zone (Figure 2b) mostly have a linear relationship, except for Zn; which is quite similar to the area representing geochemical background areas (Figure 2a).

Zone II (natural and anthropogenic sources):

This zone is characterised by currently exploited copper mines on the right of the Cam Dan tributary and unexploited copper mines in zone I. High-level springs and groundwater can affect the ore and transport elements to the Cam Dan tributary. Two Cu anomalies were identified in Yen Dinh (9.396 µg/L, sample W17) located downstream of the Cam Dan River, which is affected by the copper and gold deposit. The second Cu anomaly (2.572 µg/L, W1) was located near the Khuon Muoi copper mine and the Lang Lan copper deposit (Figure 1). A Zn anomaly was found downstream of the Cam Dan River (9.766 µg/L, W17) with a very high anomaly contrast (CMAmax = 63.7, Table 1), possibly due to the oxidation, leaching, and dissolution of natural ores in zones I and II and intensified by mining activities in zone II. The results also demonstrated three anomalies (µg/L) of Sb (1.575, W1; 1.248, W17 and 0.967, W16), and one anomaly each (µg/L) of As (3.645, W1), Ni (3.469, W1), Mo (1.903, W1) Sr (329.06, W1), and Cd (0.332, W17). Furthermore, high contrast anomalies of Zn, Cu, and Mo were found, implying the possibility of unrecognized deposits in this zone.

Table 2. Correlation between metal concentrations in stream and tributary water (n=12)

	pH	*Cr*	*Co*	*Ni*	*Cu*	*As*	*Sr*	*Mo*	*Cd*	*Sb*	*Pb*
pH	1										
Cr	-0.15	1									
Co	0.03	-0.19	1								
Ni	0.16	**0.64**	0.11	1							
Cu	-0.25	**-0.43**	0.52	0.31	1						
As	-0.01	**-0.80**	0.12	0.12	**0.72**	1					
Sr	**0.62**	0.69	-0.04	0.83	-0.10	-0.09	1				
Mo	**0.68**	0.26	0.03	0.67	0.09	0.24	**0.83**	1			
Cd	-0.36	-0.24	0.53	-0.14	**0.49**	**0.51**	-0.43	-0.40	1		
Sb	**0.63**	-0.30	0.09	0.07	0.36	**0.42**	0.23	**0.66**	0.09	1	
Pb	0.10	**-0.47**	0.31	0.01	**0.58**	**0.75**	-0.16	0.12	**0.46**	0.26	1

Table 3. Geochemistry of stream sediments in the Son Dong area (mg/kg)

Geochemical parameters	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sb	Pb	Hg
GB	**0.119**	0.015	0.061	0.047	0.176	0.011	0.052	0.004	0.016	0.097	0.032	0.00014
Max	0.120	0.022	**0.151**	0.065	0.227	0.029	0.060	0.005	0.033	0.103	0.066	0.00031
Min	0.039	0.003	0.007	0.004	0.079	0.004	0.025	0.001	0.007	0.029	0.016	0.00007
Median	0.087	0.010	0.030	0.026	0.117	0.006	0.036	0.002	0.010	0.056	0.026	0.00011
Mean	0.084	0.010	0.041	0.026	0.138	0.012	0.039	0.002	0.014	0.062	0.030	0.00012
S	0.025	0.005	0.039	0.018	0.045	0.009	0.011	0.001	0.008	0.027	0.013	0.00006
V (%)	29.72	47.89	96.43	69.82	32.64	73.38	28.44	61.03	54.82	43.00	41.76	49.37
MA	0.140	0.019	0.097	0.059	0.261	0.035	0.063	0.005	0.029	0.157	0.041	0.00016
Number of anomalies	0	1	1	1	0	0	0	0	1	0	2	3
C_{MAmax}		1.1	1.6	1.1					1.2		1.6	1.9

Table 4. Correlation between metal concentrations in stream sediments and tributary sediments (n=16)

	Cr	Co	Ni	Cu	Zn	As	Sr	Mo	Cd	Sb	Hg	Pb
Cr	1											
Co	0.11	1										
Ni	0.51	0.41	1									
Cu	0.02	0.24	0.33	1								
Zn	0.56	0.34	0.27	0.29	1							
As	0.45	-0.02	0.28	-0.27	0.35	1						
Sr	0.31	0.53	0.00	0.22	0.34	-0.31	1					
Mo	0.48	-0.05	0.12	-0.29	0.01	0.73	-0.18	1				
Cd	0.39	-0.11	-0.35	-0.46	0.23	0.43	0.30	0.51	1			
Sb	0.20	-0.09	-0.30	-0.50	-0.10	0.34	0.14	0.63	0.58	1		
Hg	-0.19	-0.37	-0.35	0.08	-0.25	-0.32	-0.25	-0.23	-0.19	-0.41	1	
Pb	0.48	0.00	-0.09	-0.41	0.37	0.76	0.10	0.67	0.74	0.73	-0.48	1

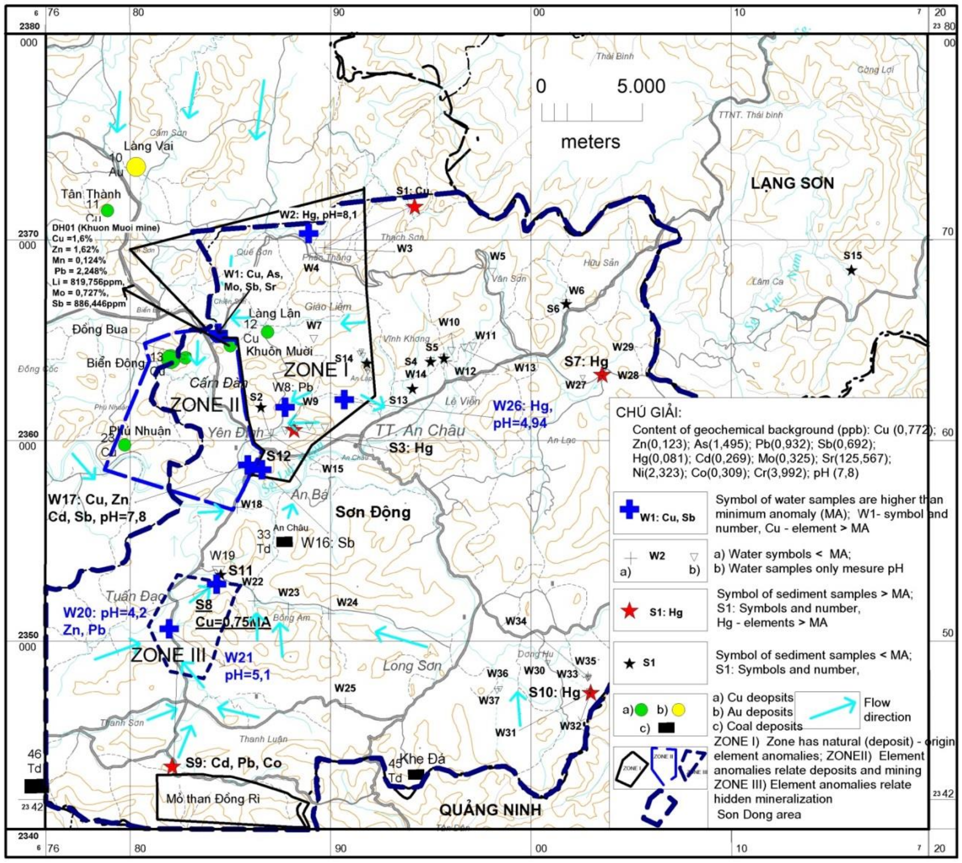

Figure 1. Anomaly origin - zoning of Son Dong (Bac Giang) based on geochemistry of water and sediments.

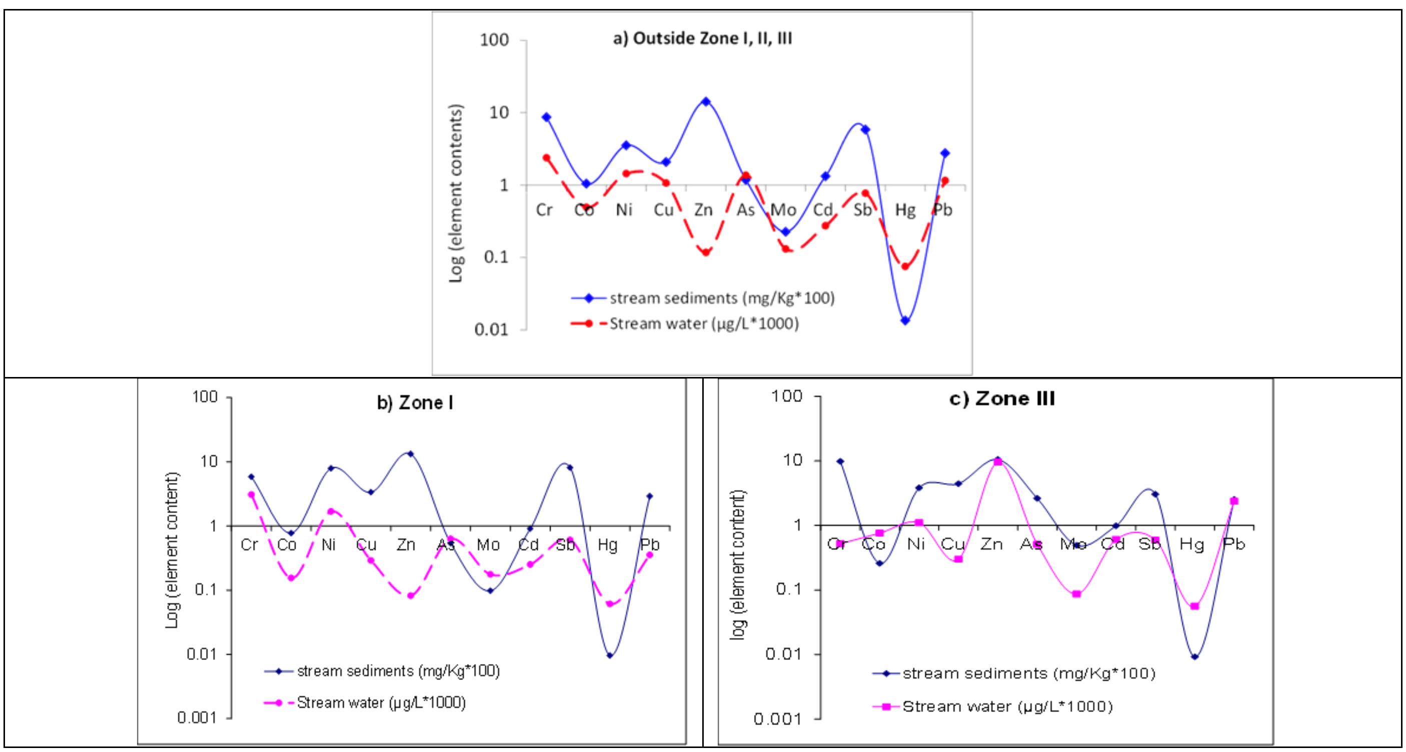

Figure 2. a), b), c) Characteristics of the distribution of elemental content in stream water and stream sediment in regions of the Luc Nam River basin in Son Dong (Bac Giang).

The anomalous water point in the Cam Dan River (W17) was possibly due to impacts from copper deposits (that is, Khuon Muoi, Dong Bua, Bien Dong, Phu Nhuan, Lang Lan, and the Tan Thanh) and Lang Vai gold deposit, which then flowed into the Luc Nam River in Yen Dinh. The anomalies in the streams flowing into the Cam Dan tributary were also related to copper mines that have been exploited for many years (temporarily stopped until 2022) and some of the unexploited mines. On the contrary, the concentrations of Cu, Zn, Mo, Sb, Pb, and Cd at the sampling point in the stream (W16) were much lower than those at the anomalous point in the Cam Dan River (W17). Additionally, the pH of the water at the W16 point dropped to a neutral level (pH=7.1). It should be noted that the sampling point (W16) was in a stream flowing from low mountain slopes without mining activity, and no signs of mineralization have been detected (Figure 1). However, W17 was characterized by an alkaline geochemical environment (pH = 7.8) along with very high anomalies of Zn and Cu, but a negative correlation between pH and Cu-Cd-As-Pb (Table 2) in the entire Luc Nam River basin (mutational impacts related to mineral exploitation and human activities were excluded when calculating the correlation), indicating the potential impact of anthropogenic activities. Mining may induce the leaching of heavy metals into the environment. Agricultural activities were also possibly another source of metal contamination in the study area using pesticides and preservation chemicals, but this impact is minimal. The sampling process selected locations in streams less affected by agricultural activities and separated samples (most samples were taken in acacia and regenerated forest areas, avoiding lychee cultivation areas and short-day plants). In addition, many pesticides containing Hg, Pb, Cd, Se, etc. have been banned in Vietnam (Decision No. 23/BVTV-KHKT/QD dated January 20, 1992, of the Ministry of Agriculture and Food Industry).

According to Kierczak and Pietranik [20], the mobility of elements in stream sediments associated with mine waste drainage flows decreases in the following order: Pb>Cu>Zn>As; the mobility of metals is inversely proportional to sediment contamination, except for Zn, which depends on the characteristics of the waste. This shows that the mining process and mineral processing technology will affect the behavior of the elements, or the level of correlation mentioned above. Along with the weak alkaline environment downstream of the Cam Dan River, the possibility of deposition of Cu, Pb, Zn, and Sb in stream sediments may increase.

Zone III (natural source with possible unrecognized mines):

This zone is characterised by the absence of mining activities, mainly consisting of acacia forests and coal-bearing sedimentary formation. The sampling point W20 in a small spring in Tuan Dao commune revealed the anomaly of pH (4.2), Cu (9.396 µg/L = 5.7MA), Zn (9.51 µg/L = 63.7MA), Pb (2.364 µg/L), and Cd (0.606 µg/L). The relatively strong acidic water (pH = 4.2) can be the result of oxidation and leaching of sulfur minerals, forming acid drainage at the mineralization sites. The Cu and Mo content in stream sediments here also increased, higher than most other locations (only lower than a few points in Zone I). Cu = 0.0443 mg/kg (0.75MA), Mo = 0.00491 mg/kg. The pH, Zn, and Cu anomalies, along with the negative correlation between pH and Cu-Cd-As-Pb (Table 2) in stream water, and the increased content of Cu and Mo in stream sediments, may indicate the possibility of hidden sulfide deposits that have not been recognized in Zone III.

Although heavy metals may be leached from coal-bearing formations in this area, it is difficult to form a very high Zn anomaly in the stream water above. However, in upstream-outside zone III, in Thanh Luan commune (S9), there are anomalies of Cd (0.0329 mg/kg), Pb (0.0656 mg/kg), Co (0.0221 mg/kg) in stream sediments that may be related to the Dong Ri coal mine and coal-bearing sedimentary rock layers containing coal (Figure 1).

The distribution characteristics of elements in the stream water and sediment of Zone III for some elements are different from Zone I and the area representing the geochemical background area (Figure 2a): Zn is positively correlated between the two environments, while Cu and Cr are opposite (Figure 2c). This may be due to the acidic environment and possibly nearby Zn-rich hidden mineralization (sampling sites near mountain slope water outcrops compared to deposit-related stream water samples in Zone I), Zn is strongly enriched in both water and sediment and is less mobile than Cu, which explains the absence of Cu anomalies here.

3.3. Governance of the river basin

The management of the river basin encompasses various issues, including changes in material composition related to the basin in terms of space, time, concentration level, and the origin of these changes. It also considers socioeconomic factors and the basin's ability to affect the ecosystem and community. The effects of material components (elements) are considered not only in terms of allowable content thresholds according to standards (many elements lack standards to determine allowable content thresholds), but also in terms of their actions, bioavailability, and unusual changes in content compared to the general characteristics of a specific ecological region. The best standardization value to apply is the geochemical background, which aims at the generality of the background environment, separates natural geological processes from technical activities that cause anomalies, and considers factors such as the existence form of elements etc.

The results of geochemical characteristics and interpretation of metal sources suggest several solutions for the governance of the Luc Nam River basin in the study area: (1) Using geochemical background and geochemical anomalies as common levels for metal source identification and environmental change management; 2) Planning to monitor environmental changes in the basin according to the space and origin of environmental pollution in the basin; 3) Establishing a database to assess environmental impacts and control them throughout the process of a project/task, as well as according to basin space; 4) Building a basis for assessing the carrying capacity of the basin. The planning process for river basin management and restoration also affects basin governance indicators [4]. The results of this study provide geochemical background data and metal sources for assessing the impacts of planning and further development of Bac Giang province in general and Son Dong district in particular on the Luc Nam River basin.

This result shows the necessity of periodically monitoring changes in the composition of the water environment, river, and stream sediments in the area, including many elements not covered by existing standards. It is essential to quickly measure field parameters such as pH, Eh, TDSat specific locations: Dong Ri coal mine, Khe Da; Cam Dan tributary in the upper and lower reaches and branch streams on both flanks related to copper mineral mines; some small streams in the Tuan Dao - Thanh Son area; and various points on the Luc Nam River (above and below the confluence of the Cam Dan River). Special attention should be paid to geochemical anomalies (Figure 1).

CONCLUSIONS

The Luc Nam River basin in the Son Dong region of Bac Giang province exhibits changes in the composition and geochemical characteristics of the elements, pH due to mineralization, hidden mineralization and mineral exploitation and processing activities (including the temporarily mine closures). Specifically, three zone relate the river basin as follows:

i) Zone I: Located on the left side of the Cam Dan tributary (that is, Lang Lan, Giao Liem, An Lap and Yen Dinh). This zone has a pH of less than 6.6, and is characterised by anomalies of Cu, Zn, Pb, Mo, Sb and As in stream water. The spatial relationships between copper deposits/mines and the correlation between pH and these elements indicate that changes in pH and element content in the surface water and sediment environment are affected by mineralisation (natural sources).

(ii) Zone II: Surrounding the Cam Dan tributary. This zone is characterised by both exploited mines (i.e., Khuon Muoi, Dong Bua, and Bien Dong) and unexploited mines such as the Phu Nhuan and Tan Thanh copper deposits and Lang Vai gold deposit. The pH increases to 7.8, and the anomaly contrast of Zn (63.7MA) and Cu (5.7MA) is very high to high. In addition, there are also anomalies of Sb and Cd, and the pH of the water is favorable for deposition of metals in sediments. These results indicate that changes in the pH and element content in stream water and sediments are influenced by anthropogeni sources. The natural metal sources of Zone I also affected this zone.

(iii) Zone III: Located in Tuan Dao. This zone has very low pH levels and anomalies of Zn and Pb in stream water, Pb in stream sediments, and increased Cu levels. This zone has not exploited mines and is mainly covered by acacia forests. Therefore, hidden mineralisation may exist here, affecting the water and sediment environment.

Based on the geochemical background content, geochemical anomalies of elements in water and sediments in the Luc Nam river basin, as well as the origin of metal dispersion in the above zones, this study will contribute to building a crucial data set for multidimensional environmental monitoring governance of the Luc Nam river basin.

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