APPLICATION OF ENVIRONMENTAL PROTECTION MEASURES FOR CLAY LOAM CAMBISOL USED FOR AGRICULTURAL PURPOSES

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Abstract. Field experiments were done at the Joniškėlis Experimental Station of the Lithuanian Institute of Agriculture (LIA) during 2004–2006. The experiments were done on a productive clay loam Gleyic Cambisol used for agricultural production and were designed to estimate the effects of various catch crops – red clover (Trifolium pratense L.) and white clover (Trifolium repens L.) mixture with Italian ryegrass (Lolium multiflorum Lamk.) and white mustard (Sinapis alba L.) biomass and wheat (Triticum aestivum L.) straw incorporated into the soil on the composition of humus. In the first year, incorporation of only catch crops biomass or together with straw increased the content of mobile humic acids (C_{HA1}) by 10.7–28.0% compared with that before trial establishment. With increasing mobile humic acids content the contents of aggressive and free fulvic acids increased too (r = 0.80, p < 0.01; r = 0.85, p < 0.01, respectively). Conditionally stable humic acids fractions (C_{HA2}, C_{HA3}) formed more intensively in the second year of effects of the measures applied. The biomass of Fabaceae family plants incorporated alone or together with straw tended to increase the content of calcium-bound humic acids (C_{HA3}). Having incorporated catch crops biomass together with straw, the fraction of humic acids C_{HA3} tended to increase or was the same as that before trial establishment. A slight reduction in the total amount of fulvic acids and an increase in the content of humic acids, compared with the levels before the trial establishment determined positive changes in the main indicators of humus quality – C_{HA3}: FA ratio and humification rate; they were the most distinct having incorporated red clover phytomass together with straw. Incorporation of mineral nitrogen fertilizer N45 together with straw increased soil organic matter mineralization rate and determined a reduction in humic acids content.

Keywords: Gleyic Cambisol, catch crops, straw, humic and fulvic acids.

1. Introduction

Soil organic matter, which is a multi-component and constantly changing part of soil, exerts a marked effect on the entire ecosystem and its stability. Carbon (C) is the main constituent of organic matter. Plant and bacteria associations existing in the soil photosynthetically fix atmospheric carbon and other elements that are returned into the soil in the form of plant and animal residues (Nieder et al. 2003). Meanwhile, soil micro-organism associations break down plant residues by catalysing major biogeochemical reactions depending on specific soil conditions. This is not simply organic matter utilisation, but also humic matter formation in the soil. It is important that new compounds form in the soil that do not exist in live organisms but which are vital for incessant existence of contemporary life forms (Шинкарев, Гнездинский 2001). Organic matter humification is a process conducive to the soil since thanks to it organic matter resources increase and as well as soil nutrient stocks available for plants. These processes determine supply of nutrient elements to plant and animal associations of the ecosystem and to large extent their quality and productivity (Baltrėnas et al. 2010). The amount of carbon which is annually incorporated into the composition of humic substances ranges from 0.6 to 2.5·10⁹ t (Орлов 1990).

In nature, organic matter accumulation depends on matter cycling in the biosphere between the above-ground and under-ground components of the ecosystem. The balance of natural ecosystems’ state is determined by balancing of soil organic matter decomposition and synthesis processes in a closed nutrient cycle. In differences agrocenoses, the largest part of phytomass produced by plants is removed from a field (farm) as a marketable produce. Therefore plant residues (carbon fixed in them) are the main source replenishing soil organic matter reserves. Moreover, intensive anthropogenic effect – mechanical soil tillage, intensive use of mineral fertilizers, especially nitrogen, nutrient leaching, shortage of organic fertilizers and other factors change organic matter introduction and transformation processes in the soil, where mineralization prevails and humification processes are inhibited (Bučienė 2003: 88–114; Feiza et al. 2005; Šlepšienė et al. 2007). Furthermore, farm specialisation in Lithuania’s intensive farming regions is narrowing, 2–3 most profitable crop species are cultivated, livestock production is being abandoned, which makes the problem of soil fertility maintenance more acute.
In agricultural land, organic matter (organic carbon) content can be replenished by increasing plant diversity and stimulating plant biomass growth (with increasing plant residue amount) or by enriching the soil with exogenous organic matter (e.g., farmyard manure). Experimental evidence suggests that the largest amounts of plant residues in the 0–40 cm layer are accumulated in the crop rotations involving perennial grasses, while the least plant residue amounts are accumulated in the crop rotation composed of black fallow, row crops and cereals (Magyla et al. 1997). Root mass of cultivated crops can be enhanced by mineral NPK fertilization. However, increased root mass does not always cover soil organic matter mineralization losses. The way the root biomass will behave in the soil – whether it will fully mineralise and increase CO₂ emission and plant nutrient reserves, will assimilate and be fixed in micro-organism biomass or partly changed will be incorporated into much more stable humic substances composition (will humify), will depend on root chemical composition and environmental conditions (Teēr 1991; Moran et al. 2005). The rate and trend of soil-incorporated organic matter transformation processes are influenced by its carbon to nitrogen ratio, lignin content, substrate surface area and environmental conditions (Пономарева, Плотникова 1998). The findings of long-term trials indicate that in specialised cereal farms the soil receives plant residues and straw with a high carbon to nitrogen rate. Due to the lack of nitrogen, this organic matter does not secure a positive humus balance (Magyla et al. 1997). A different situation is exhibited by the roots and residues of perennial and annual legumes – red and white clover, lucerne, and faba beans. Multifunctional effects of these plants in the agrosystems and an especially conducive C : N ratio for soil organic matter humification have long been known. They could be of great benefit for soil improvement; however, their use in crop production farms is limited. As a result, when organic fertilizer (farmyard manure) is not available it is vital to find ways to increase plant diversity and to enrich the soil with plant residues containing a different carbon to nitrogen ratio.

Catch crops, grown in many countries’ agrosystems, after main crop harvesting are designed to effectively utilise solar energy, reduce nutrient leaching and physical degradation of soil surface layer (Catt et al. 1998; Nieder et al. 2003; Fischbeck 2005). The objective of our study was to estimate the effects of the above-ground biomass of various catch crops on the composition of soil humic substances and their variation in agricultural, fertile heavy loam Cambisol.

2. Materials and methods

Research was done in the northern part of Central Lithuania’s lowland. The soil characteristic of the larger part of this region is Endocalci – Endohypogleylic Cambisol (CM-n-w-can) of high potential productivity. The soil texture is clay loam on silty clay with deeper lying sandy loam. The pHKCl of the topsoil is close to neutral. The soil is medium in phosphorus (P₂O₅ 118–128 mg kg⁻¹ soil), high in potassium (K₂O 213–219 mg kg⁻¹ soil) and moderate in humus (2.38%).

The study was carried out during the period 2004–2006 at the Lithuanian Institute of Agriculture, Joniškėlis Experimental Station as a bi-factor field trial with the following experimental design. Factor A: utilisation of winter wheat straw: A₁ straw removed from the field; A₂ straw chopped and spread. Factor B: Catch crops: B₁ Without catch crops (check treatment on A₁ background); B₂ Red clover (Trifolium pratense L.); B₃ White clover (Trifolium repens L.) and Italian ryegrass (Lolium multiflorum Lamk.) mixture; B₄ White mustard (Sinapis alba L.).

Catch crops were grown in the same year as winter wheat (Triticum aestivum L.), with no separate field allocated. Catch crops: undersown red clover, white clover mixture with Italian ryegrass (seed rate ratio 1:1) and post-crop white mustard. Catch crops were undersown into winter wheat early in spring when the soil had dried sufficiently. Post-crops were sown shortly after wheat harvesting (on the same day), the straw was either removed or chopped and spread (factor A). Post-sowing, ammonium nitrate (N₄₅) was applied for optimal growth of white mustard (on both straw backgrounds, treatment B₂) and straw (5 t ha⁻¹) (factor A₂) mineralization. In the middle of October the biomass of catch crops was chopped and incorporated into the soil. The effects of the measures used on the changes in humic and fulvic acids and soil organic carbon (SOC) were monitored for two years by growing spring barley (Hordeum vulgare L.) employing conventional soil and crop management practices and N₇₀, P₆₀, K₁₂₀ fertilization.

Soil samples for the determination of organic carbon content, humic and fulvic acids fractional composition were collected from 0–25 cm layer before trial establishment and in the first and second years of effect of catch crops’ biomass and straw incorporation after spring barley harvesting. Soil organic carbon (SOC) was measured by Tyurin method (ISO 10694:1995), humic and fulvic acids fractional composition by Tyurin method modified by Ponomariova and Plotnikova (Пономарева, Плотникова 1980). Chemical analyses were done at the LIA Chemical Research Laboratory.

The mean daily air temperature and precipitation during the experimental period were similar to long-term mean. The experimental data were processed by the analysis of variance and correlation-regression analysis methods using a software package “Selekcija”.

3. Results and discussion

3.1. Catch crops

In Lithuania, the main crops cover the soil for 60–70% of the warm period (when positive daily air temperature is above +5 °C), and the rest of this period (30–40%) is used unproductively when physical and chemical soil degradation occurs. Seeking to utilise solar energy as long as possible, it is expedient to cultivate catch crops for which there is no need to allocate a separate field in the crop rotation. This extends a positive effect of plants (catch crops) on soil properties. Nutrients fixed in plant biomass, used as green manure, are returned into the soil and serve as a source of nutrition for plants cultivated the
following year, and organic carbon replenishes organic matter reserves in the soil. When there are no plants which utilise and accumulate nutrients during the warm period, soil nutrients, especially nitrogen, migrate to deeper soil layers or are leached into ground water (Stancevičius, Trečiokas 1996). During the recent years, more attention has been devoted to soil conservation requirements with a special focus on the role of catch crops, however, research into their cultivation technologies is rather scarce in Lithuania.

During the experimental period, the weather conditions after winter wheat harvesting were favourable and the biomass of the above-ground part of catch crops amounted to 2.16–3.42 t ha$^{-1}$ dry matter. A large amount (4.48–5.63 t ha$^{-1}$) of dry organic matter (aboveground + underground biomass) was incorporated into the soil (Table 1).

Literature references indicate that in the course of evolution roots of most plant species have formed so that they have a C to N ratio, which is optimal for humification, compared with the above-ground plant biomass part (Rasse et al. 2005). However, the data on the effects of plant green above-ground mass on humification are rather ambiguous and inconsistent. Intensive decomposition of herbaceous plants’ above-ground biomass is affected by its high nitrogen status, which determines a narrow C to N ratio. Research findings suggest that catch crops’ above-ground mass contained 1.3–1.7 times more nitrogen and less fibre compared with roots. In agrosystems, it is important to consider different nitrogen nutrition methods of Fabaceae, Poaceae and Brassicaceae plants. Red and white clover fixed the larger part of nitrogen (2/3) from the atmosphere and supplied the agrocnose with extra nitrogen. Italian ryegrass and white mustard during the August – October months utilised the remaining nitrogen which had not been utilised by the main crops or had accumulated in the soil due to intensive micro-organism activity. All this prevented nitrogen from migrating into deeper soil layers and leaching. From the viewpoint of environmental protection, catch crops of white mustard and white clover mixture with Italian ryegrass are valuable in terms of nitrogen utilisation from the soil after cereal harvesting. Catch crops’ biomass is important for soil humic substances accumulation not only as organic carbon but also nitrogen source.

With cereal straw used as fertilizer the soil receives carbon-rich organic matter with a wide C to N ratio, which is 5.1–8.7 times higher compared with that for catch crops’ biomass. As a result, in the initial straw decomposition stages the amount of nitrogen is too little and insufficient for mineralization and does not secure a normal micro-organism metabolism and straw decomposition (Moran et al. 2005). Research evidence of Lithuanian and foreign researchers shows that mineral nitrogen or organic fertilizer rich in nitrogen needs to be additionally applied together with straw in order to increase soil biological activity and to create preconditions for soil organic matter humification (Berecz et al. 2004; Hege and Offenberger 2006; Tripolskaja et al. 2008). Moreover, straw rich in lignin, which (and its breakdown products) is humified at a higher rate than readily-metabolisable organic compounds.

3.2. Humic acids

The paper discusses humic substances – humic and fulvic acids, which vary most and take an active part in soil chemical processes. Humic acids are composed of mobile humic acids fraction ($C_{HA1}$). Humic acids are chemically bound with polyvalent cations of which the prevalent one is Ca$^{2+}$ ($C_{HA2}$) and bound with clay particles ($C_{HA3}$). The latter two fractions are attributed to stable or partially inert humus forms and are more resistant to decomposition, are characterised by a slower variation and higher humification degree compared with mobile humic acids (De Nobili et al. 2008).

Mobile humic acids are attributed to young and active humus forms and are characterised by a more rapid turnover in the soil (Olk 2006). This mobile part of soil organic matter can be utilised by micro-organisms as a source of carbon and energy. During mineralization process of these acids the soil is enriched by nutrients necessary for plant nutrition and plant above-ground mass formation.

In the first year (2004) of effect of the measures applied, mobile humic acids ($C_{HA1}$) accounted for on average 17.7% of the total humic acids content (Table 2). Nitrogen-rich, readily mineralising biomass of all catch crop species (with straw removed from the soil) incorporated into the

Table 1. Biomass of catch crops and straw incorporated into the soil and their quality

| Catch crop                     | DM t ha$^{-1}$ | Chemical composition |          |          |        | C : N |
|-------------------------------|----------------|----------------------|----------|----------|--------|-------|
|                               |                | N%       | P%       | K%       | crude fibre% |     |
| Above-ground biomass          |                |          |          |          |        |       |
| red clover                    | 3.0            | 3.58     | 0.26     | 3.15     | 17.4   | 12.5  |
| mixture of white clover and   | 2.32           | 2.90     | 0.26     | 3.54     | 24.0   | 18.1  |
| Italian ryegrass              |                |          |          |          |        |       |
| white mustard                 | 3.42           | 2.1      | 0.34     | 4.28     | 20.3   | 19.3  |
| Underground biomass           |                |          |          |          |        |       |
| red clover                    | 2.53           | 2.09     | 0.39     | 1.75     | 28.3   | 17.1  |
| mixture of white clover and   | 2.16           | 1.89     | 0.40     | 1.76     | 31.4   | 18.4  |
| Italian ryegrass              |                |          |          |          |        |       |
| white mustard                 | 2.21           | 1.62     | 0.26     | 1.17     | 39.0   | 21.2  |
| Straw                         | 5.0            | 0.41     | 0.06     | 0.90     | –      | 109   |
soil markedly increased (0.08–0.21 C g kg\(^{-1}\)) mobile humic acids content compared with the check treatment. Having incorporated straw into the soil (with mineral nitrogen fertilizer or catch crops’ biomass) the content of mobile humic acids increased, however, this content was by on average 0.22 C g kg\(^{-1}\) lower compared with the treatments where straw had not been used as fertilizer. It has been indicated that in the soils with low readily available nitrogen status nitrogen immobilization is possible in the first rapid decomposition stage. In the next decomposition stage the immobilized nitrogen becomes available to plants again (Vinten et al. 2002). With increasing mobile humic acids content, a significant increase in nitrogen concentration in the immobilized nitrogen becomes available to plants again rapid decomposition stage. In the next decomposition stage. In the next decomposition stage the immobilized nitrogen becomes available to plants again (Vinten et al. 2002). With increasing mobile humic acids content, a significant increase in nitrogen concentration in spring barley grain yield occurred (\(r = 0.69, p < 0.05\)), which suggests that mobile humic acids took part in plant nitrogen nutrition process.

The amount of the second fraction of humic acids (C\(_{HA2}\)) accounted for on average 25.8% of the total humic acids content. The amount of these acids, compared with their status before trial establishment, declined in all cases: with straw removal from the field by on average 0.12 C g kg\(^{-1}\) and with straw utilisation as fertilizer (N\(_{15}\)) by on average 0.19 C g kg\(^{-1}\). The third fraction of humic acids (C\(_{HA3}\)) in clay loam Cambisol accounted for the largest share of the total humic acids. After incorporation of catch crops’ biomass and straw the content of these acids declined by on average 0.22 C g kg\(^{-1}\), compared with the initial level before trial establishment. The effects of the measures applied were one-to-many. Their content was significantly reduced by straw fertilization (N\(_{83}\)), which was incorporated only during autumn ploughing. However, having incorporated straw together with the biomass of white clover mixture with Italian ryegrass, red clover or white mustard, their amount increased compared with the treatments where only catch crops biomass had been incorporated.

The most intensive humification processes (accumulation of humic acids) occurred in the soil having incorporated biomass of various catch crops (without straw incorporation). The amount of humic acids (ΣC\(_{HA}\)) was most appreciably influenced by mobile humic acids. Having incorporated the biomass of only catch crops – red clover, white clover and Italian ryegrass mixture and white mustard, ΣC\(_{HA}\) content increased (0.10–0.13 C g kg\(^{-1}\)), compared with the check treatment. Straw incorporated together with the biomass of white clover and Italian ryegrass mixture or Brassicaceae plants also tended to increase the total humic acids content. The lowest contents of these acids were identified in the soil where straw had been spread on the soil surface and nitrogen fertilizer had been applied for its mineralization.

In the second year (2005) of effect of the measures applied, formation of more stable humic acids was noted. The content of mobile humic acids compared with that in the first year of effect almost halved (accounted for 9.5% of the total humic acids content). However, the content of these acids when straw had been removed still remained higher compared with the treatments with straw fertilization. This suggests that incorporation of catch crops’ above-ground biomass and straw (with mineral nitrogen fertilizer or plant biomass) increased mobile humic acids content for two years in succession, which is confirmed by

### Table 2. Change of humic acids (C\(_{HA}\)) fractions (C g kg\(^{-1}\) of soil) in the soil (0–25 cm) after catch crop biomass and straw incorporation

| Catch crop (B) | Straw use (A) | Before trial establishment | Without catch crop | Red clover | Mixture of white clover and Italian ryegrass | White mustard | Means for factor A | LSD 05 |
|---------------|--------------|----------------------------|---------------------|------------|---------------------------------------------|--------------|-------------------|--------|
|               | C\(_{HA1}\)  | C\(_{HA2}\)  | C\(_{HA3}\)  | ΣC\(_{HA}\)  | C\(_{HA1}\)  | C\(_{HA2}\)  | C\(_{HA3}\)  | ΣC\(_{HA}\)  |        |
|               | 0.35         | 1.23         | 2.57         | 4.15       | 0.75         | 1.10         | 2.40         | 4.25       | 0.64   |
|               |              |              |              |            | 0.86         | 1.21         | 2.31         | 4.38       | 0.66   |
|               |              |              |              |            | 0.96         | 0.96         | 2.43         | 4.35       | 0.59   |
|               |              |              |              |            | 0.83         | 1.18         | 2.34         | 4.35       | 0.61   |
|               |              |              |              |            | 0.85         | 1.11         | 2.37         | 4.33       | 0.63   |
|               | C\(_{HA1}\)  | LSD 05 A–0.05; B–0.09; AB–0.13; C\(_{HA2}\) LSD 05 A–0.09; B–0.16; AB–0.22; C\(_{HA3}\) LSD 05 A–0.09; B–0.15; AB–0.22; ΣC\(_{HA}\) LSD 05 A–0.17; B–0.30; AB–0.43 |
|               | 0.47         | 1.40         | 2.30         | 4.17       | 0.34         | 1.25         | 2.39         | 4.39       | 2.63   |
|               | 0.52         | 1.41         | 2.26         | 4.19       | 0.30         | 1.44         | 2.51         | 4.25       | 2.60   |
|               | 0.45         | 1.23         | 2.54         | 4.22       | 0.34         | 1.37         | 2.60         | 4.31       | 2.53   |
|               | 0.47         | 1.41         | 2.37         | 4.26       | 0.34         | 1.37         | 2.53         | 4.24       | 2.53   |
| second year (2005) | | | | | | | | | |
the correlation between mobile humic acids contents in the first and second year of effect \((r = 0.98, p < 0.01)\). The content of the second fraction of humic acids \((C_{HA2})\) increased \((by on average 0.31 \text{ C g kg}^{-1}\), compared with the first year of effect\) and accounted for on average 32.7\% of \(\Sigma C_{HA}\). This agrees with the data found in literature suggesting that the content of readily metabolizable compounds declines and only stable humic substances persist and build up and secure long-term, continuous nutrient and energy supply (De Nobili et al. 2008). Straw utilization as fertilizer increased the content of humic acids bound with calcium \((C_{HA2})\) by on average 0.33 \text{ C g kg}^{-1}, in the treatments with straw removal by on average 0.30 \text{ C g kg}^{-1}, compared with the findings from the first year of effect. In the second year after catch crops’ biomass incorporation the content of these acids was by on average 0.16 \text{ C g kg}^{-1} higher compared with that before trial establishment. In the treatments where the straw had been removed from the field and no agricultural practices had been applied \(C_{HA2}\) fraction was found to be the highest. However, in a similar treatment but with straw fertilization the content of these acids was significantly lower \((0.36 \text{ C g kg}^{-1})\), compared with that in the check treatment.

Biomass of red clover and white clover mixture with Italian ryegrass incorporated into the soil tended to increase the content of these acids in the treatments both with and without straw. Statistical analysis showed that during the experimental period, with increasing humic acids content in the first \((r_1)\) and second \((r_2)\) year of effect the content of humic acids bound with clay minerals declined \((r_1 = -0.67, p < 0.05 \text{ and } r_2 = -0.64, p < 0.05)\), whereas straw utilization as fertilizer promoted the build up of these acids. Averaged data indicate that their highest content \((0.16 \text{ C g kg}^{-1} \text{ more})\) was recorded having used straw as fertilizer compared with the treatments where straw had been removed from the field. All the agricultural practices used in combination with straw increased the content of humic acids bound with soil clay particles. Humic acids fraction \(\Sigma C_{HA}\) increased having used straw as fertilizer together with red clover or white mustard biomass. Literature references suggest that decomposition cycles of readily degradable and conditionally resistant to degradation organic matter are related since readily degradable organic matter provides microorganisms, participating in aromatic polymers degradation, with carbon, energy and nutrients, so that they could degrade rather stable compounds (Орлова 1990; Olk 2006).

In the second year of effect of the measures applied, soil organic matter humification was increased by both catch crops biomass alone and in combination with straw. The total humic acids content \((y)\) was significantly increased by the fractions of humic acids bound with calcium and humic acids strongly bound with clay minerals \((r_1, r_2, \text{ respectively})\). These relationships are statistically significantly reflected by the correlation coefficients \(r_1 = 0.68, p < 0.05\) and \(r_2 = 0.67, p < 0.005\). The total content of humic acids increased by on average 0.10 \text{ C g kg}^{-1} compared with that before trial establishment. In the intensive cereal crop rotation involving straw fertilization with the addition of mineral nitrogen fertilizer \((N_{fa})\), like in the first year of effect, the total content of humic acids significantly declined \((0.46 \text{ C g kg}^{-1})\), compared with the check treatment or by 0.17 \text{ C g kg}^{-1} compared with that before the trial establishment. Mineral nitrogen fertilizer is a means to rapidly increase the productivity of arable land but it does not provide long-term and stable effect. Unused nitrogen fertilizer is often leached from the soil during the autumn-winter period. The greatest positive influence on \(\Sigma C_{HA}\) formation was exerted by straw utilization as fertilizer together with the biomass of red clover or white mustard catch crops.

Research conducted in other soils with a lower potential productivity showed that humus in sandy loam \(Luvisol\) is composed of a higher percentage of mobile humic acids \(C_{HA1}(45.2–50.5\%\) and a lesser percentage of conditionally resistant to degradation \(C_{HA3}(35.8–40.2\%)\) (Tripolskaja et al. 2008). While in gleyic \(Eutric Panosol\) humic acids composition was dominated by the fraction of humic acids bound with calcium \((41.2–49.4\%)\) (Jodaugiene et al. 2001). The findings about humic acids fractions suggest that humic substances of heavy loam are characterised as being of low mobility and strongly bound, which is determined by a high content of clay particles that interact with soil organic matter (Wiseman, Püttrmann 2006). Environmental factors, such as climatic conditions and soil properties, are thought to significantly interact with specific management practices determining soil carbon accumulation and mineralization rate (Marianni et al. 2010).

### 3.3. Fulvic acids

Fulvic acids are characterised by a lower carbon and elevated oxygen contents, are more readily-water – soluble and have a lower molecular mass compared with humic acids. Some authors attribute them to the predecessors of humic acids, others to their breakdown products (Тейт 1991). Compared with the status before trial establishment, the most variable were found to be the first three fractions \((C_{FA1a}, C_{FA1}, C_{FA2})\), especially in the treatments where green biomass of catch crops had been incorporated (Table 3). In the first year these fractions in the total fulvic acids accounted for a different share – 13.1, 20.2, 12.7\%, respectively (averaged data). Correlation regression analysis suggests that with increasing humic acids content, the content of fulvic acids \(C_{FA1a} \text{ and } C_{FA1}\) fractions increased also (correlation coefficients \(p = 0.796, p < 0.01 ; r = 0.848, p < 0.01\)). The total content of mobile fulvic acids \((C_{FA1} + C_{FA2})\) was markedly higher (by on average 0.86 \text{ C g kg}^{-1}) compared with the respective humic \(C_{HA1}\) and \(C_{HA2}\) acids. The content of “aggressive” \((1a)\) fulvic acids fraction was most significantly reduced (by on average 0.08 \text{ C g kg}^{-1}) by straw use for fertilization. The content of fulvic acids fraction \(C_{FA1}\) was enhanced by the incorporated biomass of red clover and white clover mixture with Italian ryegrass. The content of these acids also increased having incorporated straw with mineral nitrogen fertilizer \((N_{fa})\) and with red clover biomass.
The content of C\textsubscript{FA1} fraction, compared with its status before trial establishment, declined (by on average 0.31 C g kg\textsuperscript{-1}). The content of these acids was most markedly reduced by Fabaceae catch crops biomass and straw used with nitrogen fertilizer. With increasing contents of mobile humic (C\textsubscript{HA3}) and fulvic acids (C\textsubscript{FA1}), the status of C\textsubscript{FA2} fraction significantly declined (correlation coefficient \( r = -0.67, p < 0.05; r = -0.83, p < 0.01 \)). Of all fulvic acids fractions C\textsubscript{FA3} was the most abundant. It increased with an increase in humic acids fraction C\textsubscript{HA3} (correlation coefficient \( r = 0.685, p < 0.05 \)). The lowest content of this fraction was identified in the treatments with no organic additives or with straw incorporation (N\textsubscript{A3}). However, when catch crops’ biomass had been used as fertilizer or biomass together with straw, the content of these acids increased compared with the check treatment.

In the first year, after catch crops biomass incorporation the total content of fulvic acids was (by on average 0.63 C g kg\textsuperscript{-1}) higher compared with that of humic acids. Fulvic acids content \( \Sigma C_{FA} \) after the measures applied increased, except for the treatment where straw had been used as fertilizer, compared with that before trial establishment. Averaged data indicate that the highest fulvic acids content was in the treatments with only catch crop biomass incorporation. The correlation-regression analysis shows that the sum of fulvic acids increased with an increase in C\textsubscript{FA1} fraction, C\textsubscript{FA2} fraction and sum of humic acids \( \Sigma C_{HA} \) (correlation coefficients \( r = 0.913, p < 0.01; r = 0.637, p < 0.05; r = 0.658, p < 0.05 \), respectively).

In the second year after all catch crops’ biomass incorporation fulvic acids mobile fractions C\textsubscript{FA1a} and C\textsubscript{FA1} tended to decline, compared with the first year of effect of measures applied. The content of “aggressive” fulvic acids (C\textsubscript{FA1a}) declined already in the second year after catch crops’ biomass incorporation and almost reached the same level which had been before trial establishment. The lowest content of this fraction was measured having incorporated white mustard biomass together with straw. “Aggressive” C\textsubscript{FA1a} fraction increased with an increase in mobile humic acids C\textsubscript{HA1} and fulvic acids C\textsubscript{FA1} fraction in the first year (correlation coefficients \( r = 0.656, p < 0.05; r = 0.655, p < 0.05 \), respectively). The content of humic acids fractions in the first and second year influenced mobile fulvic acids C\textsubscript{FA1}, which varied in a similar pattern as mobile humic acids (correlation coefficients \( r = 0.766, p < 0.01; r = 0.818, p < 0.01 \)). The second fraction of fulvic acids C\textsubscript{FA2}, compared with its status in the first year, increased: having used catch crops’ biomass as fertilizer by on average 0.16 C g kg\textsuperscript{-1}, having incorporated straw together with catch crop biomass by on average 0.24 C g kg\textsuperscript{-1}, compared with respective data from the first year of effect. The content of these acids differed little between the treatments when catch crops’ biomass had been used together with straw. The lowest content of these acids was found having incorporated only red clover or white mustard biomass compared with the check treatment. The third fraction of fulvic acids (C\textsubscript{FA3}) tended to declined compared with the first year of effect.

The lowest content of these acids was recorded having incorporated red clover biomass together with straw, while the highest content was measured having incorporated white mustard biomass together with straw.

### Table 3. Change of fulvic acids (C\textsubscript{FA}) fractions (C g kg\textsuperscript{-1} of soil) in the soil (0–25 cm) after catch crop biomass and straw incorporation

| Catch crop (B) | Straw use (A) |removed from the field | chopped and spread |
|---------------|---------------|-----------------------|---------------------|
|               | C\textsubscript{FA1a} | C\textsubscript{FA1} | C\textsubscript{FA2} | C\textsubscript{FA3} | \( \Sigma C_{FA} \) | C\textsubscript{FA1a} | C\textsubscript{FA1} | C\textsubscript{FA2} | C\textsubscript{FA3} | \( \Sigma C_{FA} \) |
| Before trial establishment | 0.053 | 0.72 | 0.092 | 0.254 | 0.470 |
| Without catch crop | 0.67 | 0.86 | 0.73 | 2.46 | 4.72 | 0.56 | 1.00 | 0.45 | 2.13 | 4.14 |
| Red clover | 0.68 | 1.13 | 0.48 | 2.51 | 4.80 | 0.60 | 0.94 | 0.67 | 2.75 | 4.96 |
| Mixture of white clover and Italian ryegrass | 0.67 | 1.14 | 0.38 | 2.79 | 4.98 | 0.58 | 0.81 | 0.71 | 2.81 | 4.91 |
| White mustard | 0.65 | 0.99 | 0.68 | 2.72 | 5.04 | 0.60 | 0.85 | 0.76 | 2.63 | 4.84 |
| Means for factor A | 0.67 | 1.03 | 0.57 | 2.62 | 4.89 | 0.59 | 0.90 | 0.65 | 2.58 | 4.71 |
| second year (2005) | | | | | |
| Without catch crop | 0.56 | 0.98 | 0.85 | 2.36 | 4.75 | 0.51 | 0.80 | 0.83 | 2.57 | 4.71 |
| Red clover | 0.54 | 0.95 | 0.64 | 2.46 | 4.59 | 0.55 | 0.75 | 0.86 | 2.33 | 4.49 |
| Mixture of white clover and Italian ryegrass | 0.55 | 0.91 | 0.78 | 2.50 | 4.74 | 0.54 | 0.81 | 0.83 | 2.58 | 4.76 |
| White mustard | 0.55 | 0.88 | 0.66 | 2.47 | 4.57 | 0.52 | 0.65 | 1.02 | 2.77 | 4.96 |
| Means for factor A | 0.55 | 0.93 | 0.73 | 2.45 | 4.66 | 0.53 | 0.75 | 0.89 | 2.56 | 4.73 |
The content of $C_{FA1}$ declined with an increase in mobile fulvic acids $C_{FA1}$ and $C_{FA2}$ (correlation coefficients $r = -0.77, p < 0.01$; $r = -0.69, p < 0.05$). The total fulvic acids content ($\Sigma C_{FA}$) was most markedly increased by fulvic acids $C_{FA2}$ and $C_{FA3}$ (correlation coefficient $r = 0.68, p < 0.05$; $r = 0.69, p < 0.05$, respectively). The content of these acids was most markedly reduced by red clover biomass, incorporated alone or together with straw and by white mustard biomass incorporated alone. However, having incorporated white mustard biomass together with straw, the content of these acids was the highest (0.26 C g kg$^{-1}$ higher compared with that before trial establishment). Averaged data indicate that the total content of fulvic acids inappreciably declined, while the total humic acids content increased compared with their status before trial establishment.

### 3.4. Humus quality indicators

The total content of humic substances ($\Sigma C_{HA} + \Sigma C_{FA}$) in the first year of effect tended to increase after catch crop (red clover, white clover mixture with Italian ryegrass, white mustard) biomass incorporation compared with that in the check treatment (Table 4), whereas straw used as fertilizer increased humic substances content only when applied with red clover biomass. In the second year of effect, the lowest sum of humic and fulvic acids was recorded for the treatments where no soil ameliorating measures had been applied (check treatment). The largest increase in the sum of humic and fulvic acids occurred having incorporated biomass of red clover, white clover mixture with Italian ryegrass and white mustard compared with that of the check treatment and with that before trial establishment.

Having used straw as fertilizer, the sum of $\Sigma C_{HA} + \Sigma C_{FA}$ was increased only when straw had been incorporated together with red clover or white mustard biomass compared with the check treatment. Humus quality is best reflected by the ratio of humic to fulvic acids ($C_{HA}:C_{FA}$). In the first year of plant biomass incorporation the highest $C_{HA}:C_{FA}$ ratio was established in the check treatment with no soil ameliorating organic additives and in the treatment with red clover biomass incorporation. In all other cases this ratio tended to decline. In the second year of effect of measures applied the ratio of $C_{HA}$ to $C_{FA}$ tended to increase. The highest ratio was determined having incorporated straw together with red clover biomass.

When estimating soil humification processes, humification degree is an important factor, which indicates a share of humic acids in the SOC ($\Sigma C_{HA} : \text{SOC} \times 100$). Statistical analysis suggests that with increasing ratio of humic to fulvic acids humification degree increased ($r = 0.73, p < 0.05$). In the first year after various catch crops’ biomass incorporation, humification degree in most cases increased or remained unaltered, except for the treatments where straw had been incorporated with mineral nitrogen fertilizer or red clover biomass. In the second year of effect, degree of humification tended to decline. However, having incorporated straw together with red clover biomass humification degree was the highest.

Soil organic carbon (SOC) content in the first year of catch crops’ effect increased by on average 0.025 percentage point compared with that before trial establishment. However, when straw had been used as fertilizer
with mineral nitrogen addition (N₂₄₈) SOC content was the lowest (0.06 percentage point less compared with its status before trial establishment). In the second year of effect SOC content increased (by on average 0.05 percentage point) in all treatments compared with its status before trial establishment.

Organic matter humification in the soil occurs due to oxidation, reduction, hydrolysis, condensation and other chemical reactions with the participation of microorganisms. The newly formed products of various complexity are involved again into organic matter synthesis and destruction processes that occur continuously (Орлов 1990). However, the stability of humic substances in the soil is determined by a regular introduction of certain amount of organic matter, which determines formation of new humic substances and their destruction due to the formation of a stable amount of active humus forms (Marinari et al. 2010).

In Endocalcari – Endohypogleyic Cambisol used for agricultural production, biomass of catch crops (red clover, white clover mixture with Italian ryegrass, white mustard) incorporated alone or together with winter wheat straw, in the first year increased the content of mobile humic acids (C_HA), which are essential for plants and soil micro-organisms as nutrient and energy potential. With increasing mobile humic acids content an increase occurred in the amount of so-called “aggressive” and free fulvic acids (r = 0.80, p < 0.01; r = 0.85, p < 0.01, respectively). Conditionally stable humic acids fractions C_HA and C_HA formed more intensively in the second year of effect of measures applied. The biomass of Fabaceae family catch crops incorporated alone or with straw increased the content of humic acids bound with calcium (C_HA). The fraction of conditionally stable humic acids bound with clay particles (C_HA) declined in the treatments where only the biomass of catch crops had been incorporated compared with its status before trial establishment. This was determined by higher contents of mobile humic acids and free fulvic acids that formed due to nitrogen-rich plant above-ground biomass incorporation into the soil. Having incorporated catch crops biomass together with straw, C_HA fraction tended to increase or remained unaltered as it had been before the trial establishment. Inappreciable reduction in the total fulvic acids content and an increase in humic acids content, compared with their status before trial establishment, determined positive changes in the main humus quality indicators – C_HA:CF_A ratio and degree of humification; which were the most marked (0.98 and 31.1% respectively) having incorporated red clover biomass together with straw into the soil.

Mineral nitrogen N₂₄₈ incorporation together with straw increased soil organic matter mineralization rate and determined a reduction in humic acids content.

4. Conclusions

1. Biomass of catch crops (red clover, white clover mixture with Italian ryegrass, white mustard) incorporated for green manure increased the soil organic matter (4.48–5.63 t ha⁻¹ DM) and nitrogen resource. Experimental data suggest that narrow carbon to nitrogen ratio (C:N) was in the aboveground biomass of red clover (12.5), wide – in straw (109).

2. In the first year nitrogen-rich, readily mineralising biomass of all catch crop incorporated into the soil markedly increased (0.08–0.21 C g kg⁻¹) mobile humic acids content compared with the check treatment. Conditionally stable humic acids fractions C_HA and C_HA formed more intensively in the second year of effect of measures applied. The agricultural practices used in combination with straw increased the content of humic acids bound with calcium and bound with soil clay particles. In the first year of effect of the measures applied, the most intensive (4.35–4.38%) humification processes (accumulation of humic acids C_HA) occurred in the soil having incorporated biomass of various catch crops, in the second year – having incorporated catch crop biomass in combination with straw (4.25–4.40%).

3. In the first year, the total content of humic substances (ΣC_HA + ΣC_FA) was significantly dependent upon straw and cover crops, in the second upon only straw. The highest contents of humic substances were identified in the soil where straw had been applied with biomass of white mustard.

4. Inappreciable reduction in the total fulvic acids content and an increase in humic acids content, determined positive changes in the main humus quality indicators – C_HA:CF_A ratio and degree of humification, which were the most marked (0.98 and 31.1% respectively) having incorporated red clover biomass together with straw into the soil.

References

Baltrenas, P.; Pranskevičius, M.; Lietuvninkas, A. 2010. Investigation and assessment of dependences of the total carbon on pH in Neris regional park soil. Journal of Environmental Engineering and Landscape Management 18(3): 179–187. doi:10.3846/jecelm.2010.21

Berecz, K.; Kismanyoky, T.; Debreczeni, K. 2004. Studying the effect of organic matter recycling combined with mineral N fertilization in long-term field and model pot experiments, Archives of Agronomy and Soil Science 50(1): 65–72. doi:10.1080/03650340310001627603

Bučienė, A. 2003. Žemdirbystės sistemų ekologiniai ryšiai [Ecological relations of cropping systems]. Klaipėda.

Catt, J. A.; Howse, K. R.; Christian, D. G.; Lane, P. W.; Harris, G. L.; Goss, M. J. 1998. Strategies to decrease nitrate leaching in the Brimstone Farm Experiment, Oxfordshire, UK, 1988–1993: the effects of winter cover crops and unfertilized grass leys, Plant and Soil 203(1): 57–69. doi:10.1023/A:1004389426718

De Nobili, M.; Contin, M.; Mahieu, N.; Randall, E. W.; Brookes, P. K. 2008. Assessment of chemical and biochemical stabilization of organic C in soils from the long-term experiments at Rothamsted, Waste Management 28(4): 723–733. doi:10.1016/j.wasman.2007.09.025

Feiza, V.; Šimanskaitė, D.; Deveikytė, I.; Šlepetienė, A. 2005. Pagrindinio žemės dirbimo supaprastinimo galimybės [Plant growing and biodiversity in simplified agriculture]. Klaipėda.
Agriculture], Biologija in unserer Zeit 29(3): 177–183. doi:10.1002/biuz.960290308

Hege, U.; Offenberger, K. 2006. Effect of differentiated mineral fertilisation and organic manuring on yield, product quality and N balance in the international permanent organic nitrogen experiment (IOSDV) Pučh, Archives of Agronomy and Soil Science 52(5): 535–550. doi:10.1080/03650340600931650

Jodaugienė, D.; Motuzas, A.; Stanevičius, A.; Raudonius, S. 2001. skirtinės žemės dirbimas ir giliaus glėjšo pasostin-tojo palaužėnų humuso kokybė, smulkiadispersė dalis bei jos organinė ir mineralinė sudėtis [Different soil till-age and humus quality, clay fraction content and its or- ganic and mineral composition in Endohypoglycic-Endor Planosol], Žemės ūkio mokslai 4: 3–10.

Magyla, A.; Šateikienė, D.; Šlepetienė, A. 1997. Augalinių įrąsiųjų bei laisvųjų fulvinių rūgščių kiekis (atitinkamai prieš bandymą, lėmė teigiamus pagrindinių humuso kokybės rodiklių – C, FR2, FR3, FR4 kiekių pokyčius). Įterpus vien tarpinių biomases ar kartu su šiaudais, pirmaisiais metais judriųjų huminių rūgščių (CHR) kiekis, padidėjo 0,024–0,061 %. Didėjant judriųjų huminių rūgščių kiekiui, didėjo ir agresyviųjų (CHR) frakcijos intensyviai formavosi antraisiais taikytų priemonių poveikio metais. Pupinių še- nių augalų biomasė, įterpta viena ar su šiaudais, didino huminių rūgščių junginių su kalciu (CHR) kiekį. Įterpus tarpinių pasėlių biomasę kartu su šiaudais, huminių rūgščių frakcija tendencingai didėjo ar prilygo buvusiai prieš bandymą. Suminė įrąsiųjų rūgščių kiekio neįmanoma sumažėjimas ir huminių rūgščių kiekio padidėjimas, palyginti su išvystomis pries bandymą, lemė teigiamus pagrindinių humuso kokybės rodiklių – C, CHR, CFS, CHFR santykio ir humifikacijos laipsnio poky-
čius; jie ryškiausi buvo į dirvožemį įterpus raudonųjų dobilų fitomasės kartu su šiaudais. Patręšus mineralinėmis azoto trąšomis N<sub>45</sub> kartu su šiaudais, didėjo dirvožemio organinių medžiagų mineralizacijos intensyvumas ir sumažėjo huminių rūgščių.

Reikšminiai žodžiai: gležniškas rudžemis, tarpiniai pasėliai, šiaudai, huminės ir fulvinės rūgštys.