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Assessment of physicochemical and agrochemical indicators of the composting process

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Abstract

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The positive balance of soil organic matter (SOM) in arable land is the main issue of sustainable agriculture. Organic fertilization via composting is an effective method of soil productivity support. The deficit of traditional organic fertilizers creates the need to explore new sources of organic matter such as agricultural waste, sewage sludge, municipal and industrial waste.

The different types of organic materials were researched of their use as fertilizers by the method of composting with natural soils for circular economy purposes. That, on the one hand, is related to full use of resources, and on the other for a positive balance of humus in soils under conditions of intensive agriculture. The study included both environmental bioresources (biochar and compost) as well as traditionally known manure (cow and sheep mature) and sewage sludge from domestic wastewater.

The composting is done with two soil types - Alluvial-meadow soil and Smolnitza. The following phisico-chemical and agrochemical parameters were analyzed: pH in water; electrical conductivity; cation exchange capacity and base of saturation; the content and composition of the organic matter; total nitrogen; mobile forms of nitrogen, phosphorus and potassium.

The studied indicators reflect a more profound change with the addition of organic materials to Alluvial meadow soil compared with the Smolnitza soil type. This is mainly due to changes in CEC characteristics of both soil types. Changes in the content and composition of soil organic matter are highly indicative of the composting process. They are more sensitive for the Alluvial-meadow soil, where the soil organic matter from humic-fulvic type is converted to humic type by addition of all organic materials, except the cow mature.

Keywords: biochar; manure; sludge; humic acids; E_4/E_6

Introduction

The positive balance of humus in arable land is a major issue for sustainable agriculture, and organic fertilization is a good practice in this case. The deficit of traditional organic fertilizers creates the need to explore new sources of organic matter, such as agricultural waste, sewage sludge, municipal and industrial wastes. Data from the European Commission for the Agriculture Sector indicate that up to date only ~ 5% of organic waste is recycled and used as fertilizers. The statistical studies indicate that if more bio-wastes are recycled, they could replace up to 30% of inorganic fertilizers (https://ec.europa.eu/environment/circular-economy/index_en.htm). The direct addition of organic waste to the soil can have adverse effects such as phytotoxicity, nitrogen immobilization, the introduction of toxic compounds and pathogen microorganisms.

Composting is a way for recycling of organic waste materials and an effective method of increasing soil fertility. The most commonly used composts are straw, wood bark, plant residues (Senesi, 1989; Manolov et al., 2003). Biochar is a focus of studies which are looking for solutions for how to improve some soil properties, reduce fertilizer rates and increase yields (Mikova, 2014). Plant waste materials are suitable as substrates for aerobic composting, not only because of the high cellulose content but for the microorganisms needed for the decomposition processes (Roper, 1985; Kostov et al., 1994). The effectiveness of organic fertilizers for plant growth and productivity has been proven in various scientific studies (Petkova, 2016; Petkova & Ivanova, 2018; Petkova & Kutev, 2017; Ivanova & Petkova, 2019). Biochar has been increasingly applied as soil ameliorant with the purpose to sequester carbon and mitigate climate change effects (Zhang et al., 2014; Simeonova et al., 2019). Indicators for assessing the maturity of compost are changes in the composition of organic matter to control the processes of biodegradation of organic waste and the production of rich food composts. Decomposition of organic materials is faster with increasing microorganisms activity (Kostov et al., 1994).

The purpose of the study is to evaluate the agrochemical and the physicochemical parameters of soils treated with different organic waste materials as ameliorants.

Materials and Methods

The methodological approach contains composting lab experiment with five types of organic waste materials and two different soil types with contrasting physicochemical properties. Organic materials can be grouped as follows: two types of bioresources - biochar and plant compost; two types of manure - cow and sheep manure and sludge from wastewater treatment plant (WWTP).

The tested organic waste materials are included in the list of eligible bio-waste and biodegradable waste for the production of compost and fermentation product according to Regulation for separate collection of bio-waste and treatment of biodegradable waste (Regulation 20, 2017). The two soil types used for composting are Alluvial-meadow soil from the Institute's experimental field in Tsalapitsa, Plovdiv region and Smolnitsa from the experimental field at Bojurishte, Sofia region. Composting is in two variants at a ratio compost to soil 1: 9, 100 g in total according to the following scheme:

Variant 1. Alluvial-meadow soil - control
Variant 2. Smolnitza soil - control
Var.1.1 (Var.2.1) +biochar ;
Var.1.2 (Var.2.2)+plant compost ;
Var.1.3 (Var.2.3)+ cow fertilizer ;
Var.1.4 (Var.2.4) + sheep fertilizer ;
Var.1.5 (Var.2.5) + sludge from WWTP.

Organic waste materials were added to the soils at constant 10% moisture and were incubated for 3 weeks. Following the incubation process, the following parameters were analysed: pH in water (ISO 10390:2011); electrical conductivity (Popandova,1995); cationic exchange capacity (CEC) and base of saturation (BS) (Ganev & Arsova, 1980); determination of total organic carbon by the modified Turin method (Filcheva & Tsadilas, 2002); composition of soil organic matter (SOM), by mixed alkaline extraction with 0.1 M $Na_4P_2O_7$ и 0.1 M NaOH, determination of total contents of humic and fulvic acids; b) alkaline extraction with 0.1 M NaOH, determination of the free and mobile R_2O_3 humic and fulvic acids; c) acidic fraction by extraction with 0.1 N H_2SO_4.

Humic acid absorption is a spectrophotometric analysis which determines the extinction of the absorption spectra of the humic acids at 465 and 665 nm (cm^{-1}). The optical density of the humic acids and the degree of aromaticity and condensation of humic substances are reported as E_4/E_6 ratio.

Total nitrogen was determined by the Kjeldahl method; content of ammonium and nitrate nitrogen by the Bremner method (and labile phosphorus and potassium by the method of Ivanov (1984);

Working hypotheses for composted variants are related to increasing the amount of organic carbon as a major element of organic ameliorates. Content of organic carbon and C: N ratio was used as a criterion for compost quality according to the "Ordinance for separate collection of bio-waste and treatment of biodegradable waste (2017)".

Agrochemical parameters as the available forms of NPK were compared to thresholds used by National Agricultural Advisory Service: medium reserve 20-60 mg/kg $NO_3 + NH_4$: 13-30 mg/100 g P_2O_5 : 15-30 mg/100 g K_2O, low reserve below $N_{20}P_{13}K_{15,}$ and high reserve above $N_{60}P_{30}K_{30}$ (Atanasov et al., 2009).

Results and Discussion

The difference between the basic physicochemical and agrochemical parameters of the starting organic materials (bioresources), manure and sludge are shown in Table 1. Both soil types possess slightly acidic pH, the sewage sludge – near neutral pH, while the cow and sheep manure, the compost and the biochar have alkaline pH. The electrical conductivities of the manures and the sludge exceed those for natural soils and correlate with the higher contents of available N, P and K (Table 1, Table 2 and Table 3). Cation exchange capacity (CEC) decreases in the order: Sewage sludge > Compost > Cow manure > Sheep manure > Biochar. All organic waste materials are saturated with bases, but the lowest base saturation is for the sludge from WWTP (86.4%). Both soil types have contrasting physicochemical characteristics, the Alluvial-meadow soil has a medium, unlike the Smolnitza which has a high sorption capacity (Penkov, 1986). The content of total nitrogen in both soils is between 0.1- 0.2% according to the classification (Penkov, 1986). Its removal will be faster at the Alluvial Meadow soil compared to the Smolnitza depending on the soil physicochemical characteristics. Preliminary analysis suggests that composting of the Alluvial-meadow soil with the organic materials will balance the inadequate nitrogen regime since organic materials have from 0.34 to 3.23% total N. The biochar and the sludge from WWTP are organic waste materials with the least total nitrogen content. The Smolnitza soil has phosphorous deficiency because its content is below the thresholds for insignificant quantity, i.e. below 13 P_2O_5 mg/100 g (Atanasov et al., 2009). All organic materials except biochar have high amounts of mobile phosphorus, that's why we expected changes after composting (Table 1).

The Alluvial-meadow soil is of low to medium humus content, while the Smolnitza is of high humus content according to Penkov (1986). It's expected that the total carbon content in all the composted variants will increase due to its high content in the starting materials from 4.58% to 31.72%. According to the content of organic carbon the waste materials are aligned in the following order (Table 4): Cow manure < Sheep manure < Compost < Sewage Sludge < Biochar.

The total content of humic and fulvic acids (HAs+FAs) in the Smolnitza are higher than in the Alluvial meadow soil. The soluble organic acids (HAs+FAs) in organic materials exceed those in the experimental soils and range 2.63 to 3.71%, and with different qualitative characteristics (Table 5 and Table 6). The organic matter of the Smolnitza soil is of humic type, against the Alluvial-meadow soil which is of humic-fulvic type (Grishina & Orlov, 1978). While in the soils, the organic matter is represented by more stable organic acids, in the organic amendments they are more mobile because the fulvic acids predominate, which are free or bound

Table 1. Physicochemical and agrochemical parameters in organic waste materials before their composting

Type	pH H_2O	Electrical conductivity	CEC	Base saturation	Total N	NH_4+NO_3	P_2O_5	K_2O
		mS.cm^{-1}	cmol.kg^{-1}	%	%	mg.кg^{-1}	mg.100g^{-1}	
Biochar	7.9	0.13	10.9	100	0.36	47.2	15.2	427
Compost	8.7	1.61	44.7	99.6	1.18	61.0	156	1289
Cow manure	7.7	2.52	39.5	97.7	1.92	287	298	1670
Sheep manure	8.2	2.87	22.5	98.7	1.52	176	290	1855
Sludge from WWTP	6.8	0.55	51.6	86.4	3.23	247	261	181

Table 2. Physico-chemical and agrochemical parameters for composting of Alluvial meadow soil with different organic waste materials after 21 days

Variants	pH H_2O	Electrical conductivity	CEC	Base saturation	Total N	NH_4+NO_3	P_2O_5	K_2O
		mS.cm^{-1}	cmol.kg^{-1}	%	%	mg.кg^{-1}	mg.100g^{-1}	
Alluvial meadow Soil	6.1	0.10	16.5	73.9	0.100	19.6	12.7	19.4
Var.1.1 + Biochar	7.2	0.10	15.3	83.0	0.146	20.7	12.1	37.1
Var.1.2 + Compost	7.5	0.18	16.5	84.9	(0.104)	35.7	42.1	85.3
Var.1.3 + Cow manure	6.6	0.41	24.5	86.4	0.333	81.8	104	141
Var.1.4 + Sheep manure	6.7	0.46	20.4	86.8	(0.109)	40.3	69.3	90.0
Var.1.5 + Sludge from WWTP	6.6	0.15	23.3	80.7	0.164	19.6	100	25.7

Table 3. Physico-chemical and agrochemical parameters for composting of Smolnitza with different organic waste materials after 21 days

Variants	pH H_2O	Electrical conductivity	CEC	BS	Total N	NH_4+NO_3	P_2O_5	K_2O
		mS.cm^{-1}	cmol.kg^{-1}	%	%	mg.кg^{-1}	mg.100g^{-1}	
Smolnitza	6.1	0.1	51.5	90.7	0.17	35.1	3.30	43.3
Var.2.1 + Biochar	6.4	0.1	51.1	91.2	0.17	25.3	3.50	56.2
Var.2.2 + Compost	6.4	0.16	50.6	91.1	0.23	24.2	23.8	153
Var.2.3 + Cow manure	6.3	0.7	52.0	91.9	0.23	51.8	22.5	68.0
Var.2.4 + Sheep manure	6.4	0.49	50.8	92.5	0.16	48.7	67.6	145
Var.2.5 + sludge from WWTP	6.5	0.18	53.2	90	0.32	37.4	118	49.0

to R_2O_3. The optical density of humic acids is an indicator of changes in the composted variants. The soils have high optical density, the E_4/E_6 ratio is 3.51 in Smolnitza and 4.04 in the Alluvial-meadow soil.

The ratio E_4/E_6 varies from 4.78 to 7.90 and 9.14 for the compost and the cow manure, respectively. The free humic acids predominate and the ratio varies widely from 5.26 to 9.08. The results published by other authors prove that the humic acids E_4/E_6 ratios about 4.04 indicate high-quality of soil organic matter. In case that fulvic acids predominate, the E_4/E_6 ratio reaches values of 6.17, while when humic acids of higher sizes predominate, the value is 4.34 (Eshwar et al., 2017). This ratio does not depend on concentrations of humic and fulvic acids but varies depending on the humic substances from different soil types (Tahiri et al., 2016). A systematic study of humic acids in forest soils shows E_4/E_6 ratios in the range of 5.84 to 6.60 (Amran et al., 2017).

The stability of humic systems in both soils is determined by the negligible fraction of the aggressive fulvic acids, 0.01-0.02%, which varies from 0.03 to 0.40 % for the organic waste materials (Table 4, Table 5 and Table 6). Organic materials in the following Variants - Var.1.3 with cow mature; Var.1.4 with sheep manure; Var.1.6 with sludge from WWTP change the pH of the Alluvial-meadow soil has a slightly

Table 4. Content and composition of organic matter in the organic waste materials before their composting

Variants	TOC %	C:N	HAs+-FAs	HAs free or with R_2O_3	HAs with Ca	FAs	Ch/Cf	Humin	Agr.FAs	Optical density (E_4/E_6)	
										total HAs	free HAs
Biochar	31.7	88.1	3.73	2.40	-	1.33	2.33	27.99	0.34	5.57	5.26
Compost	14.0	11.8	2.62	0.93	0.67	1.02	1.57	11.33	0.30	7.90	7.85
Cow manure	4.58	2.39	3.71	1.33	0.62	1.69	1.19	0.87	0.40	9.14	9.08
Sheep manure	13.4	8.82	3.49	1.11	0.63	1.75	0.99	9.92	0.31	4.78	7.51
Sludge from WWTP	14.6	4.52	3.00	1.12	-	1.88	0.60	11.61	0.27	5.50	6.25

Table 5. Content and composition of organic matter for composting the Alluvial meadow soil with different organic waste materials after 21 days

Variants	TOC %	C:N	HA+FA	HAs free or with R_2O_3	HAs with Ca	FAs	Ch/Cf	Humin	Agr.FAs	Optical density (E_4/E_6)	
										total HAs	total HAs
Alluvial meadow soil	1.25	12.3	0.22	-	0.10	0.12	0.83	1.03	0.01	4.04	-
Var.1.1 + Biochar	2.40	16.4	0.28	-	0.17	0.11	1.54	2.12	0.04	3.25	-
Var.1.2 + Compost	3.27	38.9	0.52	0.21	0.15	0.16	2.25	2.75	0.07	2.82	5.26
Var.1.3 + Cow manure	3.00	9.01	0.76	0.23	0.14	0.39	0.95	2.24	0.03	4.93	7.77
Var.1.4 + Sheep manure	2.23	24.5	0.58	0.09	0.24	0.25	1.32	1.65	0.04	4.75	4.35
Var.1.5 + sludge from WWTP	1.27	7.13	0.35	0.16	0.07	0.12	1.92	0.82	0.04	3.81	5.13

Table 6. Content and composition of organic matter for the Smolnitza soil and different organic waste materials after 21 days

	TOC %	C:N	HA+FA	HAs free or with R_2O_3	HAs with Ca	FAs	Ch/Cf	Humin	Agr FAs	Optical density (E_4/E_6)	
										total HAs	free HAs
Smolnitza	2.73	16.5	0.68	-	0.44	0.24	1.83	2.05	0.02	3.51	-
Var.2.1 + Biochar	2.84	16.9	0.89	-	0.61	0.28	2.18	1.95	0.08	3.14	-
Var.2.2 + Compost	6.11	26.6	1.24	0.29	0.69	0.26	3.77	4.87	0.14	3.70	3,35
Var.2.3 + Cow manure	2.30	10.0	1.07	-	0.51	0.56	0.91	1.23	0.09	3.71	-
Var.2.4 + Sheep manure	3.60	22.2	0.87	0.17	0.27	0.43	1.02	2.73	0.04	3.56	5,50
Var.2.5 + sludge from WWTP	2.30	7.26	0.72	-	0.40	0.32	1.25	1.58	0.08	3.42	-

acidic reaction to neutral, and the materials of Var.1.1 with biochar, Var.1.2 with compost achieve neutralization and even slight alkalinization (Table 2, Figure 1). There CEC varies in the organic waste materials from 12.5 to 24.5 cmol/kg, but the BS in the composting variants is always higher than in the control soil. In the Alluvial meadow soil along with the need for soil organic matter increase, there is also a need to improve the nitrogen content. Composting with all the organic materials increases the total nitrogen content relative to the control, but is most significant in the variant with manure and sludge applied (Table 2, Figure 1).

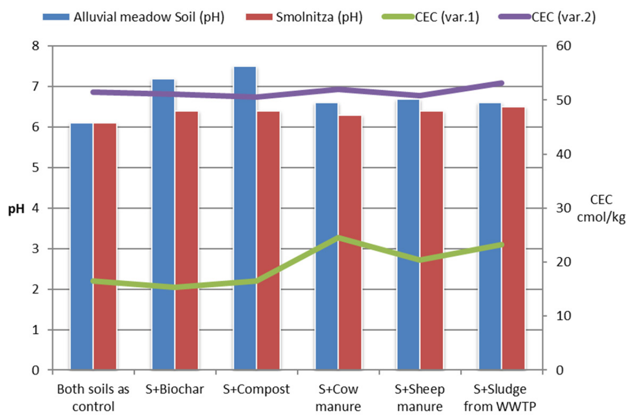

Fig. 1. Efficiency of both composting variants by pH in water and CEC meq/100 g

All the composted variants with both soils types possess disbalance in the levels of nitrogen, phosphorus and potassium compared to the thresholds for significant levels 20-60 mg/kg NO_3+NH_4 : 13-30 mg/100 g P_2O_5:15-30 mg/100 g K_2O which are needed for balanced nutrition. It should be noted that the introduction of biochar does not improve phosphorus nutrition. The sludge from the WWTP increases the phosphorus content compared to the content of nitrogen and potassium. Amendments application increases NPK in imbalanced ratios, for example, cow manure involves over-fertilization of phosphorus content, but plant compost has increased potassium content. As an optimum variant for organic fertilization in the Alluvial-meadow soil according to the physicochemical and agrochemical characteristics may be recommended the plant compost (Figure 2, Figure 3 and Figure 4).

The applied organic waste materials in the Smolnitza do not display a significant change in pH, CEC and BS (Table 3). Diagnosed phosphorus nutrition deficiency in Smolnitza is most effectively corrected by the cow manure and the in-

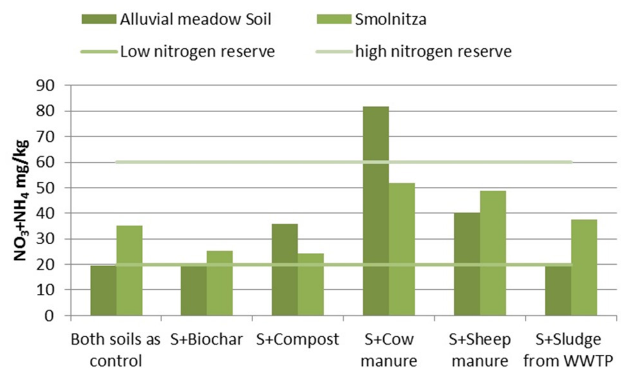

Fig. 2. Efficiency of both composting variants by the content of NO_3+NH_4 mg/kg

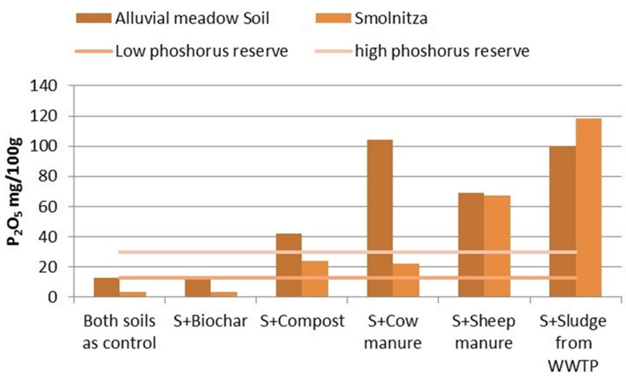

Fig. 3. Efficiency of both composting variants by the content of P_2O_5 mg/100 g

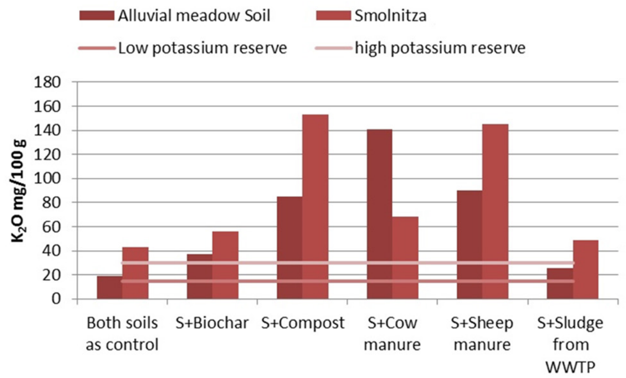

Fig. 4. Efficiency of both composting variants by the content of K_2O mg/100 g

crease of nitrogen and potassium is 1.5-1.6 times. The use of sheep manure as an organic fertilizer is associated with an increase in potassium compared to other nutrients. Similar is the situation with the use of sewage sludge, which increases the phosphorus content.

The content and composition of soil organic carbon are indicative of the composting process. The first composting variant with the Alluvial meadow soil and the organic materials on the 21st day display many changes (Table 5). The total content of organic carbon does not increase in Var.1.5 with the sludge from the WWTP. Biochar does not bring to significant increases in the humic acids, but they are most stable. Humic acids are bound with calcium and have a high optical density from 2.73 to 3.25 according to the ratio E_4/E_6. Composting demonstrates positive changes with the dominant involvement of humic acids in all the variants, except Var.1.3 with the cow manure where the Cha/Cfa ratio is below 1.0 and the fulvic acids are dominant. The suitable composting variant is considered to be Var.1.5 with the sludge from the WWTP according to the ratio C:N 7.13, because due to the insignificant content of organic carbon, the losses from nitrogen will be significant. Var.1.4 have an optimal C:N ratio of 25-35, for optimal energy and nutritional balance of the substances.

Composting organic materials with Smolnitza show a higher increase in total organic carbon from 2.84 to 7.85%, except Var.2.3 with cow manure, where there is no increase (Table 6). The variant Var.2.3 is inappropriate because there is an imbalance between the carbon and nitrogen content, also the ratio C:N is lower than in the control variant (Figure 5). The total soluble fraction of organic acids is in greater amounts from 0.72 to 1.24% relative to the control (Figure 6).

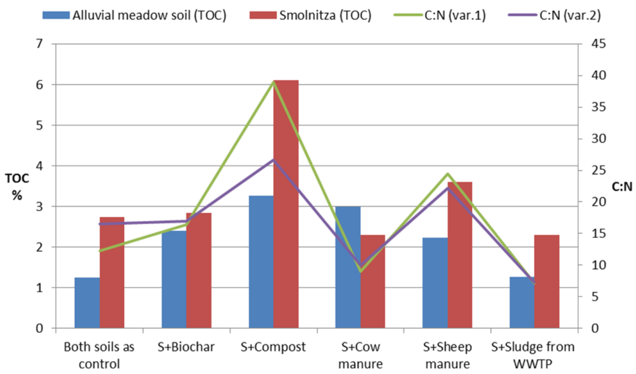

Fig. 5. Efficiency between var.1 and var.2 by the content of TOC and C:N ratio

Humic acids predominate in all variants, except Var.2.3 with cow manure. Composting of organic materials with Smolnitza shows that the composition of organic matter has higher stability than in the Alluvial meadow soil because there are no free humic acids except Var.2.2 with plant compost and Var.2.4 Sheep manure. Humic acids are calcium

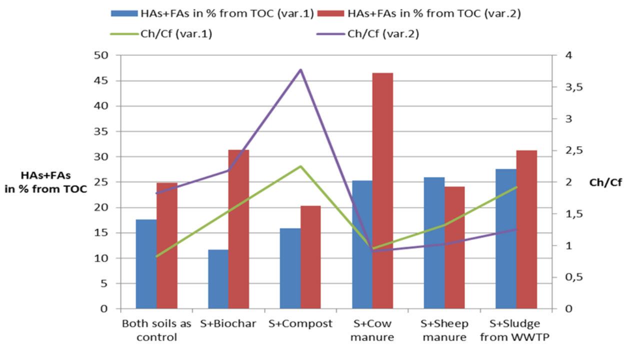

Fig. 6. Efficiency between var.1 and var.2 by the content of HAs + FAs and Ch/Cf ratio

bound and have a high optical density of 3.14 from Var.2.1 with biochar to 3.42 for Var.2.5 with sludge from WWTP according to E_4/E_6 (Table 6).

Conclusion

Different types of organic waste materials have been investigated for utilization as soil fertilizers for circular economy purposes. The chemical and agrochemical diagnostics of the two soil types show that the reclamation needs of the Alluvial-meadow soil are related to the increase of organic matter and nitrogen, while phosphorus deficiency is corrected in the Smolnitza.

Organic waste materials have different potential as organic fertilizers applied to contrast soil types with different physicochemical parameters and nutritional requirements. A stronger effect is observed on the Alluvial-meadow soil than in the Smolnitza soil. According to all the studied parameters and characteristics, the most effective is the plant compost for the Alluvial meadow soil. Many soil parameters were improved in this composting variant, e.g. soil pH, the ratio C:N, the content of the organic matter with the domination of humic acids. Organic waste materials composted with Smolnitza soil type, do not cause significant changes in pH, CEC and base saturation. Composting is associated with positive changes concerning humic acids in all the variants of Smolnitza, except the variant with cow manure, where fulvic acids are dominant, but on the other hand, the diagnosed phosphorus deficiency is corrected in the most balanced way.

Biochar stabilizes soil organic matter in a highly insoluble form but does not correct the mineral phosphorus deficiency. The organic matter in the cow manure a highly soluble and is unsuitable for application to soil with low organic matter content of predominantly humic-fulvic type. Sheep manure and plant compost have their advantages in increasing the content and composition of soil organic matter and nitrogen, but the assessment of the uptake of one or the other organic material should be tailored to the needs of the crops grown. The sludge from WWTP is ineffective as an organic fertilizer because it does not increase the organic matter and leads to imbalanced nutrients content with phosphorus predomination.

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