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Analyses and decreasing patterns of veterinary antianxiety medications in soils

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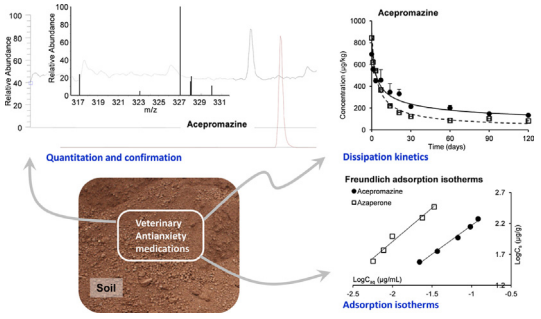
HIGHLIGHTS

- The present study is the first record for determination of antianxiety drugs in soils.
- Ultrasonic-assisted extraction and LC/MS/MS were used for extraction and analysis.
- Dissipations of the tested drugs were investigated using batch soil incubation experiments.
- Two kinetic models were calculated and validated according to SANCO guideline.
- Acepromazine was more adsorptive and degradable, while xylazine was more sustainable and mobile.

GRAPHICAL ABSTRACT



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ABSTRACT

An ultrasonic-assisted extraction method was developed to detect 16 antianxiety medications in soil samples using liquid chromatography–high resolution mass spectrometry (LC–HRMS), Orbitrap mass spectrometer. The determination method resulted in satisfactory sensitivity, linearity, recovery, repeatability, and within-laboratory reproducibility. Acepromazine, azaperone, and xylazine were incubated in control, amended, and sterilized soils. The amendment with powdered blood meal affected the relatively fast dissipations of acepromazine, azaperone, and xylazine in the soils. Dissipation kinetics of acepromazine were consistent with bi-phasic kinetics (first-order multi compartment) and the other couples were fit to single first-order kinetics. A hydroxylated acepromazine was identified from soil samples using Orbitrap mass spectrometry. According to sorption batch experiments, the adsorption of acepromazine and azaperone was greatly high, whereas that of xylazine was relatively low. Xylazine was persistent in the incubated soils, and acepromazine demonstrated fast initial dissipation; hence, xylazine could have a potential harmful effect on the environment. To the best of our knowledge, this is the first report on the dissipation and adsorption–desorption patters of animal pharmaceutical tranquilizers and α, β-blockers.

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1. Introduction

Pets and livestock food-producing animals are given veterinary medications either to care for or prevent a disease or to fatten up. Psychological stability is also an important concern for healthy animals. Moreover, protecting animal safety and promoting animal welfare have been globally emphasized to produce safe and high-quality animal products from healthy livestock. Unfortunately, however, animal welfare is unattainable to petty stock farmers, and even developed counties continue to run concentrated animal feeding operations to make a huge profit and meet the high public demand. It should be given unrelenting efforts to conduct more advanced animal farming considering animal welfare. As of now, safe and correct use of veterinary medications in accordance with guidelines, and hygienic growing environment would be best to promise freedom against diseases and stress for animal welfare and safe animal products to consumers. The thing to consider at this point is that livestock wastewater and excretions are continuously formed while animals grow, although safe meat products are manufactured as a result of observance of safe use guidelines.

Although inadmissible use of veterinary drugs is avoided actively, illegal discharge and incomplete purification of livestock wastewater and reuse of animal excretion are polluting aquatic and terrestrial environments. Active pharmaceutical ingredients can be introduced into soil through sludge land application, use of livestock wastes as fertilizers, and reclaimed water irrigation. Pollutants in soil may be accumulated in plants or migrate through soil intact or transformed and reach groundwater, finally resulting in pollution to the drinking water source [1]. The presence of significant amounts of residual pharmaceuticals and their potentially active metabolites in manure, sediment, sludge, and wastewater has been demonstrated by monitoring studies in the past few years [2–8]. Several tranquilizers and α, β-blockers have been employed to relief anxiety and stress of food-producing animals. Several hypnotic-sedatives are even injected into pigs to calm them during transportation to the slaughterhouse [9,10]. Therefore, slaughterhouse wastewater would be one of the main sources of pollution with veterinary drugs [11,12]. Likewise, on account of considerable risk of the residual veterinary medications in the environment, their environmental fate, including adsorption, desorption, transport, transformation, degradation, and biological accumulation has been comprehensively studied in water, sediment, and soil [13–20]. In particular, the mobility of contaminants in soil has been emphasized because it is directly linked to water resource quality. Vazquez-Roig et al. [7,21] were determined various type of pharmaceuticals in soils, sediments, and waters of the Spanish marshlands using pressurized liquid extraction (PLE) and liquid-chromatography tandem mass spectrometry (LC/MS/MS). They found that all pharmaceuticals (except one) were detected in waters, soils and sediments. Moreover, contamination by pharmaceuticals in that coastal wetland area affected ground, tap, and surface waters. Such contamination not only causes ecological problem to aquatic fauna but also constitutes potential risk to human health.

Environmental fate is fundamentally predicted by laboratory batch experiments, including adsorption–desorption and incubation studies. However, there were no studies on the determination and dissipation of veterinary tranquilizers and α, β-blockers in soil. In order to extract various organic pollutants, including pesticides and veterinary drugs from soil, liquid–liquid extraction using organic solvents and diverse buffers has traditionally been employed as an exhaustive extraction method. Extractability, quickness, and performance were improved and automated by mechanical approach, such as pressurized liquid extraction (PLE) and microwave-/ultrasonic-assisted extraction (USE) [22–26]. Mechanical extraction methods are attractive because they are easy to control, consume less solvent, and can avoid manual handling errors.

Herein, an USE approach was introduced to extract 16 tranquilizers and α, β-blockers from soil, and liquid chromatography–high resolution mass spectrometry (LC–HRMS) using Orbitrap MS was employed for quantitative and confirmatory analyses. The dissipation behaviors and adsorption–desorption properties were evaluated for three representative analytes, such as acepromazine, azaperone, and xylazine in soil batch experiments.

2. Experimental

2.1. Chemicals and reagents

Acepromazine maleate, carazolol, chlorpromazine hydrochloride, fluphenazine dimaleate, mesoridazine benzenesulfonate, perphenazine, prochlorperazine dimaleate, promazine hydrochloride, propionylpromazine hydrochloride, (±)-propranolol hydrochloride, thioridazine hydrochloride, trifluoperazine dihydrochloride, triflupromazine hydrochloride, xylazine, and acepromazine-d6 hydrochloride (internal standard, IS) were purchased from Sigma–Aldrich (Taufkirchen, Germany). Azaperone (98.5%) and metoprolol fumarate were supplied from Dr. Ehrenstorfer (Augsburg, Germany) and the US Pharmacopeial Convention (MD, USA), respectively. The purities of chlorpromazine and fluphenazine were 95 and ≥90%, and the others were ≥98%. Ammonium formate (AF), ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), magnesium sulfate, and sodium chloride were obtained from Sigma–Aldrich, formic acid (FA) and mercuric chloride ($HgCl_2$) were obtained from Merck (Darmstadt, Germany). Acetonitrile (MeCN), methanol (MeOH), and *n*-hexane were purchased from JT Baker (Deventer, the Netherlands), and ethylacetate (EtOAc) was from AppliChem (Darmstadt, Germany). Primary secondary amine (PSA) was obtained from Agilent Technologies (CA, USA). All solvents and reagents used were of high-performance liquid chromatography or analytical grade.

2.2. Standard solutions

Standard stock solutions of all analytes, including IS were prepared in MeOH at 100 μg/mL. A multi-compound intermediate standard solution was prepared by mixing 16 stock solutions, and then serially diluted with blank soil extracts to obtain calibration standards at the lowest calibrated level (LCL) ×1, ×4, ×10, ×20, ×100, ×200, and ×400 μg/kg. The blank soil was confirmed previously, and none of the tested analytes were in the extract. IS was added at a concentration of 25 μg/kg to all calibration standards. Every stock solution was stored at–26 °C in a dark amber bottle, and all calibration standards were kept at 4 °C.

2.3. LC–high resolution mass spectrometry

An HPLC system was operated with an Agilent 1200 Series (CA, USA), and a high resolution mass spectrometric detection coupled to LC was carried out with a Finnigan LTQ Orbitrap mass spectrometer (Thermo Scientific, MA, USA). An internal lock-mass calibration method of the high-accuracy MS was carried out using n-butyl benzenesulfonamide (*m/z* 214.0896, $[M+H]^+$); *m/z* 231.1162, $[M+NH_4]^+$) to detect the high accurate masses of the tested analytes. The details of the LC and MS conditions were the same as mentioned before in our previous study [27]. Herein the experimental set-up was shown as a supplementary material (Table S1).

Supplementary table related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.05.005.

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