

WATER-SEWAGE SLUDGE DISTRIBUTION OF SIXTEEN PHARMACEUTICALLY ACTIVE COMPOUNDS

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Abstract

Sixteen pharmaceutically active compounds belonging to different therapeutic groups including five anti-inflammatory drugs, two antibiotics, a β -blocker, two lipid regulators, four estrogens, an antiepileptic drug and a nervous stimulant were analyzed in wastewater and sewage sludge. The solid-water partition coefficients (K_d) of the pharmaceutically active compounds were determined. Log K_d values were in the ranges between 1.17 and 3.00 which correspond to naproxen and 17 α -ethynilestradiol, respectively. K_d values obtained were used to evaluate the removal rate of these compounds from the aqueous phase in wastewater treatment plants by sorption onto sludge particles.

Keywords: pharmaceutically active compound; wastewater treatment plants; water-sludge distribution.

Introduction

Wastewater treatment plants are the main source of discharge of pharmaceutically active compounds (PhACs) into the environment. In general, two processes are responsible for the removal of PhACs during these treatments: biodegradation and retention onto sludge. Several approaches based on octanol-water partition coefficients (K_{ow}) have been used to determine the capacity of the substances to be sorbed onto solids. However, in the case of compounds with polar groups, such as PhACs, these approaches reveal significant deviations (Carballa et al., 2008) because sorption onto sludge depends not only on the physical and chemical properties of the compound, but also on the characteristic of sewage sludge. As a result, the estimation of the capacity of PhACs to be sorbed onto sludge requires of experimental studies based on solid-water distribution coefficients (K_d).

Methods

Analytical methods for the determination of PhACs were based on validated methods previously reported. The method reported by Camacho-Muñoz et al. (2009) was used for the determination of PhACs in water whereas the method reported by Martín et al. (2010) was used for sludge samples.

Analytical procedure was based on sample treatment by solid-phase extraction with cartridges packed with 60mg of Oasis HLB, in the case of wastewater samples, and on ultrasonic assisted extraction and clean-up by solid phase extraction, in the case of sludge samples. After sample treatment, PhACs were determined by high-performance liquid chromatography with diode array and fluorescence detectors connected online.

Results and discussion

Concentration levels of PhACs in wastewater and sludge samples are presented in Table 1. All of the pharmaceutical compounds monitored except clofibrac acid, estrone, sulfamethoxazole and trimethoprim were detected in the samples analyzed.

Naproxen, ketoprofen, salicylic acid, propranolol and gemfibrozil were always detected in wastewater samples, while the estrogenic compounds, the anti-inflammatory drug diclofenac and the antiepileptic drug carbamazepine were found in 20–60 % of the samples measured.

Except the anti-inflammatory drugs diclofenac and ketoprofen, all of the compounds found in wastewater were also found in sludge (Table 1).

Table 1. Range, mean concentration levels and calculated log K_d values of pharmaceutically active compounds in wastewater (n=32) and sludge (n=32) samples.

Compound		Wastewater		Sludge		Log K_d
		Range ($\mu\text{g L}^{-1}$)	Mean ($\mu\text{g L}^{-1}$)	Range ($\mu\text{g kg}^{-1}\text{dm}$)	Mean ($\mu\text{g kg}^{-1}\text{dm}$)	
Antiinflammatory drugs	Diclofenac	<LOD-1.98	0.21	<LOD	<LOD	-
	Ibuprofen	<LOD-73.4	32.0	<LOD-8183	2206	1.84
	Ketoprofen	0.38-4.03	1.81	<LOD	<LOD	-
	Naproxen	0.62-6.00	3.46	<LOQ-177	50.7	1.17
	Salicylic acid	8.69-47.1	27.2	8.66-2452	560	1.31
Antibiotics	Sulfamethoxazole	<LOD	<LOD	<LOD	<LOD	-
	Trimethoprim	<LOD	<LOD	<LOD	<LOD	-
Antiepileptic drug	Carbamazepine	<LOD-3.49	0.45	<LOD-172	29.3	1.82
β -Blocker	Propranolol	0.03-0.72	0.31	<LOD-73.1	20.4	1.81
Nervous stimulant	Caffeine	<LOD-8.97	1.33	<LOD-2336	446	2.53
Estrogens	17 α -Ethinylestradiol	<LOD-0.37	0.10	8.41-355	98.0	3.00
	17 β -Estradiol	<LOD-0.52	<LOQ	<LOD-82.3	24.7	-
	Estriol	<LOD-1.07	0.41	<LOD-70.5	12.6	1.48
	Estrone	<LOD	<LOD	<LOD	<LOD	-
Lipid regulators	Clofibrac acid	<LOD	<LOD	<LOD	<LOD	-
	Gemfibrozil	0.65-3.47	2.11	<LOD-1423	<LOD	-

dm: dry matter; LOD: Limit of detection; LOQ: Limit of quantification

Anti-inflammatory drugs was the therapeutic group at the highest average concentration levels in wastewater and sludge. The anti-inflammatory drugs at the highest concentrations were ibuprofen and salicylic acid with mean concentration levels of 32.0 and 27.2 $\mu\text{g L}^{-1}$, respectively, in wastewater samples and 2206 and 560 $\mu\text{g kg}^{-1}\text{dm}$, respectively, in sludge samples. This fact could be due to the widespread use of such pharmaceuticals not only because of their medical benefits but also because no medical prescription is required to be sold. In Spain, total quantities of ibuprofen sold per year have been estimated to be about 276 tons, while other antibiotics such as trimethoprim are sold in quantities of about 3.7 tons per year.

K_d coefficients were calculated by the formula: $K_d = C_{\text{solid}}/C_{\text{water}}$; where K_d is expressed in $L\text{ kg}^{-1}$, C_{solid} is the concentration of the pharmaceutical compound in the solid phase ($\mu\text{g kg}^{-1}$ dry matter) and C_{water} is the concentration of the pharmaceutical compound in the aqueous phase ($\mu\text{g L}^{-1}$).

Log K_d values of each PhAC are shown in Table 1. From these values can be concluded that, without taking into account the persistence/biodegradability factor and for most of the encountered pharmaceuticals, sorption onto sludge can be one of the key factors controlling the removal of PhACs in wastewater treatment plants.

Conclusions

In this study the concentration levels of 16 PhACs belonging to different therapeutic groups have been determined in wastewater and sludge samples from wastewater treatment plants to evaluate their distribution between both phases. All the sixteen pharmaceutical compounds monitored, except clofibric acid, estrone, sulfamethoxazole and trimethoprim were detected in the samples analyzed. Generally all the PhACs found in wastewater were also detected in sludge, except diclofenac and ketoprofen which were found in wastewater but were not detected in sludge. Most of the pharmaceutical compounds studied present relatively high K_d values, especially the estrogenic compound 17α -ethinylestradiol, pointing out to sorption onto sludge as one of the main mechanisms for the removal of these compounds in wastewater treatment plants.

Acknowledgements

The authors wish to thank the financial support received from the Ministerio de Ciencia e Innovación, Spain (Project No. CGL2007-62281).

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