Progressive methods for investigation of migration of pharmaceuticals in soils

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Soil pollution is one of the most critical problems related to both environmental quality and human health. In the last decades, pharmaceuticals have been extensively used in large quantities which resulted in their input into environment (Drillia *et al*, 2005; Topaz *et al*, 2020). Pharmaceuticals which can be both beneficial for human health and harmful for environment, and, therefore, harmful indirectly for human health because of their potential uptake by plants from soils. Several major sources of pharmaceuticals and their metabolites can be identified. The pharmaceutical industry, from which drugs are released during their production, can be considered as first source. Other sources are drug containing waste from industries, hospitals and households, wastewater, and sewage sludges from municipal wastewater treatment plants (Gworek *et al*, 2021; Klučáková and Závodská, 2023). Their migration in soils play important roles in their toxicity and bioavailability therefore knowledge of their behaviour is essential for the prediction of their mobility, toxicity, and bioavailability in soils and surface-water and ground-water environments. It is known that soils have a "self-cleaning" ability which is related to the content of organic matter (Bulc and Slak, 2009; Lishchuk *et al*, 2023; Smirnova et al, 2022). This ability is connected to the interactions between pollutants and soil organic matter which can form in many cases highly stable complexes and immobilize pollutants in their structures. It results in a decrease in concentration of free mobile pollutants in soils and the immobilized pollutants thus remain in soil, but they are not able to enter into soil solution, ground-water, and plant roots.

In this contribution, we would like to introduce our methods how to investigate migration of pollutants in soils, their possible immobilization and (on the other hand) bioavailability. The study is focused on pharmaceuticals which are recently considered as very problematic pollutants, but our methods are universal and can be used for many different pollutants (e.g. heavy metals and dyes) as published in previous studies (e.g. Kalina *et al*, 2013; Klučáková and Pekař, 2009; Klučáková *et al* 2014; Sedláček *et al*, 2013). We combine three different approaches (in situ measurement in soil, measurement in humic hydrogels, and measurement in inert hydrogel enriched by humic substances) and four different techniques optimized to our purposes (diffusion cells, diffusion from instantaneous planar source, diffusion from constant source, and diffusion couple). All our approaches and technics are supported by mathematical simulation.

In situ measurement is based on system of vertical columns in soils insulated against their cylindrical environment (only frontal circular areas are accessible for pollutant). Upper circular area serves as an entrance for pollutant. One of the boundary conditions is usually that the column can be considered as a semi-infinite medium, it means that the diffusion distance of pollutant is shorter than the column height. Similar boundary condition is applied to all our techniques excepting diffusion cells. Other two approaches use humic substances as representants of soil organic matter in the form of hydrogels: humic gel based on the precipitation of sodium humate by an acid to achieve compact structure and agarose hydrogel enriched by humic substances. Both hydrogels are considered as experimental models of pore soil structure with homogeneously distributed organic matter as active sites for interactions with pollutants. Similarly, as in the case of soil column, the hydrogels are insulated against their environments and only frontal areas are accessible for pollutant molecules (or ions).

The technique of diffusion cells is used for the study of the diffusion through hydrogel layers. The diffusion from instantaneous planar source is used for the study of diffusion from very small sources which can be considered as a pulse and its whole amount is gradually distributed into hydrogel or soil medium. The diffusion from constant source works with constant concentration on the interface between hydrogel or soil and the diffusion source. The diffusion couple uses two compartments. One of them (donor part) contains homogeneously distributed pollutant particles, other part is pure of them. After connection, the pollutant particles can diffuse from donor to acceptor compartment. The movement of pollutant in soil or hydrogel is monitored; the concentration profiles of free movable pollutant are experimentally determined by suitable analytical method in given time. Transparent agarose hydrogels can be analysed directly in cuvettes with hydrogel after removal from donor solution using UV/VIS spectrometer equipped with the special accessory providing controlled fine vertical movement of the cuvette in the spectrophotometer. Humic hydrogels are sliced, and each slice is separately extracted with the leaching solutions (e.g. HCl). Leachates can be analyzed by UV/VIS spectrometry or liquid chromatography. Details can be found in our previous studies (Kalina *et al*, 2013; Klučáková *et al* 2014; Klučáková and Pekař, 2009; Klučáková and Závodská, 2023; Sedláček *et al*, 2013). Experimental data are processed, and the diffusion coefficients are computed. Their values are strongly affected by interactions as well as the pore structure. The diffusion pathway in pores is longer as a result of tortuous movement. Interactions between pollutant and active sites can suppress their mobility and bioavailability by the decrease in diffusion rate and concentration of free movable pollutant.

Table 1. Diffusion coefficients for sulphapyridine in different matrices based on various experimental methods.

Matrix	Method	Diffusion coefficient ($m^2 s^{-1}$)
Enriched agarose hydrogel	Diffusion couple	$(9.85 \pm 0.47) \times 10^{-11}$
	Constant source	$(3.40 \pm 0.13) \times 10^{-10}$
	Diffusion cells	$(4.49 \pm 0.12) \times 10^{-10}$
Humic hydrogel	Instantaneous source	$(4.38 \pm 0.29) \times 10^{-10}$
Soil	In situ	$(4.23 \pm 0.27) \times 10^{-10}$

A summary of diffusion coefficients obtained for sulphapyridine is shown in Table 1. As can be seen both model mediums (agarose hydrogel enriched by humic acid and humic hydrogel) can provide practically the same results as in situ measurements in soil, if a suitable experimental method is chosen. Simultaneously, results obtained for agarose hydrogel allows to differentiate between the effects of porous structure of hydrogel and interactions between humic acids and pollutants. Using agarose hydrogel, we can compare results obtained for pure medium (agarose hydrogel without humic acids) and hydrogel enriched by humic acids as representant of soil organic matter. The values of diffusion coefficients obtained for pure inert hydrogel are $(1.01 \pm 0.05) \times 10^{-10}$ $m^2 s^{-1}$, $(4.60 \pm 0.21) \times 10^{-10}$ $m^2 s^{-1}$, and $(4.93 \pm 0.38) \times 10^{-10}$ $m^2 s^{-1}$ for the diffusion couple, the diffusion from constant source, and the diffusion cells, respectively. Comparing with the diffusion coefficient (2.03×10^{-9} $m^2 s^{-1}$) obtained for aqueous solution (Ghoreishi *et al,* 2017), the strong decrease caused by the pore structure when the diffusion coefficient is dependent on its porosity (a portion of free volume to bulk volume of hydrogel) and tortuosity (the ratio of squares of real diffusion path in pore and a macroscopic distance). The addition of humic acids in porous material resulted in the additional decrease in diffusion coefficient caused by the interaction and immobilization of sulphapyridine in hydrogel structure. This finding is very usable for a prediction of the behaviour of pharmaceuticals (and other pollutants) in soil environments.

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