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JOLANTA KWIATKOWSKA-MALINA*

THE COMPARISON OF THE STRUCTURE OF HUMIC ACIDS FROM SOIL AMENDED WITH DIFFERENT SOURCES OF ORGANIC MATTER

Abstract. Soil organic matter (SOM) is an essential soil constituent. The deficiency of SOM is an essential problem in many regions in Poland. Diversity of organic matter and the environment create varying structures and compositions, and thus differences in properties of humic substances (HS) especially humic acids (HAs). It was found that soil amendment with organic matter resulted in improving of soil and HAs properties compared with non-treatment ones. The results obtained provided the following evidences. With respect to HAs: an increasing content of carboxylic groups in HAs from amended soils; a major content of aromatic ring systems; higher carbon, nitrogen, hydrogen, and sulphur and lower oxygen contents comparing to the control; the addition of straw caused an increase of carbon content in HAs particles and, consequently a decrease of the C:H ratio; higher content of oxygen functional groups compared with non-treated ones. Organic matter from straw is more resistant to fast decomposition as compared to compost and it shows higher long-term sorption capacity. Therefore, straw may be an equivalent to natural sources of SOM in terms of agriculture and ecosystems protection.

Organic matter in soil comprises a wide variety of organic components which are generally grouped in different chemical composition and reactivity, and in pools of different biological activity and stability. The amount and quality of soil organic matter (SOM) are depend on the natural input of plant, animal, and microbial residues, adequate crop management practices (e.g., reduced tillage, cover crops, prescribed grazing, and high biomass rotations), and organic amendment [18]. A growing interest in the different, alternative sources of

* Assoc. Prof. J. Kwiatkowska-Malina DSc.; Warsaw University of Technology, Department of Spatial Planning and Environmental Sciences, Warsaw University of Technology, Pl. Politechniki 1, 00–661 Warsaw, Poland.

organic matter (e.g. brown coal waste material and compost) was observed in last years [3, 8, 12]. Transformations of SOM lead to formation of humic substances (HS). Diversity of organic matter and the environment create varying structures and compositions, and thus differences in properties of HS especially humic acids (HAs) which are the most abundant and important constituents of non-living SOM [6]. Furthermore HAs are usually defined as humic substances of high molecular weight and high chemical heterogeneity compared to fulvic acids [11]. The structure of HAs is however still ill-defined and it is suggested that they consist of a heterogeneous association of molecules or small humic sub-units of different chemical nature and origin [13].

The aim of this research was to study properties of humic acids (HAs) isolated from soil amended with different sources of organic matter (farmyard manure, straw and compost) based on moisture and ash contents, elemental composition (C, H, N, S, O), total acidity and functional groups contents in comparison to those of unamended soil HAs.

MATERIAL AND METHODS

The experiments was carried out in long-term field experiments in Skierniewice located on 20°34’ E 51°58’ N (Poland) on Haplic Luvisol (WRB) developed from loamy sand on medium loam. Farmyard manure, wheat straw and municipal solid waste compost were applied once to the soil in dose of 20 tons per hectare. Not amended soil was used as a control. Soil samples were taken at the depth of 20 cm, five years after the application of amendments. The following parameters in soil samples were determined: pH_{H20} and pH_{KCl} were determined potentiometrically, the total organic carbon (TOC) by the Tiurin’s method, and the total nitrogen (Nt) content–by the Kjeldahl’s method. Additionally, C to N ratio were calculated. In organic amendments were determined: the total organic carbon (TOC) by the Tiurin’s method, and the total nitrogen (Nt) content–by the Kjeldahl’s method. Additionally, C to N ratio were calculated.

Physico-chemical properties and elemental composition of HAs extracted from soil after introduction of organic matter from sources mentioned above into the soil were studied. HAs were extracted according to the IHSS standard method [15]. HAs analysis: moisture and ash contents were measured by heating for 24 h at 105°C and 550°C, respectively, elemental composition (C, H, N, S) was determined by Analyser Fisons Instruments (Crawley, UK) model EA 1108. Oxygen content was calculated by difference: O% = 100 – (C+H+N+S)% in relation to the ashless sample weight, functional groups analyses were established by titration [22], total acidity and functional groups contents were determined according to the conventional methods [16] and the phenolic hydroxyl group content was calculated by difference.

RESULTS AND DISCUSSION

The use of different sources of organic matter such as: brown coal, Rekulter, peat and farmyard manure in the fertilization of declined soil has been described previously [6, 7, 10]. Basic properties of studied soil samples and organic amendments are given in Table 1. Applying the egzogenic organic matter as compost, farmyard manure and wheat straw into the soil resulted in changes of physico-chemical properties of the soil. Applying compost into soil did not influence significantly on soil reaction pH (pH_{H2O}=6.93; pH_{KCl}=5.95) in comparison to control soil (soil not amended with organic matter). The highest increase in soil reaction pH (pH_{H2O}=7.10; pH_{KCl}=6.43) was found in the case of farmyard manure. This was the effect of the role of organic matter in soil which has the ability to moderate major changes in the soil pH. Organic matter buffers the soil against major swings in pH by either taking up or releasing H^+ into the soil solution, making the concentration of soil solution H^+ more constant. The result of application of organic matter from farmyard manure was a stable pH close to neutral. There is the same in the literature about the effect of organic matter on soil reaction [17, 18].

Crop residues and animal manures have traditionally been applied to soil as a means for maintaining and increasing SOM content and related fertility functions. In recent years the intensive cropping of soils with consequent SOM depletion, and the need to protect soils from degradation and/or erosion has urged a series of efforts in finding alternative practices aiming to restore and/or improve SOM content and functions. As a result, recycling as soil organic amendment of the large amounts of organic residues and wastes, such as sewage sludges, composts, food industry byproducts and refuses, wood processing wastes, and agricultural crop residues, has became a very popular and efficient agricultural practice [9]. The wheat straw application in the soil caused significant increase in TOC content (Table 1). In the A horizon (0–25 cm), the contribution of TOC derived from decomposing straw's organic matter increases with dose from 6.14 (control soil) to 10.63 $g \cdot kg^{-1}$ of the total carbon. Normally accumulation of soil organic carbon at the soil surface layer is a result of surface placement of crop residues and a lack of soil disturbance that kept residues isolated from the rest of the soil profile [4]. A more rapid increase in carbon content has been published previously [1, 3, 8, 23]. As well as [14] showed the same situation of the reclamation sites. In object with compost, the TOC increased to 10.32 $g \cdot kg^{-1}$ as compare to control soil. These data may indicate that, sites ameliorated with wheat straw, accumulated carbon in light mineral soil and they content more carbon comparable to soil in natural conditions. However, a comparison of absolute amounts of TOC accumulation in soil in warmer and drier climates is smaller than in soil in cooler and moister climates [4]. It is well-known that sandy textured soils do not favour physical protection of easily biodegradable substrates and microorganisms leading to further losses of soil organic matter [21]. In general, soil organic matter turnover rates are determined by the proportion of "old" (stable) and "younger" (less resistant) organic matter. Soils with a low organic matter content contain relatively high proportions of "young" soil organic matter, resulting in rapid initial organic matter decomposition.

TABLE 1. BASIC PROPERTIES OF SOIL SAMPLES AMENDED WITH DIFFERENT SOURCES OF ORGANIC MATTER AND ORGANIC AMENDMENTS

Object	pH in H_2O	pH in KCl	TOC	Nt	TOC : Nt
			$g \cdot kg^{-1}$		
Control soil	6.88	5.93	6.14	0.64	9.4
Soil + compost	6.93	5.95	10.32	0.73	14.2
Soil + farmyard manure	7.10	6.43	9.90	0.52	18.9
Soil + wheat straw	7.08	6.40	10.62	0.49	21.5
Compost	-	-	162	8.6	18.1
Farmyard manure	-	-	155	8.0	19.4
Wheat straw	-	-	8.89	2.8	3.2

The total nitrogen (Nt) content ranged from 0.49 to 0.73 $g \cdot kg^{-1}$ (Table 1). The compost application into soil caused the highest content of Nt as compare to the control soil and other organic matter sources. Consequently, a significant increase in the TOC : Nt ratio was observed in object with wheat straw. The highest value of TOC to Nt ratio of 21.5 obtained for soil sample with wheat straw was due to the highest carbon and the lowest Nt content in this object. In other experiments with the barley straw similar results were obtained, usually found for this kind of materials [13].

Data obtained indicate that composition, functionalities, and other structural and chemical properties of HAs of organic amended soil are generally quite different from those of native soil HAs. Humic acids represent a small part of humic substances within the range between 3.6 and 5.3% TOC. The extent of the difference between properties of HAs extracted from soil with egzogenous organic matter and the corresponding properties in native soil HAs depend substantially on the origin and nature of the amendment. Briefly, the HAs samples show only some minor differences as a function of the sources of organic matter. The HAs extracted from the amended (with farmyard manure, wheat straw or compost) soil samples contained more hydrogen, sulphur, carbon and nitrogen than the HAs extracted from a control soil and were characterised by higher values of the C:O and O:H ratio (Table 2). The oxygen content and C:N ratio are lower as compare to control soil HAs. The C:H ratio was similar for HAs extracted from soil with farmyard manure and straw. Moreover, the highest value of the w parameter was observed for unamended control soil. Humic acids from soil amended with organic matter show higher content of acidic functional group, especially phenolic group, than corresponding values of the control soil HAs (Table 3).

TABLE 2. THE ELEMENTAL COMPOSITION (IN ATOMIC PERCENTAGE), ATOMIC RATIOS AND A DEGREE OF INTERNAL OXIDATION (OF HUMIC ACIDS (HAS) EXTRACTED FROM SOIL SAMPLES AMENDED WITH DIFFERENT SOURCES OF ORGANIC MATTER

Parameter	Object			
	Control soil	Soil + compost	Soil + farmyard manure	Soil + wheat straw
C %	55.08	57.30	55.42	55.11
H %	5.45	5.65	5.49	5.47
N %	4.67	4.92	5.03	4.94
O %	34.77	31.39	33.28	33.74
S %	0.73	0.74	0.77	0.74
C:N	11.79	11.65	11.02	11.15
C:H	10.11	10.14	10.09	10.07
C:O	1.58	1.83	1.67	1.63
O:H	6.38	5.55	6.06	6.17
w	1.418	1.254	1.374	1.394

Notation: w – internal oxidation degree.

TABLE 3. SOME PHYSICO-CHEMICAL PROPERTIES OF HUMIC ACIDS (HAS) EXTRACTED FROM SOIL SAMPLES AMENDED WITH DIFFERENT SOURCES OF ORGANIC MATTER

Parameter	Object			
	Control soil	Soil + compost	Soil + farmyard manure	Soil + wheat straw
Carboxyl groups cmol(+)/g	2.98	3.33	3.04	3.01
Phenolic OH cmol(+)/g	2.67	2.68	7.97	5.25
Moisture	1.61	4.83	4.10	2.94
Ash content	4.98	4.99	5.64	4.54
Total acidity	5.64	5.91	11.01	8.26

In agreement with data published previously on similar types of HAs [5, 20] obtained results suggest a greater presence of nitrogen containing groups, and a smaller content of oxygen containing groups, a smaller acidic reactivity, and a limited humification degree of HAs, with respect to the control soil HAs. The effect of egzogenous organic matter application into soil on the elemental and functional group composition of soil HAs is dependent on both the kind of amendment and management (residual versus cumulative applications). Further, the elemental composition of these HAs resemble more that of HAs from soil amended with organic matter than that of the control soil HAs. These results suggest the occured incorporation of structural and functional units such as nitrogen containing and carboxyl groups, of HAs from egzogenous organic matter (compost, farmyard manure, straw) into soil HAs, especially in the cumulative experiment [19]. Changes occurring in the properties of amended-soil HAs may be important in soil restoration processes of degraded agroecosystems [5, 9] because HAs interactions with a variety of organic and inorganic soil contaminants may change, thus affecting the mobility, bioavailability, degradation and phytotoxicity of contaminants in compost amended soils [2].

CONCLUSIONS

1. It was found that soil amendment with compost, farmyard manure or straw resulted in an increase of the: soil pH, content of organic carbon, and total nitrogen. The resulting higher values of C:N ratio within range usually found for Polish arable soils.

2. HAs extracted from the soil treated with egzogenous organic matter had higher carbon, hydrogen, nitrogen and sulphur, and lower oxygen contents comparing to the control soil. Simultaneously, the addition of organic matter caused an increase of the C:O and O:H ratio. HAs extracted from amended soils had higher contents of oxygen functional groups, a major content of aromatic ring systems comparing to the control. The addition of straw caused an increase of carbon in HAs particles and, consequently a decrease of the C:H ratio compared with non-treated ones.

3. Organic matter from straw is more resistant to fast decomposition as compared to compost and it shows higher long-term sorption capacity. Therefore, straw may be an equivalent to natural sources of organic matter in terms of agriculture and ecosystems protection.

4. Organic amendment applied to soil determines important beneficial changes in soil HAs, which contribute to ameliorate soil properties especially in degraded agroecosystems, and are expected to increase the soil fertility status with relevant effects on crop production , and to enhance soil protection versus degradation and potential contamination.

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PORÓWNANIE STRUKTURY KWASÓW HUMINOWYCH Z GLEB PO WPROWADZENIU MATERII ORGANICZNEJ Z RÓŻNYCH ŹRÓDEŁ

W zależności od rodzaju egzogennej materii organicznej (obornik, kompost, słoma) wprowadzonej do gleb wyekstrahowane kwasy huminowe charakteryzowały się różnymi właściwościami. Stwierdzono, że w kwasach huminowych wystąpił wzrost zawartości grup karboksylowych i fenolowych, większy udział struktur aromatycznych. W kwasach huminowych z gleb nawożonych stwierdzono większą zawartość węgla, wodoru, azotu i siarki oraz niższą zawartość

tlenu w porównaniu do kwasów huminowych z gleb bez dodatku egzogennej materii organicznej. Dodatek słomy spowodował wzrost zawartości węgla w składzie pierwiastkowym kwasów huminowych a w konsekwencji zmniejszenie stosunku C:H. Materia organiczna ze słomy jest bardziej odporna na szybki rozkład w porównaniu z kompostem.