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Properties of Sorption Complex and Humic Acids in Sandy Soils Fertilized with Sewage Sludge

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One of the methods of disposal of sewage sludge, which is based on its fertilizing properties, is its use in nature, e.g. in farming (if all the permissible standards are met). However, the sludge used for soil fertilization might also contain heavy metals which cause soil contamination and are accumulated in plants. The effect of application of organic fertilizers on soil reaction and other properties of sorption complex are also essential. The authors of the present study aimed at analysis of the effect of use of sewage sludge and selected organic fertilizers on changes in sorption properties in the fertilized soils. For comparison purposes, sewage sludge was introduced to sandy soil. One organic addition was also composted pine bark. The experiment was carried out under conditions of pot experiment. The following doses of organic fertilizers were used: 0, 10, 50, 100 and 200 Mg·ha^{-1}, which was calculated per pot with 10 kg of sandy soil. After 12 months from fertilization, changes in active and hydrolytic acidity were analysed in the fertilized foundations. The contents of organic matter, total of alkali in sorption complex S, soil sorption capacity T and content of humic acids in fertilized soils was also determined.

1 Introduction

Properties of the sorption complex in soils are regarded as one of the most important elements that affect soil fertility. An extended sorption complex in an element which collects a variety of soil contaminants or, for a particular time, activates them in a soil-water environment. Characteristics of a sorption complex are affected by e.g. content of organic substances, humic compounds created during decomposition of this substance, active and potential acidity (hydrolytic acidity), saturation of the sorption complex with alkaline cations (Balintova et al., 2012; Scanferla et al., 2012). Soil reaction is regarded as one of the most important indices of soil fertility. Soil acidity largely determines its physical, chemical and biological properties. Acidity of the ground affects durability of lumpy structure and air - water relations (Forsberg et al., 2006; Kabata-Pendias et al., 1993). All these elements provide optimum conditions for growth and yielding of plants. Soil reaction can be controlled by a variety of chemical agents (e.g. calcium) which deacidify mineral and organic minerals. The use of manure is claimed to reduce soil acidity. Some authors suggest using sewage sludge for soil fertilization, with particular focus on the sludge which is stabilized and hygienized with calcium (Marcinkowski, 2004; Wysokinski, 2005; Malinowska 2008). The results of the studies on fertilizing properties of sewage sludge and their effect on pH of the fertilized soil are not unequivocal. Some authors have demonstrated that sewage sludge increase reaction of the soil environment. Others point to the acidifying tendencies of sewage sludge after its introduction to the soil fertilized with it (Stanczyk-Mazanek et al., 2007a; Stanczyk-Mazanek et al., 2007b) This causes the necessity of further investigations of wastewater and sludge in terms of chemical composition. It is also necessary to constantly control the quality and content of toxic compounds, including heavy metals, in soils and plants fertilized with sewage sludge (Ociepa et al., 2008; Ociepa et al., 2010). The authors of the present study attempted to analyse the effect of the use of sewage sludge and cattle manure on changes in sorption properties and content of humic compounds in the soils fertilized with these substances after a year time from the fertilization.

2 Research Material

A sandy soil was used for fertilization under conditions of pot experiment. This was a sandy soil with granulometric composition of loose loamy soil. The soil was divided into two types. They significantly differed in their pH, modified for the study. The reaction of one of the soils was 8.31 (i.e. alkaline soil according to

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fertilization recommendations). Higher reaction was obtained when using, prior to the study, a calcium-based fertilizer according to fertilization recommendations for this type of soils. Furthermore, the reaction of the second sandy soil (natural, without addition of calcium) was 4.79 and according to (Ostrowska et al., 1991) it was categorized as acid reaction. Both types of soils were fertilized with sewage sludge and manure. The experiment was aimed at evaluation of the response of the sorption complex of soils with different pH to a variety of fertilizes and doses. The pot experiment was carried out in polyethylene pots with capacity of 10 kg. The pots were filled with two types of soils. Concentration of heavy metals in the soils was below permissible levels recommended for fertilization with sewage sludge (The Ordinance by the Minister of Environment on soil quality standart, 2002; The Ordinance by the Minister of Environment on the municipal sewage sludge, 2002). The ordinance was in effect when the experiment was started. The research objects were fertilized with increasing doses of 2 different types of sewage sludge and cattle manure. In lysimetric experiment, the authors used for fertilization purposes the sewage sludge from two wastewater treatment plants situated in the south of Poland i.e. in Pajęczno and Rokitnica. The sludge from these locations differed in treatment processes. Sewage sludge from the Pajęczno Wastewater Treatment Plant (P) was obtained from wastewater treatment using a hybrid technology of moving bed (in biological reactors) combined with the activated sludge process. Next, a simultaneous aerobic stabilization of the sludge was used. The sludge was thickened mechanically and dewatered by means of a belt press. Sewage sludge from the Rokitnica Wastewater Treatment Plant (R) was obtained after treatment and thickening in Imhoff tank and stabilized by means of a fermentation method. They were dewatered in moving filtration presses.

The doses of the fertilizer used were 10, 20, 100 and 200 $Mg \cdot ha^{-1}$ per pot. The experimental design also included 2 control objects: 2 types of soils (alkaline and acid), which were left without fertilization. Plants were not grown in any of the experimental objects in order to exclude the effect of activity of root system on changes in sorption parameters of the fertilized soils. The experiment was carried out in laboratory conditions. For the whole duration of the experiment (one vegetation season) no mineral fertilization was allowed. Humidity of all the soils in the experiment was maintained at a constant level of 60% of maximum water capacity (weight method). After completion of the experiment, the samples for chemical analyses were dried in a dryer until they reached a solid state. The following parameters were analysed in the soils (Ostrowska et al., 1991):

- soil pH in the solution of 1 mol KCL (potentiometric determination)
- hydrolytic acidity and cation exchange capacity using Kappen methodology
- content of humic acids in soils, determined by means of extraction and precipitation with HCl
- organic carbon (Tiurin's method)
- organic matter, determined by means of heating in a muffle furnace at the temperature of 550 °C

The study aimed to demonstrate the response of different types of soils (alkaline and acid) on fertilization with selected types of organic fertilizers and comparison of them with the effect of manure.

The types of the soils used were marked as:

P_{AL} - control sandy soil with alkaline reaction, non-fertilized

P_{AC} - control sandy soil with acid reaction, non-fertilized

The fertilizers used were marked as follows:

P - sludge from the Pajęczno Wastewater Treatment Plant

R - sludge from the Rokitnica Wastewater Treatment Plant

M- manure

3 Results

The use of sewage sludge and manure as fertilizers contributed to changes in chemical properties of the soils used in pot experiment. Selected properties of sorption complex of sandy soils (alkaline and acid) after fertilization with sewage sludge and manure with respect to control objects are presented in Tables 1 and 2. The study found that after a period of one vegetation season, the after-effects of the fertilizer used for fertilization remained noticeable. Control soil (alkaline with reaction of 8.30) after introduction of all the fertilizers (with different doses), despite insignificant decline in the reaction after the use of sewage sludge did not change its properties and, considering the acidity levels and pH of the soils (Kabata-Pendias et al., 1993; Ostrowska et al., 1991) it can be categorized as an alkaline soil. One exception was the sludge from Pajęczno plant with doses 100 and 200 $Mg \cdot ha^{-1}$ and Rokitnica with doses of 200 $Mg \cdot ha^{-1}$, which caused a reduction in the reduction of soil mixtures to a neutral reaction. The only agent that insignificantly increased soil reaction was manure in high doses. The response of acid control soil (Kabata et al., 1993) with pH = 4.77 to the fertilizers used points to their deacidifying effect. The increased in the dose was reflected by the rise in reaction of the soils fertilized with sewage sludge. Even the doses of 10 $Mg \cdot ha^{-1}$ increased pH of very acid soils to slightly acid soils

Table 1. Properties of sorption complex in the fertilized sandy soiled with alkaline character

Object No.	Combination of fertilizers	Parameter																	
		pH_{H2O}			pH_{KCl}			Organic substance [%]			Hydrolytic acidity H_h [mmol(+) · kg^{-1}]			Cation exchange capacity CEC [mmol(+) · kg^{-1}]			Content of humic acids [%]		
		Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.
1	P_{AL} (control)	8.30	0.01	kl	7.90	0.02	cdefg	0.63	0.06	ab	67.6	0.56	def	38.63	0.93	ab	0.06	0.01	bc
2	P_{AL} P10	7.75	0.02	hij	7.42	0.05	cdefg	0.83	0.06	c	75.37	0.64	efg	45.83	1.68	ab	0.17	0.0	f
3	P_{AL} P50	7.56	0.01	ghi	7.21	0.03	cdefg	1.10	0.10	e	105.23	0.61	i	78.03	1.59	abcde	0.28	0.02	ij
4	P_{AL} P100	7.30	0.02	defg	7.14	0.01	cdef	2.17	0.15	gh	144.33	1.85	mn	108.77	1.17	cdefgh	0.45	0.01	m
5	P_{AL} P200	7.16	0.03	def	7.05	0.02	bcde	3.77	0.15	m	182.87	2.62	pr	213.30	2.35	ijk	0.66	0.02	s
6	P_{AL} R10	7.88	0.02	ij	7.64	0.03	cdefg	0.60	0.04	a	67.7	0.53	def	45.33	0.84	ab	0.20	0.01	g
7	P_{AL} R50	7.79	0.01	hij	7.54	0.02	cdefg	0.83	0.06	c	90.67	1.59	ghi	121.03	1.81	defgh	0.30	0.02	kl
8	P_{AL} R100	7.49	0.02	fgh	7.23	0.01	cdefg	2.07	0.12	g	134.97	1.43	kl	141.20	1.68	gh	0.58	0.01	r
9	P_{AL} R200	7.30	0.02	defg	7.11	0.01	bcde	3.27	0.15	i	171.47	1.11	op	269.87	1.37	k	0.72	0.0	s
10	P_{AL} O10	8.10	0.02	jk	7.91	0.02	cdefg	0.63	0.06	ab	61.00	1.14	bcde	45.97	1.69	ab	0.19	0.01	g
11	P_{AL} O50	8.28	0.03	kl	8.15	0.02	defg	0.87	0.06	cd	52.50	1.10	bcd	81.50	1.97	abcdef	0.27	0.01	i
12	P_{AL} O100	8.38	0.02	kl	8.30	0.03	efg	2.23	0.15	gh	45.27	0.47	ab	131.03	3.48	efgh	0.58	0.02	p
13	P_{AL} O200	8.50	0.02	lm	8.38	0.03	efg	3.57	0.16	kl	30.80	0.68	a	204.07	2.86	ij	0.72	0.01	s

SD - Standard deviation (±)

g. h. - group homogeneity (based on statistical tests). Means with the same letters do not differ statistically significantly.

Table 2. Properties of sorption complex in the fertilized sandy soiled with acid character

Object No.	Combination of fertilizers	Parameter																	
		pH_{H2O}			pH_{KCl}			Organic substance [%]			Hydrolytic acidity H_h [mmol(+) · kg^{-1}]			Cation exchange capacity CEC [mmol(+) · kg^{-1}]			Content of humic acids [%]		
		Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.	Mean	SD	g.h.
1	P_{AC} (control)	4.77	0.04	a	4.69	0.02	a	0.63	0.06	ab	107.87	1.6	ij	25.73	0.87	a	0.03	0.0	a
2	P_{AC} P10	6.65	0.04	b	6.54	0.05	bc	0.73	0.15	abc	127.4	1.3	hi	33.8	1.05	fgh	0.05	0.0	b
3	P_{AC} P50	7.06	0.02	cde	7.04	0.01	bcde	1.03	0.06	de	154.9	1.92	no	68.0	0.87	abcd	0.17	0.01	f
4	P_{AC} P100	7.24	0.03	defg	7.17	0.01	cdef	2.27	0.07	h	192.20	2.74	pr	105.63	1.42	cdefgh	0.28	0.01	j
5	P_{AC} P200	7.33	0.05	efg	7.29	0.02	cdefg	4.43	0.15	k	233.0	2.49	t	202.37	2.39	ij	0.49	0.02	o
6	P_{AC} R10	6.73	0.03	bc	6.70	0.04	bcd	0.63	0.06	ab	123.47	1.56	jkl	29.40	0.92	a	0.07	0.0	d
7	P_{AC} R50	7.11	0.01	de	7.08	0.02	bcde	0.77	0.05	abc	135.83	2.48	klm	113.40	3.05	cdefgh	0.14	0.03	e
8	P_{AC} R100	7.26	0.02	defg	7.20	0.01	cdef	1.63	0.07	f	192.87	2.32	r	125.90	1.55	defgh	0.25	0.01	h
9	P_{AC} R200	7.35	0.04	efg	7.29	0.03	cdefg	2.90	0.1	i	203.27	2.14	s	253.63	2.16	jk	0.52	0.03	p
10	P_{AC} O10	6.94	0.06	bcd	6.84	0.02	bcd	0.60	0.01	a	102.57	1.8	i	31.47	1.68	a	0.07	0.01	cd
11	P_{AC} O50	7.71	0.12	efg	7.17	0.06	defg	0.80	0.1	bc	82.90	1.25	fgh	61.53	0.81	abc	0.14	0.02	e
12	P_{AC} O100	9.10	0.14	m	8.60	0.09	h	1.57	0.15	f	64.20	2.39	cde	93.40	2.07	bcdefg	0.25	0.03	h
13	P_{AC} O200	9.30	0.09	m	8.70	0.02	hi	3.20	0.2	j	47.53	1.56	abc	156.33	3.29	hi	0.45	0.02	n

SD - Standard deviation (±)

g. h. - group homogeneity (based on statistical tests). Means with the same letters do not differ statistically significantly.

The higher doses resulted in even neutral pH. Furthermore, manure exhibited the best deacidifying effect. It was the doses of 10 Mg·ha^{-1} that caused an increase in the reaction to the neutral one (6.94). Higher doses of manure after a year of fertilization caused that the reaction in the fertilized soil continued to be alkaline. An increase in the content of organic substance, which was significantly higher than the control material, was found in the case of fertilization with both manure and sewage sludge. In the case of fertilization with the sludge from Pajęczno (stabilized under aerobic conditions), the increase in the content of organic matter in the fertilized sandy soils was significantly higher than in the case of fertilization with the sludge from Rokitnica (stabilized under anaerobic conditions) and manure. The soil organic matter is one of the most important components which determine soil fertility. Soils are regarded as rich in humus if they contain ca. 3 % of organic compounds (Kabata-Pendias et al., 1993). After a year of fertilization these amounts of organic compounds, ranging from 3.27 (sludge from Rokitnica) to 3.77 (sludge from Pajęczno) were found in soil mixtures with sludge and manure only for the highest doses (200 Mg·ha^{-1}). Slightly lower amounts were observed after application of 100 Mg·ha^{-1} of both sludge and manure. The highest results of determination of hydrolytic acidity (significantly higher than the control sample) were found in the case of fertilization with sewage sludge. Both acid and alkaline soils exhibited tendencies for constant increase in potential acidity. Acidity of the fertilized soils increased with the doses of sludge (of both types). Sludge from Pajęczno (stabilized aerobically) tended to acidify the soil environment to a higher degree. Doses of 100 and 200 Mg·ha^{-1} of this sludge caused an increase in acidity by 114 and 170 % with respect to the control object (alkaline control soil). Even smaller doses of 10 and 50 Mg·ha^{-1} of the sludge from Pajęczno increased the hydrolytic acidity by 15 and 56 % compared to the alkaline control soil. In acid soils, response of the soil to fertilization with sewage sludge was similar. Only in the case of fertilization with manure a statistically significant decline in hydrolytic acidity with respect to control sample was found both in alkaline and acid soils. The cation exchange capacity in the alkaline soil was similar to its levels observed in the acid soil. Fertilization with both sludge types and manure caused an increase in the cation exchange capacity (CEC) (significantly higher than the control sample). Using sewage sludge (particularly from Rokitnica) for fertilization caused an increase in the cation exchange capacity in the fertilized soils (both alkaline and acid) which was higher than for the manure. The highest increase in this parameter, by 786% and 599% with respect to control objects (acid and alkaline soil, respectively) caused application of sewage sludge from Rokitnica (stabilized under anaerobic conditions) with the doses of 200 Mg·ha^{-1}. However, lower doses, e.g. 50 Mg·ha^{-1} of this sludge caused an increase in the cation exchange capacity in the fertilized soils (acid and alkaline) by 340 % and 213 %, respectively. The manure used with this dose (maximum dose recommended in agriculture) cause an increased cation exchange capacity in the fertilized soils by 139 % and 111% with respect to acid and alkaline control soils. After a year from fertilization of the alkaline soil, the content of humic acids was higher than in acid soil. The use of the dose of 10 Mg·ha^{-1} caused an increase in the content of humic substances from 0.06% in the control soil to 0.17% and 0.20% in soil mixtures with sludge from Pajęczno and Rokitnica. After a year of fertilization with manure with the same dose in the alkaline soil mixture, an amount of 0.19 % of humic acids was observed in the alkaline soil mixture. Fertilization with sludge from Rokitnica (stabilized under anaerobic conditions) causes formation of higher amount of humic acids compared to the application of sludge from Pajęczno. Similar effect was observed for fertilization with manure.

4 Conclusions

A significant factor that determines such effects as mobility of heavy metals and other chemical pollutants in soil is sorption properties of the soil. An increase in the reaction of the fertilized soils was observed in the study in all the fertilized soils after the use of manure. Furthermore, sewage sludge used for fertilization (both after aerobic and anaerobic processing) caused an increased acidity in the fertilized sandy soils (particularly observed in the soils already acidified), which increased with an increase in the dose of the sludge. Similar effect of sewage sludge on the levels of soil acidity was demonstrated by Iżewska (2007) who investigated the effect of fertilization with manure and sewage sludge on soil properties. Gondek (2009), who analysed fertilization use of sewage sludge, also demonstrated their acidifying effect, particular in the second year after application. Other results were obtained by Skowrońska at al. (2008), who found an increase in soil acidity after application of both sewage sludge and manure. This increase, however, was statistically insignificant. A long-term effect of fertilization on soil reaction and tendencies which might be invisible during determination of active acidity can be more measurably determined by potential acidity (so-called hydrolytic acidity). After fertilization with sewage sludge, increase in the doses caused increased acidity. Manure had an alkalinizing effect on soil environment. Only the doses of 10 Mg·ha^{-1} of sewage sludge (both after aerobic and anaerobic stabilization) did not cause increased hydrolytic acidity of the fertilized soils. Manure used for fertilization of soils in all the samples reduced hydrolytic acidity. Similar results were obtained by Gondek (2009). An increase in hydrolytic acidity by 50% in the soils after fertilization with sewage sludge compared to control samples was determined in a study by Skowrońska at al. (2008). Other observations were obtained by Baran et al. (2008) since they found a decline in hydrolytic acidity after fertilization with composts from sewage sludge compared to control objects. The opposite response can be explained by the method of preparation of composts from sewage sludge, which were added considerable amounts of ashes with alkalinizing properties. The cation exchange capacity (number of cations with alkaline character) rose with the dose of the introduced organic fertilizers. The sewage sludge used in the study, introduced in the soils in all the samples in the experiment, caused a significantly higher increase in the cation exchange capacity (CEC) compared to manure. The results obtained by Baran et al. (2008) also showed a positive effect of the sludge composts on sorption properties of the soil. The amount of the organic substance in the soils with addition of sewage sludge and manure rose with the dose of the fertilizers used in all the experiments. Parat et al. (2005) carried out fertilization of soil with sewage sludge and manure for 20 years with the amount of 10 and 100 $Mg \cdot ha^{-1}$ and demonstrated that, even after a period of 6 years after the last application, the organic matter in the soils was significantly higher than in the control objects. This was also confirmed by the results obtained in the present study. The amount of humic substances in the fertilized soils after the use of sewage sludge and manure did not differ significantly. An increase in the amount of these substances was observed simultaneously with the rise in the dose of sewage sludge and manure. Similar results of the study were obtained by Wang et al. (2010). These authors also emphasized a considerable role of the root system of plants in creation of humic substances in the soil.

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