

THE CHARACTERISTICS OF THE ADSORPTIVE COMPLEX AND THE REACTION OF SOILS SUBJECTED TO HIGH ANTHROPOGENIC PRESSURE FROM THE COPȘA MICĂ AREA

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Abstract

Anthropogenic pollution triggers a series of processes that also affect the bioavailability of nutrients, the soil being a key element in food security and sustaining biodiversity. The purpose of this research is to identify the influence of the soil reaction and the values of the adsorptive complex indices (SH, SB, CEC, V) on the nutritional status of the soils around the town of Copșa Mică in the context of over 70 years of pollution). Soil pH is a reliable indicator of chemical transformations and a predictor of possible deficiencies or toxicity of elements necessary for plant physiology. The adsorptive complex indices have a diagnostic and prognostic role on the health of the soils, reflecting the degree of nutrient supply. In the 13 sample areas, the soil reaction varies from very strongly acidic to weakly alkaline, an important role being attributed to the influence of the orography of the land and the local pollutant-dispersing microclimate. The dynamics of the determined or calculated values of the adsorptive complex indices vary depending on the sampling depth and the investigated SP.

Key words: adsorptive complex indices, soil reaction, Copșa Mică area.

INTRODUCTION

Soil reaction is the result of multiple chemical transformations with prognostic role on the danger of nutritional deficiencies or potential toxicity (Slattery et al., 1999; McKenzie et al., 2004). In agronomy, acidity is an indirect indicator of soil fertility through its impact on root exudates (Stoltz & Greger, 2002; Pansu & Gautheyrou, 2006), acting as a limiting factor on plant growth (especially roots), nutrient uptake due to the release of toxic Al³⁺ in susceptible plants (Cronan et al., 1995; Lindsay & Walthall, 1996). Islam et al. (1980) highlight the corrosive action of low pH on root membranes. Bessho & Bell (1992), Menzies et al. (1994) support the idea that in soils with similar mineralogy and highly degraded soils, pH can accurately predict Al toxicity. Humic substances in the composition of organic matter can buffer the pH. Spurgeon et al. (2006), Rooney et al. (2006) indicate industrial pollution as a determining factor in influencing soil pH with an immediate effect on the bioavailability and toxicity of metal pollutants on the soil biocenosis. Anthropogenic acid discharges have effects similar to natural soil

acidification (Kennedy, 1992; Saha, 2017) and affect soil fertility by removing essential basic cations, thus increasing the toxicity of Al and Mn (Rhode et al., 1995), and the toxic action of metals heavy impacts mineralization, nitrification, symbiotic relationships, and decreases pH value and P bioavailability (Foy, 1984; Al-Fredan, 2011; Bach et al., 2020). Heavy metals such as Pb, Cd, Cu, Ni or Zn shows a mathematical correlation with the concentration in the soil solution, with pH being the most critical factor whose increase favours the absorption of these metals (Basta & Tabatabai, 1992; McBride, 1994). In “virtually unaffected” pollution areas, soil acidification occurs as a result of the accumulation of H⁺ from the biogeochemical circuit of C, N and S (Ulrich, 1991).

Changes in pH due to the action of anthropogenic pollutants depend on the type and chemical composition of the pollutant emissions. SO₂ rich emissions from non-ferrous smelters increase soil acidity, and the presence of particulate matter containing metal oxides cannot buffer the SO₂ impact on pH. In forest soils, both wet deposition (via acid rain) and dry deposition (gases, vapours, particulate

matter, tailings) accelerate soil acidification (Davidson, 1990; Legge, 1990; Lorenz, 1995). Research has not revealed the dependence of pollutant type or pH with soil depth. (Kozlov et al., 2009). The increase in soil *pH* triggers a decrease in the solubility of most elements, thus limiting their flow into the soil solution. The mobility and bioavailability of some elements at high *pH* is due to the formation of complexes with soil organic fractions (Kabata Pendias, 2011; Bravo et al., 2017; Solly et al., 2019). Forest soils are more acidic than those intended for crop plants, the input of H⁺ being also added to that of N and heavy metals, and trees can accumulate significant amounts of Cd and other heavy metals (Mayer, 1993; Li & Li, 2005).

Adsorptive complex indices and their role in soil health and trophicity

Cation exchange capacity (CEC) represents the sum of the exchangeable cations OCa^{2+} , Mg^{2+} , K^+ , Na^+ (in Al^{3+} acid soils), adsorbed by the soil, with metals such as Mn, Fe, Cu, Zn having insignificant contribution (Osman, 2013; Hazelton & Murphy, 2016). From the perspective of agronomists and ecologists, exchangeable cations and CEC are intrinsic indicators of the health, fertility, physical and chemical status of soils, the retention capacity of nutrients, pollutants or, as the case may be, of fertilizers. Hazelton & Murphy, (2016); Mukhopadhyay et al. (2019), highlights the role of CEC in buffering *pH* fluctuations, Ca^{2+} content and soil structural changes. Revil & Leroy (2004) show the major role of CEC on plant growth, fertility and soil transport processes. Among soil colloids, organic matter presents a high CEC, between 100 and 300 cmol/kg, being influenced by clays and organic matter (Fooladmand, 2008; Sulieman et al., 2018). The adsorptive complex that regulates the degree of storage, distribution, mobility and bioavailability (Dalal & Moloney, 2000; Pansu & Gautheyrou, 2006; Ross et al., 2008) impacts potentially toxic cations from anthropogenic polluting sources (Pb).

Studying the impact of carbon black on nutrient retention in anthrosols of Amazonian Brazil, Liang et al. (2006) highlights that soils with a high carbon black load show a high CEC (i.e. *pH* 7). CEC value depends on the type of soil,

fertile soils showing values between 8 and 10 meq/100 g soil, the sandy ones <10 meq/100 g soil, and the clayey ones between 10-15 meq/100 g soil. A moderate CEC value i.e. >12 indicates a good nutrient retention capacity (Botta, 2015; Ghorbani et al., 2015). Soils with low CEC values are vulnerable lacking essential cations that are washed out of the soil.

The degree of saturation with bases (V, %) represents a proportion of CEC occupied by bases (Osman, 2013), showing a close correlation with *pH* in acidic or neutral soils, ranging between 20 and 60% at $\text{pH} \geq 5$. This index may be impacted by clays and it shows how close nutritional status is to potential fertility (Rengasamy & Churchman, 1999). Many forest soils in Central Europe have a low saturation with bases, being depleted in exchangeable cations (BML, 1996). Soils with $V, \% < 50$ are dystrophic, poorly or moderately fertile. Lukac & Godbold (2011) show that soils with high $V, \%$ buffer soil acidity more effectively by controlling the release of toxic elements, while a low $V, \%$ enhances the sensitivity of soils to acid deposition.

The characteristics of the edaphotopes of the Coșa Mică area by the time of research

According to Untaru et al. (2000), with regard *pH*, the systematic edaphic unit and the degree of pollution cause an acidification of the soil in the range of extremely acidic to neutral or weakly alkaline reaction (6.0-8.0). The negative effects of pollutant emissions on soils, observed by Alexa et al. (2004) are as follows: increased acidity and base saturation loss in adsorptive complex. In the Târnăvioara Improvement Perimeter, the slope is affected by pollution, artificial terracing and erosion. Because of the mass displacements, steep detachment ravines appear alternating with landslides as effect of slope breaks (Alexa et al., 2004). Based on data collected between 1973-1999 Cotârlea et al. (2001) cited by Alexa et al. (2004), fully covers the forestry real estate from management unit (MU) II Micăsasa, MU III Târnavă within forest district (FD) Mediaș in zone I of very strong pollution and 40% of forests within zone I and 60% in zone II on the territory of MU I Șeica Mică. It is worth mentioning that the sample areas-SP (delimited for this study) SPs 2, 6, 7 East, 7

West, 8 9 (MU III Târnavă/FD Mediaș); SPs 12, 13, 14, 15 and 16 (MU I Șeica Mică/FD Mediaș) are within the pollution zones I and II (Alexa et al., 2004).

The multi-decade aggression on the soils within the Copșa Mică area was also due to acid rains and fine powders containing Pb, Cu, Cd, Zn, and Fe. Ianculescu et al. (1994) observe that the *pH* in the horizons of the upper part of soil decreases by 0.6-2.4 units, the degree of saturation with bases (*V*, %) shows a reduction of 20-30%, the exchangeable Al content ranging between 700-800 ppm. The same author finds a high acidity (*pH*=4) in the soil Ao horizon, which is a characteristic present throughout the depth of the profiles, with some exceptions, the *pH* having values below 6.0 in the deeper horizons of the soil. Between 1985-1994, some plots showed a slightly decreasing trend of the soil reaction in the upper horizons. After reviewing the data obtained from 1996 and 2001, Alexa et al. (2003) conclude that the soil surface horizon is generally acidic, while at depths of more than 40 cm the reaction becomes weakly acidic or neutral. A recent research work by Iordache et al. (2020) finds a slightly acidic soil reaction at the depths of 0-20 cm and 20-40 cm.

The research on the physical and chemical characteristics of the edaphotopes within the Copșa Mică area was carried out in the year when the cessation of activity of the main polluter i.e. the company S.C. Sometra S.A. from Copșa Mică (26.01-31.03.2009) took place, the other polluter, i.e. the company Carbosin S.A. being decommissioned permanently since 1995.

MATERIALS AND METHODS

Soil sampling took place between 15 November and 4 December 2009 in accordance with the sampling norms proposed by the National Research-Development Institute for Pedology, Agro-chemistry and Environmental Protection (ICPA) Bucharest (xxx, 1981). Sampling depths were as follows: 0-5 cm, 10-15 cm, and 30-35 cm. The experimental device includes 14 sample areas (see Figure 1) abbreviated SP1 (MU I Veseuș/FD Aiud); SPs 2, 6, 7 East, 7 West, 8 9 (MU III Târnavă/O.S. Mediaș); SP 10 (MU VII Moșna/FD Mediaș);

SAs 12, 13, 14, 15, 16 17 (MU I Șeica Mică/FD Mediaș). SP 1 represents the control sample area located westward from the city of Blaj, 26.36 km away from the main polluter i.e. S.C. Sometra S.A.

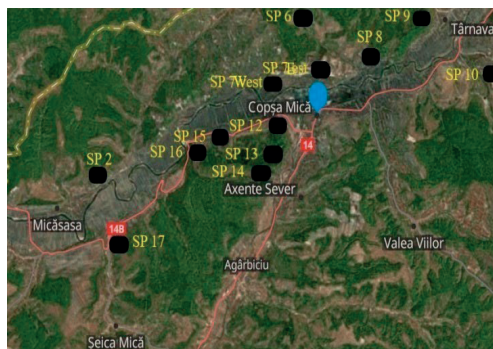


Figure 1. Location and nomenclature of the sample surfaces (SPs) in the Copșa Mică town area subject to multidecadal pollution

The following types of soil characterise the SAs taken into consideration: typical preluvosoil (SP 1-MU 1 Veseuș, FD Aiud), typical luvosoil (SP 2-MU II Micăsasa; SP 7West, SA 8, MU III Târnavă); calcareous regosol (SP 6 MU III Târnavă, SPs 15, 16 MU I Șeica Mică); stagnant luvosoil (SP 7East-MU III Târnavă); typical brown luvic soil (SP 10, MU VII Moșna); marnic phaeozems soil (SP 9 - MU III Târnavă; SPs 12, 13, 14 - MU I Șeica Mică, FD Mediaș) (**2008; **2018; **2020; Florea & Munteanu, 2003). Basic samples sampled from four different points were mixed resulting in an average sample, the laboratory samples being obtained by the four quarters method (Dean, 2002). The drying, conditioning and processing of the soil samples was carried out according to the protocols issued by ICPA Bucharest (**1981) and the undecomposed plant remains, and gravel and foreign materials were selected and removed. The soil samples thus obtained were dried, ground with a lab mill and sieved through a 2 mm mesh sieve. Afterwards, the resulting fine soil was stored and labelled in hermetically sealed plastic boxes. In order to determine the *pH*, and of the indices of the adsorptive complex (SH, SB, CEC, *V*, %) we used the working methodology indicated by Târziu and Spârchez (1987).

Determination of soil *pH*

Bélangier et al. (2006) show that forest soils tend to have the same ionic strength throughout the year and indicate the determination of soil *pH* in soil-water suspension. Couchense et al. (1995) draw attention to the shock induced by both the heat treatment and the soil sampling in terms of affecting *pH* values. The principle of the research method involves the measurement of H^+ activity using a double glass calomel electrode, immersed in the solution to be analysed. The soil suspension in H_2O has a 1:2.5 mass/ volume ratio. The results are expressed in *pH* units, with an accuracy of 0.05 (in *pH* units). As a result, we considered the average of the last two measurements, the value of which does not differ by more than 0.1 units of *pH* (Târziu & Spârchez, 1987).

Determination of total exchangeable soil acidity (SH)

KCl exchangeable acidity in agronomy is an important indicator of exchangeable phytotoxic Al (Pansu & Gautheyrou, 2006). Exchangeable acidity was determined by the Kappen's method, which entails treating the soil with a neutral KCl 1 N solution (Thomas, 1982) that activates the extraction (H^+ and Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$) and the volumetric titration of the excess HCl formed with a NaOH solution in the presence of phenolphthalein until the appearance of a faint orange colour. Drying the soil sample at $105^\circ C$ is necessary for soils rich in oxides and hydroxides (the presence of Fe oxides causing colouring errors). Pratt & Bair (1961) and Espiau & Pedro (1980) show that the KCl method is the most efficient, being often used in comparison with the $BaCl_2$ based method.

Determination of the basic cation exchange capacity (SB) (Kappen's method)

It entails treating the soil sample with a known or excess amount of 0.1 N HCl, resulting in the cation exchange of the soil adsorptive complex with H^+ ions of HCl. The excess of HCl was titrated with 0.1 N NaOH solution until the colour changed from blue-violet to persistent green for two minutes, and the amount of HCl consumed was calculated by the remainder. A control sample was also titrated separately. (Târziu & Spârchez, 1987).

The total cation exchange capacity (CEC) was determined by calculation, i.e. by summing the exchangeable bases and the total exchangeable acidity, according to the formula: $CEC (m.eq /100 g soil) = SB + SH$ (1) where: SB is the sum exchangeable bases, in m.eq. and SH the total exchangeable acidity in m.eq. /100 g soil.

The degree of saturation with bases (V, %) was determined by the ratio between the sum of exchangeable bases (SB) and the total cation exchange capacity (CEC), expressed in % according to formulas 2 and 3 below: $V\% = SB / (CEC) \times 100$ (2) or $V\% = SB / (SB + SH) \times 100$ (3) (Târziu & Spârchez, 1987).

Data analysis

The charts showing the variation of the analytical values of the researched parameters were developed in MS Excel 2019, and the dependence between the sum of cation exchangeable bases and $CEC/V(\%)$ was subjected to research using linear regression type $y = ax + b$.

RESULTS AND DISCUSSIONS

The range of variation in soil acidity at the proposed sampling depths encompasses a generous *pH* range with very strongly acidic reaction minima and moderately or weakly alkaline reaction maxima (ICPA, 1987). Maximum acidity values that fall into the slightly alkaline reaction class were also determined by Szanto et al. (2012) at sampling depths of 0-10 cm, 10-20 cm and 20-30 cm in areas partially overlapping with the SPs of this survey. The relative difference of 372% between the maximum and minimum value expresses a wide variation of *pH* values in the surveyed soils. The sample from the control sample area (SP 1) shows a slightly acidic reaction at all three sampling depths. To facilitate the reading of the charts of the statistical processing of the *pH* values and the adsorptive complex indices, the sampling depths of the soil samples at 0-5 cm, 10-15 cm and 30-35 cm were equated with sampling depths 1, 2 and 3.

In the case of the first sampling depth, the *pH* values are between 4.35 (very strongly acidic reaction in SP 2), and a maximum value of 8.65 (moderately alkaline reaction in SP 7West). At

a depth of 10-15 cm, the minimum value is 4.31 (very strongly acidic reaction) and is registered in SP 16 (i.e. the Curmătura Perimeter additionally polluted by the emissions of vehicles passing through National Road DN 14B), and the maximum value is 8.6 (moderate alkaline reaction), in SP 7East. With regard the acidity at the sampling depth 3, the minimum value of 4.61 (strongly acidic reaction) was also determined in SP 16, and the maximum value of 8.48 (weakly alkaline reaction) was found in SP 9 with intensely humic soil at the sampling depth 1. The strongly and very strongly acidic reaction determined in SPs 2, 16, 17 (located at a distance of approx. 8km West away from the polluting industrial platform) is due to the Târnavă Mare depression corridor that imprints the direction and the channelling of the dominant winds carrying the pollutants over a long distance).

To determine the dominant *pH* classes, the clustering tendency of the determined values was reviewed. Thus, about 36% of the values are within the *pH* range of 8.0-9.0 (conclusions similar to Iordache (2009) who conducted studies in the Copșa Mică area) which shows the preponderance of the slightly to moderately alkaline reaction of the soils at the time of the analytical determinations in the surveyed SPs (Figure 2). The soil reaction affects the activity and diversity of microorganisms living in the soil. Bacteria, the most useful microorganisms for the soil, are present in the weakly acidic to weakly alkaline reaction range. Descriptive statistics applied did not reveal the correlation between the *pH* and the distance or distance classes between the major polluter in the area and SA.

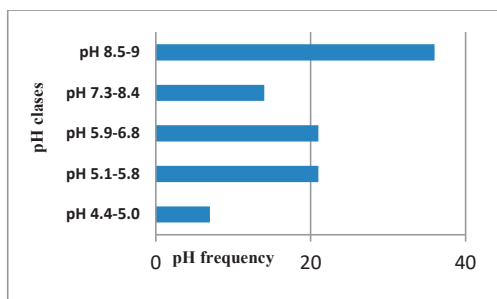


Figure 2. Weighted averages distribution frequency of *pH* for sampling depth 0-35 cm

The ratio of exchangeable bases (SB) is a valuable indicator in assessing soil fertility. The maximum values for the three sampling depths were determined in SPs 9, 14 and 15, and SP 16 obtained minimum values at all stages of soil sampling (Figure 3).

The statistical processing highlighted the fact that the sum of exchange cations did not showed a mathematical correlation with the distance between the main polluter of the surveyed area and the SA within the experimental device.

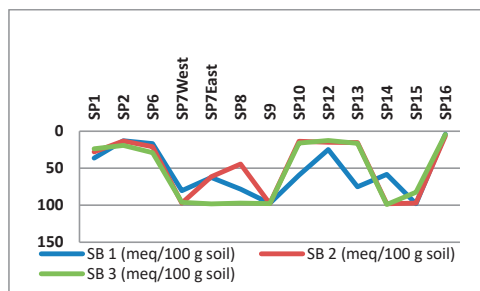


Figure 3. Variation with SPs and sampling depth of the sum of base exchange cations (SB)

Since no SB value exceeded 100, CEC was calculated by summing the base exchange cations (SB) and total exchangeable acidity (SH). CEC varies discontinuously with sampling depth. The high level of humus found in SP 8 and SP 14 correspond to high CEC values (Figure 4). In terms of CEC, SP 15 and 7East recorded maximum values and SP 16 recorded minimum values at the three sampling depths.

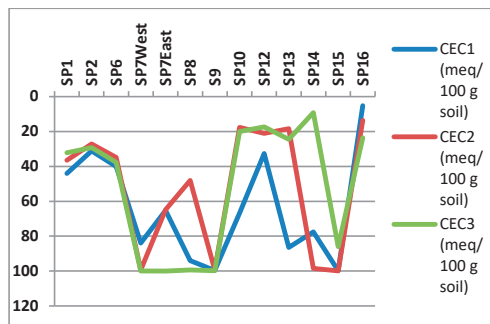


Figure 4. Dynamics of the CEC values calculated by sample plots in the experimental device for the three sampling depths considered

The downward trend of total exchange acidity SH is present in SPs 2, 6, 8, 10, 12, 13, 14 while for SAs 15 and 16, the determined values of SH increase with the sampling depth (Figure 5). Determination of SH is an important indicator since it features the presence of H^+ in the adsorptive complex of the soil, the proportion of which increases with the intensification of soil base saturation loss processes. The maximum values of SH were determined in SPs 2, 6, 16 while in SP 14 minimum values were found for the sampling depths 2 and 3.

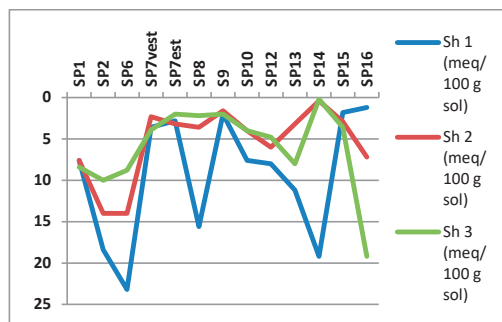


Figure 5. Variation of total exchangeable acidity (SH) by sample area and sampling depth

As in the case of the sum of exchangeable bases, the total exchangeable acidity did show a correlation with the distance between the point pollutant of the area and the SPs surveyed.

As one can notice from figure 6, and according to Metson (1961), the level of saturation with bases (V, %) is very high regardless of the SP considered or the sampling depth applied. According to the saturation with bases (V, %) calculated, the soil from the first sampling depth from SPs 2 and 6 is moderately washed by the bases, the other SPs being very weakly washed according to the classification given by Metson (1961). With regard extreme values, SPs 14 and 16 are clearly distinctive for the sampling depths 2 and 3.

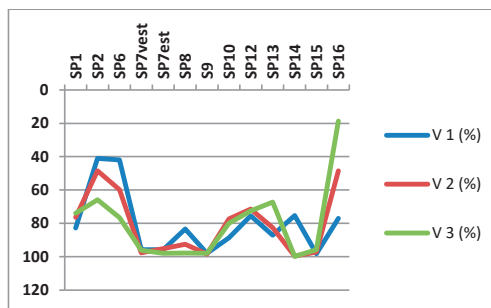


Figure 6. Fluctuation of the values of V (%) assigned to the sampling areas in the experimental device for the three sampling depths

Application of the statistical test resulted in correlation between SB and CEC, as well as between SB and V, % at all three sampling depths according to Table 1 and Figures 7 and 8.

Table 1. The value of the correlation coefficients between the studied variables

Correlation coefficient SB1-CEC 1	0.973041	Correlation coefficient SB1-V%1	0.771107
t_{exp}	14.61504	t_{exp}	4.195336
t_{table}	2.179	t_{table}	2.179
Correlation coefficient SB2-CEC 2	0.995543	Correlation coefficient SB2-V%2	0.828759
t_{exp}	36.5666	t_{exp}	5.130234
t_{table}	2.179	t_{table}	2.179
Correlation coefficient SB3-CEC 3	0.765227	Correlation coefficient SB3-V%3	0.809682
t_{exp}	4.117716	t_{exp}	4.779303
t_{table}	2.179	t_{table}	2.179

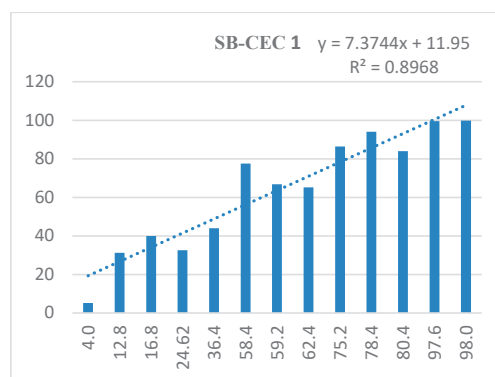


Figure 7. Correlation between SB and CEC at the soil sampling depth 1

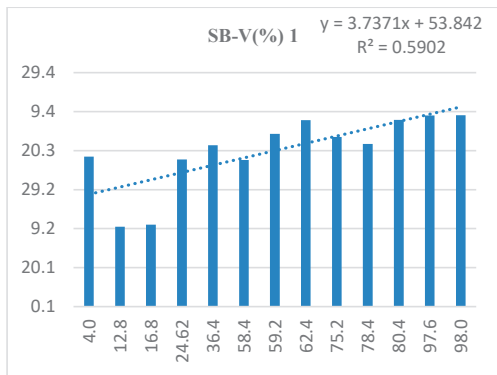


Figure 8. Statistical relationship between SB and V (%) at soil sampling depth 1

CONCLUSIONS

Through the multilateral and in-depth analysis of the physical and chemical characteristics of soils, it is possible to objectively establish the properties they possess and make available to cultivated plants. The *pH* of the surveyed soils indicates the dominance of weak-acidic to moderate-alkaline chemical reaction classes, an aspect also captured by other research conducted within the area suggesting a reduced mobilization of some potentially toxic heavy metals from the soil. Changes in terms of *pH* due to the action of anthropogenic pollutants depend on the type and chemical composition of pollutant emissions. SO_x-rich emissions from non-ferrous smelters increase soil acidity, and the presence of particles containing metal oxides cannot buffer the effect of acidic pollutants on soil *pH*.

The level of saturation with bases (V, %) of the surveyed soils is very high regardless of the SP or the sampling depth applied. The soil sampling depth 1 in SPs 2 and 6 is moderately base-washed, the other SPs being weakly base-washed. CEC varies discontinuously with sampling depth, and the high level of humus in SPs 8 and 14 corresponds to high values of CEC. The correlation coefficient (*r*) between Sb and CEC (*r* ranging 0.7652-0.9955) and between Sb and V% (*r* between 0.7711-0.8287) for the three sampling depths, indicates a very strong correlation between the variables subjected to research. Further studies may also research the influence of soil texture and organic matter content on CEC.

It is only through detailed research works that we can find the factors with optimal regimes, respectively the limiting factors by insufficiency or excess that determine both the nature of the species that can be cultivated (especially in the environmental restoring of the Copșa Mică area) and the level of the productivity thereof. The richness in humus and nutritious mineral substances in accessible forms, the depth of the physiological layer, the good loosening widen the range of species that can be selected and cultivated successfully. On the contrary, a marked friability or compactness, acidity or accentuated basicity of the soil is a limiting factor in terms of diversity of species that can be capitalised without requiring additional interventions that entails additional costs.

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