Searching for pedotransfer functions to predict sorption ofpharmaceuticals from soil properties

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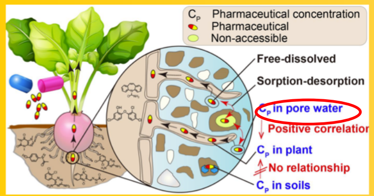
1) Introduction

Recycling of organic waste products and irrigation with treated waste waters are increasingly used by farmers (Bünneman et al., 2024) ➔ Need to better assess the risks of transfer of pharmaceutical (PPCPs) residues from soils to groundwater and plants (Verlicchi & Zaambello, 2015 ; Mejías et al., 2021)

Plant root uptake of pharmaceutical residues from soil pore



Li et al., 2022

Soil pore water concentration is controlled by coupled processes:

- **Sorption – desorption**
- Diffusion
- Biodegradation
- Uptake by organisms and plants

Sorption coefficients are among the most sensitive parameters in models used for risk assessment

For different classes of pharmaceuticals, the variations in sorption among different soil types are poorly described and understood (Kodesova et al., 2015)

Hypotheses :
Soil properties controlling sorption can implement pedotransfer functions that allow predicting sorption parameters for a wide range of soils

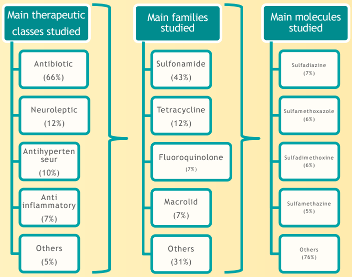
Objectives :

- To review sorption parameters for different classes of pharmaceuticals and their variation with selected soil properties
- To investigate the sorption properties of three pharmaceuticals, ofloxacin, tetracycline, diclofenac on ten soils having contrasting properties

2) Materials and Methods

Litterature Review : pedotransfer functions for PPCPs sorption by soils

Corpus n = 136 articles on PCPPs sorption in soil



Only 7 articles with pedotransfer functions

List of studied molecules :

→ Sulfachlorpyridazine, sulfamethazine, sulfadiazine, sulfamethoxazol

→ Oxytetracycline, tetracycline, chlortetracycline, trimethoprim, clarithromycin, clindamycin

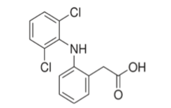
→ Atenolol, metaprolol, carbamazepine, triclosan, sertraline, venlafaxine telmisartan, atorvastatin, bisphenol S, lamotrigine, 2-phenylbenzimidazole-5-sulfonic acid, memantine, 1-methyl-1H-benzotriazole, valsartan, irbesartan, citalopram, fexofenadine

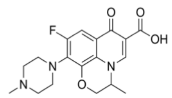
Sorption experiments : 10 different soils with contrasted properties

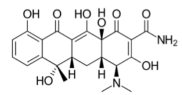
	Experimental site	Soil type	pHw	SOC	CEC	BCS*	SCS**	Clay	Silt	Sand
				g/kg	cmol⁺/kg	cmol⁺/kg	%		g/kg	
Temperate	PROSpective	Calcosol	8.4	13.9	17.2	18.3	106.0	182.0	625.0	73.0
Temperate	La Bouzule	Calcisol redoxic	7.1	17.6	15.5	16.6	107.2	349.3	533.8	326.8
Temperate	QualiAgro	Luvisol	6.4	9.7	9.1	8.3	91.3	156.3	778.3	65.5
Temperate	EFELE	Luvisol-Redoxisol	6.2	9.6	5.7	5.7	101.3	145.5	700.8	153.8
Temperate	Couhins	Luvisol dystric	6.6	13.5	4.8	3.8	80.4	43.0	67.0	890.0
Temperate	Theix	Brunisol	5.8	43.9	9.1	8.7	95.7	185.0	262.0	553.0
Temperate	Lusignan	Brunisol	6.3	18.0	6.7	6.5	97.8	140.0	630.0	230.0
Temperate	Laqueuille	Andosol	5.6	90.0	8.3	5.9	71.4	231.3	547.1	226.4
Tropical	Dakar	Arenosol	6.5	6.8	9.7	8.1	83.6	99.9	112.2	765.2
Tropical	La Réunion	Nitisol	6.4	19.1	10.7	11.1	104.0	460.1	435.0	105.0

*SEB: sum of exchangeable basic cations (Ca^{2+} / Mg^{2+}/ K^+ /Na^+) ; ** SCS : sorption complex saturation (percentage of BCS in CEC)

PPCPs ionizable with contrasted physico-chemical properties


Diclofenac *pKa 4.2; Log Kow 4.5*


Ofloxacin *pKa 6.5 ; 8.3; Log Kow -0.4*

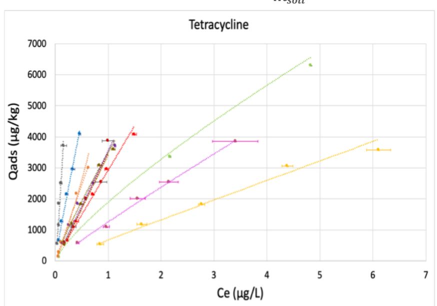

Tetracycline *pKa 3.2, 7.8, 9.6; Log Kow -1.2*

- Initial concentration ranges in aqueous solution 10^{-2} M $CaCl_2$
  - Diclofenac [5, 10, 20, 40, 80 µg/L]
  - Ofloxacine & Tetracycline [160, 300, 500, 700, and 1000 µg/L]
- LC-MS-MS analytical quantification (Bourdat-Deschamps et al., 2014)
- For strongly sorbed compounds, limitations for equilibrium concentration quantification

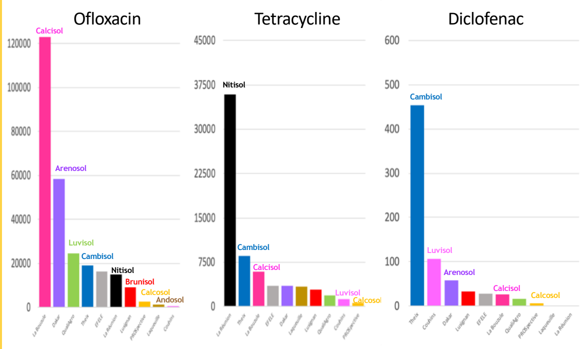
3) Results

Sorption isotherms

$$Qads = (C_i - C_e) \cdot \frac{V_0}{m_{soil}}$$



Freundlich sorption coefficients K_F



Multiple linear regression analyses

	K_F	pH	SOC	CEC	SEB	SCS	Clay	Silt	Sand
K_F	1.00	-0.49	0.92	-0.18	-0.19	-0.15	-0.03	-0.46	0.40
pH		1.00	-0.31	0.80	0.80	0.44	0.28	0.22	-0.33
SOC			1.00	0.05	0.07	0.17	0.26	-0.22	0.15
CEC				1.00	0.99	0.63	0.70	0.24	-0.37
SEB					1.00	0.72	0.75	0.31	-0.43
SCS						1.00	0.79	0.69	-0.75
Clay							1.00	0.42	-0.45
Silt								1.00	
Sand									1.00

Pearson correlations of sorption parameters with soil properties

Example of Diclofenac

Statistical significance p-value < 0.05

- **Very contrasted sorption behaviors**
- **Soil type effects specific to each compound**
- **Experimental pedotransfer functions**
  - **Diclofenac**

    K_F = 210.5 – 34.3 x pH + 10.3 x SOC – 1.3 x Silt
    R^2 = 0.94 / p value = 0.006
  - **Tetracycline**

    K_F = - 4 10^3 + 669 x Clay – 20.8 x SCS
    R^2 = 0.60 / p value = 0.040
  - **Ofloxacin**

    Weak correlation with CEC, clay (+) and SOC (-)

4) Conclusions

Pedotransfer functions based on soil organic carbon content, soil pH, exchangeable cations, clay and metal oxides are the historical approach for predicting and specifying sorption of ionizable PPCPs (Kodesova et al., 2015, Klement et al., 2018). The limited number and covariation of the soil properties considered can hinder their ability to predict and specify sorption mechanisms.

Our experimental results confirmed these findings showing that the strong variation of sorption behaviours among soil types were very specific of each compound. For ofloxacin no satisfying pedotransfer function could be identified. For tetracycline, clay content and the cationic complex saturation index were significantly correlated to sorption where as for diclofenac pH, SOC and silt fractions were the most important factors.

References

Bünnemann, E.K. (2024) Science of the Total Environment 912, 168901
Bourdat-Deschamps, M. et al. (2014) Journal of Chromatography A 1349, 11-23
Klement, A. et al. (2018) Chemosphere 195,615-623
Kodesova, R., et al. (2015) Science of the Total Environment 511, 435–443
Li et al. (2022) Environmental Science & Technology 56, 9346–9355
Mejías, C. et al. (2021) Trends in Environmental Analytical Chemistry 30, e00125.
Verlicchi, P. & Zambello, E. (2015) Science of The Total Environment 538, 750–767

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