UNESCO-IWRA ONLINE CONFERENCE

17-19 JANUARY 2023

3RD IN THE IWRA ONLINE CONFERENCE SERIES

Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Investigating the infiltration of Pharmaceuticals and Transformation products through agricultural soils

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Thursday, January 19th, 2023, 13:00

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IWRA International Water Resources Association

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1. Introduction

What are the emerging pollutants?

- Newly detected compounds, development of analytical techniques, not regulated.
- Microplastics, nanomaterial, PFAs and ***PPCPs***.

Why are pharmaceuticals an issue?

- Biologically active.
- High consumption -> Continuous introduction into the environment.

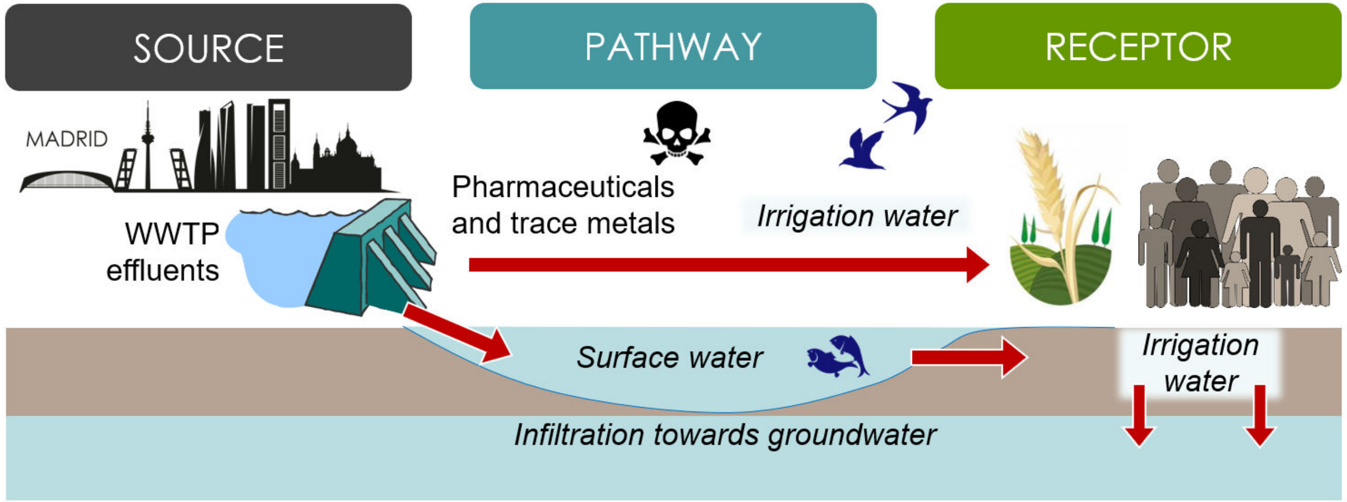
How do they reach agricultural soils?

- WWTP effluent -> Indirect reuse

Objective

To investigate the natural attenuation processes of four pharmaceuticals and two Transformation products (TPs) during their infiltration through an agricultural from data obtained in a column test.

Figure 1. "Source-pathway-receptor" system conceptualization.
Source: Project FATEPHARM (CTM2017-89995-R)



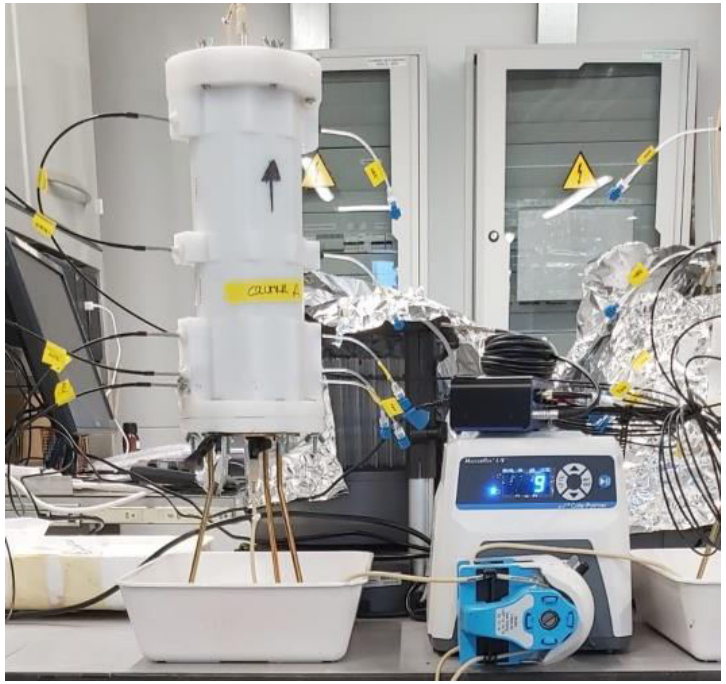
2. Materials and methods: Compounds and experimental set-up

Physicochemical properties. *Adapted from Meffe et al. (2021)*

Compound	4FAA	ATE AC	FLE	METFOR	SUL	VAL
CAS Number	1672-58-8	56392-14-4	54143-55-4	657-24-9	723-46-6	137862-53-4
Class	PTs	PTs	PHARM	PHARM	PHARM	PHARM
Molecular mass (Da)	231,10	267,15	414,14	129,10	253,05	435,23
Charge state at pH 7,7	Neutral	Anionic/ Cationic	Cationic	Cationic	Anionic	Anionic
Log K_{OW}	0,11	-1,24	3,19	-0,92	0,79	5,27
Log D_{OW}: pH=7,4/pH=8	0,11	-1,24/-1,25	1,01/1,57	-5,62/-5,37	$9x10^{-4}$/-0,11	1,08/0,5

- Agricultural soil of medium texture (silty loam), moderately alkaline (pH 8.1 ± 0.1) and not saline (0.14 ± 0.02 dS/cm).
- Organic matter content is not very high (1.2 ± 0.3%) and TOC (1.2 g/kg).

Figure 2. Soil-column experiment set-up.



- Inflow concentration 100 µg/L
- Outflow measurements, depth profiles, soil-retained content.

2. Materials and methods: Infiltration modelling

Figure 3. Physical and chemical non-equilibrium models. *Source: Šimůnek et al. (2013).*

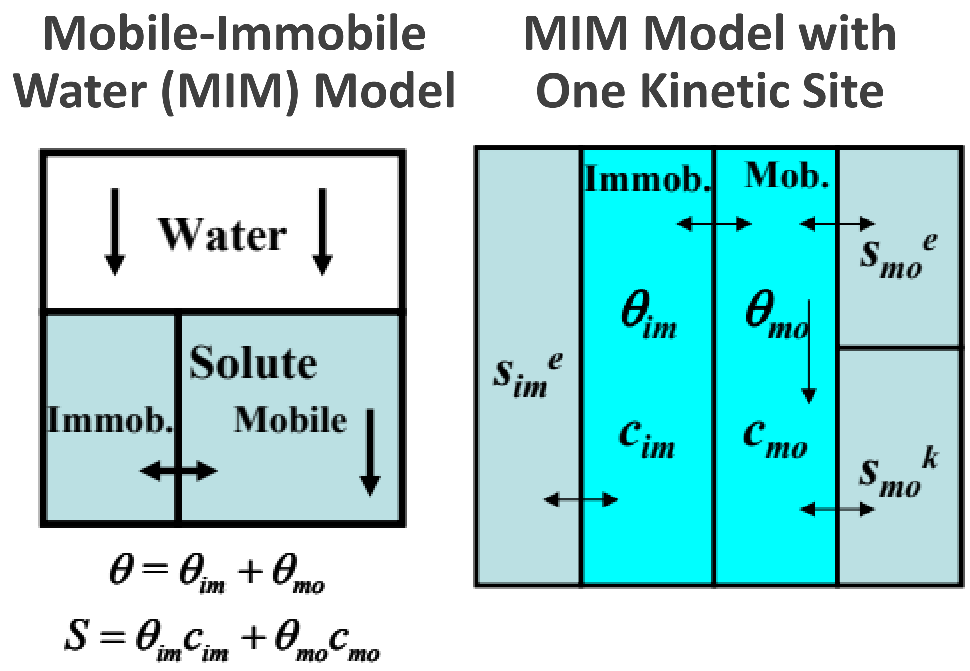
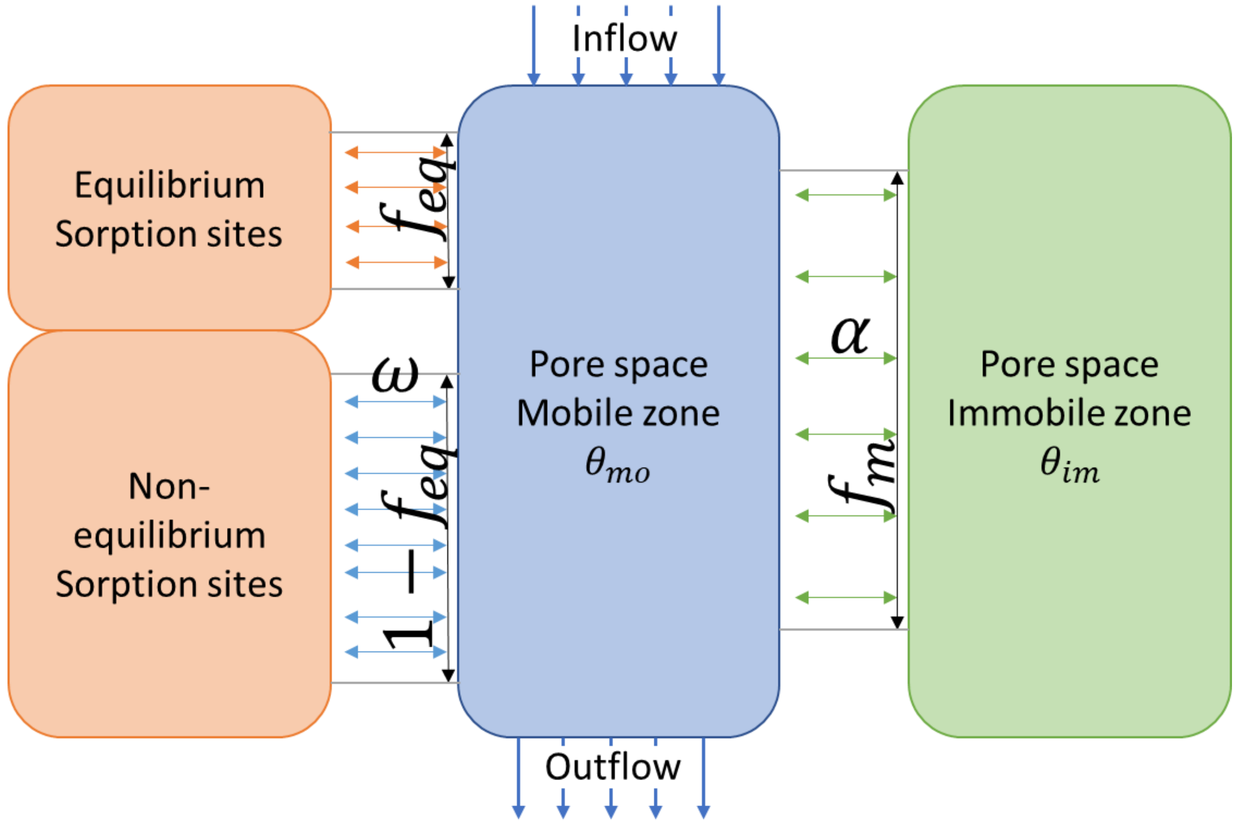


Figure 4. Conceptualization of the MIM model with two-site sorption in the mobile zone. *Source:de Rassam et al. (2018).*



2. Materials and methods: Infiltration modelling

STAGE 1: CONSERVATIVE TRANSPORT (TRACER)

Physical equilibrium
Dispersion
D_L

Mobile-immobile water
Mass transfer (physical)
α , θ_{im}

STAGE 2: REACTIVE TRANSPORT (PHARMACEUTICALS & TPs)

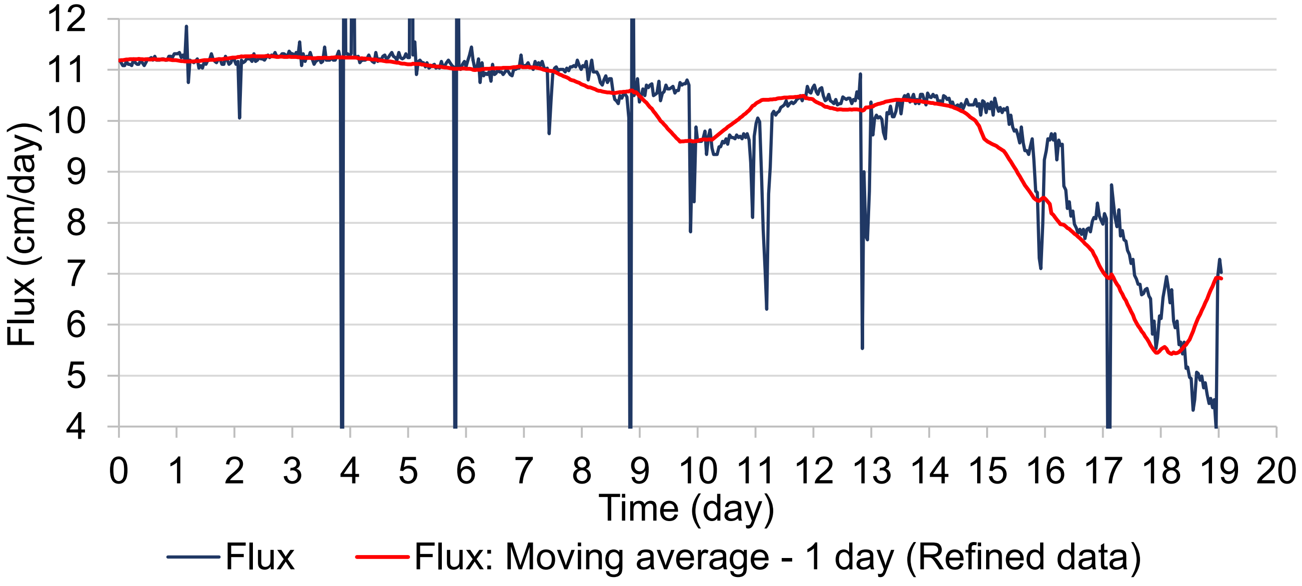
Non-kinetic sorption
Degradation
μ_w
Sorption (reversible)
K_d , β

kinetic sorption
Mass transfer(chemical)
f_{eq} , ω

Model parameters

	Parameter	Valor	Unidad
Column	Length (L)	26,3	cm
	Diameter	9,0	cm
Soil	Silt	61,9	%
	Sand	27,8	%
	Clay	10,3	%
	Bulk density	1,457	g/cm³
	Saturated water content (θ)	0,4506	cm³/cm³
Flux	Flow rate (Q)	712,9	cm³/day
	Saturated hydraulic conductivity (Ks)	11,19	cm/day
	Flux (J_w)	11,19	cm/day
	Flow velocity	24,86	cm/day
	Residence time	1,06	days

Figure 5. Flux through the Soil-column experiment.



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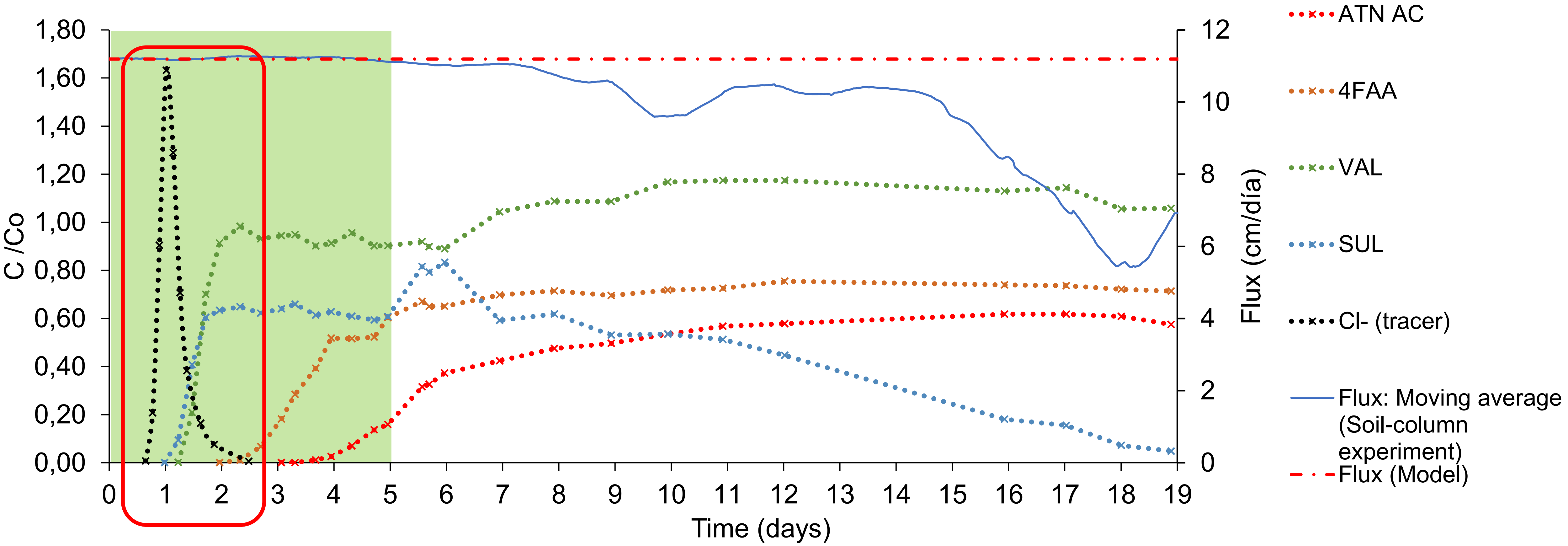
3. Results and discussion: Water flux and tracer transport

Figure 5. Outflow normalized concentration of the tracer and selected pharmaceuticals and TPs through the soil-column experiment.

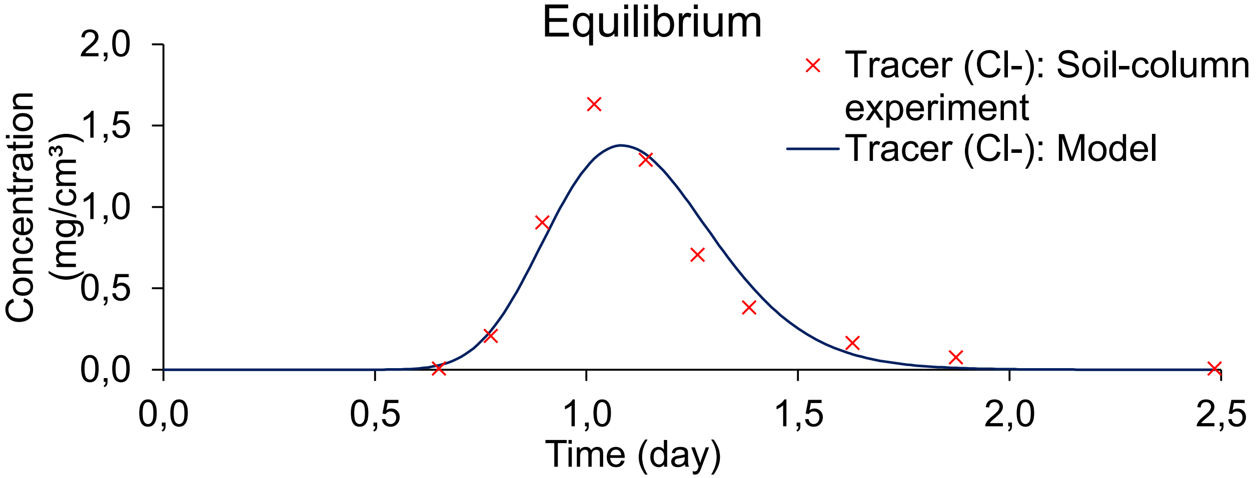


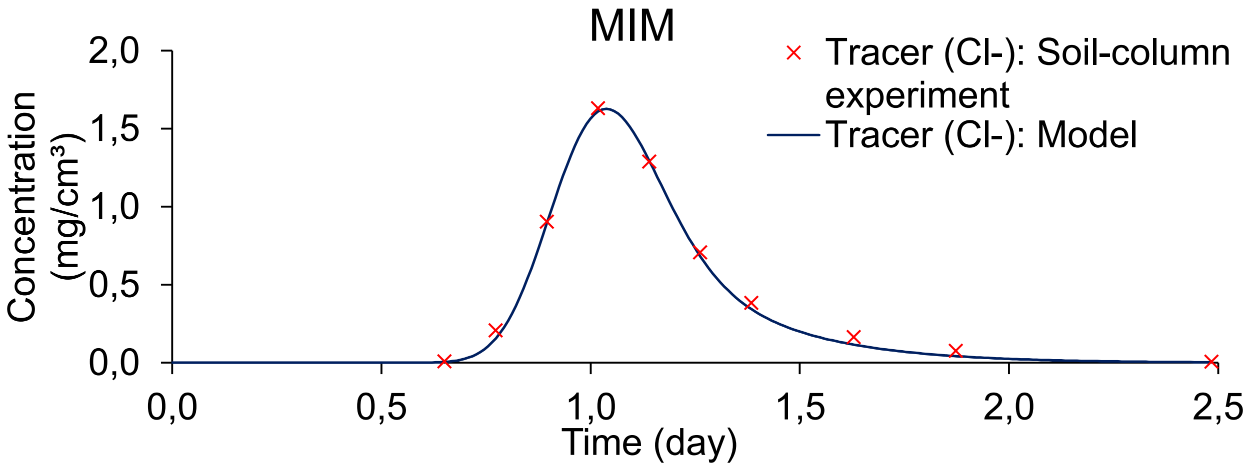
3. Results and discussion: Water flux and tracer transport

Figure 6. Results of the tracer modelling for each model.

Parameter	Equilibrium	MIM
Longitudinal dispersivity [cm]	0,47	0,21
Water content in the mobile region [cm^3/cm^3]	0,4506	0,4106
Water content in the immobile region [cm^3/cm^3]	0,0000	0,0400
First-order coefficient (α) for mass transfer between the mobile and immobile zones [day^{-1}]	*n.a.	0,21
Coefficient of determination (R^2) [-]	0,93	1,00
Root-mean-square deviation (RMSD) [-]	0,090	0,018

*Not applicable.





3. Results and discussion: Reactive transport

Parameters for each pharmaceutical and TP assuming linear (L), Freundlich (F) and kinetic sorption.

Compound	Model	K_d ($cm^{3\beta}\ \mu g^{1-\beta}\ g^{-1}$)	β	μ_w ($día^{-1}$)	f_m	f_{eq}	ω ($día^{-1}$)	R_m	R^2	RMSD
VAL	L	0,169	1,000	0,0356	1,0	1,00	n.a.	1,6	0,98	0,0040
	F	0,113	0,825	0,0395	1,0	1,00	n.a.	1,5	0,99	0,0029
	K+L	0,179	1,000	0,0364	1,0	0,95	0,0001	1,6	0,98	0,0040
	K+F	0,106	0,791	0,0402	1,0	0,96	0,0001	1,5	0,99	0,0027
SUL	L	0,119	1,000	0,4723	1,0	1,00	n.a.	1,4	0,99	0,0026
	F	0,093	0,895	0,4749	1,0	1,00	n.a.	1,4	0,99	0,0023
	K+L	0,123	1,000	0,4714	1,0	0,96	0,0110	1,4	0,99	0,0026
	K+F	0,094	0,884	0,4742	1,0	0,96	0,0001	1,4	0,99	0,0023
ATN AC	L	1,256	1,000	0,7874	1,0	1,00	n.a.	5,5	0,94	0,0026
	F	1,506	1,071	0,7497	1,0	1,00	n.a.	5,9	0,99	0,0009
	K+L	1,320	1,000	0,6877	1,0	0,87	1,341	5,7	0,98	0,0014
	K+F	1,572	1,048	0,6406	1,0	0,87	0,5242	6,3	0,99	0,0012
4FAA	L	0,727	1,000	0,4166	1,0	1,00	n.a.	3,6	0,98	0,0063
	F	1,202	1,202	0,3774	1,0	1,00	n.a.	4,3	0,97	0,0050
	K+L	0,902	1,000	0,2543	1,0	0,70	0,7970	4,2	0,99	0,0028
	K+F	0,954	1,022	0,2498	1,0	0,71	0,7524	4,3	0,99	0,0027

Figure 7. Relative concentration vs Time for valsartan (VAL) and sulfamethoxazole (SUL) assuming non-kinetic and kinetic sorption.

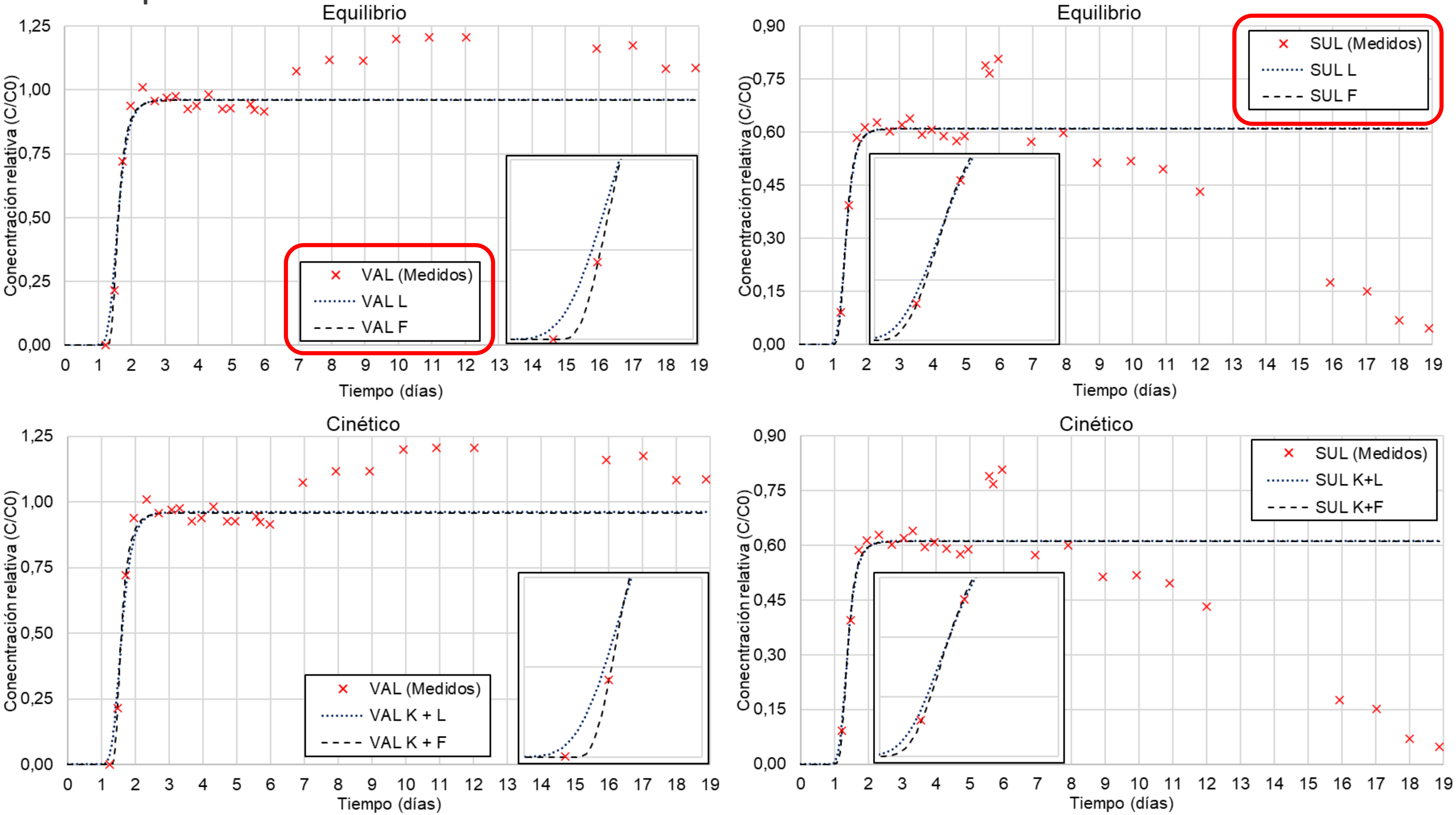
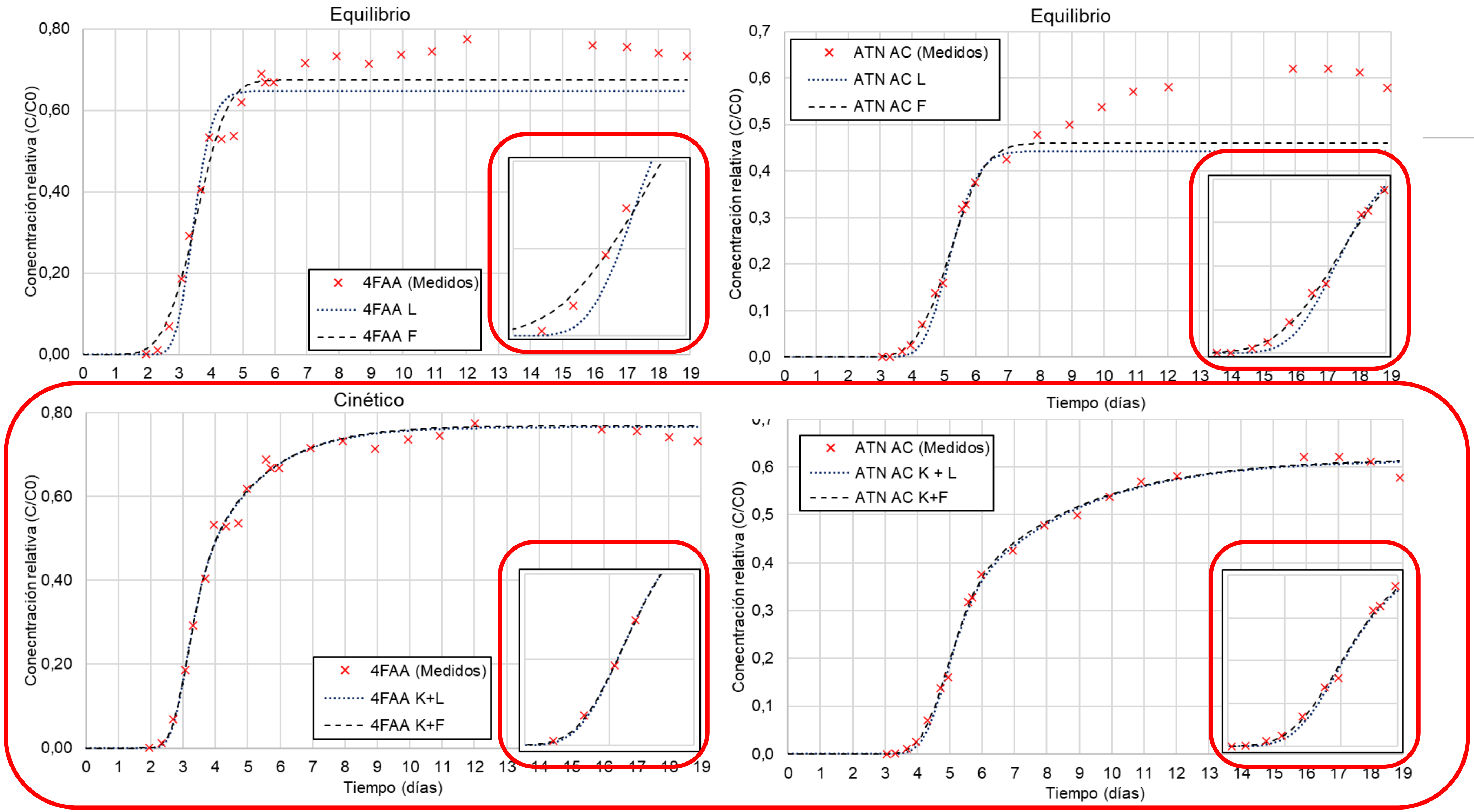
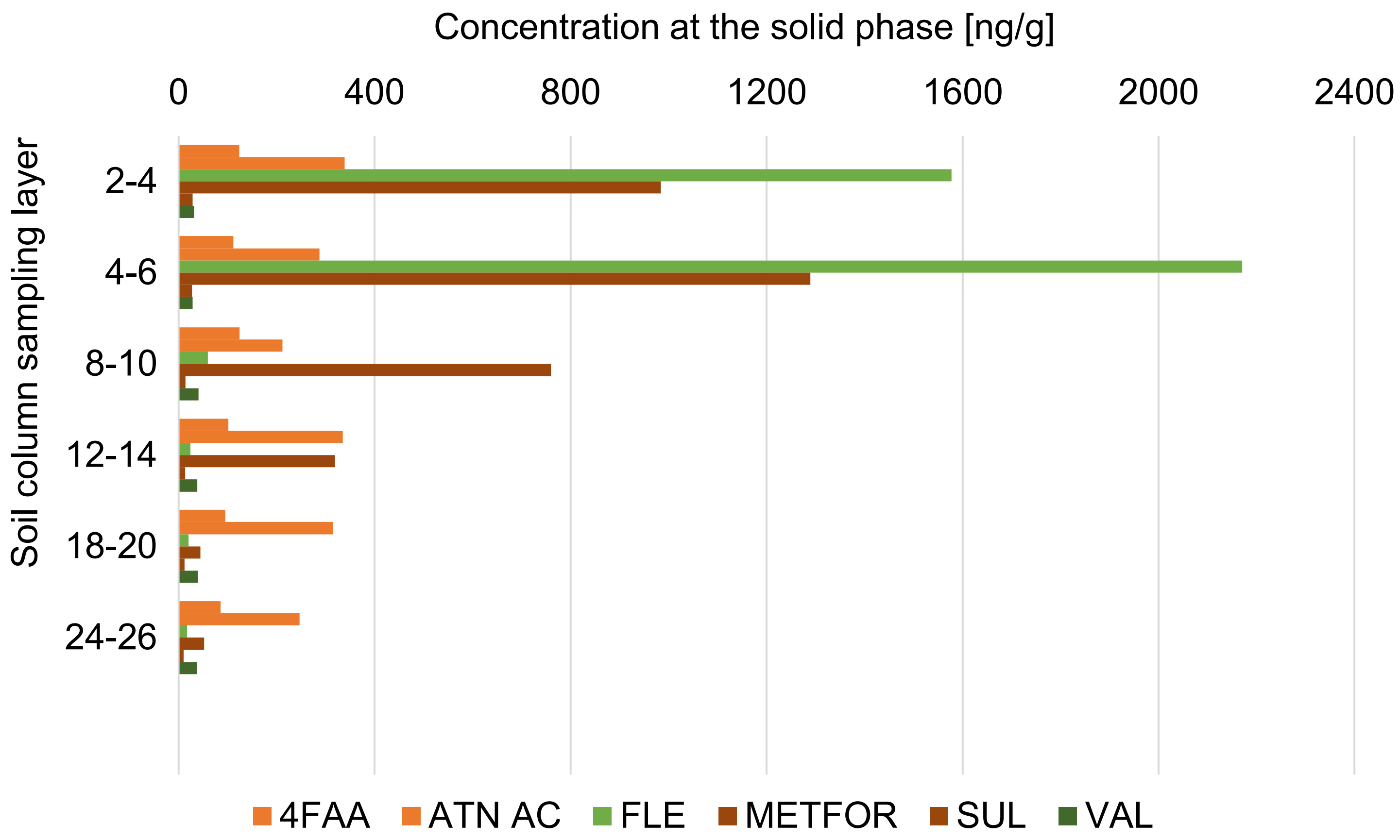


Figure 8. Relative concentration vs Time for 4-formylaminoantipyrine (4FAA) and atenoloico acid (ATN AC) assuming non-kinetic and kinetic sorption.



3. Results and discussion: Soil-retained content

Figure 9. Soil-retained content.



Accumulated soil-retained content in relation to that injected for each compound

Compound	% Soil-retained content
4FAA	10 - 20
ATN AC	50 - 60
FLE	70 - 80
METFOR	100
SUL	0 - 5
VAL	0 - 10

4. Conclusions and recommendations

- **All models** obtained fairly acceptable results R^2**> 0.90** in **all cases**.
- For the modelled **pharmaceuticals**, a better fit was obtained when considering **sorption in non-linear equilibrium**. While for the **TPs** a better fit was obtained when considering **kinetic sorption** with a **tendency towards linearity**.
- It seems that sorption processes in this type of agricultural soil are dominated by **electrostatic sorption** phenomena with the **mineral phases**, therefore, **positively ionized compounds** have a **higher affinity to sorption** in this soil.
- **Flecainide and metformin** show the **highest attenuation**; however, the **risks of their presence in the soil** must be **assessed**.
- Although **valsartan** has the highest mass (435.23 Da) and an **anionic character**, it is the **most persistent** compound, possibly due to the **absence of certain field conditions** (rhizosphere and/or organic matter).
- The modelled compounds are arranged based on their μ_w in **descending order** from the one that suffered the most **degradation** to the one that suffered the least; **Sulfamethoxazole, atenoloic acid, 4-formylaminoantipyrine and valsartan.**

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THANK YOU

Project FatePharM/ CTM2017-89995-R by MCIN/AEI/"ERDF A way of making Europe"

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Support slides: Conservative transport

Advective-dispersive transport equation:

$$\theta \frac{\partial C}{\partial t} = \theta D^w \left(\frac{\partial^2 C}{\partial z^2} \right) - J_w \frac{\partial C}{\partial z}$$

$$D^w = D_L v$$

Dual-porosity (MIM model)

$$\theta = \theta_m + \theta_{im}$$

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D^w \left(\frac{\partial^2 C_m}{\partial z^2} \right) - J_w \frac{\partial C_m}{\partial z}$$

$$\theta_{im} \frac{\partial C_m}{\partial t} = \Gamma_1$$

$$\Gamma_1 = \alpha (C_m - C_{im})$$

Support slides: Reactive transport

General system of equations for reactive transport:

$$\theta_m \frac{\partial C_m}{\partial t} + f_m \rho \frac{\partial S_m^e}{\partial t} = \theta_m D^w \left(\frac{\partial^2 C_m}{\partial z^2} \right) - J_w \frac{\partial C_m}{\partial z} - \mu_w C_m - \Gamma_1 - \Gamma_2$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1 - f_m) \rho \frac{\partial S_{im}}{\partial t} = \Gamma_1 - \mu_w C_{im}$$

$$\Gamma_2 = \rho \omega \left(S_{m,e}^k - S_m^k \right)$$

Sorption system of equations

$$S = f_m S_m + (1 - f_m) S_{im}$$

$$S_{im} = K_d C_m^\beta$$

$$S_m = S_m^e + S_{m,e}^k$$

$$S_m^e = f_{eq} K_d C_m^\beta$$

$$S_{m,e}^k = (1 - f_{eq}) K_d C_m^\beta$$