

Soil enzyme activity of urban territories of Rostov agglomeration

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Abstract. We carried out testing of the enzyme activity level (catalase, invertase, polyphenol oxidase) in natural and anthropogenically converted soils of Rostov-on-Don's (Russia) suburban, park, residential and industrial zones. The soil enzyme activity under conditions of urban pedogenesis is significantly lower (2 or 3 times) than in out-of-town analogs. Duration of soil sealing considerably influences biological activity, and, the longer this period the higher the negative impact on activity of researched enzyme is. Nevertheless, there is a close connection between soil humus condition and its enzyme activity: the activity of the above mentioned enzyme is highest in horizons containing the largest number of organic substance.

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Introduction

Urban soil biosystems are exposed to significant structural transformation which expresses itself in redistribution of biological activity in the limits of soil profile [1]. In this connection special attention should be paid to one of the indicators of soil biochemical characteristics – enzyme activity [2-4], and its interconnection with pollution and the change of soil biota under the influence of negative ecological processes occurring in the urban environment [5].

The influence of urbanization on soil enzymes is a little-studied problem. At the same time, enzyme activity is an early diagnostic indicator warning of the early stages of negative change [6]. In this connection the study of the peculiarities of enzyme activity in urban soils is highly important.

Objects and Methods

The main goal of the research, which has been conducted over the last 6 years, is the testing of soil cover specificity in Rostov-on-Don and its peculiarities within park and recreational and residential and industrial zones with special attention being focused on soil enzyme activity of the urban environment and its change according to the soil profile.

Taking into account complicity of the research object [7] we made about 40 soil profiles in different parts of the city. At every observation point we selected soil samples from all genetic horizons and anthropogenic layers and carried out compulsory morphological descriptions. In all selected samples we determined the basic soil and diagnostic

indicators. The total humus content was determined by using a wet combustion of the organic matter with a mixture of potassium dichromate and sulphuric acid at about 125°C. and content of soil carbonates according Kudrin and Sheibler. The activity of catalase enzyme ($H_2O_2:H_2O_2$ –oxidoreductase) was determined by gasometric method according Galstyan [8]; invertase enzyme ([beta]-fructofuranosidase, saccharase) – colorimetric method by Khaziev[8]); polyphenol oxidase enzyme (O-diphenol:oxygen-oxidoreductase)-colorimetric method with usage of pyrogallol by Galstyan [8].

To reveal regularities in the degree of changing enzyme activity from forty profiles we have chosen the most typically researched soils and united them in four groups depending on the type of land use and, accordingly, the transformation level of their morphological properties:

First group. Soils with natural composition that haven't been considerably affected by urbanization processes; they are represented by ordinary Chernozems conserved on watershed plains in a park and recreational city zone with adjoining arable areas. Profiles # 28, 29, 32.

Second group. Soils with natural composition overlapped by permeable anthropogenic sediments. They are represented by anthropogenically transformed soils – urbanozems and urban chernozems which keep the main genetic horizons of once scalped chernozem soils in their profile. These soil types mainly refer to residential zones of an older part of the city. Profiles #22, 30, 31.

Third group. Natural soils overlapped by asphalt and/or another impermeable covering. In their "body" at some depth under the asphalt layer sealed

soils have retained mostly full-profile chernozems that can be sometimes slightly scalped and sealed by the horizon "urbic" or gravel, lime waste or masonry. They refer to residential zones. Profiles #26, 27.

Fourth group. Mixed layers consisting of remnants of soil horizons and infused soils sealed or unsealed by asphalt coating. They are presented by anthropogenically transformed soils composed of "urbic" horizons of different thickness and interfusion with an amount of anthropogenic inclusions higher than 10%. They refer to city industrial zones Profile # 23.

Results and Discussion

Comparative analysis of urban soils catalase activity with virgin analogs indicates reduction of this characteristic under the influence of urbanization (table 1).

In urban soils the content of catalase enzyme averages approximately 75 % of the quantity of this characteristic in virgin Chernozem. Tillage preceding development of urban lands partly contributed to reduction of this enzyme activity. It is evident that this regularity has remained for urban natural soils (park soils, woodland parks, fallow land and waste areas), but the degree of enzyme activity reduction is slightly higher and this is determined by a superposed effect connected with a change in soil density [7].

For most tested profiles of both natural and anthropogenically transformed soils, the highest catalase enzyme activity according to the profile is observed in horizons A and B which is connected with an increased humus content in them, new organic substance inflow (wherever it is possible) and higher intensity of processes of organic matter transformation. At this point content reduction with greater depth is, as a rule, accompanied by weakening of enzyme activity (table 1) though such distribution according to the soil profile is not observed for all tested varieties of urban soils.

In some cases, with greater depth, an increase of catalase activity in carbonate horizons is recorded with its maximum on the horizon C_{Ca} . In our view this increase is connected with the whole complex of soil processes and phenomena. First, carbonates can have a direct impact on soil enzyme activity alkalizing soil solution which influences vital functions of biota. Second, increased catalase activity in a lower profile part can depend on a change in organic substance composition as growth in the content of movable forms of humus down profile which can initiate increased catalase activity, is observed [9].

Third, increased soil catalytic activity in carbonate horizons can depend on the character and

content of the carbonates. In T.A. Zubkova and L.O. Karpachevskiy's paper [10] when studying carbonate soils' catalytic activity by the gasovolumetric method [10] it was ascertained that the total amount of gas formed as a result of the reaction is determined not only by the volume of excreted O_2 from H_2O_2 decomposition, but also by the volume of CO_2 from decomposing carbonates.

To prove the latter it is necessary to focus on the urbanozem of the second group (profile 22) in which the highest indicator of catalase activity falls on horizon C_{Ca} (table 1). In soil horizons of sealed urban soil (ekranozem) from the third group's (profile 26) anomalously high catalytic activity is observed and this can be directly linked to the influence of sealing soil asphalt and chalkstone layers. Along with a high carbonate content of infused chalky materials, the partial permeability of asphaltic concrete with a permeability coefficient of 2×10^{-3} cm/sec [11], remains evident. Consequently, all of this could lead to permeating of carbonates into underlying horizon A as well as heightening of the catalytic activity indicator.

When characterizing soil by activity of various enzymes we applied a recompilation of given data by G.Azzi's method [12] that enabled us to convert data that were noncomparable, due to different measuring units, into percentages. The results show that the reduction factor of catalase activity in the horizon A_{buried} of urbanozems is 2,1–2,5 and the reduction factor of the same enzyme by soil sealing in comparison with unsealed urban analog is 1,4.

Examined urban soils have been estimated by a degree of catalase provision by Zvyagintsev's scale and all of them are characterized by average enrichment and some of them are even rich in the tested enzyme[9].

Urbanization process influenced soil invertase activity to a considerable degree. On the whole provision of urban soils with invertase can be characterized as very poor [7].

The highest degree of invertase activity was noticed only in upper horizons (A_p and A_d) of tillage chernozems and partly woodland park zone (profiles 28, 29) where the highest humus content of 7,5 and 3,14 % accordingly was recorded. With all this invertase activity goes down the profile up to the horizon B_2 where a dramatic drop is recorded and further in horizons BC and C this enzyme activity is zero.

Table 1. Enzyme soil activity in Rostov-on-Don

Horizon	Depth, cm	Humus, %	CaCO ₃ , %	MgCO ₃ , %	CO ₂ of carbonates, %	Catalase, ml O ₂ per 1 min/1 soil gr	Invertase mg glucose/1 soil gr per 24 hours	Polyphenol oxidase, mg purpurgallin/100 soil gr per 30 min
1	2	3	5	6	7	8	9	10
First group of soils								
Ordinary calcic deep Chernozem (arable land, profile #28)								
A _p	0-25	3,14	2,48	0,21	1,20	7,0	17,06	Undef.
A	25-55	1,95	2,63	0,21	1,27	5,9	14,44	
B ₁	55-80	1,67	7,03	0,49	3,34	6,5	14,43	
B ₂	80-105	0,98	10,8	0,6	5,06	7,8	2,35	
BC	105-135	0,66	10,93	1,47	5,57	5,7	0	
C _{ca}	135-170	0,40	11,95	1,82	6,22	9,0	0	
1	2	3	5	6	7	8	9	10
Ordinary calcic deep Chernozem (woodland park zone, profile #29)								
A _d	0-10	7,90	3,62	1,64	2,35	4,7	4,51	23,28
A	10-32	3,68	2,55	1,46	1,81	5,5	1,04	16,76
B ₁	32-50	2,65	8,11	1,16	4,01	4,01	0,65	15,80
B ₂	50-70	1,98	12,11	1,21	5,73	3,0	0,26	26,07
BC	70-95	1,33	11,80	1,24	5,61	4,3	0	26,07
C	95-145	0,55	12,79	0,77	5,79	4,8	0	28,90
Ordinary calcic deep Chernozem (fallow land, profile #32)								
A _p	0-25	3,47	2,34	0,51	1,29	5,5	1,06	10,71
A	25-50	2,97	2,24	0,26	1,12	4,5	0,15	8,85
B ₁	50-70	2,19	2,34	0,59	1,33	3,7	0,41	18,6
B ₂	70-90	1,62	9,88	1,53	5,14	4,2	0	13,03
BC	90-108	1,00	12,06	1,79	6,23	4,6	0	15,8
C _{ca}	108-150	0,34	10,35	1,28	5,22	5,0	0	17,9
The second group of soils								
Urbanozem laid on ordinary carbonate buried Chernozem (city center, profile #22)								
U _{1ha2}	0-25	2,40	6,93	0,46	3,29	1,5	2,1	Undef.
U _{2hFe2}	25-45	4,09	8,05	0,6	3,85	0,6	0,79	
U _{3iha1}	45-55	1,02	8,9	0,81	4,34	3,5	1,7	
U _{4iha1}	55-90	0,52	9,64	0,74	4,62	2,7	0,12	
A _{1emb.}	90-100	2,38	4,93	0,95	2,67	2,3	1,95	
A _{2emb.}	100-120	2,12	2,25	0,84	1,43	3,7	4,33	
B	120-140	1,58	2,6	0,42	1,36	4,2	3,11	
BC	140-160	1,19	14,68	1,05	7,01	4,8	3,55	
C _{ca}	160-200	0,69	12,1	0,77	5,19	8,3	0	
Urbanozem laid on ordinary carbonate buried chernozem (city center, profile #31)								
U _{3iha1}	40-80	1,88	12,39	1,08	5,55	1,60	0	20,02
A _{emb.}	80-95	1,95	1,94	0,88	1,25	2,20	0	5,80
B ₁	95-110	1,36	4,47	0,73	2,25	2,23	0	9,30
B ₂	110-130	0,91	10,22	1,50	5,08	3,07	0	11,17
BC _{ca}	130-160	0,60	11,23	0,92	5,21	3,50	0	11,17
Urbo-chernozem with 25% of anthropogenic inclusions (boulevard in city center, profile #30)								
U _{4iha1}	25-35	2,56	5,56	0,72	2,74	4,7	0	3,72
A _{emb.}	35-60	2,77	2,1	0,90	1,33	5,5	0	3,03
B ₁	60-75	2,09	3,33	1,57	2,20	4,0	0	7,45
B ₂	75-90	1,81	3,55	1,10	2,04	3,0	0	19,56
BC	90-110	1,26	9,46	1,13	4,57	4,3	0	14,90
C _{ca}	110-150	0,64	12,12	1,24	5,75	4,8	0	14,90

Invertase activity is closely connected with content of organic substance content and activity of soil microflora[13], and this relation is directly proportional. We established that enzyme activity decreases with the reduction of organic substance content down the profile while analyzing the biochemical properties of ordinary chernozem [9]. Therefore it is understandable that in horizons A₁ и B₁ one can observe a sharp reduction in the degree of invertase activity at the same time that the humus content recedes to 3,7%. Along with that clear inverse relationship between carbonates' content in soil and their invertase activity is found not only in lower chernozem horizons, but also in surface horizons "urbik" and in located below recarbonated buried humus stratum.

Medium deep sealed urbanozem (25% of anthropogenic inclusions) on ordinary deep carbonate clay loam buried chernozem can serve as an example (profile 27). Here buried chernozem was sealed with an asphalt layer and an underlying 15-cm sawdust layer not long ago. This explains why invertase was not found in the upper part of the given profile (horizon U_{1ha1}) as carbonates that had penetrated into the soil from a chalkstone layer, suppressed enzyme activity (see the table 1). The highest value of invertase activity is seen in the horizon A₁ where both minimal CaCO₃ content and maximal humus content occur concurrently. However, this value is significantly lower than invertase activity in the same horizon in the profile located close to the investigated soil, but not under asphalt. It's proves that soil sealing has a negative influence on invertase activity even for a short period of time. In general, this soil can be characterized as very poor from the perspective of invertase content.

In urbanozems of the second and third groups in cases where the content of carbonates in the soil horizon exceeds a certain critical value, the level of invertase activity can reduce to zero. In unsealed urbanozems invertase distribution down the profile is analogous to invertase distribution in sealing urban soil. Thus, loose anthropogenic horizons of the second group urbanozem (profile 22) are once infused soil or rock layers of varied coloring, structure, humidity and density. Invertase activity within them decreases unevenly: in horizons U_{1ha2} and U_{3iha1} it is higher than in horizons U_{2hFe1} and U_{4iha1} (see the table 1). Enzyme activity contents correlate with the content of humus and carbonates in corresponding horizons. The horizon U_{2hFe1} is the only exception as it has low invertase activity whereas its humus content is high. This phenomenon, unusual at first sight, can be explained by the fact that the obvious gleying process resulting in low values of invertase activity takes place in this layer. In buried

soil dynamics of invertase activity replicates the same in nature. The maximum is observed in horizons A_{buried}, B and BC in which there are the lowest indicators of carbonate content as well as significantly high humus content. In horizon C_{ca} and further down the profile invertase activity falls to zero.

When comparing the derived values of the invertase activity to literary data given for virgin and arable soils [9], taking into account any reappraisal of derived data by G.Azzi [12] it can be seen that the invertase decrease factor in the urbanozems horizon A_{buried} amounts to 3,3–3,4, and the decrease factor of invertase activity under sealing equals 1,6. This shows that invertase activity is the most dynamic and responsive indicator of soil anthropogenic transformation.

In all the examined profiles irregular distribution of soil profile polyphenoloxidase can be observed (table 1). Both in sealed urban and natural soils maximum polyphenoloxidase activity is detected in the upper part of the profile which is caused by introduction of a new organic substance (urban natural soils) from the surface or various specific high-molecular compounds including those of phenol type (urbanozems and sealing urban soil) from outside or delivered anthropogenic layers. In the middle of the profile the dramatic decline of this enzyme activity can be seen, but in the lower zones polyphenoloxidase activity has again increased.

Polyphenoloxidase enzyme catalyzes the processes of phenols oxidizing in the presence of atmospheric oxygen, ipso facto, collaborating in the transformation of organic aromatic compounds into soil humus components [14]. Therefore, this increase is most probably connected with the changing reductive-oxidative conditions in the lowest part of the soil profile as well as the prevalence of an anaerobic mode of organic remnants' decomposition which impedes oxidizing phenol compounds and appears to be a favourable condition for their accumulation in a free state.

When comparing polyphenoloxidase enzyme activity in natural soils and urbanozems it is evident that its heightened content in the latter ones which can be connected with pollution of the soil by aromatic substances. Therefore, it is impossible to assess a degradation factor (in these cases the increase of enzyme activity is linked to soil degradation) using existing methods which assume index reduction.

In sealing urban soil polyphenoloxidase activity in buried humus horizons decreases. The index reduction can be said to conform to the third or fourth degradation factor. According to the polyphenoloxidase enzyme of the horizon A_{buried} the sealing urban soil decrease by a factor of 1.9.

Conclusions

1. Catalase, invertase and polyphenol oxidase activity in ordinary carbonate chernozem under urban conditions is considerably less than the activity of these enzymes in out-of-town analogs.
2. Sealing duration has a considerable influence on enzyme activity, and the longer this period is the higher the negative influence on tested enzymes' activity is. The high rate of decreasing enzyme activity under soil activity compared to the unsealed urban analog by catalase 1,4; by invertase – 1,6, and by polyphenoloxidase – 1,9.
3. Under urban conditions there is a strong link between the humus content of natural and anthropogenically transformed soils and their enzyme activity: high enzyme activity is typical for horizons containing maximum amount of organic substance irrespective of the nature of its origin.
4. Catalase and invertase activity react to carbonate content in soil in different ways: the relationship between soil catalytic activity and CaCO₃ content in the soil profile is one of direct proportionality while invertase activity, contrarily, with the addition of CaCO₃ significantly decreases.

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