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Evaluation of Polycyclic Hydrocarbons in Sewage Sludge Compost

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One of the main options of sewage sludge disposal is its application as fertilizer. The Directive on sewage sludge 86/278/EEC aim is to support the use of sewage sludge as fertilizer in agriculture. This Directive regulates sewage sludge use in such a way as to control and prevents harmful effects on soil, animals and humans. Sewage sludge application as fertilizer has even been recommended as the most appropriate and suitable option in the European Directive draft “Working document on sludge” published in 2000. But this Directive sets limit values for only 7 heavy metals in soil as well as in sewage sludge itself. This Directive does not consider organic pollutants such as dioxins, polycyclic aromatic hydrocarbons (PAHs) and potentially pathogenic organisms, or newer, less investigated compounds spread deliberately or accidentally into the environment. The aim of the research was to evaluate the PAHs (benzo(a)pyrene, fluoranthene, pyrene) in compost from sewage sludge. The results was compared with the PAHs in the compost from green waste and with the EPA recommended limit values. The research results demonstrate that concentrations of PAHs in the compost are smaller than recommended concentrations by EPA. But still there is a risk because PAHs are cancerogenic for humans and animals, also there is possibility that plants can uptake this organic compound from soil which is fertilized with this compost. The possible accumulation of organic pollutants in the food chain is quite high and should be done more studies about the risk evaluation. Compost from sewage sludge can be used for the remediation of damaged sites but not as fertilizer for agricultural purpose.

1. Introduction

During the last twenty years, the use of composted sewage sludge on agricultural soils has become part of a political discussion regarding waste recovery. Quite often this discussion meets an economic need too. Existing European legislation governing land application of sludge and the monitoring of sludge quality (Directive 86/278/EEC) still rise many questions about the risks associated with the presence of organic compounds in sludge.

Sewage sludge application as fertilizer has even been recommended as the most appropriate and suitable option in the European Directive draft “Working document on sludge” published in 2000. The main Directive on sewage sludge (86/278/EEC) sets limit values for only 7 heavy metals: cadmium, copper, nickel, lead, zinc, mercury and chromium in soil as well as in sewage sludge itself. This Directive does not consider organic pollutants such as dioxins, PAHs and potentially pathogenic organisms, or newer, less investigated compounds spread deliberately or accidentally into the environment.

Large numbers of chemicals, including organic compounds (OCs) are used in modern society (Almarcha et al., 2014). According to European Chemicals Agency (ECHA) more than 120,000 chemical substances registered in the European Union (EU) are estimated to be used daily in Europe (ECHA, 2016). Many of these registered (and some not registered) substances are discharged into the waste streams handled by wastewater treatment plants.

The main purpose of wastewater treatment is to reduce or destroy nutrient loads and biochemical oxygen demand. According to Olofsson (2012) there is another important purpose – to act as a partial barrier, reducing the amounts of carcinogenic, mutagenic and reprotoxic chemicals, organic pollutants, pesticides, toxic metals

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and other potentially harmful anthropogenic substances to levels (in both effluent and sludge) that will not cause adverse environmental effects.

The amount of contaminant (or compound) in sewage streams controlled by wastewater treatment plants is dependent on the amount of chemicals used (Gottardo et al., 2015). According to Olofsson (2012), leakages from consumer products also contribute to the load. The personal care products and pharmaceuticals used directly influence the load. Indirect sources are various plastic additives incorporated in many consumer products. Additional important sources influencing wastewater treatment plants contaminant loads are the massive use of industrial chemicals and storm water pollution originating from traffic, other combustion sources and long distance air transport (Valskys et al., 2015).

Numerous studies have focused on amounts of sewage sludge contaminants, such as PAHs, PCB, AOX, LAS and others (Kapanen et al., 2013; Rhind et al., 2013). The results of these studies indicate that many compounds can be present in wastewater treatment plants effluent or sewage sludge at potentially harmful concentrations (Zinkute et al., 2015). The secondary source of anthropogenic substances released into the environment is wastewater treatment plants.

According to Olofsson (2012) traditional organic compounds are lipophilic and thus have tendency to accumulate in sludge. However levels of traditional organic compounds, such as PAHs, PCDD/Fs and PCBs in sewage sludge have substantially fallen in recent decades (Clarke et al., 2011).

The main purpose of wastewater treatment plant is to concentrate the organic pollutants in the sewage sludge. During wastewater treatment process some organic contaminants can degrade, especially in aerobic process (Pishgar et al., 2014). But some organic compounds as linear alkylbenzene sulphonates (LAS) are specifically added to detergents.

Table 1: Summary of the main organic compounds found in sewage sludge (mg/kg d.w. except where indicated) (Smith et al., 2011)

Substance	Minimum	Maximum	Mean
PAHs	6.40	72.00	130.00
PCBs	0.05	0.93	0.22
PCDD/Fs, ng/kg	2.40	80,000.00	2,178.00
TEQ contribution attributable to the PCDD/Fs and PCBs	0.70	680.00	36.50
Linear alkylbenzene sulphonates LASs	2,100.00	10,500.00	5,560.00
Di(2-ethylhexyl)phthalate DEHP	0.30	1,020.00	110.00 (median)
P/NPEs	256.00	824.00	351.00
Polycyclic musk fragrances (HHCB, AHTN)	2.00	97.00	32.00
Polychlorinated n-alkanes PCNs	0.05	0.19	0.08
PBDEs (six congeners) µg/kg	12.50	288.00	108.00 (median)
Triclosan	0.09	16.80	2.30 (median)

McNally et al. (1998) wrote that some of organic compounds (such as PAHs) can be degraded in 12-80 h. However, these experiments of PAHs were done under ideal conditions with constant temperature 20°C. Adapted bacteria were used and also were added nutrients (Smith, 2009). In practical case with low temperature the actual degradation time is much longer – from 80 to 600 h. This mean that PAHs are hardly to be degraded in a wastewater treatment plant. According to Harrison et al. (2006) for many organic compounds or hydrophobic compounds sorption to the sewage sludge is the main pathway for organic compounds removal from wastewater.

Volatile organic compounds as hydrophobic organic compounds can have a potential risk to environment (sewage sludge can be used as fertilizer in agriculture) and human health. Meanwhile there are no legal limits for organic compounds in sewage sludge and its application into soils. In 2000 European Commission released “Working document on sludge” limits for 6 organic compounds is offered (Table 2). This document was only the recommendation and the limit values for the organic compounds was not included in to the official EU Directive 86/278/EEC.

Table 2. Limit values for concentrations of organic compounds (CEC, 2000)

Organic compound	Limit value, mg/kg d.w.
AOX - sum of halogenated organic compounds	500.00
LAS - linear alkylbenzene sulphonates	2600.00
DEHP - di(2-ethylhexyl)phthalate	100.00
NPE - it comprises the substances nonylphenol and nonylphenolethoxylates with 1 or 2 ethoxy groups	50.00
PAH - sum of the following polycrylic aromatic hydrocarbons	6.00

Suciu et al. (2015) noted that EC has been planning to determine limits for organic compounds in sewage sludge (such as PAHs, LASs, DEHPs and etc.) for 14 years. However, still no regulation or legislation has been implemented.

According to EC report of pollutants in urban wastewater and sewage sludge (2001) most organic compounds are presented in environment at low concentrations, but still some of organic compounds may bioacumulate or have effect on health.

Many researches (Kapanen et al., 2013; Rhind et al., 2013) points that organic compounds are found in sewage sludge at high concentrations (PCBs, DEHPs, PAHs and etc.). Other authors like Suciu et al. (2015) highlighted that the sum of PAHs in sewage sludge not exceeding the EU and Italian recommendations. This mean that the question of safe use of sewage sludge as fertilizer in agriculture still remain open. The aim of the research was to evaluate the PAHs (benzo(a)pyrene, fluoranthene, pyrene) in compost from sewage sludge and in compost from green waste. The results was compared with the EPA recommended limit values.

2. Methodology of experimental research

The aim of experimental research is to evaluate amount of selected organic compounds – PAHs in compost from sewage sludge and compost from green waste. For the evaluation of PAH in two different compost types, samples were taken in 3 different places: start of the pile, middle of the pile and the end of the pile (Figure 1). Three samples were taken from sewage sludge compost and three samples from green waste compost. All the samples were taken in the middle of the week to minimize effects of the reductions in many industrial activities that occur during weekends and other weekend activities that may affect sewage water and sludge contents. The samples were taken from small company “Biastra plius”. This company is responsible for the composting of the sludge from the Vilnius wastewater treatment plant.

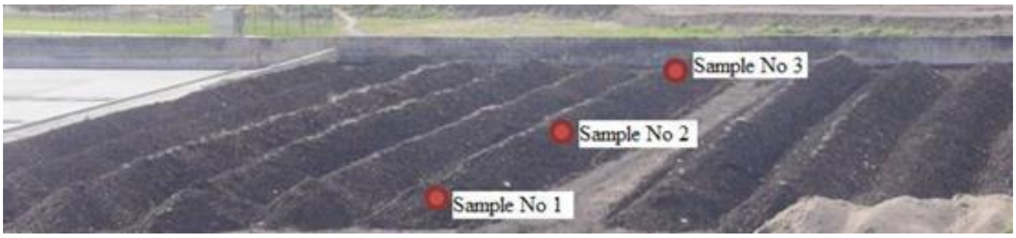

Figure 1: Places of collected samples.

All samples were collected in dark pre-treated bottles. The bottles were immediately stored at minus 2°C until analysis in order to reduce the risk of microbial degradation (Olofsson, 2012). The samples were prepared by three steps: drying and fractionation, extraction, clean-up. All samples were dried on Petri dishes in an oven at 40 °C until a constant weight is attained (after 24-72 h). Lumpy samples were crushed in a porcelain mortar with a pestle. Then, all samples were sieved to a particle size of 2 mm. After these preparations was chemical analysis which consisted gas chromatography and mass spectroscopy. The compounds were extracted using Soxhlet solid/liquid extraction (Gan et al., 2009). According Swiss Agency for the Environment recommendations (2001) 20 g of the ≤2 mm fraction were weighed into a pre-cleaned Soxhlet thimble (thimble – cellulose, diameter 28 mm), and 10-50 µL of the internal standard solution was added in the centre part of the sample. A small amount of cleaned cotton wool was placed on top of the thimble. The sample was extracted for 24 h with 300 mL of cyclohexane in a 200 mL Soxhlet extractor (≥6 cycles per hour). The extractor was lagged with a sheet of polyurethane foam. The clean-up of samples was performed according Swiss Agency for the Environment recommendations (2001). The purpose of it was to remove undesirable compounds such as lipids and other interferences to decrease chemical noise and avoid interfering compounds co-eluting in the instrumental analysis. 4 mL of sample was transferred to a 15 mL centrifuge tube, about 3 mL of dimethylformamide (DMF) and water (ratio 9 and 1: it means 180 mL of DMF and 20 mL distilled water) mixture was added in centrifuge tube. Mixture was shaken 30 s. Centrifuge tube was centrifuged at 2500 rpm for 5 min. The cyclohexane phase was sucked off with a pipette and transferred to a new centrifuge tube, then 1 mL of DMF mixture was added in new centrifuge tube. Mixture was shaken 30 s and centrifuged at 2,500 rpm for 5 min. 5 mL of distilled water and 3 mL of cyclohexane was added to the centrifuge tube with the mixture of DMF (total volume was 13 mL). Mixture was shaken 30 s and 1 mL of cyclohexane was added. Cyclohexane extract was washed with 2 mL of distilled water and transferred to a new centrifuge tube and dried with 1 g of Na_2SO_4. The sample extract was transferred to a vial and the Na_2SO_4 washed with 1 mL of cyclohexane. The sample extract was adjusted to the desired sample volume (volume 1 mL) by the Automated Evaporation System and cleaned further with a silica column. Prepared and concentrated sample extracts (one for compost from sewage sludge and other for compost from green waste) were prepared for the chemical analysis, which was performed by using gas chromatography with auto injector and mass spectrometry. The following separation capillary was used: 5-%-Phenyl-95%-methylpolysiloxane, capillary dimensions – 25 m and 0.25 mm of polyimide coated quartz capillary. The mass spectrometer with perfluorotributylamine (PFTBA) applying the fragment masses m/z 119.0, 219.0, 264.0 or 414.0 was used. The signal width at half height was adjusted to 0.55±0.03 u and the mass scale calibrated to an accuracy of ± 0.05 u. Compost quality parameters (pH, dry matter, organic matter, phosphorus, nitrogen) were measured too. These parameters were determined by EU standards: EN 13037:2012; EN 15934:2012; EN 13039:2012; EN 13654-1:2002; EN 13650:2006.

3. Results of experimental research

Two different groups of samples were analysed: compost from sewage sludge and compost from green waste. Results of compost quality parameters are shown in Table 3.

Table 3: Measured compost quality parameters

	Compost from sewage sludge				Compost from green waste			
Sample point No.	1.1	1.2	1.3	Average	2.1	2.2	2.3	Average
Compost pH	7.00	7.26	7.35	7.20	7.90	8.10	7.94	7.98
Dry matter, g/kg	651	663	723	679	756	750	750	752
Organic matter, %	37.9	37.8	38.6	38.1	46.1	45.5	44.3	45.3
Total N, gN/kg	6.14	6.15	6.13	6.14	8.28	8.30	8.24	8.27
Total P, gP/kg	0.018	0.019	0.017	0.018	0.45	0.35	0.40	0.45

As seen in Table 3 green waste compost has a higher pH value than the compost from sewage sludge. Compost pH depends on materials which were composted. The investigated composts has pH in scale from 7 to 8. Green waste compost has more dry matter than compost from sewage sludge (it is about 1.1 times more). The most composts has amount of dry matter between 40-50 %. Green waste compost has more organic matter than compost from sewage sludge (it is about 1.2 times more). Organic matter improves soil structure in compost and also water holding capacity. Organic matter in compost depends on materials which were composted and process time. According to the results of quality parameters – green waste compost has better parameters than compost from sewage sludge. Green waste has more organic matter, nitrogen and phosphorus. It means that plants can uptake more organic matter from fertilized soil.

In this experiment concentrations of three PAHs (Benzo(a)pyrene, Fluoranthene, and Pyrene) were measured. Results of measurements (compost from sewage sludge and compost from green waste) are shown in Table 4 and Table 5.

Table 4: Results of PAH concentration, µg/kg MS (compost from sewage sludge)

Sample point No.	1.1	1.2	1.3	Average	Recommended limit values by EPA
Benzo(a)pyrene	11.0	12.0	12.0	11.7	63.0
Fluoranthene	28.0	29.0	29.0	28.7	45.0
Pyrene	30.0	29.0	29.0	29.7	44.0

Table 5: Results of PAH concentration, µg/kg MS (compost from green waste)

Sample point No.	2.1	2.2	2.3	Average	Recommended limit values by EPA
Benzo(a)pyrene	7.0	8.0	8.0	7.7	63.0
Fluoranthene	12.0	11.5	11.5	11.7	45.0
Pyrene	14.0	15.0	15.0	14.7	44.0

Déportes et al. (1995) has confirmed that “the concentration of PAHs in compost from sewage sludge varies over a wide range, from 1 to 250 ppm, and for particular compounds the content range is from 0.0006 to 49.3 ppm”. Such a broad range of concentrations of PAHs in compost from sewage sludge, conditioned by their origin, has been confirmed by the results cited by Grossi et al. (1998) and Brändli et al. (2007). Compost which is produced from sewage sludge derived from towns and villages contained twice PAHs as compost made of biowaste (green waste).

Brändli et al. (2005) have also demonstrated that, “in general, compost made of sewage sludge contained more PAHs, except for naphthalene, than composted green waste and average content of the 16 analyzed PAHs in green waste composts was 1,715 µg/kg, as compared to 1,915 µg/kg in compost made of sewage sludge waste”.

There are no established limit values of PAHs for green waste composts, therefore the appropriate values are taken by comparison with compost from sewage sludge. The main indicator of organic compound for total PAHs is benzo(a)pyrene (McGowin, 2001). The value of this compound in the analysed compost from sewage sludge ranged within 12 µg/kg, thus being about 5 times lower than the recommended limit value by EPA.

Concentrations of benzo(a)pyrene, fluoranthene and pyrene are lower than recommended limit values by EPA. But still there is a risk, even concentrations are smaller than recommended. The risk is based on accumulation of pollutants in the soils. Benzo(a)pyrene (and other PAHs) is cancerogenic for humans and animals, also there is possibility that plants can uptake this organic compound from soil which is fertilized with this compost.

4. Conclusions

The European sludge Directive 86/278/EEB sets limit values for only 7 heavy metals: cadmium, copper, nickel, lead, zinc, mercury and chromium in soil as well as in sludge itself. This Directive does not consider organic pollutants such as dioxins, PAHs, nor potentially pathogenic organisms. EU Member States should implement limit values for organic compounds as well as for contaminants which were not addressed in it.

Concentrations of benzo(a)pyrene, fluoranthene and pyrene in compost from green waste are smaller than in compost from sewage sludge. They are smaller than recommended by EPA, but still, there is a risk - Benzo(a)pyrene is cancerogenic (and other PAH), also there is possibility that plants can uptake them.

Compost from sewage sludge use in agriculture has risk. The obtained concentrations of the PAHs are far below the limits but the possible risk is based on accumulation of pollutants in the soils. The possible accumulation of organic pollutants in the food chain is quite high and should be done more studies about this risk.

Reference

Almarcha D., Almarcha M., Nadal S., Poulssen A., 2014, Assessment of Odour and VOC Depuration Efficiency of Advanced Biofilters in Rendering, Sludge Composting and Waste Water Treatment Plants. Chem Eng Transactions 40, 223-228.

Brändli R.C., Bucheli T.D., Kupper T., Furrer R., Stadelmann F.X., Tarradellas J, 2007, Organic pollutants in Swiss compost and digestate. 1. Polychlorinated biphenyls, polycyclic aromatic hydrocarbons and molecular markers, determinant processes and source apportionment, Journal of Environmental Monitoring 9 (5), 456.

CEC, 2000, Working Document on Sludge, 3rd Draft, Council of the European Community, Brussels 27 April, 19.

Clarke B.O., Smith S.R., 2011, Review of emerging organic contaminants in biosolids and assessment of international research priorities for the agricultural use of biosolids, Environment International 37 (1), 226-247.

Déportes I., Benoit – Guyod J.L., Zmirou D., 1995, Hazard to man and the environment posed by the use urban waste compost: a review, Science of Total Environment 172 (2-3), 172-197.

European Commission, 2001, Final Report on pollutants in urban waste water and sewage sludge, I C Consultants Ltd, London, United Kingdom.

EU, 1986, Directive 86/278/EEC: Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, Official Journal of the European Communities 181, 6-12.

ECHA, 2016, Information on Chemicals <echa.europa.eu/information-on-chemicals> accessed: 10.03.2016

Gan S., Lau E.V., Ng H.K., 2009, Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs), Journal of Hazardous Materials 172 (2-3), 532-549.

Gottardo M., Micolucci F., Mattioli A., Faggian S., Cavinato C., Pavan P., 2015, Hydrogen and Methane Production from Biowaste and Sewage Sludge by Two Phases Anaerobic Codigestion, Chemical Engineering Transactions 43, 379-384.

Grossi G., Lichtug J., Krauß P., 1998, PCDD/F, PCB and PAH content of Brazilian compost, Chemosphere 37 (9-12), 21-53.

Harrison E.Z., Oakes S.R., Hysell M., Hay A., 2006, Organic Chemicals in Sewage Sludge, Science of The Total Environment 367 (2-3), 481-497.

Kapanen A., Vikman M., Rajasarkka M., Itavaara M., 2013, Biotests for environmental quality assessment of composted sewage sludge, Waste Management 33, 1451-1460.

McGowin A.E., Adom K.K., Obubuafo A.K., 2001, Screening of compost for PAHs and pesticides using static subcritical water extraction, Chemosphere 45, 857.

McNally D.L., Mihelcic J.R., Lueking D.R., 1998, Biodegradation of three and four ring polycyclic aromatic hydrocarbons under aerobic and denitrifying conditions, Environmental Science Technology 32 (17), 2633-2639.

Olofsson U., 2012, Removal processes in sewage treatment plants – Sludge quality and treatment efficiency of structurally diverse organic compounds, PhD Thesis, Umeå University, Umeå, Sweden.

Pishgar R., Najafpour G.D., Neya B.N., Mousavi N., Bakhshi Z., 2014, Effects of organic loading rate and hydraulic retention time on treatment of phenolic wastewater in an anaerobic immobilized fluidized bed reactor, Journal of Environmental Engineering and Landscape Management 22 (1), 40-49.

Rhind S.M., Kyle C.E., Ruffie H., Calmettes E., Osprey M., Zhang Z.L., Hamilt D., McKenzie C., 2013, Short and long –term temporal changes in soil concentrations of selected endocrine disrupting compounds (EDCs) following single or multiple applications of sewage sludge to pastures, Environmental Pollution 181, 262-270.

Smith S.R., 2009, Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling, Philosophical Transactions of the royal society a mathematical, Physical and Engineering Sciences 367 (9), 4005-4041.

Suciu A.N., Lamastra L., Trevisan M., 2015, PAHs content of sewage sludge in Europe and its use as soil fertilizer, Waste management 41 (7), 119-127.

Swiss Agency for the Environment, 2001, Determination of polycyclic aromatic hydrocarbons in soil by GC/MS. Method Recommendations, University of Basel, Basel.

Valskys V., Valskiene R., Ignatavicius G., 2015, Analysis and assessment of heavy metals concentrations in Nemunas river bottom sediments at Alytus city territory, Journal of Environmental Engineering and Landscape Management 23 (2), 147-154.

Zinkute R., Baltrunas V., Taraskevicius R., Karmaza B., Stakeniene R., Seiriene V., Kisieliene V., 2015, Quaternary interglacial sediments as possible natural sources of arsenic and molybdenum anomalies in stream sediments in Lithuania, Journal of Environmental Engineering and Landscape Management 23 (1), 60-70.