Repeated applications of organic waste products in field conditions hardly impact pharmaceutical concentrations in soil and soil leachates

S. Houot[1], M. Bourdat-Deschamps[1*], S. Ferhi[1], N. Bernet[1], V. Mercier[1], D. Montenach[2], F. Feder[3], G.D. Moussard[3], D. Patureau[4]*

(1) UMR ECOSYS, INRA, AgroParisTech, Université Paris-Saclay, 78850, Thiverval-Grignon, France
(2) UE SEAV, INRA, 68021, Colmar, France
(3) UPR Recyclage et risques, CIRAD, 97408, Saint Denis, Réunion, France
(4) LBE, INRA, 11100, Narbonne, France

**e-mail: sabine.houot@grignon.inra.fr, marjolaine.deschamps@grignon.inra.fr*

INTRODUCTION

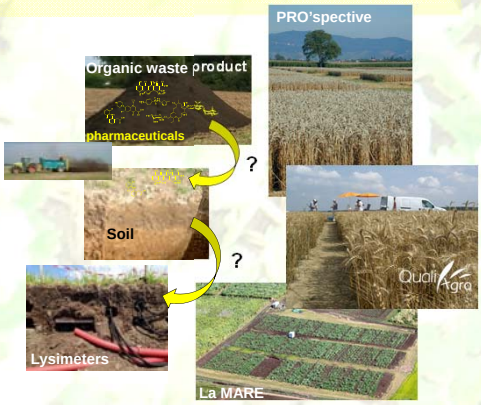
- Pharmaceuticals excreted by animal husbandries or humans are transferred to manure or wastewater.
- In wastewater treatment plants, they can be degraded and/or removed from water through adsorption to sludge.
- Organic waste products (OWP), such as manure, sludge, compost, are recycled in agriculture for their fertilizing properties.
- OWP spreading may contribute to the dissemination of pharmaceuticals in the environment (soils, surface- and groundwater) which may impact non–target organisms.

OBJECTIVE

Determination of concentration levels of pharmaceuticals in environmental matrices:
- OWP (sludge, compost, slurry, manure)
- Soils that have received the OWP for a decade
- Soil leachates

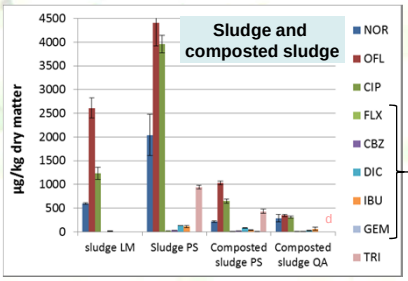
EXPERIMENTAL

- **14 pharmaceuticals:**
  - **Antibiotics** - **fluoroquinolones**: norfloxacin (NOR), ofloxacin (OFL), ciprofloxacin (CIP); **tetracyclines**: chlortetracycline (CTC), doxycycline (DOX); **sulfonamides**: sulfamethazine (SMZ), sulfamethoxazole (SMX); **macrolide**: tylosin (TYL)
  - **Other pharmaceuticals**: antidepressant (fluoxetine, FLX), anti-inflammatory (diclofenac, DIC; ibuprofen, IBU), anti-epileptic (carbamazepine, CBZ), lipid regulator (gemfibrozil, GEM), bactericide (triclosan, TRI).
- **Field-Experiment:**
  - 3 sites from the french long-term field experiment network, SOERE PRO–: **QualiAgro** (QA) – Ile-de-France, **Pro'spective** (PS) – Alsace, **La Mare** (LM) – La Réunion.
- **Matrices (sites)**:
  - **OWP**: digested and limed sewage sludge (LM); activated sewage sludge (PS), composted sludge with green wastes (PS and QA), liquid pig slurry (LM), poultry manure (LM), farmyard manure (PS and QA), composted farmyard manure (PS), composted municipal solid waste (QA), composted biowaste (PS and QA).
  - **Soils**: sampled before the application of OWP, corresponding to 2 years after the last application (QA and PS) + 1 month and 1 year after application of OWP (QA).
  - **Soil leachates**: leachates were sampled every two weeks during winter and spring from lysimeters at 45 and 100 cm depth. 276 samples were analysed over 3 years for QA and 36 samples during one year for PS.
- **Analytical method**: ultrasound assisted extraction (20 min) – QuEChERS purification – online SPE UHPLC-MS-MS analysis. Quantification by isotope dilution except CTC, DOX and TYL ([1], [2] and poster P028 [3])



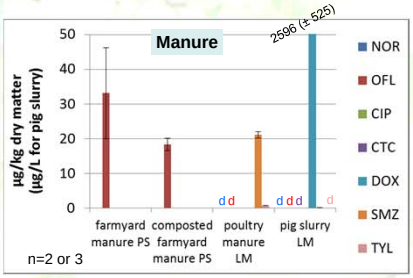
RESULTS

Organic Waste Products

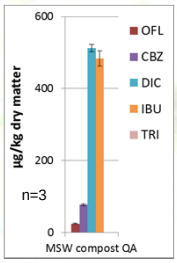


n= 2 or 3 replicates

- Contents in fluoroquinolones and triclosan were **higher in sludge and composted sludge**.
- The content in sludge was **similar to literature results**.
- The various origins of raw and treated sludge may explain the differences in pharmaceutical contents.
- The **content decrease** between sludge PS and composted sludge PS may be attributed to the dilution through addition of green wastes and/or the dissipation of pharmaceuticals during composting.



- **Doxycycline was highly concentrated in pig slurry**. It was mainly sorbed to particulate phase.
- **Composting seems to have a positive impact** on ofloxacin content in farmyard manure.



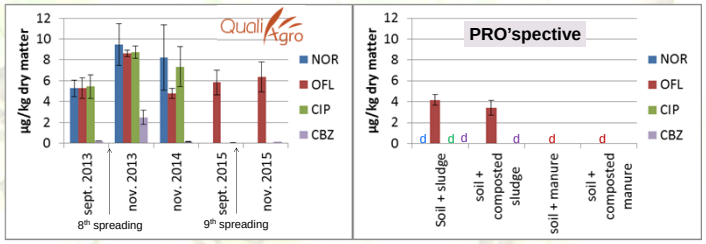
Urban composts

- **Pharmaceuticals were not detected in composted biowaste** from QA, except ibuprofen once.
- The **presence of pharmaceuticals in composted municipal solid waste** may be due to a lack of source sorting.

Summary:

- The **highest occurrences and contents in pharmaceuticals were found in sludge and composted sludge**, compared to the other OWP.
- The contents in pharmaceuticals in OWP from the same treatment plant were **similar over the years**, except for sludge and pig slurry (seasonal variation).

Amended soils



QA: Soil amended with **composted sludge** (n=4)

OFL, CBZ and IBU were also detected in soils amended with composted municipal solid waste, not with composted biowaste. Non-treated soils did not contain pharmaceuticals.
limits of quantification (µg/kg DM): NOR, 6; OFL, 4; CIP, 6; CBZ 0.1

PS: Soil sampled before the 7th spreading (n=4) of the different amendments

limits of quantification (µg/kg DM): OFL, 4; CBZ 0.1

- Soil contents were **below 10 µg/kg dry soil**.
- **Fluoroquinolones and carbamazepine** were quantified or detected in soils amended with sludge and composted sludge. Ofloxacin was detected in soils amended with manure. Carbamazepine in soil from QA in november 2013 seems to be abnormaly high.
- The **increase in soil contents of fluoroquinolone** (2013), **ofloxacin** (2015) and **carbamazepine** (2015) in QA one month after composted sludge spreading was **coherent with the flux of these compounds coming from the compost**.

Soil leachates

- Pharmaceuticals were **detected in less than 7%** of the leachate samples in (QA) and **4%** in (PS) and **quantified in less than 0.5%** (QA) and **0.2%** (PS) of the samples
- **Carbamazepine** was the most frequently detected compound in both sites followed by **ibuprofen** (QA) and **ofloxacin** (PS). Antibiotics were also detected in QA.
- Concentrations were **below 0.1 µg/L** (except ibuprofen : 0.27 µg/L). LOD and LOQ were globally in the 0.002-0.03 µg/L and 0.005-0.09 µg/L ranges, respectively.
- There were **no differences between treatments**.

CONCLUSIONS

- Pharmaceuticals are present at very different concentration levels in OWP, from few µg/kg up to mg/kg dry matter or mg/L for slurry.
  OWP containing sludge or animal effluents mainly contain antibiotics, while composted municipal solid waste contains anti-inflammatory compounds.
- The contents of pharmaceuticals in soils amended with OWP are below few µg/kg. Only the most persistent compounds are detected or quantified (fluoroquinolones and carbamazepine).
- The occurrence of pharmaceuticals in leachates is very low, with detection frequencies below 7% and concentrations rarely above 0.02 µg/L.

REFERENCES
[1] S. Ferhi, M. Bourdat-Deschamps, J.J. Daudin, S. Houot, S. Nélieu. Anal. Bioanal. Chem. 2016
[2] M. Bourdat-Deschamps, S. Leang, N. Bernet, J.J. Daudin, S. Nélieu. J. Chromatogr. A. 2014
[3] M. Bourdat-Deschams et al. Poster ICRAPHE P028.

Acknowledgments
This work was supported by ONEMA and Region Ile-de-France.
Both QA and LM sites are financed by Veolia.
The PS site is mainly supported by ADEME and AERM.

Paris
September 8-9, 2016