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Research Article

Content of heavy metals in soils of Bidoup Nui Ba National Park (Southern Vietnam)

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Abstract

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The study of technogenic pollution of soils with heavy metals (HM) is an essential task for ecology. The analysis of the content of HMs in the park's soils shows the degree of pollution and the sources of its occurrence. The study of the elemental composition of soils is an objective method for assessing the state of the ecosystem. To determine the current state of heavy metal contamination in forest soils, the concentrations of their total forms were analyzed. Heavy metals, including Zn, Pb, Cr, Cu, Hg, Cd, and As, were found in the study area. In addition, the threat of contamination with Cd and As has been identified. The calculation of the total pollution coefficient allows us to assess the level of pollution for the dry season (Zc = 18.45-28.24, average 22.45) as average (moderately hazardous) and for the wet season (Zc = 0.01-5.11, average 1.96) as permissible. This indicates an unfavorable environmental situation. The content of heavy metals in soils depends on the season. Observations show that at the end of the wet season, the concentration of heavy metals decreases, while it increases in the period after the dry season.

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Introduction

Soil serves as the primary sink for heavy metal accumulation in the environment (Qingjie and Jun, 2008; Marchand et al., 2011). The ability to accumulate heavy metals depends on factors such as soil type, physical and chemical properties, and the specific metal involved. Heavy metals are stable and resistant to biodegradation or leaching. Their accumulation disrupts biochemical processes and negatively impact biological activity (Dijkstra, 1998; Hernandez et al., 2003; Kabata-Pendias, 2011; Mmolawa et al., 2011). Heavy metal distribution within the soil profile varies due to pedogenesis, weathering of parent material, and organic matter binding capacity (Karczewska and Kabała, 2002; Zawadzka and Łukowski, 2010). Urban areas are prone to heavy metal pollution, but contamination can also occur through wind transport (Karczewska and Kabała, 2002; Wei and Yang, 2010; Zawadzka and Łukowski, 2010; Yisa et al., 2012). Vertical water movement enriches heavy metals in deeper layers. Protected areas, including national parks, are at risk of activities. contamination from human Soil characteristics and terrain features influence heavy metal distribution. Accumulation of heavy metals reduces soil quality and can lead to soil acidification. Atmospheric pollutants, including heavy metals, can affect forests and soils through long-range transport (De Vries et al., 2002; Staszewski, 2012).

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National Parks are valuable natural and cultural heritage sites, and the presence of heavy metals in these areas causes environmental problems. Monitoring is crucial to assess pollution and soil quality (Sienkiewicz et al., 2012; Gu et al., 2016). However, there are limited studies on forest soil pollution in nature reserves, possibly due to the assumption that these areas are inherently clean. Nevertheless, existing studies demonstrate significant interest in the topic. For example, soil examinations in Cat Tien National Park found As, Pb, Cu, and Zn in all types of native forest soils (Tran and Tran, 1998; Nguyen, 2013, 2015).

Another study in Kon Ka Kinh National Park and Kon Chu Rang Nature Reserve (Gia Lai Province) revealed the presence of heavy metals in forest soils (Nguyen, 2017). Separate studies focused on determining the total content of Mn, Ni, Cr, and Zn in soils in the central part of South Vietnam (Ngo, 1995). Research conducted in Bidoup-Nui Ba National Park explored the diversity of flora and fauna, as well as the concentration of biophilic microelements in the park's soils (Lebedev, 2019). The geochemical composition of soils and the migration of heavy metal elements in the "plant-leaf debris/twig-soil" system were also investigated (Lebedev, 2019, 2021a,b; Pham, 2022).

This study aimed to assess soil pollution levels in Bidoup-Nui Ba National Park according to regulatory documents in Vietnam and the Russian Federation. The results provide insights into the chemical composition of the studied subjects, enabling the assessment of soil contamination by various chemical elements and the identification of their sources.

Materials and Methods

The territory of Bidoup-Nui Ba National Park is located in the province of Lam Dong, in the southern part of Central Vietnam, with a tropical monsoon climate. This study has selected a key forest area (Figure 1) for further studies. The soil cover in this area consists of various subtypes of yellow ferralitic soils.

The rationale for choosing a territory for establishing a landscape-ecological station has been provided in previous works by the authors (Gorbunov, 2018; Kotlov, 2018). The soil cross-sections of the laid-out catena were correlated with elements of the structural-denudational relief - at the ridge top, the slope of the structural ridge, and the slope's foot. One of the cross-sections was situated at the foot of the slope on an island that emerged due to a periodic watercourse. Consequently, it can be classified as part of the structural-fluvial relief. The location of soil profiles is presented in the schematic diagram of genetic landscape types (Figure 2).

Sampling and sample preparation were carried out in accordance with GOST 17.4.4.02-84. Sampling points were positioned considering the wind rose and microrelief features. In compliance with GOST requirements, the upper part of soil horizon A was

sampled to a depth of 15 cm, where the majority of pollutants typically precipitate from the atmosphere. Element and heavy metal determination in the selected soil samples was conducted using a mass spectrometer with inductively coupled plasma (PlasmaQuant MS Elite S-NR:11-6000ST043) at the Scientific and Educational Collaborative Center "Spectrometry and Chromatography" within the Research Center of IBSS.

Concurrently, a blank analysis was conducted, including all determination stages except for sampling (Kuznetsov, 1992). For the analysis, values of several highly toxic elements were used, including Zn, Cr, Cu, Cd, Pb, Hg, and As.

To evaluate the intensity and level of hazard posed by soil contamination with heavy metals in the studied areas, this study calculated:

Coefficient of technogenic concentration of elements (Ks), according to the formula:

$$Ks = Ci / Cf$$

where: Ci is the content of the heavy metal in the sample, mg/kg; Cf is the background concentration of the heavy metal, mg/kg. Reference concentrations of heavy metals were taken as Clarke values for elements in the Earth's crust (according to Vinogradov et al., 1993).

Hazard coefficient Ko is calculated using the following formulas:

$$Ko = Ci / MPC$$

where: Ci is the content of the heavy metal form in the sample, mg/kg; MPC - maximum permissible concentration of a heavy metal form, mg/kg

The total pollution index (Zc), which allows for calculating the geochemical (background) level of pollution and comparing the degree of pollution of the soil cover, can be determined using the following formula:

$$Zc = \sum Kcn - (n-1)$$

where: Zc is the total coefficient of heavy metal contamination in the sample; n is the number of determined elements; Kc represents the concentration coefficients of heavy metals determined in the sample (Bolshakov, 1999).

The existing standards for assessing the accumulation of chemical elements in the soils of Russia are provided in the Decree of the Chief State Sanitary Doctor of the Russian Federation dated January 23, 2006, No. 1 "On the Enactment of Hygienic Standards GN 2.1.7.2041-06". Standards for the content of pollutants in the soils of Vietnam are outlined in the National Technical Regulations on the permissible limits of heavy metals. The comparison between national regulations and Clarke concentrations shown Table 1 demonstrates that the Maximum

Permissible Concentration (MPC) for heavy metals in the soils of Vietnam (MPC VN) significantly exceeds the standards adopted for soils of Russia (MPC RF).

Simultaneously, no MPC for Hg in soils has been established in Vietnam. Therefore, this study used Russian MPC values for Hg.

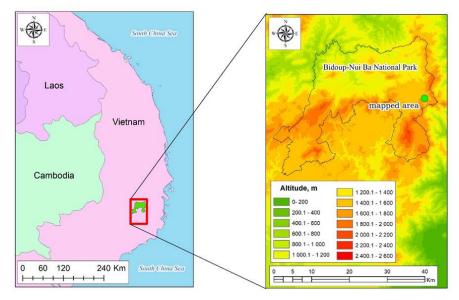


Figure 1. Study area and sampling sites.

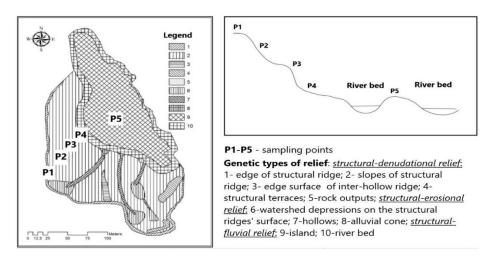


Figure 2. Genetic types of relief: structural denudation relief (Lebedev, 2019).

P1 - Thin, podzolized loamy sandy loess yellow ferralitic soil on kaolinite weathering crust; P2 - Thin, weakly podzolized, medium loamy loess soil on rubble-stony deluvium of dacites; P3 - Thin sandy loam yellow ferralitic soil on rubble-stony deluvium of dacites; P4 - Gleyic light loamy yellow ferralitic soil on the deluvium of the kaolinite weathering crust; P5 - Alluvial-fluvial light loamy soil on sandy and pebble-boulder alluvium of dacites, andesites, tuffs, and sandstones.

Table 1. Standards for the content of heavy metals in soils, in mg/kg (FH 2.1.7.2041-06, FH 2.1.7.12-1-2004, Vinogradov et al., 1993, SanPiN 2.1.7.573-96, 41, QCVN 03, 2008).

Elements	Clark by A.P. Vinogradov et al. (1993)	MPC Vietnam	MPC RF
Cu	47	70	33
Zn	83	200	55
Pb	16	100	32
As	1.7	12	2
Hg	0.083	-	2.1
Cr	83	200	100
Cd	0.13	2	0,5

Results

This study analyzed some chemical indicators that influence the mobility and adsorption capacity of heavy metals in soil. The acidity of the soil solution ranges from acidic to slightly alkaline (pH 4.2-7.8) (Table 2). The acidity of soil solutions decreases from organic to mineral horizons. This is consistent with natural conditions (rainforest) and can be attributed to the acidifying effect of leaf debris. To determine the current state of heavy metal contamination in forest

soils, the concentrations of their total forms were analyzed. All tested samples contained the studied heavy metal elements: Zn, Cr, Cu, Cd, Pb, Hg, and As. The content of the total forms of the studied heavy metals is shown in Table 3. The samples were taken in the dry and wet seasons. The content of heavy elements in soils was analyzed based on seasonal moisture. It is noted that the concentration of the studied elements in the dry season is higher than the values typical for the wet season in most of the considered cases (Figure 3).

Table 2. Actual acidity (pH_{H2O}) of the soil (for the dry season).

Point 1		Point	2	Point	3	Poin	t 4	Point 5		
Horizon	pН	Horizon	pН	Horizon	pН	Horizon	pН	Horizon	pН	
At	4.5	At	4.2	A1	5.6	Ad	6.4	Ad	5.7	
A1	5.1	A1	5.6	AcB	5.7	A	6.8	A1	6.6	
A2	4.9	AcB	6.65	C1	6.2	AB	7.1	B1	7.2	
В	5.8	BC	6.9	C2	6.3	В	7.6	B2	7.5	
C	6.7					Bg	5.8	BC	7.4	
						G	7.5			

This study noted that for a number of elements, the Clarke concentration values, MPC VN, and MPC RF were exceeded for dry or wet seasons, as well as for both seasons combined. Among the elements, cadmium should be highlighted, for which an excess of Clarke values, MPC VN, and MPC RF was observed in both the wet and dry seasons. An analysis of the content of the studied elements in the organogenic soil horizons is provided below.

Arsenic content in soil

The content of As in total forms was investigated in all samples. By the end of the dry season, a concentration range of 2.17-7.48 mg/kg was observed, while by the end of the wet season, the concentration significantly decreased to 0.25-0.51 mg/kg in all studied horizons. The average arsenic content during the dry season was 6.24 mg/kg, characterized by a threefold excess of this indicator relative to the MPC RF (2.0 mg/kg) and no excess of the MPC VN (12 mg/kg). The average arsenic content during the wet season was 0.39 mg/kg, with no excess of the MPC RF or the MPC VN noted.

Cadmium content in soil

The content of Cd in total forms was investigated in all samples, ranging from 0.96 to 3.73 mg/kg by the end of the dry season and from 0.54 to 1.29 mg/kg by the end of the wet season. The MPC VN (2.0 mg/kg) and the MPC RF (0.5 mg/kg) values differ in terms of Cd content in soils. In accordance with the MPC VN values for Cd, an excess was noted during the wet season (Figure 4). Particularly high values of Cd content were observed in riverine areas (points 4, 5). The Cd content exceeded MPC VN in all horizons of points 4 and 5 during the dry season. In accordance with the MPC RF values for Cd, an excess was noted in all the studied soils for both the dry and wet seasons.

Copper content in soil

The content of Cu in the soil was investigated in all samples in its total forms. By the end of the dry season, values were recorded within the range of 17.64-48.96 mg/kg, and from 3.29-7.99 mg/kg by the end of the wet season. The MPC VN (70.0 mg/kg) and the MPC RF (33.0 mg/kg) values for Cu content in soils differ. No exceedances in MPC VN values were recorded. Exceeding the MPC RF values was noted in all studied horizons at the end of the dry season, up to 1.6 times. By the end of the wet season, MPC values were not exceeded.

Lead content in soil

The total forms of Pb content were investigated in all samples, amounting to 3.70-39.13 mg/kg by the end of the dry season and 2.13-23.96 mg/kg by the end of the wet season. The MPC VN (100.0 mg/kg) and the MPC RF (32.0 mg/kg) values for Pb content in soils differ significantly. By the end of the dry season, no exceedance of MPC for Pb was noted for Vietnam; however, an excess of MPC RF was recorded in all studied organogenic horizons at points 4 and 5. Excesses of MPC for both Vietnam and the Russian Federation were not recorded for the wet season of the year.

Zinc content in soil

Zn content in total forms was investigated in all samples. By the end of the dry season, Zn content values were recorded in the range of 4.37-117.71 mg/kg and from 9.03-32.19 mg/kg by the end of the wet season. The MPC VN (200.0 mg/kg) and the MPC RF (55.0 mg/kg) values differ significantly in terms of total forms of Zn content in soils. Exceeding the MPC VN value for Zn was not recorded.

Table 3. The content of heavy metals in the soil of the Bidoup-Nui Ba Park in dry (Ds) and wet (Ws) seasons in total form, mg/kg.

Point	Horizon	A	\s	Cd		C	u	P	0	Zn	1	Н	g	Cr	1
		Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws
	At	1.34	0.34	2.80	0.94	36.97	5.12	10.00	8.01	18.72	29.22	0.35	0.01	7.25	0.15
1	A1	2.18	0.49	1.88	0.81	17.64	3.29	9.32	2.13	4.38	9.03	0.86	0.01	8.86	0.41
	A2	4.00	0.51	1.90	0.74	24.30	3.48	15.34	2.58	7.48	9.15	0.49	0.01	16.56	0.84
	At	3.29	0.28	2.45	1.29	28.39	4.86	8.25	7.37	43.73	27.92	0,.29	0.01	26.16	0.36
2	A1	4.47	0.27	2.56	1.00	21.12	3.46	3.70	2.90	6.94	13.47	0.15	0.01	36.78	0.23
	A_{cB}	4.48	0.31	2.02	1.03	18.96	3.63	8.24	3.23	14.24	32.19	0.37	0.01	60.39	1.98
3	Ad	9.49	0.25	2.29	0.77	30.95	6.00	15.38	7.64	11.34	12.37	0.23	0.08	72.36	1.75
	A_{cB}	9.46	0.41	2.47	0.98	44.28	7.99	23.21	9.55	21.69	14.62	0.22	0.01	146.36	2.70
	Ad	5.03	0.40	2.57	0.62	25.07	6.26	32.77	12.12	117.72	18.07	0.35	0.02	31.65	1.74
4	A	4.58	0.49	2.66	0.54	26.70	6.19	32.96	15.21	66.77	16.30	0.25	0.02	31.83	2.49
	AB	4.55	0.38	2.37	0.58	23.38	3.60	33.61	18.49	64.90	17.99	0.18	0.02	30.59	1.72
5	Ad	5.17	0.48	2.79	0.83	26.67	6.56	39.13	19.60	59.43	18.18	0.47	0.01	29.05	1.32
	A1	4.62	0.49	2.96	0.89	20.72	5.88	34.04	23.96	54.88	22.84	0.17	0.02	28.60	2.36



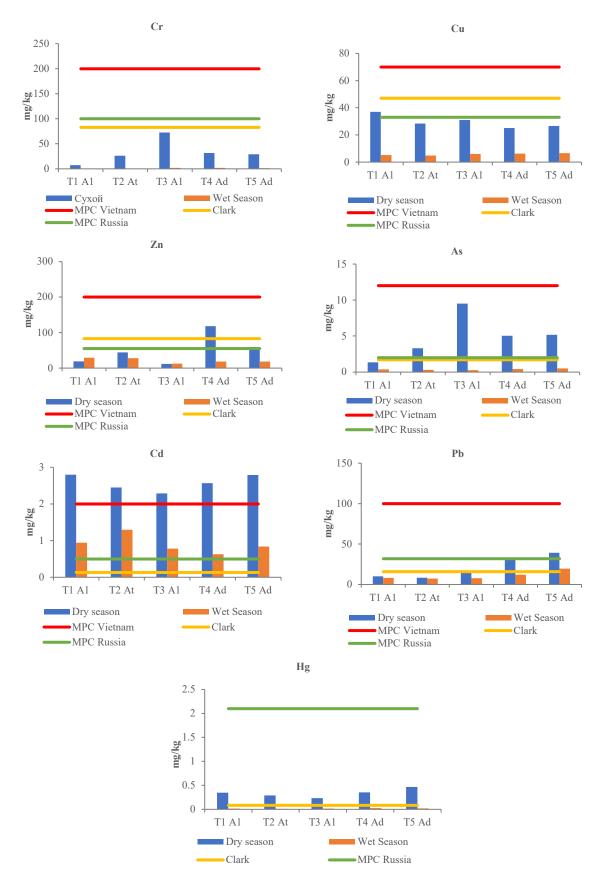
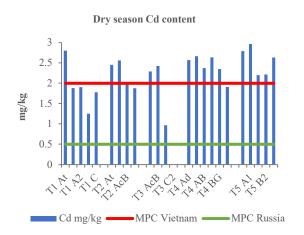


Figure 3. The content of heavy metals in the soil of the Bidoup-Nui Ba National Park compared to the MPC VN, MPC RF, and the Clarke value of concentration.



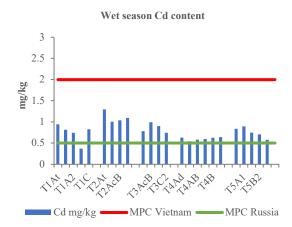


Figure 4. The content of Cd in the soil of Bidoup-Nui Ba National Park compared to the MPC VN and MPC RF values.

For all studied soil horizons at points 4 and 5, as well as organogenic horizons at points 2 and 3, by the end of the dry season, an excess of the MPC RF for total forms of Zn was noted. By the end of the wet season, the excess at point 2 in the organogenic horizon remained, and an excess of Zn content in the organogenic horizon of point 1 was also noted. These were observed at the slope of the automorphic hill and the automorphic hill, respectively.

Mercury content in soil

The content of Hg in total forms was investigated in all samples. Values ranged from 0.14 to 0.86 mg/kg by the end of the dry season and from 0.01 to 0.08 mg/kg by the end of the wet season. Exceeding the MPC RF (2.1 mg/kg) was not recorded in any sample. There is no established MPC VN for Hg in soils.

Chromium content in soil

The content of total forms of Cr was investigated in all samples. The values ranged from 8.85-123.90 mg/kg by the end of the dry season and from 0.15-2.7 mg/kg by the end of the wet season. The MPC VN (200.0 mg/kg) and the MPC RF (100 mg/kg) values differ in terms of chromium content in soils. Exceeding the MPC VN and the MPC RF was not recorded.

The determined content of the studied elements made it possible to calculate the technogenic concentration coefficients (Ks). For background territories, this coefficient does not directly reflect the degree of anthropogenic pollution but indicates a level comparable to anthropogenic pollution. Ks reveals the characteristic accumulation patterns of heavy metals in the park soil (Table 4). The higher the Ks>1, the greater the risk of soil pollution (Zakrutkin and Shishkina, 2011). The studied elements, based on this indicator, are divided into three groups:

In the first group, this study assigned Ks<1, which is typical for dry and wet seasons under the studied landscape conditions: Cu, and also, with

- the assumption Zn and Cr, since a single excess was noted.
- The second group includes Ks>1, which is typical for dry and wet seasons under the studied landscape conditions: Cd. For Cd, an excess was noted in all horizons. In the wet season, Ks reaches values from 9.61 to 28.76, and from 4.16 to 9.96 in the dry season.
- The third group includes Ks>1, which are typical for the dry season for all studied landscape conditions: As, Hg. For As, the excess has a range of 1.28-5.58, and for Hg, 1.81-10.36.

Ks made it possible to identify the elements that accumulate to a greater extent in the studied soils (Ks>1): As, Hg, and in some cases, Pb, Zn, and Cr. In particular, Cd - its Ks were noted for both dry and wet seasons. Table 5 presents the hazard coefficient (Ko). If the calculated Ko of a substance does not exceed 1, then the probability of developing harmful effects in the soil is insignificant, and such an impact is characterized as acceptable. If the Ko exceeds 1, there is a possibility of harmful effects, but it is impossible to specify the exact value of this probability.

It can be observed from the table that by the end of the dry season, Cd has Ko>1 in almost all horizons. Thus, Cd is associated with the potential for harmful effects. By the end of the dry season, the Ko for As at point 3 also has a value close to 1, but does not exceed it. For other elements, the value of Ko is much lower than one. It should be noted that the Ko values according to the MPC RF (Table 6), differ significantly from the MPCVN. Cd has Ko>1 values in all horizons for both dry and wet seasons. As has values of Ko>1 in almost all horizons during the dry season. In the dry season, the value of Ko>1 for Pb and Zn was also recorded in all horizons at points 4 and 5, and at point 3 for Cr. Therefore, there is a risk of Cd and As pollution in the area. It should be noted that weathering processes and volcanism serve as natural sources of Cd for atmospheric transport.

Table 4. Technogenic concentration coefficients (K_s) of heavy metals in dry (Ds) and wet (Ws) seasons.

Point	Horizon	A	\s	C	d	C	Cu	P	b	7	Zn	Н	g	(Cr
		Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws
	At	0.79	0.20	21.54	7.23	0.79	0.11	0.63	0.50	0.23	0.35	4.22	0.12	0.09	0.00
1	A1	1.28	0.29	14.46	6.23	0.38	0.07	0.58	0.13	0.05	0.11	10.36	0.12	0.11	0.00
	A2	2.35	0.30	14.62	5.69	0.52	0.07	0.96	0.16	0.09	0.11	5.90	0.12	0.20	0.01
	At	1.94	0.16	18.85	9.92	0.60	0.10	0.52	0.46	0.53	0.34	3.49	0.12	0.32	0.00
2	A1	2.63	0.16	19.69	7.69	0.45	0.07	0.23	0.18	0.08	0.16	1.81	0.12	0.44	0.00
	A_CB	2.64	0.18	15.54	7.92	0.40	0.08	0.52	0.20	0.17	0.39	4.46	0.12	0.73	0.02
3	Ad	5.58	0.15	17.62	5.92	0.66	0.13	0.96	0.48	0.14	0.15	2.77	0.96	0.87	0.02
	A_CB	5.56	0.24	19.00	7.54	0.94	0.17	1.45	0.60	0.26	0.18	2.65	0.12	1.76	0.03
	Ad	2.96	0.24	19.77	4.77	0.53	0.13	2.05	0.76	1.42	0.22	4.22	0.24	0.38	0.02
4	A	2.69	0.29	20.46	4.15	0.57	0.13	2.06	0.95	0.80	0.20	3.01	0.24	0.38	0.03
	AB	2.68	0.22	18.23	4.46	0.50	0.08	2.10	1.16	0.78	0.22	2.17	0.24	0.37	0.02
5	Ad	3.04	0.28	21.46	6.38	0.57	0.14	2.45	1.23	0.72	0.22	5.66	0.12	0.35	0.02
	A1	2.72	0.29	22.77	6.85	0.44	0.13	2.13	1.50	0.66	0.28	2.04	0.24	0.34	0.03

Table 5. Hazard coefficient (Ko) according to MPC VN for dry (Ds) and wet (Ws) seasons (values not given for Hg).

Point	Horizon	As		Cd		(Cu	F	Pb	Z	n	Cr	
		Ds	Ws										
1	At	0.11	0.03	1.40	0.47	0.53	0.07	0.10	0.08	0.09	0.15	0.04	0,0008
	A1	0.18	0.04	0.94	0.41	0.25	0.05	0.09	0.02	0.02	0.05	0.04	0.002
	A2	0.33	0.04	0.95	0.37	0.35	0.05	0.15	0.03	0.04	0.05	0.08	0.0042
	At	0.27	0.02	1.23	0.65	0.41	0.07	0.08	0.07	0.22	0.14	0.13	0.002
2	A1	0.37	0.02	1.28	0.50	0.30	0.05	0.04	0.03	0.03	0.07	0.18	0.001
	A_CB	0.37	0.03	1.01	0.52	0.27	0.05	0.08	0.03	0.07	0.16	0.30	0.01
3	Ad	0.79	0.03	1.24	0.49	0.63	0.11	0.23	0.10	0.11	0.07	0.73	0.01
	A_CB	0.79	0.02	1.15	0.39	0.44	0.09	0.15	0.08	0.06	0.06	0.36	0.01
	Ad	0.42	0.03	1.29	0.31	0.36	0.09	0.33	0.12	0.59	0.09	0.16	0.01
4	A	0.38	0.04	1.33	0.27	0.38	0.09	0.33	0.15	0.33	0.08	0.16	0.01
	AB	0.38	0.03	1.19	0.29	0.33	0.05	0.34	0.18	0.32	0.09	0.15	0.01
5	Ad	0.43	0.04	1.40	0.42	0.38	0.09	0.39	0.20	0.30	0.09	0.15	0.01
5	A1	0.39	0.04	1.48	0.45	0.30	0.08	0.34	0.24	0.27	0.11	0.14	0.01



Table 6. Hazard coefficient (Ko) based on MPC RF for dry (Ds) and wet (Ws) seasons.

Point	Horizon	A	\s	C	Cd	(Cu	P	P b	7	Zn.	Н	[g		Cr
		Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws	Ds	Ws
	At	0.67	0.17	5.60	1.88	1.12	0.16	0.31	0.25	0.34	0.53	0,.17	0.00	0.07	0.002
1	A 1	1.09	0.25	3.76	1.62	0.53	0.10	0.29	0.07	0.08	0.16	0.41	0.00	0.09	0.004
	A2	2.00	0.26	3.80	1.48	0.74	0.11	0.48	0.08	0.14	0.17	0.23	0.00	0.17	0.01
	At	1.65	0.14	4.90	2.58	0.86	0.15	0.26	0.23	0.80	0.51	0.14	0.00	0.26	0.004
2	A1	2.24	0.14	5.12	2.00	0.64	0.10	0.12	0.09	0.13	0.24	0.07	0.00	0.37	0.002
	A_CB	2.24	0.16	4.04	2.06	0.57	0.11	0.26	0.10	0.26	0.59	0.18	0.00	0.60	0.02
3	Ad	4.75	0.13	4.58	1.54	0.94	0.18	0.48	0.24	0.21	0.22	0.11	0.04	0.72	0.02
	A_CB	4.73	0.21	4.94	1.96	1.34	0.24	0.73	0.30	0.39	0.27	0.10	0.00	1.46	0.03
	Ad	2.52	0.20	5.14	1.24	0.76	0.19	1.02	0.38	2.14	0.33	0.17	0.01	0.32	0.02
4	A	2.29	0.25	5.32	1.08	0.81	0.19	1.03	0.48	1.21	0.30	0.12	0.01	0.32	0.02
	AB	2.28	0.19	4.74	1.16	0.71	0.11	1.05	0.58	1.18	0.33	0.09	0.01	0.31	0.02
5	Ad	2.59	0.24	5.58	1.66	0.81	0.20	1.22	0.61	1.08	0.33	2.46	0.00	0.29	0.01
	A1	2.31	0.25	5.92	1.78	0.63	0.18	1.06	0.75	1.00	0.42	2.20	0.01	0.29	0.02

Table 7. Total pollution index (Zc) for dry (Ds) and wet (Ws) seasons.

Point	T1				T2			3		T4			T5		
Horizon	At	A1	A2	At	A1	AcB	Ad	A ₂ B	Ad	A	AB	Ad	A1	value	
Ws	22.27	21.22	18.64	20.24	19.34	18.45	25.63	22.60	25.33	23.98	20.82	28.24	25.11	22.45	
Ds	2.51	0.96	0.47	5.11	2.39	2.92	2.88	1.81	0.37	0.01	0.40	2.39	3.30	1.96	

Anthropogenic sources of Cd pollution in the biosphere include mining and metallurgy of Zn, electronics and semiconductor industries, paint production, electrical industry, and superphosphate fertilizers (Zakrutkin and Shishkina, 2011). Near the park's border, there are coffee and fruit plantations as well as a fish farm. However, the concentrations are so high that they are comparable to the levels of industrial pollution, which makes it difficult to directly associate them with agriculture.

The entry into organic horizons is possible through translocation transfer from mineral horizons with native leaf debris and twig. This is concerning since point 5 is on a seasonal island in a river that runs through a fish farm. Moreover, a high Ko for Pb and Zn was noted, which is also characteristic of the territory of the seasonal island.

The total pollution index (Zc) reflects the degree of soil contamination with both chemicals and heavy metals (Table 7). This study assessed the degree of soil pollution risk in terms of Zc using an assessment scale based on a generally accepted methodology (Titova et al., 2001). The pollution level at Zc 0-16 is considered low; at Zc = 16-32, it is medium (moderately hazardous); Zc = 32-128 corresponds to a high (dangerous) level; and at Zc>128, it is very high (extremely dangerous) (Titova et al., 2001). The calculation of the Zc allows us to assess the level of pollution for the dry season (Zc = 18.45-28.24, average 22.45) as moderate (moderately hazardous), and for the wet season (Zc = 0.01-5.11, average 1.96) as permissible.

Discussion

There are relatively few studies on the content of heavy metals in the soils of reference areas in Vietnam (Nguyen, 2013, 2015a,b, 2017; Lebedev, 2021a,b; Do, 2022; Pham, 2022). However, these studies do not take seasonality into account, and there is also an emphasis on the technogenic nature of the presence of heavy metals in soils (Nguyen, 2013, 2015a,b, 2017; Do, 2022), which cannot reflect the complete picture due to the lack of research on this issue.

There are several works (Le et al., 2000; Kien et al., 2010; Cao, 2012; Nguyen, 2014, 2018, 2017a,b, 2008; Hoai et al., 2011; Do, 2016; Pham, 2017; Tran, 2018; Vu, 2018) devoted to the issue of heavy metal content in agricultural soils. Nguyen (2013, 2015a,b, 2017) and Do (2022) studied the issue of heavy metal content in the soils of reference areas; however, the conclusions suggest that the increased content of heavy metals in soils is associated with anthropogenic pollution. Nevertheless, this study has not found sources of pollution that could contribute to the accumulation and explain the significant content of heavy metals in the soils of reference areas. This study compared the obtained results with the literature data for each element studied.

Comparison of the obtained results with previously published works shows that the excess of

As content in the soils of the Bidoup-Nui Ba National Park, with the MPC RF values noted by us for the dry season, is significantly lower than in the soils of the Kon Chu Rang National Park, formed on basalts (2.01-22.53 mg/kg) and in the Kon Ka Kinh National Park (17.64-18.83 mg/kg) (Do, 2022). In the protected areas of Dong Nai province, the values of As content varies from 20.4 mg/kg for red-yellow soils formed on shale to its absence (detection threshold <0.1 mg/kg) (Do, 2022). For Bidoup-Nui Ba National Park, As levels of 5.86 mg/kg to no As have previously been reported (detection threshold <0.12 mg/kg). The content of Cd in the range of 0.15-0.26 mg/kg in the soils of the Bidoup-Nui Ba National Park was established earlier and corresponded to the values found at the end of the wet season and the beginning of the dry season (Do, 2022).

In accordance with the literature data, in the forest soils of Cat Tien National Park formed on basalt deposits, Cu content in the upper soil layer (0-20 cm) reaches 46.9 mg/kg. In the soils of Kon Chu Rang National Park, Cu content varies between 19.12 and 31.58 mg/kg. In Kon Ka Kinh National Park, Cu content reaches 61.0 mg/kg (Nguyen, 2017). According to Le Duc (1998), Cu content in ferralitic soils on limestones can reach 52 mg/kg (Do, 2022). For the soils of Bidoup-Nui Ba National Park, the values of Cu content were noted in the range of 1.05-32.51 mg/kg (Nguyen, 2017). According to the literature data, the content of total forms of Pb in the soils of Bidoup-Nui Ba National Park was noted in the range of 7.18-18.87 mg/kg (Do, 2022).

In the soils of Kon Chu Rang, Kon Ka Kinh, and Cat Tien National Parks for soils formed on metamorphic shales, the values were higher (6.65-21.41 mg/kg) than in soils formed on basalt deposits (3.22-6.30 mg/kg) (Nguyen, According to the literature data, the content of total forms of Zn in the soils of Bidoup-Nui Ba National Park was noted in the range of 9.08-52.05 mg/kg (Nguyen, 2017). The content of Zn in Kon Chu Rang and Kon Ka Kinh parks is in the range of 2.18-154.0 mg/kg. In Cat Tien National Park, the concentration of Zn reached 210 mg/kg, exceeding the MPC VN (200 mg/kg). It was also noted that the average content of Zn in the red ferralitic soil of Vietnam is 107 mg/kg (Lebedev, 2021a). In the central part of Vietnam, the content of Zn in organic horizons (0-20 cm) of ferrallitic soils formed on basalts reaches 81 mg/kg (Tra and Egashira, 2001). For brown ferrallitic soils, Zn content was noted in the range of 179-208 mg/kg (Ngo, 1995).

There have been no studies on the content of Hg in the soils of reference areas. However, no excess of the MPC RF values was noted in any of the studied samples, while the MPC VN for mercury is absent. For the Bidoup-Nui Ba National Park, the content of total forms of Cr was previously noted in the range of 5.65-12.52 mg/kg (Nguyen, 2017). The content of heavy metals in the soils of the Bidoup-Nui Ba

National Park corresponds to the range of their concentrations previously reported by the authors and does not exceed the MPC VN (Ngo, 1995; Nguyen, 2015; Pham 2017). In general, all National parks and reserves in Vietnam are located far from residential areas, industrial zones, etc. Therefore, the sources of heavy metals deposited in the soils of these areas are mainly of natural origin and are associated with weathering processes. The results obtained by us make it possible to judge the values of the content of total forms of As, Cu, Pb, and Zn in the soils of Bidoup-Nui Ba National Park, which are similar to the literature data from Vietnamese studies.

Based on the findings of the present study, it could be inferred that the forest soils of Bidoup-Nui Ba National Park were quite similar to the content of heavy metals in other National Parks of Vietnam. There was a difference in the concentration of heavy metals in surface soil by season: the content of heavy metals in the dry season is higher than the content of heavy metals in the wet season. The lower concentration of heavy metals during the wet season may be attributed to its leaching. During the dry season, heavy metals accumulate in surface soil due to its movement toward the upper layers of the soil. The discarded plastic material, lead chromium batteries, empty paint containers, and colored polythene bags act as significant sources of heavy metals in soil. The effects of rainfall during summer may facilitate the leaching of the soil and contribute to the dilution of soil solution during the wet season.

Moreover, evaporation is more intense in the dry season, thus causing soil solution to be more concentrated in terms of heavy metals in the dry season. The amount of heavy metals in surface soils was maximum during the dry and minimal in the wet season. This might be due to the runoff effect which is capable of removing heavy metals in general from the land. Transport near the forest sites may be one reason, but the concentration is negligible their presence in sites has the potential to increase toxicity in the future owing to more environmental degradation.

In terms of the studies carried out on the calculation of the coefficients: technogenic concentration (Ks), hazard (Ko), and total pollution index (Zc), this study could not find comparable works by other authors on this topic for comparison, making the results unique.

Conclusion

In this study, an assessment was conducted on the content of heavy metals (Zn, Pb, Cr, Cu, Hg, Cd, and As) in soils within the area of Bidoup-Nui Ba National Park in South Vietnam, according to the regulatory documents of Vietnam (MPC VN) and the Russian Federation (MPC RF). In the study area, a widespread excess of the MPC RF for the total forms of metals Cu, Zn, As, Pb, and Cd was observed. Comparing these values with the MPC VN, it was found that only the content of Cd exceeded the MPC. Thus, the content of Cd surpasses the MPC values for both Vietnam and the Russian Federation. According to the MPC RF and the MPC VN, the technogenic concentration coefficient (K_s) was calculated to clarify the features of heavy metal accumulation in the soil of the park, depending on the season of the year. An excess of K_s>1 for the dry and wet seasons in all landscapes for Cd was noted, as well as K_s>1 for the dry season in all landscapes for As and Hg. According to the MPC RF and the MPC VN, the hazard coefficient (K_o) was calculated. The values of K₀ differ in the MPC VN and the MPC RF, and also vary by the seasons of the year. It has been established that Cd has values of K₀>1 in all horizons for the dry and wet seasons according to the MPC RF, and according to the MPC VN only for the dry season. According to the MPC RF, As has values of K₀>1 in almost all horizons during the dry season. In the dry season, the value of K_o>1 for Pb and Zn was also recorded in all horizons at points 4 and 5, as well as for Cr at point 3.

The calculation of the total pollution coefficient made it possible to assess the level of pollution as medium (moderately hazardous) (Z_c = 18.45-28.24, average 22.45) for the dry season and as acceptable $(Z_c = 0.01-5.11, average 1.96)$ for the wet season. Thus, the presence of Cd, As, and Hg in the soil at levels comparable to technological pollution was detected in the Bidoup-Nui Ba Park area. The gross concentration values of heavy metals indicate an unfavorable ecological-geochemical situation on the park territory. However, this study has not identified the sources of technological pollution in the studied area, which suggests a natural origin of the investigated heavy metal concentrations in the soil of Bidoup-Nui Ba Park.

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