Season Dynamics of Pollution and Changes in Enzymatic Activity in Agricultural Soil near an Industrial Area

SUKIASYAN A.[1*], KIRAKOSYAN A.[1]

[1] Polytechnic University of Armenia, 105 Teryan Str., 0009 Yerevan, Armenia

*corresponding author:
e-mail: sukiasyan.astghik@gmail.com

Abstract. The aim of the study was to assess the ecological condition of soils in three regions in Armenia - Hrazdan, Gavar, and Martuni. It was shown that the soil samples from the three regions had low humus content in winter. However, in spring and summer, a significant increase in humus content was observed. The soils had a neutral pH of 7.11 to 7.83. The enzymes studied belong to the class of hydrolases (invertase and urease) and oxidoreductases (catalase). The urease activity was almost 2-3 times lower than invertase activity in all soil samples. During the winter-spring period, high catalase activity was observed in all soil samples. It was found that in Hrazdan and Martuni regions the enzyme activity was on average 62% higher than in soil samples from Gavar regions. The HMs distribution depends on seasonal variations and the wind rose in each region. In order to interpret the results, the given total contamination index (Z_c) was compared, taking into account the cloud concentration of chemical elements. The value of the total index of pollution of arable soils by HMs near the Gavar region also had a moderately dangerous value.

Keywords: Soil; humus; pH; enzymes; heavy metals; total contamination index.

1. Introduction

Enzyme systems are present and functioning in soils, constantly carrying out biochemical reactions (Datta, et al., 2017). Enzymes participate in the processes of decomposing plant residues, synthesizing and mineralizing humus, and converting unavailable forms of nutrients into forms available to plants. For this reason, the enzymatic activity of the soil is the most diagnostic indicator of the impact of the anthropogenic load on the soil system. This is particularly relevant for agro ecosystems with annual agro technical impacts on soil (Mazhari et al., 2017). The determination of soil enzyme activity is very important for the identification of the degree of influence of agro technical measures and agrochemical agents on the activity of biological processes.

An important role of enzymes in the soil is that they establish functional relationships between the components of the ecosystem, and the enzymatic activity of soil is a reflection of the functional state of its living soil population (Piotrowska-Długosz et al., 2021). Under the action of enzymes, soil organic matter, and many biota residues are broken down into various final mineralization products. As a matter of fact, these biological catalysts play a leading role in the transformation processes of organic matter. Clearly, they are sensitive indicators of the influence of various soil formation factors, including anthropogenic changes in soil heavy metal content (Wu et al. 2023). The problem of degradation of soil biological properties is relevant in the context of uncontrolled environmental pollution by a wide range of pollutants (Sukiasyan and Kirakosyan, 2020). In this context, multi-component studies can provide the necessary information to establish the link between the impact of adverse factors on biota and human economic activities. Currently, anthropogenic stress is a factor that has reached global proportions, leading directly to the degradation of the naturally fertile soil layer. One of the dominant causes of soil degradation and reduction in biological productivity is heavy metals (HMs) pollution, which has highly toxic effects on biota. Anthropogenic impacts on biota lead to changes in the physical, chemical, and biological state of soils. This affects the activity of enzymes involved in carbohydrate metabolism. They inhibit the mineralization and synthesis of various substances in soil (Trifonova et al., 2014), the respiration of soil microorganisms, and cause microbiostatic effects (Nannipieri et al., 2017). Most HMs in high concentrations irreversibly alter the activity of soil enzymes: catalase, invertase, amylase, etc. (Olaniran et al., 2013). At the same time, the sensitivity of enzymes to different doses of HMs varies (Engwa et al., 2019). The impact of pollutants on natural biochemical processes that shape fertility has not been well studied, despite the sensitivity of the environment to enzymatic diagnostics.The aim of the study was to assess the ecological condition of soils in three Armenian regions - Hrazdan, Gavar and Martuni, adjacent to private agricultural use, by combining biochemical and geo-ecological approaches to determine the degree of anthropogenic pollution of soils. Taking into account the activity of some oxidoreductase (catalase) and hydrolytic (urease and invertase) enzymes, a comparative assessment of the pollution of arable soils by some heavy metals near the industrial zone and the identification of conjugate changes with humus content and pH will be carried out.

2. Materials and methods

2.1. Preparation of soil samples

The soils studied were steppe chernozem soils of adjacent natural and cultivated landscapes. Soil samples were collected in Hrazdan (five points - site 1), Gavar (three points - site 2), and Martuni (two points - site 3). They were taken under dry weather conditions using the envelope method from the depth which averaged 0.20-0.30 cm according to (Sukiasyan et al, 2021).

2.2. Measurement of the concentration of chemical elements

The chemical elements of the fourth periodicity (chromium (Cr), magnesium (Mn), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn)) with different hazard classes were measured in soil samples (Sukiasyan, 2018). Concentrations of chemical elements in soil samples in mg/kg were analysed in accordance with (Thermo scientific sample collection and preparation tools for exploration and mining, 2012). The obtained results were compared with the adopted normative standards.

2.3. Calculation of geo-ecological coefficients

The total contamination index (Z_c) was calculated to characterize the accumulation processes of chemical elements in soil samples according to the formula

$$Z_c = \sum_{i=1}^{n} C_{ci} - (n-1)$$

where $C_{ci}= C_s/B_f$ – concentration factor; C_s – concentration of chemical elements in the soil sample, mg/kg; B_f – background content of chemical elements in the soil, mg/kg (Müller, 1981); n – number of chemical elements.

2.4. Biochemical analysis of soil samples

Determination of humus in soil samples was carried out by Tyurin's method, which is based on the oxidation of humus with a sulfur-chromium mixture prepared in a ratio of sulfuric acid with a specific weight of 1.84 and water 1:1 (Tyurin, 1951). In soil samples, determination of catalase (1.11.1.6) activity in soil samples was carried out at 18-20°C; Cm O2 per 1g of soil for 1 min. The total activity of α and β amylase (3.2.1.1), which act on glycosyl compounds, was determined. Invertase (3.2.1.26) is involved in the breakdown of hydrocarbons, and the activity of this enzyme can be used to judge the rate of decomposition of carbon-containing organic compounds. Urease (3.5.1.5) decomposes urea to CO2 and NH3, and the resulting ammonia and ammonium salts serve as a source of nitrogen nutrition for plants and microorganisms. The activities of all of these enzymes (catalase, amylase, urease, and invertase) in soil samples were carried out according to the method by Khaziev's methods (Khaziev, 1990).

2.1. Statistical Analysis

All analytical results were performed as the average of up to 5 replicates using SPSS 22.0 and Excel (Microsoft Inc.) software packages. Data are presented as means of technical replicates ± Standard error. All results were considered significant at $P<0.05$.

3. Research results and discussion

3.1. Agrochemical parameters in samples of soil

Humus is a dynamic system. It consists of a collection of plant and animal residues that have lost their anatomical structure and are in various stages of decomposition and synthesis. It is the main and most important component of the organic matter of the soil. Indicators such as humus and acid-alkaline status were determined in order to clarify certain physicochemical parameters of the soil samples studied. The results are presented in Table 1.

Table 1. Seasonal variation of some agrochemical parameters of the arable soils of different industrial zones of the regions of Armenia

The 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 investigated soil samples are characterized as weakly (<3 %) and low (3-5 %) in terms of humus content. The variations in humus content between the different soil regions are insignificant. However, the maximum values are almost twice as high as the minimum values. All soil samples from the three regions showed in winter the humus content is low. However, a significant increase in humus content was in spring and summer. This may be the result of increased agricultural activity in the fields (Table 1). In the topsoil, the pH value should ideally be kept at more than 5.5. According to the results of this study, the soil samples had a neutral pH from 7.11 to 7.83. In the spring-summer period, the soil pH increased within one standard deviation (Table 1).

3.2. The enzymatic activity in samples of soil

The enzymes studied belong to the class of hydrolases (hydrolytic cleavage of organic substances (invertase and urease)) and oxidoreductases, which play an essential role in redox reactions (catalase). The enzymatic transformation of carbohydrates in the soil is the most important part of the carbon cycle in nature. It is responsible for the movement of large quantities of organic matter into the soil and for the storage of energy in the soil. The activity of invertase is linked to the further distribution of sucrose in all biological organisms. It is a potential source of sucrose accumulation in the soil. Invertase enzyme activity is characterized as a medium in the soils we studied (fig. 1).

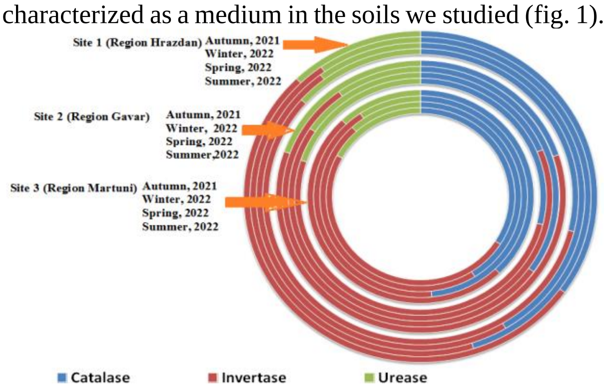

Figure 1. Seasonal variation of the activity of some enzymes in the arable soils of different industrial zones of the Armenian regions

The highest level of enzyme activity in the three regions under study was in the spring-winter period of 2022. The highest invertase activity was observed in soil samples from the Martuni region. In contrast, invertase activity in soil samples from the Hrazdan region was low. The activity of the enzyme urease is an indicator of the self-purification capacity of soils contaminated with xenobiotics of organic nature. So in agro ecosystems, an increase in urease activity indicates the ability to accumulate ammonia nitrogen in the soil. In our experiments, urease activity was almost 2-3 times lower than invertase activity in soil samples from all three regions of Armenia. However, throughout the study period from autumn 2021 to summer 2022 was observed a similar pattern of seasonal accumulation. The oxidation of the hydrolysis products of organic compounds to pre-humus substances should be taken into account when considering the enzymatic activity of soils. These reactions take place with the participation of oxidoreductases. Catalase is an important one. The activity of catalase characterizes the biogenesis of humic substances. It is directly related to the redox processes in the soil and thus describes the functional state of soil microorganisms. According to the results obtained, high catalase activity was observed in the winter-spring period in all soil samples from the three regions of Armenia. However, in the regions of Hrazdan and Martuni, the activity of the enzyme was on average 62% higher than in the soil samples from the region of Gavar.

3.3. Contamination by heavy metals in samples of soil

Transition metals can be grouped according to the highest energy valence electrons occupying the d-orbital in the electron shell. Their general functions are related to the process of formation between amino acids, proteins, nucleic acids, and the ions of the corresponding metals. HMs are of particular concern among the transition metals. As a result of human activities, they are a potentially dangerous source of contamination of biota along the water-soil-plant-animal-human food chain. They are not susceptible to degradation processes and can only be redistributed between different soil components and accumulate in different links of the food chain. In this context, research to determine HMs contamination levels in agricultural soils is relevant. According to the result (Table 3), Co was detected in trace amounts in Hrazdan region. A peculiar anomaly was detected in the overall pattern of HMs distribution. It depends on seasonal variations and was subjected to air migration as a result of the action of the wind rose in the region. From the analysis of the obtained results (Table 3), it can be assumed that some of the elements are subject to air migration as a result of the action of wind rose in the region. In order to interpret the results, the given total index of pollution (Z_c) was compared, taking into account the clark concentration of chemical elements (Sukiasyan, 2018). The value of the total index of pollution of arable soils near the Gavar region also had a moderately dangerous, which is fraught with a tendency to increase chronic diseases, caused by migration in the trophic chains of HMs.

4. Conclusions

The most advanced technological production schemes are used, a significant amount of highly toxic compounds enter the environment, polluting the atmospheric air, water and soil of the regions equally. The activity of the main soil enzymes was determined in three regions of Armenia, and conjugate changes in humus content and pH were revealed. The topsoil layer is contaminated with Mn, Cu and Zn. Probably, the processes of HM migration in the polluted areas can be attributed to the wind rose in the regions. It was found that the studied level of anthropogenic contamination does not negatively influence the activity of soil enzymes, but on the contrary, changes in their activity on arable land are accompanied by the intensification of the overall activity of biological processes in the studied soil samples.

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Table 2 Seasonal variation of some heavy metals and total contamination index of arable soils of different industrial zones of Armenian regions

The soil sampling region	Season of sampling	Concentrations of heavy metal (with configuration), mg/ml						Total contamination index (Z_c)**
		Cr (4s13d5)	Mn (4s23d5)	Co (4s23d7)	Ni (4s23d8)	Cu (4s13d10)	Zn (4s23d10)	
Site 1 (Hrazdan region)	Autumn, 2021	97.7	849.1	-*	62.0	85.1	99.3	3.5
	Winter, 2022	102.3	858.6	-*	65.8	58.5	109.6	3,0
	Spring, 2022	138.5	799.1	-*	65.8	67.3	118.1	3.8
	Summer, 2022	94.7	882.8	-*	63.1	68.6	99.9	3.0
Site 2 (Gavar region)	Autumn, 2021	113.3	819.7	137.0	80.7	84.4	87.5	15.3
	Winter, 2022	146.3	810.9	280.1	84.3	69.9	126.5	28,0
	Spring, 2022	127.2	792.5	93.7	86.7	65.5	89.5	11.4
	Summer, 2022	109.9	780.8	216.6	81.7	69.8	90.1	21.4
Site 3 (Martuni region)	Autumn, 2021	135.3	737.4	78.8	57.5	71.8	85.5	9.7
	Winter, 2022	111.9	776.1	139.8	84.3	58.7	98.6	14.9
	Spring, 2022	129.0	725.3	138.1	65.2	53.6	85.4	14.1
	Summer, 2022	132.0	741.5	182.1	76.9	57.5	83.2	18.2

Note: - has not been measured; ** the summary pollution level was classified as low with Zc< 16 contamination is considered as non-dangerous; with 16 <Zc< 32 contamination is moderately dangerous; with 32 <Zc< 128 contamination is dangerous; with Zc> 128 contamination is extremely dangerous (Müller, 1981).*

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