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AGROECOLOGIC VALUATION OF ORGANIC WASTE IN DIFFERENT TECHNOLOGIES OF STORAGE

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Abstract: A study has been conducted, based on three types of fertilizers / cow, pig and bird manure/ and bioshlam /received from clearing station/ that have been storage in different technologies in order to make an agroecologic valuation. The different types of fertilizers and wastewater in different technologies of storage have been analyzed according to the following parameters: Dry matter (DM), Organic matter (OM), Organic Carbon (OC), Nitrogen Kjeldahl (N), Nitrogen Ammonium (N -ammonium), Nitrogen nitrate (N- nitrate), Sulfates (SO₄), Calcium Oxide (CaO), Magnesium Oxide (MgO), Potassium (K), P (Phosphorus), pH (H₂O) and heavy metals – arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pb), Zinc (Zn). The received results show: variation of the percentage of dry material /from 92,12% to 4,03%/ according to the technology of storage. The way of storage has no essential influence on the content of carbon in the various stable fertilizers, where pig manure has the highest value of nitrogen in all technologies of storage. Near to the recommendable optimal values of C:N is stayed/dry/ and fresh/hard/ in all three fertilizer types. The technology of storage by the different manure types has no influence on the content of heavy metal. Exception can be observed as far as the zinc content in stale /fluid/ pig manure is concerned. High content of dry material can be observed in bioshlam received from clearing station. In both ways of production of variation in the content of dry material the ratio between the biogenic macro elements C:N remains. The free nitrogen forms (N-ammonium and N-nitrate) in bioshlam are higher to other organic waste in both technologies of storage. No values over the critically admissible in bioshlam are observed in both technologies of production.

Key words: cow manure (fertilizer), Pig manure, Bird manure, Technology for storage, agri- environmental indicators (assessment), waste water treatment plan, bioshlam

Introduction

In recent years a growing interest in organic waste received by livestock animals, grew due for environmental and agrochemical problems while they technological applications of anaerobic digestion as a raw material for biofuel production.

The energy content of manure (regardless of what kind of animals received is approximately 50%) that of the feed. Manure containing a high concentration of ammonia which has an inhibitory effect on the glycolytic pathway (Baykov, *et al.*, 2007). With simultaneous decomposition of plant materials and fertilizers. Manure provides buffering capacity and a wide range of food substances, till added plant material high carbon improves the balance of the elements C: N (Lehtomaki *et al.*, 2007). Differences in the ratio of C: N allow combine fertilizers with regard to the need of nitrogen in the soil, as well as the requirements of the EU directive Nitrate (1991) to increase the soil fertility by limiting the amount of nitrogen contributed to 170 kg /ha year EU Directive and regulation 22/2010.

The present work aims to make agri-environmental assessment of fertilizers from various livestock animals and bioslam of Treatment plant (TP) at different storage technologies to shape substrates with their participation with good agri-environmental indicators.

Materials and Methods

The study included:

1. Collecting of samples of different fertilizers - beef, pork and chicken and compost from (Sofia) at various storage technologies. The Table 1 shows the types of fertilizers and compost (sludge) at various storage technologies.

2. Analysis of samples for the following parameters and methods: Dry matter (DM) by BSS EN 14346 (Bulgarian State Standart), Organic matter (OM) determined based on estimates of BOD, Organic Carbon (OC) by BSS EN 13137, Nitrogen Kjeldahl (N) by BSS 13342, Nitrogen Ammonium (N -ammonium) BSS 3587, Nitrogen nitrate (N- nitrate) by BSS EN ISO 10304-2, Sulfates (SO₄) by BSS EN ISO 10304-2, Calcium Oxide (CaO) by EPA 6010C, Magnesium Oxide (MgO) by EPA 6010C, Potassium (K) by EPA 6010C, P (Phosphorus) by EPA 6010C, pH (H₂O) by BSS EN 12176 and heavy metals – arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Mercury (Hg), Nickel (Ni), Lead (Pd), Zinc (Zn) by EPA 6010C.

Table 1. Types of organic waste at different storage technologies

№	Identification
Fresh manure	
1	Cattle (liquid) manure obtained by water cleaning of the premises
2	Cattle (hard) manure produced with the participation of bed of straw
3	Pork (liquid) manure obtained in water cleaning of the premises
4	Pork (hard) manure after separation, obtained after dividing of manure fraction
5	Birds (hard) dry manure obtained by farming of chickens on bedding
6	Birds (hard) manure
Stayed manure	
7	Cattle (liquid) manure obtained by water cleaning of the premises - stayed 6-8 months
8	Cattle (hard) manure produced with the participation of bed of straw – stayed 6-8 months
9	Pork (liquid) manure obtained in water cleaning of the premises - stayed 6-8 months
10	Pork (hard) with a mixture of straw and sawdust– stayed 6-8 months
11	Birds (hard) dry manure obtained by farming of chickens on bedding
12	Birds (hard) manure - stayed 6-8 months
Waste from wastewater treatment plan	
13	Primary sludge
14	Secondary sludge
15	Mixed sludge dewatered by tape filter press
16	Mixed sludge (Stayed)
17	Methane tank-entrance
18	Methane tank- exit

Results and Discussion

The Table 2 presents the composition of different types of fertilizer (beef, poultry and pork) under different storage technologies as well as that of sediments from TP. For the primary indicator - Solids shows that the conservation process influenced the dry matter content for all types of fertilizer (beef, poultry and pork), regardless of the state - liquid or solid. With 1% tolerance exception substrate 11 overripe poultry manure to fresh Hard poultry manure substrate 5. Following the result of anaerobic digestion and fermentation processes ongoing loss of dry matter in standing fertilizers stayed 6 – 8 month fresh is to from 2.4% to 7.10% while the bovine solid manure they are the greatest. In terms of indicators of organic matter calculated on BOD variation is large between fresh and stayed fertilizers, the overall trend is towards a reduction of organic matter on standing manure, regardless of its type. Data for indicators of organic carbon correspond with those of the organic matter, while fresh manure carbon moves from 38,37 for pig manure to 25.25% and beef solid fertilizer on standing fertilizers, regardless of their tendency towards reduction of carbon.

Table2. Composition of organic waste in variety of storage technologies

№	DM, %	OM,% *	C, %	N,%	C:N	pH
1	6,68±0,19	44,82±0,47	35,98±0,29	4,61±0,09	5,61	8,66±0,36
2	59,30±0,76	28,43±0,13	25,25±0,98	0,99±0,01	25,51	7,76±0,13
3	4,04±0,28	33,33±0,93	26,19±0,76	7,14±0,21	3,67	7,86±0,14
4	37,46±1,13	40,80±0,11	38,37±0,65	2,43±0,06	15,79	7,36±0,09
5	48,16±0,03	44,85±1,11	38,03±0,23	6,48±0,11	5,87	8,46±0,19
6	50,50±0,01	36,00±0,27	32,38±0,91	3,62±0,13	8,94	8,35±0,24
7	4,04±0,04	43,37±0,31	30,78±0,04	6,76±0,06	4,55	8,54±0,15
8	52,20±1,02	35,21±0,23	31,92±0,19	1,25±0,02	25,54	7,46±0,11
9	1,61±0,01	39,62±0,27	36,31±0,09	3,31±0,13	10,96	7,95±0,24
10	40,47±0,28	37,07±0,93	31,92±0,76	5,09±0,21	6,27	8,24±0,14
11	49,05±1,35	37,93±0,35	26,84±0,17	4,12±0,08	6,51	8,27±0,07
12	44,59±1,35	26,99±0,35	22,87±0,17	4,78±0,08	4,78	8,47±0,07
13	4,90±0,09	29,12±0,22	28,61±0,11	0,51±0,03	55,90	5,53±0,06
14	0,90±0,01	30,18±0,14	25,37±0,31	4,81±0,78	5,27	7,52±0,09
15	41,81±0,98	30,79±0,18	28,08±0,14	2,71±0,10	10,36	7,56±0,19
16	56,46±1,13	15,60±0,11	14,50±0,19	1,14±0,05	12,72	6,63±0,11
17	2,96±0,15	35,52±1,01	30,59±0,22	4,93±0,69	6,20	7,22±0,07
18	2,20±0,03	20,58±0,20	18,48±0,31	2,10±0,27	8,80	8,60±0,16

*Organic matter is determined on the basis BOD

The percentages of reduction of the organic matter are shown in Table 5.

It is evident that the percentage of reduction of the organic compounds is higher in solid form fertilizers than in the liquid ones. Similar trends are observed in the data for mineralization of organic matter (Table 5), where the percentage of mineralization of the organic matter is highest in cow manure presented in both states – liquid and solid. Data from members of the collective from previous studies support the obtained results that cow manure is a suitable material for the production of biofuel. Table 5 clearly shows, however, that in manure from ruminants, regardless of the state (liquid or solid), the percentage of nitrogen (expressed as % from the DM – dry matter) is highest compared to other fertilizers. A tendency toward higher values is observed too in the mixture of bird manure with straw and filings.

Table 3. Contents of biogenic macro elements in organic waste

Indicators №	N, mg(kg ammonium)	N,mg(kg nitrate)	K,%	P,%	CaO %	MgO,%	Sulfates (SO ₄ ,%)
1	1,45	<6	3,11	3,14	2,93	1,35	0,21
2	0,14	<5	0,73	0,29	1,73	0,46	0,07
3	3,59	<11	4,20	1,28	3,63	1,13	0,12
4	0,13	<6	0,25	0,85	2,54	0,84	0,10
5	1,04	<4	2,04	0,98	2,74	0,78	1,12
6	0,72	<5	1,18	0,83	4,15	0,54	0,16
7	2,42	<11	3,34	0,99	4,00	0,99	0,43
8	0,02	177,8	0,68	0,49	1,42	0,62	0,03
9	2,38	27,8	0,68	3,33	5,19	3,94	0,10
10	4,76	<50	4,19	0,90	3,55	2,55	4,70
11	0,75	<5	1,30	0,52	6,31	0,66	0,12
12	0,26	382,5	0,39	5,48	9,07	3,57	0,48
13	2,354	-	0,50	1,95	4,90	1,12	-
14	2,418	-	1,05	4,10	2,59	1,04	-
15	5,844	-	1,36	8,61	1,76	0,31	-
16	<50	-	2,84	7,20	4,37	0,77	-
17	6,708	-	0,94	5,13	9,24	2,02	-
18	4,011	-	1,56	5,10	2,90	1,90	0,08

Table 3 presents some biogenic macro-elements in the different types of manure, stored in different technologies, as well as the composition of the residues in various stages of wastewater treatment. As can be seen, in fresh manure, regardless of the type, the content of the main biogenic macro-elements (with a few exceptions) is lower than the content in stagnant manure. Due to partial emission of carbon, oxygen and hydrogen (which are included in the biogas), the products of decomposition of organic matter have redistributed the studied macro-elements and correspondingly have resulted in higher levels in stagnant manure. In all three types of manure it has been found an increase in the amount of studied macro-elements. Our results for the composition of the different types of manure, obtained by different storage technologies, are a source of useful agro-ecology information. Having under consideration that C, N and O are not limiting to the plants, it can be noted that the values obtained on stagnant manures, in respect of the quantity of the tested macro-elements (nitrogen, phosphorus, potassium, calcium and magnesium

oxide), have high agrochemical value due to the relatively greater quantity of limiting macro-elements – nitrogen, phosphorus, potassium. With regard to the pH variation between the different manures from different storage methods, they are negligible (with 1% variation).

Table 4. Content of heavy metals

Components,mg(kg №	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1	<5	<0,4	3,88	57,98	<1	5,58	<10	258,1
2	<5	<0,4	4,02	10,72	<1	4,33	<10	38,33
3	<5	<0,4	6,33	183,7	<1	8,56	<10	1815
4	<5	<0,4	5,37	63,96	<1	9,26	<10	1292
5	<5	<0,4	5,62	61,16	<1	7,25	<10	352
6	<5	<0,4	6,97	33,55	<1	3,30	<10	205
7	<5	<0,4	4,41	105,35	<1	6,47	<10	397,2
8	<5	<0,4	2,06	21,93	<1	2,13	<10	121,2
9	<5	<0,4	9,81	419,4	<1	13,47	<10	1401
10	<5	<0,4	13,17	25,34	<1	10,00	<10	115,6
11	<5	<0,4	3,86	34,65	<1	3,20	<10	229,8
12	<5	<0,4	8,81	183,26	<1	7,27	<10	1068
13	19,6	4,7	83,2	494,1	<1	41,3	97,0	1546
14	<5	3,6	95,5	308,0	<1	41,8	41,0	948
15	<5	1,0	22,3	114,8	<1	10,80	24,60	385,1
16	8,9	2,6	57,6	297,5	<1	25,8	77,7	894
17	<5	6,1	174,0	778,8	<1	85,05	159,1	2588
18	4	29	448	417	3	156	47	2454

In table 2 we are presented with the data on the composition of residues obtained as a waste product during the various stages of wastewater purification. The data show that the primary and secondary residues have lower values of DM (dry matter - 5.90 and 0.90% respectively) in comparison to the mixed residue. The low values of dry matter in the secondary residue compared to the primary residue (stage one of wastewater purification) are also noticeable. Regarding the organic matter indicator there aren't significant differences between the different residues. The method of storage has had an effect on the amount of organic matter in the mixed residues. In the stagnant mixed residue the amount of organic matter has decreased by almost half. This decrease is confirmed also in regard to the nitrogen and carbon content, despite that their ratio (C:N) values are too close with a tendency for higher ones in the stagnant one. The percentage of reduction of organic matter in the primary residue is highest (substrate 13-16). A similar tendency is observed when comparing the primary with the mixed residue which was dehydrated beforehand (Table 5). The percentage of mineralization of the

organic matter in the different types of residue is within 46%-54%. The high level of mineralization in the freshly dried residue compared to the primary one makes an impression. The obtained organic waste (substrate 17 and 18) is characterised by a composition and proportion which are analogous to the others during the various stages of wastewater purification. It has been noted, however, that substrate 17 (methane tank-input) has the highest percentage of nitrogen in dry matter. Similar to our results have been reported by *Marinova (2008)*.

Table 5. Basic technology issues depending on the method of storage

substrates №	DM,% Fresh Stayed		OB,% Fresh Stayed		% of reduction of BOD (Fresh-Stayed)	% of mineralization of OM	% of N in fresh, % from DM
1 - 7	6,68	4,04	44,82	43,37	60,48	96,76	3,07
2 - 8	59,30	52,20	28,43	35,21	88,03	123,84	5,87
3 - 9	4,04	1, 61	33,33	39,62	39,85	97,87	2,88
4 - 10	37,46	40,47	40,80	37,07	108,03	90,85	2,06
5 - 11	48,16	49,05	44,85	37,93	102,00	84,57	3,12
6 - 12	50,50	44,59	36,00	27,65	88,29	76,81	1,83
13 - 16*	4,90	56,46	29,12	15,60	115,2	53,57	2,50
14 - 16*	0,90	56,46	30,18	15,60	62,27	51,69	6,50
13 - 15*	4,90	41,81	29,12	30,79	85,33	105,70	2,50
14 - 15*	0,90	41,81	30,18	30,79	46,46	46,46	4,33
17 - 18	2,96	2,20	35,52	20,58	74,32	57,94	14,59

*Fresh sludge and compost (mixed sludge out)

For an agro-ecological assessment of the analysed substrates, obtained at different stages of wastewater purification and stored as compost – freshly dried and as stagnant (substrate 15-16), the dynamics of the water-soluble fractions of the macro-nutrients, which are available to the plants, are of great importance. For this reason a leading indicator is the nutrients' content, while the water-soluble forms should be analysed as a criterion for the effectiveness of modelling the decomposition(decomposers' unit (modelling the unit of decomposition) in order to obtain an accurate dosage in soil application. Soil fertility and soil structure are determined by two main groups of products: nutrients in mineralized form and nutrients as organic compounds. In this respect the compost has an advantage as it retains all macro and micronutrients in two agro-chemically important categories: available mineral salts and the same elements in the form of organic compounds.

The movement of the toxic elements in the various types of manure, depending on the method of storage and those in wastewater at a various stage of their purification, are presented in Table 4. Their choice is based on the requirements in Ordinance 22(2001 on organic production in crop production. The

analysis of the obtained results shows that the content of arsenic, cadmium, mercury and lead are within the permissible values for the three types of manure in the different storage technologies. Essential in assessing the quantity of toxic elements is their impact on the soil at application and their potential for bioaccumulation along the trophic chain. In this respect it is important to consider the high values we obtained for chromium and nickel in the three types of manure. Pig manure has the highest chromium content (stagnant-liquid) – 9,81 mg(kg. Pig manure (fresh and liquid) and bird manure (fresh and solid) have similar chromium content, 6.33 and 6.97 mg(kg respectively. The lowest chromium content (approaching the permissible values) is in stagnant cow and pig manure (2.06 mg respectively). Nickel is also highest in pig manure (stagnant-liquid) – 13.47mg (kg and again it is the lowest in stagnant (dry) cow and pig manure (2.13 mg(kg respectively). The high levels of zinc in the fresh manure, stored in liquid or solid form makes an impression, as well as those in stagnant liquid pig manure. The deviations of the obtained values for pig manure compared to the other types of manure are in some cases almost 10 times. The levels of zinc are lowest in fresh cow manure, stored in liquid or solid state (25.12 and 38.33 mg(kg respectively). Stagnant (liquid) pig manure has the highest content of the microelement copper (419.4 mg(kg).

The results from the analysis show that the different types of manure, using different storing technologies, as well as the compost of the wastewater of the (Wastewater Treatment Plant) meet the requirements of Ordinance № 22 and EU Directive 2001(18 as sources of nutrients. Redistribution of some toxic elements depending on the method of storage was found, but their increased number in some organic waste is not a reason for them to be excluded as means to increase soil fertility.

Conclusion

The results obtained for the composition of the different types of manure (cow, pig and bird manure), stored using different technologies, as well as the organic waste (residues from wastewater) show:

- Variation of the percentage of dry matter, depending on the storage technology and the stage of wastewater purification.
- The method of storage (fresh and stagnant) has had a significant impact on the carbon content in the different types of manure and residues of wastewater.

- High levels of reduction of the organic matter, expressed in a per cent of the dry matter is observed, as well as high percentage of mineralization of the organic matter in stagnant manure and bioslam obtained from the wastewater purification plants.
- The variations in the carbon and nitrogen content in the different manures and technologies of storage, affect the indicator C:N, which has close to the recommended optimal values for biofuel production in the three types of manure stored in a solid form.
- The storage technology in the different types of manure, regardless of their form (solid or liquid) and the bioslam obtained from the wastewater of Sofia's Wastewater Treatment Plant, has not influenced the heavy metal content. All values are within the critically permissible as stated by Ordinance 35 for organic farming.

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Agroekološka vrednost organskog otpada u različitim tehnologijama skladištenja

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Rezime

Studija je sprovedena na osnovu tri vrste đubriva (stajnjaka od krava, svinja i živine) i biološkog otpada koji se skladište u različitim tehnologijama, kako bi se uradila agroekološka procena.

Različite vrste đubriva i otpadnih voda u različitim tehnologijama za skladištenje analizirane su na osnovu sledećih parametara: suve materije (SM), organske materije (OM), organskog ugljenika (OC), Kjeldahlov Azot (N), amonijačni azot (N - amonijum), azot nitrat (N-nitrat), sulfati (SO₄), kalcijum-

oksid (CaO), magnezijum oksid (MgO), kalijum (K), P (fosfor), pH (H₂O) i teški metali - arsen (As), kadmijum (Cd), hrom (Cr), bakar (Cu), živa (Hg), nikl (Ni), olovo (Pb), cink (Zn). Dobijeni rezultati pokazuju: varijaciju na procenat suve materije od 92,12% do 4,03% prema tehnologiji skladištenja. Način odlaganja nema suštinski uticaj na sadržaj ugljenika u različitim stabilnim đubrivima, gde svinjski stajnjak ima najveću vrednost azota u svim tehnologijama skladištenja. Tehnologija skladištenja različitih vrsta đubriva nema uticaja na sadržaj teških metala. Izuzetak je sadržaj cinka u ustajaloj (tečnoj osoki iz objekata gde se drže svinje). Visok sadržaj suve materije može se registrovati u otpadnim materijama iz stanica za prečišćavanje. U oba načina proizvodnje varijacije u sadržaju suve materije odnos biogenih makroelemenata C:N ostaje nepromenjen.

Slobodni oblici azota (N-amonijum i N-nitrat) u otpadnim materijama su veći u odnosu na drugi organski otpad u obe tehnologije skladištenja. Nema vrednosti preko kritički prihvatljivih za optadni materijal u obe tehnologije proizvodnje.

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