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Multimedia fate modeling and comparative impact on freshwater ecosystems of pharmaceuticals from biosolids-amended soils

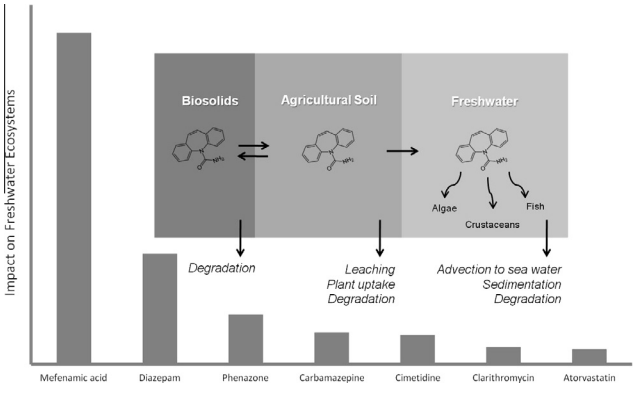
Sérgio Alberto Morais [a,b,*], Cristina Delerue-Matos [b], Xavier Gabarrell [a,c], Paqui Blánquez [c]

[a] SosteniPrA (UAB-IRTA-Inèdit), Institut de Ciència i Tecnologia Ambientals (ICTA), Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Barcelona, Spain
[b] REQUIMTE/Instituto Superior de Engenharia do Porto (ISEP), Rua Dr. António Bernardino de Almeida 431, 4200-072 Porto, Portugal
[c] Departament d'Enginyeria Química, Escola d'Enginyeria, Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Barcelona, Spain

HIGHLIGHTS

- We modeled the fate of pharmaceuticals detected in biosolids amended to soils.
- We ranked the potential impact on aquatic ecosystems of detected pharmaceuticals.
- Low mobility of pharmaceuticals in a regional EU model was estimated.
- Mefenamic acid had the highest impact and warrants further investigation.

GRAPHICAL ABSTRACT



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ABSTRACT

This study modeled the impact on freshwater ecosystems of pharmaceuticals detected in biosolids following application on agricultural soils. The detected sulfonamides and hydrochlorothiazide displayed comparatively moderate retention in solid matrices and, therefore, higher transfer fractions from biosolids to the freshwater compartment. However, the residence times of these pharmaceuticals in freshwater were estimated to be short due to abiotic degradation processes. The non-steroidal anti-inflammatory mefenamic acid had the highest environmental impact on aquatic ecosystems and warrants further investigation. The estimation of the solid-water partitioning coefficient was generally the most influential parameter of the probabilistic comparative impact assessment. These results and the modeling approach used in this study serve to prioritize pharmaceuticals in the research effort to assess the risks and the environmental impacts on aquatic biota of these emerging pollutants.

1. Introduction

The application of municipal biosolids to agricultural soils as a source of crop nutrients and organic matter is a common farming practice. Seven EU member states spread >50% of their biosolids on agricultural soils (Muller, 2007). Persistent pharmaceuticals that partition into organic matter during the sewage treatment process are present in sludge and ultimately in biosolids (Edwards et al., 2009; Sabourin et al., 2009; Wu et al., 2010). These emerging pollutants have been detected in biosolids-amended soils (Furczak and Joniec, 2007; Kinney et al., 2008). Recent research has shown the potential of several pharmaceuticals to migrate offsite in runoff

* Corresponding author at: SosteniPrA (UAB-IRTA-Inèdit), Institut de Ciència i Tecnologia Ambientals (ICTA), Universitat Autònoma de Barcelona (UAB), 08193 Bellaterra, Barcelona, Spain. Tel.: +34 935 81 37 60.
E-mail addresses: sergioalberto.cruzmonteiro@uab.cat, sergio_morais@yahoo.com (S.A. Morais).

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water following land application of biosolids (Topp et al., 2008; Wu et al., 2010).

However, few studies have experimentally characterized the fate and transport of these pharmaceuticals and the risks of contaminating adjacent surface waters (Barron et al., 2009, 2010). Furthermore, in Europe, approximately 4000 different pharmaceutical active compounds (PhACs) can reach every environmental compartment (Mompelat et al., 2009). The wide range of properties of pharmaceuticals and the lengthy analytical processes required for field-scale experiments make chemical fate modeling a valuable tool for screening and prioritizing pharmaceuticals in research efforts to understand their environmental behavior.

The aims of this study were (1) to model the environmental fate of pharmaceuticals detected in dewatered municipal biosolids (DMB) applied to agricultural soils, accounting for their dissociating properties, (2) to estimate their comparative impact on freshwater ecosystems, and (3) to identify and prioritize those compounds that warrant further investigation as well as the most sensitive fate processes, i.e., those that contribute to variance of impact results to a higher extent. For other endpoints, such as terrestrial ecosystems and humans, other modeling challenges need to be investigated and are currently out of the scope of this research. Almost no experimental data on terrestrial ecotoxicity effects are available, as well as, in human exposure routes, quantitative structure activity relationship (QSAR) models to estimate biotransfer factors for milk and meat and bioaccumulation in roots and leaves of dissociating compounds or degradation data in the vegetation compartment are also not available.

2. Methodology

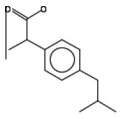
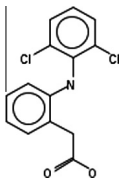
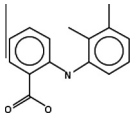
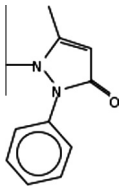
In a previous study, 43 pharmaceuticals were targeted in DMB samples, and 28 were either absent or present in concentrations below the method detection limit (Rodríguez-Rodríguez et al., 2011). The wastewater treatment plant (WWTP) in this study is located in El Prat de Llobregat, near Barcelona, Spain, and it has a treatment capacity of 2 million equivalent habitants. Table 1 shows the concentrations of detected pharmaceuticals in the DMB analysis, which did not account for human or veterinary metabolites of parent compounds.

The concentration of pharmaceuticals is higher immediately following sludge application at the beginning of the growing season and lower at the end of the year due to removal processes. However, for screening purposes, steady-state conditions and first-order kinetics for the degradation processes are assumed.

The modeled system consists of five compartments: biosolids, agricultural soil, air, freshwater, and freshwater sediment (Fig. 1). The landscape and environmental parameters of the regional scale European Union System for the Evaluation of Substances model (EUSES v2.1.1) (EC, 2004) were chosen to mimic a typical densely populated region in the EU with an area of 40400 km^2 and applied in this assessment. After biosolids have been applied to a soil, pharmaceuticals can desorb and thereby become bioavailable in the agricultural soil matrix. They can then undergo leaching and runoff in surface water. Conversely, they can remain highly bound and unavailable. To account for differences in the sorption, desorption, and degradation of compounds between the biosolid and soil matrices, the biosolids-amended soil compartment was modeled as a biosolids compartment nested in the agricultural soil compartment. The volume of the biosolids compartment was calculated for an application rate of 5000 kg dry weight per hectare per year, assumed to be typical for EU regional agricultural practices (EC, 2004), and 1.5 kg L^{-1} density of dry biosolids (EC, 2004).

In the model, the environmental compartments are assumed to be homogeneous and well mixed. Once emitted, chemicals are assumed to be instantaneously dispersed throughout the entire compartment. Therefore, spatial variations in properties of the medium and spatial differences in concentrations are disregarded. The mass distribution estimation in the five-compartment model requires a mass balance solution with five simultaneous differential

Table 1
Structures, molecular acidity, and concentrations of detected pharmaceuticals in dewatered municipal biosolids.

Compound	CAS[a]	Structure	Usage	pK_a[b]	Concentration ng g^{-1} (±SD)[c]
Ibuprofen	15687-27-1		Anti-inflammatory	4.91	85.9 (±9.2)
Diclofenac	15307-86-5		Anti-inflammatory	4.15	60.3 (±9.6)
Mefenamic acid	644-62-2		Anti-inflammatory	4.2	17.9 (±2.1)
Phenazone	60-80-0		Analgesic and antipyretic	1.4	9.6 (±2.2)

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