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Peculiarities of Plant Mineral Composition in Semi-Desert Conditions

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Abstract: Plant–soil interactions in semi-desert conditions elicit the development of plant-specific adaptation strategies, including selective accumulation of macro- and microelements. Using an ICP-MS analysis of 12 plant species belonging to Asteraceae, Fabaceae, Poaceae, Ephedraceae, Amarantaceae, and Lamiaceae families of the Baskunchak Nature Reserve, remarkable species differences in accumulation of 22 macro- and microelements were recorded. The most common *Artemisia* species and Poaceae representatives belong to two different groups of plants with high content of Na, K, Zn, Cu, V and high antioxidant status and low Si typical for the former group and the opposite characteristics for the latter one. The mentioned phenomenon indicates two diverse powerful adaptation mechanisms based on the antioxidant defense and Si protection, respectively. The high frequency of remarkable levels of Se in plants with BCF exceeding 1 (*Glycyrrhiza aspera*, *Phlomis pungens*, *Tanacetum nullifolium*, *Helichrysum nogaicum*, and *Jurinea ewersmannii*), Zn in all species except *Poa angustifolia*, and Cu in the Asteraceae plants *Phlomis pungens* and *Kraschenninikovia ceratoides* suggests the significance of these elements in plant tolerance to environmental stresses. Plant–soil positive correlations were recorded for Sr ($r = 0.866$; $p < 0.001$); plant Sr, Fe, Co, Pb levels and soil salinity ($r = 0.763$, $p < 0.001$; $r = 0.606$, $p < 0.03$; $r = 0.627$, $p < 0.02$; $r = 0.548$, $p < 0.05$, respectively); and Cr only for Asteraceae species ($r = 0.986$, $p < 0.001$). The results obtained in this research may be used in plant adaptability evaluation in conditions of environmental stress.

Keywords: plant mineral elements; semi-desert environment; salinity; soils; adaptation

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1. Introduction

Plant adaptation to the environmental stresses is greatly connected with specific peculiarities of macro- and microelement content, as a defense strategy against stress factors, whose accumulation contributes to enhancing the antioxidant defense, physical and mechanical tissue properties, soil microbial activity, and root exudates [1–4].

The complexity of both stress factor impact and relationship between elements causes a high variability of plant defense mechanisms, affecting biodiversity and ecosystem integrity. In arid conditions, typical for North and South Africa, Asia, the Near East, and the Pacific shore of the North and South America, [5] unfavorable environmental factors include high insolation, temperature, and soil salinity; low organic matter content and soil fertility; and water deficiency and drought, which negatively influence plant growth and biodiversity in these regions [6].

High salt concentration toxicity is associated with the inhibition of plant growth and K accumulation, acceleration of plant senescence, and induction of water deficiency due to osmotic stress [7]. The interaction between sodium chloride and gypsum excess in semi-arid areas has specific effect on plant growth and development. Indeed, gypsum is known to reduce Na^+ uptake by plants, improve nutrient availability as well as physical and chemical properties of soil, and promote a balanced concentration of electrolytes in the soil solution [8,9]. In this respect, the complexity of semi-arid soil characteristics and the latter effect on plant growth and mineral composition are especially important, providing useful information about ecosystem sustainability and adaptation strategies of plants [5]. Element accumulation has been the focus of numerous studies of the plant–soil relationship in controlled experimental conditions [10]. Currently, the importance of essential and beneficial element supply to plants under stressful conditions is being intensively discussed [11,12]. Notably, among the mentioned elements, Se is beneficial in plant protection against all forms of oxidative stress, supporting plant growth and survival in extreme conditions, such as the semi-desert ones [13]. The regulation of K and Na adsorption from soil is reportedly crucial in drought and high-salinity conditions [14]. The participation of essential minerals, i.e., Fe Mn, Zn, and Cu in redox reactions and in the activity of certain enzymes is considered vital in plant adaptability [15]. Particularly, Zn improves plant antioxidant status and tolerance to drought and salinity [16], and vanadium [17] and Co [12] are beneficial for plant growth in stress conditions. Nevertheless, to date, the role of macro- and microelements in natural stress conditions hampering plant development has been poorly investigated.

Based on what is mentioned above, the Bogdinsko-Baskunchak Nature Reserve (BNR) provides an opportunity to evaluate the mineral composition of plants and soils at a semi-desert territory situated in the north-east of the Caspian lowland, Astrakhan region. The area is characterized by a significant soil complexity and salinity due to remarkable salt deposits in Baskunchak lake and an uneven soil relief. The Bogdinsko-Baskunchak Nature Reserve is situated at the western part of the Kazakhstan 'semi-desert' belt, with an evaporation rate typically exceeding the mean annual precipitation level (750–900 mm and 220–270 mm, respectively), the latter being in the range between the precipitation threshold and its half value, which is in accordance with the 'semi-arid' definition [18]. The sharp continental climate, with intensive seasonal temperature fluctuations (from −40 to +40 °C), frequent winds causing erosion, and water deficiency, leads to severe drought and uneven distribution of soil vegetation cover with the predominance of grasses and shrubs [19,20]. The territory is characterized by a thin humus horizon (7–15 cm), development of rinsing water regime with the soil profile wetting of about 50–80 cm and with low plant productivity. Such conditions induce a specific plant adaptation to the conditions of oxidative stress and promote particular plant–soil interactions.

Up to date, most investigations carried out at the territory of the Baskunchak Nature Reserve were predominantly descriptive and devoted to the evaluation of flora and fauna biodiversity and studies of the karst formation [21–24], while the information about mineral composition of soils and plants was extremely scant, thus hampering the creation of a general picture devoted to mineral composition of Basunchak plants and soils. At present, only the work of Diyanova [25] can be found in the literature, reporting high local levels of boron at the territory of the Reserve and indicating the high efficiency of ephedra utilization as a B bio-indicator. A comparison of element content in *Artemisia lerchiana*, *Diploschistes ocelatus* and higher mushrooms, and mineral composition of different groundwater samples makes it suppose the existence of areas with high Cr and Sr levels [26]. In 2022, the total amount of Fe, Mn, Cu, and Zn in five soil samples of the Bogdo mountain has been published [27] without evaluation of bioavailable forms of these elements.

Due to the exclusive characteristics of the Reserve territory (a UNESCO heritage) and the scant information related to the soil–plant mineral composition, the present study aimed to evaluate the peculiarities of macro- and microelement distribution between plants

and soils in this area and plant antioxidant status to record the data to connect with plant adaptability.

2. Material and Methods

2.1. Plant and Soil Sampling

The territory of the Baskunchak Nature Reserve (BNR) is situated in the north-eastern part of the Astrakhan region near the Baskunchak salt lake (Figure 1), with Gypsic Kastanozems, Endosalic Calcisols and Calcisols Sodic, Luvic Calcisols, and Solonets unevenly distributed across the territory [20,28]. The area of the present research is located in the desert steppe subzone, at the border between the steppe and desert zones [21].

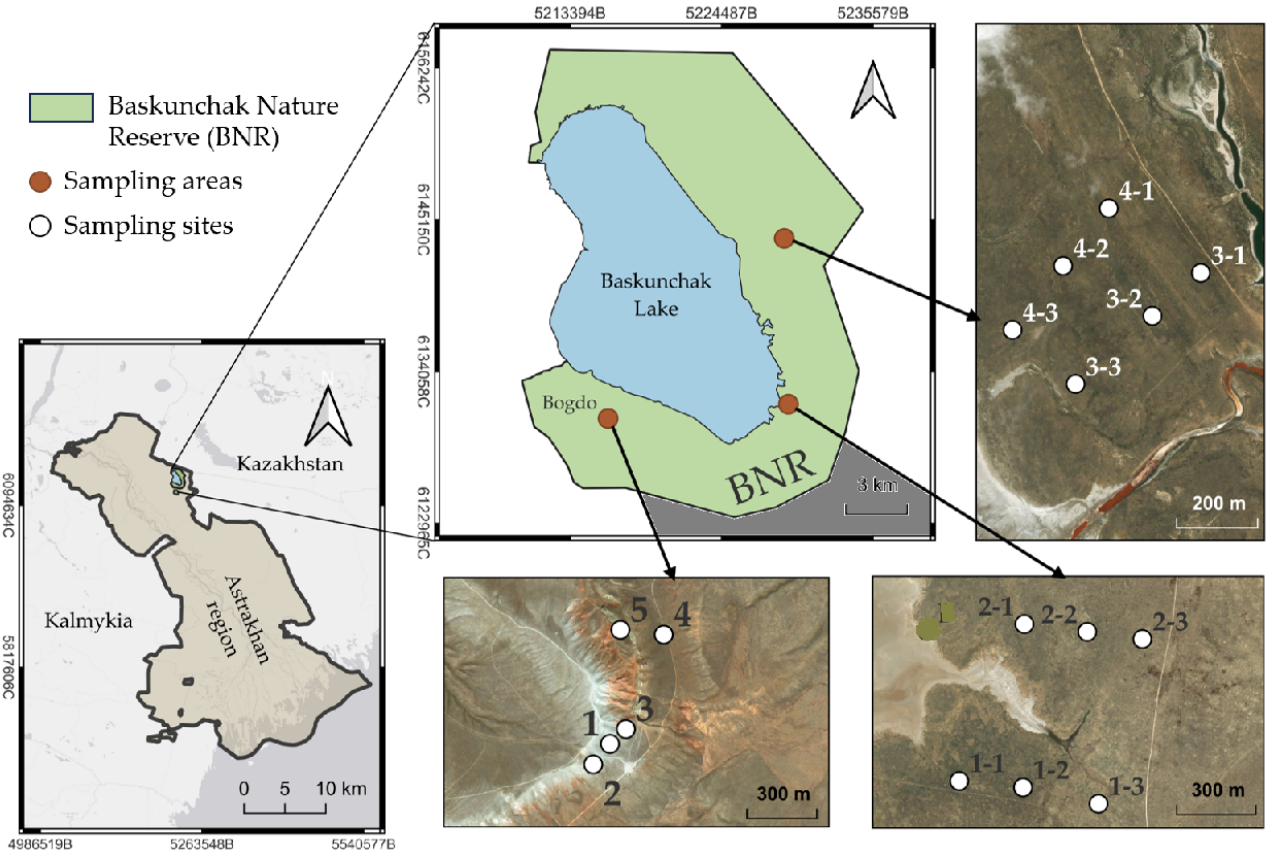

Figure 1. Sampling sites at the territory of the Bogdinsko-Baskunchak Nature Reserve. BNR: the Bogdinsko-Baskunchak Nature Reserve; Bogdo: the Big Bogdo mountain. The numbers indicate sampling places whose geographical coordinates are presented in Tables 1 and 2.

Soil and plant samples were collected during the period of active plant growth on 22–28 May 2021 and 2022, at the territory of the BNR and the Big Bogdo mountain.

The mean monthly temperatures and precipitation in 2021–2022 [29] are shown in Figure 2.

Due to both the restrictions of plant sampling at the territory of the Reserve and the need to maintain the integrity of the Reserve flora, only the aboveground parts of plants were used in this investigation. Samples of 8–10 plants per each of the 12 species investigated belonging to 6 families, i.e., Asteraceae (*Helichrysum mogaicum*, *Jurinea ewersmannii* Wge, *Artemisia Taurica*, and *Artemisia lerchiana*, *Tanacetum millefolium*), Fabaceae (*Glycyrrhiza aspera* and *Astragalus vulpinus*), Amaranthaceae (*Kraschenininkova ceratoides*), Poaceae (*Poa angustifolia*; *Eremopyrum orientale* (L.) Jaub. & Spach), Ephedraceae (*Ephedra distachya*), and Lamiaceae (*Phlomis pungens*), were gathered at the territory of the BNR and the Big Bogdo mountain (Table 1). All the Asteraceae representatives were collected at the Big Bogdo mountain, while Poaceae and Fabaceae plants were typical of the steppe zone of the

Reserve. All the investigated species are medicinal herbs belonging to a group of perennial plants, except the annual *Eremopyrum orientale*. Many of them, some also included in a list of the Red Book, have an important value due to their essential oils (*Artemisia lechiana and taurica*, *Helichrysum nogaicum*) and antioxidant properties. *Krascheninnikivia ceratoide*, *Eremopyrum orientale*, and *Poa bulbosa* are forage plants.

The geographical coordinates of plant sampling places of the Reserve were determined using GPS and are presented in Table 1.

Plant identification was carried out using the Vascular Plant Guidelines of the Bogdinsko-Baskunchak Nature Reserve [30]. Samples of plants belonging to each species were combined, cut into small pieces, and dried in the shadow at 20 °C to constant weight to minimize Se losses [31], after which dried samples were homogenized. The resulting powder was used for the determination of the plant mineral profile and antioxidant status.

To determine the peculiarities of mineral distribution along the territory of the Baskunchak Nature Reserve and evaluate the plant–soil interactions, 17 samples of soil were gathered (Table 2).

Within each area, about 1 kg of soil was collected at three different locations at the depth of 0–30 cm, air-dried, homogenized, and sieved by a 2 mm sieve. The combined soil samples taken from each location, representing a mixed sample of a given area, were used for the analysis.

Table 1. Geographical coordinates of plant sampling at the territory of the Baskunchak Nature Reserve and Big Bogdo mountain.

Family	Species	Geographical Coordinates	Localization
Fabaceae	*Glycyrrhiza aspera* L.	48.150717° N; 46.967740° E	The BNR
	Astragalus vulpinus L.	48.133747° N; 46.867745° E	
Poaceae	*Eremopyrum orientale* (L) Jaub. & Spach.	48.217313° N; 46.967313° E	The BNR
	Poa bulbosa L.	48.217313° N; 46.967313° E	
Ephedraceae	*Ephedra distachya* L.evergreen shrub	48.217253° N; 46.967485° E	The BNR
Asteraceae	*Artemisia lerchiana* L.	48.150092° N; 46.967537° E	The Big Bogdo
	Helichrysum nogaicum L.	48.233294° N; 47.418230° E	
	Jurinea ewersmannii Wge L.	48.233323° N; 47.418613° E	
	Artemisia taurica L.	48.233323° N; 47.418613° E	
	Tanacetum millefolium L.	48.233614° N; 47.4189612° E	
Lamiaceae	*Phlomis pungens* Wielld. L.	48.233606° N; 47.4218278° E	The Big Bogdo
Amaranthaceae	*Krascheninnikovia ceratoides* L.	48.233167° N; 47.418166° E	The Big Bogdo

Table 2. Geographical coordinates of soil-sampling places at the territory of the Baskunchak Nature Reserve and the Big Bogdo mountain.

Steppe Zone of the Baskunchak Nature Reserve		The Big Bogdo Mountain	
No. on the Map *	**Geographical Coordinates**	**No. on the Map ***	**Geographical Coordinates**
1-1	48°08′46″7 N; 46°58′20″0 E	1	48°14′10″65 N; 46° 85′69″96 E
1-2	48°08′46″2 N; 46°58′31″6 E	2	48°14′17″63 N; 46°85′73″79 E
1-3	48°08′44″8 N; 46°58′44″7 E	3	48°14′19″4 N; 46°85′96″8 E
2-1	48°09′05″5 N; 46°58′32″2 E	4	48°14′36″87 N; 46°85′96″71 E
2-2	48°09′04″3 N; 46°58′44″1 E	5	48°14′36″36 N; 46°85′76″67 E
2-3	48°09′03″0 N; 46°58′53″4 E		
3-1	48°13′18″2 N; 46°58′34″8 E		
3-2	48°13′15″2 N; 46°58′29″1 E		
3-3	48°13′09″9 N; 46°58′19″7 E		
4-1	48°13′22″9 N; 46°58′24″3 E		
4-2	48°13′18″8 N; 46°58′18″8 E		
4-3	48°13′13″7 N; 46°58′13″0 E		

* See Figure 1.

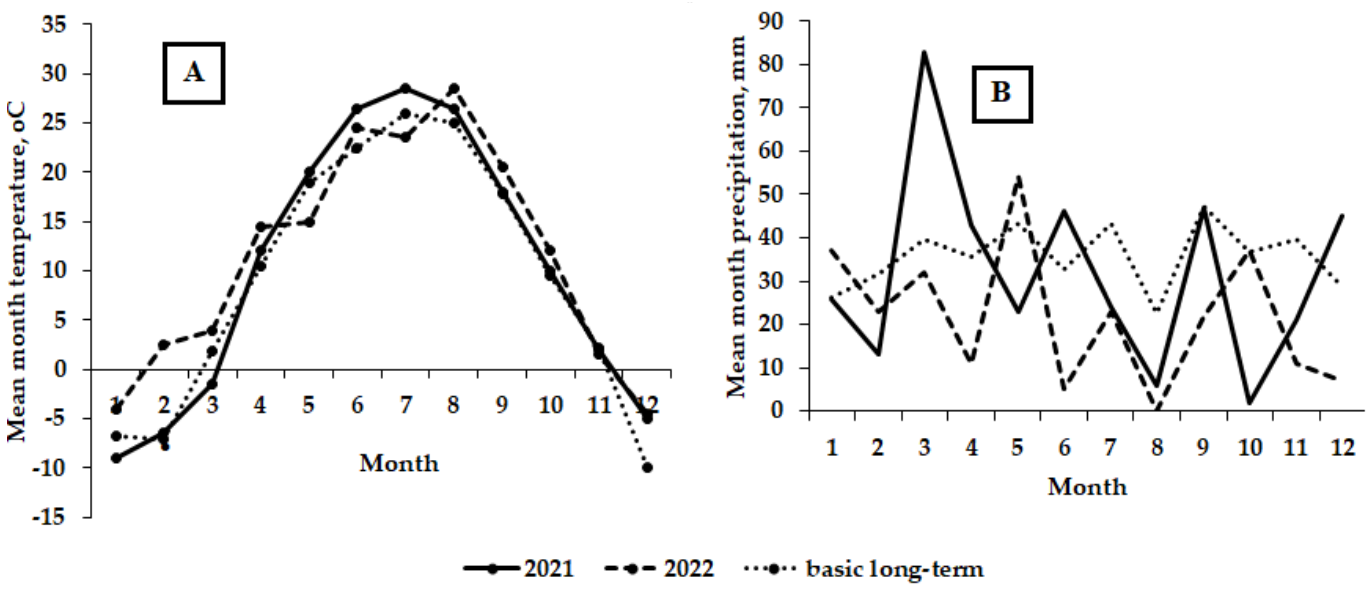

Figure 2. Mean monthly temperature (**A**) and precipitation (**B**) in 2021–2022, compared to the basic long-term values.

2.2. Plant Elemental Composition

The determination of element contents (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Si, Sn, Sr, V, and Zn) in plants was conducted in triplicate on the dried, homogenized, mixed samples of each species investigated, using the ICP-MS on a Nexion 300D quadruple mass-spectrometer (Perkin Elmer Inc., Shelton, CT, USA), equipped with a seven-port FAST valve and an ESI SC DX4 autosampler (Elemental Scientific Inc., Omaha, NE, USA). Microwave digestion of the samples was carried out with sub-boiled HNO_3, diluted at a ratio of 1:150 with distilled deionized water (Fluka No. 02, 650 Sigma-Aldrich, Co., St. Louis, MO, USA) in a Berghof SW-4 DAP-40 microwave system (Berghof Products + Instruments Gmb H, 72, 800 Eningen, Germany). Rhodium 103 Rh was used as an internal standard to eliminate instability during the measurements. Quantitation was performed using external standards (Merck IV, multi-element standard solution); the Perkin–Elmer standard solutions for P and V, and all the standard curves, were obtained at five different concentrations. Trace levels of Hg and Sn in the samples were not taken into account, and accordingly, these elements were not included in the tables.

2.3. Elemental Composition in Soils

The content of elements (Fe, Mn, Cu, Zn, Pb, Sr, Cr) in soils, bioavailable to plants, was determined by Atomic Absorption Spectrometry (AAS) using a Shimadzu GFA-7000 spectrophotometer (Shimadzu, Kioto, Japan) after extraction of soils by 3% nitric acid (1:5 ratio).

2.4. Selenium

Plant Se was analyzed using a fluorimetric method previously described for tissues and biological fluids [32]. Dried homogenized samples were digested via heating with a mixture of nitric and perchloric acids, subsequent reduction in selenate (Se^{+6}) to selenite (Se^{+4}) with a solution of 6 N HCl, and the formation of a complex between Se^{+4} and 2,3-diaminonaphtalene in the presence of 1.25% EDTA solution. The calculation of the Se concentration was performed by recording the piazoselenol fluorescence value in hexane at 519 nm λ emission and 376 nm λ excitation. Each determination was performed in triplicate. The precision of the results was verified using the Mitsuba reference standard of Se-fortified stem powder in each determination, with a Se concentration of 1865 μg kg^{-1} (Federal Scientific Vegetable Center).

Soil Se content was determined analogously using 10% EDTA solution to exclude the effect of other elements on the results of Se analysis. Soil taken at the experimental fields of the Federal Scientific Vegetable Center with Se content of 240 μg kg^{-1} d.w. was used as an external standard.

2.5. Bio Concentration Factor (BCF)

To evaluate the intensity of element accumulation in plants, a Bio Concentration Factor (BCF) was calculated using the following formula:

$$BCF = [Metal]_{shoot}/[Metal]_{soil}$$

2.6. Soil Salinity (TSS)

A five-fold amount of pre-boiled distilled water was added to a sample of soil sieved through 1–2 mm diameter holes, and the mixture was stirred intensively for 5 min. The total soluble salts were measured gravimetrically via evaporation of a soil water extract (TSS) [33].

2.7. Electrical Conductivity (EC)

To assess the soil electrical conductivity (EC), a leaching solution of 1:5 soil–water ratio was prepared [34], and the parameter was determined using a portable conductometer TDS-3 (HM Digital, Seoul, Republic of Korea).

2.8. pH

The soil pH was measured in the soil–water extract (1:5) using a pH meter Expert-0.01 (Econix Expert Co, Moscow, Russia). The precision of the determination was 0.03.

2.9. Total Polyphenols (TP)

Total polyphenols were determined in 70% ethanol extracts of dried-plant samples using a Folin–Ciocâlteu colorimetric method as previously described [35]. Half a gram of dry homogenates was extracted with 20 mL of 70% ethanol/water at 80 °C for 1 h. The mixture was cooled down and quantitatively transferred to a volumetric flask, and the volume was adjusted to 25 mL. Then, it was filtered through filter paper, and 1 mL of the resulting solution was transferred to a 25 mL volumetric flask, to which 2.5 mL of saturated Na_2CO_3 solution and 0.25 mL of the diluted (1:1) Folin–Ciocâlteu reagent were added. The volume was brought to 25 mL with distilled water. One hour later, the solutions were analyzed with a spectrophotometer (Unico 2804 UV, Suite E, Dayton, NJ, USA), and the concentration of polyphenols was calculated according to the absorption of the reaction mixture at 730 nm. As an external standard, 0.02% gallic acid was used. The results were expressed as mg of gallic acid equivalent per g of dry weight (mg GAE g^{-1} d.w.).

2.10. Antioxidant Activity (AOA)

The antioxidant activity of plant leaf homogenates was assessed on 70% ethanolic extracts of the dry samples using a redox titration method [35]. The values were expressed in mg gallic acid equivalents (mg GAE g^{-1} d.w.).

2.11. Statistical Analysis

The presented results are the mean values of three replicates of each sample. The data were processed by analysis of variance (ANOVA) and Principal Component Analysis (PCA), and mean separations were performed through Duncan's multiple range test, with reference to the 0.05 probability level, using SPSS software version 28.

3. Results and Discussion

3.1. Soils

The comparison was performed between a steppe zone (BNR) and the Big Bogdo mountain. The latter is the only peak at the Caspian lowland situated in the close vicinity of the salt-lake, is characterized by outcrops of rocks from the Triassic period (the period of the mountain formation), and is the edge of a constantly growing (about 1 mm per year) salt dome covered by sandstones, lime stones, and clay, whose height does not exceed 150 m [36].

High soil variability, low organic matter content (humus concentration is 0.66–1.45%), and the presence of easily soluble salts and gypsum are typical for this area [27,29].

Soil alkalinity (pH > 7.5) is characteristic of arid and semi-arid regions, and highly calcareous soils. High soil pH creates the conditions of decreased heavy metals accumulation affecting solubility, bioavailability, and translocation [36]. High pH levels are known to be beneficial for trace element absorption [37], encouraging their higher bioavailability, compared to acidic soil conditions [36], also referring to soil Se [37].

According to the analysis, the mean pH was significantly higher (9.4) at the Big Bogdo mountain compared to most of the BNR parts (8.1). The coefficients of variation of this parameter did not exceed 5% within each territory (Supplement Table S1).

On the contrary, variations in soil salinity at the territory were much greater: from 0.280 to 0.980 g kg^{-1} at Big Bogdo mountain up to 0.223–5.652 g kg^{-1} at the BNR area (Table 3).

Table 3. Mean concentrations of soil bioavailable elements (mg kg^{-1} d.w.), total dissolved solids (mg kg^{-1} d.w.), and electric conductivity (μS cm^{-1}) at the territory of the Baskunchak Nature Reserve.

	BNR			Big Bogdo		
	M ± SD	**Concentration Range**	**CV%**	**M ± SD**	**Concentration Range**	**CV%**
Cu	5.0 ± 0.7 a	4.0–6.3	14.0	1.7 ± 1.2 b	1.0–3.9	70.6
Zn	10.4 ± 1.2 a	8.2–12.5	11.5	3.3 ± 1.4 b	1.9–5.2	42.4
Fe	218.5 ± 58.4a	119.2–255.1	26.7	150.8 ± 106.4 ab	119.2–284.3	70.6
Mn	53.7 ± 10.9 a	33.5–67.7	20.3	80.1 ± 26.9 a	49.1–115.1	33.6
Cr	7.5 ± 1.7 b	5.0–9.9	21.8	0.78 ± 0.42 d	0.10–1.19	53.8
Sr	14.3 ± 3.9 a	10.10–20.43	27.3	4.9 ± 3.3 b	2.11–10.10	67.3
Pb	0.130 ± 0.04 c	0.074–0.212	30.8	3.937 ± 2.694 a	2.104–7.911	68.4
Se	0.542 ± 0.114 b	0.354–0.724	21.0	0.105 ± 0.020 c	0.079–0.123	19.0
TSS	1358 ± 1877 b	223–5652	138.2	568 ± 297.5 c	280–980	52.4
EC	550.5 ± 743.9 b	94.6–1998	135.1	223.2 ± 116.9 b	110–385	52.3

EC: electric conductivity; TSS: total dissolved solids. Within each line, values with the same letters do not differ statistically according to Duncan test at $p < 0.05$.

The analysis of acid-soluble mineral content also revealed high variations in soil Cu, Zn, Fe, Cr, Sr, and Pb levels, especially remarkable at the Big Bogdo mountain (CV = 33.6–70.6%), less pronounced at the territory of the BNR (CV 11.5–30.8%) (Supplement Table S2). The complexity of soil relief of the Big Bogdo mountain indicates the uneven distributions of mineral elements (Supplement Table S2).

Overall, the elemental analysis of 17 soil samples revealed the existence of several highly significant correlations between Zn, Cu, Se, Cr, Pb, and Mn ($p < 0.001$) (Table 4). Similar significant Zn, Cu, and Cr correlations were previously recorded in different urban soils of Belgrade using acid extraction of the elements [38].

The results express only the peculiarities of reactive soluble elements, providing the opportunity to evaluate the element amounts potentially available for plant absorption [39,40]. A diluted nitric acid extraction used in the present investigation was adopted as a standard to extract geochemically reactive elements in soil, allowing for excluding the inert fraction incorporated in minerals, organic matter, and oxides [39]. The obtained reactive concen-

trations are considered "potentially available" for plants [40], reflecting their geochemical association in soils and sediment-forming minerals.

The obtained data indicate that negative correlations were recorded only between Pb and Zn, Cr, Se, and between Mn and Zn, Cr, Cu, and Sr. No significant correlations between the analyzed elements and soil salinity were recorded (Table 4).

Table 4. Correlations between elements in soils at the Baskunchak Nature Reserve (n = 17).

	Zn	Fe	Mn	Cr	Sr	Pb	TSS	Se
Cu	**0.854 a**	0.412	**−0.673 b**	**0.775 a**	**0.857 a**	**−0.468 e**	0.195	**0.727 a**
	Zn	0.418	**−0.535 d**	**0.822 a**	**0.805 a**	**−0.754 a**	0.221	**0.683 a**
		Fe	−0.144	0.433	0.139	−0.138	0.263	0.322
			Mn	**−0.599 c**	**−0.689 a**	0.190	−0.119	**−0.539 d**
				Cr	**0.732 a**	**−0.765 a**	0.241	**0.842 a**
					Sr	−0.408	0.219	**0.719 a**
						Pb	−0.209	**−0.750 a**
							TSS	0.178

The significant correlations are indicated by bold letters, corresponding to 'p' lower than: (a) 0.001, (b) 0.002, (c) 0.01, (d) 0.02, (e) 0.05.

3.2. Plants

To date, 588 higher vascular plant species belonging to 77 families have been identified at the Baskunchak Nature Reserve [41]. The main territory of the Reserve is occupied by wormwood desert and fescue-feather grass steppes. Among the species inhabiting the Baskunchak Nature Reserve territory, representatives of Asteraceae, Poaceae, Fabaceae, and Lamiaceae families account for 14.6, 10.0, 6.0, and 3.1% out of the total identified species [30]. Due to low precipitation levels (Figure 2) and intensive fluctuations of temperature, most plants inhabiting the Baskunchak Nature Reserve show extremely short periods of active growth and development. Therefore, the obtained results refer to the end-of-May period, corresponding to the highest increase in biomass for most grasses. Notably, the studied area is characterized by widespread pterophitic and psammophitic plants that are able to survive in sandy and stony soils due to a powerful root system. They are characterized by small aerial extensions and limited height. Slow-growing taproot turfy herbaceous plants and subshrubs and small-turf grasses predominate.

Plant resistance to stresses greatly depends on genetic peculiarities, nutrient availability, antioxidant status, and hormonal regulation [42]. The elemental analysis of the Baskunchak Nature Reserve plant collection showed high species variability of the content of macro- (Table 5), toxic (Table 6), and microelements (Table 7), suggesting different strategies of plant defense against environmental hazards.

Among the species examined, two contrasting groups of plants can be indicated: *Artemisia* representatives, and plants belonging to Poaceae family. Indeed, while *A. taurica* and *A. lerchiana* accumulated the highest levels of ash and minerals including Na, K, Al, Ni, V, Cu, Zn, and the lowest of Si, Poaceae species showed an opposite frame. Particularly, ash, K, Ni, V, Cu, and Zn levels in Poaceae plants were 2–10 times lower than in wormwood, whereas a 25–32 times lower sodium concentration and 14–30 times higher Si one were recorded.

Furthermore, the highest antioxidant status was typical for Asteraceae plants and the lowest for Poaceae species (Figure 3). In this respect, *Artemisia* species may be considered as an appropriate example of plants with powerful antioxidant defense strategy provided by secondary metabolites (polyphenols, essential oil) and minerals. Indeed, the ability of these plants to accumulate high concentrations of potassium makes it easy to tolerate high salinity and high Na levels, activate enzymes, promote the rapid accumulation of carbohydrates, and improve osmoregulation and water transport, protecting against oxidative stress via the induction of the secondary metabolite synthesis, particularly polyphenols [43]. It is worth mentioning that among the examined plant species, *A. taurica* and *A. lerchiana* showed

an unusual ability to accumulate high levels of Na, contrary to the root salt exclusion mechanism especially typical for most of halophytes and Poaceae representatives [44]. Low levels of Na in other Baskunchak plants may also relate to the ability of halophytes to secrete salt via salt gland [44], as previously reported in several *Artemisia* species [45] and *Eremopyrum orientale*, belonging to Poaceae family [46].

Table 5. Ash and macroelement accumulation in plants grown at the territory of the Baskunchak Nature Reserve (mg kg^{-1} d.w.).

Species	Ash (%)	Ca	K	Mg	Na	P
1	4.52 a	8542 bc	26.824 a	2751 b	4319 a	2770 d
2	3.91 a	9728 b	22306 ab	1815 cd	3357 b	1938 e
3	3.10 bc	7790 c	15945 c	2113 c	1427 c	3713 ab
4	2.71 c	5823 d	15601 c	1612 de	162 e	3886 a
5	2.62 c	11192 a	8550 e	3949 a	164 e	2383 de
6	3.54 b	6070 d	21209 b	4120 a	94.5 g	3913 a
7	2.03 d	6708 d	8940 de	1516 e	56.7 h	3040 cd
8	2.06 d	5818 d	9988 d	989 g	411 d	3435 bc
9	1.91 d	6533 d	8190 e	2057 c	107 g	2184 e
10	1.89 d	9507 b	4935 g	1233 f	32.6 k	2397 de
11	1.82 d	3102 e	10118 d	855 h	134 f	3716 ab
12	1.08 e	1871 f	6202 f	574 k	136 f	2012 e

Asteraceae: 1—*Artemisia taurica*; 2—*Artemisia lerchiana*; 3—*Tanacetum millefolium*; 4—*Helichrysum nogaicum*; 5—*Jurinea ewersmannii* Wge. Amaranthaceae: 6—*Kraschenninnikova ceratoides*. Fabaceae: 7—*Glycyrrhiza aspera*; 8—*Astragalus vulpinus*. Lamiaceae: 9—*Phlomis pungens*. Ephedraceae: 10—*Ephedra distachya*. Poaceae: 11—*Eremopyrum orientale*; 12—*Poa bulbosa*. Within each column, values with the same letters do not differ statistically according to the Duncan's test at $p < 0.05$.

Table 6. Al, As, and heavy element accumulation in plants grown at the territory of the Baskunchak Nature Reserve (mg kg^{-1} d.w.).

Species	Al	As	Cd	Cr	Ni	Pb	Sr	V
1	148 c	0.110 d	0.100 cd	0.56 de	3.57 a	0.28 cd	42.4 c	1.07 b
2	346 a	0.200 b	0.120 c	1.10 b	3.03 ab	0.62 a	48.14 c	2.69 a
3	92.4 d	0.140 c	0.190 b	0.65 d	1.65 c	0.52 a	31.8 d	0.51 d
4	60.0 e	0.100 d	0.380 a	0.50 e	1.11 e	0.38 b	17.2 f	0.26 f
5	80.3 d	0.340 a	0.089 d	0.57 de	1.31 d	0.30 c	49.8 c	0.34 e
6	33.2 g	0.042 f	0.200 b	0.29 g	1.81 c	0.15 f	21.1 e	0.14 g
7	35.6 g	0.038 g	0.007 f	0.35 f	2.83 b	0.12 g	45.3 c	0.14 g
8	47.5 f	0.053 f	0.320 a	0.36 f	1.67 c	0.28 cd	61.3 b	0.15 g
9	50.4 ef	0.200 b	0.0093 d	2.20 a	0.66 f	0.33 b c	24.0 e	0.30 ef
10	190 b	0.170 b	0.100 d	0.99 b	1.35 d	0.57 a	99.6 a	0.79 c
11	55.8e	0.075 e	0.100 d	0.81 c	1.21 de	0.24 d	46.4 c	0.32 e
12	35.8 g	0.049 f	0.010 e	0.56 de	0.79 f	0.18 e	25.2 e	0.14 g

Asteraceae: 1—*Artemisia taurica*; 2—*Artemisia lerchiana*; 3—*Tanacetum millefolium*; 4—*Helichrysum nogaicum*; 5—*Jurinea ewersmannii* Wge; Amaranthaceae: 6—*Kraschenninnikova ceratoides*; Fabaceae: 7—*Glycyrrhiza aspera*; 8—*Astragalus vulpinus*; Lamiaceae: 9—*Phlomis pungens*; Ephedraceae: 10—*Ephedra distachya*; Poaceae: 11—*Eremopyrum orientale*; 12—*Poa bulbosa*. Within each column, values with the same letters do not differ statistically according to Duncan test at $p < 0.05$.

Furthermore, high levels of Cu and Zn in *Artemisia* species indicate the importance of these microelements in plant adaptability due to the participation of these elements in various redox reactions and antioxidant enzymes [15]. Particularly, Zn is an essential element participating in plant development, antioxidant status, and tolerance to drought and salinity [16], being a cofactor of many enzymes, such as Zn-superoxide dismutase, carboxypeptidase, and carbonic anhydrase. Increased plant ability to accumulate high concentrations of Zn may also relate to plant exudates, containing organic acids, phenolics, carbohydrates, amino acids, sugars, and polysaccharides, which are able to decrease pH and

improve Zn extraction ability [47]. Moreover, benefits to plant growth in stress conditions have been reported with reference to V [17] and Ni [48].

Table 7. Microelement accumulation in plants grown at the territory of the Baskunchak Nature Reserve.

Species	B	Co	Cu	Fe	Li	Mn	Mo	Se	Si	Zn
1	32.76 b	0.13 c	15.19 a	185 b	0.94 b	43.94 c	0.37 b	0.08 c	8.54 h	26.4 b
2	32.76 b	0.13 cd	15.19 a	185 b	0.94 b	43.94 c	0.37 b	0.08 c	10.06 h	33.2 a
3	25.60 c	0.17 b	5.73 c	215 b	0.33 c	76.7 a	0.13 d	0.29 b	127 b	16.1 d
4	45.22 a	0.14 c	5.19 c	185 c	0.25 d	57.9 b	0.18 c	0.36 a	18.6 e	14.1 e
5	31.50 b	0.17 b	9.32 b	217 b	2.01 a	41.5 c	0.54 a	0.28 b	16.7 ef	14.0 e
6	30.8 bc	0.12 d	4.51 ab	96.5 cd	0.18 c	35.6 a	0.17 e	0.36 b	13.9 g	19.1 c
7	36.10 b	0.06 f	4.24 ab	115 c	0.10 d	26.0 b	0.21d	1.15 a	15.5 fg	11.9 g
8	33.40 b	0.09 e	4.52 ab	118 c	0.48 a	19.1 c	0.96 a	0.34 bc	16.2 e	13.8 ef
9	20.90 d	0.10 e	4.45 d	193 b	0.11 e	12.6 d	0.12 e	0.30 ab	53.8 c	7.3 h
10	12.30 e	0.28 a	2.36 c	439 a	0.35 b	32.5 a	0.09 f	0.25 d	27.4 d	13.7 ef
11	13.20 e	0.14 c	3.75 b	141 b	0.33 b	40.6 a	0.55 b	0.26 d	255 a	12.6 fg
12	6.06 f	0.07 f	2.22 c	82.1 d	0.11 d	39.9 a	0.38 c	0.29 cd	119 b	7.8 h

Asteraceae: 1—*Artemisia taurica*; 2—*Artemisia lerchiana*; 3—*Tanacetum millefolium*; 4—*Helichrysum nogaicum*; 5—*Jurinea ewersmannii* Wge. Amaranthaceae: 6—*Krascheninnikova ceratoides*. Fabaceae: 7—*Glycyrrhiza aspera*; 8—*Astragalus vulpinus*. Lamiaceae: 9—*Phlomis pungens*. Ephedraceae: 10—*Ephedra distachya*. Poaceae: 11—*Eremopyrum orientale*; 12—*Poa bulbosa*. Within each column, values with the same letters do not differ statistically according to the Duncan's test at $p < 0.05$.

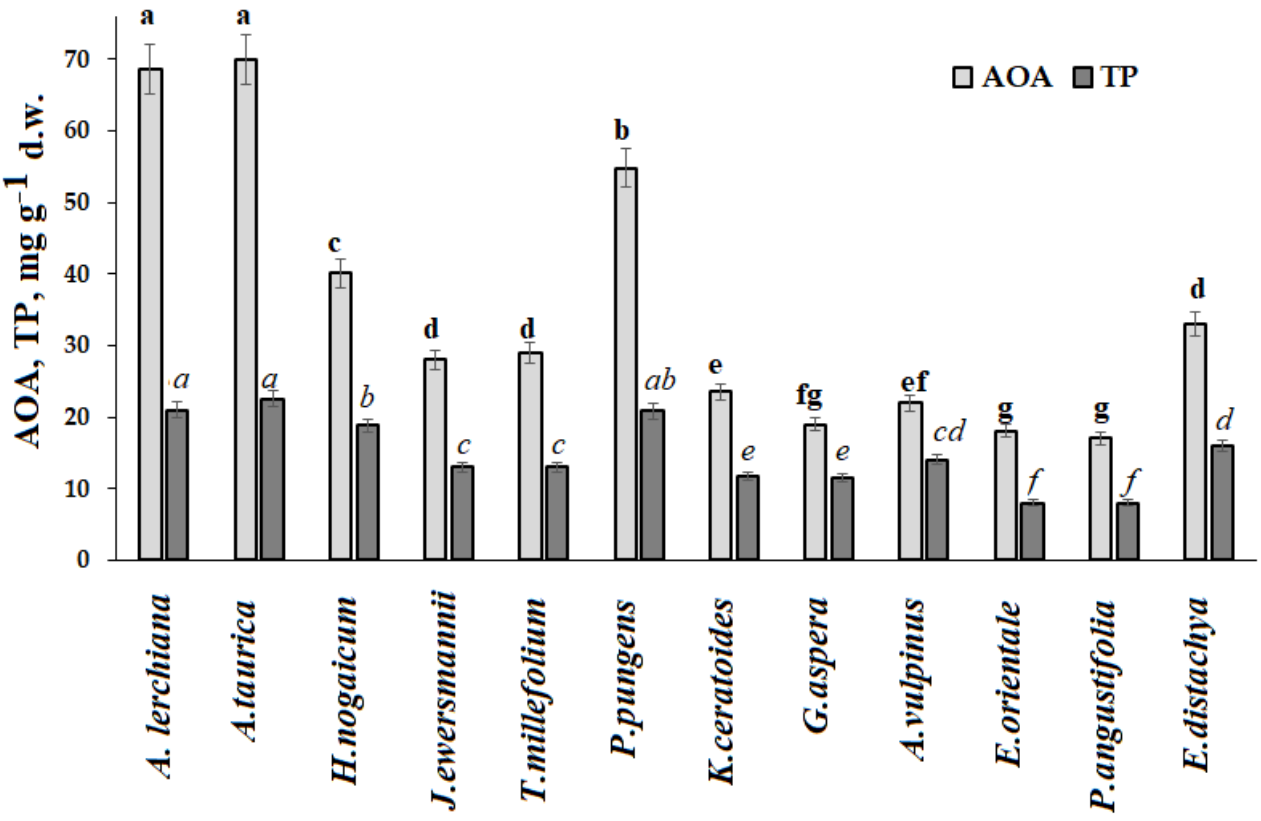

Figure 3. Antioxidant activity (AOA) and polyphenol content (TP) in plants of the Baskunchak Nature Reserve. For each parameter, values with the same letters do not differ statistically according to Duncan's test at $p < 0.05$.

The high occurrence of Poaceae plants at the territory of the Baskunchak Nature Reserve indirectly indicates their high adaptability based on a different strategy. Indeed, these species show an exclusion mechanism that prevents the accumulation of Na and

toxic elements in the aboveground part of plants [49]. *Poa angustifolia* and *E. orientale* demonstrated the ability to avoid the absorption of many elements (Na, V, Ni, Al, Zn, Cu, Mn, B, Li, Fe, Cu, Co), which is consistent with the known adaptation feature of Poaceae representatives [50,51]. However, the most typical skill of Poaceae plants is their ability to accumulate high levels of silicon. The latter element is known to enhance growth, photosynthesis and carbon assimilation, phytohormone biosynthesis, and plant tolerance to environmental stresses, including drought, high salinity, extreme temperature and insolation, nutrient deficiency and metal toxicity, and pathogen and herbivory attack [52]. Morphological changes caused by SiO_2 deposition improve stem rigidity and leaf erectness of plants [53].

It is worth mentioning that neither *Artemisia* species nor Poaceae representatives accumulate significant amounts of the powerful natural antioxidant Se [37]. Contrarily, about 50% of the tested plants had significant concentrations of this element, which may participate in plant adaptability to stress conditions. The latter protection mechanism could involve plant species belonging to the Fabaceae family, such as *J. ewersmannii*, *H. nogaicum*, *T. millefolium*, *P. pungens*, and *K. ceratoides*, with relatively high Se levels (Table 7).

More complex adaptability mechanisms may take place in other plant species. Indeed, high antioxidant activity was recorded in *H. nogaicum*, *P. pungens*, and *E. distachya*. *Tanacetum millefolium* showed high Si content. *Jurinea ewersmannii* Wge accumulated unusually high levels of Ca. *Ephedra* displayed rather high antioxidant status (Figure 3) and accumulated the highest levels of Co, Fe, Pb, and Sr and the lowest of Mo, K, Na, and Cu. Contrary to literature reports [25], *Ephedra* was not among the plants with high B accumulation at the territory of the Baskunchak Nature Reserve. According to literature reports, *E. intermedia* also demonstrated a high ability to accumulate Sr and Fe [54].

Both the Fabaceae species studied accumulated extremely low concentrations of V in leaves. The latter fact is not in contrast with V participation in nitrogen fixation via V-dependent nitrogenases of legumes, as the process proceeds exclusively in roots.

High pH and low heavy metal contents in soils result in low concentrations of the latter in the Baskunchak plants (Table 6). Nevertheless, among toxic elements, Al mostly accumulated in Asteraceae representatives and *Ephedra distachya.* Arsenic predominated in Asteraceae plants, including *Phlomis pungens* and *Ephedra distachya.* The lowest levels of chromium were recorded in Fabaceae species and *K. ceratoides*, and its concentration was the highest in *Phlomis punhems*. The leaves of the latter plant, grown in a primrose clay at the Bogdo mountain, accumulated up to 2.2 mg Cr kg^{-1}, which was 2–7 times higher than Cr accumulation levels in other plants. Nevertheless, it is worth highlighting that Cr predominantly accumulates in plant roots but not leaves [55]. Therefore, the obtained data may reflect both differences in translocation of the element from roots to shouts and species variations.

The mineral composition of individual plants within a species may vary considerably depending on the habitat location reflecting the phenotypic adaptation development. On the other hand, the ratio between different elements is less affected by this geographic variation due to plant ability to absorb and accumulate nutrients selectively, providing a balance of intracellular concentrations to optimize metabolism, protein synthesis, and tissue production [56].

3.3. K/Na, Ca/Sr, Ca/Na, and Fe/Mn Ratio

In the conditions of the Baskunchak Nature Reserve, the K/Na ratio characterizing the adaptability of plants to high salinity levels was the highest in *Kraschenninikova ceratoides*, *Ephedra distachya*, and *Glycyrrhiza aspera*, reaching 151.4–224.4, and the lowest in two *Artemisia* species (*A. lerchiana* and *A. taurica*) and *Tanacetum millifolium* (6.21–11.2; Table 8); the latter three plants demonstrated the ability to accumulate high levels of Na without growth inhibition. High K/Na and Ca/Na ratios are essential for normal plant metabolism [57].

Table 8. Ratios between elements in plants growing at Baskunchak Nature Reserve.

	Plant Family	Plant Species	K/Na	Ca/Sr	Ca/Na	Fe/Mn
Big Bogdo mountain	Asteraceae	*Artemisia lerchiana*	6.64 g	202.1 d	2.90 h	7.7 b
		Artemisia taurica	6.21 g	201.4 d	2.02 h	4.2 e
		Helichrysum nogaicum	96.3 c	338.5 a	35.94 d	3.2 fg
		Jurinea ewersmannii Wge	52.1 e	224.7 d	68.24 c	5.1 d
		Tanacetum millefolium	11.2 h	245 c	5.46 g	2.8 g
	Lamiaceae	*Phlomis pungens* Wielld	76.5 d	272 bc	61.06 c	15.3 a
	Amaranthaceae	*Kraschenninnikova ceratoides*	224.4 a	287.7 ab	64.23 c	2.7 g
	Fabaceae	*Glycyrrhiza aspera*	157.7 b	148.1 e	118.3 b	4.4 de
		Astragalus vulpinus	24.3 f	94.9 f	14.16	6.2 c
	Poaceae	*Eremopyrum orientale* (L) Jaub. & Spach	75.5 d	66.9 h	23.15 e	3.5 f
		Poa angustifolia L.	45.6 e	123.1 e	11.55 f	2.1 h
	Ephedraceae	*Ephedra distachya*	151.4 b	95.5 f	291.63 a	13.5 a

Within each column, values with the same letters do not differ statistically according to Duncan's test at $p < 0.05$.

In conditions of environmental gypsum excess, the Ca/Sr ratio is an important parameter of plant adaptability. In this respect, all the tested Asteraceae representatives in addition to *Kraschenninnikova ceratoides* (Amaranthaceae) showed the highest Ca/Sr values (201.4–338.5). These observations were consistent with the similar high Ca/Sr ratio detected in a collection of *Artemisia* species grown at Nikitsky Botanic Garden, Crimea [45].

The Ca/Sr ratio in plants depends on their concentration in soil, the ability of plants to discriminate between Ca and Sr, and environmental factors either stimulating or inhibiting Sr bioavailability. Indeed, high variations in the plant Ca/Sr ratio were recorded in Turkey in the vicinity of a silver-mining area [58]. Strontium bioavailability was shown to be greatly improved in the presence of calcium carbonate [59]. Furthermore, plants may greatly differ in the ability to distribute Sr between leaves and roots [60]. In this respect, it may be highlighted that plants at the Big Bogdo mountain contain significantly lower levels of Sr (33.5 ± 13.3; 17.2–49.8 mg kg^{-1} d.w.), compared to the steppe zone of the Reserve (55.6 ± 27.7; 25.2–99.6 mg kg^{-1} d.w). Relatively high variations in Sr content within each area may reflect uneven distribution of Sr, Ca, and, in particular, gypsum deposits.

Despite the low bioavailability of Fe in soils with high pH, the Fe/Mn ratio in most plants tested was high and reached 2.1–7.7, while extraordinary ratios (13.5–15.3) were recorded in *Ephedra distachya* and *Phlomis pungens.* Taking into account that either an Fe/Mn ratio of 1.5–2.5 is considered physiologically adequate for plants [57] or the Fe/Mn antagonism is well documented, the presented data allow to reveal the existence of significant plant Fe uptake [57]. Furthermore, the Fe/Mn ratio positively correlated with the Ca/Na one (r = 0.559, $p < 0.04$), suggesting a positive correlation of Ca and Na with Fe and Mn assimilation in plants in semi-desert conditions. To date, no relationships between Ca/Na and Fe/Mn ratio have been revealed.

According to the literature data [61], high levels of Ca promote the increase in K/Na ratio in plants, improving their resistance to salinity stress. The present results showed a significant positive correlation between Ca/Na and K/Na ratios (r = 0.605, $p < 0.04$). Gypsum is known to regulate the replacement of sodium (Na^+) with calcium (Ca^{2+}) on clay surfaces, thereby increasing the Ca^{2+}/Na^+ ratio in the soil solution. Intracellularly, Ca^{2+} also promotes a higher K^+/Na^+ ratio. Moreover, the presence of sulfur (S) in gypsum improves plant growth through the increased production of phytohormones, amino acids, glutathione, and osmoprotectants, which are vital elicitors in plant responses to salinity stress.

3.4. Relationship Between Elements in Plants

Differently from most investigations, where the relationship between mineral elements in plants have been assessed only within a single species in different environmental conditions, in this research, 12 plant species belonging to 6 families and grown at the territory of the Baskunchak Nature Reserve were examined. Significant correlations ($p < 0.01$) have arisen between macroelements (Na, K, Ca), essential microelements (Cu, Fe, Zn, Co),

and beneficial elements (V, Al) (Table 9). The detected correlations between elements are supposed to reflect similar element accumulation efficiency in the tested plants.

Table 9. Correlations between mineral elements in 12 plant species at the Baskunchak Nature Reserve.

	Ca	K	Mg	Na	P	B	Co	Cu	Fe	Li	Mn	Mo
K	0.253	1										
Mg	**0.550 d**	0.461	1									
Na	0.391	**0.794 a**	0.154	1								
P	−0.294	0.232	0.107	−0.234	1							
B	0.310	0.417	0.423	0.112	0.492	1						
Co	**0.640 c**	0.131	0.086	0.283	−0.242	−0.229	1					
Cu	**0.741 a**	**0.741 a**	0.482	**0.865 a**	−0.191	0.373	0.188	1				
Fe	−0.039	0.086	−0.039	0.355	−0.461	−0.220	**0.934 a**	0.218	1			
Li	−0.247	0.087	**0.554 d**	0.260	−0.247	0.223	0.278	**0.643 c**	0.192	1		
Mn	0.099	0.465	0.100	0.408	0.240	0.099	0.408	0.301	0.266	0.121	1	
Mo	−0.269	−0.118	−0.187	0.007	0.074	0.062	−0.269	0.114	−0.307	0.374	−0.265	1
Se	−0.387	−0.353	−0.117	−0.463	0.212	0.324	−0.508	−0.387	−0.396	0.301	−0.317	−0.134
Si	−0.247	−0.279	−0.433	−0.223	0.229	−0.580	−0.107	−0.365	−0.247	−0.240	0.196	−0.123
Zn	0.345	**0.841 a**	0.314	**0.849 a**	−0.085	0.214	0.498	**0.745 a**	0.503	0.328	0.453	−0.012
Al	0.286	0.402	−0.018	**0.671 b**	−0.482	−0.172	**0.799 a**	0.477	**0.889 a**	0.286	0.359	−0150
As	0.134	−0.096	0.428	0.112	−0.505	−0.030	0.547	0.379	**0.562 d**	**0.752 a**	0.134	−0.078
Cd	0.255	0.294	0.033	−0.030	**0.669 b**	**0.587d**	0.086	−0.004	−0.054	0.027	0.314	0.255
Cr	−0.281	−0.204	−0.117	0.013	−0.508	−0.387	0.213	−0.057	0.387	−0.170	−0.283	−0.330
Ni	−0.407	**0.700 b**	0.211	**0.786 a**	−0.051	0.353	0.115	**0.716**	0.206	0.159	0.183	0.015
Pb	−0.309	−0.284	−0.084	−0.181	0.165	−0.063	0.398	−0.186	0.293	0.075	0.204	−0.257
Sr	0.422	−0.336	0.243	0.007	−0.271	−0.282	**0.587 d**	−0.057	**0.594 d**	0.219	−0.226	0.200
V	0.345	0.520	0.009	**0.752 a**	−0.460	−0.123	**0.664 c**	**0.557 d**	**0.773 a**	0.295	0.376	−0.114
AOA	0.489	**0.620 c**	0.196	**0.794 a**	−0.414	0.144	0.372	**0.734 a**	0.530	0.172	0.160	−0.247
TP	**0.571 d**	0.523	0.202	**0.640 c**	−0.254	0.351	0.365	**0.619 c**	0.524	0.118	0.120	−0.280

	Se	Si	Zn	Al	As	Cd	Cr	Ni	Pb	Sr	V
Si	−0.102	1									
Zn	−0.412	−0.346	1								
Al	−0.467	−0.259	**0.791 a**	1							
As	−0.376	−0.210	0.144	0.406	1						
Cd	−0.189	−0.200	0.170	−0.065	−0.197	1					
Cr	−0.281	0.101	−0.138	0.242	0.442	−0.407	1				
Ni	0.094	−0.407	**0.789 a**	0.507	−0.115	−0.070	−0.304	1			
Pb	−0.233	0.094	−0.309	−0.058	0.266	0.248	0.176	−0.395	1		
Sr	−0.057	−0.148	0.091	0.422	0.223	−0.106	−0.001	0.146	0.353	1	
V	−0.457	−0.225	**0.850 a**	**0.971 a**	0.345	−0.084	0.248	**0.575 d**	−0.233	0.238	1

(a) $p < 0.001$; (b) $p < 0.01$;(c) $p < 0.02$; (d) $p < 0.05$. Bold values correspond to the significant relationship between the parameters.

Notably, similar highly significant V-Al-Fe-Co interactions were recorded previously in a collection of *Artemisia* species at the Nikitsky Botanic Garden [45], while Fe-Co correlation was confirmed in a couch grass [62]. Taking into account the specific environmental conditions at the Baskunchak Nature Reserve, the mentioned elements may participate in plant protection against stresses in semi-desert areas.

Cobalt is a transition metal located in the fourth line of the periodic table, a neighbor of Fe, and it is an essential element for Fabaceae plants which improves N_2 fixation [63]. The same ionic radius of Co^{2+} and Fe^{2+} (both 0.76 Å) may explain the significant correlation between these two elements and the known replacement of iron by cobalt in the active sites of enzymes.

The high Fe-Al correlation may be attributed to the similar ionic radius of the hydrated ions of Fe and Al or the same charge [64]. Fe and Al hydroxides are considered strong primary sorbents of V in soils [65]; precisely, Fe and Al (hydr)oxides are the main

compounds determining the mobility of V in soil. Vanadium bioavailability increases in soils with high pH [66].

3.5. Soil–Plant Interaction

The relationship between mineral element content in plants and soils depends on soil characteristics, level of salinity, climate, and plant species differences. Using a singular extraction technique with diluted HNO_3, only the significant correlation between plant and soil Sr was revealed (Figure 4).

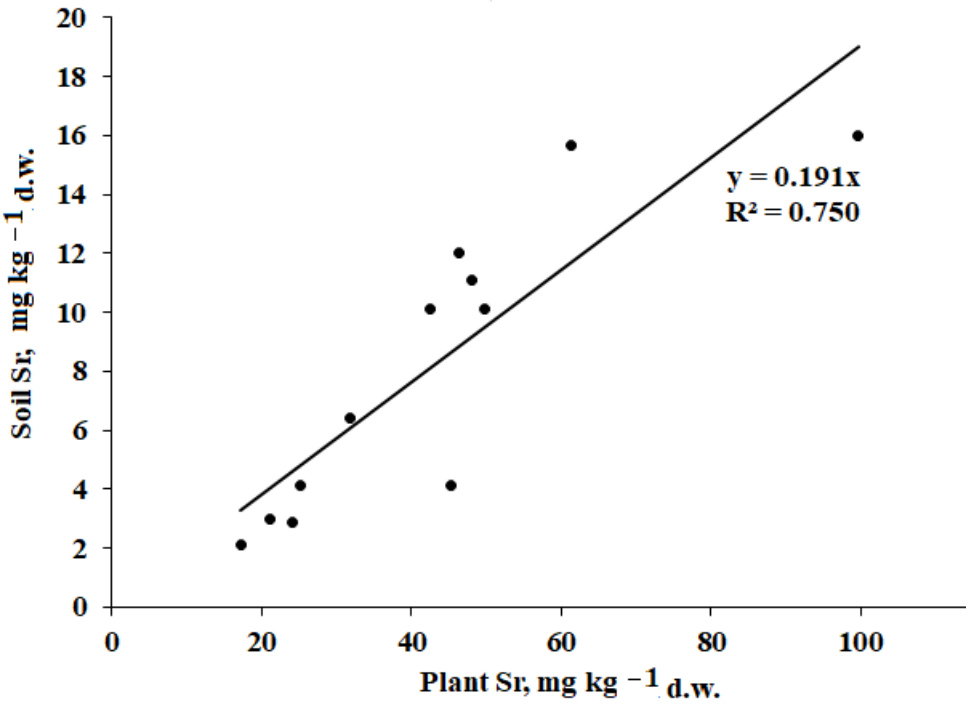

Figure 4. Correlation between soil and plant Sr levels at the BNR and the Bogdo mountain (r = 0.866, $p < 0.001$). The linear relationship is based on data for all studied plant species (n = 12) and corresponding soil samples.

The statistically significant correlation between plant and soil Sr levels suggests similar conditions of Sr absorption by plants at the territory of the Baskunchak Nature Reserve. Plants accumulate stronthium through Ca^{2+} channels as a free divalent ion and to a lesser extent as a complex with low-weight organic compounds [67,68]. Contrary to Ca, Sr is not essential to plants and is able to replace Ca and co-precipitate with Ca in soils [69]; the intensity of its accumulation depends on the competition with Ca, absorption on organic chelators [70], plant exudates, and soil electric conductivity [71].

The present results revealed a positive correlation between plant Sr levels and soil salinity (TSS; r = 0.763, $p < 0.001$), in accordance with the Yasuda et al. reports [71], which is the most significant among the plant–soil interactions examined, in agreement with a significant correlation between the values of Sr content in plants and soils (Figure 4). Moreover, a weak effect of soil salinity on the content of Co, Fe, and Pb in plants was recorded (r = 0.627, $p < 0.02$; r = 0.606, $p < 0.03$; r = 0.548, $p < 0.05$, respectively).

Notably, the effect of salinity on plant mineral composition has not been fully understood, and, indeed, it may consist of either an increase or decrease in plant element accumulation ability [72]. According to numerous investigations, salinity inhibits plant Se accumulation [72,73]. The present results did not demonstrate any relationship between soil salinity and plant Se content, which indirectly indicates a significant role of species differences in the ability to accumulate Se [37] and a beneficial effect of gypsum on plant growth. However, it is worth highlighting that complex soil fractionation is necessary to

reveal other relationships between soil and plant elements (Cu, Zn, Mn, Pb, and Se) [74]. Furthermore, soil–plant interaction is greatly governed by genetic factors, so that lack of significant correlations between soil/plant elements in all the plants tested is not unexpected. In this respect, it is necessary to mention a positive Cr soil–plant correlation ($r = 0.986$, $p < 0.001$) relevant to Asteraceae plants of the Big Bogdo mountain. Nevertheless, further investigations are needed to confirm the mentioned relationship.

3.6. Biological Concentration Factor (BCF)

The elements analyzed in soil samples allowed us to evaluate the coefficients of biological accumulation or a biological concentration factor (BCF) of only 8 elements: Sr, Zn, Pb, Fe, Cu, Mn, Cr, and Se (Table 9). All the mentioned elements, except Sr, Pb, and Cr, are known to participate in plant antioxidant defense. Indeed, Mn is a plant-essential element, which is involved in photosynthesis and acts as a cofactor in several enzymes with antioxidant properties [75]. Copper is another essential element which also plays an important role in photosynthesis, respiration, antioxidant activity, protein metabolism, carbohydrate distribution, and nitrogen fixation, etc. [76,77]. Zinc is a constituent of many enzymes affecting gene regulation and activation, protein synthesis, and carbohydrate metabolism, providing the enhancement of membrane stability [16,47,78]. Though Se is not an essential element in plants, it is actively involved in alleviating both biotic and abiotic environmental stresses via improvement of antioxidant defense and enhancement of water uptake by plants [37,79]. High Se BCFs were recorded in 6 species (*T. millefolium*, *Jurinea ewersmannii*, *H. nogaicum*, *G aspera*, *P. pungens*, *K. ceratoides*) (Table 10). In the latter list, the first three representatives belong to Asteraceae family, the fourth one to Fabaceae family, and *K. ceratoides* to Amaranthaceae, which include plant species/accumulators of Se [45,72,80,81]. Nevertheless, the ability of these plants to accumulate Se has never been studied before.

Table 10. Bio-concentration factors (BCFs) for eighth elements in different plant species residing at a semi-arid area of the BNR.

Family	Species	Sr	Zn	Pb	Fe	Cu	Mn	Cr	Se
Asteraceae	*Artemisia lerchiana*	4.34 d	3.57 c	3.37 a	3.07 b	2.16 c	0.95 b	0.2 g	0.13 f
	Artemisia taurica	4.2 de	8.25 a	0.035	0.97 e	3.89 b	0.73 c	5.6 a	0.92c
	Jurinea ewersmannii Wge	4.93 d	4.38 b	0.038	0.90 e	2.39 c	0.69 c	5.70 a	3.22 a
	Helichrysum nogaicum	8.15 b	7.42 a	0.18 f	5.59 a	4.21 b	0.59 c	0.71 c	3.2 ab
	Tanacetum millefolium	4.97 d	8.05 a	0.16 f	2.20 c	5.20 a	1.56 a	0.55 d	3.36 a
Poaceae	*Poa angustifolia*	6.3 c	0.83 g	1.34 d	0.30 g	0.47	0.59 c	0.076	0.82 c
	Eremopyrum orientale	3.87 e	1.54 de	2.35 b	0.67 f	0.93 d	0.69 c	0.40 e	0.40 e
Fabaceae	*Glycyrrhiza aspera*	11.0 a	1.27 f	0.90 e	0.43	0.90 d	0.38 e	0.05 k	3.25 ab
	Astragalus vulpinus	3.92 e	1.14 fg	1.88 c	0.81 e	0.72 e	0.38 e	0.06 h	0.65 d
Ephedraceae	*Ephedra distachya*	6.23 c	1.37 ef	4.00 a	1.54 d	0.48 f	0.69 c	0.27 g	0.46 e
Lamiaceae	*Phlomis pungens* Wielld	8.36 b	1.79 d	0.13 g	0.68 f	4.45 ab	0.11 f	2.2 b	3.8 a
Amarantaceae	*Krascheninnikova ceratoides*	7.1 bc	3.67 c	0.88 e	0.95e	3.76 b	0.45 d	0.32 f	2.95 b
Number of accumulators		12	11	5	4	6	1	3	6

Within each column, values with the same letters do not differ statistically according to Duncan's test at $p < 0.05$.

A bio-concentration factor exceeding 1 was recorded for Mn only in one species (*T. millefolium*), for Cu and Zn in all Asteraceae species.

In this respect, the possibility of element participation in plant protection against environmental stresses in semi-desert conditions is the most pronounced in Asteraceae representatives that are able to actively accumulate Zn, Cu, and Se, while, among other species, only *K. ceratoides* and *P. pungens* showed similar ability.

In conditions of high pH and low soil organic matter, Cr is present in soil predominantly in a mobile toxic Cr(VI) form [55,82]. In this respect, the exclusion of toxic Cr (BCF < 1 in the aerial plant parts) was recorded in most of the species examined, which may be partly connected to the main accumulation of this element in roots and active

reduction in Cr(VI) to Cr(III) [83]. Only three species, *J. ewersmannii*, *A. Taurica*, and *P. pungens*, displayed BCF values > 1 at extremely low soil Cr contents. Among the latter species, *P. pungens* also showed a remarkable ability to accumulate Zn, Cu, and Se, which supposedly participate in plant defense.

Pb exclusion was recorded only in half of the species investigated. The BCF value of Pb decreased according to the following sequence: *Ephedra distachya* > *Artemisia lerchiana* > *Eremopyrum orientale* > *Astragalus vulpinus* > *Poa angustifolia*.

Among Fe accumulators, it is worth highlighting the high accumulation abilities of *E. distachya*, *H. nogaicum*, and *A. lerchiana*.

Despite the linear correlation between soil–plant Sr levels, the distribution of the parameters suggests significant differences in the BCF among the plants tested. Unexpectedly, the broad BCF range of values, from 4.5 in *Astragalus vulpinus* to 11 in *G. aspera*, was in accordance with the detected effect of species variability and the external factors [84]. In the conditions of the Bogdinsko-Baskunchak Nature Reserve, the BCF values of Sr were the highest (8–11) in *G. aspera*, *P. pungens*, and *T. millefolium*, which may be beneficial in phytoremediation of radioactive Sr with similar behavior as stable Sr [84]. A positive correlation between Sr levels in plants and soils at the Baskunchak Nature Reserve suggests high availability of this element in semi-desert conditions at the beginning of summer (25–28 May) with sufficient water supply. Indeed, high soil pH and low organic matter content enhances Sr bioavailability [84].

The high Se, Zn, Cu, and other element concentrations in plant tissues may relate to phenotypic adaptability, leading, in certain cases, to the formation of genotypic changes. In this respect, high Se levels in plant tissues may reflect not only a phenotypic answer of plants to environmental stress but also changes in the expression of genes, encoding Se transport proteins, and the assimilation of selenate, encoding enzymes for the conversion of selenocysteine into non-toxic methylated forms or volatile derivatives [85]. Among the plant families examined, Amaranthaceae, Asteracea, and Fabaceae reportedly contain Se accumulators [86]. A high BCF value for *Phlomis pungens* Wielld, the representative of the Lamiaceae family, has been recorded in the present research for the first time. The mineral composition of the examined species has never been studied previously, which indicates the need of further investigations in plant genetics.

3.7. Principal Component Analysis

The behavior of the 12 sampled plant species is shown in Figure 5. The five species belonging to Asteraceae family (*Artemisia lerchiana* L., *Artemisia taurica* L., *Helichrysum nogaicum* L., *Jurinea ewersmannii* Wge., and *Tanacetum millefolium* L.) demonstrated an affinity for the accumulation of the elements Ca, V, Li, Ni, Na, Zn, Cu, Mn, K, Mg, B, Cd, and Mo and a higher Ca/Sr ratio than the other species examined.

The species belonging to the Lamiaceae family (*Phlomis pungens* L.) are graphically represented at the opposite end of the spectrum compared to the species of Asteraceae, regarding the accumulation of the aforementioned elements, with a slight affinity referring to the higher Ca/Na and K/Na ratios.

The two Fabaceae species (*Glycyrrhiza aspera* L. and *Astragalus vulpinus* L.) exhibited a common trend to accumulate Se and P, with a greater propensity for Se in the case of *Glycyrrhiza aspera* L. and P in *Astragalus vulpinus* L.

Furthermore, the species belonging to the Poaceae family (*Eremopyrum orientale* L. and *Poa angustifolia* L.) showed the highest K/Na ratio.

Finally, *Ephedra distachya* L. (Ephedraceae) and *Kraschenninikova ceratoides* L. (Amaranthaceae) exhibited contrasting behavior in the accumulation of mineral elements. Indeed, the first species was characterized by a higher relative accumulation of Cr and Sr, and greater Ca/Na and Fe/Mn ratios, whereas the latter showed a higher accumulation of P and Mo.

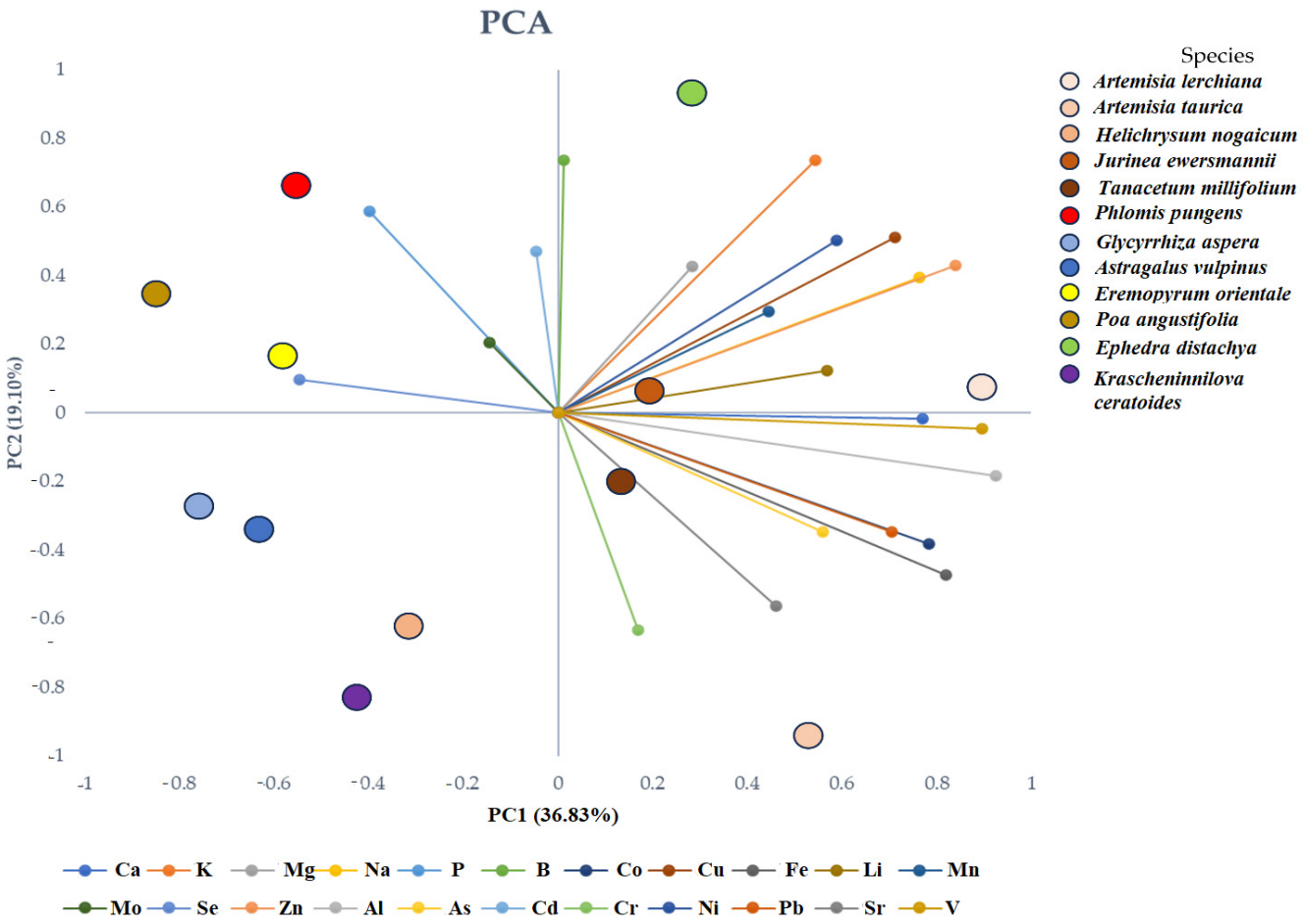

Figure 5. Principal component analysis (PCA).

4. Conclusions

The present results showed clear relationships between mineral elements in soil and plants of different families at the territory of the Baskunchak Nature Reserve, with positive correlations between soil and plant Sr levels and between plant Sr, Fe, Pb, and Co contents and soil salinity. Two contrasting groups of plant species were identified, representing examples of different protection mechanisms in a semi-desert condition: *Artemisia*, with an unusually high antioxidant status, including polyphenols, Zn, Cu, K, and V, is able to accumulate high levels of Na; and Poaceae representatives have insignificant content of antioxidants but an extremely high Si accumulation level. Frequent cases of Se-accumulator plants at the Baskunchak Nature Reserve allow to hypothesize a Se-protection effect. Suppressed levels of Cr in most plant species reflect another possible mechanism of plant defense. Further investigations are needed to reveal other peculiarities of element participation in plant adaptability in semi-desert conditions.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijpb15040085/s1. Table S1: Soil pH and salinity; Table S2: Elemental profile of Baskunchak soils

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