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Organic carbon in soil aggregate fractions under native vegetation and agricultural use in Pitimbu, Paraiba, Brazil

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ABSTRACT

Agriculture is a very representative activity in Brazil, one of the main economic resources of the country. However, the improper management of agricultural areas has negative effects on key soil properties such as soil organic matter. The aim of this research was to identify changes in soil organic carbon and its distribution in soil aggregates, depending on the transformation of native vegetation areas on pasture lands and croplands. The study was conducted in Pitimbu, State of Paraíba, Brazil. Three representative management systems were selected in a Ultisol: bean crop under conventional tillage (TIL), planted pasture (PAS) and native forest in Atlantic Forest biome (NAT). In each plot, samples of soils were collected at depths of 0-20 and 20-40 cm. Total organic carbon (TOC) was determined in the soil fraction <2 mm, according to Walkley & Black (1934). Aggregates between 8.00 and 4.76 mm were subjected to a 15 minutes wet sieving with vertical oscillation (Yoder, 1936), and fractions of aggregates were obtained in the following classes: (A) 4.76 to 2.00 mm, (B) 2.00 to 1.00 mm , (C) 1.00 to 0.50 mm, (D) 0. 50 to 0.25 mm, (E) < 0.25 mm. The TOC of each class of soil aggregates were determined by the same method used in the total mass of soil. The results were subjected to ANOVA and mean comparison by Tukey test at 5%. There was no significant difference in TOC content of the total soil mass between TIL, PAS and NAT, and no significant effect of the sampling depth. However, TOC content in NAT (3.71 mg kg-1) was higher than TIL (1.85 mg kg-1) and PAS (2.66 mg kg-1) along the sampled profile in A aggregate class (P≤0.0006). NAT also surpassed TIL in both B aggregate class (P≤ 0.0445, only in the layer of 20-40 cm) and C class (P≤0.0287). Plant diversity observed in the forest, the dense layer of leaf litter and the abundant presence of the root system of native species make NAT very protective of the carbon contained in the aggregates, especially in larger aggregates. The introduction of annual cropping and pasture in forest native vegetation areas in similar conditions to this research alters the distribution of organic carbon in soil aggregates. Studies on the sustainability of environments must consider not only the content of TOC in total mass of the soil, but also within aggregates.

INTRODUCTION

Agriculture is a very representative activity in Brazil, one of the main economic resources o f the country, currently representing 5.7% of Gross Domestic Product (GDP). During the first quarter of 2014, GDP in the Agriculture sector grew by 3.6 % compared to the fourth quarter of 2013 with 4.8 % cumulative growth over the last four quarters, indicating the strength and importance of the sector for the Brazilian economy (IBGE, 2014). According to the Ministry of Agrarian Development of Brazil, family farms grew 52 % over the last ten years, and now accounts for 4.3 million production units (84% of farms in the country) and 33% of GDP in the Agriculture sector, employing 74% of the labor force field (BRASIL, 2013). Although rates of deforestation are suffering reductions in Brazil from the 2004-2005 period, deforestation is still a worrying form of land use change in the country, having contributed in 2008 to a loss of 40% of soil carbon to atmosphere, causing over recent decades accelerated reductions in the area of major biomes such as the Amazon, the Cerrado and the Atlantic Forest (World Bank, 2010). In this context, soil quality indicators are useful to monitor early changes in key soil properties (Islam & Weil, 2000) such as soil organic matter (SOM) and aggregate stability indices (Karlen & Stott, 1994).

In the transformation of areas of native vegetation on agricultural land, increased rates of SOM oxidation causes reductions on aggregate stability, particularly in macroaggregates, which are very sensitive to management, increasing in number in the case of areas with grasses and reducing when the soil is disturbed by intensive cultivation (Oades, 1984). Several conditions of soil quality reductions have been observed in Brazil because of intensive soil management in agricultural areas, leading to negative effects on SOM, aggregation and microbial biomass (D 'Andrea et al 2002a, b; Wendling et al, 2005; Costa Junior et al, 2012). Passos et al. (2007) noted a marked reduction in the organic carbon of smaller aggregates (<0.106 mm) compared to the larger size aggregates, due to the fact that larger body reserves are mainly related to clay so that there is an increase in the rate of mineralization with decreasing particle (clay> silt> sand). Maia et al. (2009) argue that factors such as spatial variability, climate and soil types, in addition to management history, are seen as the main factors responsible for differences in the soil organic C content, indicating that few studies have been developed in soils under pasture taking into consideration soil aggregation and the dynamics of C. Moreover, the gradual reduction of native ecosystems due to land use changes contributes to the reduction of biodiversity, loss of natural habitats and significant changes in regional water balance, by the expansion of agricultural areas or by the pressure of disordered urban growth. The aim of this research was to identify changes in soil organic C and its distribution in soil aggregates, depending on the transformation of native vegetation areas on pasture lands and croplands.

MATERIAL and METHODS

The study was conducted in the municipality of Pitimbu, State of Paraíba, Brazil, located in the middle region of Zona da Mata Paraibana, micro-region of the South Coast (Litoral Sul) and metropolitan area of João Pessoa. The climate is As' according to Köppen Climate Classification (tropical climate with rain season on fall-winter), with average annual rainfall of 1,634 mm mm yr^{-1} and an average annual temperature between 25 and 29°C. The study area belongs to the geomorphological unit of the Coastal Tablelands (Tabuleiros Costeiros), geological formation Grupo Barreiras Indiviso (BRASIL, 1981). The study area is located on a Ultisol (Argissolo Vermelho Amarelo, Brazilian soil classification), in the agricultural settlement of APASA, occupied by small farmers with agroecological approach (Lima, 2008). For sampling we selected three representative management systems: bean crop under conventional tillage (TIL), planted pasture (PAS) and native forest in Atlantic Forest Biome (NAT). The average contents of clay, silt and sand were 182 g kg^{-1}, 4 g kg^{-1} and 814 g kg^{-1} for managed areas (TIL and PAS) and 269 g kg^{-1}, 46 g kg^{-1} and 685 g kg^{-1} for the NAT area. In each selected management system, samples of soils were collected at depths of 0-20 and 20-40 cm. Total organic carbon (TOC) was determined in the soil fraction <2 mm, according to Walkley & Black (1934). Aggregates between 8.00 and 4.76 mm were subjected to a 15 minutes wet sieving with vertical oscillation (Yoder, 1936), and fractions of aggregates were obtained in the following classes: (A) 4.76 to 2.00 mm, (B) 2.00 to 1.00 mm , (C) 1.00 to 0.50 mm, (D) 0, 50 to 0.25 mm, (E) < 0.25 mm. The TOC of each class of soil aggregates were determined by the same method used in the total mass of soil. The results were subjected to ANOVA and mean comparison by Tukey test at 5%.

RESULTS and DISCUSSION

The analysis of variance (ANOVA) of total organic carbon (TOC) of the total mass of the soil revealed no significant difference between NAT, TIL and PAS ($P \leq 0.0907$) systems. The average TOC in NAT, TIL and PAS systems were 3.16 g kg^{-1}, 2.97 g kg^{-1} and 2.41 g kg^{-1}, respectively. Also no significant differences were observed in average TOC of the total mass of soil between the two sampling depths ($P \leq 0.1794$), with mean values of 3.00 g kg^{-1} for the 0-20 cm layer and 2, 69 g kg^{-1} for the 20-40 cm layer. In contrast to levels of TOC in the total mass of soil, ANOVA of total organic carbon TOC in the different fractions of aggregates revealed significant differences among the systems studied, mainly in fractions of larger aggregates (Figure 1).

The TOC content in the fraction of aggregates> 2.00 mm was significantly higher in NAT system (3.71 g kg^{-1}) compared to more intensive systems PAS (2.66 g kg^{-1}) and TIL (1.85 dag kg^{-1}). The trend was repeated in the fraction of aggregates with size between 2-1 mm, although there was a significant interaction of the management systems and the sampling depth ($P \leq 0.0421$). In this case, there was effect of soil management on soil carbon only in the 20-40 cm layer, where TOC in aggregates of 2-1 mm was higher in NAT system (2.20 g kg^{-1}) and lowest in TIL (1.12 g kg^{-1}). Significant differences in TOC concentrations were also found in the fraction of aggregates between 1-0.5 mm, with higher carbon content in the NAT (1.74 g kg^{-1}) compared to the TIL system (0.97 g kg^{-1}), in the average of the two depths. In the fractions of aggregates between 0.5-0.25 mm and <0.25 mm, no significant differences were found in the TOC.

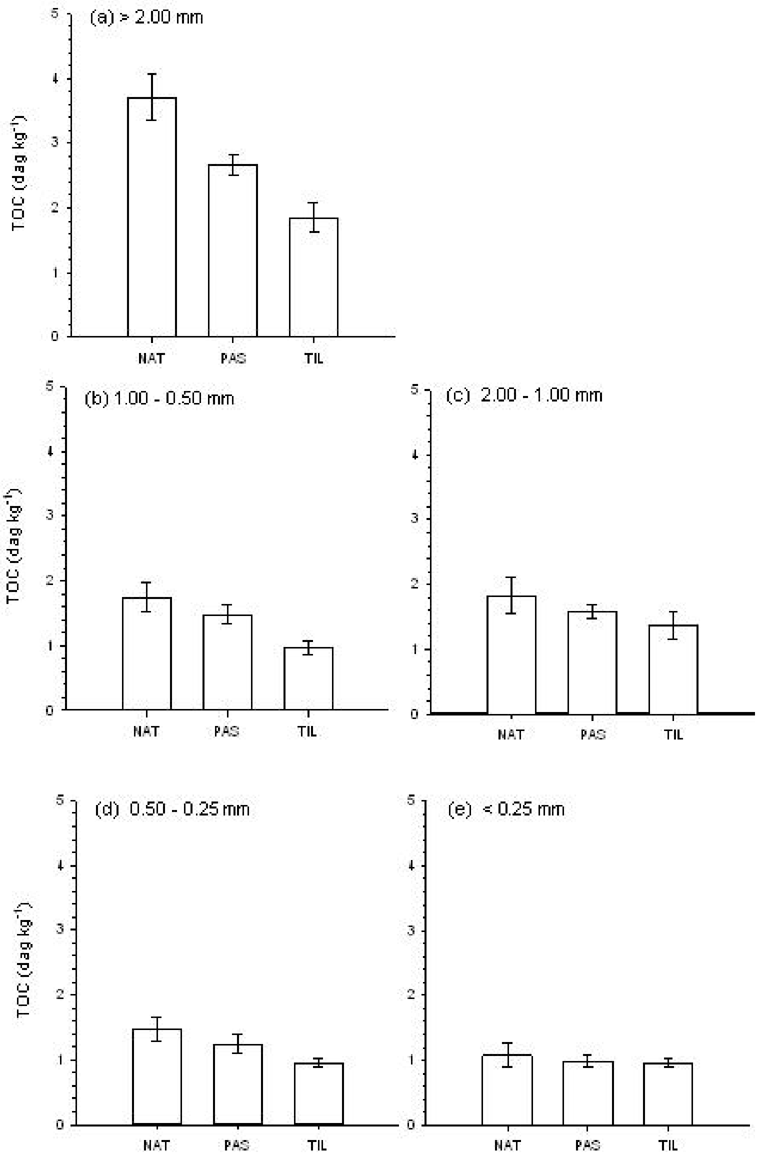

Figure 1. Distribution of total organic carbon content (TOC) in soil aggregates under different tillage systems in Pitimbu, Paraiba, Brazil. NAT: native Forest; PAS: pasture; TIL: conventional cultivation of beans

The results clearly indicate differences between the management systems in relation to TOC content in classes of aggregates larger than 0.50 mm. Larger aggregates stored more organic carbon in NAT than in more intensive systems, especially TIL, being soil aggregates TOC a good indicator for the preservation of forest environments. Taking into account the hierarchical classification of aggregates proposed by Tisdall & Oades (1982), in which the diameter of 250 μm separates the microaggregates of macroaggregates (the latter formed by the union of smaller aggregates), one sees easily that the macroaggregates of the studied soil are less resistant to carbon loss resulting from the action of cultivation. In the present work, the results are consistent with those found by Costa Junior et al (2012). These authors observed in a Brazilian Oxisol with clay contents ranging from 541 $g\ kg^{-1}$ and 641 $g\ kg^{-1}$ (in the top 0-20 cm), that aggregates larger than 0.25 mm may be more sensitive to land use change, offering less protection of soil organic carbon, especially in the layer of 0-5 cm of soils under native vegetation converted into cultivated and pasture systems. In the present work, less TOC in the larger aggregates can reduce its stability, which should be further investigated. In this sense Bastos et al. (2005) argue that the polysaccharides are the active agents involved in the stability of aggregates that are rapidly decomposed, being directly linked to the stability of soil macroaggregates. Other agents such as fungal hyphae and roots that take longer to decompose remain in soil for weeks and even months and are also associated with macroaggregates.

On soil, management systems that add organic matter mainly through plant residues can increase the content of TOC, contributing to the maintenance of agricultural soil sustainability and reduction of CO_2 emissions to the atmosphere (Loss, 2011). Moreover, the absence of soil disturbance into native forest or even in conservation farming systems such as no-till systems may contribute to increasing organic carbon within aggregates (Costa Junior et al., 2012). Thus, the dynamics with which the aggregates are renewed can be a major factor that controls the relationship between the occlusion of organic matter in aggregated to control its decomposition dynamics (Rilling & Mummey, 2006).

In this work, the soil aggregates in bean crop area had low levels of carbon in all size fractions, being significantly lower than TOC content of native forest in the larger size aggregates. It was observed in the field that the diversity of vegetation in native forest is abundant, and the root system of native species makes the forest a very protective system of the carbon contained in the aggregates, especially in the larger ones. In the present study, the pasture was shown as an intermediate system between the forest and the conventional cultivation of beans, especially in fractions larger than 0.5 mm aggregates. The transformation of areas of native forest to pasture or annual crops under similar conditions to those in this study alters the distribution of organic carbon in soil aggregates, although no significant differences were observed with respect to values of total soil mass. Studies on the sustainability of environments must consider not only the content of TOC in the total mass in the soil, but also its distribution within the aggregates. Further studies can be conducted to evaluate the state of soil aggregation through indexes aggregate stability in the systems under study, as well as the evaluation of the microbial biomass of the soil, the rate of soil respiration and decomposition rate of soil organic matter. Authors have reported changes in the microbial components of soil in the surface layers of both sandy and clay soils in Brazil after the transformation of areas with native vegetation into agroecosystems (D'Andrea et al, 2002a; Frazão et al 2010).

Concerned with issues relating to the transfer of carbon from the terrestrial compartment to the atmosphere, the Brazilian Ministry of Agriculture, Livestock and Supply (MAPA) produced in 2012 the Sectoral Plan for Mitigation and Adaptation to Climate Change for the consolidation of an low carbon agriculture economy, also called Plan ABC (Low Carbon Emission Agriculture). This plan aims to reduce greenhouse gases emissions in agriculture in accordance with the National Policy on Climate Change through the adoption of sustainable production technologies to meet the commitments made by the agricultural sector in Brazil (BRASIL, 2012). Among the commitments are: a) encouraging the introduction of planted forests (target area increase of approximately 3 million ha); b) the recovery of degraded pastures (target area increase of approximately 15 million ha) and c) crop-livestock-forest (with goals of increased area of about 4 million hectares). Such policies in the agricultural sector should contribute significantly to improve the physical state of the soil, maintain or increase carbon stocks in terrestrial compartment, and reduce its osses to the atmosphere, with direct impacts related to encouraging the adoption of practices of conservation agriculture.

CONCLUSION

The introduction of annual cropping and pasture in forest native vegetation areas in similar conditions in this research alters the distribution of organic carbon in soil aggregates, with a significant reduction of the levels of TOC in aggregate classes greater than 0.5 mm. Studies on the sustainability of environments must consider not only the content of TOC in total mass of the soil, but also within aggregates.

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Research Article

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Fertility of calcareous chernozem of the Rostov region under different tillage systems

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fertility, black soil, tillage methods, physical and chemical properties

ABSTRACT

In this paper we study the fertility factors of common calcareous black soil including humus content, the content of mobile phosphorus and mineral nitrogen, and also the results of monitoring physical properties of the soil depending on various methods used for its primary cultivation. It has been demonstrated that in comparison with moldboard ploughing the selection of minimum tillage and direct seeding caused certain changes in the agrophysical properties of the soil, and accumulation of total mineral nitrogen content in the plough layer. We have revealed the tendency towards the growth of mobile phosphates content with the increase of tillage intensity, which is particularly remarkable in the upper organic soil horizons.

INTRODUCTION

Tillage represents an essential part of the soil cultivation system. Among numerous agricultural methods, it always played the main role in yield formation being a universal tool affecting physical, chemical and biological properties of the soil, which considerably determines transformation of the plant residues entering soil and eventually affects its fertility. For a long time mechanical soil treatment was considered an efficient method mobilizing the soil fertility in crop rotation; however, anthropogenic changes in the physical and chemical properties of black soils in the process of agricultural production are often negative and result in degraded soil fertility. Therefore, it is necessary to develop location-tailored technologies ensuring minimum cost of agricultural production without sacrificing the productivity of the crops in field rotation (Komissarova, 2012; Oliveira Ferreira et al., 2013).

The purpose of the paper is to study the influence of power saving technologies used for primary soil cultivation on the fertility aspects of calcareous black soil of the Lower Don territory.

MATERIAL and METHODS

The target of research is deep common calcareous heavy loamy black soil on loessial loam. Appropriate sampling sections were arranged in the winter wheat areas using traditional, minimum and No-till treatment and also the virgin land lot of S.M. Kirov JSC in the Peschanokopsky region of the Rostov Province. Granulometric soil composition was analyzed using the pipette method with pyrophosphate preparation, soil bulk density was identified with the method proposed by A.N. Kachinsky (Vadyunina and Korchagina, 1986). Mobile phosphorus content was identified according to the Machigin method; humus content - according to Tyurin's method; nitrate nitrogen - according to the Grandval-Lajoux method; ammonium nitrogen – according to GOST 26489 in the edition of the Central Scientific Research Institute of Agricultural Chemistry (Mineyev, 2001)..

RESULTS and DISCUSSION

According to the N.A. Kachinsky classification, the soil in question granulometrically belongs to heavy loam class with physical clay content of 48,87 - 59,58% treated using varied methods. Weight ratio of particles of various sizes does not change radically under the influence of treatment, but inside their category the particles do change. No-till treatment decreases the content of silt fractions down the profile, minimum treatment increases it insignificantly. Density of the A_{pl}

horizon was characterized according to the N.A. Kachinsky scale as dense ploughland and varied from 1,20 to 1,28 g/cm^3 depending on the soil treatment method. Horizon A demonstrates slight increase of soil density when resource-saving cultivation is used, while ploughing increases the indicator by 0,24 g/cm^3. Further down the profile demonstrates density increase for all treatment methods.

Humus status serves as an important indicator of soil fertility and stability as a component of biosphere. Humus content belongs to a group of indicators having more dynamic nature compared with granulometric and mineralogical composition but less flexible than the content of essential nutrients. Thus, as one of the most stable indicators suggested for analysis humus content will reflect the level of anthropogenic impact (Bezuglova, 2001). In natural ecosystems the concentration of organic carbon typically decreases from the topmost horizon towards lower levels. This phenomenon is caused by continuous supply of carbon from plant residues and droppings in the absence of pedoturbation. Such patterns can be observed in the profile of the virgin land lot.

The influence of primary soil cultivation intensity on humus distribution in common calcareous black soil is displayed in the Figure 1.

Revealed average humus content in the plough layer in case of No-till treatment reached 3,01%, 4,51% with minimum treatment, and 3,43% with traditional treatment. Calcareous black soil within the lots with minimum treatment was characterized as low-humic, in case of ploughing and direct seeding - as slightly humic. These differences indicate considerable influence of the treatment method on the humus status of soil. Down the soil profile, we observed regular decrease of humus content for all treatment methods. Sharper decrease revealed for traditional treatment indicates stronger mineralization processes and more remarkable disruption of biological cycle of the matter. High level of humus resources is noted in meter-deep soil stratum of all lots. By the influence of treatment methods on the indicator, they can be arranged as: minimum > traditional > No-till.

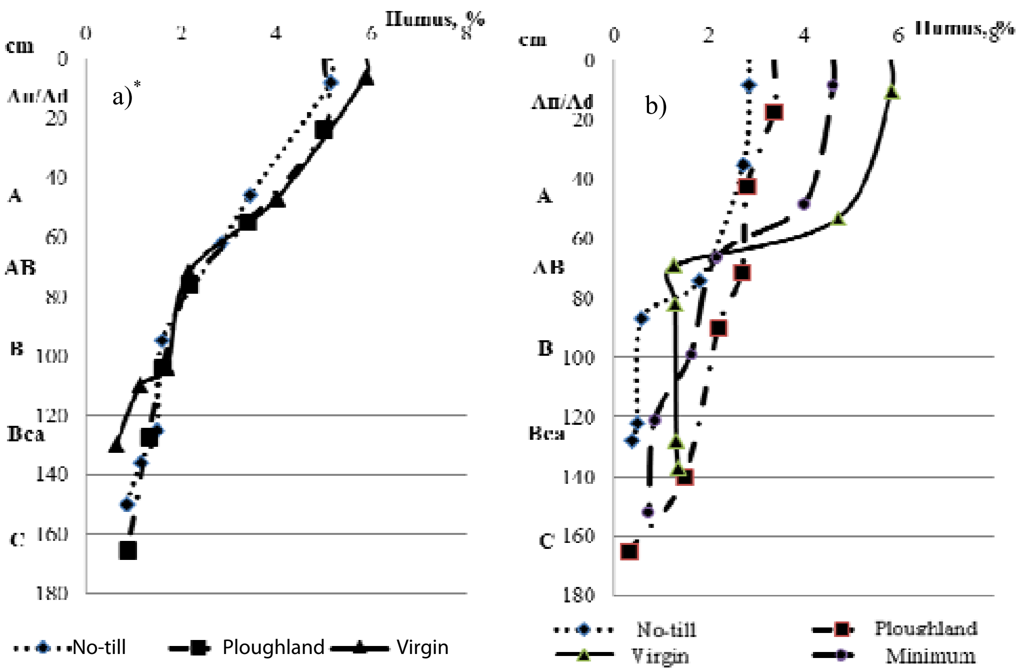

Figure 1. Depthwise humus distribution, %
* Here and in the figures further a) – spring, b) – summer samples

Essential role of phosphorus follows from its participation in the carbohydrate and energy metabolism on the cell level facilitating seed sprouting, better development of plants, especially the root system during early development stages, faster formation of reproductive organs, and other important functions. This determines the topicality of researching mobile phosphorus content in soil as influenced by different methods selected for its primary cultivation (Ilyinskaya et al. 2013).

Figure 2 demonstrates the graphs of mobile phosphorus distribution down the profile of common calcareous black soil of S.M. Kirov JSC in the Peschanokopsky region.

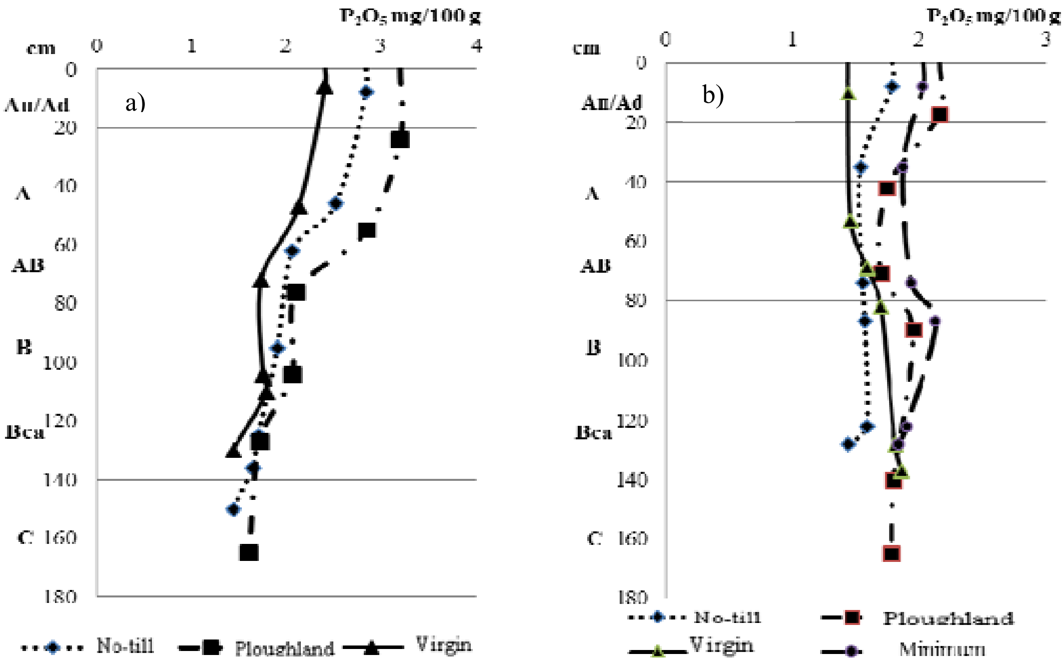

Figure 2. Depthwise mobile phosphorus distribution, mg/100 g of soil

Common calcareous black soil of the virgin land lot during the spring period is characterized by average availability of mobile phosphorus to the crops (2,4 mg/100 g). Upon ploughing we registered maximum accumulation of mobile phosphorus with availability change to increased level (3,2 mg/100 g). In case of No-till treatment, mobile phosphorus content also increased but its availability to crops remained on the previous level. Mobile phosphorus content in the horizon A of the virgin land plot during summer sampling reached 1,44 mg / 100 g of soil. No-till, minimum and traditional soil treatment improved availability of mobile phosphorus to crops. Maximum changes were registered in case of ploughing where availability reached the average level (2,15 mg /100 g).

Although plants utilize nitrogen efficiently, usually it is the most scarce nutrient. Higher plants use inorganic compounds (ammonia/ammonium, nitrites, and nitrates) as the source of nitrogen. Some published sources also mention data indicating that plants can assimilate low-molecular nitrogen compounds (carbamide, certain amino acids). A number of papers demonstrate that ammonia and nitrates can act as equivalent sources of nitrogen for plants (Komissarova, 2012; Dieckow, 2005; Simakin, 1988).

Ammonium content in soil depends on its moisture; therefore soil humidity was analyzed prior to detection of assimilated ammonium quantity. N-NH_4 is generated as a result of ammonification processes due to the activity of aerobic and anaerobic bacteria, ray fungi and mold fungi occurring at different pH values in sufficient humidity and optimal temperature conditions. During spring sampling of organic soil horizons we found no considerable differences in the ammonification process intensity at 0-15 cm depth, N-NH_4 content in case of various soil treatment systems was 13-17 mg/kg (Figure 3).

When No-till soil treatment is used, N-NH_4 accumulation depth of 45-60 cm becomes distinctly notable (18 mg/kg). Down the soil profile, we observe a uniform decrease of ammonium content to 130-145 cm (10 mg/kg), after which N-NH_4 decreases further at 160 cm (8 mg/kg). When minimum soil treatment is used, N-NH_4 accumulation depth of 40-50 cm also becomes distinguishable (19 mg/kg). Towards the lower layers nitrogen content decreases gradually, with a sharp drop at 120-130 cm from 12 to 4 mg/kg.

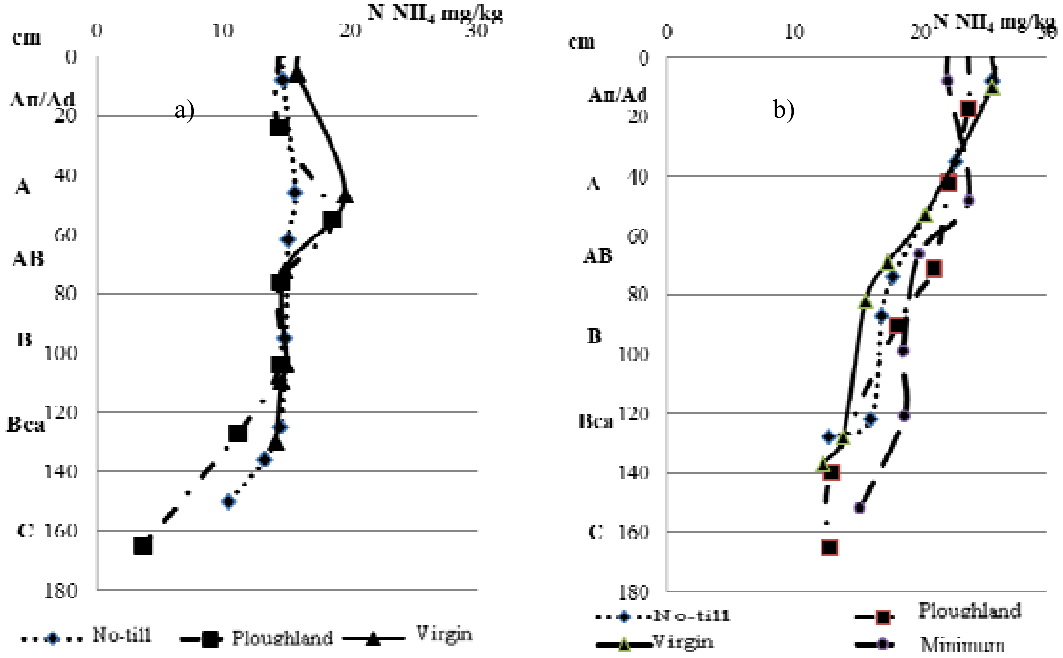

Figure 3. Depthwise distribution of ammonium nitrogen, mg/kg of soil

During the summer period, N-NH_4 content in organic soil horizons at 0-20 cm treated using various methods and in the common calcareous black soil of the virgin land lot reached 22-26 mg/kg. When direct seeding, minimum treatment, and ploughing is used, N-NH_4 content decreases gradually. In case of minimum treatment slight accumulation of ammonium nitrogen also occurs at the depth of 30-35 cm.

Although ammonium nitrogen has certain advantages, it is unable to supply plants with nitrogen alone. N-NO_3 does not produce marginally soluble compounds in soil, it exists in the soil solution acting as the main nitrogenous nutrition source for plants. Its content in soil depends on the availability of organics in soil, its humidity, temperature and the soil solution reaction (Dieckow, 2005). Nitrification process is intensive at favourable soil moisture level of 60-70% of capillary moisture capacity, good aeration, optimal temperature of 25-32° C, and the soil solution reaction close to neutral (6,2-8,1). If nitrification proceeds intensively, the main part of ammonium nitrogen quickly becomes oxidized to nitrates. Soils in the Rostov Province demonstrate high ability for generation of nitrates up to June, then the ability decreases (Simakin, 1988).

Nitrification process in common calcareous black soil of the virgin land lot during spring has low intensity (Figure 4).

No-till treatment allowed to reach the average level of N-NO_3 content (27 mg/kg) in the upper horizon. Downwards the profile, nitrates content sharply decreases to 12-13 mg/kg at 45-50 cm. Similar type of distribution is observed in case of traditional treatment, too.

During summer black soil of the virgin land lot is characterized by average content of nitrate nitrogen (21 mg/kg) in humus layers with gradual decrease down the profile. All cultivation procedures allowed to increase N-NO_3 content to 26-33 mg/kg, but its availability remained on the same level.

Analysis of depthwise distribution of mineral nitrogen in calcareous black soil tilled using various treatment methods revealed the following tendencies: in humic layers ammonium nitrogen prevails while in the lower profile part nitrate nitrogen content is higher; power saving technologies of soil cultivation distinguish the depth of mineral nitrogen accumulation (ammonium + nitrates) at 30-50 cm.

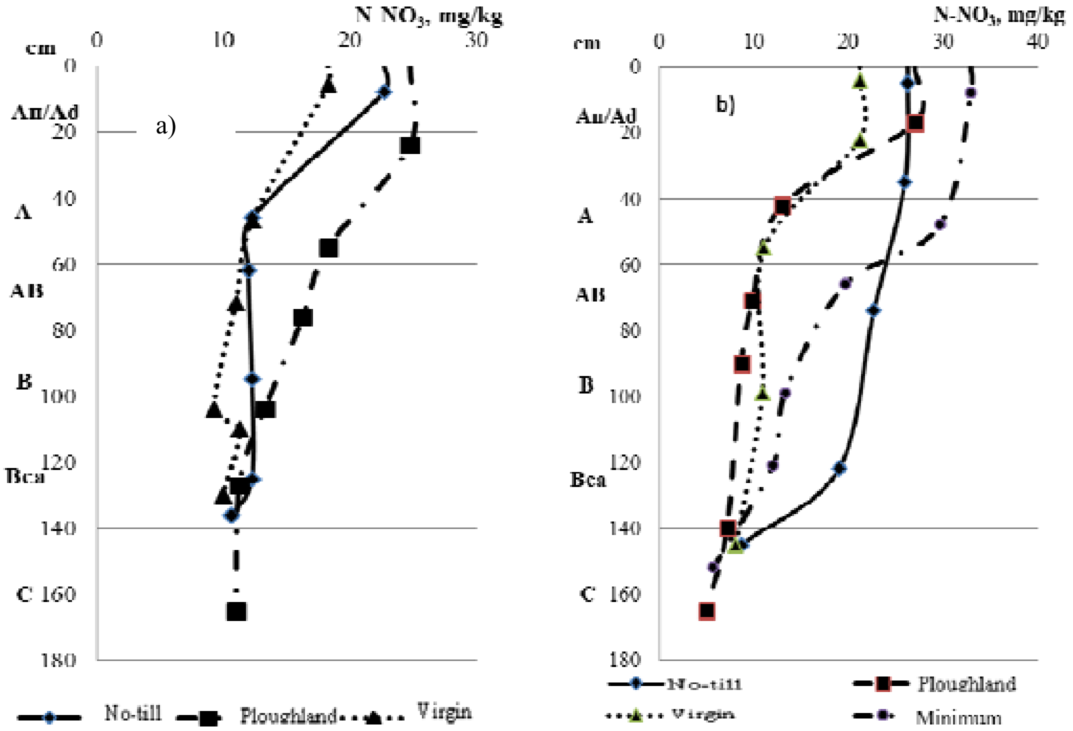

Figure 4. Depthwise distribution of nitrate nitrogen, mg/kg

CONCLUSION

Thus, physical and chemical properties of calcareous black soil depend on the primary cultivation method.

Primary cultivation intensity affected the organic matter content in the profile of common calcareous black soil. Maximum changes are observed in humus horizons where No-till treatment is used, and the largest decrease of humus content (by 0,75%) is registered compared with a virgin land lot.

We have revealed the tendency towards the growth of mobile phosphorus content with the increase of cultivation intensity, which is particularly remarkable in the upper organic soil horizons.

Intensity of ammonification processes in common calcareous black soil does not significantly depend on the primary cultivation method. Ammonium nitrogen content in case of the agricultural technologies in question is practically identical.

Resource-saving cultivation (No-till, minimum treatment) creates favourable conditions for microorganisms accelerating nitrification processes, as a result a lot of nitrate nitrogen is accumulated.

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Research Article

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Soil properties and development of some coniferous tree species in Kolubara coal basin

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ABSTRACT

From all energy sources, coal is still the most important energy resource in the world, since it accounts for about 46% of the total reserves of all resources used for energy. Large lignite basins are in our country, as well as in many other countries, the energy potential of strategic importance. The development of open pit mining as an energy-industrial complexes and the large volume of adverse impacts on the environment, obliged that through integrated planning and restoration of degraded areas enable their comprehensively usage in the period after the ending of exploitation. Serbia is rich in low calorie coal (lignite) that is mainly used for electric power generation. Their participation in the total reserves of all types of coal expressed in tons, and observed through geological (85%), balance (92%) or exploitation reserves (94%) is the largest. About 93% of total lignite reserves are located in three large basins, out of which the Kolubara -Tamnava basin is the largest. The exploitation interesting lignite deposits in this basin occupies about 520 km^2. In this area have been made impressive work on the revitalization and development of degraded land surfaces. The totally reclaimed area is more than 1,300 hectares, of which forests cover 75% of the area, while agricultural reclamation carried out on 25% of the area. These initial relates of different ecosystems are justified considering the fact that the forest ecosystems are of the greatest importance for protection and maintenance a healthier environment. Depending on the micro-ecological conditions and the type of mine soils, for afforestation has been used a larger number of tree species. The paper presents the researching results of physical, chemical and microbiological soil properties and development results of several coniferous trees species used in biological recultivation by afforestation.

INTRODUCTION

In the technology applied in the opencast lignite exploitation in Serbia, overburdening of barren soil deposits is carried out in a non-selective manner, which results in an occurrence of mixed or partially grouped layers of overburden from various geological periods on the surface of barren soil deposits, whose physical-chemical properties range from sterile inert sands from the Pontian geological period to heavy clay Pliocene substrata, of a very adverse hydrological and mineralogical composition. Thus deposited pedosubstrate, of degraded structure and water/air regime, is very unfavourable in terms of survival of plants established in the process of biological re-cultivation by afforestation.

The relatively large number of species has been used for biological recultivation by afforestation not only because of the great variability of the micro-ecological conditions caused by nonselective disposal of overburden, but also because of the tendency to enrich landscapes with the newly created forest ecosystems whose valorization should be moving towards the use of the landscape in post-mining period as the excursion and recreation areas..

MATERIAL and METHODS

The researches were realized in the area of the Kolubara lignite basin. The experimental field was formed on the mine soil of lighter texture, at the altitude of about 185m. There were analyzed nine coniferous species with a total of 62 trees. The trees were planted in groups of 5 to 7.

The environmental conditions has been analyzed – climate and soil conditions, as well as the development of dendroflora species.

Climatic Conditions. Based on the analysis of the following parameters: insolation, temperature conditions, pluviometric regime (rainfall and relative humidity), cloudiness, wind speed and frequency.

Soil Characteristics. On the experimental field samples were taken from two layers of soil profile, from 0-38 cm and 38-86 cm. The accredited laboratory of the Institute of Forestry made the analysis of physical, chemical and microbiological characteristics of soil. The laboratory analyses of soil included: active and substitution acidity - potentiometrically, hydrolytic acidity and sum of adsorbed base cations by Kappen method (Živković 1996), content of total humus by Tyurin method (Škorić, Sertić 1966), content of total nitrogen by Kjeldahl method (Džamić 1966), content of available forms of phosphorus and potassium by AL-method by Egner-Riehm (Džamić et al 1996). Textural composition of fine soil was determined by sedimentation method using Na-pyrophosphate as peptisation agent, and soil textural class using Ferre's triangle (Racz 1971).

In especially taken soil samples number of physiological groups of saprophytic microorganisms was determined as follows: number of ammonifyers on meat-peptonic agar, total number of mineralogenic microorganisms on the soil agar, number of oligonitrophiles on Eshbi agar, total number of fungi on Chapek's agar, number of actinomycettes on Krasilnikov's agar.

The development of some coniferous trees species. Within the park formed on the mine soil of lighter texture, we analyzed the development of the following coniferous trees species at the age of 10 years: *Abies nordmanniana* (Stev.) Spach., *Cedrus atlantica* Man., *Chamaecyparis lawsoniana* (Murr) Parl., *Cupressus arizonica* Greene, *Libocedrus decurrens* Torr., *Picea omorika* (Panic) Purkyne., *Pinus excelsa* Wall., *Pinus ponderosa* Law. and *Sequoiadendron giganteum* (Lindl.) Buchh. We analyzed the development and increase in diameter (at the height of 1.30 m), the height and volume of listed species, as well as analysis of their condition of health, vitality, decorativeness and functionality. Based on these analyzes, a general rating and ranking position has been determinated.

The rating of vitality was given with the assessment of the average condition, health, registered damages of biotic and abiotic nature and adaptability for the existing site conditions, and was expressed in scale from 1.0 to 5.0.

The rating of decorativeness was expressed by visual-aesthetic impression of an individual tree or the group of plants, putting it in relation to the impression that manifests under optimal environmental conditions. It is also expressed in scale from 1.0 to 5.0.

The rating of functionality was given on the basis of the previous parameters, taking into account: the size of the trees, the size and density of the crown and in relation to that the amount of oxygen that is produced, the amount of solid particles that can be absorbed, the feelings of pleasure that causes, the amount of sunlight reaching the land, the presence of ground flora species, particularly flowering plants which occur at different times of the year, pleasantness of color of the leaves, bark or the other details, essential oils, fragrances and phytoncides characteristic for the certain species, attractiveness for spending time in nature and so on. Functionality is also expressed in the scale from 1.0 to 5.0.

The general assessment is the result of evaluation of the vitality, decorativeness and functionality and represents an arithmetic mean of the above parameters. The general assessment is also evaluated from 1.0 to 5.0, which automatically determined the ranking place of species.

RESULTS and DISCUSSION

Environmental Conditions

Climate

Insolation

The average value of the insolation during the year is 2073 hours. Maximum radiation is in July, after the summer solstice, and a minimum in December, before the winter solstice. The highest solar radiation is during the summer (802.2 hours), and the lowest in the winter (on average in December is 62.7 hours). The amount of insolation during the vegetation period is very suitable for the plants, because over this period complex physiological processes take place.

Temperature conditions

The average annual air temperature is 11.8ºC. The lowest average value of the temperature is in January (-2.9°C), while the maximum average values of air temperature is in August (27.7ºC). Subzero temperatures occur from October to April, which could have a negative impact on the plants in the spring. Dates for the first and last frost can be expected in the following intervals: the earliest date of the first frost - 20th October; latest date of the first frost – 27th December; the earliest date of the last frost – 4th February; latest date of the last frost – 12th April.

Average maximal temperatures occur during the summer months (21.3°C), while the lowest temperature is in the winter period (1.3°C).

In the vegetation period average monthly temperatures are in the range from 6.5 to 22.1°C.

Pluviometric regime

Pluviometric regime presents the average amount of precipitation distributed by month, seasons and an average year. Together with the temperature/energy conditions over the year is the most important limiting factor for the biological development of the plant. If any of these three factors isn't at least in the required minimum, plants will not be able to survive, which is particularly evident in the vegetation period.

Precipitation

Cyclonic activities of various origins are reflected on the precipitation regime. This influence is manifested by the cross of cold and moist air masses from the Atlantic Ocean from the west and northwest, the warm from the south and southwest from the Mediterranean area, and winter cross of the air masses from the north and northeast.

The studied area belongs to the continental, slightly modified type of the pluviometric regime which is characterized by the appearance two maximums and the two minimums during the year. The main peak is in June (95.0mm), while the secondary peak is in November/December (56.7mm).

The main minimum of precipitations is at the end of the winter, in February (40.3mm), and the secondary minimum is in September (39.9mm).

The average mean annual precipitation is 694.3 mm. It is characteristic that during the vegetation period fall more than 50% of the total annual rainfall, which is very favorable for the development of plants. Atmospheric deposits during the year are usually in the form of rain, and then as snow. During a transitional period from autumn to winter and from winter to spring wet snow falls which is negative for representatives of evergreen trees and shrubs of the area.

The average relative humidity (%)

Humidity of the air is considered as the most important higric characteristics of air masses. It connects energy/temperature air characteristics with the process of sublimation and condensation of water vapor in the atmosphere. Relative air humidity is closely related to the physiological processes in plants.

The highest average humidity is in the winter period (81.1) and autumn (74.9). The spring is slightly drier (67.7), and also the summer (66.0). In the vegetation period the relative humidity is 69.5%, which is satisfactory quantity which ensures normal growth and development of forest vegetation.

Cloudiness

The average annual cloudiness is 5.6, which is not a great value. The clearest is summer (4.3), then autumn (5.3), spring (5.9) and winter (6.3) which is cloudiest. In the vegetation period average cloudiness is 4.98.

Such distribution of cloudiness by months fully corresponds with the development of plants because in the period when the life processes that require the greatest amount of sunlight occurs, it is found in sufficient quantities.

Winds

The average annual wind speed is 2.2 m/s. The month with the maximum wind is the month of March (3.1m/s), while in January is the lowest wind speed (1.3). Regarding the seasons, the winter is with maximum winds, then fall, spring and summer. During the vegetation period the average wind speed is 2.2 m/s. The average highest frequency of wind during the year is from ESE direction - 78%, then from the WNW direction - 55%, N and NW direction - 32%, while winds from other directions have significantly smaller share. The average frequency of silence is significant and amounts 629% during the year.

Vegetation

Macroclimatic conditions correspond to the conditions of the oak belt, or climatogene community *Quercetum frainetto-cerris* Rud. However, in the relief depressions, where the influence of groundwater are stronger there are conditions for the development of significantly hydrophilic communities.

Soil

During the process of surface mining, the original image of the landscapes is drastically changed. As a part of these processes, the natural soils completely disappear. Their place is taken by some other substrates which follow the new configuration of the field.

In contrast to the technology of selective waste disposal, which implies that the most fertile part of the soil (surface layer) is re-deposited on the surface of the landfills, followed by the rough and fine planning, in Serbia is still mostly in the use unselective waste disposal with or even without technical reclamation, creating in that way very difficult conditions for the successful completing of the reclamation process.

By the technology the surface coal excavation, overburden (in the mining terms: "unproductive soil layer") is removed by the powerful excavators in order to reach a layers of coal which is in Kolubara basin located at a depth of 21.20 to 201.90 meters. Overburden is disposed next to the pit. As a rule, the most productive layers of the original natural soils are buried dipper, and over them unproductive layers of overburden. In this way, there were created irregular overburden dumps ("kippe"), with characteristic relief of the desert dunes.

In Serbia, these soils are determinated as *mine soils* (Antonović, 1972), *koposols* (Korunović, R., Filipović, B., 1979), or *depo-regosols*, *depo-rendzinas*, *depo-rankers* (Resulović, 1979). Resulović (1984), more precisely interprets types within the class of *technogenic soils*, which is divided into: *mine soils*, *rekultisols* and *flotisols*.

Antonović (1980) puts them to on the level of type and includes in the class *anthropogenic land*, while they Resulović (1984) and Škorić (1985) classified into the *class of technogenic land, type mine soil, subtype mine soil resulting from the surface mining of lignite coal*, which is accepted in this paper.

Mine soils of the studied area show a wide variability of properties as a result of the diverse starting characteristics of the deposited material. It is characteristic that they have very deep solum. As a consequence of the method of disposal, they present a mosaic of various lithological layers, different in texture and mineralogical composition. Composition, physical and chemical properties of the newly formed substrate depends on mineralogical composition of the overburden and the lithological characteristics of the geological profile above coal layer.

The experiment field was established on the mine soil of lighter texture, with the following characteristics:

Table 1. Particle size composition

Depth cm	Particle size composition						Textural class
	Coarse sand	Fine sand	Silt	Clay	Total sand	Total clay	
	%						
0-38	0.3	67.5	14.12	18.0	67.8	32.2	Sandy/loam
38-86	1.1	21.3	30.0	47.6	22.4	77.6	Clay

Table 2. The soil chemical properties

Depth cm	Adsorptive complex				Y_1 cm^3	pH		Humus	N	Available	
	T	S	T-S	V		H_2O	KCl	%		P_2O_5	K_2O
	equiv. centimol/1kg			%						mg/100 gr	
0-38	13.74	12.09	1.65	87.99	2.54	6.5	5.2	0.29	0.05	1	5.73
38-86	29.83	26.53	3.30	88.94	5.08	6.8	5.1	0.56	0.00	1	11.46

The chemical properties of the soils are characterized by a neutral pH of the soil solution in the water. The adsorption capacity is low, as well as the total content of humus is extremely low, especially in the surface layer with the light texture. As a result of higher content of clay in texture composition, the adsorption capacity is significantly higher in the deeper layers of the analyzed soil. The soil has a very low content of humus, with a low content of total nitrogen, and especially in the deeper layers where the amount of this element is below detectable limits. The surface layer of soil is poorly provided with easily accessible potassium to the plants, while in deeper layers easily available forms of potassium are on the border between medium and low. Amounts of the phosphorus available to the plants are below detectable limits throughout the depth of the analyzed soil.

Table 3. Microorganisms population size in the soil (1000 microorganisms/ 1 g air-dry soil)

Depth	Mineralogenics (2)	Ammonifyers (1)	Oligonitrophiles (3)	Actinomycettes (5)	Fungi (4)
0-38	418	488	267	75	23
38-86	356	167	6	69	-

1. Number of ammonifying microorganisms on meat-peptone agar
2. Total number of microorganisms on soil agar
3. Number of oligonitrophilic microorganisms on Eshbi agar
4. Total number of fungi on Chapek's agar
5. Actinomycettes on synthetic agar

Photo 1. Pedological profile

In both analyzed layers of the soil there have been registered all the basic physiological groups of microorganisms. Their number is, as expected, significantly higher in the surface layer, while with the depth decreases. This is also, characteristics of natural, undisturbed soil. The microorganisms which assimilate mineral nitrogen (total number of microorganisms on the soil agar) are the most numerous. These also means that it is a mineralogenic soil, with a much smaller number of ammonifyers. Such a number of ammonifyers may result from the low content and the influx of fresh organic matter that is energy material for this group of microorganisms, or even faster dehumification, considering very high content of actinomycetes that decompose the same organic matter, and even substances such as the humus which are more difficult to be decomposed.

The Researching Results of Tree Species Development

The table 4. shows the comparative overview of diameter, height and volume in the tenth year the age of trees.

The table shows that at the age of 10 years, the largest diameter reached redwood (10.7) and the Arizona cypress (10.6cm), the Himalayan pine (10.4cm), American yellow pine (9.4cm), Atlas cedar (7.3cm), Lawson's cypress (6.9cm), incense cedar (6.3cm), Caucasian fir (4.8cm) and finally Serbian spruce (4.4cm). Mean diameter for the analyzed conifer species is 7.9cm. The greatest height at this age reached Atlas cedar (6.00m), followed by Lawson's cypress (5.67m), Arizona cypress (5.58m), Himalayan pine (5.05m), redwood (5.00m), incense cedar (4.03m), American yellow pine (4.00m), Caucasian fir and Serbian spruce (3.00m). Average height for the analyzed conifer species is 5.00m. The largest volume has redwood (28.8dm^3), and Himalayan pine (25.8 dm^3), then Arizona cypress (24.3 dm^3), American yellow pine (21.5 dm^3), Atlas cedar (11.7 dm^3), Lawson's cypress (11.0 dm^3), incense cedar (7.4 dm^3), Serbian spruce (5.2 dm^3) and Caucasian fir (4.6 dm^3). The mean value for the volume for the analyzed coniferous species is 15.6 dm^3.

Table 4. Comparative overview of diameter**,** height and volume values

	The development of the diameter (d_g without bark) in the cm					The development of the height (h_g) in the m					The development of the volume (v_g without bark) in the dm^3				
Species	Age (years)														
	2	4	6	8	**10**	2	4	6	8	**10**	2	4	6	8	**10**
Abies nordmanniana	0.0	0.1	1.1	3.0	4.8	0.20	0.60	1.35	2.10	3.00	0.0	0.4	0.9	2.1	4.6
Cedrus atlantica	0.0	0.5	1.6	4.6	7.3	0.75	1.87	3.00	4.33	6.00	0.0	0.2	0.8	4.2	11.7
Chamaecyparis lawsoniana	0.0	0.9	2.0	4.3	6.9	1.25	3.00	4.00	5.00	5.67	0.0	0.2	1.0	3.9	11.0
Cupressus arizonica	0.0	2.1	5.1	7.8	10.6	1.26	2.43	3.67	5.00	5.58	0.1	1.3	5.2	12.2	24.3
Libocedrus decurrens	0.0	1.0	2.9	4.6	6.3	0.75	1.64	2.32	3.00	4.03	0.0	0.2	1.1	3.3	7.4
Picea omorika	0.0	0.7	2.0	2.9	4.4	0.75	1.58	2.15	2.72	3.00	0.1	0.5	1.3	2.4	5.2
Pinus excelsa	0.0	1.2	4.3	7.6	10.4	0.80	2.00	3.05	4.30	5.05	0.0	0.6	4.2	12.6	25.8
Pinus ponderosa	0.0	2.3	3.8	6.3	9.4	0.75	1.65	2.50	3.50	4.00	0.1	2.0	4.8	10.2	21.5
Sequoiadendron giganteum	0.0	0.5	2.8	6.0	10.7	0.75	1.64	2.32	3.00	5.00	0.0	0.4	3.0	10.3	28.8

The Research of Vitality, Functionality and Decorativeness of Analyzed Species with a General Assessment and Ranking Positions

The basic function of all different types of tree used in the process of biological re-cultivation of open pits in the Kolubara lignite basin is not the utilitarian function, i.e. the production and the economic function is secondary. Plantations are primarily in the function of revitalization, environmental protection in general and the aesthetic enhancement of the degraded areas and the restoration of ecosystems damaged by surface mining. Starting from the premise that in the a later phase of forest cultures development and the comprehensive spatial development, these regions in the post exploitation phase can be used also for recreational purposes, the evaluation of vitality, decorativeness and functionality of each species has been done, according to which was given its general score and ranked position.

According to the vitality, in the first place are cedar and the incense cedar, followed by Lawson's cypress, redwood, Himalayan pine, American yellow pine, Caucasian fir, Serbian spruce and in last place according these criteria is the Arizona cypress. Results of the decorativeness give different order. In the first place are also Atlas cedar and incense cedar, then redwoods, Lawson's cypress, Serbian spruce, Himalayan pine, Caucasian fir, American yellow pine and in the last place, as well as in the previous case, is Arizona cypress. According to functionality, cedar is in the first place, in the second there are incense cedar and the redwoods, in the third Lawson's cypress and the Himalayan pine, then Serbian spruce, American yellow pine, Caucasian fir and at the end the Arizona cypress. With a general assessment of 5.00 in the first place is the Atlas cedar, immediately followed with libokedar (4.87), then redwood (4.70), Lawson's cypress (4.33), Himalayan pine (4.17), Caucasian fir (3.57), the American yellow pine (3.50) and the on the last place the Arizona cypress (2.93).

Table 5. The rating of vitality, decorativeness and functionality of the analyzed species with a general assessment and the ranking positions

Species	Vitality	Decorativeness	Funkctionality	General assessment	Ranking positions
Abies nordmanniana	3.50	3.80	3.40	3.57	VI
Cedrus atlantica	5.00	5.00	5.00	5.00	I
Chamaecyparis lawsoniana	4.50	4.00	4.50	4.33	IV
Cupressus arizonica	2.80	3.00	3.00	2.93	VIII
Libocedrus decurrens	5.00	5.00	4.60	4.87	II
Picea omorika	3.20	4.00	3.50	3.57	VI
Pinus excelsa	4.00	4.00	4.50	4.17	V
Pinus ponderosa	3.50	3.50	3.50	3.50	VII
Sequoiadendron giganteum	4.50	5.00	4.60	4.70	III

CONCLUSION

The researching results of the development, vitality, decorativeness and functionality of nine coniferous tree species on mine soils of the Kolubara lignite basin showed that despite very unfavorable soil characteristics, some of the analyzed species have achieved very good results and can be recommended for further use in reclamation processes, taking into consideration the micro ecological conditions.

During the ten years of the park existence, the pedological processes have been initiated. Increased content of some nutrient elements and humus activated microbiological processes and included these substrates into biological cycling. The increase of humus and organic matter favorably affects to the physical properties of soil, which is reflected in beginning of the creation of structural aggregates.

This contributes to the revitalization of the whole reclaimed area, the development of forest and park plantations, spontaneous succession, increasing biodiversity and improving of the environment in general.

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Research Article

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Effect of calculation models on particle size distribution estimated by laser diffraction

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Key Words:

particle size analysis, laser diffraction method, Mie model, Fraunhofer model, refraction index, absorption index

ABSTRACT

Nowadays, laser diffraction stands for fast and repeatable method of soil texture analysis. Two different models are used for calculation of particle size distribution: the Fraunhofer and Mie model. The first assumes a complete diffraction of laser beams and thus no knowledge on the optical properties of examined soil is required. To estimate the particle size distribution using Mie model, that takes into account diffraction, transmission and absorption, refraction and absorption indices of the soil must be known. This paper describes the effect of Mie and Fraunhofer calculation model on the particle size distribution. The comparison is based on various combinations of refractive and absorption indexes. Laser particle sizers use laser light with a wavelength between possibly 500 and 700 nm. Therefore the transition between Fraunhofer and Mie should take place in the region of about 0.5 – 1µm. However, the decision of which method to use depends not only on particle size but also on heterogeneity of the sample material and the particular application. Four samples of coarse and medium fine soil from the Nitra River catchment in Slovakia were used for analysis and the distribution of particle size fractions was determined according to USDA classification. The analyses were conducted using ANALYSETTE22 MicroTec plus particle sizer (FRITSCH, Oberstein, Germany) that performs measurements in the range from 0.08 up to 2000 µm. The measured data were processed and evaluated in the software MaS control and Microsoft Excel, respectively. After reviewing the available literature on particle size distribution estimated by various devices applying laser diffraction principle, the effect of refractive and absorption indices on particle size distribution was tested in the range from 1.3 to 1.8, respectively from 0.001 to 0.2. Generally, higher clay content in samples was estimated when using Mie calculation model. Low value of refractive index (1.3) resulted in very significant increase of clay fraction. Less of clay fraction was estimated for those combinations when the absorption index was lower than 0.008 and the refractive index higher than 1.5, respectively. Using the refractive index equal to 1.5 and absorption indices in the range 0.1 – 0.2 resulted in very similar estimates in comparison to Fraunhofer model. In the contrary, very low values of absorption index had significant effect on the distribution of particle size fractions, the course of this distribution altered significantly with the tendency to isolate the size fractions into higher amount of individual peaks.

INTRODUCTION

Particle size distribution (PSD) is one of the most fundamental physical properties of a soil, defining, for example, the soil's texture, and strongly affecting many physical and chemical soil properties. Determination of PSD is not trivial task because of the heterogeneity of the shape and density of particles (Eshel et al., 2004). Classification of soils according to particle size is one of the oldest systems of soil classification and it identifies and determines the soil types.

Nowadays, there are various available techniques to determine the PSD. Significant progress in computer technology led to the progressive development of the laser diffractometry. This optical method uses scattering of electromagnetic waves on the particles to determine the particle size distribution. Angle of scattered light is inversely proportional to size of particle at which the incident light beam is scattered. The partial deflection of the laser light results in a characteristic, ring-shaped intensity distribution behind the sample which is measured by a specially shaped detector. This image of the scattered light is called Fraunhofer diffraction pattern, in the middle there is located the zero maximum and then the course decreases sharply. Measured particle size is calculated based on the size of the gaps between the circles: large particles form rings with smaller spaces, small particles form rings with bigger spaces. Analysis of a large set of particles is based on the fact that particles of the same size are converging light beam to the same point. The advantages and disadvantages of this method are well documented e.g. in Beusenlick et al., 1998; Eshel et al., 2004; Arriaga et al., 2006. Potential advantages of laser diffraction method (LDM) include simplicity, small sample size, and rapid analysis and information on the full range of particle size distibution. According to Segal et al., 2009, the potential disadvantages include a required initial expensive investment, the need to make assumptions about particle geometry (sphere) and refractive indexes, overestimation of certain size categories because of competition between two light sources as well as lack of particle size databases determined by laser diffraction method that could be used for comparison purposes. Although the usage of LDM to estimate PSD has increasing trend, there are problems that makes the comparison of obtained results and methods used difficult. Various soil preparation methods prior to analysis have been used in a variety of studies to show the effect on resulting PSD. These procedures include drying, grinding, weighting, mechanical dispersion (mixing by various mixers, using an ultrasonic bath) and chemical dispersion (adding of appropriate detergent). Together with the choice of theory to calculate the PSD, as well as setting of measuring device during the analysis, all of them have a significant influence on the measurement (e.g. Ryzak et al., 2007; Eshel et al., 2004; Di Stefano et al., 2010; Vdovic et al., 2010; Kondrlova et al., 2013; Madarasz et al., 2012).

For calculating particle sizes from light intensity sensed by detectors, two diffraction theories are commonly used: the Fraunhofer diffraction model and the Mie theory (Di Stefano et al., 2011). Both theories assume that the particles have a spherical shape; in other words, the particle dimension is the optical spherical diameter, i.e. the diameter of the sphere having a cross-section area equivalent to the measured one by laser diffraction. The Fraunhofer theory (Fig. 1) describes the portion of light deflection that occurs exclusively as a result of diffraction. If light encounters an obstacle or an opening, this results in diffraction and interference effects. If the incoming light is parallel (even wave fronts), this is referred to as Fraunhofer diffraction. Since for sufficiently large particles the light deflection is dominated by diffraction, Fraunhofer theory can be used for particle size distribution down to the lower micrometre range. One major advantage of Fraunhofer theory lies in the fact that no knowledge of the optical properties of the examined material is required. For particles with diameters that are not significantly larger than the wavelength of the light used, the Mie theory is applied for the analysis of the measurements (Fig. 2). This theory is the complete solution of the Maxwell equations for the scattering of electromagnetic waves by spherical particles. It can be used to analyse the characteristic intensity distributions for even very small particles, which, in contrast to Fraunhofer theory, are not restricted to scattering angles of less than 90° (forward scattering). In fact, scattering angles of greater than 90° also occur (backward scattering).

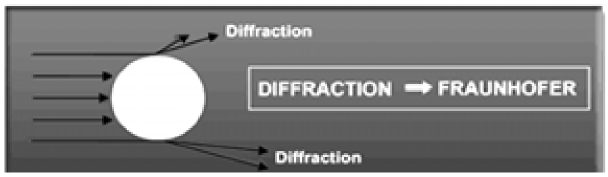

Figure 1: Behavior of laser beam obstructed by soil particle according to the Fraunhofer theory (Beatop Electric Limited, 2012)

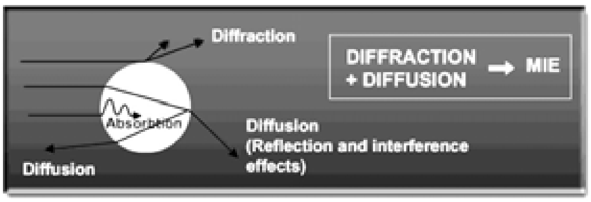

Figure 2: Behavior of laser beam obstructed by soil particle according to the Mie model (Beatop Electric Limited, 2012)

Selection of the Mie theory entails the necessity of defining optical parameters: the refractive index for the dispersing medium, and the refractive and absorption indexes for the medium being dispersed. The refractive indexes for the two mediums should differ considerably from each other (Ryzak, Bieganowski, 2011). The particle sizers manufacturers provide a comprehensive database containing the refraction indexes of numerous different materials (e.g. FRITSCH n.d.). On the other hand, it is very difficult to estimate these values for heterogenic mixtures, such as soil. Typically, laser particle sizers use laser light with a wavelength between possibly 500 and 700 nm. Therefore the transition between Fraunhofer and Mie should take place in the region of about 0.5 – 1µm (Crolly n.d.). However, the decision of which method is used depends not only on particle size but also on the heterogeneity of the sample material and the particular application.

Study of available papers on laser diffraction to estimate PSD of soil shows that there is not only lack of standard method of measurement, but also the problem of choosing the calculation theory was still not sufficiently solved. While some authors still prefer the Frauhhofer theory in their methodologies (e.g. Vandencasteele, De Vos, 2001; Di Stefano et al., 2010, Ryzak, Bieganowski, 2011), the other more or less confidentially recommend the usage of Mie model with proposed indexes (Eshel et al., 2004; Arriaga et al., 2006; Ryzak et al., 2007; Di Stefano et al., 2010; Vdovic et al., 2010, Junakova et al., 2014).

This paper describes the effect of Mie and Fraunhofer calculation model on the particle size distribution. The comparison is based on various combinations of refractive and absorption indexes.

MATERIAL and METHODS

To date, the standard method of soil sample preparation for laser diffraction has not yet been specified. Sample preparation methods that were used for our analysis were derived from the established practices used in standard sedimentation methods. In order to derive a rapid and simple method of soil sample preparation prior analysis, some steps (e.g. removal of carbonates and organic matter) were omitted or simplified. As an example, randomly selected two samples of coarse soil (light soils in the Slovak soil science terminology) and medium fine soil (medium heavy soils) collected in the Nitra River catchment, West Slovakia were used for analysis. Prior to laser analysis, samples were sieved and from fraction < 2 mm 5 g of soil was weighted, pretreated by 0.05 M sodium polyphosphate solution (Graham's salt, ($(NaPO_3)_n$), mixed and covered 24 hours prior to analysis.

The analyses were conducted using ANALYSETTE22 MicroTec plus particle sizer (FRITSCH, Oberstein, Germany) using wet dispersion and the ultrasound was set to at very low intensity. This particle sizer performs measurements in the range from 0.08 up to 2000 µm. The measured data were processed and evaluated in the software MaS control and Microsoft Excel, respectively. After reviewing the available literature on particle size distribution estimated by various devices applying laser diffraction principle, the effect of refractive and absorption indices on particle size distribution was tested in the range from 1.3 to 1.8, respectively from 0.001 to 0.2 (Table 1). The refractive index of water was set to 1.333 (FRITSCH n.d).

Table 1: Overview of various calculation algorithms and indices used for PSD estimation

Number of setup	Calculation method	Refractive index (IR)	Adsorption index (IA)
1	Mie1	1.5	0.1
2	Mie2	1.5	0.001
3	Mie3	1.42	0.1
4	Mie4	1.42	0.001
5	Mie5	1.3	0.001
6	Mie6	1.3	0.1
7	Mie7	1.8	0.001
8	Mie8	1.8	0.2
9	Mie9	1.5	0.2
10	Mie10	1.544	0.008
11	Mie11	1.544	0.1
12	Fraunhofer	---	---

RESULTS and DISCUSSION

The calculation results were compared with focus on differences in clay fraction content according to USDA soil fractions classification. The resulting PSD according to Fraunhofer model and Mie theory varied significantly depending on indexes combinations used. The figure 3 and figure 4 show the PSD and its course for example of sandy soil and medium fine soil sample respectively. Generally, higher clay content (particles smaller than 0.002 mm) in samples was estimated when using Mie calculation model. The calculation method Mie11 gave very similar results to Fraunhofer model and in contrary the methods Mie8, Mie7, Mie10 and Mie2 resulted in lower clay content (by 1; 5; 6 and 7% respectively – the percentage shown is averaged for all samples). The lower clay fraction was estimated for those combinations when the absorption index was equal or lower than 0.008 and the refractive index was equal or higher than 1.5, respectively. In these cases, the course of PSD altered significantly with the tendency to isolate the size fractions into higher amount of individual peaks.

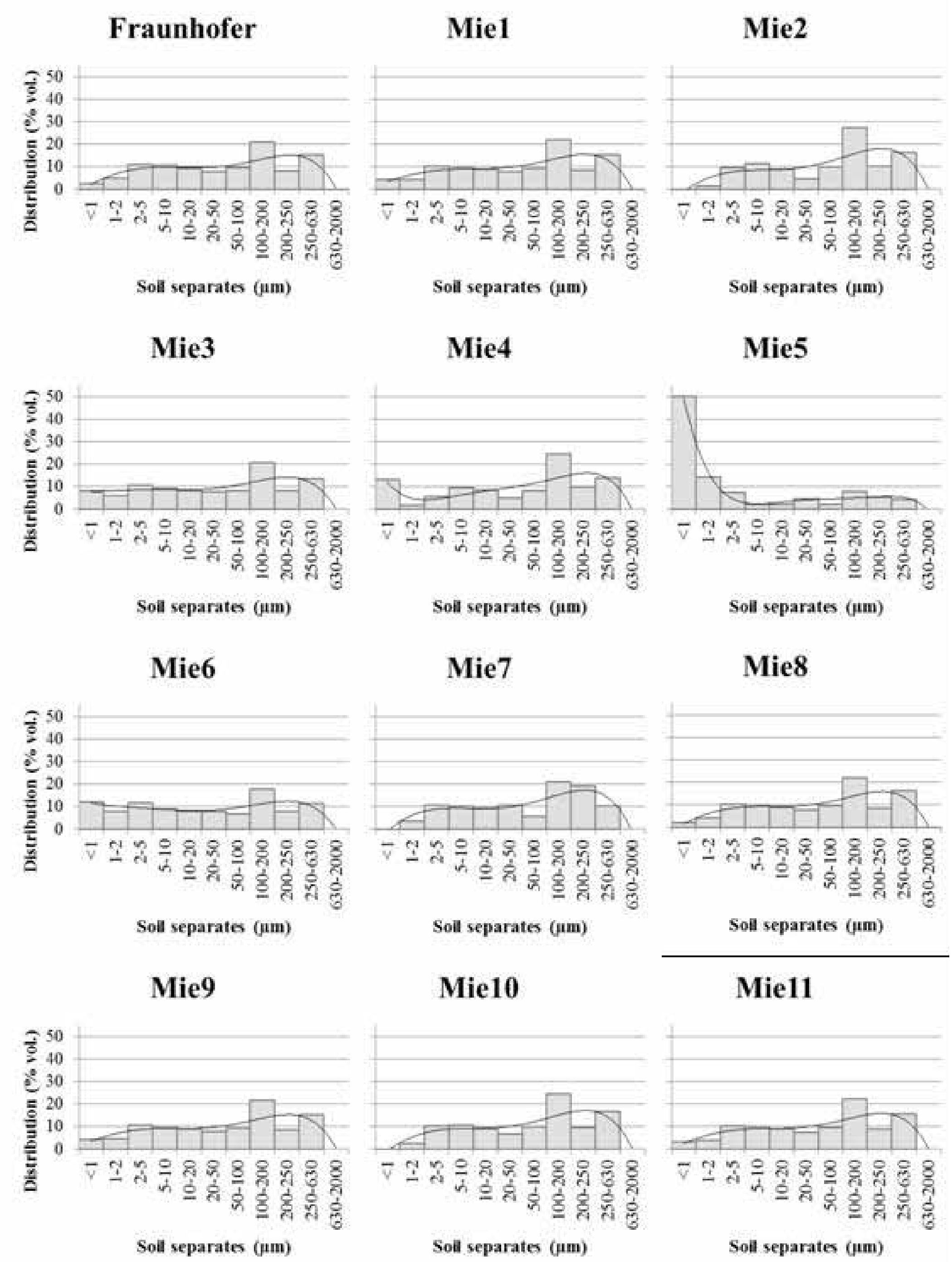

Figure 3: Volume percentage distribution of selected soil separates in sandy soil sample (33/40) according to various calculation algoritms of particle size distribution

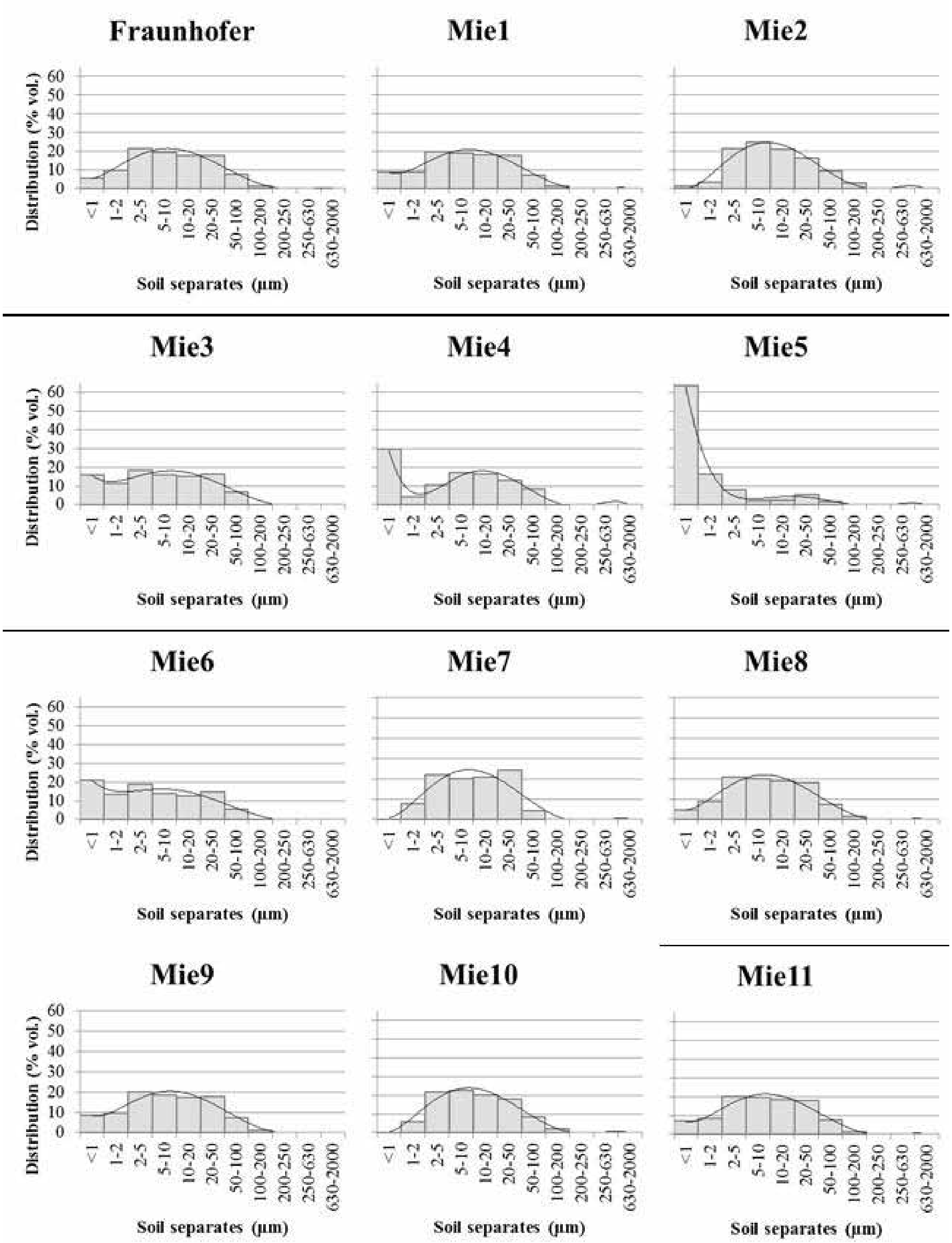

Figure 4: Volume percentage distribution of selected soil separates in medium fine soil sample (59/15) according to various calculation algoritms of particle size distribution

The lowest value of refractive index – 1.3 (Mie6 and Mie7) resulted in very significant and highest increase of clay fraction by 58%, resp. 16% in comparison to Fraunhofer model. Decreasing of the refractive index resulted in increasing of clay content. When the absorption index was set to 0.1, the decrease of refractive index from 1.5; 1.42 down to 1.3 (Mie1, Mie3 and Mie6) resulted in increase of clay fraction by 17 %. This increase was much steeper when the lower absorption index equal to 0.001 was used. The clay content rose by 51% as the refractive index decreased from 1.5; 1.42 down to 1.3 (Mie2, Mie4, Mie5).

Using the refractive index equal to 1.5 and absorption indices in the range 0.1 – 0.2 resulted in very similar estimates in comparison to Fraunhofer model. At such a setting, the change of refractive indexes did not have a significant effect on the distribution of particle size fractions. Such results were observed also by Di Stefano et al. (2010) although he used particle sizer made by different manufacturer and different soil sample preparation. According to their findings they suggested to use Fraunhofer model because of its simplicity and similar results.

The comparison of measurement results show that the PSD estimation according to different calculation theories and indexes combinations may vary up to different extent. The difference is even more obvious when the PSD results are plotted into the USDA triangle. For clarity, we show the results for one coarse soil sample and medium fine soil sample (Figure 5). The closest values to Fraunhofer model were obtained by refractive/absorption index combination in Mie1 (1.5/0.1), Mie11 (1.544/0.1), Mie9 (1.5/0.2) and Mie8 (1.8/0.2). For coarse soils the method Mie7 (1.8/0.001) showed also similar results like Fraunhofer model. In contrary, the biggest difference was observed at method Mie5 (1.3/0.001), when all samples were placed in the clay soil group..

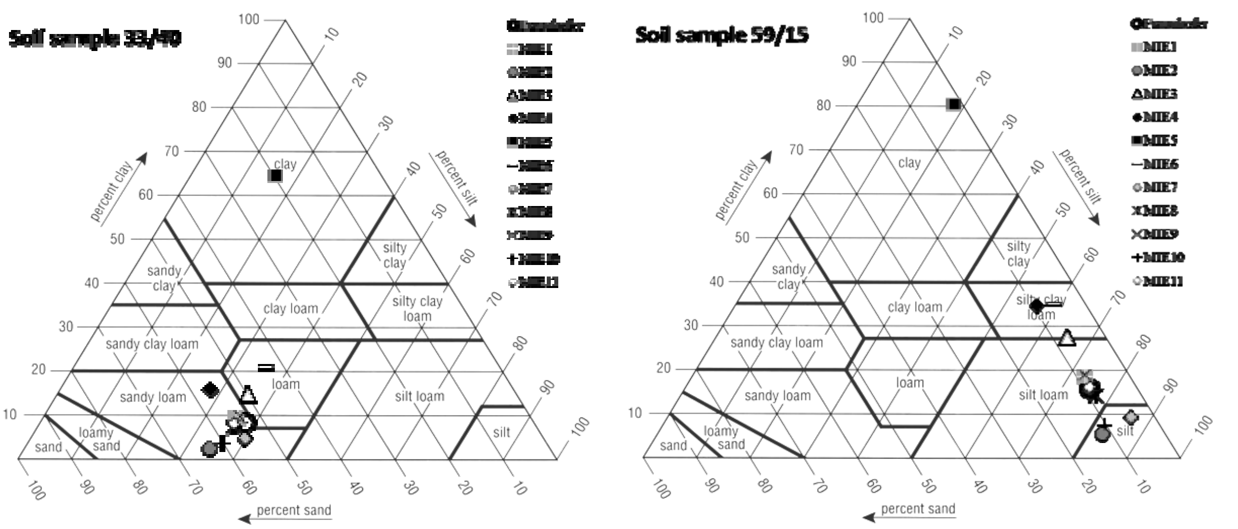

Figure 5. Comparison of particle size distribution according to various calculation algorithms for samples of coarse (33/40) and medium fine soil (59/15).

CONCLUSION

The comparison of measurement results show that the PSD estimation according to different calculation theories and indexes combinations may vary up to different extent. In this paper, we have used some of the indexes combinations proposed by the authors using Mie model that was suitable for their soil samples, apparatures and methodology of soil sample preparation. Unfortuantelly, it is very difficult to determine the correct and best fitting indexes combination. Thus, the need for good estimates of the refractive indices of both the sample and the solution is yet another obstacle in the "proper" use of laser diffraction (Kelly, Etzler, 2000). Several authors dealt with comparison of laser diffraction and pipette method (e.g. Arriaga et al., 2006; Eshel et al., 2004; Mihalache et al., 2010), or hydrometer method (Di Stefano et al., 2010) to find also the best combination of indexes. Because sedimentation methods and laser diffraction are based on different principles, the distribution of grain size fractions determined by the laser diffraction is not comparable with the sedimentation methods in the ratio 1:1 (Vandecasteele, De Vos, 2001). Kelly and Etzler (2000) suggest to use microscopy and compare the PSD results with quantitative microscopy results. In the final we can conclude, that it is really neccesary to deal with issue of PSD calculation method for soil samples, otherwise many professionals will be still discouraged to accept the laser diffraction as a method of determining soil texture, despite its many benefits.

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Research Article

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Conceptual model of water stable soil aggregate

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Key Words:

Soil structure, aggregate, soil organic matter, hydrophilic and hydrophobic properties of the soil solid phase

ABSTRACT

Water stability of the aggregate structure is directly related to the surface properties of elementary soil particles (ESP) in the solid phase (SP) of the soil. In the case of ESP hydrophilicity, water flows through the capillaries in the dry aggregate and leads to an increase of water pressure in the aggregate and its destruction. When ESP are hydrophobic, water and ions cannot get into the aggregate, and the "dead space" is created. Two forms of organic substances determine ESP architecture of soil aggregate and a combination of hydrophilic and hydrophobic surface properties of SP. Organic compounds adsorbed on the surface of mineral ESP provide film moisture migration, and hydrophobic organic ESP localized in the pore space of the aggregate provide the water repellent function and prevent the rapid migration of capillary moisture in the soil pore space.

INTRODUCTION

The phenomenon of the aggregate structure of the soil has always held and continues to hold one of the main places in the exploratory research of soil scientists. Origin, formation and stability of aggregates and, conversely, the processes of aggregate structure degradation - are the processes that directly affect the complex fundamental physical-chemical and biological processes in the soil, and at the same time are actually practical. However, there is no universally accepted and comprehensive theory of the aggregate formation and the structure formation control. There are a number of hypotheses on the aggregates formation, based on the works of V.P. Williams on the structure formation.

Unique natural formation that gives the soil a specific form of structural and hierarchical organization underlying all soil functions - soil unit - has a spatial organization, where the main role of "adhesives" is played by humic substances (HS), silt and cations such as Ca, Al, Fe-ions (Afanasyeva, 1966; Koolman, 1998; Voronin, 1986). The mineral skeleton, in most cases represented by elementary particles of mineral (quartz grains, feldspar, etc.). This is how the soil unit is formed: primary mineral particles are connected with each other with "adhesives" of different nature. This is confirmed by the huge amount of meso- and micromorphological observations, granulometric and mineralogical analysis of soil in general and the microaggregate fractions. This structure of the aggregates can be considered an indisputable fundamental fact of soil science (Kaurichev and Tararina, 1972; Voronin, 1986). Based on the morphological structure of soil aggregates, the hypotheses of soil structure formation appeared. Among these hypotheses, the three main or most common can be selected. Initially, the coagulation theory of structure formation was dominant; K.K.Gedroyts can be regarded as the founder of this theory, which was subsequently developed by Antipov-Karataev and colleagues (Afanasyeva, 1966; Kachinskii, 1965). It can be assumed that this hypothesis allowed to develop new schemes of analysis of soil aggregates, to classify and identify their characteristic types.

The most significant contribution to the theory of structure formation was V.R.Williams theory (1936), who emphasized the role of biological factors. He emphasized the importance of the plants root systems as a macro factor of granular structure formation, as well as the role of the so-called "fresh" organic matter, which is formed under anaerobic conditions, and is a metabolic product of anaerobic bacteria functioning. According to the assumptions of VR Williams, anaerobic zones are localized within soil aggregates, and aerobic processes go on their surfaces. This ingenious guess of V.R.Williams was subsequently confirmed experimentally (Kaurichev and Tararina, 1972; Stepanov, 1997; Williams, 1936), and it was proven that when humidity exceeds 70% of the total moisture, the redox potential inside the unit is 100-200 mV lower as compared with the surface. Moreover, soil microbiologists experimentally established the presence of facultative anaerobic bacteria in soil aggregates (Serdobolsky, 1953) which form local anaerobic zones of microcenosis (Stepanov, 1997). These facts indirectly indicate that the genesis of stable soil aggregates may be associated with specific properties of organic matter, which is formed in a lack of air and with the participation of specific microbiota.

However, the question of the physical and chemical properties, origin and mechanism of structure involving a "fresh organic matter" (by V.R.Williams) is not fully understood as of now.

To date, studies of humic substances (HS) allow to regard them as a multicomponent system. The strategy of the study of such objects is simplification by separation into components and their independent research. This approach involves the consideration of the initial multicomponent system as a mixture of a number of discrete states, the number of which is defined and limited by sufficiency to describe the currently available experimental data. Basic and fundamental problem here is the choice of criteria on which to carry out the separation.

Since the middle of last century to the present day separation of HS system is based on their solubility in acid and alkali. Although this property is never realized in a real natural setting, solubility parameter was adopted in soil science as a genetic characteristic of humus and soils of different genesis. With the widespread use of acid-base HS separation into components, this feature does not reveal the mechanisms of formation of humus soil profile, to explain the reasons for differences in the components of HS in soils of different genesis.

Indeed, most if not all soil processes involve soil water. The nature of interaction of the substance with water depends on the intensity of its hydrophilic or hydrophobic properties. Organic substances, of which HS are formed as a result of humification, have only biological origin. Most biological molecules are amphiphilic compounds, i.e. are capable of exhibiting both hydrophilic and hydrophobic properties (Koolman, 1998; Rudakov, 1951). Amphiphilicity is caused by the presence of both hydrophilic (polar) groups and hydrophobic (nonpolar) zones in their structure. The ratio of the hydrophilic and hydrophobic portions in the molecule determines its solubility, spatial organization and diversity of functional properties. Apparently, the have more pronounced hydrophilic properties HS have, the more these substances are mobile in the profile of the soil, the more they act as acidic hydrolysis agents, the more they interact from the aqueous phase with the solid phase surface. Hydrophobic HS will, on the contrary, be fixed at the place of their formation, forming accumulative characteristics of the profile. Apparently, this constitutes the significance and the role of amphiphilic properties in the formation of humus (accumulative, eluvial, eluvial-illuvial) soil profile.

Because mineral components are hydrophilic, organic matter plays the role in the formation of the hydrophobic surfaces in the soil. The degree of surface hydrophobicity of organic particles will depend on their ability to interact with each other through hydrophobic binding and formation water-stable aggregates, or susceptibility to peptization, due to the formation of hydrogen bonds. In this paper, we adhere to the assumption that the hydrophobic HS cause structural bonds and are responsible for the formation and stability (water resistance) of the soil structure. The formation of aggregates through hydrophobic interaction between elementary HS-coated soil particles is caused by the formation of the energetically most favorable, in an aqueous environment, surface of the resulting aggregate. Strong bonds existing between the water molecules are broken upon "dissolution" of a substance in water. In the case of ionic (hydrophilic) compounds these breakages are compensated by replacing water-water interaction by ion-water interaction. Upon "dissolution" of non-polar (hydrophobic) substances there is no such compensation and dissolution of substance in water does not occur. Association of hydrophobic particles to one another whereby the interaction between the water molecules are broken to the least degree is more energetically favorable (Milanovskii et al. 1993). In general, the hydrophobic binding can be defined as the interaction between the particles, which is stronger than the interaction of these particles with water, and which can be caused by covalent or hydrogen bonding, electrostatic attraction, or charge transfer. On this basis, it is the severity of hydrophobicity properties of HS will determine water resistance (and, apparently, all resistance to external influences) of soil structure.

It is believed that the main role of organic matter (OM) supplier in soils, particularly in the cultivation of herbs, is played by plant roots waste. OM of the root waste, entering the soil in situ, is subsequently converted by soil biota, passing the step of biotransformation with insufficient oxygen; therefore mainly humic acids and fulvic acids are formed, which, in the modern understanding of the properties of the newly formed soil organic matter, are amphiphilic substances containing hydrophobic and hydrophilic components (Antipov-Karataev et al. 1948; Kaurichev and Tararina, 1972; Milanovskii et al. 1993). All this data indicate that the formation of stable soil aggregates is caused by the special properties of OM, which is produced by specific biota in the lack of air. To date, these hypotheses are supplemented with data about the importance of the fungi hyphae in the primary (first mechanically and then biochemical) formation of aggregates, the data on the role of hydrophobization in the creation of the structure stability, primarily by increasing the duration of moistening, reducing the "discontinuous" action of entrapped air (Milanovskii et al. 1993; Williams, 1936), the importance of anaerobic processes in the formation of water-stable aggregates. Aggregate forming function of OM is associated with the acquisition of the hydrophobic properties by SOM components in anaerobic conditions through hydrophobic interactions formation (Gedroits, 1926; Serdobolsky, 1953). However, this is little to no data on participation of the hydrophilic and hydrophobic components in the formation of the soil aggregate structure and their change upon its degradation. The purpose of this work is to substantiate the value of the amphiphilic properties of soil organic matter in the formation and degradation of the water stable soil structure.

Objectives:

- To assess the value of the hydrophilic and hydrophobic components of SOM in the formation of the soil structure;
- To study the mechanism of structure formation with participation of hydrophilic and hydrophobic components;
- To identify the preferred mechanisms of desaggregation of soil properties (on the case of the typical chernozem) under anthropogenic load.

MATERIAL and METHODS

The object of study is typical chernozem (Alekhin Central Chernozemic Reserve, Kursk region) which is located under native steppe vegetation and bare (since 1947) fallow. These objects are described in detail in (Afanasyeva, 1966; Margolina et al. 1988). Humic substances were isolated from mineral genetic soil horizons by 0.1M $Na_4P_2O_7$ +0.1 M NaOH solution at 1:10 soil:solution ratio. For organic horizons, the ratio of 1:40 was used. Humic substances were purified from the extract of mineral impurities by centrifugation (8000 rpm., 15 min) and filtered through a membrane filter with 0.45μm pores. Chromatography of the hydrophobic interaction was conducted on Octil-Sepharose CL-4B (Pharmacia). Fractionating was conducted for the humic acid preparations, dissolved (5mg/ml) in 0.05M Tris-HCl buffer, pH = 8 and OM directly extracted from the soils. Sample volume was 0.5 ml, filtration rate 1ml/min., eluate detection was conducted at 280 nm, column 1x10 cm.

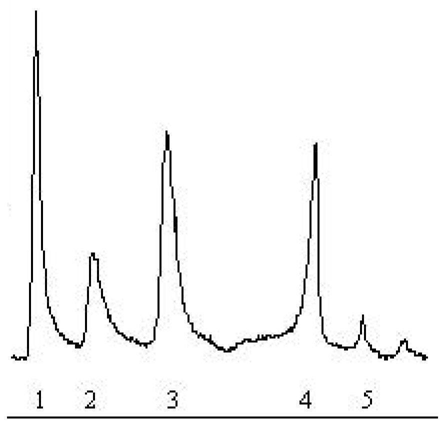

Figure 1. Chromatogramms of soil organic matter of the typical chernozem. 1-2 – chromatographic peaks of hydrophilic components, 3-5 - chromatographic peaks of hydrophobic components

As a result of chromatographic separation, the chromatograms clearly reveal five fractions differing in hydrophilic-hydrophobic interactions (Figure 1): fractions 1-3 interacted demonstrated the least hydrophobic interactions and were regarded as hydrophilic fractions, whereas fractions 4-5 were regarded as hydrophobic fractions.

RESULTS and DISCUSSION

Long-term bare fallow conditions of chernozem in comparison with chernozem under native vegetation led to a decrease in humus content (Figure 2) and a significant compaction of the upper layer (0.60-0.75 g/cm^3 – native steppe, 1.05-1.31 g/cm^3 – bare fallow).

A free filtering capability of upper chernozem horizons under native steppe is reduced in the bare fallow to 1.3-0.3 mm/min. Both amplitude and depth of profile freezing and heating increased. Aggregates of >2 mm lost the property of water-stability. According to microaggregate analysis, there was an increase in fraction of physical clay and silt and a significant decrease in content of fractions of medium and coarse sand. Decrease in SOM content within the plow layer is accompanied by accumulation of carbon in the lower horizons of the profile. The migration process of humic substances in the lower horizons of the profile was observed not only for the typical chernozem under bare fallow, but also for ordinary chernozem and dark chestnut soil, which were under long-term agricultural use (Figure 3).

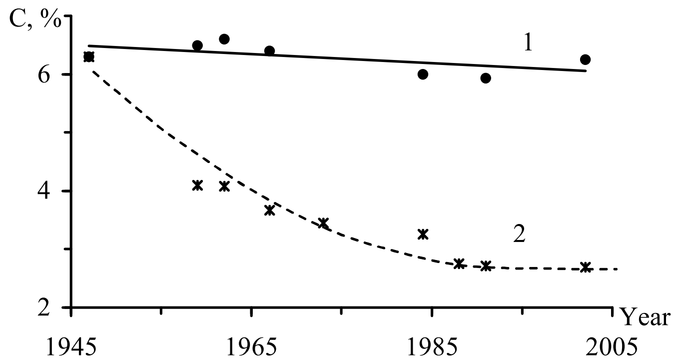

Figure 2. The carbon content in $A1_1$ (1) and A_{fallow} (2) of a typical black soil under virgin vegetation and resting fallow

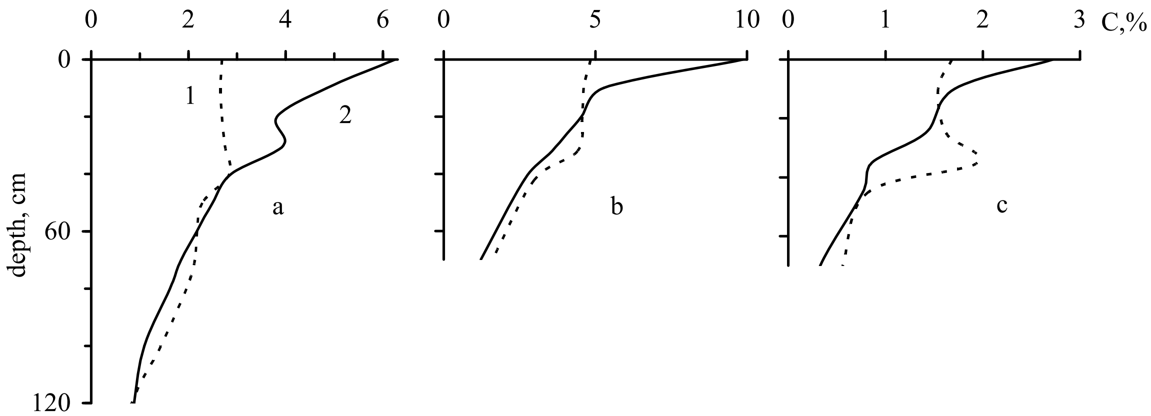

Figure 3. Carbon distribution in the soil profile under tillage (1) and native vegetation (2); *a* - typical chernozem, *b* - ordinary chernozem, *c* - dark chestnut soil

Significant changes in the structure of the chernozem under plowing, primarily related to the reduction of its water resistance, are characteristic consequences of anthropogenic degradation processes (Bezuglova, 2001; Serdobolsky, 1953).

Although water resistant chernozemic aggregate structure is associated with the humic acids, identification of the humus composition in the virgin and arable chernozems reveals decline in Aarable value of nonhydrolyzable residue and a significant reduction of fulvic acids (by 22-46%) as compared to their content in virgin soils. The absolute content of humic acids was less decreased (4-26%). As a result, the index value Chumic / Cfulvic in Aarable as compared to Al1 of virgin soil increases (1,14,21). According to some reports [21] long-cultivated chernozems demonstrate the carbon loss of about 4-5% in silt fractions and of 25% in clay fraction, indicating a more rapid mineralization of organic matter of the clay fraction and of microbiological and chemical stability of the humus composition in silt fractions. At our objects the carbon loss of the clay fraction is about 32% (10.24% in the virgin lands, 6.93% in fallow).

Chromatographic analysis (Figure 4) of HS from virgin chernozem profile and arable chernozem demonstrated that prolonged exposure of a typical chernozem as black fallow led to a substantial decrease in the absolute content of hydrophilic components (fraction 1 and 2) as part of HS of arable horizon and their increase in the underlying horizonts. Content of the hydrophobic components did not change in fraction 3 and increased in fraction 4.

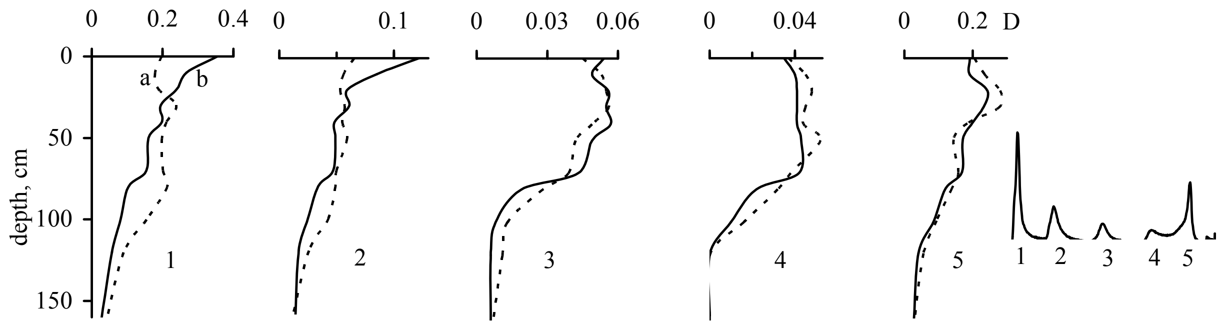

Figure 4. Distribution of chromatographic fractions (1-5) HS along the profile of a typical chernozem; *a* – bare fallow, *b*-native steppe

Reduction of hydrophilic HS in A_{arable} with their accumulation in the lower profile horizons indicates lesser stability of these components of HS to chemical and microbiological processes of mineralization on the one hand, and the migration of hydrophilic components through the profile on the other. This data is consistent with well-known facts about changing fractions of HS under degradation of the aggregate structure. Although traditionally chernozemic aggregate structure is associated with humic acids, determination of the humus composition in the virgin and arable chernozems shows a significant decrease in fulvic acids in the latter (22-46%) as compared to their content in virgin soils.

Thus, in conditions of the black fallow, under the deficit of the incoming fresh organic material primarily the mineralization of HS hydrophilic components localized on the surface of the mineral matrix occurs. Obviously, this process is a major cause of loss of water-resistance properties of the soil aggregates..

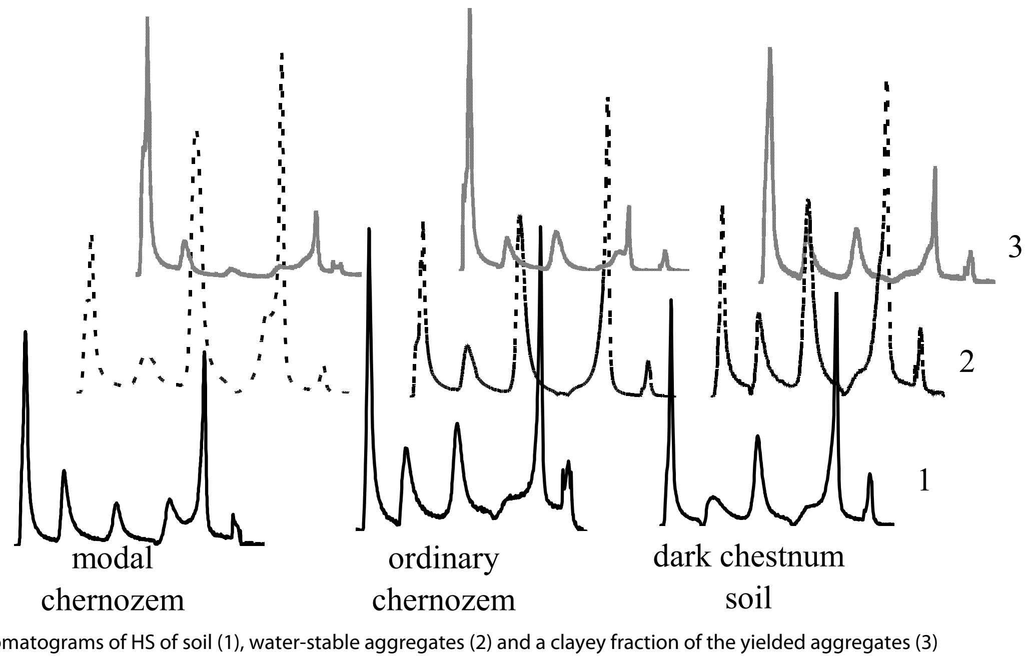

Figure 5. Chromatograms of HS of soil (1), water-stable aggregates (2) and a clayey fraction of the yielded aggregates (3)

Accumulation of HS of hydrophobic nature in the SOM of water-stable aggregates is confirmed by results of HIC (Figure 5). The content of hydrophobic HS in water-stable aggregates is greater (especially the third HS fraction) than in the soil as a whole. HS from clay fraction of aggregates are predominantly hydrophilic in nature (clay fraction from water-stable aggregates was isolated by decantation). We believe that hydrophobic components of water-stable aggregates HS are represented by the products of SOM humification *in situ* and correspond to particles of organic nature with size of 2-10 µm. HS of hydrophilic nature are mainly localized in clay-organic compounds.

The data obtained allow to create highly schematized model of the structural and functional organization of the hydrophobic-hydrophilic components in the chernozem aggregate formation. In the mineral horizons profile during humification of organic material *in situ* the heterogeneous system of SOM is formed whose components differ by hydrophobic-hydrophilic properties. Water-soluble (hydrophilic) products are removed from humificated plant residues and, hitting the surface of the mineral particles, form sorption and organo-mineral complexes with this surface, reducing its hydrophilic properties due to mutual locking of polar groups of the mineral matrix and organic molecules, covering her surface. In other words, the surface of mineral solids becomes hydrophobizated. In turn, the hydrophobic products of organic material humification, incapable of water migration, remain at the place of formation. This hydrophobical components are spatially "isolated" from mineral particles, beeing caught between them. Accumulation of hydrophobic components of HS in the internal volume of the aggregate is helped by quasianaerobical conditions of organic material humification. It was described previously that the central part of water-stable chernozem aggregates is an ecological niche for anaerobic microorganisms. Additional 4 species of anaerobes were found in the center zone of aggregates compared to soil in whole and initial aggregates (2 species of clostridia - primary anaerobes, as well as ferroreducers and sulphatereducers - secondary anaerobes). Concentration of clostridia in "nuclei" of aggregates is 10-17 times its content in the original soil (Milanovskiy, 2009).These conditions of the formation of "fresh" humus were described in works of V.R.Williams. Nonpolar molecular fragments, on the one hand, determine their hydrophobic properties, and on the other - their resistance to oxidative, microbiological waste mineralization, especially in quasianaerobical conditions.

Presence of non-polar HS in the aggregate volume causes distortions in the structure of water that can be transmitted over considerable distances along chains of hydrogen bonds and cause long-range hydrophobic interaction. The combined action of HS, which hydrophobize the surface of mineral matrix and isolated in the micro areas, nonpolar molecules, stochastically distributed in the aggregate, cause its water-stable properties. In the aqueous environment, the non-polar areas gravitate towards each other, as the approaching minimizes their thermodynamically unfavorable contacts with water. The total effect inside the hydrophobic areas of the aggregate is countering the rapid flow of water in the aggregate, reducing its swelling and promoting its stability in a saturated state. The last point is proven by data on water-resistant aggregates. Mineralization of the hydrophilic HS components, localized on the surface of the mineral particles, leads to the exposition of the hydrophilic surfaces of mineral solid soil phase, the efficiency of hydrophobic interactions within the aggregate drops and it is dispersed by water.

One should specifically highlight the role of hydrophilic components in soil humus. The role of hydrophobic interactions in soils, in particular, is emphasized by the fact that the stability of soil aggregates correlates with the content of hydrophobic humus fraction in the soil (Capriel et al. 1990). Water-stability of aggregates increases by adding nonpolar liquids in the soil (Biederbeck, 1990). In addition, as a prerequisite for modifying the surface properties of soil solid phase by organic matter, it should be located in the liquid phase of soil, i.e. hydrophilic fraction or water-soluble organic matter.

CONCLUSION

Prolonged (from 1947) typical chernozem soil exposure in the black fallow conditions led to a decrease in humus content, the formation of subsoil compaction, compaction of the upper layer and a sharp decrease in water stability of aggregates. In conditions of arable black fallow, with a deficit of fresh-organic material, mineralization and partial migration down through the profile of hydrophilic HS components, localized on the surface of the mineral matrix, primarily occur.

Hypothesis of V.R. Williams on the role of "fresh" organic matter in the process of aggregation is confirmed by physico-chemical models of formation of black soil aggregate structure, where the role of sorbed on mineral surfaces matter is played by hydrophilic components of HS, and the links between the particles "mineral surface-hydrophilic components" are formed by hydrophobic HS components. Therefore organo-mineral water-stable aggregate has the following organo-mineral composition: "mineral particle surface – (hydrophilic-hydrophobic components) = (hydrophobic-hydrophilic components) – mineral surface" where the symbol denotes a molecule of SOM, and the symbol "=" represents hydrophobic interactions.

A conceptual model of water stability of soil aggregates associated with the ratio of hydrophilic and hydrophobic components and their spatial localization is proposed. The combined action of hydrophobic components of SOM, which hydrophobize the surface of the mineral matrix and nonpolar molecules, isolated in microzones, stochastically distributed in the aggregate, cause its water-stable properties.

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Research Article

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Soil microbiological consequences of a long-term fertilization experiment in Hungary

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long-term experiment, chemical soil properties, soil microbes, parameters of C- and N cycle, activity of soil enzymes

ABSTRACT

The results of long-term experiments in all over the world demonstrate that the fertilization have direct and indirect effect on soil as a life community, mainly influence the plant population and quantity occurrence and activity of soil microorganisms. According to the environmental–friendly approach of the sustainable agricultural production it is very important to investigate the secondary effect of applied fertilization doses and methods in long-term fertilization experiments in order to prevent the dynamic of microbial population and fertility of soils. The objective of the study was to evaluate the chemical and soil microbiological consequences of a 25-year old long-term fertilization experiment, where five increasing doses of NPK-fertilizers have been applied in maize monoculture.

INTRODUCTION

Different crop management practices (fertilization, crop rotation, crop protection, etc.) are applied in the agricultural production and the consequences of these practices on soil properties can be investigated in long-term field experiments. With environment-friendly technologies, are able to maintain the nutrient status and fertility of soils achieving higher yields and quality crops. These expectations, however, are influenced by several biotic and abiotic natural ecological factors, agrotechnics and also by the economy of production. The soil physical, chemical and biological properties play a key role among the ecological factors. According to Biró, (2005) a more thorough knowledge is required for establishing the relationships among these factors and for a realistic assessment of the quality and fertility of soil. Among the management practices the quantity and quality of applied fertilizers is one of the most important parameter on the yield. Fertilizers have direct and indirect positive or negative effects on soil characteristics, including the activity of plants and microorganisms (Virág, 1981). Through their chemical composition and solubility they primarily have direct effects on the development and growth of the crops; the indirect effects of fertilization are shown by the changes in soil environment.

Chemical and microbiological studies were made in long term fertilization experiment by several home and foreign researchers (Hickisch and Müller 1990; Müller 1991; Kautz et al. 2004, Li-Xiu et al. 2005; Janusauskaite et al. 2013; Lásztity et al., 1981; Gulyás et al., 1984; Kátai 1999, 2006.) which demonstrated that the balanced nutrient supply (both macro-and microelements) had favourably affected the processes of the soil material and energy conversion, biodynamic, as well as the development of plants.

From the 1990s a considerable decrease in the amount of applied fertilizers has been experienced. Nowadays fertilizer use is at a constantly low level in

Hungary (Pepó and Nagy, 1997). The resulted negative soil nutrient balance is due to the fact that only half of the extracted nutrients are returned to the soils in general with inorganic fertilizers and organic manures. Soil organic matter shows a decreasing trend across Europe. This is valid for Hungarian soils, as agricultural production mainly relies on plant residues for soil organic matter supply. Toth and Kismányoky (2001) and Kátai et al., (2014) examined some soil properties in long-term field experiments in different cropping systems and stated that soil organic matter content was greater in crop rotation, than maize monoculture and increased with the rise of fertilization rates. The highest organic matter content was measured when legumes were in the crop rotation. Palmer et al. (2013) stated that organically fertilized crops yield was significantly higher following grass/red clover leys, then winter wheat.

In the present paper the results of four years in a 25-years long-term fertilization experiment are discussed concerning the changes in some soil chemical properties and microbiological characteristics of the carbon and nitrogen cycles. In order to evaluate the effects of agrotechnical factors, it was aimed to establish the possible correlations between the measured soil chemical and microbiological properties.

MATERIAL and METHODS

The objective of the study was to evaluate the chemical and soil microbiological consequences of a 25-year old long-term fertilization experiment which was set in 1988 in the Eastern part of Hungary about 30 km far from Debrecen, in Görbeháza. In the experiment five increasing doses of NPK-fertilizers have been applied in maize monoculture. The soil type of the experiment is a typical meadow soil according to the genetic soil classification (Vertisols in WRB).

The effects of different fertilizer levels on soil properties were compared to control and evaluated [1. control (0), 2. (N_{40} P_{25} K_{30}), 3. (N_{80} P_{50} K_{60}), 4. (N_{120} P_{75} K_{90}), 5. (N_{160} P_{100} K_{120}) 6. (N_{200} P_{125} K_{150}) doses as N, P_2O_5, K_2O], in maize monoculture under non-irrigated conditions.

Soil samples were taken from the soil under maize. Some soil chemical properties were measured: soil pH (in distilled water (H_2O) and 1 M potassium chloride (KCl), ratio of soil/water 1/2,5 w/w), hydrolytic acidity (according to Buzás, 1988), the available nitrate (NO_3-N, based on Felföldy, 1987), phosphorus, potassium (AL-P_2O_5 and AL-K_2O based on Egnér et al., 1960), organic carbon (according to Székely et al., 1960) and nitrogen (according to Tyurin, cit. Filep, 1988) contents. The abundance of some soil microbiological physiological groups was also investigated. The amount of microbial biomass carbon and nitrogen, the carbon dioxide release, the capacity of nitrate exploration, and the activity of three soil enzymes (saccharase, urease and dehydrogenase) were determined.

The aerobic cellulose decomposing and nitrifying bacteria were investigated according to Pochon and Tardieux (1962). The rate of soil respiration (CO_2-production) was measured after 10 days incubation with NaOH trapping (Witkamp, 1966 cit. Szegi, 1979). Microbial biomass carbon (MBC) and nitrogen (MBN) were assessed by the fumigation-extraction method according to Vance et al. (1987). The nitrate exploration was measured after incubation, as suggested by Felföldy (1987). Saccharase activity was measured by the method of Frankenberger and Johanson (1983), urease activity was estimated on the quantitative determination of ammonia, as the modified method of Kempers (cit. Filep, 1988).

Soil samples were taken for four years (2009-2012) from the 0–20 cm soil layer twice yearly [in spring and autumn, resulting in 192 soil samples (6 treatments, 4 repetitions and 8 sampling times along the four years)] and analysed. Changes in some soil chemical and microbiological properties (Tables 1, 2 and 3), are discussed and evaluated.

In this paper the effects of different fertilization' levels on the chemical and microbiological soil properties are evaluated. Data analysis was performed using Microsoft Excel 2003 (mean values and standard deviation). Two factors variance analysis was used to get significant effect on measured parameters.

RESULTS and DISCUSSION

Examined physical and chemical properties of soils from field experiment

In the evaluation the result of the fertilizer-treatments (2, 3, 4, 5, 6, treatments) are compared to control (1) treatment. The texture of soils did not change in the treatments significantly according to the Arany-type plasticity index and clay & silt fraction, the texture of the soil is clay-loam. There was no significant change in the average moisture content of treatments in the examined four-year. In the treatment 2, the pH_{KCl} decreased significantly, but in the other higher fertilizer doses did not cause significant decrease in the pH and what is more, the pH increased. It should be noted that the parent material of soil is loess.

Regarding the easily available soil nutrients, generally an increased nutrient content was recorded in each NPK treatment. Concerning the phosphorus, and nitrate contents of soil a significant increases where detected in each fertilizer treatment. While the phosphorus content of soil increased 3-4 fold, the nitrate content increased in higher rate, in the 4-6 fold, but in the treatment 5 the increase was tenfold.

Concerning the potassium content of soil only the medium-large, large and largest doses of fertilizers caused significant increase in this parameter. On the bases of correlation analyzes, among the measured soil parameters close correlation were established in several cases. Regarding the physical and chemical soil properties, close correlation was proved between the following measured parameters, moisture content and clay & silt fraction (r = 0,896), AL-P_2O_5 and nitrate content (r = 0,843), and AL-P_2O_5 and AL-K_2O (r = 0,946).

Table 1. Moisture content, physical and chemical characteristics of a typical meadow soil (Vertisols in WRB) under maize monoculture in Görbeháza long-term fertilization field experiment (average values of four years)

Number of treatments	K_A	Silt & clay %	Moisture content %	pH_{KCl}	AL-P_2O_5 mg kg^{-1}	AL-K_2O mg kg^{-1}	NO_3^- mg kg^{-1}
1.	43,8	48,14	20,58	6,62	44,04	233,36	24,39
2.	44,07	51,99	22,29	5,89*	80,07	228,45	89,18*
3.	44,20	51,76	22,45	6,28	139,25*	256,64	157,33*
4.	43,77	50,26	21,93	6,50	171,64*	279,50*	114,32*
5.	44,43	50,75	21,63	6,80	196,36*	278,32*	241,04*
6.	44,50	52,64	22,09	7,08	181,50*	286,00*	137,94*
$LSD_{5\%}$	2,64	2,49	2,01	0,45	40,43	33,47	23,08
f-ratio	0,10	1,74	1,74	0,64	1,36	1,29	0,71

Examined soil microbiological parameters of the C-cycle

Soil microbial parameters of carbon-cycle are shown in table 2. Total bacteria number could be evaluated both at the carbon and nitrogen-cycle; we do it in the C-cycle. The total number of bacteria increased in each treatment but only the small and medium (2 and 4 treatments) doses of fertilizers increased significantly this microbial parameter. Organic carbon content of soil increased in all treatments, from 11-27%, but only in the 4, 5, 6-treatments increased significantly this parameter. The number of aerobic cellulose decomposing generally increased in the treatments except the 2-treatment. This parameter increased significantly in the higher doses of fertilizer treatments 3, 4, 5, 6), in the treatment with highest fertilizer dosage the increase was six fold. The activity of saccharase enzyme was the only parameter among the examined parameters of C-cycle, where each treatment caused significant increase. The CO_2-production increased in each treatment, but significantly in the treatment 3, 4, 5. The microbial biomass carbon increased in the treatment of the lower and middle doses of fertilizers (2, 3, 4 treatments), but decreased in the larger doses of fertilizers (5, 6 treatments), the decrease was significant by the effect of largest fertilizer dose (6).

Summarizing the results of the parameters in the carbon–cycle, generally positive effects were measured by the effect of increasing doses of fertilizers especially the organic carbon, the number of cellulose decomposing bacteria, the activity of saccharase activity and CO_2-production increased, in most cases significantly, but the microbial biomass carbon (MBC) decreased significantly in the largest dose of fertilizer's treatment.

Table 2. Some soil characteristics of the carbon cycle in a typical meadow soil (Vertisols in WRB) under maize monoculture in Görbeháza long-term fertilization field experiment (average values of four years)

Number of treatments	Total bacteria number, x 10^6	Organic carbon, g kg^{-1}	Cellulose decomposing bacteria x 10^3	Saccharase glucose (mg $100g^{-1}$)	CO_2 mg 100g $soil^{-1}$ $10day^{-1}$	MBC (extr.) (µg g^{-1})
control	7,26	22,7	2,98	10,67	12,48	123,52
$N_{40}P_{25}K_{30}$	10,69*	26,4	2,71	15,20*	14,68	145,35*
$N_{80}P_{50}K_{60}$	9,05	25,3	5,64*	14,17*	15,77*	169,78*
$N_{120}P_{75}K_{90}$	11,13*	28,9*	12,69*	14,34*	15,71*	170,23*
$N_{160}P_{100}K_{120}$	8,95	28,1*	9,74*	14,04*	15,69*	117,44
$N_{200}P_{125}K_{150}$	8,85	27,1*	17,76*	15,50*	14,90	106,33*
$LSD_{5\%}$	2,45	3,9	1,15	3,04	3,29	9,93
f-ratio	1,63	2,2	1,96	0,56	0,915	0,63

Examined soil microbiological parameters of the N-cycle

Soil microbial parameters of nitrogen-cycle are shown in table 3. In the nitrogen cycle five parameters were investigated. It is clear that the different level of fertilization had positive effects in maize monoculture on these examined soil biological properties. On the bases of the mathematical statistical evaluation, the organic nitrogen content and number of nitrifying bacteria increased significantly in each fertilized treatment. The nitrate production and the quantity of microbial biomass nitrogen (MBN) also increased in each treatment, but significantly in the 3, 4, 5, 6 treatments. Regarding the urease enzyme, the treatment 3 and 4 had significantly positive effect on the activity of urease.

Summarizing the parameters of nitrogen-cycle, all analyzed soil biological properties positively responded to fertilization in maize monoculture, significant growth was proved in the majority of the treatments..

Table 3. Some soil characteristics of the nitrogen cycle in a typical meadow soil (Vertisols in WRB) under maize monoculture in Görbeháza long-term fertilization field experiment (average values of four years)

Number of treatments	Organic nitrogen g kg^{-1}	Nitrifying bacteria x 10^3	Urease NH_4^+ mg $100g^{-1}$	Nitrate production NO_3^- μg g^{-1}	MBN (μg g^{-1})
control	2,266	4,15	28,85	13,78	6,81
$N_{40}P_{25}K_{30}$	2,641*	10,88*	41,79	14,41	8,96
$N_{80}P_{50}K_{60}$	2,539*	8,42*	46,35*	40,80*	11,95*
$N_{120}P_{75}K_{90}$	2,888*	11,17*	52,09*	66,84*	11,40*
$N_{160}P_{100}K_{120}$	2,805*	12,30*	40,06	29,06*	11,95*
$N_{200}P_{125}K_{150}$	2,707*	8,96*	39,91	37,91*	16,05*
$LSD_{5\%}$	0,278	1,15	17,10	5,39	4,39
f-ratio	0,220	0,47	0,41	0,90	0,32

Among the parameters of the carbon and nitrogen cycles and physical and chemical properties of soils also close correlations were proved. Close correlation was between the microscopic fungi number and moisture content (r = 0,950), as well as the clay and silt content (r = 0,874). Further close correlation was between the aerobic cellulose decomposing bacteria and AL-K_2O (r = 0,923), the nitrifying bacteria and total bacteria number (r = 0,757). The CO_2-production was close correlation with AL-P_2O_5 and nitrifying bacteria (r = 0,818), (r = 0,830) respectively. There was strong correlation between the MBC and moisture and CO_2-production of soils (r = 0,872), (r = 0,901). The MBN was close correlation with AL-P_2O_5 (r = 0,843), with AL-K_2O (r = 0,840), and number cellulose decomposing bacteria (r = 0,878). Among the measured enzymes activities, the dehydrogenase had the most of the close correlations with the soil parameters. So dehydrogenase was close correlation with moisture content (r = 0,964), total bacteria number (r = 0,841), number of microscopic fungi (r = 0,976), CO_2-production (r = 0,814), MBC (r = 0,901) and with saccharase activity (r = 0,900). It was not the exhaustive list.

Some ratio among the examined soil microbial parameters

The ratio of MBC/MBN gradually decreased with the increasing doses of fertilizers. While this rate was 18,14 in the control, only 6,62 in the treatment 6. It means that the quantity of microbial biomass nitrogen increased parallel with the increasing doses of fertilizers.

The ratio in microbial biomass carbon and organic carbon (MBC/OC) confirmed that the increasing doses of fertilizers decreased the MBC, so this MBC/OC ratio also decreased in the treatments of 5 and 6.

Table 4.Some microbial indexes between the parameters of the carbon and nitrogen cycles in a typical meadow soil (Vertisols in WRB) under maize monoculture in Görbeháza long-term fertilization field experiment

Number of treatments	Dehydrogenase activity	MBC/MBN	MBC/ OC(%)	CO_2 /MBC qCO_2
control	35,04	18,14	5,441	0,101
$N_{40}P_{25}K_{30}$	49,01*	16,22	5,505	0,100
$N_{80}P_{50}K_{60}$	48,13*	14,20	6,710	0,093
$N_{120}P_{75}K_{90}$	48,17*	14,92	5,890	0,092
$N_{160}P_{100}K_{120}$	43,21*	9,82	4,179	0,133
$N_{200}P_{125}K_{150}$	46,02*	6,62	3,923	0,140
$LSD_{5\%}$	4,49			
f-ratio	0,93			

CONCLUSIONS

The objective of the study was to evaluate the chemical and soil microbiological consequences of a 25-year old long-term fertilization experiment, through a four year-experiment, where five increasing doses of NPK-fertilizers have been applied in maize monoculture. The soil type of the experiment was a typical meadow soil (Vertisols in WRB), it was set in 1988 in the Eastern part of Hungary on the "Hajdúság loess plateau" in Görbeháza and the results of the 2009-2012 years were evaluated.

The examined Arany-type plasticity index as well as the silt and clay content stayed in the same level and in the majority of treatments the pH were not changed by treatments either. It should be noted that the parent material of soil is loess. The easily available soil nutrients (NPK) generally increased, concerning the phosphorus, and nitrate contents of soil significant increases were detected in each fertilizer treatment. The phosphorus content of soil increased 3-4 fold, the nitrate content increased in higher rate, in the 4-10 folds. The increase in potassium content was more moderate than the increase of phosphorus and nitrogen.

Summarizing the results of the parameters in the carbon and nitrogen–cycle, generally positive effects were measured by the effect of increasing doses of fertilizers. The organic carbon, the number of cellulose decomposing and nitrifying bacteria, the activities of the saccharase and urease enzymes, the CO_2-production, microbial biomass nitrogen and nitrate production in most cases increased significantly, but the microbial biomass carbon (MBC) decreased significantly in the largest dose of fertilizer's treatment. Regarding the physical and chemical soil properties, close correlation was proved several cases. Only few important relationships are output. The moisture content was close correlation with clay & silt fraction (r = 0,896); the AL-P_2O_5 with nitrate content (r = 0,843); and AL-P_2O_5 with AL-K_2O (r = 0,946). There was strong correlation between the MBC and moisture and CO_2-production of soils (r = 0,872), (r = 0,901) respectively. The MBN was close correlation with AL-P_2O_5 (r = 0,843), with AL-K_2O (r = 0,840), and number cellulose decomposing bacteria (r = 0,878). Among the measured enzymes activities, the dehydrogenase had the most of the close correlations with the soil parameters. So dehydrogenase was close correlation with moisture content (r = 0,964), total bacteria number (r = 0,841), number of microscopic fungi (r = 0,976), CO_2-production (r = 0,814), MBC (r = 0,901) and with saccharase activity (r = 0,900).

In maize monoculture the application of mineral fertilization seems to be an effective method to increase the soil nutrient content and to intensify the soil biological processes through the soil biological activity according to the results of 19 investigated soil physical, chemical and microbiological parameters of four years (2009-2012). Several cases were proved close correlation among the investigated physical, chemical and microbiological soil parameters..

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Research Article

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Bioavailability of heavy metals (Cu and Zn) after amelioration of contaminated soil

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ABSTRACT

The soil in the region of Zlatitza (Western Bulgaria) is characterized by long term contamination and is hygienically loaded by heavy metals (especially by Cu) resulting from the activities of the nearby copper producing factory. An important factor which further increases the mobility and the bioavailability of metals in the soil is its acidity (pH_{H2O} = 4.0). Thus, in the region, areas without any vegetation are formed. The objective of this experiment was to investigate the impact of different soil amendments on the bioavailable forms of heavy metals Cu and Zn measured in three soil extractants 0.01M $CaCl_2$, 1M NH_4NO_3 and 0.05M EDTA. In a pot experiment the polluted soil was ameliorated with three kinds of ameliorative mixtures – CaO, peat and zeolite with three doses in 12 treatments. A mixture of grasses was used as a test crop and heavy metals concentrations in the biomass were analyzed. The mobility of Cu and Zn increased with soil pH decrease. A strong negative corelation was found between the soil exchangeable Cu and Zn (in 0.01M $CaCl_2$ and 1M NH_4NO_3) and the soil pH which is expressed with (R = -0.861 and -0.852 for Cu) and (R = -0.906 and -0.868 for Zn). A positive correlation was found between Zn concentrations in plants and Zn extracted with 0.01M $CaCl_2$ (R = 0.730) and 1M NH_4NO_3 (R = 0.702).

INTRODUCTION

Contamination of soil by heavy metals is a question that has attracted considerable attention in recent years. A common feature of heavy metals as contaminants is their permanent presence in soil difficultly to be removed due to their nature of simple substances. In contrast to the organic contaminants and the radionuclides, they are not degradable in the soil and at certain concentrations may be toxic to plants (Takáč et al., 2009). The bioavailability of heavy metals and their potential uptake by plants is largely determined by the fraction of free metals present in the soil solution (Lake at al., 1984; Hare and Tessier, 1996). Detailed analysis showed that the chemical properties of the metals in the soil and their retention by the solid phase are influenced by the combination of the physical and chemical properties of the soil such as soil acidity, soil structure, content and nature of the clay minerals, organic matter content. These factors determine the mobility and the intensity of their biological uptake (Novozamsky et al., 1993; Kaplan et al., 1995; Xiao-quan Shan et al., 2003). The changes in the chemical properties of soil affect the concentration of free metals and as a result, their bioavailabilities to plants alter (Fries at al., 2003). By increasing the soil pH, the concentration of organic matter and clay, the solubility of most heavy metals decreases because of their increased adsorption.

Copper and zinc are essential elements for the growth of plants. However, their presence in soil in concentrations higher or lower than the optimum could affect adversely their development. The phytotoxicity of copper depends on its bioavailability, which is closely related to the distribution of this element in its various chemical forms (Alva et al., 2000).

There is a number of methods for determining the bioavailable forms of heavy metals. According to many authors, the strongest is the relationship between the extracted amount of heavy metals from soil and their contents in plants during the extraction with neutral unbuffered electrolyte solutions, such as 0.01M $CaCl_2$ (Novozamsky et al., 1993). Another recommendable method for the extraction of exchangeable forms of heavy metals is the use of 1M NH_4NO_3 (Ure, 1996). Synthetic chelating agents such as EDTA are widespread as extractants, mainly because of their ability to form very stable water-soluble and well-defined complexes with a wide range of multivalent cations (Novozamsky et al., 1993; Ure, 1996). Their disadvantage is the ability to dissolve the solid soil phase, mainly carbonates and the Fe-and Al-oxides, which afforded the very high concentrations of the studied metals.

The purpose of this study was to evaluate the influence of different ameliorants added to polluted, acid soil on the bioavailable forms of heavy metals - copper and zinc, as defined in three soil extractants (0.01M $CaCl_2$, 1M NH_4NO_3 and 0.05M EDTA pH -7).

MATERIAL and METHODS

The object of this study is acidic, polluted by heavy metals (especially by Cu) Alluvial meadow soil (Dystric Fluvisols - FAO) from the region of Zlatitza, Western Bulgaria. The contamination of the soil is due to the activity of the nearby copper smelter. The mobility of heavy metals in the studied soil is greatly increased, because of its low pH (pH in H_2O = 4.0), which is mainly a result of the release of SO_2 from the copper smelter. Thus, in the course of multiannual period there were formed a complete deforestation territories in the region. Some of the general physico-chemical characteristics of the soil are presented in Table 1.

Table 1. General physico-chemical characteristics of the investigated soil *

Physico-chemical characteristics	C%	pH H_2O	$T_{8,2}$	T_{CA}	T_A	Exch. $H_{8,2}$	Exch. Al^{3+}	Exch. Ca^{2+}	Exch. Mg^{2+}	V%	Cu	Zn
			cmol/kg								mg/kg	
Investigated soil (0 - 20 cm)	0.80	4.0	22.8	15.5	7.3	11.2	3.7	9.5	2.2	51	1339.0	146.8
	in % of $T_{8,2}$											
	-	-	-	68	32	49	16	47	10	-	-	-

*Some of the physico-chemical characteristics of the studied soil are taken from (Benkova, 2005).

The investigated soil refers to strongly acidic soils, with enhanced, toxic to plants exchangeable acidity (mainly represented by exch. Al^{3+} = 3.7 cmol/kg) and hydrolytic acidity ($H_{8.2}$ = 11.2 cmol/kg) – Table 1. The organic content of soil is low (C_{org} = 0.80%). The soil texture is defined as slightly sandy-clay, according to (Kachinski, 1965). The content of physical clay (particles < 10μm) in the surface two horizons is between 26.7% and 29.3 % and of clay (particles < 1 μm) – 9.2 – 10.7%. The concentration of Cu in the analyzed soil is on average 1339.0 mg/kg and this value far exceeds not only the background but also the maximum permissible concentrations for the Bulgarian soils (Soil Protection Act, 2007). The concentration of Zn is 146.8 mg/kg and it exceeds the average background for Bulgarian soils, but is lower than the maximum permissible concentrations for this element.

For the purpose of the study a pot experiment was conducted with a large volume lyzimetric vessels (V = 42.39 dm^3). The pots were filled with 65 kg of the contaminated soil collected from the surface horizon (0 - 20 cm) of the investigated area, as the polluted soil was previously homogenized with the tested ameliorants. Three kinds of ameliorative mixtures – CaO, peat and zeolite with three doses in 12 treatments were tested. The scheme of the ameliorants is: CaO1 -75 g/per pot; CaO2 – 150g/per pot; CaO3 – 225 g/per pot; Peat1 – 500 g/per pot; Peat2 – 1000 g/per pot; Peat3 – 1500g/per pot; Zeolite – 400 g/per pot. Grass mixture was used as a test crop. The effect of the ameliorations was assessed by comparison with the control. The concentrations of Cu and Zn in the biomass were determined after biomass digestion with HNO_3 and H_2O_2 and subsequent measurement on AAS (Methods of soil analysis, 1982). Physico-chemicals characteristics of soil were determined according to Ganev and Arsova, 1980.

After the end of the experiment a soil sample from a depth 0 - 30 cm was taken from each of the variants. The soil samples were analyzed for the bioavailable forms of Cu and Zn by the following methods – extraction with 0.01M $CaCl_2$, at a soil: solution ratio (1: 10) and shaking for two hours (Houba et al., 1996); extraction with 1M NH_4NO_3 at a soil: solution ratio (1: 2.5) (Fries et al., 2003) and extraction with 0.05M EDTA with pH = 7 at a soil: solution ratio (1: 4) (Andreu and Gimeno-Garcia, 1996).

The results obtained were processed statistically (correlation and regression analysis) using Statgraphics centurion XV.I and Statistica 7.

RESULTS and DISCUSSION

Changes in some physico-chemical characteristics of the soil occurred as a result of the amelioration applied (Table 2).

Table 2. General physico-chemical characteristics after amelioratioin of the polluted soil (at the end of the experiment)

Variants	pH H_2O	$T_{8.2}$	T_{CA}	T_A	$H_{8.2}$	Exch. Al^{3+}	Exch. Ca^{2+}	Exch. Mg^{2+}	V in % from $T_{8.2}$
		cmol/kg							
1.Control	4.15	22.0	14.8	7.2	10.2	3.2	9.4	2.2	53.64
2. CaO1	5.50	21.8	16.2	5.6	6.6	0.9	12.9	2.3	69.72
3. CaO2	6.70	21.8	18.3	3.5	3.4	0.0	16.0	2.3	84.40
4. CaO3	8.00	21.3	-	-	0.0	0.0	19.1	2.2	100.00
5. CaO2+Peat1	6.90	21.8	18.8	3.0	3.1	0.0	16.1	2.3	85.78
6. CaO2+Peat2	7.20	21.9	19.7	2.2	2.0	0.0	17.5	2.3	90.87
7. CaO2+Peat3	7.10	22.0	20.0	2.0	1.9	0.0	17.8	2.2	91.36
8. Peat1	5.00	21.9	15.4	6.5	8.9	2.5	10.3	2.3	59.36
9. Peat2	5.20	21.5	15.0	6.5	8.5	2.4	10.7	2.3	60.77
10. Peat3	5.80	21.4	15.3	6.1	7.4	1.06	11.4	2.3	65.42
11. Zeolite	4.80	21.8	15.8	6.0	9.0	2.8	10.6	2.3	58.72
12.CaO2+Peat2+Z	7.20	21.7	19.4	2.3	2.5	0.0	16.5	2.2	88.48

Considerable increase of the pH values of soil is observed in all the variants as compared to the Control due to the ameliorants added (Table 2). The soil remains acidic in the variants of self-addtion of zeolite (Z) - pH = 4.80 and at the low dose of self-addition of peat (Peat1) - pH = 5.00. Moderately acidic is the soil reaction in the variant of self-addition of lime (CaO1), in which a complete neutralization of exchangeable acidity in the soil with liming was not reached, as well as in the two levels of peat added individually (Peat2 and Peat3). In all the others variants a neutral or slightly alkaline reaction of soil was reached - over pH = 6.5, which is favorable for the plant growth. In the variant CaO3 was applied liming over the optimum dose which leads to a full saturation of the exchangeable positions of the soil adsorbent with bases (V% = 100). Thus prevents the uptake of important amphoteric micronutrients from plants, due to their hydroxide precipitation and leads to a receiving of an excess of basic elements into the plant roots (Ganev, 1990).

Complete neutralization of the exchangeable acidity in the studied soil (exch.Al^{3+} = 0) is reached in the variants CaO2; CaO3; CaO2+Peat1; CaO2+Peat2; CaO2+Peat3 and CaO2+Peat2+Z.

When studying the optimum soil acidity for plants it is concluded (Ganev,1989) that with thermodynamic logic one common optimum for plants could be established. This optimum is defined by the complete neutralization with bases of the strong acidic system of the soil adsorbent (bases = T_{CA}) and saturation with protons of the weak acidic system of the soil adsorbent (exch.$H_{8.2} = T_A$) corresponding to analogous neutralization state of the different acidic ion exchange positions of plant roots. Near to one such acidic optimum leads the amelioration in the following variants - CaO2; CaO2 + Peat1; CaO2 + Peat2; CaO2 + Peat3 and CaO2 + Peat2 + Z.

Changes in bioavailable forms of Cu and Zn after the amelioration of the polluted soil

The application of ameliorants to the polluted soil leads to a significant immobilization of the bioavailable forms of Cu, determined in the two soil extractants (0.01M $CaCl_2$ and 1M NH_4NO_3) – Table 3. The concentrations of Cu, extracted with 0.01M $CaCl_2$ decreases from 10.7 mg/l in the Control to 0.05 mg/l in the variant - CaO3. Only in the variant with self-addition of Zeolite (Z) the mobility of Cu compared to the Control increases (12.0 mg/l). This could be due to the high natural content of the Zeolite material of Na^+, which leads to a dispersion of the soil aggregates. The same is the tendency when using the extraction with 1M NH_4NO_3, but in this case the results are 10 times higher, because of the higher concentration of the reagent and its ability to lower the pH and to promote the hydrolysis of clays (Ure, 1996). It could be seen from Table 3 that in most of the variants Cu extracted with 0.05M EDTA (pH = 7) varies within narrow limits. Only in the variants Peat1 and Peat2 its values are significantly greater, because of the possibility of this reagent to extract organically complexed Cu.

Table 3. Biovailable forms of Cu and Zn (mg/l) in soil after the amelioration and concentrations of Cu and Zn (mg/kg) in plants

Variants	Cu (mg/l) in different soil extractants			Cu, (mg/kg) in plants	Zn (mg/l) in different soil extractants			Zn, (mg/kg) in plants
	0.01M $CaCl_2$	1M NH_4NO_3	0.05M EDTA		0.01M $CaCl_2$	1M NH_4NO_3	0.05M EDTA	
1.Control	10.70	89.00	490	78.0	0.48	1.70	44.80	168.4
2. CaO1	1.33	8.40	428	63.6	0.36	1.86	8.40	155.2
3. CaO2	0.21	1.80	468	56.7	0.07	0.22	6.20	116.5
4. CaO3	0.05	3.07	310	77.5	0.02	0.02	6.20	102.6
5. CaO2+Peat1	0.14	0.63	412	74.4	0.05	0.07	4.24	140.1
6. CaO2+Peat2	0.05	1.09	322	74.5	0.03	0.02	4.16	105.1
7. CaO2+Peat3	0.07	1.13	444	62.0	0.03	0.02	4.92	116.7
8. Peat1	7.60	70.50	712	41.2	0.70	3.30	8.20	147.8
9. Peat2	7.10	67.50	862	52.7	0.60	2.80	8.80	128.6
10. Peat3	0.69	4.43	420	47.0	0.25	1.34	6.24	109.7
11. Zeolite	12.0	95.25	514	53.4	0.59	3.0	6.32	184.0
12.CaO2+Peat2+Z	0.09	1.09	386	62.2	0.02	0.02	4.40	101.0

The values of the soil pH play a major role when determining the bioavailability of heavy metals to plants. A strong negative correlation (expressed by R = -0.861 and R = -0.852) was found between pH values of the ameliorated soil and the concentration of 0.01M $CaCl_2$ and 1M NH_4NO_3 extractable Cu. Most preferably, this statistical dependence is described by the exponential curves and the regression equation presented in Figures 1 and 2 demonstrating the rapid reduction of the bioavailable concentration of copper in soil extracted with 0.01M $CaCl_2$ and 1M NH_4NO_3 when increasing the soil pH. Much weaker negative correlation (R = -0.624) was found between the pH values of the studied soil and the forms of copper, defined using the extraction with 0.05M EDTA (pH - 7). In this case, in addition to the bioavailable forms of Cu, other forms of copper associated with aluminum and iron oxides were extracted too.

Bioavailable forms of zinc are also influenced by the ameliorants added (Table 3). In general, after the soil amelioration the concentration of both 0.01M $CaCl_2$ and 1MNH_4NO_3 extractable Zn decreases but in three of the variants - Z, Peat1 Peat2 the mobility of the metal increases. The reason for this could be the introduction of small additional quantities of zinc with the ameliorative materials themselves. The concentrations of Zn, extracted with 0.05M EDTA (pH - 7) showed the restraining impact of the imported ameliorants.

As with the copper, the bioavailable forms of zinc depends highly on the soil pH which is expressed with correlation coefficients -0.906 and -0.868 for the two soil extractants 0.01M $CaCl_2$ and 1M NH_4NO_3 respectively. Regression relationships are described very well by exponential curves (Figures 3 and 4). EDTA extraction of Zn gave significantly higher and low varying values of that metal between the variants, which are not correlated with the changes of the pH values of the soil.

The addition of ameliorants in the studied soil slightly affects the concentration of copper and zinc in the produced biomass (Table 3). Probably the reason for the results obtained for Cu is the fact that, there is a threshold of the accumulation of copper in the soil (up to about 900 mg/kg), over which the toxicity of the copper to plants is difficult to overcome. Generally, the variants ameliorated with peat only - Peat1, Peat2 and Peat3 accumulate the lowest concentration of copper in the biomass, because the ability of organic matter to form stable complexes with Cu. The results obtained for the copper concentration in the biomass even under the best variants - Peat1 and Peat3 are considered as critical for the feed. In most of the variants, the concentration of zinc in the biomass is considered as normal. A moderate to strong positive correlation between the concentrations of zinc in the biomass and in the 0.01M $CaCl_2$ (R = 0.730) and NH_4NO_3 (R = 0.702) extractable Zn was established. For copper such a connection wasn't observed.

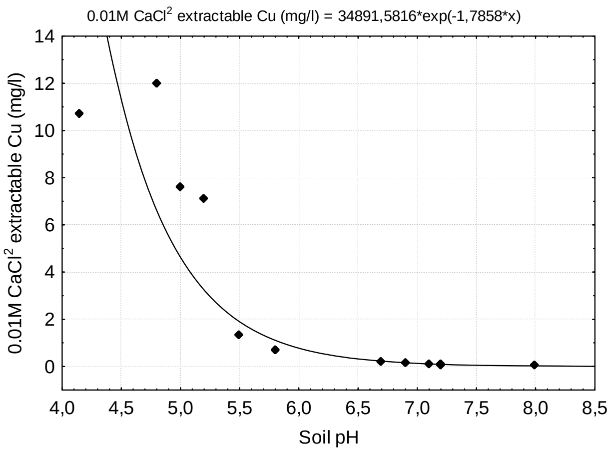

Figure 1. Relationship between 0.01M $CaCl_2$ extractable Cu (mg/l) and the pH values of the soil after amelioration

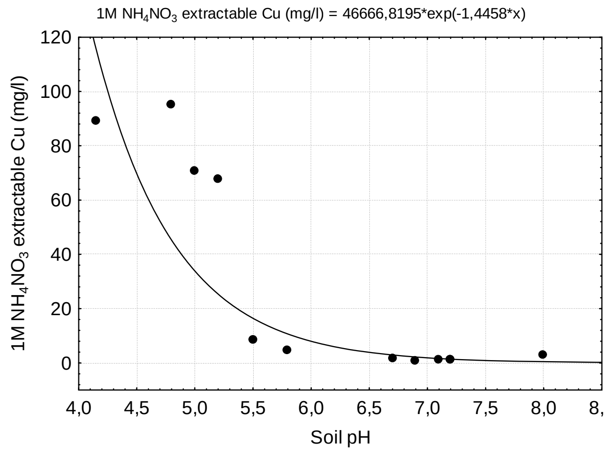

Figure 2. Relationship between 1M NH_4NO_3 extractable Cu (mg/l) and the pH values of the soil after amelioration

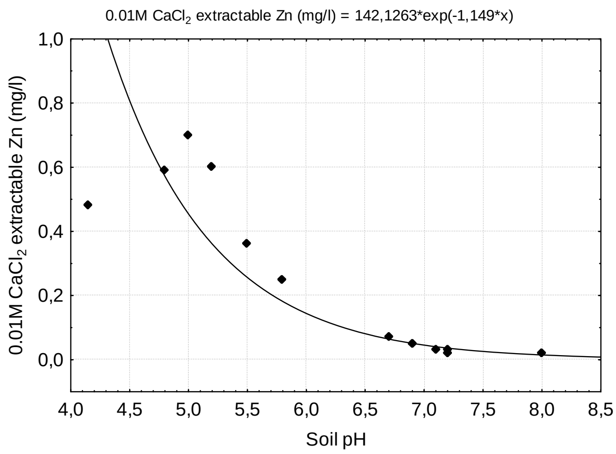

Figure 3. Relationship between 0.01M $CaCl_2$ extractable Zn (mg/l) and the pH values of the soil after amelioration

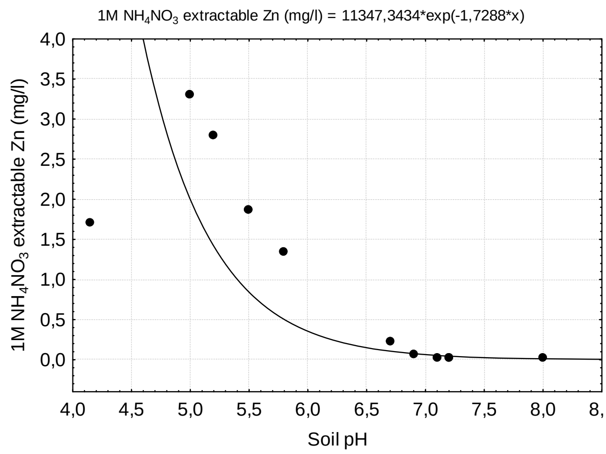

Figure 4. Relationship between 1M NH_4NO_3 extractable Zn (mg/l) and the pH values of the soil after amelioration

CONCLUSION

Considerable changes in soil physico-chemical characteristics compared to the Control were observed after the amelioration. The soil pH increased in all the variants and reached a neutral or slightly alkaline reaction (over pH = 6.5), which is favorable for the plant growth and development in the variants CaO2; CaO2 + Peat1; CaO2 + Peat2; CaO2 + Peat3 and CaO2 + Peat2 + Z.

The application of ameliorants to the polluted soil leads to a significant immobilization of the bioavailable forms of Cu determined in the two soil extractants (0.01M $CaCl_2$ and 1M NH_4NO_3) with the exception of the variant of self-addition of zeolite (Z). Bioavailable forms of Zn also decreased after the amelioration. Only in the variants Peat1 and Peat2 the opposite was determined.

A strong negative correlation (expressed by R = -0.861 and R = -0.852) was found between pH values of the ameliorated soil and the concentration of 0.01M $CaCl_2$ and 1M NH_4NO_3 extractable Cu. Similar correlation relationship was expressed by R = -0.906 regarding the 0.01M $CaCl_2$ extractable Zn and R = -0.868 for 1M NH_4NO_3 extractable Zn.

The addition of ameliorants slightly and unsignificantly affects the concentration of copper and zinc in the grass biomass. A moderate to strong positive correlation between the concentrations of Zn in the biomass and the 0.01M $CaCl_2$ (R = 0.730) and NH_4NO_3 (R = 0.702) extractable Zn ware established while for Cu such a relationship was not observed.

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Research Article

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Different pasture amelioration methods effects on soil and water conservation in natural pasture area of minoz creek basin

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ABSTRACT

In this study, effects of fourdifferent pasture amelioration methods on sediment and water losses in natural pasture soil of Minöz Creek Basin were investigated. Experiment was conducted with six treatments; control under uncontrolled grazing (C), control under controlled grazing (CG), fertilizing (F), spread seeding (SS), cultivation or aeration (A) and spread seeding+fertilizing (SSF) on sandy loam textural soil (Lithic Ustorthent). In the study, erosive rainfall between 2008 and 2011 were evaluated and their effects on sediment and water losses were investigated.The rainfall values of the study area are 517,40 mm in 2008 for the lowest and 710,30 mm in 2011 for the highest. According to the results, it was determined that the lowest sediment value is 10,2 kg/ha for SS and the highest value is 18,6 kg/ha for CG application. According to the water losses, the lowest value is 20,5mm for F and the highest value is 70,6 mm for SSF application.Consequently, results of this study showed thatthe most effective amelioration methods are SS application for decreasing the sediment movement and F application fordecreasing water losses.

INTRODUCTION

Soil is a complex, dynamic and living system that should contain certain amounts soil, air, water and organic matters for its sustainability. Soils are one of the most important parts in many ecosystems as dynamic Natural body and fundamental resource. They have some physical, chemical and biological properties. By these properties, they resist to water effects which are erosive and transporter.

Soils with good drainage are extremely prone to nutrient loss. Percolation in a soil profile is higher in rainy conditions. Therefore, loss of nutrients through soil profile in tropical and rainy climate zones, especially in light textured soils, is more pronounced (Brohi et al., 1997). Soil aggregation is important for the resistance of land surfaces to erosion and influences the ability of soils to remain productive (Pinheiro et al., 2004).

Soil structural degradation tends to accelerate the high soil strength, poor infiltration, increased runoff and soil erosion problems. The effectiveness of pasture species like ryegrass in improving soil structure has been well reported (Haynes and Beare, 1997). Cover crops such as grass and legume have been maintained successfully in many regions for soil reclamation (Lal et al., 1979). They reduce sediment production by reducing the amount and the velocity of runoff and also increase soil quality by improving soil physical, chemical and biological properties (Dabney et al., 2001).Studies have shown the potential value of grass in cropping systems for improvement or maintenance of soil structure (Tisdall and Oades, 1979; Stone and Buttery, 1989). The effects of one or more factors including soil properties, climatic conditions, biological characteristics of the grass species, pasture and cattle management can result in declining pasture quantity or quality (Martinez and Zinck, 2004).

Water erosion, land use changes, extensive cultivation and high decomposition rates lead to the reduction of organic matter and microbiological activity resulting in deterioration of soil structure (Garcia et al, 1997). Water infiltration is defined as the process by which water enters the soil. It's rate depends on soil type, soil structure and soil water content. Infiltration is important for reducing run-off and consequent erosion. Increased soil compaction and loss of surface structure (reduced aggregation) are the main factors in reducing water infiltration rates in soil (Franzluebbers, 2002).

Drewry et al. (2004) reported that soil compaction and recovery may occur in a cycle under grazing systems. While deterioration in soil physical condition can occur during wet spring periods under dairy cattle grazing, natural recovery of soil physical condition occurred over summer and autumn for many soil properties. Grazing or tampling in pasture lands cause changes in physical soil properties with reducing infiltration and increasing runoff, erosion and bulk density. The magnitude of the trampling effect depends on the number of cattle per area, the grazing system, soil texture and soil moisture content (VanHaveren, 1983).

Soil erodibility is a complex concept; it is influenced by many factors, such as soil properties and human activities. In many studies, relations among erodibility indices, structural stability and several pedological properties of soils (clay content, cationexchange capacity, organic matter content, $CaCO_3$ content, pH etc.) were searched and studied (Toy et al., 2002; Morgan, 1986; Özdemir,2002). Soil erosion is the most widely recognized and most common form of land degradation and therefore, a major cause of falling productivity (Stocking and Murnagham. 2001). Soil erosion, refers to the process during which soil particles are separated from their original context and cause a factor to be carried to another place (Esnali and Abdollahi, 2010).

Soil erosion and sedimentation are two processes that follow each other. It's possible to minimize soil erosion and to reduce sedimentation in the basin with conservation methods. The objective of this study was to determine effects of fertilizing, spread seeding, spreadseeding+fertilizing and cultivation or aeration treatments on sediment movement and water losses under uncontrolled and controlled grazingby determining the sediment yield and potential soil loss in natural pasture area of Minöz Creek Basin..

MATERIAL and METHODS

A field experiment in a natural pasture was conducted on Lithic Ustorthent in Minöz Creek Basin in a randomized block design with six treatments; two controls (uncontrolled (C) and controlled grazing (CG)) and the treatments of fertilizing (F), spread seeding (SS), cultivation or aeration (A) and spread seeding+fertilizing (SSF) under controlled grazing plots (10.0x1.5 m^2). Sheep grazing in controlled grazing treatments was allowed between April 20 and October 30 in each year. Spread seeding of natural cover plants and aeration plots were established in the first year. Aeration treatment was done cultivating the plot at 30 cm row spacing. The rates of spread seeding for the natural cover plant species were 20% for sainfoin (*Onobrychisviciifolia*), 15% for salad burnet (*Poteriumsanguisorba*), 40% for crested wheatgrass (*Agropyroncristatum*) and 25% for smoot brome (*Bromusinermis*). Map of Minöz Creek Basin is given in Figure 1.

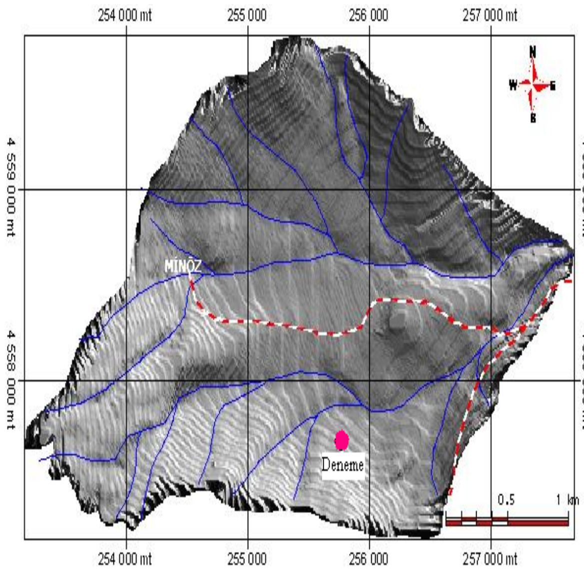

Figure 1. Map of Minöz Creek Basin

Selected soil properties of the experimental field on Lithic Ustorthent are given in Table 1. According to soil analyses, the textural class is sandy loam; neutral in pH and non-saline (Soil Survey Staff., 1993). Statistical analyses of the experimental data were performed using SPSS software package program.

Table 1. Some soil properties of the experimental field

Sand %	Silt %	Clay %	Soil texture	pH (1:1)	EC dS/m	OM. %	CEC cmol/kg^{-1}	$CaCO_3$ %
67.68	22.46	9.86	SL	6.89	0.200	1.68	7.39	3.98

Soil sediment samples and precipitations were taken every day between 2008 and 2011. Sediment samples were calculated from the water taken from collecting tanks under the plots.

Soil samples oven dried by two days and the rest samples weighed. This is the sediment value by kg/ha for each plots. Precipitations were determined by pluviographs nearby the plots. Erosive rainfalls were calculated from the diagrams using the daily precipitations. Potential soil loss for the Basin was estimated using USLE developed by Wischmeier and Smith (1978).Design of runoff plot and collecting tank are given in Figure 2.

Monthly precipitation values from 2008 to 2011 are given in Table 2.

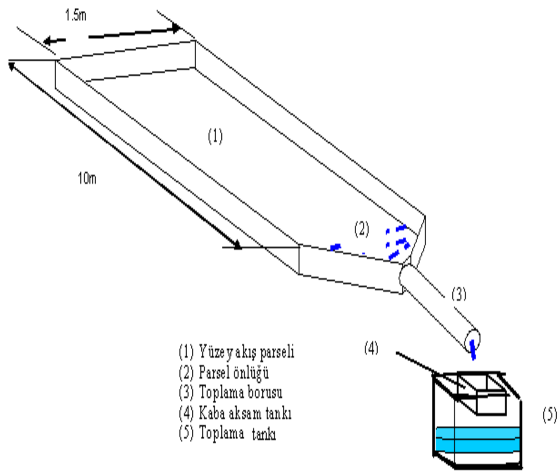

Figure 2. Runoff plot and collecting tank

Table 2. Monthly precipitation between 2008 and 2011 (mm)

Years	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Total
2008	45,1	87,7	39,0	44,5	17,0	36,2	54,1	46,5	48,4	14,5	2,2	82,2	517,4
2009	48,0	66,8	79,7	87,3	85,3	59,1	34,9	75,8	21,3	69,3	10,8	51,9	690,2
2010	35,6	89,1	67,0	60,1	24,7	90,3	79,4	30,3	117,8	16,9	2,7	30,7	644,6
2011	123,9	7,3	57,5	91,5	25,4	71,4	57,3	82,1	87,3	18,8	27	60,8	710,3

RESULTS and DISCUSSION

Research area soils classified as Lithic Ustorthent, with a slope of 30%, high drainage and susceptible to the erosion. Usually surface soils of these areas have 10% of clay content. Particularly the rough material and sand content approaches 70% in profile. This situation leads to a low water retention capacity. For this reason during the rainy periods excess water going to runoff and caused to the fine soil materials transporting to the less slope areas. In the fertilizing plot; fertilizing and improving existing vegetation applications without disturbing the natural structure of the soil has positive effects to reduce losses of sediment and runoff. In the SSF and A plots the natural structure of the soil disturbed by tillage. Significant reduction in bulk density, mechanical effects of the roots in the soil and microbial activity occurred due to the higher increase in root growth than in other plots. In this layer with developing roots; substituted attenuated soil particles transported as sediment.

At the end of the experiment; sediment yield (kg/ha) and runoff (mm) values are given in Figures 3 and 4, respectively. According to the results; there was a significant differences between subjects. The lowest sediment yield determined from F application by 7,1 kg/ha in 2009. The highest sediment yield value determined from F application by 24,3 kg/ha in 2010. According to the average values of subjects; lowest average sediment value determined from SS by 10,2 kg/ha and the highest average sediment value determined from CG by 18,6 kg/ha as shown in Figure 3. The highest sediment values are determined in 2010 due to the extreme daily rains.

During the study, increases in sediment yield values of treatments according to the years as follows; SS < C < F < A < SSF < CG. The average sediment yield values according to the years are given in the following order; 13,56 in 2009, 13,71 in 2008, 15,4 in 2011 and 17,52 in 2010. As reported by Nunes et al., (2011), inappropriate land management, destruction of forests, forest fires and such as improper land use factors that cause erosion tillage is most effective.

Sparovek et al., (2007), in pastures in Brazil a significant improvement in soil conservation in perennial plant species were obtained by reducing the soil tillage. Munoz-Robles et al., (2011), studied the relationship between rainfall and sediment by creating simulations of rainfall among a newly created pasture, old pastures, damaged degraded forest and in open land. In the study they did not find a significant relationship between runoff and sediment yield. Maximum sediment yield found in the newly formed pasture. They reported that the most effective pasture management method to reduce runoff and sediment yield were controlled grazing and minimum tillage. Coşkun et al. (2010), according to their findings pasture amelioration methods results very important to prevent erosion and C application (control under uncontrolled grazing, closed to grazing) is more advantageous than CG application (control under controlled grazing, open to sheep grazing) in terms of both quantity and quality of pasture and erosion prevention. Grazing pressure and fragmentation of topsoil in C application is less than CG application. The fertilizing application gave the best results between the subtitles of the research. To create artificial pasture increased erosion.

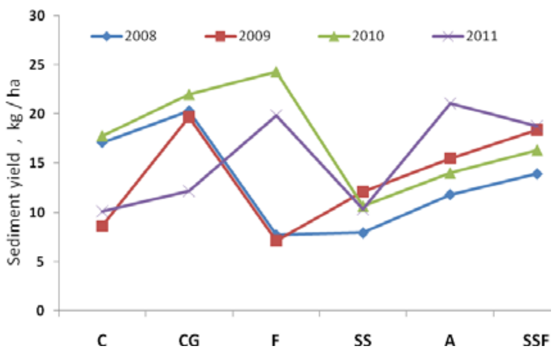

Figure 3. Comparison of subjects and sediment obtained from erosive rainfall between 2008 and 2011

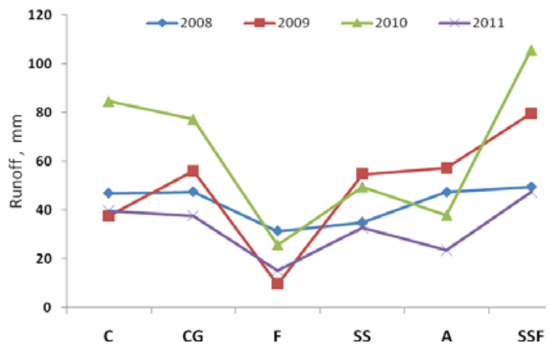

Figure 4. Comparison of subjects and runoff obtained from erosive rainfall between 2008 – 2011.

According to the all years, the lowest mean sediment losses were determined in 2008 due to lack of rainfall. Erosive rainfall were measured between 2008 and 2011. When we examine the relationship between sediment yield and years, the highest sediment yield was determined by 18.8 kg ha^{-1} in 2010. There was no significant differences among other years at 1% level statistically. The differences between subjects was significant at 1% level. Higher average sediment yields were determined with SSF and CG applications and the lowest value was determined in SS application.

According to the runoff results; there was a significant difference between subjects. The lowest runoff was determined with F application by 9,6 mm in 2011. The highest runoff value was determined with SSF by 105,8 mm in 2010 (Figure 4). The relationship between years and runoff by rainfall was statistically significant at 1% level. The highest average runoff was determined with SSF application by 70,6 mm and the lowest average value was determined with F application by 20,5 mm. The highest runoff values were determined in 2010 due to the extreme daily rains.During the study, increases in runoff values of treatments according to the years as follows; F < A < SS < C < CG < SSF. The average runoff values according to the years are given in the following order; 32,7 in 2011, 42,9 in 2008, 49,1 in 2009 and 63,45 in 2010.

Coşkun et al., (2010), reported that the best results were determined in fertilizing plots to prevent erosion with increasing quantity and quality of pasture with different amelioration methods in Erzurum conditions.

CONCLUSION

Pasture amelioration applications with cultivating in sloping areas increased the erosion in the first year, but decreased next years due to the soil stabilization. Application of no-tillage pasture amelioration method in problematic areas is very important. The effectiveness of the treatments to reduce the sediment and runoff values of pasture area were significantly important. In conclusion, it is strongly recommended that fertilizing application itself confidently be the best subject for both decreasing sediment yield and runoff values.

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Soil contamination study around the Buchim Copper Mine, Republic of Macedonia

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ABSTRACT

One of the major emission sources of some metals in the eastern part of the R. Macedonia is Bucim copper mine and flotation, near the town of Radovis. Ore excavation is from open pit and the ore tailings are stored in the open, in mine vicinity. The produced copper ore from the mine is processed in the flotation plant; after the flotation of copper minerals, the flotation tailings are separated, disposed of and deposited on a dump site in an adjacent valley near the village Topolnica. During the 35 years of continuous exploitation around the Buchim Mine was created surface waste dump were have been stored more than 150 Mt and more than 100 Mt material within the hydro-tailling dam. Within this study a total content of 20 elements was determined in soil samples taken from the vicinity of the "Bucim" mine, covering an area of 14.2 km^2. Analyses were performed by the ICP-AES. The results have been compared to new Dutchlist and NOAA standards and the following was concluded: As values ranged 13.1÷225 mg kg^{-1} with 20 samples above the optimum (29 mg kg^{-1} As) and 7 above action value (55 mg kg^{-1} As), in that context Cd values ranged 0.67÷17.9 mg kg^{-1} with 17 values above optimum (0.8 mg kg^{-1} Cd) and 1 over the action value (12 mg kg^{-1} Cd), Cr with range 30.1÷171 mg kg^{-1} with 6 over optimal value (100 mg kg^{-1} Cr) and none above action value (380 mg kg^{-1} Cr), Cu with range 17.8÷1734 mg kg^{-1} with 16 over optimal value (36 mg kg^{-1} Cu) and 3 above action value (190 mg kg^{-1} Cu), Ni with range 9.8÷69.4 mg kg^{-1} with 5 over optimal value (35 mg kg^{-1} Ni) and none above action value (210 mg kg^{-1} Ni), Pb with range 46÷3456 mg kg^{-1} with 19 over optimal value (85 mg kg^{-1} Pb) and 1 above action value (530 mg kg^{-1} Pb), Zn with range 88÷3438 mg kg^{-1} with 12 over optimal value (140 mg kg^{-1} Zn) and 1 above action value (720 mg kg^{-1} Zn), Mn with range 169÷998 mg kg^{-1} with 25 over optimal value (33 mg kg^{-1} Mn) and none above action value (48 mg kg^{-1} Mn), Fe range 0.73÷5.02% with 21 over optimal value (1.8% Fe) and none above action value (3.2% Fe). The V, Al, Co, also, showed some increased values, but not more than optimal concentration.

INTRODUCTION

There are many different sources of heavy metal contaminants, including mining and metallurgical industries (Kabata-Pendias and Pendias, 2001). It is obvious from the papers published recently that mining and metallurgical activities lead to enormous soil contamination (Li et al. 2005, 2006; Wilson et al. 2005; Pruvot et al. 2006; Aryal et al. 2006; Cemek and Kizilkaya 2006; Cappuyns et al. 2006; Tembo et al. 2006). Particular emphasis is given on ore deposits, mining, processing and flotation plants as significant anthropogenic sources of dust. Copper mine with open ore pit type present a potentially emission source of heavy metals in the air, soil and water. Main processes that allow it are: minerals blasting, drilling and crushing, their loading and transportation to processing and flotation plants. From other hand, large amounts of ore waste and flotation tailings are deposited at open, continuously exposited to air flow and winds caring-out. Heavy metals emitted in the atmosphere by combustion processes usually have relatively high solubility's and reactivity's; especially under low-pH condition (Athar and Vohora, 1995; Hršak et al., 2003; Hou et al., 2005). They can be carried to places far away from the sources by wind, depending upon whether they are in gaseous form or as particulates. Metallic pollutants are ultimately washed out of the air by rain and deposited on the land (Balabanova et al., 2011b). Deposited dust refers to any dust that falls out of suspension in the atmosphere. Solid and liquid particles or dust that falls out of suspension in the atmosphere can get into the environment and lead to its contamination. Atmospheric total deposition (deposited dust) is very useful mechanism for monitoring the fate of anthropogenic elements introduced into the atmosphere (Čačković et al., 2009).

The intent of this article is to present the results of 2010 study of spatial distribution of different chemical elements in surface soil in the Buchim mine region (Figure 1), located in the eastern part of the Republic of Macedonia, known for its copper industrial activity in the last three and half decades.

The mine and the ore processing plant have been functioning since 1979 and and process 4 million tons of ore annually. It is assumed that the mine at the moment have about 40 million tons of ore reserves. The deposit is a porphyry copper type deposit and mineralization is related to Tertiary sub-volcanic intrusions of andesite and latite in a host of Pre-Cambrian gneisses and amphibolites (Serafimovski et al., 1995). The open ore body is approximately 500 m in diameter and 250 m in vertical extent, which actually allows direct exposure of ore particles to the atmosphere. The content of copper in ore is at on the average of 0.3 % Cu. Characteristic metallic minerals are chalcopyrite, pyrite, and bornite, with small amounts of galena, sphalerite, magnetite, hematite, and cubanite (Serafimovski et al., 1996; Alderton et al., 2005). Ore tailings are disposed at open site near the mine, that occupies a surface of 0.8 km^2. The tailing dam has about 130 million tons of ore tailings. Exposure of this great mass of ore tailings to constant air flow and wind leads to the distribution of fine dust in the air.

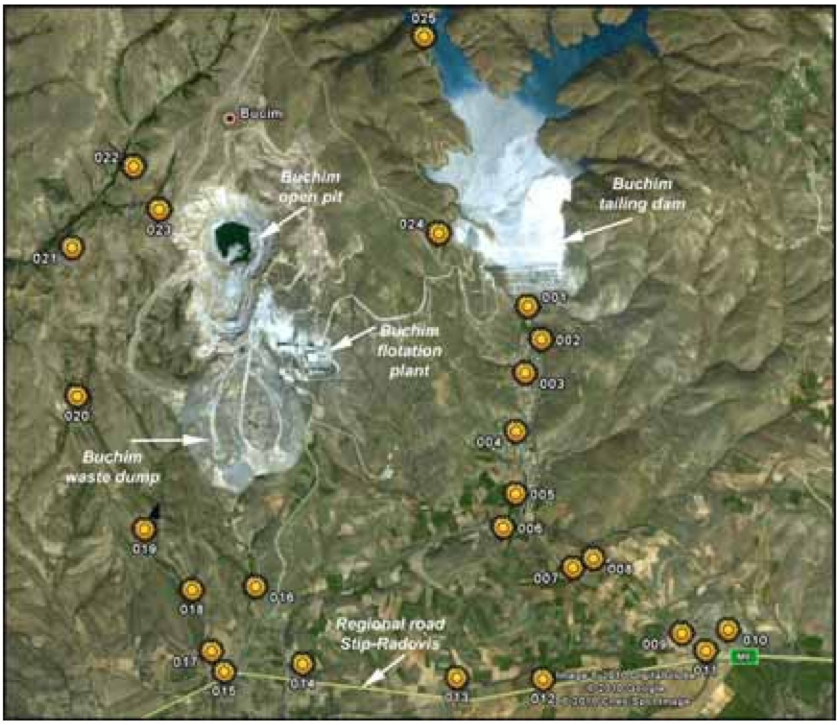


Figure 1. Location of the soil samples around the Buchim copper mine

MATERIAL and METHODS

Sampling was carried out at the begining of February 2010. Soil surface samples (0 cm to 5 cm depth) were collected in around the Buchim Mine and its surrounding region (Figure 1). In total, 25 samples were collected from 25 locations, including locations near the mining center of Buchim over an area of 14.2 km^2. Samples were located using the Global

Positioning System (GPS), topographic maps at scale of 1:25 000 and Google Earth maps. Each sample represented the composite material collected at the central sampling point itself together with at least four points collected around a central one with a radius of 1 m towards N, E, S and W directions. The composite material of each sample (about 0.5 kg) was placed into plastic self-closing bags and brought to the Faculty of Natural and Technical Sciences, University "Goce Delcev" Stip, Republic of Macedonia, where they were prepared for atomic spectroscopy.

All of the collected soil samples were then shipped to the Institute of Chemistry at the Faculty of Natural Sciences, University "Sts.Cyril and Methodius" Skopje, R. Macedonia. Analyses were conducted using emission spectrometry with inductively coupled plasma (ICP-AES) after Aqua Regia Digestion. All samples (n=25), replicates (n=3) and geological standards (n=4) were submitted to the laboratory in a random order. This procedure assured an unbiased treatment of samples and a random distribution of the possible drift of analytical conditions for all samples. Eleven randomly selected samples were replicated for precision estimation. The precision was less than 5%.

RESULTS and DISCUSSION

The latest study of soils around the Buchim mine complex was performed on 25 locations and for each sampling point samples were analyzed for a geochemical package of 20 elements.

Table 1. Statistical data from the soil samples around the Buchim copper mine

Element	min	max	average	Optimum (Dutch list)	Action (Dutch list)	above optimum	above action
Al (%)	0,72	5,9	2,8928	4,7	-	5	0
Ca (%)	0,07	4,28	1,3024	-	-	0	0
Fe (%)	0,73	5,02	3,148	1,8		21	0
K (%)	0,79	3,28	2,008	-		0	0
Mg (%)	0,12	1,97	0,9708	-		0	0
Na (%)	0,77	2,09	1,7624	-		0	0
Ag (mg kg^{-1})	0,1	0,1	0,1	-	15	0	0
As (mg kg^{-1})	13,1	225	63,904	29	55	20	7
Ba (mg kg^{-1})	131	485	304,68	160	625	24	0
Cd (mg kg^{-1})	0,67	17,9	2,1908	0,8	12	17	1
Co (mg kg^{-1})	3,62	22,3	12,3884	9	240	22	0
Cr (mg kg^{-1})	30,1	171	80,684	100	380	6	0
Cu (mg kg^{-1})	17,8	1734	129,064	36	190	16	3
Li (mg kg^{-1})	0,07	0,25	0,1264	-	-	0	0
Mn (mg kg^{-1})	165	998	552,72	33	-	25	0
Ni (mg kg^{-1})	9,8	69,4	29,548	35	210	5	0
Pb (mg kg^{-1})	46	3465	288,252	85	530	19	1
Sr (mg kg^{-1})	17,6	132	75,804	-	-	0	0
V (mg kg^{-1})	14	144	83,612	42	250	22	0
Zn (mg kg^{-1})	88	3438	319,872	140	720	12	1

During the study of results and their statistical processing it was determined that very representative are particular elements such are copper, arsenic, cadmium, lead and zinc that are given in more details within this paper while there are elements such are iron, manganese, chromium, vanadium, nickel, cobalt, which display slightly elevated concentrations, but without any significant impact, as well as elements such are aluminium, calcium, sodium, barium, strontium etc being direct product of geological setting and without any anthropogene enrichment (Table 1).

As it can be seen from the table above, there were analyzed 20 elements and their minimal, maximal, average and referent values according to the New Dutchlist (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm), are given. Distribution of particular anthropogenically introduced elements is given as follows:

Arsenic (As): It is well known that an arsenic in nature usually occurs in the form of sulphides such as arsenopyrite, FeAsS, realgar, As_4S_4, orpiment, As_2S_3, and that the exposure to As by ingestion can cause problems in the digestive and nervous systems and activity of the heart while prolonged long-term exposure could result in nerve damage and may lead to lung, skin, or liver cancer (Goyer, 1996; Frumkin and Gerberding, 2007). Contamination of the environment by arsenic from both anthropogenic and natural sources has occurred in many parts of the World and is now recognized as a global problem. The principal anthropogenic sources for soil contamination by As include base metal smelters, mining of arsenic, lead and zinc, gold and other types of mines (Stafilov et al. 2010a). The average amount of As in the world's soils is 5 mg kg^{-1} (Bowen, 1979), and in the European topsoil is 12 mg kg^{-1} (Salminen et al., 2005). The average amount of As in the topsoil for the entire study area is 63.904 mg kg^{-1}, with a range of 13.1–225 mg kg^{-1} (Table 1; Figure 2). .

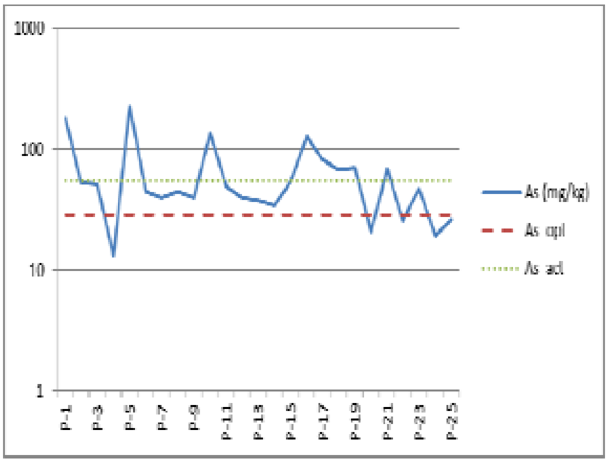


Figure 2. Diagram of arsenic distribution in the soil compared with optimal and action values

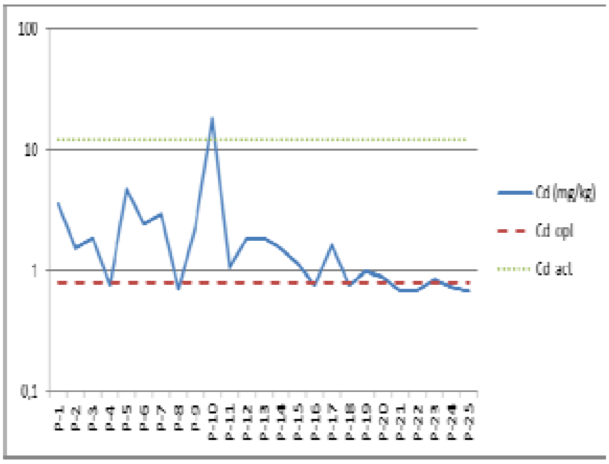


Figure 3. Diagram of cadmium distribution in the soil compared with optimal and action values

As it is displayed at the diagram arsenic concentration at particular sampling points were higher than optimal as well as over the action values according the New Dutchlist (http://www.contaminatedland.co.uk/ std-guid/dutch-l.htm). Also, it was found that the content of arsenic in topsoil is high in the areas of the copper mine and flotation plant, but also in the topsoil from around the flotation dam that follows the wind rose. In several anomalous areas it could be seen that the highest values are in the area closest to the outflow of flotation dam (from 51 to 225 mg kg^{-1}) and so-called Buchim Lake and dry riverbed draining open pit mine and in the south-western part of the area (67.4–82.8 mg kg^{-1}). According to this data, it is evident that the source of high arsenic in this region is directly related with processing of copper ores in the Buchim Mine. In the mineral association of the Buchim deposit it was determined one phase of low-temperature pyrites, which in its chemical composition have up to 2.5% As. During the processing of ore, probably one part of that arsenic have been released and distributed into the adjacent environment.

Cadmium (Cd): is a heavy metal that is dispersed throughout the modern environment mainly as a result of pollution from a variety of sources (Bhattacharyya et al., 2000; Järup et al. 1998). Cadmium is produced mainly as a by-product from mining, smelting, and refining sulphide ores of zinc, and to a lesser degree, lead and copper. The metal has no known beneficial biological function and prolonged exposure to this element has been linked to toxic effects in both humans and animals (Zadorozhnaja et al., 2000). Cadmium and cadmium compounds are, compared to other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate.

The average amount of Cd in soils in the world is 0.35 mg kg^{-1} (Bowen, 1979), in the European topsoil is 0.12 mg kg^{-1} (Salminen et al., 2005). The average amount of Cd in the topsoil for the entire study area is

2.19 mg kg^{-1}, with a range of 0.67–17.9 mg kg^{-1} (Table 1). In the main polluted area, the average concentration of Cd is more than 18-times higher than the European cadmium average and up to 7.5-13 times more than Macedonian average of 0.16 mg kg^{-1} (study in 2002, Barandovski et al. 2008) and 0.29 mg kg^{-1} (study in 2005, Barandovski et al. 2012). It is evident from the obtained results (Table 1; Figure 3) that the content of cadmium is very high in the topsoils from the areas of the copper mine facilities, as well as in the topsoils from the flotation dam vicinity.

In this region several topsoil samples with extremely high content of cadmium are present. It should be noted that sample No. 10 with the content of 17.9 mg kg^{-1} is 150-times higher than the European topsoil average of 0.12 mg kg^{-1}. These higher contents of cadmium in soil samples are the result of anthropogenic origin where cadmium inputs from mine industrial complexes as it was confirmed elsewhere (Šajn et al., 2011).

Copper (Cu): The most important statement on Cu contamination of soils is the great affinity of surface soils to accumulate this metal. Soil contamination by Cu compounds, which has been the subject of detailed studies for several decades confirmed several significant sources: fertilizers, sewage sludge, manures, agrochemicals, industrial by-product wastes etc that have contributed to increased Cu levels. However, the highest increased levels of Cu are observed in soils surrounding Cu mines and smelters (Kabata-Pendias and Pendias, 2001). As Cu is only slightly mobile under most soil conditions elevated contents may persist for a long time. The average amount of Cu in the world's soils is 30 mg kg^{-1} [Bowen, 1979], in the European topsoil is 17 mg kg^{-1} (Salminen et al., 2005) and in Macedonia is 31.8 mg kg^{-1} (Stafilov et al., 2010c). The average amount of Cu in the topsoil for the entire study area is 129.064 mg kg^{-1}, with a range of 17.8–1734 mg kg^{-1} (Table 1; Figure 4).

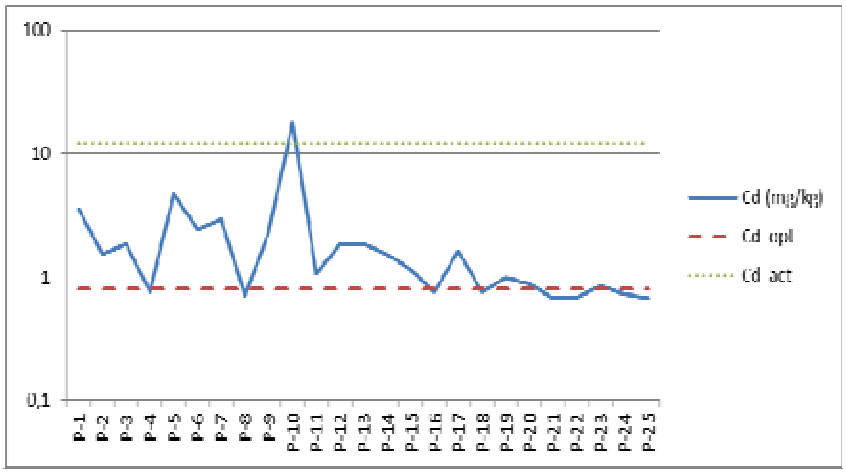


Figure 4. Diagram of copper distribution in the soil compared with optimal and action values

Obviously, there is no large difference in concentration within the studied mine and flotation ares (Table 1; Figure 4), except in three positions (sample 15, 17 and 18) dry riverbed draining open pit mine. In the main polluted area, the average concentration of Cu exceeds the European Cu average by a factor of 15.3 and Macedonian average for 8.2-times. The highest content of copper is present in the topsoils from the areas of the copper mine drainage dry riverbed, which is close to the mine.

Lead (Pb): In mining areas, Pb may be dispersed due to the erosion and chemical weathering of tailings. The severity of these processes depends on chemical characteristics, and the minerals present in the tailings (Kabata-Pendias and Pendias, 2001). In general, several observations of Pb balance in various ecosystems show that the input of this metal greatly exceeds its output. The strong Pb adsorption in soils may mean that Pb additions to soil are permanent and irreversible. The average amount of Pb in the world's soils is 35 mg kg^{-1} (Bowen, 1979), in the European topsoil is 33 mg kg^{-1} (Salminen et al., 2005) and in Macedonia is 44.3 mg kg^{-1} (Stafilov et al., 2010c). The average amount in the topsoil for the entire study area is 288 mg/kg, with a range of 46–3465 mg kg^{-1} (Table 1). Similarly to cadmium distribution, the differences between the content of lead in the studied areas are very significant (Table 1; Figure 5).

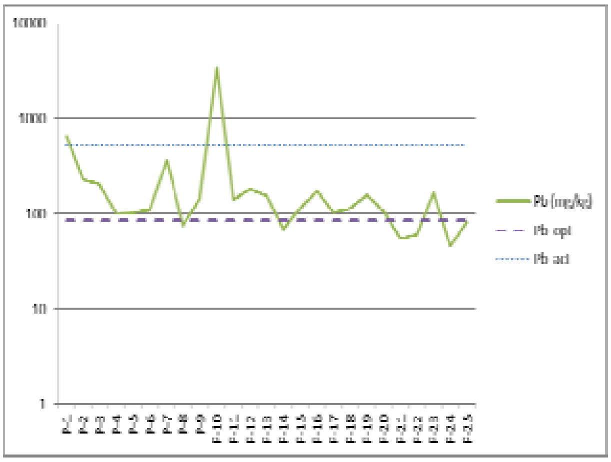


Figure 5. Diagram of lead distribution in the soil compared with optimal and action values

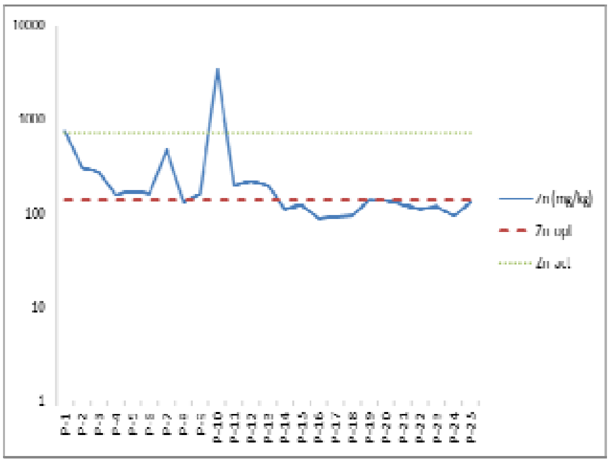


Figure 6. Diagram of zinc distribution in the soil compared with optimal and action values

In the main polluted area the average concentration of Pb is 8.7-times higher than the European Pb average and Macedonian average for 6.5-times. Although the average content of lead in the topsoil for the entire study area was found to be about 288 mg kg^{-1}, there are areas with very high contamination, as it was for example, for the main polluted area (sample 10) with content of 3465 mg kg^{-1} (Table 1). The highest values for Pb content were established in the topsoils in the eastern and south-western part of an area.

Zinc (Zn): The most important anthropogenic sources of Zn are the metallurgy industry, burning of fossil fuels, mines and Zn ore processing (Aliu et al., 2010). Zn is an essential element for most living organism (plants, animals and humans) with important role in enzymes processes and cellular metabolism, in immune function, protein synthesis, DNA synthesis, and cell division and daily intake of zinc is required to maintain a steady state because the body has no specialized zinc storage system (Rink and Gabriel, 2000). Even the toxicity of Zn is relatively low, there are cases when poisoning with Zn can occur in both acute and chronic forms (Prasad, 1995).

The average amount of Zn in the world's soils is 90 mg kg^{-1} (Bowen, 1979), in the European topsoil is 68 mg kg^{1} (Salminen et al., 2005) and in Macedonia is 31.8 mg kg^{-1} (Stafilov et al., 2010c). The average Zn amount in the topsoil for the entire study area is 319.8 mg kg^{-1}, with a range of 88–3438 mg kg^{-1} (Table 1). For the main polluted area, the average concentration of Zn is 4.7-times higher than the European Zn average and Macedonian average for 10.1-times. Similarly to the findings for lead, although the average content of zinc in the topsoil for the entire study area was found to be about 319.8 mg kg^{-1}, there are areas with very high level of contamination (Table 1; Figure 6).

These areas are especially pronounced in the main polluted area around flotation on the east and south western parts of the area.

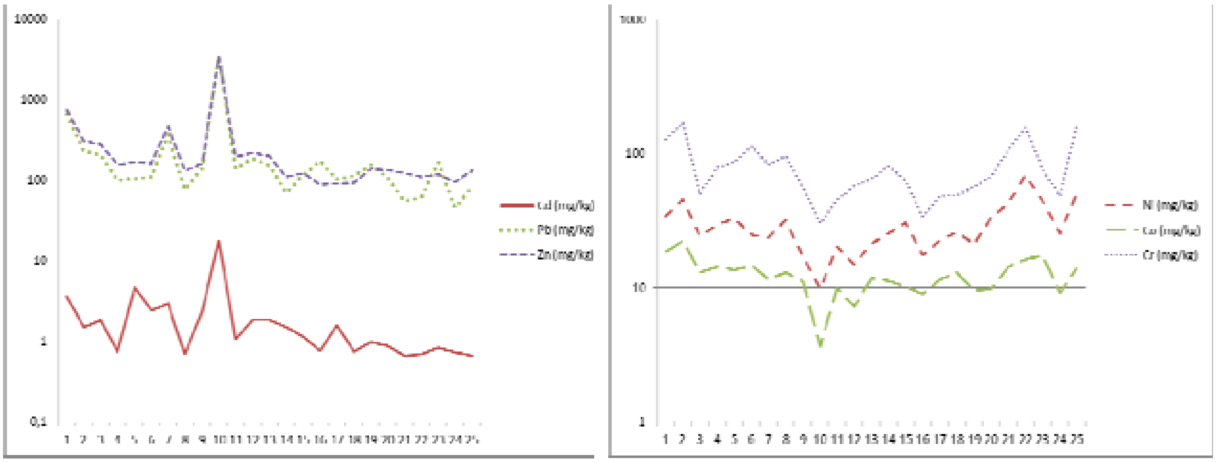
The high contents of Cu and Pb are not only due to mining works, but also the town works, traffic, industry and developed technological processes which aloud emission of higher amounts of these heavy metals in air (Balabanova et al., 2009; 2010; 2011; Stafilov et al, 2010b).

Correlations: Data from geochemical analyzes were statistically processed in regular Excel calculations procedure going through the Data menu where we chose Data analysis option with an array of Analysis tools where we continued with Correlation and selected data range for that particular type of data analysis. The results of correlation analysis are displayed in Table 2.

From the table above can be seen that in the whole correlation calculation where included 13 elements, which pointed out two correlation elemental suites (Figure 7). The first suite encloses Cd-Pb-Zn with correlation coefficients for Cd-Pb of 0.967, Zn-Pb of 0.998 and Zn-Cd of 0.970. These values indicate a high elemental correlation for this suite where zinc and cadmium have "historical" roots of their high correlation even in their primary sources. The second elemental suite consists of Ni-Co-Cr with correlation coefficient for Ni-Co of 0.708, Ni-Cr of 0.821 and Co-Cr of 0.773. All these correlation coefficients are relatively high and reflect the and the clear geochemical relationship of these elements, which basically belong to ultramafites or they are metals that are representative of primary mantle (oceanic crust).

Table 2. Matrix of correlation coefficients in soil samples (n=25) around the Buchim copper mine

	Al	Fe	Ag	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Al	1												
Fe	**0,822**	1											
Ag	0,000	0,000	1										
As	0,205	-0,041	0,000	1									
Cd	-0,139	-0,419	0,000	0,467	1								
Co	**0,774**	**0,854**	0,000	0,003	-0,415	1							
Cr	**0,775**	**0,808**	0,000	-0,087	-0,234	**0,773**	1						
Cu	-0,074	-0,023	0,000	-0,018	-0,085	-0,110	-0,134	1					
Mn	**0,825**	**0,881**	0,000	0,075	-0,327	**0,829**	**0,656**	0,095	1				
Ni	**0,688**	**0,836**	0,000	-0,163	-0,365	**0,708**	**0,821**	0,008	**0,758**	1			
Pb	-0,195	-0,423	0,000	0,361	**0,967**	-0,416	-0,235	-0,068	-0,327	-0,330	1		
V	**0,863**	**0,948**	0,000	-0,035	-0,351	**0,843**	**0,870**	-0,039	**0,796**	**0,772**	-0,362	1	
Zn	-0,170	-0,404	0,000	0,357	**0,970**	-0,394	-0,201	-0,083	-0,316	-0,315	**0,998**	-0,336	1



a) b)

Figure 7. Correlation diagrams for the geochemical suite one Cd-Pb-Zn (a) and suite two Ni-Co-Cr (b) from the soil analytical data around the Buchim copper mine

However, here we are dealing with their anthropogenic input in soils around the Buchim mine, which clearly indicates their connection with the processing of copper ore from the mine, which in turn seems a fact that copper is the metal of oceanic crust.

CONCLUSION

Analytical data of the soil study around the Buchim mine displayed contamination with heavy metals on two fronts. The first one regarding the contaminated soil around the tailing dam where have been determined increased concentrations of Pb, Zn, Cd and Co and the second one around the waste dump with increased concentrations of Cu, As, Cr and V. These contaminations coincide with the so-called rose of winds in the Buchim mine area and display reflection through increased concentrations of above mentioned metals in soil, air and water.

Several geochemical pairs have shown high correlation coefficients: Cd-Pb 0.967, Zn-Pb 0.998 and Zn-Cd 0.970 as well as Ni-Co 0.708, Ni-Cr 0.821 and Co-Cr 0.773 and group in two basic geochemical suites: Pb-Zn-Cd and Ni-Co-Cr. Copper did not manifested correlation with any element of the analyzed association, but however it is present in both. Increased concentration of all analyzed metals in soil around the Buchim mine implies direct correlation to the processing of porphyry copper ore in the Buchim mine, while metal deposition in soil the most frequently comes through the airborne contamination.

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Research Article

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The effect of soil and foliar application of magnesium on yields and quality of *Vitis vinifera*, L. grapes

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ABSTRACT

The three-year field trial with the vine variety Müller Thurgau was focused on the effect of various methods of application of magnesium fertilisers on yields and quality of grapes. In the past visual symptoms of Mg deficiency appeared repeatedly on leaves of vine (intercostal chlorosis) grown on light soil with a low supply of Mg in the experimental locality Žabčice (South Moravia, Czech Republic). The experiment consisted of five treatments: i) unfertilised control; ii) spring soil application of Kieserite - 20 kg Mg.ha^{-1}; iii) spring soil application of Kieserite - 20 kg Mg.ha^{-1} + 5 foliar applications of a 5% solution of Epso Combitop – Mg, S, Mn, Zn; iv) 5 foliar applications of a 5% solution of Epso Combitop – Mg, S, Mn, Zn; v) 5 foliar applications of a 5% solution of Epso Top – Mg, S. No visual symptoms of magnesium deficiency appeared on the leaves after magnesium applications. The average three-year yield of grapes of the unfertilised control was 7.39 t.ha^{-1}. In all the fertilised treatments (2-5) the yields increased significantly in contrast to the control, i.e. as follows: 8.37-8.96-8.31-8.24 t.ha^{-1}. The yields of treatment 3 were significantly higher (8.96 t.ha^{-1}) than of the other fertilised treatments. The average sugar content of grapes of the unfertilised control was 16.6 °NM. The sugar content of the fertilised treatments (2-5) increased significantly as follows: 17.6-18.4-17.4-18.3 °NM. No significant differences were seen in the contents of titratable acids (6.20-6.82-6.63-6.89-6.86 g.l^{-1}) and pH of must (3.23-3.33-3.36-3.36-3.26) among the treatments. The results showed that the best yields and sugar content were achieved in treatments where soil and foliar applications were combined (Kieserite + Epso Combitop). For magnesium nutrition of vine crucial is the soil application of magnesium because tens of kg is required per 1 ha. Foliar application is a complementary method of fertilisation suitable particularly for nutrition with microelements (Zn, Mn).

INTRODUCTION

Balanced nutrition and fertilisation is an essential component of vineyard technology if we are to achieve the required yields of grapes and their quality (Custic et al., 2008; Krempa et al., 2009).

Magnesium is an important macroelement with a number of physiological functions in the plant. In many aspects the importance of magnesium in the plant is connected with photosynthesis. It is the central atom of chlorophyll and activates enzymatic processes. On top of that magnesium has a favourable effect on assimilation activity (Marschner, 2002; Mengel et al., 2001; Dorenstouter et al., 1985).

As a rule the average content of Mg in vine leaves ranges around 0.3 % in dry matter and magnesium is more mobile than calcium (Hlušek et al., 2002). In terms of magnesium uptake we can see differences among the varieties (Kocsis, 2003). Magnesium deficiency reduces the content of chlorophyll in the leaves and changes the ratio of a:b chlorophyll in favour of chlorophyll b; visually it appears as intercostal chlorosis on the leaves, especially on older leaves, and causes their premature shedding. The cause of chlorosis is either absolute deficiency of soil Mg, high content of soil Ca (calcareous soils) or a combination of these factors (Gluhić et al., 2009;

Ksouri et al., M., 2005; Marschner, 2002). The antagonistic action of Ca and K also affects Mg uptake by the plant; it was confirmed by Garcia *et al.* (1999) who discovered that the Mg content was considerably reduced in berries on soils with a high supply of Ca and was associated with an increase in the total content of berry acids. Likewise Skinner and Matthews (1990) reported Mg deficiency in vineyards where the soil reaction and phosphorus content were low. Magnesium deficiency or unbalanced K : Mg ratio are said to be among the causes of stalk necrosis and berry shrivel (Hlušek et al., 2002). In terms of the mode of application we distinguish between soil and foliar application (Takacs-Hajos et al., 2007).

The objective of the field trial was to compare soil and foliar applications of magnesium fertilisers (including their combinations) on yields and qualitative parameters of grapes..

MATERIAL and METHODS

The field trial was established with the vine variety Müller Thurgau and conducted in 2010-2012 in Žabčice (Czech Republic) in a vineyard belonging to Mendel University in Brno. The village of Žabčice [49°0´43´´N, 16°36´8´´E] lies ca 25 km south of Brno (south Moravia) in a maize-growing region; the soil and climate conditions are as follows: altitude - 185 m, annual sum of precipitation 450-550 mm, average annual air temperature 9.3 °C, soil type – light soil. The berry-bearing vineyard (established in 1999) lies on sandy subsoil which has a limited sorption capacity for water and nutrients. Table 1 gives the agrochemical characteristics of the soil prior to trial establishment.

Table 1. Agrochemical characteristics of soil prior to trial establishment (Mehlich III)

Depth	$pH/CaCl_2$	mg.kg^{-1}			
		P	K	Ca	Mg
0 – 0.3 m	5.95	80	124	1,159	118
	slightly acid	satisfactory	satisfactory	satisfactory	satisfactory
0.3 – 0.6 m	4.82	181	94	1,267	100
	strongly acid	high	low	satisfactory	satisfactory

The content of Mg both in the topsoil and subsoil was satisfactory; the application of Mg is necessary on this soil (the soil is rated as follows: very high – high – good – satisfactory – low). The variety Müller Thurgau is very sensitive to Mg deficiency. In the past years visual symptoms of magnesium deficiency appeared repeatedly on a regular basis on the leaves of this variety and it was also confirmed by leaf analysis. In terms of microelements Mn and Zn deficiency was proved.

The experiment consisted of 5 treatments, and each treatment was repeated 4 times; one replication involved 10 vines.

The experiment consisted of five treatments:

1) unfertilised control
2) spring soil application of Kieserite (40 kg Mg.ha^{-1})
3) spring soil application of Kieserite (40 kg Mg.ha^{-1}) + 5 foliar applications of a 5% solution of Epso Combitop (11.8 kg Mg.ha^{-1})
4) 5 foliar applications of a 5% solution of Epso Combitop (11.8 kg Mg.ha^{-1})
5) 5 foliar applications of a 5% solution of Epso Top (14.8 kg Mg.ha^{-1})

The combination of fertilisers was as follows:

Kieserite - 25 % MgO, 20 % S

Epso Combitop - 13 % MgO, 13 % S, 4 % Mn, 1 % Zn

Epso Top - 16 % MgO, 13 % S

Foliar nutrition as a 5% solution (600 l.ha^{-1}) was applied 5 times after blossom shedding from late June to early August in 7-10 day intervals. Tables II and III give the total rates of magnesium applied in the respective treatments (kg Mg.ha^{-1}).

Every spring the vineyard was fertilised with 108 kg N.ha^{-1} in the form of ammonium nitrate with limestone (27% N). After the spring surface application the magnesium fertiliser Kieserite was incorporated into the soil with a cultivator. During vegetation pest control was applied in the experimental treatments and was the same as in the rest of the vineyard. The grapes were picked manually and the yield was converted to ha; the average number of vines was 3.133 ha^{-1}. In terms of quality the grapes were analysed for the content of sugar, acids and pH. The content of sugar in the must was assessed in fresh must from 100 berries refractometrically in each repetition and the results were converted to normalised mustmeter degrees (°NM). 1 °NM corresponds to 1 kg of sugar in 100 liters of must. The content of all titratable acids in the must with the exception of H_2CO_3 was assessed by titration of 0.1M NaOH in $g.l^{-1}$. The pH of the must was assessed on a pH-meter (Zatloukalová, 2013).

The results were processed statistically using analysis of variance followed by testing according to Scheffe (P = 95%).

RESULTS and DISCUSSION

Yield

Magnesium deficit not only reduces yields, but also increases the risk of tendril atrophy (Májer, 2004; Füri and Hajdú, 1980). With regard to the requirement of (macro) elements the basic method of vineyard nutrition is soil application. According to Hubáčková (1996) the annual rate of magnesium for maintenance fertilisation of the vineyards is 20 – 30 $kg.ha^{-1}$. As an accompanying ion the magnesium fertilisers contain sulphates; sulphur stimulates nitrogen utilisation thereby it stimulates yields and reduces the danger of its losses, e.g. such as nitrate leaching into ground water (Mengel et al., 2001). Grape yields (Table 2) in treatments 1-5 were as follows: 7.39-8.37-8.96-8.31-8.24 $t.ha^{-1}$. The yields were significantly the lowest in the unfertilised control treatment. The yields of treatment 3 were significantly higher (8.96 $t.ha^{-1}$) than of the other fertilised treatments. It was proved that on soil with satisfactory (second lowest) supply of Mg soil application of magnesium fertilisers is necessary to top up the soil supply. Krempa *et al.* (2009) pointed out the importance of soil applications of organic and mineral fertilisers for vine. In three-year trials Ložek (2010) observed that the yields of berries of Riesling italico increased by 4.1 % after soil application of N, Mg and by 14.9 % after the application of N, P, K, S. In their two-year experiments Krempa *et al.* (2009) also monitored that the yields of grapes of the variety Lipovina increased by 10.9 % after soil application of N, Mg and by 16.3 % after the application of N, Mg and S.

Foliar nutrition has an irreplaceable function in vine fertilisation, not only with magnesium but particularly with microelements - Zn, Mn, Fe (Hlušek et al., 2002). Foliar application of Mg had the best effect on yields in combination with soil application of Mg (+ 21.2% against the unfertilised control), Table 2 Foliar application of both fertilisers increased yields by 11.5-12.4% as against the control and there were no differences between the fertilisers (Table 2).

Table 2. 3-year average yields

Treatment No.	Type of fertilization	Rate of Mg ($kg\ Mg.ha^{-1}$)	Yield	
			$t.ha^{-1}$	rel. %
1	-	0	7.39 a	100.0
2	soil	40	8.37 b	113.3
3	soil + foliar	40 + 11.8	8.96 c	121.2
4	foliar	11.8	8.31 b	112.4
5	foliar	14.8	8.24 b	111.5

Different letters (a, b) indicate significant differences among treatments

In his field trials with Riesling italico Májer (2004) explored the effect of both soil (control, 10 - 20 - 30 - 40 kg $Mg.ha^{-1}$) and foliar application (5% solution applied three times after blossom shedding) of magnesium in the form of bitter salt (Epso Top) on yields and qualitative parameters of grapes. The results were positive after soil application of 30 – 40 kg $Mg.ha^{-1}$.

Content of sugar, acids and pH of must

The flavour of the wine is mellow and well-balanced if the content of sugar and acids in the grapes is in direct proportion. The average sugar content of grapes of the unfertilised control was 16.6 °NM. The sugar content of the fertilised treatments (2-5) increased significantly as follows: 17.6-18.4-17.4-18.3 °NM (Table 3). The content of sugar in the grapes was the highest in treatments 3 and 5. Takacs *et al.* (2007) reported that foliar application of Mg during summer (also for prevention purposes) increased the content of Mg in vine leaves, increased photosynthesis and increased the sugar content in the grapes; this was confirmed in our experiments too. In contrast, in their 2-year trials Krempa *et al.* (2009)

reported minimal differences in the sugar contents in the variety Muscatel yellow (22.65 °NM) after the application of NMg (22.30 °NM) and NMgS (22.50 °NM).

There were no differences in the contents of titratable acids (6.20-6.89 g.l^{-1}) among the treatments (Table 3); the lowest content was detected in the control treatment. In their 2-year trials Krempa *et al.* (2009) discovered minimal differences in the content of acids between the unfertilised variety Muscatel yellow and Furmint (8.09 and 9.20 g.l^{-1}, respectively) after the application of NMg (8.04 and 9.31 g.l^{-1}, respectively) and application of NMgS (8.22 and 9.26 g.l^{-1}, respectively). Among treatments 1-5 there were no differences in the pH of must: 3.23-3.33-3.36-3.36-3.26. Zatloukalová *et al.* (2011) did not detectany changes in the contents of titratable acids (12.78-13.25 g.l^{-1}) and pH of must (3.02-3.11) after soil or foliar application of Mg in the variety Riesling italic.

Table 3. 3-year average qualitative results

Treatment No.	Type of fertilisation	Rate of Mg (kg Mg.ha^{-1})	Content of sugar in must (°NM)	Content of titratable acid (g.l^{-1})	pH of must
1	-	0	16.6 a	6.20 a	3.23 a
2	soil	40	17.6 b	6.82 a	3.33 a
3	soil + foliar	40 + 11.8	18.4 c	6.63 a	3.36 a
4	foliar	11.8	17.4 b	6.89 a	3.36 a
5	foliar	14.8	18.3 c	6.86 a	3.26 a

Different letters (a, b) indicate significant differences among treatments

CONCLUSION

The results of three-year trials imply that on soil with a low or satisfactory supply of magnesium this macronutrient must be applied to the soil. A combination of soil and foliar application of magnesium resulted in the highest yields and content of sugar in the grapes. Foliar application is a complementary source of nutrition with macroelements, but can cover the demands of vine for microelements (Zn, Mn). While the yields of grapes and their sugar content were affected by magnesium fertilisation, the contents of titratable acids and pH of must did not change.

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