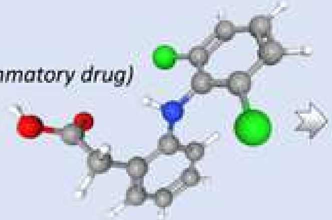
Reversible Degradation of Diclofenac in Groundwater Under Uncertainty

1. MOTIVATION

Diclofenac

- *Contaminant of Emerging Concern (Anti-Inflammatory drug)*
- suspected to promote **bioaccumulation**
- detected in groundwater worldwide
- **recalcitrant** in aqueous bodies
- difficult to foresee its fate in aquifers



Development of geochemical models and predictive tools

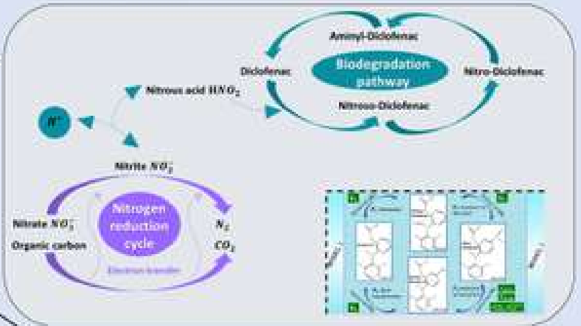
2. METHODOLOGY

- Development of a robust geochemical model M_1 considering the **molecular dynamics** of multi-stage chemical reactions → kinetic reaction rates:

$$RR_i(t) = \frac{dC_i(t)}{dt} = f_i(\underbrace{C_i, C_{i+1}, \dots, C_{N_i}}_{\text{Aqueous concentrations}}, \mathbf{p})$$

Reaction rate of species *i*-th

Vector of uncertain parameters involved in the reaction leading to species *i*-th



- Formulation of **inverse problem** $\quad C = M_1(\mathbf{p})$

Model operator

Vector of aqueous concentrations (state variables)

Objective: estimation of $\mathbf{p}$ given several measurements of $\mathbf{C}$

Given:
- 14 observations of state variables
- 7 uncertain parameters encompassed in the 4 main processes of the Diclofenac biotransformation cycle

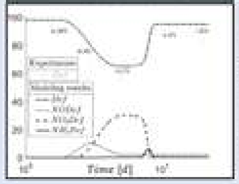
Assuming:
- independent, identically distributed prior probability distributions of the uncertain parameters

Model calibration in a ***stochastic*** context through **Bayesian inference** (Acceptance-Rejection Sampling - ARS)

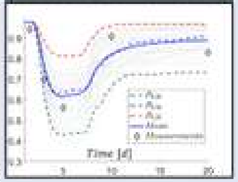
1. **Numerical implementation** of the geochemical model in the PHREEQC Software
2. Running the direct model (numerically) to sample the prior parameter space → to obtain a **Monte Carlo** collection of realizations of the phenomenon under study
3. Reject realizations which do not fulfill the ARS criterion (based on the sum of the squared residuals between measured and modeled concentrations)
4. Evaluate empirical probability distributions of the uncertain parameters included in $\mathbf{p}$ → **posterior** (i.e., **conditional on data**) multivariate **distribution** of $\mathbf{p}$ → Assessment of **predictive uncertainty** based on **percentiles** associated with concentration histories

3. RESULTS

Diclofenac concentrations from calibrated model M_1 against measurements

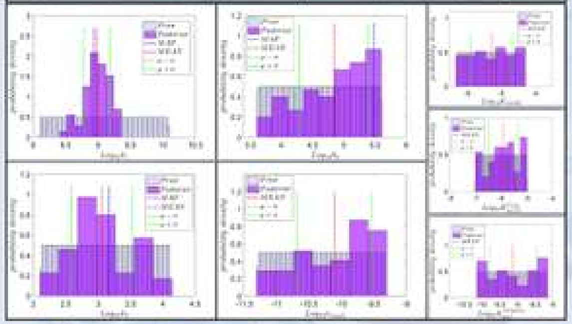


Associated uncertainty quantified by posterior distributions of Diclofenac concentration



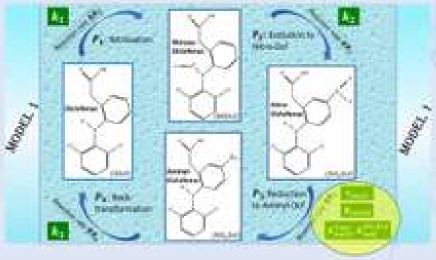
*Normalized values against the initial concentration of Diclofenac

Posterior distributions of uncertain parameters enclosed in p



4. ONGOING RESEARCH & ASSOCIATED RESULTS

- ***Motivation***: Data scarcity limits the quality of posterior parameter estimates associated with process P_3

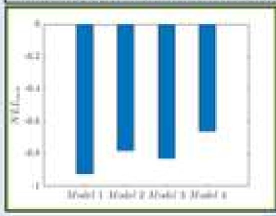


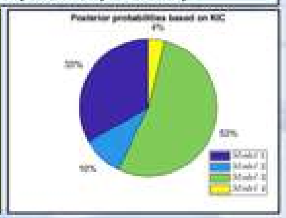
- ***Objective***: Simplifying the **complete geochemical model** M_1 through:

(1) **Global Sensitivity Analyses** in a **multi-model** context
(2) Ranking of model candidates through **Maximum Likelihood** and classical **Model Identification Criteria** (e.g., KIC)

Considering **3 competing models** (M_2, M_3, M_4), each characterized by a mathematical formulation of the reaction rate RR_3 of process P_3 obtained by progressively simplifying model M_1.

Negative-Log-Likelihood (NLL) and posterior probability





Model M_3 appears to be **favored** by post-calibration analyses, possibly due to:
(1) calibration dataset quality and/or
(2) parametrization redundancy in model M_1
→ Significant simplification of P_3 (up to first order reaction rate RR_3)

5. CONCLUSIONS & FUTURE PERSPECTIVES

- The proposed geochemical model correctly interprets the **reversible behavior** exhibited by Diclofenac
- **Stochastic calibration** of the complete model is **successful** (**quantifying predictive uncertainty**) even as dataset quality appears to favor a more streamlined geochemical model than M_1
- The proposed methodology can be applied to **customized** reactive systems under uncertainty

Underground space: from resources to structures and infrastructures – March 8th, 2022

POLITECNICO MILANO 1863
Ceresa Laura, Guadagnini Alberto, Porta Giovanni, Riva Monica
Department of Civil and Environmental Engineering