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Evaluation of catalase activity and antioxidant properties of soils located in the buffer zone of the Roztocze National Park depending on their use

Ocena aktywności katalazy i właściwości antyoksydacyjnych gleb położonych na terenie otuliny Roztoczańskiego Parku Narodowego w zależności od ich użytkowania

Summary: Currently, one of the most sensitive indicators assessing the usable quality of soil is the assessment of enzymatic activity and total antioxidant capacity (TAC). They reflect, to a large extent, the possibility of producing high-quality plant materials, which is particularly important in protected areas, such as the buffer zone of a national park. The aim of the study was to assess catalase activity (CA) and antioxidant properties of brown soils depending on its use, located in the buffer zone of the Roztocze National Park. The material for the study consisted of soil samples collected from the humus horizon (A), browned horizon (Bw) and parent material (C) of three research plots.

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Experimental plots were marked out in an arable field (plot I), in a garden (plot II) and on fallow land (plot III). Basic chemical properties were determined in the soil samples, CA (biotic and abiotic) and TAC were analysed in soil extracts (ethanol, acetone and aqueous). The statistical analysis showed that CA and TAC of the soils were highly significantly positively correlated with most of the chemical properties tested, particularly organic carbon content.

Key words: brown soil, buffer zone, catalase activity, total antioxidant capacity

INTRODUCTION

Soil is the biologically active surface layer of the lithosphere. It is formed from the parent material as the result of pedogenetic factors, mainly living organisms, climate and water [Schoonover and Crim 2015]. Pedogenetic processes take place continually and are an integral element of the transformations occurring in ecosystems [Kajak 2016]. Soil is a complicated biological system composed of a vast number of microscopic environments formed due to accumulation of organic matter and to the stimulating activity of the root system of plants, as well as individual interactions of microorganisms [Strzelczyk 2001, Mohammadi at al. 2011]. Indicators of biological and biochemical activity include not only the quantity and composition of soil microbiota, but soil enzyme activity as well [Wielgosz and Szember 2001]. Enzyme activity is one of the most sensitive and reliable indicators of changes taking place in the soil, as well as a measure of its productivity and fertility [Furtak and Gałązka 2019]. According to Brzezińska and Włodarczyk [2005], catalase released from cells exhibits considerable stability in the soil owing to sorption on the surface of clay minerals and association with soil organic colloid.

Evaluation of physicochemical, biochemical and antioxidant parameters should be an integral element in the monitoring of the soil environment, where plants cultivated for food grow and develop [Skwaryło-Bednarz and Krzepiłko 2007]. Furthermore, such evaluation is an essential element of research on environmental protection. The literature concerning problems associated with protection of the soil environment provides numerous examples confirming the usefulness of this type of assessment. By analysing the physicochemical properties of soil, enzyme activity, number of microorganisms, and organic matter content, we can assess the quality of the soil to determine the degree of human impact on the soil environment [Skwaryło-Bednarz and Krzepiłko 2007]. This takes on particular significance in protected areas, such as the buffer zone of Roztocze National Park.

In one of our previous studies we proposed that soil could be analysed using a biochemical method for determining total antioxidant capacity (TAC) of biological material [Skwaryło-Bednarz and Krzepiłko 2007]. This parameter may be useful in evaluating the rate of redox processes taking place in the soil. Soil antioxidant content is of key importance for food quality and human health [Skwaryło-Bednarz 2019].

The aim of the study was to evaluate catalase activity and antioxidant properties in brown soil in relation to how it is used. The material for the study consisted of soil samples collected from the humus horizon (0–20 cm), browned horizon (20–45/75 cm) and parent material (<45/75 cm) of three research plots.

MATERIAL AND METHODS

Field research

The study plots were established on brown soils made of loess. According to the international taxonomy, these soils are classified as Cambisols [FAO 2015] located in the buffer zone of the Roztocze National Park (50°40'46"N, 22°58'48"E – 50°39'5"N 22°57'41"E), Lublin Voivodeship, south-eastern part of Poland. These soils were used in various ways: as an arable field (plot I), a garden (plot II) and fallow land (plot III). The material for the study consisted of soil samples collected from three horizons: the humus horizon (0–20 cm), browned horizon (20–45/75 cm) and parent material of each plot (<45/75 cm). From each horizon 25 samples were collected, from which weighted average samples were prepared. Chemical properties, catalase activity (CA) and antioxidant properties were determined in an average mixed sample of each of the soils.

Chemical properties

The following soil properties were determined:

– pH in 1 mol dm^{-3} KCl – potentiometric method [Ostrowska et al. 1991],

– sorption capacity (T) by the Kappen method [Ostrowska et al. 1991],

– organic carbon ($C_{org.}$) content by the Tiurin method [Sapek and Sapek 1997],

– total N content by the Kiejdahl method [Ostrowska et al. 1991],

– content of available P and K forms in the soil was determined based on the results of their extraction from the soil according to the Egner-Riehm method, and content of Mg by the Schachtschabel method [Kabała and Karczewska 2019]. The content of available forms of nutrients in the soil was compared with threshold values.

Preparation of soil material for determination of catalase activity (CA)

The soil material, after sampling from each genetic horizon of the tested soils, was transported to the laboratory, and then sieved through a sieve with a mesh diameter of 1 mm. The soil material prepared in this way was used to determine the activity of catalase in fresh soil at individual genetic horizons. In order to obtain air-dried soil material, it was laid out in the form of a thin horizon and dried for 14 days, and then sieved again. The control was quartz sand (humidified to fresh soil moisture or air dry).

Catalase activity (CA)

The decomposition of hydrogen peroxide in the soil (catalase test) to water and oxygen was studied according the modified Beck method [Brauner and Bukatsch 1987]. For this purpose, 1 g of fresh or dried and sieved soil was placed in a calibrated Eykman test tube (Labor Szklo, Lublin) and 25 ml of 3% H_2O_2 were added. The height of the oxygen gas column released from the solution in centimeters was measured every minute. The unit of catalase activity (CA) is the volume of oxygen in centimeters released in 1 min by 1 g of a fresh (biotic catalase activity – biotic CA) or dried (abiotic catalase activity – abiotic CA) soil sample (cm min^{-1} g^{-1}).

Soil extract

The soil extracts (soil mixed with solvent in a weight ratio of 2 : 1) – ethanol, acetone and aqueous – for determining TAC were prepared according to a procedure described by Baran [2000].

Total antioxidant capacity (TAC)

TAC was determined according to Rice-Evans and Miller method [1994] with a modification by Bartosz [2003]. A methanol solution of DPPH (2,2-diphenyl-1--picrylhydrazyl) was added to a extract of ethanol, acetone and aqueous soils. After 30 min, the decrease in absorbance relative to the control sample was measured at 515 nm. TAC (mM Trolox 1 cm^{-3} g^{-1} soil) of 1 cm^3 of extract prepared from 1 g of soil was expressed as mM Trolox equivalent.

Statistical analysis

Data for statistical computations were taken from at least three independent experiments, each performed in three replications. Statistical analysis was performed using one-way analysis of variance (ANOVA) in STATISTICA 10.0 software, at a significance level of $p < 0.05$. Homogeneous groups were determined using the Tukey test.

RESULTS

While the soil horizons tested in the arable field (plot I) had acidic pH, the humus horizon and parent material had similar pH, while that of the browned horizon was lower (Tab. 1). In the soil from the garden (plot II), the humus horizon and browned horizon had neutral pH, while the parent material was slightly acidic. The soil samples collected from the humus horizon and parent material of plot III (fallow land) had acidic pH, and the browned horizon samples were highly acidic (Tab. 1).

Table 1. Chemical properties of the soils analysed – mean values

Parameters	Plot I Arable field			Plot II Garden			Plot III Fallow land		
	L1	L2	L3	L1	L2	L3	L1	L2	L3
pH_{KCl}	5.3	5.0	5.2	7.1	7.1	5.6	5.5	4.4	5.4
Organic carbon (g kg^{-1})	16.2	5.2	–	18.6	6.4	–	14.5	4.1	–
CEC (cmol(+) kg^{-1})	5.04	7.04	7.58	6.95	9.56	7.95	4.75	4.08	3.85
Total N (g kg^{-1})	3.8	4.1	0.9	4.6	5.2	1.1	2.2	1.9	0.7
P (mg kg^{-1})	87.6	34.4	23.5	232.8	242.0	27.9	41.0	17.0	26.2
K (mg kg^{-1})	190.1	54.0	165.2	36.5	195.1	37.4	92.1	30.7	28.2
Mg (mg kg^{-1})	103.0	102.0	121.0	87.0	90.0	124.0	103.0	71.0	120.0

L1 – humus horizon, L2 – browned horizon, L3 – parent material; CEC – cation exchange capacity

Organic carbon ($C_{org.}$) content in the humus horizons of the soils studied was highly varied. It was highest (18.6 g kg^{-1}) in the soil from the garden, lower in the soil from the arable field (16.2 g kg^{-1}), and lowest in the fallow soil (14.5 g kg^{-1}). Organic carbon content in the browned horizons ranged from 4.1 to 6.4 g kg^{-1} and was dependent on its content in the humus horizons (Tab. 1).

The sorption capacity of the soils analysed was varied. In the humus horizon of the arable field (plot I) it was 5.04 (cmol(+)·kg^{-1}) and increased with the depth of the soil profile, achieving a value of 7.04 (cmol(+) kg^{-1}) in the browned horizon and 7.58 (cmol(+) kg^{-1}) in the parent material. The highest sorption capacity in the soil horizons was noted in the soil from the garden (plot II); it was 6.95 (cmol(+) kg^{-1}) in the humus horizon, increased substantially in the browned horizon – 9.56 (cmol(+) kg^{-1}), and decreased in the parent material, while remaining higher than in the humus horizon – 7.95 (cmol(+) kg^{-1}). The lowest values for this parameter were observed in the fallow soil (plot III). Moreover, the sorption capacity on this plot decreased with the depth of the soil profile (humus horizon – 4.75 (cmol(+) kg^{-1}), browned horizon – 4.08 (cmol(+) kg^{-1}), parent material – 3.85(cmol(+) kg^{-1}) (Tab. 1).

The highest total nitrogen (N) content was noted in the soil horizons of plot II, with the highest level in the browned horizon (5.2 g kg^{-1}), and the lowest in the parent material (1.1 g kg^{-1}). A similar relationship was demonstrated for plot I, but the amounts of total N were lower. In the case of the fallow soil (plot III), the total N content decreased with the depth at which the soil was collected (Tab. 1).

Determination of basic nutrients in each research plot showed that the humus horizon of the arable field (plot I) had high content of available phosphorus (P) forms, which decreased with the depth of the soil profile, attaining a low level in the browned horizon and parent material. In the case of the soil from the garden (plot II), the humus horizon and the browned horizon had very high content of available P forms, with a higher level noted in the browned horizon. The parent material of this plot had low content of available forms of P. The content of available P forms in the fallow soil (plot III) was low in the humus horizon, very low in the browned horizon and low in the parent material (Tab. 1).

The content of available forms of potassium (K) in the humus horizon of the arable soil (plot I) was high, but was very low in the browned horizon and intermediate in the parent material. The content of available K forms in the humus horizon and parent material of the garden soil (plot II) was very low, while that of the browned horizon was high. Low content of available K forms was noted in the humus horizon of the fallow soil (plot III), and it decreased with the depth of the soil profile, attaining a very low value in the parent material (Tab. 1).

The studied horizon of arable soil (plot I) were characterized by a very high abundance of available forms of magnesium (Mg), the garden soil (plot II) was abundant in the humus and browned horizon levels, and very high from the parent material. The fallow land (plot III), on the other hand, showed a very high abundance of available forms of Mg in the extreme level and high in the browned horizon (Tab. 1).

Catalase activity (CA) in the three soil horizons of plots I–III was determined in fresh and dried soil material (biotic and abiotic catalase activity). The highest biotic CA from the humus horizon (1.14 cm min^{-1} g^{-1}), was noted for the fallow field (plot III). CA in the fresh soil samples from this plot decreased with soil depth, attaining a value of 0.35 cm min^{-1} g^{-1} in the parent material. Biotic CA in the humus horizon of research plot III was over 3 times greater than in the parent material. In plot I biotic CA was 1.10 cm min^{-1} g^{-1} in the humus horizon, and in the browned horizon was slightly higher and amounted 1.16 cm min^{-1} g^{-1}, and in the parent material more than twice lower than in the browned horizon – 0.57 cm min^{-1} g^{-1}. The lowest CA in fresh soil samples from the humus horizon was noted for research plot II – 0.89 cm min^{-1} g^{-1}. The value for activity of this enzyme decreased with the depth of the soil profile, attaining a value of 0.63 cm min^{-1} g^{-1} for the browned horizon and 0.25 cm min^{-1} g^{-1} for the parent material, which was 3.5 times less than in the humus horizon (Tab. 2).

Table 2. Catalase activity (CA) of the soils analysed – mean values

Horizons	Catalase activity – CA (cm·min^{-1}·g^{-1})							
	biotic (fresh soil)				abiotic (dry soil)			
	arable field	garden	fallow land	mean	arable field	garden	fallow land	mean
L1	1.10 ^{a}	0.89 ^{a}	1.14 ^{a}	1.13 ^{a}	0.33 ^{a}	0.37 ^{b}	0.51 ^{a}	0.40 ^{a}
L2	1.16 ^{a}	0.63 ^{b}	1.14 ^{c}	0.98 ^{b}	0.35 ^{a}	0.40 ^{a}	0.37 ^{b}	0.37 ^{a}
L3	0.57 ^{b}	0.25 ^{c}	0.35 ^{b}	0.39 ^{c}	0.35 ^{a}	0.18 ^{c}	0.28 ^{c}	0.27 ^{b}
$LSD_{0,05}$	0.10	0.09	0.06	0.26	0.05	0.03	0.04	0.08

L1 – humus horizon, L2 – browned horizon, L3 – parent material
Values marked with the same letters for the experimental factor (a, b, c) do not differ significantly at $p \leq 0.05$

The highest abiotic CA was noted for plot III, attaining a value of 0.51 cm min^{-1} g^{-1} in the humus horizon, 0.37 cm min^{-1} g^{-1} in the browned horizon and 0.28 cm min^{-1} g^{-1} in the parent material. In plots I and II the browned horizon exhibited higher activity of this enzyme than the humus horizon (Tab. 2).

TAC of the soil horizons analysed was determined by preparing soil extracts – ethanol, acetone and aqueous. Estimation of TAC based on analysis of the ethanol extracts showed the highest value for this parameter in the browned horizon of the garden soil (plot II) – 4.90 mM Trolox cm^{-3} g^{-1}. This was 1.8 times higher than the value noted for the humus horizon and 2.4 times higher than in the parent material of the garden soil (Tab. 3). In plot I the highest TAC measured in the ethanol extracts was also found in the browned horizon (2.92 mM Trolox cm^{-3} g^{-1}), while the values obtained for the humus horizon and parent material were lower and very similar. In the fallow soil antioxidant capacity was also highest in the browned horizon, at 2.69 mM Trolox cm^{-3} g^{-1}, compared to 2.49 mM Trolox cm^{-3} g^{-1} in the parent material and 2.58 mM Trolox cm^{-3} g^{-1} in the humus horizon (Tab. 3).

Measurements made in soil extracts prepared using acetone also indicated that the browned horizon of the garden soil had the highest TAC, at 2.86 mM Trolox cm^{-3} g^{-1}, compared to 2.38 mM Trolox cm^{-3} g^{-1} in the parent material and 2.64 mM Trolox cm^{-3} g^{-1} in the humus horizon. The data in Table 2 show that TAC of the acetone extracts from the three horizons of arable soil were similar. In the case of the fallow soil, the highest antioxidant capacity was noted in the acetone extracts prepared from the browned horizon (2.70 mM Trolox cm^{-3} g^{-1}), followed by the humus horizon (2.62 mM Trolox cm^{-3} g^{-1}) and the parent material (2.46 mM Trolox cm^{-3} g^{-1}) – Table 3.

Estimation of TAC using aqueous soil extracts confirmed the highest capacity in the humus horizon of plot III, with a value of 3.09 mM Trolox cm^{-3} g^{-1}. This was 1.1 times higher than in the browned horizon and 1.8 times higher than for the parent material. As in the case of the fallow land, the highest antioxidant capacity in the aqueous soil extracts was noted in the humus horizon of the arable field (2.95 mM Trolox cm^{-3} g^{-1}). The antioxidant capacity in plot I decreased with the depth of the soil profile (browned horizon – 2.49 mM Trolox cm^{-3} g^{-1}, parent material – 1.67 mM Trolox cm^{-3} g^{-1}). In the case of plot II the highest antioxidant capacity of the soil extracts prepared using water was observed in the browned horizon as well – 2.66 mM Trolox cm^{-3} g^{-1}, in comparison with the humus horizon (about 1.3 times higher) and the parent material (1.5 times higher) – Table 3.

Table 3. Total antioxidant capacity (TAC) of the soils analysed – mean values

Horizons	Total antioxidant capacity (mM Trolox cm^{-3} g^{-1})											
	ethanol extract				acetone extract				aqueous extract			
	arable field	garden	fallow land	mean	arable field	garden	fallow land	mean	arable field	garden	fallow land	mean
L1	2.77 [b]	2.70 [b]	2.58 [b]	2.68 [b]	2.57 [a]	2.64 [b]	2.62 [a]	2.61	2.95 [a]	2.05 [b]	3.09 [a]	2.70 [a]
L2	2.92 [a]	4.90 [a]	2.69 [a]	3.50 [a]	2.56 [a]	2.86 [a]	2.70 [a]	2.71	2.49 [b]	2.66 [a]	2.87 [b]	2.67 [a]
L3	2.80 [b]	2.05 [c]	2.49 [c]	2.45 [b]	2.57 [a]	2.38 [c]	2.46 [b]	2.47	1.67 [c]	1.77 [c]	1.70 [c]	1.71 [b]
$LSD_{0.05}$	0.05	0.08	0.04	0.75	0.03	0.07	0.09	0.11	0.04	0.16	0.12	0.36

L1 – humus horizon, L2 – browned horizon, L3 – parent material
Values marked with the same letters for the experimental factor (a, b, c) do not differ significantly at $p \leq 0.05$

Many significant correlation coefficients were found between the analyzed basic chemical properties and CA and TAC (Tab. 4). CA in fresh soil was significantly positively correlated with organic carbon content (r = +0.650) as well as CA in dry soil (r = +0.760), and negatively correlated with Mg content (r = –0.591). TAC measured in the prepared ethanol extracts was positively correlated with pH_{KCl} (r = +0.540), cation exchange capacity (r = +0.558), N (r = +0.654), P (r = +0.671), K (r = +0.617). However, TAC determined in acetone extracts was positively correlated with the content of N (r = +0.652), P (r = +0.637), CA in dry soil (r = +0.684), but negatively with the content of Mg (r = –0.759). TAC determined in aqueous soil extracts was positively correlated with the content of $C_{org.}$ (r = +0.565), CA in fresh soil (r = +0.841), CA in dry soil (r = +0.667), but negative with Mg content (r = –0.637). A significant positive relationship was also found between the content of $C_{org.}$ and N (r = +0.635) – Table 4.

Table 4. Correlation coefficients of chemical properties and catalase activity with organic carbon content and total antioxidant capacity ($\alpha_{0.05}$)

Parameters	pH_{KCl}	Organic carbon	CEC	N	P	K	Mg	Biotic CA	Abiotic CA
Organic carbon	0.405	–	–0.138	0.635	0.532	0.180	–0.453	0.650	0.654
Biotic CA	–0.246	0.650	–0.382	0.396	–0.026	0.060	–0.591	–	0.760
Abiotic CA	0.132	0.654	–0.144	0.374	0.250	0.285	–0.508	0.760	–
TAC									
1. ethanol extract	0.540	0.064	0.558	0.654	0.671	0.617	–0.380	0.009	0.381
2. acetone extract	0.403	0.332	0.265	0.652	0.637	0.455	–0.759	0.395	0.684
3. aqueous extract	0.133	0.565	–0.265	0.474	0.107	0.285	–0.637	0.841	0.667

DISCUSSION

Soil is the basic production resource of agriculture, and its good quality provides the potential for high-quality food production. Degraded soil, on the other hand, is a source of adverse effects on human health. In the Lubelskie Voivodship, where the research was conducted, there are many good quality soils for agricultural production, according to the IUNG-PIB scale in Puławy, the quality index of agricultural production space in this voivodship is 74.1 points (nationally 66.6 points), which is one of the highest in Poland [Guzal-Dec et al. 2015]. Awareness of the importance of environmental values can be used in taking specific actions in the field of agricultural production, especially in the buffer zone of, for example, the Roztocze National Park or other nature reserves. These areas can be used to produce high-quality food, from farm to table.

Valuable soils in the buffer zone of the Roztocze National Park, in terms of agricultural usefulness, are brown soils, which, next to podzolic soils, dominate in terms of area occupied. They are found in various places of the buffer zone. They are medium-value soils, and their quality depends primarily on water conditions [Uziak 2001].

The analyzed brown soils were characterized by typical values of chemical properties, shaped also by agrotechnical treatments, including fertilization, which is most noticeable in garden soils. It should be noted that in addition to these properties, a general indicator of environmental conditions in the context of obtaining good quality crops is the assessment of the enzymatic activity of soils, including catalase [Skwaryło-Bednarz et al. 2022].

The analyzed soils were characterized by average (pH_{KCl}, C_{org} content) or slightly lower (CEC) values of chemical properties for brown soils, also shaped by agricultural practices, including fertilization (organic, mineral), which is most noticeable in garden soils.

It is also important to study these activities in fresh and air-dry soil. According to Bartosz [2003], the decomposition of hydrogen peroxide in a fresh soil sample is caused by microorganisms containing the catalase enzyme, but also organic compounds with antioxidant properties and mineral compounds, such as heavy metal oxides or transition metal ions – Fe^{2+} or Cu^{1+}. For this reason, the rate of hydrogen peroxide decomposition in a fresh soil sample is usually faster than in an air-dried sample, where the activity of microorganisms is usually low [Skwaryło-Bednarz and Krzepiłko 2007, Skwaryło-Bednarz et al. 2018].

According to Lemanowicz [2019], the assessment of catalase activity in the soil is very important, because it informs about the activity of soil microorganisms, and catalase is one of the most resistant enzymes in soil to anthropogenic factors, which results from the value of the resistance index – RS.

Catalase activity in fresh and dried soil decreases with the depth of the soil profile, which results from the presence of organic matter in the surface horizons and the abundance of soil microorganisms [Skwaryło-Bednarz et al. 2014]. Similar relationships were found in this study. Purev et al. [2012] research shows, however, that catalase activity decreases faster with increasing depth in soils subjected to strong anthropopressure compared to soils from natural sites.

This is confirmed by the results obtained in the present study. The statistical analysis showed significant positive correlations between organic carbon content in the soils from the plots and soil horizons tested and CA in fresh and dry soil. Such correlations have also been found in other studies [Martyn and Skwaryło-Bednarz 2005, Skwaryło--Bednarz and Krzepiłko 2007, Krzyżaniak and Lemanowicz 2013].

Catalase activity in soil depends not only on the organic matter content, but also on total N, available P and K [Formánek and Vranova 2003, Borowska et al. 2013]. Such relationships were not found in this study.

How soil is used has been shown to affect its enzyme activity [Saviozzi et al. 2001]. The authors found that in general all the biological properties tested had the highest activity levels in native grassland soil, followed by forest soil and then cultivated soil. Soil on which maize was grown intensively had the lowest values for such parameters as total N, water-soluble organic C (WSOC), phenolic substances, and enzyme activity (alkaline phosphatase, protease, β-glucosidase, urease, catalase and dehydrogenase). The authors postulate that parameters such as total and humified organic carbon, water-soluble organic carbon and soil enzyme activity can serve as indicators of the effectiveness of soil cultivation. In own research, the CA of fresh and dry soil depended on soil use. It is interesting that the uncultivated soils were characterized by the highest CA value in fresh and dry soil. Similar conclusions are noted from studies by other authors who emphasize that in fallow soils there is an increase in biological activity [Landgraf and Klose 2002, Jian-gang et al. 2004]. Even a 2-year fallow, compared to soils used for agriculture (under maize cultivation and cocoa plantation), increases the enzymatic activity of the soil expressed in the assessment of the activity of various enzymes and the values of chemical properties parameters [Gonnety et al. 2012].

In the present study TAC of soils used in different ways was measured in three different horizons. Only TAC determined in water soil extracts was positively correlated with organic carbon content.

Water-soluble organic carbon (WSOC) contains mainly organic acids and soluble carbohydrates [Horník et al. 2021]. The quantity of WSOC in the different soils is influenced by a number of factors, including how the soil is used and climate conditions. Content of WSOC in intensively exploited soils (e.g. for vegetable production) has been shown to be significantly lower than in the soil of meadows and forests [Cardelli et al. 2012]. Similar relationships were demonstrated by Riffaldi et al. [2002]: arable soils were characterized by substantially lower content of this fraction of organic carbon in comparison with undisturbed areas. Saviozzi et al. [2001] noticed that this parameter is strongly influenced by intensive leaching of soluble compounds from the soil profile by precipitation.

Rimmer [2006] put forth the hypothesis that antioxidants present in the soil have a role in protecting soil organic matter (SOM) against oxidation. A study by Aeschbacher et al. [2012] confirmed that organic components of soil containing phenolic groups are the main sorbent for organic contaminants in soil and sediment. During the sorption process irreversible reactions may take place reducing quinones to hydroquinones that make up humic acid. These changes affect not only the sorption capacity of soil but also its redox potential and pH.

Soil chemical parameters are of great importance in assessing the antioxidant capacity of the soil. In own research, significant positive correlations were found between TAC determined in water soil extracts and pH_{KCl} and CEC.

Studies by Schepetkin et al. [2002] as well as by Rimmer [2006] have demonstrated strong antioxidant properties in humus containing humus acids. Many analyses of different soil horizons have shown that the greatest quantity of antioxidant substances in soil is found in humus. Schepetkin et al. [2002] showed that a large quantity of antioxidant humus substances can affect various chemical and biochemical processes taking place in the rhizosphere (movement of water and nutrients, oxidation and reduction reactions, secretion by plant roots of organic acids, sugars, phenols and amino acids, or chelate formation).

In the study of Skwaryło-Bednarz and Krzepiłko [2007], the chemical and microbiological properties of soils were compared and the TAC was measured in three soil types from the buffer zone of the Roztocze National Park. Soil TAC was significantly positively correlated with the content of organic carbon, CA and the number of soil microorganisms.

Saviozzi and Cardelli [2014] investigated the effect of pelleted cow manure (PCM), peat, municipal solid waste compost (MSWC), wet olive husk compost (WOHC) and green waste compost (GWC) on soil biochemical activity and total antioxidant capacity (TAC). They also evaluated organic carbon content in these organic materials. Their tests showed that TAC was closely correlated with phenol content and organic carbon content. The present study showed significant correlations between soil organic carbon content and TAC of soil extracts.

Cardelli et al. [2012] evaluated soil organic matter content, biochemical activity and antioxidant capacity in Mediterranean land use systems. Soil quality characteristics were measured in adjacent agricultural (horticultural cropping sequence), native grassland (naturally grazed) and forest (indigenous wood of holm oak) soils. TAC of the soils was highest in the native grassland and correlated with the amount of alkali-soluble phenols. The rate constant of organic matter mineralization (k) appeared to depend on TAC rather than on the relative amounts of the labile C pools. These results seem to explain the role of phenols as controllers of the mineralization rate of organic matter.

There are many positive relationships between the TAC determined in ethanol and acetone extracts of soils and their content of N, available P and K. Skwaryło-Bednarz and Krzepiłko [2009] in their studies also showed positive relationships between fertilization and the TAC of brown soil under amaranth cultivation. However, the authors did not find a solution concerning negative correlations between the TAC value in acetone and aqueous solutions and the content of available forms of Mg. Only Hailes et al. [1997] found that available Mg is not significantly correlated with the content of organic carbon in the soil. This may indicate a close relationship between TAC and soil organic matter, and Mg with primary and secondary clay minerals, from which Mg passes into the soil solution. The uptake of Mg by plants depends also on the pH of the soil, and in acidic and alkaline soils it becomes unavailable for plants [Nurzyński 2008, Senbayram et al. 2015]. Moreover, in brown soils, the content of available Mg forms in deeper levels is higher than in the surface layer. This indicates leaching of this element to deeper soil layers under the influence of rainwater [Krzywy 2007].

Soil fertilization, particularly with organic fertilizers, plays a fundamental role in increasing the content of antioxidant compounds in various plant raw materials. Adding compost to arable soil (in proportions of 1:1) or cultivation on compost alone has been shown to increase the concentration of ascorbic acid and glutathione, and in consequence the content of antioxidant compounds in the fruits of two varieties of strawberries, Allstar and Honeoye [Wang and Lin 2003].

It can suppose that in our own research a significant impact on the TAC (ethanol extract, acetone extract) had the way of soil use, which was noticeable in the case of garden soils, where organic fertilization is usually used, which positively affects this parameter.

The present study found numerous significant, positive correlations between TAC of the ethanol, acetone and aqueous extracts of the soils analysed and their chemical properties and CA (Tab. 4). Particularly worth noting is the significant positive correlation between total N content in particular soil horizons and TAC. According to Sykut [1993] and Sapek [1996], nitrates are easily leached from the soil because they are not absorbed by it and always occur in soluble form. This means that water permeating through the soil transports them deeper into the soil profile. The amount of nitrates permeating into the groundwater depends mainly on their concentration in the soil. Water permeating through the soil probably transported N compounds down the soil profile, which is why high antioxidant capacity was noted in the solutions of soil from the browned horizon.

In our own research, significant positive correlations were also obtained between TAC in soil water extracts and biotic and abiotic CA, and TAC in acetone extracts and abiotic CA, which clearly indicates a strong relationship between organic carbon content and direct enzymatic activity and indirect soil TAC.

CONCLUSIONS

1. The tested brown soils were characterized by typical values of the assessed chemical properties, i.e. pH_{KCl}, organic carbon content and CEC. The content of total N and available forms P, K and Mg in the horizons of brown soils, especially arable fields and garden soils, were shaped by agrotechnical factors.

2. Biotic catalase activity (CA) from humus horizons depended on the intensity of cultivation, its highest value was recorded in fallow lands, and the lowest in garden soils. Biotic CA outside the arable fields decreased with the depth of the soil profile.

3. Abiotic catalase activity (CA) from the humus horizons was as follows (from the highest to the lowest value): fallow land→garden soil→arable field, in the case of brown horizons: garden soil→fallow land→arable field, and in the parent material: arable field→fallow land→garden soil.

3. Biotic and abiotic CA were closely and positively correlated with the organic carbon content.

4. The highest total antioxidant capacity (TAC) in soils, measured in ethanol, acetone and water extracts, was generally observed in most brown horizons.

5. Significant positive correlations were found between the total antioxidant capacity (TAC) of water soil extracts and the organic carbon content and TAC of acetone extract and available forms of P content and ethanol extract as well as pH_{KCl}, CEC, total N content and available P and K forms in the soil.

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