Faculty of Chemistry
Instrumental Analytical Chemistry

UNIVERSITÄT DUISBURG ESSEN

Sorption of non-ionic organic compounds onto carbon-based nanomaterials

Presentation at the Norman Workshop:
"Engineered Nanoparticles in the Environment"

Koblenz, Germany

Thorsten Hüffer

Outline

- Introduction
  - What are CNM?
  - Properties
  - Environmental relevance?
- Review
- Concept
- Expected Outcome

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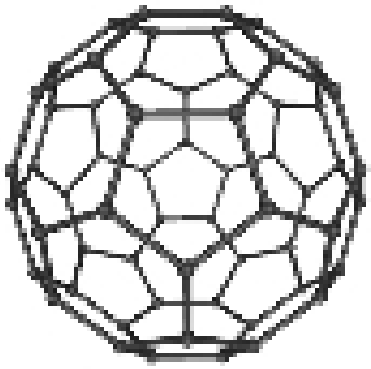
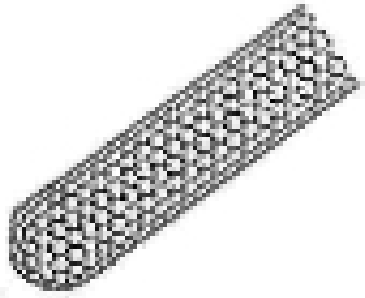
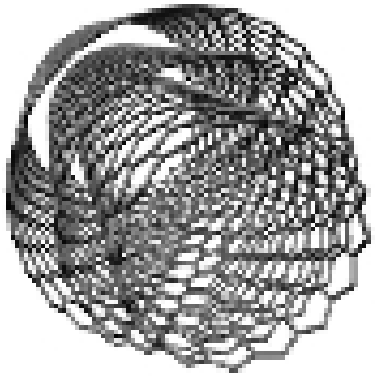
Carbon-based NanoMaterials (CNM)



Fullerene C_{60}



Single-walled carbon nanotubes (SWCNT)



Multi-walled carbon nanotubes (MWCNT)

Mauter & Elimelech (2008)

Environmental relevance?

- Due to an increasing application, an input of CNM into the environment becomes more likely
  - Focus on the potential environmental relevance of CNM (UBA, 2009)

    „the interaction with chemicals depending on shape, size, charge, and/or surface configuration“
- Problem:
  - Interaction of CNM with organic contaminants in the environment?
  - Impact of CNM on the fate and transport of organic contaminants in the environment?

Systematic approach on the sorption onto CNM is missing!

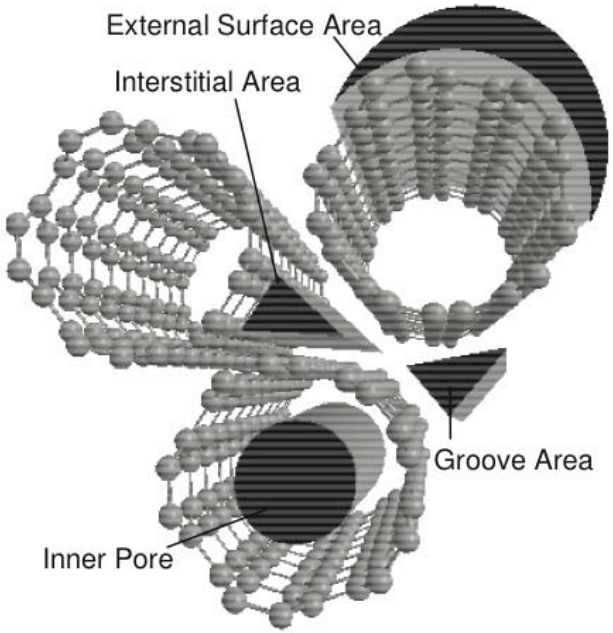
Outline

- Introduction
- Review
  - Sorption mechanism
  - Sorbent Influence
  - Sorbate Influence
- Own Concept
- Expected Outcome

Heterogeneity

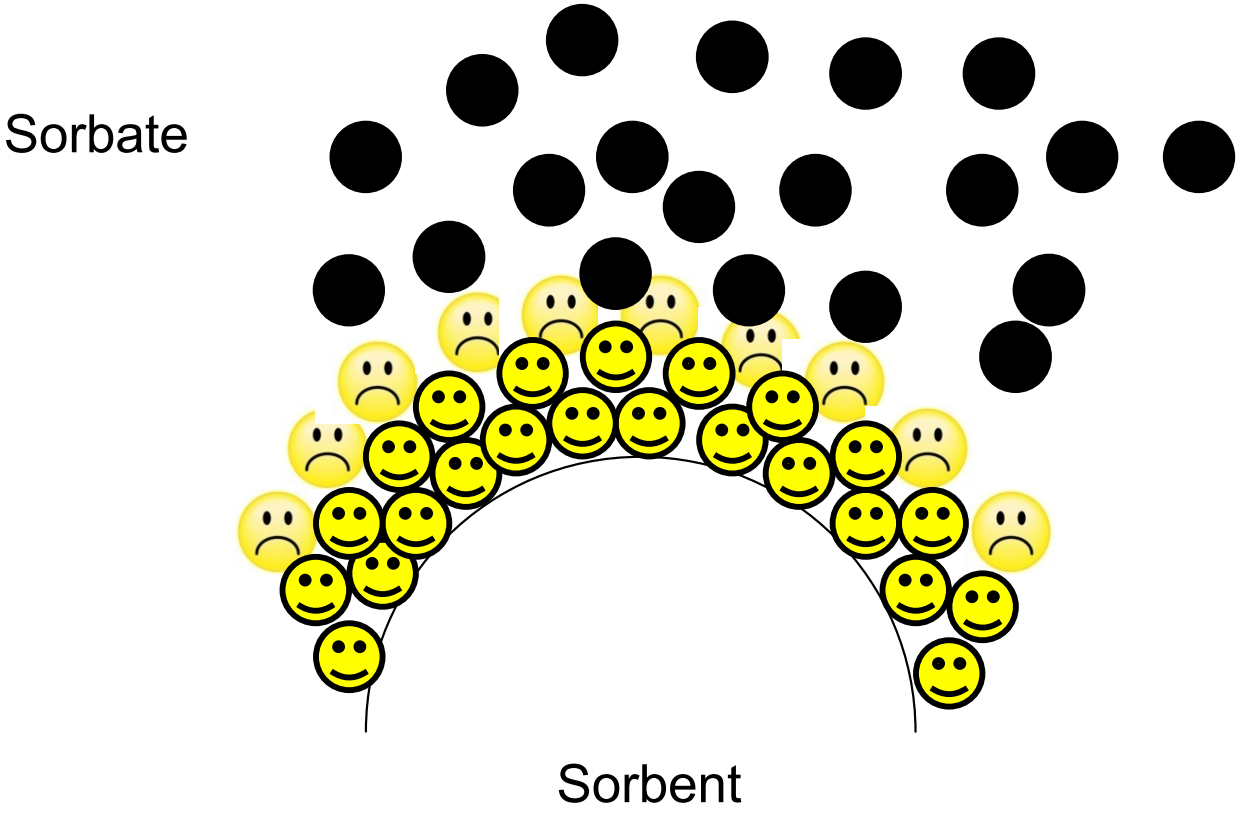
(Various models used to describe sorption (Freundlich, Langmuir, Polanyi-Manes…)

- High energy surface sites, such as
  - Defects on CNM surface
  - Functional groups
  - Space of bundles



Pan & Xing, 2008

Condensation



First sorbate layers: Interaction with surface

Following layers: Interaction with each other

=> Distribution of sorption energy

Sorption Mechanisms

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Even distribution of hydrophobic surface sites

=> Prediction of sorption *only* based on one mechanism or parameter (e.g., hydrophobicity: K_{OW} or K_{HW})? **Insufficient!**

Other possible mechanisms:

-*Electron donor-acceptor (EDA)*

-*Hydrogen bonds* (functional groups)

-*Electrostatic interactions* (Charged sorbent surfaces, organic ions)

Relative contribution of each mechanism to the overall sorption is fundamental to predict sorption on CNM

Sorbent Influence

- Physical Properties
  - oSurface area — No direct correlation to sorption
  - oPore volume/diameter — Dimensional restrictions?
- Morphology — **Available for sorption?**
  - oMWCNT layers — Not available
  - oInterstitial and groove areas — Not available
  - oInner pores — Available
  - oSurface area — Available
- Functionalization
  - Decreased hydrophobicity
  - Decreased accessibility

Sorbate Influence

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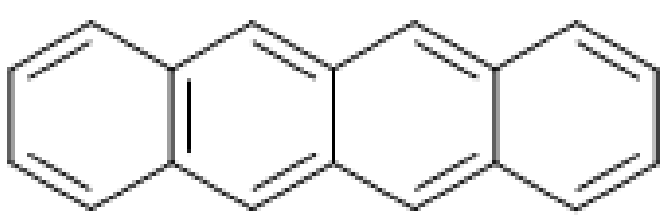
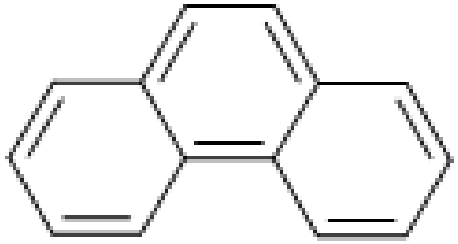
Availability of sorption sites on sorbent depends on:

- Molecular Morphology
  - Size: large vs. small
  - Shape: linear/planar vs. bulky





➢ Contact with sorbent surface to allow strong sorption

Gotovac et al. 2007

Sorbate Influence

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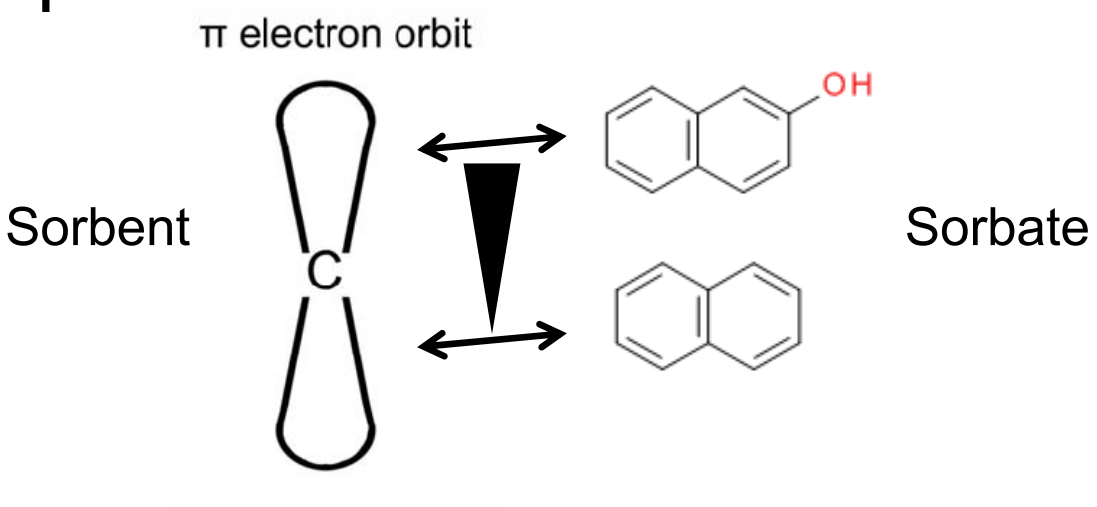
Strength of sorption depends on:

- Functional Groups
  - EDA
    - π-π



Chen et al. 2008

Summary

Various mechanisms control sorption

- EDA
- Hydrophobicity

Mechanisms may be affected differently by controlling parameters

- Sorbate characteristics
- Sorbent characteristics
- Water chemistry

Organic chemical sorption cannot sufficiently be described by a single mechanism (coefficient)!

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Linear free-energy relationships (LFER)

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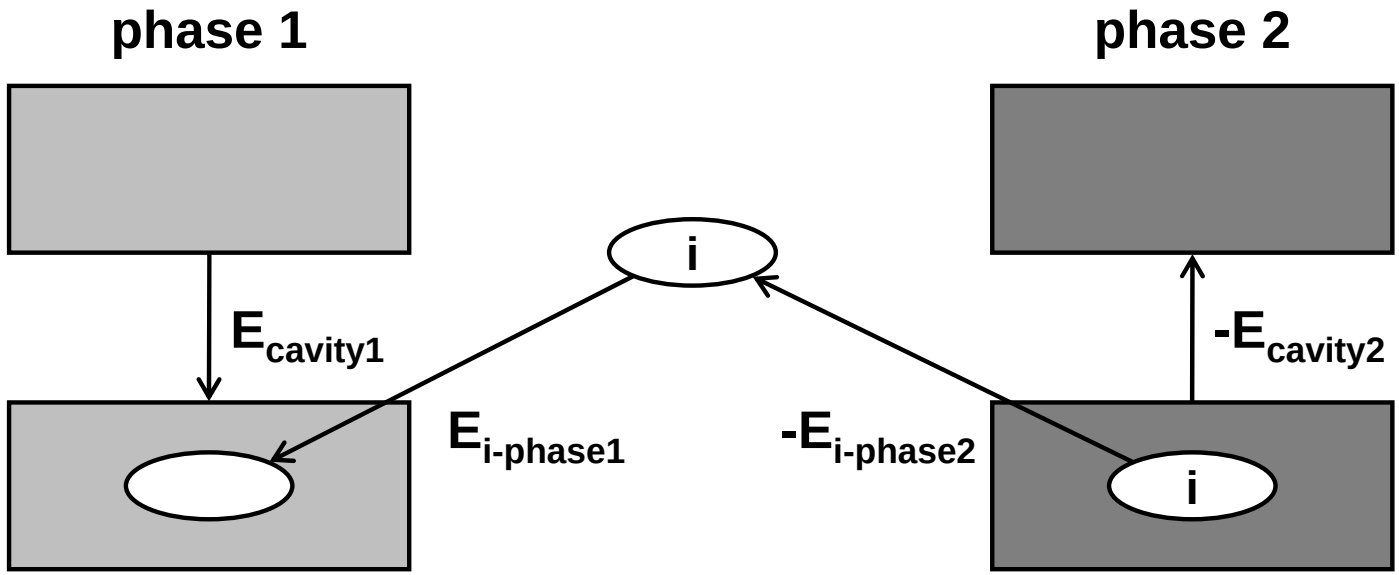
For the partitioning between two bulk phases:



$$\Delta G_{i12} = E_{cavity1} + E_{i-phase1} - E_{cavity2} - E_{i-phase2}$$

Relevant interactions of non-ionic organic compounds:

van der Waals & specific polar interactions (EDA)

$$E = E^{vdW} + E^{EDA}$$

Goss & Schwarzenbach 2001

Linear free-energy relationships (LFER)

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- Poly parameter linear free-energy relationship (ppLFER)

$$\log K_{ijw} = e_{jw}E_i + s_{jw}S_i + a_{jw}A_i + b_{jw}B_i + v_{jw}V_i + c_{jw}$$

$e_{jw}E_i$	$s_{jw}S_i$	$a_{jw}A_i$	$b_{jw}B_i$	$v_{jw}V_i$
excess molar refraction	dipolarity/ polarizability	H-bond acidity	H-bond basicity	molar Volume (McGowan)

Solute descriptors: E, S, A, B, V

Phase descriptors: e, s, a, b, v

spLFER vs. ppLFER

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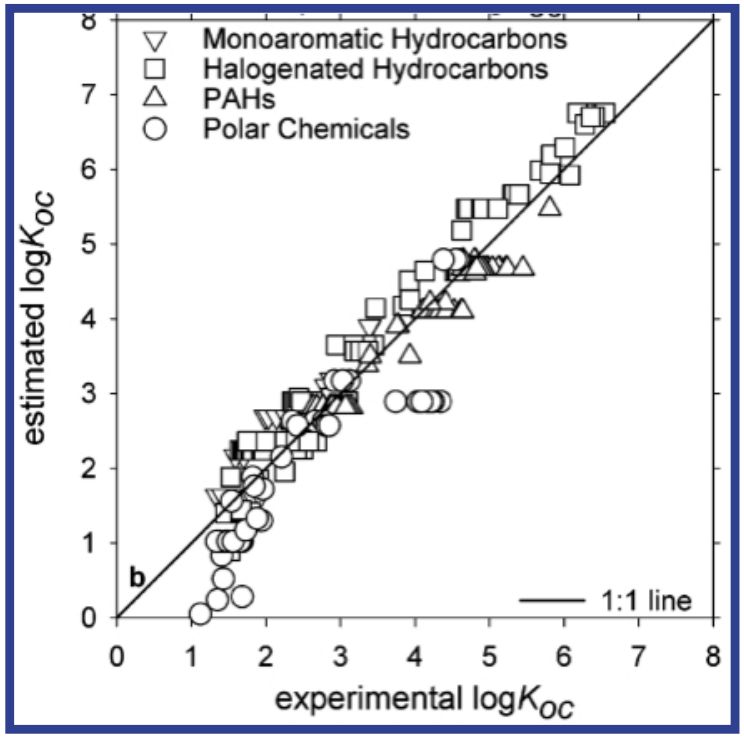
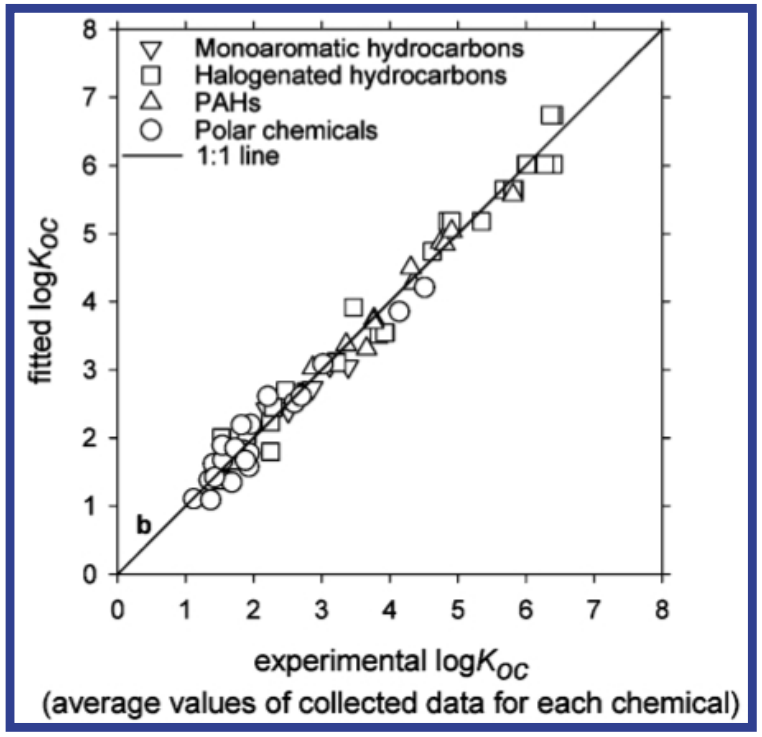
Partitioning of Organic Compounds between Water and NOM in soil/sediment





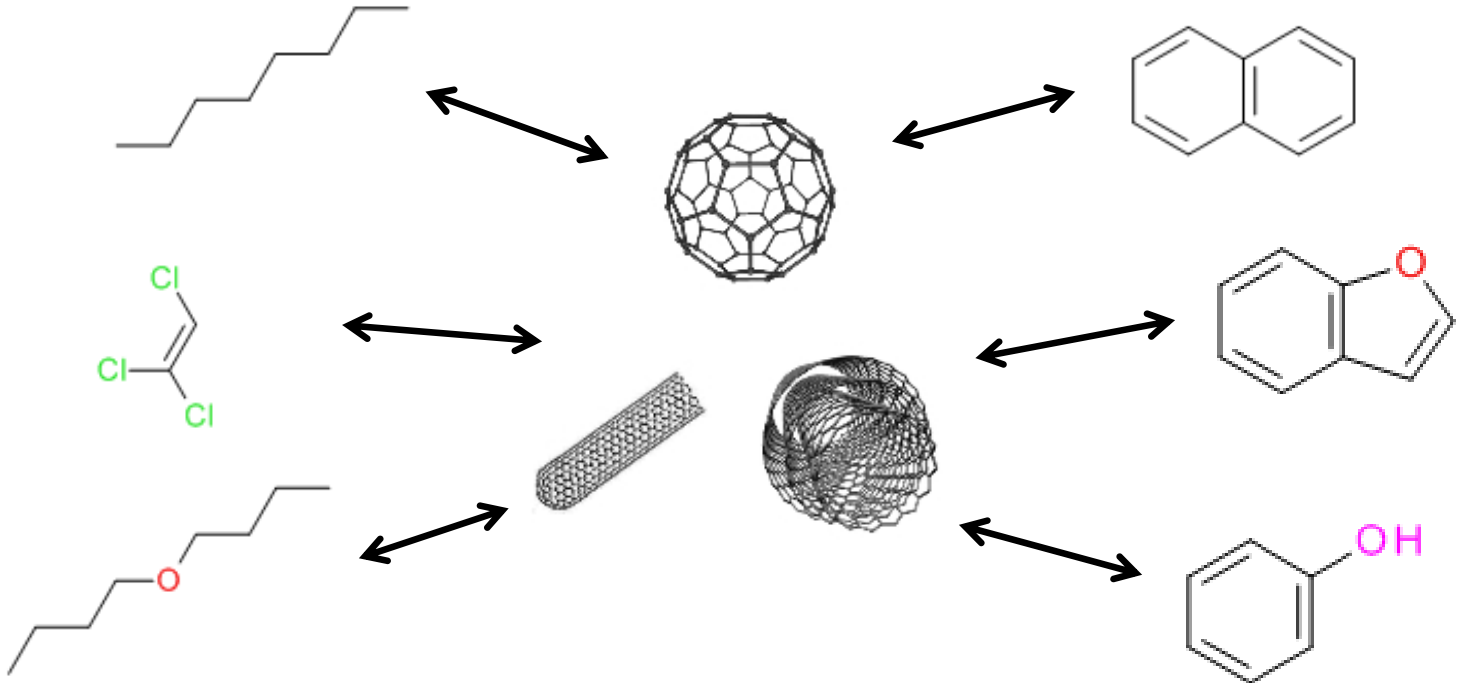
spLFER with Kow

$$\log K_{ijw} = a \log K_{iow} + c$$

ppLFER

Nguyen et al. 2005

Probe Compound Approach



- Various classes to cover all relevant molecular interactions (e.g., H-bond acidity etc.)

Outline

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Expected Outcome

The systematic investigation of sorption of non-ionic compounds on CNM

- **Determination of phase descriptors of various CNM**
- **Relative contribution of different molecular interactions to the overall sorption**

- ***Impact of CNM of transport of organic chemicals in the environment***

Acknowledgement

Instrumental Analytical Chemistry

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Organizing and Scientific Committee

Thank you very much for your attention!

Presentation at the Norman Workshop:
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