Retention of a model pesticide on artificial hydrophobic soils

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Background

- Soil retention of pesticides mainly controls their dispersion to other environmental compartments
- The retention of neutral molecule is usually related to the physico-chemical properties of molecules
- But it also depends on the soil properties, like its hydrophobic feature
- The hydrophobicity of soils is mainly attributed to organic matter that interacts with mineral particles
- Organic matter of soils usually bears negative charges and is sorbed on negative mineral surfaces (clays) through calcium binding

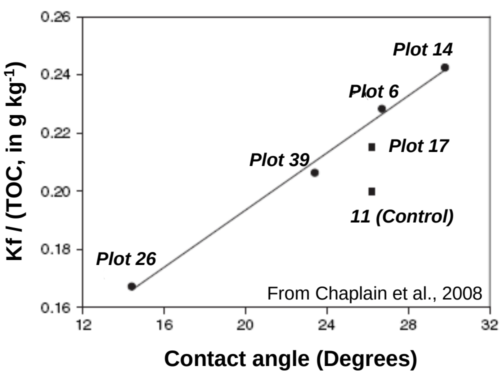
Background

- Recent experiments showed that equilibrium retention of diuron was governed by the hydrophobicity of clay fraction, and soil structure (Chaplain et al., 2008, EJSS)

42 plots long-term experiment (since 1928)
(INRA, Versailles, France)

➡ One same soil ➡ Variation of pH (from 3.5 to 8.2) and hydrophobicity due to various amendments and fertilizers

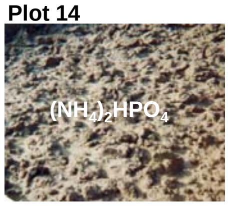
Background



Hydrophilic → *Hydrophobic*

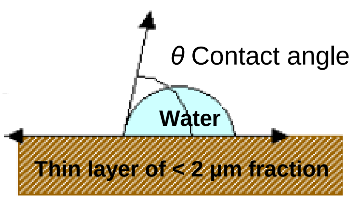
Plot 26

Plot 14



Plot 11

Plot 17



- Plot 17: Same hydrophobicity as Control
  But ≠ structure ➡ ↘ Adsorption rate

Objectives

To study using artificial organo-silica particles:

- The influence of the hydrophobic characteristics of surfaces on the retention of a neutral pesticide (lindane)

- The influence of diffusion on the kinetics of adsorption

➡ Silica particles covered by cationic polymers having contrasted hydrophobic features were used

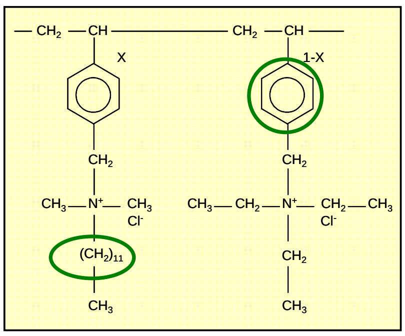
These particles are the sorbent phase of artificial soils

Artificial organic matter

- Polymers derived from poly (vinyl benzyl chloride)

- X is the molar fraction of dimethyldodecylammonium (1-X) is the molar fraction of triethylammonium

  X is a well-controlled parameter that could vary from 0 to 100
  In this study X = 20 and 80



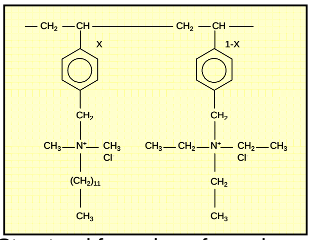
Structural formulae of synthetic copolymers

- Hydrophobic side chains are randomly distributed along the polymer backbone

- Hydrophobicity had two chemical natures: aliphatic chains and aromatic cycles

Artificial organic matter

- These amphiphilic polymers are soluble in water



Structural formulae of copolymers

- Their 3D conformation in water solution depends on electrostatic repulsions between charges, ionic strength and, hydrophobic interactions

- They are strongly adsorbed on silica surfaces by electrostatic interactions
  - High affinity adsorption
  - The adsorbed amount does not depend on hydrophobicity (X)
  - The conformation of adsorbed polymers is flat due to the cationic charges

Main characteristics of organo-silica sorbents

- Porous and non-porous particles were used to study the influence of diffusion on pesticide sorption kinetics in the case of hydrophobic interactions

Characteristics of covered silica particles:

Name	Kind of particles	Diameter (µm)	Coverage with polymer (mg m^{-2})	Total organic carbon (g C / 100g soil)
A20	Non porous	0.1	0.23 ± 0.03	0.44
A80	Non porous	0.1	0.38 ± 0.04	0.61
B80	Micro-porous	0.9	0.39 ± 0.04	0.61

} X (A20, A80)
} Porosity (A80, B80)

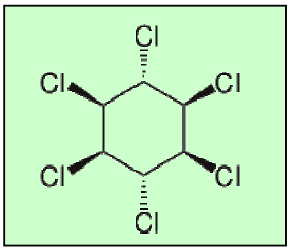
➡ The A20 sorbent was less hydrophobic than A80 and B80 sorbents

Model pesticide

Lindane

- Insecticide

- M = 290.83 g mol^{-1}
  Sw = 2-10 mg L^{-1}
  logKow = 3.8
  Koc = 1352-2139 L kg^{-1} (Data from Fabre et al., 2005)



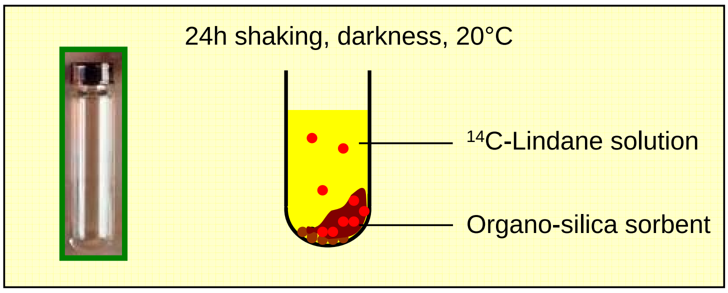
Structural formulae of lindane

➡ Chosen because its adsorption was assumed to be mainly due to hydrophobic interactions

Retention of lindane on organo-silica sorbents

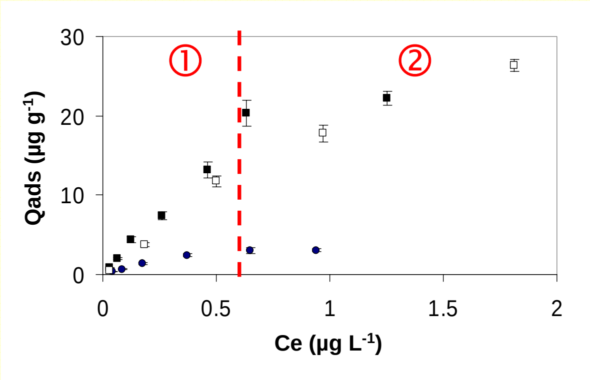
- Solutions of ^{14}C-lindane in 10^{-3}M KCl at concentrations from 0.05 to 2.2 mg L^{-1}

- Batch experiment ➡ Adsorption kinetics & Isotherms



- Suspensions of the organo-silica sorbent used in retention measurements were completely dispersed without any polymer in solution

Adsorption isotherms of lindane



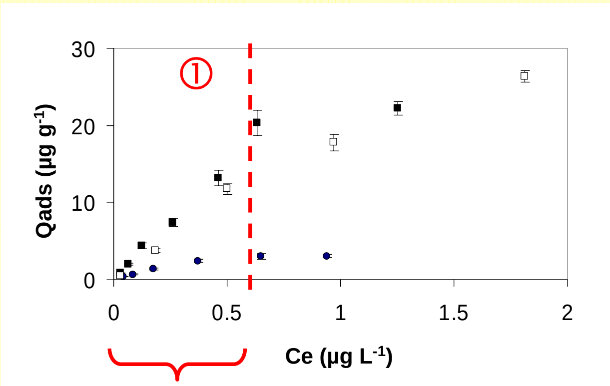
● A20, low hydrophobicity, non porous
■ A80, high hydrophobicity, non porous
□ B80, high hydrophobicity, micro-porous

Qads: Amount of adsorbed lindane (µg g^{-1})
Ce: Equilibrium concentration (µg L^{-1})

- 2 parts in adsorption isotherms
- The first part was described by linear isotherm

Introduction • Materials & Methods • **Results & Discussion** • Conclusion

Adsorption isotherms of lindane



Koc (L kg^{-1}) = Qads / Ce

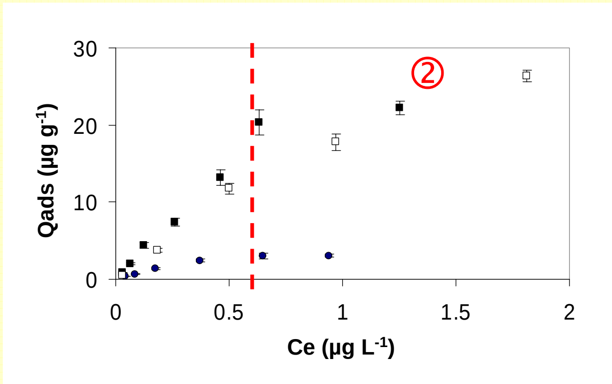
● A20, low hydrophobicity, non porous
■ A80, high hydrophobicity, non porous
□ B80, high hydrophobicity, micro-porous

Qads: Amount of adsorbed lindane (µg g^{-1})
Ce: Equilibrium concentration (µg L^{-1})

A20: Koc = 1778 L kg^{-1}
A80: Koc = 4898 L kg^{-1}
B80: Koc = 3236 L kg^{-1}

- Koc in agreement with literature (Fabre et al., 2005)
- Retention of lindane on A80 & B80 > A20 ➨ Due to their hydrophobic feature

Adsorption isotherms of lindane

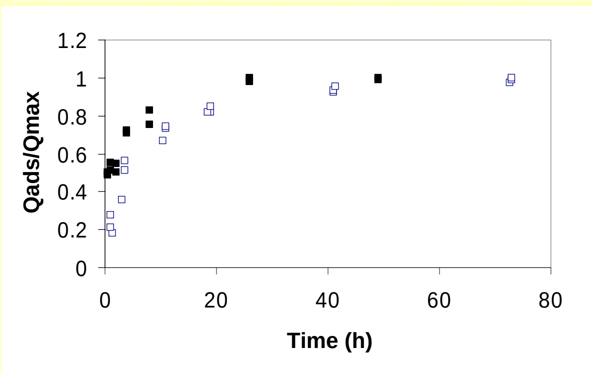


● A20, low hydrophobicity, non porous
■ A80, high hydrophobicity, non porous
□ B80, high hydrophobicity, micro-porous

Qads: Amount of adsorbed lindane (µg g^{-1})
Ce: Equilibrium concentration (µg L^{-1})

- Phase ②: 0.002 ± 0.001 mol lindane mol^{-1} of alkyl chains adsorbed on A20
  0.003 ± 0.001 mol lindane mol^{-1} of alkyl chains on A80 & B80
- The porous nature of silica B80 did not affect the retention of lindane

Adsorption kinetics of lindane



■ A80, non porous
□ B80, micro-porous

Qads: Amount of adsorbed lindane (µg g^{-1})
Qmax: Maximum amount of adsorbed lindane after 72 hours (µg g^{-1})

➡ Measured in the linear range of isotherms

- A plateau was reached after 24 h for both organo-silica sorbents
- Sorption initially delayed in porous particles (B80) ➡ Due to molecular diffusion inside the micropores (1 µm) & Diffusion into the polymer layer (10 nm)
- Small ≠ between curves ➡ Diffusion through the polymer is dominant process

Hydrophobic interactions

- Alkyl chains: Hydrophobic zones ➨ Sorption through partition mechanism
- Aromatic cycles: Sorption through pi-stacking molecular interactions

Hypotheses:

- Lindane sorption is supposed mainly governed by pi-stacking molecular interactions
- Alkyl chains might increase the accessibility of aromatic rings

Conclusion

- The measured Koc were close to typical values found for lindane in soils ➨ Relevance of such organo-silica sorbents that could be used as “artificial soils” in retention modelling
- Additional measurements, including desorption kinetics, are needed for lindane and other selected pesticides to improve the description of hydrophilic and hydrophobic interactions
- Suspension of organo-silica particles should be used as reference materials to compare the reactivity of pesticides and soils

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