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Combining sorption experiments and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to study the adsorption of propranolol onto environmental solid matrices – Influence of copper(II)

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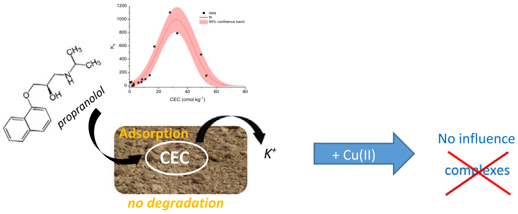
HIGHLIGHTS

- Propranolol adsorption was mainly governed by solid CEC.
- A cationic exchange mechanism was evidenced for propranolol adsorption.
- The presence of copper did not modify propranolol adsorption.
- No propranolol degradation product was evidenced at the soil surface by ToF-SIMS.
- No propranolol-copper complex was evidenced at the soil surface by ToF-SIMS.

GRAPHICAL ABSTRACT



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ABSTRACT

The bioavailability of pharmaceuticals is governed by their sorption in soils/sediments, as the retention processes determine their concentration in surface- and ground-water. The adsorption of these contaminants can involve various solid components such as organic matter, clays and metallic oxides, and their distribution among these solid components depends on contaminant and solid properties. In this paper we studied the adsorption of the pharmaceutical propranolol – a beta-blocker – on eight different solids (six soils, one sediment and one kaolinite-based sample) by batch experiments. The influence of contact time, propranolol concentration and pH was considered, as well as the presence of copper(II). The investigated solids displayed a wide variability in terms of CEC (cationic exchange capacity) and organic carbon and carbonates contents. The influence of pH was negligible in the pH range from 5.5 to 8.6. The adsorbed amounts were greatly dependent on the solid and two groups of solids were evidenced: three soils of high CEC and organic carbon contents which retained high amounts of propranolol, and three soils, the sediment and the kaolinite-based sample (low CEC and organic carbon content) displaying a low adsorption capacity for the beta-blocker. A linear model enabling the determination of the sorption parameters K_d and K_{oc} was pertinent to describe the adsorption isotherms but the K_{oc} values showed a great variability. It was shown that organic carbon content alone could not explain propranolol adsorption. The CEC value was identified as influent parameter and a simple empirical model was proposed to describe propranolol adsorption. At microscopic and molecular scales, ToF-SIMS experiments indicated (i) a decrease of potassium on the surface upon propranolol adsorption with a distribution of the beta-blocker similarly to alumino-silicates, iron and organic carbon on the surface confirming a cation exchange mechanism and (ii) the absence of degradation products and copper-propranolol complexes.

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1. Introduction

In recent decades, the widespread occurrence of pharmaceuticals in the environment has become an important concern and presents a potential toxicity for aquatic and soil ecosystems and a risk for human health (Lin et al., 2010). Human pharmaceuticals enter the aquatic environment through various routes. After ingestion they are excreted to the sewer system in the form of the non-metabolized parent compound or as metabolites (Pérez and Barceló, 2007). They reach waste water treatment plants (WWTPs), which are not yet well-adapted for their retention/degradation, and finally finish their way into receiving waters or land by the application of sewage sludge or by irrigation with reclaimed wastewater (Chen et al., 2011). They can subsequently reach groundwaters by leaching and surface waters by run-off then sediments by adsorption (la Farré et al., 2008).

We focus here on propranolol as pharmaceutical ($pK_a = 9.53$, Hansen et al., 2006), a beta-blocker extensively used in medicine and widely detected in the environment (Azzouz and Ballesteros, 2012; Maszkowska et al., 2014; Mendoza et al., 2015). Beta-blockers are widely used for the treatment of heart rhythm disorders, angina pectoris, hypertension, tachycardia or acute myocardial infarction (Kyzas et al., 2015). They are detected in effluents of WWTPs and in surface waters in the ng L^{-1} to μg L^{-1} range because of incomplete removal during treatment processes (Godoy et al., 2015). Consequently, they are persistent in the environment (Maszkowska et al., 2014) and their common presence can lead to unexpected effects towards different organisms (Maszkowska et al., 2014; Santos et al., 2010).

Adsorption is a key process governing the fate of pharmaceuticals in soils because it can slow down the migration of chemicals, limit their degradation and determine the available amounts for exposure. The prediction of the adsorption behavior of pharmaceuticals remains a challenge to researchers since not only it depends on the soil composition, but also it varies from one compound to another with a pH-dependent speciation. In soils, it has been evidenced in few papers a limited adsorption of propranolol which can be considered as more or less mobile in the soil structures with distribution coefficient K_d of 48–160 L kg^{-1} depending on the soil properties (Maszkowska et al., 2014; Carter et al., 2014). By contrast, Drillia et al. (2005) showed that it was more strongly adsorbed (K_d of 200 L kg^{-1}) on soils with a relatively high organic carbon content (7%). In river sediments, it has been highlighted a significant adsorption of beta-blockers including propranolol (Yamamoto et al., 2009; Lin et al., 2010), with distribution coefficient reaching values of 270 L kg^{-1}. Adsorption studies of beta-blockers were also reported, with different adsorption rate, on different type of sorbents encountered in the environment such as kaolinite (Maszkowska et al., 2014), metallic oxides, framework and ring silicates (Kibbey et al., 2007), and montmorillonite (Vicente et al., 1984). Despite the number of studies on the adsorption of beta-blockers (>150 publications), the mechanisms involved in the adsorption process remain ambiguous.

It has long been known that organic micropollutants can form more or less stable complexes with metallic cations present in the environment. Gölcü et al. (2004) revealed the structure of cobalt(II)- and copper(II)-propranolol complexes using various spectroscopic techniques. Recent studies demonstrated that the presence of such metallic cations could enhance the retention of pharmaceuticals (e.g. Perez-Guaita et al., 2011; Graouer-Bacart et al., 2013). However, Graouer-Bacart et al. (2016) showed that copper(II) had no influence on the retention of diclofenac onto soils despite the formation of stable Cu-diclofenac complexes, meaning that each system metallic cation-pharmaceutical should be studied on a case by case basis.

Finally, in most of cases the mechanisms involved in the sorption processes were studied using macroscopic methods (batch and/or column experiments) and final conclusions are still in debate. Indeed, soil properties can influence adsorption of organic and inorganic contaminants. The characterization of different chemicals on mineral and organic surfaces of environmental samples is an important challenge. At microscopic scale, the heterogeneity or variability of the soil surface chemistry can lead to misinterpretation, introducing confusion in the characterization process (Cerqueira et al., 2011). The use of physico-chemical and/or spectroscopic techniques can overcome the uncertainties remaining with the indirect methods. In this sense, to our knowledge, very few attention has been focused on providing information about the interactions between pharmaceuticals and metallic cations by such techniques. To this end, time of flight secondary ion mass spectrometry (ToF-SIMS) is a powerful technique which can provide precise information on the distribution of contaminants on soil surfaces such as natural minerals and organic matter. This technique was used for the distribution and stability of pharmaceutical actives within solid matrices (Barnes et al., 2011).

The aim of the present study was to investigate the adsorption behavior of propranolol in the environment. For that purpose, eight different environmental solids (six soils, one sediment and a clay sample) were studied as a function of different parameters such as contact time, pH and concentration using batch experiments. We also studied propranolol adsorption in presence of copper – a ubiquitous contaminant present in soils, sediments and water compartments – on two selected soils. Another objective was to evidence the associations of both contaminants with the main soil components using ToF-SIMS. A better understanding of the involved processes in their retention onto soils and sediments will make it possible to predict their behavior and propose measures to control their mobility and thus their plant uptake and leaching to groundwater.

2. Materials and methods

2.1. Materials and reagents

Propranolol hydrochloride, 1 isopropylamino 3 naphthyloxy propan 2 ol (Fig. 1) (purity 99.5%), and $CuSO_4.5H_2O$ (Normapur) were purchased from VWR and Prolabo, respectively. The stock solutions of propranolol (1 mmol L^{-1}; 259.3 mg L^{-1}) and of $CuSO_4$ (1 mmol L^{-1}; 63.5 mg L^{-1} of Cu) were prepared in distilled water. Acetonitrile (HiPerSolv CHROMANORM®) was obtained from VWR. HCl and KOH (Normadoses) were purchased from Prolabo.

In this work, eight different solids were studied: six soils, one river sediment and one kaolinite-based sample. A kaolinite-based sample (named kaol-based) was preferred to a whole kaolinite sample in order to be more representative of clay contents encountered in natural solids. It was prepared by mixing 10% of kaolinite and 90% of quartz in weight; quartz was chosen to complete the weight because it represents the main component of soils originating from the sampling region in France (El Arfaoui et al., 2009), and the absence of propranolol retention on this mineral was preliminary checked. Kaolinite and quartz were purchased from Sigma-Aldrich and Merck, respectively. The soils and the sediment were collected in the 5–20 cm horizon, in France (S_1, S_3, S_4, S_5, S_6, sediment), and in Germany (S_2). They were dried at 40 °C for 24 h and passed through a 2 mm sieve. They were characterized for particle size distribution (without decarbonation), pH, CEC, organic carbon (OC) and carbonate contents according to French and International standard methods, following NF X31-107, ISO 10390, ISO X31-

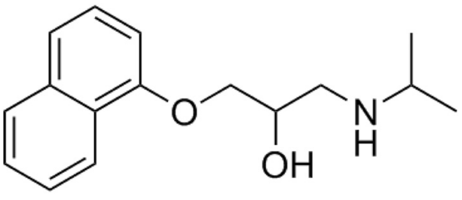

Fig. 1. Structure of propranolol.