TG ENVIRONMENTAL RESEARCH

Microplastic particles as vectors of transport for hydrophobic organic chemicals

Todd Gouin

Microplastic and chemicals – Is there an intrinsic risk?

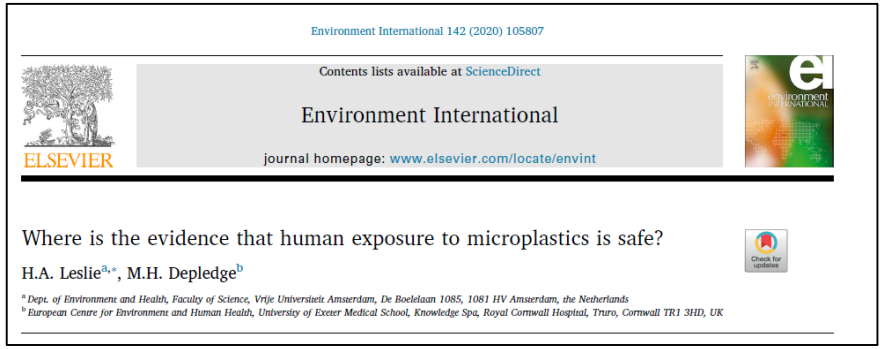
No, really, I have evidence

There must be a rational explanation for this

Dedicated to investigating the unexplainable

Microplastic and chemicals – Is there an intrinsic risk?

- Leslie and Depledge (2020)
  - The ability of microplastic to be chemical vectors needs to be seriously considered as part of the overall assessment of microplastic safety.
  - Bibliography of >3500 publications related to microplastic particle research, with >1300 which broadly include some aspect of chemicals (about 35%).



Environment International 142 (2020) 105807

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Where is the evidence that human exposure to microplastics is safe?

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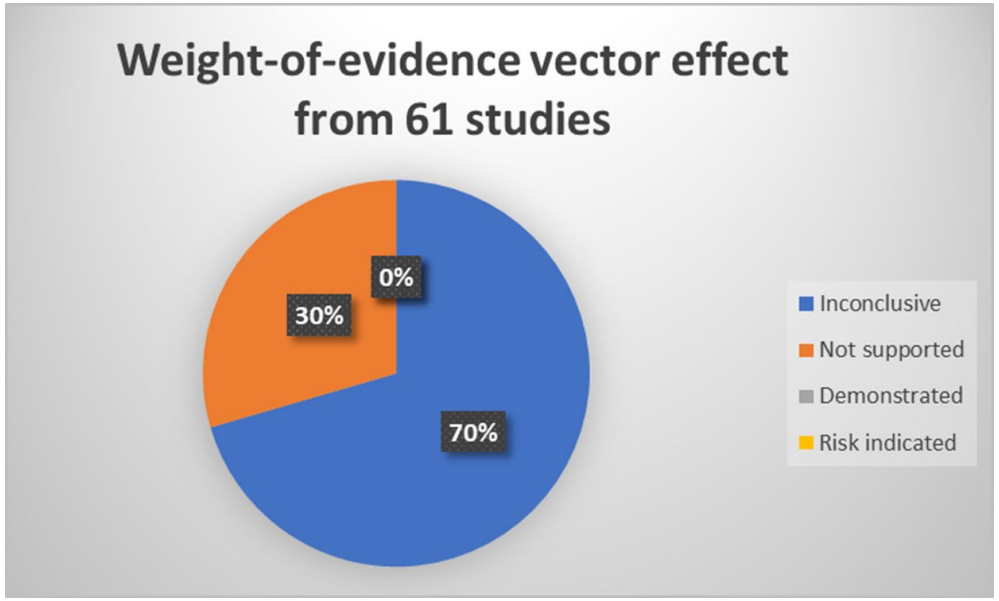
[a] Dept. of Environment and Health, Faculty of Science, Vrije Universiteit Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, the Netherlands
[b] European Centre for Environment and Human Health, University of Exeter Medical School, Knowledge Spa, Royal Cornwall Hospital, Truro, Cornwall TR1 3HD, UK

- Kolemans et al. (2020)
  - Reviewed 61 studies specifically related to the vector issue



Microplastic and chemicals – an evolving story

- Carpenter and Smith (1972) – Many plastics contain considerable concentrations of PCBs as plasticizers. If the plasticizers have been lost to seawater…the incorporation of PCBs by marine organisms is possible.

- Teuten et al. (2007)

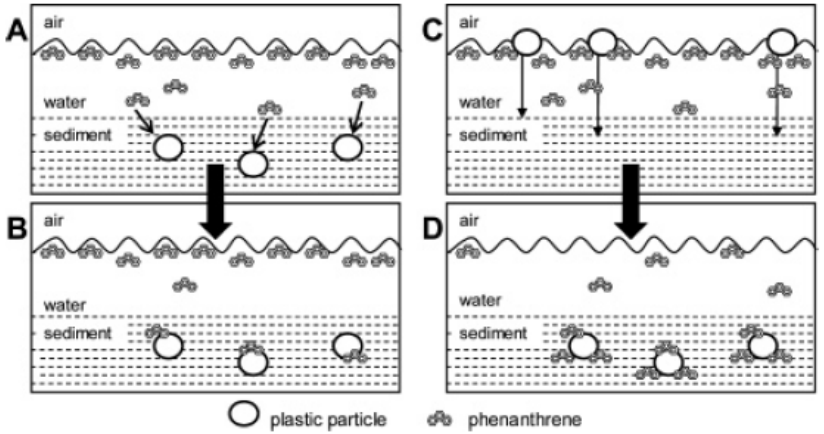
537 citations

Environ. Sci. Technol. 2007, 41, 7759–7764

Potential for Plastics to Transport Hydrophobic Contaminants

EMMA L. TEUTEN,*,† STEVEN J. ROWLAND,‡ TAMARA S. GALLOWAY,§ AND RICHARD C. THOMPSON†

School of Biological Sciences and School of Earth, Ocean, and Environmental Sciences, University of Plymouth, Plymouth PL4 8AA, United Kingdom, and School of Biosciences, University of Exeter, Exeter EX4 4PS, United Kingdom



PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Transport and release of chemicals from plastics to the environment and to wildlife

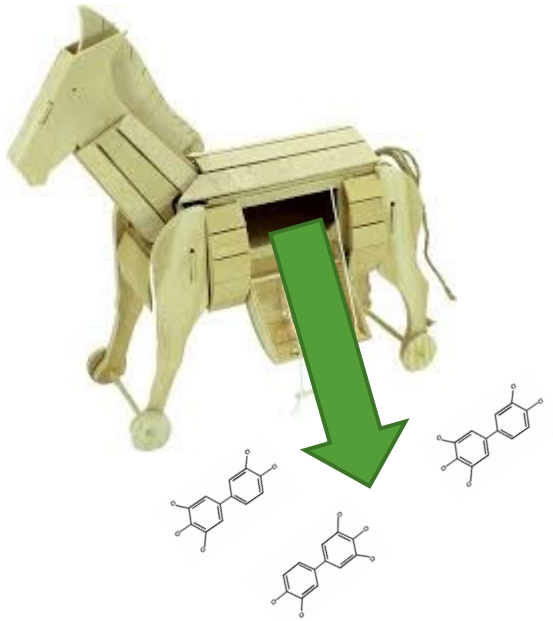
Emma L. Teuten, Jovita M. Saquing, Detlef R. U. Knappe, Morton A. Barlaz, Susanne Jonsson, Annika Björn, Steven J. Rowland, Richard C. Thompson, Tamara S. Galloway, Rei Yamashita, Daisuke Ochi, Yutaka Watanuki, Charles Moore, Pham Hung Viet, Touch Seang Tana, Maricar Prudente, Ruchaya Boonyatumanond, Mohamad P. Zakaria, Kongsap Akkhavong, Yuko Ogata, Hisashi Hirai, Satoru Iwasa, Kaoruko Mizukawa, Yuki Hagino, Ayako Imamura, Mahua Saha and Hideshige Takada

Phil. Trans. R. Soc. B 2009 **364**, 2027-2045
doi: 10.1098/rstb.2008.0284

1043 citations

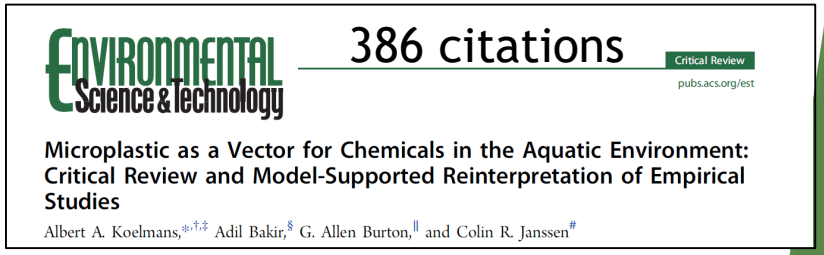
Microplastic – “Trojan Horse” analogy

- During the 10-year siege of troy the Greeks constructed a wooden horse, in which a select force of men were concealed. The Greeks pretended to sail away, and the Trojans pulled the horse into the city as a victory trophy. That night the Greek force crept out of the horse and opened the gates for the rest of the Greek army to enter and destroy the city of Troy – ending the siege.

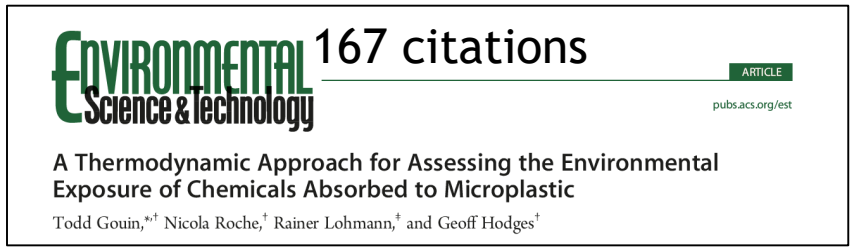


Microplastic and chemicals – an evolving story

- Koelmans et al. (2016)
  - "We conclude that overall the flux of HOCs bioaccumulated from natural prey overwhelms the flux from ingested microplastic for most habitats, which implies that microplastic ingestion is not likely to increase the exposure to and thus risks of HOCs in the marine environment."



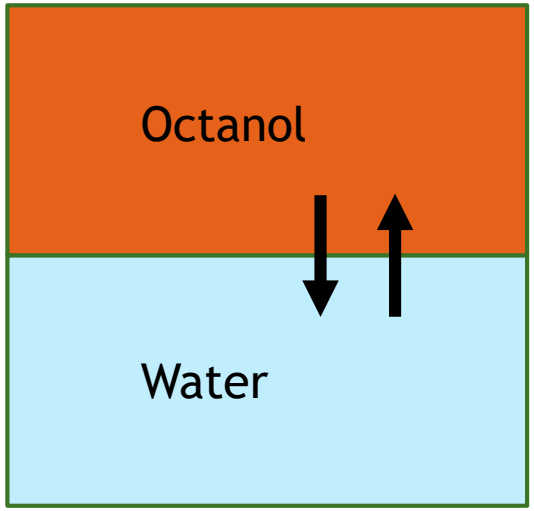
- Gouin et al. (2011)
  - "Using a multimedia modelling approach, we define a chemical space aimed at improving our understanding of how chemicals partition in the marine environment with varying volume ratios of air/water/organic carbon/polyethylene, where polyethylene represents a main group of microplastic

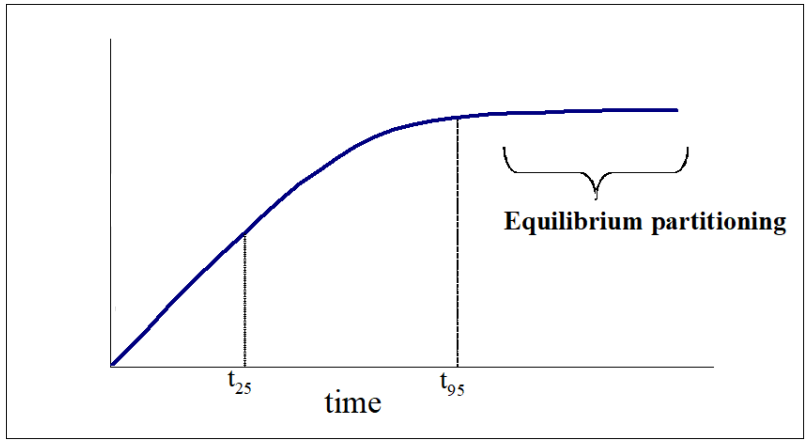


Thermodynamics and Fugacity

- Concept of fugacity introduced in 1901 by G.N. Lewis
  - Refers to the escaping tendency of a chemical
  - Units of pressure (Pa)
  - Convenient method for defining thermodynamic equilibrium criterion
- Thermodynamic equilibrium occurs between two matrices when the fugacities in each matrix is equal

Fugacity 101





At equilibrium:

$$f_O = f_W$$

and $C_O / C_W = K_{OW}$

Fugacity is also proportional to concentration

$$C \propto f$$

$$C = Zf$$

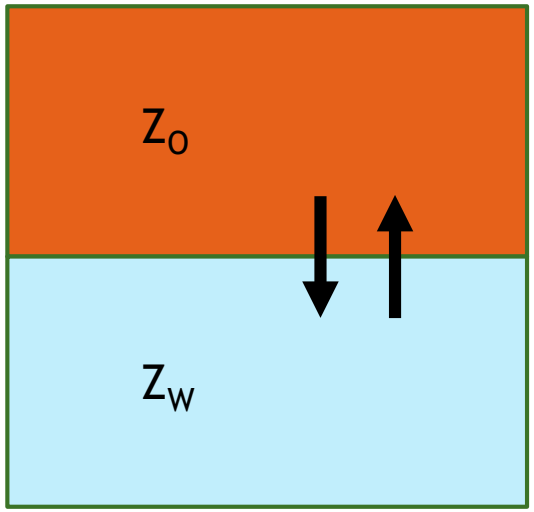
Where:

Z = fugacity capacity

Fugacity 101: Fugacity capacity

- Fugacity capacity (Z) is media specific

- HOCs concentrate in octanol because $Z_O >> Z_W$



$$K_{OW} = C_O / C_W$$

$$K_{OW} = Z_O / Z_W$$

- Where $Z_O >> Z_W$ a higher mass of chemical will concentrate

- Generally $K_{OW} \approx K_{PW} \approx K_{lip\text{-}w} \approx K_{oc}$
  - Alternatively, the fugacity capacity of octanol, plastic, lipid, and organic carbon are all similar

- Importance of volume in relation to concentration
  - Concentration = mass / volume
    - Volume and mass are not constant
    - Fugacity capacity is constant

  - Consequently, the concentration at equilibrium varies depending on the magnitude of Z relative to Z in the other media and the media-specific volume ratios.

Fugacity 101: Fugacity capacity

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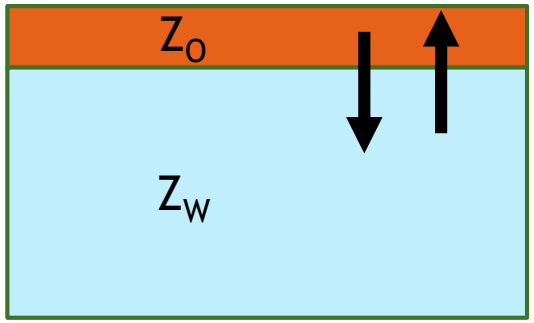

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    - Consequently, the concentration at equilibrium varies depending on the magnitude of Z relative to Z in the other media and the media-specific volume ratios.

Multimedia mass fraction – influence of volume ratios

Environmental Science & Technology
ARTICLE
pubs.acs.org/est

A Thermodynamic Approach for Assessing the Environmental Exposure of Chemicals Absorbed to Microplastic

Todd Gouin,*† Nicola Roche,† Rainer Lohmann,‡ and Geoff Hodges†

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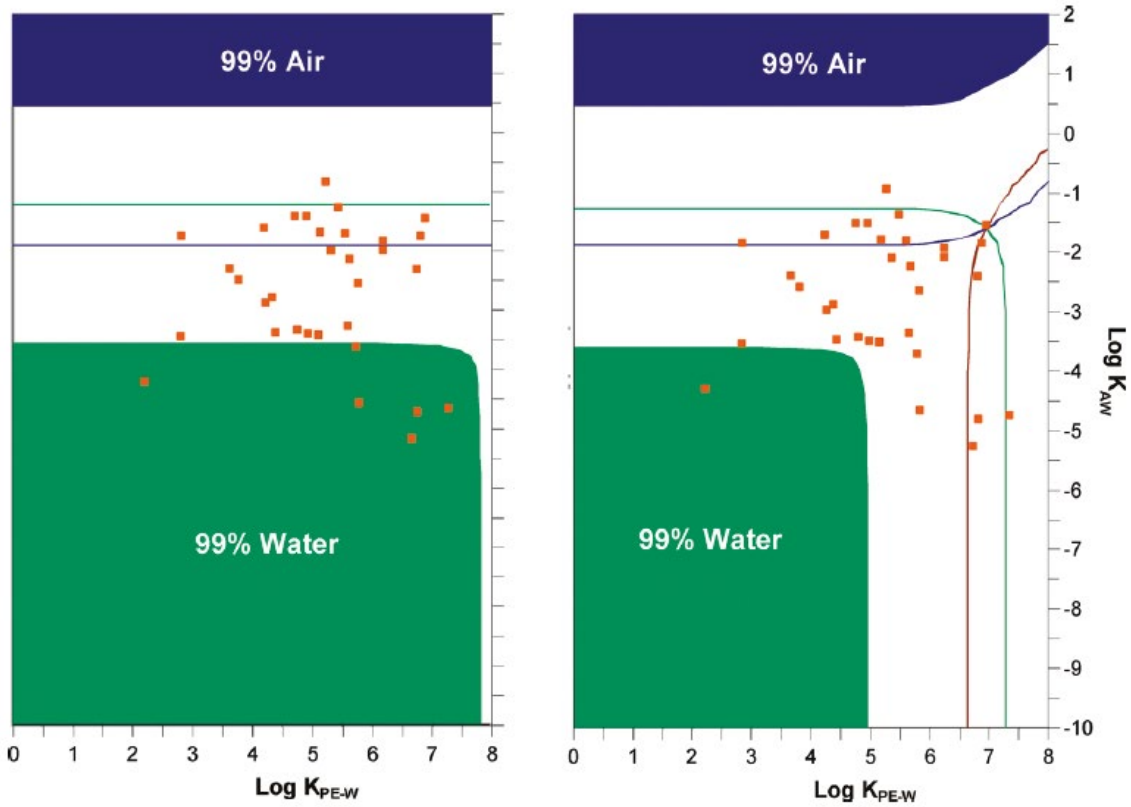
‡Graduate School of Oceanography, University of Rhode Island, South Ferry Road, Narragansett, Rhode Island, 02882 United States

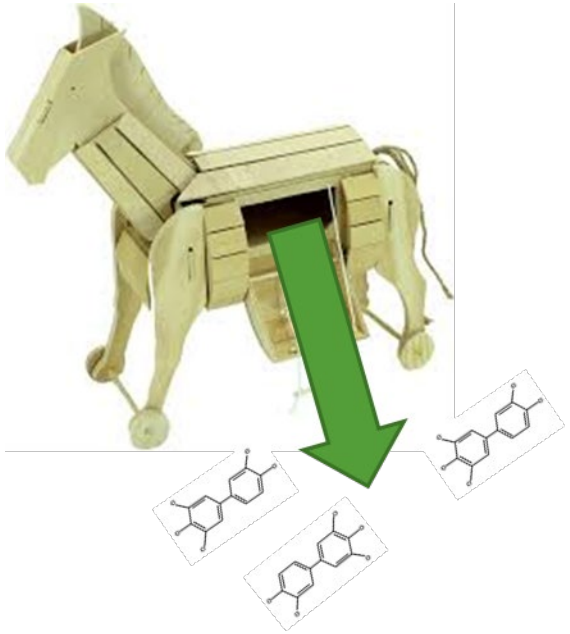
Open ocean environment - 360,000 km^2
Water depth = 20 m; no organic carbon



1200 m^3 plastic

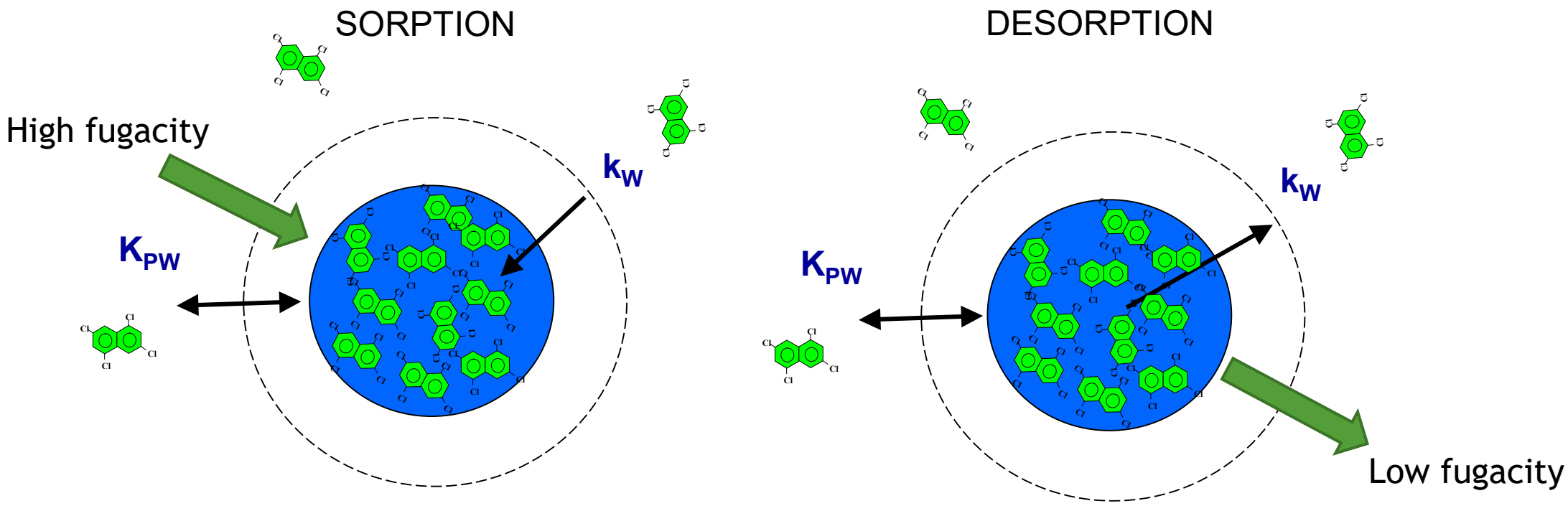
10^6 m^3 plastic

What do the Greeks have to do with it again?



It’s coming…I hope!?!

The extent of sorption and desorption depend on the relative fugacity of the surrounding environment

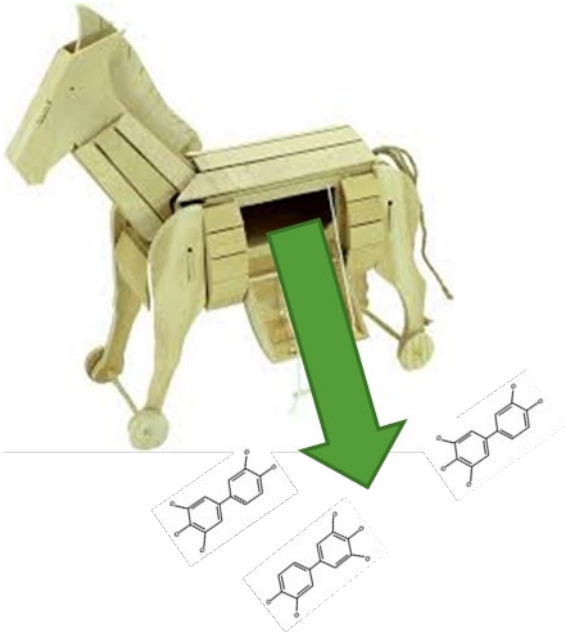


If fugacity is low in the plastic then bioavailability is reduced

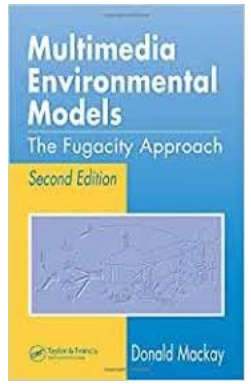
If fugacity is high in the plastic then leaching will occur

And fugacity is?

Analogy to the Trojan Horse implies that the fugacity is >> fugacity in surrounding environment – is this really the case?

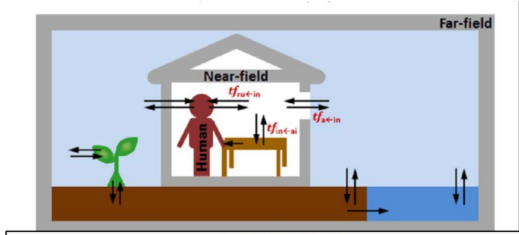


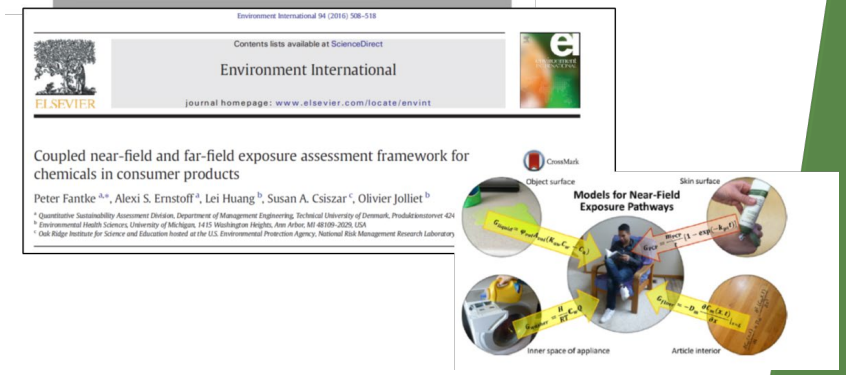
See Mackay (2001)

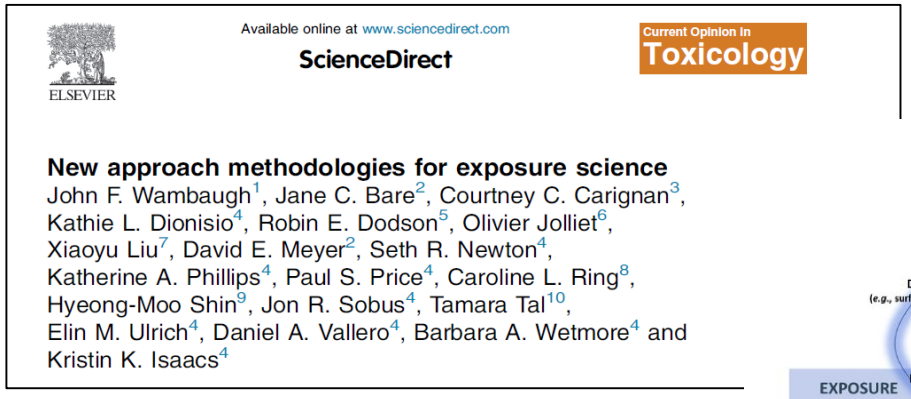


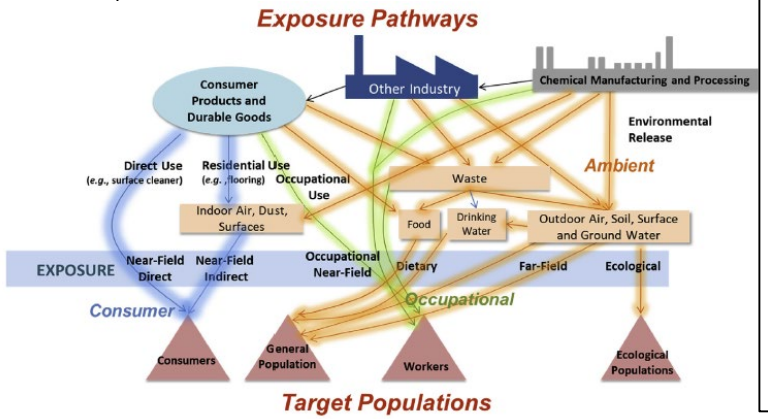
Exposure to chemicals from microplastic versus other pathways

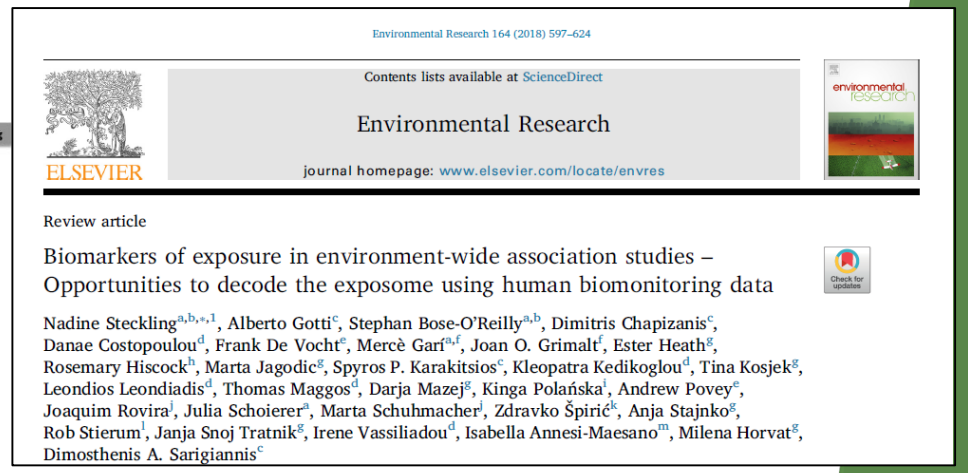
- Exposure to chemicals used in commerce is ubiquitous
- Most chemicals are used in a wide variety of applications/products
- Human biomonitoring data provides an indication of actual exposure
- New approach methodologies are being developed better quantify and characterize chemical exposure and exposure pathways











Quantifying the differences between exposure routes

- Characterization and quantification of the relative strength of the different exposure pathways, requires derivation of:
  - Mass distribution in the different compartments, which depends on
    - FUGACITY GRADIENTS
    - MEDIA-SPECIFIC VOLUME RATIOS

Influence of volume ratios – passive dosing/sampling

- Microplastic dosed with HOCs added to a test system will:
  - Partition between the various media in the test system according to the laws of thermodynamics
  - Biological uptake is influenced by the mass of chemical that becomes freely available
  - Free concentrations of HOCs can be controlled by manipulation of the volume ratios of the various media – passive dosing

Environ. Sci. Technol. **1999**, *33*, 2284–2290

Establishing and Controlling Dissolved Concentrations of Hydrophobic Organics by Partitioning from a Solid Phase

PHILIPP MAYER,* JURGEN WERNSIN
JOHANNES TOLLS,
P. GERT-JAN DE MAAGD,† AND
DICK T. H. M. SIJM‡
Environmental Toxicology and Chemistry, RITOX, Utrecht University, P.O. Box 80058, NL-3508 TB Utre The Netherlands

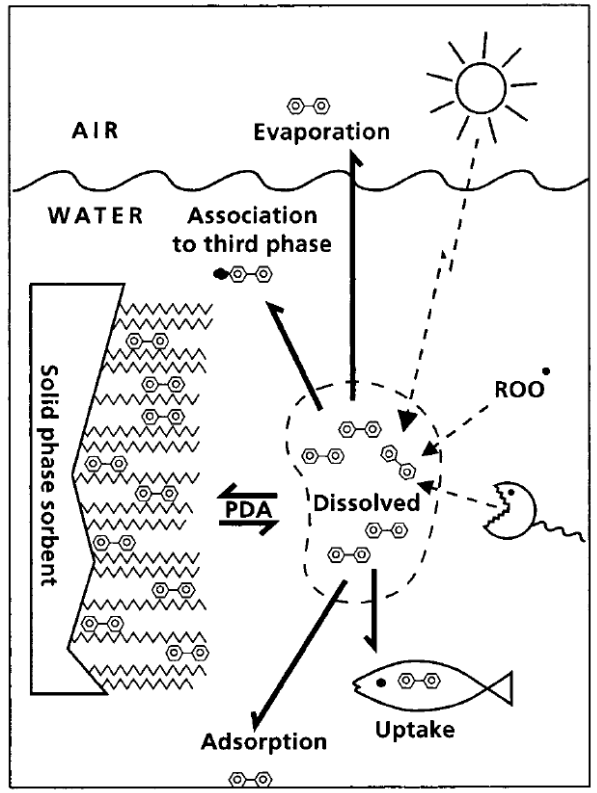


FIGURE 1. Batch experiment presented as multiphase system. Partitioning driven administering controls the dissolved concentrations of hydrophobic organics against a number of degrative (— —) and nondegrative (—) depletion processes by partitioning from a dominating solid phase.

Integrated Environmental Assessment and Management — Volume 10, Number 2—pp. 197–209

Passive Sampling Methods for Contaminated Sediments: Scientific Rationale Supporting Use of Freely Dissolved Concentrations

Philipp Mayer,†§§§ Thomas F Parkerton,‡ Rachel G Adams,§ John G Cargill,‖ Jay Gan,# Todd Gouin,†† Philip M Gschwend,‡‡ Steven B Hawthorne,§§ Paul Helm,‖‖ Gesine Witt,## Jing You,††† and Beate I Escher‡‡‡*

Aquatic Toxicology 98 (2010) 15–24

Contents lists available at ScienceDirect

Aquatic Toxicology

journal homepage: www.elsevier.com/locate/aquatox

Controlling and maintaining exposure of hydrophobic organic compounds in aquatic toxicity tests by passive dosing

Kilian E.C. Smith[a,*], Nathalie Dom[b], Ronny Blust[b], Philipp Mayer[a]

[a] *Department of Environmental Chemistry and Microbiology, National Environmental Research Institute, Aarhus University, Frederiksborgvej 399, PO Box 358, 40000 Roskilde, Denmark*
[b] *Department of Biology, Ecophysiology, Biochemistry and Toxicology group, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerpen (Wilrijk), Belgium*

Influence of volume ratios – in vitro

Environmental Science & Technology
Article
pubs.acs.org/est

Application of Mass Balance Models and the Chemical Activity Concept To Facilitate the Use of in Vitro Toxicity Data for Risk Assessment

James M. Armitage,*[,†] Frank Wania,[†] and Jon A. Arnot[†,§]

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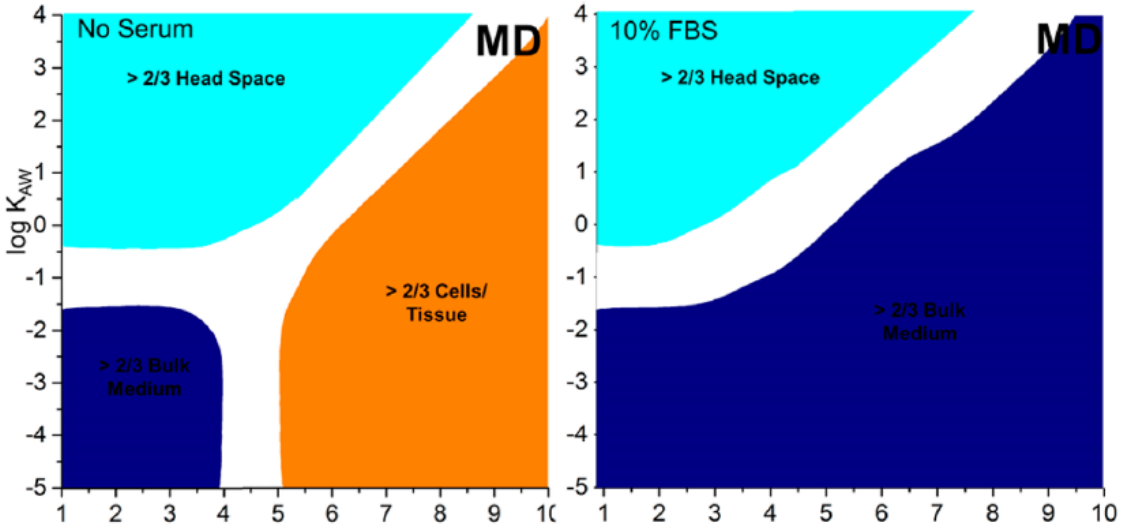
[§]ARC Arnot Research and Consulting, Inc., 36 Sproat Avenue, Toronto, Ontario M4M 1W4, Canada

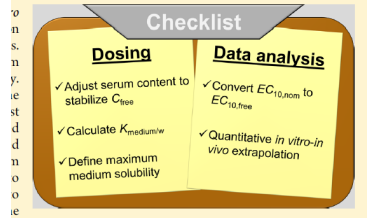


Chemical Research in Toxicology
Perspective
Cite This: Chem. Res. Toxicol. 2019, 32, 1462−1468
pubs.acs.org/crt

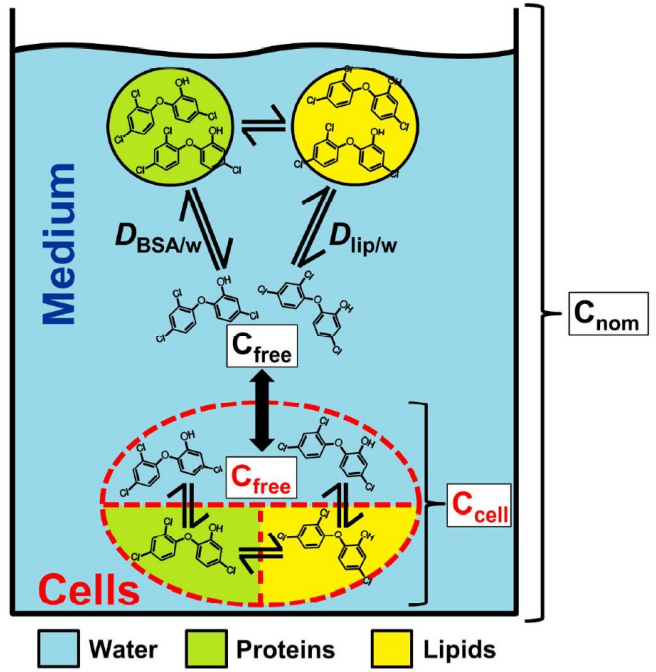
How To Improve the Dosing of Chemicals in High-Throughput *in Vitro* Mammalian Cell Assays

Fabian C. Fischer,[†] Luise Henneberger,[†] Rita Schlichting,[†] and Beate I. Escher*[,†,‡]

[†]Department Cell Toxicology, Helmholtz Centre for Environmental Research - UFZ, Permoserstraße 15, 04318 Leipzig, Germany
[‡]Centre for Applied Geoscience, Eberhard Karls University Tübingen, 72074 Tübingen, Germany



conversion of *in vitro* effect data to freely dissolved effect ve *in vitro* to *in vivo* extrapolation models and compared to



Fischer, F. C., L. Henneberger, M. Konig, K. Bittermann, L. Linden, K. U. Goss and B. I. Escher (2017). "Modeling exposure in the Tox21 in vitro bioassays." Chem Res Toxicol.

Reflections

Is there a scenario where the fugacity in plastic is >> fugacity of the surrounding environment (occupational)

Should we continue to prioritize the influence of microplastic to act as vectors/Trojan horses for chemicals?

Do we know enough about the physical effect of microplastic particles – does the polymer composition/shape/size represent a toxicity for microplastic that is more potent then any other particle?

Do we know enough about chronic exposure to bioavailable chemical mixtures that occur from diet and inhalation to even begin to assess the additional stressor that exposure to particulates represents?

Does the issue represent an opportunity to develop risk assessment frameworks better able to address the complexity related to the adverse effects associated with both chemical and non-chemical stressors?