The fate of selected pharmaceutical residues during composting of sewage sludge

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Sludge from the wastewater treatment process after appropriate treatment can represent a significant source of organic matter and nutrients for agricultural land. However, the use of these materials is associated with known risks such as the content of risk elements, organic pollutants, and pathogenic microorganisms (Yakamercan *et al*, 2021; Zennegg *et al*, 2013; Selambakkannu *et al*, 2022). Legislation in many countries of the world sets limit values for these risk parameters.

But the issue of micropollutants is little explored and not regulated by legislation. Important micropollutants not only in sewage sludge, but in the entire environment include pharmaceutical residues (Prasad *et al*, 2019). This includes medicines not only from the health sector, but also from veterinary care, as well as analgesics, fat regulators, beta-blockers, contrast agents used in radiology and hormonal substances (Ellis, 2006). The consumption of pharmaceuticals in the world is increasing every year. These substances reach the waste water treatment plant in the waste water in the form of urine and faeces, in which an average of 80% of the pharmaceuticals can be excreted. The specific percentage depends on the type of pharmaceutical (Zuccato *et al*, 2000). Guasch *et al* (2012) summarized the results of observing the concentration of pharmaceutical residues in wastewater in many countries of the world. More than 150 types of pharmaceuticlas belonging to different therapeutic groups were detected in raw wastewater in concentrations reaching up to the order of mg/L. The most common were ibuprofen, naproxen and ketoprofen. Rate of pharmaceutical residues removal from wastewater varies from 0% to 70% at a conventional wastewater treatment plant. The degree of residue removal from waste water usually correlates with its content in sewage sludge. This can be an obstacle to the direct use of such sludge as fertilizer.

The aim of this study was to find out whether composting can reduce the content of some pharmaceutical residues and thus produce a safer product for application to agricultural land.

Materials and methods

Two feedstocks were used for composting:

– sewage sludge (SS), which came from a town sewage treatment plant with a load of 3,500 equivalent inhabitants. It was a mechanical-biological treatment plant with aerobic sludge stabilization technology. After dewatering, the sludge had a solids content of 13.3%, pH/H_2O = 7.0, C/N = 6.1.

– straw pellets (SP), that came from wheat straw and were moistened to a dry weight of 21.2% before use in the experiment, which improved their disintegrability and degradability. The pH/H_2O of pellets was 8.3 and C/N 53.7.

The experiment was conducted in 5 different ratios:

(1) Sewage sludge 100%,
(2) Sewage sludge 75% by weight + straw pellets 25% by weight,
(3) Sewage sludge 50% by weight + straw pellets 50% by weight,
(4) Sewage sludge 25% by weight + straw pellets 75% by weight
(5) Straw pellets 100%

Each variant was prepared in duplicate. The feedstocks and their mixtures were composted for 4 months in aerobic composters with a working volume of 70 l and a radius of 23 cm. Air was brought into the composter from below. Air flow conditions were set at 4 l/min for 14 days. The air flow lasted for 5 minutes every half an hour. Subsequently, the air flow time interval was shortened to 3 minutes every half an hour.

Samples (n=6) were taken at the beginning (M0) of the experiment and at the end of the experiment after 4 months (M4) and stored in a freezer at -25°C. They were then homogenized and lyophilized.

Samples were extracted into methanol (VWR Chemicals, HPLC-gradient grade) using a Dionex ASE 200 (pressure 1500 psi, temperature 80°C) and, after treatment, were analyzed on a liquid chromatograph (Shimadzu Nexera x2) with a mass detector (Sciex 4500) on triple quadrupole basis for targeted analyses.

Although 34 pharmaceutical residues (PRs) were detected in the samples, only 12 PRs were used in this proceeding article, namely: Bisphenol (BPA), Caffeine (CAF), Carbamazepine (CBZ), Cetirizine (CETI), Citalopram (CITA), Diclofenac (DCF), Ibuprofen (IBF), Mirtazapine (MIRT), Sulphapyridine (SPD), Telmisartan (TE), Triclosan (TCS), and Venlafaxine (VEN). In SS itself 32 micropollutants were detected, the most for TE (10,161±226 ng/g), TCS (543±36 ng/g) and CITA (440 ±2.8 ng/g). Five pharmaceutical residues were detected in SP (CAF, MIRT, SPD, TE, and VEN).

Results and discussion

Table 1 shows the content of 12 pharmaceutical residues (PRs) in initial materials and compost samples. For some PRs, the final content in compost (after four months) decreased in comparison to the initial content, while for others, it increased. As evidenced by the data, the content of some PRs (CAF, CITA, DCF, MIRT, and VEN) was reduced from its initial content, with the percentage of reduction compared to the initial being: CAF (24–64%), DCF (12–80%), CITA (20–37%), MIRT (27–100%), and VEN (9–14%). CAF and DCF were decreased in all variants except the 100% SP variant, and MIRT was decreased in all variants except the 75% SS variant; however, CITA was increased in the 75% SS and 100% SP variants, and VEN was increased in the 75% SS variant but remained constant in the 100% SP variant (Table1).

Table 1: Content of pharmaceutical residues (PRs) (ng/g) before and after composting

	100% SS		75% SS + 25% SP		50% SS + 50% SP		25% SS +75% SP		100% SP	
PRs	M0	M4	M0	M4	M0	M4	M0	M4	M0	M4
BPA	89±18	467±56^{a}	58±12	384±46^{a}	34±7.1	186±34^{b}	15±3.2	69±13^{c}	nd	nd
CAF	142±13	60±5.3^{a}	96±8.9	41±1.6^{b}	61±6.3	22±2.0^{c}	33±4.2	25±1.5^{c}	10±2.6	13±2.6^{c}
CBZ	39±0.7	51±2.3^{a}	25±0.5	44±1.2^{b}	15±0.3	31±0.8^{c}	7±0.1	15±0.4^{d}	nd	2±0.2^{e}
CETI	79±0.7	79±11^{a}	51±0.5	65±3.9^{a}	30±0.2	34±0.9^{b}	14±0.1	13±0.7^{b}	nd	2±0.1^{c}
CITA	440±2.8	354±9.3^{a}	287±1.9	296±16^{b}	169±1.1	107±6.2^{c}	76±0.5	51±2.4^{d}	nd	3±0.4^{e}
DCF	284±9.8	250±6.4^{a}	185±6.4	142±9.2^{b}	109±3.8	38±1.8^{c}	49±1.7	10±0.3^{d}	nd	3±0.2^{d}
IBF	87±6.7	287±15^{a}	57±4.4	127±12^{b}	34±2.6	130±13^{b}	15±1.2	38±3.4^{c}	nd	nd
MIRT	63±2.8	46±5.7^{a}	42±1.8	46±1.5^{a}	25±1.1	18±0.5^{b}	12±0.4	6±0.4^{c}	2±0.1	nd
SPD	15±0.92	33±1.2^{a}	10.5±0.6	15±0.9^{b}	6.9±0.3	6±0.3^{c}	4.0±0.2	3±0.1^{d}	1.7±0	nd
TE	10162±226	15018±1231^{a}	6628±147	11432±285^{b}	3910±87	9114±442^{c}	325±7.2	2687±62^{d}	4±0.2	57±12^{e}
TCS	543±36	770±23^{a}	354±23	599±16^{b}	209±14	408±5.2^{c}	94±6.2	162±12^{d}	nd	3±0.4^{e}
VEN	34±3.7	31±1.9^{a}	23±2.4	25±1.1^{b}	14±1.4	12±0.3^{c}	7±0.6	6±0.2^{d}	2±0.0	2±0.1^{d}

Mean value followed by different letters is statistically different at ($p < 0.05$). Values indicate mean ± standard error (n = 6). nd= not detected

BPA and IBF levels were significantly ($p < 0.05$) higher in all variants except the 100% SP variant, which was below detection limit. CBZ, TE, and TCS levels were also significantly higher in all variants. The content of CETI remained constant in the variant with 100% SS even after four months of composting but decreased by 7% in the variant with 25% SS and increased in the other remaining variants. The content of SPD was reduced by 13%, 25%, and below the detection limit in variants with 50% SS, 25% SS, and 100% SP, respectively. However, it increased in variants with 100% SS and 75% SS. The content of these micropollutants may increase as the weight and volume of compost are reduced. Depending on the studies and substances, the removal/reduction of such micropollutants ranges from nearly complete to insignificant. According to Carballa *et al* (2007) as cited in Hammer and Palmowski (2021), the removal/reduction range was classified into five categories: Insignificant removal (0–20%), low removal (20–40%), medium removal (40–60%), high removal (60–80%), and very high removal (80%) during anaerobic digestion of sewage sludge (Hammer and Palmowski 2021). The reduction/removal efficiencies of CAF, CITA, DCF, MIRT, and VEN vary among variants, ranging from no removal to high or very high removal. Given such heterogeneous behavior, it is recommended that additional research be conducted to determine the range of values for specific sewage sludge.

Conclusions and perspective

Composting decreased the content of some pharmaceutical residues, particularly CAF, CITA, DCF, MIRT, and VEN, however, the content of some pharmaceutical residues increased due to organic matter loss. Considering such heterogeneous behaviors, it is recommended to conduct further studies to find out in which range the values will be for specific sewage sludge.

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List of references

Carballa, M. et al., 2007. Chemosphere, 67, 1444–1452.

Ellis, J.B. 2006. Environ. Pollut., 144, 184–189.

Hammer, L. and Palmowski, L., 2021. Water Environ. Res., 93, 1910–1924.

Guasch, H., Ginebreda, A., Geiszinger, A. 2012. Emerging and Priority Pollutants in Rivers, Bringing Science into River Management Plans. Springer-Verlag, Berlin, 270 pages. ISBN: 978-3-642-25722-3.

Prasad, M.N.V. et al., 2019. Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology: Emerging Contaminants and Micro Pollutants. Oxford, UK: Butterworth-Heinemann, 467 pages. ISBN: 978-0-12-816189-0.

Selambakkannu, S. et al, 2022. Radiat. Phys. Chem., 199, 110358.

Yakamercan, E.et al, 2021, J. Clean. Prod., 319, 128568.

Zennegg, M. et al, 2013, Environ. Int., 60, 202–208.

Zuccato E. et al, 2000, The Lancet 355, 1789–1790.