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Degradation of carbamazepine and triclosan in sewage sludge mixtures used for fertilizing agricultural soils

Lembit Nei[1]*, Egge Haiba[1], Jane Raamets[1], Koit Herodes[2]

[1] Tallinn University of Technology/School of Engineering/Tartu College, Puiestee 78, 51008, Tartu, Estonia

[2] University of Tartu/Institute of Chemistry, Ravila 14a, 50411, Tartu, Estonia

* Corresponding author: Prof. PhD Lembit Nei, lembit.nei@taltech.ee, ORCID iD: https://orcid.org/0000-0002-6399-7093

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Abstract

Global deficit of fertilizers is evident and as a result of the war in Ukraine the situation is worsening. At the same time, not all the possible major resources of nutrients have found appropriate application in agriculture, as for example sewage and its sludge, which are among the most promising sources of P, N and organic matter. Sewage sludge (SS) usage as an agricultural fertilizer has a number of limitations. Amongst them persistent organic pollutants (POPs) have a special role due to their ability to affect living organisms. Ongoing work directed to eliminating POPs present in SS is widely reported, but due to the complexity of these compounds no universal success has been achieved. In the case of several undesired residual compounds promising results have been gained using SS composting with different bulking agents. The current study was concentrated on the degradation of some widely used persistent POPs that are present in SS, namely carbamazepine (CBZ) and triclosan (TCS). Peat alone as a bulking agent widely used in the mixture with sewage sludge in Estonia is not suitable for initiating the process of composting. Additions of carbon-rich matter, as for example draff, might provide the relevant conditions needed for launching this process.

1. Introduction

Soil pollution has clear impact on food quality and ongoing research in this field is of utmost importance (Golbiak and Rutkowska, 2023; Haiba et al., 2018; Nei et al., 2009). The global deficit of fertilizers, leading to acute food insecurity, is evident. The war in Ukraine only worsens the situation (Osendarp et al., 2022). At the same time, several major perspective resources of nutrients have not found appropriate exploitation in agriculture. Among them, sewage sludge (SS) could be one of the most significant sources of phosphorus (P), nitrogen (N) and organic matter. SS is the major product of sewage treatment plants that anyhow must be utilized (Kicińska et al., 2018). Municipal SS can be a source of micronutrients for plants with high nutrient requirements, and the use of macronutrients from SS by energy crops is an alternative form of nutrient recycling from organic waste (Antonkiewicz et al., 2019) . A considerable drop in the use of P fertilizers can be followed in Estonia since the beginning of 1990s (Haiba et al., 2016). Due to this fact the relevant agricultural production takes place at the expense of soil P. It is expected that the valorization of SS, which is a renewable secondary raw material from biological wastewater treatment plants, will be compulsory (Kratz et al., 2019). The problem of SS management lies mainly in the complex composition of the material (Kicińska et al., 2019). SS land application has several limitations due to a large number of organic pollutants present in this matrix, including pharmaceutically active compounds (Haiba et al., 2016). These have a great impact on the environment and human health (Golbiak and Rutkowska, 2023). SS tends to concentrate persistent organic pollutants (POPs) present in wastewater, which could be accumulated into soils (Santos et al., 2023) and food plants (Wei et al., 2023; Kipper et al., 2010; Lillenberg et al., 2010). Pharmaceuticals and personal care products (PPCPs) have generated considerable interest not only because they are permanently being released into the environment but also because they have been designated to affect living organisms.

Due to the said above the studies involving the elimination of pharmaceutical residues from SS that is utilized as an organic fertilizer is of utmost importance. The achievement of this goal might realize via composting procedures that are specially designed for this purpose. This is extremely important in the case of relatively persistent pharmaceuticals, which do not undergo to the degradation under essential field conditions. In the current study we have selected a couple of more or less persistent compounds, namely carbamazepine (CBZ) and triclosan (TCS), commonly present in SS, to show if they could be degraded in the mixture of peat and SS in the case that some draff, ethanol or effective microorganisms are added to this mixture.

The high persistence of antiepileptic CBZ has been reported by several authors (Santos et al., 2023; Malvar et al., 2021; Haiba et al., 2018; Shao et al., 2018). Still, it has been shown by Butkovskyi et al. (2016) that the degradation of CBZ during the composting of SS with waste wood under temperature-controlled conditions reaches up to 88%. Several attempts have been made to remove CBZ from different media, but they have been only partly successful (Jiang et al., 2023; Dao et al., 2022; Thomas et al., 2020; Butkovskyi et al., 2016). In a study carried out by Paltiel et al. (2016), the content of CBZ increased in human urine due to ingestion of food crops irrigated with reclaimed sewage. As for pregnant women, CBZ is considered to be potentially teratogenic, especially at high doses (Tomson et al., 2011).

TCS is a broad-spectrum antibacterial agent that is widely used in PPCPs. Verlicchi and Zambello (2015) reported that TCS was difficult to degrade during SS composting and its biodegradation can take place with different kinetics depending on the microenvironment. TCS tends to sorb onto soil and sediment and may be subjected to very low biodegradation in aerobic conditions, whereas in anaerobic conditions it is more resistant (Ying and Kookana, 2007). Aerobic composting was found to be a way to partly degrade TCS in SS (Zheng et al., 2020). Moreover, the composting process benefited the microbial activity (Yu et al., 2019; Zheng et al., 2018) and increased the relative abundance of TCS-degrading microorganisms (Zheng, et al., 2020). Correlation studies have shown that the half-lives ($t_{1/2}$) of CBZ and TCS were positively related to TOC (total organic carbon) (Shao et al., 2018). Sawdust might be one potential organic source able to initiate efficient composting, as exhibited by elevated composting temperatures, and consequently resulted in the reduction of residual concentrations of different pharmaceuticals to reasonable levels in a relatively short composting period of livestock manure (Kim et al., 2012).

The objective of the current study was to clarify weather SS composting in the mixtures with peat could support the degradation of commonly persistent compounds CBZ and TCS that are present in sewage and its sludge. The results of these experiments were compared with outcomes of previous work where two different portions of sawdust were used in mixture with SS (Haiba et al., 2017 and 2018).

2. Materials and methods

2.1. Chemicals and materials

Standard substances (CBZ and TCS) were obtained from Labochema Estonia Ltd: CBZ (99.9%) and TCS (99.7%). Effective microorganisms were purchased from Agri Partner LLC, draff was obtained from A. Le Coq Ltd (Estonia), peat from Tootsi Turvas Ltd, sawdust from Ralgetor LLC and ethanol (96.7%) from Estonian Spirit LLC. The anaerobically digested and dewatered by centrifugation SS samples were collected from the Tartu municipal wastewater treatment plant. All solvents were of reagent grade or higher quality.

2.2. Sample preparation and treatment

The description of sample collection and treatment is given in detail in Haiba et al., 2017 and Haiba et al., 2018. The SS was mixed with (1) peat at a single ratio (1:1 SS:peat, v:v); and this SS and peat mixture was also blended with (2) draff; or (3) effective microorganisms; or (4) C_2H_5OH (Table 1) and submitted to a process of aerobic treatment. The initial concentration of both CBZ and TCS was 0.2 mg kg^{-1} in relation to dry weight (dw) in all these samples.

The preparation of calibration and quality control samples is described in detail in Haiba et al., 2017. They were prepared by diluting stock solutions of analytes. Stock solutions were made by dissolving appropriate amount of analytes in ethanol. Working standards were prepared by diluting stock solution with MilliQ water. Similarly to preparation of sample solutions, all solutions were prepared by weight, vortex-mixed and filtered through syringe filters. Concentration of calibration and quality control solutions were chosen according to the linear range for each analyte. The average recovery rates were for CBZ−91%, and for TCS−94%.

Experiments with the studied mixtures were performed in non-transparent plastic containers during a one-month period. With the aim of preventing heat loss from the sides and bottom of the containers, a 5 cm thick insulation (glass wool) was used. Two samples of 50 L were prepared with each mixture. The solutions of CBZ and TCS were prepared as follows: 0.2 mg of each pharmaceutical was dissolved in 100 ml ethanol and after that 400 ml distilled water was added to the solution. The Sonorex ultrasonic bath (Germany) was used to enhance the solubility of CBZ and TCS. Then the solutions of the studied compounds (CBZ and TSC) were mixed with the SS and bulking agent samples. The temperature of the surrounding was 21–23°C. Samples were turned periodically (2−3 times per week) to provide sufficient aeration and homogenization. The moisture content of the mixtures was maintained at 60–70% of their water holding capacity throughout the period of the experiment.

Table 1
Samples of sewage sludge (SS) and bulking agent

Sample No	Mixture	Mixture ratio (v:v)	Dry matter*, %
1	SS : peat	1:1	27
2	SS : peat+draff	1:1+7%	27
3	SS : peat+microorganisms	1:1+7%	26
4	SS : peat+C_2H_5OH	1:1+0.3%	26

* dry matter in the beginning of experiment

2.3. LC-MS/MS analysis

The procedure of CBZ and TCS chemical analysis is given in detail in Haiba et al., 2017 and Haiba et al., 2018. Sample extracts were analyzed in three parallels using liquid chromatography – tandem mass spectrometry (LC–MS/MS) system consisting of ultra-high performance liquid chromatograph UHPLC Agilent 1290 Infinity and mass spectrometer Agilent 6495 Triple Quad. Chemical analyses were performed at the Testing Centre of Tartu University.

3. Results and discussion

In the case of a number of PPCPs present in SS the impact of composting on their degradation is evident (Butkovskyi et al., 2016; Dalahmeh et al., 2022). According to Dalahmeh et al. (2022), SS has very low concentrations of hormones, antibiotics, and pharmaceutically active substances after one year of composting. Still, CBZ is not among them. Negative values of degradation percentage can be followed for CBZ due to the decrease of the mixture weight during the composting process. In SS and peat mixtures that do not undergo or are only partly a subject to the composting process, modest TCS degradation can be followed in the presence of draff and effective microorganisms (Fig. 1 and Table 2)

The temperature profiles in Fig. 1 show that peat is not a good bulking agent in SS composting. Still, in Estonia sewage treatment plants usually use it in the mixture with SS. This mixture is used as a fertilizer in parks and forestry, but is unsuitable for application in agriculture, as the formation of compost does not take place. Draff is among the studied additives the only one that leads to the almost sufficient increase of the temperature of the SS and peat mixture that is needed for composting, and in this case slight decrease of the concentrations of TCS and even CBZ can be followed during one-month period of the experiment.

In the case of SS-sawdust mixtures, two higher temperature regions were observed (Fig. 1), one at the beginning of fermentation (from 2 to 4 days), and the other later during the first month of the experiment. The first temperature increase is typical for a fast biodegradation of the studied mixtures by microorganisms

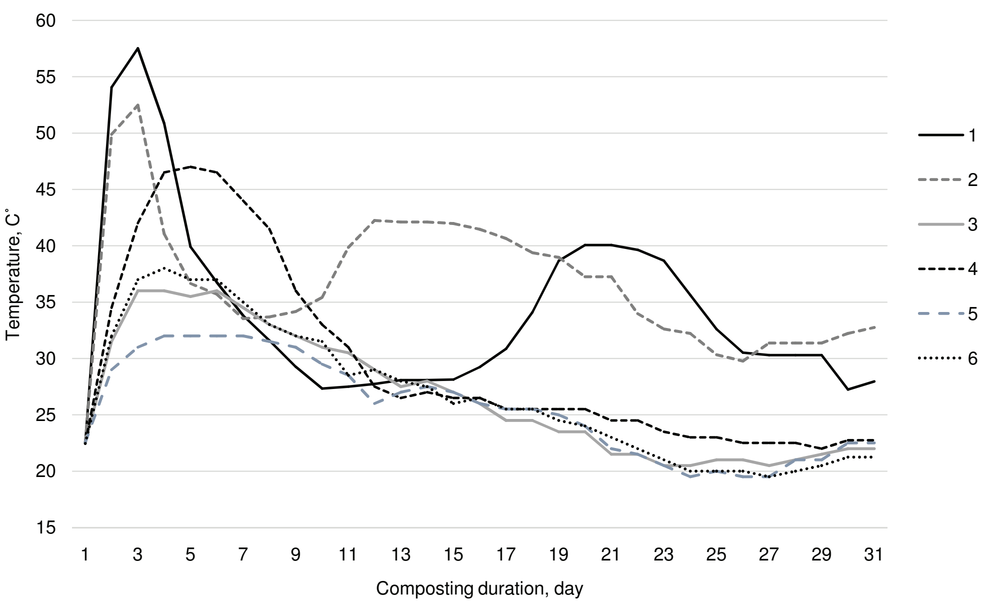

Fig. 1. Temperature profiles during one month composting for the mixtures of: **1** – 1:2(v:v) sewage sludge/sawdust; **2** – 1:3(v:v) sewage sludge/sawdust; **3** – 1:1(v:v) sewage sludge/peat; **4** – 1:1(v:v) sewage sludge/peat+7% draff; **5** – 1:1(v:v) sewage sludge/peat +7% microorganisms; **6** – 1:1(v:v) sewage sludge/peat+ 0.3% C_2H_5OH

Table 2
Concentrations of TCS and CBZ in SS–peat mixture samples (mg kg^{-1}, dw)

Compound	Sample No	1 day	1 week	1 month	Degradation, %
TCS	1	6.7±0.3	not tested	6.8±0.2	–2
	2	9.4±0.5	8.1±0.4	6.8±0.2	28
	3	8.2±0.4	6.9±0.2	7.0±0.4	15
	4	8.3±0.5	9.1±0.3	8.0±0.2	4
CBZ	1	0.6±0,1	not tested	0.6±0,1	0
	2	2.1±0.2	3.0±0.3	1.8±0.1	14
	3	2.1±0.2	2.1±0.2	2.3±0.1	–10
	4	2.1±0.3	2.6±0.1	2.3±0.1	–10

(Bachelart et al., 2020). The second temperature increase might be caused by a resuming of the biological activity. Therefore, the operating conditions that were no longer favorable to maintain a biological activity after the first increase of temperature became briefly acceptable to the microorganisms again.

At the same time, it can be taken into account that the total weight of the composted mixture decreases over time. Butkovsky et al. (2016) have shown that the reduction of CBZ in a mixture of SS with waste wood at 5:9 mass ratios reached to 88% by weight during 3-months period, and the corresponding number for TCS was 97%. This indicates that higher amounts of wood or sawdust would be able to provide more favorable conditions for successful SS composting. A well-designed composting process leading to a sufficient decrease of POPs present in compost mixture needs additional source of organic matter, as the organic matter can initiate the increase of temperature and provide a wide range of additional binding sites during composting (Kim et al., 2012). The results of previous studies (Haiba et al., 2017 and 2018) showed that sawdust could be one potential organic source able to initiate efficient composting, as exhibited by elevated composting temperatures, and consequently resulted in the reduction of residual concentrations of various organic pollutants to reasonable levels in a relatively short composting period. Still, unfortunately, the application of sawdust in SS composting makes the price of the final product relatively high due to its wide applicability as a fuel in central heating plants or in making different building materials. Additions of draff to peat-SS mixtures also lead to elevated temperatures (Fig. 1), showing the possibility of modifying these mixtures so that the process of the compost formation could take place.

In the case of the studied mixtures with peat that are commonly applied by sewage treatment plants in Estonia, the composting process did not take place. Alternatively, in the mixtures with sawdust, the composting process was evident and leaded to the degradation of TCS, and to the lesser extent, to the degradation of CBZ (Haiba et al., 2017 and 2018). Further studies are needed with the aim of solving the problems arising due to the extremely high persistence of such pollutants, as for example CBZ. Still, the results presented in this paper and previous studies (Butkovskyi et al., 2016; Haiba et al, 2018; Santos et al., 2023) show that the intelligent treatment of SS might lead to its much wider and safer usage in agriculture.

4. Conclusions

The current study was to show if CBZ and TCS could be degraded in the mixture of peat and SS in the case that some draff, ethanol or effective microorganisms were added to this mixture. In these mixtures the composting process did not take place. The degradation of TCS was very slow and the degradation of CBZ was negligible. Still, in the case of SS and peat mixtures, additions of draff were able to slightly catalyze the degradation of TCS.

Peat alone as a commonly used bulking agent in the mixture with SS in Estonia is not suitable for initiating the process of composting. Additions of carbon-rich matter might provide the relevant conditions needed for launching this process, and further studies should be carried out with the aim of solving this task.

The application of sawdust in previous studies instead of peat in the mixtures with SS has shown more promising results, as the degradation of TCS was apparent, but still no degradation of CBZ took place. This is to confirm that in spite of partial success gained by some authors, the problem concerning the sufficient degradation of CBZ present in SS remains unsolved. Further attempts should be made with the aim of completing this task. Relevant solutions might also lead to the successful degradation of other POPs present in sewage and its sludge.

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