Reactive transport of dichloromethane in porous media under dynamic hydrogeological conditions: from experiments to modelling

M. Prieto-Espinoza[1]*, S. Weill[1], R. Di Chiara[1], B. Belfort[1], F. Lehmahn[1], J. Masbou[1], E. Muller[2], S. Vuilleumier[2], G. Imfeld[1]*

[1] University of Strasbourg, CNRS/EOST, LHyGeS UMR 7517, Laboratory of Hydrology and Geochemistry of Strasbourg, Strasbourg, France

[2] University of Strasbourg, CNRS, GMGM UMR 7156, Génétique Moléculaire, Génomique, Microbiologie, Strasbourg, France

Motivation

- **Dichloromethane** (DMC) is one of the most common chlorinated methanes often detected in groundwater as a result of extensive use, inappropriate disposal and accidental spills.[1,2]

- In surface-groundwater interfaces, **water table variations** can strongly impact the transfer of gases (e.g. oxygen), the evolution of redox conditions and the evolution/adaptation of bacterial/microbial populations that control biodegradation pathways of contaminants.

- In this study, **numerical modelling** is used to investigate DCM reactive transport under steady-state and fluctuating conditions based on our experimental study.

- Compound-stable isotope analysis **(CSIA)** has been used to derive the extent of DCM degradation and reaction mechanisms using a carbon-chlorine isotope approach.[5]

- This study **aims** to i) integrate a dual-element isotope modelling approach, ii) to validate the model with our experimental data and iii) to prove its feasibility under dynamic hydrogeological conditions.

Methods: Experimental study

Two laboratory aquifers under near-natural setting (injection of field groundwater).
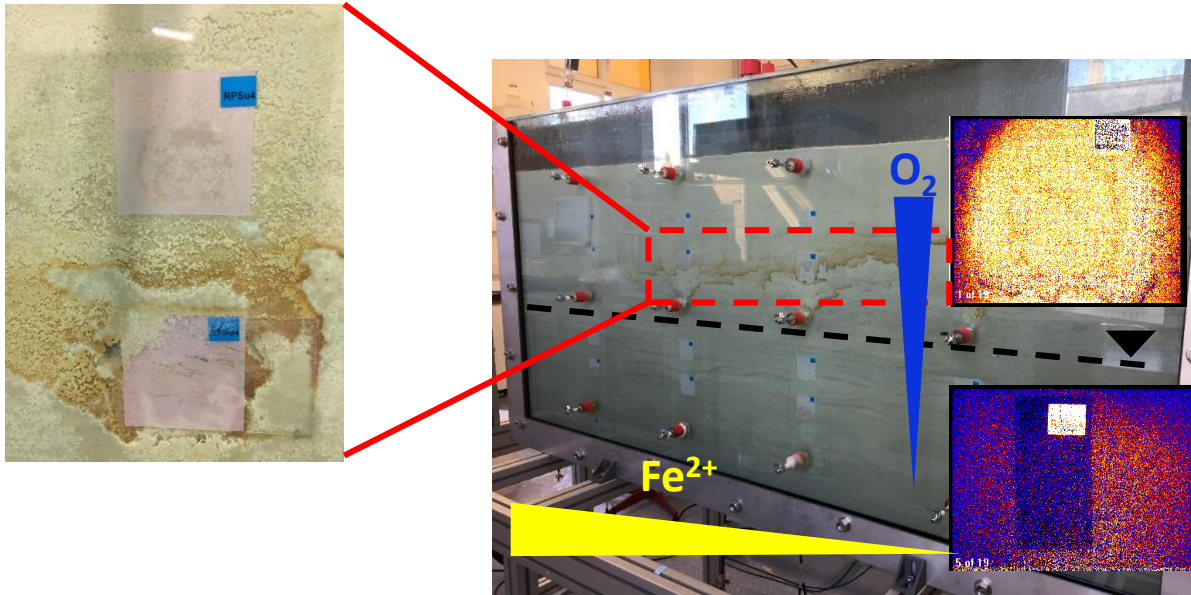
Dimensions: 160 x 80 x 7 cm³
Flow rate: 0.33 mL/min
DCM injection: 0.45 mM/L
Oxygen content: **< 0.3 mg/L**
Residence time: 31 days

Highlights:

- Iron-reducing conditions prevailed in the systems.

- Water table fluctuations enhanced DCM biodegradation and influenced DCM degradation pathways compared to steady-state conditions.
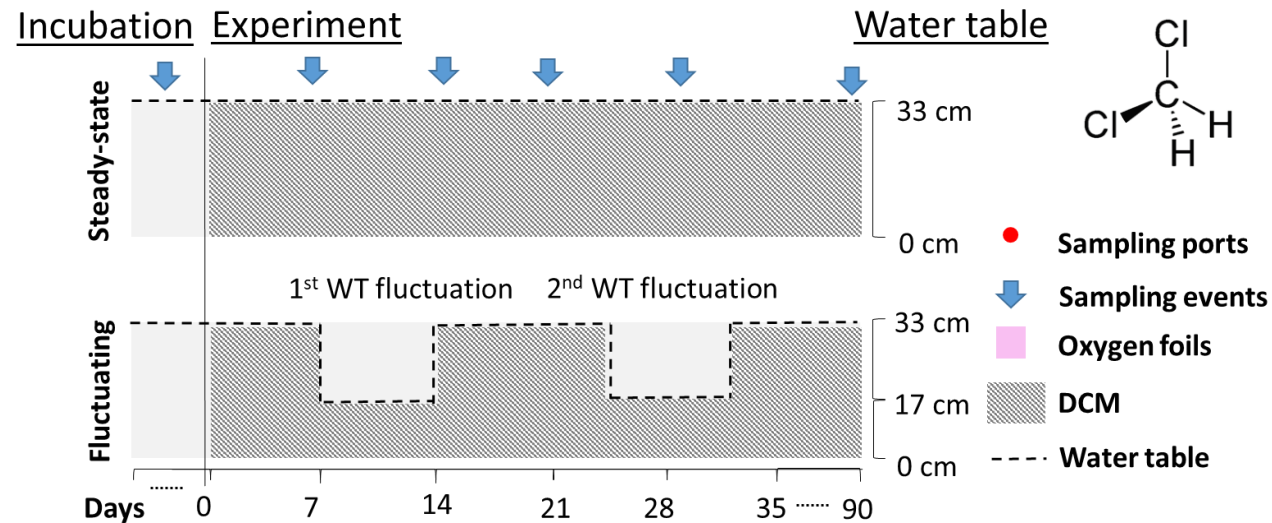
Scheme of the operation of two laboratory aquifers.

Methods: Numerical simulations - 2D CubicM model[8]

- The presented numerical simulations account for:
  i)   transport processes (e.g., advection, dispersion) and
  ii) reactive transformations (e.g., microbial transformation).

- Microbial transformation is derived from changes in isotopic composition[3] of two elements: ^{13}C and ^{37}Cl. We also account for isotope fractionation by molecular diffusion.[4]

- Kinetics of biodegradation are described by Monod kinetics[3].

- Simulation of the 4 most abundant DCM isotopologues. The abundance of each isotopologue is computed accounting for the occurrence of C and Cl isotopes.[5]
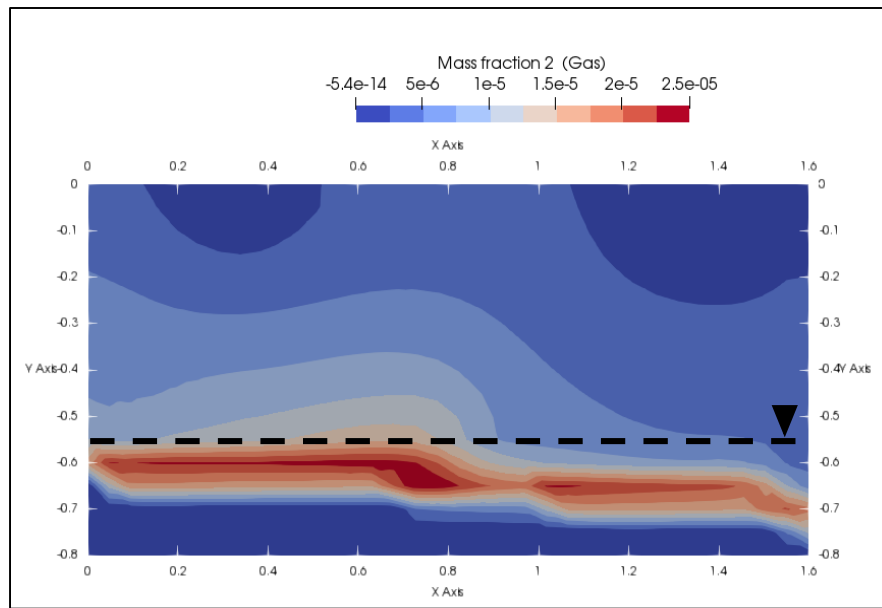
DCM –water phase
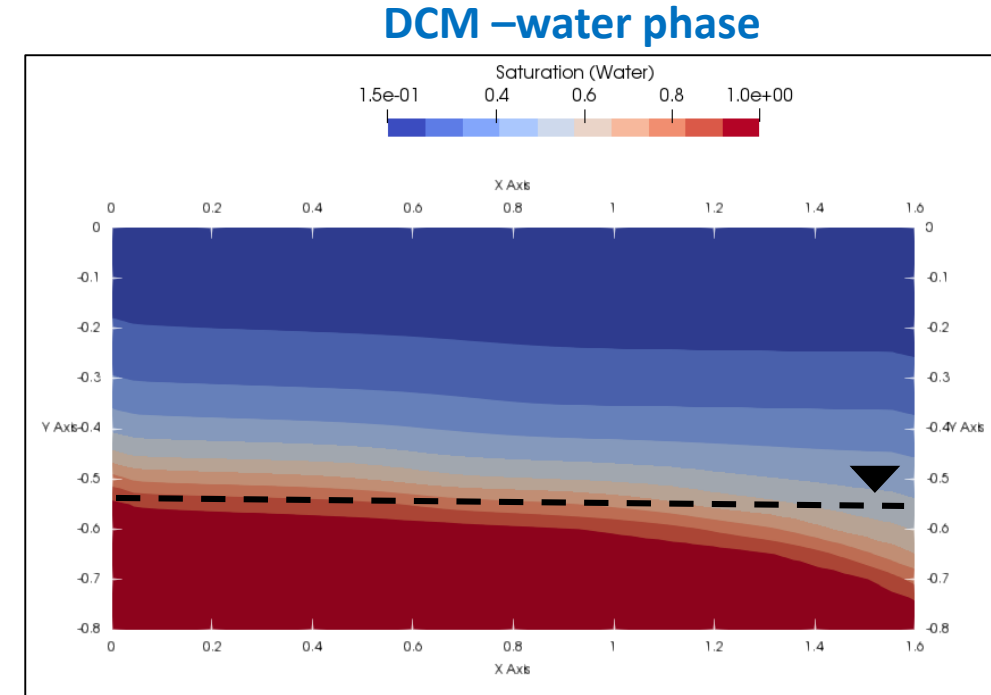
DCM plume in the saturated zone after 12 days of steady-state injection.

Two-phase flow: accounting for transient conditions

Current model simulation (12 days) under steady-state conditions have proven to grasp two-phase flow of water and gas > DCM volatilization and oxygen intrusion from the surface of the aquifer models.
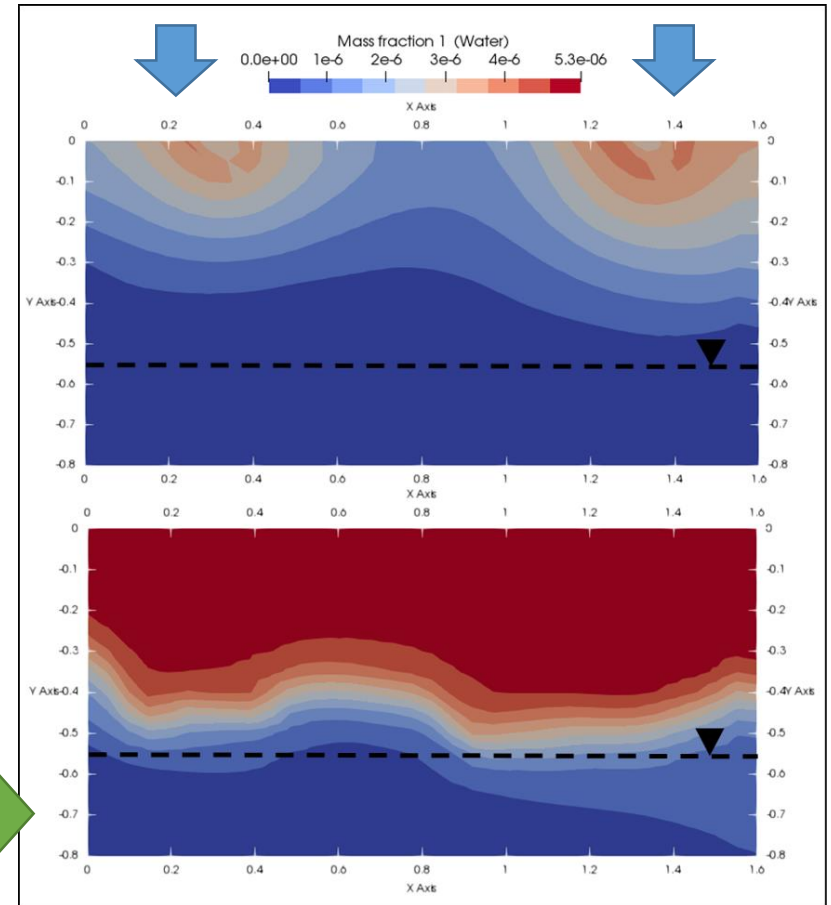
Ambient air

DCM – gas phase

DCM transport in the gas phase – DCM volatilization.

Anoxic groundwater

O₂

Oxygen intrusion from two ports (top).
Gradient of oxic to anoxic conditions from top to bottom.

Dual-element CSIA and DCM degradation pathway

- A simple 2D simulation of the 4 DCM isotopologues to validate the model isotope approach[5]:
    - ✓ DCM degradation pathways (under oxic and iron-reducing conditions).
- Preliminary results are in agreement with our experimental study where DCM degradation pathway followed the one described by the DCM degrader *Ca.* Dichloromethamonas elyunquensis[6,7].
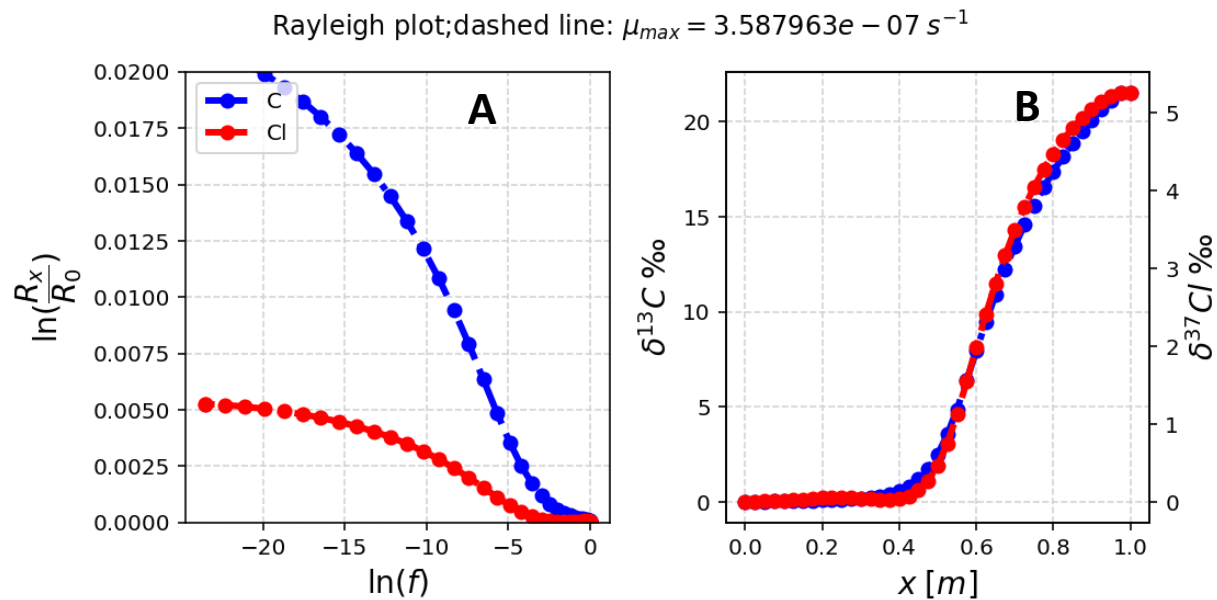
A) Distinct ^{13}C and ^{37}Cl isotope fractionation.
B) ^{13}C and ^{37}Cl isotope fractionation over distance of domain.
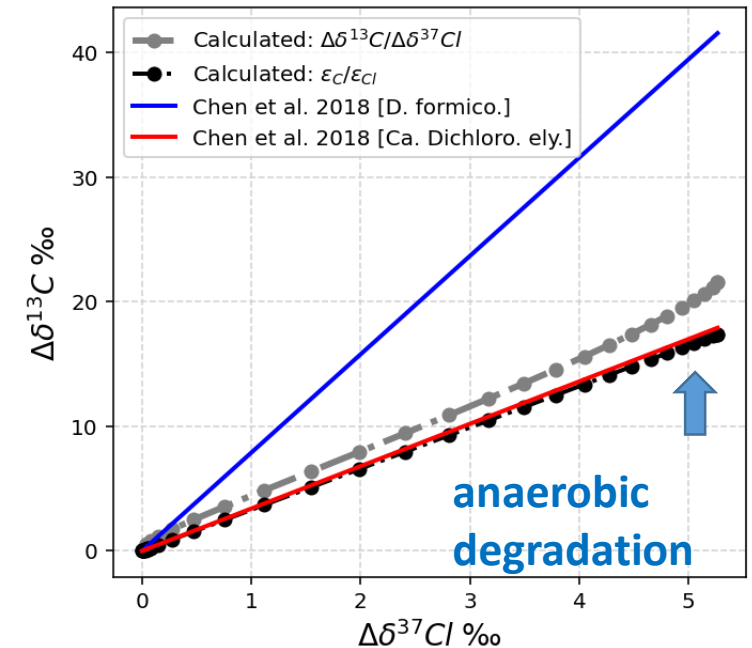
Simulation of dual C-Cl isotope plot of DCM degradation.

Outlook

- The dual-element isotope modelling approach will be tested on the 2D-CubicM model (accounting for isotope evolution under transient conditions).

- Longer simulation times are needed to grasp differences between the steady-state and fluctuating system:
  - $\Rightarrow$ hydrochemistry (i.e., oxygen and reduced iron)
  - $\Rightarrow$ DCM mass balance
  - $\Rightarrow$ isotope signatures
  - $\Rightarrow$ Difference in microbial distribution and biomass evolution

- Coupling isotope data (dual-element) and bacterial kinetics may help to understand the highlighted results of our experimental study:
  - $\Rightarrow$ distinct DCM degradation pathways under steady-state and fluctuating conditions?
  - $\Rightarrow$ mechanistically distinct C-Cl bond cleavage reactions subjected to microbial adaptations during dynamic hydrogeological conditions?

- By considering dynamic hydrogeological conditions, our model may prove useful for improved assessment of natural attenuation of DCM at contaminated sites.

References

1. Hermon, L.; Denonfoux, J.; Hellal, J.; Joulian, C.; Ferreira, S.; et al. (2018). Dichloromethane biodegradation in multi-contaminated groundwater: Insights from biomolecular and compound-specific isotope analyses. Water Res. 142, 217–226.

2. Blázquez-Pallí, N., Shouakar-Stash, O., Palau, J., Trueba-Santiso, A., Varias, J., Bosch, M., Soler, A., Vicent, T., Marco-Urrea, E. and Rosell, M., (2019). Use of dual element isotope analysis and microcosm studies to determine the origin and potential anaerobic biodegradation of dichloromethane in two multi-contaminated aquifers. Science of The Total Environment, 696, p.134066.

3. Eckert, D., Rolle, M., & Cirpka, O. (2012). Numerical simulation of isotope fractionation in steady-state bioreactive transport controlled by transverse mixing. Journal Of Contaminant Hydrology, 140-141, 95-106.

4. Worch, E.A., (1993). A new equation for the calculation of diffusion coefficients for dissolved substances. Vom Wasser 81, 289–297.

5. Jin, B., Haderlein, S., & Rolle, M. (2013). Integrated Carbon and Chlorine Isotope Modeling: Applications to Chlorinated Aliphatic Hydrocarbons Dechlorination. Environmental Science & Technology, 130122142002006.

6. Chen, G., Shouakar-Stash, O., Phillips, E., Justicia-Leon, S.D., Gilevska, T., Sherwood Lollar, B., Mack, E.E., Seger, E.S., Löffler, F.E., (2018). Dual carbon-chlorine isotope analysis indicates distinct anaerobic dichloromethane degradation pathways in two members of the Peptococcaceae. Environ. Sci. Technol. 52, 8607–8616.

7. Kleindienst, S., Higgins, S., Tsementzi, D., Chen, G., Konstantinidis, K., Mack, E. and Löffler, F., (2017). ' *Candidatus* Dichloromethanomonas elyunquensis' gen. nov., sp. nov., a dichloromethane-degrading anaerobe of the Peptococcaceae family. Systematic and Applied Microbiology, 40(3), pp.150-159.

8. ADEME, LHyGeS, BURGEAP, IMFT, 2017. CUBICM User's guide v2.17.

THANK YOU!

[1]LHyGES:

Gwenaël Imfeld
Sylvain Weill
Benjamin Belfort
François Lehmahn
Raphaël Di Chiara
Benoit Guyot
Jérémy Masbou
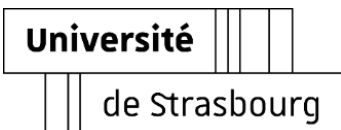Colin Fourtet
Thierry Perrone

[2]GMGM:

Stéphane Vuilleumier
Emilie Muller
Carmen Lazaro

*We thank Raphaël di Chiara Roupert for providing the source code of the 2D - CubicM model.

*E-mail corresponding authors:

M. Prieto-Espinoza: prietoespinoza@unistra.fr
G. Imfeld: imfeld@unistra.fr

Governing equations

We solve the following system of partially ordinary equations:

$$^{12}C^{35}Cl_2 \; : \; \frac{\partial\, ^{12}C_s}{\partial t} + \mathbf{u}\nabla\, ^{12}C_s = \nabla\cdot\left(^{12}D_s\nabla\, ^{12}C_s\right) - r_{deg}\frac{^{12}C_s}{C_s^{\,tot}}$$

$$^{13}C^{35}Cl_2 \; : \; \frac{\partial\, ^{13}C_s}{\partial t} + \mathbf{u}\nabla\, ^{13}C_s = \nabla\cdot\left(^{13}D_s\nabla\, ^{13}C_s\right) - r_{deg}\frac{^{13}C_s}{C_s^{\,tot}}\alpha_C$$

$$^{12}C^{37}Cl^{35}Cl \; : \; \frac{\partial\, ^{12}C_s^*}{\partial t} + \mathbf{u}\nabla\, ^{12}C_s^* = \nabla\cdot\left(^{12}D_s^*\nabla\, ^{12}C_s^*\right) - r_{deg}\frac{^{12}C_s^*}{C_s^{\,tot}}\alpha_{Cl}$$

$$^{13}C^{37}Cl^{35}Cl \; : \; \frac{\partial\, ^{13}C_s^*}{\partial t} + \mathbf{u}\nabla\, ^{13}C_s^* = \nabla\cdot\left(^{13}D_s^*\nabla\, ^{13}C_s^*\right) - r_{deg}\frac{^{13}C_s^*}{C_s^{\,tot}}\alpha_C\alpha_{Cl}$$

in which $C_s^{tot} = {}^{12}C_s + {}^{13}C_s + {}^{12}C_s^* + {}^{13}C_s^* \; [M/L^{-3}]$

$$\frac{\partial C_{O_2}}{\partial t} + \mathbf{u}\nabla C_{O_2} = \nabla\cdot\left(D_{O_2}\nabla C_{O_2}\right) - r_{deg}^{O_2}f_{deg}^{O_2}\left(\frac{^{12}C_s}{C_s^{\,tot}} + \frac{^{13}C_s}{C_s^{\,tot}}\alpha_C + \frac{^{12}C_s^*}{C_s^{\,tot}}\alpha_{Cl} + \frac{^{13}C_s^*}{C_s^{\,tot}}\alpha_C\alpha_{Cl}\right) - k_{dec}f_{dec}^{O_2}X$$

$$\frac{\partial C_{Fe^{3+}}}{\partial t} + \mathbf{u}\nabla C_{Fe^{3+}} = \nabla\cdot\left(D_{Fe^{3+}}\nabla C_{Fe^{3+}}\right) - r_{deg}^{Fe}f_{deg}^{Fe}\left(\frac{^{12}C_s}{C_s^{\,tot}} + \frac{^{13}C_s}{C_s^{\,tot}}\alpha_C + \frac{^{12}C_s^*}{C_s^{\,tot}}\alpha_{Cl} + \frac{^{13}C_s^*}{C_s^{\,tot}}\alpha_C\alpha_{Cl}\right) - k_{dec}f_{dec}^{Fe}X$$

* $$\frac{\partial X}{\partial t} + \mathbf{u}\nabla C_X = \nabla\cdot\left(D_X\nabla C_X\right) + r_{deg}Y_s\left(\frac{^{12}C_s}{C_s^{\,tot}} + \frac{^{13}C_s}{C_s^{\,tot}}\alpha_C + \frac{^{12}C_s^*}{C_s^{\,tot}}\alpha_{Cl} + \frac{^{13}C_s^*}{C_s^{\,tot}}\alpha_C\alpha_{Cl}\right)\left(1 - \frac{X}{X_{max}}\right) - k_{dec}X$$

* All kinetic parameters are currently under revision.

Université de Strasbourg

cnrs

LHyGeS

ENGEES
ÉCOLE NATIONALE DU GÉNIE DE L'EAU
ET DE L'ENVIRONNEMENT DE STRASBOURG

gm
Génétique Moléculaire ■ Génomique ■ Microbiologie