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Assessment of the Macro- and Microelement Composition of Fly Ash from 50-Year-Old Ash Dumps in the Middle Urals (Russia)

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Abstract: The paper considers the macro- and microelement composition of two ash dumps in the Middle Urals, where meadow and forest communities have been spontaneously forming for 50 years, as well as the effect of the plants on the changing composition of the ash. Higher contents of Cu, Co, Sn, Ga, and Yb were found in the deep ash layers of both dumps, while in the upper 20-cm layer, the trace element composition depended on the influence of different plant communities. Higher contents of Sr, Cr, Ni, Sn, and Co were revealed under meadows, and Ba, Zr, and La were found under the forest. The levels of element accumulation in the aboveground and underground parts of dominant plants were revealed. Increased content of Be, Ce, Ga, La, Sc, Y, and Yb was detected in areas where meadow plants were dominant and Zn and Ba in forest areas. The toxic elements Cd and Pb were highly accumulated in both communities, whereas Co was found only in meadows. The studied materials can serve as a base to assess the feasibility of processing and/or utilizing fly ash from ash dumps in the Middle Urals and similar ash dumps in other regions situated in the southern taiga.

Keywords: ash dumps; fly ash; Technosols; macronutrients; trace elements; plant communities; Middle Urals

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1. Introduction

The Russian Federation, like many other countries, produces electric power mainly by using solid-fuel natural resources such as brown and bituminous coals. Their share in global power production was 36.4–41% for 2000–2019 [1–3]. Coal combustion creates a large amount of ash waste, which is difficult to dispose of, stored in ash dumps covering significant areas and affecting the environment [3–8]. The large amount of ash and slag waste that has accumulated, and is being constantly added to, has become a problem. The question of recycling and reusing this waste as a secondary raw material has recently attracted a large amount of attention in different countries, including Russia [3,9–21]. Innovative approaches to use ash wastes demonstrate the possibility of achieving 100% recycling and applying ash and slag dumps at different geographical points [3]. However, as reflected in numerous publications, the study of ash dumps in different countries and regions differs significantly in methodological approaches, detail, and the extent of techniques and tools used [9,13,18,22–25]. At the same time, despite the voluminous scientific literature, there are still many gaps in understanding various issues related to

the possibility of maximizing ash dump recycling and restoring their locations to a normal ecological state.

The features of ash dumps depend on several factors: the type of solid fuel sources used, their ash content, technological techniques, and stored ash properties, as well the environment of the thermal power plants (TPP) sites. Therefore, information about ash dumps of different scales and diverse combinations of natural conditions and ash properties is of high scientific and practical value. Although the presence of substances toxic to humans in coal ash has been known since the middle of the last century [26], assessing ash deposits in terms of their content levels and changes over time still requires attention to assess the possibility of using the ash substrate. It is well known that ashes and slags contain components with unique properties and that modern technologies make it possible to use them in building construction, industry, agriculture, and the population's domestic needs [9,27–30].

Analyzing the chemical composition and the levels of macro- and micro-elements in the ash to assess the possibility of its use as a substance (raw material) to implement various practical tasks, and identifying the changes in the ash's composition and properties as it accumulates under different plant communities are subjects of interest. It is possible to assess the levels of the most valuable elements and the changing trends of the stored ash composition and properties over time.

The need to reuse and recycle the accumulated ash and slag masses in the Middle Urals to the greatest extent possible has become an incentive to study detailed macro- and micro-element composition of fly ash in the two oldest (50-year-old) ash dumps of thermal power plants (TPP) in the Middle Urals.

The ash dumps of two large TPPs in the Middle Urals, the Verkhnetagilskaya thermal power plant (VTTPP) and the Sredneuralskaya thermal power plant (SUTPP), whose vegetation, physicochemical properties, component composition, and ratio of humus substance system, etc., have been investigated for almost half a century, are poorly studied from the standpoint of their macro- and micro-element composition. To establish practical measures for ash disposal and recycling, it is necessary to have as much detailed knowledge as possible about the ash dump's state, composition, and properties at a given moment to use as a starting point to implement the methods of its use and recycling.

The macro-and micro-element composition of the ash, located at a depth outside the effect of vegetation during the entire 50-year period, the state of ash after experiencing the influence of the process of pedogenesis for five decades, especially the effect of plant communities and their impact on the current state of ash dumps, as well as an assessment of the ability of individual plants to concentrate different elements in their underground and aboveground parts, are all subjects of great interest. This article addresses these issues.

The purpose of this study is to assess the state of the macro-and micro-element composition of fly ash from ash dumps after 50 years of spontaneous vegetation in the southern taiga of the Middle Urals and to reveal the influence of different plant communities on its specific properties.

2. Objects and Methods

The problem of assessing the chemical composition of ash dumps and their transformation under the effect of the natural colonization of plant communities over the past 50 years, as well as the transformation of ash under the influence of natural processes, such as leaching and element migration, is considered in the example of ash dumps in the Middle Urals (Figure 1).

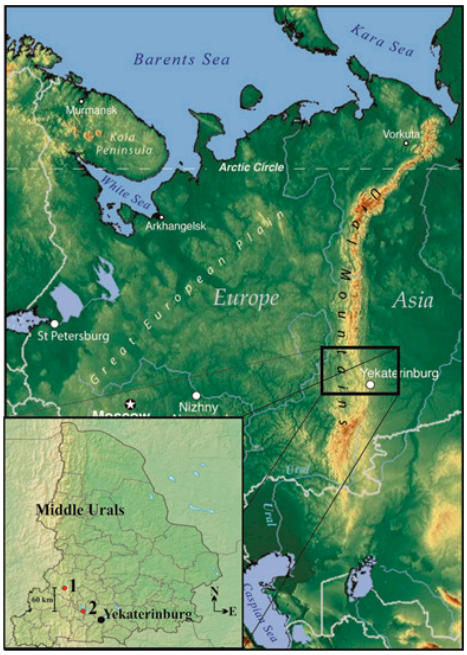

Figure 1. The location of the objects: (1) ash dump of the Verkhnetagilskaya thermal power plant (VTTPP); (2) ash dump of the Sredneuralskaya thermal power plant (SUTPP).

The objects of study were the ash dumps of two large thermal power plants (TPP) in the Middle Urals, the Verkhnetagilskaya thermal power plant, hereafter referred to as VTTPP or object No. 1, and the Sredneuralskaya thermal power plant, hereafter referred to as SUTPP or object No. 2, which have not been sufficiently studied in terms of their macro- and micro-element composition. These sites were chosen due to their administrative and geographical locations.

The VTTPP ash dump (57°20′N, 59°56′E) consists of fly ash from brown coal from the Chelyabinsk and Bogoslovskoye deposits (Ural, Russia) and occupies an area of 125 ha.

The SUTPP ash dump (57°00′N and 60°27′E) consists of fly ash from brown coal from the Ekibastuz deposit (now located in the territory of the Republic of Kazakhstan), has an area of 104 ha.

These ash dumps were selected from 10 similar sites for a detailed, comprehensive study of the transformation of their chemical compositions under different conditions because they are the result of burning high-ash brown coals with various properties from different deposits. At the same time, they are located on territories with the same (southern taiga) bioclimatic conditions, both are 50-years old, are under the influence of spontaneous vegetation, and both sites have been occupied by meadow and forest communities.

The two research sites are located in the temperate continental boreal climate zone. The average annual temperature is 1.7–2.4 °C, and the average annual precipitation is 510–580 mm. Their location is forested by typical indigenous vegetation, represented by southern taiga pine, and less often, pine-spruce forests, secondary birch, and mixed birch–pine forests [31]. At the end of operations, one part of the leveled surface of both ash dumps was subjected to reclamation, and the other was left for natural colonization. By the time of the study, areas with both herb–grass meadow communities and mixed forest phytocenoses, with a predominance of small-leaved trees (*Betula and Pendula*) and a small admixture of conifers, were formed at the ash dumps of VTTPP and SUTPP as a result of spontaneous vegetation on the uncultivated ash surface. For convenience, when describing an area with meadow communities, the term"meadow" is used; for forest communities, "forest" is used.

The ash dumps at both sites are composed only of fly ash since the coal used at VTTPP and SUTPP are classified as low-caking coals and exclude the formation of slags [32,33].

It was previously established that plant communities formed on ash dumps in the Urals affect only the upper 20-cm layer in the first 5–10 decades of growth [34]. Based on this, we consider the properties of ash at a depth of 0–20 cm and at 30–50 cm. The first depth corresponds to the level where the ash was influenced by the plant communities formed on the ash dumps and includes the horizons of Technosols formed over 50 years. The second depth reflects the current state of the ash, which during this period is only under the influence of physicochemical processes, mainly leaching, migration, and/or physical weathering.

Three sample plots were chosen in both the meadow and forest areas of VTTPP and SUTPP ash dumps. The plots measured 10 × 10 m for a meadow and 20 × 20 m for a forest. Morphological descriptions were completed for one or two soil sections in each sample plot (10 on the first object and 6 on the second).

Poorly differentiated low thickness soils (Technosols in accordance with WRB) [35] were formed in the upper 20-cm layer of the meadow and forest areas under the effect of the corresponding plant communities at the VTTPP and SUTPP ash dumps over 50-years. They have horizons with a high content of organic matter and transitional horizons (AC), underlaid by parent rock (C).

Sampling from the ash dumps was carried out within the 20-cm thickness of young soils from each horizon and from ash at a depth of 30–50 cm, which is outside the influence of soil-forming processes. In total, 18–20 samples were taken from both the meadow and forest areas of each ash dump. The samples were air-dried at room temperature, and visible organic residues were removed. An average of 20 g was taken from each field sample for C and N analysis, ground in a porcelain mortar, and sifted through a 0.25 mm diameter sieve. The remaining samples were also ground and sifted through a 1 mm diameter sieve. Part of the homogenized samples from the same horizons of one area were mixed to obtain a composite sample for further analyses. The main physical-chemical characteristics of the ash were obtained according to [36,37]. The pH was determined in a supernatant of soil and water in a ratio of 1:2.5 by pH meter ANION 4100 (Russia). Particle size distribution was determined by the pipette method [38]. Total organic carbon was found by wet combustion in a mixture of potassium dichromate and sulfuric acid. Total N was determined by Kjeldahl's method with termination on a spectrophotometer UNICO 2100 (United Product & Instruments, Dayton, NJ, USA).

The peculiarities in the chemical composition of the aboveground and underground parts of different plant species that were dominant in the studied areas of the VTTPP ash dump were also studied. *Calamagrostis epigejos* L. *Roth*, *Poa pratensis* L., *Pimpinella saxifraga* L., *Silene nutans* L., *Plantago media* L., and *Erigeron acris* L. were determined to be the dominant species in the meadow; *Betula pubescens Ehrh.*, *Betula pendula Roth*, *Populus tremula* L., *Orthilia secunda* L. *House* and *Pyrola rotundifolia* L. were the dominant species in the forest area. Approximately 15 to 30 plant specimens from the meadow and the forest areas of the ash dump (5–10 from each plot) were chosen, depending on their size, and combined to produce a composite sample for further analysis. Samples were dried at 60 °C, ground, and ashed in a muffle furnace at 450 °C. The resulting ash was ground to a powder.

The macronutrient and trace element composition of the mineral part of the fly ash and plants was found using atomic emission spectrometry (AES) and X-ray fluorescence analysis using synchrotron radiation (storage ring VEPP-3, BINP SB RAS) – (SR XRF-).

Macronutrients, as well as Ce, B, Be, Sn, La, Sc and Yb, were determined by the AES method using a setup including a spectral excitation source—an argon arc two-jet plasmatron (DDP, Novosibirsk, Russia), a device for spraying and feeding into the plasma jet a finely dispersed powder, spectrometer (PGS-2, Jena, Germany) and multichannel analyzer of emission spectra (MAES, Novosibirsk, Russia). Sample preparation was carried out in accordance with [39]. The remaining trace elements were determined by the SRXRF method using X-ray fluorescent elemental analysis in the Siberian Centre of Synchrotron and Terahertz Radiation (Budker Institute of Nuclear Physics SB RAS). This equipment was manufactured at the Budker Institute of Nuclear Physics SB RAS. All standard and

test samples were presented as dry powder with a particle size of 25 μm (GSO 7126-94 Bil-1). All samples were pressed into tablets with a diameter of 8 mm under a pressure of ≈150 kg/cm^2. The tablets were placed between two layers of mylar film and fixed in fluoroplastic rings. All instruments used in sample preparation: a scalpel (steel grade EI-515), tweezers (with a fluoroplastic tip), were treated with "OSCH" grade (GOST 10749-80) ethyl alcohol. Before packing the samples into mylar films, the latter were also treated with ethyl alcohol [40,41].

In total, the contents of 34 macro- and micro-elements in the ash dumps and 32 in the aboveground and underground parts of plants growing in the meadow and forest areas of the VTTPP ash dump were studied.

To characterize the macro-element composition of ash, the molar ratios of SiO_2 to Al_2O_3, Fe_2O_3 and to R_2O_3 (sum of aluminum and iron oxides), which are used in the practice of deposit and soil studying, were calculated [36,37]. The degree of predominance of silicon over other elements allows us to judge the transformation of the chemical composition of the deposits.

To estimate the levels of elements in the fly ash compared to the Earth's crust, the Clarkes, according to Kasimov and Vlasov [42], were used, which were proposed based on the analysis of Clarke numbers from nine sources. For elements missing from the list of these authors, the Taylor [43] and Vinogradov [44] Clarkes were used.

Analysis, illustrative materials, and interpretation were carried out on the basis of averaged materials. The use of averaged materials for objects of different genesis, thickness, and volume made it possible to generalize, compare and evaluate different sources of information from individual plants to plant communities as a whole and from individual soil horizons to soil profile; the whole stratum transformed by pedogenesis, as well as fly ash which is outside the influence of plant communities. The Statistica 8. package (StatSoft Inc., Tulsa, OK, USA, 1984-2007) and Microsoft Excel 2016 (Microsoft, Redmond, WA, USA) were used to calculate the averaged values and present them graphically.

3. Results and Discussion

Morphological examination of the fly ash from both ash dumps shows it to be a structureless mass, with shades from light gray to dark gray, in which impurities of unburned coal may be present in the form of inclusions or thin interlayers. In terms of other properties, the ash differs to varying degrees, depending primarily on the properties of the initial coal source and the technology of its processing. At the time of the study, ash dumps had different medium values: object 1 had a pH of 7.7, object 2, a pH of 6.2, as well as different carbon contents (on average, 1.02 and 1.91, respectively) and nitrogen contents (0.04 and 0.02). The presence of carbon and nitrogen may indicate coal underburning.

The ash in the deep layers of the VTTPP ash dump was dominated by particles with a diameter of >0.01 mm (Table 1). Their share of fine earth is 87%. Medium sand dominates among particles of this size. The ash in the upper 20-cm of the VTTPP ash dump, which is in the vegetation effect zone, contains 23% particles with a diameter of <0.01 mm, almost 2 times higher than the ash located below. The texture of the deep layer ash can be attributed to sandy, overlying ash and loamy sand.

In the composition of deep layer ash at the SUTPP ash dump, particles larger than 0.01 mm made up 82% on average, and coarse and medium sand were dominant (Table 1). In the ash of the dump's upper stratum, the content of particles with a diameter of less than 0.01 mm, including the clay particles prevalent there, is greater than 23%. The ash texture of the SUTPP ash dump is loamy sand, at depths of both 30–50 cm and 0–20 cm.

Table 1. Particle size distribution in ash dumps. VTTPP: Verkhnetagilskaya thermal power plant. SUTPP: Sredneuralskaya thermal power plant.

Percentage Share of Fraction (mm)						
1.00–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	<0.01
VTTPP ash dump, 0–20 cm						
9.4	51.4	16.2	6.7	8.3	8.0	23.0
VTTPP ash dump, 30–50 cm						
17.5	47.9	21.8	5.3	3.5	4.0	12.8
SUTPP ash dump, 0–20 cm						
10.8	35.9	30.2	6.0	6.6	10.5	23.1
SUTPP ash dump, 30–50 cm						
9.5	32.6	39.9	7.9	5.7	4.4	18.0

Thus, at the VTTPP and SUTPP ash dumps, the ash in the vegetation effect zone is more enriched with clay particles than the underlying ash and belongs to a different textural class than the first subject. It should be noted that the most finely dispersed mass from which plants can extract and accumulate substances necessary for life in their organs, in the ash of deep layers of both areas, does not exceed 4.5% on average.

As to gross chemical composition, the ash of both subjects can be defined at present as aluminosilicate formations (Table 2). Attention is drawn to the high content of aluminum and silicon oxides in the dump ash, a relatively lower content of SiO_2 and Na_2O and a higher MgO, TiO_2 and P_2O_5 in the ash of subject 1 compared to the other ash dump, as well as more than twice the amount of iron in the mineral portion of ash dump 2. A comparison of ash composition from different depths using the indicators showed a relative increase in the proportion of silicon oxide in the upper 20-cm layer of the ash dump by 3.5–5.0%. At the same time, the proportion of aluminum oxide in the 30–50 cm layer increased on average by 2–7%. Calculated molar ratios of basic oxides (SiO_2:Al_2O_3 and SiO_2:Fe_2O_3 and SiO_2:R_2O_3**)** showed a regular decrease in their absolute values with depth, indicating an increase in the proportions of iron and aluminum in this direction. These differences may indicate the possibility of the aluminium leaching process (its migration with depth) which is quite natural in a humid climate with high average annual precipitation [45]. The values of the calculated molar ratios SiO_2:Al_2O_3 and SiO_2:Fe_2O_3, as well as SiO_2:R_2O_3, confirm this assumption (Table 2). The results also show that the leaching and migration of iron oxides are extremely low, especially in the SUTPP ash dump.

Table 2. Chemical composition of ash dumps.

Indicators	Element Oxides	VTTPP Ash Dump			SUTPP Ash Dump		
		Depth, cm					
		0–10	10–20	30–50	0–10	10–20	30–50
Content, %	SiO_2	46.4	42.9	41.1	52.2	54.9	48.9
	Al_2O_3	30.3	30.3	31.8	29.8	31.6	37.6
	Fe_2O_3	13.0	14.1	14.0	5.2	5.2	5.4
	CaO	3.6	5.1	5.5	4.9	2.9	2.7
	MgO	2.2	2.7	2.7	1.6	0.9	0.9
	K_2O	1.4	1.6	1.4	1.4	1.0	1.0
	Na_2O	0.4	0.2	0.3	4.3	2.3	2.1
	TiO_2	2.2	2.2	2.4	0.6	1.0	1.1
	P_2O_5	0.8	0.4	0.3	0.3	0.3	0.3
Mole Ratio	SiO_2/Al_2O_3	2.60	2.40	2.19	2.97	2.95	2.21
	SiO_2/Fe_2O_3	9.49	8.12	7.80	26.68	27.79	24.07
	SiO_2/R_2O_3 *	2.04	1.85	1.71	2.67	2.67	2.02

* R_2O_3—sum of aluminum and iron oxides.

Comparison of molar ratios in the following series: weathered ash (depth 30–50 cm)—ash from the plant community effect zone without morphological signs of changes (horizon C of the forming Technosols, depth 10–20 cm)—the upper 10-cm of ash dump—showed that leaching processes and migration of elements take place during ash dump functioning, affecting the chemical composition of ash at the 30–50 cm depth (Table 2). The results also show that the leaching and migration of iron oxides are extremely low, especially in the SUTPP ash dump.

The main macronutrients involved in the formation of ash (Si, Al, Fe, Ca, Mg, S, K, Na, Ti and P) constitute up to 98–99% of its mass. These are of increased interest when assessing the possibility of using it in construction, industry, agriculture, and recycling, as well as identifying the resultant effects of various natural factors on its composition (plant communities in particular), to compare their content with Clarke values in the Earth's crust, and when solving a wide range of other issues. In these cases, it is more convenient to operate with data characterizing the elements rather than their oxides (Table 3).

Table 3. Content of macroelements in fly ash of the studied ash dumps.

Element	Average Content, kg·t^{-1}		Clarke Values in the Earth's Crust, kg·t^{-1}		
	Object 1	Object 2	[Kasimov and Vlasov, 2015]	[Vinogradov, 1962]	[Taylor,1964]
Si	192.3	228.6	288.3 *	295.0	281.5
Al	165.6	195.8	76.10	80.50	82.30
Fe	103.2	39.79	40.60	46.50	56.30
Ca	39.31	19.30	25.66	29.60	41.50
Mg	16.29	5.43	14.95	18.70	23.30
K	11.57	8.26	23.24	25.0	20.90
Na	2.23	15.58	24.26	25.0	23.60
Ti	14.40	6.60	3.90	4.50	5.70
P	1.31	1.31	0.69	0.93	1.05

* average data obtained by calculation.

The levels of macroelements vary significantly in different ash dumps. The ash of object 1 contains increased amounts of almost all elements (except for Si, K and Na), which exceed the Clarke values of the earth's crust by 1.1 to 3.7 times. The content of most macronutrients in the ash of subject 2, on the contrary, has a lower Clarke value. Only Al exceeds the value by 2.5 times, as Ti and P (by almost 1.7 and 2 times, respectively).

Issues related to the accumulation and behavior of trace elements, both those toxic to living organisms [46] and those that may have value for use in innovative technological processes [3,47–49], are of no less interest in the study of the chemical composition of fly ash. Macroelement compositions of ash dumps differ significantly; the absolute majority of trace elements (except for Sr, Co, Pb, Sn and Cd) are contained in higher amounts in the VTTPP ash (Table 4). The elements V, Cu, Cr, Ni and Sc are 2.5–3 times higher than in the SUTPP ash dump. The content of the remaining elements exceeds analogs by no more than 1.5 times.

Table 4. The content of trace elements in fly ash of the studied ash dumps.

Element	Average Content, g·t^{-1}		Clarke Values in the Earth's Crust, g·t^{-1}		
	Object 1	Object 2	[Kasimov and Vlasov, 2015]	[Vinogradov, 1962]	[Taylor,1964]
Mn	984.2	656.5	770	1000	950
Ba	1224.6	1036.4	628	650	425
Sr	611.2	622.1	270	340	375
V	370.6	150.9	106	90	135
Zr	262.2	250.7	-	170	165
Cu	251.5	95.2	27	47	55
Cr	127.8	42.3	92	83	100
Ni	96.0	30.9	50	58	75
Zn	83.1	64.0	75	83	70
Sc	53.1	19.2	-	10	22
Y	52.9	32.6	-	29	33
Ce	40.4	36.4	-	70	60
La	34.8	24.4	32	29	30
Ga	33.1	27.0	-	19	15
Co	28.6	47.3	15	18	25
B	24.2	22.7	34	12	10
Pb	21.3	25.3	17	16	12.5
As	17.1	13.6	5.6	1.7	1.8
Sn	9.3	37.6	2.5	2.5	2
Yb	7.9	3.6	-	0.33	3
Nb	7.3	0.5	-	20	20
Be	3.3	2.3	2.3	3.8	2.8
Mo	1.9	2.1	1.1	1.1	2.5
Cd	0.3	0.4	0.09	0.13	0.2

The ash of subject 2 is distinguished by the fact that the tin content exceeds that of subject 1 by 4.4 times (Table 4). The presence of arsenic was not detected in any analyzed samples of fly ash from either ash dump, but its concentration in all detected cases exceeded Clarkes in the Earth's crust. This is reflected in the data averages from different sources, which exceed the Clarkes by 5–10 times (Table 4).

Using Clarke values to compare levels of other trace ash dump elements deep in the Earth's crust revealed that in the first subject, a maximum accumulation exceeding the Clarke by more than 9 times was noted for Cu; exceeding 3.5–3.7 times for V and Sn; 2–2.5 times for Yb, Ga, Sc and Sr. In the ash of subject 2, the tin content exceeded its Clarke value by 15 times. In addition, this ash dump has an increased content of Sr, Co and Cu by 2, 3 and 3.5 times, respectively. Thus, Cu, Co and Sn largely exceed the Clarke value at both ash dumps. Among the rare elements, in addition to those mentioned above, Sc, Ga, Yb were found in relatively high concentrations in the ash of the first subject, along with Zr, Ga, Yb and Mo in the second (Table 4).

Low thickness soils, or Technosols, formed in the upper (20-cm) part of the ash dumps over 50 years through the process of spontaneous vegetation. In the formation process, under the influence of past period pedogenesis, the transformation of ash dumps took place, affecting the macro- and micro-elements of ash composition. Any soils, wherever they are formed, accumulate in their upper humus-accumulative thickness a number of elements, primarily biogenic, necessary for plant life [34,50], and ash dumps are no exception. Plants growing in soils act as one geochemical barrier [51]; they absorb various elements from substrates, accumulate them in their aboveground and/or underground portions and, after dying off, return them to the upper layer of sediments, gradually transforming it.

A comparison of the concentrations of a wide range of elements accumulated by soils formed at different ash dumps, where the ash located at the depth has been influenced by only natural physicochemical processes for 50 years, showed that the differences between subjects are ambiguous. In subject 1, as a rule, they are usually insignificant (no more than

0.9%), but there is a clear tendency of increased Al, Fe, Ca and Mg at a depth of 30–50 cm (Figure 2Aa). Macronutrients such as K, Na and P are also relatively highly concentrated in the upper layer of the ash dump, processed by pedogenesis (Figure 2Ab). In subject 2, only Al and Na prevail in the dump ash at rates greater than their content in the soil, but this predominance is also not major (no more than 0.25%). It can be assessed as a tendency in the redistribution of macronutrients within the ash dump (Figure 2Ba,b). In both dumps, the silicon content is increased in the zone of plant influence (0–20 cm), which is usual for soils, as Si is involved in the construction of their structural element.

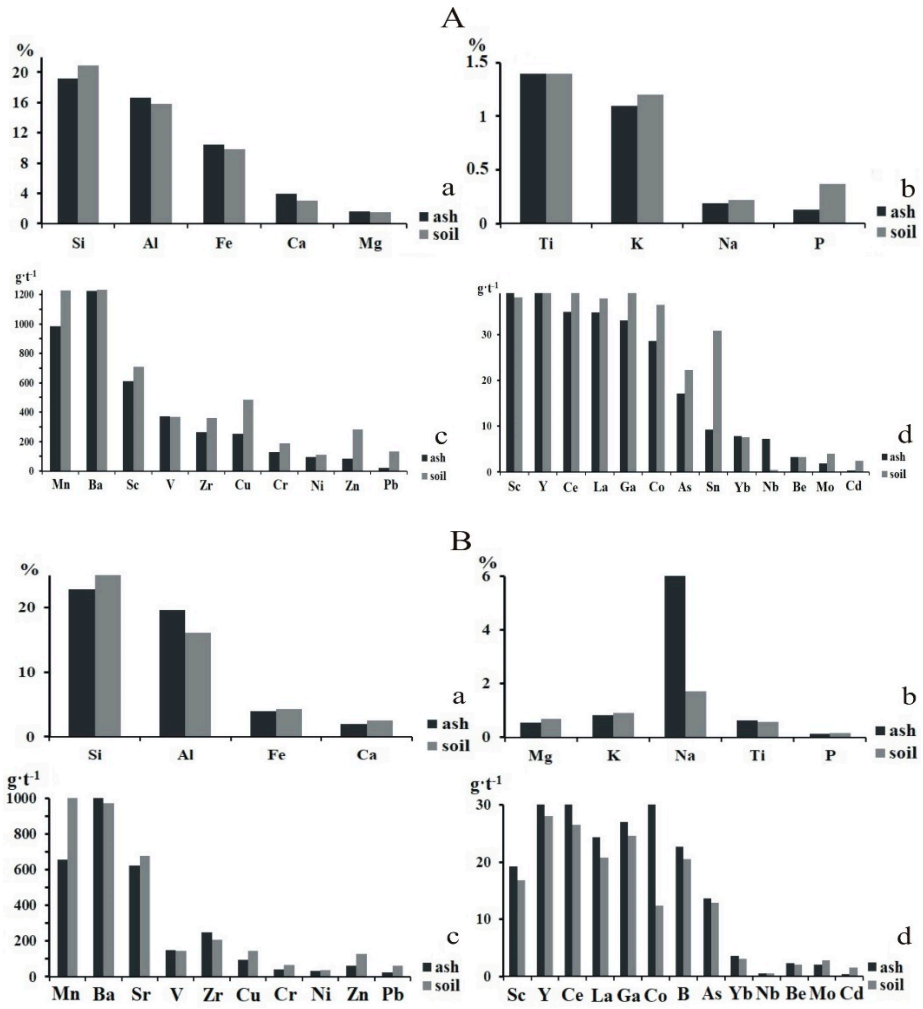

Figure 2. Content of elements in ash and soil of ash dumps: (**A**) VTTPP; (**B**) SUTPP. Legend: macroelements in ash dumps: (**a**) with high concentrations; (**b**) with low concentrations; trace elements in ash dumps; (**c**) with high concentrations; (**d**) with low concentrations.

The differences between ash and soil in terms of trace element composition (Figure 2ABc,d) are that at the VTTPP ash dump, all microelements except Sc, Yb and Nb significantly (although to varying degrees) prevail in the upper soil part of the ash dump. The most significant differences concern Pb and Cd (more than 6 times), as well as Zn and Sn (more than 3 times). The distribution of trace elements between the deep ash layer and the soil is more ambiguous at the SUTPP ash dump. Only 9 microelements out of 23 predominate in the soil; the rest in ash. Elements of the first hazard class, such as Cu, Zn, Pb, Cd, as well as toxic Cr, Ni and Mo, predominate in the soil. In the deep layer ash of the ash dump, in contrast to the soil, most rare elements have increased concentrations, in particular Sc, Y, Ce, La, Ga, Co, Yb, Be, as well as toxic As. Thus, the redistribution of toxic and other microelements between ash and soil is probably determined not only

due to vegetations' ability to absorb and accumulate various elements, including toxic ones, in the process of soil formation, but also by the initial properties of coals. To identify the role of soil formation in the redistribution of microelements throughout the thickness of ash dumps, an analysis of differences in the accumulation of elements in deep ash layers and soil in areas formed under meadow and forest communities was carried out (Figures 3 and 4).

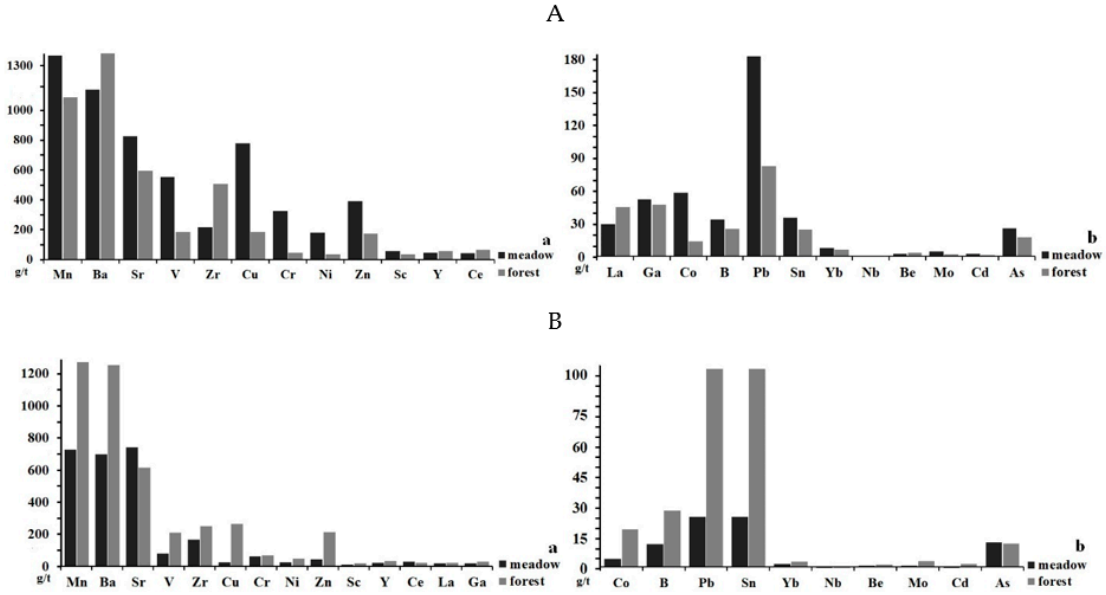

Figure 3. The content of elements in the soil of the ash dumps. (**A**) VTTPP; (**B**) SUTPP; Legend: (**a**) elements with high absolute concentrations; (**b**) elements with low absolute concentrations.

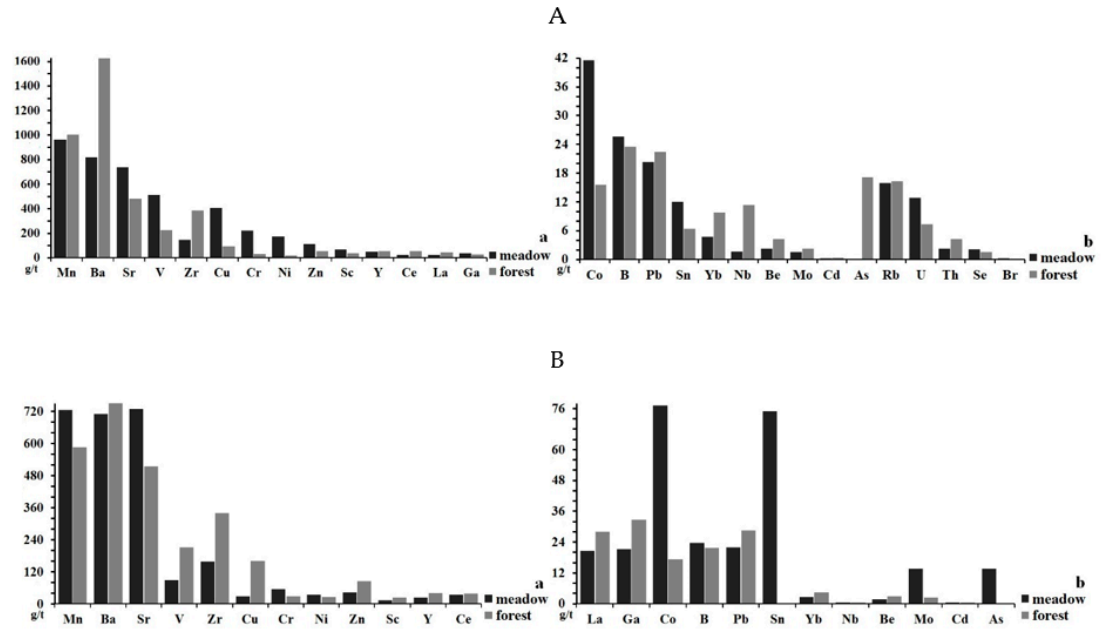

Figure 4. The content of microelements in the ash of the ash dumps. (**A**) VTTPP; (**B**) SUTPP; Legend: (**a**) elements with high absolute concentrations; (**b**) elements with low absolute concentrations.

The obtained data showed that only Sr accumulated in both meadow areas while the set of other elements with increased concentrations was significantly different. The ash of the first subject is characterized by higher concentrations of 15 more elements (Mn, V, Cu, Cr, Ni, Zn, Sc, Co, B, Pb, Sn, YB, Mo, Cd, As) in the meadow area, and of 8 elements (Ba, Zr,

Y, Ce, La, Ga, Nb, Be) in the forest area. The predominance of rare elements in the last set of elements is noteworthy in that the process of their accumulation is more pronounced in the forest. In the second subject, practically no elements accumulated in the meadow area soil (the predominance of three of them - Co, Nb, As - is insignificant), while in the forest area, the accumulation process is more strongly pronounced; the absolute majority of element content is increased in the soil mass.

The elemental composition of the underground and aboveground portions of plants was determined in order to understand the role that plant communities play in the transformation of fly ash through accumulative processes. Consider, as an example, the behavior in the soil/plant system at the VTTPP ash dump. The macro- and micro-elemental composition of the underground and aboveground portions of meadow and forest-dominated plants were analyzed. It was revealed (Table 5) that almost all trace elements (except boron) predominated in the underground portion of plants in ash dumps under meadows. The increased concentrations of most trace elements in the roots, relative to the aboveground portion of herbaceous plants, were noted by earlier researchers [46,50,52] and are confirmed by further early materials related to the VTPTT ash dump [53]. Elevated concentrations in the aboveground portions of forest plants (except B) were revealed for Cr, Zn and Ni. Due to the thick stem of woody plants, analyzed in the composition of the aboveground mass, Mn, Ba and B also prevail in the aboveground portions of the forest plants, except for the earlier mentioned elements. The situation related to the distribution of macro-elements between the aboveground and underground portions is more complicated and diverse. Only Al, Fe and Ca are more highly concentrated in the underground portions of plants (Table 5).

Table 5. Element contents and accumulation coefficients in the ash of aboveground and underground plant parts of the VTTPP ash dump.

Element	Meadow Plants				Forest Plants			
	Content		$K_{ac.}$		Content		$K_{ac.}$	
	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots
	Trace elements, $g \cdot t^{-1}$							
Mn	346	651	0.25	0.48	2038	1273	1.88	1.17
Ba	1156	1529	1.01	1.34	3236	2390	1.69	1.25
Sr	1305	1630	1.58	1.97	2219	1503	3.74	2.53
V	80	198	0.14	0.36	35	177	0.19	0.96
Zr	33	70	0.15	0.32	23	43	0.05	0.08
Cu	137	279	0.18	0.36	171	251	0.92	1.35
Cr	83	96	0.25	0.29	60	33	1.24	0.68
Ni	28	64	0.16	0.36	89	57	2.34	1.50
Zn	557	1155	1.42	2.94	4132	3265	23.86	18.85
Sc	3.39	11.6	0.06	0.20	1.7	7.2	0.05	0.20
Y	6.1	16.5	0.13	0.35	5.5	35	0.09	0.60
Ce	15	25	0.34	0.57	31	176	0.49	2.75
La	4.4	11.2	0.15	0.37	5.8	35	0.13	0.77
Ga	5.6	9.8	0.11	0.19	2.5	7.3	0.05	0.15
Co	5.1	13.2	0.09	0.23	8.6	19.5	0.61	1.37
B	242	218	7.08	6.37	484	369	18.69	14.25
Pb	135	198	0.74	1.08	551	555	6.65	6.69
Sn	124	383	3.43	10.58	24	30	0.95	1.19
Yb	0.69	2.09	0.08	0.25	0.46	3.12	0.07	0.45
Nb	0.32	0.34	1.07	1.13	0.25	0.28	0.42	0.47
Be	0.72	1.38	0.26	0.49	0.56	1.39	0.15	0.37
Mo	21	23	3.89	4.26	13	17	5.00	6.54
Cd	10.9	19.4	3.41	6.06	28.8	36.3	16.00	20.17

Table 5. *Cont.*

Element	Meadow Plants				Forest Plants			
	Content		$K_{ac.}$		Content		$K_{ac.}$	
	Shoots	Roots	Shoots	Roots	Shoots	Roots	Shoots	Roots
	Macroelements, $kg \cdot t^{-1}$							
Si	160.7	153.2	0.91	0.86	23.36	51.88	0.10	0.22
Al	10.58	19.88	0.07	0.13	7.85	20.93	0.05	0.12
Fe	9.59	16.93	0.07	0.13	5.44	14.15	0.08	0.21
Ca	136.6	153.9	2.81	3.17	21.06	162.4	1.73	13.37
Mg	27.26	22.91	1.13	0.95	43.93	31.38	8.09	5.78
K	119.0	45.68	7.20	2.76	134.3	135.5	18.06	18.22
Na	3.87	2.68	1.74	1.20	3.65	3.95	1.64	1.77
Ti	0.82	1.70	0.07	0.14	0.37	0.65	0.02	0.04
P	34.97	24.37	8.02	5.58	45.88	32.83	15.02	10.75

Plants in ash dumps are mostly associated with maintaining and changing their chemical composition in their upper layer. That is, in the situation under consideration, with a stratum transformed by the process of soil formation. We emphasize once again that as a result of this process, various macro- and micro-elements accumulate in the upper humus-accumulative thickness. Plants absorb these elements from the soil, and relevant to the macroelements, they usually absorb and accumulate nutrients from any substrates.

Comparing the concentrations of macro-and microelements in the ash of the aboveground and underground portions of plants with their content in the upper part of the ash dump (Technosols) allowed us to determine the accumulation coefficients ($K_{ac.}$) of each element and evaluate the process of their accumulation by plants, which along with leaching and migration of elements, participated in the transformation of fly ash for 50 years (Table 5). The highest accumulation coefficient in meadow plants, exceeding 6–7 units, was revealed only for boron, which accumulates in both the underground and aboveground plant portions, although its accumulation in the shoots is somewhat higher (K = 7.08 versus 6.37). The rest of the microelements have relatively high accumulation coefficients exclusively in the roots.

A different pattern is observed in the soil-plant system relationship in a forest community. Seven microelements (Mn, Ba, Sr, Cr, Zn, Ni and B) showed increased accumulation coefficient values both in the aboveground and underground portions of these plants, although they are higher in the shoots. Zn, B and Cd have very high accumulation coefficients, both in the aboveground and underground portions of meadow and forest plants, and Pb—only in the latter—(with $K_{ac.} > 6$). Thus, plants are actively involved in changing the chemical composition of ash dumps due to their ability to accumulate elements, depending on the conditions of the plant community formation.

A comparison of the levels of element content in both soil (the uppermost part of the ash dump) and in plants showed that some elements accumulate in the latter, which can eventually exceed the concentration in soils by up to 20–24 times. Toxic elements such as Zn, B and Cd, as well as biogenic elements K and P, accumulated most actively in the ash dump-studied plants. High concentrations in plants exceeding the soil element content by 2–5 times were detected for Sr, Ce, Sn, Mo, Ca and Mg.

Thus, the accumulation of elements in the soil in relation to ash and in plants relative to the soil of studied ash dumps is not unambiguous and very individual. This means that a wide study of local territory ash dumps with different combinations of formation conditions and functional duration is required to justify forecasts of possibly using fly ash as a secondary raw material.

4. Conclusions

For the first time, the study obtained material allowing for the investigation of the macro- and micro-elemental composition of fly ash at two ash dumps, formed after the

burning of high-ash brown coals from separate deposits with varying properties under the bioclimatic conditions in the Middle Urals southern taiga. They are influenced by their meadow and forest communities, formed and grew on their own for 50 years, and as a result, have numerous features that should be taken into account when monitoring ash dump conditions and, if necessary, fly ash processing or complete disposal.

Among the elements found in higher concentration in fly ash, the research has identified those associated with increased migration under taiga conditions (for example, Ba, Cd, Sr, V), as well as elements (Cu, Co, V, Zr) accumulated in the lower (illuvial) horizons of soils. These compounds could well affect the transformation of fly ash at depths of 30–50 cm, although it is outside the effect zone of the soil formation process and the influence of plant communities. Highly hazardous contaminants, such as As, Cd, Pb, Cu, Zn and hazardous B, Co, Mo and Cr, are identified in the ash composition at both ash dumps.

Comparing concentrations of the elements accumulated in the soil (0–20 cm) with fly ash at a 30–50 cm depth has shown that areas under meadows at both sites have presented higher accumulations solely of strontium. The remaining set of elevated element concentrations differs significantly; toxic heavy metals (V, Cu, Ni, Zn, Co, Pb, Sn, Mo, Cd) pre-dominate in meadows; rare elements (Zr, Y, Ce, La, Ga, Nb, Be) at forested sites. It is worth noting that the process of rare element accumulation in the forest is more pronounced.

Comparison of trace element concentrations in plants growing on ash dumps, with their content in the upper layer changed by the soil formation process, made it possible to assess the role plant communities play in transforming the fly ash due to processes of accumulation occurring under plant influence.

The calculated accumulation coefficients (Ac) of macro- and micro-elements in plants showed that boron, the highest coefficient, exceeded 6–7 units. In meadows, the clear majority of plants have higher Ac values for all elements (except boron) in their underground portions. In forests, increased Ac in the aboveground plant mass is revealed for only 7 elements (Mn, Ba, Sr, Cr, Zn, Ni and B). The rest are associated with plant roots.

The highest Ac, both in underground and aboveground plant portions, in meadows and forests, are revealed as Zn, B and Cd, also for Pb, Ac, which exceeds 6 units only for forest vegetation. Thus, plants have significant potential to accumulate toxic metals, which can reduce the toxic effect of fly ash and make it possible to adapt it for economic aims.

The considered material should serve as a basis for evaluating the feasibility of ash recycling and utilization at TPP dumps in the Middle Urals, along with other ash dumps situated in other regions of the southern taiga, and to develop methods for the most rational use of such areas.

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