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Influence of different fertilization on the dissolved organic carbon, nitrogen and phosphorus accumulation in acid and limed soils

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Abstract

Soil quality has become an important issue in soil science. Dissolved organic carbon (DOC) is believed to play an important role in soil processes and in the C, N and P balances, their supplies to plants in all types of soils. It is much more sensitive to soil management than is soil organic matter as a whole, and can be used as a key indicator of soil natural functions. This study aimed to assess the influence of different organic fertilizers on DOC and N, P accumulation. The study was carried out on a moraine loam soil at the Vezaiciai Branch of Lithuanian Research Centre for Agriculture and Forestry in 2012. Farmyard manure (FYM) (60 t ha $^{-1}$) and alternative organic fertilizers (wheat straw, rape residues, roots, stubble, perennial grasses) were applied on two soil backgrounds - acid and limed. DOC was analysed using an ion chromatograph SKALAR. Application of organic amendments resulted in a significant increase of soil organic carbon (SOC) content, which demonstrates a positive role of organic fertilizers in SOC conservation. The combination of different organic fertilizers and liming had a significant positive effect on DOC concentration in the soil. The highest DOC content (0.241 g kg^{-1}) was established in the limed soil fertilized with farmyard manure. The most unfavourable status of DOC was determined in the unlimed, unfertilized soil. The limed and FYM-applied soil had the highest nitrogen (1.47 g kg^{-1}) and phosphorus (0.84 g kg^{-1}) content compared to the other treatments. Organic fertilizers gave a significant positive effect on SOC and DOC content increase in the topsoil. This immediate increase is generally attributed to the presence of soluble materials in the amendments. Application of organic fertilizers in acid and limed soil increased the nutrient stocks and ensured soil chemical indicators at the optimal level for plant growth and thus may provide a mechanism as well as prediction opportunities for soil fertility, conservation, sustainability, and protection against degradation.

Keywords: soil, SOC, DOC, N, P, organic fertilizers, liming

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Introduction

Soil organic carbon (SOC) determines the functioning of large parts of biogeochemical interfaces in the soil. SOC is an important source of plant nutrients, which stabilizes soil structure and plays a central role in soil surface-atmosphere exchange of greenhouse gases (Grandy and Robertson, 2006, Liaudanskiene et al., 2013). Because soil organic matter can be associated with different soil chemical, physical and biological processes, it has been widely considered as one of the best soil quality indicators. Land management can significantly influence dynamics of organic carbon and nitrogen, phosphorus cycle. However, changes in

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total soil organic carbon contents in response to land management may be difficult to detect because of the natural soil variability. In the short to medium term, biological properties and readily decomposable fractions of SOC, such as dissolved organic carbon (DOC), are much more sensitive to soil management than is SOC as a whole, and can be used as a key indicator of soil natural functions (Silveira, 2005, Rékási, 2011).

DOC represents one of the most mobile and reactive organic matter fractions in the ecosystem. DOC as a heterogeneous mixture of organic molecules with different sizes, structures and functional properties is often defined operationally as "the part of organic matter that is able to pass through a filter with a pore size of 0.45 μm". DOC consists of low molecular weight substances, such as organic acids and amino acids, as well as complex molecules of high molecular weight, such as humic substances and enzymes (Zsolnay, 2003, Bi et al., 2013). As a relatively mobile fraction of the soil organic carbon, DOC plays an important role in the transport of nutrients, such as nitrogen, phosphorus and pollutants (Kaiser, 2003). In particular, DOC strongly complexes heavy metals, influencing metal exchange processes between the soil and soil solution and facilitating metal leaching through the soil profile and further transport towards streams and ground water (Worrall et al., 2009, Kaiser and Kalbitz, 2012). Though dwarfed in size by total SOC, it plays an important intermediary role between physically stable and labile C pools through its fast turnover rate, high mobility and broad reactivity in the soil (Boddy et al., 2007) and could be a potential source of the stabilized carbon occurring in soils (Schmidt et al., 2011).

DOC carries not only C, but also nitrogen (N), phosphorus (P), playing therefore a major role in determining accumulation, transport and balance of these elements in soils. DOC is an important factor in determining the balance of soil N and P and it can contribute to cycling of soil nutrients. Actually, sorption of DOC is an important mechanism to control losses of organic nutrients from soil. The extent of this mechanism regulates N and P mineralization and varies according to soil characteristics. Some studies have shown that P dynamics is not closely related to DOC, and P contents are much more variable than N contents. This difference in N and P behaviour occurs because mineralization of N takes place in conjunction with biological N mineralization, while P mineralization involves both biological and enzymatic (biochemical) processes (Qualls and Richardson, 2003; Silveira, 2005).

One of the common strategies for enhancement of SOC includes optimal fertilization, which increases C input by enhancing biomass production. In general, application of organic fertilizers and especially manure, either alone or in combination with inorganic fertilizers, increase SOC concentration (Gong et al., 2009, Liang et al., 2012). Input of organic amendments can occur through transport of DOC from the topsoil and through better crop growth. Fertilization could affect the content of DOC, leading to alterations in the formation of complexes between organic ligands and metals, and the SOM sequestration (Yu et al., 2012, Wen et al., 2014). On the other hand, increased decomposition of stabilized material induced by addition of fresh organic material triggering microbial activity can result in higher C losses from soil (Schlüter et al., 2011; Kirchmann et al., 2013).

Over the past few decades the need has risen for comprehensive studies on the soil properties and environmental factors controlling DOC quantity and quality. However, there is limited information available about the effects of different fertilization on the changes of DOC, and the data on the dynamics of DOC in soils are often contradictory, especially in arable soils. The aim of this research is to assess the influence of different organic fertilizers on DOC and N, P accumulation in acid and limed soil.

Material and Methods

Study site

The field experiment was carried out at the Vezaiciai Branch of Lithuanian Research Centre for Agriculture and Forestry in 2012. The soil of the experimental site is *Dystric Epihypogleyic Albeluvisol* (Jin – g) (ABd – gld – w) (texture – moraine loam (clay 13–15%). Farmyard manure (FYM) (60 t ha $^{-1}$) and alternative organic fertilizers (wheat straw, rape residues, roots, stubble, perennial grasses) were applied on two soil backgrounds - acid and limed. The experimental design included the following treatments: 1) unlimed soil; 2) unlimed soil + FYM (60 t ha $^{-1}$); 3) unlimed soil + alternative organic fertilizers; 4) limed soil (1.0 rate in 5 years); 5) limed soil + FYM (60 t ha $^{-1}$); 6) limed soil + alternative organic fertilizers.

The soil was limed at 1.0 rate to maintain optimal soil pH_{KCl} (5.8 – 6.0). The amount of manure applied per rotation amounted to 60 t ha^{-1}. Alternative organic fertilizers were applied every year. The mineral fertilization in both acid and limed soil was the same: $N_{60}P_{60}K_{60}$ for cereals, $N_{60}P_{60}K_{60}$ for barley, $N_{30}P_{60}K_{60}$ for lupine + oats mixture, $N_{60}P_{90}K_{120}$ for rape, $P_{60}K_{90}$ for perennial grasses.

Soil sampling

Soil samples were taken using a steel auger from three replicates of the topsoil (0 – 20 cm) in the autumn of 2012 (after the lupine – oats mixture harvesting). All samples were air-dried, visible roots and plant residues were manually removed. Then the samples were crushed, sieved through a 2-mm sieve and homogeneously mixed. For the analyses of SOC content the soil samples were passed through a 0.25-mm sieve.

Methods of analyses

Chemical analyses were carried out at the Chemical Research Laboratory of Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry. Soil pH was determined in 1M KCl (soil – solution ratio 1:2.5) using a pH – meter IONLAB, mobile aluminium by Sokolov method. Soil total nitrogen (N) was determined by the Kjeldahl method, and soil total phosphorus (P) was determined spectrophotometrically using Cary 50 (Varian) after wet digestion procedure. SOM content was determined by photometric procedure at the wavelength of 590 nm using the UV-VIS spectrophotometer Cary 50 (Varian) equipped with a computer program, and glucose as a standard after wet combustion according to Nikitin (1999).

Dissolved organic carbon was analyzed using an ion chromatograph SKALAR. For determination of DOC, the samples were shaken with distilled water at a ratio of 1:5 for one hour using a shaker "PSU – 20i multi – functional orbital shaker" (BioSan). The extract was obtained after filtration through 0.45 micrometer cellulose filters. The automated procedure for the determination of DOC is based on the following reaction: the sample is first acidified with a sulfuric acid solution and sparged with nitrogen. This liberates and disperses any inorganic or volatile organic carbon. The sample solution is then mixed with a persulfate / tetra borate reagent and passed through an UV digestion coil. This process oxidises the organic carbon to carbon dioxide. The carbon dioxide is expelled from the solution by acidification and sparging. The amount of carbon dioxide is measured by infra - red detection.

Statistical analysis

Statistical analysis was done using the computer program ANOVA from the package Selekcija. One-way analysis of variance was then used to analyze the differences in the tested parameters among the treatments. The least significant difference method (LSD) at the 5% probability level was used to test the significance of differences between treatment means. Correlation and regression analysis between data sets was done using the statistical programme STAT_ENG for EXCEL program version 1.55 (Tarakanovas and Raudonius, 2003)

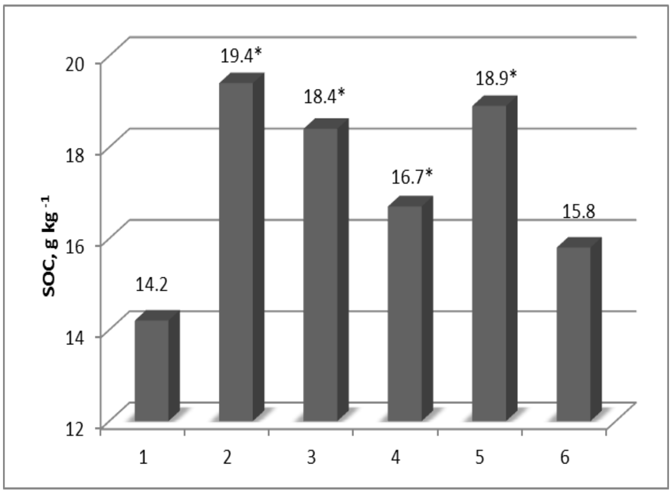
Results and Discussion

Soil organic matter accumulation is a slow process and considerably slower than the rate of decline. Fortunately, accumulation can be enhanced by positive land management techniques, such as green manures and applications of farmyard manure. The application of organic amendments to soil has beneficial effects, mainly because such amendments supply organic matter and other nutritive elements to the soil – plant system (Purakayastha et al., 2008, Powlson et al., 2012).

There was found a positive statistically significant effect of fertilization on soil organic carbon amount in the soil (Figure 1). SOC amount was 14.2 g kg^{-1} for the non-fertilized treatment and in fertilized treatments it varied from 15.8 to 19.4 g kg^{-1}. SOC content in the fertilized plots was thus approximately by 3 - 5 g kg^{-1} higher compared to the unfertilized plots. In the limed soil (1.0 rate to maintain optimal soil pH), the content of SOC increased by 2.5 g kg^{-1} compared with the control treatment. The highest amount of soil organic carbon (19.4 g kg^{-1}) was obtained in the limed soil applied with FYM. Our results agree with those from the studies done in Michigan, where fertilization was found to increase soil organic carbon stocks in the soil (Smemo et al., 2007, Pregitzer et al., 2008).

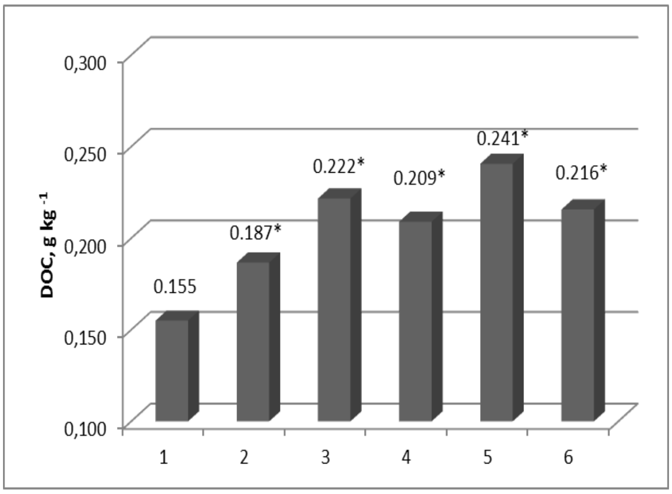
The reasons for the higher SOC in soils with farmyard manure possibly due to the presence of more humified and recalcitrant C forms in animal manure as compared to the other organic fertilizers (Powlson et al., 2012). Significant increase of soil organic carbon content demonstrates the positive role of organic fertilizers in SOC.

It was revealed that the combination of different organic fertilizers with liming had a significant effect on DOC amount in the soil. The quantity of DOC was tightly related to soil – and management – associated factors. The greatest treatment effects on DOC found in this study were the increased concentrations in the fertilized treatments compared to the non-fertilized (Figure 2). The highest amount of DOC (0.241 g kg^{-1}) was obtained in the limed soil fertilized with farmyard manure. The most unfavourable status of DOC was determined in the unlimed, unfertilized soil. The same results, i.e. an increase in the DOC content, have been recorded in the literature after liming and fertilization of arable soils. Various mechanisms have been suggested to explain this phenomenon, such as increased organic matter solubility, increased microbial activity, an increase in the production of soluble molecules due to the decrease in biologically toxic Al at higher pH, and the displacement of the previously adsorbed DOC by other mobilised anions (Filep and Rekasi, 2011).



* Differences significant at 95 % probability level

Figure 1. The influence of organic fertilisers on SOC amount in the soil, where: 1) unlimed soil; 2) unlimed soil + FYM (60 t ha^{-1}); 3) unlimed soil + alternative organic fertilizers; 4) limed soil (1.0 rate in 5 years); 5) limed soil + FYM (60 t ha^{-1}); 6) limed soil + alternative organic fertilizers



* Differences significant at 95 % probability level

Figure 2. The influence of organic fertilizers on DOC content in *Dystric Albeluvisol,* where: 1) unlimed soil; 2) unlimed soil + FYM(60 t ha^{-1}); 3) unlimed soil + alternative organic fertilizers; 4) limed soil (1.0 rate in 5 years); 5) limed soil + FYM (60 t ha^{-1}); 6) limed soil + alternative organic fertilizers

Addition of alternative organic fertilizers resulted in lower DOC content compared to farmyard manure. These differences in soil dissolved organic carbon content mainly reflect the decomposability of the organic amendments. The important soil chemical properties influencing soil fertility are soil acidity and the amount of mobile aluminum. The pH can affect the soil environment in many ways through influences on sorption potential, cation availability and microbial degradation rates (Sanderman et al., 2008). Our study showed that soil liming had a significant positive effect on soil acidity index (Table 1): pH increased by 1.65 units, mobile aluminum decreased to 0.00 mg kg^{-1} compared with unlimed soil.

Table 1. The effect of manuring and liming combination on topsoil chemical properties

Treatments	pH_{KCl}	Mobile Al, mg kg^{-1}	Total N, g kg^{-1}	Total P, g kg^{-1}	C/N ratio
1) Unlimed	4.02	88.4	1.16	0.69	12.3
2) Unlimed + farmyard manure (60 t ha^{-1})	4.51*	6.59*	1.44*	0.78*	13.5*
3) Unlimed + alternative organic fertilizers	4.29*	49.6*	1.33*	0.72	13.8*
4) Limed (1.0 rate in 5 years)	5.67*	0.00*	1.29*	0.73*	12.9
5) Limed + farmyard manure (60 t ha^{-1})	5.91*	0.00*	1.47*	0.84*	12.8
6) Limed + alternative organic fertilizers	5.78*	0.00*	1.34*	0.68	11.8

*Differences significant at 95 % probability level

The greatest soil acidity neutralizing effect resulted from the combination of manuring and liming, when after incorporation farmyard manure and alternative organic fertilizers in limed soil, pH increased by 1.89 and 1.76 units respectively. The pH is an important chemical factor for the solubility and production of DOC and the relationship between pH and DOC is generally thought to be a complex one, partly because of the influence on charge density of the humic compounds, partly because of stimulation of the microbial activity.
In our study we found a significant positive relationship between pH and DOC (Figure 3). Similar consistent patterns on relationships between soil pH and DOC concentrations have been identified in others studies (Solinger et al., 2001, Kemmitt et al., 2006, Löfgren and Zetterberg, 2011). This relationship could be attributed to differences in decomposition rates (higher at elevated pH), differences in DOC sorption to the soil complexes and complex formation with aluminium, and differences in DOC quality (phenol content lower at high pH and therefore more readily decomposable DOC).

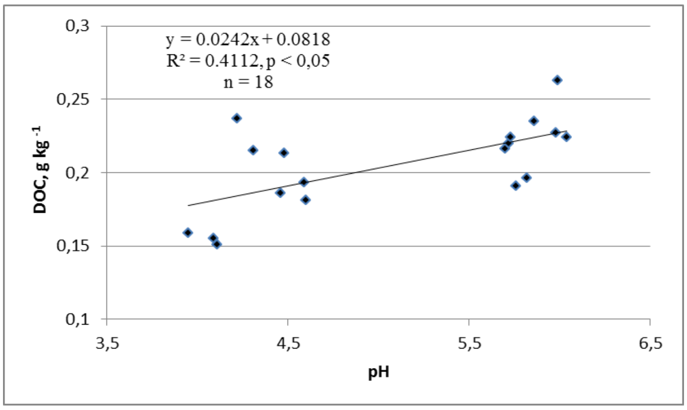


Figure 3. The relationship between DOC amount (g kg^{-1}) and soil pH. The equation of the fitted line is y = 0.0242x + 0.0818 (R^2 = 0.4112, $p < 0.05$)

There is also a possibility that not only the amount of soil organic carbon but also the N status influences DOC amount in soil, for either biological or physicochemical reasons. Furthermore, N limited sites may respond differently to sites where N availability is already high. Possible effects as a result of altered enzyme activities include however both changes in production of DOC and changes in mineralization of DOC (Zak et al., 2011). In the present study, the DOC content in soil was increased by increasing soil N. The limed and FYM - applied soil had a higher nitrogen (1.47 g kg^{-1}) content compared to the other treatments (Table 1). In this treatment we also determined the highest DOC amount (0.241 g kg^{-1}). It is possible that increase of total N content favour the microbial degradation of both DOC and solid organic matter, the latter resulting in the production of DOM (Filep and Rekasi, 2011). The total P content showed similar patterns as for N content. The highest P content (0.84 g kg^{-1}) was determined in the organic fertilization system, having incorporated farmyard manure (60 t ha^{-1}) in the topsoil.

In all acid soil, C/N ratio is one of the controlling factors of DOC mobility (Sowerby et al., 2010). Soil C/N ratio is conventionally used to characterize the degree of decomposition of the organic carbon. At high C/N ratios, mineralisation of the available DOC is limited and DOC concentrations increase. In our research, the C/N ratio of soil varied from 11.8 (limed soil + alternative organic fertilizers) up to 13.8 (unlimed soil + farmyard manure) (Table 1). Significant differences were established in unlimed soil +FYM and in unlimed soil + alternative organic fertilizers. In our study we did not find a significant relationship between C/N ratio and DOC. This agrees with Xi et al. (2007) who also did not find a relationship between C/N ratio and DOC values.

Conclusion

Amendment of soil with organic fertilizers exerted a significant positive effect on soil fertility. Application of organic amendments had a positive effect on SOC amount in the soil. Soil organic carbon content in the fertilized plots was by approximately 3 - 5 g kg^{-1} higher compared to the unfertilized plots. The quantity of dissolved organic carbon was tightly related to soil – and management – associated factors which induced an increase in dissolved organic carbon content in the topsoil. The highest amount of DOC (0.241 g kg^{-1}) was determined in the limed soil fertilized with farmyard manure. This immediate increase is generally attributed to the presence of soluble materials in the amendments, leading to alterations in the formation of complexes between organic ligands and metals, and the SOM sequestration. Application of organic fertilizers in acid and limed soil increased the nutrient stocks and ensured soil chemical indicators at the optimal level for plant growth. The combination of soil liming and manuring increased pH by 1.65 units and removed mobile aluminium compared with unlimed soil. Our study showed a significant positive relationship between pH and DOC content in the soil (R^2 = 0.41), which is an important factor for the solubility and production of DOC. The DOC content in the soil increased with increasing soil N and P. The limed soil applied with farmyard manure had a higher nitrogen (1.47 g kg^{-1}) and phosphorus (0.84 g kg^{-1}) content compared to the other treatments. Considering given environmental conditions, these data can be used for deducing scenarios of future soil processes in an efficient way, for dissolved organic carbon being a small but highly sensitive fraction of organic matter in soil and thus may provide a mechanism as well as prediction opportunities for soil fertility, conservation, sustainability, and protection against degradation.

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