Contaminants Associated with Microplastics

→ How concerned should we be?

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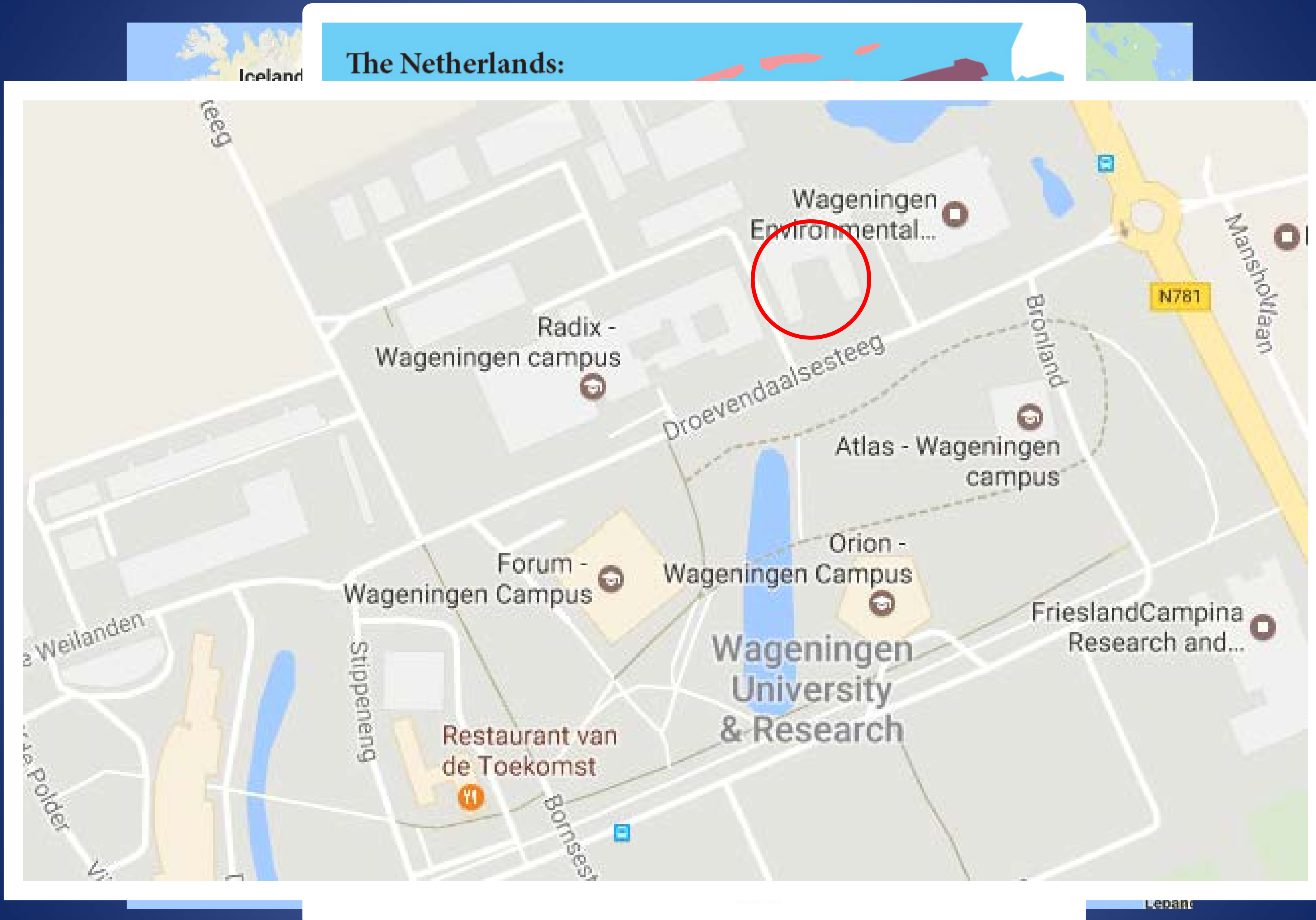
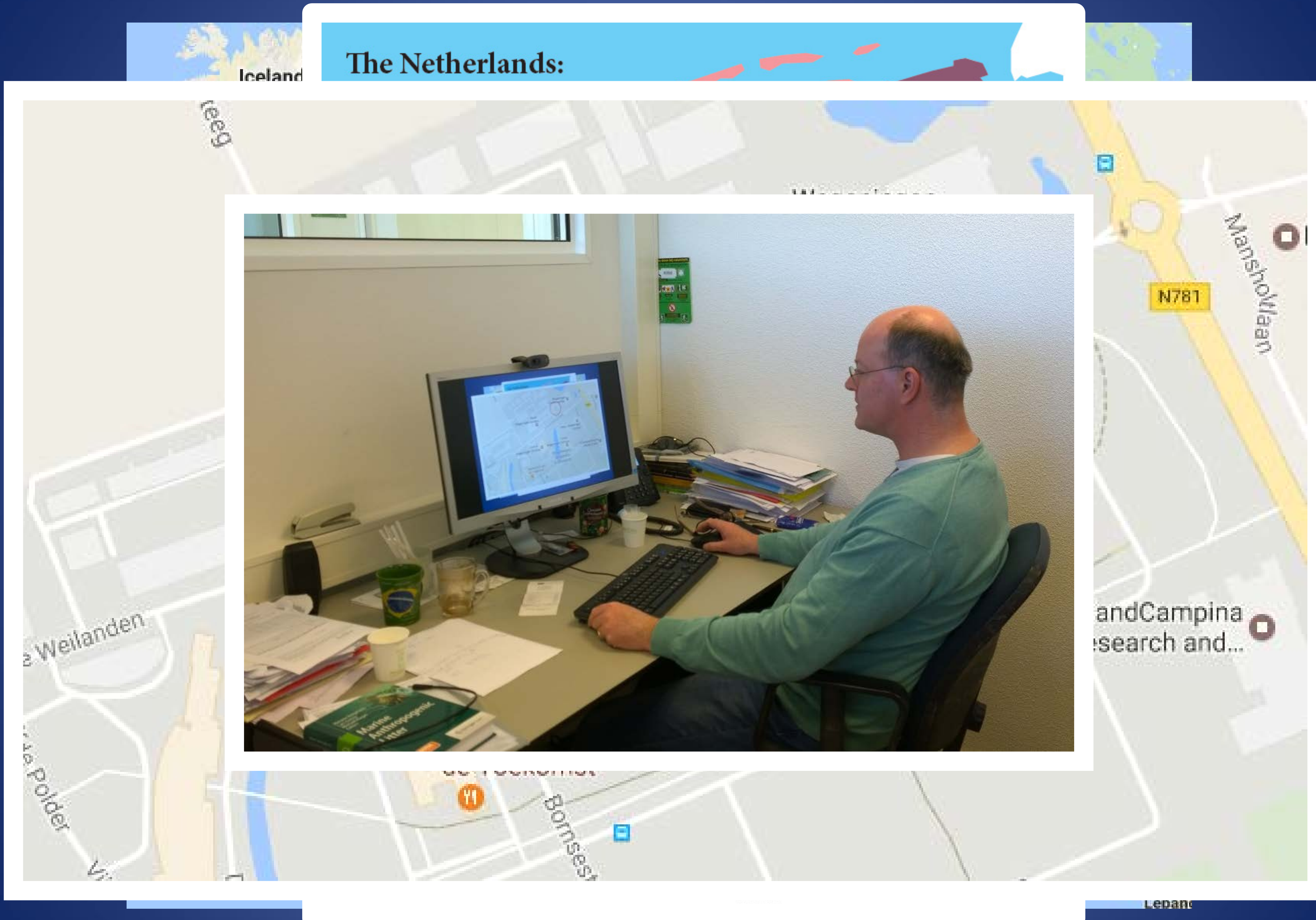
Iceland
Sweden
Norway
Finland
Baltic Sea
Estonia
Latvia
North Sea
Lithuania
Denmark
United Kingdom
Ireland
Netherlands
Belarus
Poland
London
Germany
Belgium
Prague
Czechia
Paris
Slovakia
Ukraine
Austria
Moldova
Hungary
France
Romania
Croatia
Serbia
Black Sea
Italy
Barcelona
Rome
Bulgaria
Portugal
Madrid
Spain
Istanbul
Tyrrhenian Sea
Greece
Mediterranean Sea
Tunisia

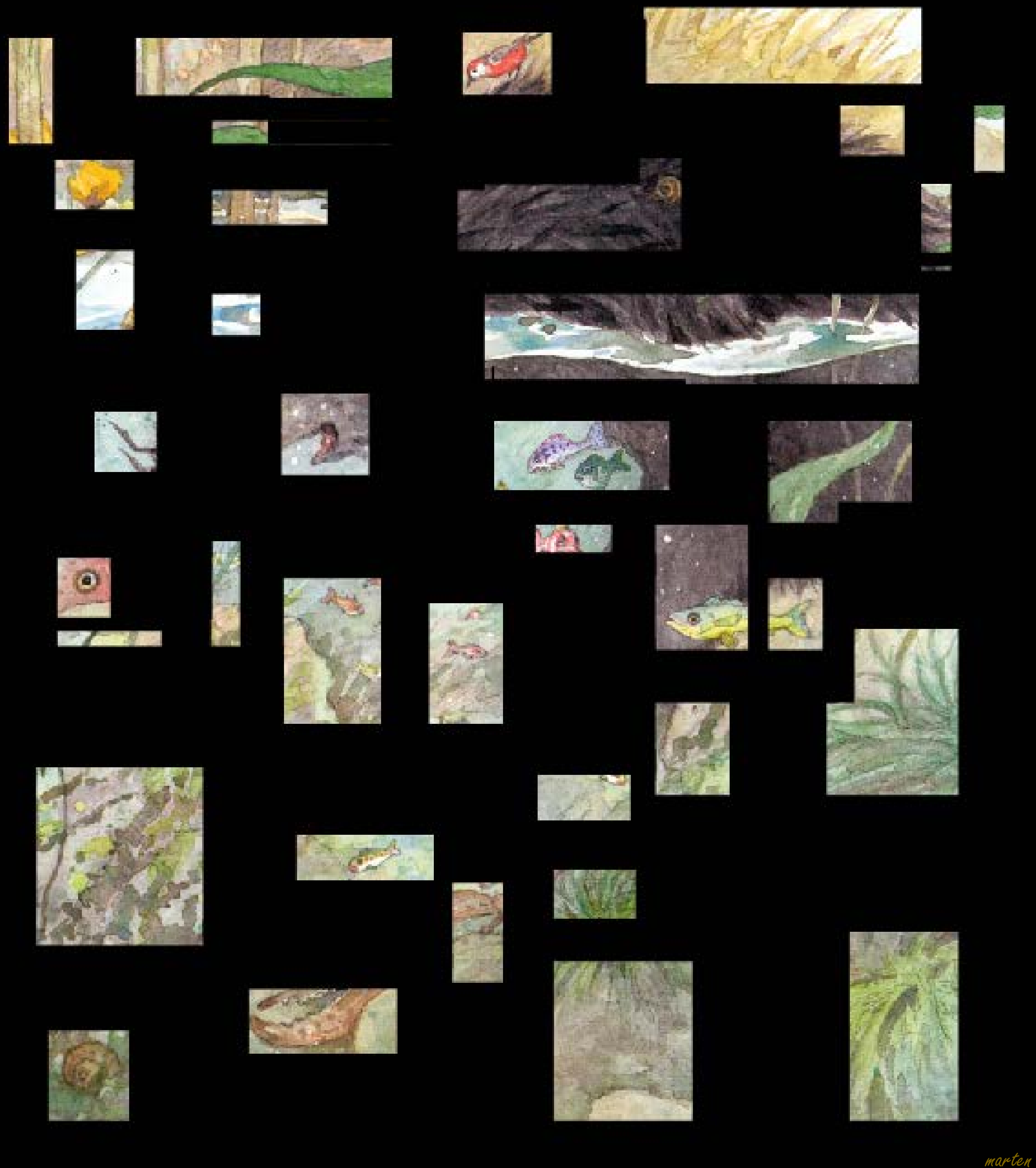

The Netherlands:
if there were no dikes...
Iceland
GRONINGEN
Groningen
Leeuwarden
FRIESLAND
Assen
DRENTHE
NORTH-
HOLLAND
FLEVOLAND
Zwolle
OVERIJSSEL
GELDERLAND
Utrecht
UTRECHT
[redacted]rnhem
The Hague
SOUTH-HOLLAND
Rhine
's-Hertogenbosch
Germany
BRABANT
ZEELAND
Scheldt
LIMBURG
Belgium
Water
70 Kilometers
43.5 Miles
Maastricht
Maas
Ukraine
Black Sea
Turkey


The Netherlands:
Iceland
Wageningen
Environmental...
Radix -
Wageningen campus
Droevendaalsesteeg
Bronland
N781
Manshoflaan
Atlas - Wageningen
campus
Forum -
Wageningen Campus
Orion -
Wageningen Campus
FrieslandCampina
Research and...
Wageningen
University
& Research
Weilanden
Stippeneng
Restaurant van
de Toekomst
Bornsest


The Netherlands:
N781
Mansholtlaan
Weilanden
Marine Anthropogenic Litter

Content & aim:

- **The big picture: what is the problem and what are the questions?**
- **What are the basic mechanisms you need to know of?**
- **Does plastic affect (global) transport of contaminants in nature?**
- **Is ingestion of microplastic dangerous because of the associated chemicals?**
- **Implications for hazards and risks**


marten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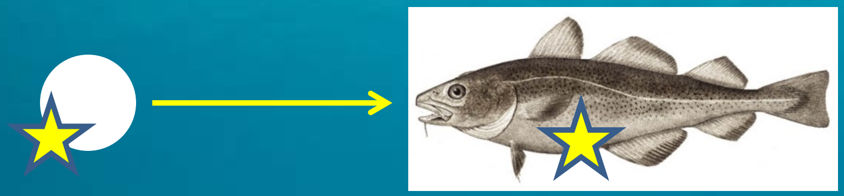
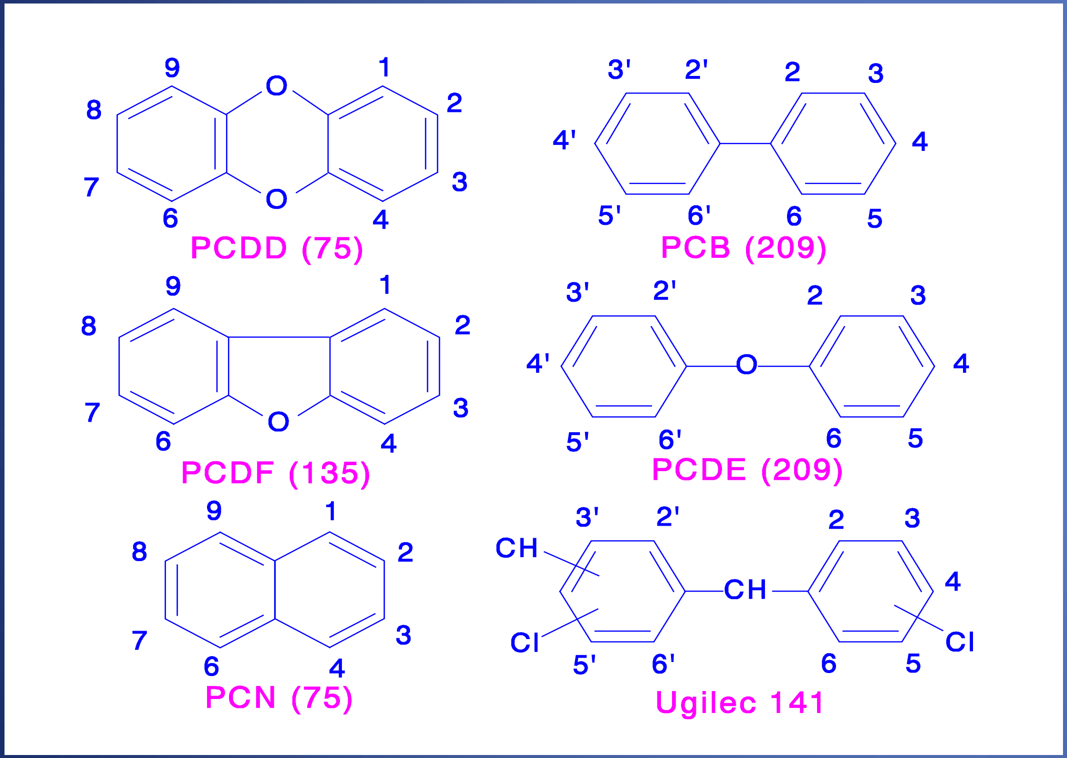


Concerns:

1. **Plastic carries contaminants to previously clean places**
2. **Plastic carries contaminants to previously clean organisms**

Contaminants?



These chemicals are big and they don't like water

They are referred to as 'hydrophobic'

Where do they go?

Organic matter (in sediments, in soils, free floating in water)

Body fat or lipids (in biota; plants, man, animals)

And... Since the 1950's... Plastic

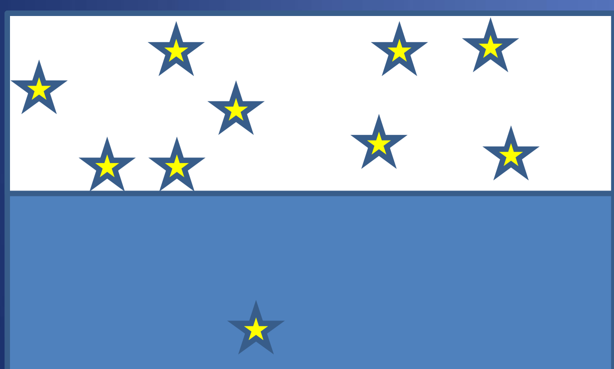
They absorb from to water to plastic, or they desorb from plastic to water, which takes time (sorption kinetics)

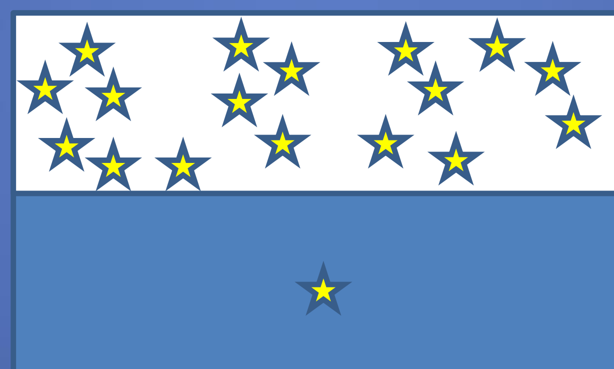
Contaminants are absorbed by plastic like water by a sponge

$$K_P = \frac{493\,782}{1}$$

$$K_P = \frac{33\,871\,648}{1}$$

$$K_P = \frac{317\,598\,000}{1}$$



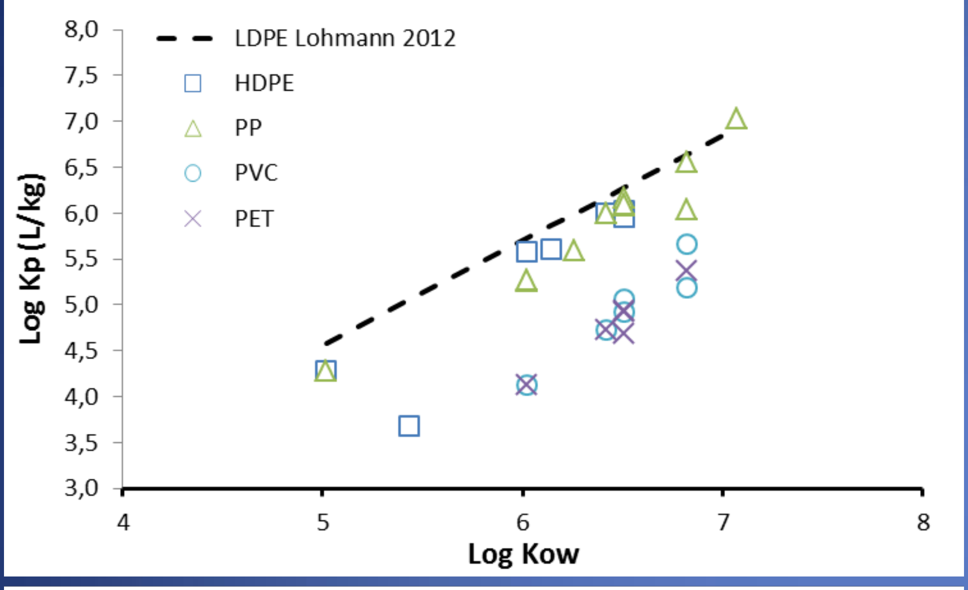


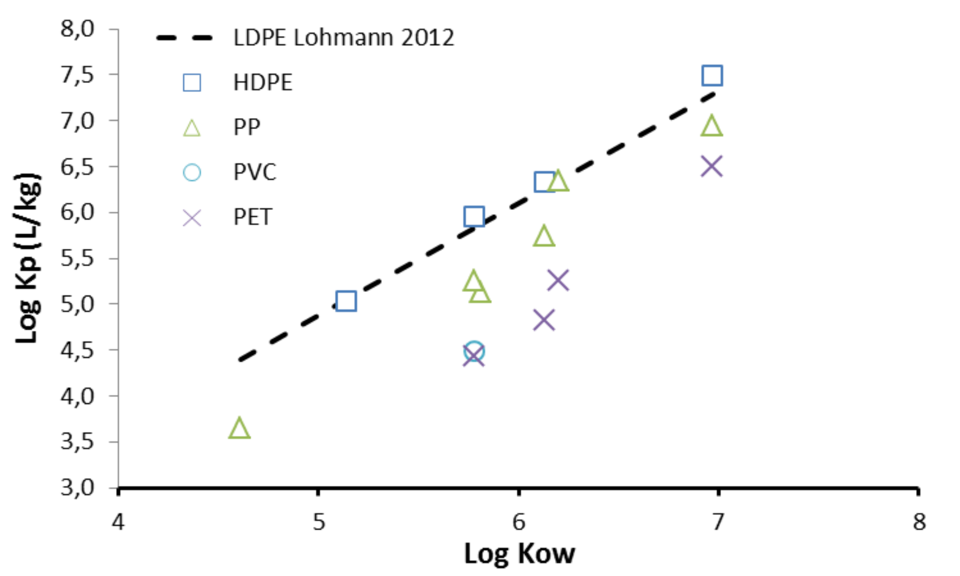
$$Log\ K_P = 5.5$$

$$Log\ K_P = 7.5$$

$$Log\ K_P = 8.5$$

Sorption Equilibrium – in situ

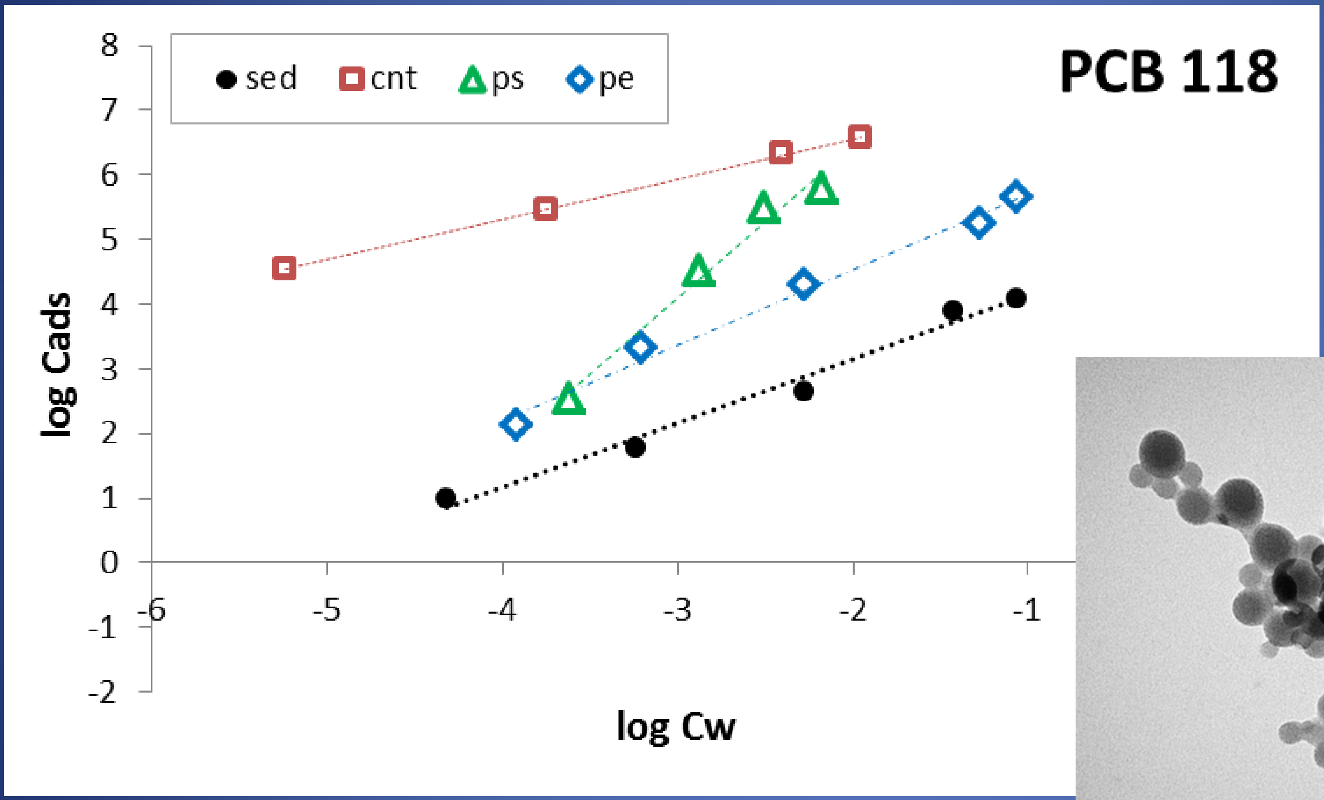


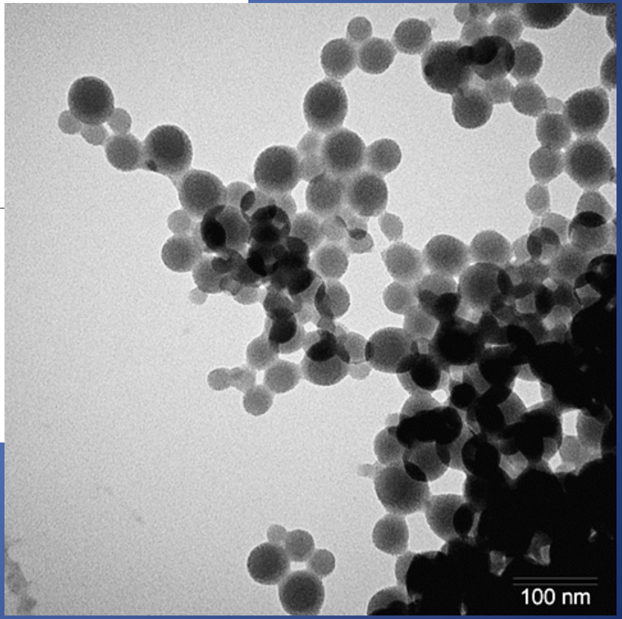


Recalculated from in situ data published by Chelsea Rochman et al, ES&T, 2013.

Endo, S., Koelmans, A.A. 2016. Sorption of hydrophobic organic compounds to plastics in marine environments: equilibrium/mechanism/monitoring. In: H.Takada and H.Karapanagioti (Eds.), Hazardous Chemicals Associated with Plastics in the Environment, *The Handbook of Environmental Chemistry, In prep.*

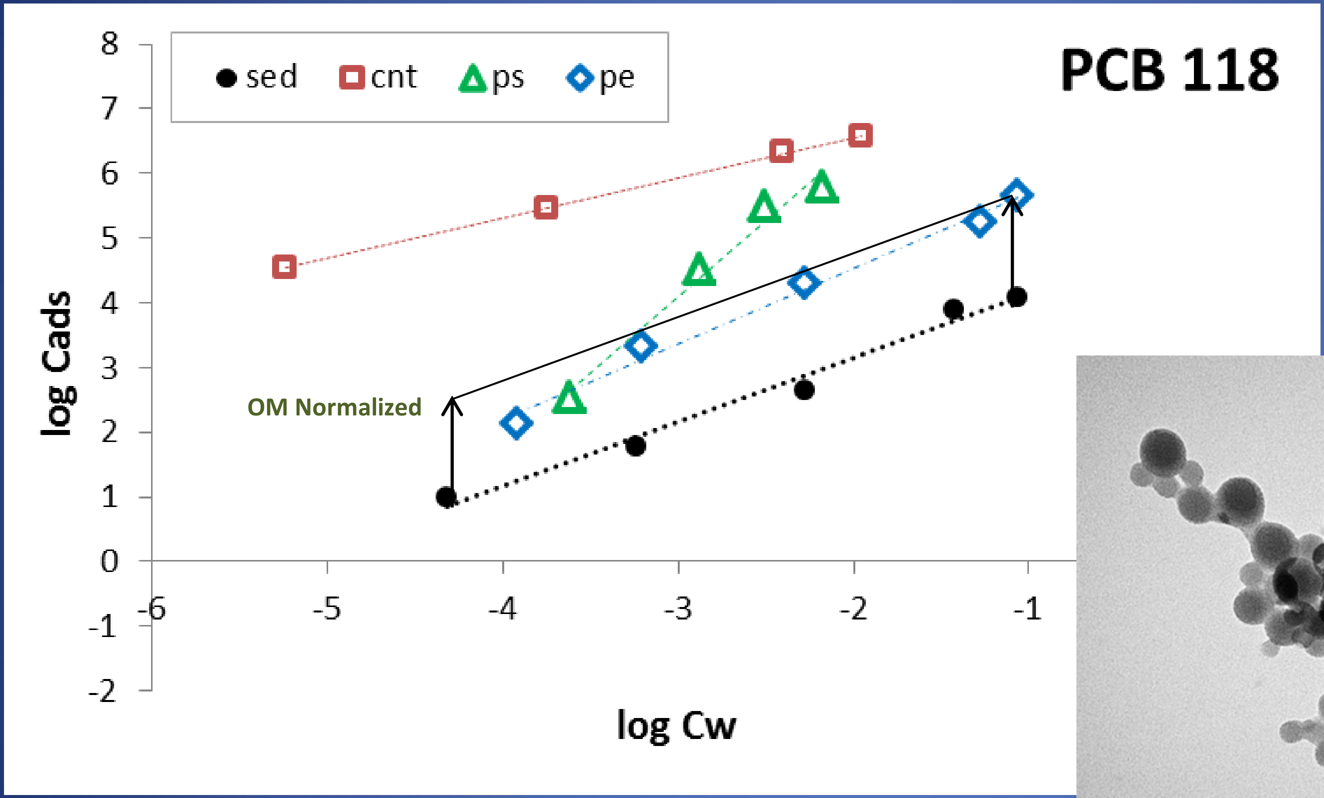
Compared to other particles?

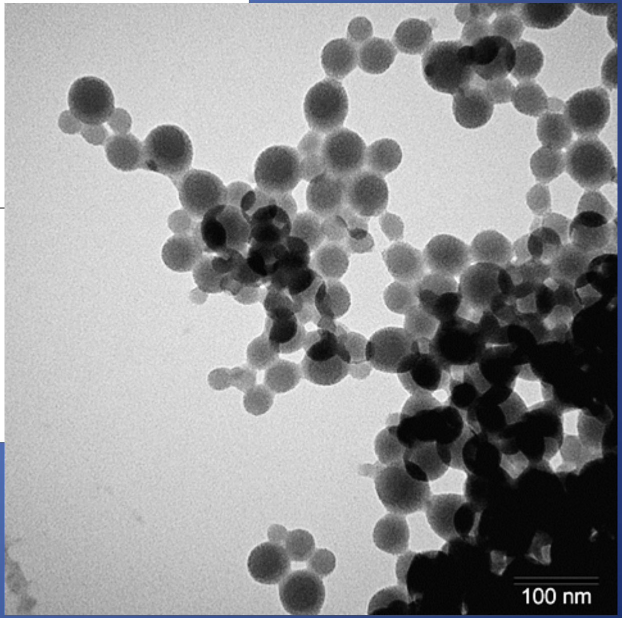




Velzeboer, I., C.J.A.F. Kwadijk, A.A. Koelmans. 2014. Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes and fullerenes. *Environ. Sci. Technol.* 48, 4869−4876.

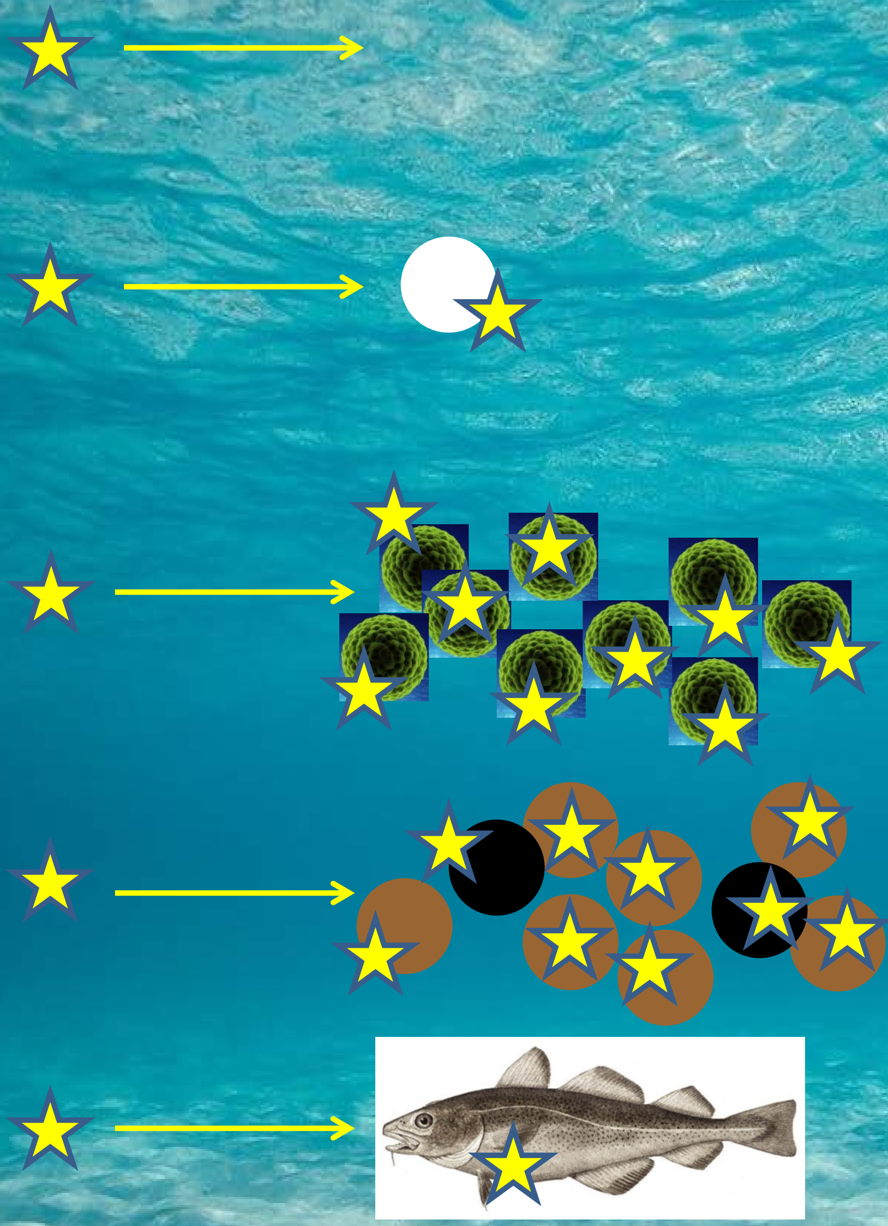
Compared to other particles?



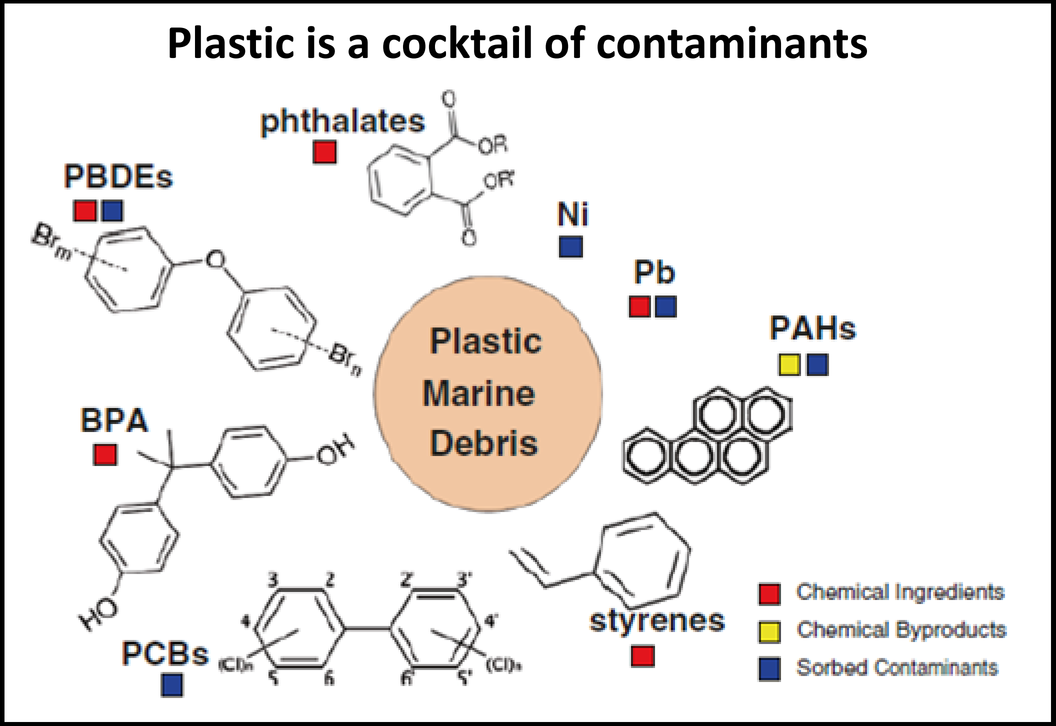


Velzeboer, I., C.J.A.F. Kwadijk, A.A. Koelmans. 2014. Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes and fullerenes. *Environ. Sci. Technol.* 48, 4869−4876.

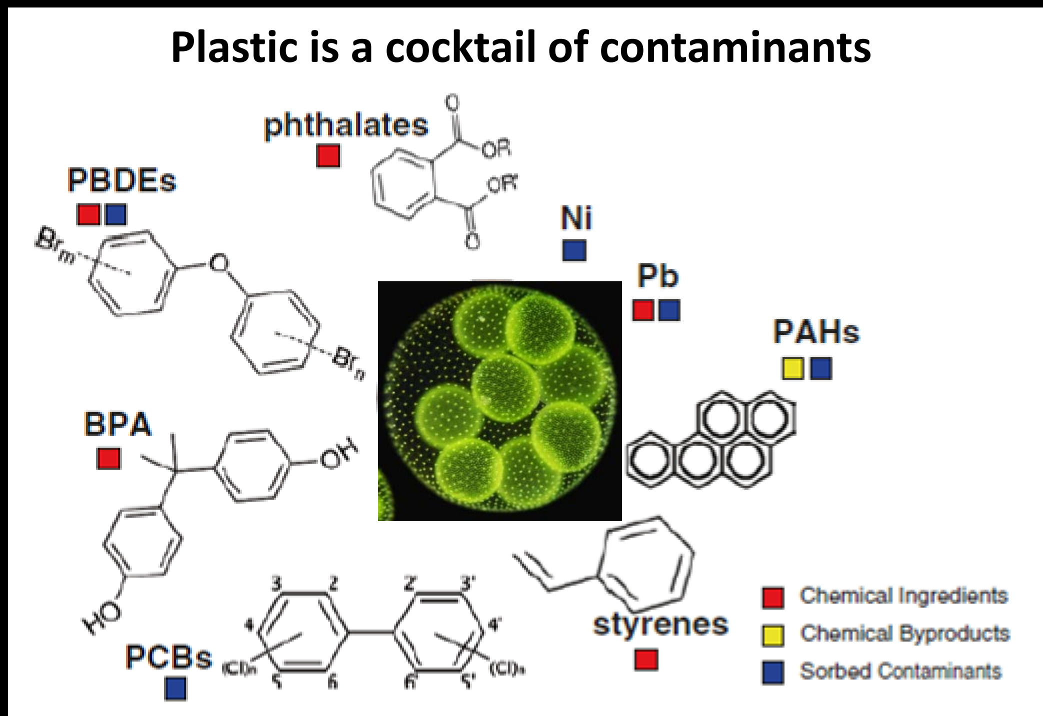
Chemicals bind to organic matter, algae, black carbon in a similar way as they do to plastic



Context: The *Environment* is a cocktail of contaminants



Context: The *Environment* is a cocktail of contaminants



Is plastic a relevant carrier medium for contaminants?

- Importance of a carrier medium depends on the strength of the binding
- Importance depends on the age of the plastic (was there enough time to completely absorb or desorb?)
- Importance of a carrier depends on the abundance of that carrier medium

→ Evaluate these criteria on an average ocean scale

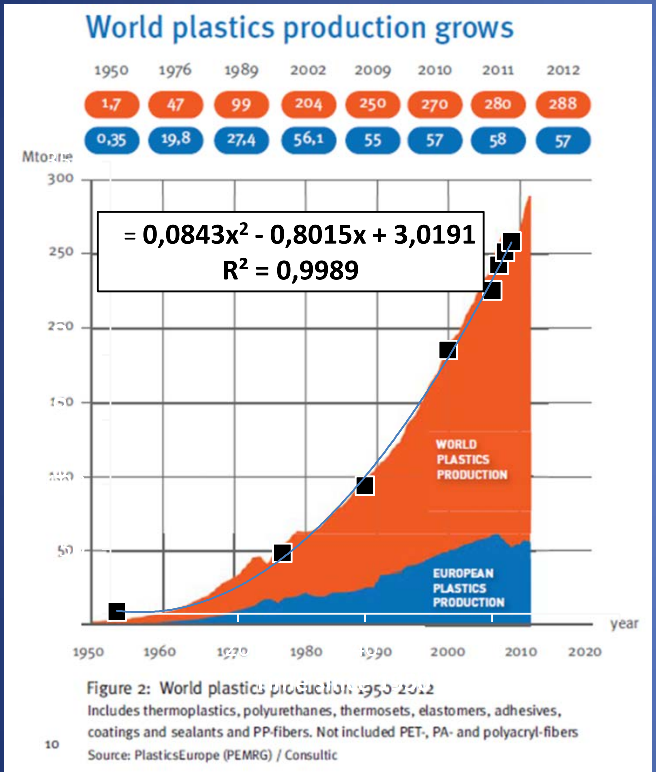
→ Evaluate them on more local scales

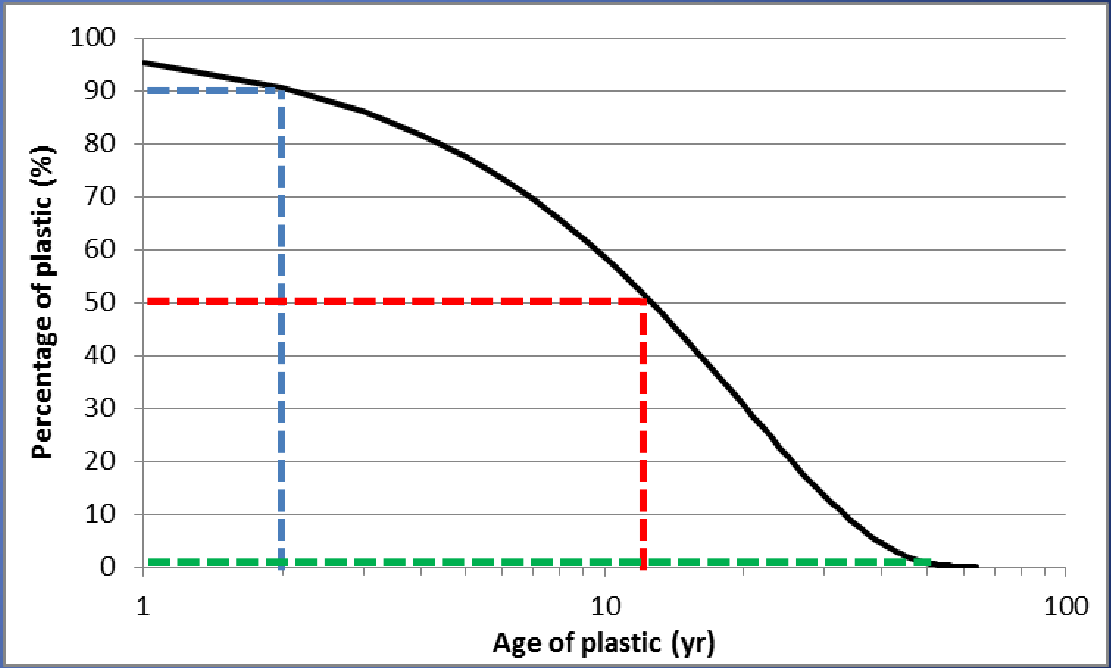
Can we assume (near-)equilibrium?

Probably 'Yes', for microplastic because:

- **Sorption half lives: 0.5 – 5 mm: months - 2 yr (Endo, 2005; Rochman, 2013)**
  < 0.5 mm: weeks - months
- **The smaller plastic is the older plastic → equilibrium**
- **The fraction of 'young' < 2 yr plastic is small considering emissions becoming substantial in the 1950s → so most plastic must be 'older' plastic**
- **→ Most ingestible plastic is 'small' and 'old' plastic, and therefore at or close to equilibrium.**

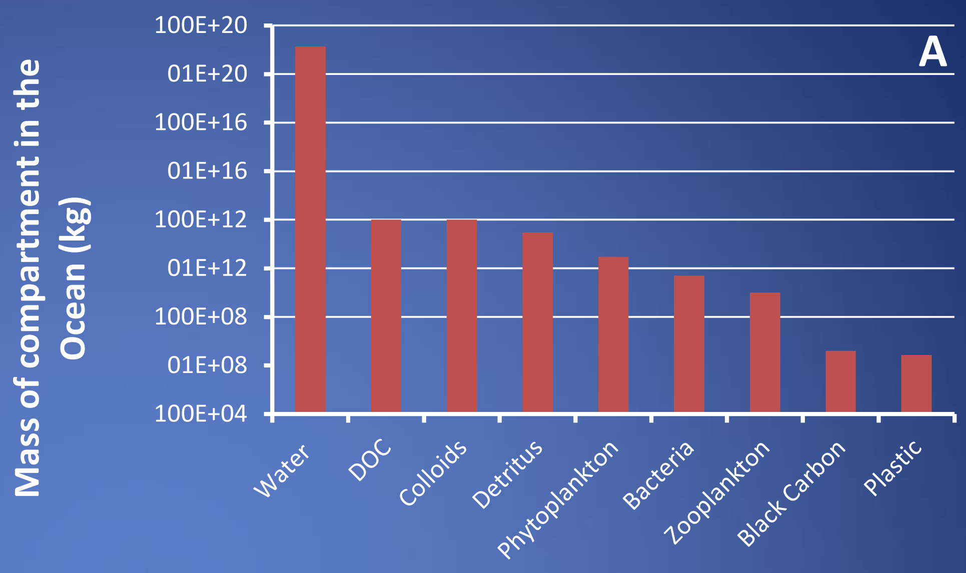
How old is the plastic? – A closer look



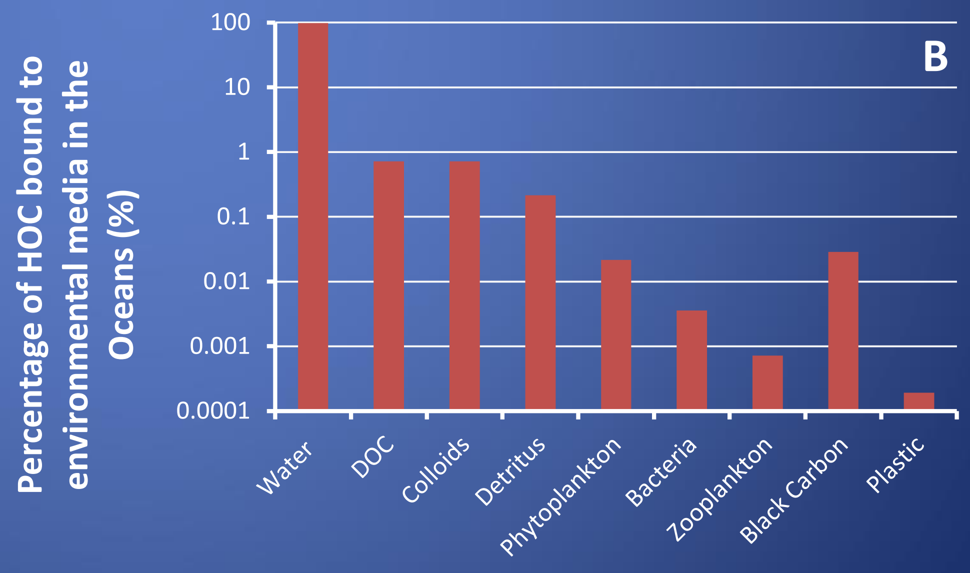


Koelmans et al., ES&T, 2016

Mass Distribution of Oceanic Media



Chemical Mass Distribution in Oceanic Media



Koelmans et al., ES&T, 2016

Is plastic a relevant carrier to a remote vulnerable system like the Arctic?

Are marine plastic particles transport vectors for organic pollutants to the Arctic?

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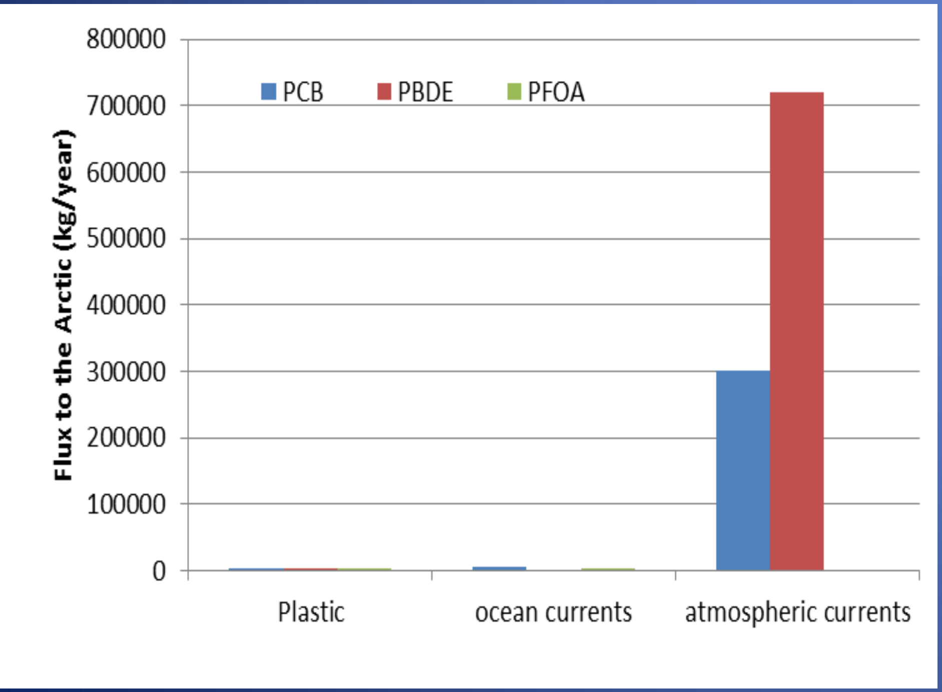
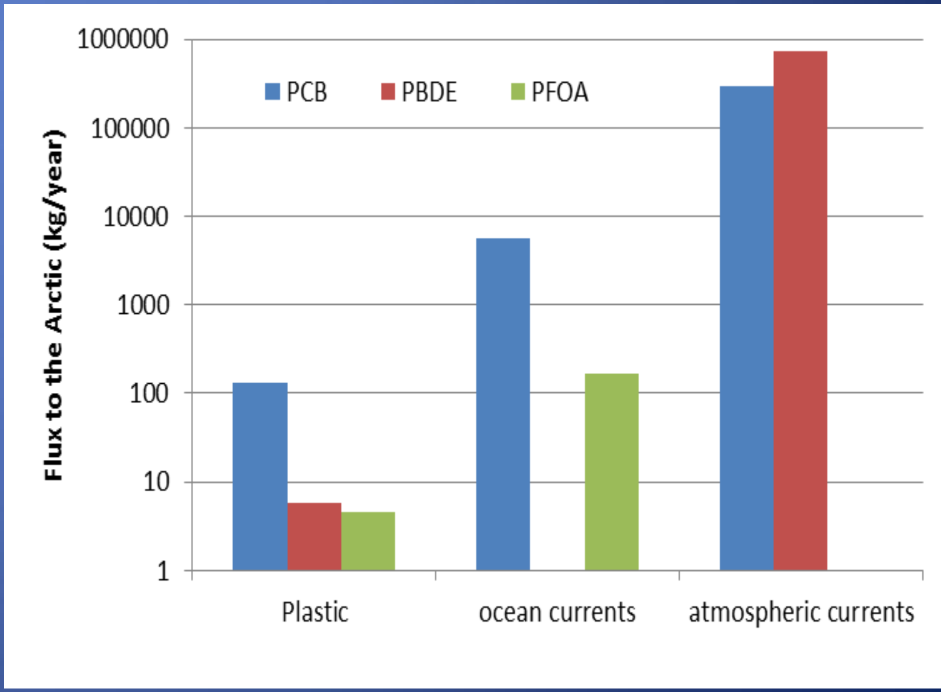
Institute of Environmental Systems Research, University of Osnabrück, Barbarastr. 12, 49076 Osnabrück, Germany





Is ingestion of microplastic dangerous because of the associated contaminants?

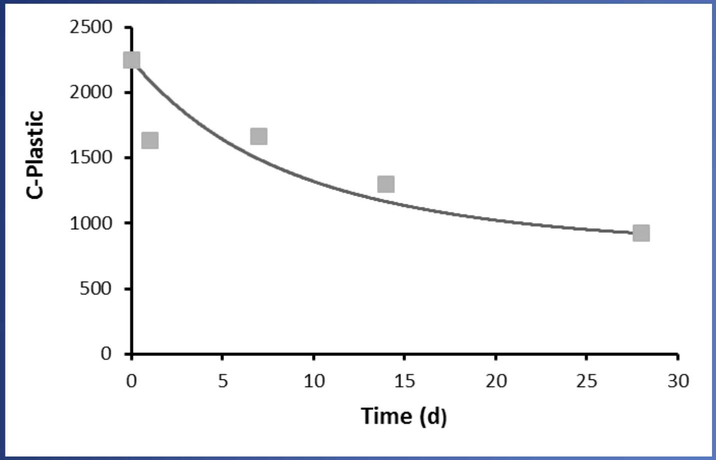
- The chemicals are hazardous, but the hazard does not necessarily imply a risk
- The plastics are hazardous, but the hazard does not necessarily imply a risk

→ Does plastic modify hazard and/or risk of contaminants?

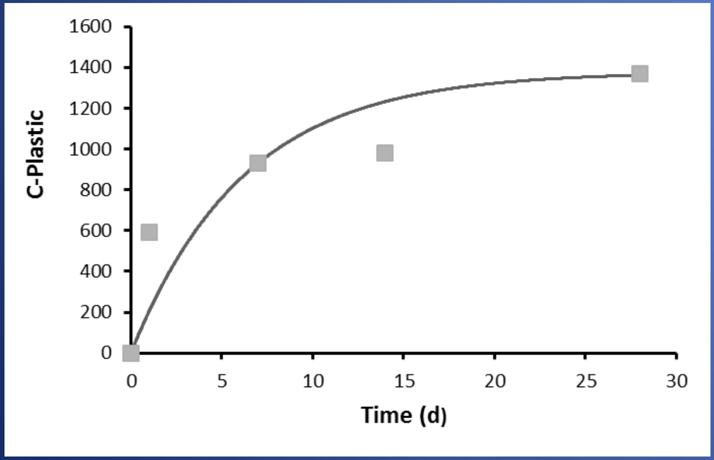
Prerequisites for an effect on risk

- Need a gradient (water flows downhill, not uphill)
- Need plastic to be a substantial carrier compared to other carriers (e.g., dermal uptake or dietary uptake)
- Needs to be bigger than biological variability (in lab experiments, more than a factor of two; in nature probably much more)
- Needs the exceeding of a toxicity threshold (for the whole cocktail), due to the ingestion of plastic

1. Chemical transfer requires a gradient



Contaminated plastic in clean gut fluids leads to desorption
→Plastic contaminates the organism

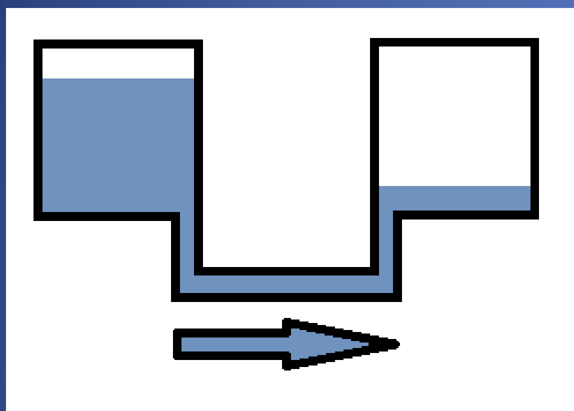


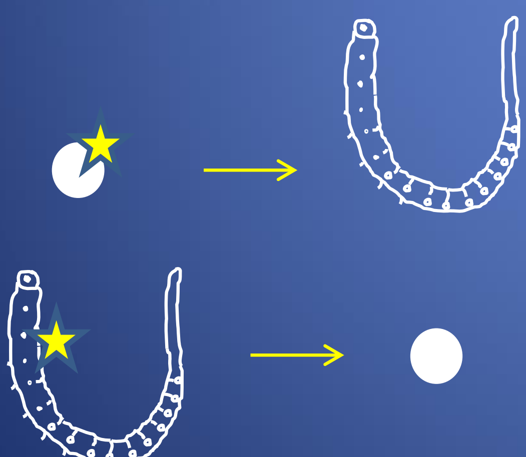
Clean plastic in gut fluids with contaminated food
→Plastic cleans the organism

Environment: Cocktail of ab- and desorbing chemicals, so both directions of transfer occur simultaneously

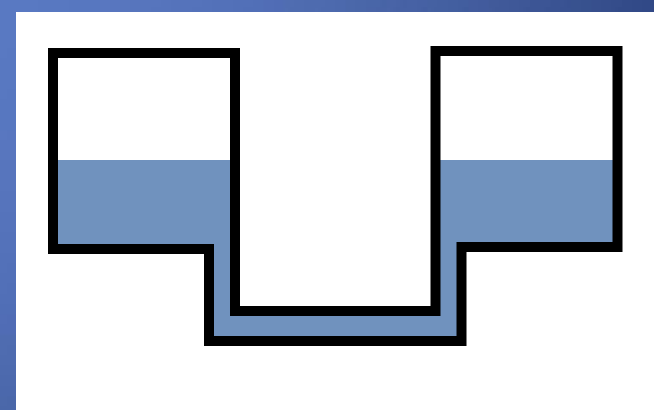
Tsaroucha, Chen, Huang, Koelmans, 2017 in prep.

1. Chemical transfer requires a gradient





Shorter term

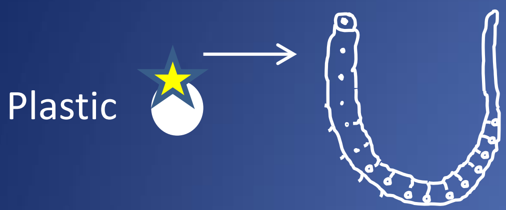


Longer term;
<u>nothing happens</u>

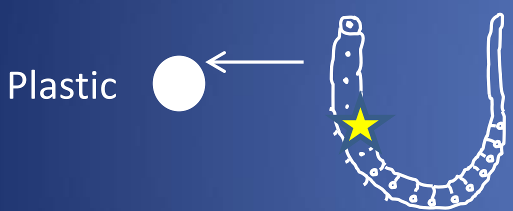
1. Chemical transfer requires a gradient

- As of birth, fish is ‘loaded’ (equilibrated) with contaminants from its (contaminated) environment
- Like a sponge can be loaded with water
- Once ‘saturated’ with contaminants a fish cannot take up <u>more</u> chemicals, not from food, not from water, not from plastic.
- Like a wet sponge cannot take up more water
- Plastic thus will not increase chemical uptake

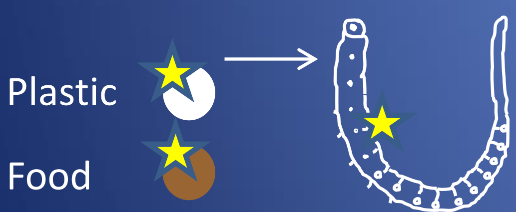
Approaches used in lab studies



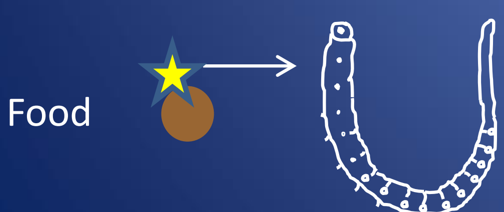
Teuten et al, 2009; Browne, 2013; Chua et al, 2014; Wardrop et al, 2016



Teuten et al, 2007; Chua et al, 2014

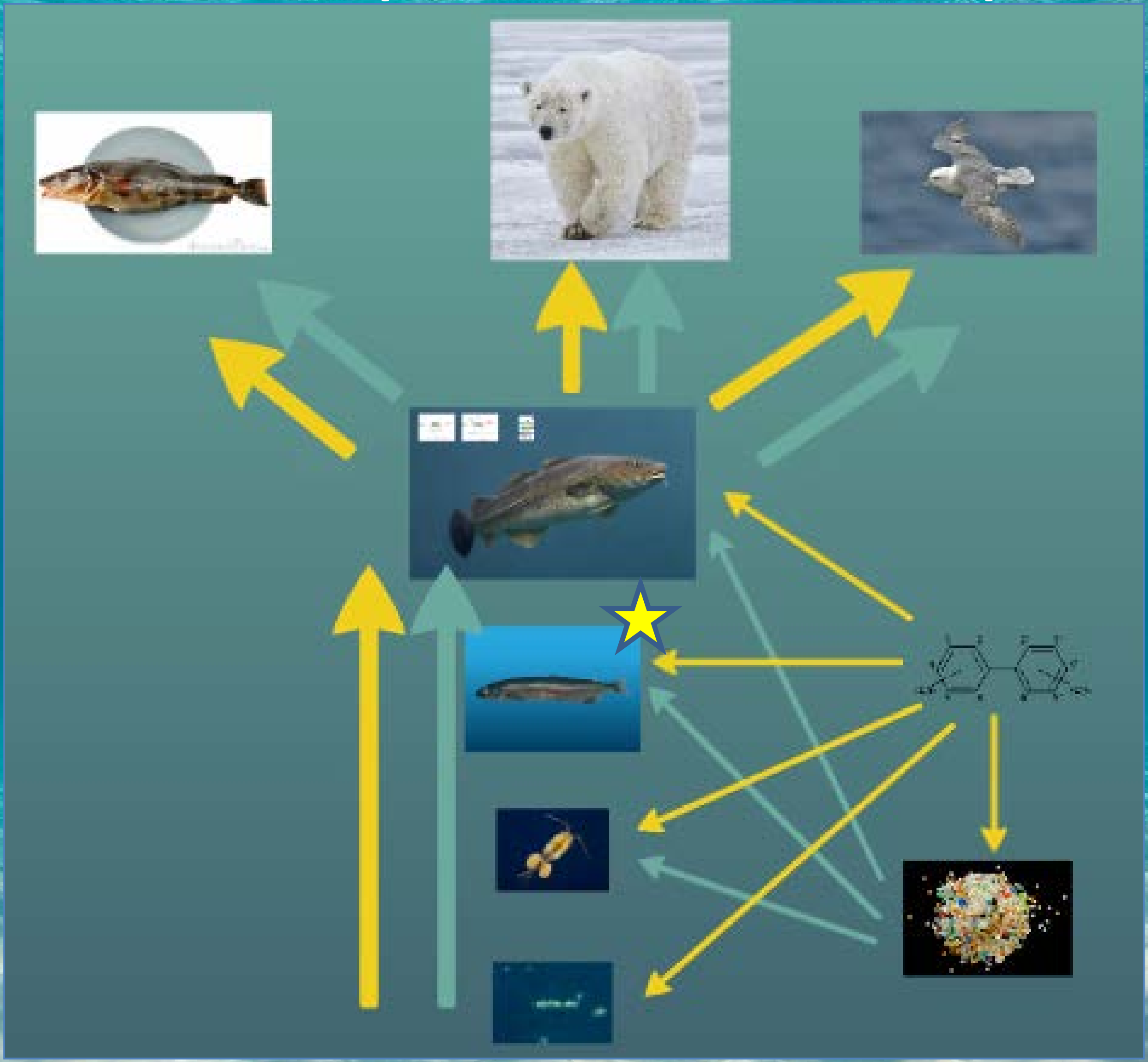


Rochman et al, 2013; Besseling et al, 2013, 2017; Paul-Pont et al, 2016



Numerous studies (Kukkonen, Landrum, Ingersoll, Ankley…)

2. Uptake through plastic needs to be substantial compared to other pathways



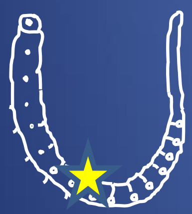
Diepens & Koelmans, 2017. Accumulation of microplastic and microplastic-associated contaminants in marine food webs, in prep.

Implications of plastic-associated chemicals for bioaccumulation?

Well-established

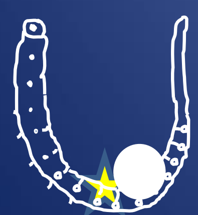
Principles of organic matter sorption

Principles of polymer sorption



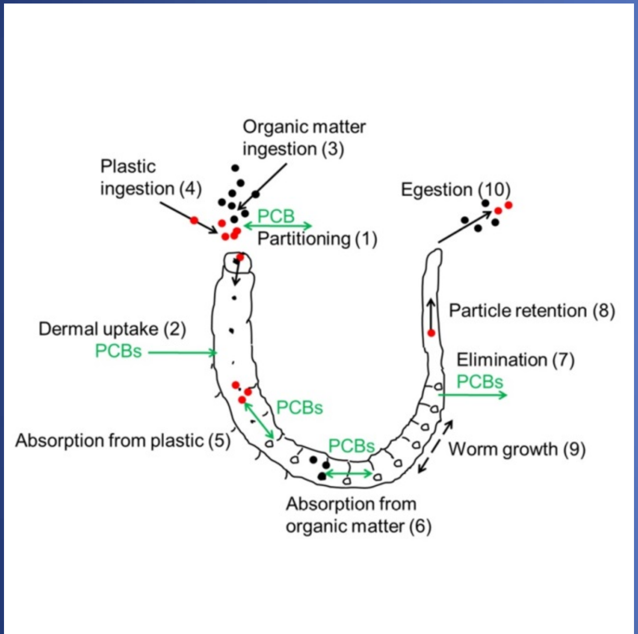
Principles of bioconcentration/bioaccumulation

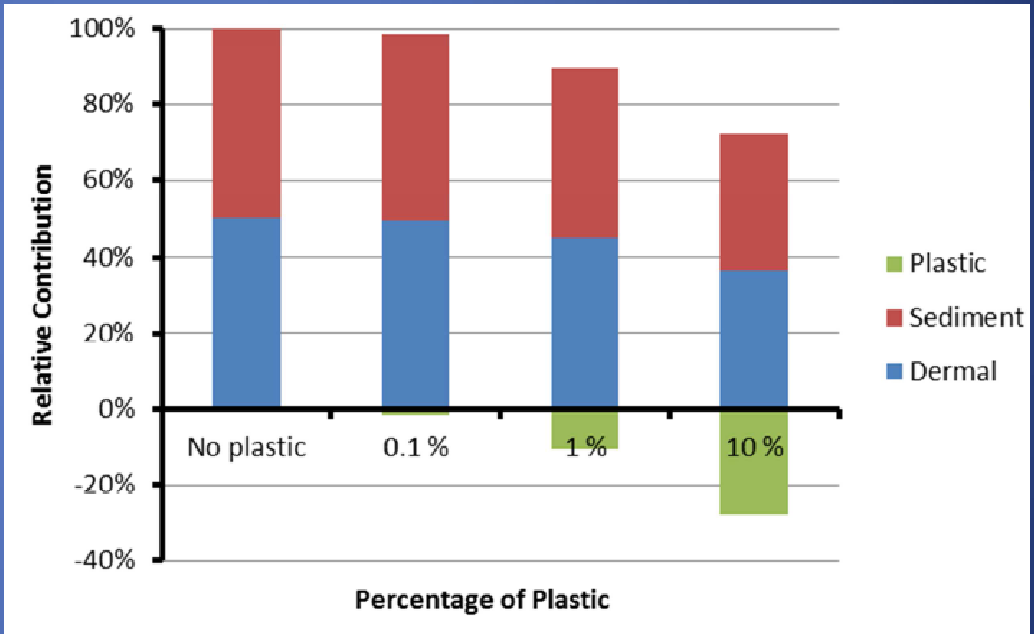
Fairly well-established



Mass transfer in the gut - toxicodynamics

Calculate & compare pathways: (a) Lugworm





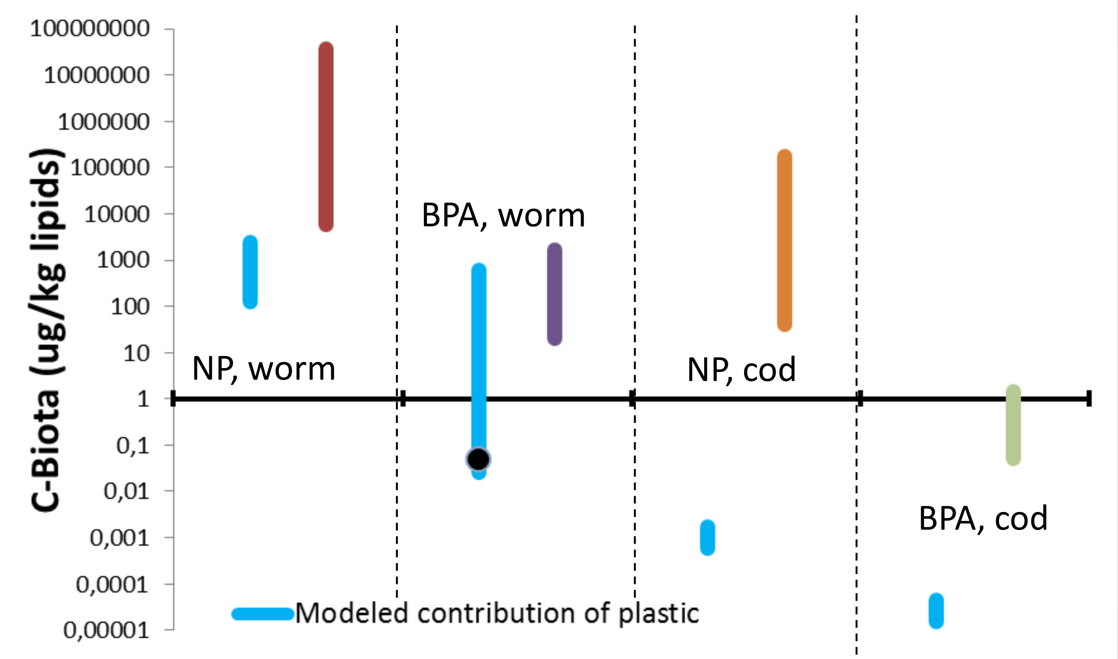
→ Marginal role of plastic ingestion at environmentally realistic MP concentrations

Koelmans, A.A., E. Besseling, A. Wegner, E.M. Foekema. 2013. Plastic as a carrier of POPs to aquatic organisms. A model analysis. Environ. Sci. Technol. 47, 7812–7820.

Calculate & compare pathways: (b) Lugworm & cod

Simulations with validated model for lugworm and North Sea cod:

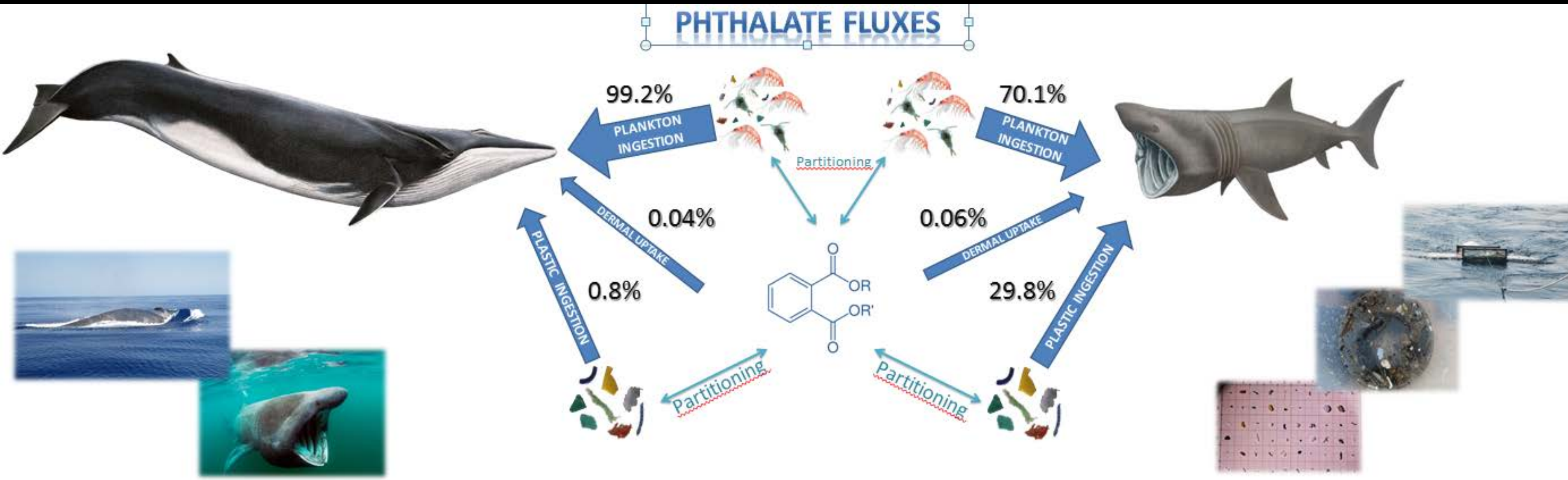
- Take environmental NP & BPA concentrations in all media
- Calculate contribution of leaching of NP and BPA to con-centration in species
- Cover uncertainties by Monte Carlo Probabilistic modelling
- Compare with concentrations in the field
- Assess relative importance



→ Marginal role of plastic ingestion at environmentally realistic MP concentrations

Koelmans, A.A., E. Besseling, E.M. Foekema. 2014. Leaching of Plastic Additives to Marine Organisms. *Environmental Pollution*, 187, 49-54.

Calculate & compare pathways: (c) Fin whale and basking shark



→ Marginal role of plastic ingestion at environmentally realistic MP concentrations

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WAGENINGEN UR For quality of life

Microplastic as a vector of chemicals to fin whale and basking shark in the Mediterranean Sea: A model-supported analysis of available data

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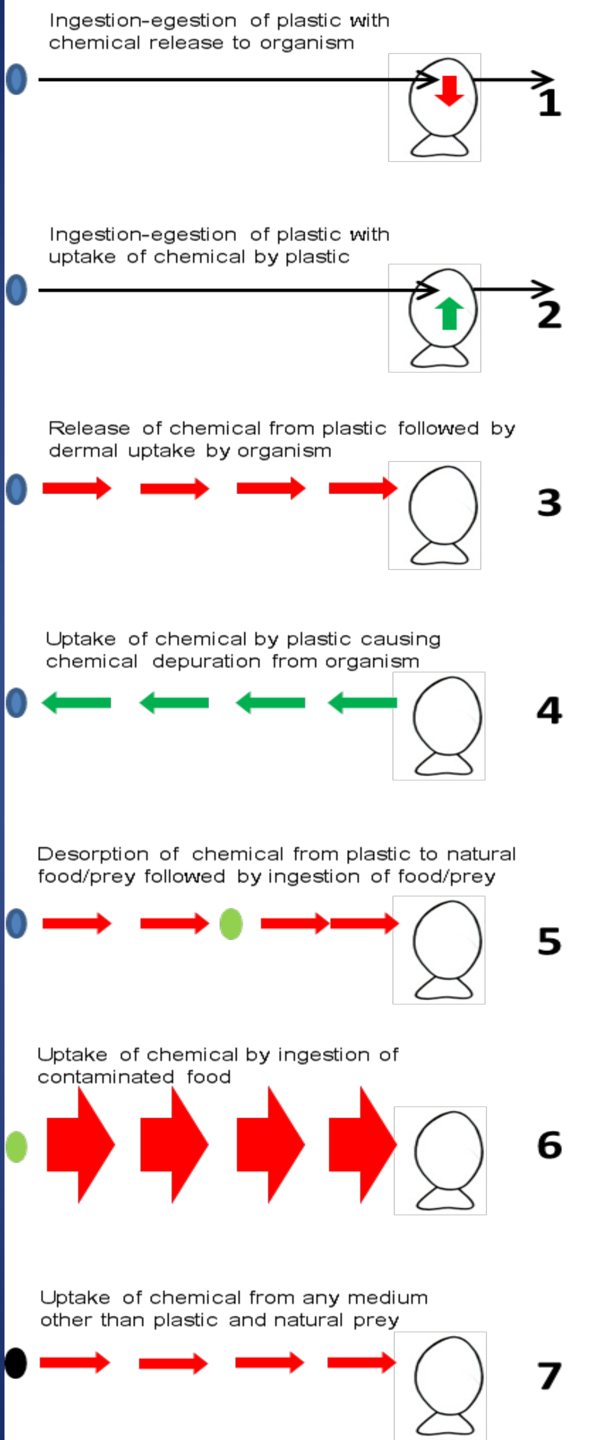
2) Aquatic Ecology and Water Quality Management Group, Dept. of Environmental Sciences, Wageningen University, 6700 AA, Wageningen, The Netherlands



Can we ever measure this in nature?

Probably not

(a) Problem of Multiple Causality
(b) Biological variability

Koelmans et al., 2016.., ES&T.

Biological variability

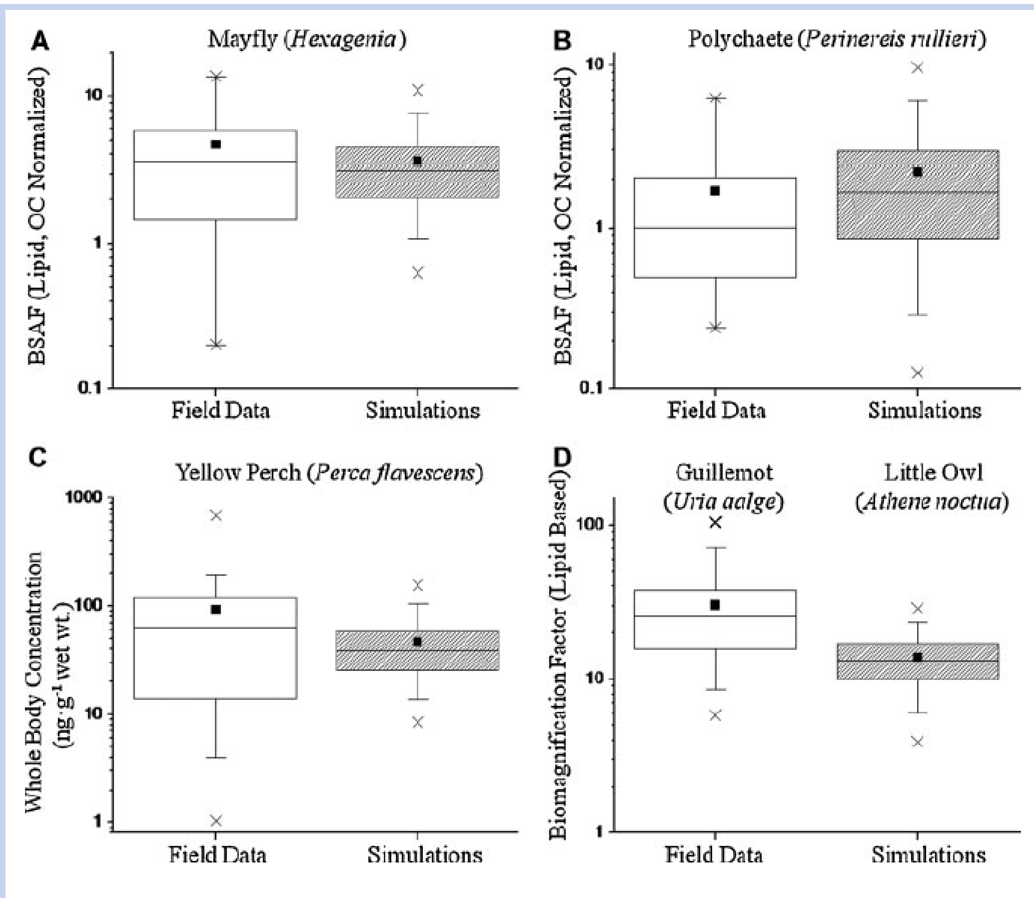


Figure 1. Comparison of PCB-153 bioaccumulation metrics between selected field data sets and model simulations for the model organisms (**A**) mayfly, (**B**) polychaete, (**C**) yellow perch, and (**D**) birds. Box charts present mean (■), median (horizontal line), 25th and 75th percentiles (box edges), 5th and 95th percentiles (whiskers), and 1st and 99th percentiles (×). Mayfly and yellow perch raw field data from the Detroit River (*n* = 13 mayfly BSAFs; Drouillard 2010; *n* = 24 yellow perch; Kashian et al. 2010); Raw polychaete BSAF data from Nesto et al. 2010; Guillemot data generated from Lundsted-Enkel et al. (2005).

Measured variability in uptake of contaminants by organisms is two to three orders of magnitude
→In many cases effects of plastic on uptake are likely to be small
→ Undetectable

Integrated Environmental Assessment and Management
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Explaining Differences Between Bioaccumulation Measurements in Laboratory and Field Data Through Use of a Probabilistic Modeling Approach

Henriette Selck,† Ken Drouillard,‡ Karen Eisenreich,§ Albert A Koelmans,‖ Annemette Palmqvist,† Anders Ruus,# Daniel Salvito,†† Irv Schultz,‡‡ Robin Stewart,§§ Annie Weisbrod,‖‖ Nico W van den Brink,## and Martine van den Heuvel-Greve†††*

Summary

- Transfer may occur into or from the organism, dependent on the concentration gradient, so the exposure scenario matters
- Relative magnitude of plastic-mediated transfer compared to other pathways matters
- Retrospective risk assessment: quantify fluxes and relative importance of pathways for different exposure scenarios (realistic, 'hot spot', worst case…) —**Tools are available**
- Prospective risk assessment: same, yet take future emissions into account; use probabilistic models.

Concluding Notes

- Chemicals and plastic contribute to a ‘multiple stress’ environment, thus are a concern
- Present data seem not to support high concerns for plastic acting as vectors for extra transport or bioaccumulation
- This cannot be fully generalized, however; Specific ‘higher risk’ cases may exist and plastic abundances will rise

Thanks to colleagues, co-workers and collaborators:

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- Muzhi Sun
- Anna Wegner
- Renske Vroom
- Enya Hermsen
- Lijing Liu
- Fani Tsaroucha
- Ilona Velzeboer
- Michiel Kotterman
- Huerta Lwanga, E
- Violette Geissen
- Annemarie van Wezel
- Carolien Kroeze
- Claudia Halsband
- Colin Janssen
- Chelsea Rochman
- Adil Bakir
- Richard Thompson
- Todd Gouin
- Courtney Arthur
- Ann-Marie Cook
- Julia Reisser
- Serena Consulo
- Satoshi Endo
- Won-Joon Shim
- Cristina Fossi
- Cristina Panti
- Arianna Bellingeri
- Ilaria Corsi
- Allen Burton
- Dorte Herzke
- …..