# Sources and Fate of Geogenic Arsenic in Groundwater

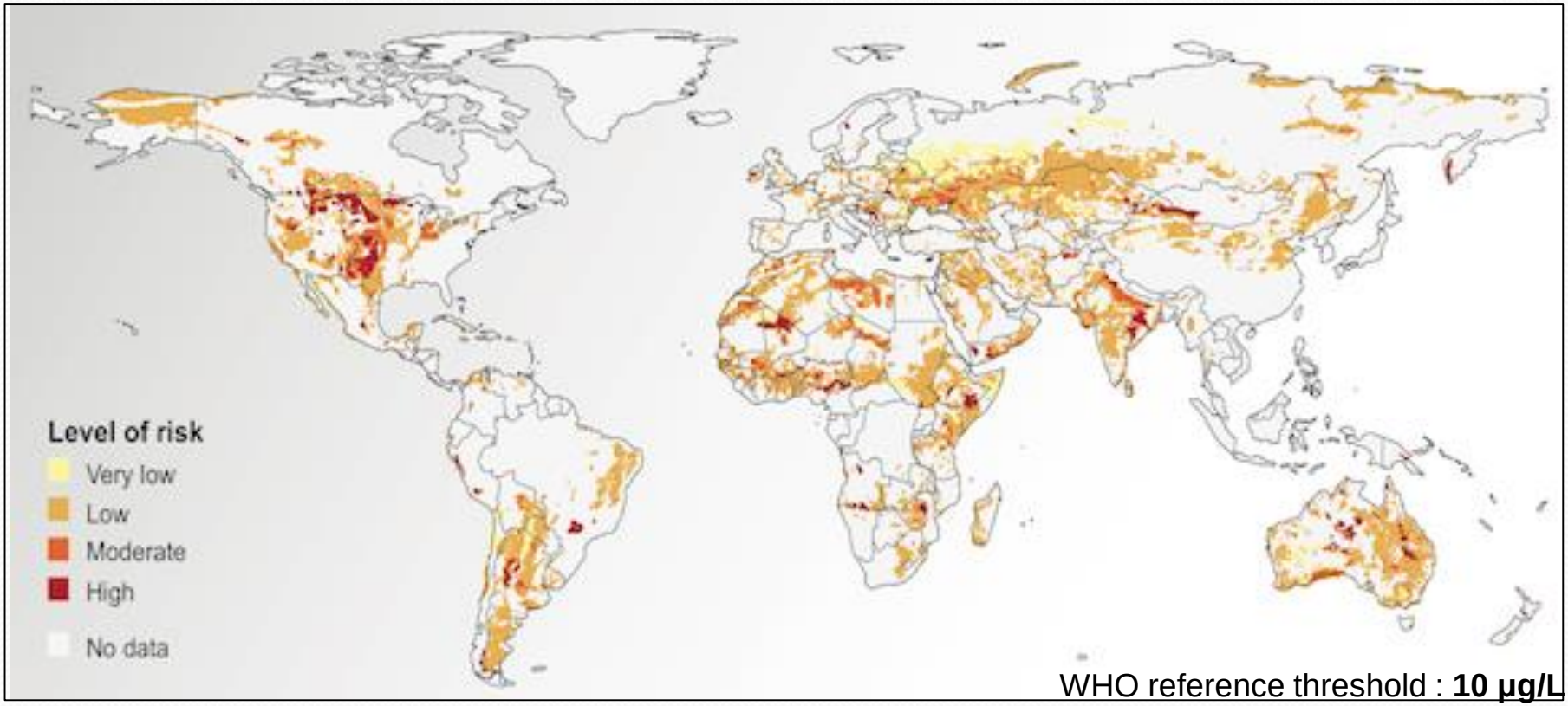
## a Focus on the Case Study of Lecco

## WE-NEED


Giulia Ceriotti
Julie Regis
Alberto Guadagnini

# Arsenic around the World

140 million people are exposed to arsenic contamination




WHO reference threshold : **10 µg/L**

# Arsenic around the World

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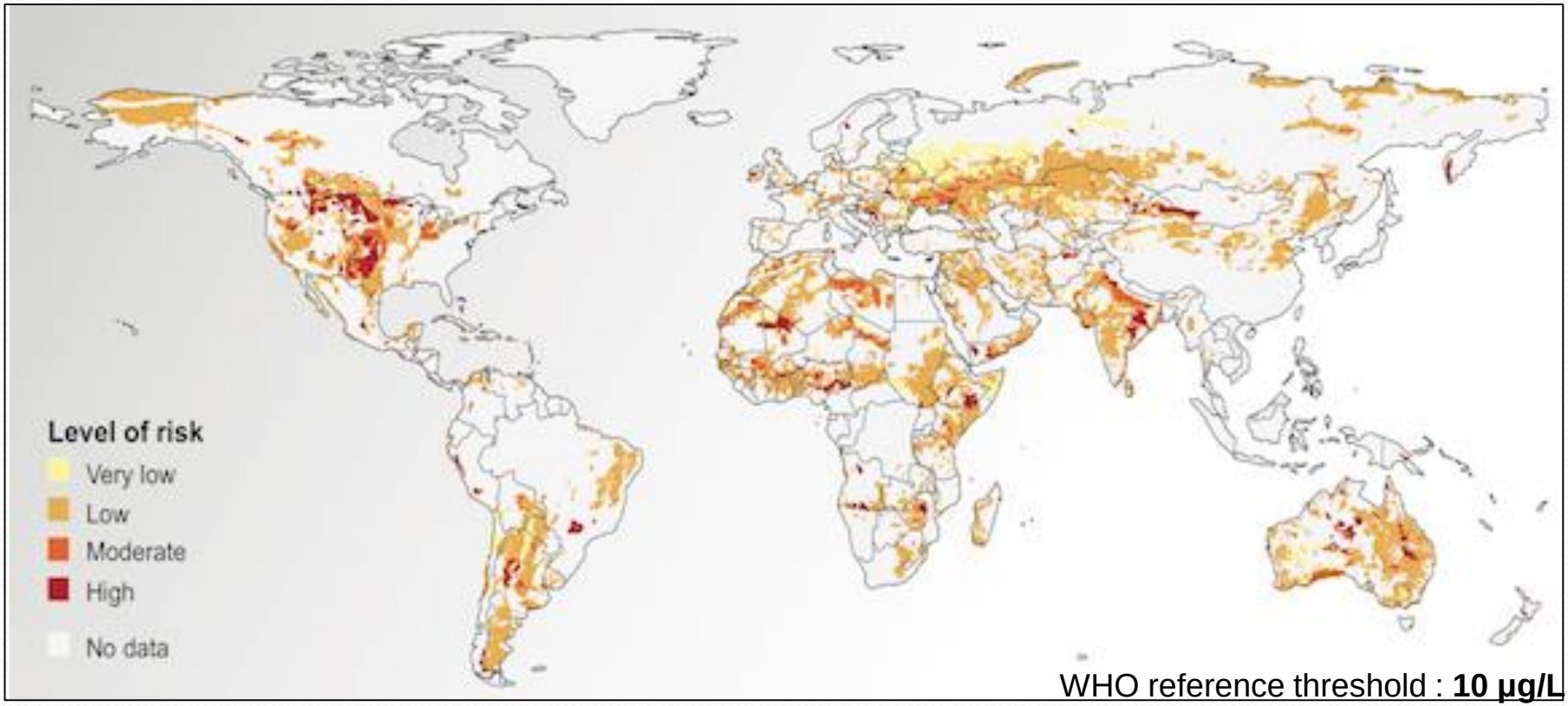
Forms of arsenic in groundwater: As(III) and As(V) are toxic

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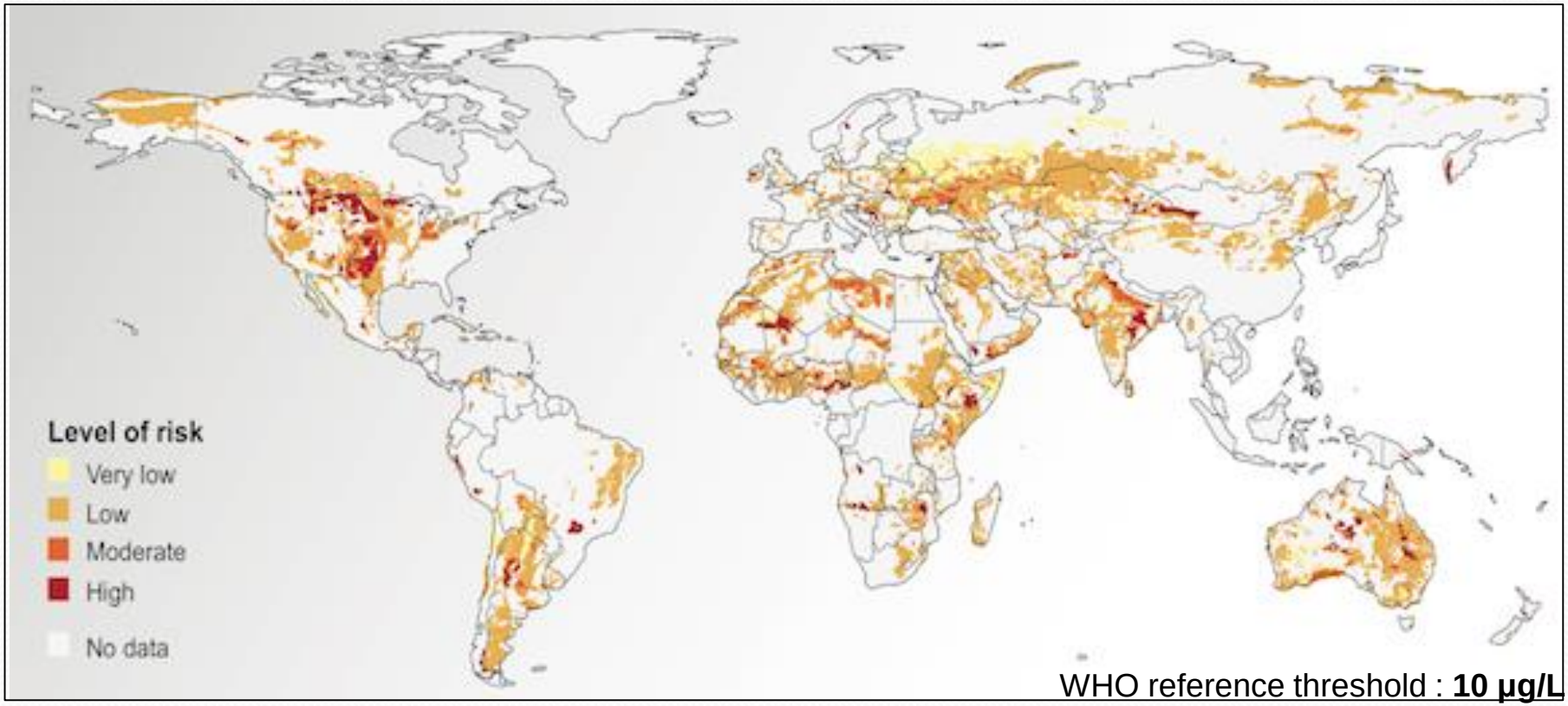
**Aim:** To identify Arsenic sources and control the contamination is one of the most important modern challenges.

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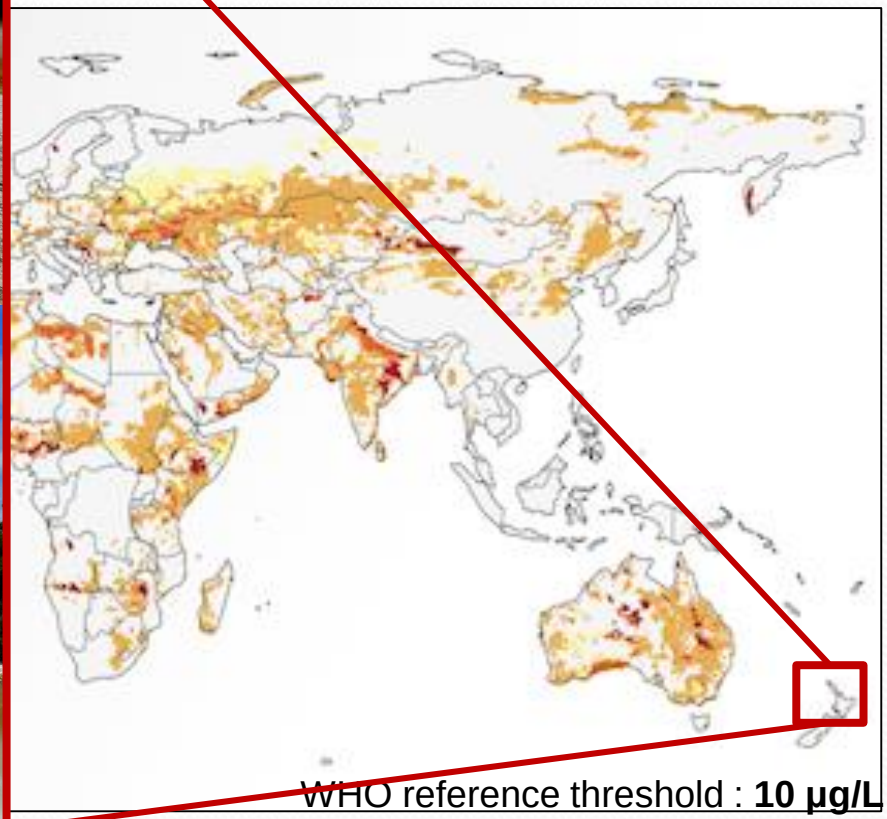
# Origin of Arsenic around the World

- Hydrothermal Fluids
  e.g., New Zealand



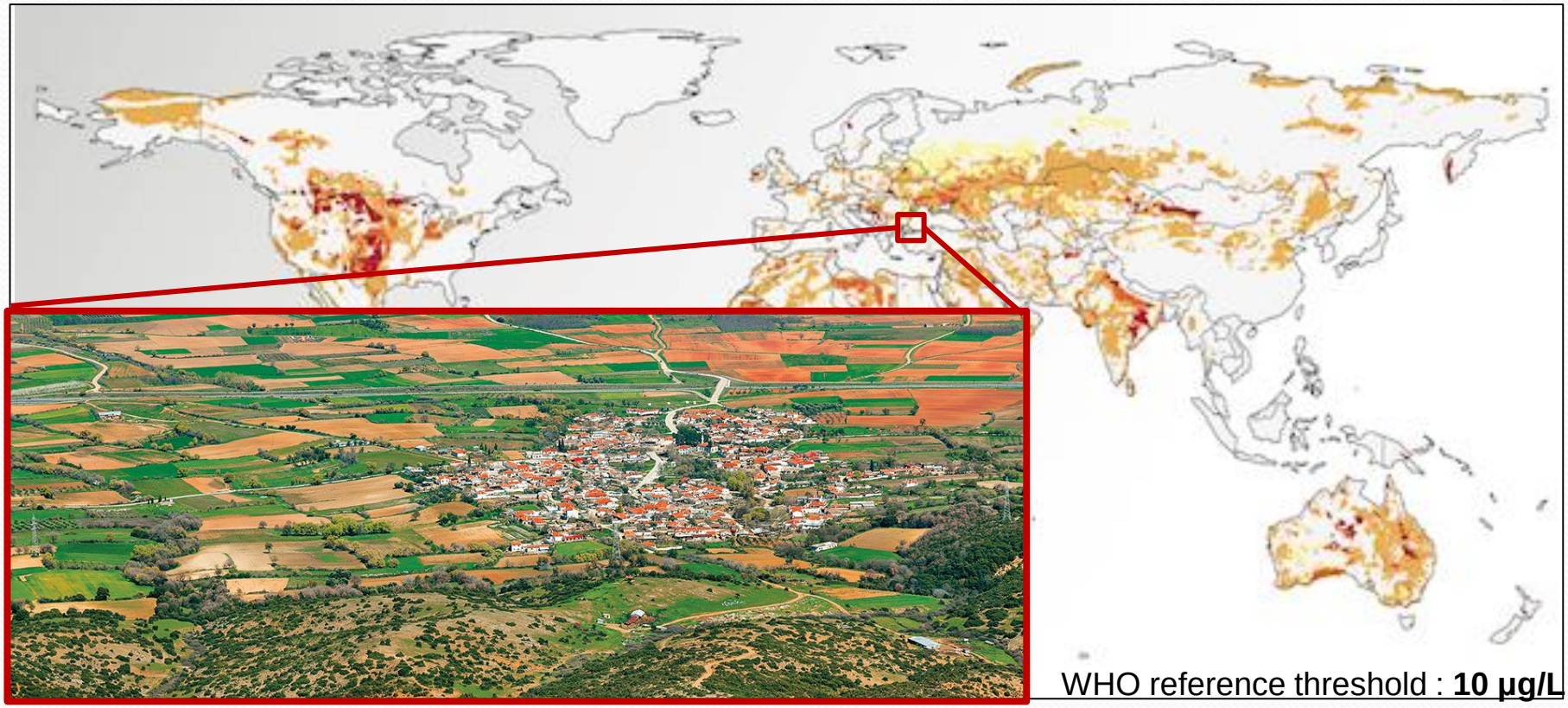
WHO reference threshold : **10 µg/L**

New Zealand Hydrothermal waters: **8500 µg/L**

**Robinson et al. (2006)**

# Origin of Arsenic around the World

- Anthropic Contamination
  e.g., Greece
- Hydrothermal Fluids
  e.g., New Zealand



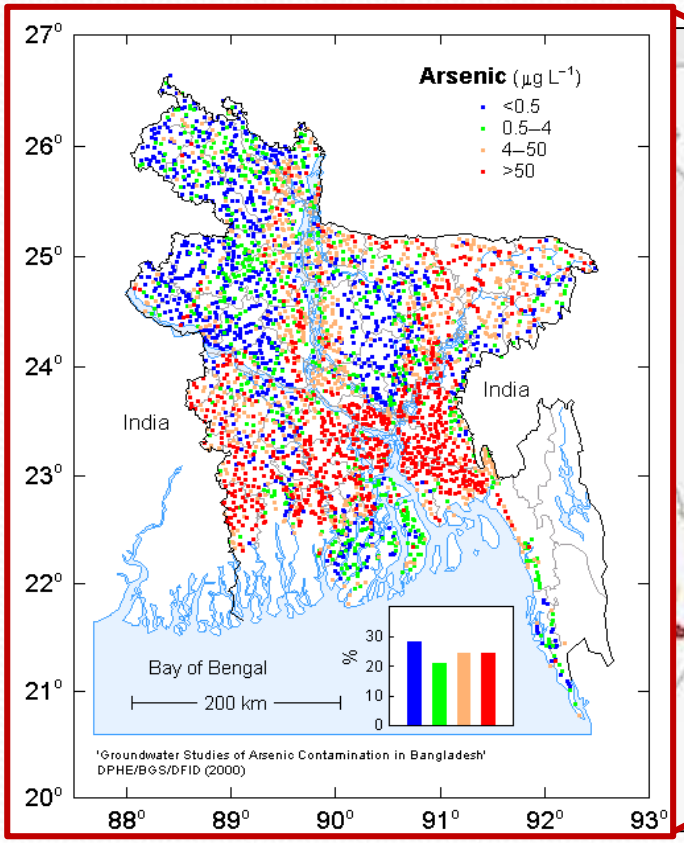
WHO reference threshold : **10 µg/L**

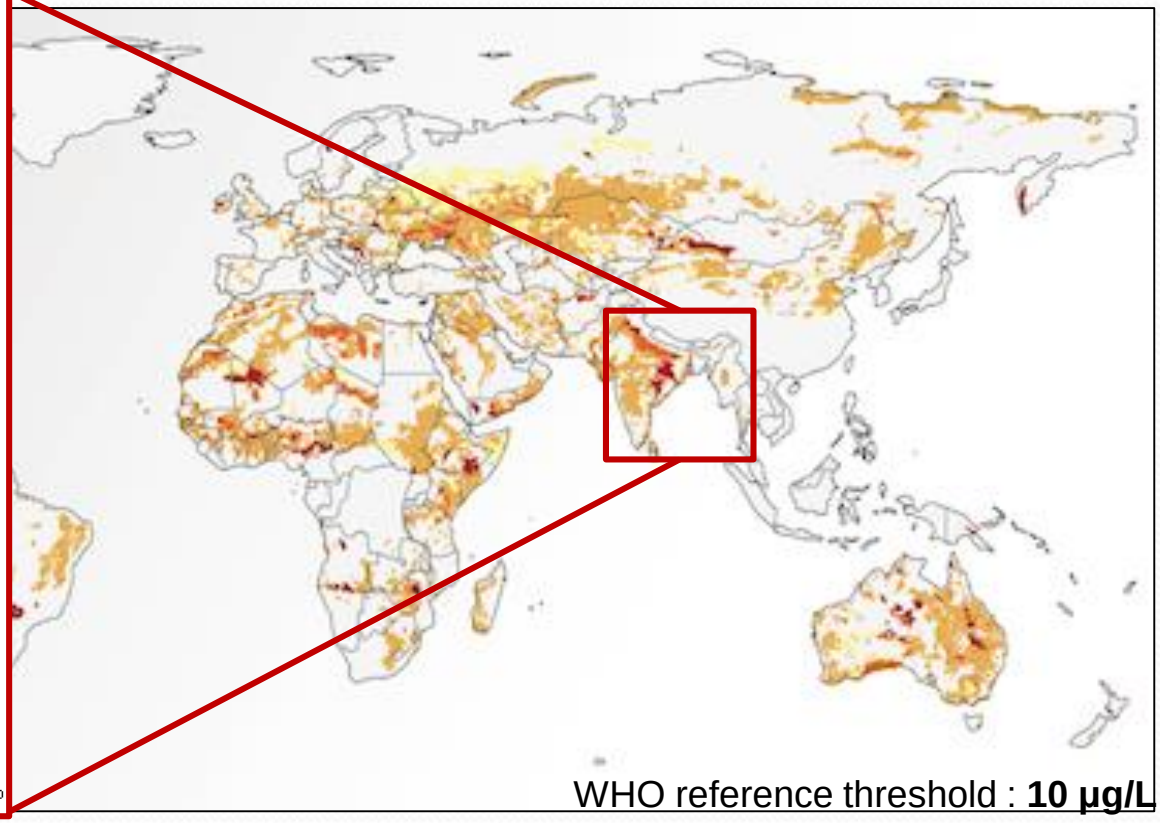
Greek groundwater: **250 µg/L**

**Mukherjee et al. (2006)**

# Origin of Arsenic around the World

- ❑ Geochemical Mobilization
  e.g., Bengala Basin
- ❑ Anthropic Contamination
  e.g., Greece
- ❑ Hydrothermal Fluids
  e.g., New Zealand



WHO reference threshold : **10 µg/L**

Bangladesh groundwater: **>200 µg/L**

**Hossain et al. (2015)**

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- ❑ Geochemical Mobilization
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  e.g., Greece
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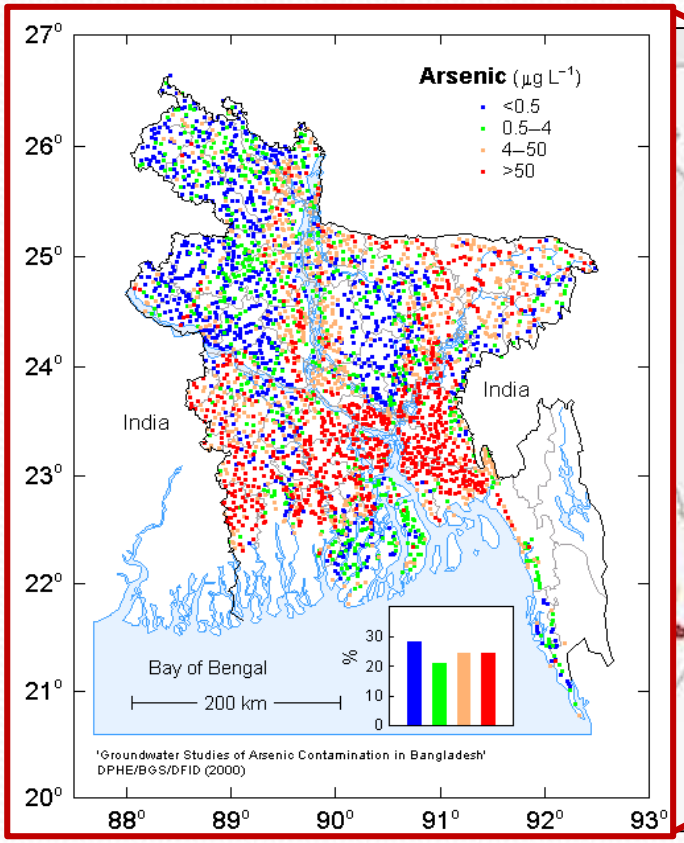
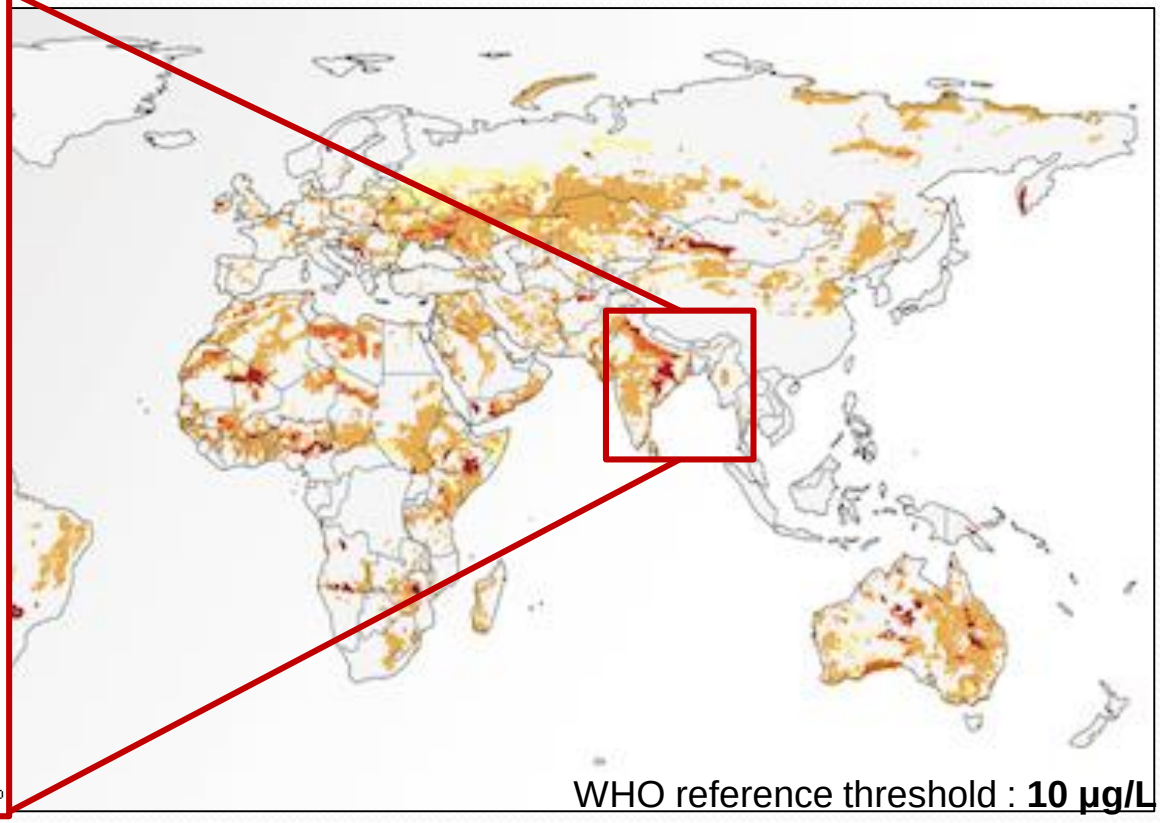
Occurrence of specific conditions that mobilize arsenic through geochemical processes.



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# Geochemical Mobilization of Arsenic

**Reductive Dissolution of Iron-oxides**

Iron-oxides

Iron-reducing Bacteria

# Geochemical Mobilization of Arsenic

## Oxidation of Pyrites

Pyrite
&
Arsenopyrite

Oxidizing
Conditions
($O_2$, Nitrates or $Fe^{3+}$)

## Reductive Dissolution of Iron-oxides

Iron-oxides

Iron-reducing
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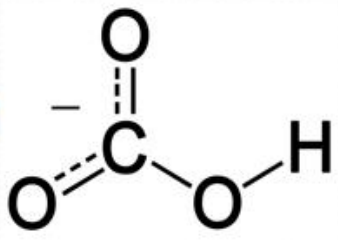
## Dissolution of Arseno-sulphides

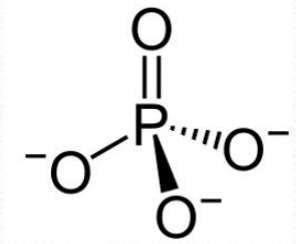
Arseno-Sulphides




Alkalinity

## Ion Exchange / Arsenic Desorption

Arsenic Adsorbents:
Metal-oxides,
Clays,
Carbonates,
Silicates
& humic substances




Competitive ions:
Phosphates,
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Change pH/Eh

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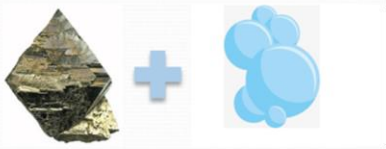
**Oxidation of Pyrites**



Pyrite & Arsenopyrite

Oxidizing Conditions ($O_2$, Nitrates or $Fe^{3+}$)

**Reductive Dissolution of Iron-oxides**

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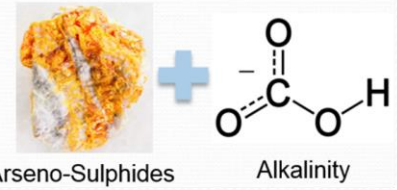
**Dissolution of Arseno-sulphides**




Arseno-Sulphides

Alkalinity

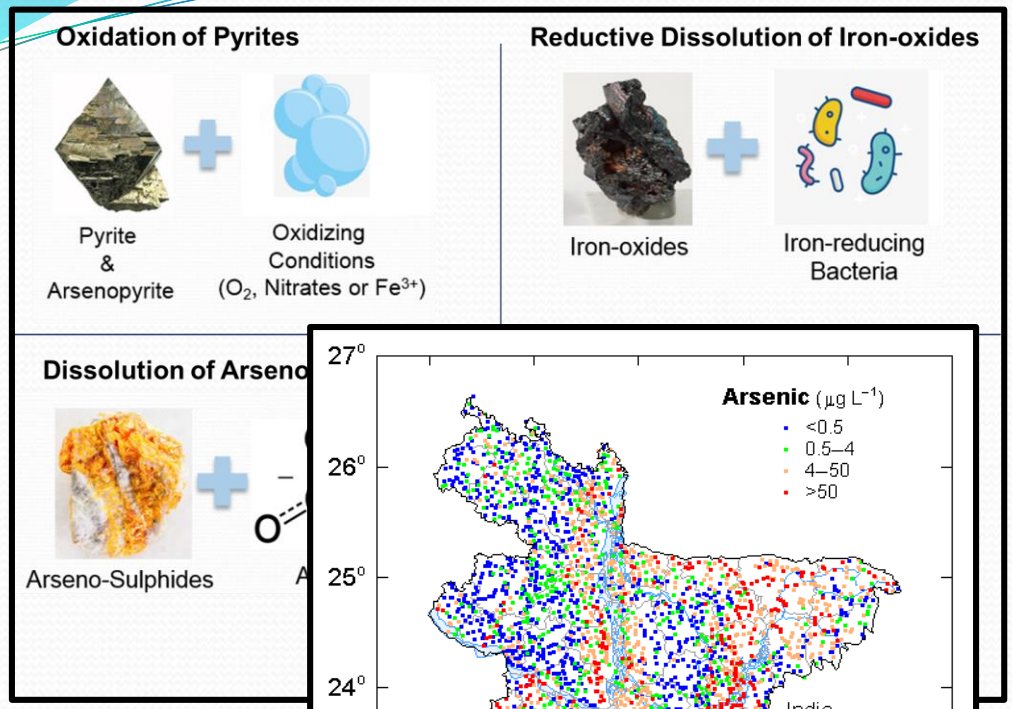
**Ion Exchange / Arsenic Desorption**

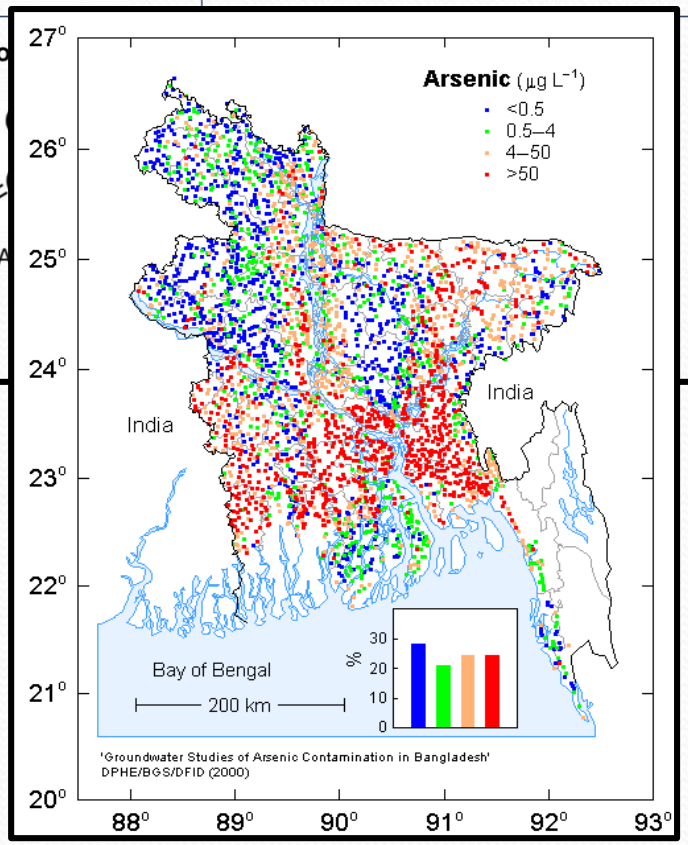

Arsenic Adsorbents: Metal-oxides, Clays, Carbonates, Silicates & humic substances

Competitive ions: Phosphates, Bicarbonates, Silica. or Change pH/Eh

- Many diverse type of mechanisms
- Any value of pH and Redox Potential
- Sources and sinks
- Both As(III) and As(V) are toxic, mobile and reactive

# Geochemical Mobilization of Arsenic

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Water JPI

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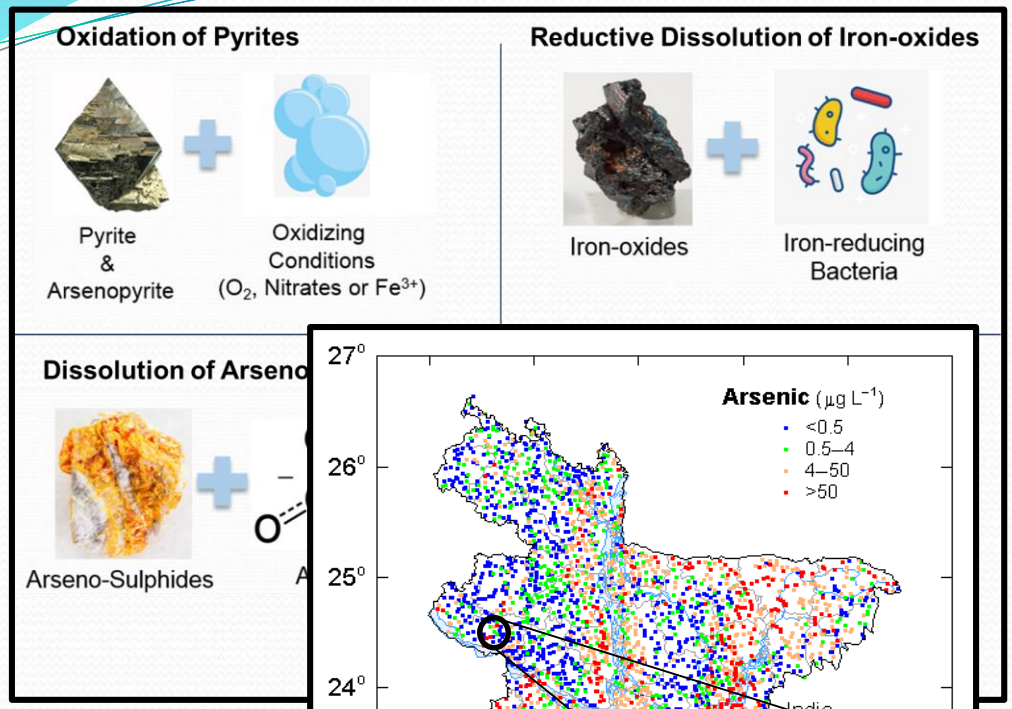


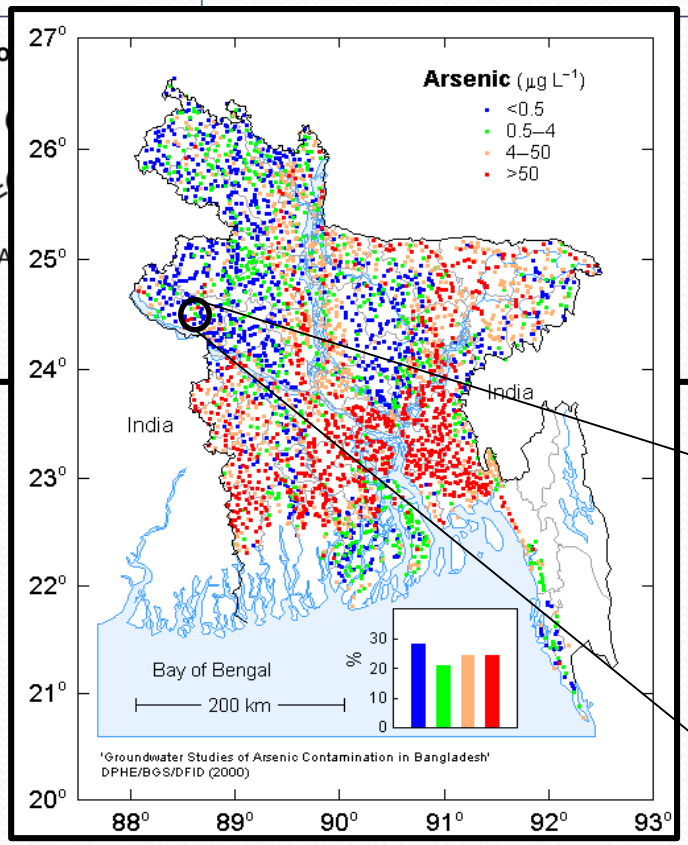


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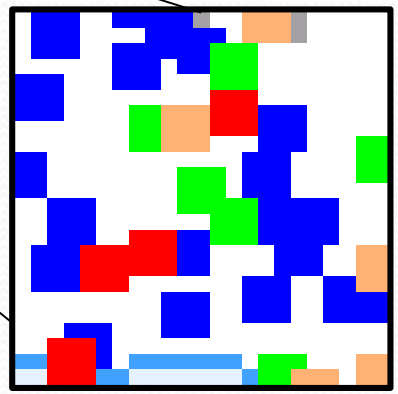

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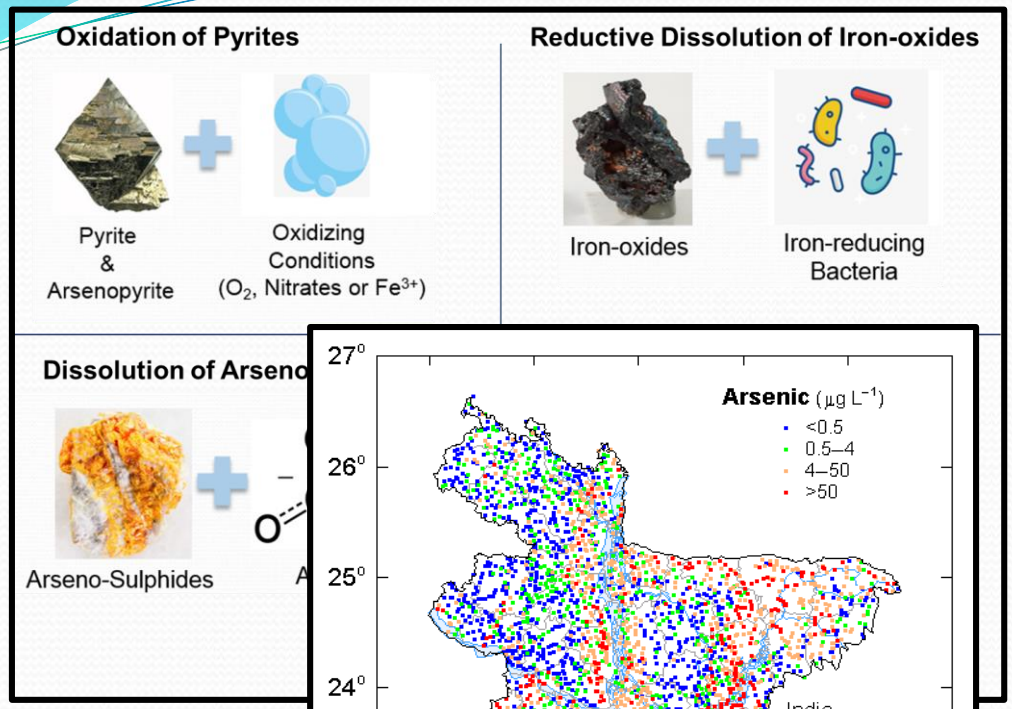


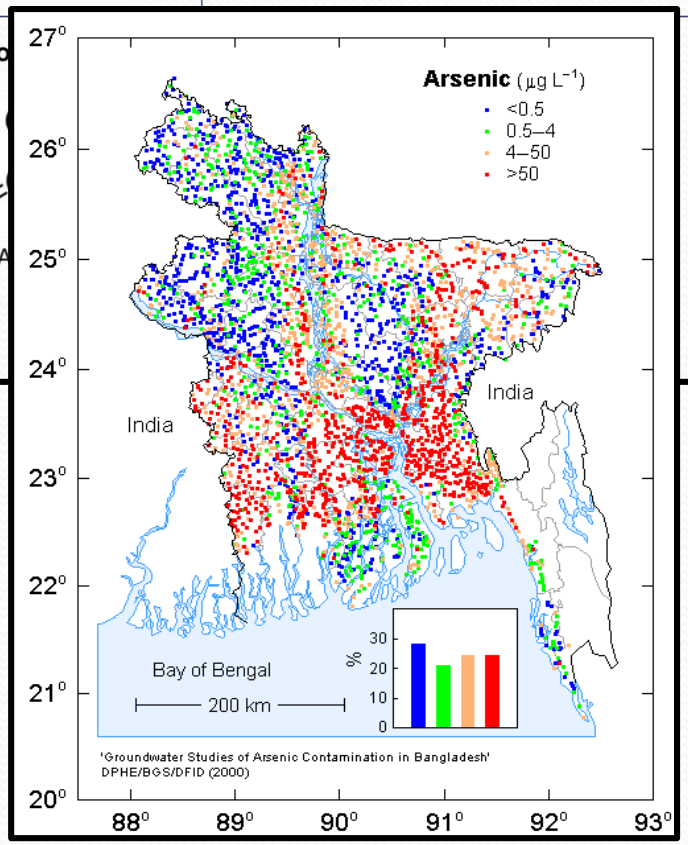


- Many diverse type of mechanisms
- Any value of pH and Redox Potential
- Sources and sinks
- Both As(III) and As(V) are toxic, mobile and reactive
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Each site is UNIQUE and identifying the source of arsenic is markedly challenging

Water JPI

# The Project Planning

Collect all existing data on the case study of interest

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Gan et al. 2014; Duan et al., 2017; Nickson et al., 2000, McArthur et al., 2001; Angelone et al., 2008; Armienta et al., 2001; Bondu et al., 2018; Bundschuh et al., 2004; Hafeznezami et al., 2016; Jia et al., 2014; Aiuppa et al., 2006; Moncur et al., 2015; Patel et al., 2019; Price and Pichler et al., 2006; Ravenscroft et al., 2005; Romic et al., 2011; Rowland et al., 2011; Sappa et al., 2014; Sengupta et al., 2014; Smedley et al., 1996; Smith et al., 2003; Welch et al., 2000; Zhou et al., 2017; Schaefer etal., 2016; Appleyard et al., 2006; Carraro et al., 2013; Chakraborty et al., 2015; Vega et al., 2017; Harvey et al., 2006; Jia et al., 2014; Pi et al.,2018

Interpretation of geochemical data available

Select a compatible source mechanisms

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Interpretation of geochemical data available

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Modeling arsenic mobilization and transport in the case study

- Check if we reproduce the spatial distribution of arsenic
- Predict arsenic where no sampling are available
- Define strategies for future water supply

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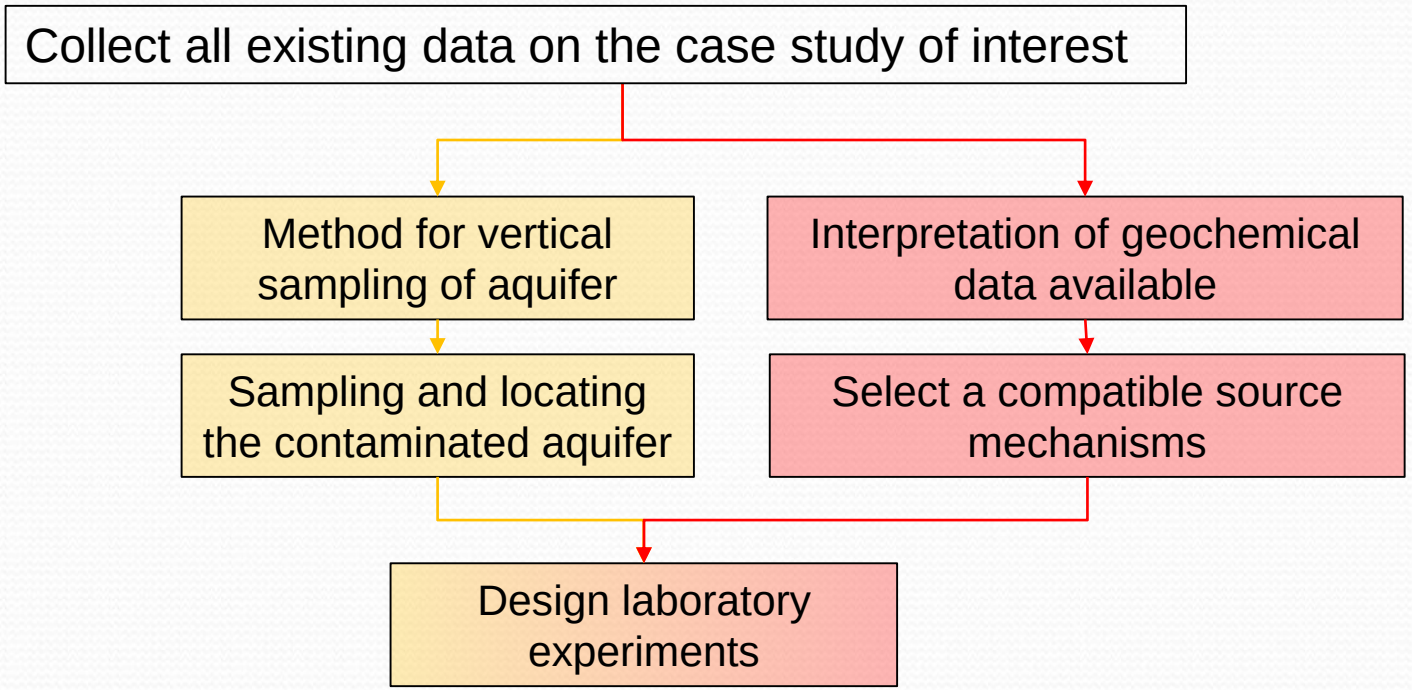


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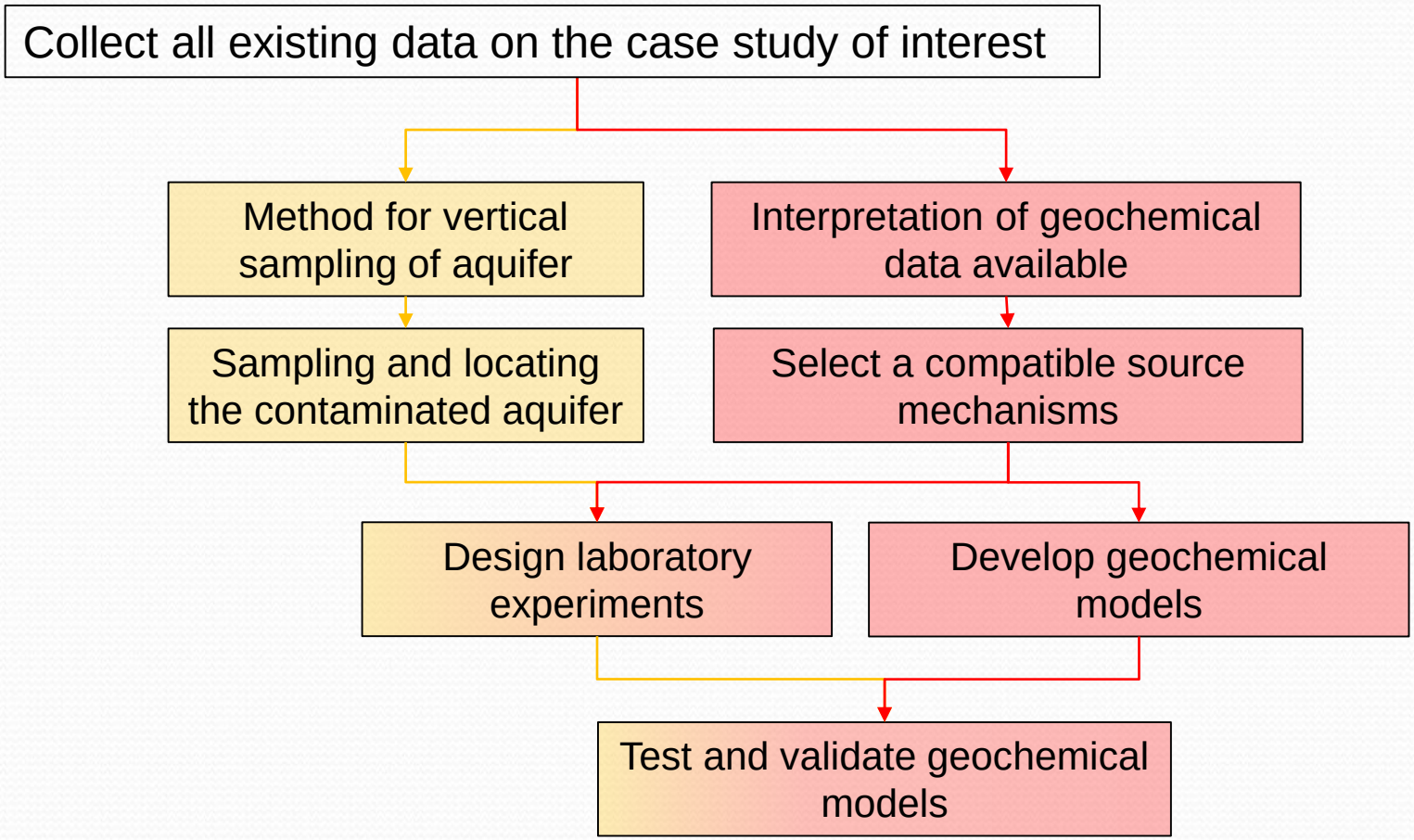


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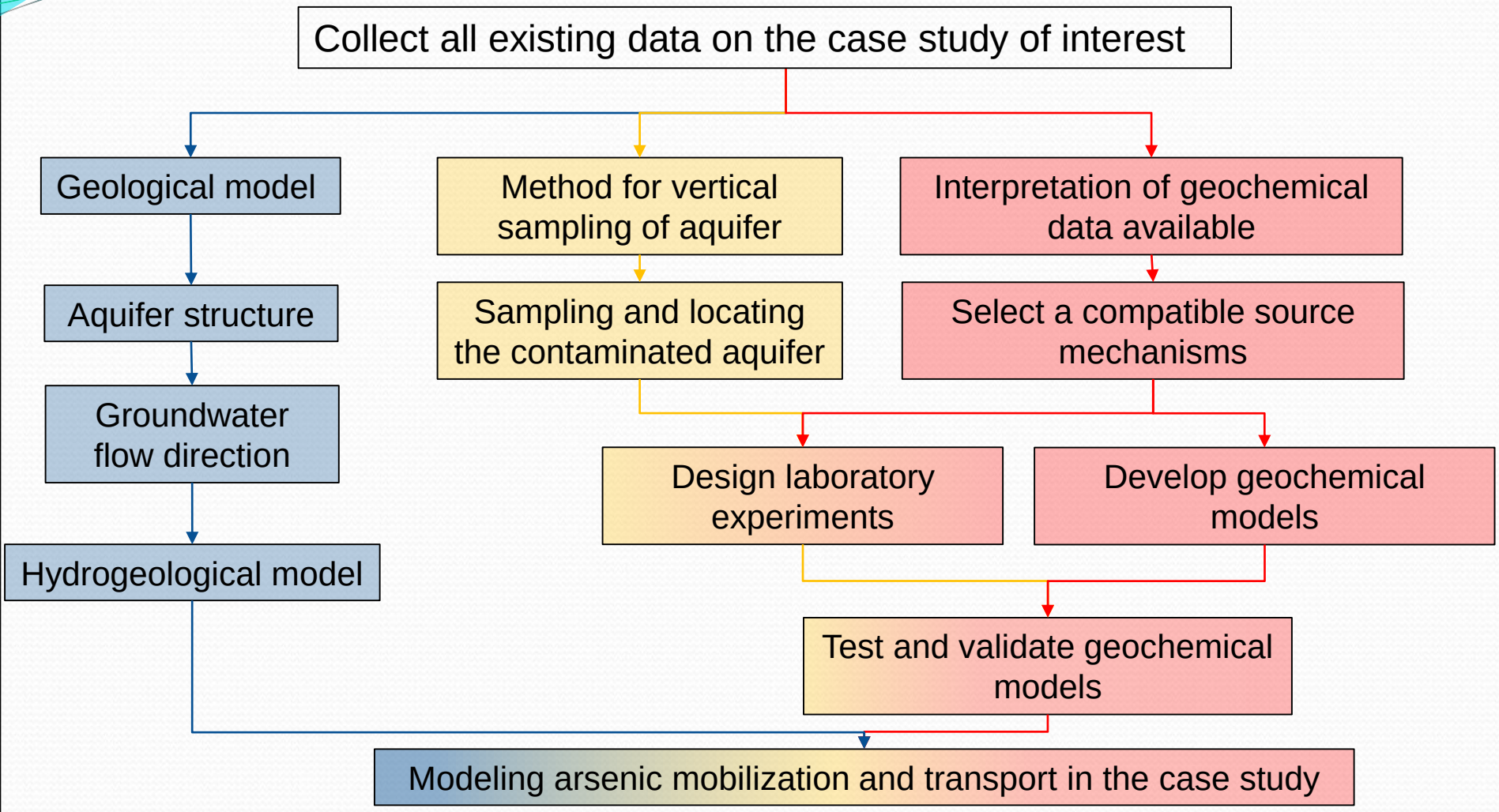


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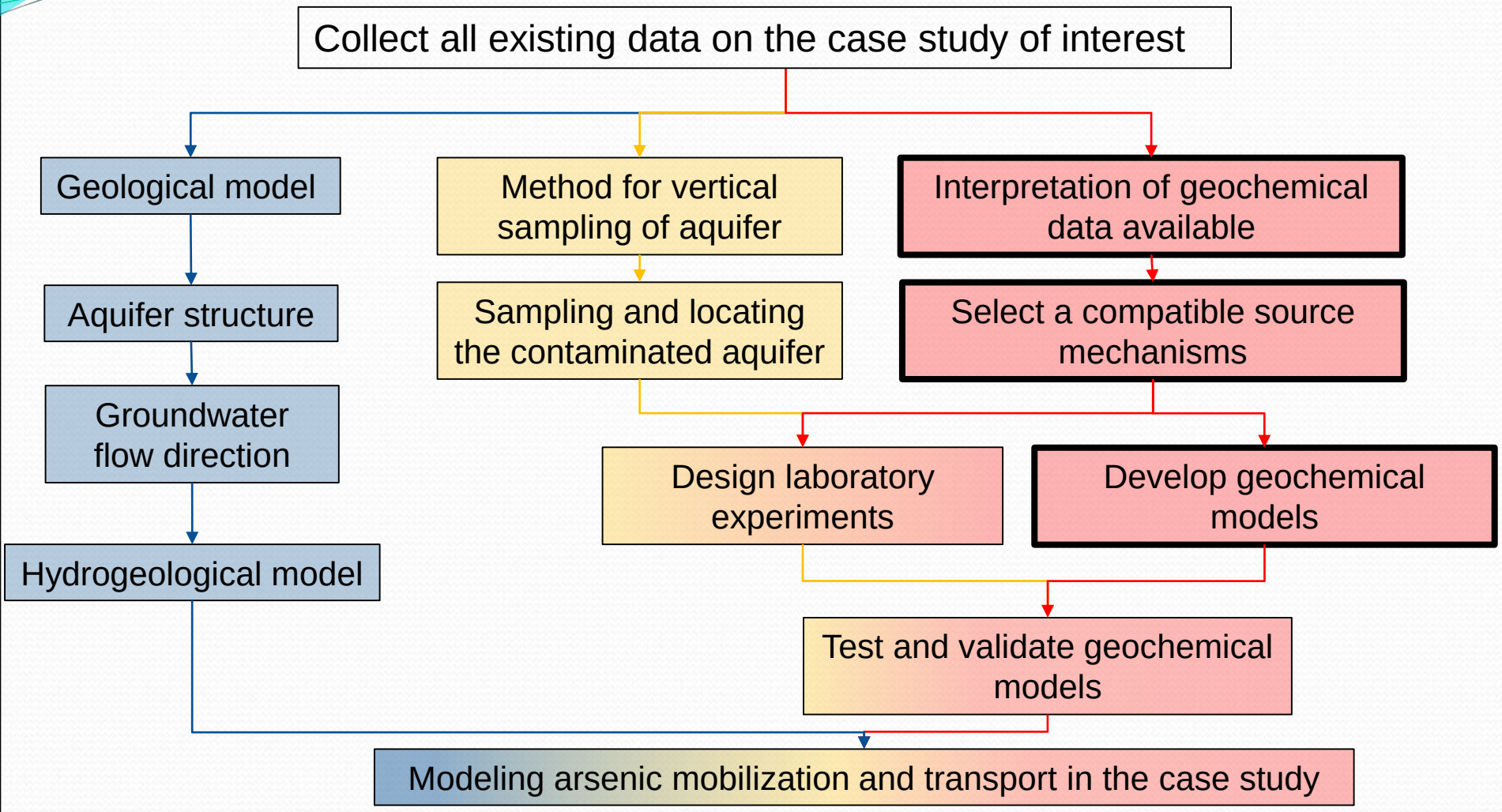


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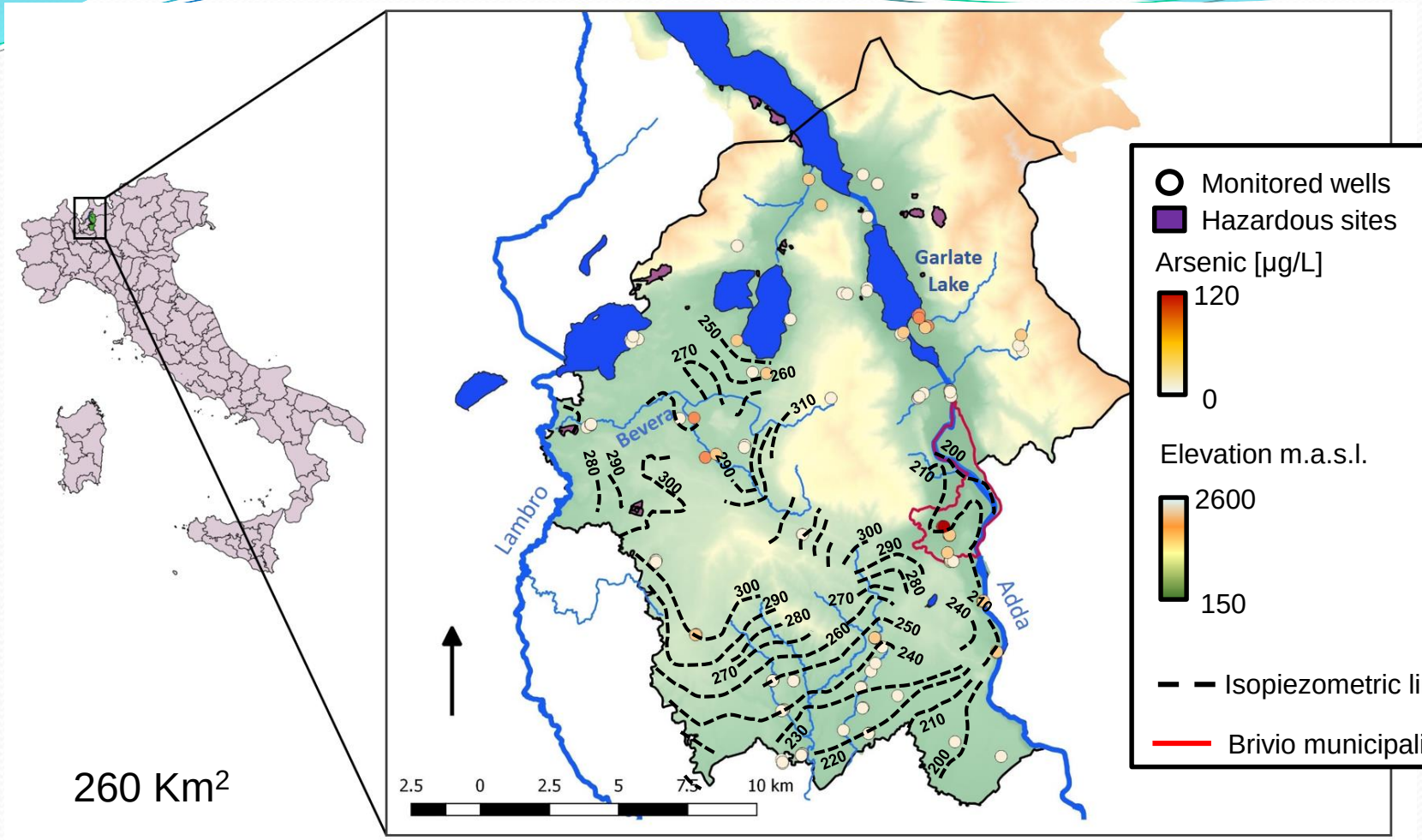
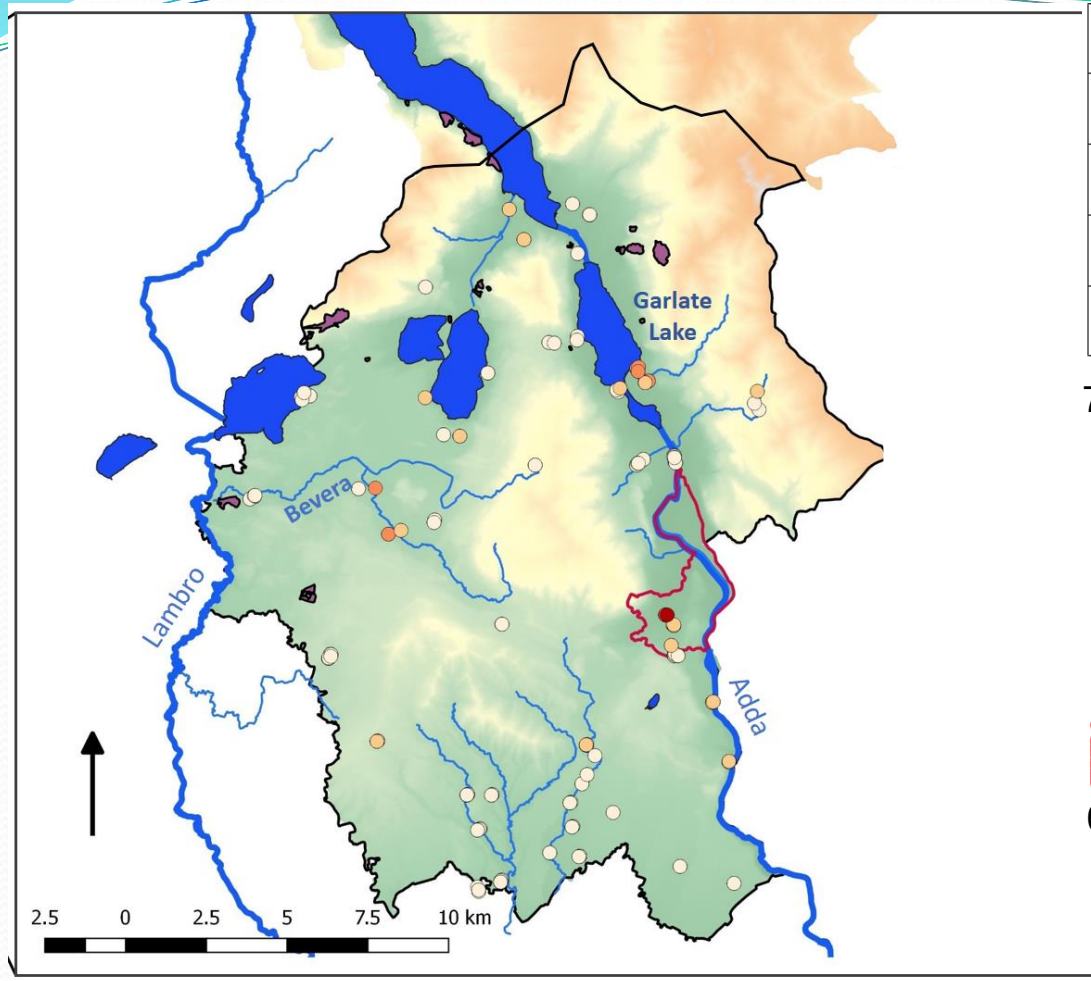
# The case study of the South Lecco Province

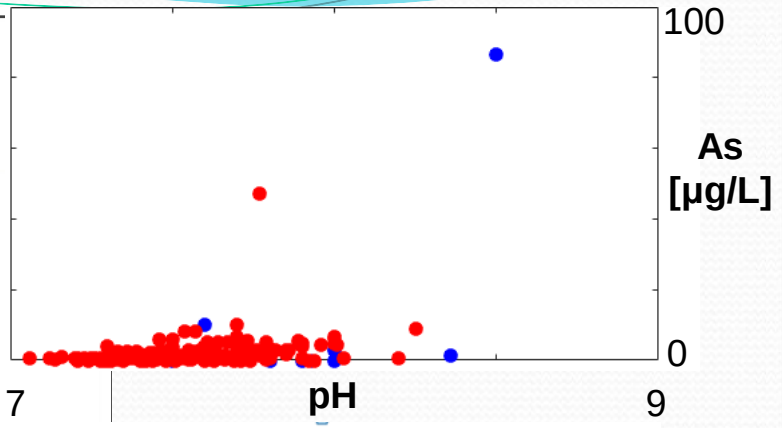


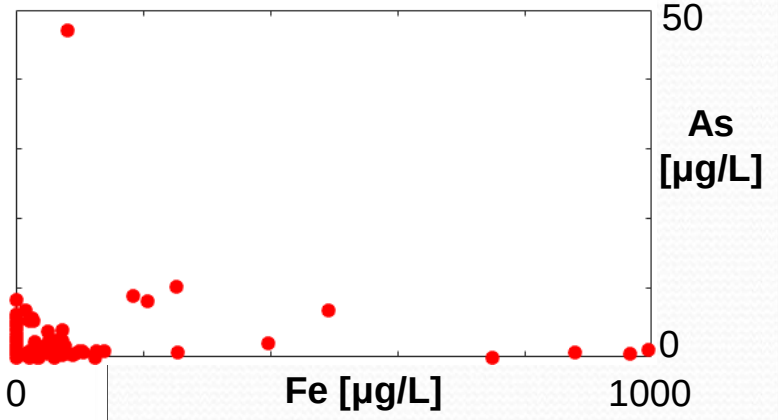

- Alluvial / Glacial aquifer → No Hydrothermal Sources
- Highest content of arsenic far from hazardous sites → No Anthropogenic Sources

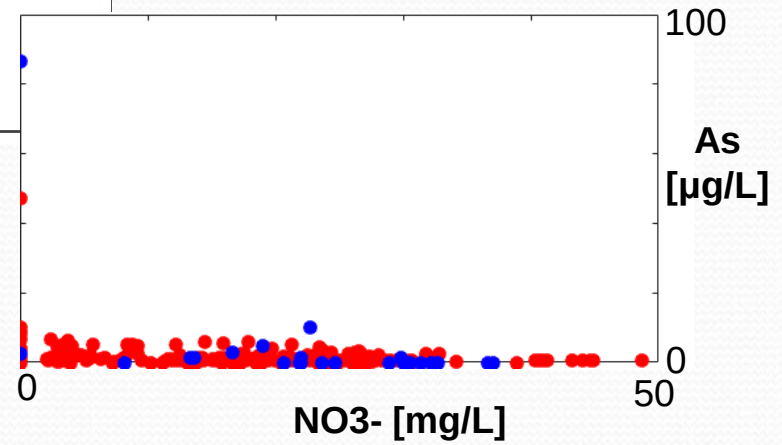
Geochemical mobilization

# Interpretation of geochemical data

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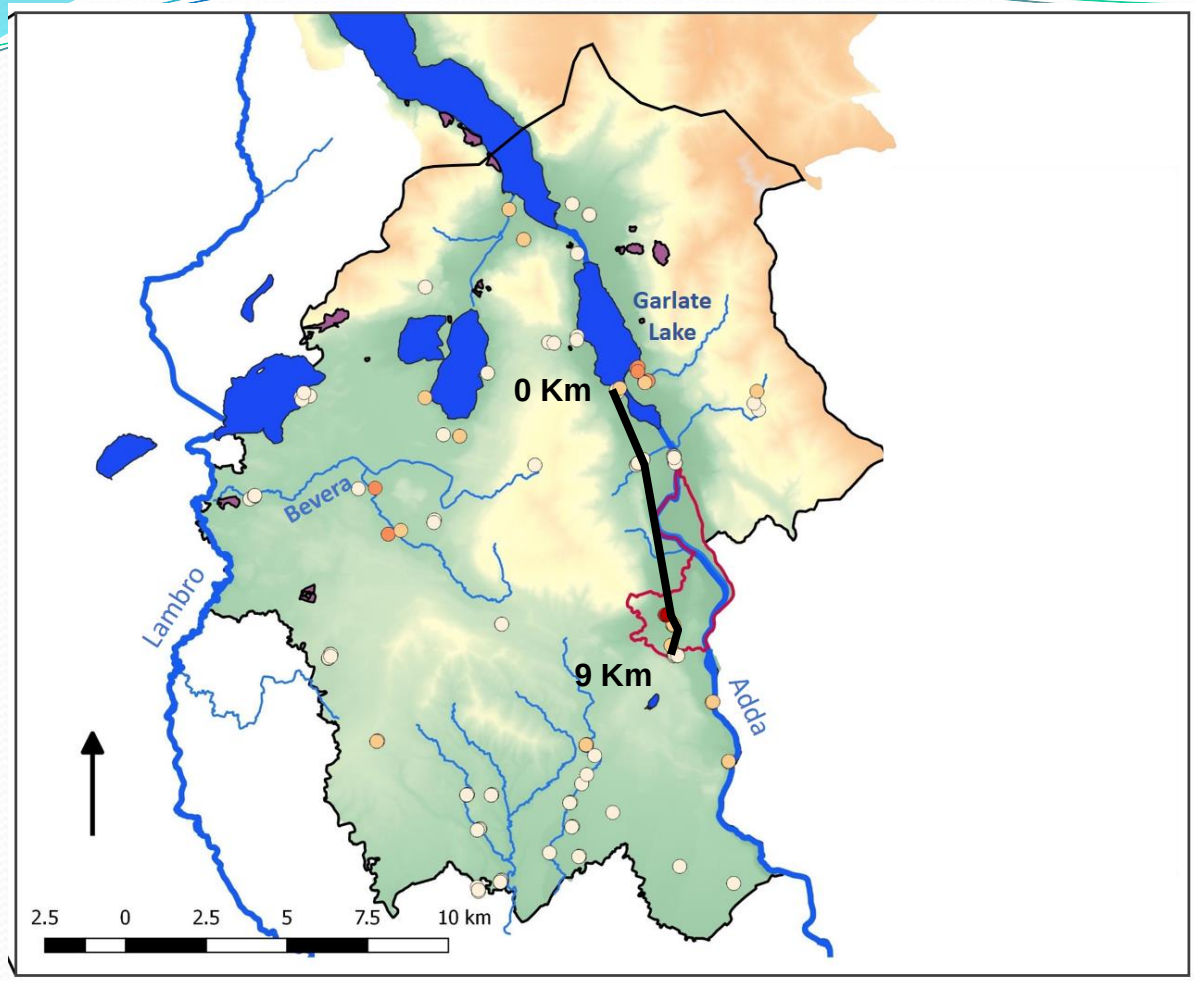


Jia et al., 2014; Postma et al., 2007; Chakraborty et al., 2015

**Reduce the scale of observation**

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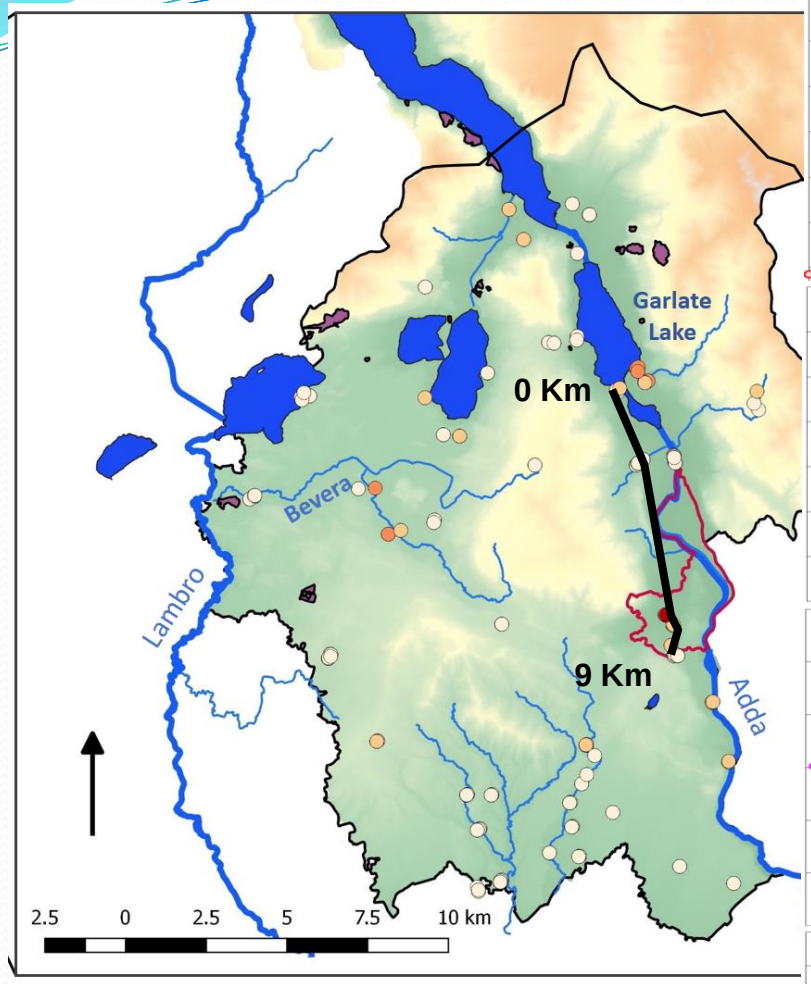


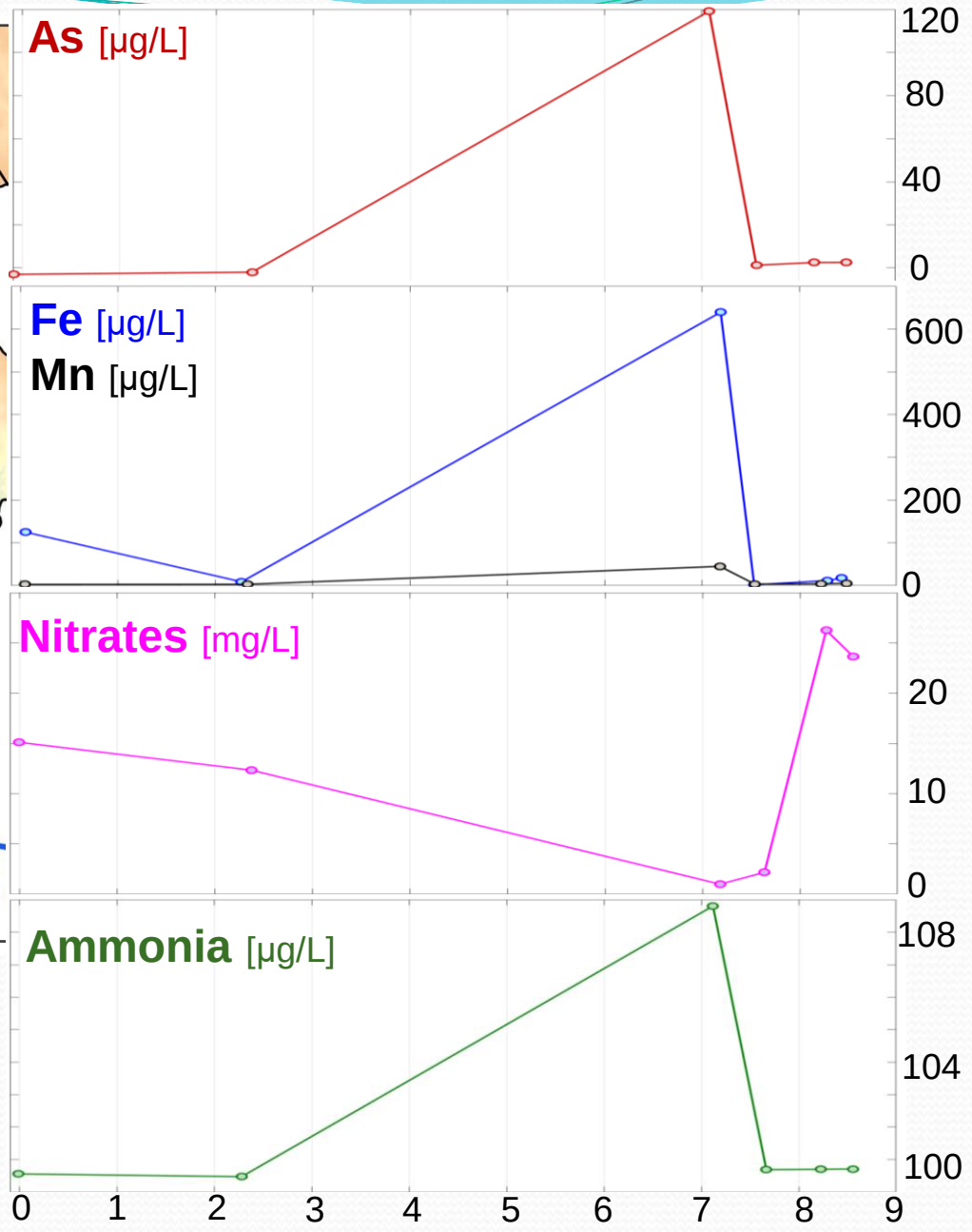


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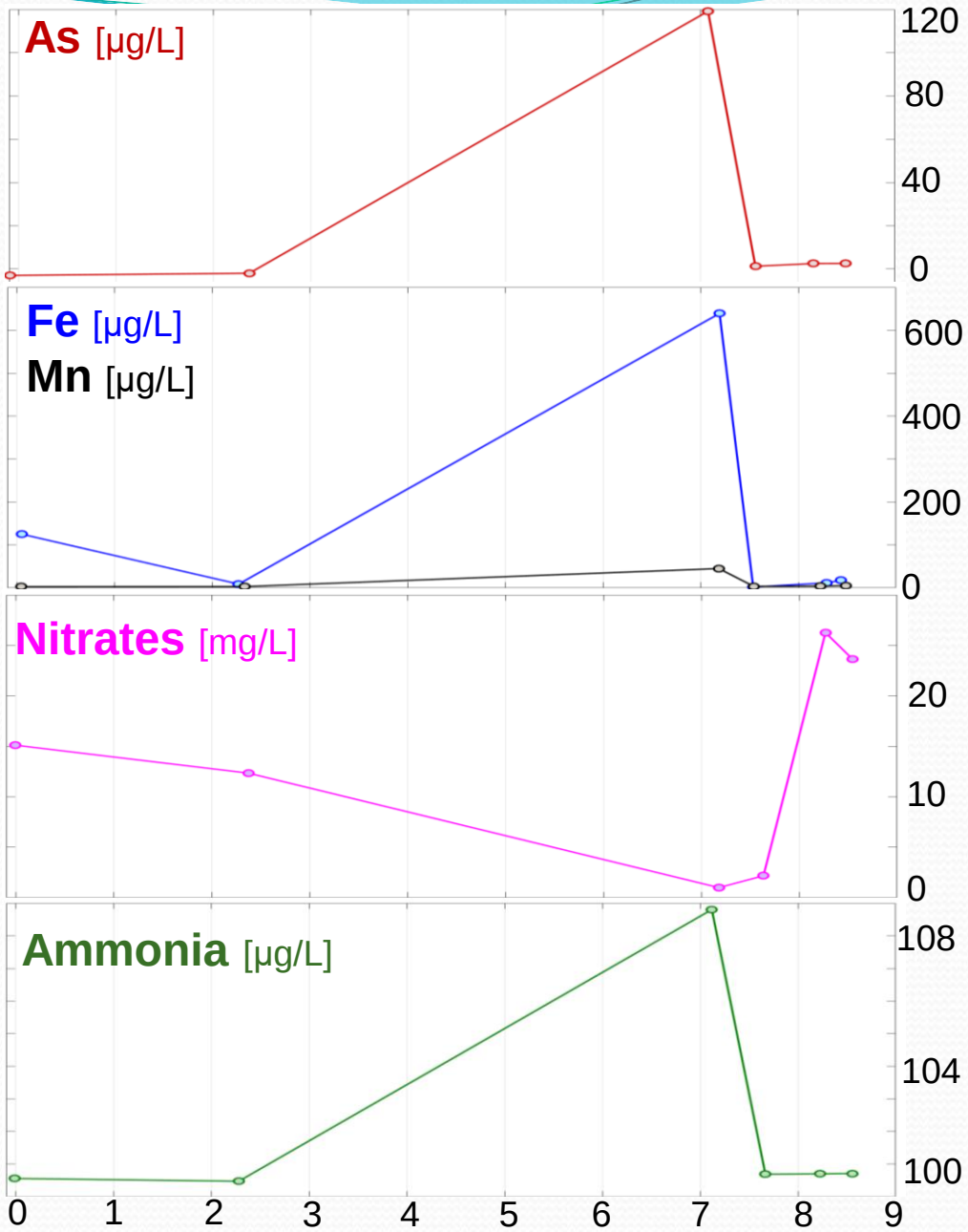


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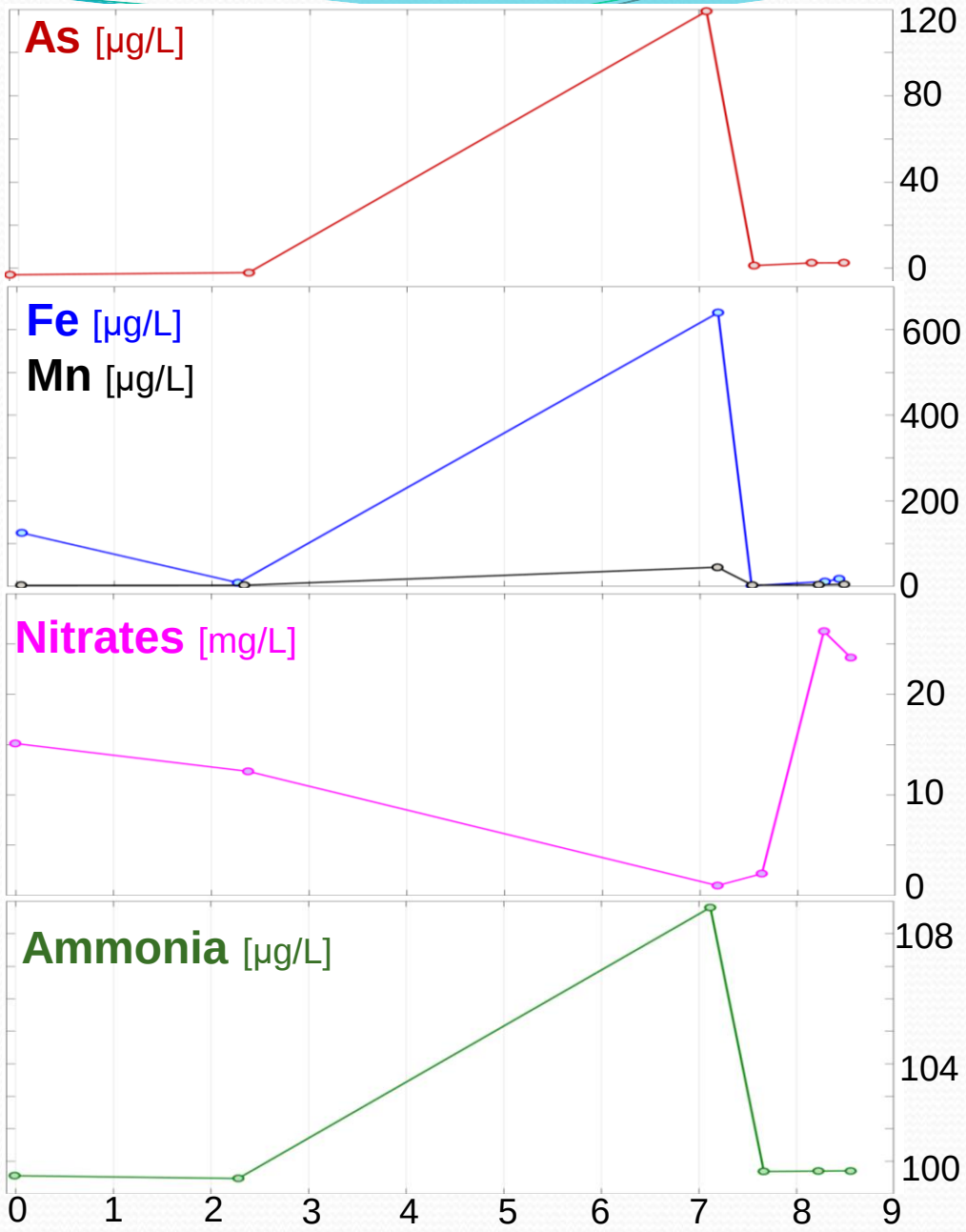


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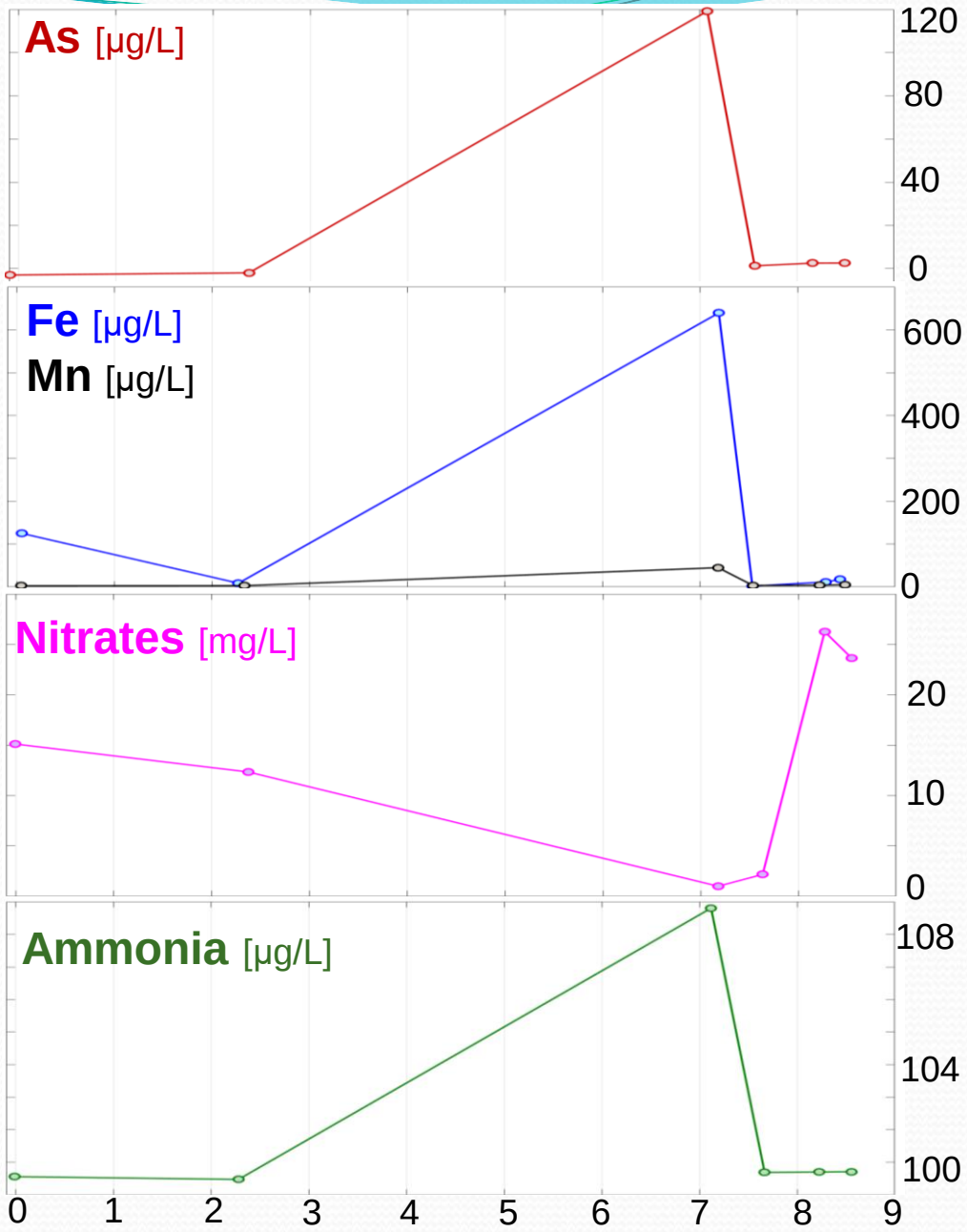


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Iron-oxides

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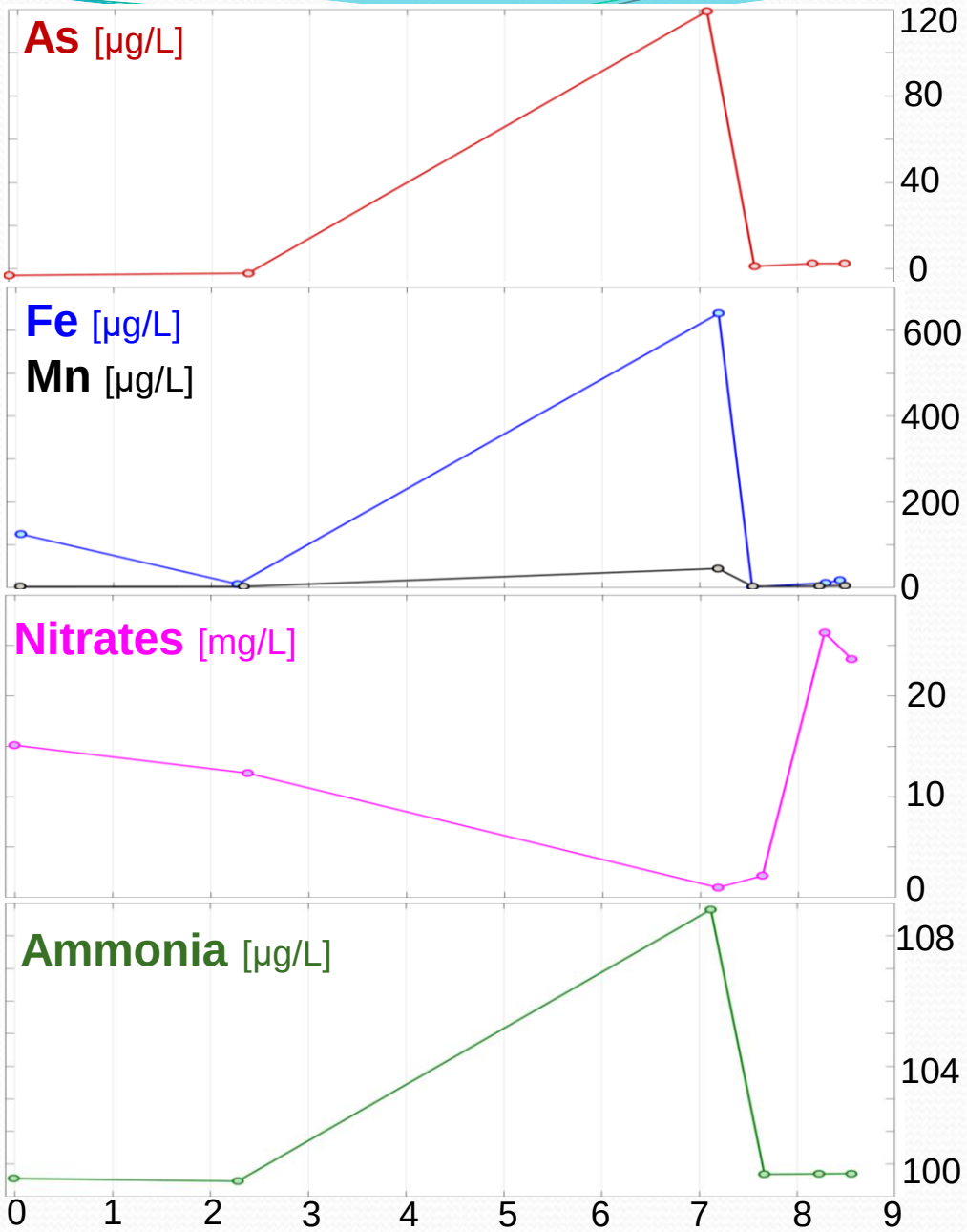

# Modeling Iron-oxides Reductive Dissolution

**Geochemical arsenic mobilization modeling:** Wallis et al., 2010; Gupta and Joshi, 2017; Sathe et al., 2019; Stollenwerk et al., 2007; Jung et al., 2009; Postma et al., 2007

**Reductive dissolution of Fe-oxides**

- A kinetic process
- A microbial-mediated process (bacteria)
- Release of arsenic

$$CH_2O + 4FeOOH + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+}$$

*From the experimental work of Liu et al. (2001)*

$$\frac{d[FeOOH]}{dt} = -S_{FeOOH}^{free} \cdot V_m \frac{[CH_2O]}{[CH_2O] + K_S}$$

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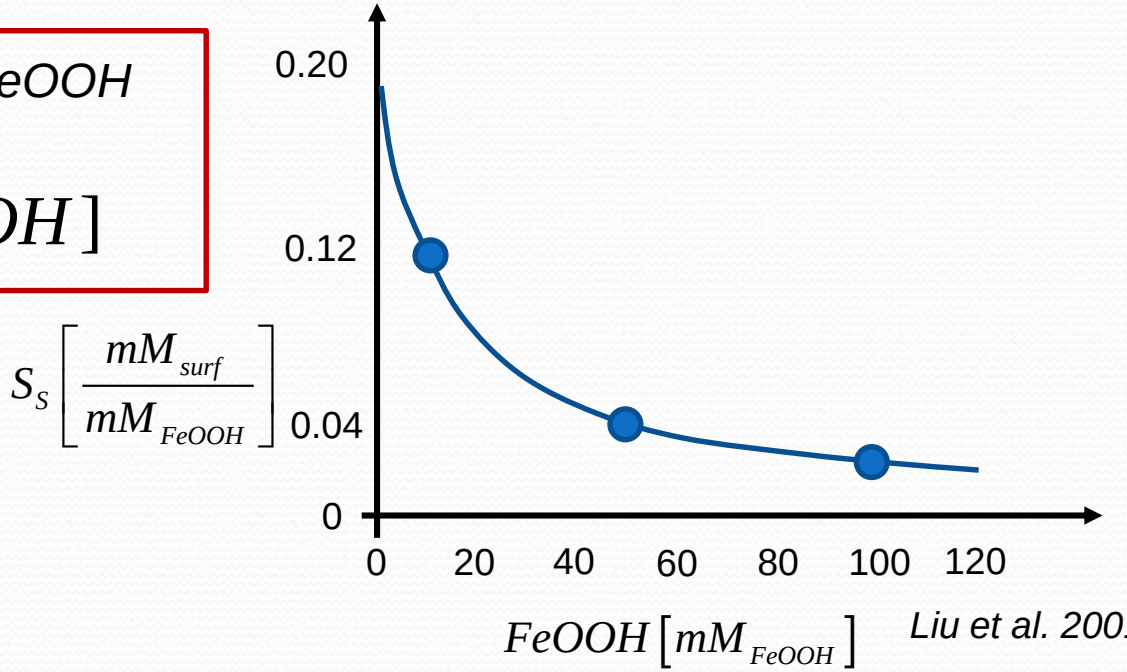


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Kinetic 2: Michaelis-Menten for $CH_2O$

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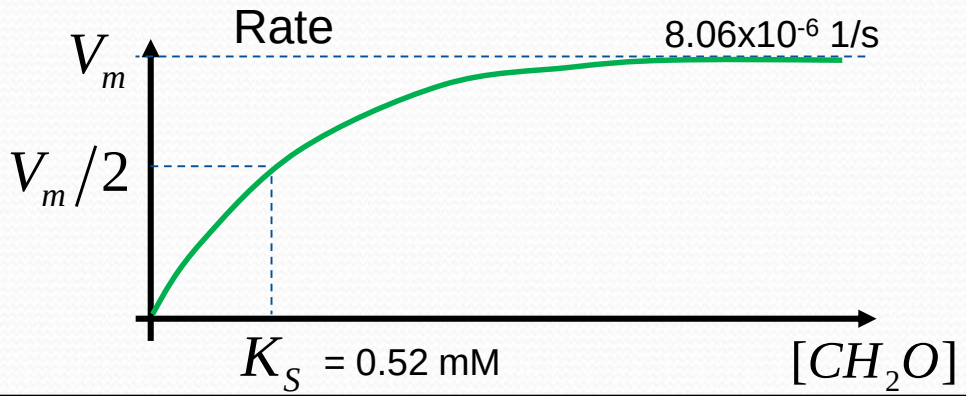

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$$CH_2O + 4FeOOH + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+}$$

*From the experimental work of Liu et al. (2001)*

$$\frac{d[FeOOH]}{dt} = -S_{FeOOH}^{free} \bullet V_m \frac{[CH_2O]}{[CH_2O] + K_S}$$

$$CH_2O + 4FeOOH \cdot (HAsO_4^{2-})_{xx} + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+} + xxHAsO_4^{2-}$$

$1.1 \times 10^{-4}$ $mol_{As}/mol_{Fe}$

3 $\mu g_{As}/g_{sed}$ & 20 $mg_{Fe}/g_{sed}$

(Swartz et al., 2004)

# Modeling Iron-oxides Reductive Dissolution

**Geochemical arsenic mobilization modeling:** Wallis et al., 2010; Gupta and Joshi, 2017; Sathe et al., 2019; Stollenwerk et al., 2007; Jung et al., 2009; Postma et al., 2007

**Reductive dissolution of Fe-oxides**

- A kinetic process
- A microbial-mediated process (bacteria)
- Release of arsenic

**Other processes**

- The pre-existing sediments
- The precipitation of authigenic phases

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Water JPI

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- Thermodynamic equilibrium for all mineral phases
- precipitation of siderite ($FeCO_3$) as authigenic phase

## Initial and boundary conditions

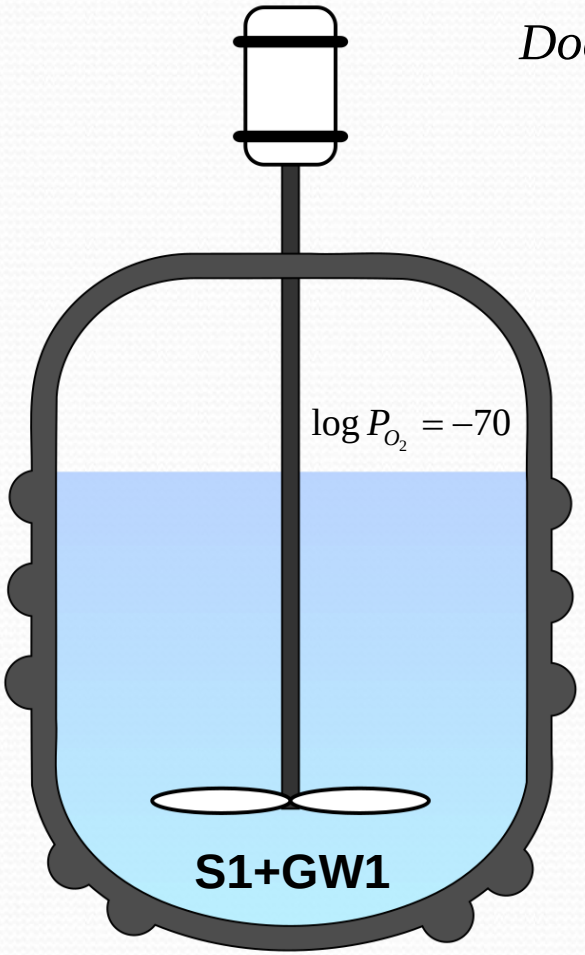
- Initial sediment composition → **S1**
- Initial groundwater composition → **GW1**
- Reducing conditions → **Fixing $O_2$ partial pressure**

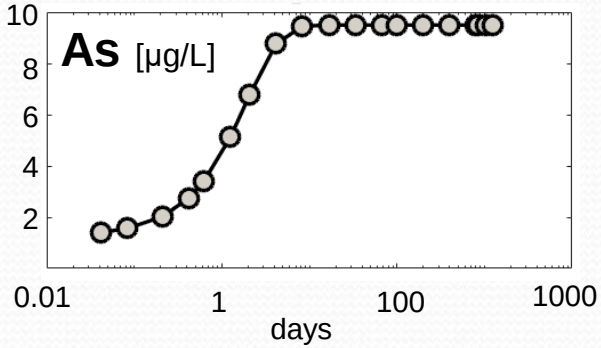
# Modeling Iron-oxides Reductive Dissolution

Assess the design of the reaction network using a batch reactor

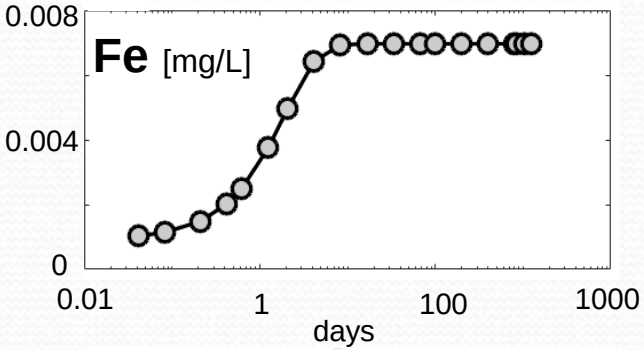
$As \rightarrow 3\mu g_{As} / g_{sed}$ *Swartz et al. (2004)*

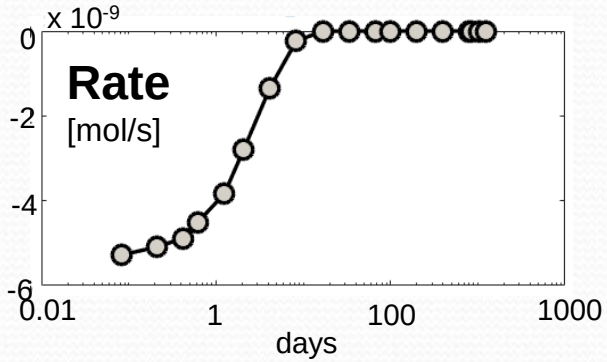
$Doc \rightarrow = 0.25 mg_C / L$

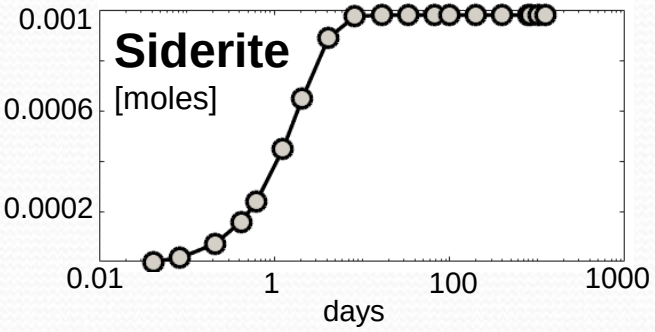


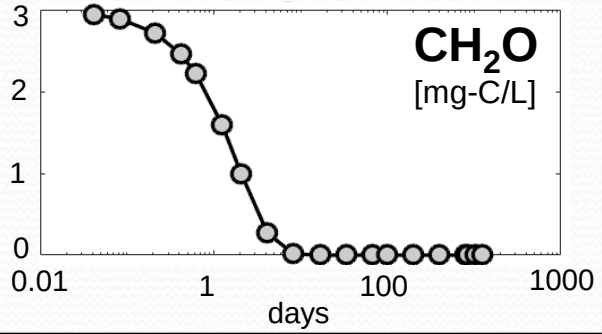




$$CH_2O + 4FeOOH \cdot (HAsO_4^{2-})_{xx} + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+} + xxHAsO_4^{2-}$$



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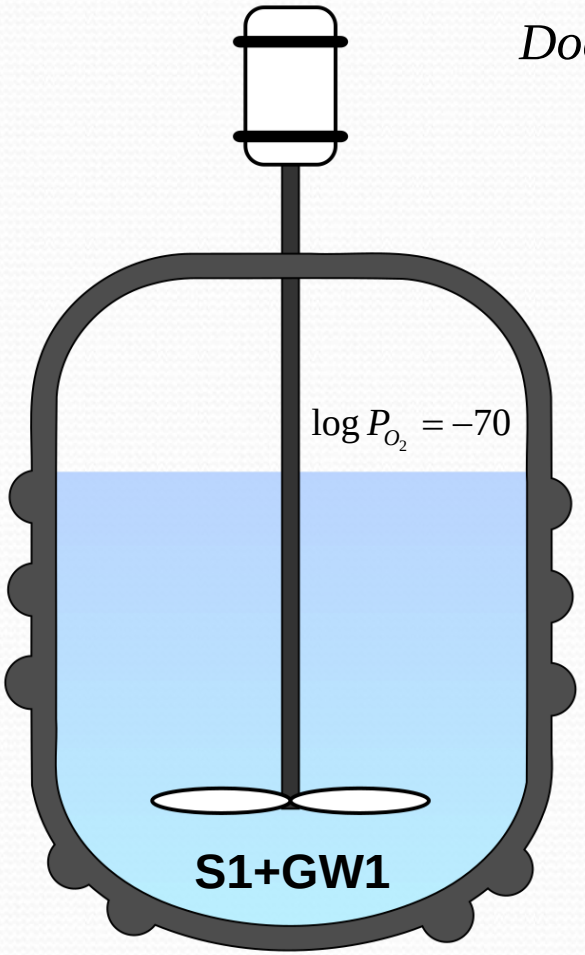
Assess the design of the reaction network using a batch reactor

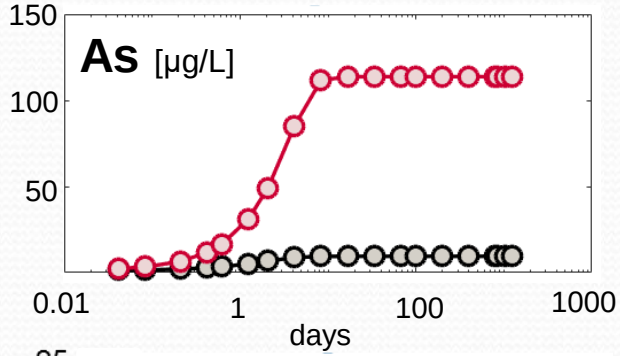
$As \rightarrow 3\mu g_{As} / g_{sed}$

$Doc \rightarrow = 0.25 mg_C / L$

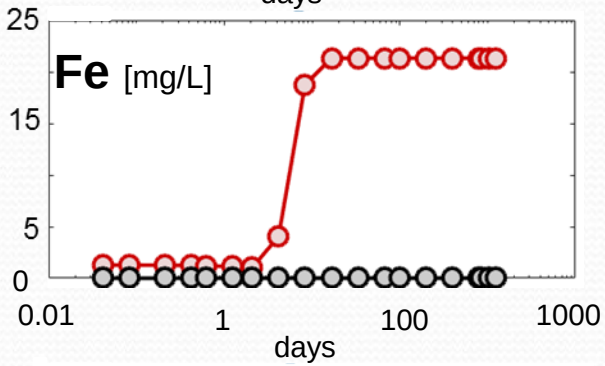
$As \rightarrow 8\mu g_{As} / g_{sed}$ *Swartz et al. (2004)*

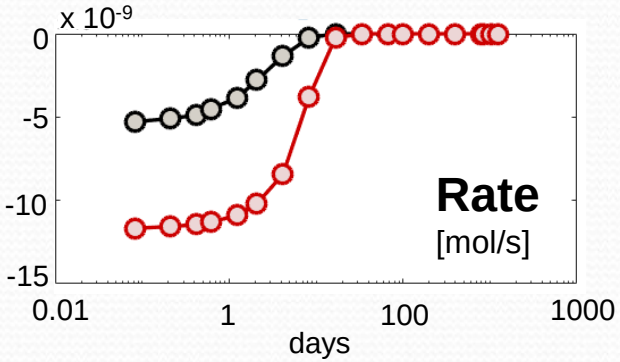
$Doc \rightarrow = 1.25 mg_C / L$

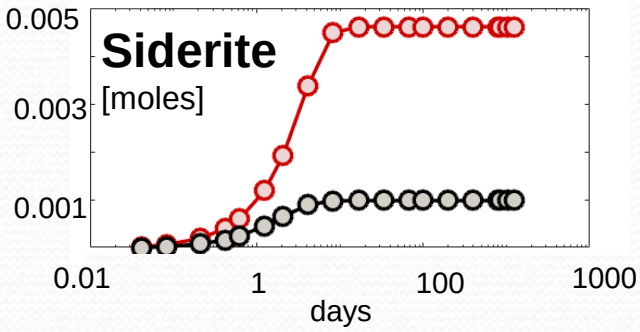


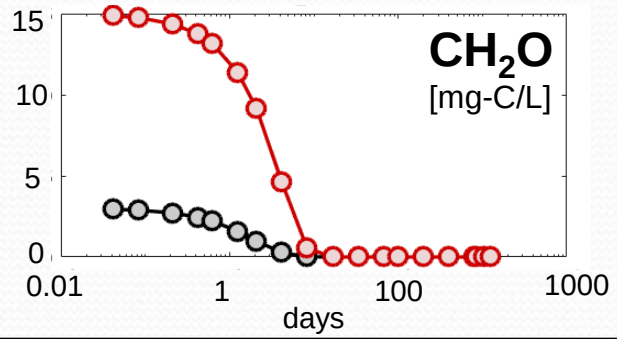




$$CH_2O + 4FeOOH \cdot (HAsO_4^{2-})_{xx} + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+} + xxHAsO_4^{2-}$$

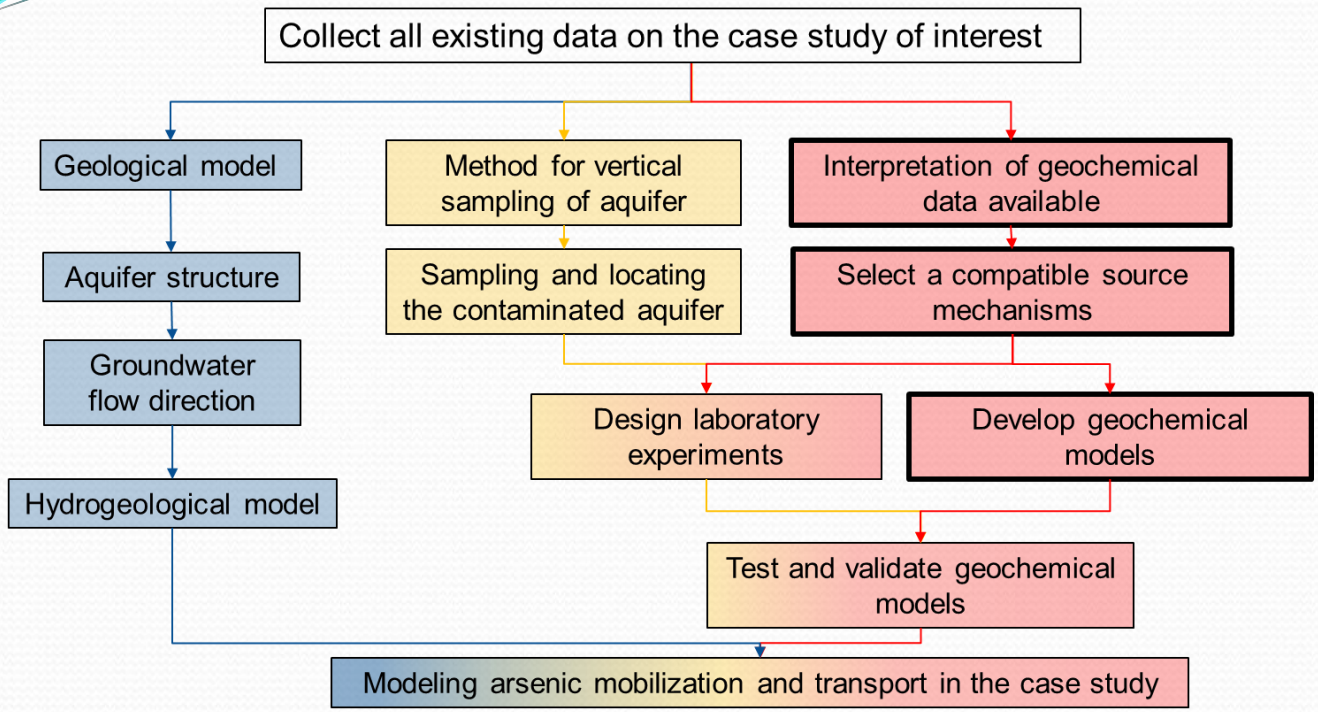


# To conclude…




Ongoing project…

Thanks to:

Julie Regis
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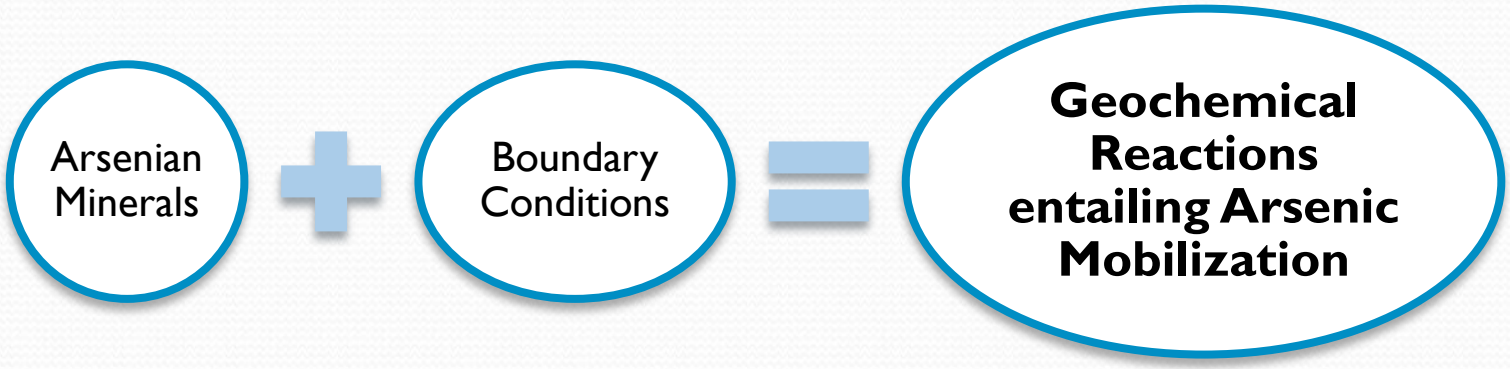
Selene Patani

Alberto Guadagnini
Monica Riva

LARIO RETI HOLDING
la tua acqua, la nostra passione

# Geochemical Mobilization of Arsenic

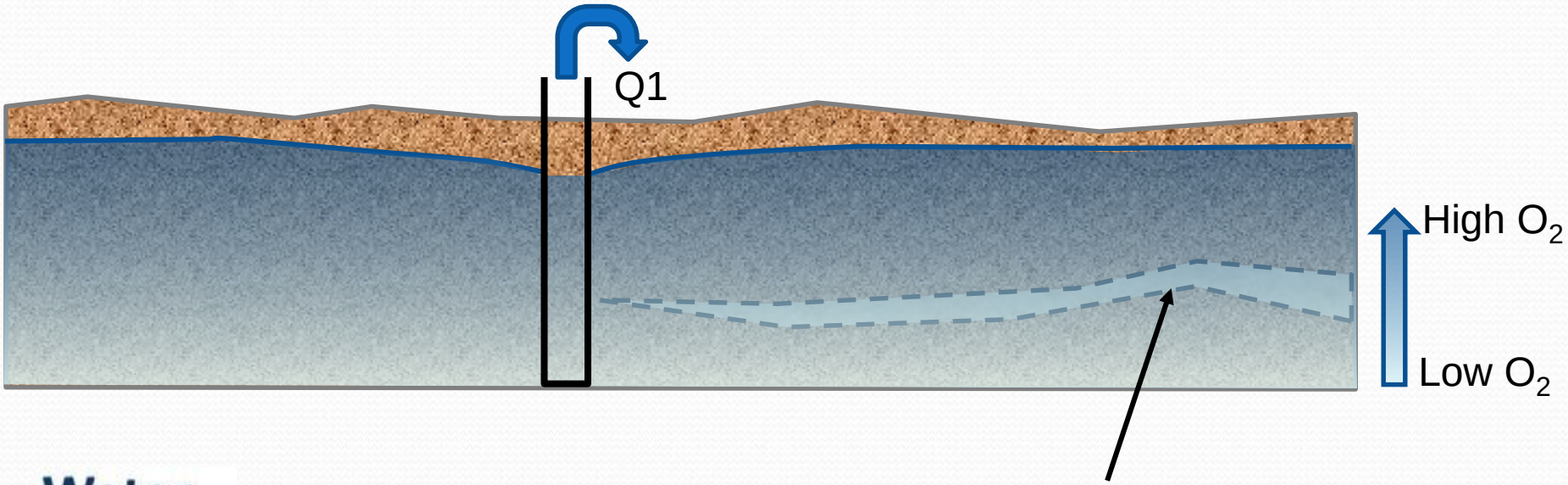


# Geochemical Mobilization of Arsenic

Pyrite
&
Arsenopyrite

Oxidizing
Conditions
($O_2$, Nitrates or $Fe^{3+}$)

**Oxidation of Pyrite & Arsenopyrite**



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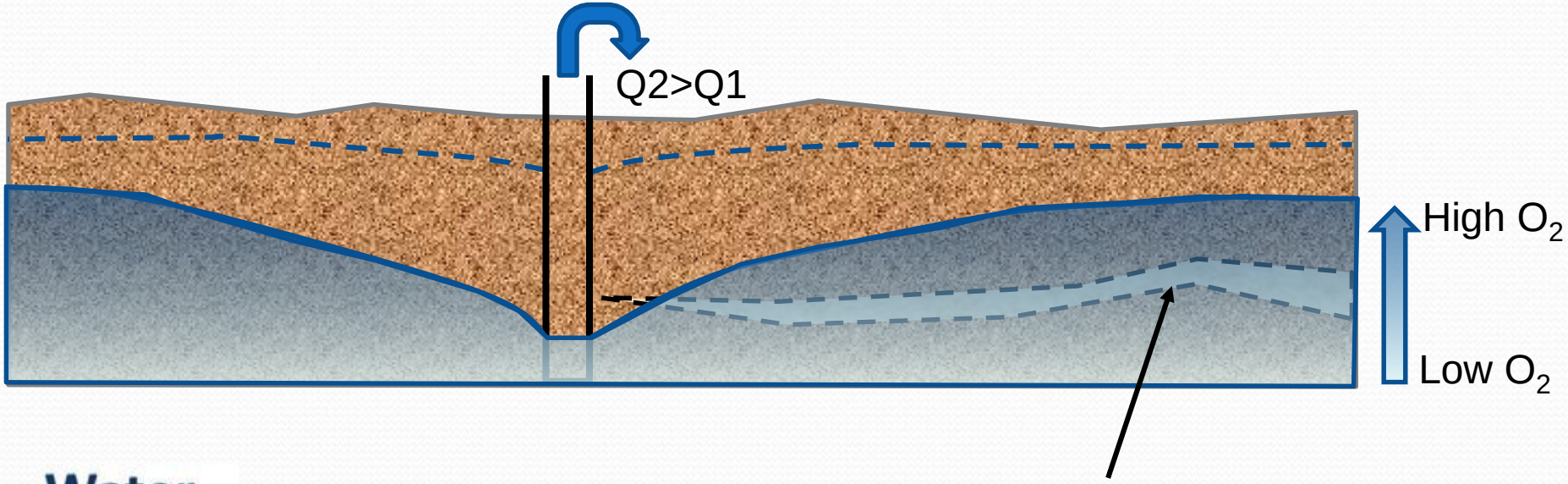

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## Reductive dissolution of Fe-oxides

- A kinetic process
- A microbial-mediated process (bacteria)
- Contextual release of arsenic

$$CH_2O + 4FeOOH + 7H^+ \rightarrow HCO_3^- + 6H_2O + 4Fe^{2+}$$

*From the experimental work of Liu et al. 2001*

$$\frac{d[FeOOH]}{dt} = -S_{FeOOH}^{free} \bullet V_m \frac{[CH_2O]}{[CH_2O] + K_S}$$

## Other processes

- The pre-existing sediments
- The precipitation of authigenic phases

- Thermodynamic equilibrium for all other mineral phases
- precipitation of siderite ($FeCO_3$) as authigenic phase

## Initial and boundary conditions

- Initial sediment composition
- Initial groundwater composition
- Reducing conditions

Partial pressure of $O_2$

Uncontaminated real GW sample

Equilibrium

**Realistic GW**

**Realistic Composition**

Silica 90%
Calcite 6%
Dolomite 3%
Illite 0.8%
Al-oxides 0.1%
Fe-oxides 0.1%

*Ravazzi et al. (2012)*