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Heavy metal contaminants in organic fertilizers

Naliana LUPASCU[a], Elisabeta CHIRILA[b] and Marilena MUNTEANU[b,c]

[a]*Pedological and Agrochemical Studies Office, 17-19 Revolutiei Street, 900735 Constanta, Romania*
[b]*Chemistry Department, Ovidius University, 124 Mamaia Blvd, 900527 Constanta, Romania*
[c]*National Sanitary Veterinary Authority and for Food Safety 78, Mangaliei Street, Constanta, Romania*

Abstract When using animal manures as organic fertilizers, heavy metal content could influence the soil quality, may contaminate crops and cause health risks to both livestock and humans. The paper aims to report original results concerning Cadmium (Cd), Copper (Cu), Lead (Pb) and Zinc (Zn) occurrence in animal manures collected from a pig farm located in Mihail Kogalniceanu village, Constantza district. Standardised protocols were followed for sample preparation and analysis of metal content. Concentrations of heavy metals have been measured using flame atomic absorption spectrometry (FAAS). In the same time, nutrients have been determined (phosphorus, potassium and nitrogen) in soil and pig manures as well as other soil characteristics (pH, calcium carbonate, salinity, humus) in order to follow the further potential influence of pig manure on the soil characteristics. The results showed that, in the investigated organic fertilizers, heavy metal levels are not higher than the "attention limit" accepted for soil pollution and they can be used for soil quality improvement.

Keywords: pig manures, heavy metals, soil, nutrients, FAAS

1. Introduction

Enrichment of heavy metals in the environment is of major concern because of their toxicity and threat to human life and the environment.

Animal manures and sewage sludge (bio solids) are the main organic fertilizers which may contain contaminants as heavy metals [1-3]. Excessive heavy metal concentrations from animal manures make vulnerable the good functioning of soils by crops contamination and cause health risks to both livestock and humans [4-8]. These heavy metals may accumulate in soil with repeated fertilizer applications. Some countries have set tolerance limits on heavy-metal additions to soil because their long-term effects are unknown. These limits usually are set for the tillage layer (surface 20–30 cm) of soil where most root activity occurs.

The objectives of the study were to assess the soil characteristics before the use of pig manures for the fertility improvement and to report original results concerning Cadmium (Cd), Copper (Cu), Lead (Pb) and Zinc (Zn) occurrence in animal manures collected from a pig farm located in Mihail Kogalniceanu village, Constantza district.

2. Experimental

Analytical grade chemicals (HCl 37%, HNO_3>69%, hydrogen peroxide 30%, Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} certified analytical standard solutions 1000 mg/L purchased from Merck and Fluka) have been used.

In 2008, two samples of fresh pig manures from a farm located in Mihail Kogalniceanu village, Constantza district, have been collected.

Samples of soil in 5 depths (0-13, 13-29, 29-35, 35-75 and 75 120 cm) from the same farm have been collected in order to evaluate the characteristics before the use of pig manures for the improvement of the soil quality.

For metals determination, 2 grams of each dried pig manure samples have been processed as described in [9] to obtain aqueous solutions.

Metal concentrations have been measured by flame atomic absorption spectrometry (FAAS) technique using a GBC Avanta flame atomic absorption spectrometer, after the previous internal validation [10]. The main characteristics of the equipment for metals determination are presented in table 1.

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Table 1. Technical characteristics for metal determination using FAAS

Ion	λ (nm)	Optimal concentration range (μg/L)	Gases flow (L/min)	
			Air	Acety-lene
Cd^{2+}	228.8	0 – 1.8	10.0	1.0
Cu^{2+}	324.8	0 – 5.0	10.0	1.0
Pb^{2+}	217.0	0.2 – 2.0	10.2	1.1
Zn^{2+}	241.0	0 – 1.5	10.0	1.0

In order to characterise soil quality, pH was determined by electrometric method with pH Cond 707 equipment, humus concentration by titrimetric method Walklei and Black and total calcium carbonate concentration was measured using gas volumetric method (Schleibler). Available potassium was determined by atomic emission spectrometry using a flame photometer Sherwood and the total nitrogen has been measured by Kjeldahl method. Total available phosphorus concentration was determined in the solution obtained by extraction from soil samples with ammonium acetate lactate solution (AAL) at pH 3.75. The phosphate anion was determined as "molybdenum blue" [11]. The spectrometric measurements were done with Cintra 404 UV-Vis equipment.

3. Results and Discussions

a. Soil quality

The soil fertility is very important for plants nutrition. Soil fertility depends on how many nutrients are available in the soil. **Table 2** presents the obtained results concerning the chemical characteristics of the investigated soil samples.

The results show that the soil is low alkaline and has low salinity being appropriate for plant development.

As expected, the humus content has an optimum value (2-4% for normal growth of plants) only in the 0-13 cm depth soil samples (3.2 %) having a decreasing shape to 0.95 %.

The phosphorus and potassium concentrations in the soil profiles samples have variations as follows: in depths of 0-13 cm and 13-29 cm are high (100-126 mg/kg P_2O_5, respectively 184-256 mg/kg K) and continuously decrease in the next depths until 21 mg/kg P_2O_5 and 100 mg/kg K in the deepest soil sample (75-120 cm).

The lack of nutritive elements and especially the nitrogen deficit, intensifies the mineralization process of humus, reducing its quantity, what leads to the worsening of the soil quality. The depleted soil not only in NPK, but also in microelements accessible for plants doesn't ensure the plant productivity, resulting in a decrease of the quality of agricultural production.

b. Nutrients occurrence in pig manures

The key property of a fertile soil is its ability to support abundant plant life and chemical, biological and physical parameters contribute to the soil fertility. The nutritive elements could be magnified by the addition of adequate amount of inorganic or organic fertilizers. Therefore, many farms apply organic fertilizers, due to their contribution to the soil fertility, increasing and influencing the plant growth. For our study, the nutrients concentrations in the analyzed animal manure samples (P_2O_5, K_2O and total nitrogen) are in admitted limits (**table 3**). The manure samples correspond to the same source, but were collected from different locations.

Table 2. Investigated soil characteristics

Soil depth (cm)	pH	$CaCO_3$ (%)	Salinity, (mg/100 g soil)	Humus (%)	Total Nitrogen (%)	Mobile P (as P_2O_5) (mg/kg)	Mobile K (mg/kg)
0 – 13	7.9	4.20	74.46	3.20	0.18	126	256
13 – 29	8.0	4.27	79.90	2.50	0.17	100	184
29 – 35	8.1	5.60	84.66	1.20	0.17	51	156
35 – 75	8.2	9.81	86.02	1.10	0.16	31	120
75 – 120	8.3	10.74	116.96	0.95	0.16	21	100

Table 3. Nutrients occurrence in pig manures

Sample	P_2O_5 (%)	K_2O (%)	Total Nitrogen (%)
1	0.911	2.111	3.569
2	1.026	1.200	5.124
Accepted limits [12]	0.6 – 2.5	0 – 3.2	2-10

c. Heavy metals content

Heavy metals in animal manures or in sludge (bio solids) may be found in the form of metal ions or of inorganic or organic complexes. In soil there are the same metal forms which are also adsorbed to the surface of clay minerals or clay-humus complexes.

The studied heavy metals were Cd, Cu, Pb and Zn, each of them having particular importance in soil economy. Cadmium and lead are the heavy metals of most concern because they may affect human health. Copper and zinc represents necessary microelements which could be harmful only if the concentration is too high. Some countries have established tolerance limits on heavy metal additions to soil because their long-term effects are unknown.

These limits usually are set for the tillage layer (surface 20–30 cm) of soil where roots activity mostly occurs. In general, heavy metal cations are the most mobile in acid conditions and their mobility and availability decreases with the pH increase.

The analysed pig manures samples had total Cd, Cu, Pb and Zn concentrations lower than the admitted limits (Table 4).

Table 4. Heavy metals occurrence in pig manures

Sample	Pb (mg/kg ± SD)	Cd (mg/kg ± SD)	Cu (mg/kg ± SD)	Zn (mg/kg ± SD)
1	0.525 ± 0.047	0.172 ± 0.011	12.90 ± 0.72	4.35 ±0.12
2	0.325 ± 0.029	0.159 ± 0.010	11.50 ±0.64	3.56 ± 0.10
Accepted limits* [12]	0.1 – 300	0 – 10	4 – 365	2 - 323

4. Conclusions

Heavy metal levels in investigated organic fertilizers are not higher than the "attention limit" for soil pollution and they can be used for soil improvement.

Pig manure has a very high nutrient content and is rich in potassium and phosphorus. Not only does pig manure enrich the soil which helps plants to grow but it also helps improve the soil structure as the straw (plant material content) in the manure assure the water retention in the soil. Pig manure can be applied to root crops especially leeks and potatoes

It is important to remember not to apply fresh manure to plants and crops as the manure will scorch the plants.

5. References

*E-mail address: naliana_lupascu@yahoo.com

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