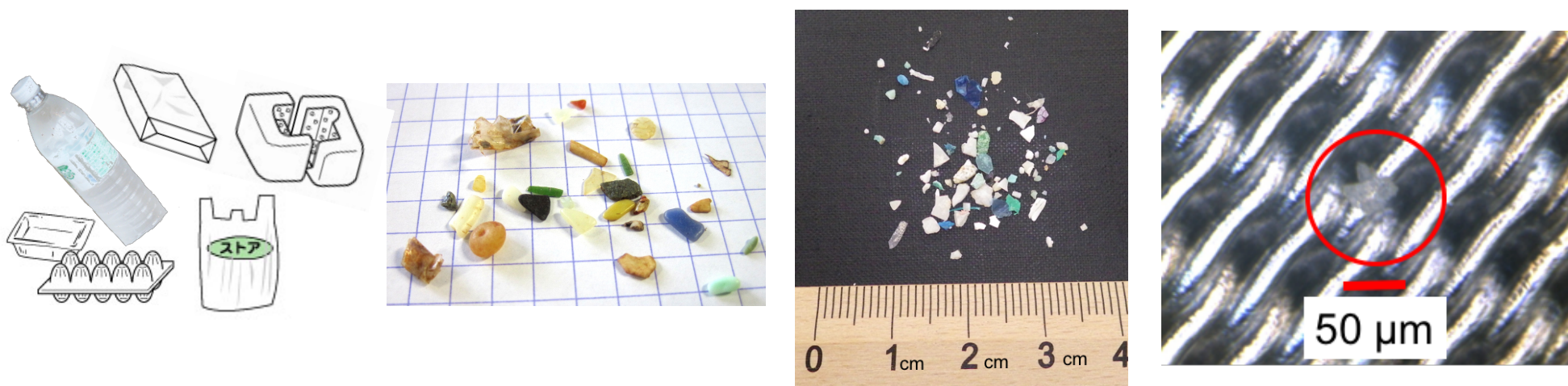


# Hazardous chemicals in marine plastics and their threat to marine organisms



**Shige TAKADA**

Laboratory of Organic Geochemistry (LOG)  
Tokyo University of Agriculture and Technology

Presented on

**International Workshop “The Science of Microplastics in the World Ocean  
Woods Hole Oceanographic Institution, Oct. 16, 2019**

## **Major Conclusion**

Plastic-mediated chemical exposure does occur and its significance depends on locations, background pollution, chemicals, species of biota, especially trophic levels.

## Topics

- Hazardous chemicals in marine plastics
  - Chemicals adsorbed from seawater
  - Additive chemicals
- Transfer of the chemicals from ingested plastics to internal tissue of biota
  - Experimental evidences
  - Mechanism
- Significance of the plastics as exposure media :  
Field observations
- Effects of the plastic-mediated chemical exposure

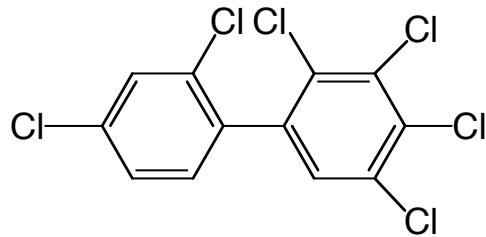
# Topics

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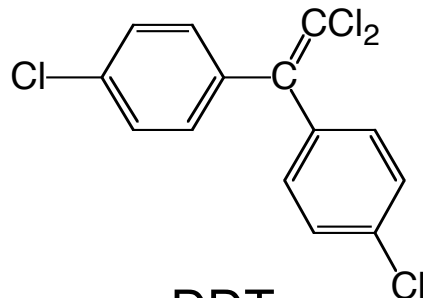


# Plastics carry two types of chemicals in marine environment

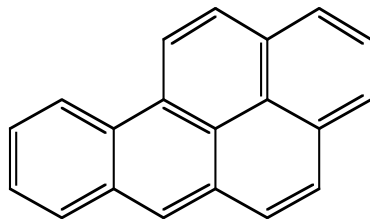
## Sorption from seawater



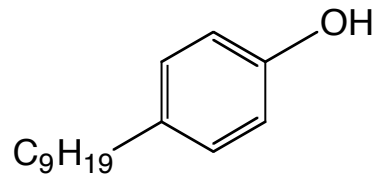
Polychlorinated biphenyl (PCBs)



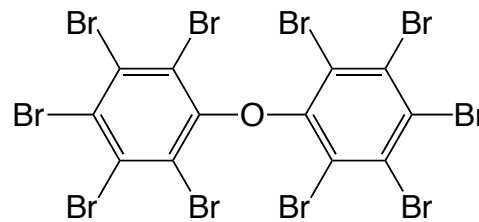
DDTs



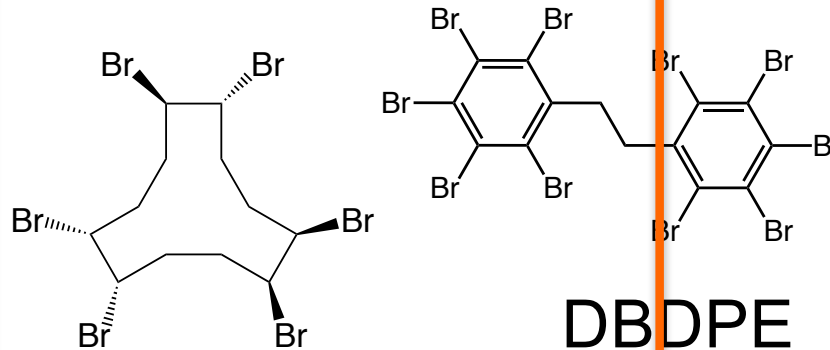
Polycyclic aromatic hydrocarbons (PAHs)



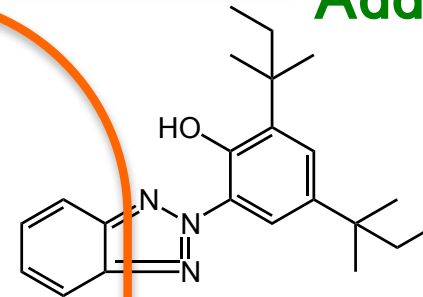
Nonylphenol



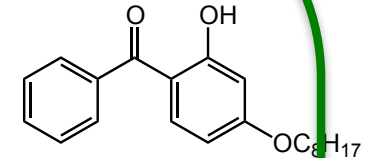
Polybrominated diphenyl ethers (PBDEs)



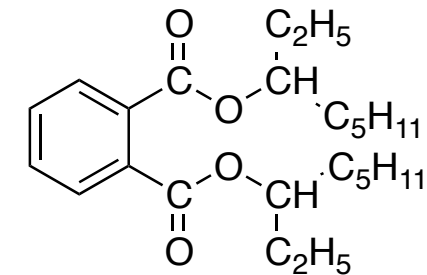
Hexabromocyclododecanes (HBCDs)



Benzotriazoles (e.g., UV-328)

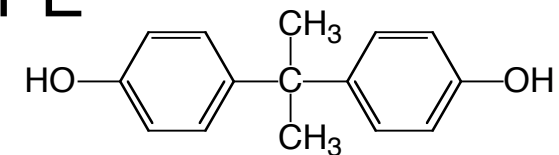


Benzophenones (e.g., BP-12)



Phthalates (DEHP)

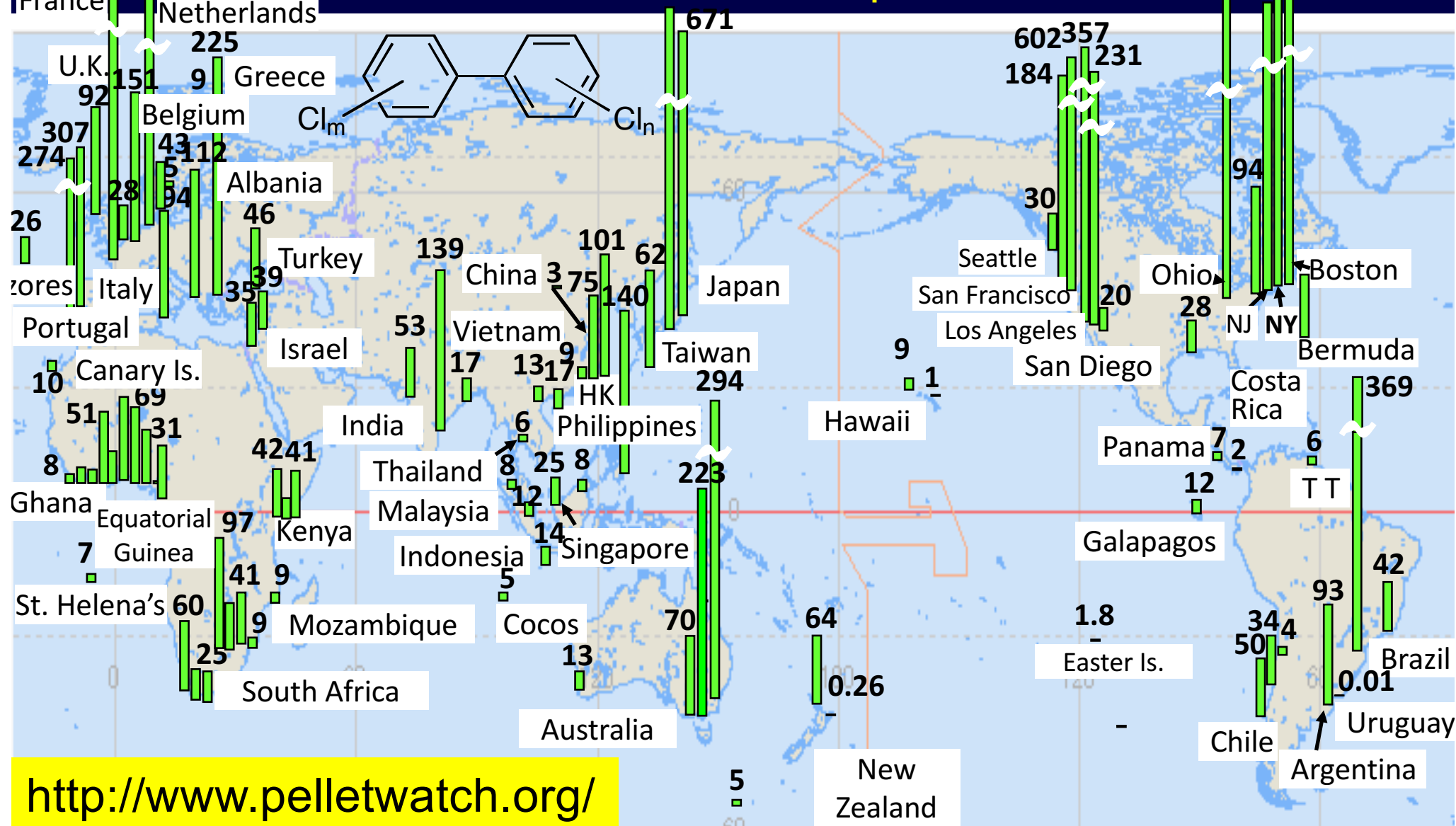
DBDPE



Bisphenol A

## Additives

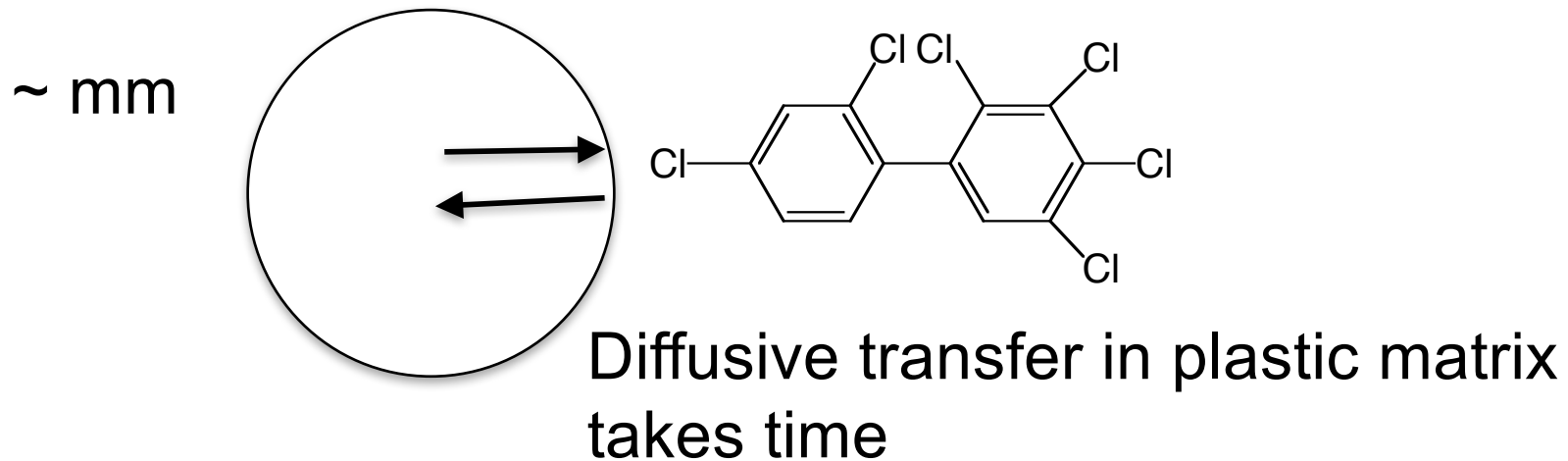
## International Pellet Watch demonstrates sorption of POPs to microplastics



## PCBs concentrations in beached plastic pellets (ng/g)

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

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



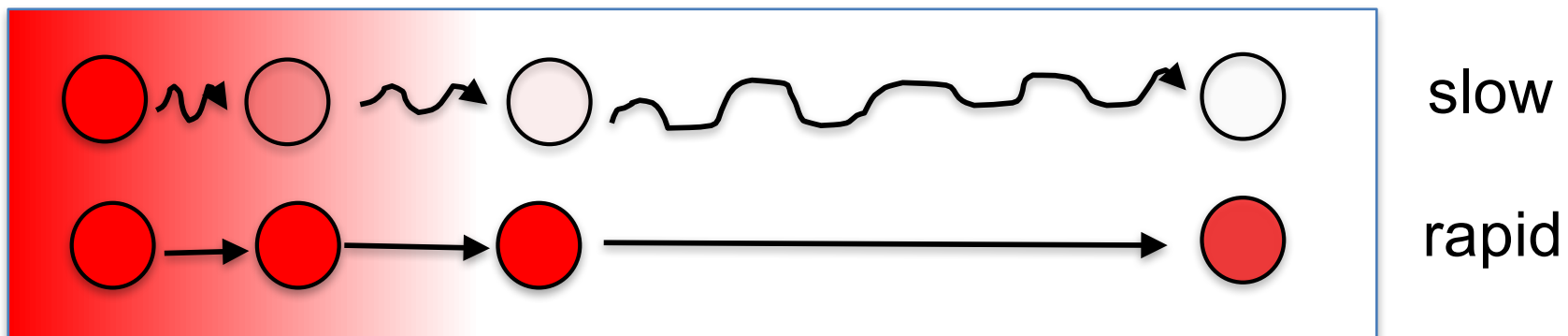
Plastic fragment/pellet with 3 mm diameter

Long time (~ 1 year) to reach equilibrium

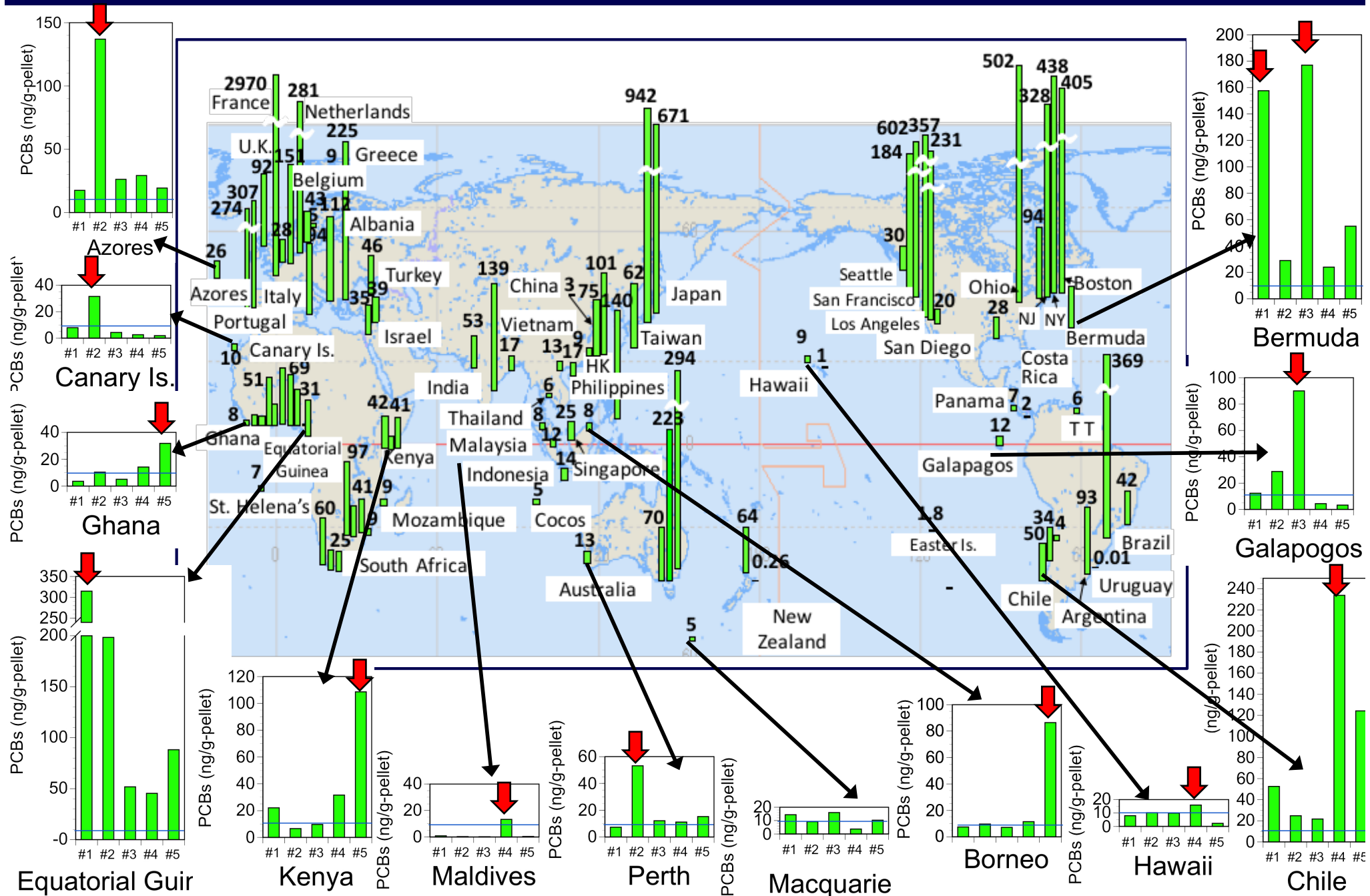
**Non-equilibrium : slow sorption/desorption**

Polluted waters

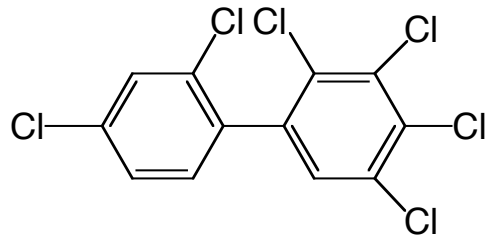
Open ocean



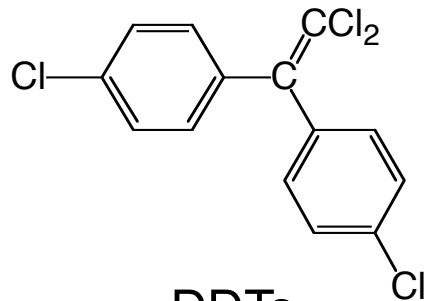
# Sporadic high concentrations of PCBs found in pellets from remote areas : Microplastics carry contaminants to remote areas



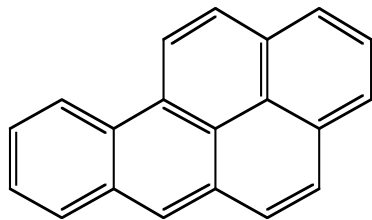
# Plastics carry two types of chemicals in marine environment



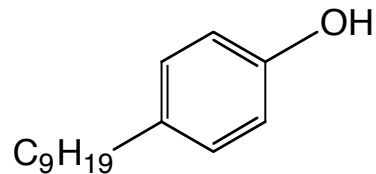
Polychlorinated biphenyl (PCBs)



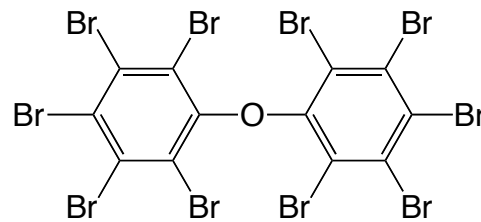
DDTs



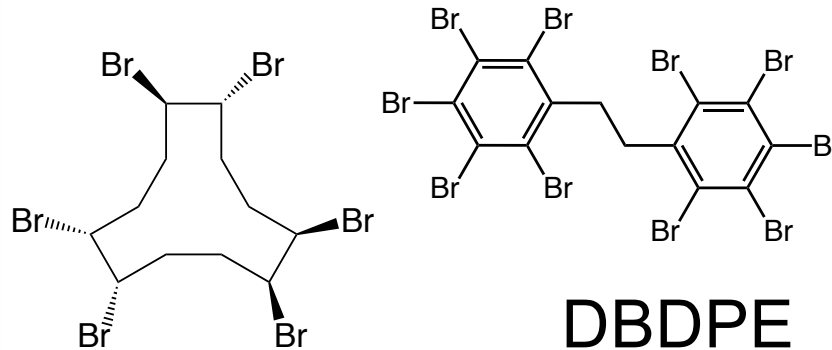
Polycyclic aromatic hydrocarbons (PAHs)



Nonylphenol

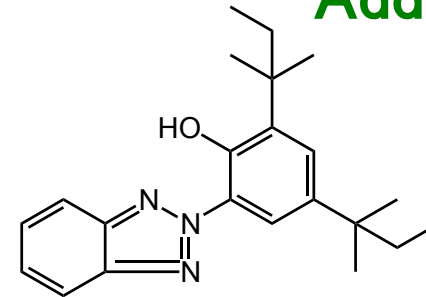


Polybrominated diphenyl ethers (PBDEs)

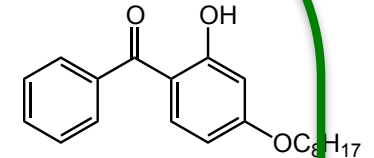


DBDPE

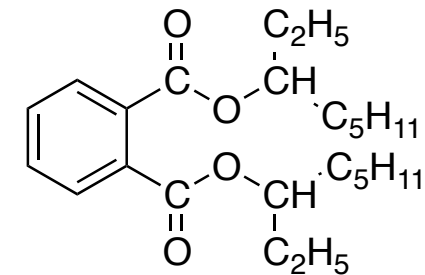
Hexabromocyclododecanes (HBCDs)



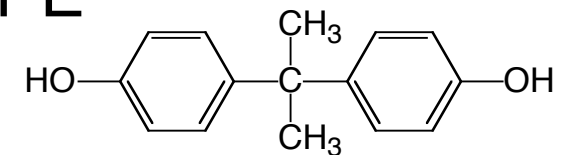
Benzotriazoles (e.g., UV-328)



Benzophenones (e.g., BP-12)



Phthalates (DEHP)

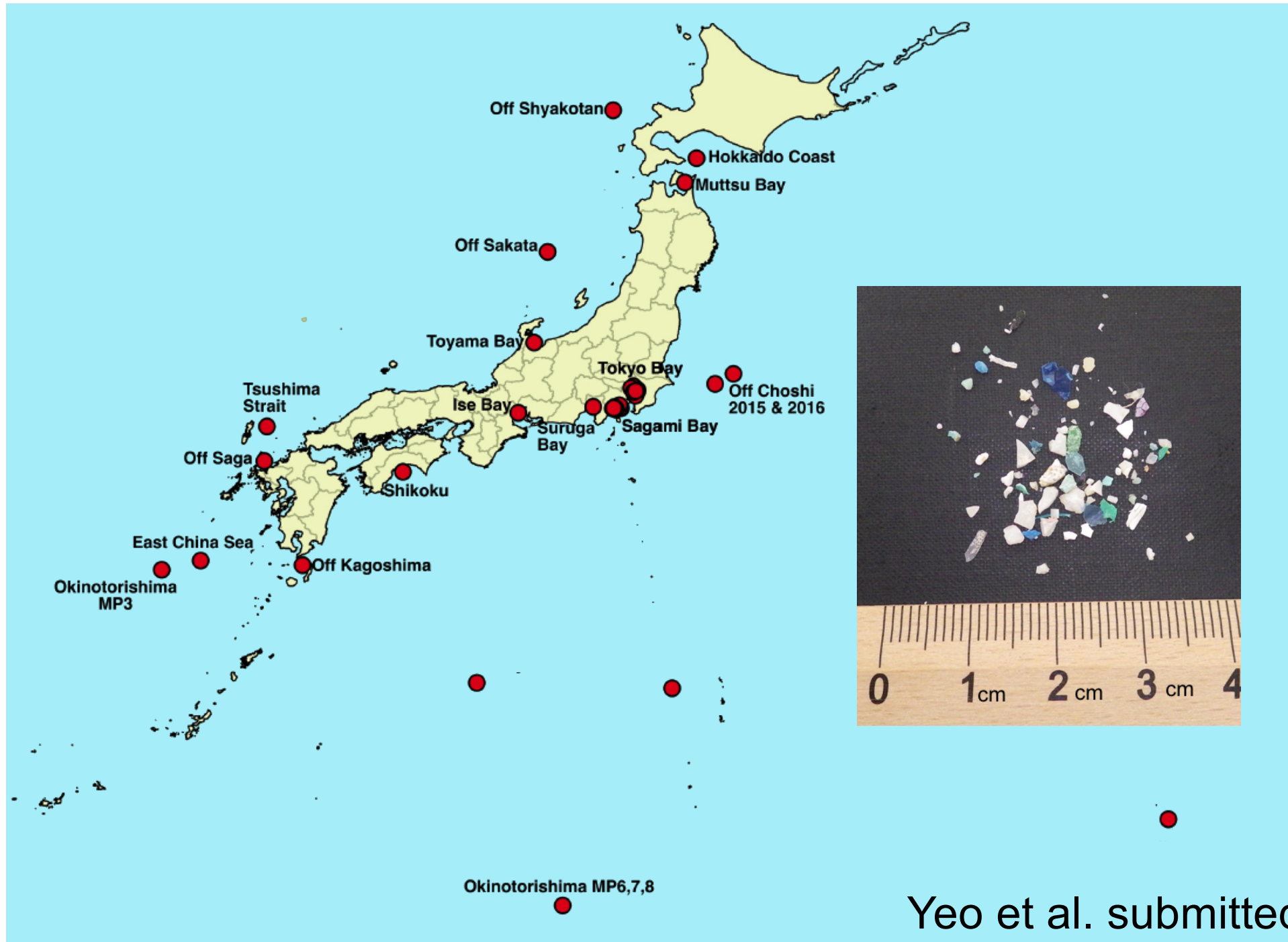


Bisphenol A

## Additives

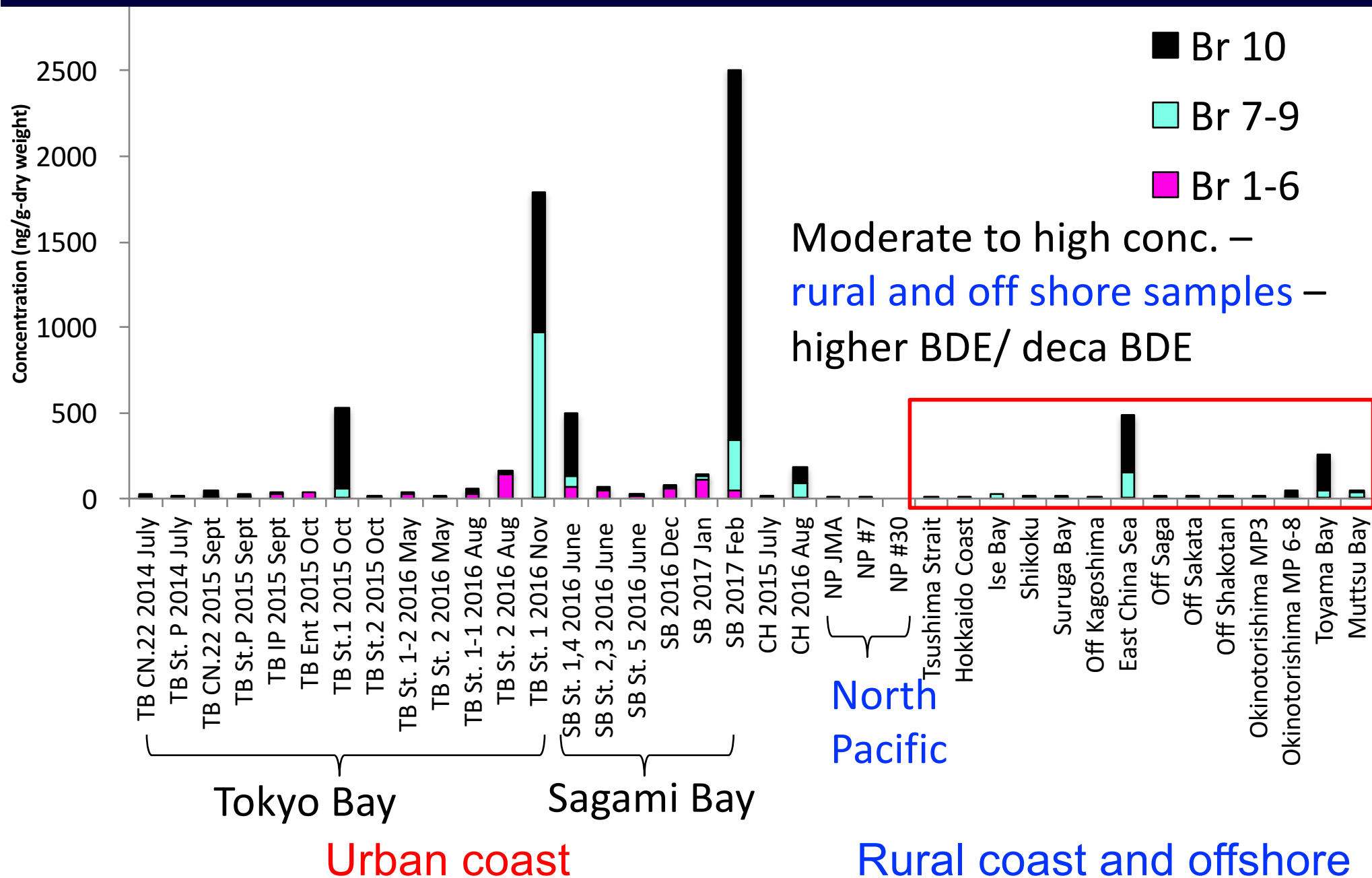


# Buoyant microplastics from Japan coasts and pacific ocean



Yeo et al. submitted

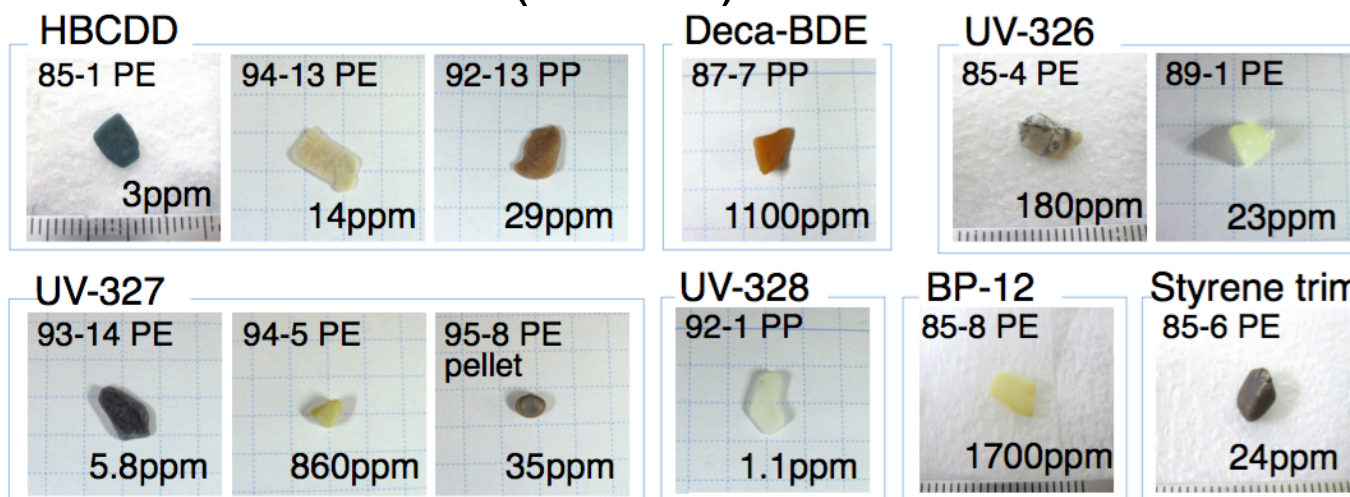
# BDE209 was sporadically detected in suspended microplastics in seawater



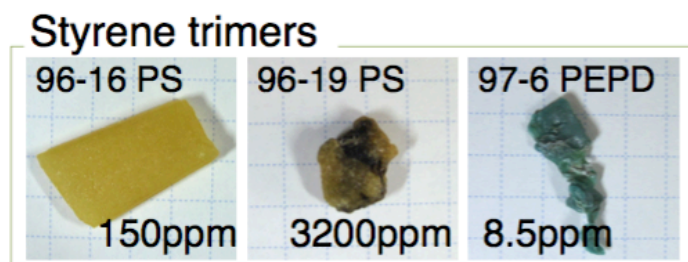
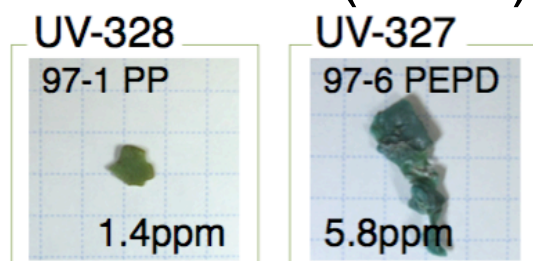
Additives (e.g., UV-326, UV-327, UV-328, BP-12, BDE209) are **sporadically** detected in plastics in seabirds' stomach

Detection frequency : ~ 2 %

## Northern fulmar (n=159)



## Albatross (n=35)



PE: polyethylene  
PP: polypropylene  
PS: polystyrene  
PEPD: polyethylene propylene diene

## Bolus

Tanaka, K., van Franeker, J.A., Deguchi, T., and Takada, H., **2019**. Piece-by-piece analysis of additives and manufacturing byproducts in plastics ingested by seabirds: Implication for risk of exposure to seabirds.

***Marine Pollution Bulletin* 145, 36-41.**

Table3. Ingestion frequency of plastic with additives.

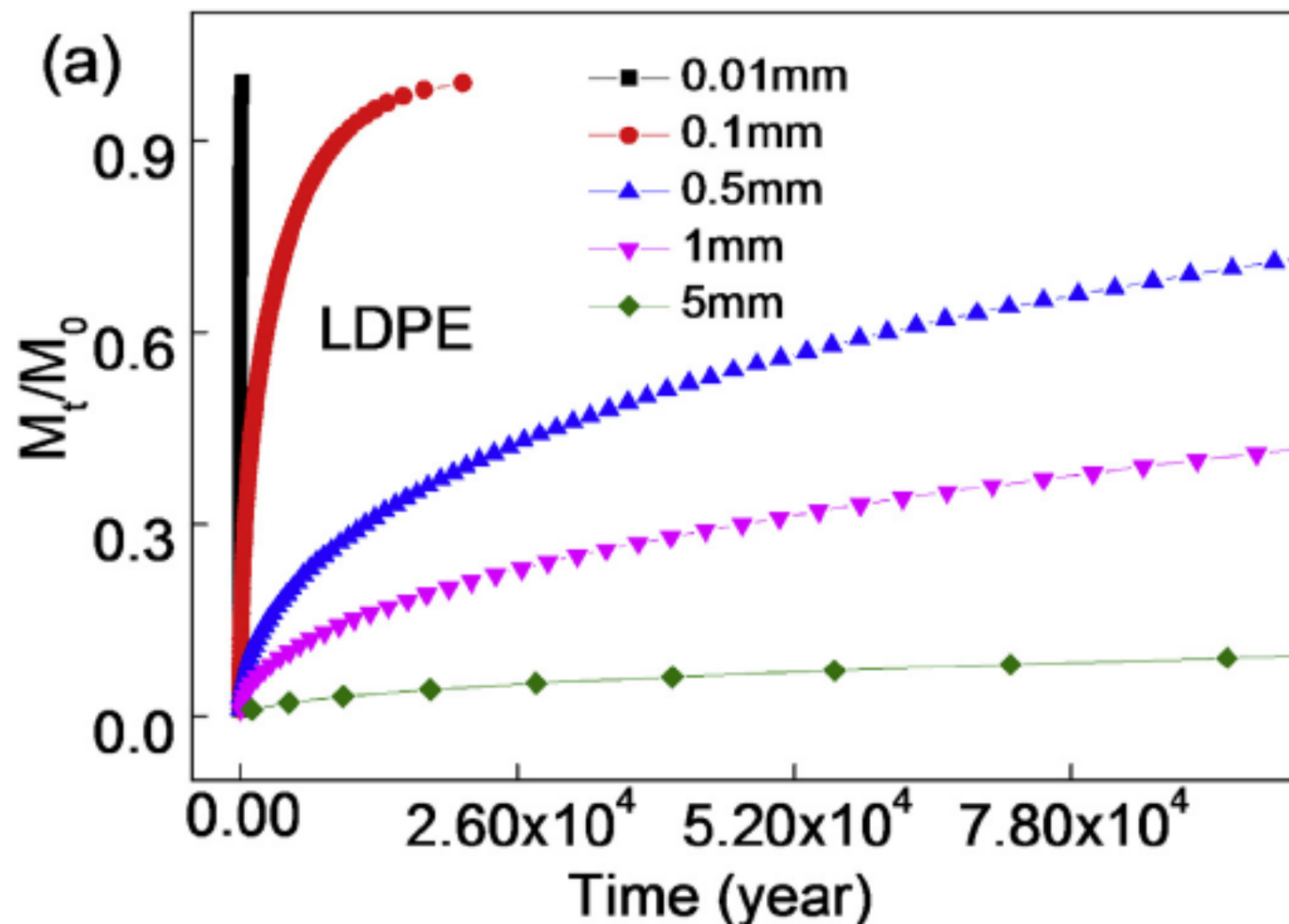
	Detection % in fragments	Ingestion %
<b>Northern fulmar</b>		
<b>Deca-BDE</b>	0.6%	9%
<b>HBCDD</b>	1.9%	27%
<b>UV-328</b>	0.6%	9%
<b>UV-326</b>	1.3%	18%
<b>UV-327</b>	1.9%	27%
<b>BP-12</b>	0.6%	9%
Σ STs	0.6%	9%
<b>Albatross</b>		
UV-328	2.9%	17%
UV-327	2.9%	17%
Σ STs	8.6%	50%



# Topics

- Introduction of plastic pollution and microplastics
- Spread of plastics in marine environments:
  - Sediment cores
  - Marine organisms : seabirds, fish, bivalves
- Hazardous chemicals in marine plastics
  - Chemicals adsorbed from seawater
  - Additive chemicals
- **Transfer of the chemicals from plastics to internal tissue**
  - Experimental evidences
  - Mechanism
- Significance of the plastics as exposure media :  
Field observations
- Effects of the plastic-mediated chemical exposure

Hydrophobic and large molecule additive such as BDE209 is difficult to leach from plastic to water.



Sun, B., Hu, Y., Cheng, H., and Tao, S., 2019. Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: Kinetics and molecular-size dependence of diffusion. *Water Research* 151, 215-225.

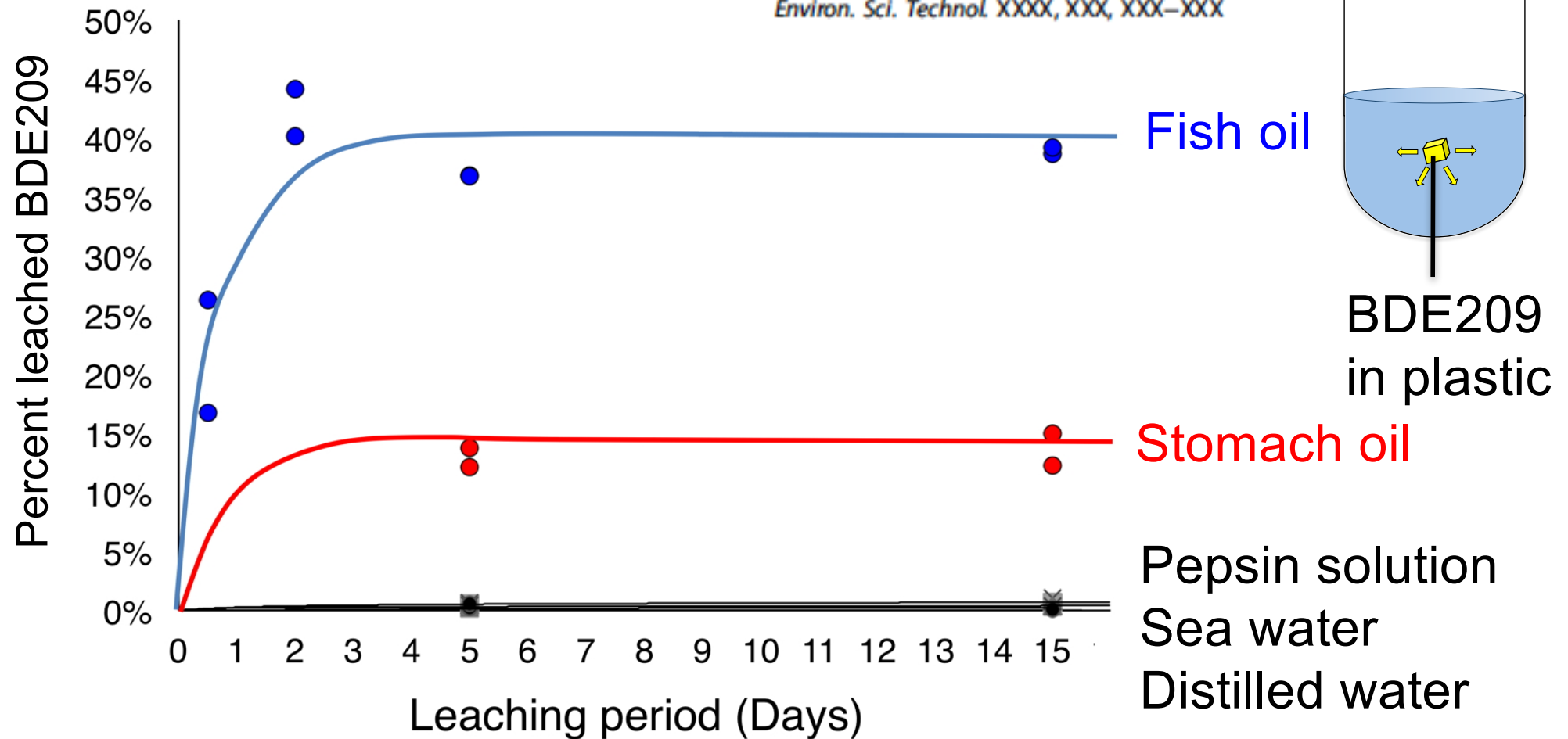
# Stomach oil and fish oil accelerated the leaching of BDE209

## Facilitated Leaching of Additive-Derived PBDEs from Plastic by Seabirds' Stomach Oil and Accumulation in Tissues

Kosuke Tanaka,<sup>†</sup> Hideshige Takada,<sup>\*,†</sup> Rei Yamashita,<sup>†</sup> Kaoruko Mizukawa,<sup>†</sup> Masa-aki Fukuwaka,<sup>‡</sup> and Yutaka Watanuki<sup>§</sup>

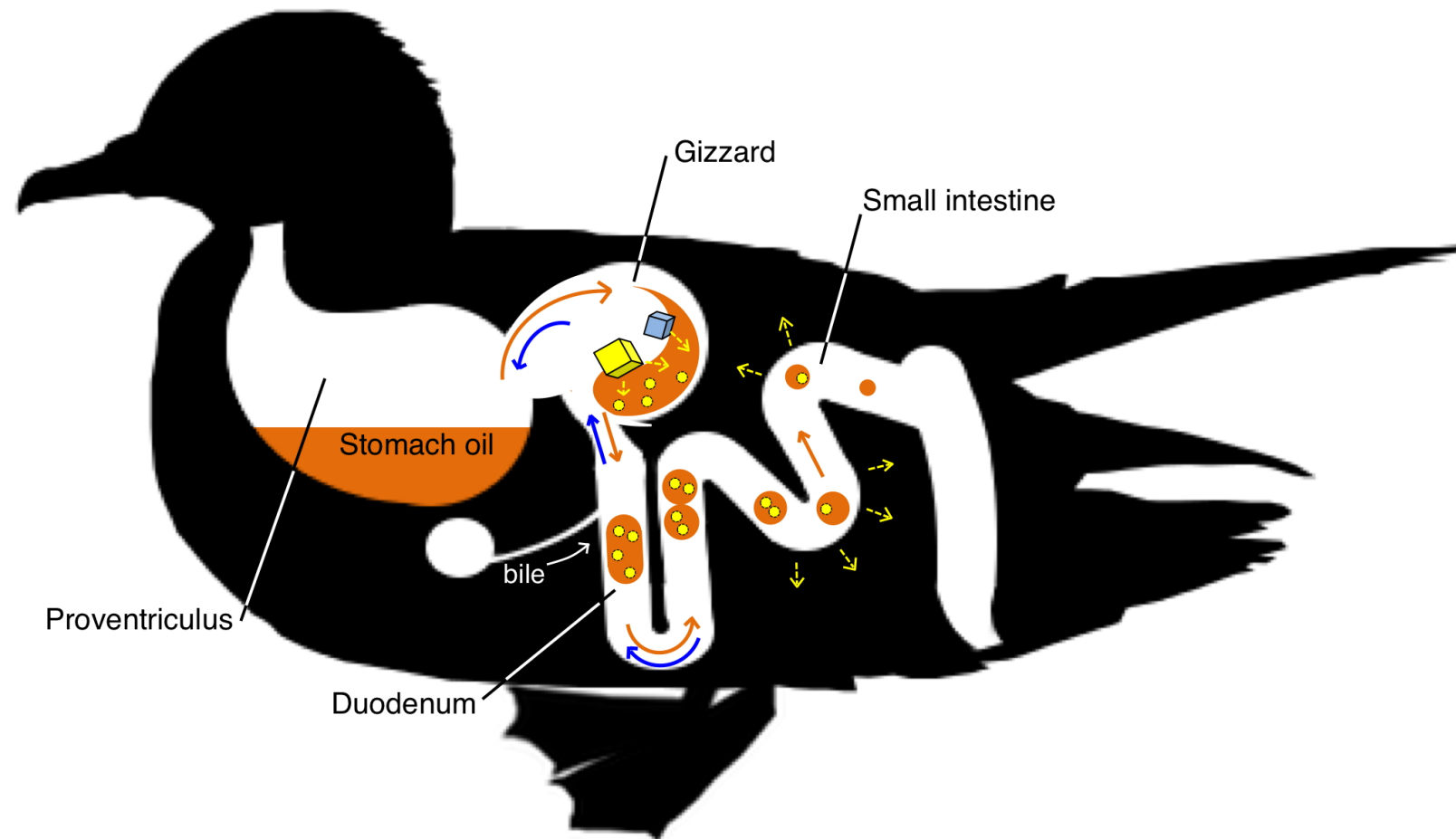
DOI: 10.1021/acs.est.5b01376

*Environ. Sci. Technol.* XXXX, XXX, XXX–XXX



This suggests that **fatty components** in digestive tract facilitates leaching of hydrophobic additives.

# Oily components in digestive fluid facilitate leaching of hydrophobic additives and their accumulation in adipose and liver



Tanaka, K., Yamashita, R., and Takada, H., *Transfer of hazardous chemicals from ingested plastics to higher-trophic level organisms*, in *Hazardous chemicals associated with plastics in environment*, H. Takada and H.K. Karapanagioti, Editor. 2018, Springer Berlin Heidelberg: p. 267–280.

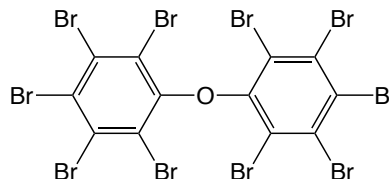
# Plastics compounded with 5 additives

## Polyethylene pellets with 5 additives

Additives:

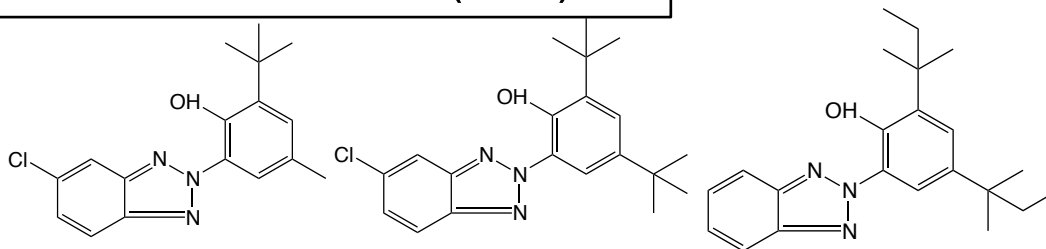
Brominated flame retardants

- BDE209



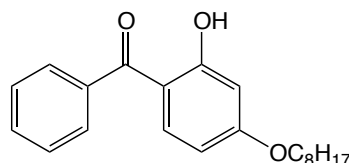
Benzotriazole UV-stabilizers (BTs)

- UV-326
- UV-327
- UV-328



Benzophenone UV-stabilizers (BPs)

- BP-12



**Additives**  
+  
**PE powder**

mixed  
melted,  
molded  
↓ by using extruder



Concentration of each chemical was 0.4 % by weight in polymer.

# Field Feeding Experiment of additive-compounded plastic to chicks of streaked shearwater

## Exposure group

PE pellets compounded with 5 additives



(5 pieces  
/individual)

+



natural diet

Chicks

### Additives

BDE209

UV326, UV327, UV328

BP12

→ Liver

→ Adipose

→ Preen Gland oil

16 days

## Control group

natural diet



natural diet

Chicks

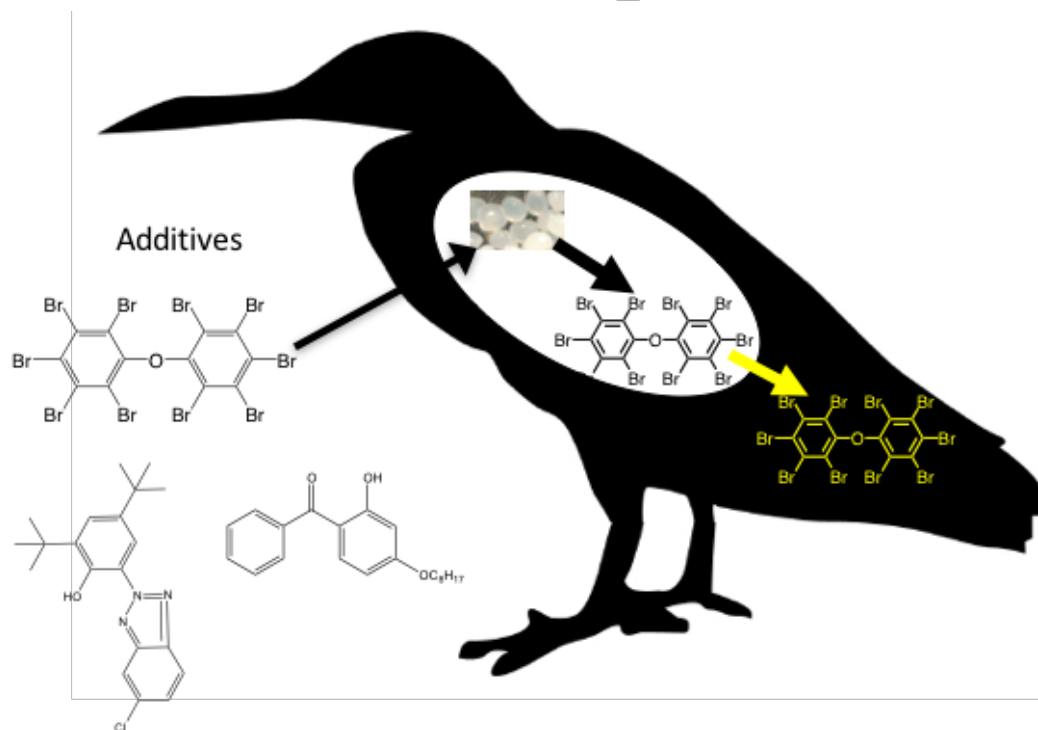
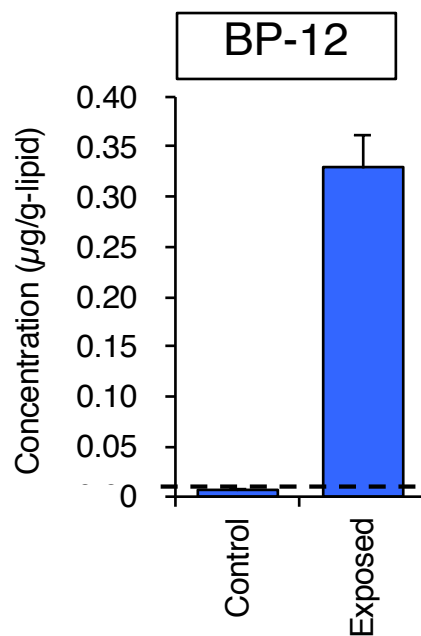
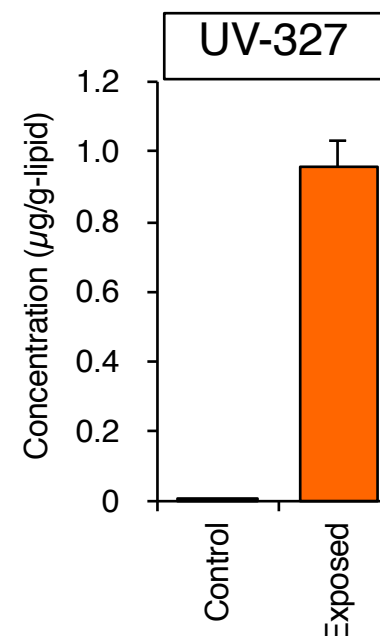
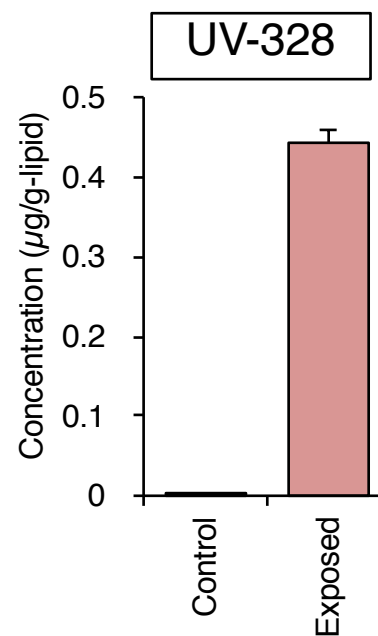
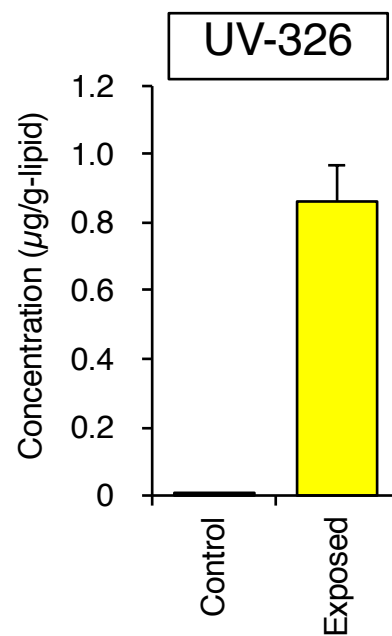
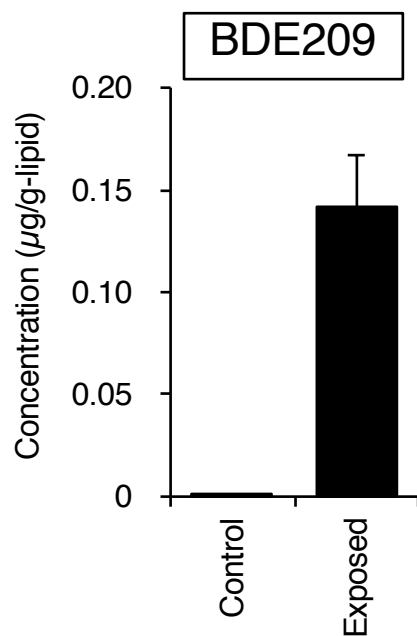
→ Liver

→ Adipose

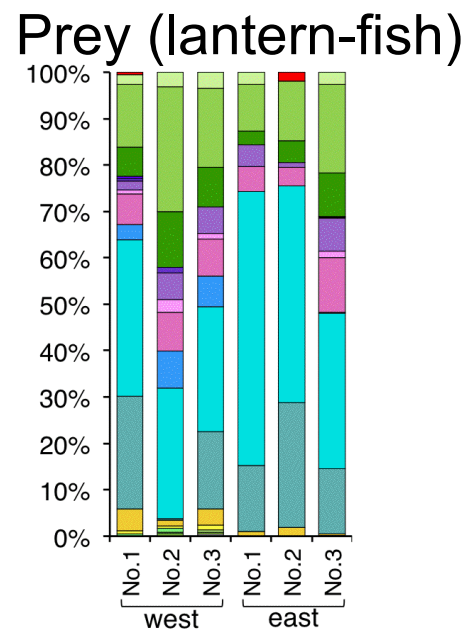
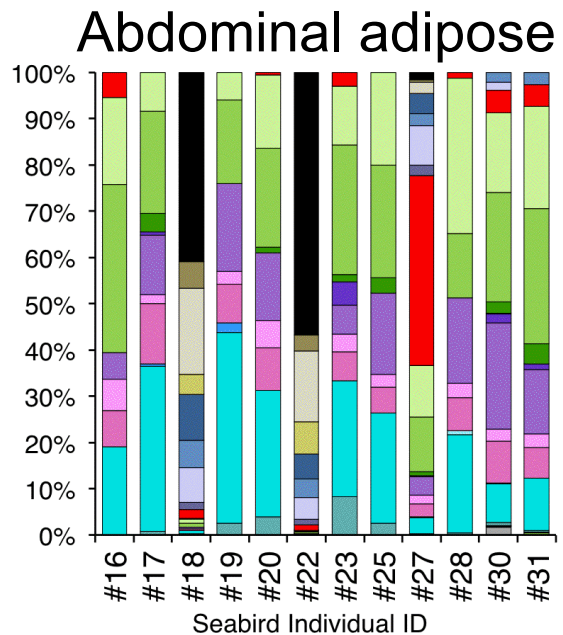
→ Preen Gland oil

16 days

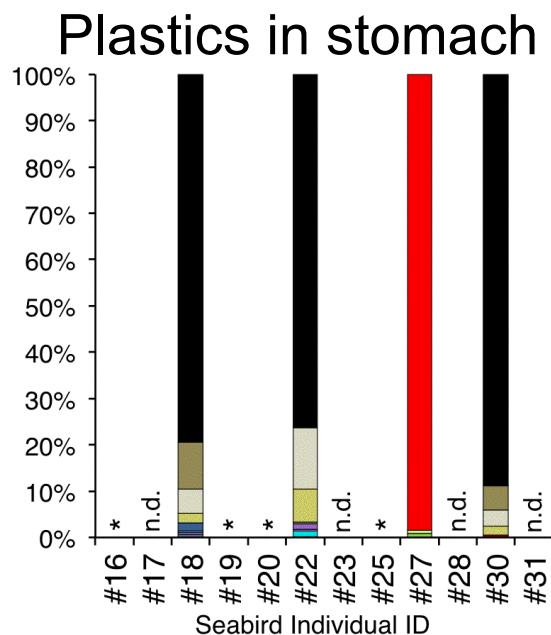
# Results\_abdominal adipose (16 day)



# Composition of BDE congeners in seabird adipose, plastics in the stomachs, and their prey.



10Br	209	206
9Br	207	208
8Br	196	203
	197	202
7Br	179	188
	190	181
	183	166
6Br	138	153
	154	155
5Br	126	85
	118	116
	99	119
	100	77
4Br	66	47
	71	49
	75	37
3Br	35	33/28
	17/25	32
	30	15
2Br	12/13	8
	11	7
	10	3
1Br	2	1



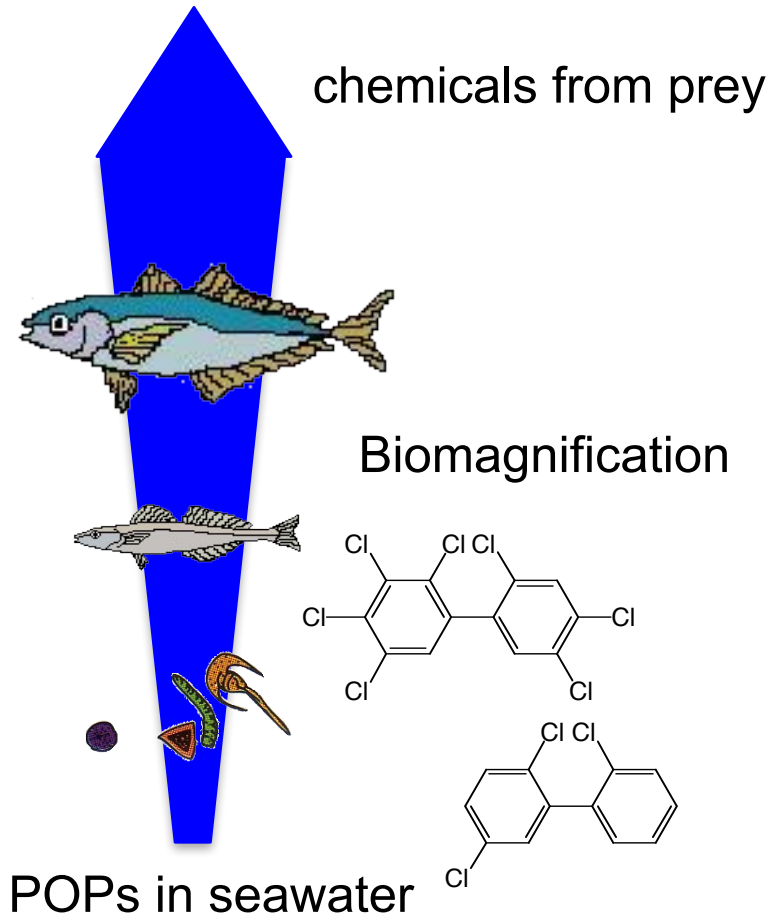
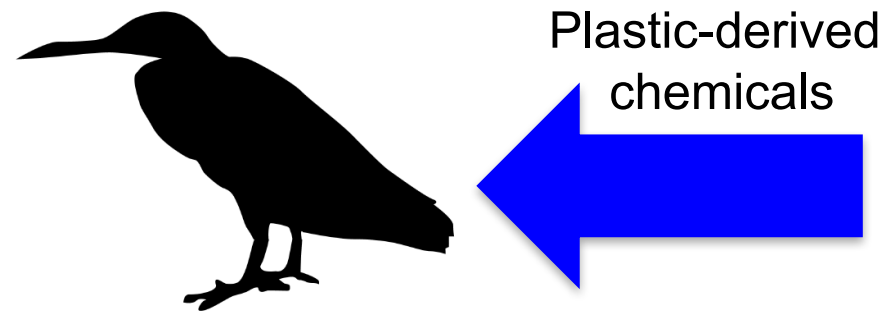
Lower brominated congeners were derived from natural prey, whereas higher brominated congeners were derived from ingested plastics.



# Topics

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  - Chemicals adsorbed from seawater
  - Additive chemicals
- Transfer of the chemicals from plastics to internal organs
  - Experimental evidences
  - Mechanism
- Significance of the plastics as exposure media :  
Field observations **Higher trophic level organisms**
- **Lower trophic level organisms**
- Effects of the plastic-mediated chemical exposure

# Exposure of contaminants both from plastics and prey



Significant of ingested plastics as exposure source of chemicals depend on target chemicals, background pollution, study area, and target biota

## Summary 1. Plastic contribution to PCBs depends on locations and trophic levels

Location	Animal	Species	Compounds	Significance	
Gough Island	Seabird	Great Shearwater	PCBs	Yes	{Ryan, 1988 #68}
Bering Sea	Seabird	Short-tailed Shearwater	PCBs (LCC)	Yes	{Yamashita, 2011 #453}
Bering Sea	Seabird	Short-tailed Shearwater	PCBs (HCC)	No	{Yamashita, 2011 #453}
Coastal Norway	Seabirds	Northern Fulmars	PCBs, DDTs, PBDEs (LBC)	No	{Herzke, 2016 #654}
Pacific	Seaturtle	olive ridley, loggerhead turtles, blue turtle	PCBs, DDTs, PBDEs	No	{Clukey, 2018 #719}
South Atlantic Ocean	pelagic fish	lantern fish	PCBs, DDTs	No	{Rochman, 2014 #718}
North Pacific Ocean	pelagic fish	lantern fish	PCBs (HCC))	No	{Gassel, 2019 #722}
North Pacific Ocean	pelagic fish	lantern fish	PCBs (LCC)	Yes	{Gassel, 2019 #722}
Remote island, Japan	bivalves	clam	PCBs	Yes	Mizukawa et al., 2019
Remote island, Japan	Crustacea	coenobita	PCBs	Yes	Mizukawa et al., 2019

## Summary 2. Plastic contribution to BDE209, phthalates, Benzotriazole UV-stabilizers is significant in most cases.

Location	Animal	Species	Compounds	Significance	
Bering Sea	Seabirds	Short-tailed Shearwater	BDE209	Yes	{Tanaka, 2015 #612}
South Atlantic Ocean	pelagic fish	lantern fish	BDE209	Yes	{Rochman, 2014 #718}
Coastal Australia	Seabirds	short-tailed Shearwater/wedged-tailed shearwater	Phthalates (DEHP)	Yes	{Hardesty, 2015 #643}
Hawaii	Seabirds	Black footed albatross, Laysan albatross	UV-stabilizer (UV-326, UV-328)	Yes	{Tanaka, 2019 #715}
Mediterranean	basking shark	Cetorhinus maximus	MEHP	Yes	{Fossi, 2014 #610}
Remote island, Japan	Crustacea	coenobita	PBDEs	Yes	Mizukawa et al., 2019
Coastal Norway	Seabirds	Northern Fulmars	BDE209	Yes	{Herzke, 2016 #654}
Pacific	Seaturtle	olive ridley, loggerhead turtles, blue turtle	BDE209	No	{Clukey, 2018 #719}



**remote island in Okinawa**

Control beach





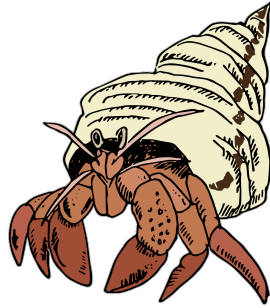
remote island in Okinawa

Plastic contaminated beach





# Microplastics in digestive tract of Hermit Crab



0 – 13 pieces/g-wet

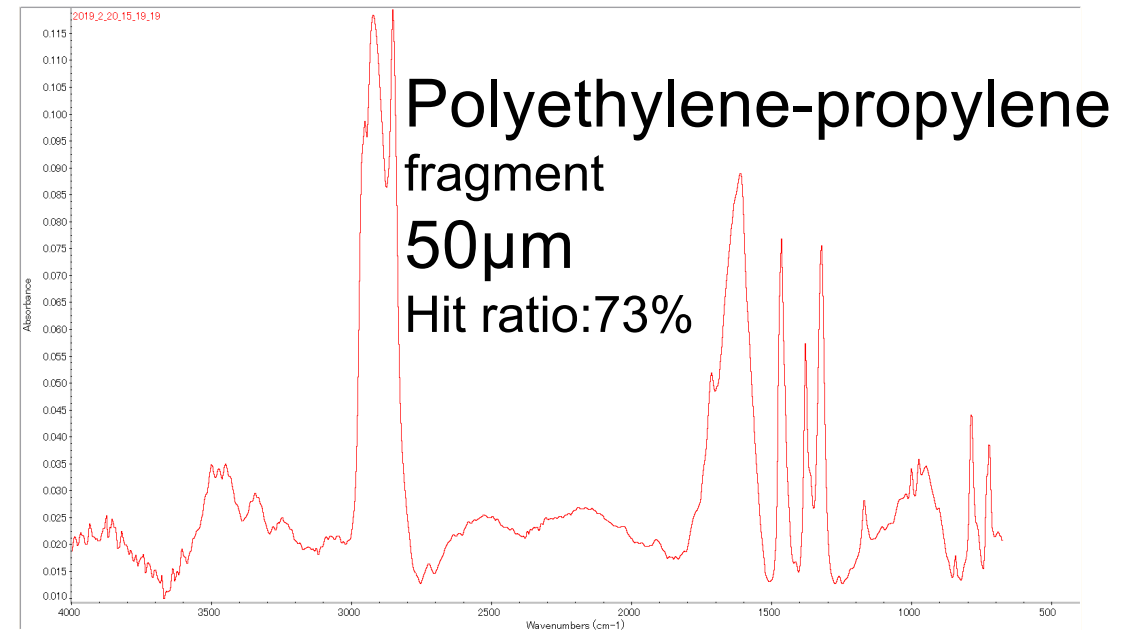
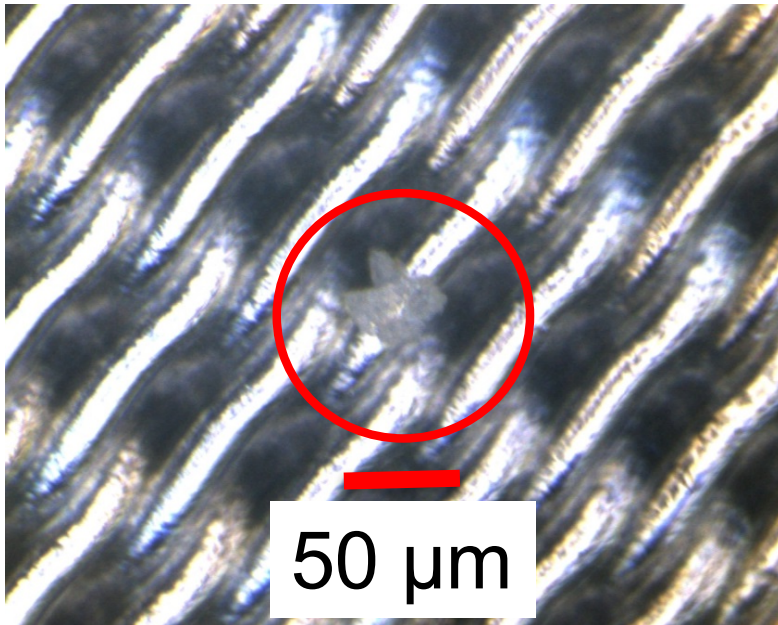
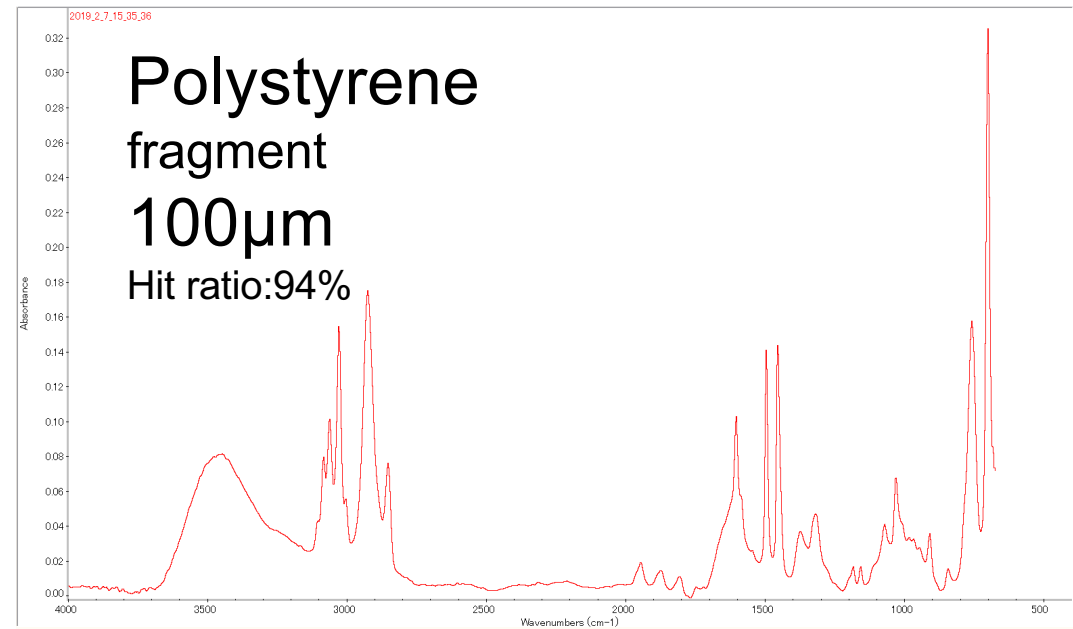
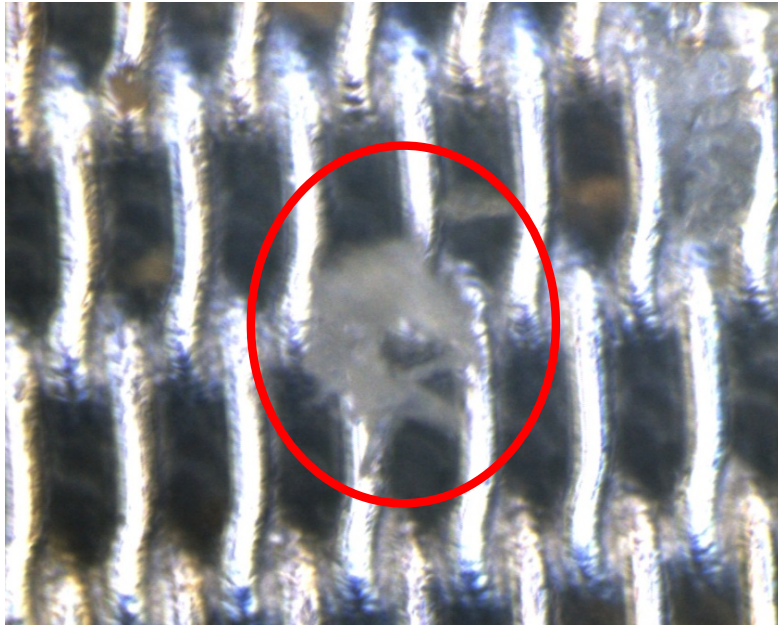
Control  
beach



293 - 482 pieces/g-wet

Plastic  
contaminated  
beach

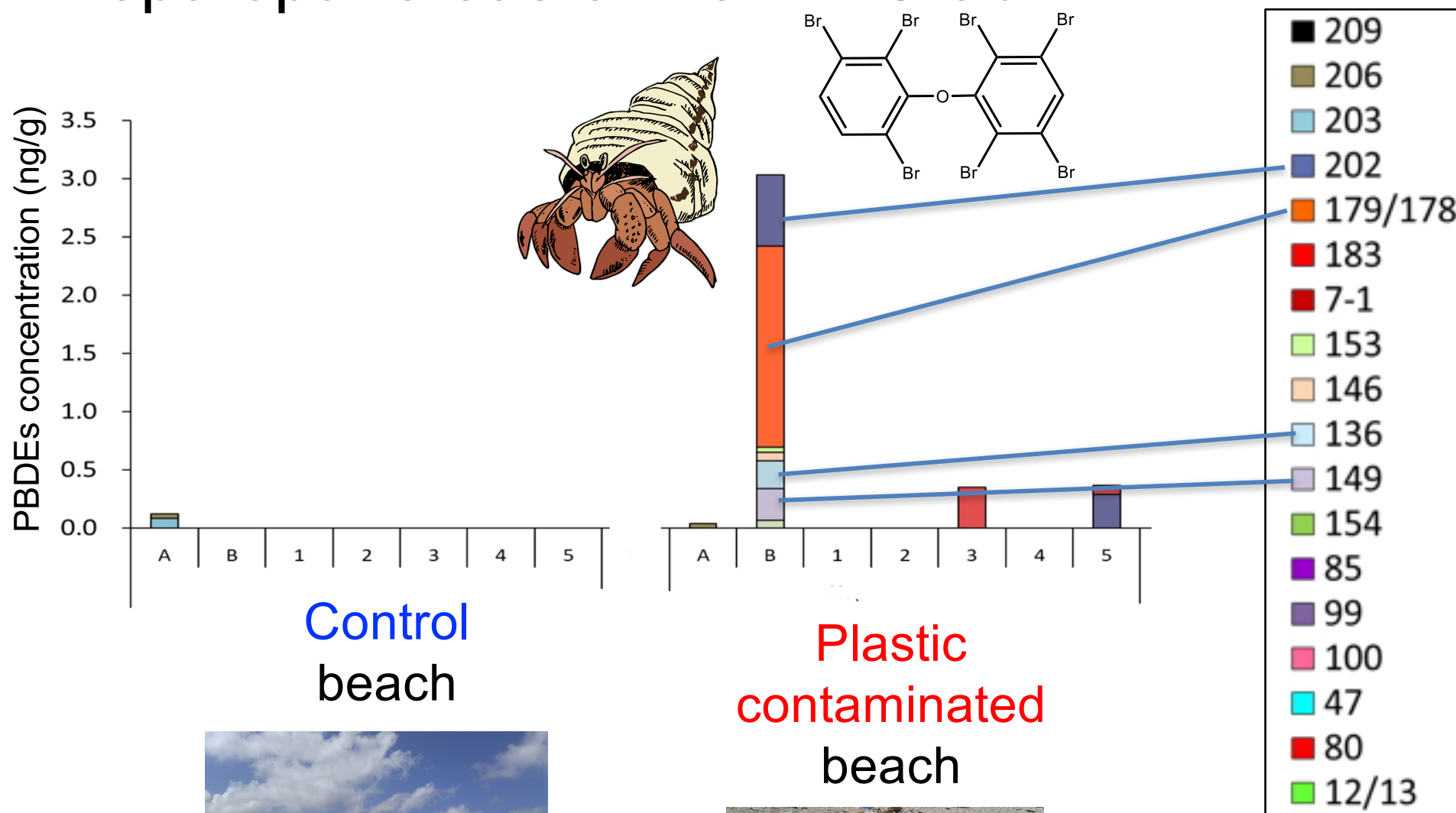




Images and FTIR spectrum of microplastics found in stomach  
of Hermit Crab

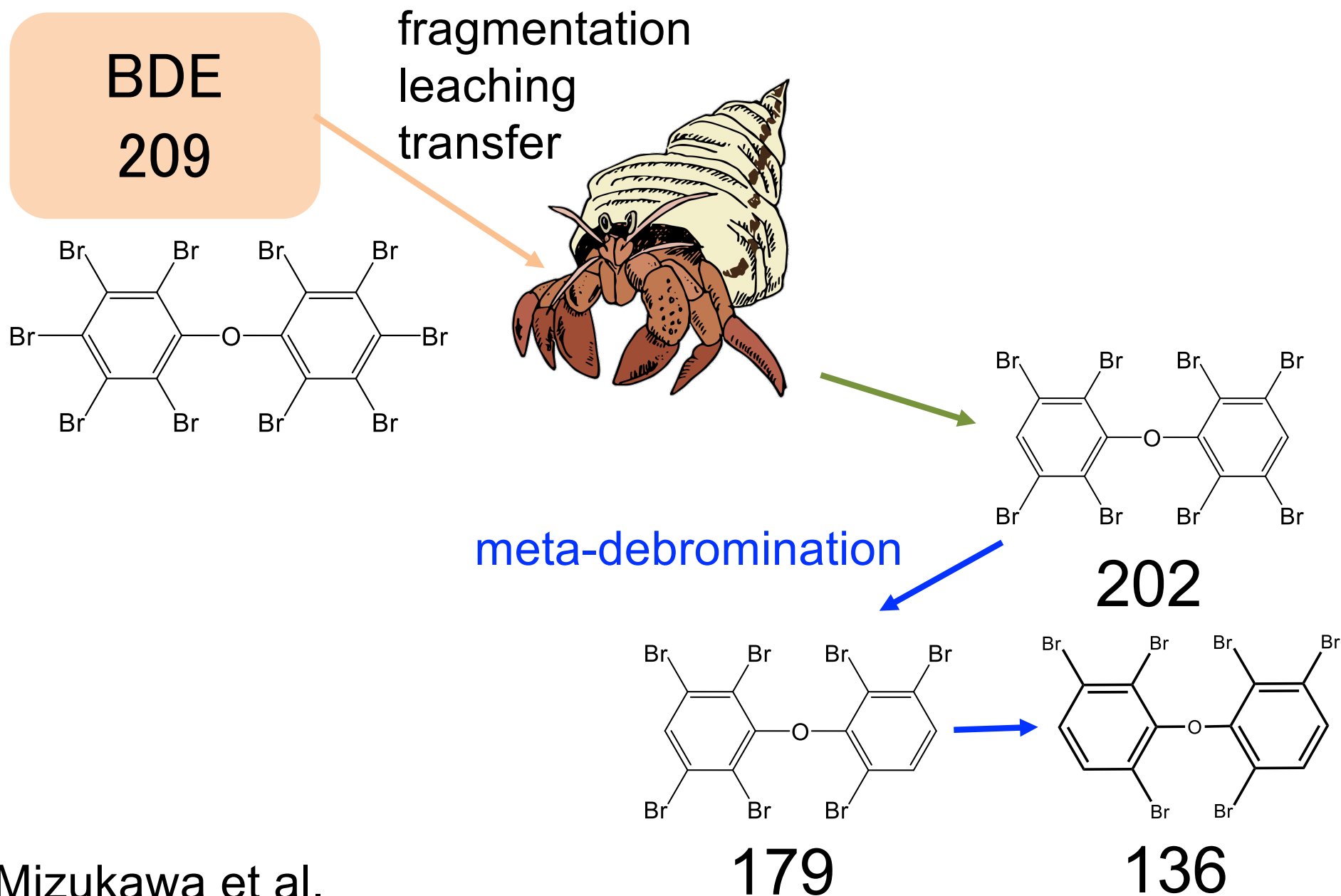


# PBDEs (Additives : Brominated flame retardants) in hepatopancreas of Hermit Crab



Mizukawa et al.

# BDE209 was transferred to internal metabolic system and debrominated

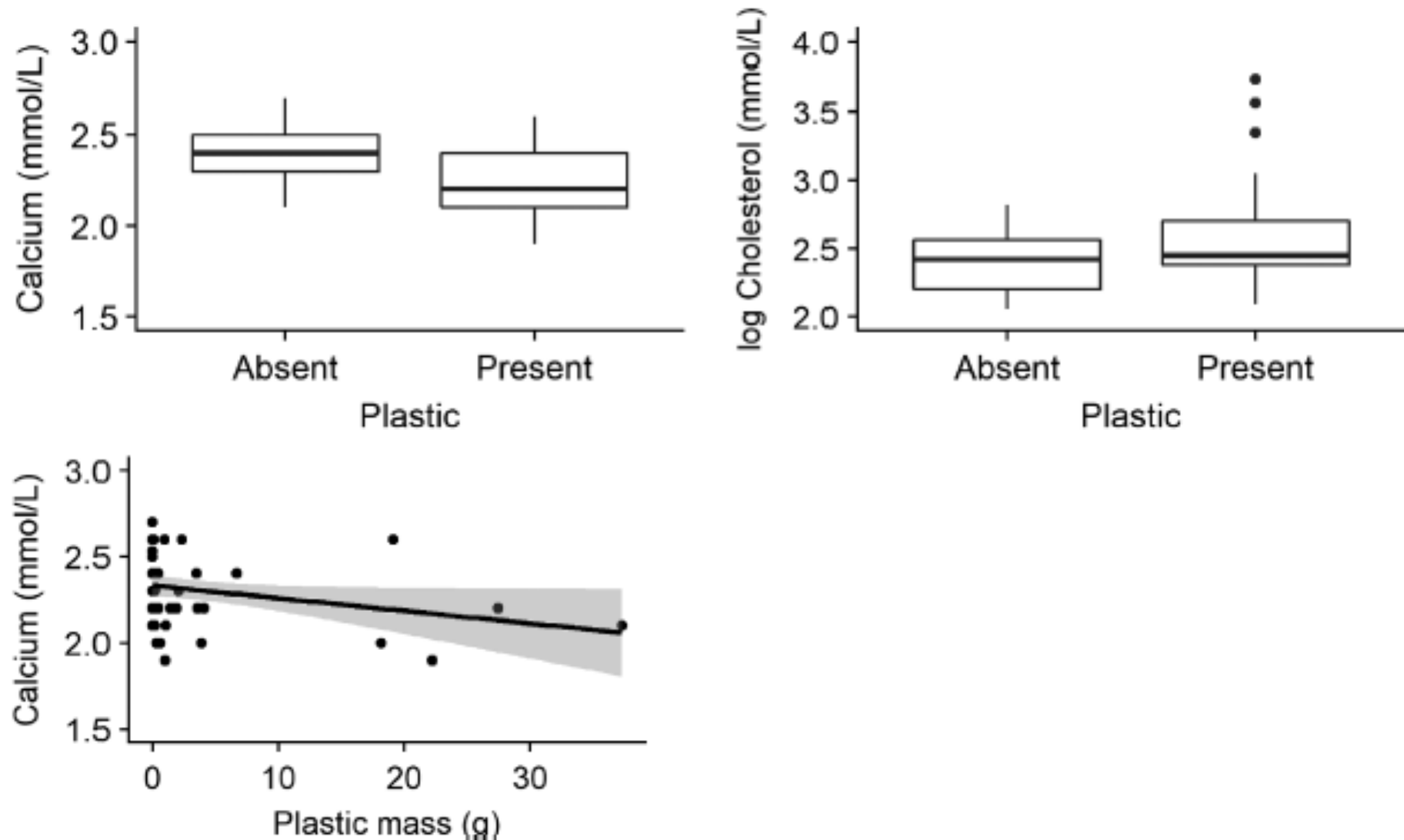


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  - Experimental evidences
  - Mechanism
- Significance of the plastics as exposure media :  
Field observations
- **Effects of the plastic-mediated chemical exposure**

# Clinical Pathology of Plastic Ingestion in Marine Birds and Relationships with Blood Chemistry

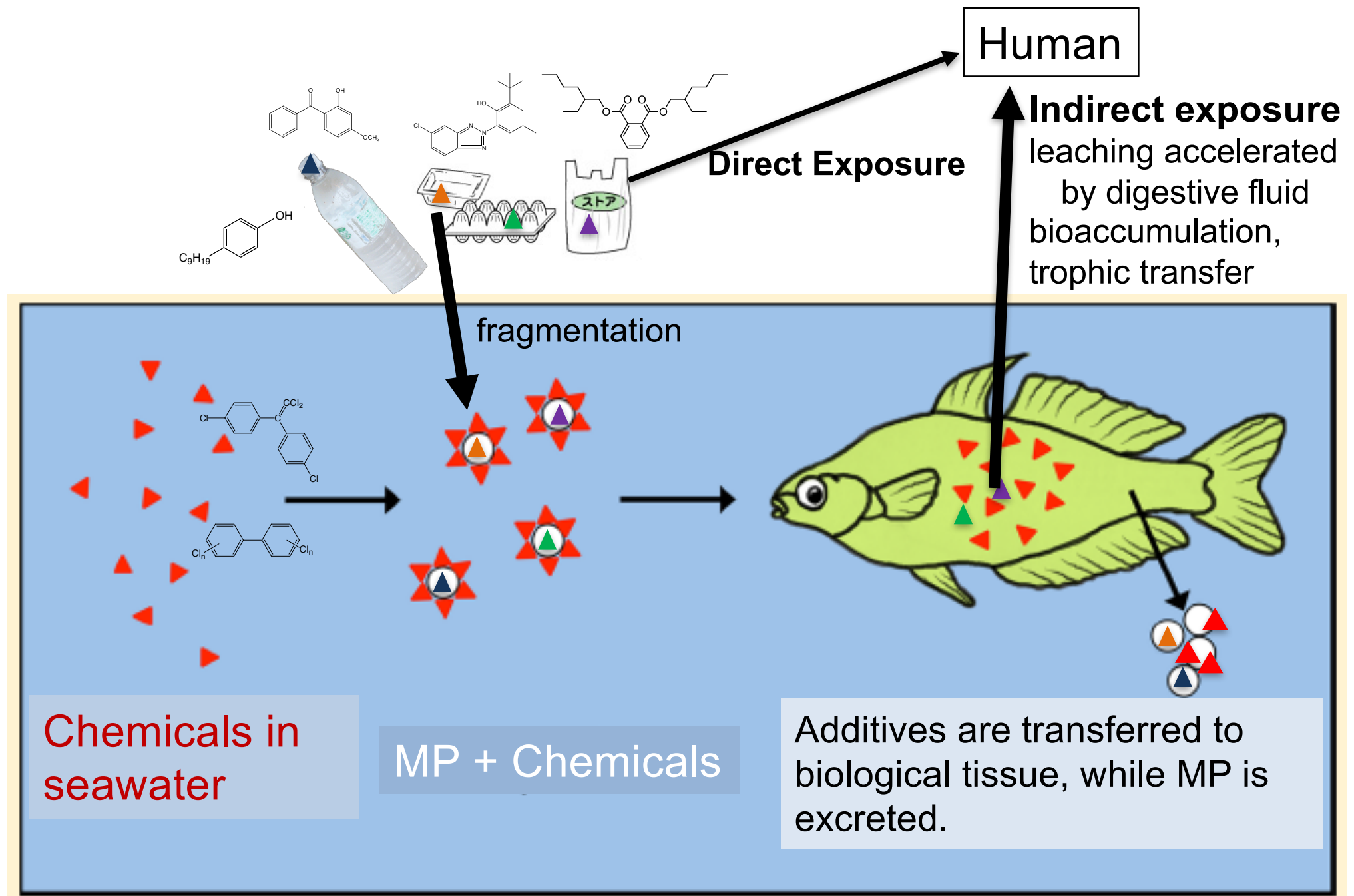
Jennifer L. Lavers,<sup>\*,†</sup> Ian Hutton,<sup>‡</sup> and Alexander L. Bond<sup>†,§</sup>



## Conclusions

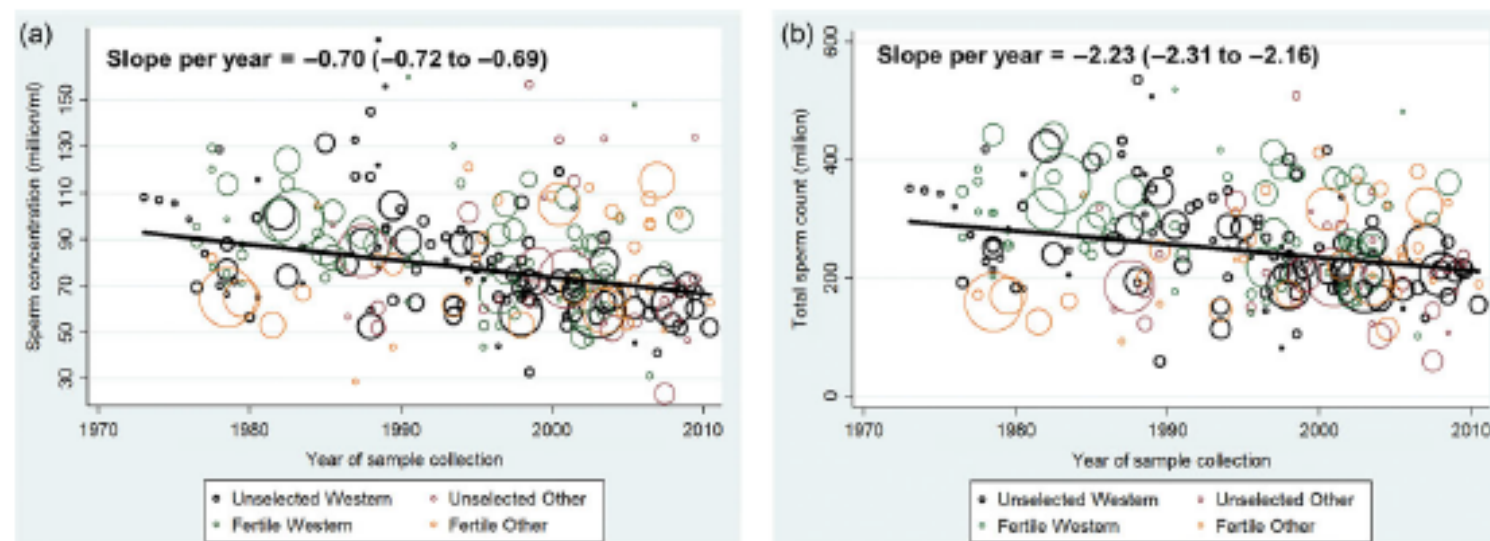
1. Both sorption- and additive-derived chemicals were retained in microplastics (PCBs, BDE209; 0.3 mm – 5mm).
2. Sporadic occurrence of microplastics with high concentrations of additives and sorbed chemicals were observed. Their exposure to remote ecosystem was suggested.
3. Transfer of hydrophobic additives to internal tissue of marine organisms was confirmed and it is facilitated by oily components in digestive fluid.
4. Plastic-mediated chemical exposure does occur and its significance depends on locations, background pollution, chemicals, species of biota, especially trophic levels.

# Microplastic pollution : Acceleration of exposure of additives to human



# Temporal trends in sperm count: a systematic review and meta-regression analysis

Hagai Levine <sup>1,2,\*</sup>, Niels Jørgensen <sup>3</sup>, Anderson Martino-Andrade<sup>2,4</sup>, Jaime Mendiola<sup>5</sup>, Dan Weksler-Derri<sup>6</sup>, Irina Mindlis<sup>2</sup>, Rachel Pinotti<sup>7</sup>, and Shanna H. Swan<sup>2</sup>



**Figure 2** (a) Mean sperm concentration by year of sample collection in 244 estimates collected in 1973–2011 and simple linear regression. (b) Mean total sperm count by year of sample collection in 244 estimates collected in 1973–2011 and simple linear regression.

## **Direction of future efforts**

Methodology to detect insidious biological effects on the field and by epidemiological survey

Endocrine disruption of variety of additives

Fate of additives

Leaching from  $\mu\text{m}$ -size plastics  
transfer to lower trophic level organisms,  
biomagnification

More field observations

Nano-size plastics

Measurement  
biological effects

Yo-yo-effects of microplastics and legacy pollution



# Acknowledgement

