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Risk assessment of persistent pharmaceuticals in biosolids: Dealing with uncertainty

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HIGHLIGHTS

- Biosolids containing significant levels of PPCPs are reused in agriculture.
- Those persistent PPCPs can be accumulated in soil and biotransferred in the long-term.
- A probabilistic screening-level risk assessment of this scenario was developed.

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ABSTRACT

A screening-level risk assessment of biosolids-borne PPCPs in agricultural scenarios was developed in this work. While several of these compounds are efficiently removed in sewage treatment plants (STPs), others are recalcitrant to degradation and can be found in sludge at significant levels. As the rate of biosolids reuse for fertilising and/or amendment purposes is increasing, it is necessary to evaluate the fate in soil and possible biotransfer of this type of pollutants in the long-term. The study includes six compounds that were selected considering data availability, presence in sludge and persistence. Due to the scarce data still present in literature, a probabilistic assessment to address uncertainty was developed. A 95th percentile of the hazard index (HI) exceeding 1 was obtained, with main contributions of triclosan and carbamazepine. Although these estimates were obtained under a worst-case approach, and that they can vary depending on scenario characteristics, they change the least-concern classification associated to the presence of PPCPs in biosolids. A sensitivity analysis indicates the high influence of application rate and sludge concentration level on the results. Thus, the importance of developing new strategies of removal in advanced STPs and the establishment of a specific biosolids reuse regulation including this type of compounds acquires an added significance.

1. Introduction

Fate and trends of pharmaceutical and personal care products (PPCPs) and other emerging contaminants in the environment and their effects on biotic matrices have been object of intensive research in these years [1–5]. There is still an open and strong debate on the impact that the presence of these compounds in the different media might have. For example, focussing on pharmaceuticals, it is not clear whether undegraded products released in STPs effluents cause significant adverse effects on representative end-points of receiving waters. A high number of conservative risk assessments of micropollutants in several locations around the world can be found in literature, involving both environmental end-points and human receptors [6–10]. Most of them reveal that the risk of adverse effects in the different trophic levels or in human health is low or very low, advocating this to their small concentrations (enhanced by the dilution effect in surface waters) and its low-toxic profile. However, although obtained risk ratios are well below the critical value of 1, some authors are concerned with the long-term exposure to these compounds [6,7] and their possible synergistic effects between them or with other micropollutants [11,12]. In a recent work [13], risk quotients exceeded 1 in several occasions, when the concept of mixtures was considered, instead of the individual risk of each compound. Indeed, these compounds are always present in the environment as mixtures [14,15], and therefore, simultaneously exposure to several substances must be

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assessed [16]. Although, PPCPs are formulated for direct human consumption, multiple exposure to them (especially to pharmaceuticals) can cause interactions and side effects.

Apart from direct discharge to water streams, effluent and sludge reuse for soil fertilising is another route of transfer and accumulation of microcontaminants in soil-related compartments. These two scenarios, and especially the latter, were extensively evaluated in terms of exposure and risk to both organic and inorganic (metals) persistent pollutants [17–19]. In fact, biosolids application rate and use (amendment or fertilising) are limited depending on their pollutant content by legislation [20].

Many pharmaceutical compounds, present at microgram levels as the highest value found in biosolids, are readily degraded once applied on soil [21]. However, some of them can persist for longer periods of time [21,22]. Hence, despite their low levels and toxicity, a specific evaluation considering relevant human exposure pathways of this scenario should be developed. The goal would be to assess the incidental exposure to pharmaceuticals, where even the therapeutic effects of these substances are considered undesirable [23]. Although PPCPs levels in biosolids or reclaimed water are not restricted to date, accumulation in soil [24] and transfer to water [25], soil-earthworms [24], crops and grass [26,28] was demonstrated, although in some cases, levels of no concern were reported [29]. While plant accumulation but not toxicity was reported [30], phytotoxicity was observed in plants exposed to a mixture of these compounds [31]. Hence, ecological risks derived from the accumulation of these compounds in the long-term should also be analysed. Few risk assessment studies were carried out evaluating these scenarios for this type of compounds [32]. Snyder and O'Connor [33] developed a human and ecological screening level risk assessment for biosolids-borne triclocarban, evaluating 16 exposure pathways. Prosser et al. [34] evaluated the uptake and risk of several PPCPs in a biosolids-amended soil scenario, focusing on crops transfer.

On the other hand, micropollutant environmental fate is still a field of novel research. This means that a high variability in model parameterisation currently exists, especially in those factors related with biota or human exposure. In fact, some factors can differ orders of magnitude depending on the research study. Therefore, uncertainty and sensitivity analysis must be performed in order to identify those parameters most affecting the results and to provide potential value distributions. In this work, a probabilistic worst-case exercise to assess the environmental fate and the risks of persistent cosmetic and pharmaceutical compounds considering sludge application for soil fertilising was performed, paying attention to concepts like biotransfer and multicomponent exposure. The results obtained will help to elucidate whether persistent PPCPs should be included in future legislations related with biosolids application in soil.

2. Methodology

2.1. Selection and characterisation of compounds

The present study is focused on those PPCPs where no or low biodegradation in STPs was observed. The selection of persistent compounds was based on the results obtained in several research studies [35,36], on the levels found in different sludge samples, and finally, on the availability of relevant properties needed for modelling purposes. The considered compounds were: carbamazepine (CBZ), fluoxetine (FLX), triclosan (TCS), miconazole (MCZ) and ciprofloxacin (CPX). Naproxen (NPX), which was present at comparable levels to those of persistent PPCPs found in sludge, was also included as not persistent compound to evaluate model response. A characterisation of each compound, including a compilation of main physicochemical properties and the origin of the data (experimental or estimated) is shown in Table S.1. of the Supporting information.

2.2. Description and modelling of the scenario

The conceptual model describing the scenario to be evaluated, including the main exposure pathways, is described next. Selected PPCPs fate and biotransfer derived from the application of sludge (once per year) for agricultural purposes was estimated following the recommendations of the TGD [37]. Two main possibilities were considered: biosolids application for (i) grass growth and (ii) crops growth. The end-points were in both cases human receptors. In the first case, transfer routes and exposure pathways include grass uptake from soil, and biotransfer from soil, water and grass intake to meat and milk cattle, and ingestion of both products by humans. In the second case, direct consumption of crop vegetables grown in the area was considered the main route of human exposure. Besides, intake, inhalation and dermal contact with soil particles were also considered as exposure pathways in both scenarios, taking into account that some compounds can be preferentially accumulated in the soil matrix. Detailed fate model equations can be consulted in TGD (Part II), while exposure model equations and general model parameterisation (Tables S.2 and S.3) are shown in the SI. Nonetheless, a briefly description of some modifications and specific characteristics is provided in the following.

2.2.1. Fate model

Application rate ($APPL_{sludge}$) and concentration of the compounds in biosolids (C_{sludge}) defined the pollutant input to soil. The term biosolids was employed throughout the text instead of sludge since the concentration of the six compounds was mainly measured in digested sludge or biosolids, according to the studies included in Table 1. To perform the analysis under a screening level approach, only first order removal rate constants from the topsoil were considered in the fate model. Where needed, the pH-adjusted octanol–water partition coefficient (Dow) was used for ionisable compounds instead of Kow (Table S.4). For its calculation, both the Kow of the neutral and ionic species and the neutral fraction of the molecule were considered [34]. Experimental data of Dow for ciprofloxacin was available in the range of considered soil pH [66]. Regressions for the estimation of these parameters are presented in the SI. However, experimental data for soil-water partitioning coefficients was employed, when available in similar conditions to those of the evaluated scenario (Table 1).

To evaluate the potential accumulation of the different compounds and if steady-state was reached, a time horizon of 20 years was established. The different removal processes that may affect the fate of PPCPs in the environment were volatilization from soil, leaching to groundwater, degradation, and plant uptake. The study case evaluated was sited in NW Spain, where the leaching of some contaminants to groundwater may be more important due to both higher precipitation rates and a higher infiltration factor than the European average (TGD). The degradation of the substances was considered mainly by biodegradation, since abiotic degradation processes like hydrolysis and photo-oxidation are not significant for soil [67]. Furthermore, recent studies indicate that the biodegradability of compounds decreases when they are introduced into soils in the form of biosolids [49]. Compiled data for half-lives ($t_{1/2}$) (Table S.1) were employed to calculate a first order degradation rate constant to account for this mechanism. Plant uptake through advection (transpiration) was considered as a removal mechanism from soil [68].

2.2.2. Exposure model

To calculate total exposure through the considered pathways, concentration and transfer factors for different biotic compart-