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# Enhanced and retarded transport of hydrophobic pesticides caused by particle transport in saturated porous media: laboratory experiments and model-based analysis

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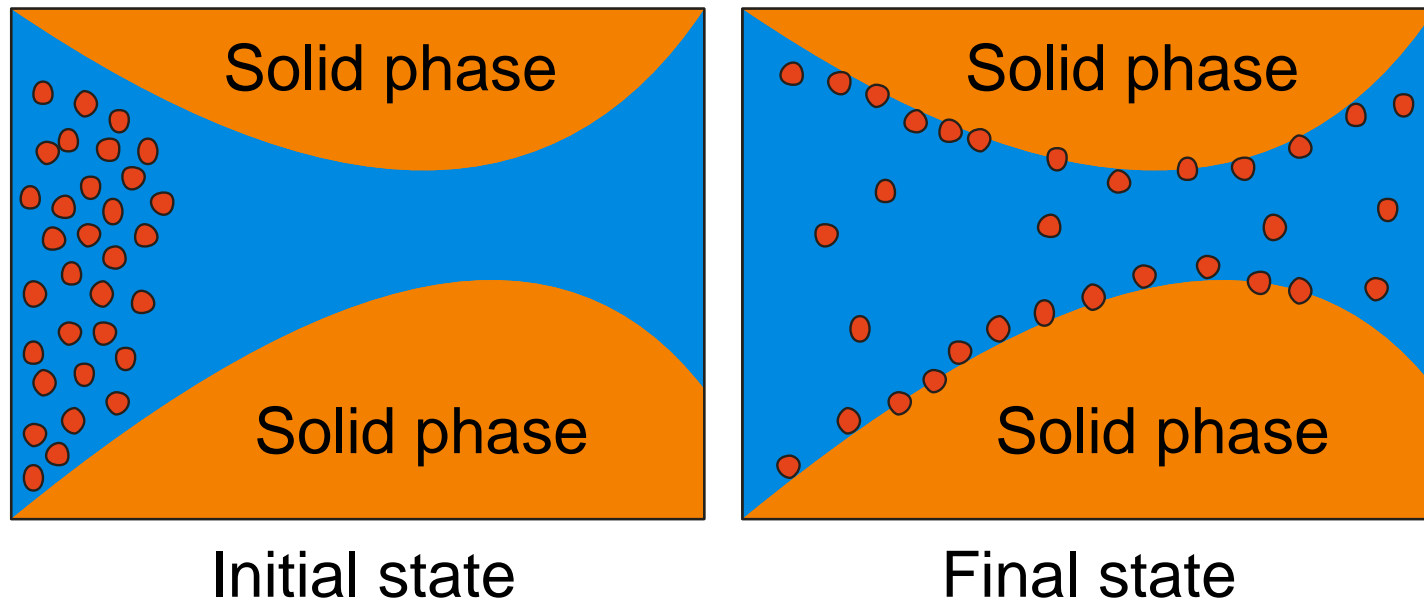
# Outline

- ▶ **Motivation**
- ▶ **Objectives**
- ▶ **Materials and Methods**
- ▶ **Results and Discussion**
- ▶ **Conclusions**

# Motivation

## Sorption...

... is the mass-transfer process of a compound that undergoes physico-chemical reactions with a solid phase (e.g. grains of soils and aquifer matrices).





# Motivation

E.g. of sorbing compounds are hydrophobic pesticides.



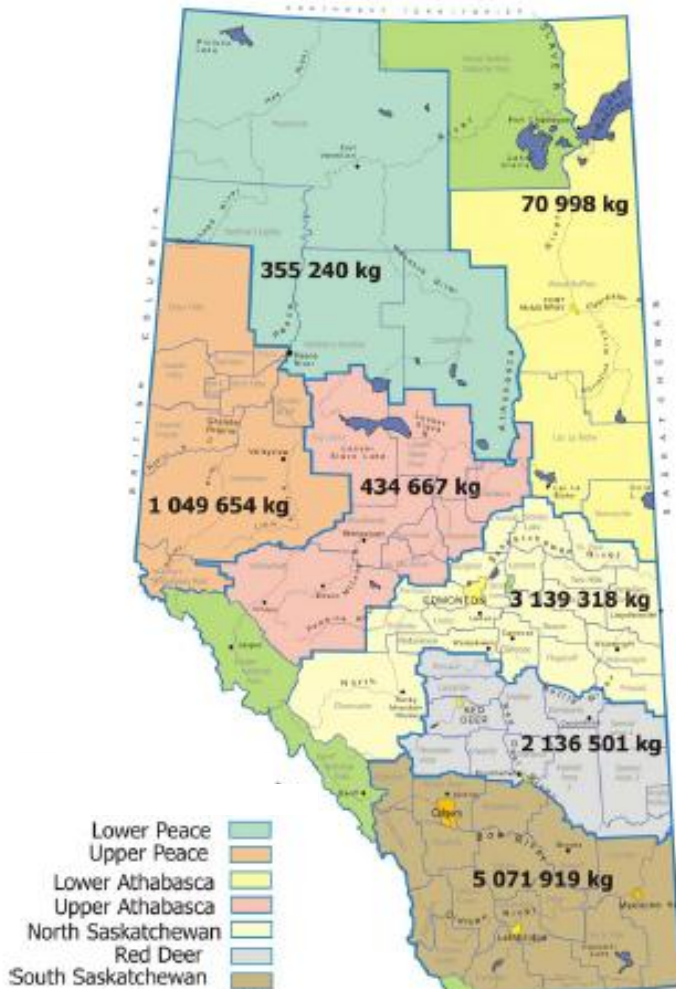
<http://www.tn.gov/agriculture/regulatory/aip.shtml>



[en.wikibooks.org](http://en.wikibooks.org)

# Motivation

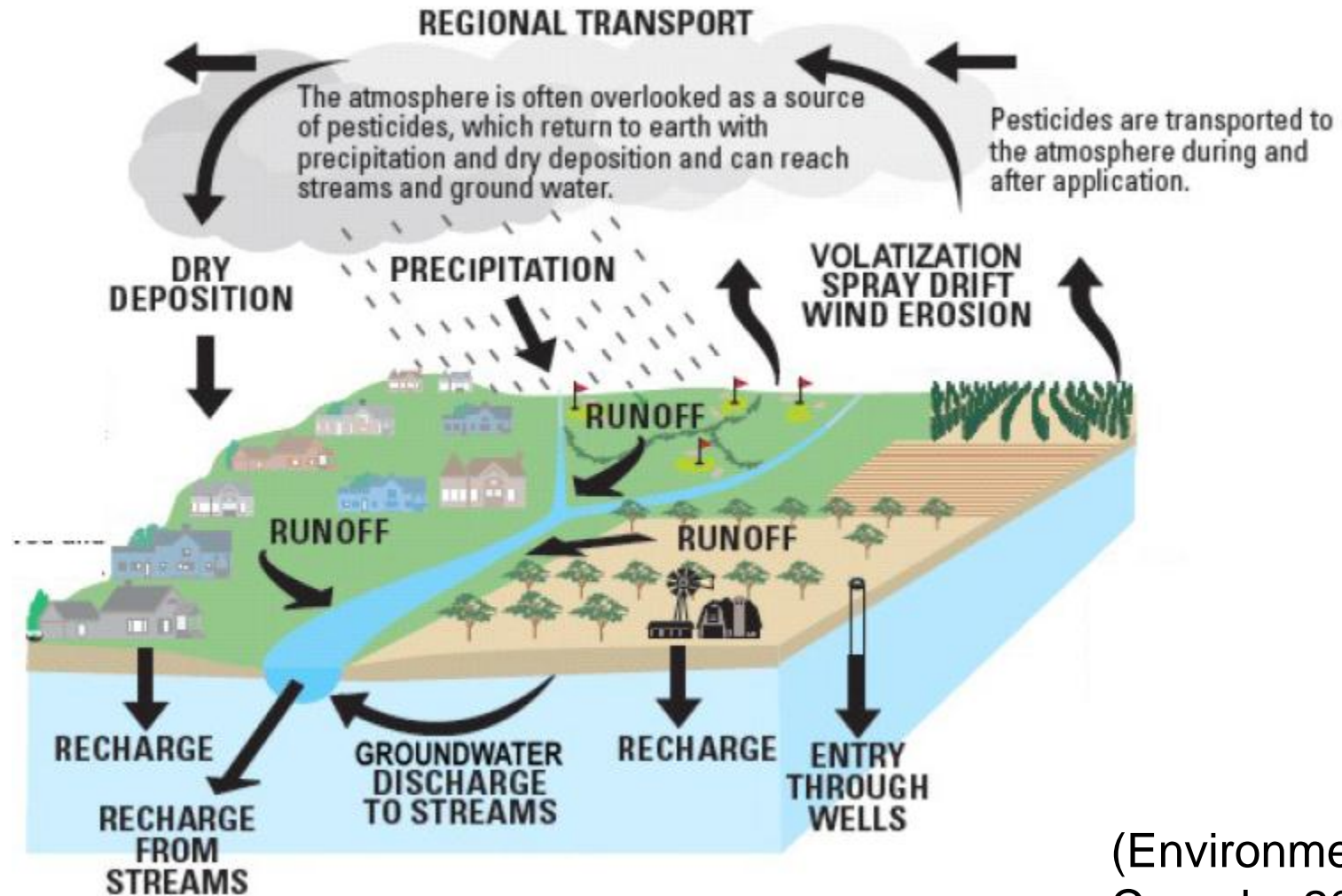
## 2008 Total Pesticide Sales by Land Use Framework region



96% for the agricultural sector.

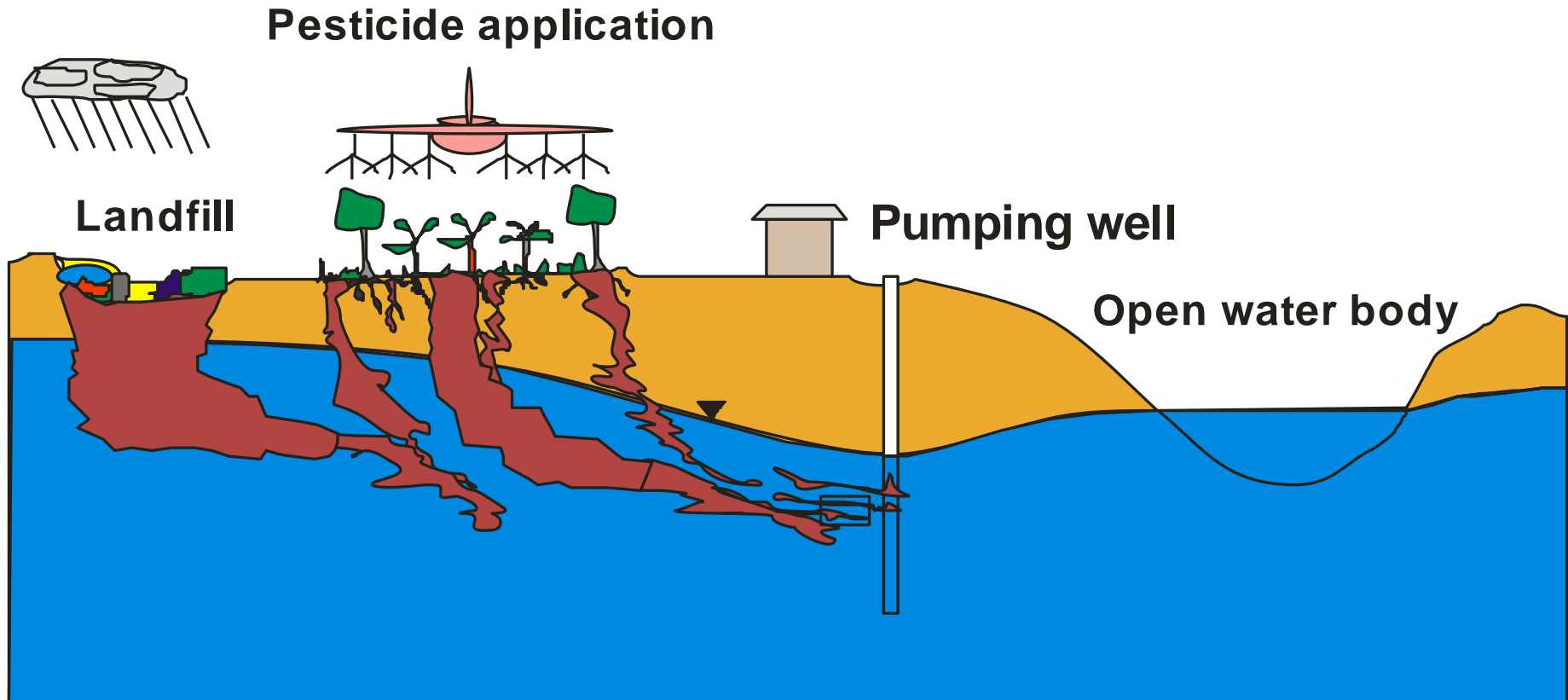
(Byrtus, 2001, Alberta Environment)

# Motivation



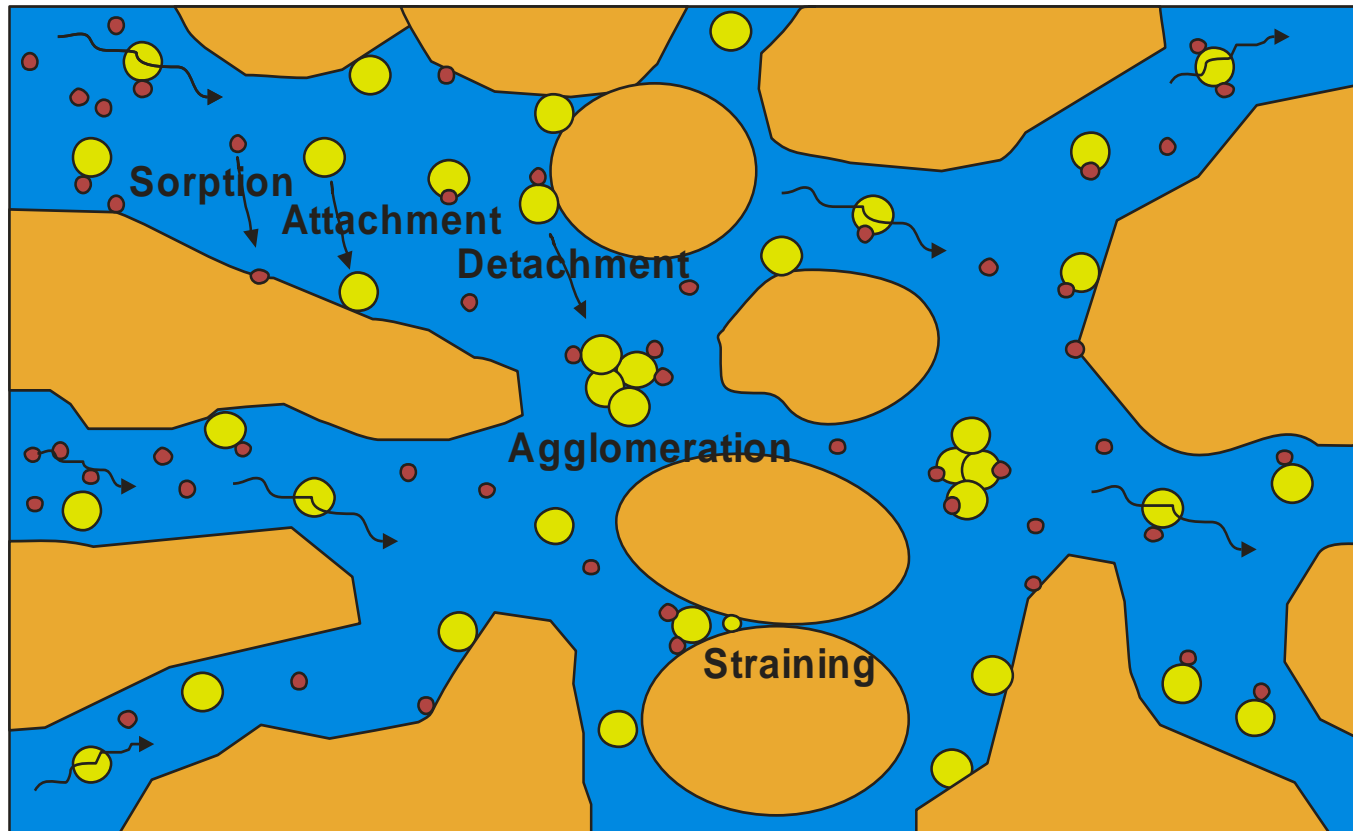
(Environment  
Canada, 2011)

# Motivation



**Travel time and concentration to well and surface water?**

# Motivation



**Compound** •

**Particle** ●  
(size up to 10  $\mu\text{m}$ )

**Aquifer material** ●

**Followed path line** ~~~~~→



# Objectives

- Effect of **natural organic particles** on the transport of **sorbing pesticides** in saturated porous media using lindane.
- **Model-based analysis** of the experimental results to understand the processes involved.

# Materials and Methods

## ➤ Laboratory experiments

- **Porous medium:** natural sand, grain size between 0.25 and 0.80 mm.

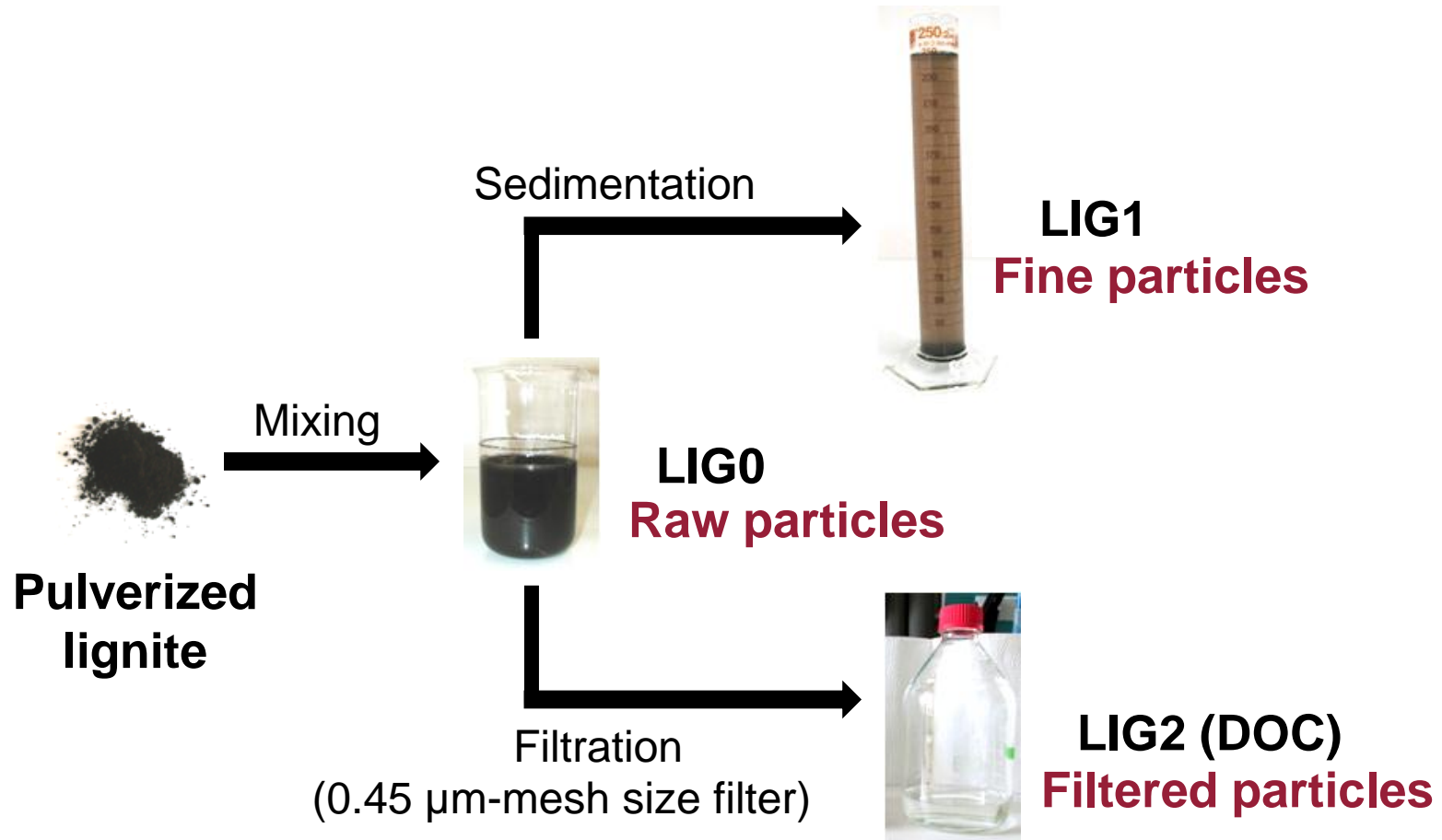
Organic carbon content ( $f_{OC}$ ) [weight%]	Particle density [g cm <sup>-3</sup> ]	CaCO <sub>3</sub> [weight%]
0.06	2.66	38



- ✓ Quartz
- ✓ Carbonate minerals

# Materials and Methods

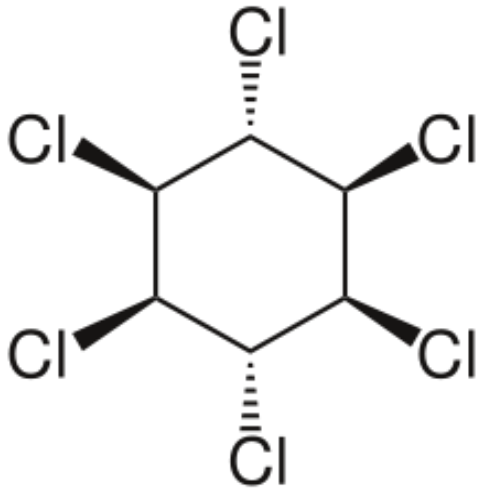
- **Particles:** natural lignite (brown coal), with  $f_{OC} = 60.5$  weight%.



DOC: dissolved organic carbon

# Materials and Methods

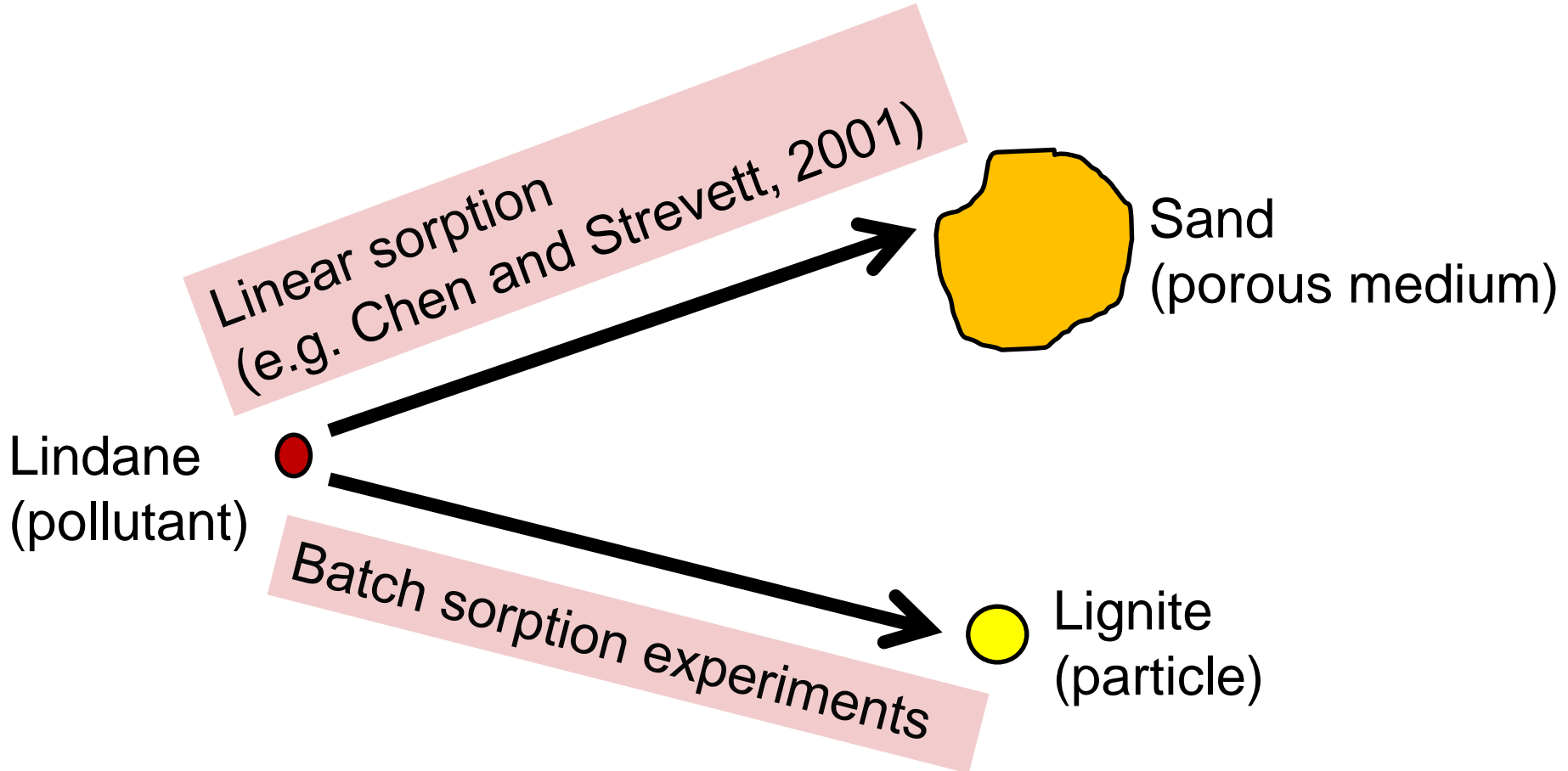
- **Pesticide:** lindane, very hydrophobic in water.





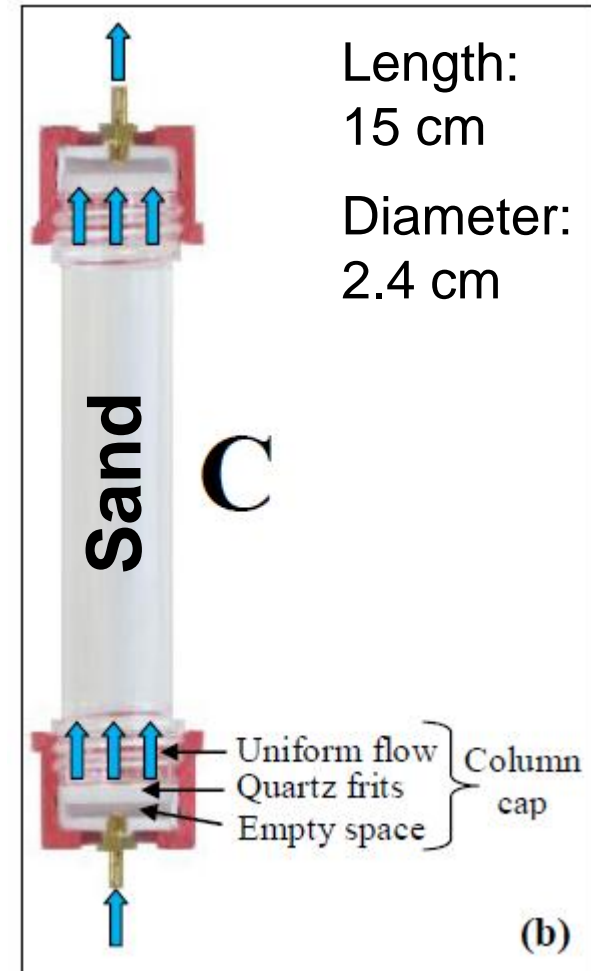
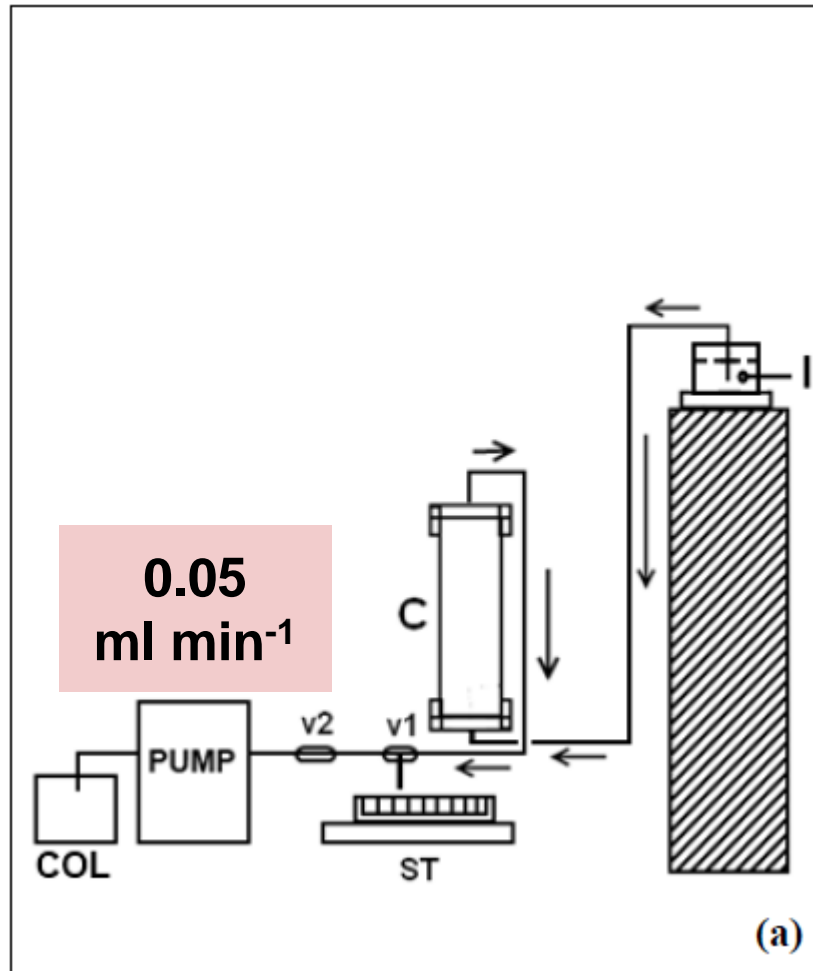
# Materials and Methods

- Sorption behaviour



# Materials and Methods

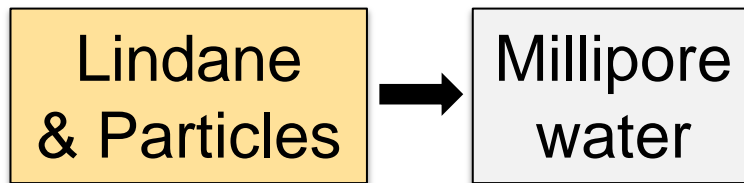
- Column experiments



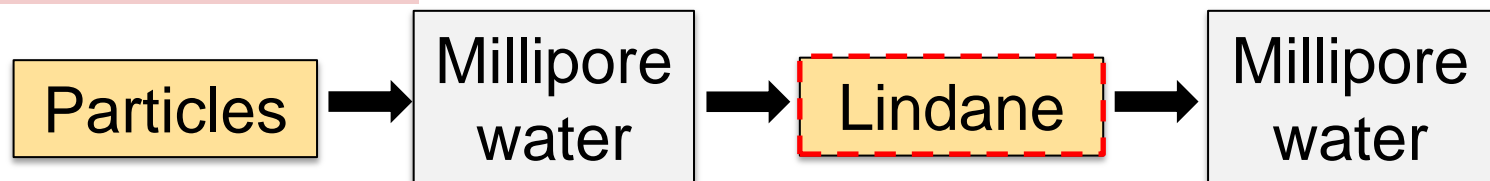
# Materials and Methods

- Two phases: injection and elution.
- Conservative transport: Cl<sup>-</sup> tracer from NaCl.
- Non-conservative transport: lindane **or** particles.
- Non-conservative transport: lindane **and** particles

## Synchronous:

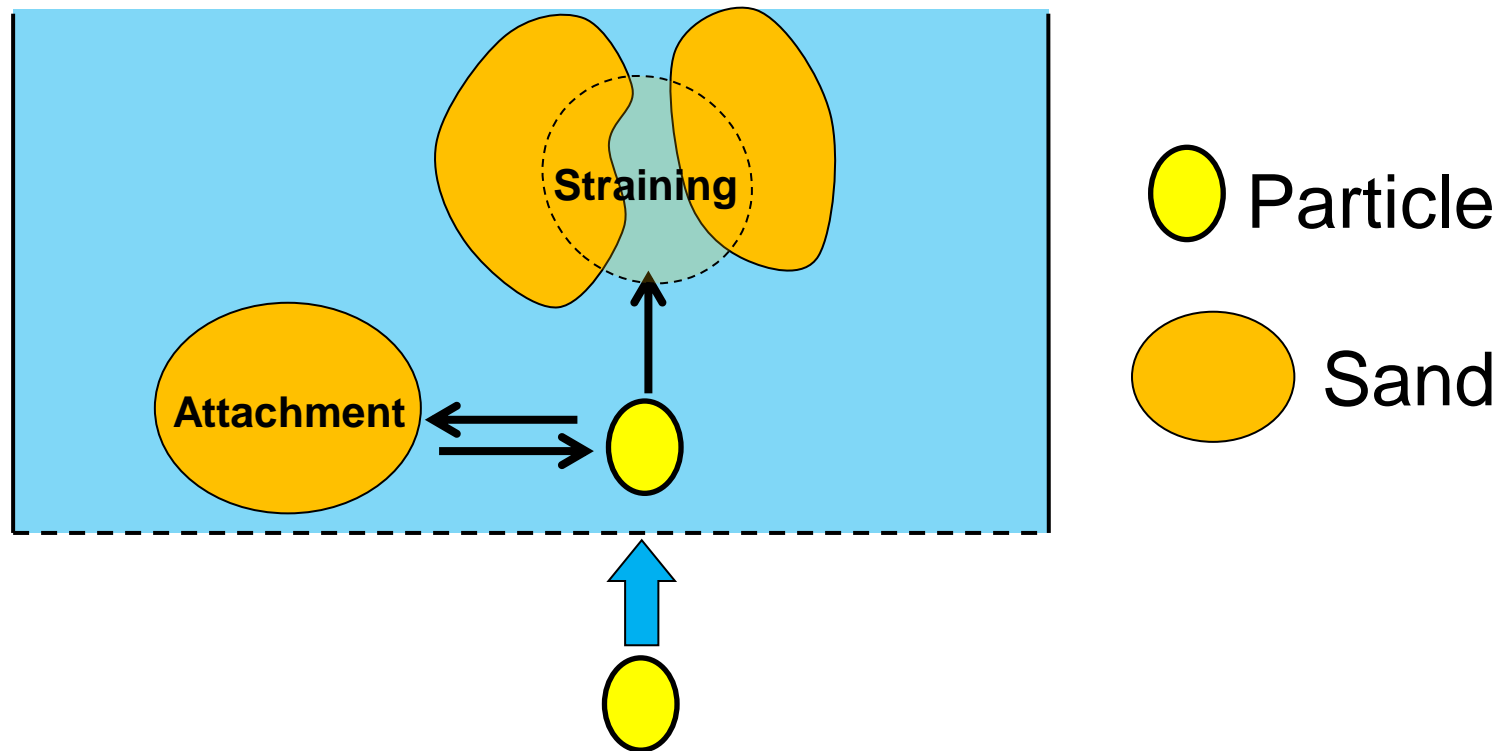


## Asynchronous:



# Materials and Methods

- **One-dimensional transport modelling**
  - **Transport of lignite particles alone (MATLAB)**

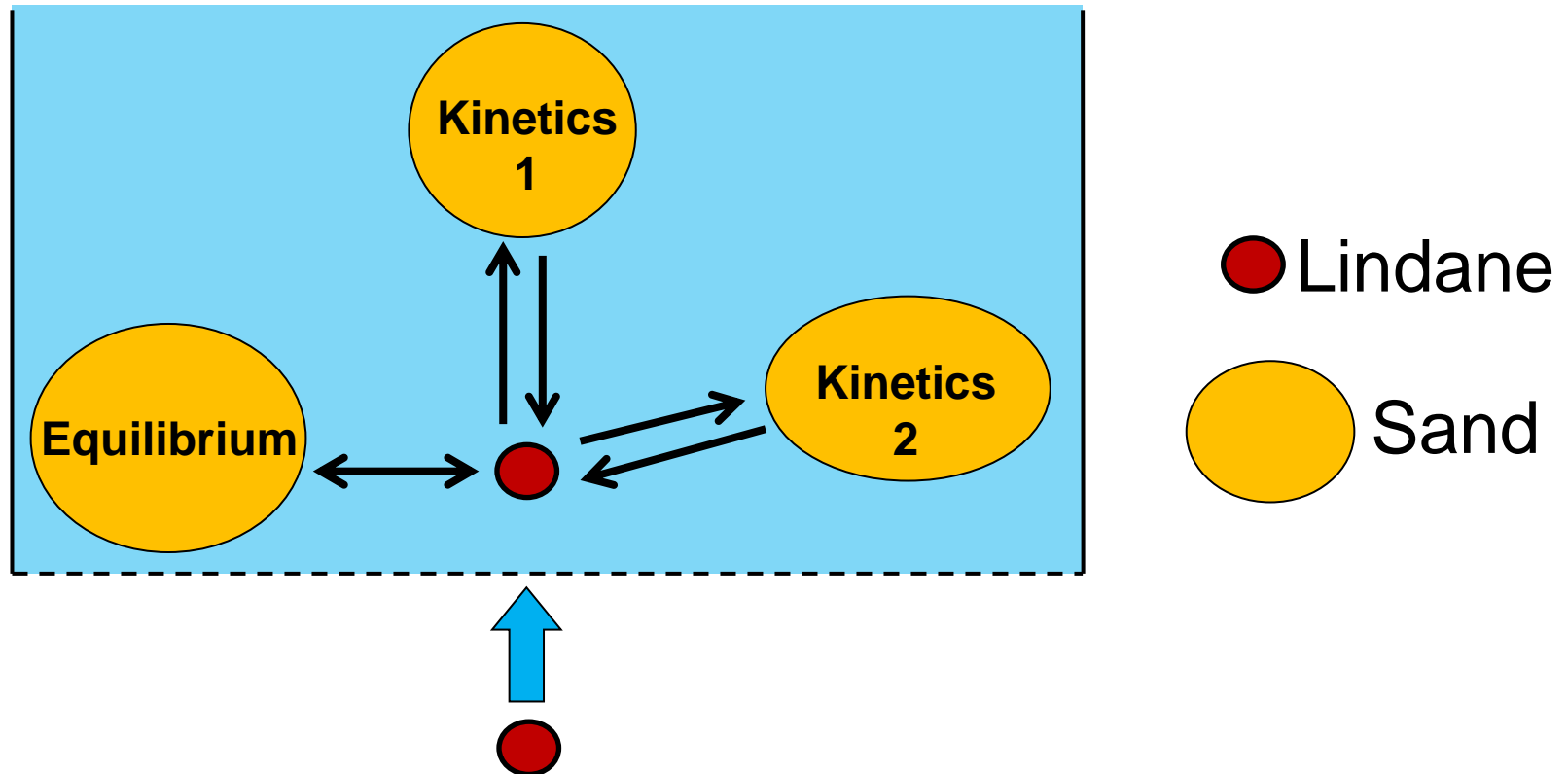


(Simunek et al., 2006)



# Materials and Methods

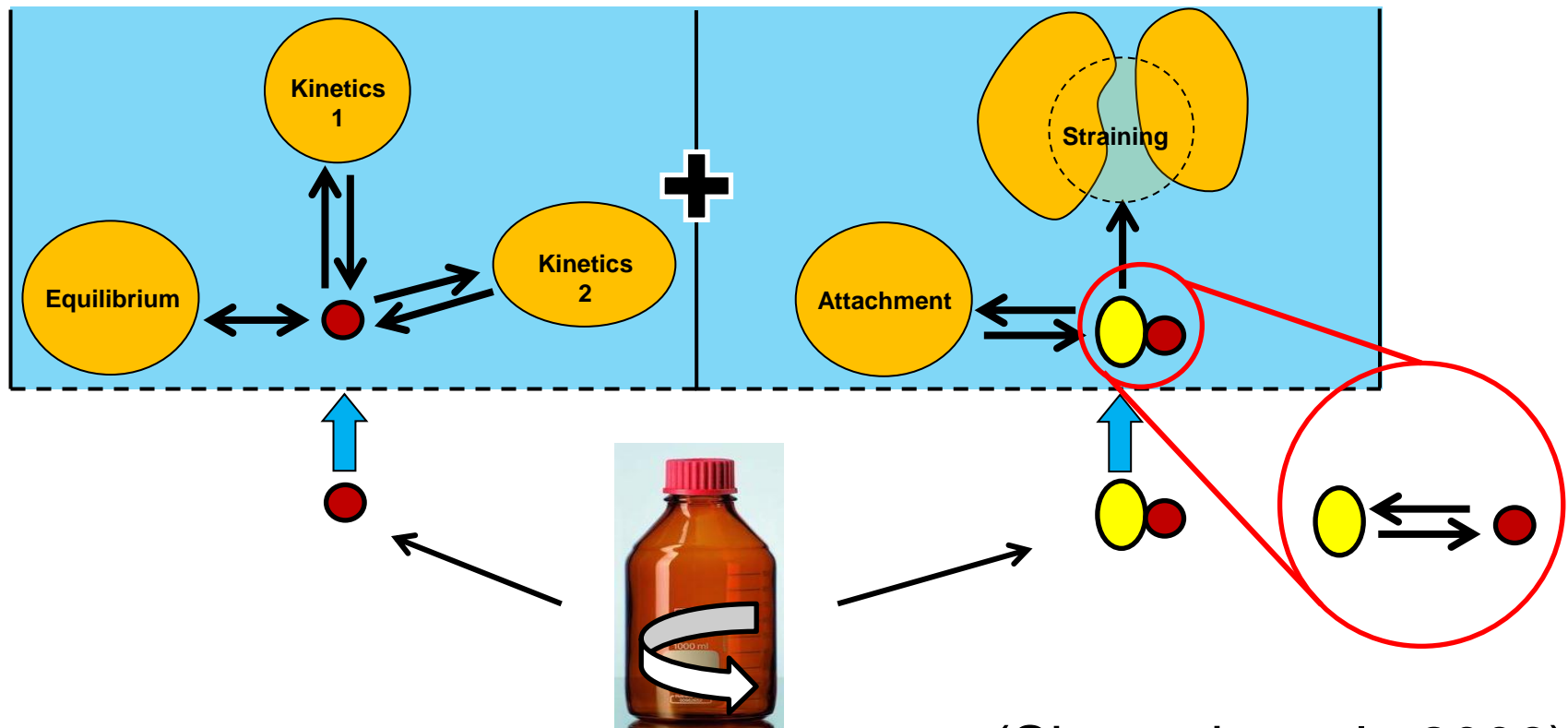
- Transport of lindane alone (MATLAB)



(Selim et al., 1990)

# Materials and Methods

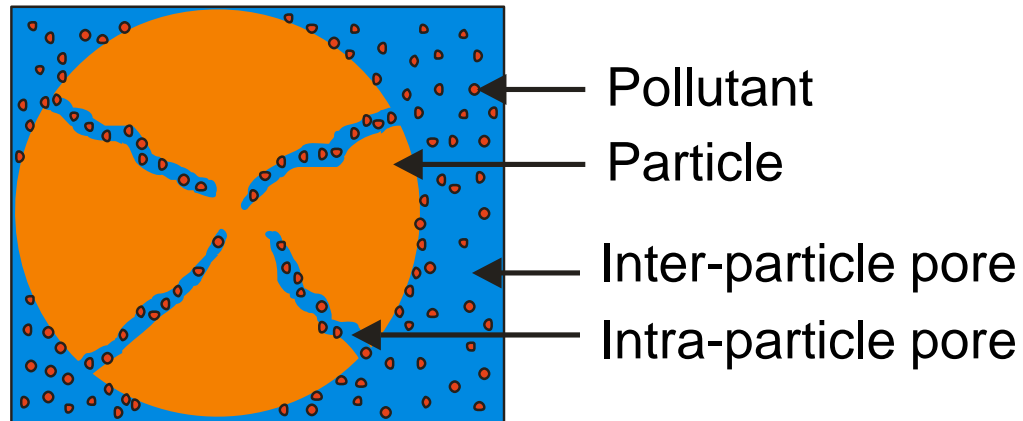
- Synchronous transport of lindane and lignite particles (MATLAB)



(Simunek et al., 2006)

# Materials and Methods

- **Asynchronous transport of lindane and lignite particles (SMART)**



## **Sorption and intra-particle diffusion**

- ✓ Lignite particles
- ✓ Sand (carbonate)

# Results and Discussion

## ➤ Equilibrium sorption of lindane

- **Sand:**

- Calculated linear distribution coefficient:  $0.14 - 1.99 \text{ L kg}^{-1}$
- Modelled linear distribution coefficient:  $0.07 \text{ L kg}^{-1}$
- **Low sorption!**

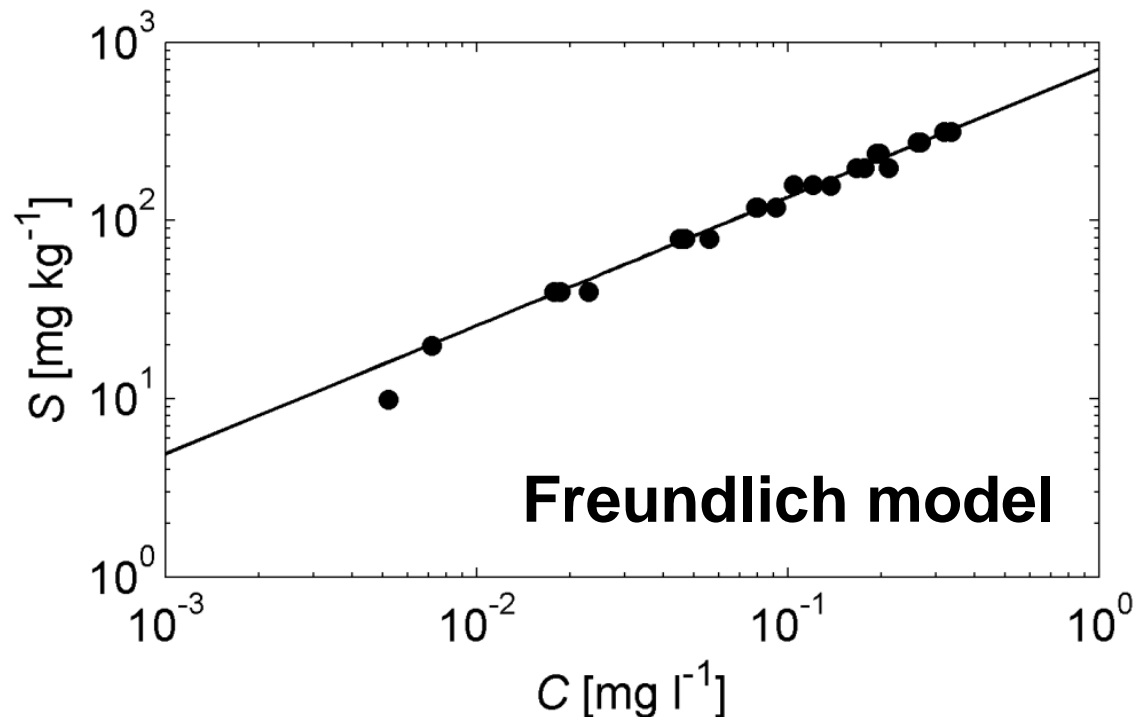


# Results and Discussion

- **Lignite:**

- Freundlich distribution coefficient:  $707 \pm 18 \text{ mg}^{1-1/n_{\text{Fr}}} \text{ L}^{1/n_{\text{Fr}}} \text{ kg}^{-1}$
- Freundlich exponent:  $0.72 \pm 0.02$

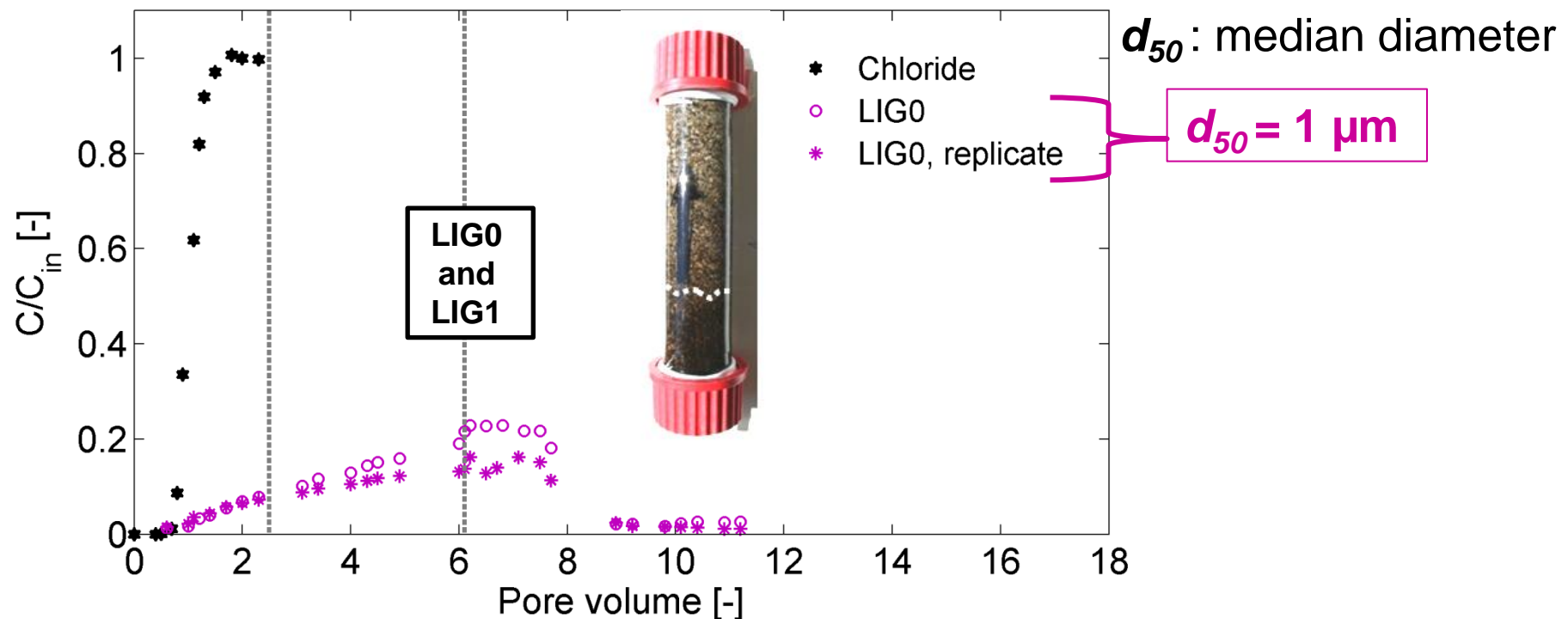
- **High sorption!**



# Results and Discussion

## ➤ Column experiments

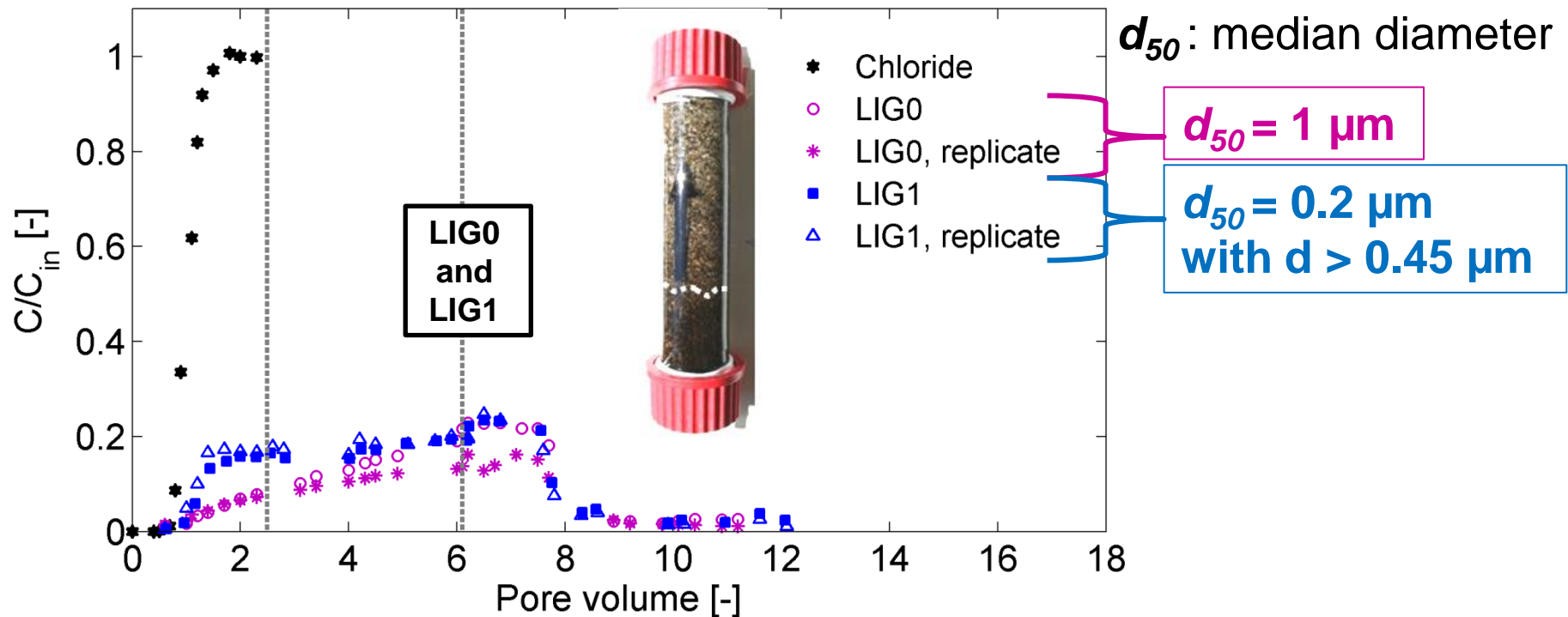
### • Transport of lignite particles alone



✓ Porosity of the sand  $\approx 0.32$

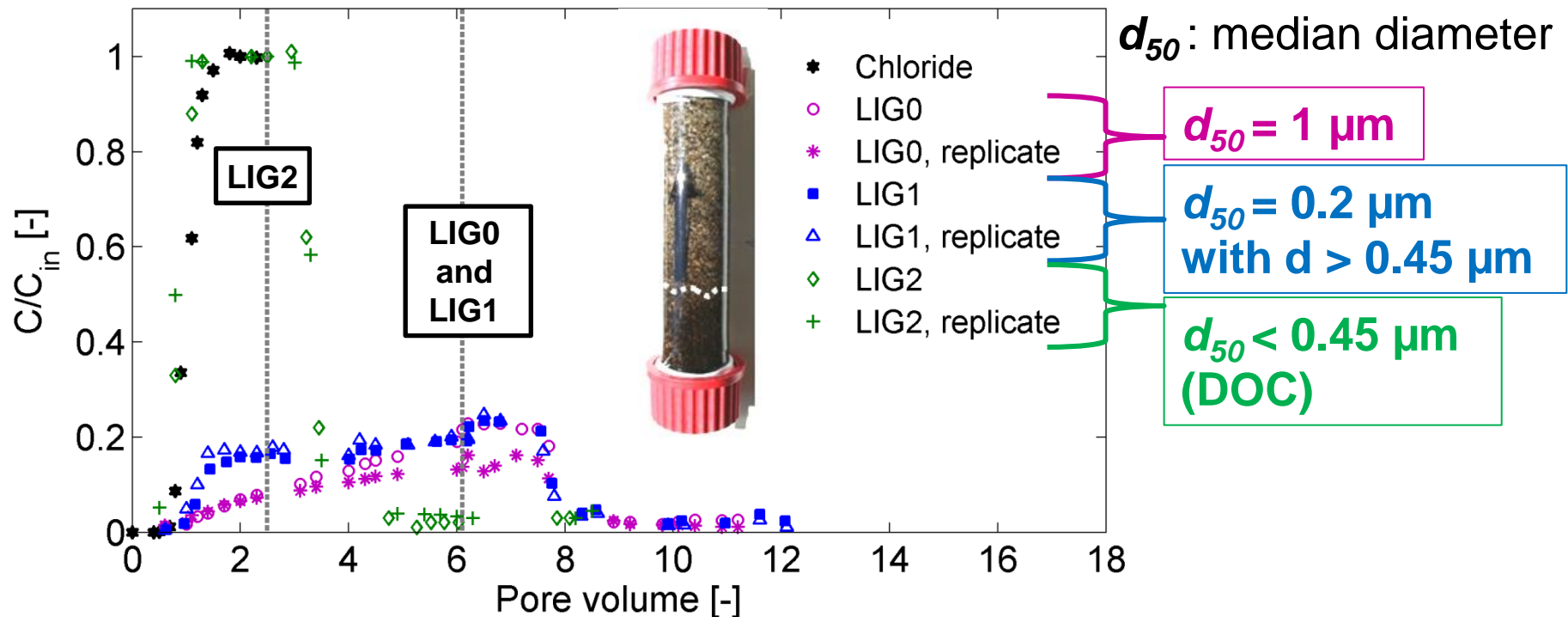
# Results and Discussion

## • Transport of lignite particles alone



# Results and Discussion

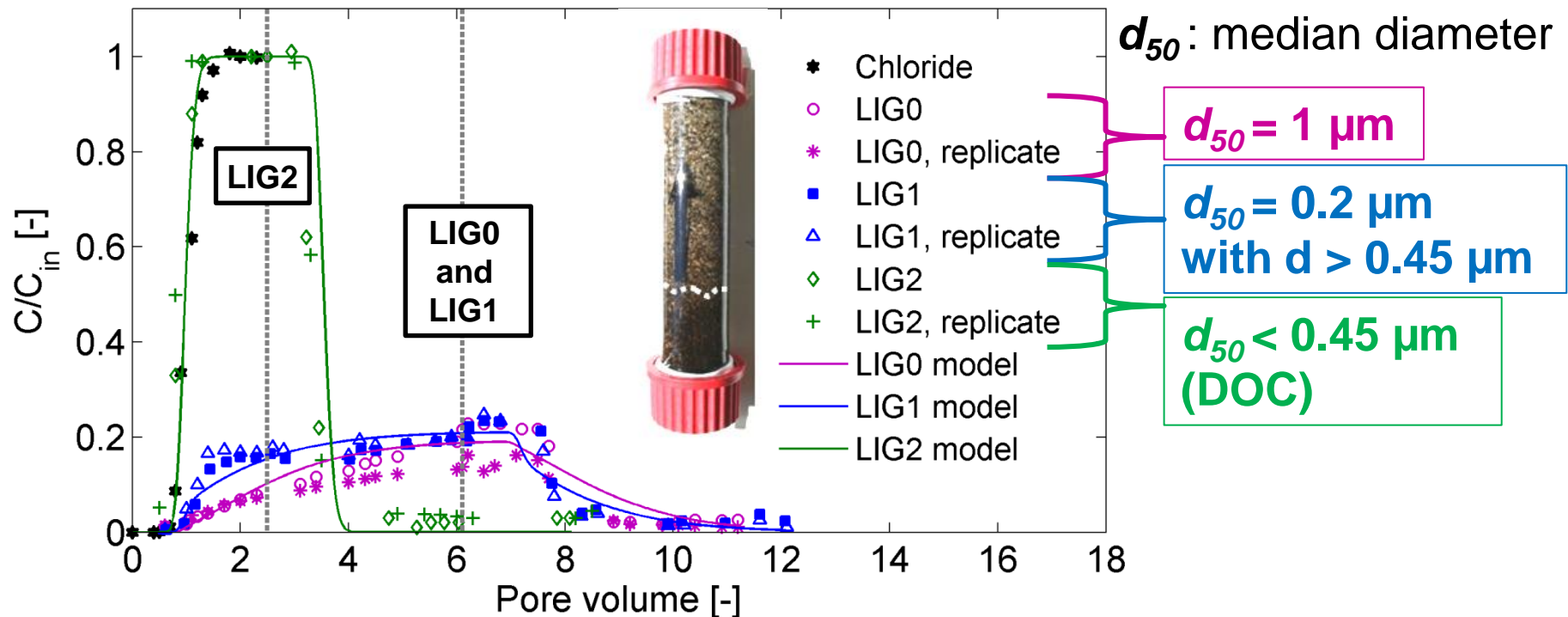
## • Transport of lignite particles alone



✓ Particle retention increased with increasing particle size

# Results and Discussion

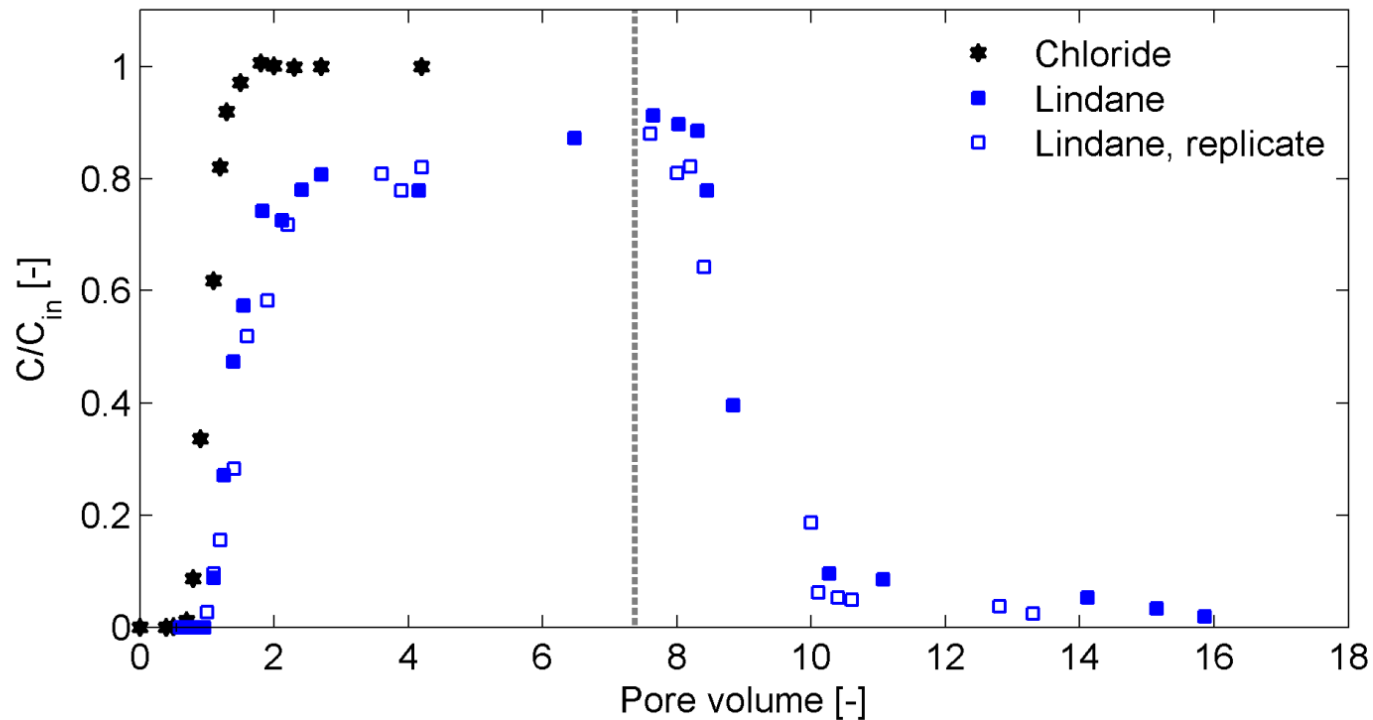
## • Transport of lignite particles alone



✓ Reversible attachment and irreversible straining

# Results and Discussion

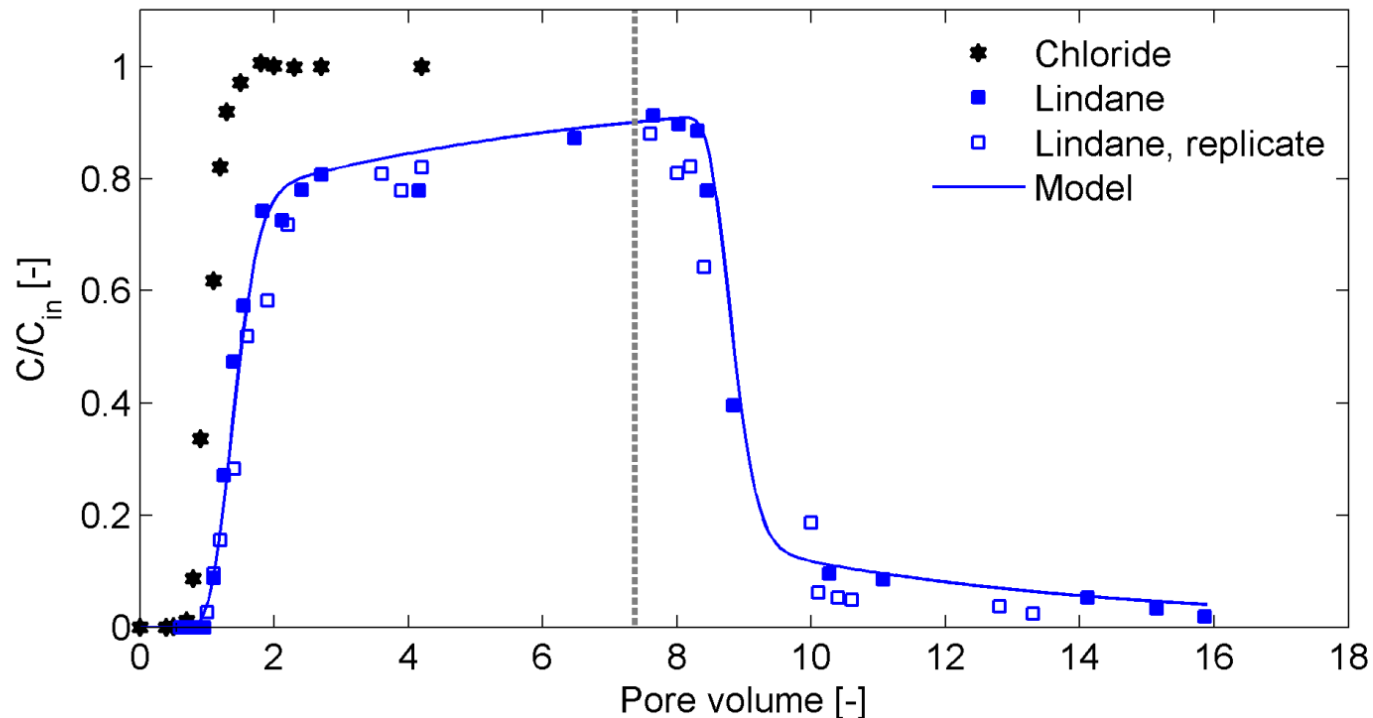
- Transport of lindane alone



✓ Slow sorption kinetics

# Results and Discussion

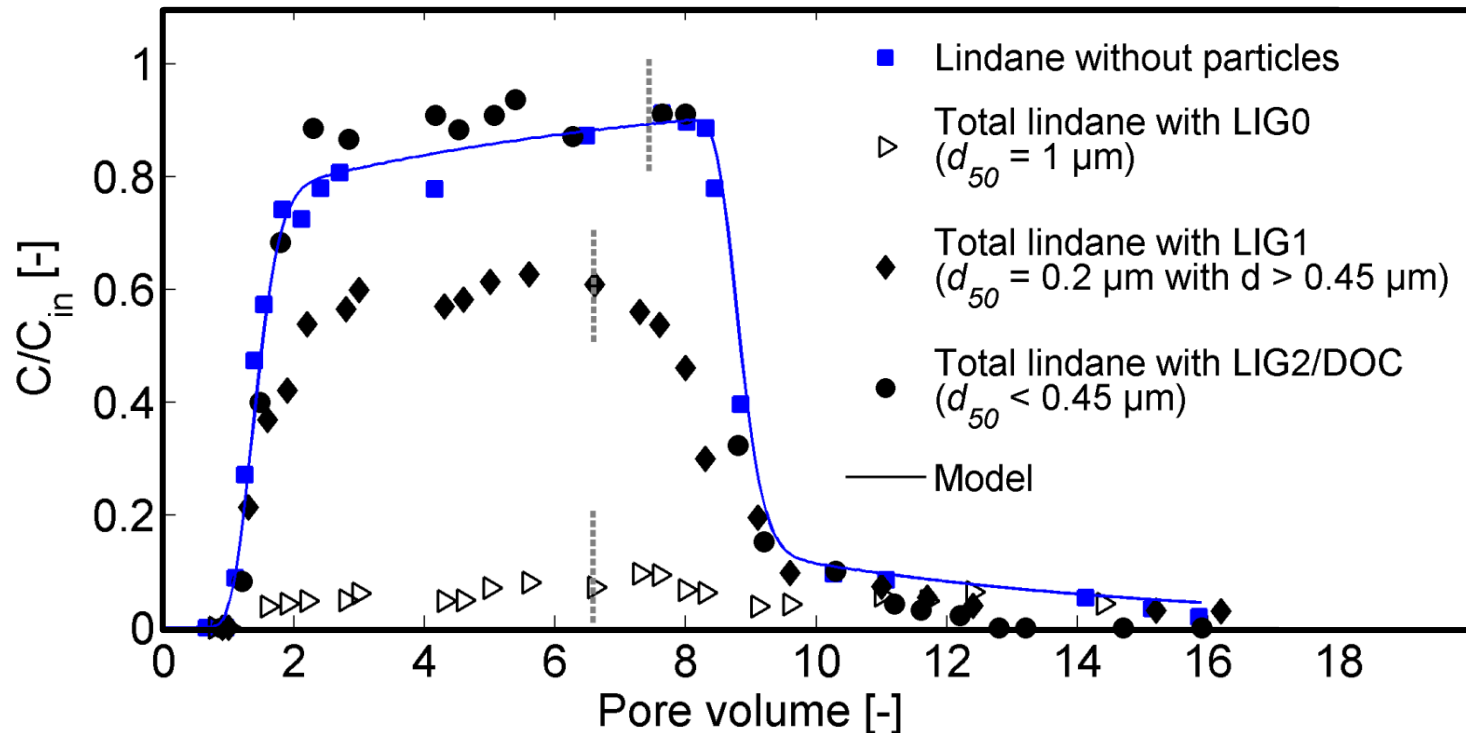
- Transport of lindane alone



✓ Linear three-site sorption onto the sand

# Results and Discussion

- Synchronous transport of lindane and lignite particles

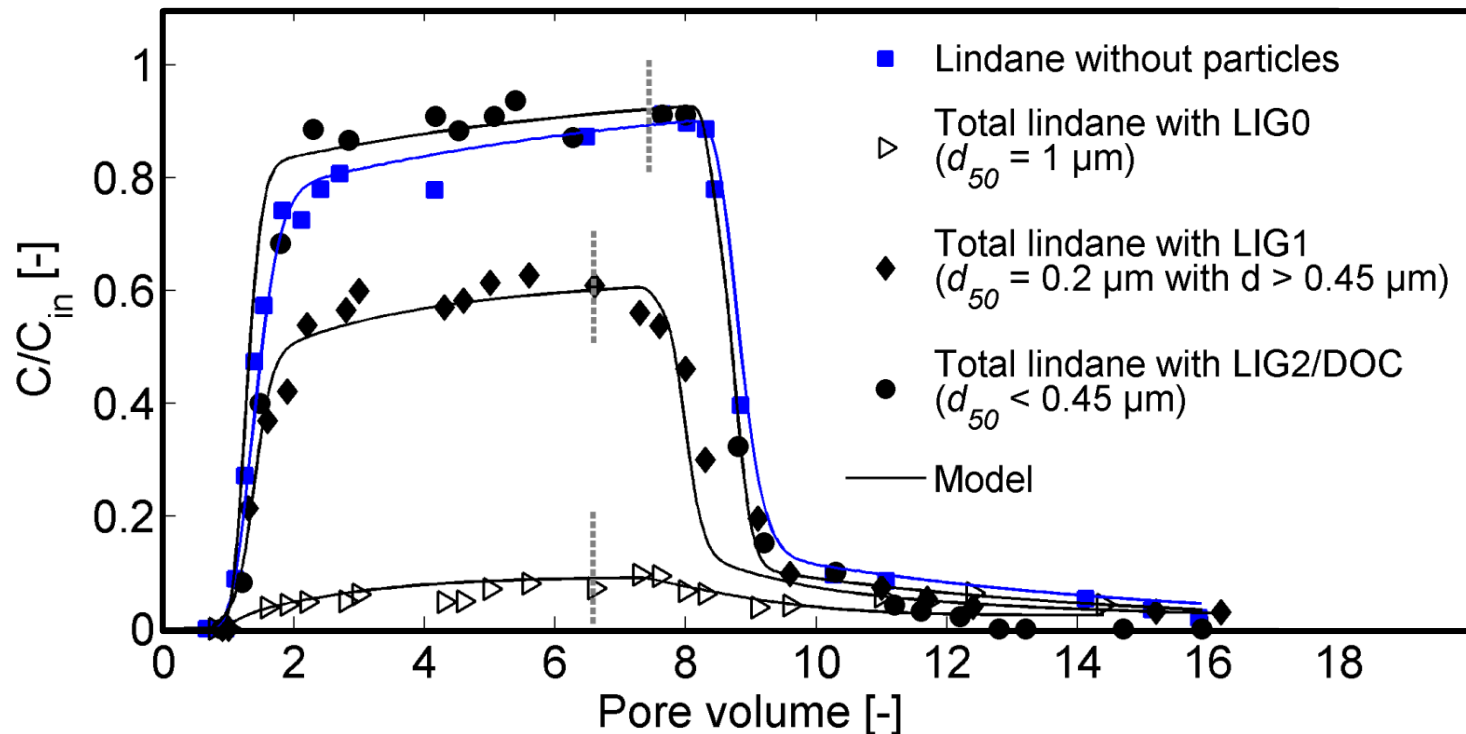


Total lindane = (dissolved lindane) + (particle-bound lindane)



# Results and Discussion

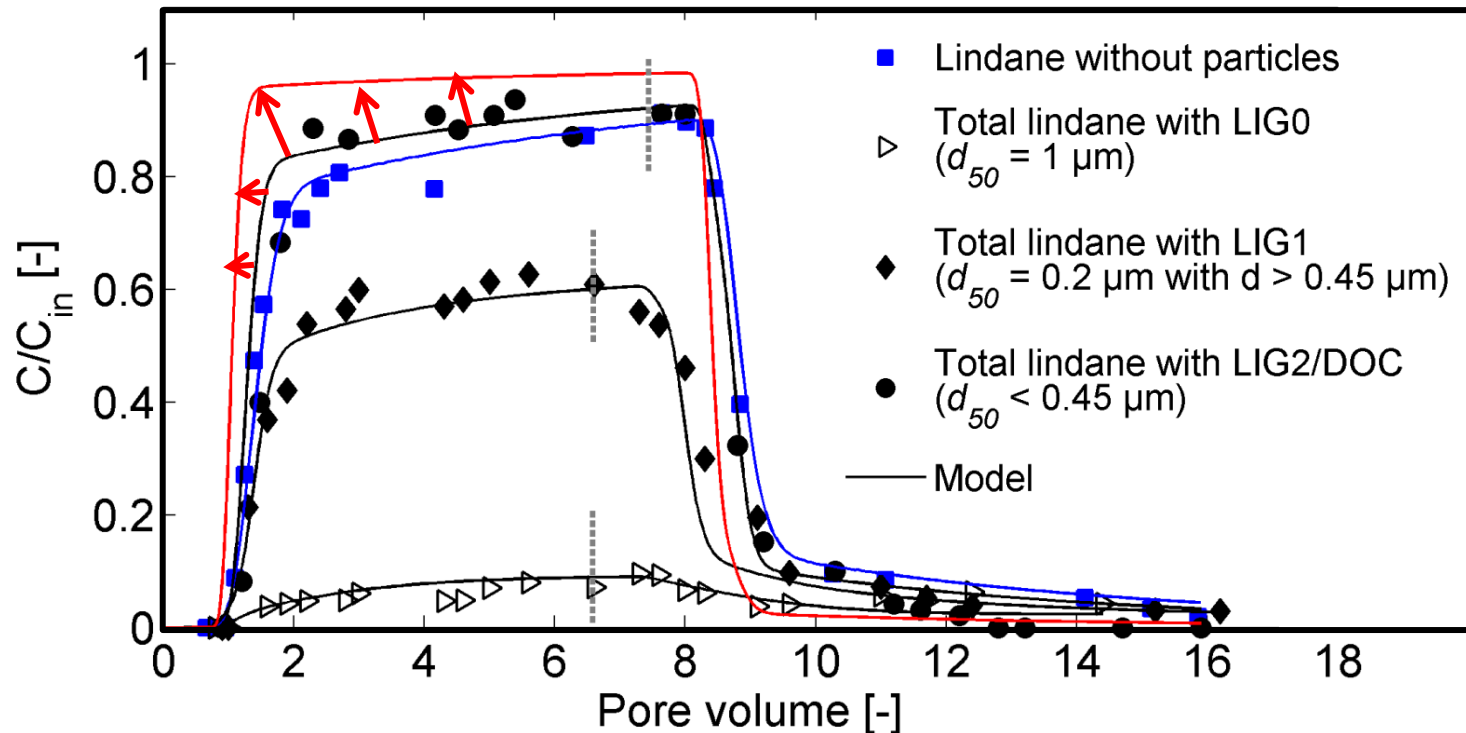
- Synchronous transport of lindane and lignite particles



✓ Root mean square error: 0.05 – 0.09

# Results and Discussion

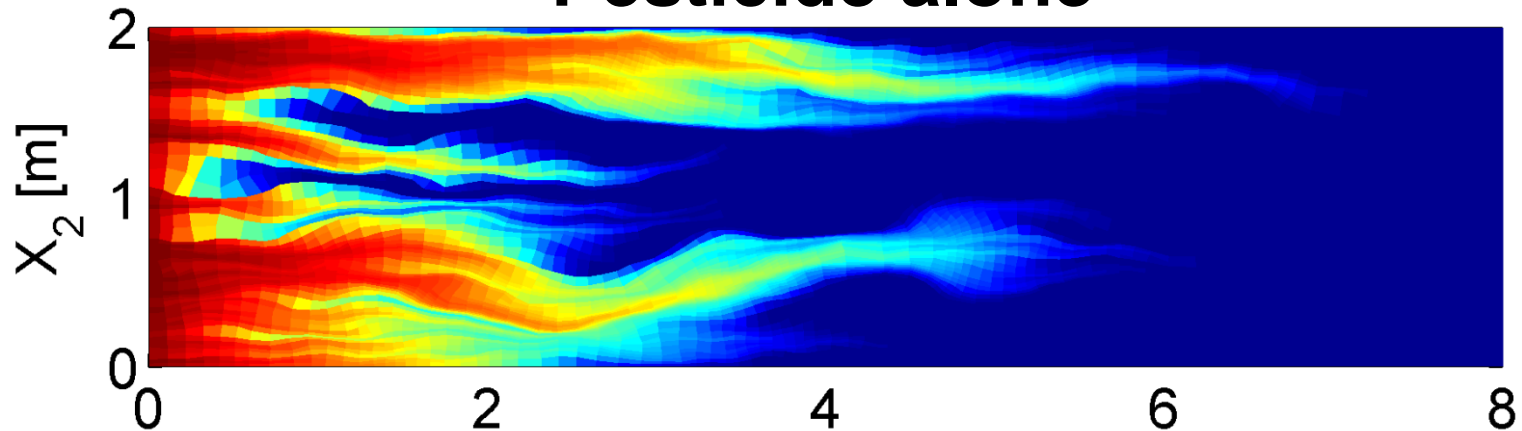
- Synchronous transport of lindane and lignite particles



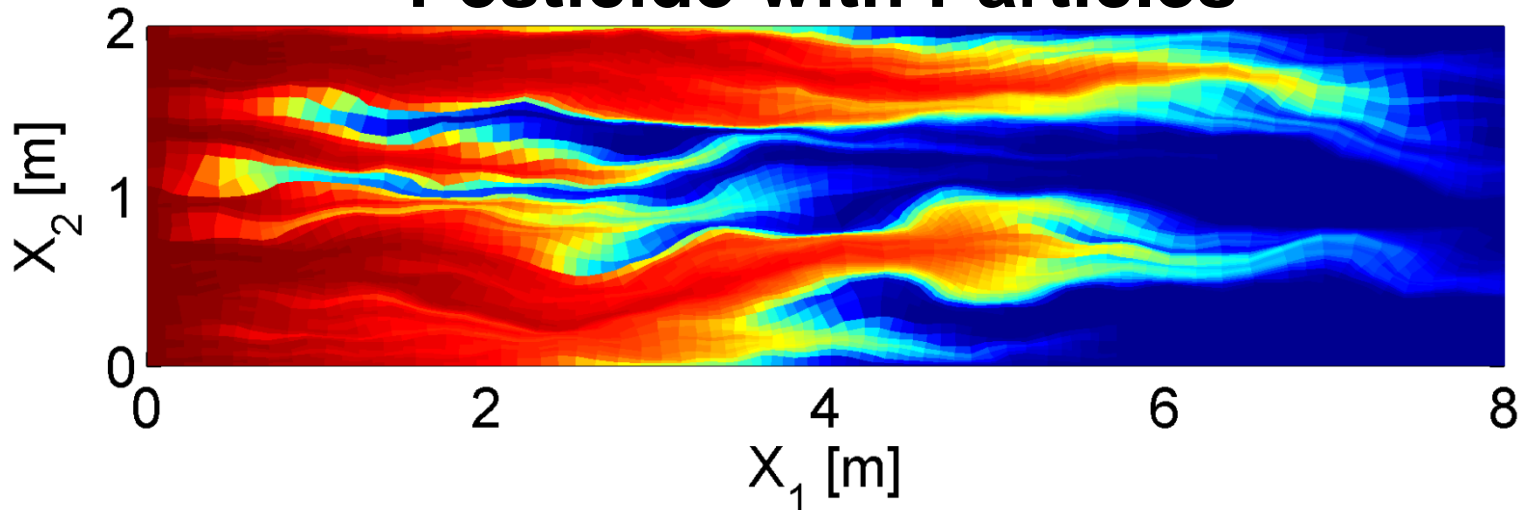
✓ Sensitivity analysis:  $C_{LIG2} = 10 \times C_{LIG2}$

# Results and Discussion

## Pesticide alone

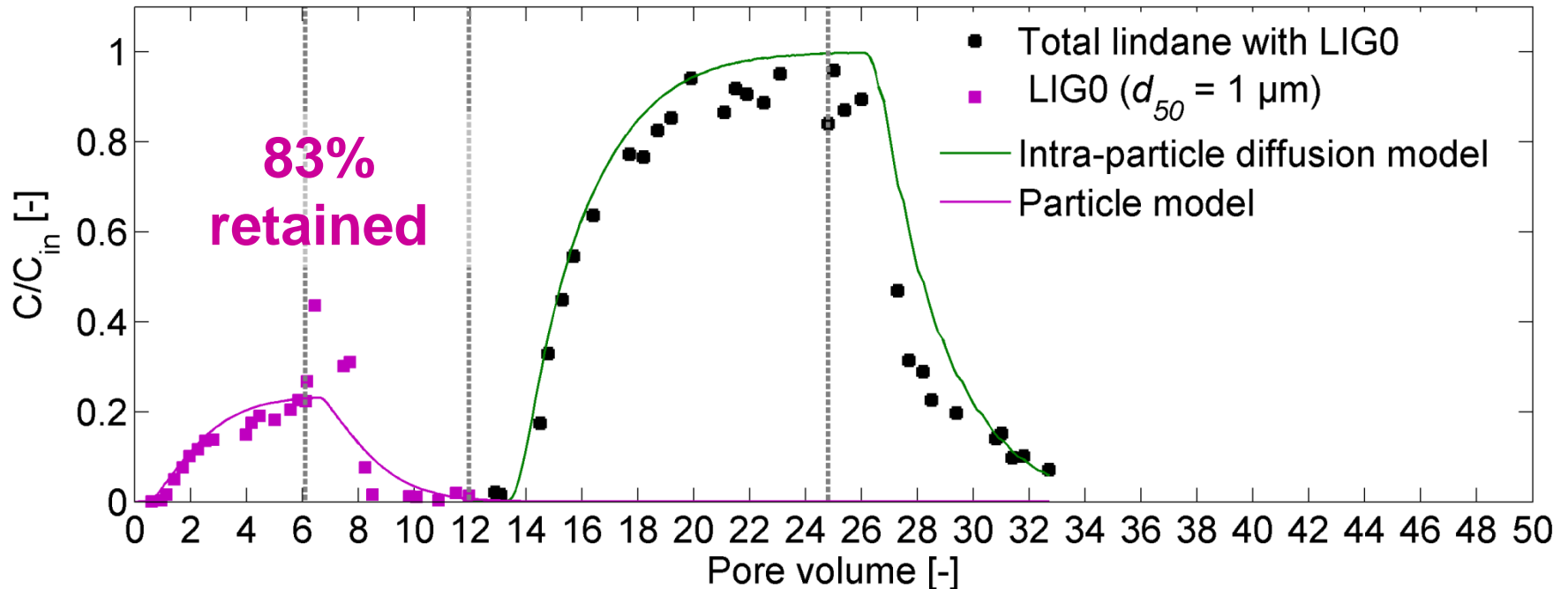


## Pesticide with Particles



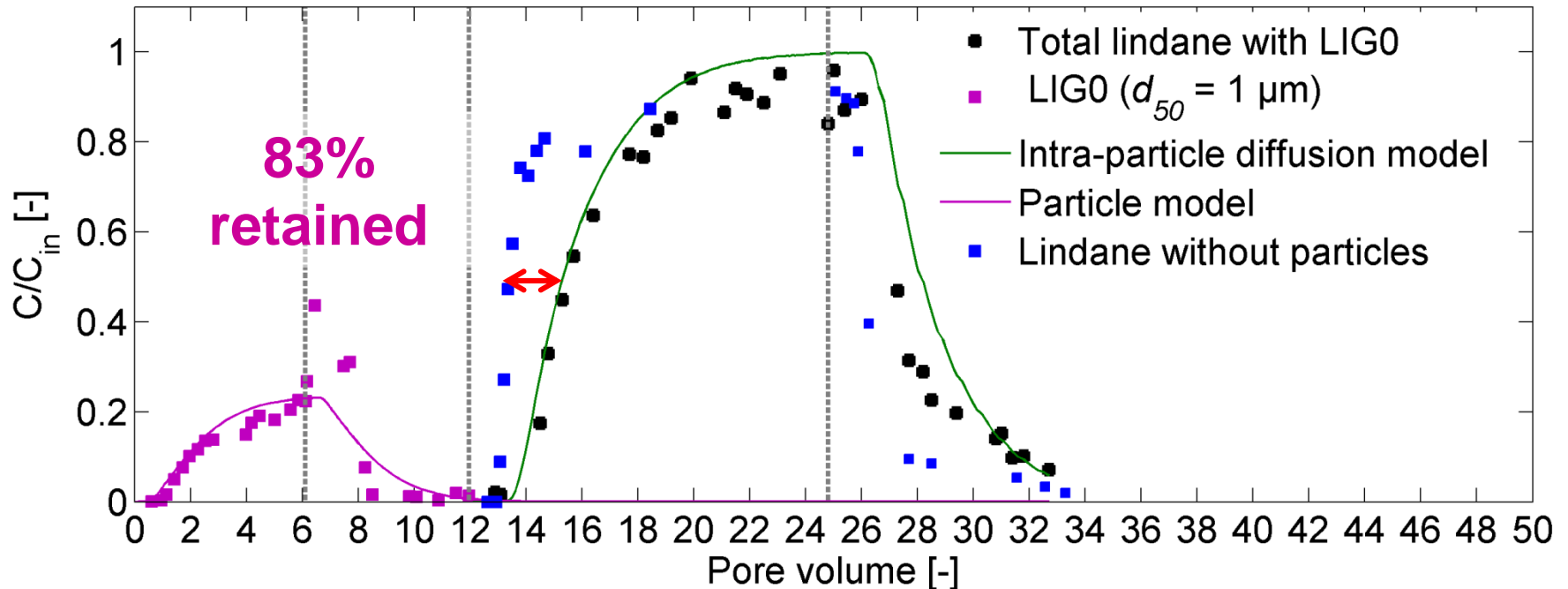
# Results and Discussion

- Asynchronous transport of lindane and lignite particles



# Results and Discussion

- Asynchronous transport of lindane and lignite particles



✓ Organic carbon content increased from 0.06 to 0.11 weight% → increased lindane sorption

# Conclusions

- The transport of **colloidal organic particles** in saturated porous media depends considerably on their **size**.
- **Particles  $> 0.45 \mu\text{m}$**  undergo strong retention, leading to retarded transport of sorbing compounds.
- **Particles  $< 0.45 \mu\text{m}$  (DOC)** enhance the transport of sorbing compounds.

# Conclusions

- Implication in the proposed application of **biochar** for soil amendment:



- Biochar ~ lignite (brown coal): may also release DOC.

# Conclusions

➤ Further implications in Alberta:

**Natural facilitating organic particles** can be found for e.g. in peat bogs and oil sand fields and include:

- particulate organic matters;
- clay colloids;
- carbonate colloids.





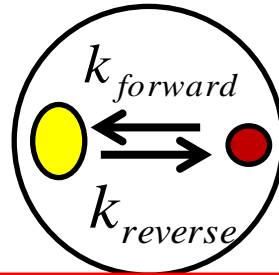
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Thank you.

# Supplementary Information

- **Modelling:**



$$r = k_{forward}[P][L_{P,eq}] - k_{reverse}[P][L_P]$$

$[P]$ : particle concentration

$[L_p]$ : particle-bound lindane concentration

$k_{forward}$ ,  $k_{reverse}$  : rate coefficients

- **Finding:**  $k_{forward} \approx k_{reverse} \approx k_p$

✓ Model simplification:

$$r = k_p ([P][L_{P,eq}] - [P][L_P])$$