

OCCURRENCE AND SEASONAL TREND OF TRICLOSAN AND TRICHLOROCARBAN IN WASTEWATER AND SLUDGE FROM WASTEWATER TREATMENT PLANTS IN GAUTENG PROVINCE, SOUTH AFRICA.

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Introduction

Triclosan [5-chloro-2-(2,4-dichlorophenoxy)phenol, TCS] and Triclocarban [3-(4-chlorophenyl)-1-(3,4-dichlorophenyl) urea, TCC] are broad spectrum antimicrobial agents that are commonly added in personal care products such as shampoos and mouth wash¹. Large quantities of these biocides have been produced for various applications since the late 1950s and early 1960s for TCS and TCC respectively^{2, 3}. Both compounds are relatively soluble in water with $\log K_{ow}$ of 4.9 and 4.8 for TCC and TCS respectively at neutral pH⁴. The usage of personal care products results in the discharge of these compounds into domestic wastewater treatment plants. Ineffective removal and partitioning of these biocides in sewage effluents and sludge during wastewater treatments introduces these contaminants into the receiving waters and biosolids-amended agricultural soils^{5, 6, 7}. The two compounds have been found to co-occur^{8, 9} and are most frequently detected in the environment¹⁰. Detection concentrations in aqueous environment are in the region of ng/L to $\mu\text{g/L}$ ^{11, 6} and ng/g to mg/kg in solids^{12, 13, 14}. High levels in solids have been reported as due to the adsorption of these compounds onto sewage sludge^{12, 15- 17}. Their presence in environmental matrices calls for concern since they have been found to be lipophilic, relatively stable, resistant to degradation, persistent and have endocrine disrupting properties^{8, 18}. Both antimicrobials have indicated the ability to be toxic to organisms at trace levels⁸. TCS has been found to modulate thyroid function in amphibians, interfere in hormone production in rats, while TCC has been found to cause a reduction in the rate of reproduction^{13, 19}. Occurrence of TCS and TCC in aquatic environment calls for immediate attention since they have the potential to form dioxin after photochemical and biological degradation.

The environmental relevance of TCS, TCC and their main metabolites in the environment calls for routine monitoring in order to determine their presence and levels in the environment such that some means of their removal from water systems can be devised. The need to remove these compounds from wastewater treatment plants is of utmost importance so that effluents discharged into water sources used for drinking water abstraction are free of these compounds. With little or no routine monitoring of organic contaminants in most wastewater treatment plants in South Africa, the focus of the present study was, therefore, to monitor the presence and levels of triclosan and triclocarban in influent and effluent wastewater and sewage sludge collected from different wastewater treatment plants over winter and summer seasons in Gauteng province, South Africa.

Materials and methods

Influent and effluent water and sludge samples (raw, activated/digested/treated and dried) were collected using grab method into nitric acid pre washed and acetone rinsed amber glass bottles and jars respectively. The samples were collected from six wastewater treatment plants using biological nutrient removal and trickling bio-filters technology for treatment in Gauteng Province South Africa and stored in cooler boxes and transported to the laboratory. Water samples were stored at 4 °C while sewage sludge samples were kept at -18 °C until lyophilised using a freeze drier. Once dried, the samples were sieved (200 mm, diameter size) and, thereafter, stored at -18 °C until analysis.

Different parameters were optimized during extraction and those which provided high recovery were used through the experiment.

Liquid-liquid extraction and Soxhlet extraction techniques were employed for liquid and solid sample extractions respectively. LC-MS/MS (Shimadzu, China, Shimadzu, South Africa) was used for quantitative analysis. Optimization of the LC-MS/M was carried out with external calibration method. About 20 μ L volume of the sample was injected using an autosampler (SIL-20AC) and separated on Inertsustain-C₁₈ column; 2.11 mm \times 150 mm, 3 μ m particle sizes (GL Sciences Inc, Japan) at a temperature of 35°C (Held in a Shimadzu CTO-20AC). Binary mobile phase comprising 20 mM ammonium acetate (B) and Methanol (A) at a flow rate of 0.400 mL/min was used. The elution gradient was as follows: initial mix of 40% mobile phase A and 60% mobile phase B, increasing to 100% mobile phase B within 5 min and held for 13 min, then decreased to 60% mobile phase B within 2 min and held for 10 min. Analytes were detected by ESI-MS/MS in the negative ion mode with interface temperature of 350 °C; heating block source and desolvation temperatures of 400°C; and 250 °C respectively; a nebuliser gas flow of 3.00 L/min, and a drying gas flow of 15.00 L/min. The mass spectrometer was operated at high mass resolution. Argon pressure in the collision cell was kept at 17KPa for MS/MS measurements. Quantification of all compounds was made by multiple reactions monitoring (MRM). Three transitions used were 287.10 \rightarrow 35.15, 287.10 \rightarrow 227.40, 287.10 \rightarrow 255.50 and 313.10 \rightarrow 160.15, 313.10 \rightarrow 126.15, 313.10 \rightarrow 31.10 for TCS and TCC respectively. Prior to and after sample analysis, an initial solvent blank, a laboratory performance standard quality control was performed. Quality control check standard was run after every five samples to monitor retention time deviation. Statistical analysis was performed using Microsoft windows statistical package.

Results and discussion

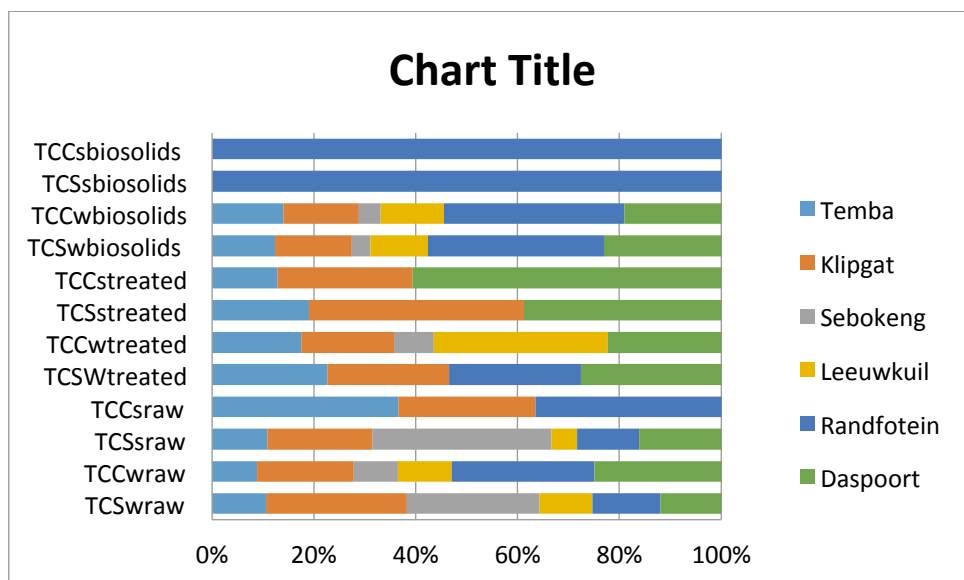
The external calibration method conducted gave good linear regression of 0.9984 and 0.9996 for TCS and TCC respectively. Results obtained indicated that both targeted analytes were present in influent and effluent in all water samples (Table 1). As can be seen in Table 1, all WWTPs influent samples had the highest level in the range of 2.74-17.6 μ g/L for TCS and <LOD-1.80 μ g/L for TCC. Furthermore, the levels of the analytes decreased from influent (0.03-17.6 μ g/L) to effluent (<LOD-13.0 μ g/L). This trend was also observed for both winter and summer levels. The observed trend indicated some removal of TCS and TCC during the treatment process (20-61 % and 11-97 % for winter and summer for TCS; 34-75 % and >90 % for winter and summer for TCC) and sample dilution effect from storm water during the rainy summer. More TCS and TCC were removed in the summer than in winter. The usage of the consumer products that may contain TCS and TCC per area, amount of waste treated per WWTP, and the treatment technology employed may have also contributed to the observed trend²⁰. The aforementioned factors may have also influenced the high levels observed for Dasport and Randfontein for TCS in winter. Dasport WWTPs is located in highly urbanized area, treating wastes from the central business district of Pretoria and its surrounding areas. Randfontein treatment plant is second to Dasport with a concentration value of 17.6 μ g/L for TCS in winter. Randfontein is followed by Leeuwkuil treatment plant with TCS and TCC levels of 15.8 μ g/L and 12.0 μ g/L for influent and effluent respectively for winter and summer. The trend for other treatment plants are as follows: Temba>Klipgat>Sebkeng. No sampling was done in the summer season for Sebokeng and Leeuwkuil WWTPs due to repairs at the treatment plants during sampling period.

Table 1: Concentrations (μ g/L) of triclosan and triclocarban in influent and effluent water samples from different wastewater treatment plants in Gauteng Province, South Africa

	TCS				TCC			
	Winter		Summer		Winter		summer	
	influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent
Dasport	16.2	13.0	2.74	2.43	1.80	0.798	1.80	0.046

Temba	8.58	6.38	6.49	2.97	0.374	<LOD	0.300	<LOD
Klipgat	8.21	3.42	5.57	3.48	0.096	0.063	0.096	<LOD
Sebokeng	5.10	2.97	-	-	0.032	<LOD	-	-
Leeuwkuil	15.8	12.0	-	-	0.987	0.248	-	-
Randfontein	17.6	6.83	9.76	7.04	1.01	0.315	1.01	0.030

Target analytes were again present in all different types of solid samples collected as can be seen in Figure 1. The concentrations of TCS and TCC in sludge and biosolids samples ranged from 3.70-15.0 $\mu\text{g/g}$, 2.70-7.81 $\mu\text{g/g}$, and 3.14-8.99 $\mu\text{g/g}$ for TCS and 4.21-11.8 $\mu\text{g/g}$, 4.25-9.20 $\mu\text{g/g}$, 1.43-11.94 $\mu\text{g/g}$ for TCC in primary raw sludge, treated sludge and biosolid respectively. The percentage distribution of TCS and TCC in various sludge types from different treatment plants are shown in Figure 1. Studies have shown TCS concentrations in activated sludge within the range of 0.62-1.49 $\mu\text{g/g}$ ⁶, 51 $\mu\text{g/g}$ ²¹ while TCC concentration range of 2.17-4.82 $\mu\text{g/g}$ was recorded⁶. TCS concentrations of 1.17-32.9 $\mu\text{g/g}$ and 0.09-16.79 mg/kg have also been reported^{10, 21}. These concentration ranges are comparable with the concentration ranges obtained in the current study.



W= winter, S= summer

Figure 2: Percentage distribution of analytes in sludge samples obtained from WWTPs

Conclusion

TCS and TCC biocides were detected in all samples collected from six operating wastewater treatment plants in Gauteng Province, South Africa. High levels were observed in influent samples than in the effluent. Daspoort, Randfontein and Leeuwkuil treatment plants exhibited the highest concentrations of TCS and TCC both for winter and summer seasons. Seasonal trends were observed with winter season having higher levels across all board. The usage of the consumer products that may contain TCS and TCC per area, amount of waste treated per WWTP, and the treatment technology employed may have also contributed to the observed trend in the levels of biocides analysed. Sample dilution effect from storm water during the rainy summer may have also contributed to lower levels observed for summer.

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