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Seasonal comparative geochemistry of ultra trace elements content in agricultural soils near Lake Sevan.

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Abstract. The contamination status of the soils from Hrazdan, Gavar, and Martuni regions has been investigated by comparing UTEs indicators with % humus and pH in soil samples during different seasonal intervals steppe chernozem soil type was studied. It was found that the maximum of % humus exceeded the minimum % almost twice in the soil samples. The soil samples were found to be neutral in terms of pH character. The results for the Hrazdan region show on 10% increase of barium content and 70% decrease of arsenic content in soil samples taken in winter 2022 compared to the whole period studied. For spring 2022, the same variant shows on 27% increase of chromium and 19% of vanadium. The change in nickel content was within the average for the whole period. The results for the Gavar region show an average dynamic increase of 22% of barium content in soil samples from autumn 2021 to spring 2022 compared to the whole sampling period. The change of the content other UTEs was within the average value for the whole sampling period. Alternating decreases (winter and summer 2022) and increases (autumn 2021 and spring 2022) of the barium content were observed in the soil samples from the Martuni region. The change of UTEs content in the soil was within the average value for the whole period sampled. The increased value of the Z_c coefficient in autumn was found to be typical for all investigated regions, although the values vary. The highest value of the coefficient is observed in the Hrazdan region and the lowest value in the Martuni region.

1 Introduction

Irrigated soils can contain high concentrations of inorganic ultra trace elements (UTEs). UTEs accumulated in plants to levels that cause phyto-toxicity, that threaten the quality and quantity of agricultural production [1]. There is evidence that UTEs in plants can have adverse effects on humans and animals that consume these plants [2, 3]. All of these situations are dangerous in the first place because they threaten human health. On another

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hand, the soil has a dynamic system, humus, consisting of a collection of plant and animal residues. All have lost their original anatomical structure. They are in different stages of decomposition and synthesis [4]. Depending on the season, the rate of decomposition can vary.

The aim of the study was to assess the ecological condition of soils of three Armenian regions - Hrazdan, Gavar, and Martuni - by comparing indicators of UTEs with humus content and pH in soil samples. During four different seasonal intervals, steppe chernozem type of soils of agro-systems of private agricultural use was studied.

2 Materials and methods

The concentrations of five UTEs barium (Ba), chromium (Cr), vanadium (V), arsenic (As) and nickel (Ni) were determined by instrumental [5]. These elements have been identified as pollutants associated with irrigated agriculture [6].

Soil for the experiment was collected in Hrazdan (five points – site1), Gavar (three points – site2) and Martuni (two points – site3) (see fig. 1) from autumn 2021 to summer 2022. In general, the arable soils were located to the left of Lake Sevan and varied in their level of contamination [7].

Fig. 1. Soil sampling regions in Armenia.

Soil samples under dry-weather conditions were taken from a depth of up to 20 cm at control points using the envelope method. Point sampling was performed by using non-metallic tools. A combined soil sample was prepared by mixing at least five incremental samples taken from the same site. Afterward, the samples were placed in dark glass containers and transported at +4°C for laboratory measurements for 24 hours [8]. All the experimental data had up to 5 technical replicates and were statistically processed.

The integral anthropogenic pollution was calculated, since soil pollution has a high content of many of the UTEs:

$$Z_c=\Sigma (K_c) – (n–1) \quad (1)$$

where n is the number of elements measured, K_c is the concentration coefficient [9].

The total toxic pollution index Z_{ctox} is calculated by introducing a correction factor for toxicity according to the formula

$$Z_{ctox}=\Sigma (K_c \text{ x } K_{tox}) – (n–1) \quad (2)$$

where K_c is the ratio of the content of UTEs in the studied soil samples to the value of their background content; K_{tox} is a toxicity coefficient of UTEs, with values of 1.5 for class I (Cr, As, and Ni), -1.0 for class II and -0.5 for class III (Ba and V) [10].

3 Results and discussion

Some physico-chemical parameters, such as humus and acid-alkaline status, were determined in the soil samples studied in different seasons (Table 1). The soil samples studied are characterized weakly (<3 %) and low (3-5 %) in terms of humus content. Variations in humus content in different soil regions are insignificant, where the maximum values exceed the minimum values almost twice. There is a significant increase in humus content in spring and summer, which may be related to the intensification of agricultural activities in the fields. Topsoil pH should ideally be maintained above 5.5. Based on the results of this study, samples of soils had neutral meaning of pH (Table 1).

Table 1. The soil parameters from the different regions.

Soil sampling region	Season of sampling	pH	Humus
Site 1 (Hrazdan region)	Autumn, 2021	7.24±0.28	3.20±0.16
	Winter, 2022	7.44±0.24	2.57±0.05
	Spring, 2022	7.83±0.26	3.11±0.03
	Summer, 2022	7.62±0.42	2.68±0.07
Site 2 (Gavar region)	Autumn, 2021	7.59±0.34	3.62±0.15
	Winter, 2022	7.58±0.99	2.19±0.04
	Spring, 2022	7.77±0.24	2.51±0.02
	Summer, 2022	7.80±0.99	4.43±0.27
Site 3 (Martuni region)	Autumn, 2021	7.11±0.28	3.93±0.18
	Winter, 2022	7.60±0.21	2.32±0.02
	Spring, 2022	7.62±0.21	4.18±0.05
	Summer, 2022	7.39±0.53	3.46±0.05

The results for the Hrazdan region show on 10% increase of barium and on 70% decrease of arsenic in soil samples taken in winter 2022 compared to the entire period studied. For the same variant, chromium is reported to increase by 27% and vanadium to increase by 19% in spring 2022. In this case, the change in nickel content was within the average for the whole sampling period. The results for the Gavar region show an average increase of 22% in the dynamics of barium in soil samples from autumn 2021 to spring 2022, in comparison with the whole sampling period. On the other hand, the change in the content of nickel, chromium, vanadium and arsenic was within the average value for the whole sampling period. In the Martuni region, soil samples showed alternating decreases (winter and summer 2022) and increases (autumn 2021 and spring 2022) of barium content. The change content of UTEs in soil was within the average for the whole sampling period.

In order to assess the integral level of anthropogenic UTEs contamination in soil samples, the total contamination index (Z_c) has been calculated (Table 2). According to the results, an increased meaning of the Z_c in autumn is typical for all studied regions, although the values differ. The highest meaning of the Z_c is found in the Hrazdan region and the lowest in the Martuni region. This can be related to the anthropogenic load in the industrially saturated region of Gavar.

Table 2. Concentrations of ultra trace elements (mg/kg) and value of total pollution indexes (Z_c and Z_{ctox}) in soil from the different regions.

Soil sampling region	**Season of sampling**	**Concentrations of ultra trace elements (mg/kg)**					**Total pollution indexes**	
		Ba	**Cr**	**V**	**As**	**Ni**	**Z_c***	**Z_{ctox}**
Site 1 (Hrazdan region)	Autumn, 2021	434.8	104.1	126.9	44.9	65.7	8.37	6.78
	Winter, 2022	500.3	102.3	125.9	12.9	65.8	2.75	3.19
	Spring, 2022	468.6	143.5	153.1	13.4	70.15	3.54	3.94
	Summer, 2022	462.5	107.6	122.0	13.4	64.2	2.76	3.06
Site 2 (Gavar region)	Autumn, 2021	457.4	117.9	134.6	27.1	82.5	5.78	5.19
	Winter, 2022	538.7	146.3	128.3	6.6	84.3	2.57	3.20
	Spring, 2022	560.5	127.2	121.9	4.8	86.7	2.08	2.86
	Summer, 2022	504.8	110.0	122.8	5.8	81.7	1.87	2.59
Site 3 (Martuni region)	Autumn, 2021	346.6	135	116.6	20.2	71.2	4.14	3.61
	Winter, 2022	427.1	112.0	104.6	10.5	84.3	2.48	2.59
	Spring, 2022	279.3	129.0	114.7	10.0	65.2	1.99	1.98
	Summer, 2022	399.2	132.0	108.7	9.6	76.9	2.37	2.49

In this case, there may be some uncertainty associated with the use of the total contamination index. This is due to the fact that it does not take into account the varying toxicity of the elements. Very toxic and less toxic elements may be present in soil simultaneously. As a result, the degree of environmental contamination may be underestimated. Therefore, if an area is predominantly polluted with poly-elements, the overall pollution index will not reflect the real severity of the environmental situation. For this reason, their toxic concentrations are part of the calculation of the overall index [11].
However, the degree of toxicity (hazard) of the UTEs is different. Therefore, for the same concentration values, the total pollution will be more dangerous if the soils accumulate more elements of hazard class I than elements of hazard classes II and III. Based on these assumptions, a kind of correction for elemental toxicity has been included in the calculations. The final calculated composite index (Zctox) differentiates soil contamination taking into account the degree of toxicity of the elements. By incorporating toxicity corrections for each element, this approach eliminates the distorting effect of abnormally high concentration ratios (Table 2).

4 Conclusions

This study compared the anthropogenic pressure on the environment with the results and soil samples from three different regions of Armenia. The comparative analysis revealed no significant deviations in acid-alkaline balance and % humus content of the soil samples over the whole period of the study. According to obtained results estimation of the degree of anthropogenic pollution of UTEs of agricultural land will be an informative parameter if must be based on the values corrected for the toxicity of each element.

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