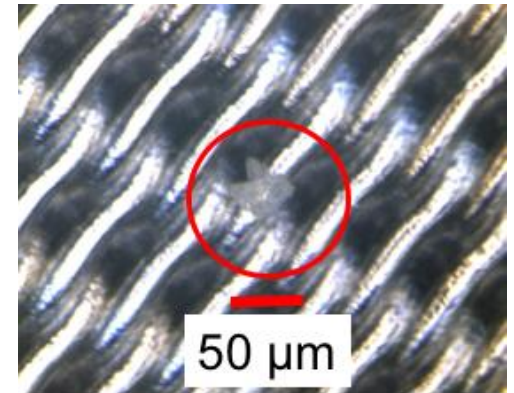
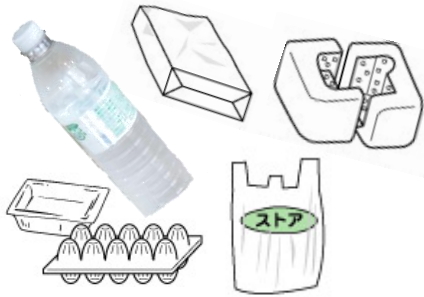


Hazardous chemicals in marine plastics and their threat to marine organisms



Shige TAKADA

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

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

Major Conclusion

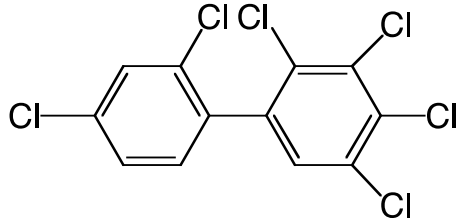
Plastic-mediated chemical exposure does occur and its significance depends on locations, background pollution, chemicals, species of biota, especially trophic levels.

Topics

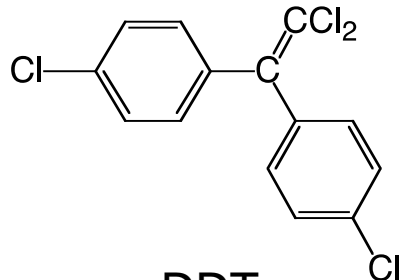
- Hazardous chemicals in marine plastics
 - Chemicals adsorbed from seawater
 - Additive chemicals
- Transfer of the chemicals from ingested plastics to internal tissue of biota
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Field observations
- Effects of the plastic-mediated chemical exposure

Plastics carry two types of chemicals in marine environment

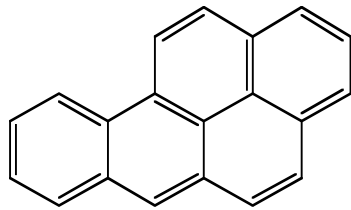
Sorption from seawater



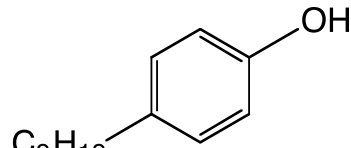
Polychlorinated biphenyls (PCBs)



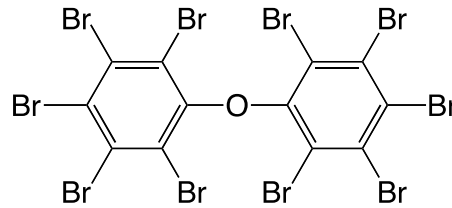
DDTs



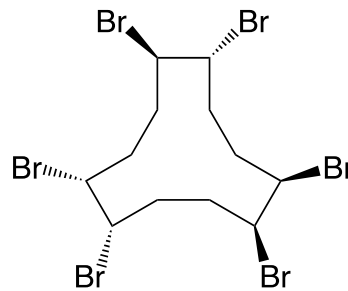
Polycyclic aromatic hydrocarbons (PAHs)



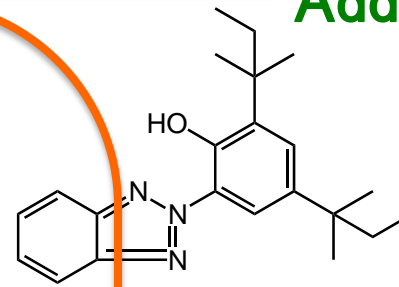
Nonylphenol



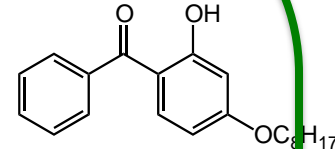
Polybrominated diphenyl ethers (PBDEs)



Hexabromocyclododecanes (HBCDs)

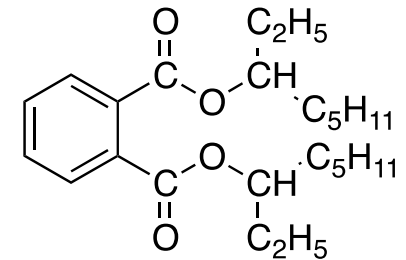


Benzotriazoles (e.g., UV-328)

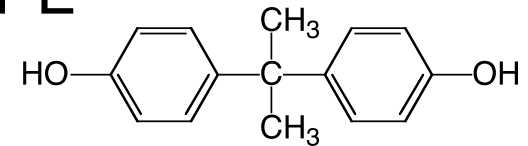


Benzophenones (e.g., BP-12)

Additives



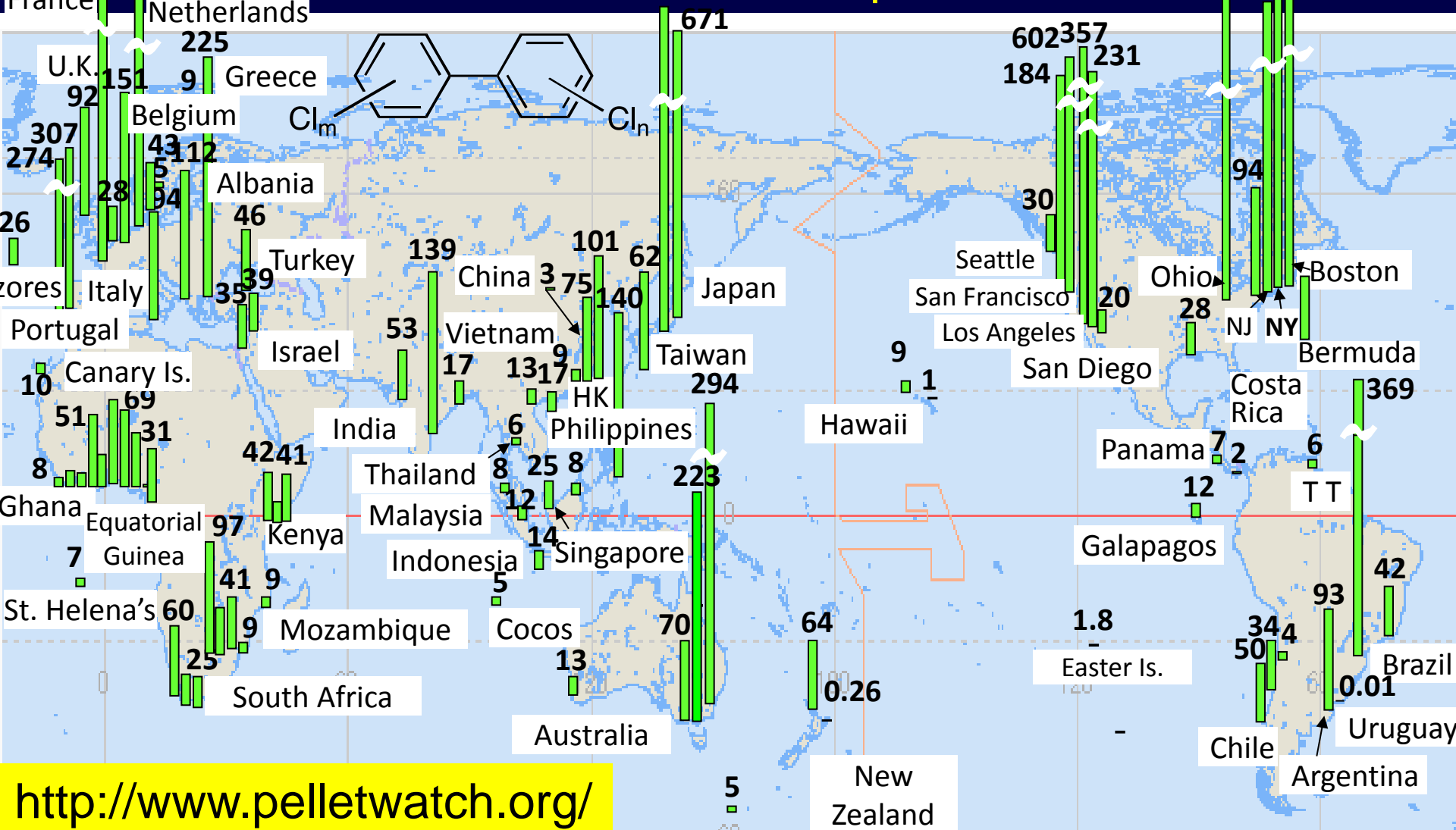
Phthalates (DEHP)



Bisphenol A

DBDPE

International Pellet Watch demonstrates sorption of POPs to microplastics

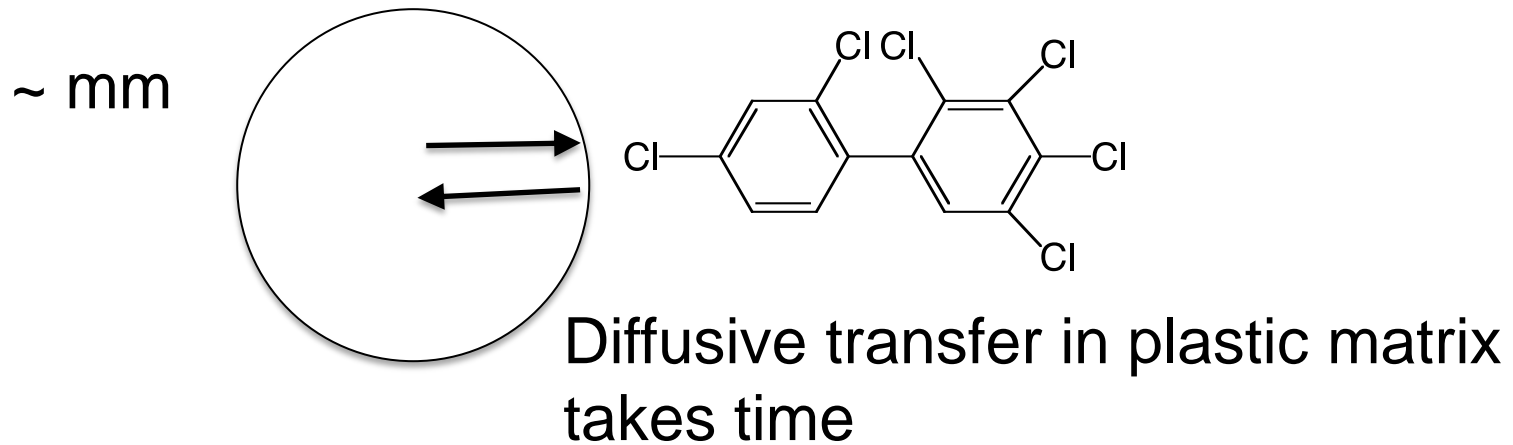


<http://www.pelletwatch.org/>

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

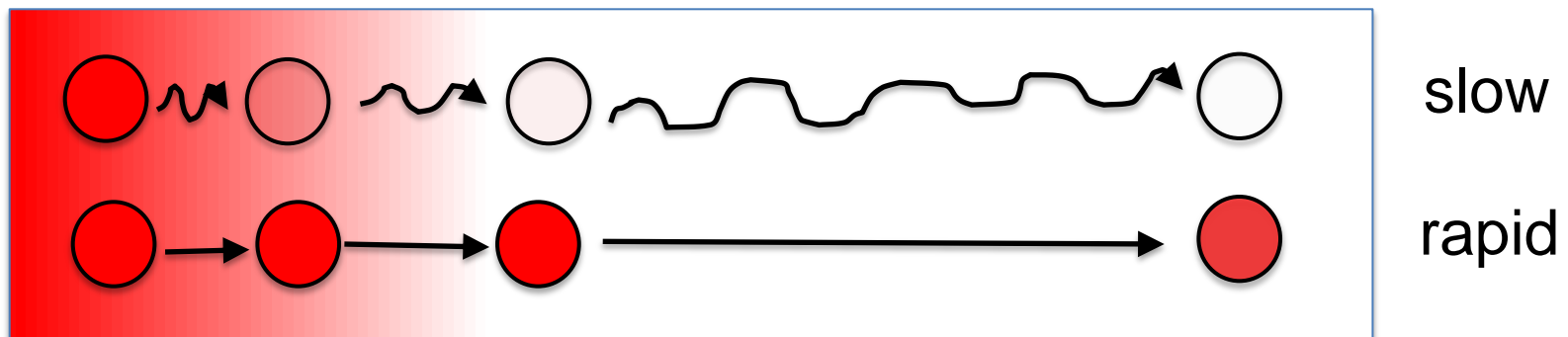


Plastic fragment/pellet with 3 mm diameter
Long time (~ 1 year) to reach equilibrium

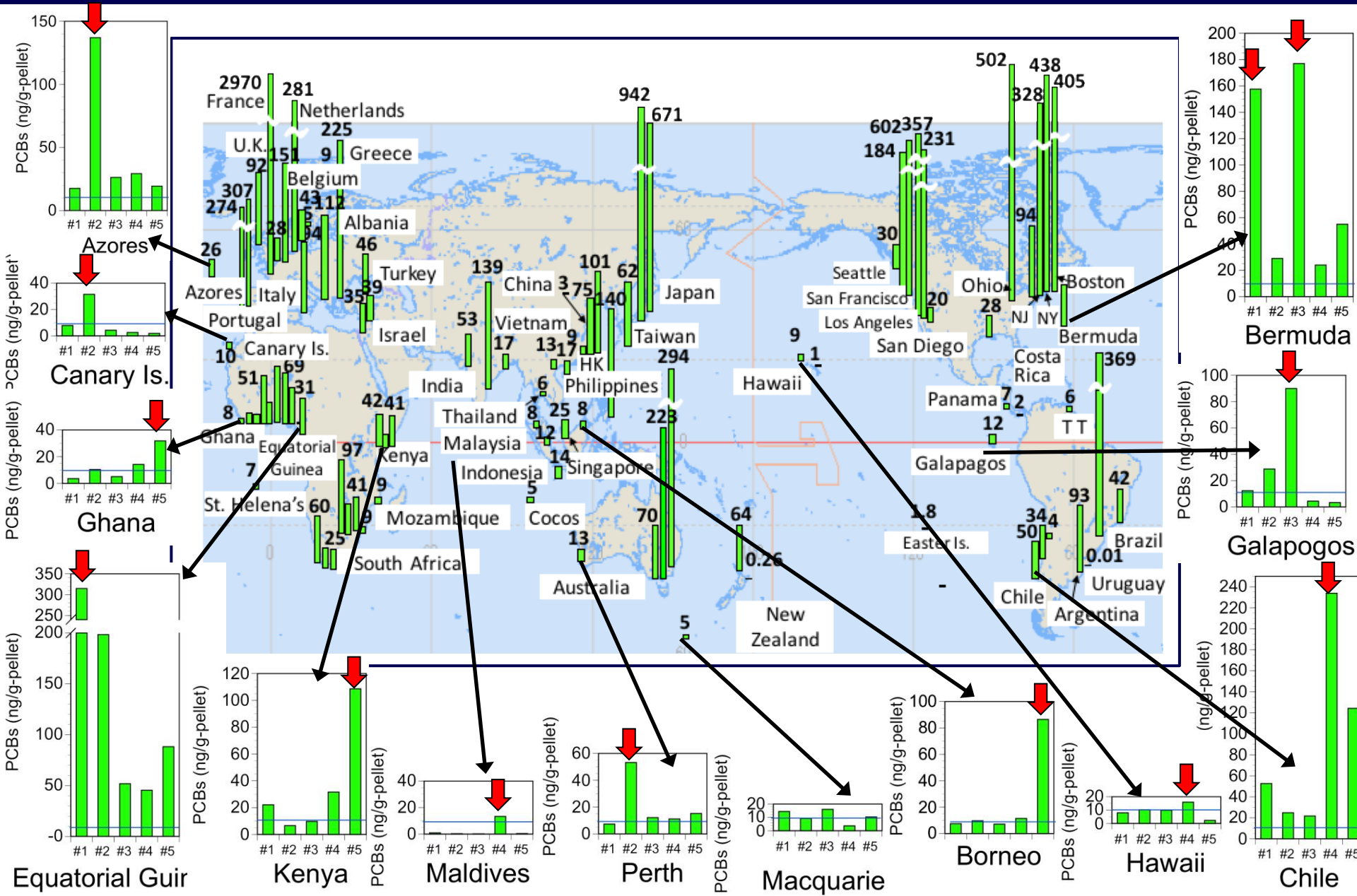
Non-equilibrium : slow sorption/desorption

Polluted waters

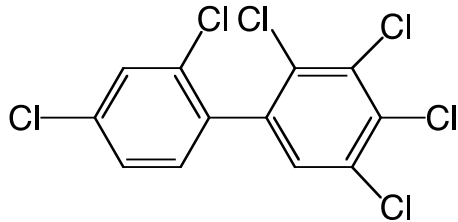
Open ocean



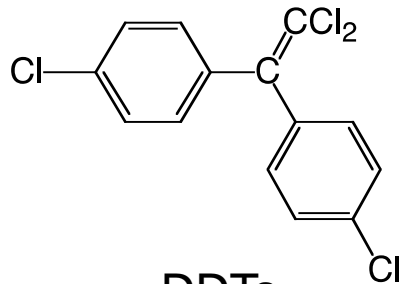
Sporadic high concentrations of PCBs found in pellets from remote areas : Microplastics carry contaminants to remote areas



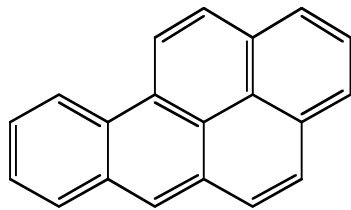
Plastics carry two types of chemicals in marine environment



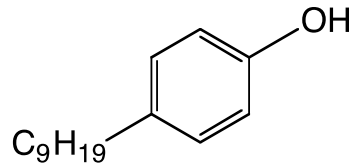
Polychlorinated biphenyl (PCBs)



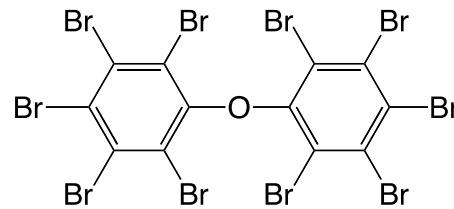
DDTs



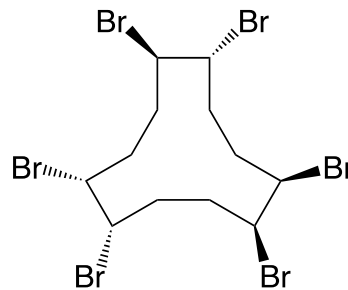
Polycyclic aromatic hydrocarbons (PAHs)



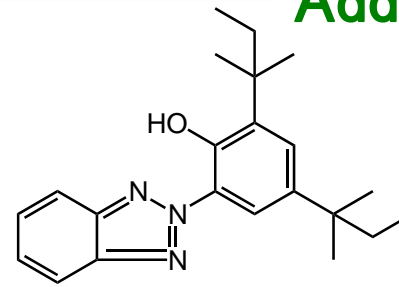
Nonylphenol



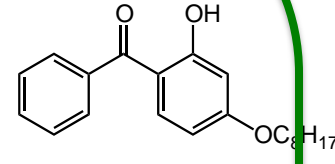
Polybrominated diphenyl ethers (PBDEs)



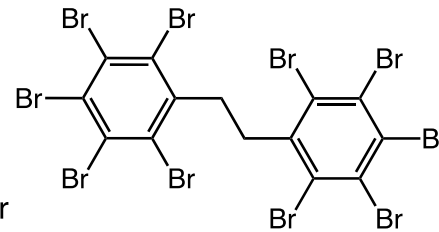
Hexabromocyclododecanes (HBCDs)



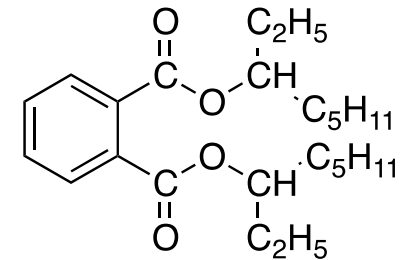
Benzotriazoles (e.g., UV-328)



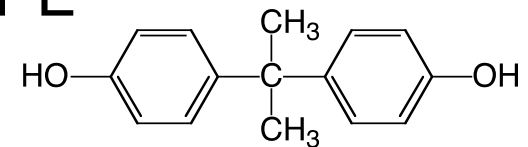
Benzophenones (e.g., BP-12)



DBDPE



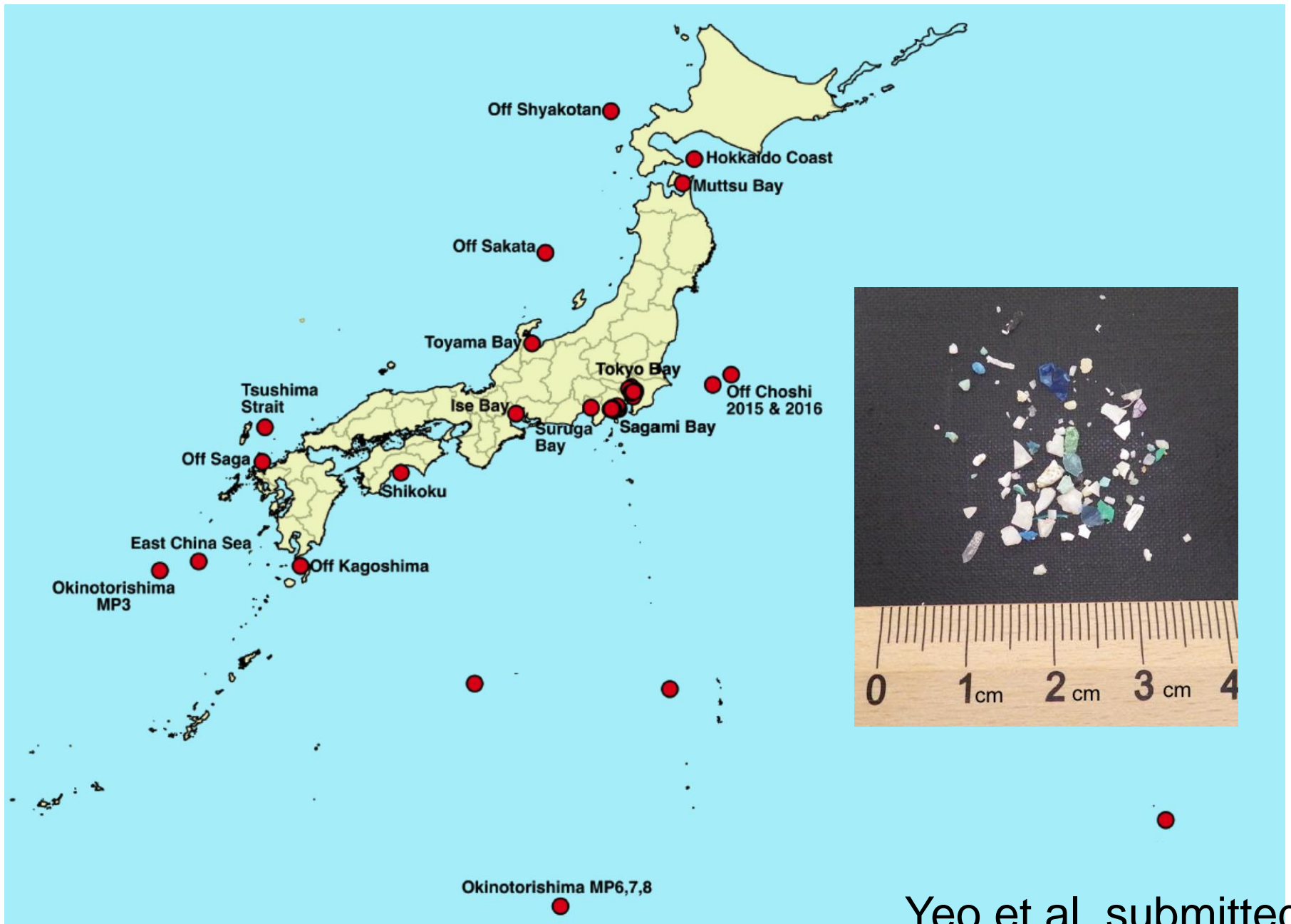
Phthalates (DEHP)



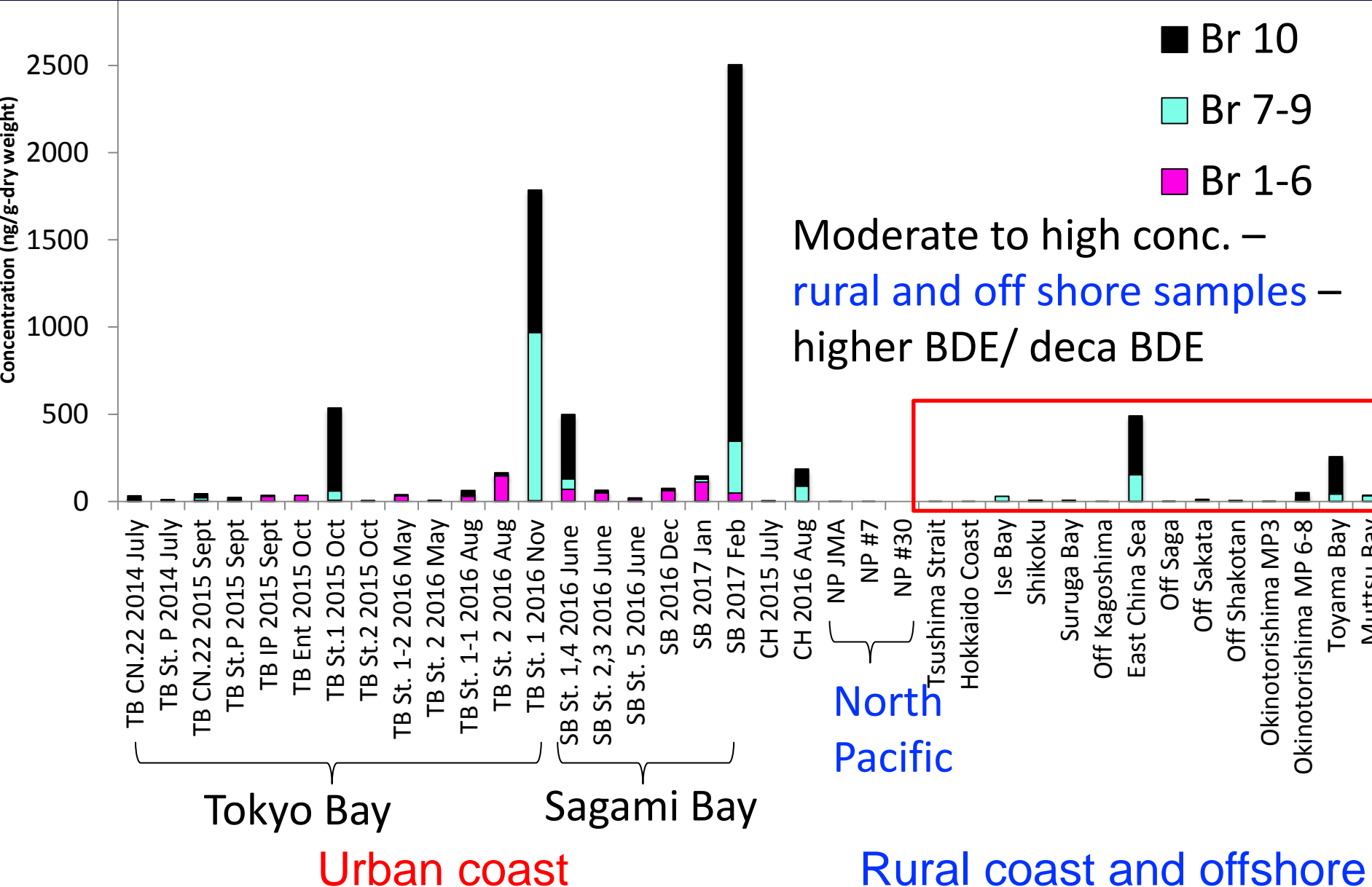
Bisphenol A

Additives

Buoyant microplastics from Japan coasts and pacific ocean



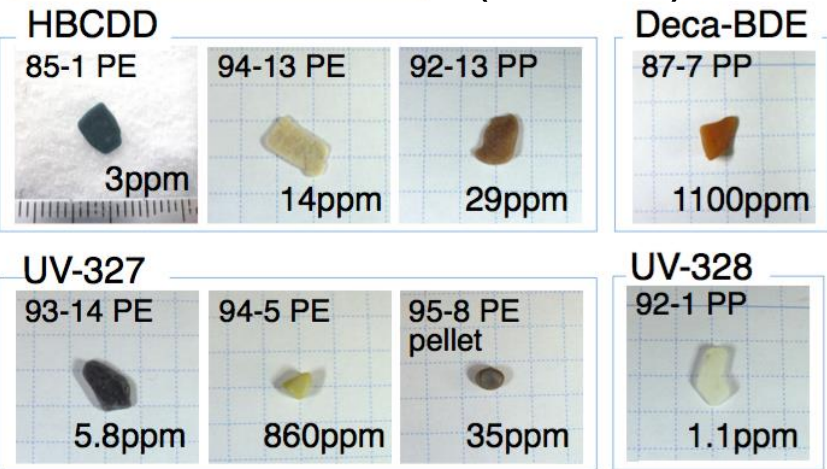
BDE209 was sporadically detected in suspended microplastics in seawater



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)

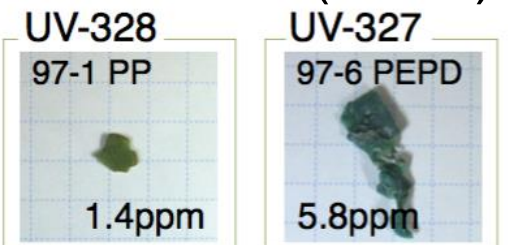


dissected

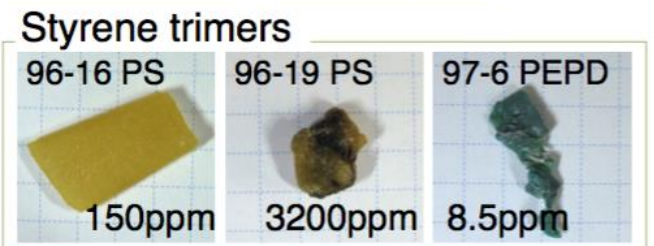
Tanaka, K., van Franeker, J.A., Deguchi, T., and Takada, H., **2019**. Piece-by-piece analysis of additives and manufacturing byproducts in plastics ingested by seabirds: Implication for risk of exposure to seabirds.

Marine Pollution Bulletin 145, 36-41.

Albatross (n=35)



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



Bolus

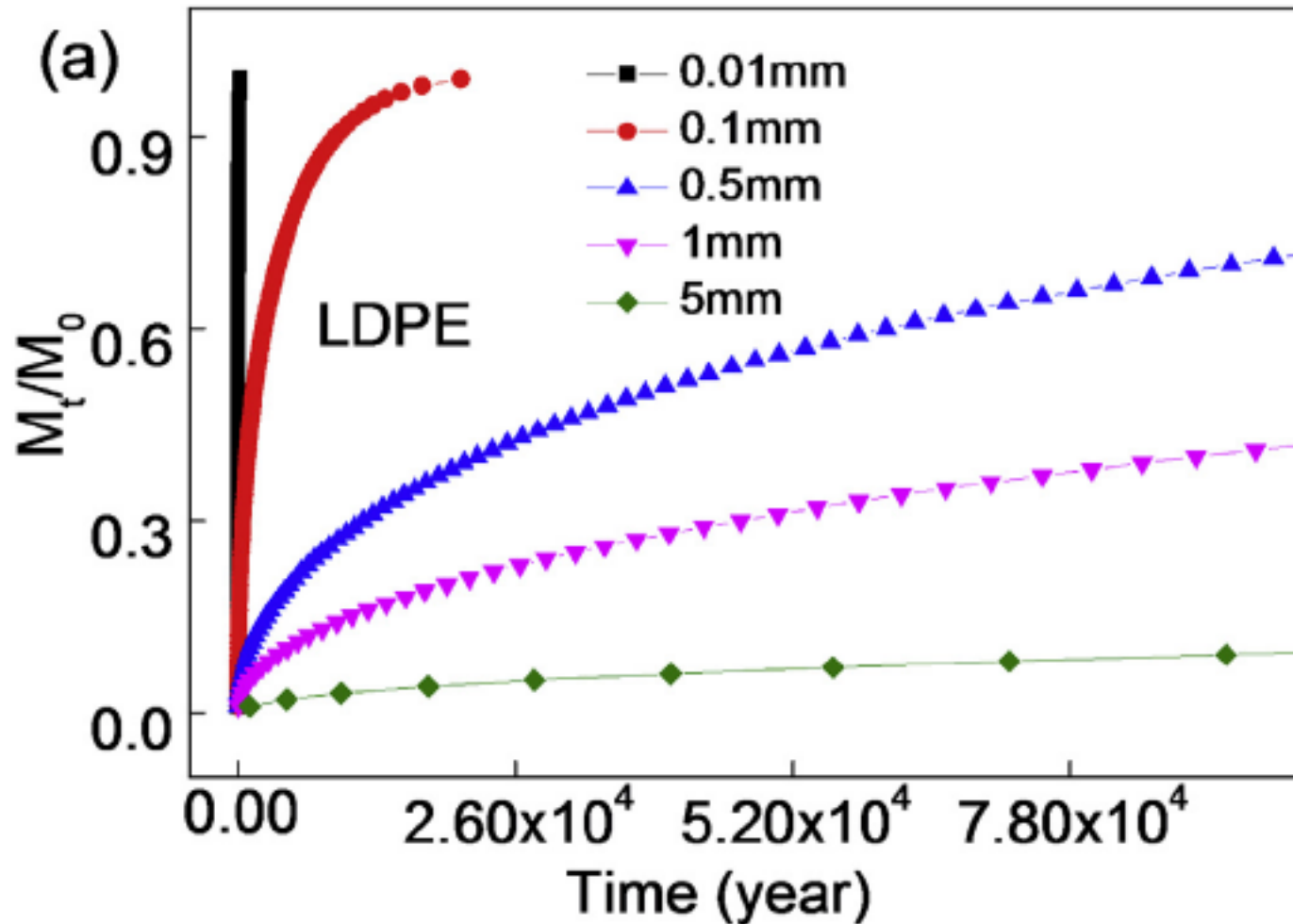
Table3. Ingestion frequency of plastic with additives.

	Detection % in fragments	Ingestion %
Northern fulmar		
Deca-BDE	0.6%	9%
HBCDD	1.9%	27%
UV-328	0.6%	9%
UV-326	1.3%	18%
UV-327	1.9%	27%
BP-12	0.6%	9%
∑ STs	0.6%	9%
Albatross		
UV-328	2.9%	17%
UV-327	2.9%	17%
∑ 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.



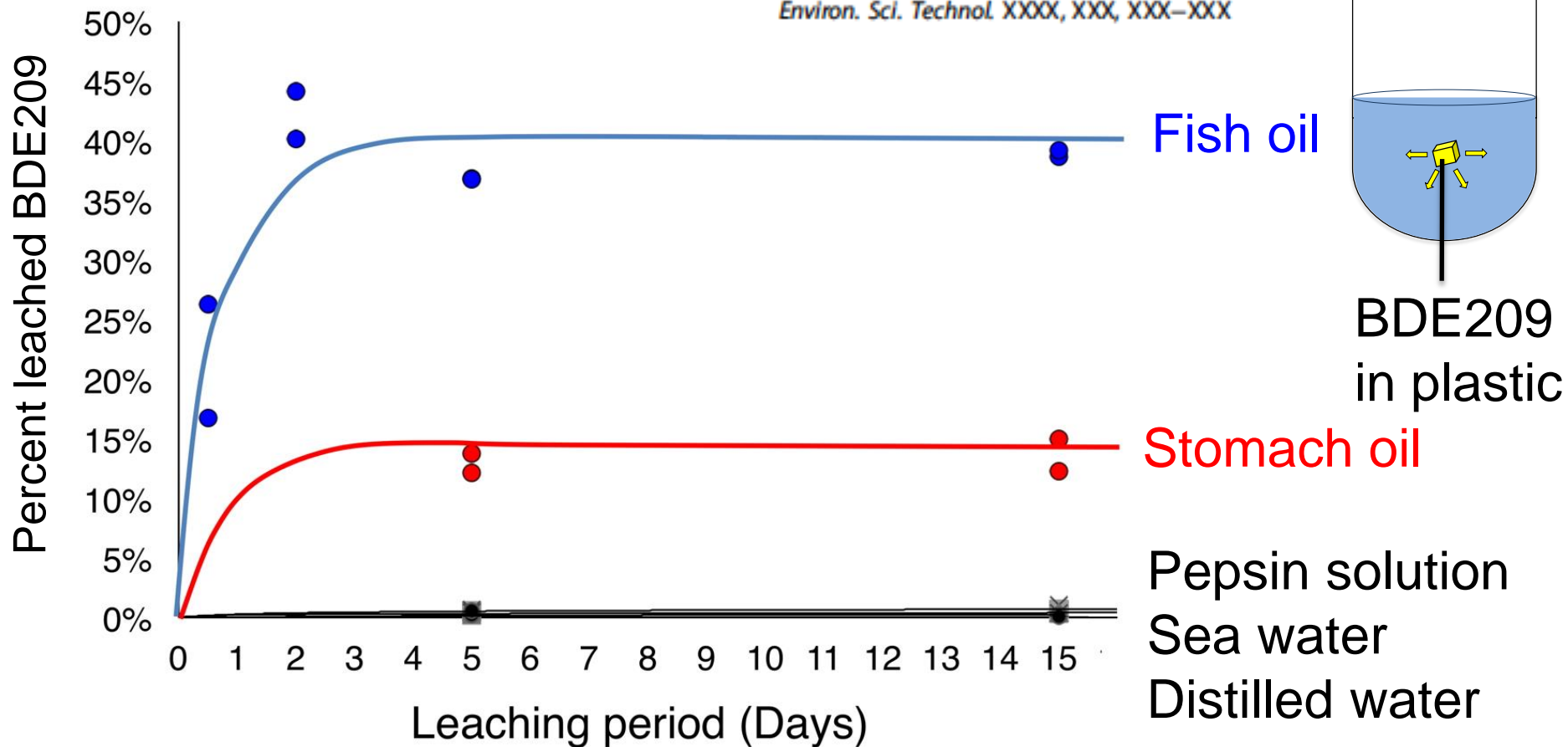
Sun, B., Hu, Y., Cheng, H., and Tao, S., 2019. Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: Kinetics and molecular-size dependence of diffusion. *Water Research* 151, 215-225.

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

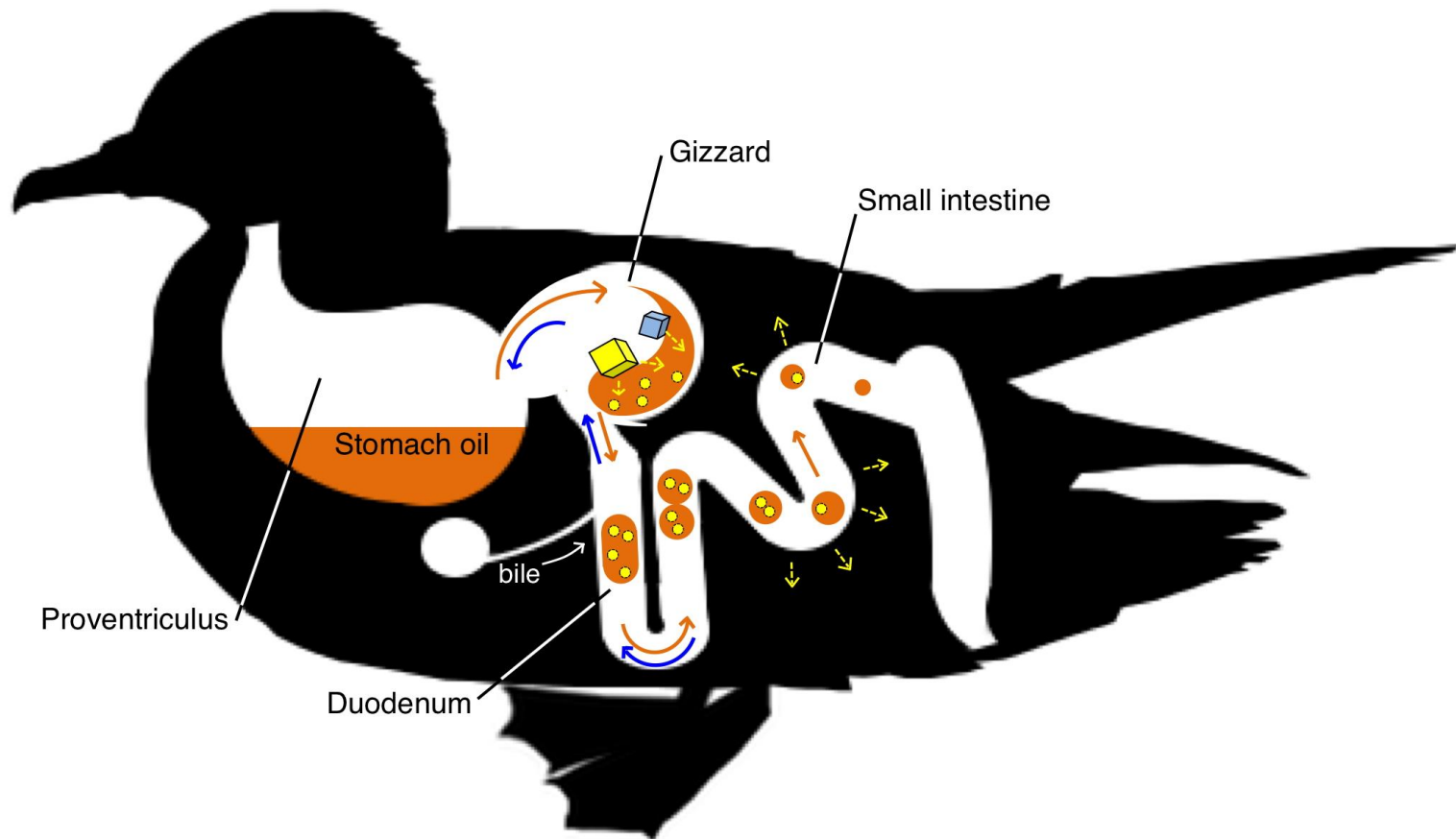
Kosuke Tanaka,[†] Hideshige Takada,^{*,†} Rei Yamashita,[†] Kaoruko Mizukawa,[†] Masa-aki Fukuwaka,[‡] and Yutaka Watanuki[§]

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.

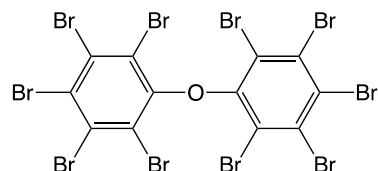
Plastics compounded with 5 additives

Polyethylene pellets with 5 additives

Additives:

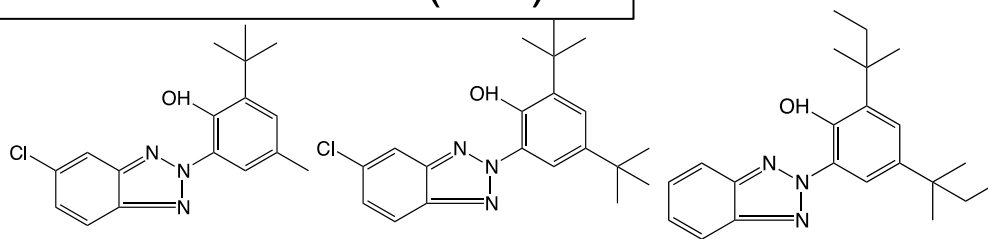
Brominated flame retardants

- BDE209



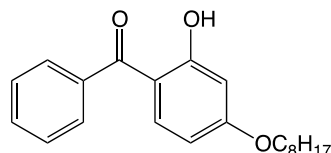
Benzotriazole UV-stabilizers (BTs)

- 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

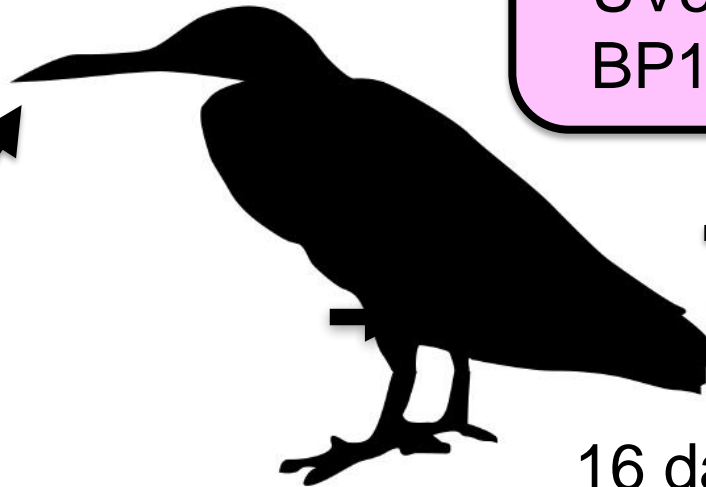
Control group

natural diet



natural diet

Chicks



16 days

→ Liver
→ Adipose
→ Preen Gland oil

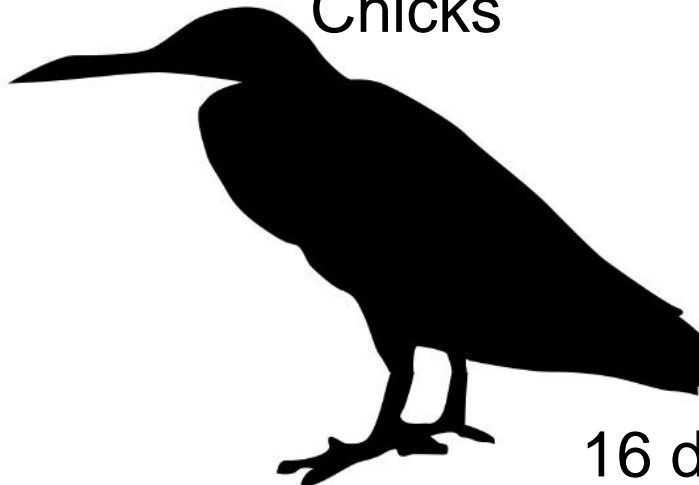
Additives

BDE209

UV326, UV327, UV328

BP12

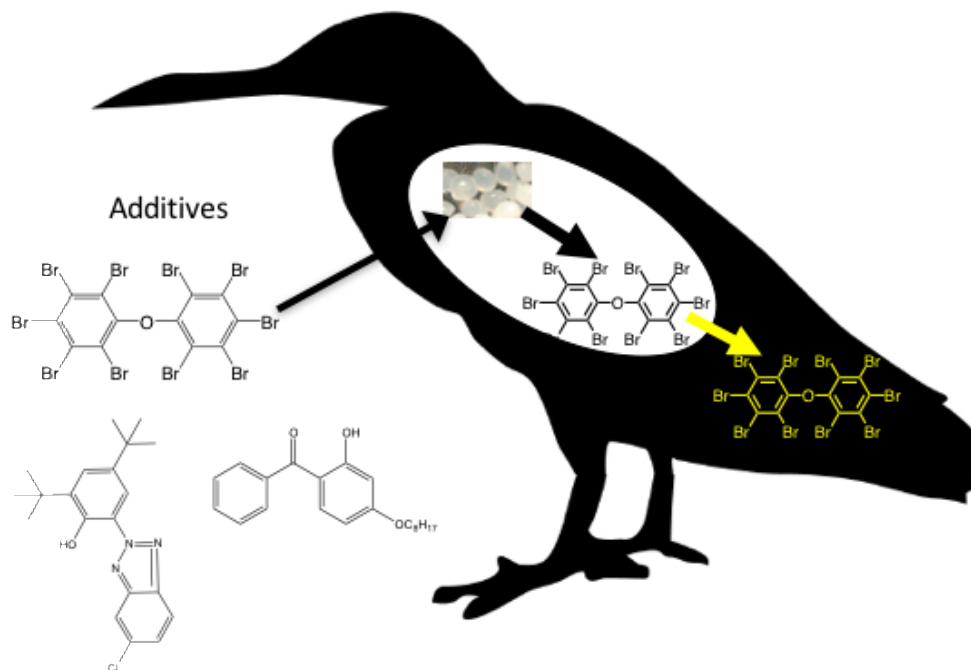
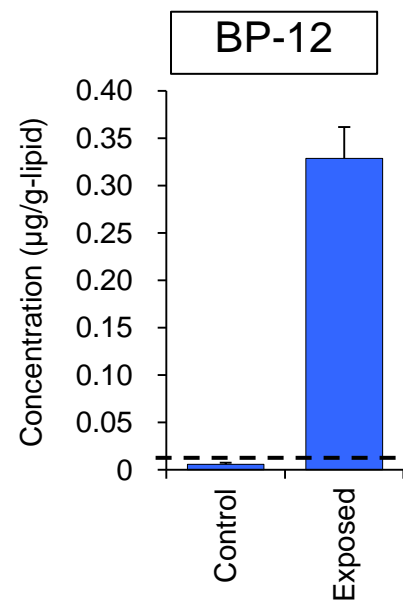
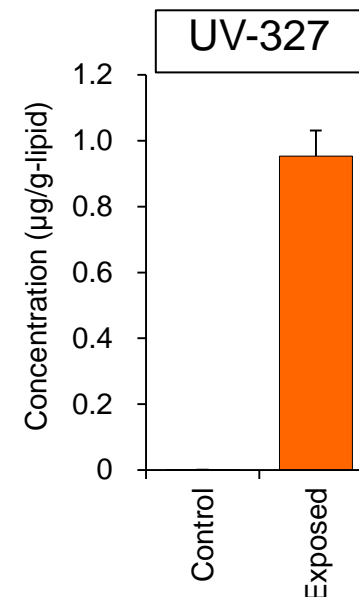
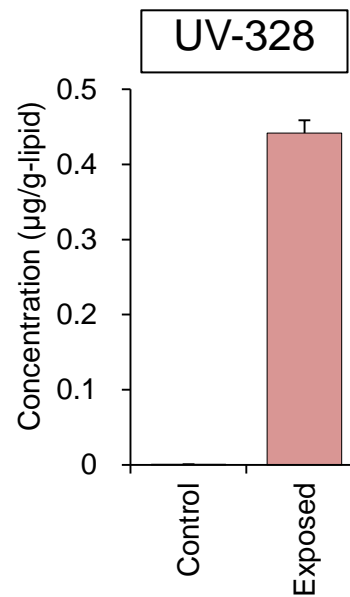
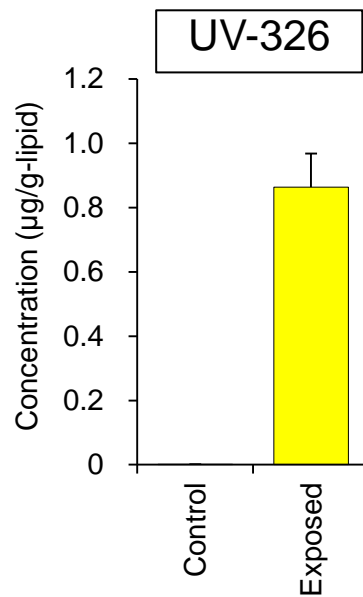
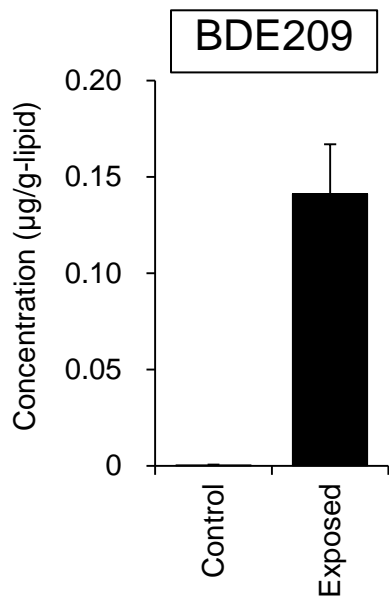
Chicks



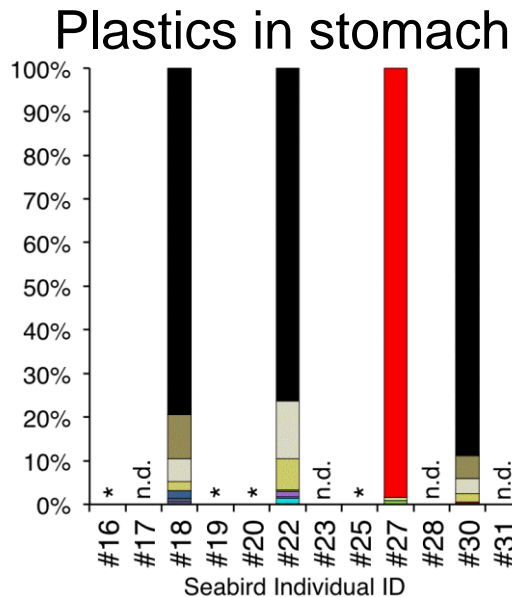
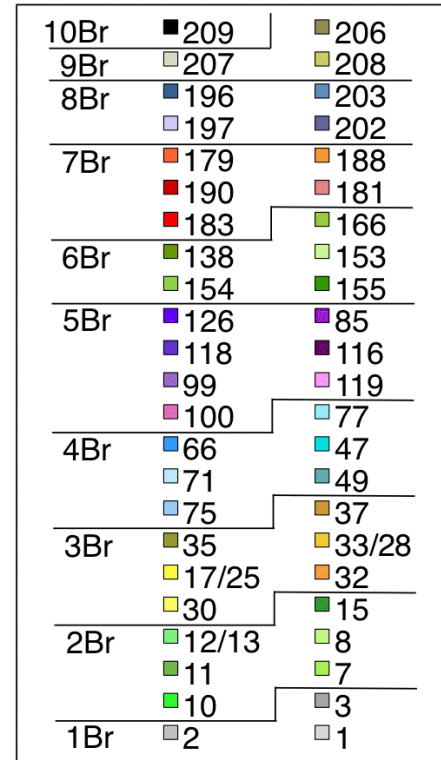
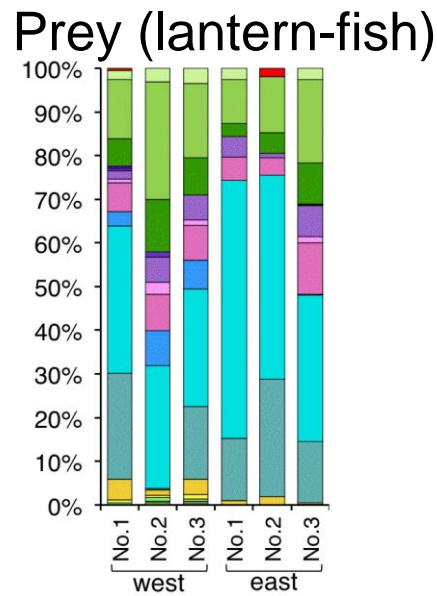
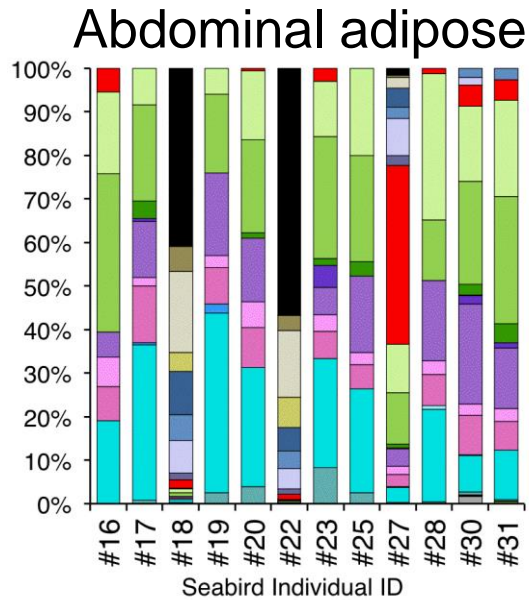
16 days

→ Liver
→ Adipose
→ Preen Gland oil

Results_abdominal adipose (16 day)



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

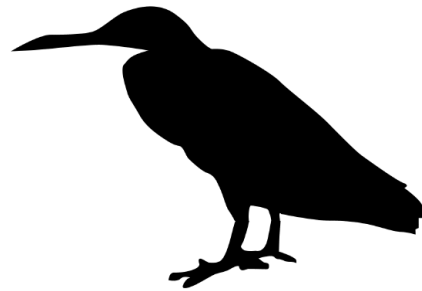


Lower brominated congeners were derived from natural prey, whereas higher brominated congeners were derived from ingested plastics.

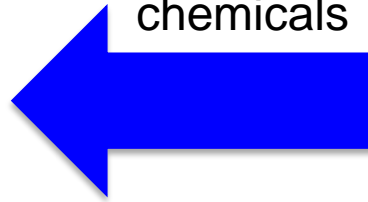
Topics

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- Significance of the plastics as exposure media :
Field observations **Higher trophic level organisms**
- **Lower trophic level organisms**
- Effects of the plastic-mediated chemical exposure

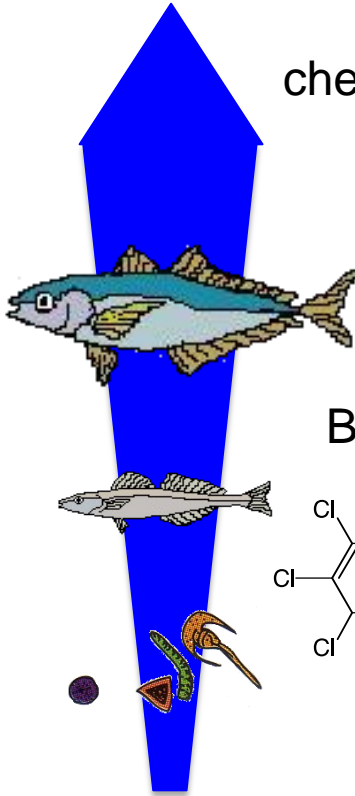
Exposure of contaminants both from plastics and prey



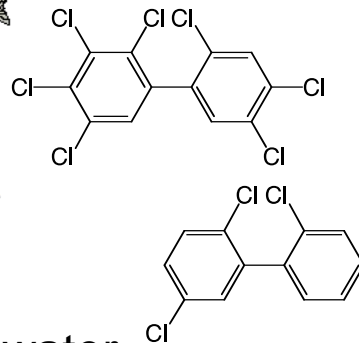
Plastic-derived
chemicals



chemicals from prey



Biomagnification



POPs in seawater

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

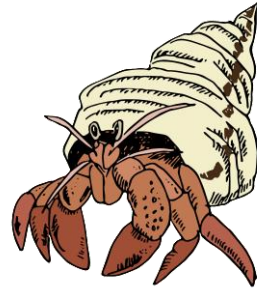


remote island in Okinawa

Plastic contaminated beach



Microplastics in digestive tract of Hermit Crab



0 – 13 pieces/g-wet

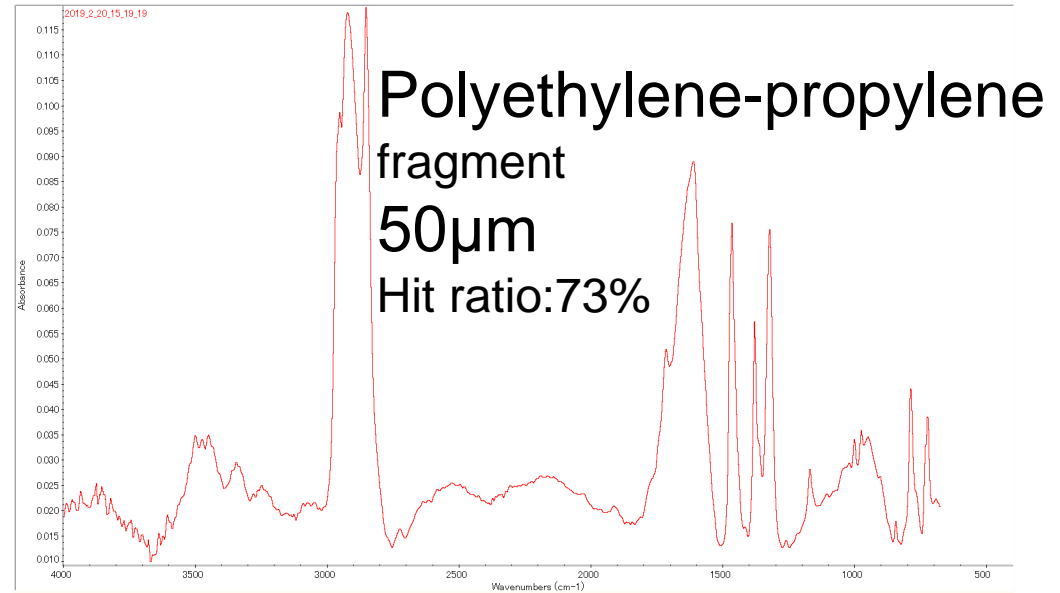
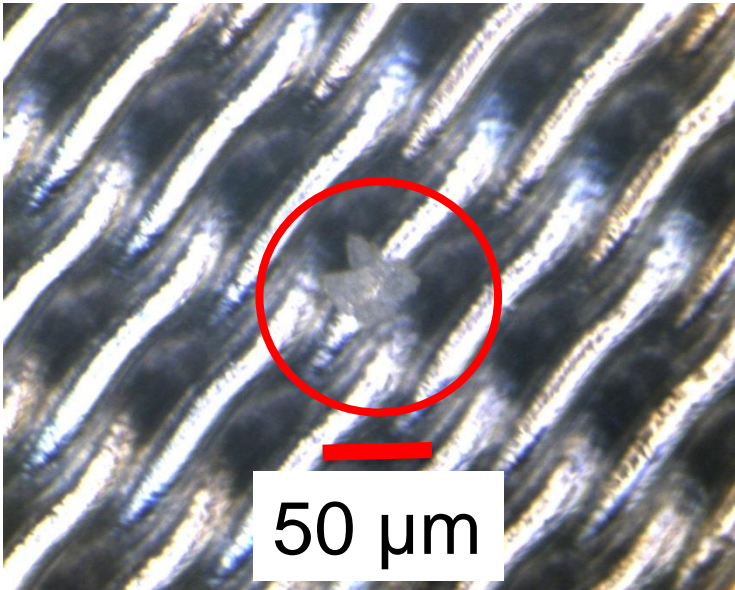
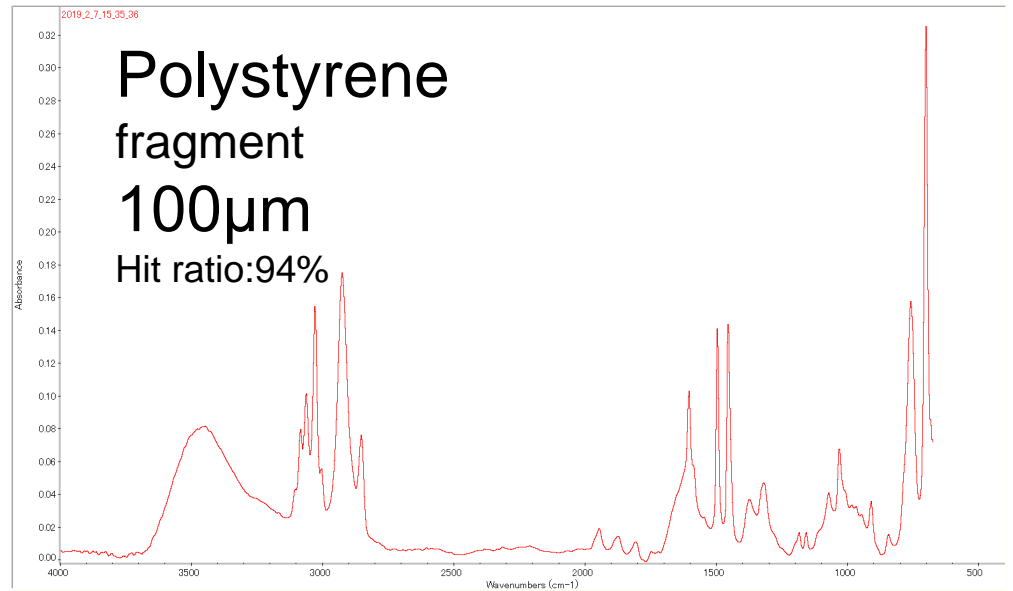
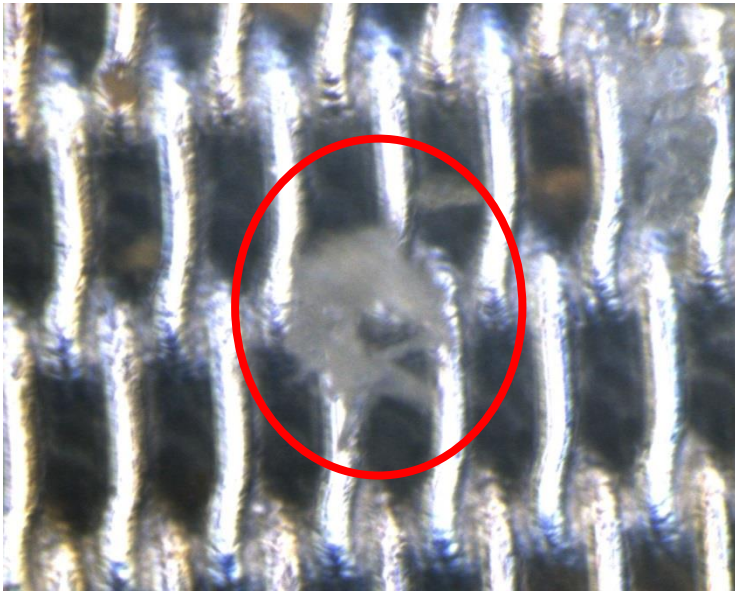
Control
beach



293 - 482 pieces/g-wet

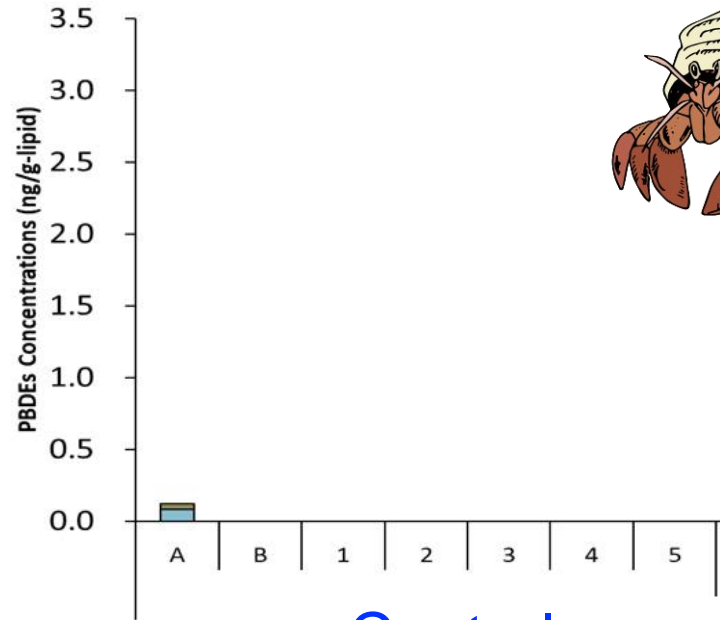
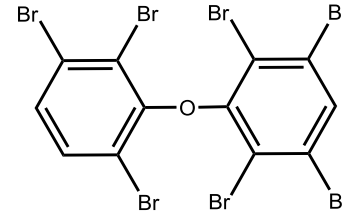
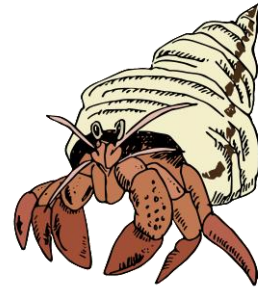
Plastic
contaminated
beach



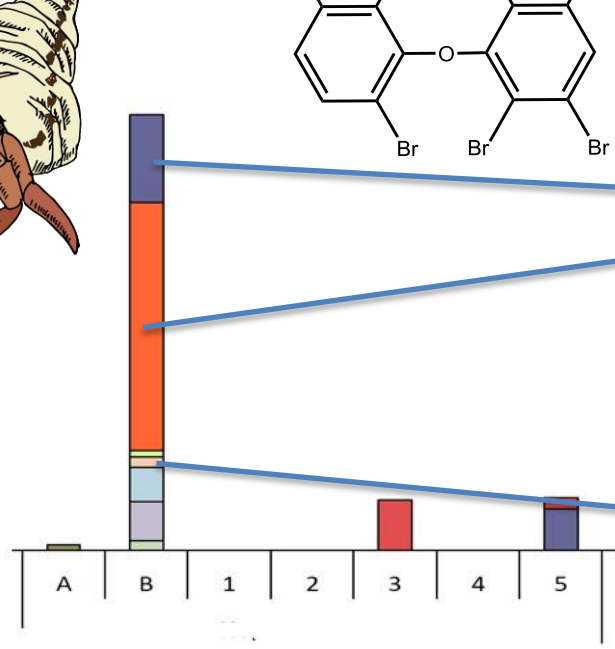


Images and FTIR spectrum of microplastics found in stomach of Hermit Crab

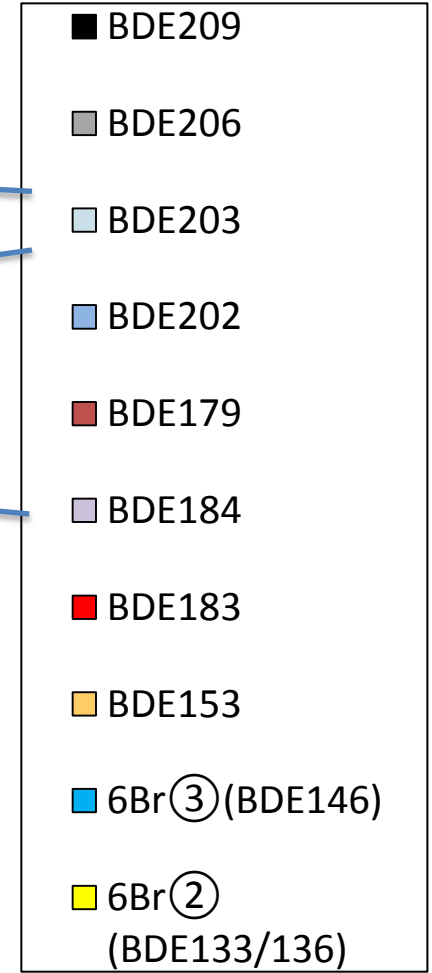
PBDEs (Additives : Brominated flame retardants) in hepatopancreas of Hermit Crab



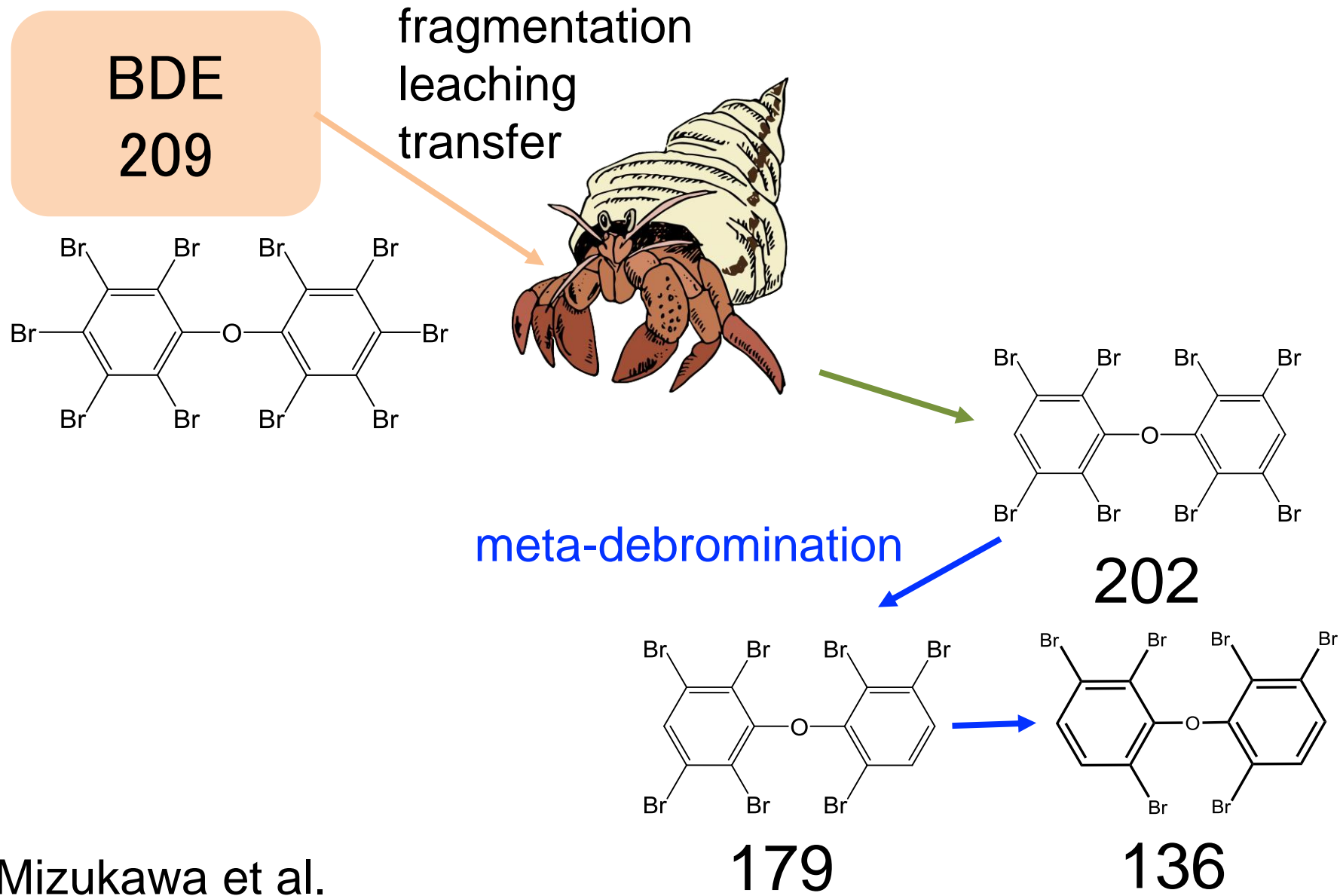
Control beach



Plastic contaminated beach



BDE209 was transferred to internal metabolic system and debrominated



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

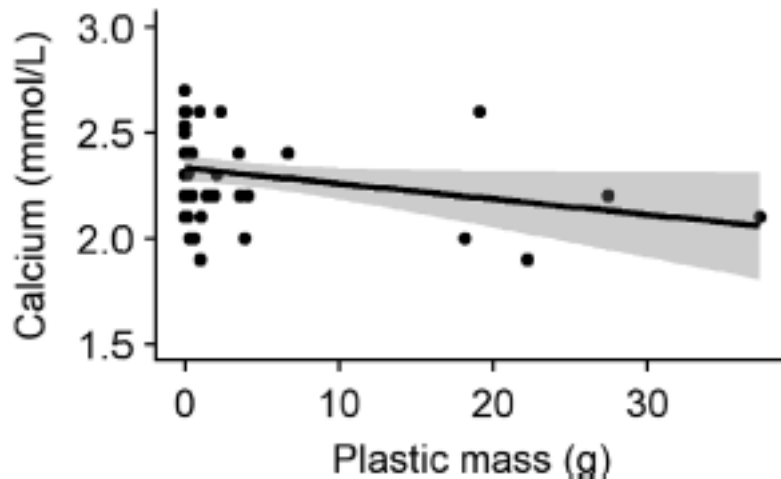
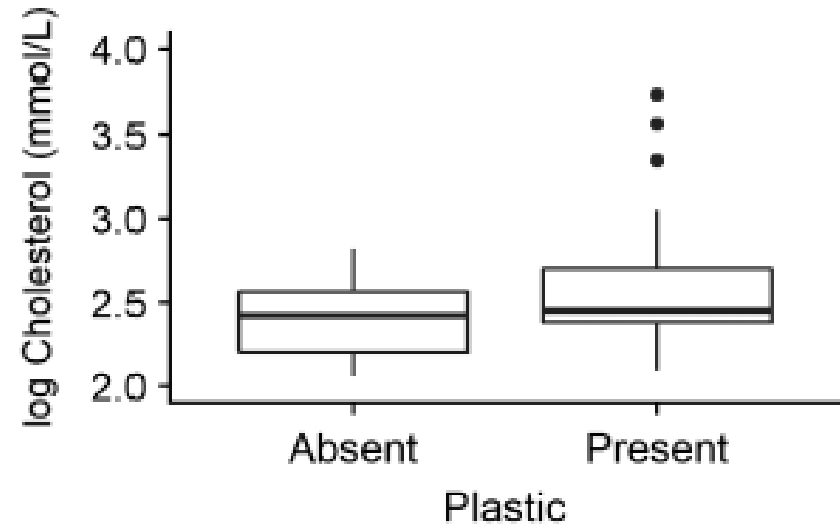
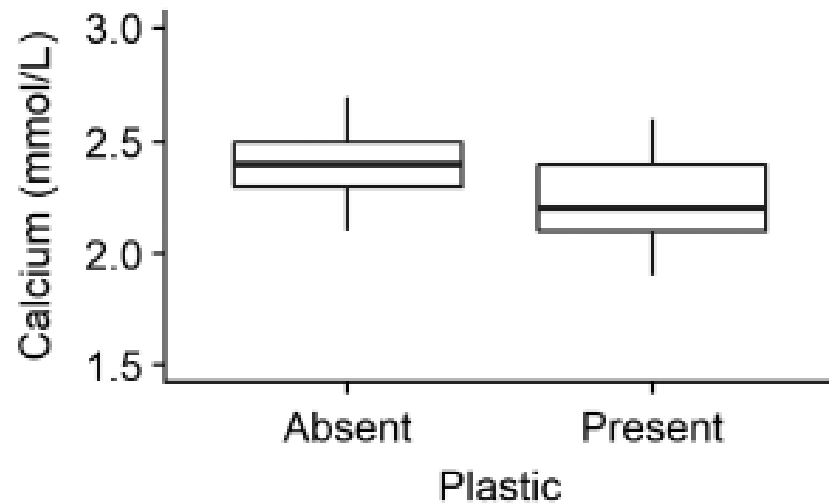
Flesh-footed shearwater from Southern pacific



Flesh-footed Shearwater
March 2005 Photo: Chris Collins

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

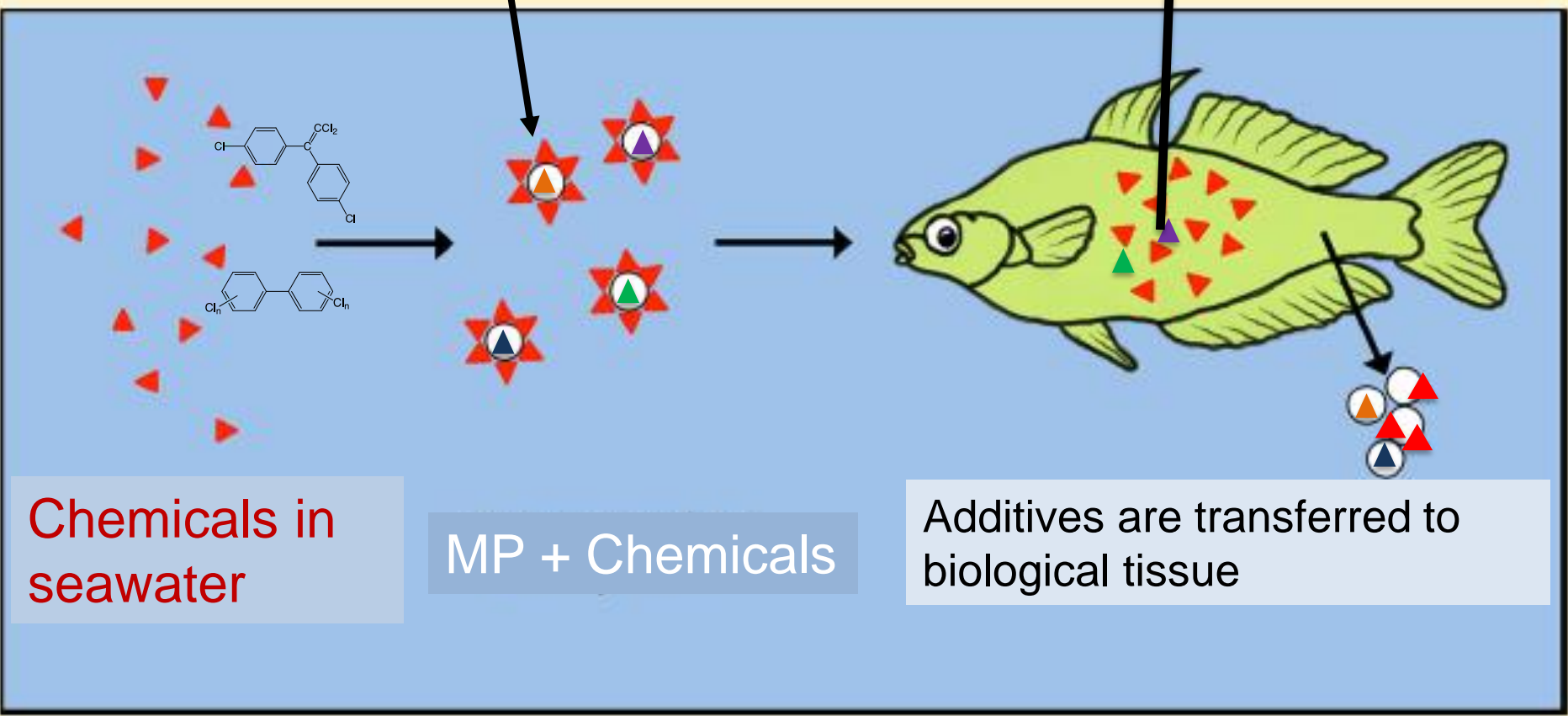
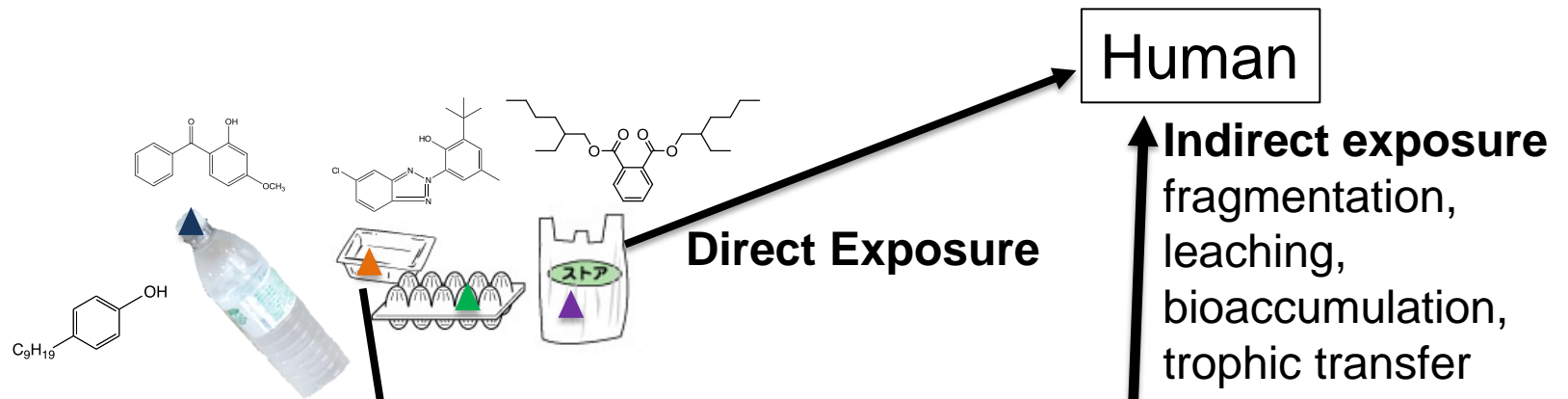
Jennifer L. Lavers,^{*,†}  Ian Hutton,[‡] and Alexander L. Bond^{†,§} 



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 ^{1,2,*}, Niels Jørgensen ³, Anderson Martino-Andrade^{2,4}, Jaime Mendiola⁵, Dan Weksler-Derri⁶, Irina Mindlis², Rachel Pinotti⁷, and Shanna H. Swan²

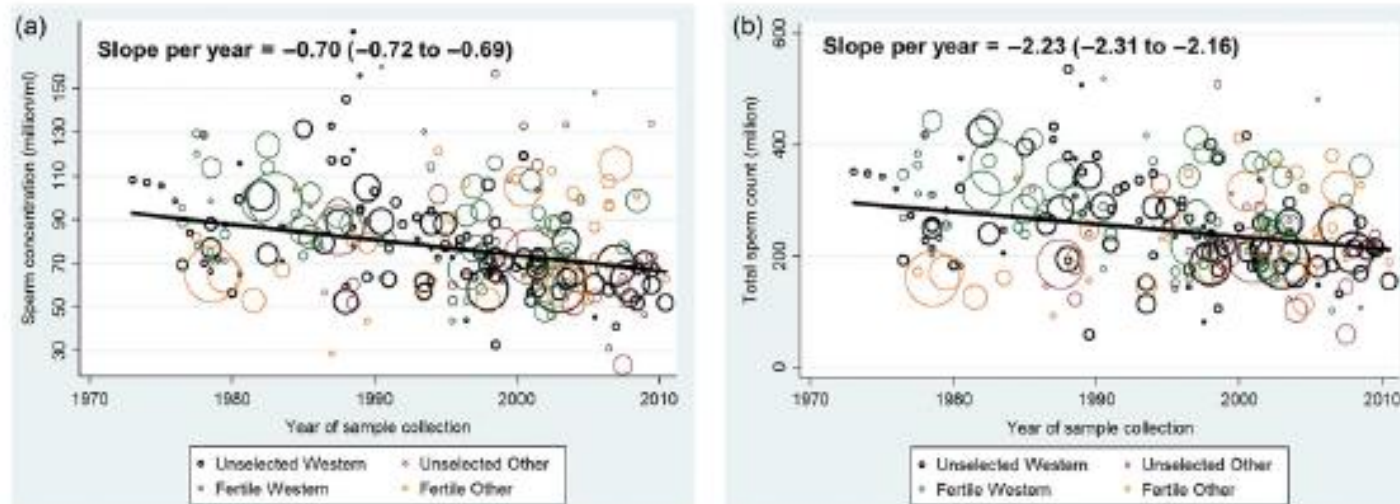


Figure 2 (a) Mean sperm concentration by year of sample collection in 244 estimates collected in 1973–2011 and simple linear regression. (b) Mean total sperm count by year of sample collection in 244 estimates collected in 1973–2011 and simple linear regression.

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 μm -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

