WatEr NEEDs, availability, quality and sustainability

WE-NEED

Monica Riva

Water JPI

WaterWorks2015 Cofunded Call

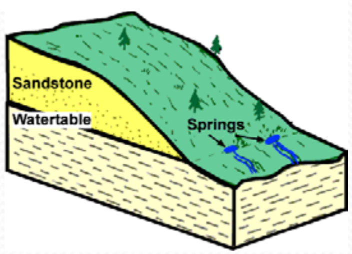
8 May 2018, Lanarca

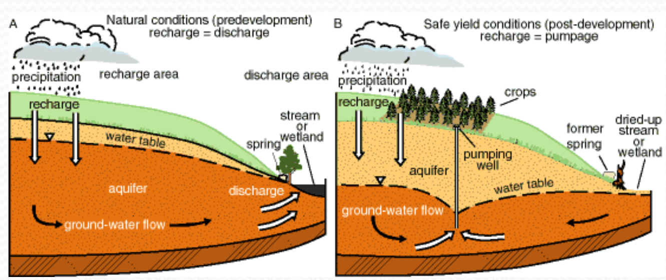
SCOPE

Develop innovative management strategies to assist the sustainable use/protection of two key components of groundwater resources (springs – wells)

WATER QUANTITY : Over-exploitation of groundwater resources
WATER QUALITY : Regulated and emerging contaminants (pharmaceuticals, …)

KEYWORDS: Management/Protection of Groundwater Resources – Sustainability – Uncertanty Quantification - Risk Assessment - Multiscale Statistical Analysis
Relevant Study Cases (real scenarios)





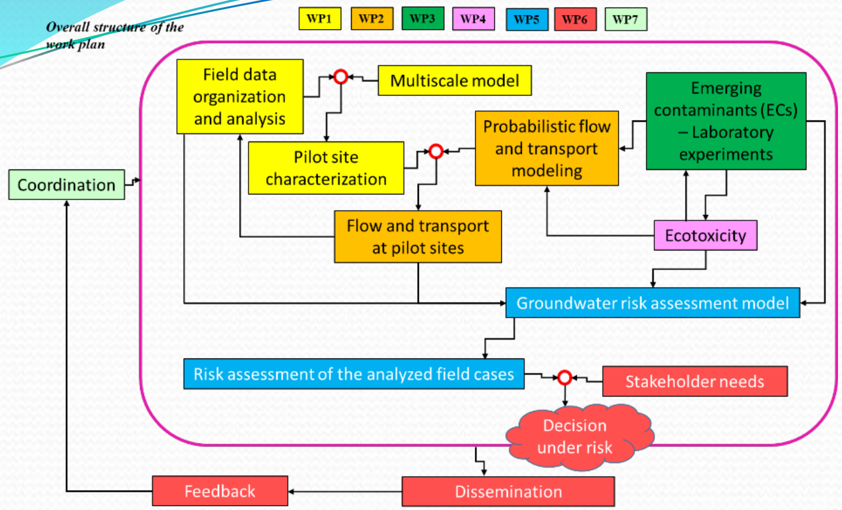
Consortium Description

ACRONYM	TOPIC	Coordination	Partners
WE-NEED	**2**		
Water Needs, Availability, Quality and Sustainability		**water management; risk assessment; emerging contaminants; multiscale characterization; ecotoxicity**	

PRINCIPAL INVESTIGATOR	INSTITUTION	COUNTRY
Monica Riva	**Politecnico di Milano - Polimi**	**Italy**
Brian Berkowitz	Weizmann Institute of Science - Weizmann	Israel
Susana Loureiro	Universidade de Aveiro - UAVR	Portugal
Daniel Fernandez-Garcia	Universitat Politecnica de Catalunya - UPC	Spain

www.we-need.polimi.it

WPs / Collaboration and Co-ordination



Activities are being coordinated with other international research projects. (Israeli and Czech Ministries of Science are funding a project that focuses on possible nanoparticle uptake by plants, and ultimate fate and transport nanoparticles in irrigation water, Polimi are also collaborating within the Interreg project AMIIGA, aimed to develop cost-effective remediation strategies for contaminated aquifers)

Each partner participates in several WPs

		Lead Partner	Participating Partner
WP1	Data collection and multiscale characterization	Polimi	UPC, UAVR, Weizmann
WP2	Probabilistic flow and transport modeling	UPC	Polimi, Weizmann
WP3	Fate of Emerging Contaminants (ECs) - laboratory experiments and modeling	Weizmann	UAVR
WP4	Ecotoxicology	UAVR	Weizmann
WP5	Multidisciplinary risk assessment and decision making	Polimi	UPC, UAVR, Weizmann
WP6	Dissemination of results, communication with stakeholders/general public	Polimi	UPC, UAVR, Weizmann
WP7	Project management	Polimi	UPC, UAVR, Weizmann

SITES

We ground our activities on observations linked to two sites, representing different but complementary realities

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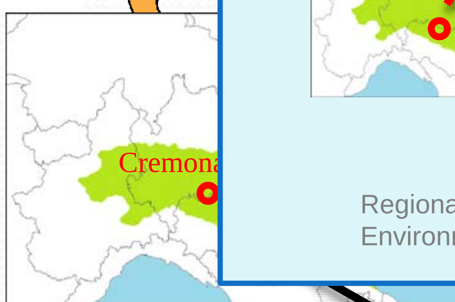
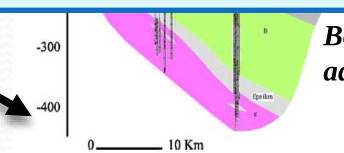




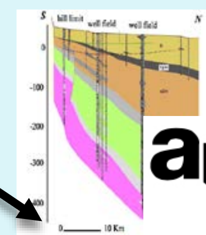
Bologna aquifer system

The *Bologna Aquifer* is a key source of water for the metropolitan area of Bologna.

Consorzio di Bonifica Dugali, Naviglio, Adda Serio

CONSORZIO IRRIGAZIONI CREMONESI

Water derivation and distribution for irrigation



arpae
agenzia prevenzione ambiente energia emilia-romagna

Regional Agency for Environmental Protection

Two diverse methodologies have been adopted in order to characterize the two systems.

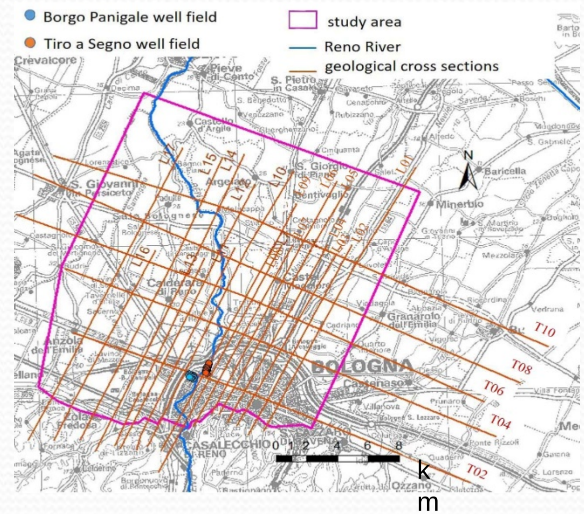
WE-NEED

BOLOGNA SITE

High-medium alluvial Po Plain

Surface area 400 km^2

Two major well fields: Borgo Panigale and Tiro a Segno

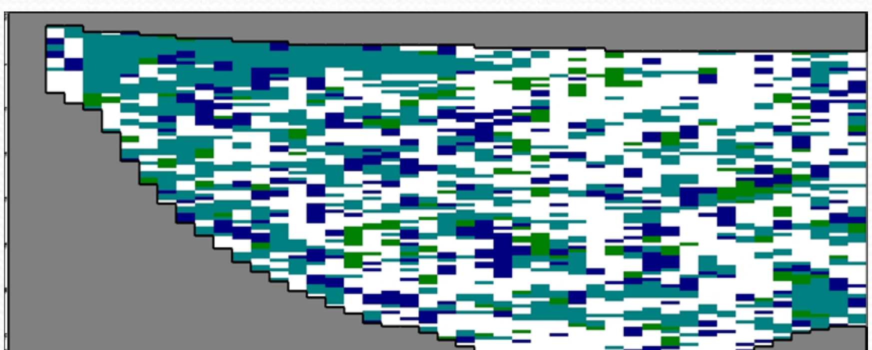


4 main categories (facies/class or geomaterial)

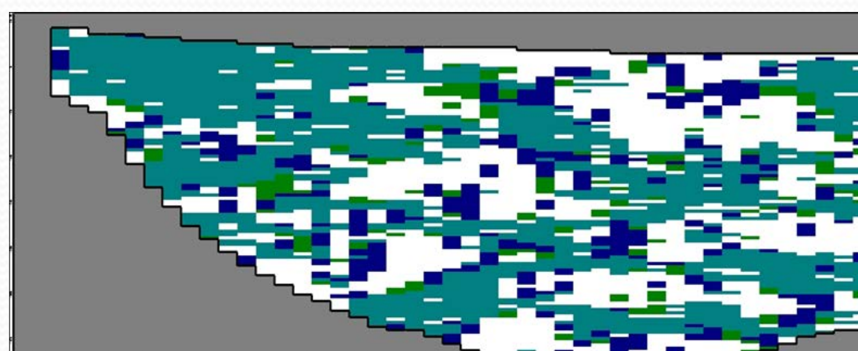
- Clay 52%
- Silt 13%
- Sand 7%
- Gravel 28%

Model Uncertainty:
Two probabilistic methodologies

(1) Sequential indicator (sample variogram)

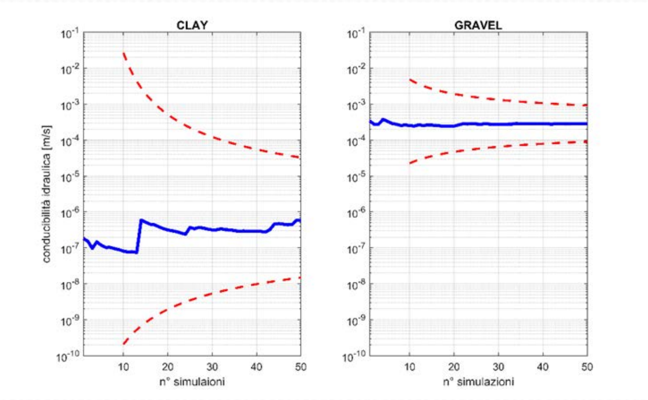


(2) Transitional probability

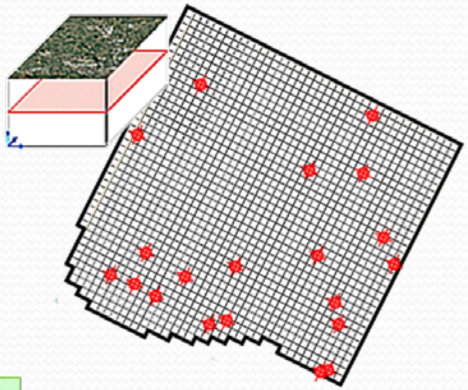


BOLOGNA SITE

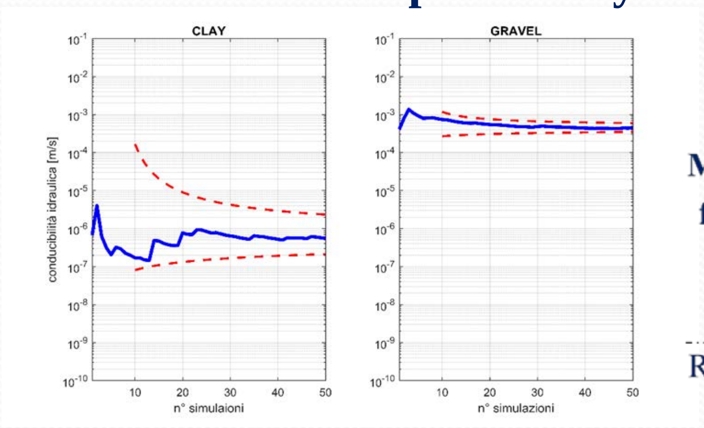
Sequential indicator

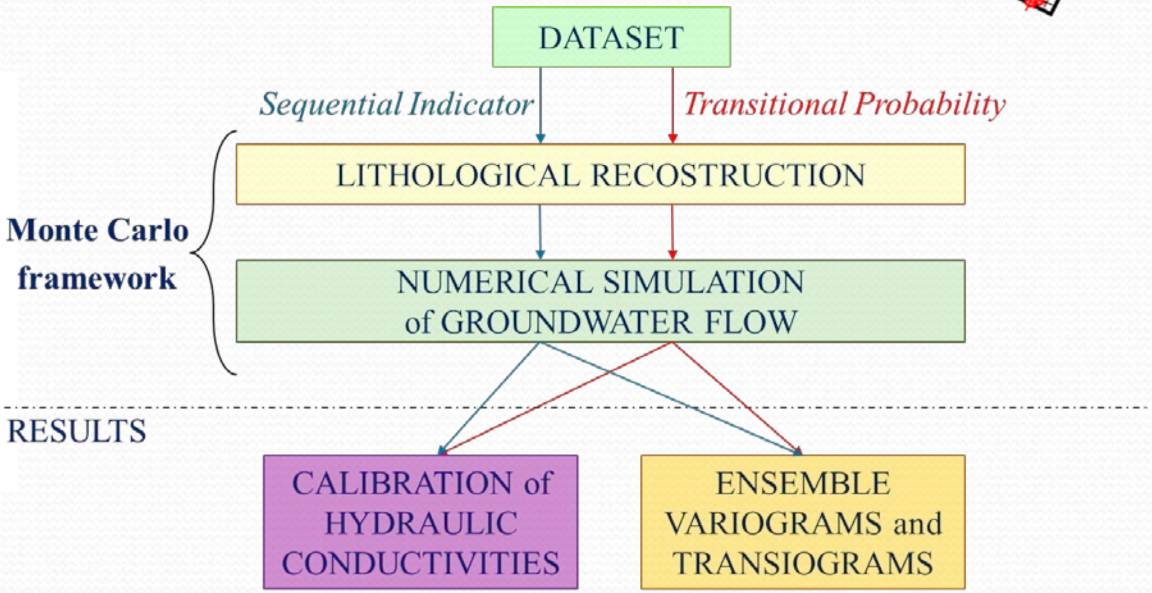


Hydraulic conductivity distributions of each MC realization have been calibrated on the basis of available piezometric data.



Transitional probability





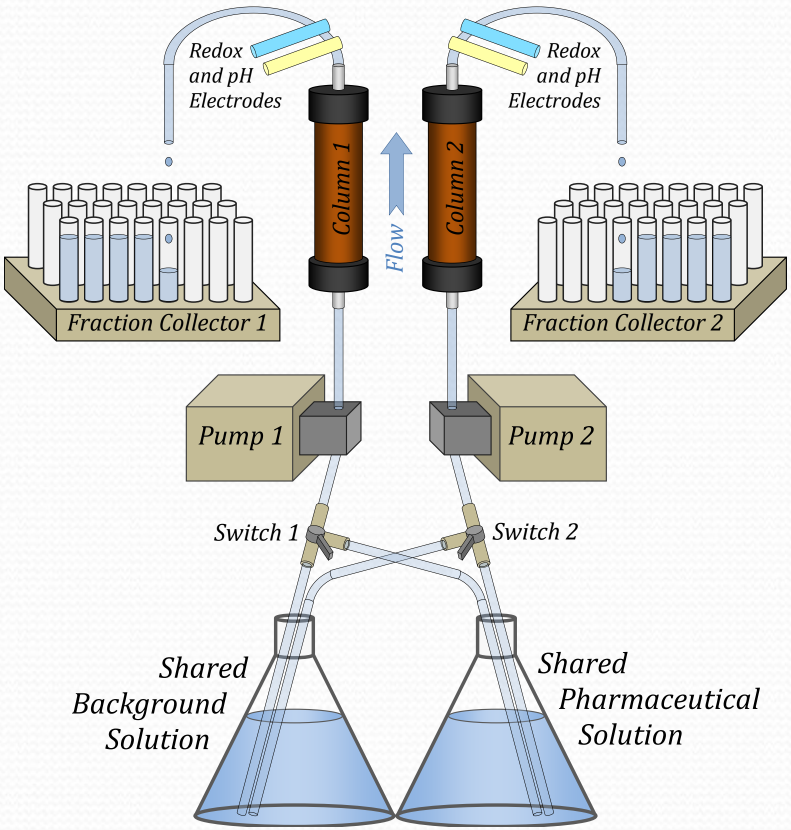
WE-NEED

LABORATORY EXPERIMENTS

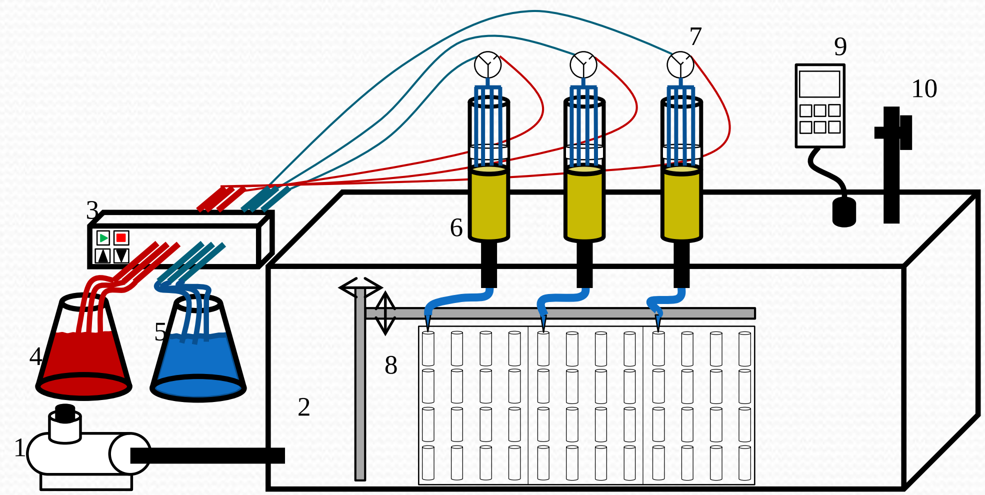
Sample	Core	Depth from ground [m]	Geological Description	
1	220-S10	51.8-52	The sample is mainly formed by sand (fluvial channel sands) with very few pebbles (maximum length 2 cm)	
2	220-S10	48.4-48.6	Sandy silt with some pebbles	
3	220-S10	35.3-35.5	Fluvial channel gravel. Heterometric gravel with grain size ranging from fine gravel (about 2 mm – the most abundant fraction) to pebbles (2-3 cm), in sandy-silt matrix	
4	220-S10	24.5-24.7	Clay and silt of alluvial plain. Fine grained material (silt)	
5	221-S6	8.3-8.6	reddish sand	
6	221-S6	15.6-16	clay	

Experimental set-ups column experiments

Fully saturated conditions



Partially saturated conditions

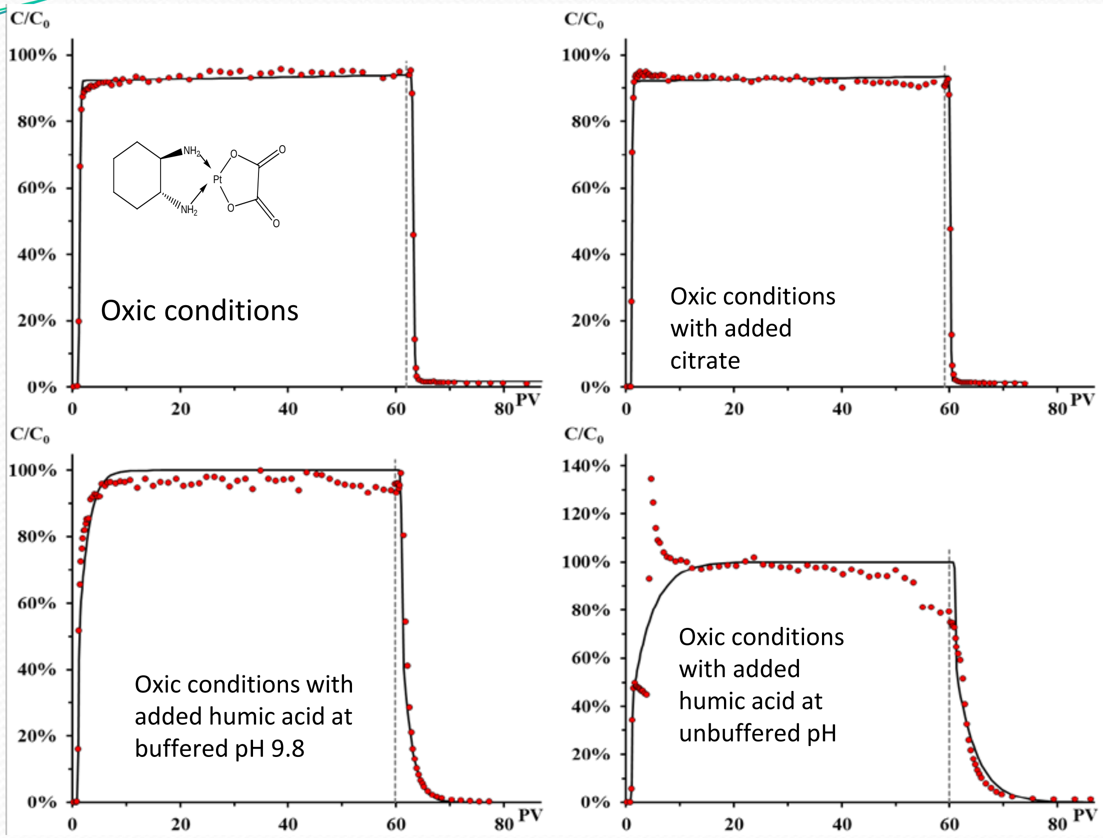


1) vacuum pump; 2) low pressure chamber; 3) multichannel peristaltic pump; 4) ENP suspension; 5) background solution; 6) cylindrical acrylic glass columns; 7) valve to control inlet source solution; 8) fraction collector consisting of stationary tube trays and moving arms; 9) vacuum meter, and 10) valve to control the pressure inside the chamber.

Water JPI

WE-NEED

BTCs – total Oxaliplatin in (quartz) sand columns



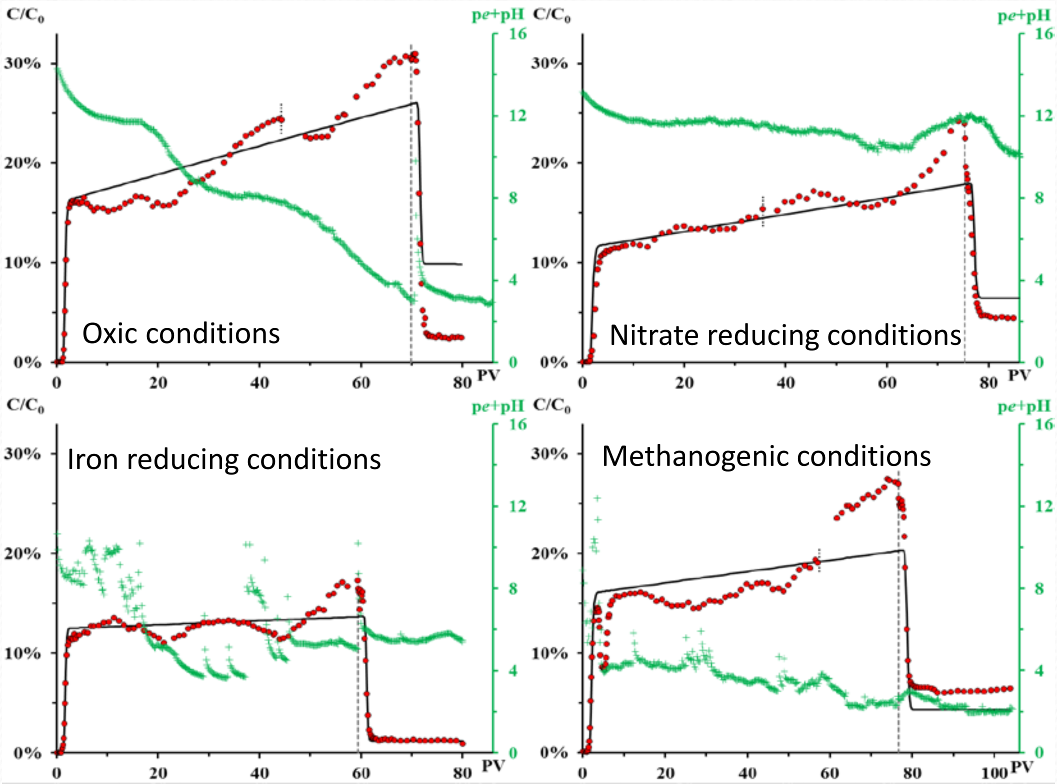
Oxaliplatin is a platinum-based chemotherapy pharmaceutical, typically used to treat colorectal cancer.

Experiments were carried out with chelating agents added to the inlet solution composition. These agents are likely to be present in wastewaters and the natural environment.

Oxaliplatin retention: about 7%, and affected only mildly by added citrate, and by humic acid under buffered pH.
Transport with unbuffered humic acid was affected significantly by pH variations, and exhibited strong retention at pH<8.

WE-NEED

BTCs – total Oxaliplatin in soil vs PV



In soil, oxaliplatin interaction with the porous medium was significantly stronger than in sand, and indicated variability in sorption sites and sorption mechanisms

Sorption does not follow a linear model

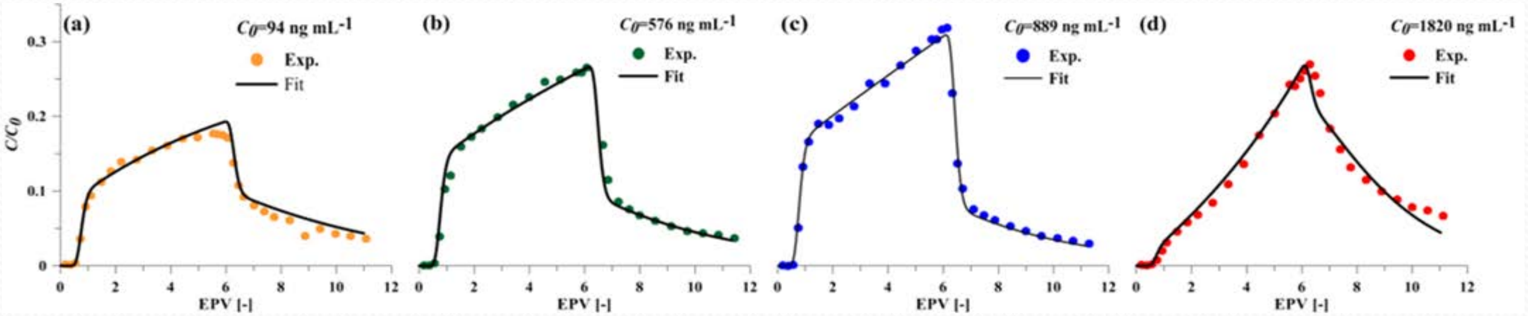
Diverse redox conditions. The redox conditions were chosen according to their potential to affect pharmaceutical transport in soil-water environments, and cover most of the range of natural redox conditions present in aquifer systems.

Water JPI

WE-NEED

BTCs – ENP (Ag-NP) in partially saturated soil columns

Varying input concentrations (C_0, in ng mL^{-1}) (a) 94, (b) 576, (c) 889, and (d) 1820.



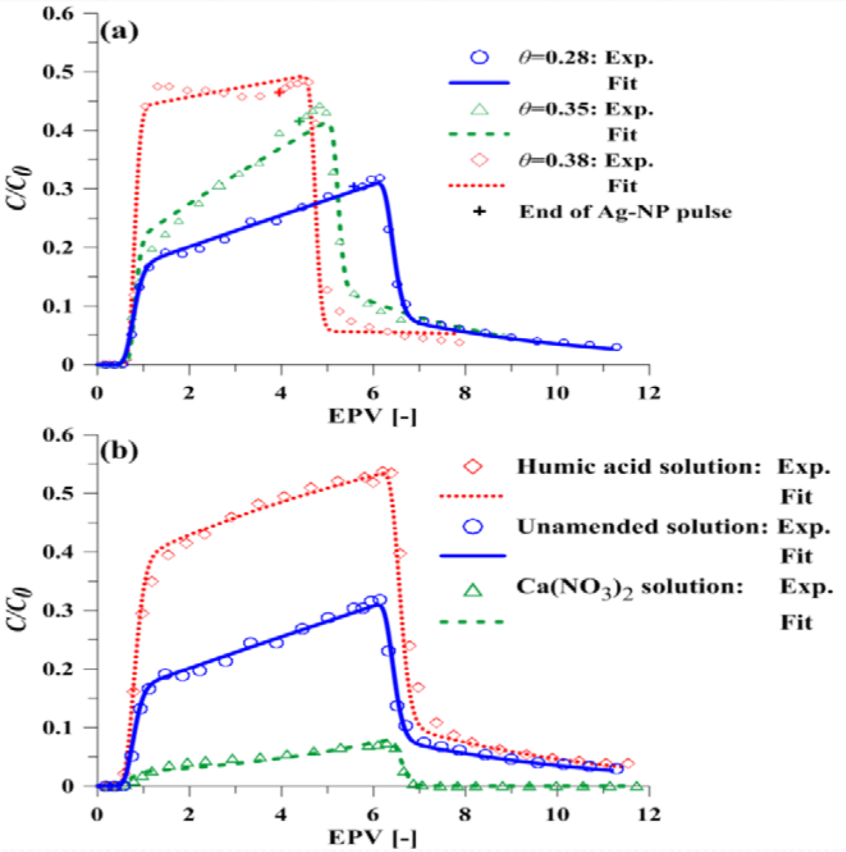
Long tailing with an initial sharp drop in Ag-NP concentration, followed by a gradual decrease during the flushing phase. This pattern indicates that Ag-NPs are released and remobilized after the Ag-NP pulse ends (detachment mechanism).

Mobility first increases with input concentration (which may be related to a decrease in the attachment rate due to repulsion between Ag-NPs). When the concentration of the Ag-NPs is increased to almost 2000 ppb the pattern of the breakthrough curve changes and fewer particles elute from the column.

WE-NEED

BTCs – ENP (Ag-NP) in partially saturated soil columns

Varying (a) water content levels; (b) in the presence of humic acid (30 mg L^{-1}), $Ca(NO_3)_2$ (425 mg L^{-1}) and unamended solution.



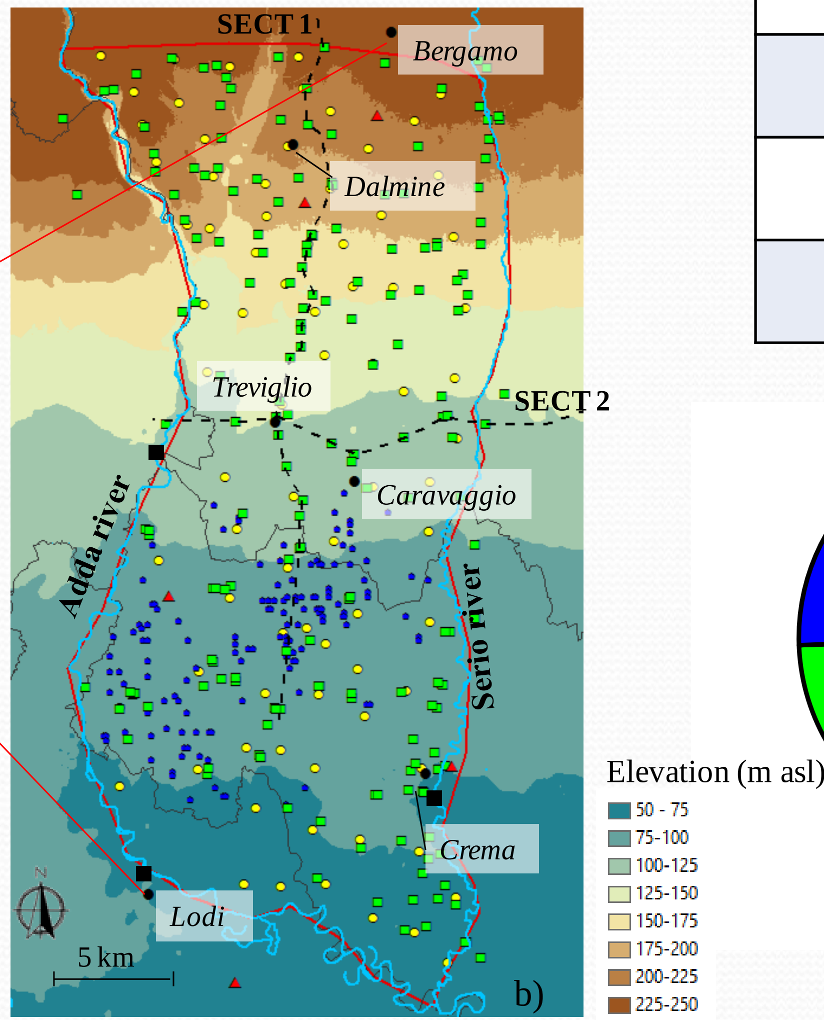
Decreasing number of attachment sites with increasing saturation (consistent with the expected decrease in air-water interface area).

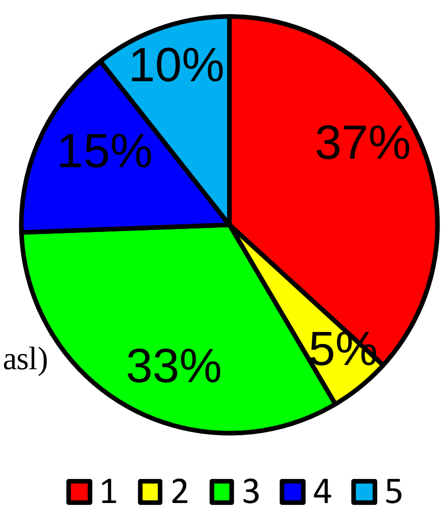
Higher mobility was observed in the presence of humic acid, which prevents the aggregation and interaction of Ag-NPs with soil grains.

Note that Ag-NP pulse duration, indicated by the cross symbol, decreases from 5.5, to 4.4, and then to 3.9 effective PVs with increasing water content. Therefore, differences on the horizontal axis are due to different EPV values in each experiment.

CREMONA SITE

FACIES	GEOLOGICAL MATERIAL
1	Clay and silty deposits
2	Fine Sands, Clay Sands, Silty Sands
3	Gravel, Gravel and Sand, Medium Sand
4	Compact Conglomerates
5	Fractured Conglomerates





CREMONA SITE: multi-model

MODEL 1: COMPOSITE MEDIUM

Each block is formed by a geomaterial. The conductivity value assigned to each cell of the model domain consists in one value for each facies.

MODEL 2 AND 3: OVERLAPPING CONTINUUM

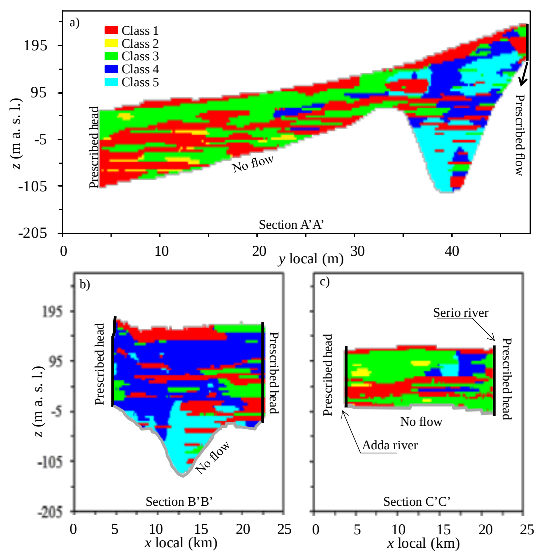
- The system can be modelled as many composite media coexisting in space. The idea is that each point in the domain represents a finite volume in which each one of the (five) geomaterials can coexist in different volumetric percentage.
- The hydraulic conductivity value of a grid cell (or block), K_j, is then calculated as a weighted mean of the conductivities of materials occurring in the block, k_i.

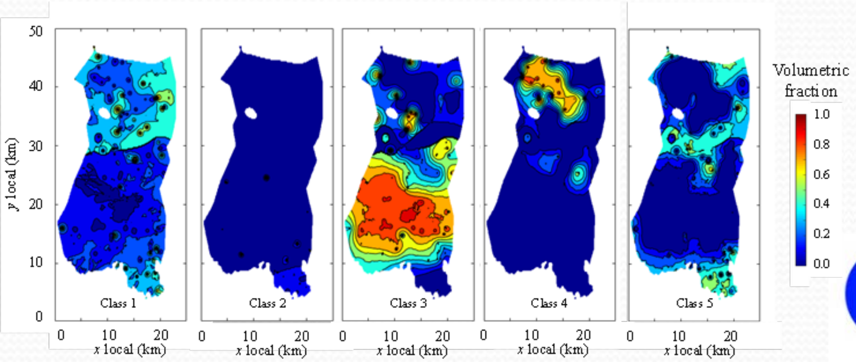
AM

$$K_j = \sum_{i=1}^{n_f} I_{i,j}\, k_i$$

GM

$$K_j = \prod_{i=1}^{n_f} k_i^{I_{i,j}}$$





CREMONA SITE: Sensitivity Analysis

- Quantitative assessment of the impact of model parameters on model outputs
- Uncertain parameters are associated with (*i*) 5 hydraulic conductivities and (*ii*) 2 selected boundary conditions

7 sources of uncertainty:

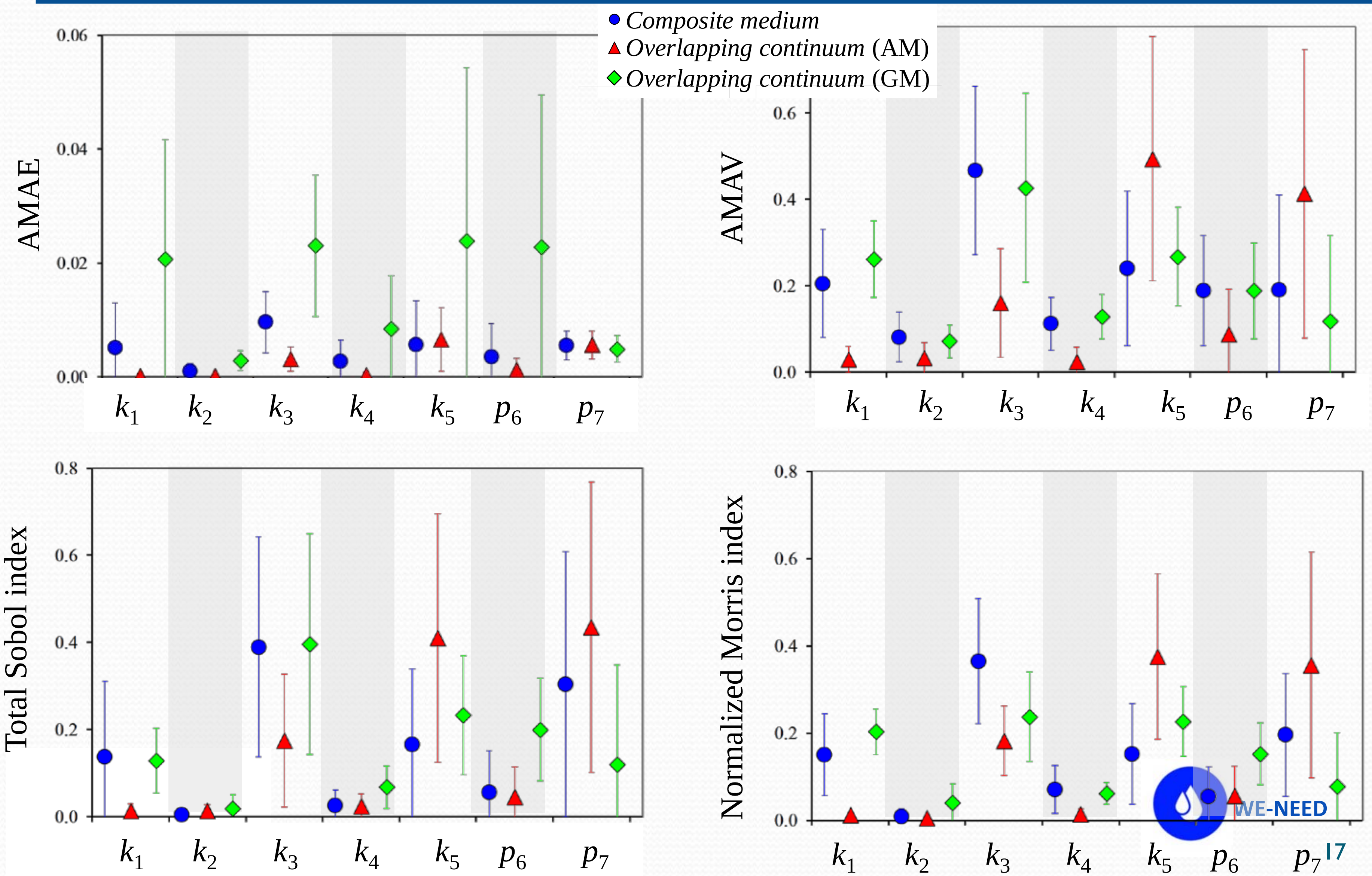
Parameter	Short name	Description	Lower bound	Upper bound	Unit
p_1	k_1	Clay and silt conductivity	10^{-8}	10^{-5}	m/s
p_2	k_2	Fine and silty sand conductivity	10^{-7}	10^{-4}	m/s
p_3	k_3	Gravel, sand and gravel conductivity	10^{-4}	10^{-2}	m/s
p_4	k_4	Compact conglomerate conductivity	10^{-6}	10^{-3}	m/s
p_5	k_5	Fractured conglomerate conductivity	10^{-3}	10^{-1}	m/s
p_6	p_6	Total flow rate from northern boundary	4.83	14.47	m^3/s
p7	p_7	Height of the river	0.0	3.0	m

Facies conductivity values

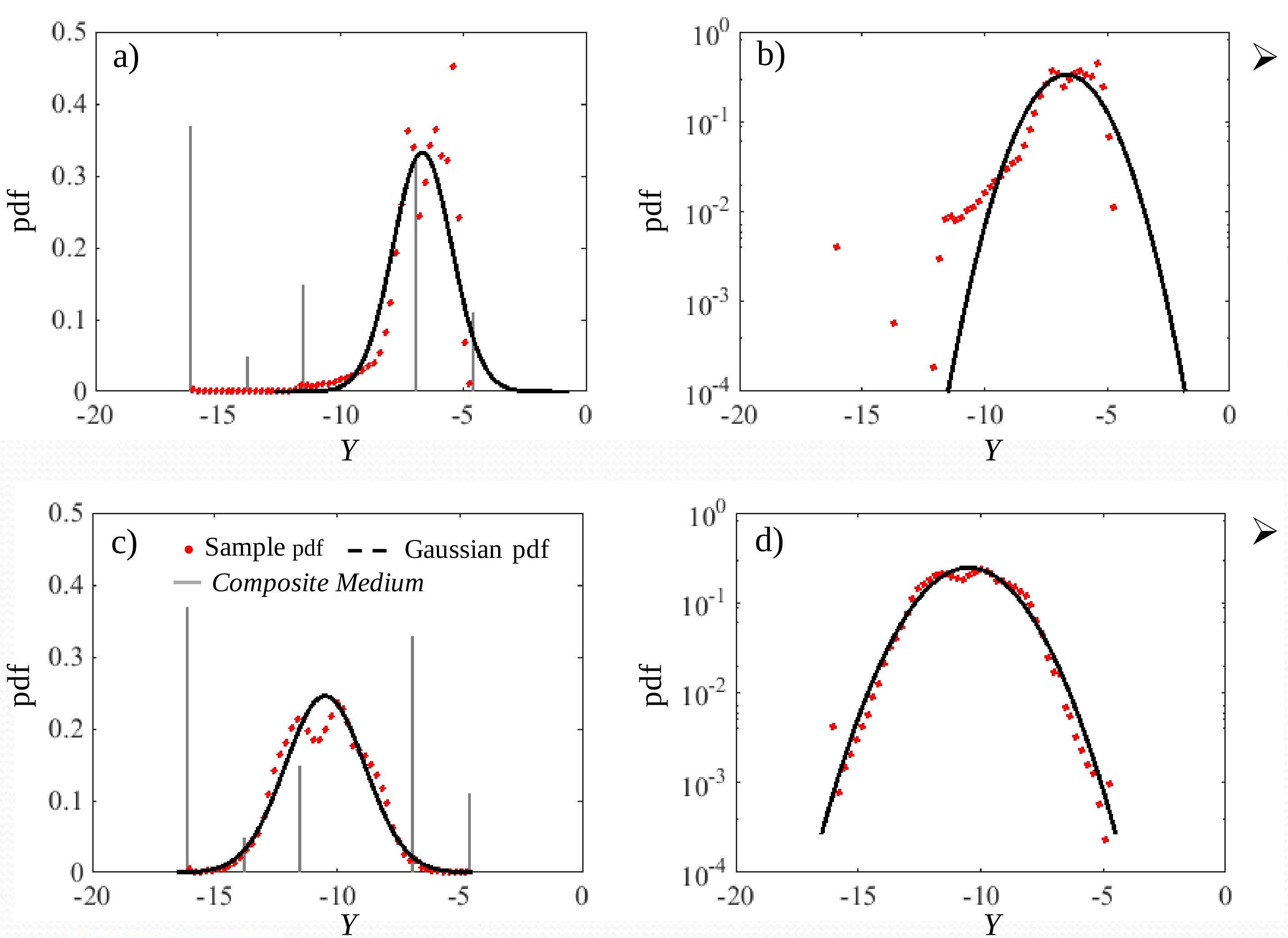
Boundary conditions

WE-NEED

Sensitivity Analysis (all observation wells)



lnK probability density function



- The sample pdf of *Y* for **AM**, sample pdf of *Y* is clearly non Gaussian and displays a long left tail.
- The sample pdf of *Y* for **GM** presents a slightly bimodal behavior with tails that decay nearly following a Gaussian pdf.

Water JPI

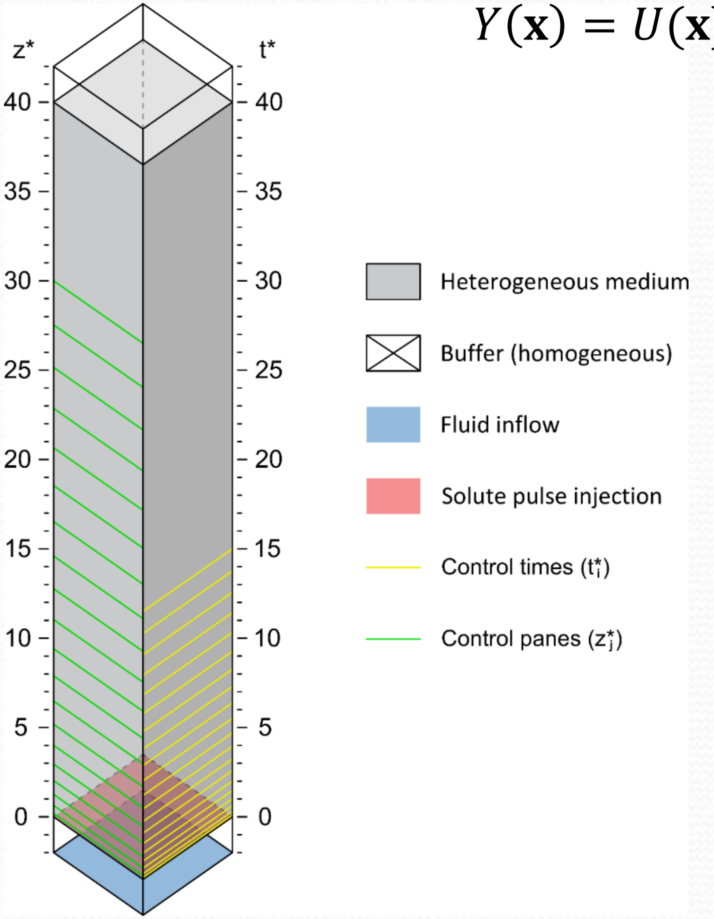
WE-NEED

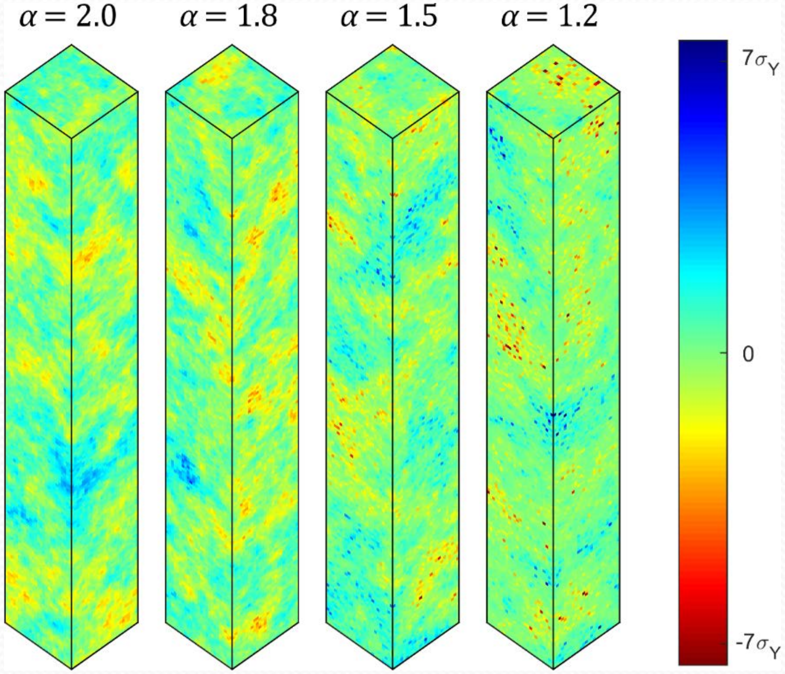
Non-Gaussian random fields

- Theoretical-Numerical model
- Effect on flow-solute transport

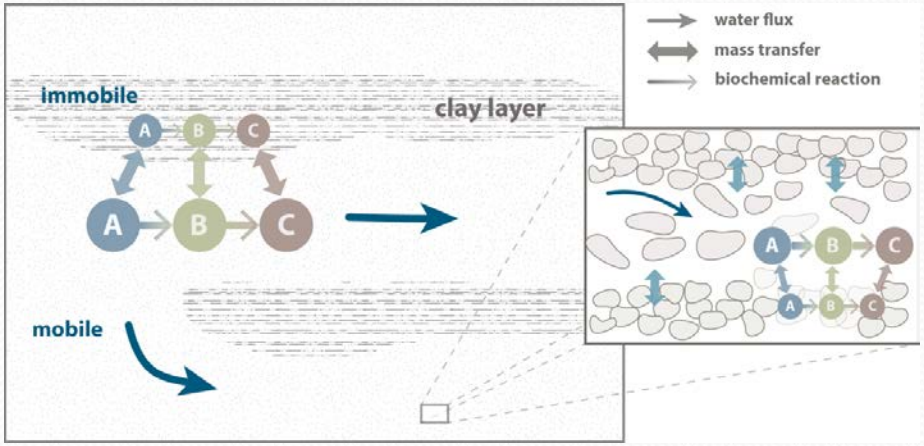
$$Y(\mathbf{x}) = U(\mathbf{x})\, G(\mathbf{x})$$

$U(\mathbf{x})$ subordinator follows a lognormal distribution of zero mean and variance $\sigma_U^2 = (2-\alpha)^2$





Particle tracking methods for complex non-linear problems



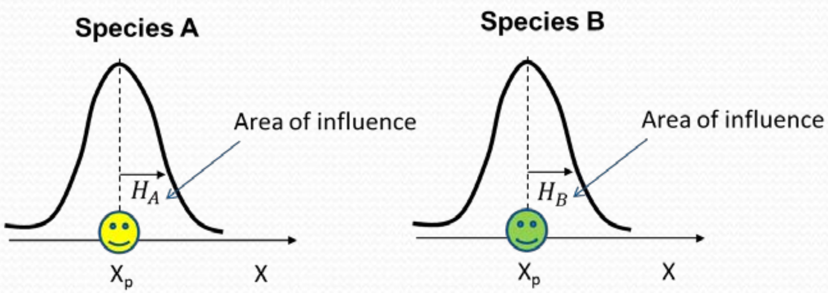
We have developed a Random Walk based on Particle Tracking schemes (RWPTM) capable of simulating different sorts of complex kinetic reactions

Lagrangian approaches are suitable for modeling transport in heterogeneous porous media.

WE-NEED

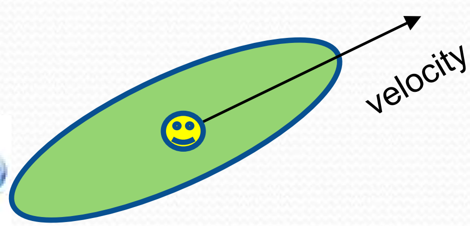
Particle tracking methods for complex non-linear problems

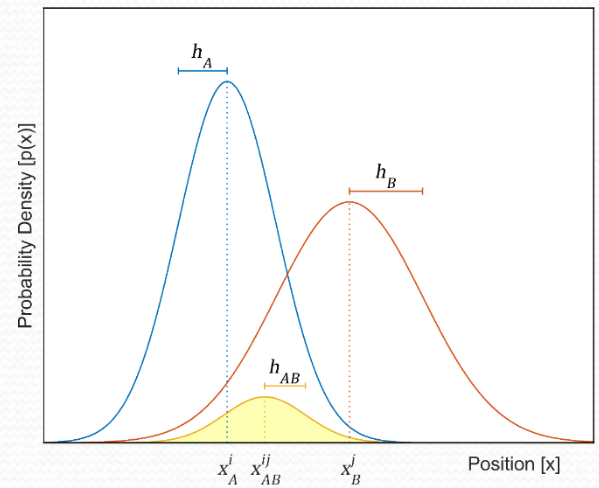
Incorporation of chemical reactions requires interaction between particles.



What is the probability of reaction of complex non-linear kinetic reactions ?

Particle support should locally adapt its shape and size according to fluid dynamics





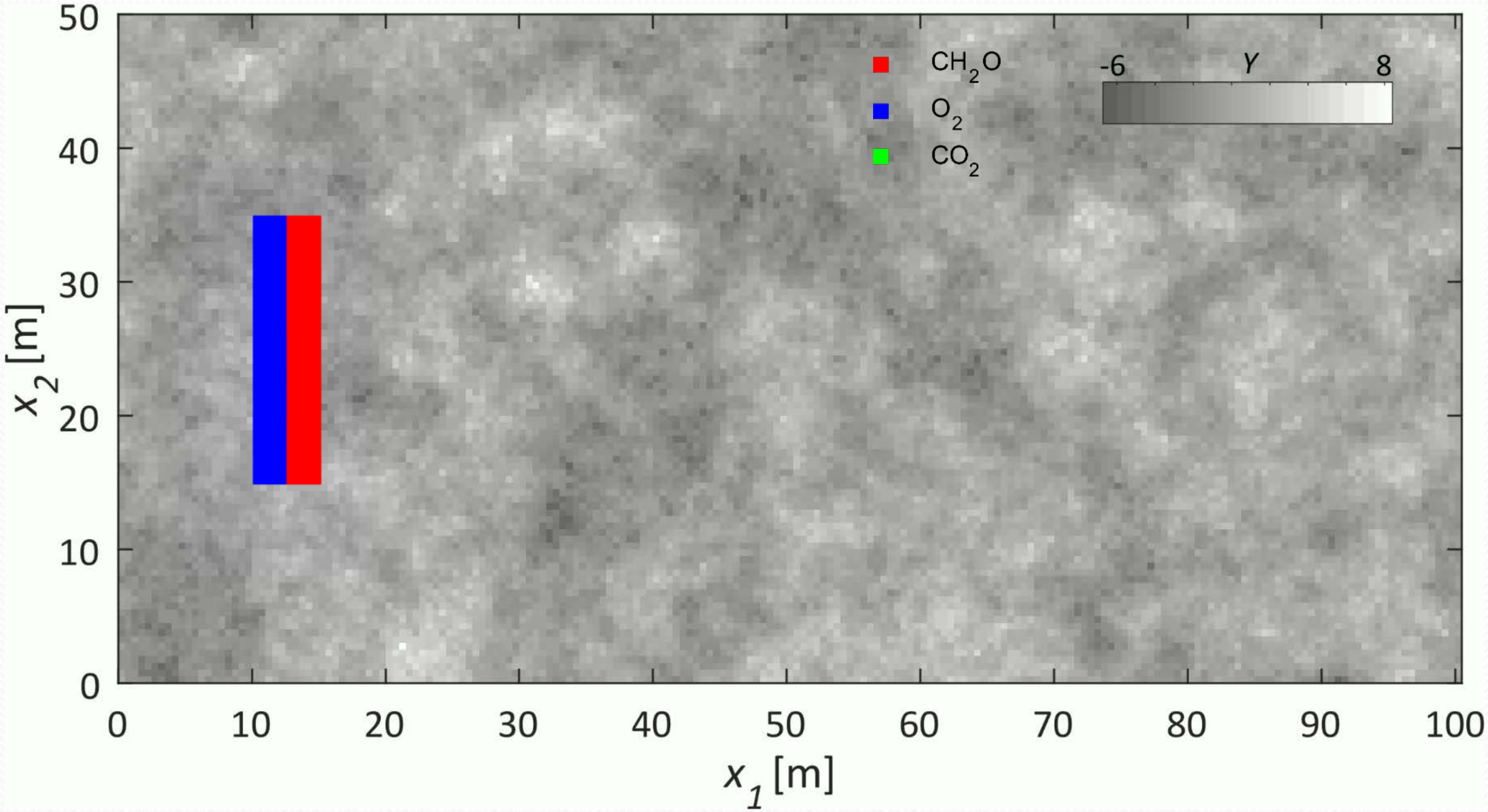
Kernel Density Estimation theory.

Idea: to equip each particle with an optimal kernel function that defines the particle support (change in time, function of the shape of the solute plume)

WE-NEED

Organic chemical compound (CH_2O)

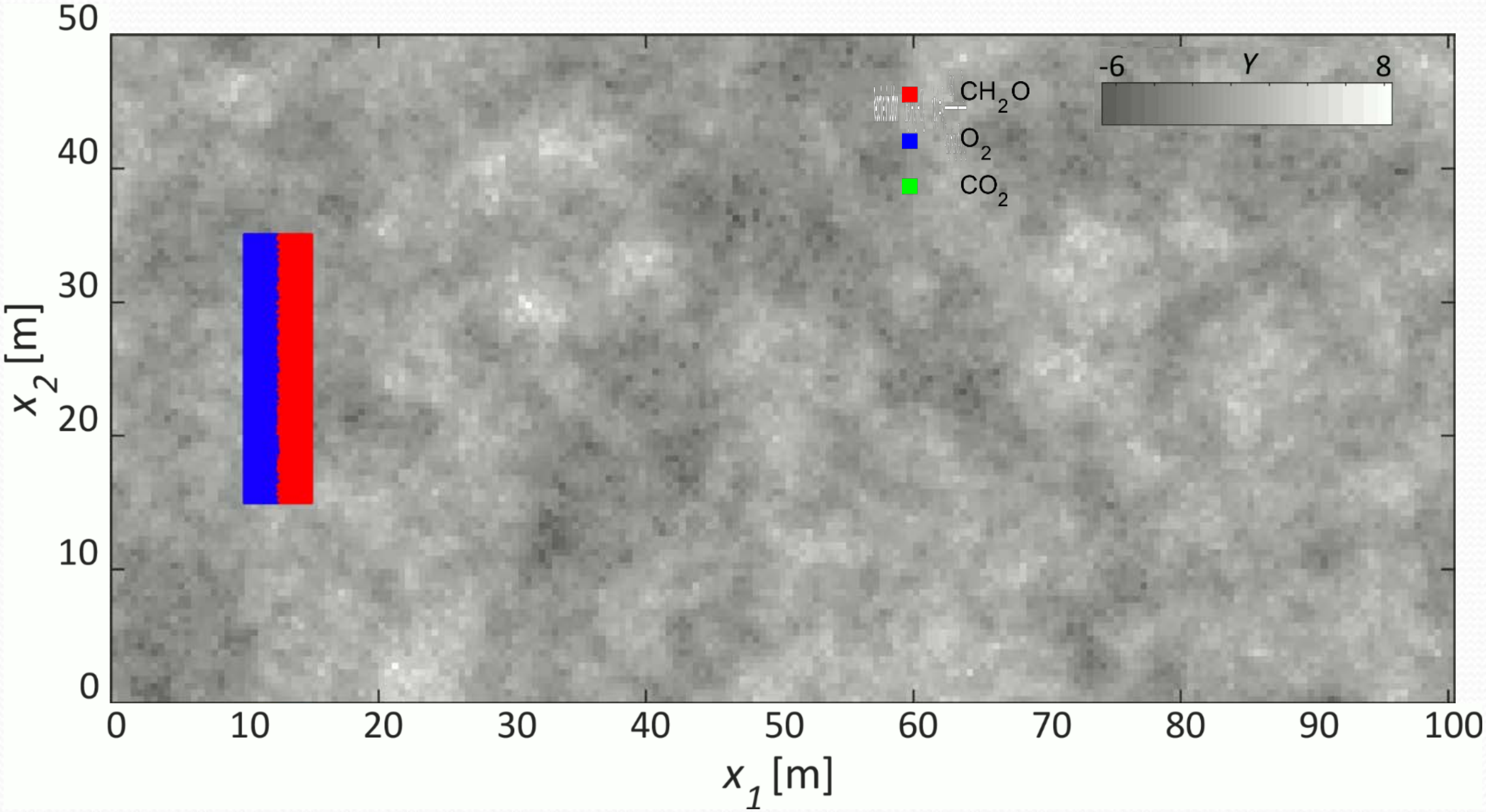
Reactive simulation: $CH_2O + O_2 \rightarrow CO_2 + H_20$, $r(\mathbf{x},t) = k_f \frac{c_{CH_2O}}{K_{CH_2O}+c_{CH_2O}} \frac{c_{O_2}}{K_{O_2}+c_{O_2}}$



Aerobic biodegration of organic an chemical compound. Dissolved organic carbon react with dissolved oxygen to form carbon dioxide

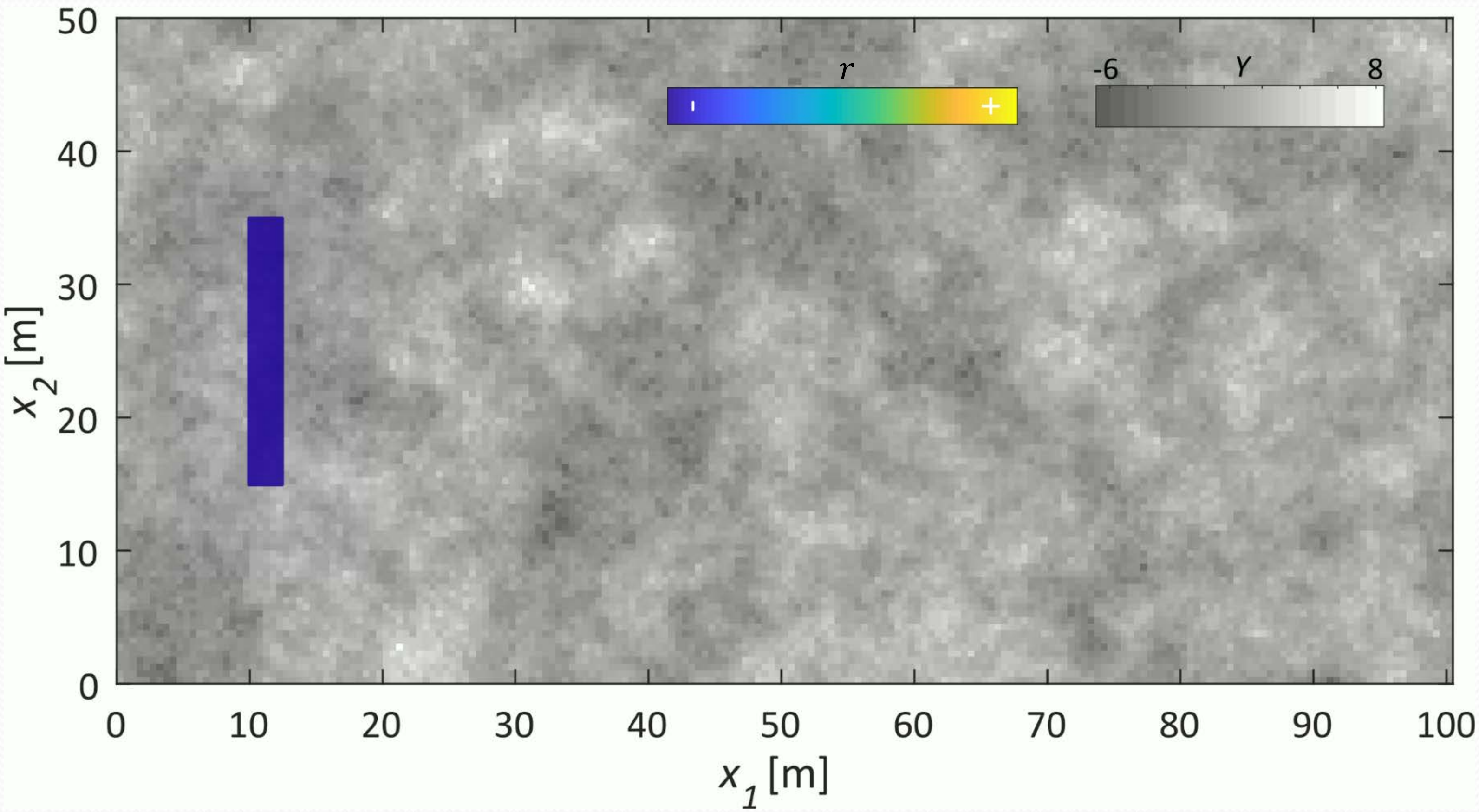
Organic chemical compound (CH_2O)

Reactive simulation: $CH_2O + O_2 \rightarrow CO_2 + H_2O$, $r(\mathbf{x}, t) = k_f \frac{c_{CH_2O}}{K_{CH_2O} + c_{CH_2O}} \frac{c_{O_2}}{K_{O_2} + c_{O_2}}$



Dissolved organic carbon react with dissolved oxygen to form carbon dioxide

Reactive simulation: $CH_2O + O_2 \rightarrow CO_2 + H_2O$, $r(\mathbf{x},t) = k_f \frac{c_{CH_2O}}{K_{CH_2O}+c_{CH_2O}} \frac{c_{O_2}}{K_{O_2}+c_{O_2}}$



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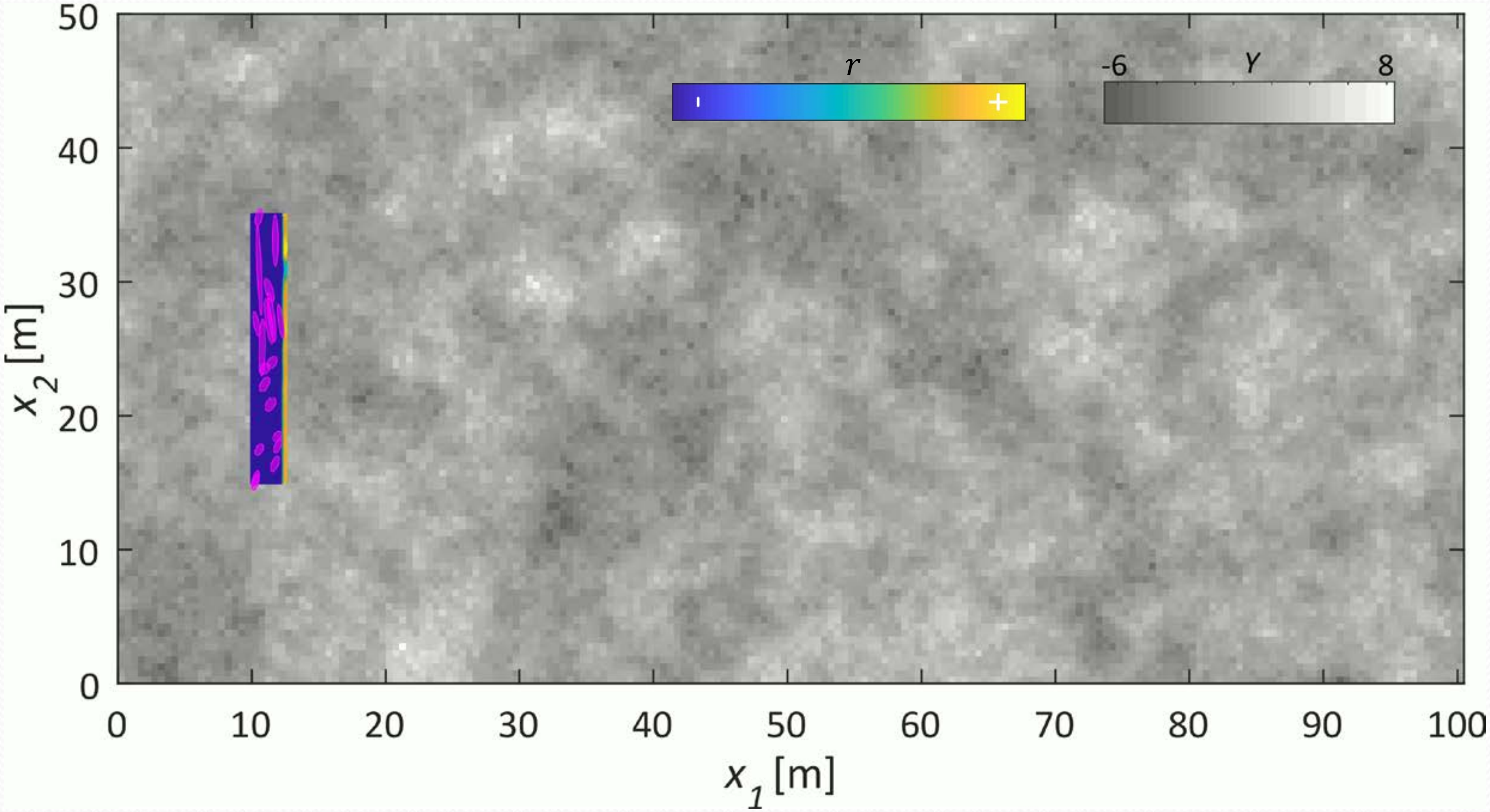


Assess the toxicity of groundwater samples

Assessment of toxicity of groundwater samples and potential toxicity synergisms due to multiple chemical exposure.

Ecotoxicity tests with *Daphnia magna* and *Danio rerio*, using ECs detected in Cremona and Bologna groundwater.

	Bologna		Cremona	
Composition	Concentration		Concentration	
	(mg/L)	mM	(mg/L)	mM
CaCO3	475	4.75	158.3	1.6
MgSO4	138	1.15	46.1	0.4
Ca(HCO3)2	673	4.15	224.2	1.4
NaCl	67	1.15	22.4	0.4
NaNO3	34	0.4	11.3	0.1
Humic acid (sodium salt)	5		5	5
	µg/L		µg/L	
tetrachloroethylene (PCE)	30		10.0	
NaF	75		25	
(NH4)OH	100		33.3	
H3BO3	800		266.7	

Anthropogenic contaminants

PCE could not be used since it was not possible to dissolve it in water with or without solvents (the amount of solvent within the test system must not exceed 10%)

Bologna and Cremona water – EC one by one

LC_{50} values (i.e. concentration causing 50% effect on mortality, mg/L, and confidence intervals registered after exposing *Daphnia*) for 48h.

ECs when occur in the Cremona groundwater appear to cause higher toxicity to *Daphnia magna*

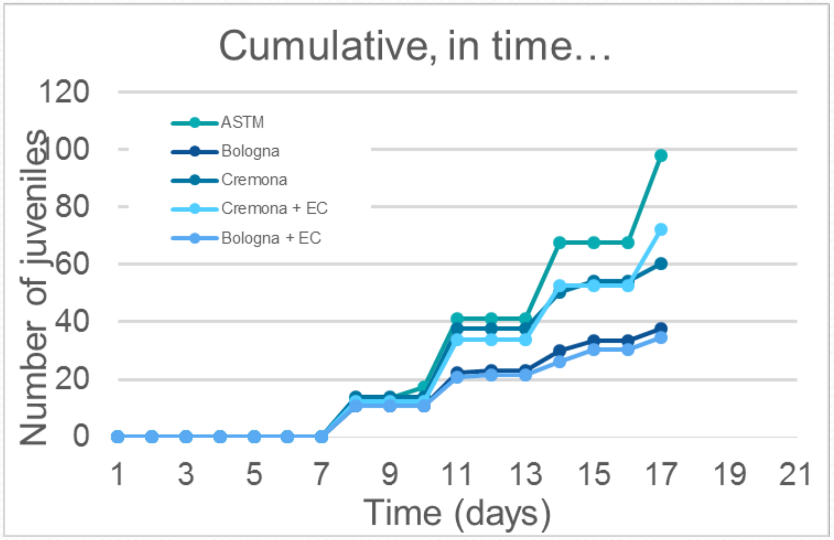
	ASTM	CREMONA	BOLOGNA
Boric acid	705.73 (479.49-792.14)	668.4 (632.52- 706.97)	686.5 (651.17- 724.95)
Ammonium hydroxide	99.31 (89.54-108.91)	111.2 (107.63- 114.95)	322.6 (293.01-359.54)
NaF	649.4 (553.33-808.26)	508.06 (487.88- 529.77)	587.62 (538.22-646.05)
Acetaminophen	2.66 (n.d.)	3.26 (2.91-3.64)	4.52 (3.83-5.37)
Triclosan	*	0.98 (0.9-1.1)	1.43 (1.27-1.69)
Phenanthrene	*	>2.83	2.73 (2.28-2.90)
PFOA	*	428.7 (363.7-506.9)	*

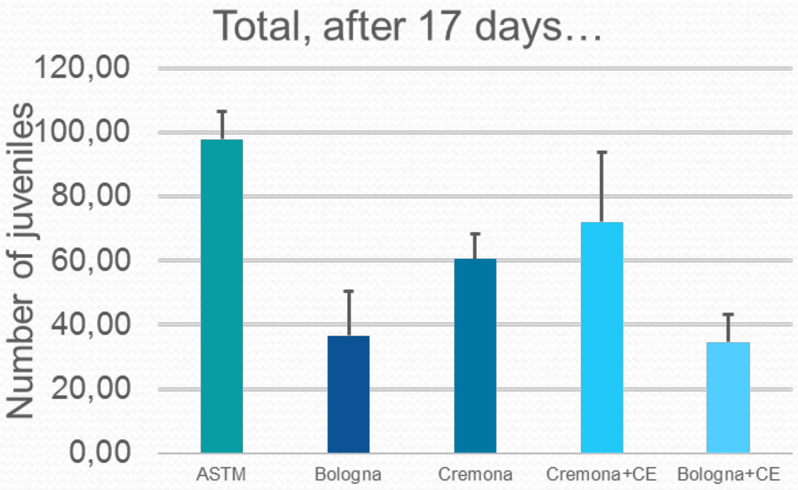
Results indicate that the lower concentration of water constituents in the Cremona water are possibly responsible for the increased toxicity observed in most of the ECs tested.

* On going, as well as with the compound PFOS

ASTM medium (standardized media, as control)

Chronic toxicity experiments in *Daphnia magna* testing four-component mixtures (Boric acid, NaF and Ammonium hydroxide). Similar results with *Danio rerio*





with contaminants

The composition of the Bologna water induced the production of less juveniles than ASTM or Cremona, no differences were attained with the introduction of ECs

WE-NEED

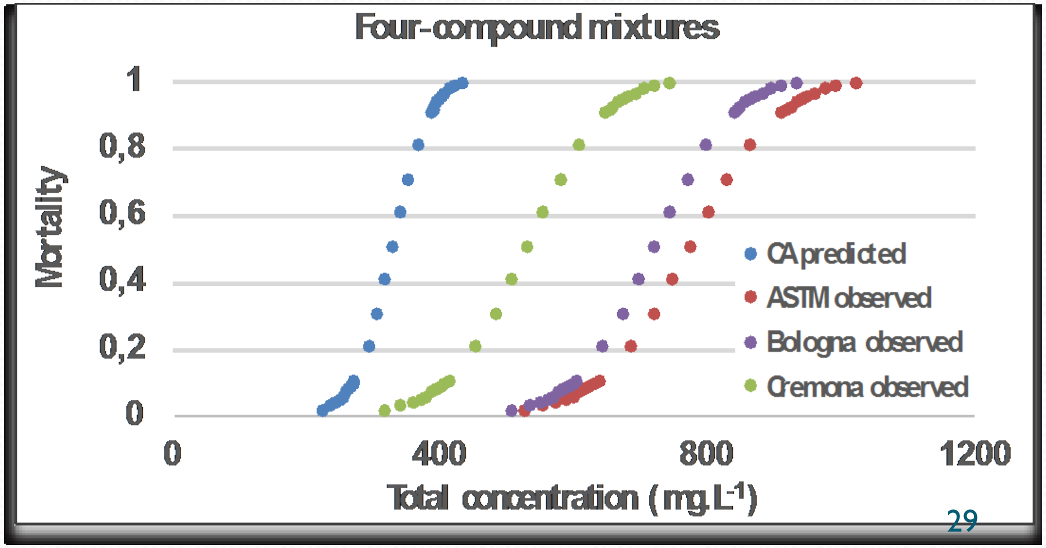
Complex Mixtures

Experimental design for acute toxicity experiments in *Daphnia magna* testing four-component mixtures containing boric acid, ammonium hydroxide, sodium fluoride and acetaminophen.
Fixed-ratio design based on TU (Toxic Unit) derived from ASTM data.

Mixture	Boric acid ($mg.L^{-1}$)	Ammonium hydroxide ($mg.L^{-1}$)	Sodium fluoride ($mg.L^{-1}$)	Acetaminophen ($mg.L^{-1}$)	∑ TU
M1	5.51	0.70	4.13	0.02	0.03125
M2	11.02	1.41	8.26	0.04	0.0625
M3	22.04	2.82	16.52	0.08	0.125
M4	44.09	5.64	33.05	0.17	0.250
M5	88.17	11.27	66.09	0.33	0.5
M6	176.34	22.54	132.18	0.67	1
M7	264.52	33.82	198.27	1.00	1.5
M8	352.69	45.09	264.37	1.33	2
M9	705.37	90.18	528.73	2.66	4
M10	1410.75	180.35	1057.46	5.32	8

Concentration Addition (CA) conceptual model

CA-predicted vs observed acute toxicity four-compound mixture *Daphnia magna*



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Stakeholder/Industry engagement

ARPAE Emilia Romagna, Consorzio Irrigazioni Cremonesi and Consorzio di Bonifica Dugali, Naviglio, Adda Serio are intensively involved in WE-NEED .

Metropolitana Milanese and Lario Reti Holding, dealing with the integrated water services for the city of Milano and the province of Lecco (Italy), respectively.

In collaboration with the Municipality of Milano we are also organizing a series of events aimed to increase in the population the awareness of the need of rational management and protection tools for water resources.

Israel Water Authority

WE-NEED

Deliverables completed

D1.1 Provision of storage and curation of data (Polimi, April 2017)
D1.2 Report on new sub-Gaussian Models (Polimi, April 2017)
D1.3 Software to generate unconditional and conditional sub-Gaussian fields (Polimi, October 17)
D1.4a Report on characterization of field sites (Polimi, October 2017)
D2.1 Report on particle tracking methods for complex non-linear problems (UPC, October)
D3.1 Report on detection and characterization protocols of the selected ECs including detailed sample preparation for analysis, analytical methods and parameters used for characterization (Weizmann, October 2017)
D3.2 Report on application of the analytical methods of the selected ECs in complex matrices, including sample preparation (Weizmann, October 2017)
D3.3a Report on transport experiments including modeling and analysis (Weizmann, May 2018)
D4.1 Report on EC toxicities from bibliography and laboratory experiments (Aveiro, April 2017)
D4.2 Report on the toxicity of samples from the two field sites (Aveiro, October 2017)

WE-NEED

Dissemination

13 papers - ISI Journals

1. Bianchi Janetti E., M. Riva, A. Guadagnini (2017) Effects of Pore-Scale Geometry and Wettability on Two-Phase Relative Permeabilities within Elementary Cells, *Water,* 9, 252.
2. Dell'Oca A., M. Riva, A. Guadagnini (2017) Moment-based Metrics for Global Sensitivity Analysis of Hydrological Systems, *Hydrol. Earth Syst. Sci*., 21, 6219–6234.
3. Dell'Oca A., M. Riva, J. Carrera, A. Guadagnini (2018) Solute dispersion for stable density-driven flow in randomly heterogeneous porous media, *Adv*. *Water Res*, 111, 329–345.
4. Hassane Maina F., P. Ackerer, A. Younes, A. Guadagnini, B. Berkowitz (2017) Benchmarking numerical codes for tracer transport with the aid of laboratory-scale experiments in 2D heterogeneous porous media, *J. Contam. Hydrol*., in press.
5. Guadagnini A., M. Riva, S.P. Neuman (2018) Recent Advances in Scalable Non-Gaussian Geostatistics: The Generalized Sub-Gaussian Model, Journal of Hydrology, in press.
6. Libera A., de Barros F.PJ, M. Riva, A. Guadagnini (2017) Solute concentration at a well in a non-Gaussian aquifer under constant and time-varying pumping schedule, *J. Contam. Hydrol*., 205, 37-46.
7. Riva M., A. Guadagnini, S.P. Neuman (2017) Theoretical analysis of non-Gaussian heterogeneity effects on subsurface flow and transport, *Water Resour. Res*., 53(4), 2298-3012.
8. Rodríguez-Escales P., D. Fernàndez-Garcia, J. Drechsel, A. Folch, X. Sanchez-Vila (2017) Improving degradation of emerging organic compounds by applying chaotic advection in Managed Aquifer Recharge in randomly heterogeneous porous media, *Water Resour. Res*., 53.
9. Sanchez-Vila X., D. Fernàndez-Garcia (2016) Debates: Stochastic subsurface hydrology from theory to practice—Why stochastic modeling has not yet permeated into practitioners?, Water Resources Research 52.
10. Stepka, Z., I. Dror, B. Berkowitz (2017) The effect of nanoparticles and humic acid on technology critical element concentrations in aqueous solutions with soil and sand, *Sci. Total Environ.*, 610-611, 1083-1091.
11. Sole-Mari G., D. Fernàndez-Garcia, P. Rodríguez-Escales, X. Sanchez-vila. (2017), A KDE-based random walk method for modeling complex kinetic reactions in porous media, *Water Resources Research*, 53, 9019–9039.
12. Ding, D., Benson, D. A.,Fernàndez-Garcia, D., Henri, C. V.,Hyndman, D. W., Phanikumar, M. S., and Bolster, D. (2017). Elimination of the reaction rate ''scale effect'': Application of the Lagrangian reactive particle-tracking method to simulate mixing-limited, field-scale biodegradation at the Schoolcraft (MI,USA) site. Water Resources Research, 53,10,411–10,432.
13. Yecheskel, Y., I. Dror and B. Berkowitz (2018). Silver nanoparticle (Ag-NP) retention and release in partially saturated soil: Column experiments and modelling*, Environ. Sci.: Nano*, 5, 422-435.

Oral – Poster presentations in 15 international conferences – workshops

5 PhD Students, 6 MSc Students

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Outreach Activities

Public presentations: *Meetmetonight* (Milano, Sept 30th, October 1st 2016), *WordWater day* (Milano, March 22, 2017), *Stockholm Junior Water Prize 2017* (August 2017, Stockholm, Sweden), *Watec 2017*, Water Technology & Environment Control, Exhibition & Conference. (September 2017, Tel Aviv, Israel).

Laboratories: "Traveling with water" laboratory activity for primary/middle school students, with small experimental facilities to illustrate subsurface flow and transport processes and groundwater contamination (Polimi, April 3th, 10th, March 8th , 30th 2017). A lecture and laboratory activity for middle school students on transport of pharmaceuticals in the environment (Davidson Institute of Science Education, August 1st-2nd, 2017).

Mentor of high school students: Catalytic Degradation of Organic Contaminants in Water by Gold Nanoparticles and Hydrogen Peroxide (Davidson Institute of Science Education, 2016), Catalytic Ozonation of halogenated contaminants in water (Davidson Institute of Science Education, 2017), Gd-DTPA transport in soil (Davidson Institute of Science Education, 2017).


research&innovation

Sustainable groundwater management

European project looks at impact of new pollutants

MONICA RIVA, WE-NEED PROJECT COORDINATOR

Recent debate surrounding PFASs - chemicals used in industrial processes which are extremely persistent and do not readily degrade - brought the problem of groundwater contamination back into the headlines.

Groundwater is a strategic water source in Europe and mismanaging it could cause enormous damage to the environment and society.

For this reason, a group of scientists are seeking innovative ways of managing precious groundwater resources - such as springs and aquifers from which drinking water is pumped to the surface - in a sustainable way.

The project on which the European pool of researchers is working is called WE-NEED, led by the Department of Civil and Environmental Engineering at Politecnico di Milano.

"We are looking at how vulnerable groundwater is to new contaminants like PFASs," explained project coordinator Monica Riva, "and we are using probability theory to develop new and innovative ways to manage water resources and protect them from pollution. Our approach allows us to assess the risk of contaminants impacting the quality of groundwater and damaging the ecosystem."

PLATINUM n.60,
"Il Sole24Ore"

WE-NEED

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www.we-need.polimi.it

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GOBIERNO DE ESPAÑA
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FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

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