Biogeochemical Migration of Some Rare Elements in the “Leaf Debris–Soil” System of the Catenary Landscapes in Tropical Mountainous Forests in Southern Vietnam

Yaroslav Lebedev 1,2,3,4, Anna Drygval 1,2,3,4, Cam Nhunh Pham 1, Roman Gorbunov 1,2,3, Tatiana Gorbunova 1,2,3,4,* , Andrei Kuznetsov 2,3, Svetlana Kuznetsova 2,3, Van Thinh Nguyen 5,6 and Vladimir Tabunshchik 1,4

1 A.O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol 299011, Russia; ya.o.lebedev@yandex.ru (Y.L.); drygval95@mail.ru (A.D.); nhunh5782@gmail.com (C.N.P.); karadag_station@mail.ru (R.G.); tabunshchyk@ya.ru (V.T.)
2 Joint Russian-Vietnamese Tropical Research and Technology Center, Hanoi 110000, Vietnam; forestkuz@mail.ru (A.K.); tropcenterhanoi@mail.ru (S.K.)
3 Severtsov Institute of Ecology and Evolution, Russian Academy of Sciences, Moscow 119071, Russia
4 Institute of Environmental Engineering, Peoples’ Friendship University of Russia Named after Patrice Lumumba, Moscow 117198, Russia
5 Southern Branch of the Joint Vietnam-Russia Tropical Science and Technological Research Center, Ho Chi Minh 700900, Vietnam; thinh39b@gmail.com
* Correspondence: gorbunovatyu@ibss-ras.ru

Abstract: Expeditionary studies of the functioning of landscapes of mid-mountain monsoon (including fog) forests have been being conducted within the landscape and ecological station in the territory of the Bidoup-Nui Ba National Park and the adjacent Hon Giao since 2018 and are currently underway. One of the research objectives is to clarify the biogeochemical migrations of the material composition of soils in the “leaf debris–soil” system. We have consistently studied natural objects for their material composition as well as the intensity and rate of involvement of chemical elements in physicochemical migration processes in the “leaf debris–soil” system. Our findings indicate an active influx of a select group of examined elements (Se, Pd, Ag, Cd, Sn, Bi), particularly Bi, Pd, Se, and Cd, through the leaf debris and the detachment of aboveground plant organs, warranting their integration into organogenic soil horizons. Subsequently, lateral migration (Pd, Cd, Se) ensues. Slope processes within subordinate landscape facets, in addition to soil moisture and aeration processes, contribute to the subsequent redistribution of elemental volumes introduced into organogenic soil horizons.

Keywords: tropical forests; leaf debris and twigs; biogeochemical migration; scattered elements; geochemical catena; Vietnam; Bidoup-Nui Ba National Park

1. Introduction

Tropical rainforests are recognized for their global role as climatic and geochemical stabilizers of the biosphere [1]. Soil geochemical processes are one of the pathways for the mass migration of substances into and their distribution in the “vegetation–detritus–soil” system, with their subsequent release into the atmosphere and surface waters. The characteristics of soil formation are determined by a set of factors that either facilitate or hinder the processes of geochemical migration and redistribution of substances in soils, which creates objective difficulties in establishing cause-and-effect relationships and identifying the dominant factors of soil formation. Numerous studies [1–8] dedicated to the investigation of the individual factors and components of tropical forest nature have not aimed to identify the processes and conditions of substance and energy migration, despite the noted significant rates of their turnover in tropical environments. At the same time, forest landscapes play a special role in the migration processes of chemical elements...
between interacting components of the biosphere, including regulating the geochemical mass flows of certain heavy metals [9,10].

The sustainable functioning and rate of change of biogeoecosystems in mid-mountain forest landscapes depend on numerous interdependent factors. Studying the “leaf debris–soil” system can help evaluate the volumes and migration speeds of the substances involved. The complexity lies in the continual, heterostatic manifestation of geochemical migrations, which are initiated and influenced by multiple interconnected factors. As substances move, natural and/or anthropogenic changes occur in biogeoecosystems, affecting the intensity of the migration-initiating factors.

The individual native factors that initiate substance migration processes are the objects of research that enable the assessment of the temporal state of biogeocenoses. These factors include climatic seasonality, microclimate, soil properties, hydrological regime, landscape conditions, plant community characteristics, anthropogenic impact, and the speed and intensity of their transformation. The intensification of substance migration in the “leaf debris–soil” system may be influenced by biogeochemical fixation, CO$_2$ and energy exchange between biogeocenoses and the atmosphere, the water cycle, soil erosion, and elementary soil processes.

The selective biological uptake of substances by various plant species through soil solutions, followed by the subsequent release of some of these substances in leaf debris and branches, leads to an uneven distribution of chemical elements within the soil profile. This significantly complicates the task of identifying the patterns and features of biogeochemical migrations of these substances. A considerable amount of research has focused on studying biodiversity and the organization of biogeocenoses within mountain landscapes in the study area [1,11–15]. These studies specifically address the facies-determined diversity of tropical mountain biogeocenoses and the reasons for their succession and regression, which are associated with both natural and anthropogenic transformations. Separate studies explore the climatic and microclimatic landscape conditions in tropical mountain biogeocenoses, enabling an assessment of the influence of incoming solar radiation on the intensity of interconnected biological and soil processes [2,16–19]. Numerous investigations have delved into the dependency of sustainable plant community functioning on the physicochemical properties and geochemical characteristics of soils, as well as the integrity of the soil cover, the accumulation of humus, and the migration of soil matter within tropical mountain landscape facies [6,11,20–27]. Some works also examine the impact of anthropogenic influences on tropical mountain biogeocenoses [23,28,29]. Despite revealing the essential aspects of the questions addressed in these studies, they do not allow for the identification of causal relationships and patterns that form during continuous biogeochemical migrations within the “leaf debris–soil” system.

The knowledge gap in the study of the biogeochemical migration of some rare elements in the “leaf debris–soil” system of the catenary landscapes in tropical mountainous forests in southern Vietnam lies in understanding the intricate processes that govern the sustainable functioning and rate of change of biogeoecosystems. The objective of this study is to evaluate the potential volumes and rates of substance migration within this system. This research addresses the complexity of geochemical migrations, which are characterized by their continual manifestation and the heterostatic state of elements involved in these processes.

This study aims to unravel the initiation and flow of migration processes influenced by multiple interconnected factors and their direct relation to geochemical migrations. It acknowledges that as substances migrate, they induce changes in biogeoecosystems, which in turn affect the intensity of the factors initiating substance migration processes. This research seeks to establish the interrelated factors that influence the polycosmic nature of substance and energy migration processes and their transformation under the influence of these processes.

This research focuses on the native factors that initiate substance migration processes, enabling the assessment of the temporal state of biogeocenoses in relation to the contin-
uous process of migration. These factors include climatic seasonality, microclimate, soil properties, hydrological regime, landscape conditions, characteristics of plant communities, anthropogenic impact, and the speed and intensity of the transformation of these factors.

This study also considers how the intensification of substance migration processes in the “leaf debris–soil” system may be influenced by biogeochemical fixation processes, CO₂ and energy exchange, the water cycle, soil erosion, and hypergenesis of mountain rocks, among others.

Furthermore, this research investigates the selective biological uptake of substances by various plant species and the subsequent release of these substances in leaf debris and branches, leading to an uneven distribution of chemical elements within the soil profile. This aspect greatly complicates the task of identifying patterns and features of biogeochemical migrations.

The proposed work is a continuation of comprehensive studies since 2018, aimed at investigating biogeochemical migrations of biophilic chemical elements, including toxic, trace, and rare earth elements, within the unique environment of mid-mountain foggy forests in southern Vietnam. This study analyzes the content of elements in the soils and compares it to their reference values.

2. Materials and Methods

The materials studied (soil, leaf debris, and twig) were sampled at the territory of Bidoup-Nui Ba National Park (Figure 1) during the dry season in the territory of the landscape–ecological station at points located within different catenary landscape facies. Average samples of leaf debris and twigs were collected from stationary leaf debris sites using the quartering method. Samples were then fractionated into leaf debris (leaves) and twigs (branches) for subsequent sample preparation.

![Figure 1. Study area and sampling sites [30].](image)

The soil profiles along the catena were associated with the features of the structural–denudational landscape, including the ridge crest, the structural ridge slope, and the base of the slope. One profile was situated at the base of the slope on an island formed by an intermittent stream, making it part of the structural–fluvial landscape. The positioning of the soil profiles is illustrated in a schematic of the genetic landscape types (Figure 2) [30]. The characterization of the soil sampling sites has the criteria presented in Table 1.
The genetic types of the relief were as follows: (1) crest of structural ridge, (2) slopes of structural ridge, (3) surface of crest of interbasin ridge, (4) structural terraces, and (5) rock outcropping. The genetic types of the structural–erosion relief were as follows: (6) catchment depressions on the surface of structural ridge, (7) hollows, and (8) alluvial cones. The genetic types of the structural–fluvial relief were as follows: (9) island and (10) riverbed.

Under laboratory conditions (in accordance with GOST ISO/IEC 17025-2019) [31], sample preparation was carried out for the further study of the elemental composition of the soil samples, ash from leaf debris, and twigs. Additionally, the physicochemical properties of the materials under investigation, including soil, leaf debris, and twigs, were determined.

Soil and plant samples were dried in a drying cabinet to a constant weight, and sample preparation was carried out according to GOST 17.4.4.02-2017 [32] and according to GOST R 58588-2019 for the selection and preparation of plant samples for agrochemical research and agroecological surveys [33], respectively. The plant samples were further
prepared using the “dry-ashing” method. Therefore, in the present study, the results of all tests are expressed in mg/kg dry weight (d.w.). A technique was used to measure the content of metals in the solid objects using inductively coupled plasma spectrometry in accordance with PND F 16.1.2.3:3.11-98 [34] (which brings it closer to the GOST ISO 22036-2014 soil quality; the definition of trace elements in the soil extracts was conducted using inductively coupled plasma atomic emission spectrometry (ICP-AES)) [32]. The determination of the material composition of the samples under study 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” of IBSS.

Standard deviations (SD) and %CV were calculated. The relationship between the concentrations of elements in the soil and leaf debris was evaluated by means of correlation (Pearson’s r) and linear regression analyses.

The local content of the studied elements in the selected samples was compared with their clarke concentration in the Earth’s crust. This comparison aimed to clarify the processes of the biological absorption and deposition of rare elements by green plants through their aboveground vegetative organs followed by their subsequent release into the biogeochemical cycle through leaf debris and twigs.

3. Results

The ash content of leaf debris allows for the estimation of the volume of matter accumulated by plants, which is involved in migration processes. Previous studies have indicated that the ash content of leaf debris and twigs decreases from automorphic conditions at the top of a ridge to trans-accumulative conditions on the slopes of the ridge. It then increases towards accumulative conditions, reaching its maximum values there. Additionally, the contents of specific rare elements in the genetic horizons of the soils in this study surpassed their clarke concentrations. For instance, the ash content of the leaf debris and twigs increased by 1.5–2 times from the automorphic to accumulative–semihydromorphic conditions and by 2–3 times in the accumulative conditions. From a broad sample of the rare element content in the studied soils, an excess of the clarke concentration was observed for Se, Pd, Ag, Cd, Bi, and Sn [35].

The content of specific rare elements can be directly linked to the geological characteristics of the study area. In the geological base of the landscape–ecological station we considered, the medium–high slope is characterized by a weathering crust. To ascertain the source of entry for this group of rare elements, we conducted an analysis of the volumes of the lateral intrasoil migration of labile forms of these elements, their overall accumulation in the genetic horizons of the studied soils, and the material composition of the leaf debris and the decomposition of aboveground vegetative plant organs at the soil sampling sites.

It should be noted that the content of several of the identified elements (Se, Sn, Bi, and their alkylated forms) significantly surpassed their clarke concentrations [36]. This presents a serious issue of widespread toxic pollution caused by these elements [37], including through freshwater river systems (Cd, Sn, and others) [38].

3.1. Rare Elements in Soils

The comparative analysis of the distribution of rare elements indicated that the contents of Se, Pd, Ag, Cd, Sn, and Bi in all the studied soils significantly exceeded their clarke concentrations (in bulk form). The elements Se, Pd, Cd, Sn, and Bi are of great ecological importance, as they act as markers of toxic pollution in study areas. The content of Ag in the studied soils, in general, did not exceed the clarke concentration of the element in the Earth’s crust [36].

The analysis of the content and vertical distribution of the studied elements allowed us to assess the sources of these elements and their subsequent migration, considering the landscape characteristics identified within the key area of the landscape–ecological station (Figure 1).
The analysis of the Se content revealed the following trends (Figure 3) in the distribution of the soils at the landscape-ecological station. Under the automorphic conditions (point 1), Se exhibited the following two concentration peaks: a decrease from the organogenic horizon, At, and an increase towards the mineral horizon, C. The distribution of labile forms of Se suggests an activation of migration processes from the organogenic horizon to the mineral one. At a depth of 60 cm, it was possible to assess the accessibility of the surveyed soil horizons to the root systems of the majority of the plant species in this area. An assumption can be made about the active transfer of Se from the mineral horizons to organogenic horizons through leaf debris and the decomposition of aboveground vegetative plant organs. Furthermore, the dominant position of the automorphic conditions compared to the subordinate landscape facies suggests the significant importance of the aerial transfer (dispersion) of leaf debris masses towards subordinate landscapes.

Under the trans-accumulative conditions of the gentle slope (point 2), a significant decrease in Se influx into the organogenic horizon, At, was observed, while a high Se content in the BC organo-mineral horizon was retained. The distribution of labile Se forms also indicates the activation of migration processes from the organic horizons to the mineral ones. The decrease in the Se content in the organogenic horizon may be a consequence of
the active removal of leaf debris material to the subordinate landscape facies, but further studies are needed to confirm this. With a depth of 66 cm exposed, it was possible to assess the accessibility of the soil horizons to the root systems of the majority of the plant species in this area. The results obtained also suggest the active transfer of Se from the mineral horizons to the organogenic ones through the leaf debris and twigs of aboveground vegetative plant organs.

In the trans-eluvial conditions of the middle part of the steep slope (point 3) with a shallow occurrence of source rocks, some features of the lateral migration processes for Se were observed. Se exhibited a single concentration peak, increasing towards the C1 mineral horizon. Additionally, the distribution of labile Se forms indicates active migration processes from the organogenic horizon to the mineral one. Similar to the trans-accumulative conditions, the decrease in the Se content in the organogenic horizon may have resulted from the active removal of leaf debris material to the subordinate landscape facies, but further studies are required to confirm this. The thickness of the soil section, reaching up to 140 cm, suggests limited accessibility of the exposed soil horizons to the root systems of the plant species growing there. In general, the obtained results lead to the conclusion that the transfer of Se from the mineral horizons to the organogenic horizons occurred through the accumulation of leaf debris and twigs from the aboveground vegetative organs of plants, facilitated by the relative accessibility of the mineral horizons, including parent rocks, with high Se concentrations. Nevertheless, the significant presence of labile forms of Se in the organogenic horizon indicates active lateral migration.

Under the accumulative conditions at the foot of the slope (point 4), the Se content had two concentration peaks, decreasing from the organogenic horizon, Ad, increasing toward the mineral horizon, B, and then decreasing due to gleying (G). The distribution of labile Se forms indicates the activation of migration processes from the organogenic horizon to the mineral (organo-mineral) horizon with a peak in the A(e)B alluvial horizon. The thickness of the soil section (up to 160 cm) made it possible to judge the limited accessibility of the exposed soil horizons to the root system of the plant species growing here. The revealed values may indicate an active transfer of Se from the mineral horizons to the organogenic horizons through the leaf debris and twigs of the aboveground vegetative organs of plants. The data obtained made it possible to put forward an assumption about the active transfer of Se from the organic–mineral horizons to the organic one through the leaf debris and twigs of the aboveground vegetative organs of plants. A significant content of labile forms of Se in the organic horizons (Ad–A(e)B) indicates its active lateral migration.

In the accumulative–semihydromorphic conditions of the island in the periodic water-course (the island of a bypass channel) (point 5), the Se content, similarly to the trans-eluvial conditions, had certain features of lateral migration. The Se content had one concentration peak with an increase towards the organo-mineral horizons, B2 and BC. The distribution of labile Se forms indicates active migration processes from the organic to the mineral horizons. The exposed thickness (up to 90 cm) made it possible to judge the limited accessibility of all the soil horizons to the root system of the plant species growing there. The results obtained allowed us to conclude that the transfer of Se from the mineral horizons to the organogenic horizons was limited by the falling and decaying of the aboveground vegetative organs of plants due to the relative accessibility of the mineral horizons to the plant root system. The significant content of labile forms of Se in the organic horizons explains its further active lateral migration.

The concentration of total selenium (Se) in all the examined horizons surpassed the clarke concentration of Se in the Earth’s crust by a considerable margin. Specifically, in the organogenic horizons, the excess ranged from 13 to 29 times; in the organo-mineral horizons, it varied from 7 to 30 times; while in the mineral horizons, it reached as much as 30 to 54 times the clarke concentration. The substantial presence of labile Se forms across all the horizons suggests a high degree of migratory activity for this element. For Se, there was a consistent increase in the ratio of labile forms to total forms in the organogenic horizons from automorphic to accumulative landscape conditions from 1:0.2–1:0.4 to 1:0.6–1:0.7.
and from 1:0.15–1:0.25 to 1:0.6–1:0.7 in the mineral horizons. In the semihydromorphic–accumulative conditions, the organogenic horizons and mineral horizons had the opposite ratio, i.e., 1:0.5–1:0.9 and 1:0.2–1:0.3, respectively. Overall, for Se, horizontal migration predominated over lateral migration.

The analysis of the palladium (Pd) content revealed the following trends (Figure 4) in the distribution within the soils of the landscape–ecological station. Under the automorphic conditions (point 1), the Pd content exhibited a single concentration peak, with an increase observed towards the organo-mineral horizon, B. The distribution of labile forms indicates a stable fixation of Pd in bulk forms, with minimal migration processes from the organogenic horizon to the mineral horizon. The exposed thickness (60 cm) allowed us to infer the accessibility of the surveyed soil horizons to the root systems of the majority of the plant species growing there. Nevertheless, there was no recorded evidence of Pd transfer from the mineral horizons to the organogenic ones through the accumulation of the leaf debris and twigs of aboveground vegetative plant organs. However, the predominant prevalence of automorphic conditions over the subordinate landscape facies suggests the potential significance of the aerial transfer (drifting) of leaf debris in the direction of the subordinate landscape facies.

Under the trans-accumulative conditions of the gentle slope (point 2), the palladium (Pd) content in all the examined horizons was relatively low. The distribution of labile forms of Pd suggests active migration processes from the organogenic horizon to the organo-mineral horizon. However, it is worth noting that the content of labile forms of Pd decreased as we approached the organo-mineral horizon. The decrease in the Pd content within the organogenic horizon may be attributed to the potential active removal of leaf debris material to the subordinate landscape facies, though further research is required to confirm this hypothesis. With the soil thickness exposed to a depth of 66 cm, we could infer that the soil horizons were generally accessible to the root systems of the majority of the plant species in this area. The results obtained suggest a transfer of a certain amount of Pd from the mineral horizons to the organogenic horizon through the accumulation of leaf debris and twigs from aboveground vegetative plant organs followed by a reverse migration back into the mineral horizons.

In the trans-eluvial conditions of the middle part of the steep slope (point 3) with shallow parent rocks, both Pd and Se exhibited characteristics of lateral migration. The Pd content had a single concentration peak, increasing towards the mineral horizons, i.e., C1 and, especially, C2. The distribution of labile Pd forms indicates active migration processes from the organogenic horizon to the mineral ones. The Pd content in the organogenic horizon was comparable to that in the organogenic horizons of the landscape facies located above. Thus, it can be assumed that the biological absorption of Pd by plants was limited, but this assumption requires further investigation. Additionally, these values may be a result of the active removal of leaf debris material to the subordinate landscape facies. The soil section’s thickness (up to 140 cm) suggests a limited accessibility of the exposed soil horizons to the root system of the plant species growing there. The overall results allow us to conclude that the transfer of Pd from the mineral horizons to the organogenic ones was limited, primarily occurring through the falling and decaying of aboveground vegetative plant organs due to the relatively high concentrations of Pd in the mineral horizons, including parent rocks. Nonetheless, the significant presence of labile Pd forms in the organogenic horizon indicates active lateral migration. In general, the gradual increase in the content of labile Pd forms in the studied subordinate landscape facies can be attributed to both increased soil moisture and the lateral migration of Pd.
Under the accumulative conditions at the foot of the slope (point 4), the Pd content had two concentration peaks, with a slight decrease from the organogenic horizon, Ad, and an increase towards the mineral horizons, BG, G. The distribution of labile forms of Pd indicates its active migration from the organogenic horizon to the mineral (organogenic-mineral) one, with a peak in the most-watered horizons, i.e., BG, G. The thickness of the soil section (up to 160 cm) made it possible to judge the limited accessibility of the exposed soil horizons to the root system of the majority of plant species growing there. The revealed values may indicate both the active transfer of Pd from the mineral horizons to the organogenic one through the leaf debris and decaying of the aboveground vegetative organs of plants and that it could be a consequence of the active removal of the leaf debris material from the subordinate landscape facies located above. The data obtained make it possible to put forward an assumption about the active transfer of Pd from the organic–mineral horizons...
to the organic one through the leaf debris and death of the aboveground vegetative organs of plants. The significant content of labile forms of Pd in the organic horizons indicates its active lateral migration, which was facilitated, in particular, by an increase in the moisture content in the soil horizons.

In the accumulative–semihydromorphic conditions of the island within the periodic watercourse (the island of a bypass channel) (point 5), the Pd content exhibited certain features of lateral migration, similar to the trans-eluvial conditions. Pd, in its bulk forms, was relatively evenly distributed throughout the entire depth of the studied soil profile. Simultaneously, the distribution of labile forms of Pd indicates active migration processes from the organic to the mineral horizons, with their content naturally increasing from the organic to the mineral horizons as the humidity increased. With the soil thickness exposed up to 90 cm, it was apparent that all the soil horizons had limited accessibility to the root system of the plant species growing there. The results obtained suggest a restricted transfer of Pd from the mineral horizons to the organic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs owing to the relative accessibility of the mineral horizons to the plant root system. However, the volumes of lateral migration were substantial.

The observed correlation between the concentration of labile palladium (Pd) forms and the soil moisture levels may suggest an active subsequent translocation of Pd through the river waters [39]. The concentration of total Pd forms in all the examined horizons significantly surpassed the clarke concentration of Pd in the Earth’s crust. Specifically, in the organogenic horizons, the excess ranged from 15 to 70 times; in the organo-mineral horizons, it varied from 12 to 84 times; while in the mineral horizons, it reached as much as from 25 to 181 times the clarke concentration. Additionally, the concentrations of labile Pd forms in the studied soil horizons appeared to exhibit a direct correlation with the degree of soil moisture. For Pd, there was a consistent increase in the ratio of labile to total forms in the organogenic horizons from automorphic to accumulative landscape conditions from 1:0.03 to 1:0.44 and from 1:0.03 to 1:0.6–1:0.7 in the mineral horizons, indicating the active horizontal and lateral migration and high mobility of the element. In the semihydromorphic–accumulative conditions, the ratio changed from 1:0.2 to 1:0.5–1:0.7 from the organogenic to the mineral horizons as a result of active lateral migration.

The silver (Ag) content data in the soils of the landscape–ecological station were also subjected to analysis for the identification of patterns (Figure 5). Ag, which participates in biogeochemical migration, represents a thermodynamically unstable colloidal silver solution (sol) that can undergo oxidation upon contact with atmospheric oxygen.

Under the automorphic conditions (point 1), silver (Ag) exhibited a distinct concentration peak in the organic horizon, A1, along with a notable presence in the the organic–mineral horizon, B. The distribution of labile Ag forms suggests a stable fixation of Ag in bulk forms from the organic horizon to the mineral horizon, with migration processes remaining inactive. With the soil thickness exposed to a depth of 60 cm, we can infer that the surveyed soil horizons were generally accessible to the root systems of the majority of plant species in this area. However, the transfer of Ag from the mineral to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs cannot be confirmed, or its volumes are negligible. It is possible that migration processes become more pronounced with seasonal increases in soil moisture levels. Additionally, the dominant presence of automorphic conditions relative to the subordinate landscape facies leads us to speculate on the significant importance of the aerial transfer (drifting) of leaf debris in the direction of the subordinate landscape facies.
Figure 5. Distribution of silver (Ag) across the horizons (mg/kg (dw: dry weight)).

Under the trans-accumulative conditions of the gentle slope (point 2), the silver (Ag) content in all the examined horizons was relatively low. The distribution of labile Ag forms suggests a stable fixation of Ag in bulk forms from the organic horizon to the mineral horizon, with migration processes remaining inactive. The results obtained may indicate the potential transfer of some amount of Ag from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs, or they may suggest the active removal of leaf debris material to the subordinate landscape facies. However, further research is needed to confirm these hypotheses. With the soil thickness exposed to a depth of 66 cm, we could assess the accessibility of the soil horizons to the root systems of the majority of the plant species in this area. A consistent trend was observed in the increase in the Ag content in the organic horizons within the subordinate landscape facies relative to the automorphic conditions.
In the trans-eluvial conditions of the middle part of the steep slope (point 3) with occurrences of shallow source rock, certain features of lateral migration were observed for silver (Ag). In terms of bulk forms, the Ag content exhibited two concentration peaks: a decrease from the organogenic horizon, Ad, and an increase towards the C1 mineral horizon. The distribution of labile Ag forms suggests conducive conditions for the formation of water-soluble forms and the activation of migration processes from the organogenic horizon to the mineral horizons. The Ag content in the organogenic horizon exceeded the values found in the organogenic horizons situated above in the landscape facies. These values may be attributed to the active removal of leaf debris from the subordinate landscape facies located above. With the soil thickness extending to a depth of up to 140 cm, it is apparent that the exposed soil horizons offered limited accessibility to the root systems of the plant species growing in this area. The data obtained lead us to conclude that Ag was transferred from the mineral to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs due to the relative accessibility of the mineral horizons, including parent rocks, containing high concentrations of labile Ag forms. The significant presence of labile Ag forms in the AeB organo-mineral horizon may indicate active lateral migration, potentially associated with both an increasing moisture content in the soil horizons with depth and the influx of organic acids during their horizontal and lateral migration. Nevertheless, the precise factors initiating these migration processes are not entirely evident and necessitate further research.

In the accumulative conditions at the foot of the slope (point 4), the silver (Ag) content exhibited a single concentration peak, with a substantial decrease observed from the organogenic horizon, Ad, to the mineral horizons, BG and G. The distribution of labile Ag forms indicates a stable fixation of Ag in bulk forms from the organogenic horizon to the mineral horizon, with migration processes remaining inactive. It is important to note that the increase in the moisture content of the soil horizons did not appear to stimulate the activation of migration processes. The Ag content in the organogenic horizon surpassed the values found in the organogenic horizons located above in the landscape facies. With the soil thickness extending to a depth of up to 160 cm, it is evident that the exposed soil horizons offered limited accessibility to the root systems of the plant species growing in this area.

The results obtained may suggest the active removal of leaf debris from the subordinate landscape facies located above, although this requires further research for confirmation. There was no recorded evidence of Ag transfer from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs. The factors driving the initiation of subsequent migration processes from the organogenic to the mineral horizons are not fully understood and necessitate further research. During this study, indications of periodic flooding of the area by a seasonal stream during the wet season of the year were noted.

In the accumulative–semihydromorphic conditions on the island within the periodic watercourse (specifically, the island within the bypass channel) at point 5, the silver (Ag) content exhibited characteristics similar to those in the accumulative conditions, with some noteworthy features of lateral migration. Notably, Ag in bulk forms presented an uneven distribution throughout the depth of the studied soil profile, with a pronounced concentration in the Ad organogenic horizon, where it reached remarkable values. The distribution of labile Ag forms indicates a stable fixation of Ag in bulk forms from the organogenic horizon to the mineral horizons, and migration processes remained inactive due to the infrequent formation of water-soluble Ag compounds involved in migration processes. An increase in soil moisture levels did not appear to stimulate the activation of migration processes. The Ag content in the organogenic horizon exceeded the values found in the organogenic horizons of the landscape facies located above, with the maximum recorded value being 0.938 g/kg, surpassing the clarke concentration by 13,410 times. With the soil thickness extending to a depth of up to 90 cm, it is evident that all the soil horizons had limited accessibility to the root systems of the plant species growing in this area. The
results obtained suggest a constrained transfer of Ag from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs, primarily due to the relative accessibility of the mineral horizons to the plant root system. Additionally, traces of periodic flooding of the area by a seasonal stream during the wet season of the year were also noted, which may account for the significant concentrations of Ag in the organogenic horizon.

The content of total silver (Ag) forms in all the examined horizons significantly exceeded the Clarke concentration of Ag in the Earth’s crust. Specifically, for the organogenic horizons, the excess ranged from 14 to 13,410 times; for the organo-mineral horizons, it varied from 6 to 159 times; while in the mineral horizons, it ranged from 6 to 71 times. This discrepancy may indicate both gradual lateral migration followed by translocation transport with the river waters and a gradual accumulation in the organic horizons. The conditions and factors responsible for initiating the formation and migration of water-soluble forms (colloidal) of Ag in this context require further study and clarification. For Ag, there was a consistent increase in the ratio of labile forms to total forms in the organogenic horizons from the automorphic to the accumulative landscape conditions from 1:0.015 to 1:0.087% (with a sharp decrease towards the semihydromorphic–accumulative conditions) and from 1:0.038 to 1:0.264 in the mineral horizons, indicating minor horizontal and more significant lateral migration. In the semihydromorphic–accumulative conditions, the pattern persists with an almost complete absence of labile forms in the organogenic horizon.

The study of the cadmium (Cd) content revealed certain distribution trends in the soils of the landscape–ecological station, as shown in Figure 6. Under the automorphic conditions (point 1), the Cd content exhibited two concentration peaks, decreasing from the organogenic horizon, A, and increasing towards the mineral horizon, C. The distribution of labile Cd forms indicates the activation of migration processes from the organogenic horizon to the mineral one. With the soil thickness exposed to a depth of 60 cm, it was possible to assess the accessibility of the surveyed soil horizons to the root systems of the majority of the plant species growing there. It is plausible to assume that Cd was actively transferred from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs. Moreover, the dominant presence of automorphic conditions relative to the subordinate landscape facies suggests the significant importance of the aerial transfer (drifting) of leaf debris mass in the direction of the subordinate landscapes.

Under the trans-accumulative conditions of the gentle slope (point 2), an elevated content of cadmium (Cd) was observed in the organogenic horizons, A and A1, compared to the organo-mineral horizons, AeB and BC. Similarly, the distribution of labile Cd forms in this context also indicates the activation of migration processes from the organogenic horizons to the mineral ones. However, in the A1 and AeB horizons, there was an accumulation of bulk Cd forms. The increased Cd content in the organogenic horizon may be a result of the active removal of leaf debris material from the subordinate landscape facies, but further studies are needed to confirm this. With the soil thickness extending to 66 cm, it was possible to assess the accessibility of the soil horizons to the root systems of the majority of the plant species growing in this area. The results obtained also suggest an active transfer of Cd from the mineral horizons to the organogenic ones through the accumulation of leaf debris and twigs from aboveground vegetative plant organs. There was no clear indication of a dependence of Cd accumulation and migration on the soil moisture regime and the degree of moisture.
In the trans-eluvial conditions of the middle part of the steep slope (point 3) with shallow source rocks, similarities to the lateral migration processes seen in the trans-accumulative conditions were observed for cadmium (Cd). Specifically, in bulk forms, Cd exhibited a concentration peak, with a decrease observed from the organogenic and organo-mineral horizons (Ad and AeB) to the mineral horizon C2. The distribution of labile Cd forms indicates the activation of migration processes from the organogenic horizon to the mineral ones. It is important to note that the content of total Cd forms in the organogenic horizon was lower than that in the organogenic horizons located above the landscape facies. The values observed may be a result of the active removal of leaf debris from the subordinate landscape facies situated above. With the soil thickness extending to 140 cm, it is evident that the exposed soil horizons offered limited accessibility to the root systems of the plant species growing in this area. The data obtained suggest that Cd was transferred from the mineral to the organogenic horizons through the accumulation of...
leaf debris and twigs from aboveground vegetative plant organs, likely due to the relative accessibility of the mineral horizons. It may also be a consequence of the active removal of leaf debris material from the subordinate landscape facies. However, these assumptions require further research. Nevertheless, the factors initiating these migration processes are not entirely evident and warrant additional investigation.

In the accumulative conditions at the foot of the slope (point 4), the cadmium (Cd) content exhibited a single concentration peak, notably decreasing from the organogenic horizon, Ad, to the mineral horizons, BG and G. The distribution of labile forms indicates a gradual activation of migration processes towards the organo-mineral horizons and a subsequent decrease towards the mineral horizons, which may be attributed to the development of the gleying process. However, at this stage, it is not possible to establish a direct link between gleying (or an increase in the soil horizon moisture content) and the activation of migration processes, necessitating further research.

The Cd content in the organic horizon was comparable to that in the automorphic landscape facies located above. These data suggest the possibility of an active transfer of Cd from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs. With the soil thickness extending to 160 cm, it is evident that the exposed soil horizons provided limited accessibility to the root systems of the plant species growing in this area.

The results obtained may indicate the active removal of leaf debris from the subordinate landscape facies located above, but this also requires additional research for confirmation. The significant presence of labile Cd forms in the organo-mineral horizon, B, may suggest the active lateral migration of Cd.

In the accumulative–semihydromorphic conditions of the island within the periodic stream (specifically, the island of the encircling channel) at point 5, the content of cadmium (Cd), similar to that in the accumulative conditions, exhibited some peculiarities related to lateral migration. Specifically, Cd in bulk forms displayed an uneven distribution throughout the depth of the studied soil profile. It predominantly existed in the organogenic horizons, Ad and A, and then its content decreased in the illuvial horizons and rose again towards the mineral horizons. This variation may be related to its presence in soil-forming rocks or accumulation processes. The distribution of labile forms indicates a stable fixation of Cd in bulk forms from the organogenic horizons to the mineral ones and was proportionally correlated with the content in bulk forms. Migration processes were active throughout the entire profile depth. The presence of Cd in high concentrations across the soil profile suggests active input with leaf debris and subsequent lateral migration, likely associated with plant uptake due to established soil-forming factors. An increase in the soil horizon moisture content did not appear to directly affect Cd’s involvement in migration processes. The Cd content in the organogenic horizons exceeded the values found in the organogenic horizons located above the landscape facies, with the highest value recorded here being 2.999 mg/kg. The observed soil thickness (up to 90 cm) indicates the limited accessibility of all the soil horizons to the root systems of the plant species growing in this area, thereby limiting the transfer of Cd from the mineral horizons to the organogenic horizons through leaf debris and twigs from aboveground vegetative plant organs. However, the consistently high concentrations of Cd throughout the considered horizons increase the likelihood of its involvement in the biological cycle. In the accumulative–semihydromorphic conditions of the island, traces of periodic inundation by a seasonal stream during the wet season of the year were also noted, which may have contributed to the significant concentrations of Cd in the organogenic horizons.

The content of Cd in gross forms in all the horizons of the studied soils significantly exceeded the clark concentrations of Cd in the Earth’s crust. For the organogenic horizons, the excess ranged from 14 to 22 times; for the organo-mineral horizon, it ranged from 9 to 20 times; and for the mineral horizon, it ranged from 7 to 20 times. This may indicate a gradual lateral migration of Cd with subsequent translocation with the river waters as well as its input from leaf debris and shedding in the organogenic horizons. However, the
conditions and factors that initiate Cd migration are highly diverse, and we can only note the established distribution of its concentrations within the studied landscape conditions in connection with the aforementioned assumptions. For Cd, there was no strict pattern in the change in the ratio of labile forms to total forms in both the organogenic and the mineral horizons when moving from the automorphic to the accumulative landscape conditions. Against the background of values of 1:0.13–1:0.25 and 1:0.16–1:0.4, respectively, an increase in the ratio can be noted due to horizontal migration into the subordinate horizons, primarily in the mineral horizons. In the semihydromorphic–accumulative conditions, horizontal migration diminished, and the ratio averaged as 1:0.22 for all the studied horizons.

The analysis of the distribution of labile and gross forms of Sn allowed us to refine the trends of their distribution in the soils of the associated landscape facies of the landscape–ecological station (Figure 7). In the automorphic conditions (point 1), the gross forms of Sn had a clear concentration peak in the mineral horizon, C; there was a gradual increase in concentration from the organogenic to the mineral horizon. In contrast, the distribution of labile forms indicates the opposite pattern, namely, a decrease in the content of labile forms of Sn from the organogenic to the mineral horizon. Migration processes, judging by the gradual decrease in the Sn content during lateral migration, were inactive. The revealed thickness (60 cm) allowed us to judge the accessibility of the studied soil horizons to the root system of the vast majority of the plant species growing there. However, the translocation of Sn (as well as the other elements described above) from the mineral horizons to the organogenic horizon through the shedding of aboveground vegetative plant organs was not verified nor insignificant. It is possible that migration processes are triggered by a seasonal increase in soil moisture. In addition, the dominant position of the automorphic conditions in relation to the associated landscape facies suggests the significant role of the aerial transport (drifting) of leaf debris mass towards the associated landscape facies.

In the trans-accumulative conditions of the gentle slope (point 2), the content of Sn in all the researched horizons was higher than in the automorphic conditions. Similarly, there was a gradual increase in the Sn concentration from the organogenic to the mineral horizons. The distribution of labile forms indicates the stable fixation of Sn in gross forms from the organogenic horizon to the mineral horizon, with the peak being in the organo-mineral horizons. Migration processes were inactive. The obtained results suggest the translocation of a negligible amount of Sn from the mineral horizons to the organogenic horizon through the shedding of aboveground vegetative plant organs or the active transport of leaf debris mass to the associated landscape facies; however, this requires additional research. The revealed thickness of the soil profile (66 cm) allowed us to judge the accessibility of the studied horizons to the root system of the vast majority of the plant species growing there. A trend of an increasing total content of Sn in the organogenic horizons was observed, as well as an intensifying lateral migration to the mineral horizons in the associated (in relation to the automorphic) landscape facies.

In the trans-eluvial conditions of the middle part of the steep slope (point 3), there was a change in the trend of accumulation of bulk forms of tin (Sn). The peak of labile forms was found in the organogenic–organo-mineral horizons. The migration activity decreased from the organogenic to the mineral horizons. The content of total forms of Sn in the organogenic horizon exceeded its content in the organogenic horizons of the landscape facies located above, which is a characteristic feature for Sn. The observed values may be a result of the active removal of leaf debris from the subordinate landscape facies situated above or horizontal matter displacement (solifluctional displacement). With the soil thickness extending to 140 cm, it is evident that the exposed soil horizons offered limited accessibility to the root systems of the plant species growing in this area. This limited accessibility may also be influenced by an increase in the moisture content of the soil horizons with depth. The data obtained suggest that Sn can be transferred from the mineral horizons to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs, likely due to the relative accessibility
of the mineral horizons. This may also be a consequence of the active removal of leaf debris material from the subordinate landscape facies. However, the factors initiating these migration processes are not entirely clear and warrant further research.

![Figure 7. Distribution of Sn across the horizons (mg/kg (dw: dry weight)).](image)

In the accumulative conditions at the foot of the slope (point 4), the Sn content exhibited two concentration peaks, namely, in the organogenic horizon, Ad, and the organo-mineral horizon, B, followed by a gradual decrease towards the mineral horizons. The distribution of labile forms indicates a gradual deceleration of migration processes from the organogenic to the mineral horizons, possibly due to the development of gleying. However, it is currently not possible to evaluate the relationship between soil horizon gleying and the slowdown of Sn migration processes; further research is needed.

The Sn content in the organic horizon was higher than in the organic horizon of the automorphic landscape facies, confirming the observed trend. These data suggest the potential for the active transfer of Sn from the mineral to the organogenic horizons through the
accumulation of leaf debris and twigs from aboveground vegetative plant organs, without excluding the possibility of horizontal material removal due to solifluction processes. With the soil section thickness up to 160 cm, it was evident that the exposed soil horizons had limited accessibility to the root systems of the plant species growing there. The obtained results may also imply the active removal of leaf debris from the subordinate landscape facies located above, though further research is required. The significant presence of labile forms of Sn in the organo-mineral horizon, B, may also indicate its active lateral migration.

Under the accumulative–semihydromorphic conditions (point 5), the Sn content, similar to the accumulative conditions, displayed specific features of lateral migration. Specifically, Sn in its bulk forms exhibited an uneven distribution throughout the depth of the studied soil profile, increasing towards the organo-mineral (illuvial) horizon, B, and subsequently decreasing towards the mineral horizons, including those showing signs of gelation. This distribution likely indicates deposition processes during lateral migration. This is supported by the fact that the content of labile Sn forms naturally decreased from the organogenic to the mineral horizons and appeared to be influenced by the moisture content and mechanical composition of the soil. Migration processes are currently inactive, with increased moisture in the soil horizons inhibiting Sn migration, in contrast to organic acids in the organic horizons. The significantly higher Sn content in the organogenic horizon (3.293 mg/kg) compared to the organogenic horizons of the subordinate landscape facies located higher up the slope confirmed this observed trend. The presence of Sn in high concentrations throughout the studied soil profile suggests the possibility of its transfer from the mineral horizons to the organic horizons through the decomposition of aboveground vegetative plant organs followed by lateral migration and inflow into the organic horizons via seasonal stream waters during floods in the humid season of the year. The location of the point excludes the possibility of horizontal material removal due to solifluction processes. With the soil thickness exposed up to 90 cm, it was evident that all the soil horizons had limited accessibility to the root system, and there was a limited transfer of Sn from the mineral to the organogenic horizons through the accumulation of leaf debris and twigs from aboveground vegetative plant organs. Nevertheless, the high concentrations of Sn in all the considered horizons increase the likelihood of its involvement in the biological cycle.

We observed that the content of total Sn forms increased both during lateral migration and during the transition from the automorphic to the accumulative–semihydromorphic conditions. The Sn concentration in the Earth’s crust was exceeded in all horizons of the studied soils developing under accumulative and accumulative–semihydromorphic conditions. The excess was relatively small, with some organic horizons exceeding it by from 1.3 to 1.5 times, the organo-mineral (including illuvial) horizons exceeding it by from 1.9 to 2.0 times, and the mineral horizons exceeding it by from 1.1 to 1.9 times. This suggests the possibility of both a gradual lateral migration of Sn and subsequent translocational transport via river waters, as well as its input from twigs and other sources into the organic horizons. The conditions and factors we have identified as initiating the migration of Sn allow us to conclude that its distribution is currently established in the studied landscape facies without considering the contribution of each of them. For Sn, there was a pattern in the change in the ratio of labile forms to total forms in the organogenic horizons when moving from the automorphic to the accumulative landscape conditions from 1:0.009 to 1:0.06. Lateral migration diminished, and in the mineral horizons, the ratio did not exceed 1:0.06. In the semihydromorphic–accumulative conditions, Sn migration practically ceased.

The analysis of the Bi content revealed the following trends (Figure 8) in the distribution within the soils of the landscape–ecological station. Under the automorphic conditions (point 1), the Bi content exhibited two concentration peaks in bulk forms: a decrease from the organogenic horizon, At, and an increase towards the mineral horizon, C, similar to the distribution of Cd and Se. The distribution of labile forms of Bi indicates the activation of migration processes from the organogenic horizon to the mineral one. With the soil thickness exposed to a depth of 60 cm, it was possible to assess the accessibility of the
surveyed soil horizons to the root system of the vast majority of the plant species growing here. It can be assumed that Bi is actively transported from the mineral horizons to the organogenic horizons through the decomposition of aboveground vegetative plant organs. However, the increase in the concentration of labile Bi forms in the mineral horizons did not allow us to draw an unequivocal conclusion about the role of organic acids in initiating migration processes. The dominant position of the automorphic conditions compared to the subordinate landscape facies suggests the significant importance of the aerial transfer (drifting) of leaf debris mass in the direction of the subordinate landscapes.

Figure 8. Distribution of Bi across the horizons (mg/kg (dw: dry weight)).

In the trans-accumulative conditions of the gentle slope (point 2), the Bi content in the studied horizons was generally lower than that in the automorphic conditions. Additionally, there was a gradual decrease in the element’s concentration from the organogenic horizon to the mineral horizon. The distribution of labile forms indicates a consistent fixation of Bi in bulk forms, extending from the organogenic horizon to the mineral horizon, with the
concentration peak of labile forms occurring in the mineral horizons. Migration processes exhibited a lateral vector of development. The results obtained suggest the possibility of a limited transfer of Bi from the mineral horizons to the organogenic horizons through the decomposition of leaf debris and twigs from aboveground vegetative plant organs. Alternatively, this could indicate a limited removal of leaf debris material to the subordinate landscape facies. However, further research is necessary to confirm these hypotheses. The observed soil profile thickness (66 cm) allowed for an assessment of the accessibility of the studied horizons to the root system of the majority of the plant species growing in this area. There was a consistent pattern of a decreasing total Bi content in the organic horizons along with a reduction in the volume of lateral migration to the mineral horizons in the subordinate landscape facies compared to the automorphic ones.

In the trans-eluvial conditions of the middle part of the steep slope (point 3), the trend of accumulating bulk forms of Bi continued, with a gradual increase in the element's concentration towards the mineral horizons. In contrast, the peak of labile forms was found in the organic horizons. The migration ability decreased from the organogenic to the mineral horizons. The content of bulk Bi forms in the organogenic horizon was lower than in the organogenic horizons located above the landscape facies of the slope, which is a characteristic feature of Bi in this context. These observed values could be a result of either the inactive removal of leaf debris from the overlying subordinate landscape facies or horizontal matter displacement (solifluctional displacement), or, conversely, they may indicate a generally limited ability of the element to undergo horizontal migration. With the soil section thickness up to 140 cm, it was evident that the exposed soil horizons had limited accessibility to the root system of the plant species growing in this area. The data obtained led to the conclusion that the transfer of Bi from the mineral horizons to the organogenic horizons was limited to occurring through the deposition of leaf debris and twigs of aboveground vegetative plant organs due to the relative accessibility of the mineral horizons. Alternatively, this may suggest the gradual lateral migration of the element during horizontal migration (during the solifluction process). In any case, the reasons for the initiation of migration processes are not entirely clear and require further research.

Under the accumulative conditions at the foot of the slope (point 4), the Sn content exhibited two concentration peaks: one in the organogenic horizon, Ad, and the other in the organo-mineral horizon, B, followed by a gradual decrease towards the mineral horizons. The distribution of labile forms suggests a gradual slowdown in migration processes from the organogenic to the mineral horizons, possibly influenced by the development of the gleying process. However, it is currently not possible to assess the relationship between soil horizon gleying and the deceleration of Sn migration processes at this stage, and further studies are needed. The Sn content in the organic horizon was higher than in the organogenic horizon of the automorphic landscape facies, confirming the observed trend. These findings indicate the potential for the active transfer of Sn from the mineral to the organogenic horizons through the decomposition of leaf debris and twigs from aboveground vegetative plant organs, and they do not rule out the possibility of horizontal matter removal due to solifluction processes. With the soil section thickness up to 160 cm, it was evident that the exposed soil horizons had limited accessibility to the root system of the plant species growing in this area. The results obtained may also suggest the active removal of leaf debris from the subordinate landscape facies located above, but further research is necessary to confirm this hypothesis. The significant presence of labile forms of Sn in the organo-mineral horizon, B, may also indicate the active lateral migration of the element.

Under the accumulative–semihydromorphic conditions (point 5), the Bi content exhibited specific features of lateral migration, resembling both the accumulative and trans-accumulative conditions. Notably, Bi in bulk forms showed a uniform distribution throughout the depth of the studied soil profile, increasing towards the organo-mineral (illuvial) horizon, BC. There were no signs of gelation due to the mechanical composition of the soil, likely due to the presence of a buried gravel–pebble fraction in the preluvium underly-
ing this horizon. This distribution probably indicates deposition processes during lateral migration, as the content of labile Bi forms naturally decreased from the organogenic to the mineral horizons. Migration processes were active, and the rate of element migration appeared to depend on the mechanical composition and periodic moisture levels of the soil. Interestingly, an increase in the soil horizon moisture content tended to inhibit Bi migration, in contrast to the effect of organic acids in the organic horizons. The Bi content in the organogenic horizon was 0.520 mg/kg, and although it did not exceed the content found under the accumulative conditions (0.568 mg/kg), it was higher compared to the organogenic horizons of the slope subordinate landscape facies, confirming the observed trend towards gradual accumulation. The presence of Bi in elevated concentrations throughout the studied soil profile suggests the possibility of its transfer from the mineral horizons to the organogenic horizons through the decomposition of aboveground vegetative plant organs followed by lateral migration. It may also enter the organogenic horizons through the waters of the seasonal stream during floods in the humid season of the year. The location of the point rules out the possibility of horizontal matter removal due to solifluction processes. With the soil thickness exposed to a depth of up to 90 cm, it was evident that all the soil horizons had limited accessibility to the root system, and the transfer of Bi from the mineral to the organogenic horizons through the leaf debris and twigs of aboveground vegetative plant organs was limited. However, the presence of high concentrations of Bi in all the considered horizons increases the likelihood of its involvement in the biological cycle.

The content of total forms of Bi in all the horizons of the studied soils was significantly higher than the clarke concentration of Bi in the Earth’s crust. In the organogenic horizons, the excess ranged from 29 to 60 times; in the organo-mineral horizons, it ranged from 29 to 70 times; and in the mineral horizons, it ranged from 36 to 75 times. This suggests the possibility of a gradual lateral migration of Bi followed by translocation transport with the river waters, as well as its input through twigs and residues into the organic horizons. Nevertheless, the conditions and factors that initiate the migration of Bi are highly diverse, and we can only describe the current distribution of its concentrations within the studied landscape conditions in connection with the assumptions described above. For Bi, there was a pattern in the change of the ratio of labile forms to total forms in both the organogenic and the mineral horizons when moving from the automorphic to the accumulative landscape conditions, i.e., from 1:0.2 to 1:0.5 and from 1:0.02 to 1:1.07, respectively. Moderate horizontal and lateral migrations were noted, with horizontal migration prevailing over lateral. In the semihydromorphic–accumulative conditions, the ratio remained stable.

During this study, several features of the lateral and horizontal distribution of elements in the soil horizons were observed:

The Se content increased in both the organic and mineral horizons and gradually rose from the automorphic to the accumulative landscape facies.

The Pd concentrations were influenced by the geological and hydrological conditions of the area, with the peak Pd concentration being associated with its content in the parent rocks of the region and with active transport via river runoff. The maximum values were noted in the near-channel areas.

The Ag content generally tended to increase from the automorphic to the accumulative conditions, with the concentration peaks observed in the organic horizons.

Cd exhibited lateral migration, as its concentration decreased from the organic to the mineral horizons. The content of Cd decreased when transitioning from the automorphic to the trans-eluvial conditions and increases again in the accumulative conditions. It was also influenced by geological features.

The increased Cd content in the organogenic horizons of the soil profiles suggests its input into the soil, primarily through plant leaf debris, but it could also be associated with horizontal migration in the subordinate landscapes.
The lateral migration of Sn was expressed as an increase in concentration from the organogenic to the organo-mineral horizons, followed by a decrease in the mineral horizons. Horizontal migration had led to a total increase in the Sn concentration from the automorphic to the accumulative–semihydromorphic conditions of the soil formation. Increased moisture, along with reduced acidity and larger solid-phase fractions of soils, presumably reduce Sn’s migratory activity.

The content of Bi indicates inactive migration from the automorphic to the accumulative landscape facies. The total Bi content decreased in the subordinate landscape facies and during lateral migration. However, in the accumulative and accumulative–semihydromorphic conditions, the total Bi content increased, with lateral migration processes gradually fading from the organogenic horizon to the mineral one. Given the periodic flooding in the lowland landscape facies, this may be attributed to the translocation transportation of Bi with the river waters.

3.2. Rare Elements in Leaf Debris and Twigs

Analyzing the material composition of ash (from leaf debris and twigs) in terms of the content of the studied elements in the plant leaf debris allowed us to not only quantify the volumes of the biogeochemical accumulation of these elements by plant vegetative organs, surpassing the Clarke concentration, but also to assess the influence of different landscape settings (facies) on the extent of their biogeochemical accumulation.

Our previous studies have shown that the chemical composition of green plants and plant litter and debris, as well as the ash content values for various landscape environments, may indicate significant differences in the concentration of certain elements depending on their bioavailability and selective (or indiscriminate) absorption by plants. In addition, the rate of release of various chemical elements into organic soil horizons may be related to the soil moisture regime (humidification, in particular) [40].

Under the automorphic conditions, leaf debris and twigs contributed significant amounts of Se, Pd, Cd, and Bi to the soil, exceeding the Clarke concentration for these elements in the Earth’s crust (Figure 9). Ag also originates from plant twigs in the form of branches. The content of Sn in the leaf debris and twigs did not surpass the Clarke concentration. The total content of all the studied elements in the plant twigs from branches exceeded that in the leaf debris. There was a proportional relationship between the content of labile and total forms of Se and Cd in the leaf debris and twigs. However, no proportional relationship existed between the content of labile and bulk forms of Pd, Ag, and Sn in the leaf debris and twigs. The content of labile forms of Bi in the plant leaf debris was several times higher than in the twigs.

![Figure 9. Content of total and labile forms of elements in plant leaf debris (mg/kg (dw: dry weight)).](image-url)

**Figure 9.** Point 1. Content of total and labile forms of elements in plant leaf debris (mg/kg (dw: dry weight)).
Both the leaf debris and twigs contributed the entire range of the studied elements to the organic horizons, with the elements from the leaf debris showing more active migration, especially Bi. The concentrations of the elements in the leaf debris and twigs that actively entered the organogenic horizons significantly exceeded the clarke concentration in the Earth’s crust. For example, the content of the gross form of Se exceeded the clarke concentration in the leaf debris and twigs by 40 and 58 times, respectively. The Pd content exceeded it by 65 and 137 times, the Cd content exceeded it by 29 and 38 times, and the Bi content exceeded it by 27 and 86 times. The content of Sn did not exceed the clarke concentration. In contrast, the content of Ag in the twigs did not exceed the clarke value, whereas in the twigs, it exceeded it by more than four times. In terms of the excess over the clarke concentration, the order of the studied elements (gross form) in the leaf debris was as follows: Pd > Se > Cd > Bi; in the twigs, it was as follows: Pd > Bi > Se > Cd > Ag.

In the trans-accumulative conditions on the gentle slope, the distribution of the content of the studied elements in the leaf debris and twigs exhibited similar features to those observed in the automorphic conditions (Figure 10). However, notable quantitative differences and an excess Ag content in the leaf debris compared to the twigs were observed. All the studied elements entered the organic horizons when plant leaf debris and twigs were present, with only the Sn content in the leaf debris not exceeding the clarke concentration in the Earth’s crust. A conditionally proportional relationship between the content of labile and bulk forms of Se and Cd in the leaf debris and twigs was apparent, but these proportions did not correlate with the content of these elements in the automorphic landscape conditions. There was no proportional relationship between the content of labile and bulk forms of Pd, Ag, Sn, and Bi in the leaf debris and twigs. The content of labile forms of Bi in the plant leaf debris was comparable to the content in the twigs. Both the trans-accumulative and automorphic conditions were characterized by an excess of the content of the studied elements in the leaf debris and twigs (except for Sn in the leaf debris) compared to their clarke crustal values. Specifically, the content of the gross form of Se exceeded the clarke concentration in the leaf debris and twigs by 61 and 49 times, respectively. The Pd content exceeded it by 58 and 176 times, the Ag content exceeded it by 13 and 10 times, the Cd exceeded it by 29 and 38 times, and the Bi content exceeded it by 91 and 182 times. In terms of the excess over the clarke concentration, the order of the studied elements (gross form) in the leaf debris was as follows: Bi > Se > Cd > Pd > Ag; in the twigs, it was as follows: Bi > Pd > Se > Cd > Ag.

In the trans-eluvial conditions of the middle part of the steep slope, the distribution of the studied elements in the leaf debris and twigs (Figure 11) indicated a more variable distribution of the elements in the leaf debris. Similar to the landscape conditions considered earlier, on the steep slope with plant leaf debris and branch decay, all the studied elements entered the organogenic horizons, while only the Sn content in the leaf debris and branch...
decay did not exceed the clarke concentration. There was no proportional relationship between the content of labile and bulk forms of Pd, Ag, Sn, and Bi in the leaf debris and twigs. The content of labile forms of Bi in the plant leaf debris was significantly higher (by six times) than in the twigs. A conditionally proportional relationship between the content of labile and bulk forms of Se and Cd in the leaf debris and twigs was observed; however, these proportions did not correlate with the content of these elements in the automorphic and trans-accumulative landscape conditions. In the leaf debris, the content of labile forms of Ag decreased, while in the twigs, the content of labile forms of Pd increased. The trans-eluvial conditions were characterized by an excess content of the studied elements (except Sn) in the leaf debris and twigs compared to the clarke value in the Earth’s crust. Specifically, the content of the gross form of Se exceeded the clarke concentration in the leaf debris and twigs by 45 and 38 times, respectively. The Pd content exceeded it by 58 and 73 times, the Ag content exceeded it by 7 and 6 times, the Cd content exceeded it by 32 and 26 times, and the Bi content exceeded it by 221 and 57 times. Thus, concerning the excess over the clarke concentration, the order of the studied elements (gross form) in the leaf debris was as follows: Bi > Pd > Se > Cd > Ag; in the twigs, it was as follows: Pd > Bi > Se > Cd > Ag.

Figure 11. Point 3. Content of total and labile forms of elements in plant leaf debris and twigs (mg/kg (dw: dry weight)).

Under the accumulative conditions at the foot of the slope, the distribution of the studied elements in the leaf debris and twigs (Figure 12) followed a distribution pattern similar to that under the automorphic conditions. Analogous to the automorphic and trans-eluvial conditions, under the accumulative conditions with plant leaf debris and decay, all the studied elements also entered the organic horizons, and the Sn content in the leaf debris and branch decay did not exceed the clarke concentration. There was no proportional relationship between the content of labile and bulk forms of the studied elements in the leaf debris and twigs. However, quantitative differences were noted in the content of labile forms of Se, Pd, Sn, and Bi in the leaf debris and Se, Pd, Ag, and Sn in the branch debris. Specifically, the content of labile forms of Se and Bi in the leaf debris of the accumulative landscape setting decreased compared to the trans-eluvial conditions, while the content of Pd and Sn increased. In the twigs, the content of Se and Pd decreased, while the content of Ag and Sn increased. The accumulative conditions were characterized by an excess content of the studied elements (except Sn) in the leaf debris and twigs compared to the clarke value in the Earth’s crust. Specifically, the content of the gross form of Se exceeded the clarke concentration in the leaf debris and twigs by 53 and 39 times, respectively. The Pd content exceeds it by 158 and 103 times, the Ag content exceeded it by 2 and 5 times, the Cd content exceeded it by 34 and 29 times, and the Bi content exceeded it by 49 and 14 times. In terms of the excess over the clarke concentration, the order of the studied elements (gross form) for the leaf debris was as follows: Pd > Se > Bi > Cd > Ag; for the twigs, it was as follows: Pd > Se > Cd > Bi > Ag.
In the accumulative–semihydromorphic landscape facies of the island within the periodic watercourse (the island of a bypass channel), the distribution of the studied elements in the leaf debris and twigs (Figure 13) exhibited a distribution pattern similar to that of the trans-eluvial conditions. With the presence of plant leaf debris and twigs, all the studied elements entered the organogenic horizons, as in the previously described landscape settings. The Sn content in the leaf debris and branch debris did not exceed the clarke concentration.

Figure 13. Point 5. Content of total and labile forms of elements in plant leaf debris and twigs (mg/kg (dw: dry weight)).

There was no proportional relationship between the content of labile and bulk forms of the studied elements in the leaf debris and twigs. Quantitative differences in the content of labile forms of Pd, Ag, and Sn in the leaf debris and Se, Ag, Sn, and Bi in the branch debris were noted. Specifically, the content of labile forms of Pd, Ag, and Sn in the leaf debris of the accumulative–semihydromorphic landscape setting decreased compared to that in the accumulative conditions. In the twigs, the content of Ag and Sn decreased, while that of Se and Bi increased.

The accumulative–semihydromorphic conditions were characterized by an excess content of the studied elements (except Sn) in the leaf debris and twigs compared to the clarke value in the Earth’s crust. Specifically, the content of the gross form of Se exceeded the clarke concentration in the leaf debris and twigs by 46 and 34 times, respectively. The Pd content exceeded it by 54 and 110 times, the Ag content exceeded it by 3 and 7 times, the Cd content exceeded it by 37 and 31 times, and the Bi content exceeded it by 332 and 135 times. In terms of the excess over the clarke concentration, the order of the studied
elements (gross form) for the leaf debris was as follows: Bi > Pd > Se > Cd > Ag; for the twigs, it was as follows: Bi > Pd > Se > Cd > Ag.

The obtained sequences of elements for the plant leaf debris and twigs in the various landscape facies are presented in Table 2. The sequences of the elements for the organic soil horizons are also provided here. The sequences are presented in order of the elements based on their degree of excess compared to the clark concentration in the Earth’s crust.

Table 2. Series of elements accumulated in plant leaf debris and twigs and organogenic soil horizons in various landscape facies (elements not exceeding the clark concentration are given in parentheses).

<table>
<thead>
<tr>
<th>Landscape Facies</th>
<th>Leaf Debris</th>
<th>Twigs</th>
<th>Soils</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1—Automorphic</td>
<td>Pd &gt; Se &gt; Cd &gt; Bi &gt; (Ag &gt; Sn)</td>
<td>Pd &gt; Bi &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Se &gt; Cd &gt; Pd &gt; Ag &gt; (Sn)</td>
</tr>
<tr>
<td>T2—Trans-accumulative</td>
<td>Bi &gt; Se &gt; Pd &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Pd &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Ag &gt; Cd &gt; Pd &gt; Se &gt; (Sn)</td>
</tr>
<tr>
<td>T3—Trans-eluvial</td>
<td>Bi &gt; Pd &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Pd &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Ag &gt; Cd &gt; Pd &gt; Se &gt; (Sn)</td>
</tr>
<tr>
<td>T4—Accumulative</td>
<td>Pd &gt; Se &gt; Bi &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Pd &gt; Se &gt; Cd &gt; Bi &gt; Ag &gt; (Sn)</td>
<td>Ag &gt; Pd &gt; Bi &gt; Se &gt; Cd &gt; Sn</td>
</tr>
<tr>
<td>T5—Accumulative—semihydromorphic</td>
<td>Bi &gt; Pd &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Bi &gt; Pd &gt; Se &gt; Cd &gt; Ag &gt; (Sn)</td>
<td>Ag &gt; Pd &gt; Bi &gt; Cd &gt; Se &gt; Sn</td>
</tr>
</tbody>
</table>

According to the obtained sequences of the elements found in the plant leaf debris and twigs, we identified Bi, Pd, Se and Cd as the most biogeochemically labile among the studied rare elements. The least biogeochemically labile elements included Ag and Sn. It is also worth noting that despite the significant presence of individual elements such as Pd, Cd, and Se in the plant leaf debris and twigs, they actively participated in migration processes (under certain conditions). This is indirectly supported by their low concentrations in the organogenic horizons of the examined soils.

4. Discussion

Selenium (Se) is a biologically significant element, and its deficiency in plants can lead to various diseases and a reduction in drought tolerance [41]. It should be noted that the Se content in plants can vary across different natural zones [42,43] and ranges from 0.1 to 15,000 mg/kg [38]. In the leaf debris and twigs we studied, the Se content ranged from 2.03 to 3.07 mg/kg and from 1.70 to 2.93 mg/kg, respectively. These values classify these plants as moderate Se accumulators [44]. This is consistent with the high content of total forms of Se in the examined soils, which exceeded the clark concentration by a factor of from 3 (for the organic–mineral horizons, 0.1792 mg/kg) to 54 times (for the mineral horizons, 2.7312 mg/kg), with the excess concentrations being 13–29 times higher for the organic horizons. In light of these values, the excess Se content (compared to the clark concentration in the Earth’s crust) in the leaf debris and twigs, ranging from 40 to 61 times and from 34 to 58 times, respectively, is natural and can be attributed to its biological availability.

Palladium (Pd) belongs to the elements of the platinum group and is known for its involvement in biosorption processes [45]. The established content of Pd in soils and various plant parts ranges from 0.27 to 7.0 mg/kg and 0.065 to 6.0 mg/kg, respectively [46]. In the leaf debris and twigs we studied, the Pd content ranged from 0.54 to 1.58 mg/kg and from 0.73 to 1.76 mg/kg, respectively. These values align with the high content of total Pd forms in the examined soils, exceeding the clark concentration by a factor of from 12 (for the organic–mineral horizons, 0.1238 mg/kg) to 181 times (for the mineral horizons, 1.8186 mg/kg), with the concentrations exceeding the clark values by 14–70 times for the organic horizons. Given these values, the excess Pd content (compared to the clark concentration in the Earth’s crust) in the leaf debris and twigs, ranging from 54 to 158 times and from 73 to 176 times, respectively, is natural and can be attributed to its high concentration in soils.

Silver (Ag) belongs to the biophilic elements that are available to plants in colloidal forms and that also actively participate in migration through natural waters [47]. The
content of Ag in soils varies widely, ranging from 1.5 to 7.4 µg/kg [48]. Additionally, the Ag content varies significantly in various vegetative organs of plants [49], with an average content in plant ash of up to 5 mg/kg. In the leaf debris and twigs we studied, the content of total forms of Ag ranged from 0.04 to 0.94 mg/kg and from 0.31 to 0.69 mg/kg, respectively. These values correspond to the high (and very high) content of total forms of Ag in the examined soils, exceeding the clark concentration by a factor of from 6 (for the organic–mineral horizons, 0.439 mg/kg) to 13,410 times (in a single case for the organic horizons, 938.74 mg/kg). The concentration exceeded the clark values by 6–21 times for the mineral horizons. Thus, the excess Ag content (compared to the clark concentration in the Earth’s crust) in the leaf debris and twigs, ranging from 0 to 13 times and from 4 to 10 times, respectively, is natural and can be attributed to its high concentration in soils, its biological absorption, and, in specific cases, its active translocation migration through natural waters.

Cadmium (Cd) is considered a labile and weakly labile element under oxidizing and gley conditions. It is a heavy metal known for its toxic, teratogenic, and carcinogenic properties, and it has a poorly understood biological role, but it actively participates in biological absorption. The content of Cd in soils varies widely depending on the mechanical composition, ranging from 0.03 to 0.15 µg/kg for light and heavy mechanical compositions, respectively [50]. In the dry biomass of vegetative plant organs, Cd content typically falls within the range of 0.1–0.8 mg/kg [51]. In the leaf debris and twigs we studied, the content of total Cd forms ranged from 3.58 to 4.85 mg/kg and from 3.41 to 4.99 mg/kg, respectively. These values correlate with the high content of total Cd forms observed in all the horizons of the examined soils, surpassing the clark concentration for Cd in the Earth’s crust by many times. It was observed that the presence of high Cd concentrations throughout the soil profile may indicate its active input through leaf debris and subsequent lateral migration. This migration is associated with Cd uptake by plants due to existing soil-forming factors [46]. The Cd content exceeded the clark concentration by a factor of from 9 (for the organo-mineral horizons, 1.250 mg/kg) to 22 times (for the organogenic horizons, 2.959 mg/kg), exceeding the clark concentration by 7–20 times for the mineral horizons. The excess Cd content (compared to the clark concentration in the Earth’s crust) in the leaf debris and twigs, ranging from 27 to 37 times and from 26 to 38 times, respectively, is consistent and can be attributed to its high concentration in soils, its biological absorption, and its active translocation through natural waters.

The behavior of tin (Sn) is not fully understood. Sn is categorized as a weakly labile anionic element and is also involved in biogenic accumulation. Typically, the content of Sn in soils falls within the range of from 1.0 to 11.0 mg/kg, while in plants, it ranges from 10.0 to 20.0 mg/kg, leading to a biological absorption coefficient of Sn = 1.85 [47]. We observed that the clark concentration of Sn was only present in the soil horizons developing under accumulative and accumulative–semihydromorphic conditions. The excess was minimal, ranging from 1.3 (for the organogenic horizons, 3.6515 mg/kg) to 2.0 times (for the organo-mineral horizons, 5.0998 mg/kg), with an excess over the clark concentration ranging from 1.1 to 1.9 times for the mineral horizons. An excess content of Sn (compared to the clark concentration in the Earth’s crust) in the leaf debris and twigs was not observed. This lack of excess may be attributed to its low content in soils, its moderate involvement in biological absorption, and its selective translocation through natural waters.

Bismuth (Bi), like Cadmium (Cd), falls under the category of rare elements that are both labile and weakly labile under oxidizing and gley conditions. It is also one of the less studied elements. In soils, its content is typically around 0.2 mg/kg, and it does not exceed 0.02 mg/kg in the dry mass of plants [47]. However, in the leaf debris and twigs we studied, the Bi content was notably higher, ranging from 0.26 to 3.31 mg/kg and from 0.13 to 1.82 mg/kg, respectively. These values nevertheless aligned with the high content of total Bi forms in the examined soils. The excess over the clark concentration ranged from 29 (for the organogenic and organo-mineral horizons, 0.2884 mg/kg) to 70 times (for the organo-mineral horizons, 0.7025 mg/kg), surpassing the clark concentration.
by 36–75 times for the mineral horizons. The excess Bi content (compared to the clarke concentration in the Earth’s crust) in the leaf debris and twigs ranged from 27 to 332 times and from 14 to 182 times, respectively. This excess is consistent and can be attributed to its high concentration in soils, its involvement in biological absorption, and its translocation migration through natural waters, particularly when appropriate redox conditions of soil solutions are established.

The relationship between the metal concentrations in the soils and leaf debris/twigs was assessed using Pearson’s correlation coefficient (r), which was considered statistically significant at \( p < 0.05 \). The calculation of Pearson’s correlation coefficient allowed us to establish that, in some cases, there were indeed significant correlations between the elements under consideration at the significance level of \( p < 0.05 \). Specifically, in the study area, a positive correlation was observed between the gross concentrations of Pd–Bi \( (r = +0.90) \), Cd–Bi \( (r = +0.63) \), Sn–Bi \( (r = +0.84) \), and Pd–Sn \( (r = +0.99) \), as well as between the gross and mobile forms of Pd–Pd \( (r = +0.81) \), Pd–Ag \( (r = +0.69) \), Pd–Bi \( (r = +0.94) \), Sn–Bi \( (r = +0.95) \), and Bi–Bi \( (r = +0.71) \). This means that in the soils of the study area, an increase in gross Bi was accompanied by an increase in gross Pd, Cd, and Sn; an increase in gross Sn was accompanied by an increase in gross Pd; and an increase in the amount of gross Pd led to an increase in its mobile forms as well as to an increase in the mobile forms of Ag. Meanwhile, an increase in the amount of gross Bi led to an increase in the mobile forms of Pd, Sn, and Bi. The nature of the relationships between the trace elements in “leaf litter–soil” systems is somewhat different from that in soils. In the study area, the soil accumulation of Pd was found to be directly dependent on the content of its mobile forms in the litter \( (r = +0.97) \) as well as on the content of mobile forms of Sn and Bi in the litter \( (r = +0.96, r = +0.96, \text{ and } +0.91, \text{ respectively}) \). On the other hand, an increase in mobile Ag in the litter led to a restriction of Sn \( (r = -0.79) \) and Ag \( (r = -0.79) \) intake into the soil. The nature of the relationships between the trace elements in the “debris–soil” system differed from that in the “leaf litter–soil” system. In the study area, the accumulation of Cd by debris led to a restriction of Pd \( (r = -0.72) \), Sn \( (r = -0.78) \), Bi \( (r = -0.78) \), and also Cd \( (r = -0.66) \) intake into the soil. The soil accumulation of Se was found to be directly dependent on the content of Ag in the debris \( (r = +0.71) \).

Therefore, the values we obtained were consistent with the widely available literature information. The significant excesses in the content of specific elements in the soil horizons or leaf debris reflect the unique characteristics of the study area and the soil formation factors in the subordinate landscape facies of the mid-mountain foggy forests of southern Vietnam.

5. Conclusions

Our study revealed significant correlations between the material composition of plant leaf debris, twigs, and organogenic soil horizons. We found that the soil samples contained high levels of Se, Pd, Ag, Cd, Bi, and Sn, exceeding their clarke values in the Earth’s crust. This study highlighted the biogeochemical migration and accumulation of these elements, influenced by landscape settings and soil moisture regimes. In the course of the study, we observed several features related to the lateral and horizontal distribution of elements in the soil horizons, as follows:

- The selenium (Se) content increased in both the organogenic and mineral horizons. It also gradually increased from the automorphic to the accumulative landscape facies due to active biogeochemical migration. In this case, the Se content in the plant twigs decreased.

- The selenium (Se) concentrations depended on the geological and hydrological conditions of the territory. The peak concentration of Pd was associated with its content in the parent rocks that make up the area and active transport through river runoff (the maximum values were observed in near-river territories). Additionally, the Pd concentrations increased due to biosorption, consistently rising from the plant leaf debris to the accumulative conditions.
- The silver (Ag) content generally exhibited an overall increase in concentration from the automorphic to the accumulative conditions. It was also characterized by concentration peaks in the organic horizons due to biological absorption (especially significant in the twigs) and active translocation migration with natural waters.

- Cadmium (Cd) showed a lateral migration that was evident through a decrease in its concentration from the organogenic horizons to the mineral ones, which was attributed to active translocation migration with natural waters. The increased Cd content in the organogenic horizons of the soil sections indicates significant biological absorption by vegetation and a reverse input with leaf debris and twigs (though the concentrations in the twigs decreased from the automorphic conditions to the base).

- The tin (Sn) concentrations tended to increase from the organogenic to the organomineral horizons and subsequently decrease in the mineral horizons. During horizontal migration, the Sn concentration increased overall from the automorphic to the accumulative–semihydromorphic landscape facies. Sn was moderately involved in biological uptake and selective translocation migration with natural waters.

- The bismuth (Bi) content was observed in the plant leaf debris and twigs as well as consistently in the horizons of the studied soils. However, the total content of the element decreased both in the subordinate landscape facies and during lateral migration. The initiation of Bi migration activity was established to coincide with the seasonal development of gleying. In the leaf debris, the Bi concentration increased from the automorphic conditions to the foot of the slope, while in the twigs, on the contrary, its concentration decreased.

The separate data and results obtained by us require additional studies to further investigate the factors initiating migration processes in the subordinate landscape facies of the mid-mountain foggy forests of southern Vietnam.

**Author Contributions:** Conceptualization, R.G.; methodology, R.G. and Y.L.; validation, T.G. and A.D.; formal analysis, Y.L., A.D. and C.N.P.; investigation, Y.L., R.G., T.G., C.N.P. and V.T.N.; resources, Y.L., A.D., A.K., S.K. and V.T.N.; data curation, Y.L. and C.N.P.; writing—original draft preparation, Y.L.; writing—review and editing, A.D., R.G., T.G., C.N.P., A.K., S.K., V.T.N. and V.T.; visualization, T.G. and V.T.; supervision, R.G.; project administration, R.G. and A.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was carried out within the framework of the Research Work of Joint Russian-Vietnamese Tropical Research and Technological Center—ECOLAN E-1.2 «Conservation, restoration and sustainable use of tropical forest ecosystems based on the study of their structural and functional organization», section «Study of the structure and functioning of lowland and mountain ecosystems in Vietnam (Bidoup Nui Ba National Park)». This work was carried out within the framework of the IBSS state research assignment “Studying the features of the functioning and dynamics of subtropical and tropical coastal ecosystems under the climate change and anthropogenic load using remote sensing, cloud information processing, and machine learning to create a scientific basis for their rational use”, registration number: 124030100030-0. The RUDN University Strategic Academic Leadership Program has supported this research.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflicts of interest.

**References**

3. Naumov, V.D. *Soils of the Tropics and Subtropics and Their Agricultural Use*; RSAU-MSHA: Moscow, Russia, 2010; p. 361.
5. Sokolov, I.A. Tropical Soil Formation and Weathering (on the Example of Laos); RAS, V.V. Dokuchaev Soil Institute: Moscow, Russia, 2004; p. 376.

6. Fridland, V.M. Soils and Weathering Crusts of the Humid Tropics (Using the Example of Northern Vietnam); Science, Russia: Moscow, Russia, 1964; p. 312.

7. Shishov, L.L.; Andronikov, S.V.; Belobrov, V.P.; Kulenkamp, A.Y.; Panteleev, L.S.; Sokolov, I.A.; Shevchenko, T.N. Soils of the Alternately Humid Tropics of Laos and Their Natural Use; V.V. Dokuchaev Soil Institute, RAS: Moscow, Russia, 1996; p. 275.


9. Dobrovolsky, V.V. Geography of Trace Elements. Global Dispersion; V.V. Dobrovolsky; Mysl: Moscow, Russia, 1983; p. 272.

10. Dobrovolsky, V.V. Geography of Soils with Fundamentals of Soil Science; V.V. Dobrovolsky; VLADOS: Moscow, Russia, 1999; p. 384.


20. Lopes de Gerenyu, V.O.; Anichkin, A. Termites as a factor of spatial differentiation of CO2 andnbsp;fluxes from the soils of monsoon tropical forests in southern Vietnam. Eurasian Soil. Sci. 2015, 48, 208–217. [CrossRef]


36. Vinogradov, A.P. Average contents of chemical elements in the main types of igneous rocks of the earth’s crust. Geochemistry 1962, 7, 555–571.
38. Moiseenko, T.I.; Dinu, M.I.; Gashkina, N.A.; Kremleva, T.A. Aquatic environment and anthropogenic factor effects on distribution of trace elements in surface waters of European Russia and Western Siberia. Environ. Res. Lett. 2019, 14, 065010. [CrossRef]
48. Chernyakhov, V.B.; Shcheglova, E.G. Main parameters of the distribution of microelements (Zn, Pb, Ag, Mo and Co) in the vegetation cover of the Yaman-Kasinsky copper pyrite deposit. Izv. OGAU 2016, 4, 162–164.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.