Eötvös Loránd University, Faculty of Science

Doctoral School of Environmental Science

Program of Environmental Earth Sciences

Investigation of factors influencing the adsorption-desorption processes of Pharmaceutically Active Compounds (PhACs) in soils

-PhD thesis-

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Introduction

Due to the increasing number of healthcare treatments, Pharmaceutically Active Compounds (PhACs) have been introduced in almost all environmental compartments. PhACs can be released into the environment in a variety of ways, but their actual source is often unidentified. Currently, even the most modern municipal wastewater treatment plants cannot fully remove these compounds. Discharges of treated wastewater back into surface watercourses and the use of these waters as irrigation water can be a significant source of pollution. The fate of PhACs in the soil may depend on several interrelated processes. The environmental risk from pharmaceuticals is mainly controlled by adsorption and desorption processes in the soil and changes in environmental parameters affecting these processes. Soils with different physical and chemical parameters were sampled to investigate the factors influencing sorption processes. The soils studied were formed under different redox conditions, with quantitative and qualitative differences in organic matter. To provide general description of the behaviour of pharmaceuticals, adsorption and desorption studies were carried out with nine PhACs with different physicochemical parameters.

The objectives of the study were to investigate how (i) the soil properties, (ii) the quantity and quality of soil organic matter and (iii) the physicochemical properties of PhACs control the sorption processes of the pharmaceuticals.

Materials and methods

Soil samples were collected from three different types of environment (climazonal, swamp, marsh) and two different land uses (pasture and arable). Eleven soil samples were taken from different soil depths at four different locations in Ceglédbercel, Hungary. The soil type of the samples were Calcaric Arenosol (Humic), Mollic Oxygleyic Calcic Gleysol (Epiloamic, Endoarenic), Calcaric Calcic Histic Gleysol (Endoarenic, Epiloamic) and Calcic Histosol (Calcaric, Fluvic), respectively, according to the World Reference Base (WRB) soil classification. Humic acids (HA) were extracted from the soil samples with 0.1 M NaOH and purified using standard methods of the International Humic Substances Society (IHSS). The commercial goethite standard (α-FeOOH) was also used as an adsorbent because the selected soils contained measurable amounts of this mineral.

Nine pharmaceuticals were selected based on their physicochemical properties, namely: carbamazepine (CBZ), diclofenac (DFC), 17α-ethynyl estradiol (EE2), 17β-estradiol (E2), estrone (E1), lidocaine (LID), tramadol (TRA), oxazepam (OXA) and lamotrigine (LAM). The adsorption and desorption of PhACs were measured in dark at constant temperature in an incubator using a batch equilibrium method according to the OECD international standard (OECD 106, 2000). The concentrations were measured with HPLC (Shimadzu Prominence LC-20AR), using a PDA and a fluorescence detector.

The Langmuir, Freundlich and Dubinin-Radushkevich models were used to evaluate the adsorption of PhACs on selected soils. Differences in the soils types and PhACs were tested by one-way ANOVA with Duncan's post hoc test ($p<0.05$). Principal component analysis (PCA) was applied to reveal the relationship between soil parameters and adsorption parameters. A multiple linear stepwise regression was used to evaluate the effect of soil variables on the sorption processes. The relationship between the physicochemical properties of PhACs and the adsorption parameter was analysed using redundancy analysis (RDA).

Results

The adsorption and desorption processes of PhACs have been investigated as affected by both soil properties (the quantitative and qualitative properties of soil organic matter) and the physicochemical properties of PhACs. PhACs (CBZ, DFC, EE2) adsorbed with significantly different amounts on the three types of soils of distinct parameters. The tested PhACs adsorbed to the higher extent on the topsoil samples with high organic matter content. The adsorbed amount decreased with depth in the soil profile. The extent of desorbed pharmaceuticals was also lower in the surface levels of soils. The extent of desorption increased gradually with depth, due to decreasing organic matter content. Higher clay content also decreased the desorption of PhACs.

The quality of organic matter in soils formed in hydromorphic areas (Gleysol, Histosol) differed from soils formed under aerobic conditions (Arenosol). Due to the anaerobic and partially anaerobic decomposition of organic matter, the organic matter was enriched in aromatic and phenolic compounds in the hydromorphic soil samples. The hydrophobic EE2 showed increased adsorption in these hydromorphic soil samples. The sorption of hydrophobic compounds is independent of changes in environmental factors (e.g. pH), whereas for fully or partly ionised compounds, such as TRA, LID or DFC, sorption processes are not independent of these factors. For these compounds, the number of charged sites controls the sorption processes. The results of my doctoral research can be summarized:

1. The extent of desorption of hydrophobic PhACs (CBZ, EE2) increased gradually with depth in the examined aerobic soil (Arenosol) and partially anaerobic soil (Histic Gleysol): for Arenosol CBZ: 94→100%, EE2: 62→86%, for Histic Gleysol CBZ: 57→95%, EE2: 3→26%. This is due to a decrease in organic matter from the surface to the lower levels (Arenosol SOC%: 1.47→0.26, Histic Gleysol SOC%: 9.26→1.78). Consequently, as the organic matter content decreases, the risk of desorption and leaching of hydrophobic

pharmaceuticals increases.

2. Based on principal component regression, desorption of hydrophobic PhACs (CBZ, EE2) was significantly reduced by higher specific surface area and swelling clay mineral content. However, the amount of soil organic matter was found to be a crucial factor in the release of PhACs.

3. Anaerobic decomposition of organic matter has resulted in a significant difference in the quality of organic matter in hydrophobic soils compared to aerobic soils. FTIR analysis showed that the humic acid fractions of the hydromorphic soils (Gleysol (G_20), Histosol (H_20)) had high relative amounts of aromatic ($rA3070>0.45$) and phenolic ($rA1220>12.5$) compounds. These components are considered to be the most active binding sites for EE2. The adsorption energy for the G_20 sample was 13.4 kJ/mol, while that of the H_20 sample was 12.8 kJ/mol. Hence, EE2 can be adsorbed to an increased extent in hydromorphic soils.

4. The redundancy analysis revealed that the adsorption mechanism of highly hydrophobic PhACs, such as EE2, is identical on both the mineral and organic

phases of soils. This is due to their structure being less dependent on the chemistry of the soil environment.

5. In the case of DFC, TRA and LID, the size of the fraction of charged species was modified with the pH change. The adsorption mechanism of these compounds was mainly determined by soil pH, since changes in the chemical properties of the PhACs cannot be separated from changes in environmental parameters.

Publications related to the dissertation

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