OCCURRENCE AND ENVIRONMENTAL RISK ASSESSMENT OF PHARMACEUTICALS IN SEWAGE SLUDGE AND SOIL - A CRITICAL REVIEW

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ABSTRACT

Pharmaceuticals administered for treating and preventing numerous diseases are only partially assimilated in human body and the remaining part is excreted through urine and feces and occurs in urban wastewater. This is conveyed to a municipal wastewater treatment plant where activate sludge system is the most adopted treatment due to its simplicity and economical convenience. Unfortunately it is not able to efficiently remove these micropollutants and other persistent compounds from wastewater.

Removal efficiency of pharmaceuticals has been extensively investigated in the last years with respect to the liquid phase, whereas their fate in activated sludge process and their partitioning between aqueous and solid phases has been less frequently studied. It should be very important to investigate the presence of these compounds in the sewage sludge and the potential environmental risk posed by their residues on terrestrial organisms as sludge may be applied in agriculture.

This study collects and discusses available literature data on the occurrence of about 100 pharmaceuticals in untreated and treated sewage sludges derived from urban wastewater treatment plants in different countries. It was found that variability range of concentration varies depending on pharmaceuticals and on adopted treatment level. This is the case of ciprofloxacin and triclosan. Attempts to correlate pharmaceutical concentrations in sludge and pharmaceutical properties were carried out.

Moreover, environmental risk posed by pharmaceuticals in sludge and soil is also evaluated through the Risk Quotient approach. Based on this study, the most critical compounds in sludge and soil are antibiotics and hormones, respectively.

Finally, a comparison between risk posed by sludge, land disposal and that previously assessed by secondary effluent is reported and discussed. This allows to identify the most critical compounds in the two matrixes.

Keywords: Pharmaceuticals, sewage sludge, environmental risk assessment, land disposal.

1. Introduction

Pharmaceuticals (PhCs), administered for treating and preventing diseases, are only partially assimilated in human body and the remaining part is excreted through urine and feces and occurs in urban wastewater. Through the sewage network, it generally reaches municipal wastewater treatment plants (WWTPs). Activate sludge system (ASP) is the most common treatment adopted in municipal WWTPs due to its simplicity and economical convenience. Unfortunately, ASP is not able to efficiently remove most of these persistent micropollutants as documented in recent studies (among them Verlicchi *et al*. 2012). Due to environmental persistence of most PhCs, WWTPs, one of the main source, should reduce their load released into the environment, although legal requirements do not exist yet for them.

Up to now, most of the investigations referred to PhC removal from the liquid phase, whereas fate of PhCs in ASP and their partitioning between aqueous and solid phases has been less frequently studied (Gao *et al*., 2012). It was found that some of these compounds are more prone to stay in

the liquid phase, while others tend to adhere onto the solid one. For this reason it should be very important to investigate the occurrence of these compounds in the sewage sludge as, if applied in agriculture, it could represent an additional pathway for PhCs into the environment.

As long as this disposal practice is allowed worldwide, a better knowledge on potential environmental risk (ER) posed by PhC residues is needed (Golet *et al*., 2003, Lindberg *et al*., 2006).

The aim of this study is to contribute to the scientific debate, by raising issues to evaluate the impact due to occurrence of selected PhCs in urban sludge in case of land application. Nevertheless, data reported and analyzed in this study should provide a snapshot of the current situation and also a springboard for further debate on this issue.

2. Study description

This study collects and discusses literature data from international peer reviewed papers on occurrence of about 100 PhCs in primary, secondary (excess) and treated sludge derived from urban WWTPs of different countries (Verlicchi *et al*., 2013; Martin *et al*., 2012a, b; Lindberg *et al*., 2006).

Attempts to correlate PhC concentrations in sludge, partitioning between water and solid phases with the main chemical and physical PhC properties were carried out.
Moreover, ER posed by PhCs in sludge and also in soil, after sludge disposal on soil, is evaluated through the Risk Quotient RQ approach.

The study completes with a comparison between the risk due to sludge and that previously assessed for secondary effluent (Verlicchi *et al*. 2012) in order to identify the most critical PhCs in the two matrixes.

2.1. Pharmaceutical compound included in the study

Selected PhCs include a wide spectrum of highly active substances designed to interact with receptors in humans. They belong to 11 therapeutic classes according to their physiological activity: analgesics/anti-inflammatories (A), antibiotics (B), antidiabetics (C), antihypertensives (D), beta-blockers (E), diuretics (F), lipid regulators (G), psychiatric drugs (H), receptor antagonists (I), hormones (J) and antiseptics (K).

3. Results

3.1. Pharmaceutical occurrence in sewage sludge

The main results, in terms of concentration variability and means for a selection of PhCs are reported in Figure 1. The number in brackets after the name in the X-axis corresponds to the logarithm of solid–liquid distribution coefficient of the compound Log Kd (with K_d in L/kg_{ss}). K_d expresses the affinity of a compound for a solid phase: according to Ternes and Joss (2006), if Log K_d >2.67 the compound has a high sorption potential. Antibiotics have been the most analyzed and found to be the most abundant.

Martin *et al*. (2012a) and Gao *et al*. (2012) found that the time of year may influence PhC concentration in sludge, mainly due to different seasonal consumption (as for ibuprofen and salicylic acid or some antibiotics) and, to a lesser extent, the changes in degradation rates at the elevated temperatures during the summer season (as for carbamazepine and ethinyl estradiol, whose consumption is not influenced by the season). Martin *et al*. (2012a) found that the concentrations of most of the selected compounds increased between primary and secondary sludge, with the exception of diclofenac, ibuprofen, and salicylic acid. They ascribed this behavior to the different physical–chemical properties of the investigated compounds (namely, chemical structures, pKa, and K_{ow} values) and the different chemical compositions of primary and secondary sludges. PhC retention mainly occurs in the organic fraction that is higher in the secondary sludge. On the contrary, a higher concentration of diclofenac, ibuprofen, and salicylic acid in primary sludge could be due to a retention mechanism based on electrostatic interactions. Triclosan is present at high concentrations in digested sludge; it has a Log K_{ow} of 4.8 and a pK_a of 7.9 and under wastewater conditions (pH about 7) can be considered a hydrophobic compound

prone to sorption onto sludge. As for the psychiatric drugs, paroxetine and fluoxetine were the antidepressants most retained on sludge (they have a high sorption potential as shown by their Log K_d>4), whereas carbamazepine showed a wide variability, but in general, its sorption to solids remained quite modest.

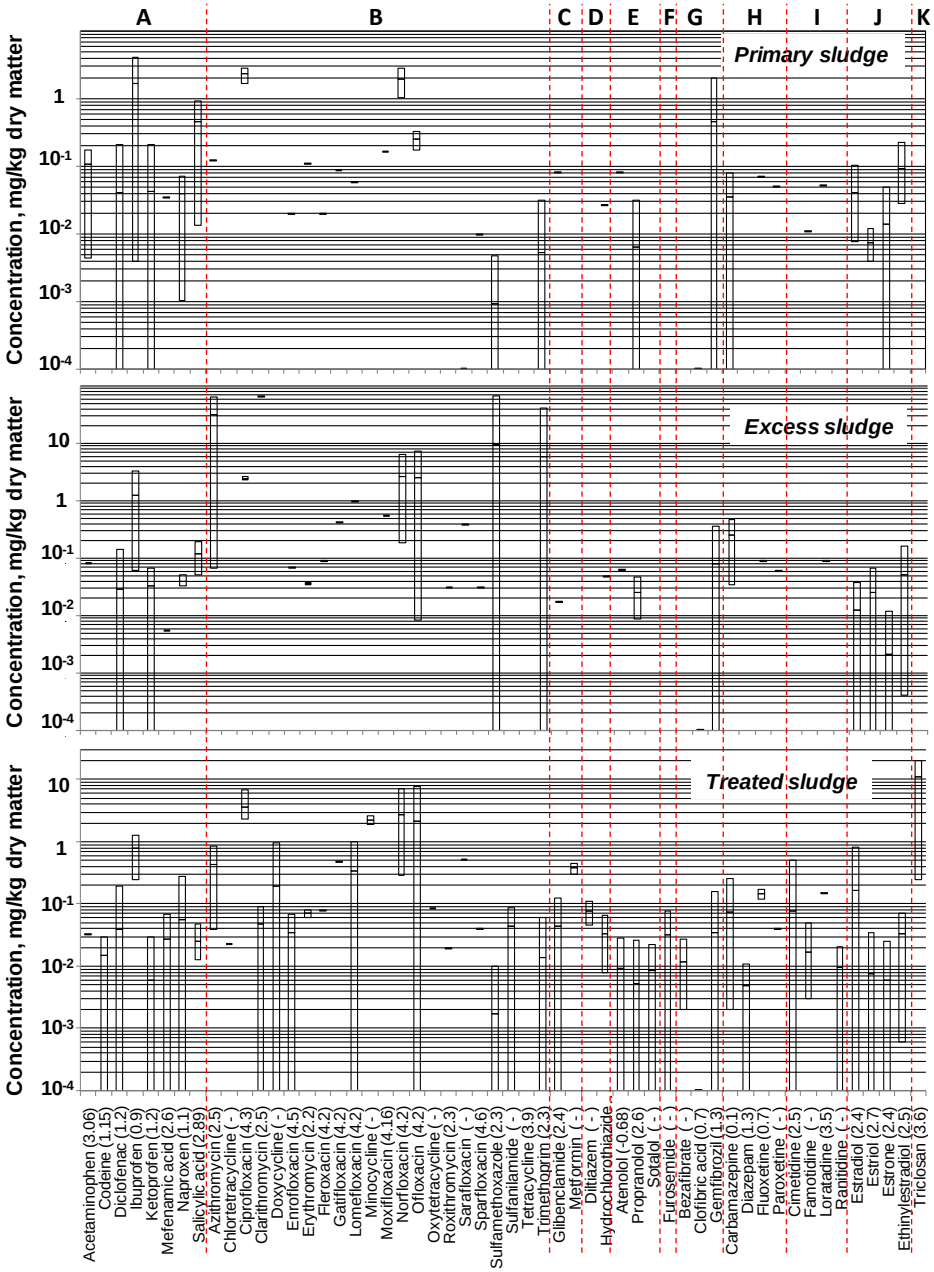

Figure 1: Occurrence of selected compounds in primary, excess, and treated sludge.

3.2. Environmental Risk Assessment for Sludge

ER was assessed by means of risk quotient approach. For each selected compound, RQ for sludge was assessed by means of the ratio between measured PhC concentration and its predicted no effect concentration in the sludge (eq. 1):

$$PNEC_{sludge} = PNEC_{water} \cdot K_{d_{sludge}} \quad (1)$$

ER due to land application of sludge was assessed according to European Commission Technical Guidance as the ratio between PhC predicted environmental concentration in soil (PEC_{soil},

evaluated by means of eq. 2 and its corresponding $PNEC_{soil}$ evaluated one year after one sludge-dose.

$$PEC_{soil} = \frac{c_{sludge} \times APP_{sludge}}{DEPTH_{soil} \times RHO_{soil}} \quad (2)$$

where c_{sludge} is PhC measured concentration in the treated sludge (mg/kg dry matter), APP_{sludge} is the application rate of dry sludge onto soil (0.5 kg/m^2 for agricultural soils), $DEPTH_{soil}$ is the mixing depth (0.20 m for agricultural soils), and RHO_{soil} is the bulk density of wet soil (1700 kg/m^3 for agricultural soils).

$PNEC_{soil}$ is evaluated by means of an equation similar to eq. 1, where $K_{d,sludge}$ is replaced by $K_{d,soil}$. RQ ranges for treated sludge are reported in Figure 2.

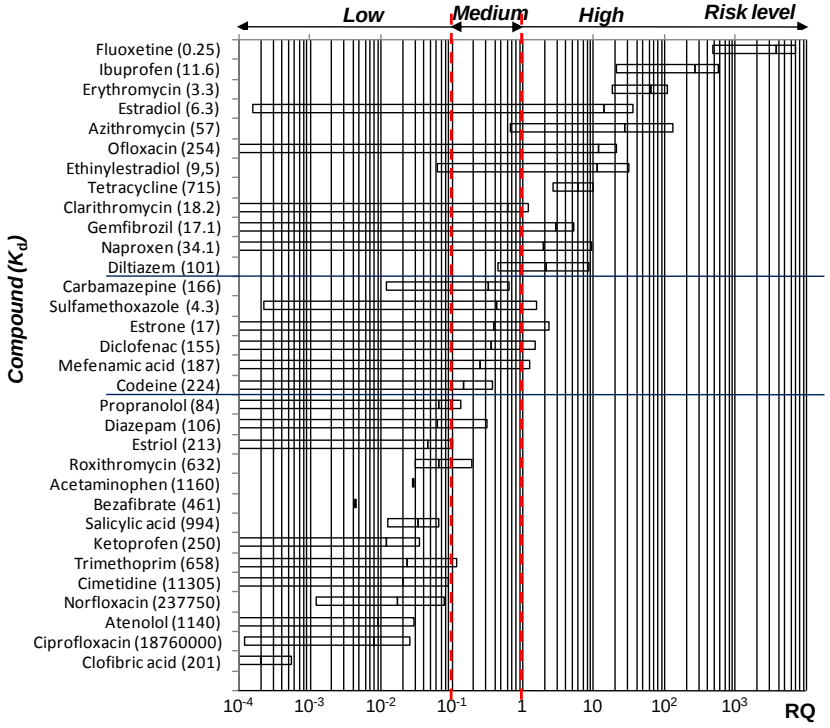

Figure 2: Risk quotient of selected PhCs, in descending order of risk, in digested sludge.

The only toxic effect expected is the one caused by estradiol, since its RQ has been calculated as 2.7. This means that an ecotoxic risk is still present to terrestrial ecosystem in spite of the significant decrease in the concentration of estradiol from digested to amended digested sludge. *The most critical compounds for environment in secondary effluent and sludge* -. Comparing the current results with those referred to WWTP final effluent by Verlicchi *et al*. (2012), it emerges that the most critical compounds are ibuprofen (high RQ_{water}, high RQ_{sludge}, and high load); fluoxetine, ofloxacin, erythromycin, tetracycline, and azithromycin (high RQ_{water} and high RQ_{sludge}); and gemfibrozil, estradiol, and ethinyl estradiol (high RQ_{water} and medium RQ_{sludge}).

4. Conclusions

Most of the municipal WWTPs includes an ASP with the final effluent being released into a surface water body and the treated sludge often land-applied. Common wastewater and sludge treatments are not able to efficiently remove all of many PhCs from liquid effluent as well as sludge. Observed removal efficiencies vary in a wide range for the selected compounds, as well as for the same substance, due to the different chemical and physical characteristics of PhCs and to operational conditions that influence partitioning behaviour. According to the results of this overview and in particular of this attempt to evaluate the environmental risk posed by PhC occurrence in sludge applied on soil, it emerges that the most critical compounds are antibiotics.

Up to now, PhCs are not included among those compounds to be regularly monitored, notwithstanding their occurrence has been documented since more than 20 years in many European countries. For this reason, further researches are necessary to widen knowledge on these issues and at the same time on adequate technologies able to reduce PhC load released in the environment by WWTP different outputs.

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