Application of Wastewater Sludge to Crop- Monitoring Changes in the "Soil-Fertilizer-Plant" System and Phosphorous Control Options

Nicholas KATHIJOTES[1], Elena ZLATAREVA[2], Svetla MARINOVA[3], Vera PETROVA[4],

1, Cyprus University of Technology, POB 50329, 3603 Limassol, Cyprus

2,3,4, 'N. Poushkarov' Institute of Soil Science Agrotechnology and Plant Protection - Shosse Bankja, Sofia 1080, Bulgaria.

Corresponding author: Nicholas Kathijotes, e-mail: nkathijotes@gmail.com; Nicholas.kathijotes@cut.ac.cy

Abstract

The aim of the study is to investigate the effects on the "soil-fertilizer-plant" system after a long application of wastewater sludge as well as the options in the recovery of phosphorous. Initially experimental plots with different soil types planted with experimental crops were investigated in order to evaluate the suitability of sludge as a fertilizer and detect possible problems.
Any changes that might have occurred in the "soil-fertilizer-plant" system as a result of this fertilization with wastewater sludge were to be recorded , in terms of soil, plant together with any relevant consequences on the environmental. This was done in view of the great energy potential contained in this wastewater sludge and the risks associated with its use.
Since 2006 sludge from the Wastewater Treatment Plant (WWTP) in Kubratovo Bulgaria, was applied as a soil conditioner to selected arrays cultivated with corn soils in the Sofia region, in accordance with the local legislation. The rate of application of sludge was calculated on the basis of chemical analysis for nitrogen content, and taking into consideration soil types, crop needs, and other requirements.
After 5-6 years of cultivation, samples were taken and analyzed for the same chemical properties as were the initial samples. No chemical fertilizer was applied during the experimental period. The results show that the use of sludge as a soil improver in accordance to local legislation does not pose any serious environmental risks but can maintain and improve soil fertility and crop yield. Slight increase in Cu and Zn, in plants were detected, however content of heavy metals for all plant samples were below Maximum Allowable Limits (Bulgarian Ordinance, 1979) and no signs of phytotoxicity were observed.

***Keywords**: wastewater sludge, organic matter, fertilization, heavy metals.*

Prolegomena

Periodic application of organic fertilizers to soils is necessary in order to maintain and improve their fertility. Incorporation of organic material also contributes towards the increase of soil organic matter and the preservation of the quality and quantity of soil nitrogen. The lack of organic fertilizers requires seeking of alternative options. Such reserve is sludge produced during biological wastewater treatment. Land application of raw or treated sewage sludge can reduce significantly the sludge disposal cost component of sewage treatment as well as providing a large part of the nitrogen and phosphorus requirements of many crops. Apart from soil enrichment in nutrients (Fytili and Zabaniotou 2008), an addition of sewage sludge results in an increase in organic matter content in soil (Kathijotes 2006; Epstein 2003). Sewage sludge however will contain, in addition to organic waste material, traces of many pollutants used in our modern society. Some of these substances can be phytotoxic and some toxic to humans and/or animals so it is necessary to control the concentrations in the soil of potentially toxic elements and their rate of application to the soil. Apart from those components of concern, sewage sludge also contains useful concentrations of nitrogen, phosphorus and organic matter.
Under intensive use of chemical fertilizers the balance of organic matter is disturbed thus resulting in degradation of the chemical and physical properties of the soil profile. Studies on the balance of soil nutrients are a part of a larger issue of a major nutrients balance, namely nitrogen. Nitrogen balance is particularly important as compared to other nutrients and plays a key role in the development of plant production. Nitrogen is extracted from soil in large quantities during harvest and is exposed to high losses due to its high mobility.
In order to maintain and improve soil fertility, regularly import of organic fertilizers is then necessary. Incorporation of organic material contributes to the increase and storage of soil organic matter and especially improves the content of soil nitrogen.

The lack of sufficient organic fertilizers then, leads to the necessity for seeking other alternatives.

The application of sewage sludge to land in member countries of the European Economic Commission (EEC) is governed by Council Directive No. 86/278/EEC (Council of the European Communities 1986). This Directive prohibits the sludge from sewage treatment plants from being used in agriculture unless specified requirements are fulfilled, including the testing of the sludge and the soil.
The above Directive specifies the requirements regarding chemical, agrochemical and microbiological characteristics that sludge should meet in order to be suitable as a soil improver. Numerous studies in terms of pots, vegetation and fields experiments were conducted in order to evaluate the suitability of sludge as a fertilizer and soil improver (Marinova, S., 2008; Kathijotes N.,Marinova S., Petrov K., 2005).

The problem of the effect of sewage sludge on seed germination and plant growth has also been addressed by numerous researchers (Fjällborg and Dave 2004; Fuentes et al. 2006; Hu and Yuan 2012; Oleszczuk 2008; Ramirez et al. 2008). However, those studies were focused primarily on the estimation of the toxicity of sewage sludge as such, without taking into account other important parameters that may be of major significance
in the utilisation of such material. Soil type, plant species used, kind of sewage sludge, effect of plants grown on soil amended with sewage sludge (especially if a given study addresses the problem in a long-term approach) are highly important issues whose role should be studied (Oleszczuk et.al 2012). Studies here then were conducted with different soil types and maize as the experimental crop, in order to evaluate the suitability of sludge as a fertilizer under various circumstances (Marinova, S. et al 2013; Ordinance № 3, 1979).
More and more farmers are now interested in organic farming and in particular to apply sludge as organic fertilizer.
The main aim of the study is to establish any changes that may occur in the "soil-fertilizer-plant” system as a result of fertilization with wastewater sludge.

Materials and Methods

Starting 2006, arrays of arable soils owned by private producer were selected in the Chepinci and Negovan villages -Sofia District as experimental areas for the application of wastewater sludge to soils. Wastewater sludge from the Waste Water Treatment Plant (WWTP) located in the village of Kubratovo was introduced in these areas as soil fertilizer.
Phytotoxicity of sewage sludge and its changes over time are significantly determined by the soil type. In this case, the soil type is one of the most important factors regulating the phytotoxicity of sewage sludge, especially in the long-term aspect. The soils from Negovan village are represented by Fluvisol - medium strong, light to medium sandy clay soil. The soils from Chepinci are medium to slightly leached cinnamon forest soils.
Growing experimental crop was maize, a common and widely cultivate crop in Bulgaria.
The sludge was incorporated in soil at different quantities (from 6 to 10 tones per ha) for various arrays. The rate of application was calculated on the basis of imported nitrogen and was consistent with the characteristics of the sludge, soil diversity, growing crop requirements, and other factors.
In order to evaluate this soil-fertilizer-plant system, certain basic chemical and agrochemical properties - pH, organic matter, total quantities of nitrogen, phosphorus and potassium and their mobile forms, and the content of heavy metals and toxic elements were determined.
For this purpose, the following methods were used:

- Determination of the pH reaction - *BS EN 12176:2000;*
- Determination of dry residue and water content - *BS EN 12880:2003;*
- Determination of total organic carbon - *BS EN 13137:2005,*
- Determination of total nitrogen- *BS ISO 11261:2002;*
- Determination of mineral nitrogen forms: ammonium /NH_4^+-N/ and nitrate /NO_{3-}-N/ nitrogen- *BS ISO 14255:2002;*
- Determination of mobile forms of phosphorus / P / - *BS ISO 11263:2002;*
- Determination of a mobile potassium / K / - *determination is carried out by methods of M. Milcheva used in ISSAPP "N.Pushkarov.";*
- Determination of the solubility of sulfur / S / as sulphate / SO_4 / *-VM-1: 2007;*
- Determination of total phosphorus content P, K, Ca, Mg, heavy metals - Cd, Cr, Ni, Cu, Zn, Pb, Hg, As - *BS EN-13346: 2000, BM-1: 2007,*

Results and Discussion

Laboratory chemical and agrochemical results from the examination of sludge resulting from the producing WWTP, are presented in Table 1.

Table 1. Agrochemical and chemical characteristics of the sludge

Indicators	Value	Indicators	Value
Dry matter%	66,96	Mg %	10 001
pH/H20/	7,34	S-SO$_{4\%}$	6 971
Organic C %	5,63	Pb mg/kg	78
Total N %	0,79	Cd mg/kg	1
N-NH$_{3\%}$	50	Cu mg/kg	179
N-NO$_{3\%}$	291	Ni mg/kg	24
Total P %	0,37	Cr mg/kg	35
Total K %	0,18	Zn mg/kg	461
Mobile P mg/kg	210	As mg/kg	<5
Mobile K mg/kg	500	Hg mg/kg	<1
Ca %	42 379		

The data shows that the sludge presents an organic soil improver with substantial amounts of total nitrogen of 0, 79%, total phosphorus 0, 37% and total potassium 0, 18%. The mobile forms of macronutrients which is actually used by the plants are respectively -291 mg / kg N-NO3, 50 mg / kg N-NN4, 210 mg / kg P and 500 mg / kg K, this means that the plants are good directly supply with N, P, K. Organic carbon is 5, 63% and it is sufficient to reduce the deficit of organic matter in the soil. The sludge used in experiment is a stable source of organic matter. The content of calcium and magnesium is high, because the fresh sludge is treated with lime solution for decontamination, which makes the sludge applicable to acidic soils.

The sludge was also analyzed for heavy metals and toxic microelements. The toxicity of heavy metals does not only depend on their properties, but primarily on the concentration in the sludge. Their high concentration puts barriers to the use of sludge in agriculture. The availability of increased levels of heavy metals in sludge used for agricultural purposes can disrupt and delay the mineralization of organic matter, also transformation and redistribution of nutritious for plants elements (Panayotova, G. et al 2008). All tested heavy metals were below the maximum admissible concentrations .Sludge is not representing risk to the soil and plants.

The data obtained from chemical analysis of soil arrays before conduct of the experiment are presented in table 2.

Table 2. The parameters investigated in soil arrays in Negovan village at the beginning of the experimental period (2006).

Arrays № / Parameter	16	17	18	19	31	32	46
pH (H_2O)	7,22	7,22	7,37	7,37	6,05	6,05	6,67
Org. matter%	1,27	1,27	1,15	1,15	0,66	0,66	1,19
Total N %	0,17	0,17	0,17	0,17	0,1	0,1	0,12
Total P %	0,1	0,1	0,1	0,1	0,08	0,08	0,06
Total K %	0,14	0,14	0,17	0,17	0,08	0,08	0,08
NO_3-N mg/kg	3,12	3,12	2,18	2,18	3,16	3,16	3,74
NH_4-Nmg/kg	3,3	3,3	3,8	3,8	7,41	7,41	5,06
P_2O_5 mg/100g	29,5	29,5	29	29	8,22	8,22	10,8
K_2O mg/100g	15,5	15,5	14,9	14,9	8,79	8,79	35,5
Cu mg/кg	56,3	56,3	67	67	36,5	36,5	23
Zn mg/кg	53,5	53,5	62,5	62,5	37,8	37,8	31,3
Pb mg/кg	18	18	24,3	24,3	20,3	20,3	14,8
Cd mg/кg	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50	<0,50
Ni mg/кg	10,3	10,3	12,8	12,8	7,5	7,5	10,3
Cr mg/кg	21	21	26	26	14,8	14,8	13
Hg mg/кg	0,026	0,026	0,023	0,023	0,019	0,019	0,022
As mg/кg	2,91	2,91	2,91	2,91	2,67	2,67	1,88

The soils of plots 16, 17, 18 and 19 (Negovan village) are with neutral to slightly alkaline pH reaction and in plots 31, 32 and 46, the reaction is slightly acidic.
Specific arrays are stocked with various amounts of essential nutrients. Very well stocked with phosphorus is soils are arrays 16, 19, 67, 68, well stocked array, 90 weak stocks are arrays 125, 31, 46 and very poorly stocked-106, 122. Very well stocked with potassium is only plot 46, well stocked are 67 and 68, average stocks are plots 16, 17, 122, 125 and with very slightly stocks- 90, 31 and 32. All arable arrays had a low content of mineral nitrogen. The concentration of heavy metals Hg, Cd, Pb, Ni, Cr, Cu, Zn and As are minimal and below MAC for all studied soil arrays. The amount of heavy metals and arsenic in soils plots have demonstrated a slight increased after the introduction of sludge, but the measured values were still below MAC for these indicators presented in the legislation. There is no environmental risk for soil resources and agricultural production of contamination with heavy metals and toxic microelements.
During 2013 (after 6 years of land use) from the same arrays was taken and analyzed the average soil samples. Besides sludge for research period 2007-2013 in the plots any other fertilizers are not imported. The results of analysis are presented in Table 3.

Table 3. The parameters investigated in soil arrays in Negovan village at the end of the experimental period (2013).

Plots № / **Parameter**	**16**	**17**	**18**	**19**	**31**	**32**	**46**
pH (H_2O)	6,27	6,06	6,23	6,22	6,17	6,04	6,4
Org. matter%	1,4	1,24	1,33	1,33	1,47	1,4	1,45
Total N %	0,11	0,1	0,1	0,11	0,11	0,11	0,1
Total P mg/kg	275,44	263,93	300,4	296,77	281,98	253,4	276,33
Total K %	0,25	0,22	0,26	0,24	0,24	0,24	0,25
NO_3-N mg/kg	<10	<10	<10	<10	<10	<10	<10
NH_4-Nmg/kg	21,62	24,57	24,89	22,6	26,86	24,57	21,29
P_2O_5 mg/100g	<5	<5	<5	<5	<5	<5	<5
K_2O mg/100g	11,06	13	11,02	9,42	15,51	10,54	13,31
Cu mg/кg	13	13	13	14	13	13	14
Zn mg/кg	64	37	40	39	35	35	35
Pb mg/кg	51	47	44	36	42	46	43
Cd mg/кg	<4	<4	<4	<4	<4	<4	<4
Ni mg/кg	20	19	21	20	23	23	23
Cr mg/кg	10	9	10	9	21	22	22
Hg mg/кg	<1	<1	<1	<1	<1	<1	<1
As mg/кg	7	10	12	10	9	6	8

Data shows that in all soil missives pH decreases, and organic matter rises. In terms of total and mobile forms of nutrients, we observe a general decrease between the initial and final stages of this research. That is, in (fig.1) nitrogen had a decrease from an average of 0.14% to 0.10%. Phosphorous also decreased from an average of 0.08% to 0.03%. The values for Potassium, showed an increase from 0.12 to 0.24%. During this period of land use, the agricultural crops have utilised significant amounts of nutrients from soil reserves and from applied sludge. Soil reserves with nitrogen and phosphorus then, have significantly decreased. Further addition of sludge actually improves plant nutrition.
The amounts of heavy metals and arsenic in soils plots have demonstrated a slight increased after the introduction of sludge, but the measured values are below the EU allowable limits. We can therefore summarize that no heavy metals or toxic microelements environmental risk to soil resources and agricultural production is evident.

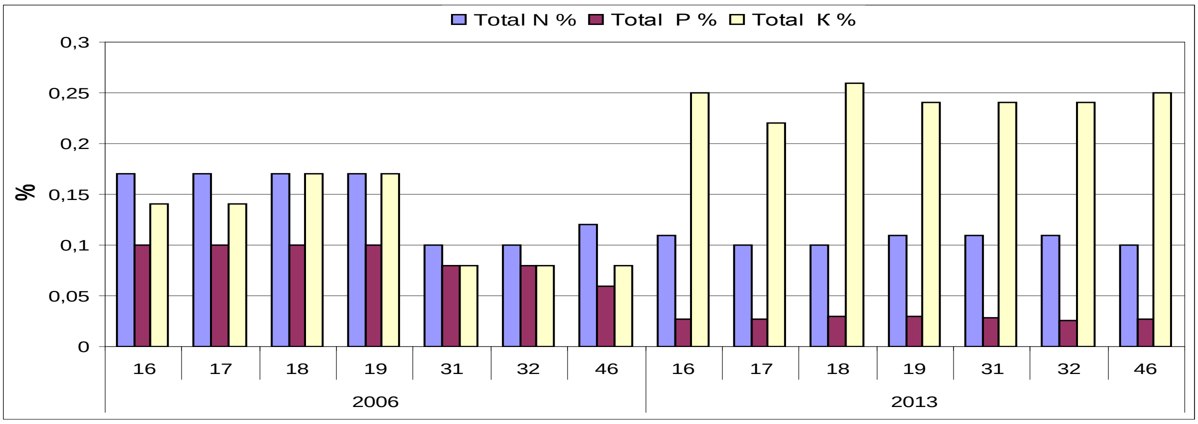

Fig.1 Evaluation of basic nutrients from arrays in Negovan village -2006-2013

In 2008 after harvesting of selected plots plant samples were taken in order to identify the impact of sludge on the quality of crop production in terms of nutrients and heavy metals. For comparison purposes plants samples outside of the experimental plots were analysed. The results are presented in Table 4.

Table 4 Chemical characterizations of maize plant samples from selected soil missives treated with sludge versus plants grown in untreated with sludge plots (Control).

Name and Plots №	**Indicators**	**N %**	**P%**	**K%**	**Ca%**	**Mg%**	**Zn g/kg**	**Cu mg/kg**	**Mn mg/kg**	**Fe mg/kg**
Negovan	Control	0,6	0,29	3,8	0,46	0,23	24	3	67	254
	17	1,5	0,39	4,5	0,57	0,26	34	4	45	169
	18	2	0,41	5,3	0,54	0,37	36	5	52	112
	19	2,5	0,43	5	0,48	0,37	43	5	68	166
	46	2,6	0,4	5,8	0,49	0,37	40	4	62	100

Significant amounts of nutrients (N, P, K, Ca and Mg) were found in all plants.
The natural background concentration of metals found in soil is normally less available for crop uptake and hence less hazardous than metals introduced through sewage sludge applications (Scheltinga, 1987).
Slight increase in Cu and Zn, compared to the controls elements were detected, with content of heavy metals for all plant samples being below Maximum Allowable Limits and with no signs of phyto-toxicity observed. The levels of heavy metals in plant production are not prohibitive for the use of corn as animal feed. The measured Cd values in all arrays are <2, and presence of Pb is not detected.

Phosphorous recovery options:

Issues like, Water Quality (delivering safer drinking water and meeting the good water status), Value Recovery (reducing chemical and energy consumption in secondary treatment, generating more biogas from sludge, and phosphorus recovery), Product Quality Enhancement and Application (adding value to and making efficient use of the recovered products), and Sustainability (techno-economic assessment of the innovative processes) should be addressed when considering a holistic approach in environmental management. In managing nutrients, public safety, closed loop phosphorus management reducing carbon dioxide emissions (climate change) and improving the security of the land recycling route together with economic opportunities developed by changing the technology basis of water and wastewater treatment should be closely considered.

By observing our initially available sludge (table 1), it appears that there is an imbalance between chemical elements with high amounts of ammonium, but low amounts of potassium and phosphorous.
Figure 1 too, shows decreasing amounts of Phosphorous in soils between the years of 2006 and 2013. It is evident then that controlling the amounts of phosphorous movement in the "Soil-fertilizer-plant” system can be improved in maintaining a better nutrient balance that will result in a healthier agricultural soil.

The applied sludge when properly treated, it is expected to provide significant improvement in biogas yield while at the same time producing marketable products. BIOPOL, is obtained through a recovery process using a micro-milling technique that causes cell disruption a breakthrough innovation in sludge-derivatives. This blend of biopolymers, has many exciting potential applications in wastewater treatment. It exposes intracellular products to enzyme actions and leads to a significant enhancement in the biogas yield during digestion while substantially raising the soluble phosphorus content in the digested liquor. Phosphorus recovery becomes then more viable (BIOPHOS), and may play may play a very important role in sludge and phosphorus management in Europe that should be moving towards a circular economy (COM 2014).

In view of the criticality of phosphorus as a raw material and the need to deliver the resource efficiency agenda established under the ‘Europe 2020 Strategy’ for smart, sustainable and inclusive growth, the investigation and application of the underpinning technologies for recovering, enhancing their functionalities, and delivering the phosphorus products as marketable commodities to suit local condition as well as to provide flexibility in its agricultural use is absolutely essential.

Using BIOPOL, BIOPHOS can be produced and can recover soluble phosphate from digested sludge liquor. BIOPHOS having at least 20% Phosphorus (as P_2O_5, dry weight basis) of which at least 80% is Citric Soluble.

Digested sludge that has been treated by micro-milling from the BIOPOL when used with further anaerobic digestion will lead to at least 40% increase in biogas yield while also raising the soluble phosphorus content in the digested liquor by at least 100%. It is believed that such a treatment will solubilise at least 75% of the phosphorus content of surplus activated sludge. Further, and after P recovery, the sludge residue would give rise to a sludge cake with a considerable reduced P content (at least 50% lower) and would make a more suitable alternative to conventional biosolids for agricultural recycling.

Conclusions and Epilogue

- Sludge from urban wastewater treatment plants, can be used as a soil improver, for directly supplying the crop with nitrogen, phosphorus and potassium. Sludge can be a stable source of organic matter which improves the organic matter content in soils.
- The results clearly demonstrate that the application of municipal sludge on fluvisols and cinnamon forest soils, increase crop yield and stimulate the formation of high-quality biomass.
- Slight increase in concentrations of the total amounts of trace elements and heavy metals such as Cu, Zn, Pb, Cd, Ni, Cr, Hg, As were detected in the soil, although these values were below MAC.
- The concentration of heavy metals in maize plants is below toxic levels, and there is no plants tissue accumulation. This however requires closer monitoring.
- Huge amounts of nutrients stored in municipal sludge can be exploited.
- Further research is necessary in order to develop a thorough scientific understanding of the mechanisms of phosphorus release and uptake from BIOPHOS

Summarising, it is stated that the use of sludge from urban wastewater treatment plants as a soil improver does not represent a serious environmental risk. It can be used in agricultural practice in order to maintain and improve soil fertility and crop yield, but after close monitoring and in adherence to local legislation. Further improvements to sludge quality should be investigated at the treatment plant level.

Acknowledgement
The authors express their appreciation to the Bulgarian National Science Fund for financial support in the frame of Scientific project FFNIPO_12_01283: “Ecology of agro-ecological systems and increase efficiency by applying a revised bio organic waste from fertilization, introduction of energy plants and complex utilization of biomass as an energy carrier” (Contract SFSR– E01/3 from 27.11.2012).

References

Bulgarian Ordinance № 3 SG 36 PSC (1979) ‘Admissible Contents of harmful substances in the soil’. Sofia, Bulgaria

COM (2014) 398. Towards a circular economy: A zero waste programme for Europe. COMMUNICATION FROM THE COMMISSION, Brussels, 2.7.2014.

Epstein, E. (2003). Land application of sewage sludge and biosolids. Lewis: Boca Raton.

Fytili, D., & Zabaniotou, A. (2008). Utilization of sewage sludge in EU application of old and new methods—a review. Renewable and Sustainable Energy Reviews, 12, 116–140.

Fuentes, A., Llorens, M., Sacz, J., Aguilar, M. I., Perez-Marin, A. B., Ortuno, J. F., et al. (2006). Ecotoxicity, phytotoxicity and extractability of heavy metals from different stabilized sewage sludges. Environmental Pollution, 143, 355–360.

Fjällborg, B., & Dave, G. (2004). Toxicity of Sb and Cu in sewage sludge to terrestrial plants (lettuce, oat, radish), and of sludge elutriate to aquatic organisms (Daphnia and Lemna) and its interaction. Water Air Soil Pollution, 155, 3–20.

Hu, M., & Yuan, J. (2012). Heavy metal speciation of sewage sludge and its phytotoxic effects on the germination of three plant species. Advances Mathematical Research, 347–353, 1022–1030.

Kathijotes N., Marinova S., Petrov K. (2005). “Effects of Treated Wastewater and Sludge in Agriculture: Environmental and Growth Evaluation of Selected Cultures”. International Scientific Conference on Agricultural Engineering Problems, (Agris Information Center Record #LV2006000102, LUA), Proceedings 9984-596-93-1.- p.149-152, Latvian University of Agriculture, 2-3 June 2005 Jelgava, Latvia

Kathijotes N. (2006), "Wastewater Reuse for Irrigation: an Acceptable Soil Conditioner?" Conference on Water Observation and Information System for Decision Support BALWOIS 2006, 23-26 May 2006 Ohrid, F.Y.Republic of Macedonia

Marinova, S., R. N. Kathijotes, E. Zlatareva, D. Stoicheva, V. Kolchakov. (2013). Comparative assessment of sludge from different places of treatment in wastewater plant in Sofia regard to their use in agriculture. INTERNATIONAL SIMPOSIUM ISB-INMA TEN Agriculture and Engineering. 1st - 3rd November 2013, 193-200

Marinova, S., 2008. The sludge from WWTP and rules for their use in. Publishers by "Publish ScieSet Eco", Sofia, 123 p.

Oleszczuk, P. (2008). Phytotoxicity of municipal sewage sludges compost related to physico-chemical properties, PAHs and heavy metals. Ecotoxicology Environmental Safety, 69, 496–505.

Oleszczuk P. ,Malara A., Jośko I., Lesiuk A. (2012).The Phytotoxicity Changes of Sewage Sludge-Amended Soils Water Air Soil Pollut 223:4937–4948 DOI 10.1007/s11270-012-1248-8

Panayotova, G., E. Zlatareva. 2008. Estimation the effect of sewage sludge on the properties of pellic vertisols and durum wheat productivity. XII International ECO-Conference „Save food", 24-27th September, Novi Sad, 2008, 193-198

Ramirez, W. A., Domene, X., Andrés, P., & Alcañiz, J. M. (2008). Phytotoxic effects of sewage sludge extracts on the germination of three plant species. Ecotoxicology, 17, 834–844.

Scheltinga HMJ, 1987; Sludge in agriculture: the European approach. Water Sci. Technol., 19 (1987), pp. 9–18. St-Yves and Beaulieu.