



*Can we measure bioavailability of organic
contaminants in soil?*

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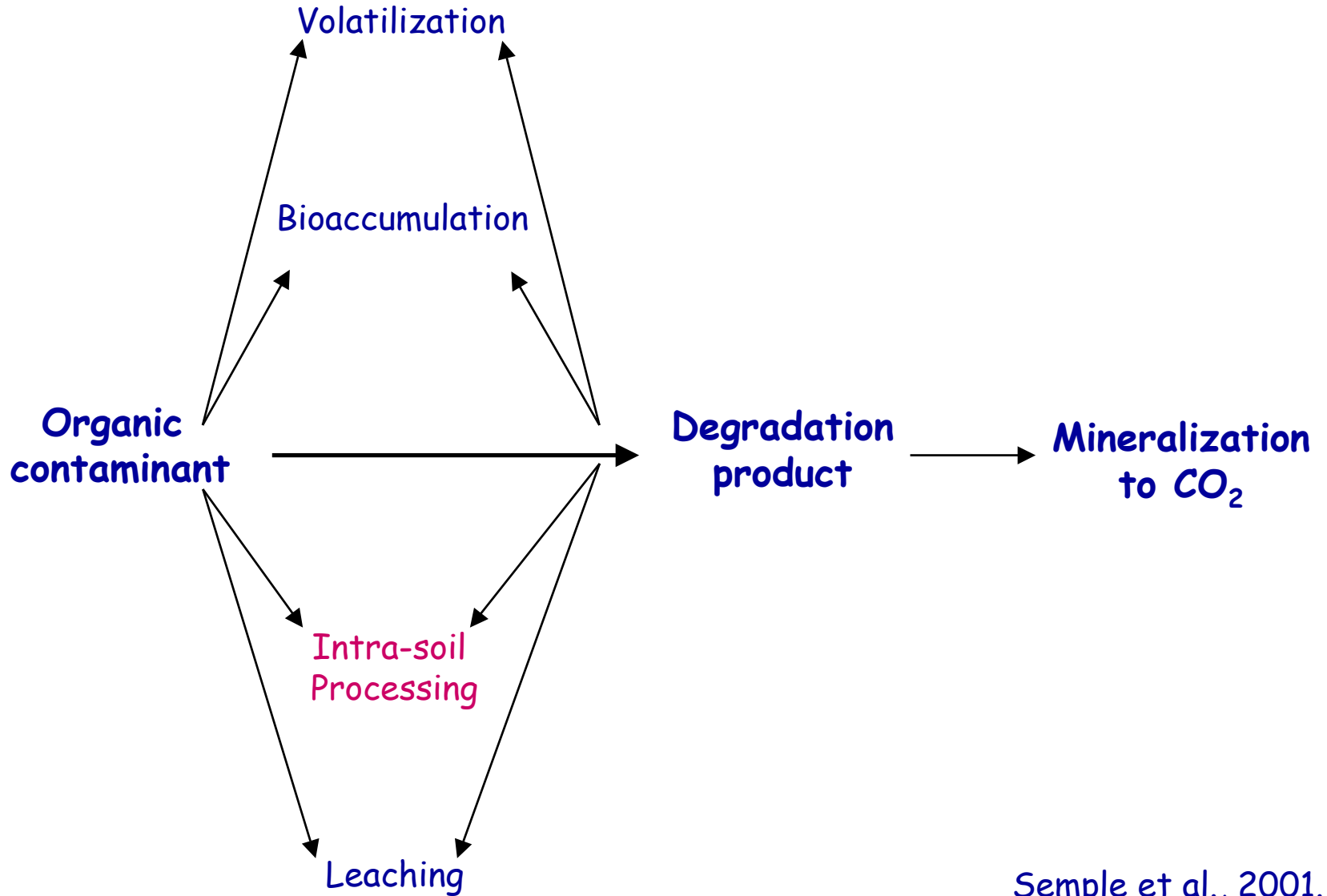


Content

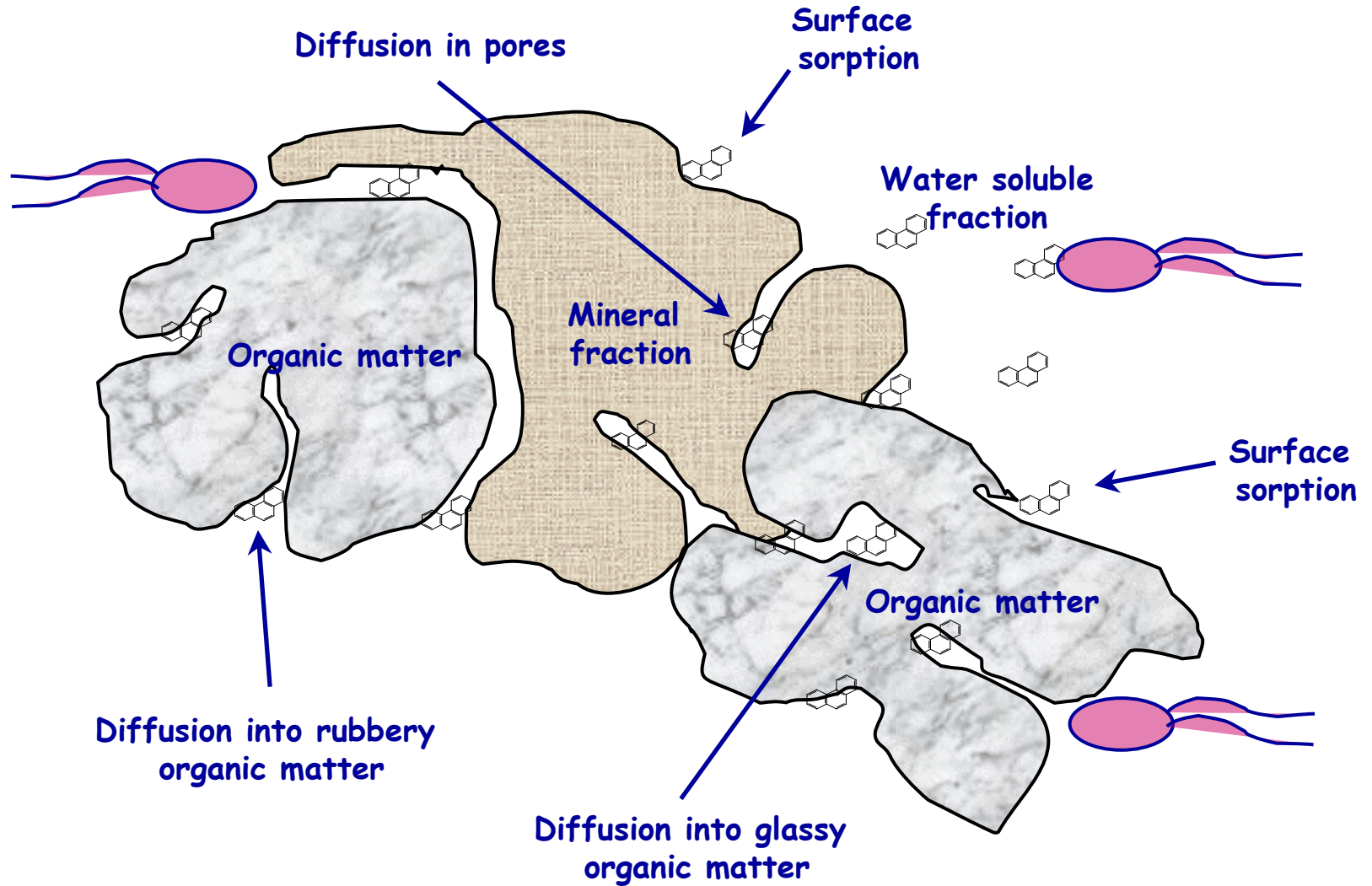
- Introduction
 - ↳ fate and behaviour of contaminants in soil
 - ↳ why do we want to be able to predict of bioavailability
- Methods for determining putative bioavailability
 - ↳ cyclodextrin extraction technique
- Can we actually measure bioavailability *chemically*?
 - ↳ definitions
- Conclusions



Fate and behaviour in soils



Semple et al., 2001.



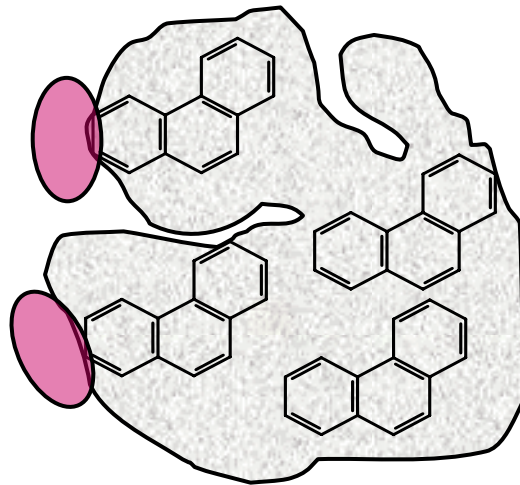


Understanding processes



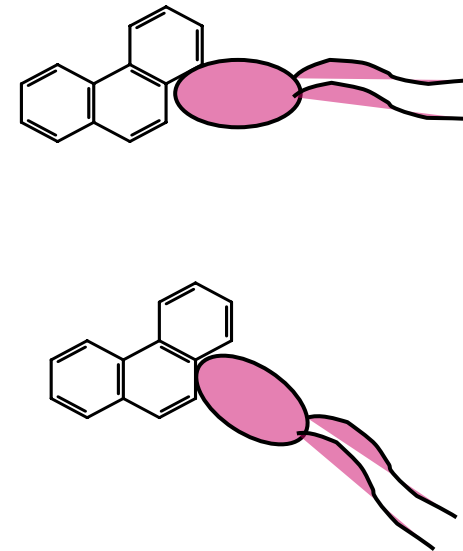
Modes of degradation

Soil-associated HOC



Degradation by direct contact

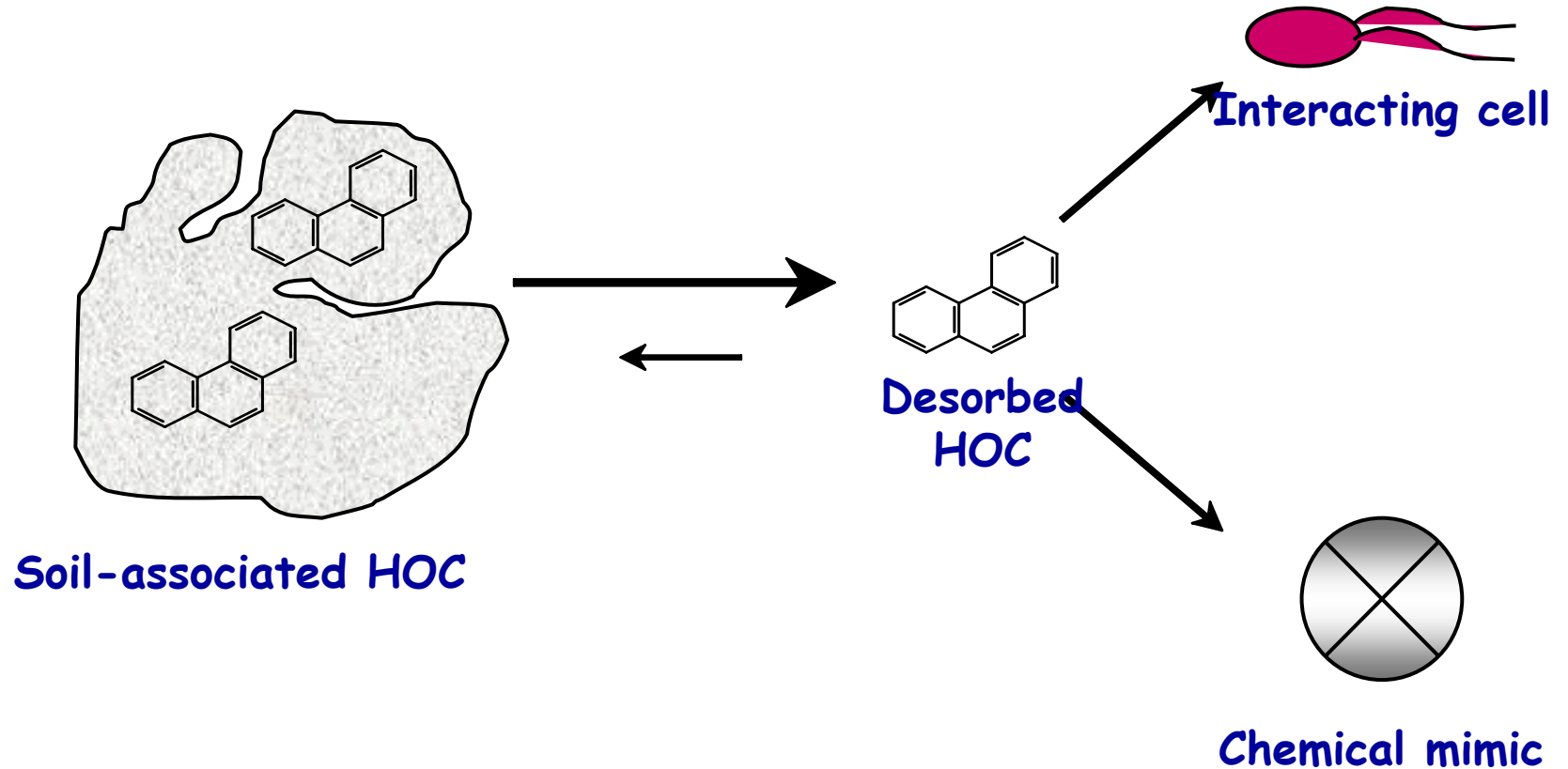
Dissolved HOC



Degradation in the aqueous phase



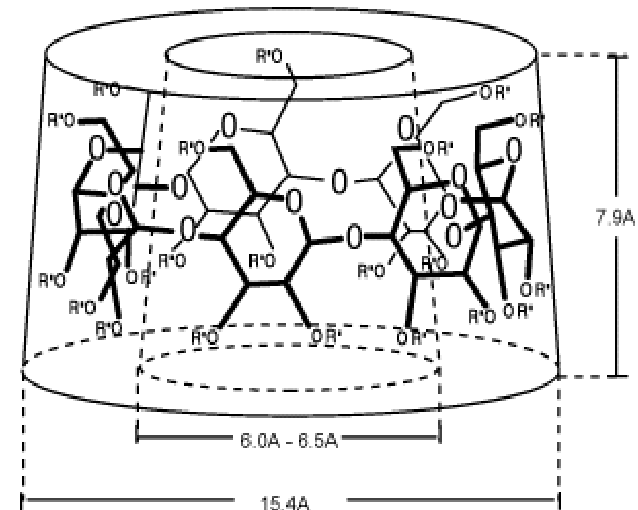
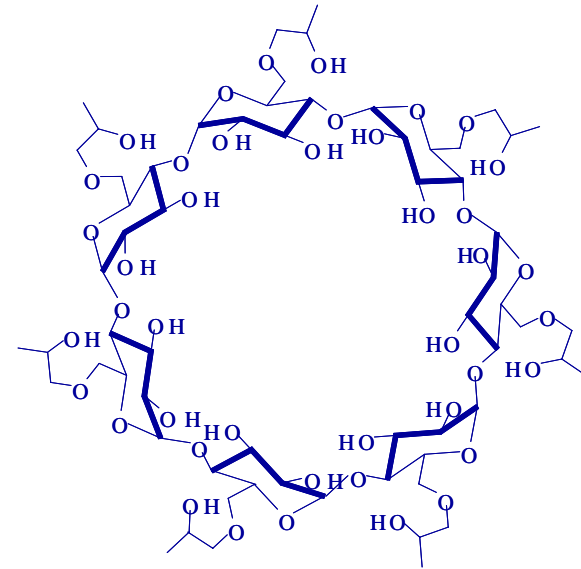
Chemical mimicry??



Semple et al., 2003

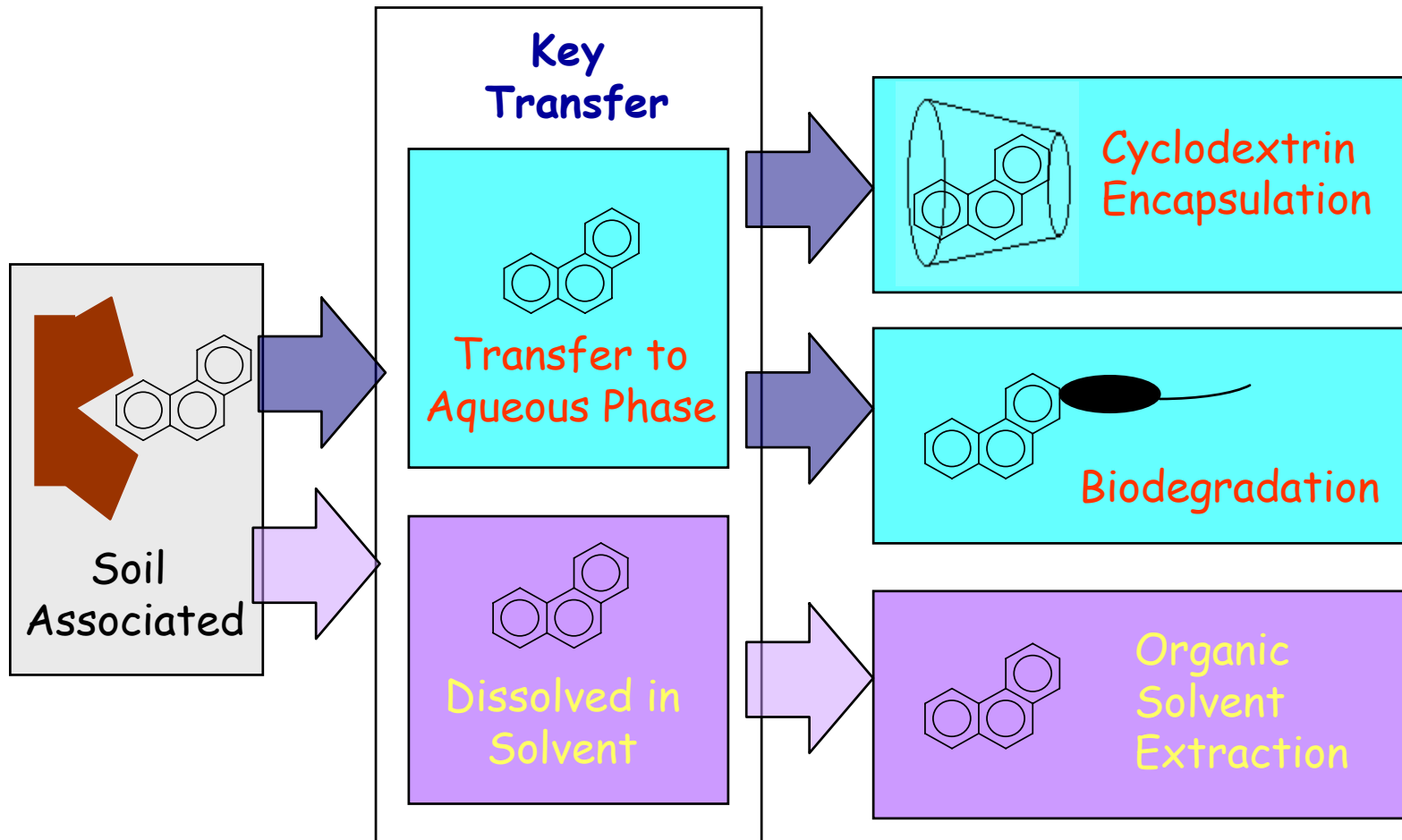
The cyclodextrin extraction technique

- Cyclodextrins are a group of macrocyclic compounds comprising a torus α -1,4-linked glucose units
- Increases the solubility of hydrophobic organic molecules
- Bucket-shaped molecule with an hydrophilic exterior and a hydrophobic cavity





Chemical mimicry of biological processes



Reid et al., 2000

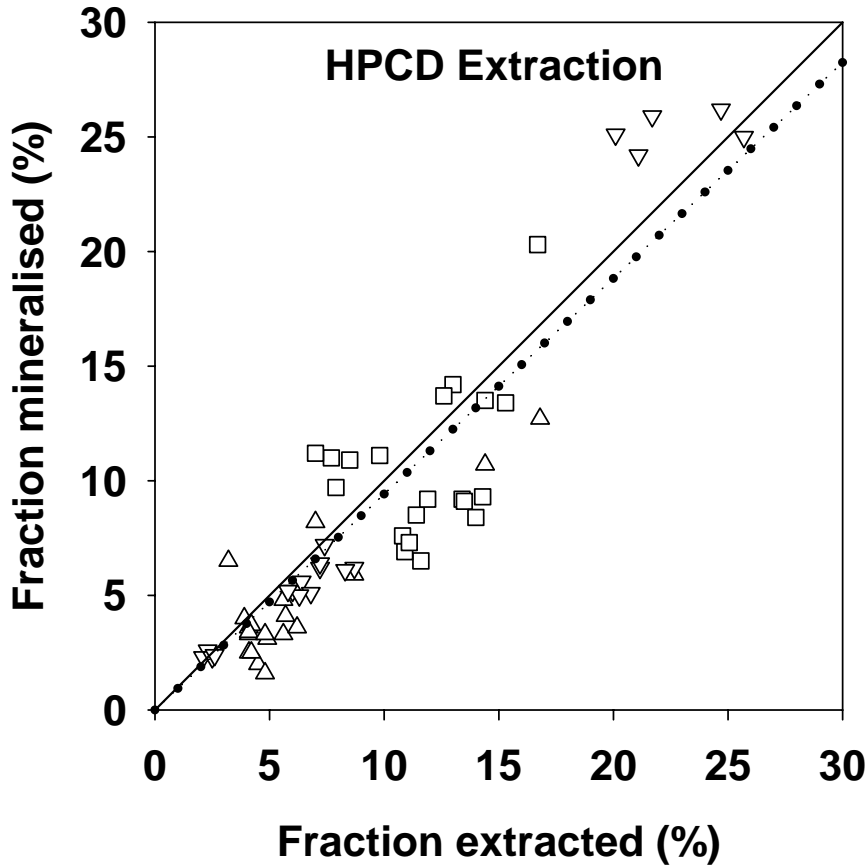


Supporting data

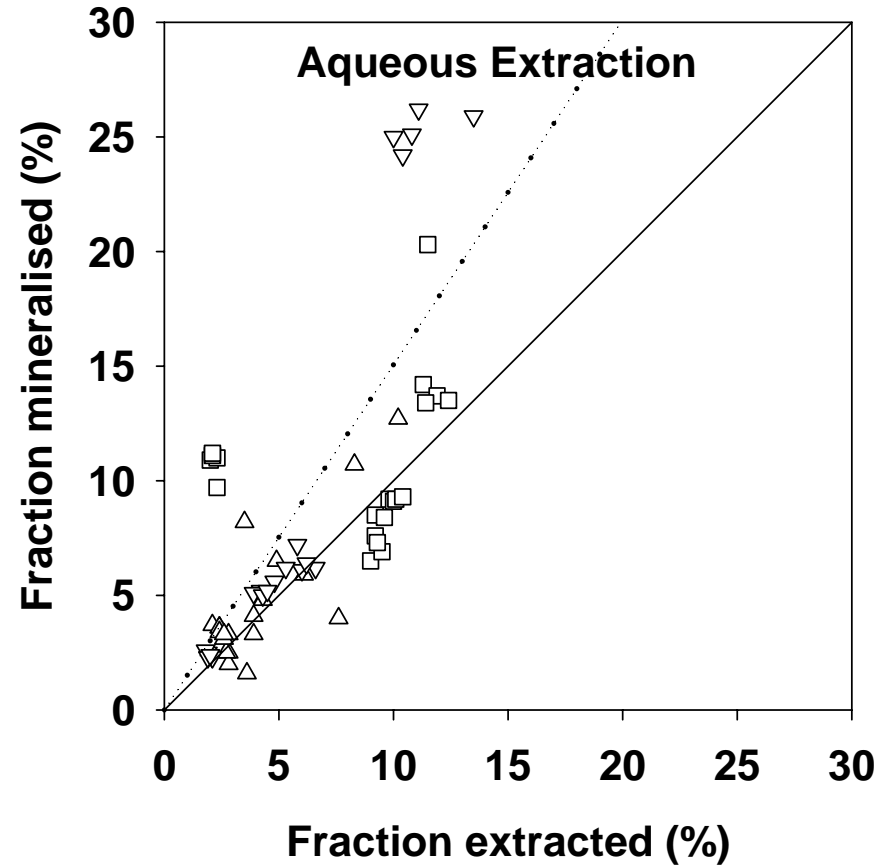


p-CRESOL EXTRACTABILITY VS. BIODEGRADATION

$y = 0.94 x$ ($R^2=0.84$)



$y = 1.21 x$ ($R^2=0.36$)

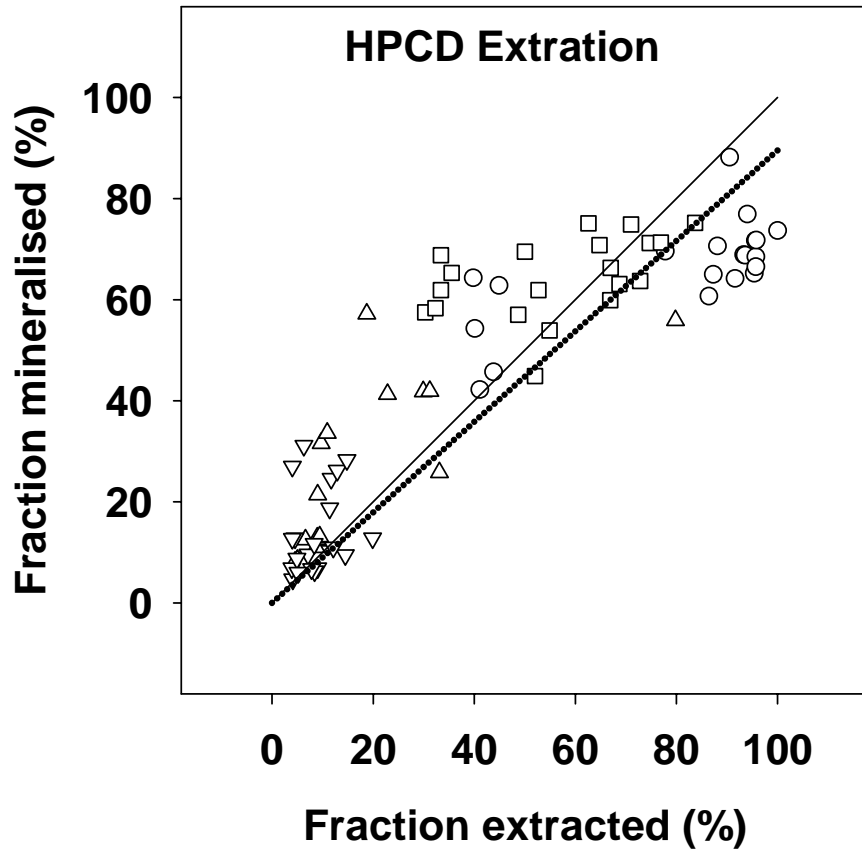


Allan et al., in prep

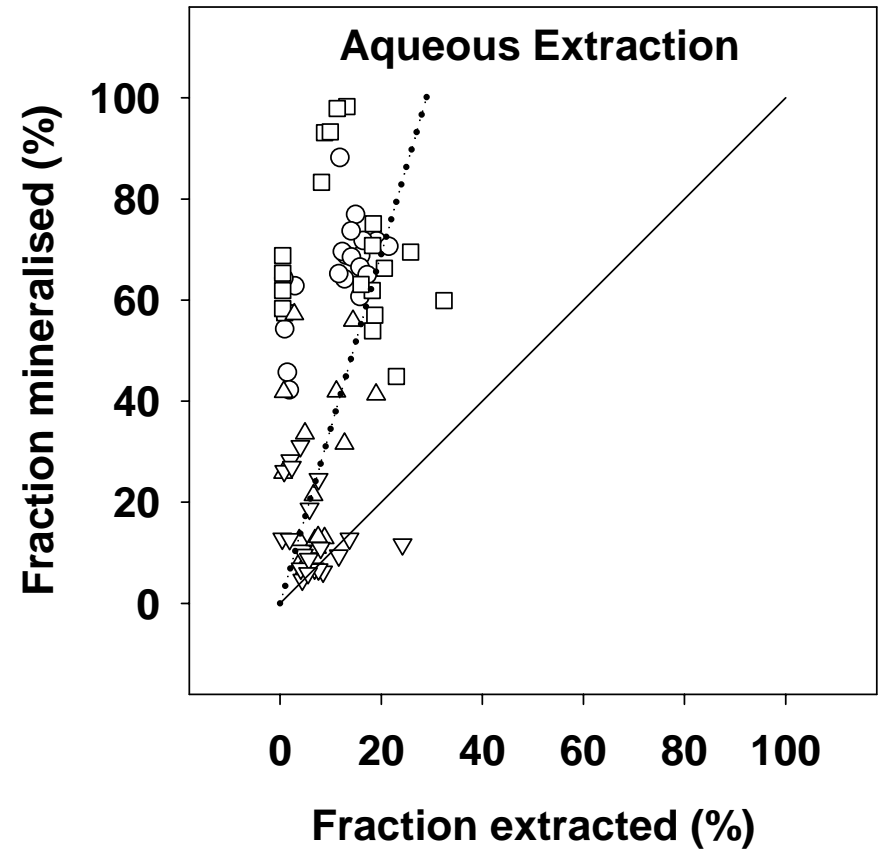


PHENANTHRENE EXTRACTABILITY VS. BIODEGRADATION

$y = 0.93 x \quad (R^2=0.66)$



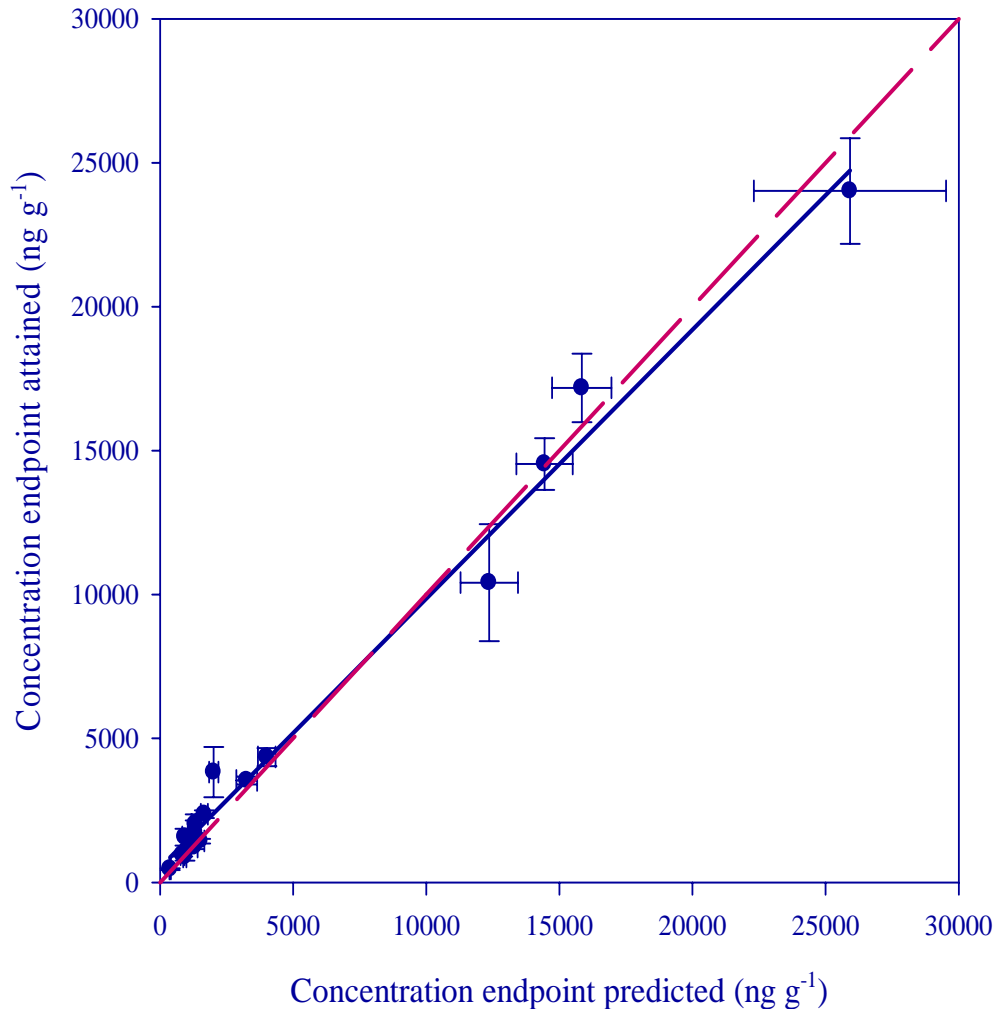
$y = 3.45 x \quad (R^2= -0.22)$



Allan et al., in prep



Correlation between predicted (cyclodextrin) and attained biodegradation endpoints in PAH-contaminated soil (QC soil LGC6140)



17 different compounds analysed in triplicate

Compounds physically and chemically very distinct

Strong linear relationship
 $r^2 = 0.986$

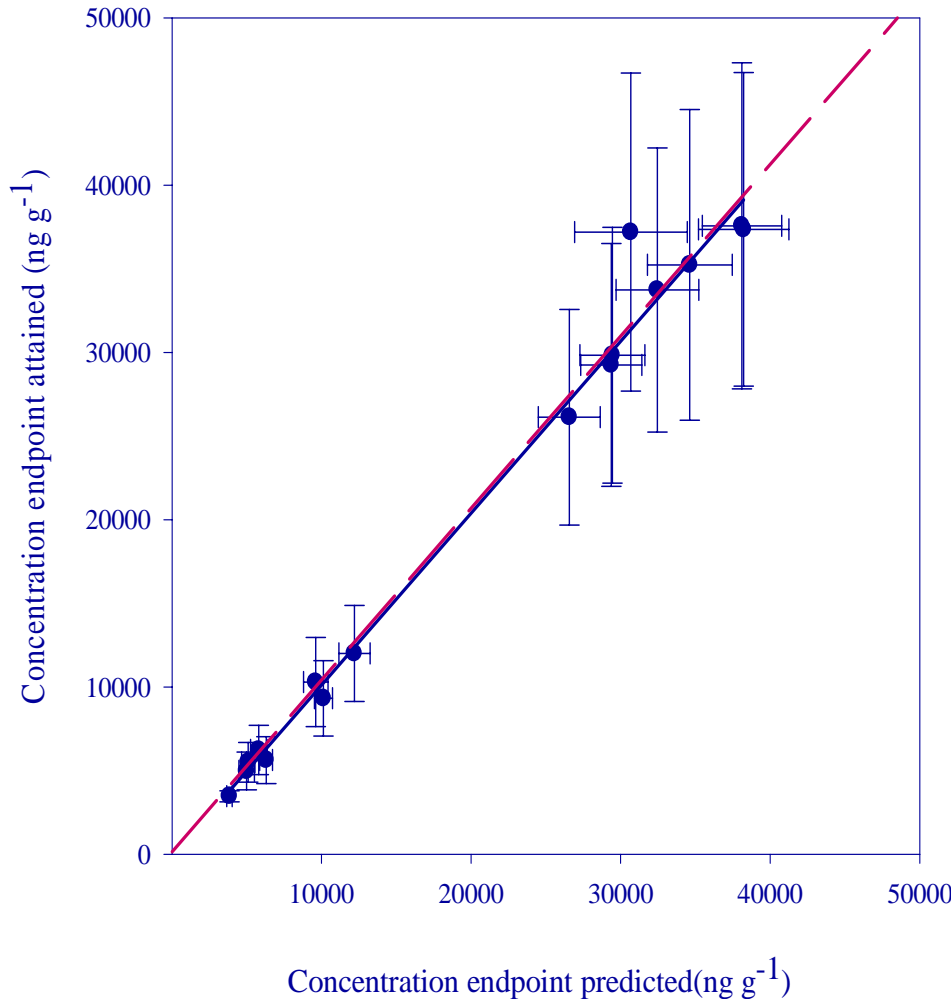
Slope = 0.934
Approximately = 1

i.e. direct prediction
no scaling factor required

Stokes et al., 2005



Correlation between predicted (cyclodextrin) and attained biodegradation endpoints in PAH-contaminated soil from a former coke plant site



16 Different compounds analysed in triplicate

Compounds physically and chemically very distinct

Strong linear relationship
 $r^2 = 0.985$

Slope = 1.027
Approximately = 1

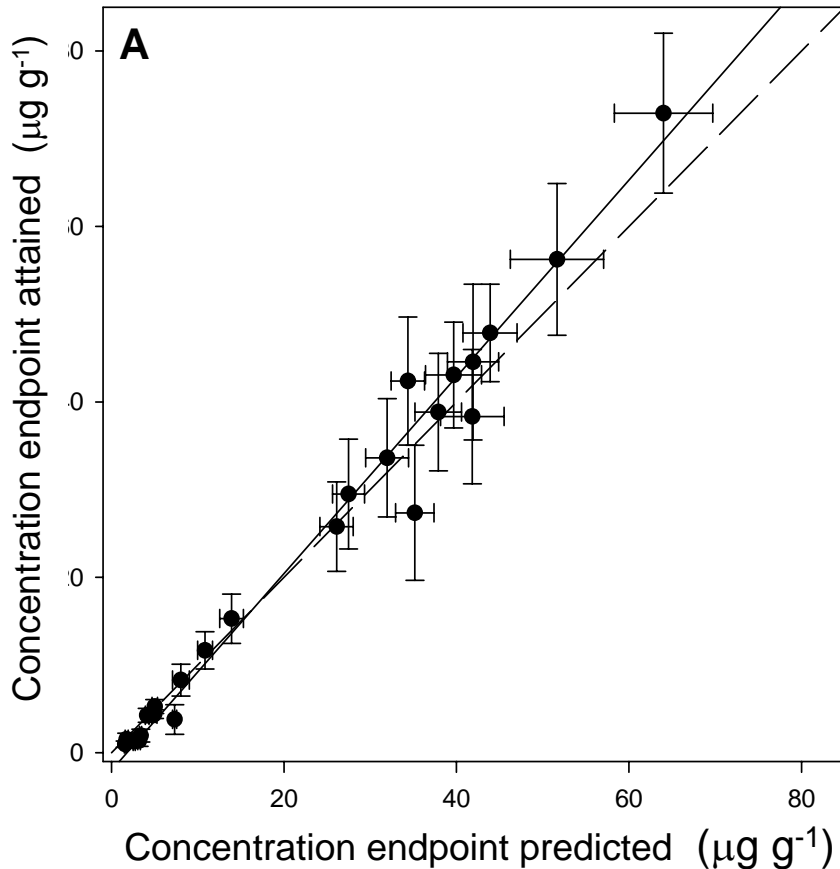
i.e. direct prediction
no scaling factor required

Stokes et al., 2005

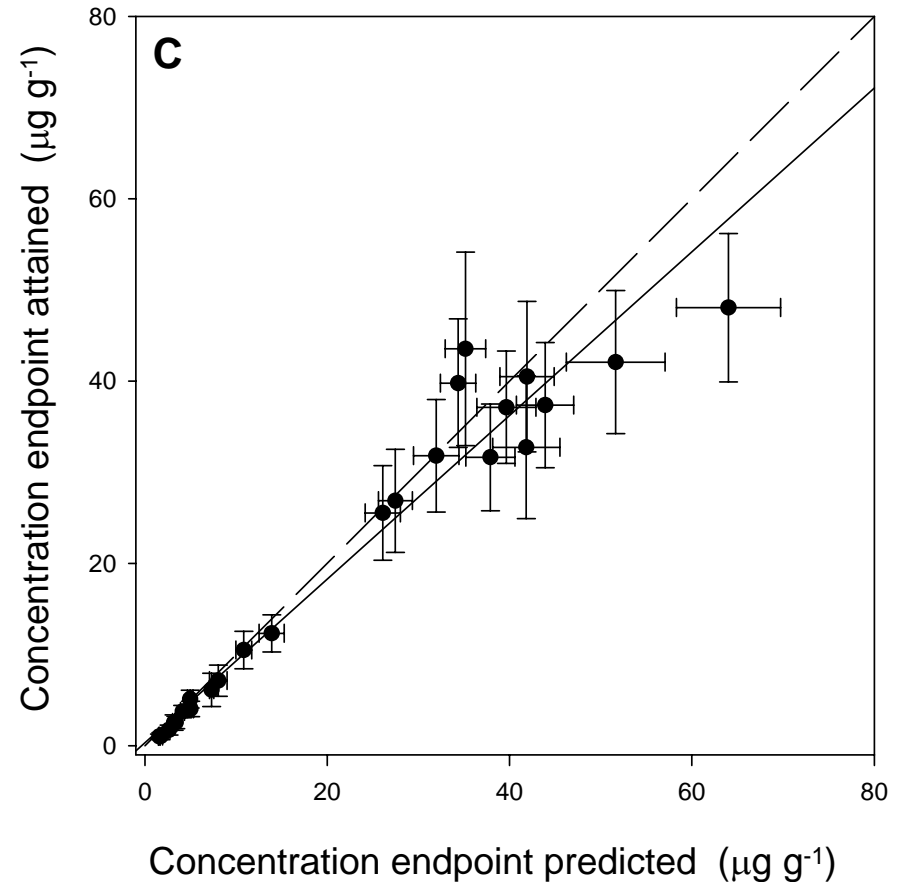


Predicted (cyclodextrin) and attained endpoints in a former coke plant soil in the presence of transformer oil

$y = 1.12x$ ($R^2=0.94$)



$y = 0.90x$ ($R^2=0.87$)



Doick et al., in prep



Bioavailability - can actually we measure it?



New definitions: Bioavailability v bioaccessibility

- **Problem** – Inconsistency and imprecision are apparent in several other usages for the term 'bioavailability' applied to contaminants in soil and aquatic systems.

- The following are examples from a recent Technical Report published by ECETOC (2002):
 - (i) 'the ability of a substance to interact with the biosystem of an organism' (Van Leeuwen and Hermens, 1995);

 - (ii) 'the portion of the total concentration of a chemical in the environment that is potentially available for biological action...'
(Spacie and Hamelink, 1995);

 - (iii) 'the fraction of a compound that is actually taken up by an organism as the outcome of a dynamic equilibrium of organism-bound uptake processes, and soil particle related exchange processes, relation to a dynamic set of environmental conditions' (Herrchen et al., 1997).



Proposed definitions (I)

Bioavailable: The word **available** is defined in the Concise English Dictionary (1982) as 'capable of being employed; at one's disposal; at hand'.

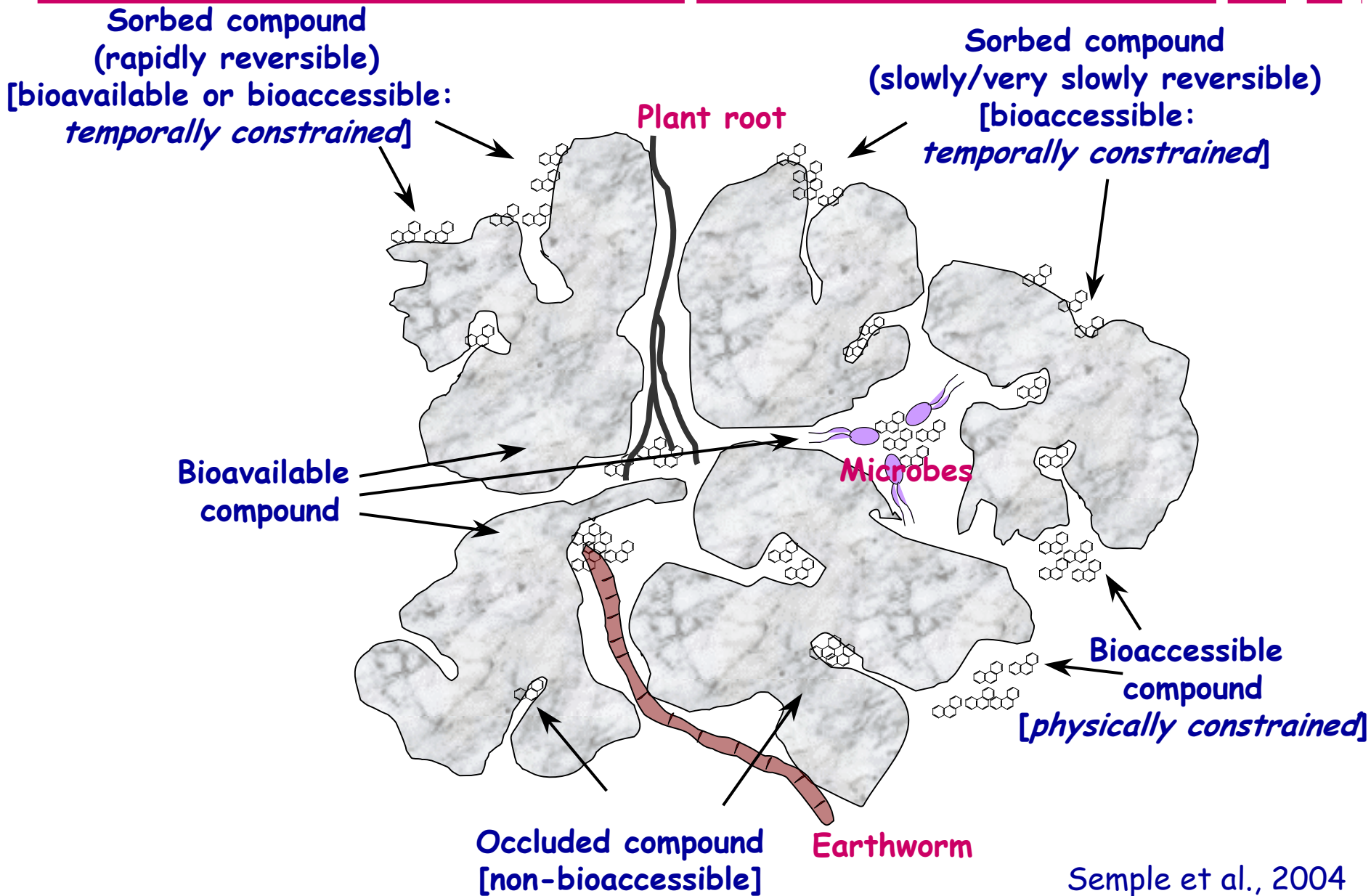
- There is an implied immediacy to the term; what is available is available *now*.
- Hence, we define the *bioavailable compound* as that which *is freely available to cross an organism's (cellular) membrane from the medium the organism inhabits at a given point in time*



Proposed definitions (II)

Bioaccessible: The word **accessible** is defined in the Concise English Dictionary (1982) as 'capable of being *approached* or *reached*, approachable, attainable.

- There is the sense that some of what is accessible *can* be reached, but is often not quite within reach from a given place, or at a given time. In our context, there is an implied *constraint* in time and/or space, preventing the organism from gaining access to the chemical *now*.
- Hence, we define the *bioaccessible compound* as that which *is available to cross an organism's (cellular) membrane from the environment it inhabits, if the organism has access to it; however, it may be either physically removed from the organism, or only bioavailable after a period of time.*
- 'Physically removed' in this context may refer to chemical which is occluded in soil organic matter, and hence is not available at a given point in time, or because the organism is occupying a different spatial range of the environment than the contaminant

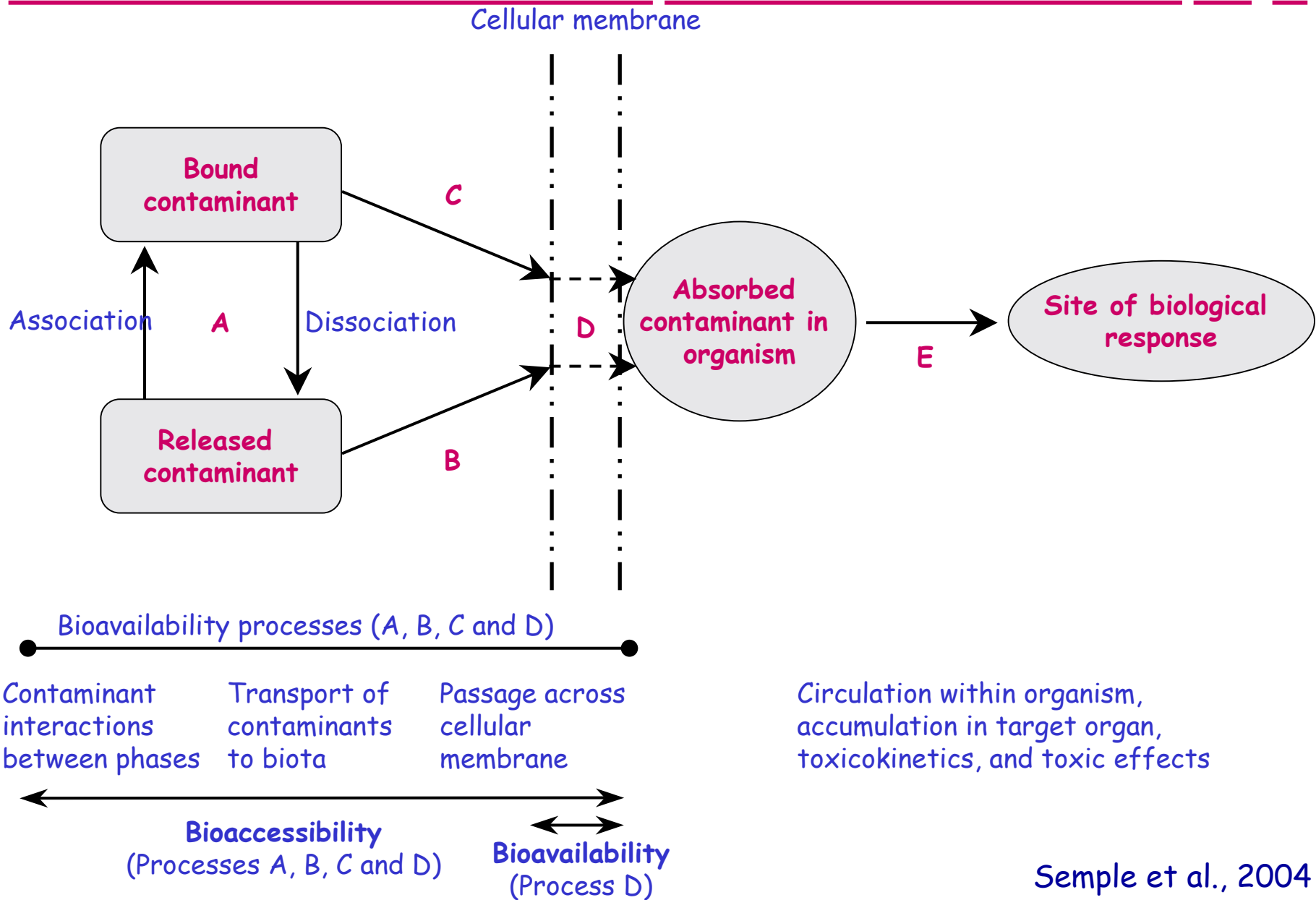


Semple et al., 2004



Summing up

- Bioavailability is the fraction of a contaminant actually available at a given moment in time in soil.
- Bioaccessibility encompasses what is actually bioavailable now **plus** what is '*potentially* bioavailable'.



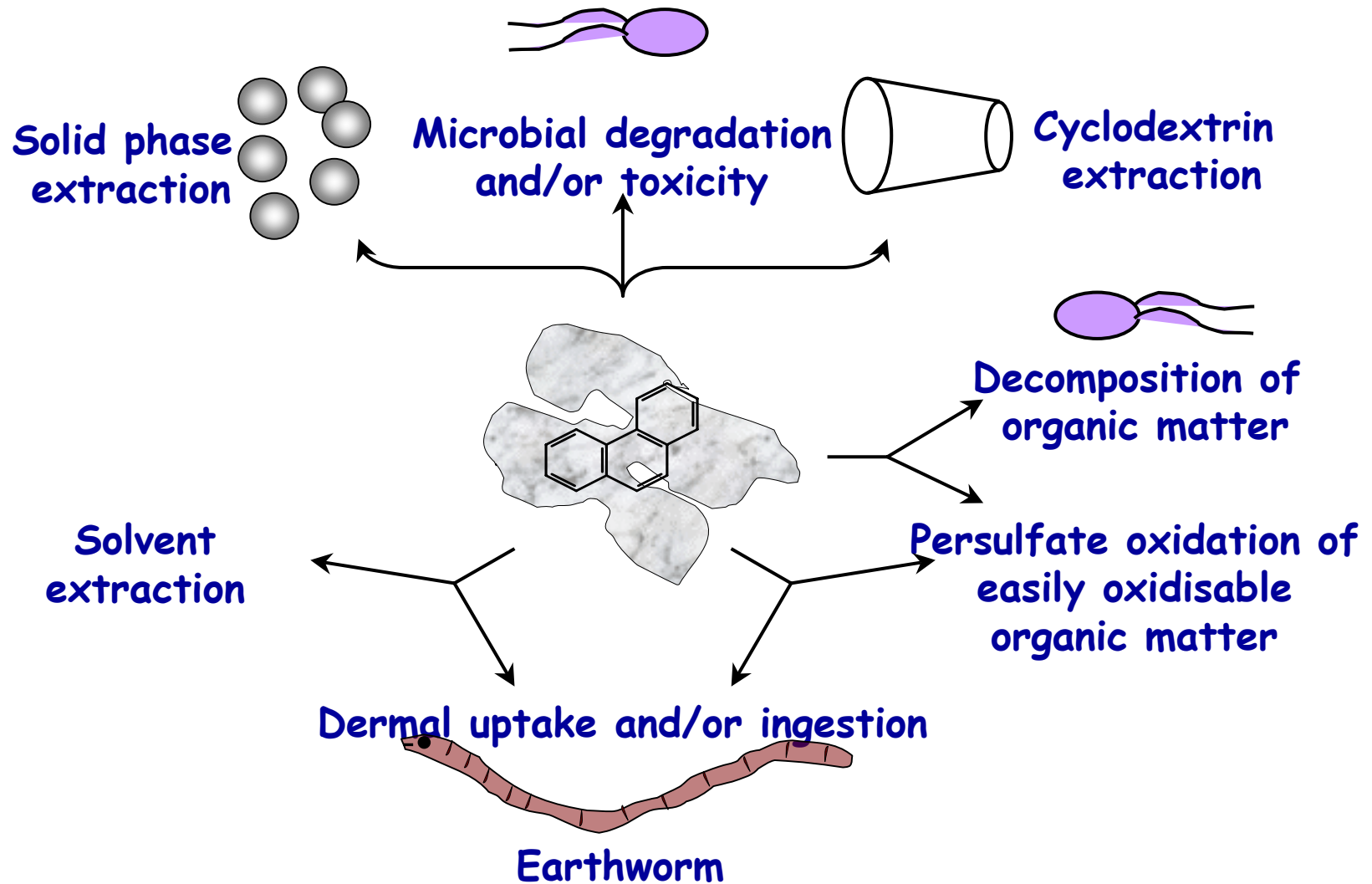
Semple et al., 2004



**So, is it possible to measure bioavailability
chemically?**



Different biotic interactions require different chemical approaches

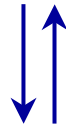




Methodologically defined?

Bioavailable
Biologically defined?

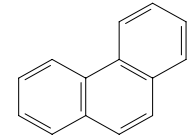
Bioaccessible
(aqueous phase and/or rapidly desorbable)



Recalcitrant
(slowly desorbable)

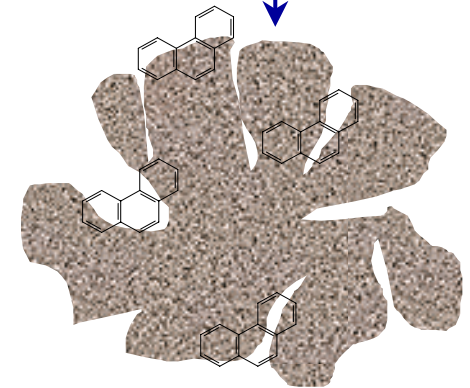


Non-extractable
(very slowly / non-desorbable)



Ageing

Chemically defined?





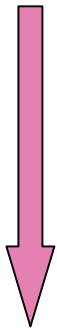
Methodologically defined?

Disruption of 3-D
soil structure

Maintenance of 3-D
soil structure

Bioavailability

BIOAVAILABILITY??



Slurry-based bioassays
Solvent extractions

Intact-soil bioassays



BIOACCESSIBILITY??

Bioaccessibility



Conclusions

- It is possible to chemically measure specific contaminant-biota interactions
- It is not possible to measure all contaminant-biota interactions using a single chemical technique
- Can *bioavailability* be measured chemically?
 - ↳ probably not
- If not, then what?
 - ↳ *Bioaccessibility?*
- It is important to understand what is *actually* being measured as this has implications for the risk assessment and putative remediation of contaminated land.



Acknowledgements

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