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SUPPLY AND DISTRIBUTION DEGREE OF SOME MACRONUTRIENTS IN SOILS POLLUTED WITH HEAVY METALS NEARBY THE CITY OF COPȘA MICĂ

Ioana Andra VLAD[1], Győző GOJI [2], Szilard BARTHA[1]

[1]University of Oradea, 26 General Magheru Street, Oradea, Romania
[2]Tehnological High School "Stefan Manciulea", Blaj, Romania

Corresponding author email: ggyozo2000@yahoo.com,

Abstract

Nitrogen (N), potassium (K), and phosphorus (P) are macronutrients that are paramount for plant physiology. The aim of this research is to evaluate the content and distribution of total N, and mobile K and P in soils historically polluted in the Copșa Mică area. We also calculated an average content of mobile P and K, highlighting the variation of the C/N ratio in the shallow depth layers of the soils within the sample surfaces. The negative impact on the soils of the main polluter of the Copșa Mică area is corroborated with a low total N content, minimal K concentration at the first depth layer, following a trend characterised by extremely low concentrations at the depth of 10-15 cm to extremely low to very low concentrations at the depth of 30-35 cm. The same trend is also noticed in the content of mobile P, the lower concentration classes being favoured in terms of average P content.

Key words: *soil nutritional status, total N, mobile K and P, polluted area.*

INTRODUCTION

Carbon (C), Nitrogen (N), Phosphorus (P), and Sulphur (S) are vital macronutrients required in vital doses for the life cycle of plants. The main source in soil nutrients generationis the decomposition of litter and humus followedbytheirfermentation, and fossil fuel extraction provides a 1000-fold surplus of C and N and 10-fold for P over the rate of natural rock degradation processes (Sposito, 2008). The biogeochemical cycles of these elements are impacted in areas facing high anthropogenic pressure or in the case of soil supplementation with exogenous fertilizers (Robertson and Vitousek, 2009). Pollutants, by means of interacting with soil components, but also microorganisms and plant root cells modulate the dynamics and bioavailability of nutrients (Saha et al., 2017; Aslam et al., 2014). Kozlov and Zvereva (2007a) and Zverev (2009), showed that the toxicity of polluting heavy metals is the main factor containing the natural regeneration of areas heavily destroyed by pollution, the research highlighting a significant decrease in the thickness of the organic soil layer by an average of 40% compared to control surfaces nearby non-ferrous smelters. In case of the reduction and total disappearance of the topsoil, Hein and van Ierland (2006) noticed a complete regression and a full cessation of forest regeneration.

Carbon in soil

Humus is the main source of C, N, S, and P for plants (Sposito, 2008; van de Wal and de Boer, 2017). The term of humus underwent several approaches synonyms and interpretations in the dedicated literature (Tan, 2011; Yarow, 2015; Paul, 2016). Thus, several researchers consider humus associated with the extractable fraction of organic matter synonymous with humic substances or soil organic matter (Whitehead and Tinsley, 1963; Kumada, 1987; Haider, 1994). The increase in organic matter is largely due to soil biodiversity, root exudates and microbiological nitrogen fixation (Safari and Rashidi, 2012; Thiele-Bruhn et al., 2012). Soil decomposition, washing, erosion, and runoff phenomena depletes the carbon from soil. Significant amounts of heavy metals i.e. Al, Fe, Cu, Zn, Mn, Hg, Cd from acidic soils are inactivated by chelation with humic acids, thus diminishing the solubility, bioavailability, and toxicity thereof (Zhang et al., 2009; Shan, 2016; Mikkelsen et al., 2020).

N dynamics in soil

Nitrogen is the macronutrient of plant growth and reproduction (Osman, 2013). Processes that are part of the N cycle are dry or wet atmospheric deposition, biological fixation such as degradation/decomposition.

In soil, N is represented by organic forms susceptible to slow mineralization into bioavailable forms (Stevenson, 1982b), and minerals (soluble NO_2^-, NO_3^-, exchangeable/non-exchangeable NH_4^+). Mineral N is less than 5% of total N, being used by plants but potentially harmful to the environment. Târziu (2006), showed that in the case of forest soils more than 50% of the total N is found in the first 20 cm of the soil profile. N leaves the soil in gaseous form (N_2, N_2O_5, and NH_3) and through soil leaching due to high mobility (Qafoku et al., 2000; Sposito, 2008). Sedimentary rocks, the activity of microorganisms and symbiotic mycorrhizae along with anthropogenic addition can increase N content in soil (Vitousek and Howarth, 2007; Morford et al., 2011).

The C/N ratio quantifies the relative content of N in organic matter, regulating the balance between N bioavailable to plants and N, which is leached or denitrified (Qafoku et al., 2000). Generally, C/N ratio in soil ranges from 10.5 to 31.5, with values between 10-12 in uncultivated soils that decrease with depth. Forest soils have a higher C/N ratio i.e. from 20 to 30, much higher ratios (i.e. ≥ 150) being characteristic in case of forest soils with acidic litter. Wet acidic deposits with NO_x or SO_x content can be beneficial for the soil N budget, although they are quantitatively lower than the amount of 100-300 kg N/ha/year required for agricultural crops, or even lower amounts needed for forest ecosystems. The harmful action of acid deposition manifests through foliar lesions, poorer resistance to pathogenic or entomological aggressions.

Characteristics of P in soil

After N, P is the second limiting element of terrestrial production (Kvakic et al., 2018). The total concentration of P in the soil varies between 50-3,000 mg/kg, the inorganic form reaching 50-70% while the share of available P is only 2.5-5%. Due to the current status Cox (2001) and Prasad et al. (2016) suggest for quantitative studies to determine the P level available in soil. Guertal (1991) noticed a stratification of P concentration values in the case of unploughed soils, at the depth of 0-2 cm the level of extractable P being extremely high, which can predict the risk of losing significant amounts of P. The P load of the soil may increase through the mineralization of organic P from plant residues, the secretion of phosphatases by plants, the activity of soluble microorganisms (Zaidi et al., 2009; Bhattacharyya and Jha, 2012) or inorganic P immobilization in microbial biomass (van der Heijden et al., 2015). Losses of P through leaching, erosion or gaseous emissions are insignificant (Sposito, 2008). Soluble compounds with P manifest a high reactivity and low mobility triggering the retention of Cu, Zn in the soil (Ullah et al., 2017; Sohail, 2019).

Presence of K in soil

K is the macronutrient that plays an important role in various plant metabolic processes (Rehm and Schmitt, 2002). According to Sparks and Huang (1985), K in soil represents a dynamic equilibrium between the exchangeable form, in solution, as mineral (from where it can be mobilized by K-solubilizing bacteria), and non-exchangeable form. Foth and Ellis (1997) showed that 98% of total soil K is unavailable to plants, and extractable-available K represents only 0.1-2%. The amount of K available to plants is in exchangeable form and K^+ from the soil solution, and depends on K content, the rhizospheric microbiome, mycorrhizal associations and organic root exudates (Sheng et al., 2003; Yousefi et al., 2011; Gundala et al., 2013), cation exchange capacity (CEC) or the level of other cations. K leaves the soil through leaching and erosion. The pH values in the range of 6.5-7.5 are optimal for the bioavailability of N, P, K. (Hochmuth et al., 2014).

The impact of multi-decadal pollution on the edaphotopes in the Copșa Mică area

The quality of the soils around the city of Copșa Mică in terms of historical pollution impact (i.e. over 70 years) was targeted by several scientific research works conducted especially by Răuță et al. (1987), Comănescu et al. (2010), Szanto et al. (2012). Barbu (2006) and Ianculescu et al. (2009), noted that forestry is most affected by pollution. The area where the experimental site was placed largely coincides with the territory of maximum pollution of approx. 7,900 ha, a fact highlighted by Alexa et al. (2004), Szanto et al. (2012). In this context Alexa et al. (2004) noticed the reduction of the supply of nutrients and the damage to the soil humification as obvious markers of pollutants impact on local edaphotopes. Regarding the heavy metals with toxic potential (i.e. Pb, Cd and Zn), Nedelescu et al. (2017), Alexa et al. (2004), Muntean et al. (2010) found concentrations that far exceed the maximum limits allowed for the upper horizon of the soil around the town of CopșaMică, but also for the Micăsasa commune.

The point sources of pollution within the area were the following: Carbosin S.A. companywhich activity was the production of blackcarbon through the chemicalization of methane until 1993, which made its mark on an area of approx. 20 km long and 6 km wide (Iordache, 2020) with polluters traces that are reminiscent even today and Sometra S.A. company which suspended its major activity since 2009. Some species used in the ecological restoration of the area between 1988-2008 such as: black locust (*Robiniapseudacacia* L.), Russian olive (*Eleagnus angustifolia* L.), desert false indigo (*Amorpha fruticosa* L.) or the white sea buckthorn (*Hippophaë rhamnoides* L.) aimed at improving the quality of soils through their ability to fix atmospheric N_2 (Alexa et al., 2004).

MATERIALS AND METHODS

In a holistic assessment of soil health, certain standard nutrient tests were put forward by various authors (Ashrad and Martin, 2002; Bajracharya et al., 2007; Fine et al., 2017; Frost et al., 2019) which subsequently have been widely tested in the US and India. These tests include, among others the determination of organic matter, P and extractable (bioavailable) K of soils. Determination of extractable nutrient values provides clear indications of soil capacity to support plants and one can find first those threshold or critical values and secondarily the environmental impact of some soil compounds (Dalal and Moloney, 2000).

The soil sampling took place between November 15 and December 4, 2009, in compliance with the rules for collecting soil samples issued by the National Research-Development Institute for Pedology, Agrochemistry and Environmental Protection - ICPA Bucharest (^{xxx}, 1981). The experimental site includes 13 sample plots(SPs) as follows: SP1 (Management unit - U.P.1 Veseuș/ Forestry District O.S.Aiud); SP 2 (Management unit U.P. II Micăsasa/Forest districtO.S. Mediaș), SP 6, 7East, 7West, 8 9, (Management unit U.P.III Târnava/ Forestry district O.S. Mediaș); SP 10 (Management unit U.P.VII Moșna/Forestry district O.S. Mediaș); SP 12, 13, 14, 15, and 16 (Management unit U.P.I Șeica Mică/Forest district O.S. Mediaș). For the comparison of the analytical values, a control surface SP1 protected from intense pollution was also required, and the site is located west to the city of Blaj, at 26.36 km away from the source of pollution. Sampling was carried out outside cold season and minimal plant physiological activity (Pennock et al., 2006), with maximum accuracy to prevent mixing soil layers from different depths.

Elemental samples were taken from the sample surfaces from four (4) different sampling points and mixed to obtain an average sample. Through the point-centered quarter (PCQ) method, this average sample was halved until obtaining the laboratory samples subject to analytical determinations (Dean, 2022). Sampling depths were between 0-5 cm; 10-15 cm; 30-35 cm, with a total of 45 average samples being taken, belonging to the following soil types: typical preluviosol (SP 1- Management unit UP 1 Veseuș, Forest district - O.S. Aiud); typical luvisol (SP 2 - Management unit - UP II Micăsasa; SP 7 West, SP 8, Management unit - UP III Târnava); typical brown luvisol (SP 10 - Management unit UP VII Moșna); calcaricregosol (SP 6 - Management unit UP III Târnava, SP 15, 16 Management unit UP I Șeica Mică); stagnant luvisol (SP 7 East- Management unit - UP III Târnava); marnic-phaeozem (SP 9 - Management unit UP III Târnava; SP 12, 13, 14 - Management unit UP I Șeica Mică, Forest district O.S. Mediaș) (Florea and Munteanu, 2003; ^{xxx}, 2008; ^{xxx}, 2018; ^{xxx}, 2020).

The rules for soil samples processing issued by ICPA Bucharest (^{xxx}, 1981) were observed, with compulsory preparatory stages for the selection and removal of non-decomposed plant remains, gravel and foreign materials; indoor drying with drying racks and ventilation system was used; grinding the samples was made via a laboratory mill, and sieving on a 2 mm mesh sieve; samples was stored in an hermetically sealed and labelled plastic boxes (by mentioning SP number, and sampling date).

To assess the trophicity of the soil and the bioavailability of some macronutrients for plants in the context of the historical pollution of the Copșa Mică area, the analytical determinations aimed at assessing the content of humus, total N, P, and mobile (extractable) K.

Determination of organic C level and the estimation of humus content was carried out by the Schollenberger-Jackson method (Târziu and Spârchez, 1987) which is a hot wet oxidative method and consists in the digestion of soil samples with an oxidizing mixture $K_2Cr_2O_7$ - H_2SO_4 (Târziu and Spârchez, 1987) the cooled digestate is titrated with a 0.2N Mohr's acid solution in the presence of the phenyl anthranilic acid as indicator. The source of interference for this method consists of the presence of chlorides or oxidizing or reducing agents in the surveyed sample. The results are expressed in percentage in total humus = % organic C x 1.724 (van Bemmelen factor).

Determination of total N was carried out by the wet Kjeldahl digestion method. The three steps of the method comprise digestion to convert N to HNO_3, distillation to retain the NH_3 formed following digestion, and estimation of NH_3 by volumetric analysis. The method related equipment used was the Kjeldahl digestion apparatus and the NH_3 distillation apparatus.

Determination of mobile (accessible) P from soil by the Egner-Riehm-Domingo method consists in the formation of coloured compounds in reaction with specific reactants whose intensity is proportional to the concentration of the determined element. The mobile (accessible) phosphates in the soil were extracted with an ammonium lactate (AL) solution (Mamo et al., 1996) buffered with acetic acid at pH 3.75.

Determination of mobile (accessible) K by the Egner - Riehm - Domingo method is based on the passage of excess H^+ and NH_4^+ from the extractant solution of ammonium acetate-lactate (AL), upon exchange, with K^+ from the exchangeable form of the soil. The dosage of these ions is carried out using the acetylene flame atomic absorption spectrometry (FAAS) (Jeffery et al., 1989).

RESULTS AND DISCUSSIONS

Total humus (%) was determined at depths of 0-5 cm and 10-15 cm. At the former sampling depth, the variation amplitude of the total humus content is between 0.12% (poorly humiferous) and 37 % (excessively humiferous), 31% of the samples having a moderate total humus content, and 23% being weakly humiferous. At a depth of 10-15 cm, the soil is weakly humic in proportion to 31%, (Figure 1 shows a downward trend as the depth increases).

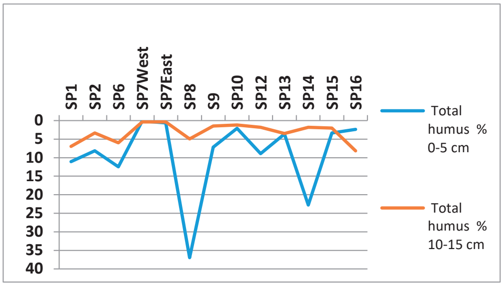

Figure 1. Variation of total humus (%) content between SPs in the experimental sites

The exceptions occurred in SP 16 where a reversal of the downward trend is obvious. The excessively humic soils belong to SP 8 and SP 14 (SP 8 is very polluted, affected by a forest fire produced in a year before the sampling, and SP 14 is located to the SW of Copșa Mică, in the Visa valley, the soil sampling being carried out in area with rich acacia and hawthorn litter). The sample areas in the Târnăvioara Improvement Perimeter, show highly degraded and polluted soils are consequently very poor in humus.

From the analysis of the correlation coefficients of the total humus content with the Cd concentrations established from the same samples, the mathematical connection between the humus content and the Cd content resulted only in the first depth step (Table 1), confirming the protective, sorbent and immobilizing role of humus against toxic substances entering the soil (Ge and Hendershot, 2005).

Table 1. Values of correlation coefficients between the total humus content and the concentrations of Cd and Pb in the sampled soils

Main characteristic	**Sam-pling depth**	**Heavy metal determined**	**Consis-tency factors *r***	***T test***	**Level of significance**
Total humus (%)	0-5 cm	Cd	0.89	6.76	***Significant***
	10-15 cm		-0.02	-0.08	ns
	30-35 cm		-0.34	-1.24	ns

Figure 2 shows the values of the total N content determined at the depths of 0-5 and 10-15 cm. The comparison with the content classes according to ICPA (1987) shows that in the heavily polluted areas (SP7East and SP7West) located on the territory of the Ecological Reconstruction Perimeter Târnăvioara, near the main polluter, the total N content of the soil is low (lower than the values presented by Alexa et al. (2004) which are between 0.13-0.27% at the depth of 0-25 cm), and the humus content is reduced due to surface erosion combined with frequent landslides, especially in SP 7West.

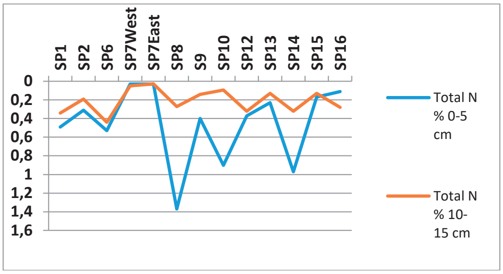

Figure 2. Total N content (%) of the surveyed soils at the first two sampling depths

Average content of total N was determined in SP 15 located at the edge of national road DN 14B, also affected by emissions from road traffic. SP 2, 9, 13, shows a lower concentration of total N. High values were quantified at the 0-5 cm depth of sample plots no. 8, 10, and 14. The soil supply of total N from the control sample plot is high in the case of the two sampling depths (Figure 2).

The values of the weighted C/N ratio of the surveyed soil samples do not exceed the value of 17 (Figure 3), which shows a good supply of N. According to Xu et al. (2013), values of C/N ratio <20 indicate a positive mineralization of N. A low C/N ratio indicates the release of significant amounts of soluble N that can be lost from the soil through various ways (Qafoku et al., 2000) which are reflected in the low total N content of SP 7 East and SP 7 West, SP 9, SP 12, SP 14, and SP 15 with C/N ratio <10. In SP 7 East and SP 7 West of the Târnăvioara Improvement Perimeter, mineralized N is lost due to soil erosion and surface soil washing.

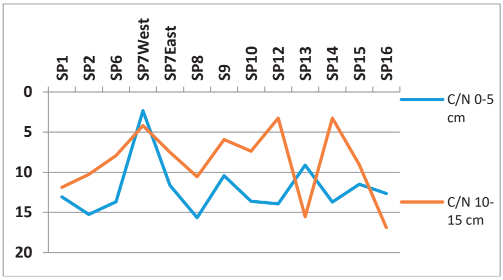

Figure 3. Weighted average values of the C/N ratio at the sampling depth of 0-15 cm in relation to the sample plots

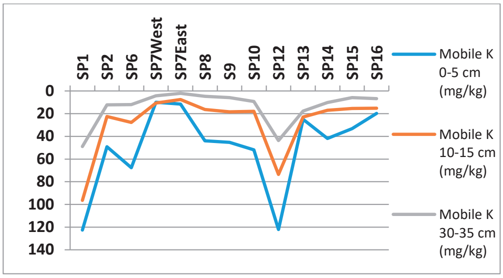

Figure 4. The mobile K content (mg/kg) of the soils surveyed at sampling depths.

Figure 4 highlights maximum values of mobile K at the first depth level, which follows an obvious decreasing trend in terms of depth so that based on the limits of interpretation of the state of supply of soils with mobile K (ICPA, 1981) at the depth of 10-15 cm, the determined values fall into the class of extremely low and low content, and for the depth of 30-35 cm between extremely low and very low content. By comparing the weighted average values at 0-35 cm between the SP, SP 7 East and SP 7 West from the Târnăvioara Improvement Perimeter strongly affected by pollution and erosion with the poorest supply of mobile K stand out clearly, 90% of the SP being marked by an extremely low K content (<40 mg K/kg, ICPA, 1981).

In the soil sampled from the first sampling stage in SP 8 and SP 13, the concentration of mobile P is very high (Figure 5), the remaining values ranging between extremely low and medium content classes (ICPA, 1981). Control SP 1 shows an extremely low concentration of mobile P.

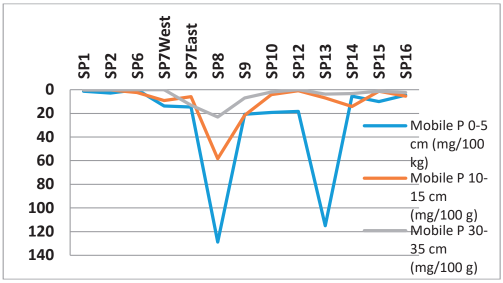

Figure 5. The degree of mobile P supply of the surveyed soils according to SP and sampling depth

The very high concentration established in SP8 may be caused by the input of P originating from the mineralization of the plant material following a forest fire started one year before the collection of the soil samples. For the second and third sampling depths, a general trend of decreasing values is observed in relation to the first depth (except for SP 14 and SP16 and SP7East from the Târnăvioara Improvement Perimeter strongly affected by erosion and horizon inversions (a phenomenon also noted by Smejkal (1982) and Alexa et al.(2004) with very low content specific value)). In the sample plots within the experimental site, soils with extremely low and very low content of average mobile P are dominant (i.e. 66.66%).

CONCLUSIONS

Although the literature on the soils of the Copșa Mică area is substantial, we consider it inappropriate, even inadequate, to compare and report the data of this study with existing values and results due to the inconsistency of the sampling depths. At an overview, there are highlighted both the SP7East and SP7West from the territory of the Târnăvioara Improvement Perimeter located in the vicinity of the main source of pollution within the area with very weak humic soils and a content of very low total N, low mobile P and mobile, bioavailable K, which is very small at all sampling depths, these outcomes being to some extent consistent with the results of the research conducted by Alexa et al. (2003) which characterizes the area as excessively or strongly eroded with sloughs in some places, bare or grassy terrain, and with de-structured and slippery soil.

The aforementioned elements, as a result of the aggressiveness of pollutants on the frequent edaphotopes, especially in SP 7 East and SP 7 West, depletes the superficial soil in humus that contains large amounts of assimilable N, decreasing its trophicity degree. Sample plot 1 (SP 1) considered as a control plot located in an area protected against the influence of a major polluter presents a high total N content, an extremely low mobile K content, and a very low mobile P. Field data and observations show that the presence of rich litter or forest fires can increase the content of N, P or humus in the soil (see cases of SP 8 and SP 14). The content of mobile K is extremely low at a depth of 0-5 cm and extremely low to very low at a depth of 30-35 cm, the downward trend in terms of analytical values while going in depth being obvious. The same downward trend also is present in the case of total N (except in SP 16), mobile P except SP 7 East and SP 14 and total humus, less in SP 7 East; SP 7 West and SP 16. Excessively humic soils are found in sample plots with rich litter or with exogenous C supply following a forest fire.

REFERENCES

Alexa, B., Cotârlea, I., Bàrbătei, R. (2004). *Forest pollution in the Mediaș Forest Ring and the ecological reconstruction works carried out.* Sibiu, Constant Publishing House.

Aslam, U., Ahmad, I., Hussain, M. (2014). Effect of heavy metal pollution on mineral absorption in sunflower (*Helianthus annuus* L.) hybrids. *Acta Physiol Plant, 36*(1), 100–108.

Arshad, M.A. and Martin, S. (2002). Identifying Critical Limits for Soil Quality Indicators in Agro-Ecosystem. *Agriculture Ecosystems and Environment*, *88*. 153–160.

Barbu, C.H. (2006). Preliminary study. Screening assessment of the existing data and studies concerning the Copşa Mică industrial area. Proposal of actions to be taken for the accurate determination of the degree of pollution and estimated costs. Sibiu, Lucian Blaga University of Sibiu Publishing House.

Bajracharya, R.M., Sitaula, B.K., Sharma, S., Jeng, A. (2007). Soil quality in the Nepalese context-An analytical review. *Int. J. Ecol. Environ. Sci., 33*(*2-3*), 143–158.

Bhattacharyya, P.N., Jha, D.K. (2012). Plant growth-promoting rhizobacteria (PGPR): emergence in agriculture. *World J. Microbiol Biotechnol, 28*. 1327–1350.

Cox, M. S. (2001). The Lancaster soil test method as an alternative to the Mehlich 3 soil test method. *Soil Sci., 166*(7), 484–489.

Comănescu, l., Nedelea, A., Paisa, M. (2010). Soil pollution with heavy metals in the area of CopșaMică town Geographical considerations. *Metalurgia International*, *XV*(4), 81–85.

Dalal, R.C., Moloney, D. (2000). *Sustainability indicators of soil health and biodiversity*. In: Hale P., Petrie A., Moloney D., Sattler P. (eds) Management for sustainable ecosystems. Centre for Conservation Biology, The University of Queensland, Brisbane, 101-108.

Dean, J. R. (2022). Extraction Techniques for Environmental Analysis, John Wiley & Sons Ltd, 368 p.

Fine, A.K, van Es, H.M., Schindelbeck, R.R. (2017). Statistics, scoring functions, and regional analysis of a comprehensive soil health database. *Soil Sci. Soc. Am J., 81*. 589–601.

Florea, N., Munteanu, I. (2003). *Romanian Soil Taxonomy System (SRTS)*. Bucharest, Estfalia Publishing House, 76 p.

Frost, P.S.D., van Es, H. M., Rossiter, D. G., Hobbs, P.R., Pingali, P.L. (2019). Soil health characterization in smallholder agricultural catchments in India. *Appl. Soil Ecol., 138*. 171–180.

Foth, H. D., Ellis, B.G. (1997). *Soil fertility*. 2nd Edition, Lewis CRC Press LLC, Boca Raton.

Gundala, P.B., Chinthala, P., Sreenivasulu, B. (2013). A new facultative alkaliphilic, potassium solubilizing, *Bacillus spp*. SVUNM9 isolated from mica cores of Nellore district, Andhra Pradesh, India. *J. MicrobiolBiotechnol, 2*(1), 1–7.

Guertal, E.A., Eckert, D.J., Traina, S.J., Logan, T.J. (1991). Differential phosphorus retention in soil profiles under no-till crop production, *Soil Sci. Soc. Am. J.,* 55(2), 410413.

Ge, Y., Hendershot, W. (2005). Modeling sorption of Cd, Hg and Pb in soils by the NICA-Donnan model. *Soil & Sediment Contamination (formerly Journal of Soil Contamination)*, *14*(1), 53–69.

Haider, K. (1994). *Advances in the basic research of the biochemistry of humic substances*. In: Humic Substances in the Global Environment and Implications on Human Health, N. Senesi, and T. M. Miano (eds.). Proc. 6th Intern. Meeting of the Intern. Humic Substances Soc., Monopoli, Bari, Italy, September 20-25, 1992. Elsevier, Amsterdam, 91-107.

Hein, L., van Ierland, E. (2006). Efficient and sustainable management of complex forest ecosystems. *Ecol Model, 190*(3), 351–366.

Hochmuth, G, Mylavarapu, R, Hanlon, E. (2014). The four Rs of fertilizer management. University of Florida, Electronic Data Information Source.

Ianculescu, M., Ionescu, D., Lucaci, S., Neagu, C.M. (2009). Dynamic of pollutants concentration in forest stands from CopșaMică industrial area. *Ann. For. Res., 52*. 207–226.

Iordache, M., Sandru, C., Miricioiu, M., Nechita, C., Ionete, R.E., Botoran, O.R. (2020). Influence of anthropogenic activity to the macronutrient loading in water and soil-Case study of industrial area. *Smart Energy and Sustainable Research*, *23*(2), 81–92.

Jeffery, G.H., Bassett, J., Mendham, J., Denny, R.C. (1989). Vogel's textbook of quantitative chemical analysis, 5thedn. Wiley, New York.

Kumada, K. (1987). Chemistry of Soil Organic Matter. Japan Scientific Societies Press and Elsevier, Tokyo.

Kozlov, M.V., Zvereva, E.L. (2007). Industrial barrens: extreme habitats created by non-ferrous metallurgy. *Rev Environ Sci Biotechnol, 6*. 231–259.

Kvakic, M., Pellerin, S., Ciais, P., Achat, D.L., Augusto, L., Denoroy, P., Gerber, J.S., Goll, D., Mollier, A., Mueller, N.D., Wang, X., Ringeval, B. (2018). Quantifying the limitation to world cereal production due to soil phosphorus status. *Global Biogeochem Cycles, 32*. 143–157.

Morford, S.L., Houlton, B.Z. and Dahlgren, R.A. (2011). Increased forest ecosystem carbon and nitrogen storage from nitrogen rich bedrock. *Nature*, *477*(7362), 78–81.

Mikkelsen, F.N., Rieckmann, M.M., Laursen, K.H. (2020). Advances in assessing nutrient availability in soils. In: Achieving sustainable crop nutrition. Burleigh Dodds Science Publishing, Cambridge, 481-514.

Mamo, T., Richter, C., Heiligtag, B. (1996). Comparison of extractants for the determination of available phosphorus, potassium, calcium, magnesium and sodium in some Ethiopian and German soils. *Commun Soil Sci. Plant Anal., 27*(9-10), 2197–2212.

Nedelescu, M., Baconi, D., Neagoe, A., Iordache, V., Stan, M., Constantinescu, P., Ciobanu, A.M., Vardavas, A.I., Vinceti, M., Tsatsakis, A.M. (2017). Environmental metal contamination and health impact assessment in two industrial regions of Romania. *Sci. Total Environ.,* 580. 984–995.

Muntean, E., Muntean, N., Mihăiescu, T. (2010). Cadmium and lead soil pollution in CopșaMică area in relation with the food chain. *Research Journal of Agricultural Science, 42*(3), 731–734.

Osman, K.T. (2013). Soils Principles, Properties and Management Springer Science+Business Media Dordrecht, p.295.

Paul, E.D. (2016). The nature and dynamics of soil organic matter: plant inputs, microbial transformations, and organic matter stabilization. *Soil BiolBiochem., 98*. 109–126.

Pennock, D., Yates, T. and Braidek, J. (2006). Soil Sampling Design. In: Carter, M.R. and Gregorich, E.G., Eds., Soil Sampling and Methods of Analysis, 2nd Edition, Taylor and Francis Group LLC, London.

Prasad, R., Shivay, Y.S., Majumdar, K., Prasad, S. (2016). Phosphorus Management. pp.81-113.

Qafoku, N.P., Malcolm, E.S., David, E.R. (2000). *J. Environ. Qual.*, *29*. 484–493.

Răuţă, C., Mihăilescu, A., Cârstea, St., Toti, M., Neaţă, G., Gamenţ, E., Mihalache, G., Dumitrescu, F., Zelinski, C., Dancău, H. (1987). Industrial pollution of soils and forest vegetation in the CopșaMică area. *ICPA Annals*, *XLVIII*. 269–280.

Robertson, G.P., Vitousek, P.M. (2009). Nitrogen in agriculture: balancing the cost of an essential resource. *Annu. Rev. Environ. Res., 34*. 97–125.

Rehm, G., Schmitt, M. (2002). Potassium for crop production. University of Minnesota Extension,www.extension.umn.edu/distribution/cropsystems. 46, pp 229-236.

Safari, S.A.A., Rashidi, T. (2012). The relationship between available P and selected biological properties in the rhizosphere of ten crop species under glasshouse conditions. *Span J. Soil Sci. 2*. 74–89.

Saha, J.K., Selladurai, R., Coumar, M. V., Dotaniya, M. L., Kundu, S., Patra, A. K. (2017). Soil Pollution - *Emerging Threat to Agriculture, Environmental Chemistry for a Sustainable World, 10*, 386 p.

Shan, H., Su, S., Liu, R., Li, S. (2016). Cadmium availability and uptake by radish (*Raphanus sativus*) grown in soils applied with wheat straw orcomposted pig manure. *Environ Sci. PollutRes. Int.*, *23*(15). 15208–17.

Sheng, X.F., Xia, J.J., Chen, J. (2003). Mutagenesis of the *Bacillus edphicaus* strain NBT and its effect on growth of chili and cotton. *Agric. Sci.* China, *2*. 40–41.

Sohail, M.I., Arif, M., Rauf, A., Rizwan, M., Ali, S., Saqib, M., Zia-ur-Rehman, M. (2019). Organic manures for cadmium tolerance and remediation. *Cadmium Tolerance in Plants (19-67*). Academic Press.

Szanto, M., Micle, V., Gament, E., Prodan, C.V. (2012). Investigations on the state of soil quality in the CopșaMică area. *Ecoterra Journal of Environmental Research and Protection*, *31*. 110–116.

Stevenson, F.J. (1982b). Organic forms of soil nitrogen. In *Humus Chemistry*, Wiley, New York, 55-119.

Sparks, D.L., Huang, P.M. (1985). Physical chemistry of soil potassium. In: Munson R.D (ed) Potassium in agriculture. Wisc, ASA, Madison, pp 201-265.

Sposito, G. (2008). The Chemistry of Soils 2nd Edition. Oxford University Press, New York, p. 342.

Smejkal, G. (1982). *Forest and industrial pollution*. Bucharest, Ceres Publishing House, 194 p.

Târziu, D.R. (2006). *Pedology and Forest Resorts*. Brasov, Silvodel Publishing House, 394 p.

Târziu, D. R., Spârchez, Gh., (1987). *Pedology - Guide for practical works.* Brasov, Reprography of Brasov University, 162 p.

Thiele-Bruhn, S., Bloem, J., de Vries, F.T., Kalbitz, K., Wagg, C. (2012). Linking soil biodiversity and agricultural soil management. *Curr. Opin. Environ. Sustain., 4*(5), 523–528.

Ullah, M.A., Shamsuzzaman, S.M., Islam, M.R., Samsuri, A.W. & Uddin, M.K. (2017). Cadmium availability and uptake by rice from lime, cowdungand poultry manure amended Ca-contaminated paddy soil. *Bangladesh Journal of Botany*, *46*(Suppl. 1), 291–296.

van der Heijden, M. G. A., Martin, F. M., Sanders, I. R. (2015). Tansley review: Mycorrhizal ecology and evolution: The past, the present, and the future. *New Phytologist,* 205(4) 140,6–1423.

van der Wal, A., de Boer, W. (2017). Dinner in the dark: illuminating drivers of soil organic matter decomposition. *Soil BiolBiochem,* 105. 45–48.

Vitousek, P.M., Howarth, R.W. (2007). Nitrogen limitation on land and in the sea: How can it occur? *Biogeochemistry*, *13*. 87–115.

Whitehead, D.C. and J. Tinsley. (1963). The biochemistry of humus formation. *J. Sci. Food Agric*. *14*. 849–857.

Xu, X., Thornton, P. E., Post, W. M. (2013). A global analysis of soil microbial biomass carbon, nitrogen and phosphorus in terrestrial ecosystems. *Global Ecology and Biogeography, 22*. 737–749.

Yarrow, D. (2015). Geology into biology: carbon, minerals, and microbes-tools to remineralize soil, sequester carbon, and restore the earth. In: Goreau T.J., Larson R.W., Campe J. (eds) Geotherapy: innovative methods of soil fertility restoration, carbon sequestration, and reversing CO_2 increase. CRC Press/Taylor and Francis Group, Boca Raton, 195-223.

Yousefi, A.A., Khavazi, K., Moezi, A.A., Rejali, F., Nadian, N.H. (2011). Phosphate solubilizing bacteria and arbuscular mycorrhizal fungi impacts on inorganic phosphorus fractions and wheat growth. *World Appl. Sci. J., 15*(9), 1310–1318.

Zaidi, A., Khan, M.S., Ahemad, M., Oves, M. (2009). Plant growth promotion by phosphate solubilizing bacteria. *Acta Microbiol Immunol Hung, 56*. 263–284.

Zhang, H., Dang, Z., Zheng, L.C. Yi, X Y. (2009). Remediation of soil co-contaminated with pyrene and cadmium by growing maize (*Zea mays* L.). *Int. J. Environ. Sci. Technol., 6*. 249–258.

Zverev, V.E. (2009). Mortality and recruitment of mountain birch (*Betula pubescens* ssp. *czerepanovii*) in the impact zone of a copper-nickel smelter in the period of significant reduction of emissions: The results of 15-year monitoring. *Russ J. Ecol., 40*. 254–260.

*** (1981). Methods, Reports, Guidelines; Research Institute for Pedology and Agrochemistry, Methodology for agrochemical analysis of soils to determine the need for amendments and fertilizers, Bucharest.

*** (2008). Forestry management of Forestry district O.S. Medias. I.C.A.S. Brasov.

*** (2018). Forestry management of Forestry district O.S. Medias. I.C.A.S. Brasov.

*** (2020). Forest management of Forestry district O.S. I Aiud I.C.A.S. Brasov.

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