

Fate of pharmaceuticals after applications of human urine-based fertilisers in long-term field experiments

M. Bourdat-Deschamps^{1*}, F. Esculier², A. Goulas¹, G. Delarue¹, D. Müller-Stöver³, J. Magid³, S. Houot¹

(1) Université Paris-Saclay, INRAE, AgroParisTech, UMR EcoSys, 91120 Palaiseau, France

(2) Ecole des Ponts ParisTech, Université Paris-Est Créteil, UMR LEESU 77420 Champs-sur-Marne, France

(3) University of Copenhagen, Department of Plant and Environmental Science, Plant and Soil Science, 1872, Frederiksberg, Denmark

*e-mail: marjolaine.deschamps@inrae.fr

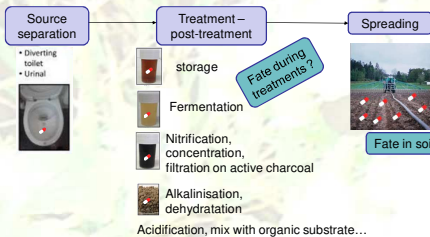
INTRODUCTION

- Current agriculture is heavily dependent on the use of **fertilisers derived from fossil resources**
- Most of the nutrients in food are excreted in urine, mostly collected and mixed with wastewaters → little recycling of the nutrients + environmental impacts
- Use of **urine-based fertilisers in agriculture would enhance the recycling of these nutrients** and develop **more circular management of crop fertilization** (cheaper and more sustainable source of nutrients than fossil based fertilisers)
- Most of pharmaceuticals or metabolites are excreted in urine → using human urine in agriculture **could contribute to disseminate pharmaceuticals** in the environment (soil, soil water...)
- Urines are at least stored to be sanitised, but they can undergo different processes: primarily to stabilise nitrogen, concentrate the nutrients and also to lower concentrations of organic pollutants

OBJECTIVES : To quantify pharmaceuticals contained in urine-based fertilisers and in the receiving soils after one or several applications

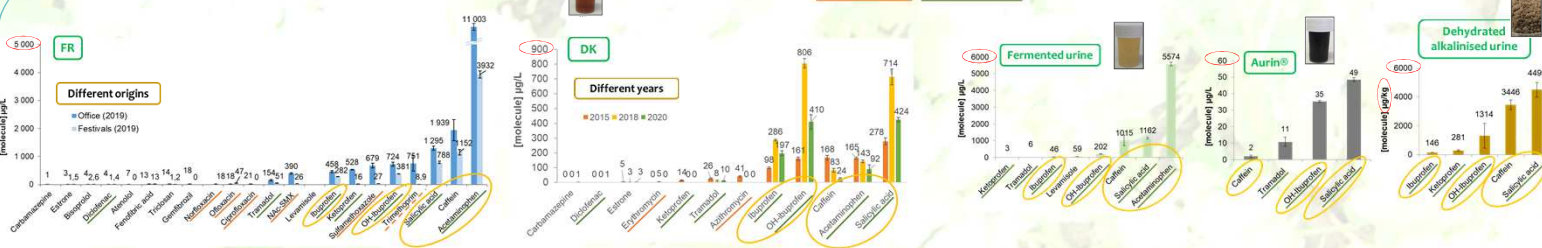
EXPERIMENTAL

- **Pharmaceuticals and other molecules:**
 - 52 pharmaceuticals or metabolites: 28 antibiotics from 5 families (fluoroquinolones, tetracyclines, sulphonamides, macrolides –lincosamides and β-lactamines), 9 anti-inflammatories, 5 neuroleptics, 3 antiparasitics, 2 β-blockers, 2 lipid regulators, 1 diuretic, 1 corticoid, 1 antidiabetic)
 - 2 bactericides
 - 2 hormones
 - Caffein
- **Urine-based fertilisers:** stored urines (from France and Denmark), fermented urine (from FR), Aurin® (nitrified, concentrated and filtered on active charcoal) and dehydrated alkalinised urine (Granurin® from Sweden)
- **Soil fertilised with urine based fertilisers:**
 - FR: 1 application in 2019; sampling before and one month after fertilisation
 - DK: "CRUCIAL" long-term field experiment [1]; repeated spreading of alternative fertilisers including human urine since 2003; sampling after the 16th fertilisation (in 2018) and before and after the 18th fertilisation (in 2020).
- **Analytical method:**
 - Urine-based fertilisers: dilution in water after pH adjustment (pH 3 or 7 or 9) / dilution in water for solid product - online SPE UHPLC-MS-MS analysis
 - Soil: ultrasound assisted extraction – QuEChERS purification – online SPE UHPLC-MS-MS analysis [2]
 - Quantification by isotope dilution for most of the compounds



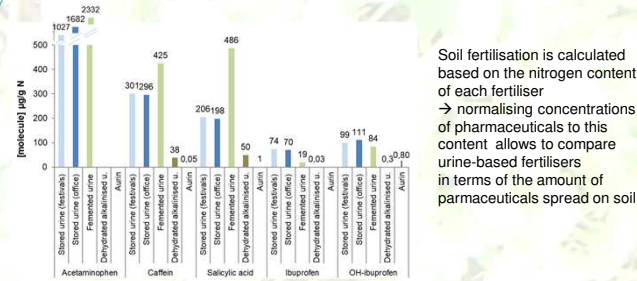
RESULTS

Concentrations in urine-based fertilisers



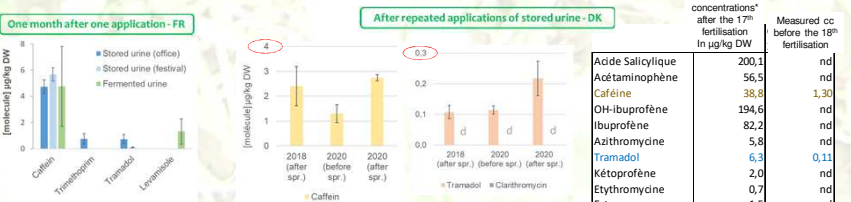
- 5 molecules (circled in orange) quantified in almost all the urine-based fertilisers: acetaminophen, salicylic acid, caffeine, ibuprofen and its metabolite
- 8 to 20 molecules quantified in stored urines between <1 µg/L and 11 mg/L
- Mainly anti-inflammatories, antibiotics and caffeine
- Less molecules and generally lower concentrations in Danish than in French urines
Possible reason: in DK, urines were collected in an eco-village
- Variation of concentrations depends on the origin of the urine and the year
- Concentration levels are similar to published studies (e.g. Winker et al. 2008, Schümann et al. 2012, Mullen et al. 2017)
- 4 to 20 molecules quantified in treated liquid urines between 2 and 5500 µg/L
→ decrease in pharmaceutical concentrations in urine-based fertiliser depends on the treatment
- Mainly anti-inflammatories and caffeine
- The lowest concentrations are observed where specific micropollutant treatment was applied (Aurin®)

Comparison of concentrations normalised to the nitrogen content



- Fermented urine seems to be equivalent to stored urines
- Aurin® seems to be the most efficient treatment to decrease concentrations due to filtration on active charcoal (Etter et al. 2015)

Concentrations in fertilised soil



- A few molecules at very low concentrations in fertilised soil (< 8µg/kg DW)
- None of the compounds are detected in control soils
- Predicted concentrations are highly above measured ones
→ Importance of long-term field experiments to evaluate dissipation of molecules that implies formation of non-extractable residues, leaching or degradation

CONCLUSIONS

- There is a wide range of number and concentration levels of pharmaceuticals and caffeine in urine-based fertilisers
- Some treatments seem to be efficient to decrease concentrations of pharmaceuticals while maintaining nitrogen contents
- Only a few molecules are found at low concentrations in fertilised soil even after decades of urine fertilisation, indicating degradation, leaching or conversion into non-extractable residues

REFERENCES
[1] Peitre et al. AGEES 2015
[2] Ferhi et al. Anal. Bioanal. Chem. 2016

Acknowledgments
This work was supported by

