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PHARMACEUTICALS RESIDUES AND BIOCIDES FROM BIOSOLIDS AND MANURE SPREAD AS FERTILIZERS: FIRST RESULTS AFTER ONE YEAR FIELD STUDY

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ABSTRACT

The Telesphore project aims to identify and to quantify the transfers of pharmaceuticals residues and biocides and their related processes from biosolids and manure spread on grassland as fertilizers. Real land-spreading conditions were reproduced on six in-situ lysimeters and the pathway of pharmaceuticals and biocides was tracked by sampling infiltrated water and soil over one year. The study has focused on 32 pharmaceuticals, biocides and their transformation products, selected from their previous detection in several organic fertilizers. Six months after biosolids and manure spreading, the soil concentrations were in the range of nanograms per gram of soil and only few compounds were detected in infiltrated water. Ketoprofen was found to be the most mobile and persistent pharmaceutical compound after biosolids application whereas thiabendazole was the most frequently detected substance in infiltrated water after manure amendment.

Keywords: *land spreading, drugs, sludge, infiltration, soil contamination, lysimeters.*

1. INTRODUCTION

The Telesphore project aims to identify and quantify the transfers of selected human and veterinary pharmaceuticals and biocides after land spreading of biosolids and manure. Some studies have already been conducted in situ (Gros et al. 2019) but they focus on pharmaceuticals only. Moreover, comparison of biosolids and manure regarding the same micropollutants is rare. In this paper, we present the first results of an experiment with six in situ lysimeters after two applications of solar dried biosolids from an urban wastewater treatment plant (WWTP) and liquid manure from a dairy farm applying strict rules for PDO (Protected Designation of Origin) reblochon cheese production. Sampling of both infiltrated water and soil at different depths allow exploring the fate of these selected micropollutants within the lysimeters under real agricultural operation of a pasture according to times and rates of application.

2. MATERIAL AND METHODS

The study site is located in Scientrier, French Alps. Six 1-m deep lysimeters of 2 m x 2 m area have been built and filled with sandy loam soil excavated from the same location, by ensuring that the initial succession of layers of soils and degrees of compaction were reproduced within

the lysimeters. Lysimeters MA and MB receive manure, lysimeters SA and SB receive biosolids, and lysimeters RA and RB are used as reference without spreading. MA, SA and RA have a concrete invert and are used for monitoring micropollutants in infiltrated water samples. MB, SB and RB have no invert and are used to monitor micropollutants at different depths in soil carrots, sampled just before the next land spreading. Solar dried biosolids from the local WWTP and dairy cow manure were applied two times, on 5 Nov. 2020 and on 03 Jun. 2021, following the rates and calendar of local agricultural practices.

32 pharmaceuticals and biocides compounds have been selected for monitoring from a preliminary suspect screening approach (Guirronet, 2021) carried out on 5 urban WWTP sludge samples, 5 liquid manures and on 1 manure with bedding material, all produced in the region: antibiotic (fluoroquinolones, cyclines, macrolides, sulfonamides, diaminopyridines class), anti-parasitic (ivermectine, imidiazothiazole, benzimidazoles, triazoles, tetrahydropyrimidine class), disinfectant (bisbiguanidine, organochlorine class), herbicide/insecticide (sulfaximine, uracil, organophosphate class).

Infiltrated water was collected 16 times during the first year of experiment in lysimeters MA, SA and RA. The soil was sampled in lysimeters MB, SB and RB on 03 Jun. and 28 Oct. 2021. The carrots were sliced in four layers: 0 – 10 cm, 10 – 40 cm, 40 – 60 cm, 60 – 100 cm depth.

3. RESULTS AND DISCUSSIONS

Only 17 compounds among 32 are detected in biosolids, including 4 transformation products, and only 11 in liquid manure. The same pharmaceuticals and biocides are detected in sludge applied in Nov. 2020 and Jun. 2021, with similar concentration levels, except 3-amino-5-methylisoxazole (a sulfamethoxazole metabolite) whose concentration is below LoQ (10 ng/g DW-dry weight) in Nov. 2020 and 1.5 µg/g DW in Jun. 2021. For comparison, in dewatered municipal biosolids Gottschall *et al.* (2012) reported higher concentrations (in ng/g) for ofloxacin (1400 versus 377 – 474 for this study), triclosan (10900 vs. 13-42), ciprofloxacin (3260 vs. 28 - 59), tetracycline (513 vs. 17 - 30), and epitetracycline (334 vs. 19 - 31 ng/g). Concentrations in liquid manure are very low (which is consistent with the strict rules applied at the farm), ranging from 0.1 ng/g DW for thiabendazole to 14.4 ng/g DW for 3-amino-5-methylisoxazole. As an example of available local data of veterinary drug administration, tetracycline represents 22 % of prescribed antibiotics but the concentration in liquid manure was only 1.0-1.4 ng/g.

Between Nov. 2020 and Oct. 2021, eight compounds were found in infiltrated water sampled in lysimeter SA (A first assessment of the mass balance for pharmaceutical residues and biocides between organic fertilizers spread and the amount recovered in soil and infiltrated water is in progress and will be presented at the conference.

Table 1). Only two pharmaceuticals were quantified in the samples from Jun. to Oct. 2021: thiabendazole (14 – 33 ng/L) in three samples from lysimeters with manure application and trimethoprim (120 ng/L) in the last sample of SA.

The number of compounds detected in soil is higher 210 days after the first spreading (05 Nov. 2020 – 03 Jun. 2021) than 147 days after the second one (03 Jun. – 28 Oct. 2021). Anhydro-erythromycin and trimethoprim are found in all layers of all lysimeters including the

reference, which suggests their persistent presence in soil prior to the experiments. An unexpected concentration profile is found for ketoprofen at the end of the first year of experiment in both lysimeters MA and SA. This compound is detected at all depths in a range of concentration between 0.36 and 2.43 ng/g DW with the liquid manure application, and between 0.35 and 0.53 ng/g DW after the application of biosolids. The predominant mechanism for this compound is assumed to be biodegradation, with low lixiviation (Wassenaar *et al.* 2015).

A first assessment of the mass balance for pharmaceutical residues and biocides between organic fertilizers spread and the amount recovered in soil and infiltrated water is in progress and will be presented at the conference.

Table 1. Detection frequency of pharmaceuticals and biocides in infiltrated water (n = 16)

Compounds	Liquid manure	Biosolids
Albendazole-2-aminosulfone	6.3%	-
Anhydroerythromycin	6.3%	-
Desmethyl-ofloxacin	-	12.5%
Flubendazole	-	12.5%
Ketoprofen	-	31.3%
Levamisole	6.3%	18.8%
Thiabendazole	50.0%	12.5%
Trimethoprim	-	6.3%

4. CONCLUSIONS

Diversity and loads of pharmaceuticals and biocides are higher in solar dried biosolids than in the liquid manure. Concentrations in soil and infiltrated water are very low and close to the LoD. Some transformation products (anhydroerythromycin, albendazole-2-aminosulfone and desmethyl-ofloxacin) were found in leachate and/or soil samples, emphasizing the importance of tracking both parent compounds and transformation products. No quantifiable accumulation is observed between the first land-spreading and the second one. Further exploration of processes under controlled conditions is needed to fully understand the processes related to and transfers of pharmaceuticals residues and biocides from urban sludge and manure used as fertilizers. The *in-situ* experiments will continue for two years, along with additional tests in lab scale columns under controlled conditions.

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