Chemicals in marine plastics : carrier of toxic chemicals to marine organisms

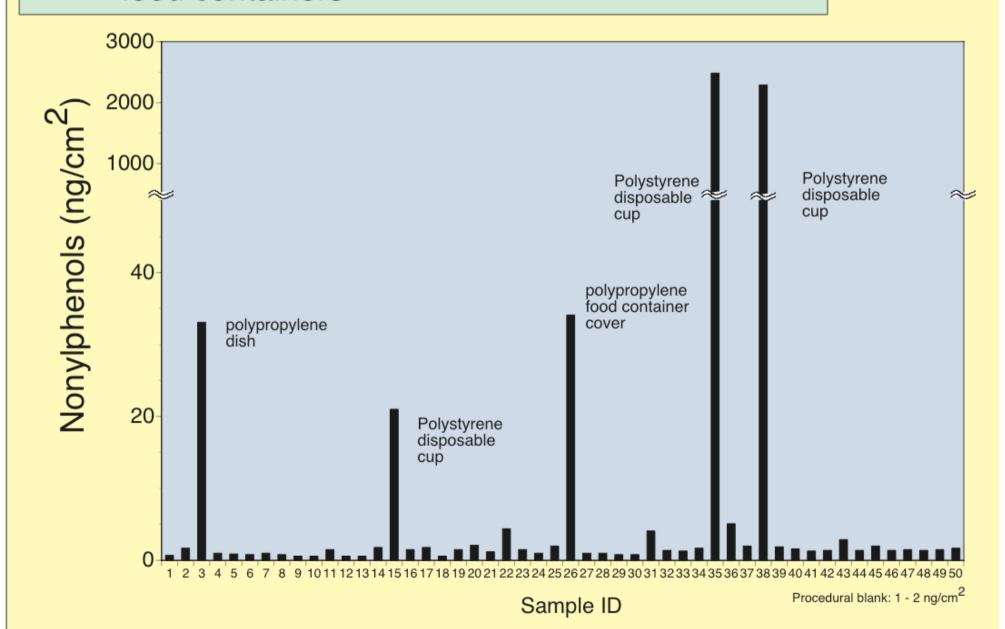
Shige TAKADA

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Nonylphenols released from plastic cups, dishes and food containers

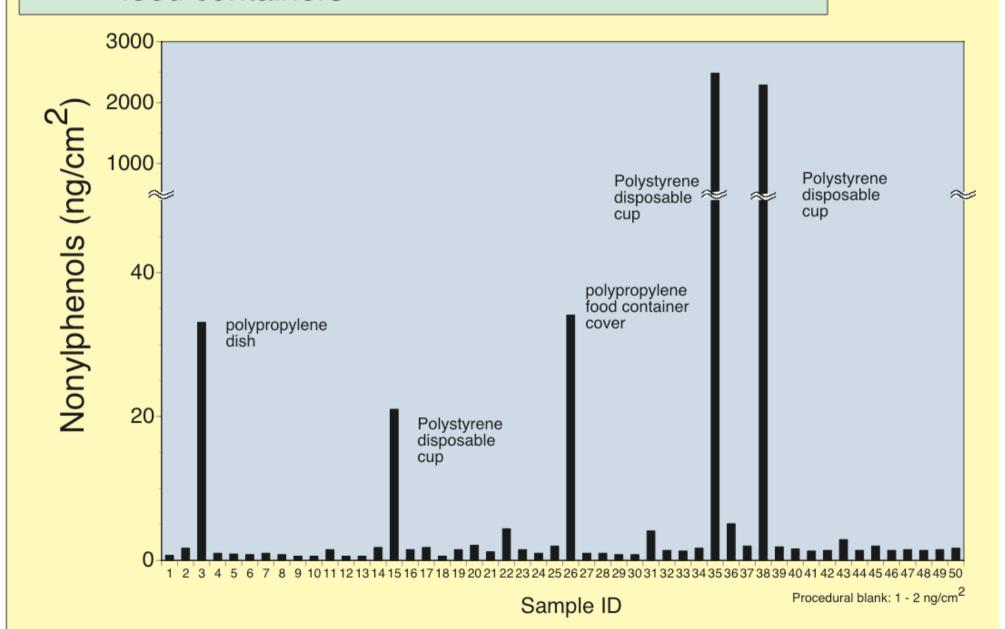


Nonylphenol: Endocrine disrupting chemicals

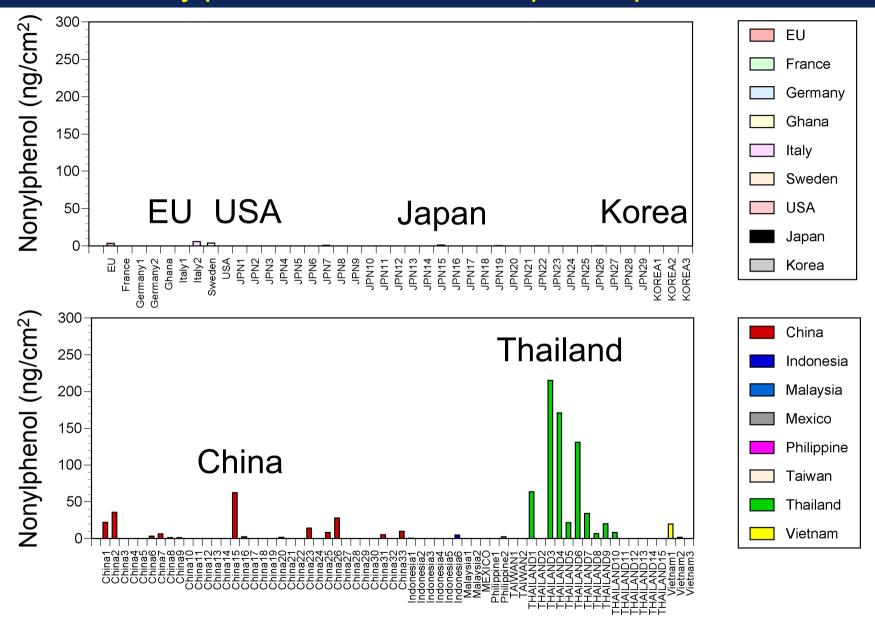
Additives to plastic

Antioxidants
Antistatic agents

Nonylphenols released from plastic cups, dishes and food containers

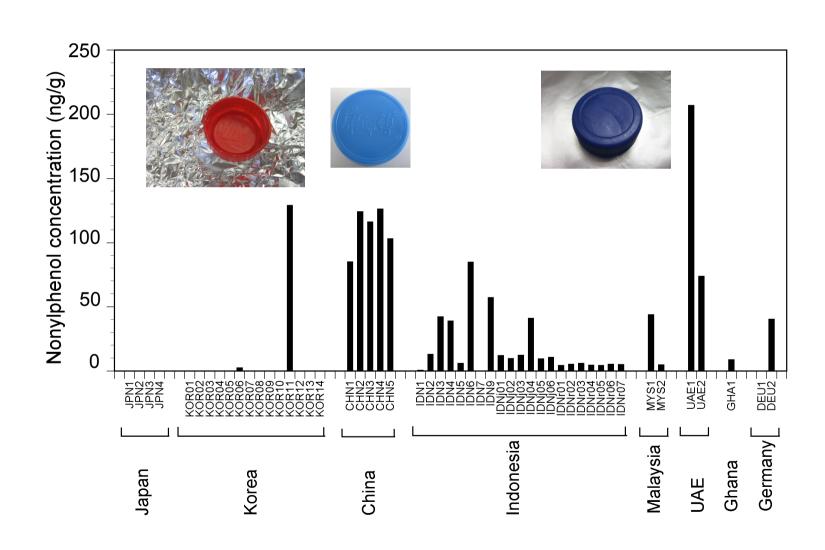


Nonylphenols leached from plastic products



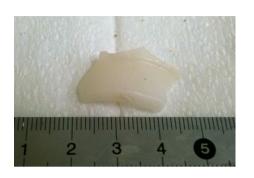
Nonylphenols are still leached from imported plastic products

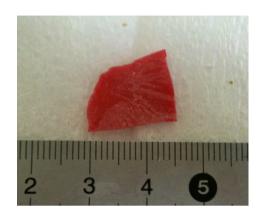
World Cap 2012 nonylphenols leached from screw cap of bottled water



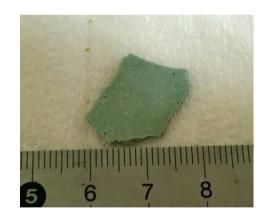
Sampling locations of user plastic fragments Northern Pacific Long Beach, Central Gyre Tokyo, Japan USA Kanagawa, Japan Atlantic **Central Pacific** Tonkin Bay, Vietnam Marbella, Costa Rica Urban beach Rural beach Open ocean

Examples of analyzed plastic fragments



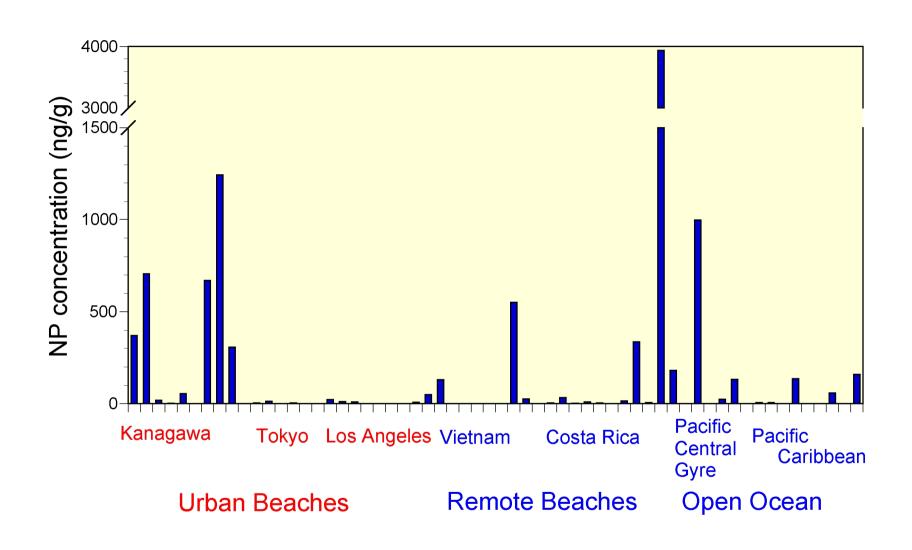








Distribution of Nonylphenols in plastic fragments



Marine plastics carry two types of chemicals

Sorption from ambient

seawater

Polychlorinated biphenyl (PCBs)

Polycyclic aromatic hydrocarbons (PAHs)

C₈H₁₇OH Octylphenol

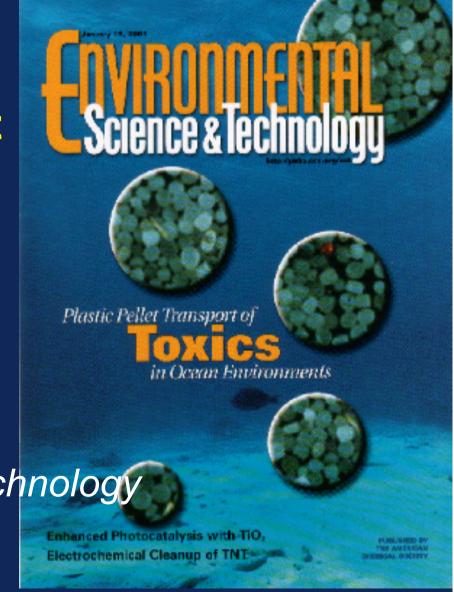
Polybrominated diphenyl ethers (PBDEs)

Additive-derived chemicals

$$HO \longrightarrow CH_3 \longrightarrow OH$$

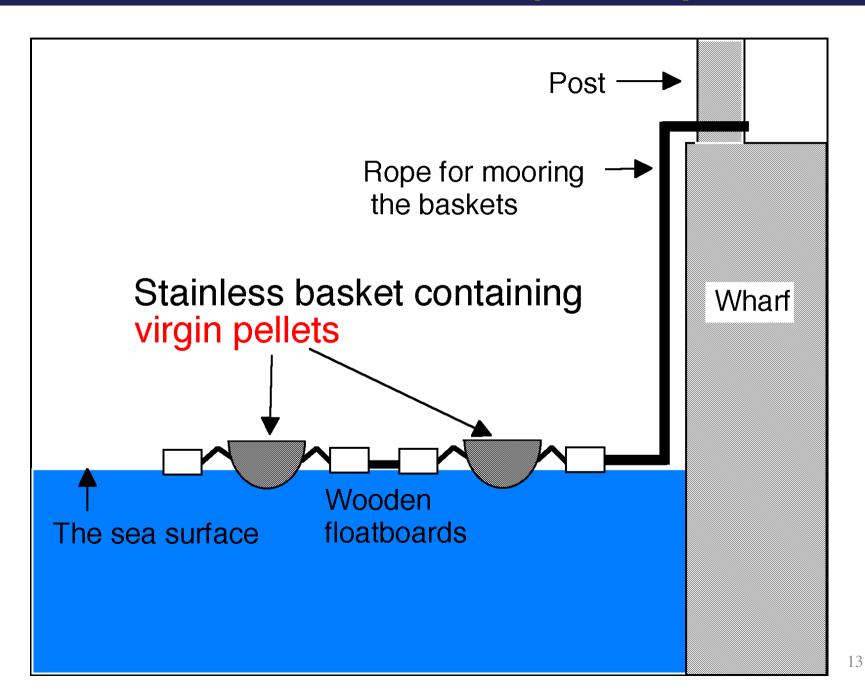
Bisphenol A

Plastic Resin Pellets as a Transport Medium for Toxic Chemicals in the Marine Environment

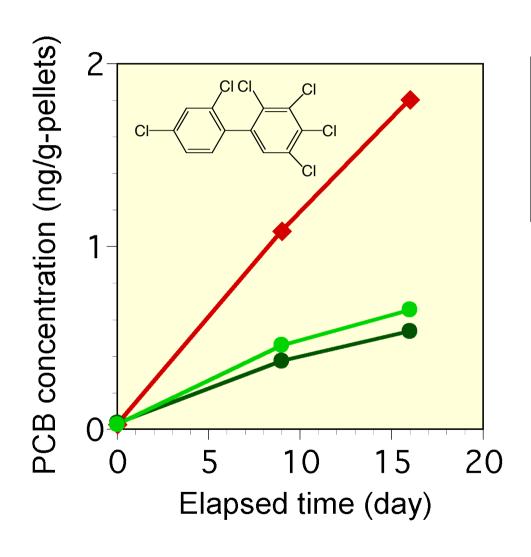


Environmental Science & Technology 2001, vol.35, 318-324

Schematic illustration of adsorption experiment



Adsorption of PCBs onto marine plastics





Persistent organic pollutants (POPs)

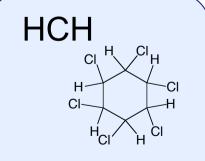
PCBs

$$CI_n$$
 CI_n

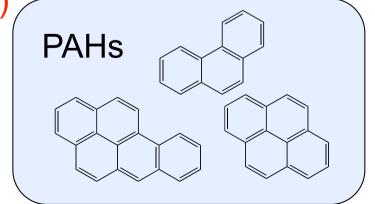
- •Industrial products for a variety of uses including dielectric fluid, heat medium, and lubricants.
- Endocrine disrupting chemicals

DDTs

- •DDT and its metabolites such as DDE and DDD.
- ·DDT was used as insecticides
- •Endocrine disrupting chemicals
- ✓ Man-made chemicals
- ✓ Persistent (stable, resistant to degradation)
- √ Toxic to human and marine organisms
- √ Hydrophobic (lipophilic)



· Insecticide



Plastics accumulate organic pollutants from seawater

PCBs

$$CI_n$$
 CI_n

- ·Industrial products for a variety of uses including dielectric fluid, heat medium, and lubricants.
- Endocrine disrupting chemicals

adsorption from ambient seawater

DDTs

- •DDT and its metabolites such as DDE and DDD.
- ·DDT was used as insecticides
- •Endocrine disrupting chemicals

Plastics

Mato et al. (2001), ES&T

$$+CH_2-CH_2$$

Polyethylene (PE)

$$\begin{array}{c} \text{CH}_3 \\ \leftarrow \text{CH}_2\text{-CH} \xrightarrow{}_\text{n} \end{array}$$

Polyprorylene (PP)

Pellets accumulate POPs from seawater

PCBs

- ·Industrial products for a variety of uses including dielectric fluid, heat medium, and lubricants.
- Endocrine disrupting chemicals

HCH

DDTs

- •DDT and its metabolites such as DDE and DDD.
- ·DDT was used as insecticides
- •Endocrine disrupting chemicals

adsorption from ambient seawater

Plastics

PAHs

Concentration factor is estimated to be $\sim 10^5$ to $\sim 10^6$.

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Plastic Resin Pellets



Trashes on high-tide line on our beaches



Trashes on high-tide line on our beaches



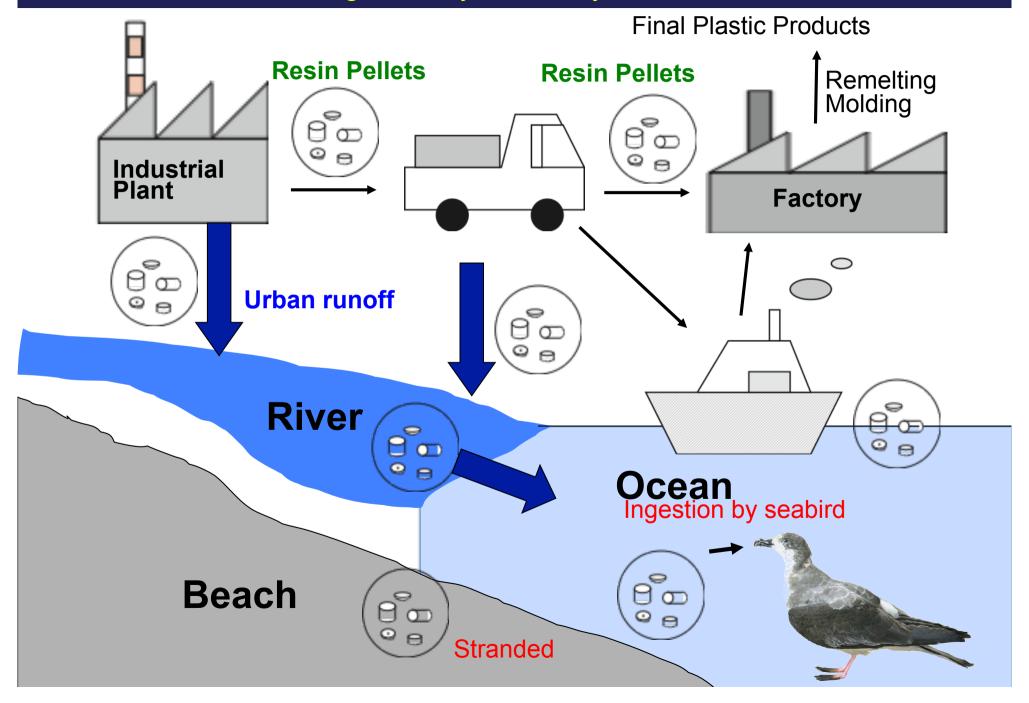
Trashes on high-tide line on our beaches



Plastic Resin Pellets



Resin pellets, industrial feedstock of user plastics, are spilled during transport and manufacturing and they are widely distributed in the ocean



International Pellet Watch

Global Monitoring of Persistent Organic Pollutants (POPs) Using Beached Plastic Resin Pellets



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Laboratory of Organic Geochemistry Dr. Hideshige Takada, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan



More than 50 pieces (~100 pieces) per one location

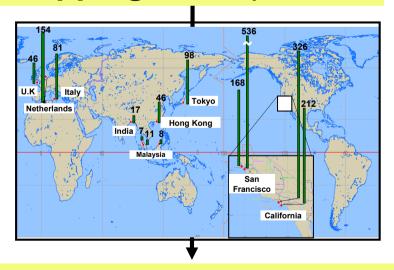
Sorting

PE, yellowing pellets

Analysis for POPs (PCBs, organochlorines, PAHs)

By GC-MS/MS, GC-MS, GC-ECD more than 5 pools of 5 pellets to exclude sporadic high concentration

Mapping POPs pollution



- Sending the data via Internet to the collaborators
- Releasing the results on web

~200 locations from 40 countries



Polychlorinated biphenyls (PCBs)

$$CI_{m}$$

$$m + n = 1 - 10$$

Commercial PCBs mixtures were used in a wide variety of applications, including

Dielectric fluids in capacitors and transformers

Heat transfer fluid

Copying paper

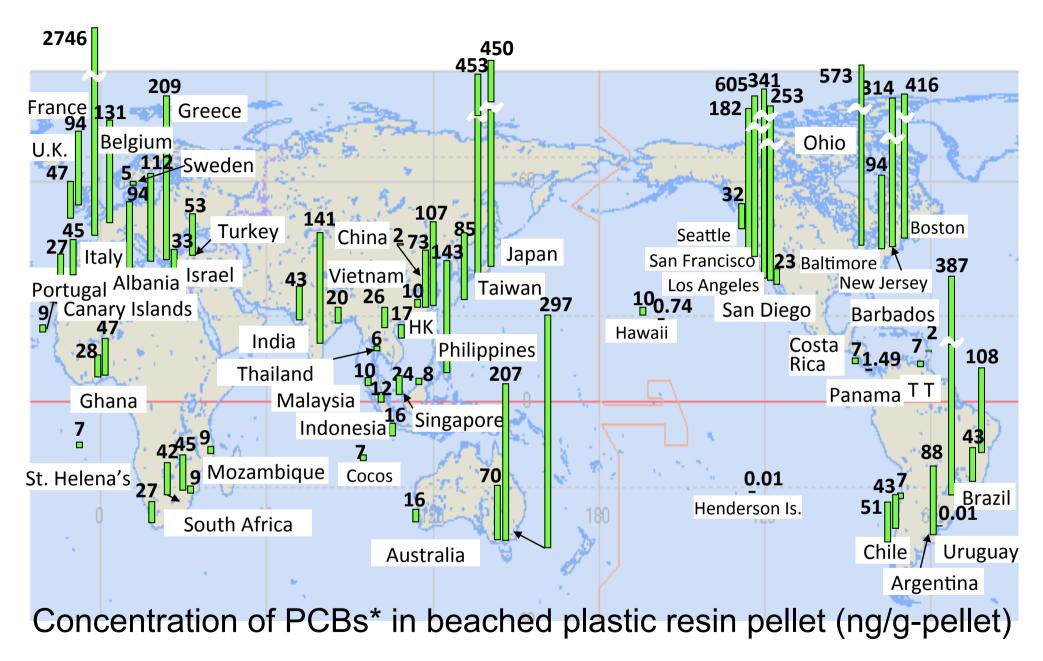
Carbonless copy paper

Adhesives

Sealant

PCBs were used from 1950s to early 1970s in industrialized countries.

Their usage was banned in 1970s



*sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206

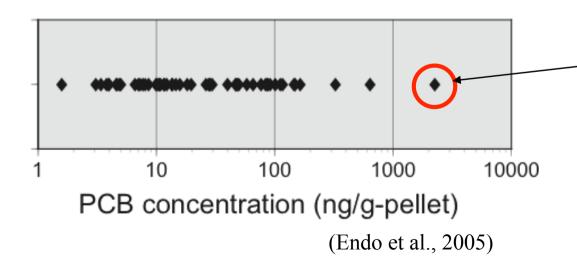
To minimize the effects of piece-to-piece variation and to get areal representative values, 5 pools of yellowing PE pellets are analyzed and median concentrations are used.



Sorting

Polyethylene (PE) Yellowing

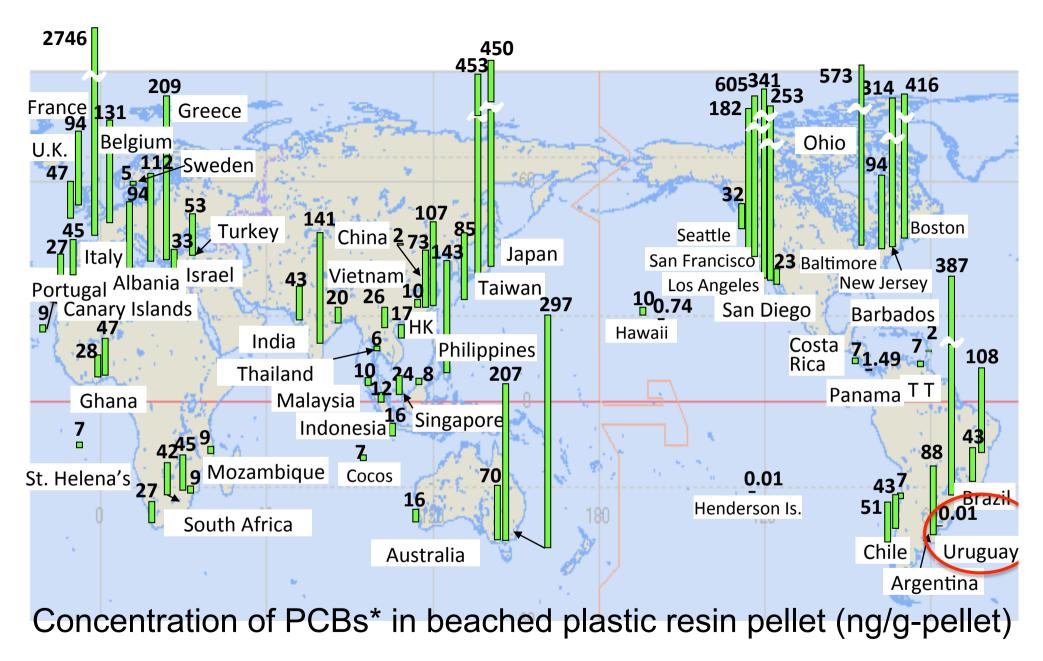




To exclude sporadic high concentrations of PCBs

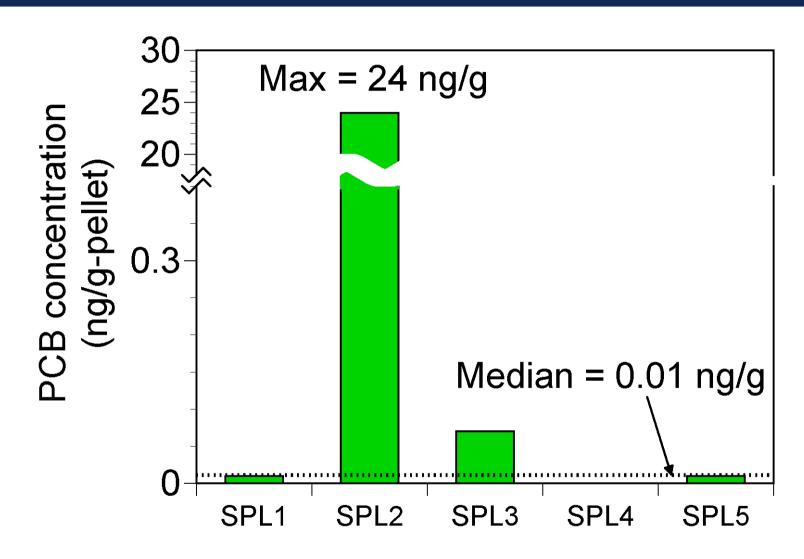
Multiple 10-pellet pools are analyzed for PCBs

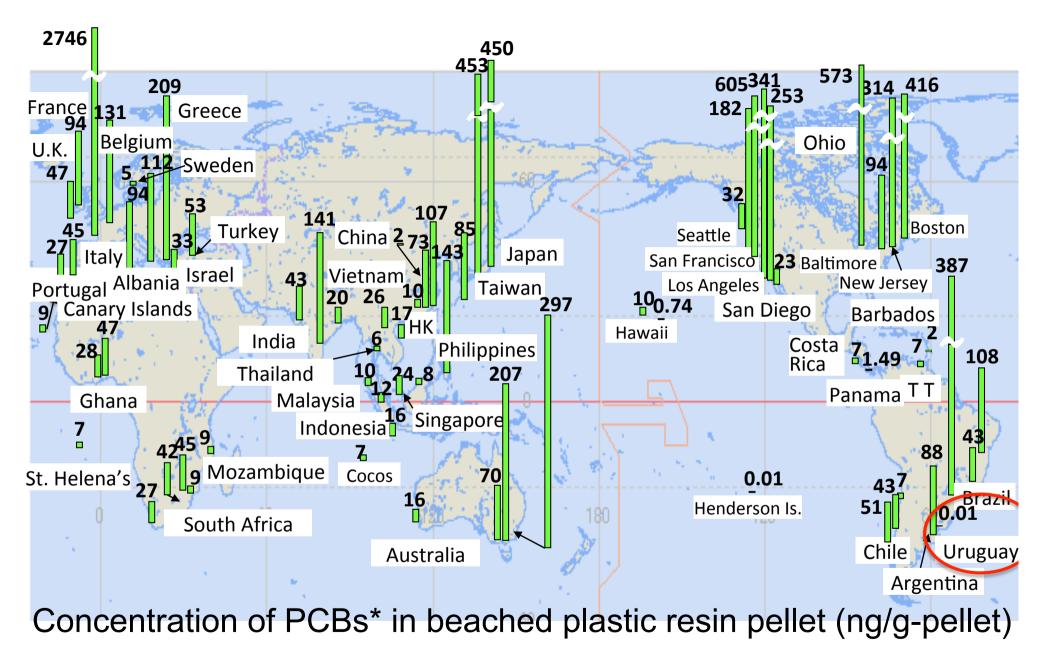
Median concentrations



*sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206

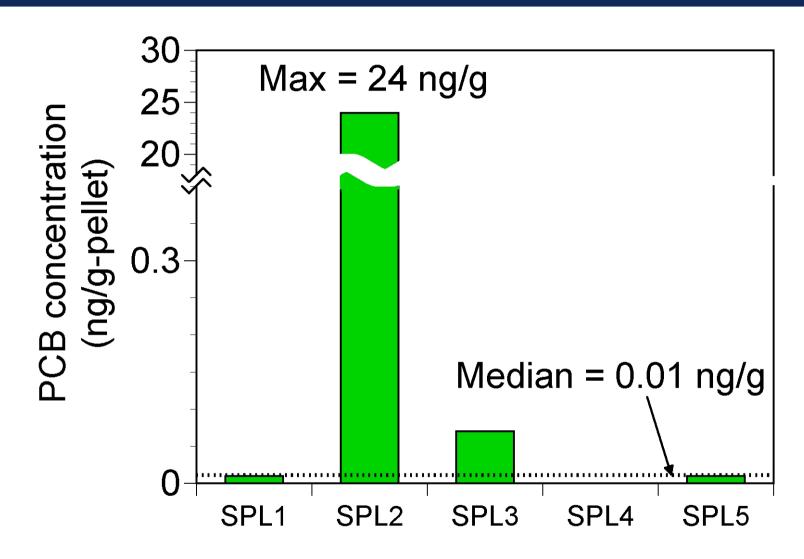
Sporadic high concentrations of POPs are often observed in pellets from remote beaches





*sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206

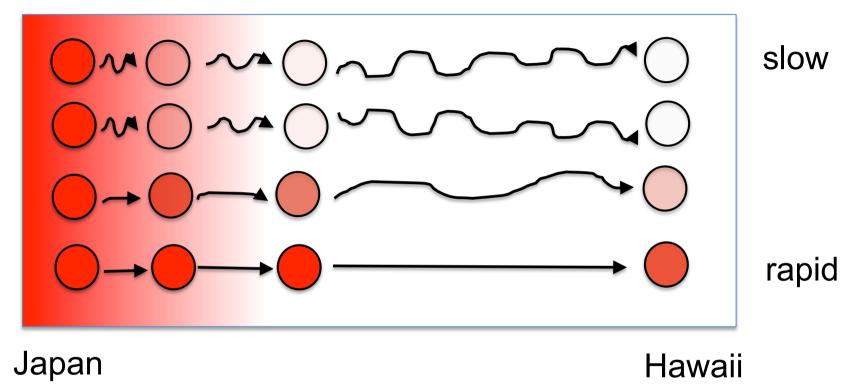
Sporadic high concentrations of POPs are often observed in pellets from remote beaches



Slow desorption and fast transport may cause sporadic high concentration of PCBs in plastic from open ocean

Polluted waters

Open ocean



Different speed/route of transport Non-equilibrium : slow sorption/desorption

Sporadic high concentrations of PCBs were detected even in remote beaches and open ocean

Larger diameters and slow diffusive transport cause non-equilibrium

Plastic fragment/pellet with 3 mm diameter

Long time (~ 1 year) to reach equilibrium

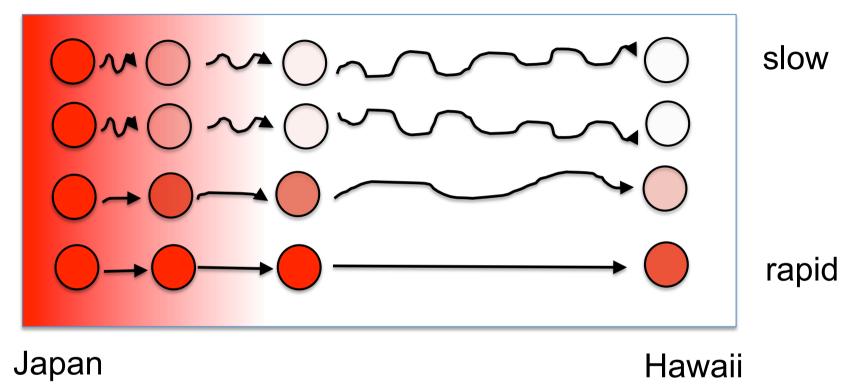
surface process

Conventional vector : sediment particle with a few µm Fast (~ hours) to reach equilibrium

Slow desorption and fast transport may cause sporadic high concentration of PCBs in plastic from open ocean

Polluted waters

Open ocean



Different speed/route of transport Non-equilibrium : slow sorption/desorption

Sporadic high concentrations of PCBs were detected even in remote beaches and open ocean

Unique characters of marine plastics as transport media of organic micropollutants

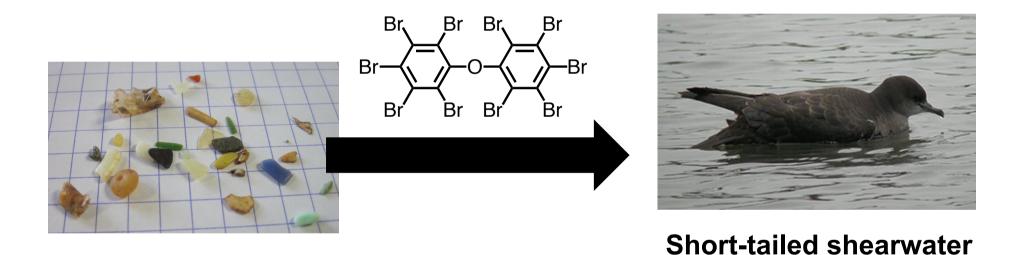
✓ Slow sorption/desorption and sporadic high concentrations of pollutants

✓ Additive-derived chemicals

Previous assessment missed these characters.

Marine plastics carry toxic chemicals to remote ecosystem

Detection of polybrominated diphenyl ethers (PBDEs) in tissue of seabird ingesting plastics

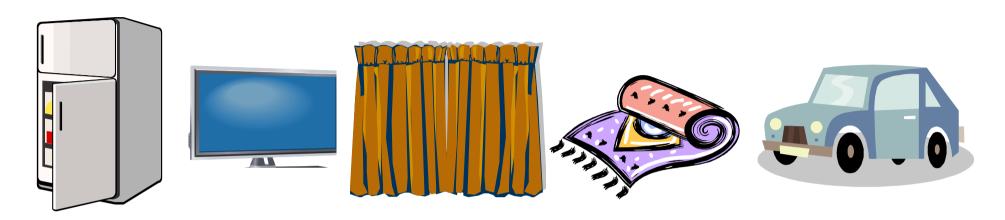


We got the evidence to the transfer, though it has not yet published

Puffinus

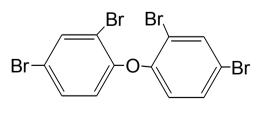
PBDEs: Flame retardants

applied in various electric products and fabrics.



3 technical products (mixtures of congeners)

Penta BDE (Br4, Br5)



e.g., BDE47

Octa BDE

(Br7,8)

e.g., BDE183

DecaBDE

(Br10)

Conclusions

Marine plastics contain various toxic chemicals including additives and POPs sorbed from surrounding seawater.

Marine plastics carry toxic chemicals to remote ecosystem

Transfer of the chemicals from plastics to internal tissue of seabirds which ingest marine plastics was strongly suggested.