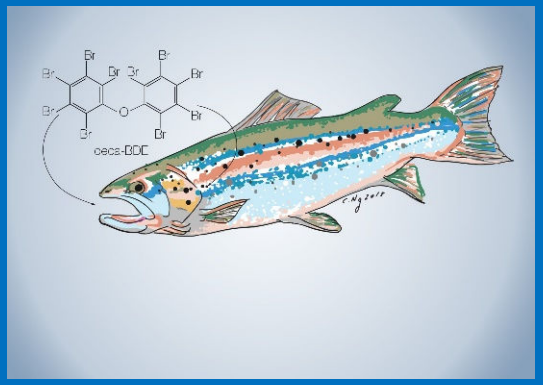
Perspectives on legacy & emerging contaminants in Virginia waters



Rob Hale, Professor
VIMS, Ecosystem Health Section
Hale@vims.edu

Potomac Watershed Roundtable
July 12, 2024

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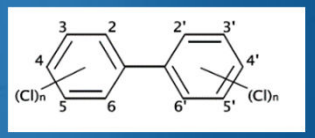
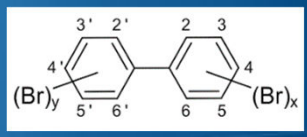
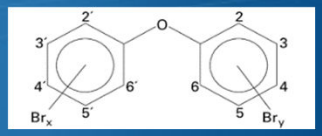
"Trace" pollutants

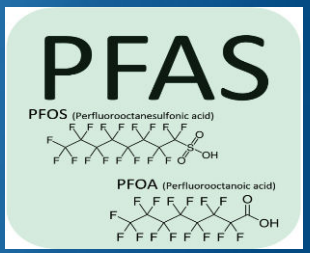
- Metals
  - Pb, Hg, Cu, Cd, As, Ni, Se, Ag, Th, Cr, Zn

+ Cl, Br, F

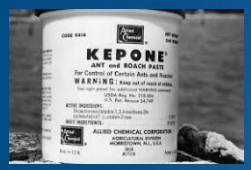








- "Organic" chemicals contain *Carbon*
  - Immense variety: ~350,000 used commercially
    - Plus impurities, breakdown products…
  - Only 126 EPA Priority Pollutants
  - 96,000 in 1976 Toxic Substances Control Act (TSCA) inventory



  - 1975 VA Kepone incident convinced US House of Representatives to pass TSCA

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Kepone: insecticide produced in Hopewell, VA circa 1966-1975, polluted James River

Human health/economic/ecological disaster

Kepone banned in U.S. in 1975

Upper James

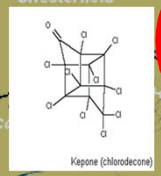
Middle James

James River Closed to Fishing

Lower James

Hopewell

VIMS



Kepone Firm Workers' Kin To Be Tested

By James Ezzell
Times-Dispatch State Staff

HOPEWELL — Members of the families of employes and former employes of Life Science Products Co., Inc., of Hopewell are being examined to determine if they might be affected by Kepone poisoning.

Chemical poisoning from Kepone, a pesticide ingredient

charges and was examined and taken to the Medical College of Virginia Hospital in Richmond.

Doctors said James Rodgers' symptoms were "as bad if not worse" as those of some of the employes already hospitalized.

Dr. Robert S. Jackson, chief

Continued on Page 7, Col. 1

James River
Middle Reach

Shoals, Placement Areas, & Landmarks

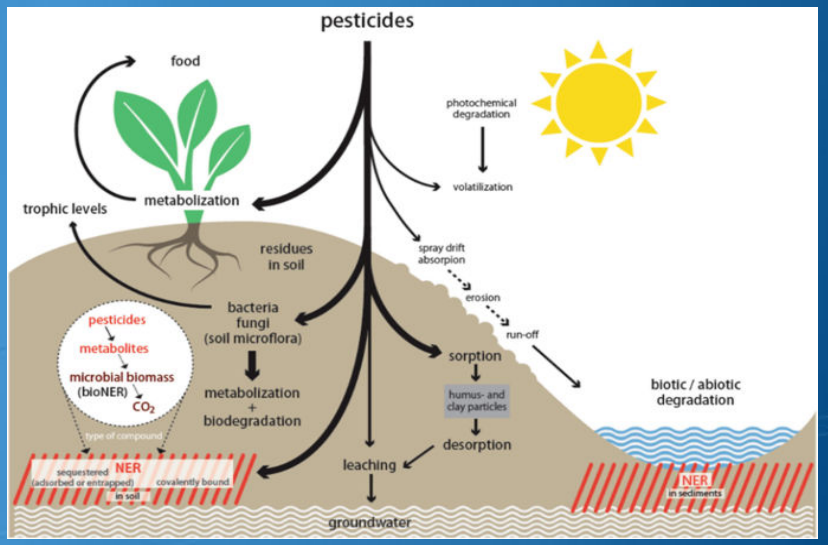
Legend

Major Roads
County Boundary
Placement Site
Maintained Channel Sections
Lower
Middle
Upper

Miles

Norfolk District
US Army Corps of Engineers

- **Chemicals exhibit different properties**
  - Water solubility
  - Volatility (air)
  - Environmental persistence
  - Bioaccumulation potential
  - Toxicity



- Affects how chemicals move in environment, expose & affect organisms

- "PBT" chemicals (persistent, bioaccumulative, toxic)
  - e.g., Kepone, PCBs, PBBs, PBDEs, microplastics, PFAS

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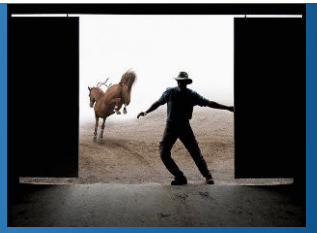
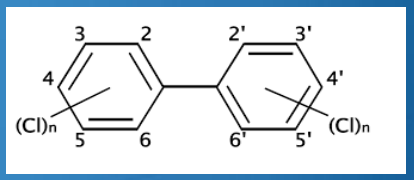
Legacy Pollutants



Historical environmental contaminants with health risks

- e.g., polychlorinated biphenyls (PCBs)



- Regulations limiting their usage/disposal/releases
  - Note that EPA Priority Pollutant List created in 1977
    - not updated since

An Industrial Poison Lingers On... and On

PCB: We May Never Get Rid of It

By Hugh Grambau

It's in fish and chickens and cows. It's in fluorescent light fixtures, envelopes, and fork-lift trucks. And if you've been drinking the water and breathing the air, it's probably in you.

It's one of those versatile synthetic hydrocarbons, like plastic and DDT. This one is called polychlorinated biphenyl, or PCB for short.

Because of PCB, you can't buy Coho salmon at the grocery store, and fishermen are advised not to eat it more than once a week. The success of Michigan's effort to restock the lakes with game fish is threatened. And workers in factories here and elsewhere may be showing signs of Yusho disease—PCB poisoning.

We've known PCB was harmful for 40 years, but we're just getting around to banning it.

Chester Georgic, a retired operating engineer, used to take care of a boiler-heater system for melting resins at the Inmont Paint Corporation plant on Milford (near Livernois and Warren) in Detroit.

The heater, like many others in the auto plants around the city, operated much like a home hot-water heating system—except that instead of circulating water, it circulated a clear, smooth-flowing liquid with the consistency of thin oil called Aroclor.

Aroclor is the trade name that Monsanto Chemical Corporation gave to PCB, which was first produced in 1929 and found many industrial applications during and after the second World War, due to its chemical and thermal stability, non-flammability, and non-conductivity.

Georgic worked on the heater from May 1958 until he left work in January 1971, suffering from a back injury, a persistent skin condition, and a feeling of weakness and lethargy.

His responsibilities on the job included drawing samples of Aroclor out of the system into a bucket to test the viscosity about once a month. He wore no protective mask and inhaled whatever fumes blew his way. On other occasions, when he would have to add more Aroclor to the theoretically "closed" system,

continued on page 3

1976
Ann Arbor Sun
article

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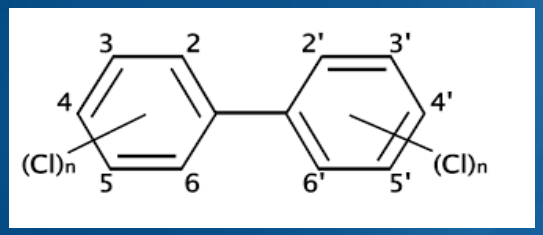
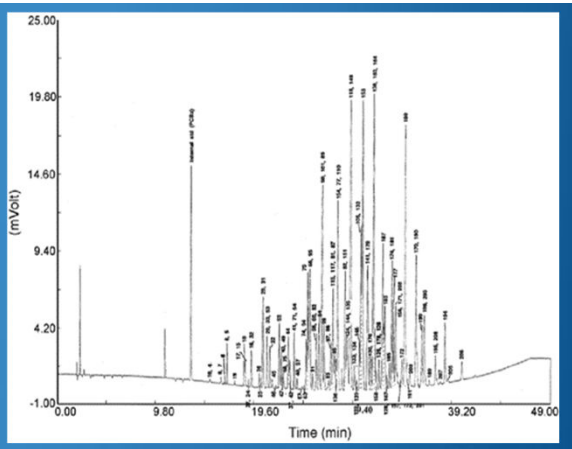


PCBs



- 1929: Monsanto produces first mixtures

  >209 possible "congeners"

  Wide uses: plastics, transformer & hydraulic fluids, inks, sealants, carbonless copy paper, paint…

- 1966: detected in Swedish fish & eagles Million-fold concentration from water

- 11 years later Monsanto stopped PCB production. But in-place uses continue
- 1979: EPA banned new uses of PCBs

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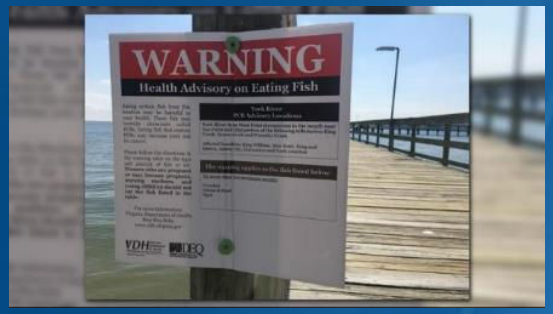
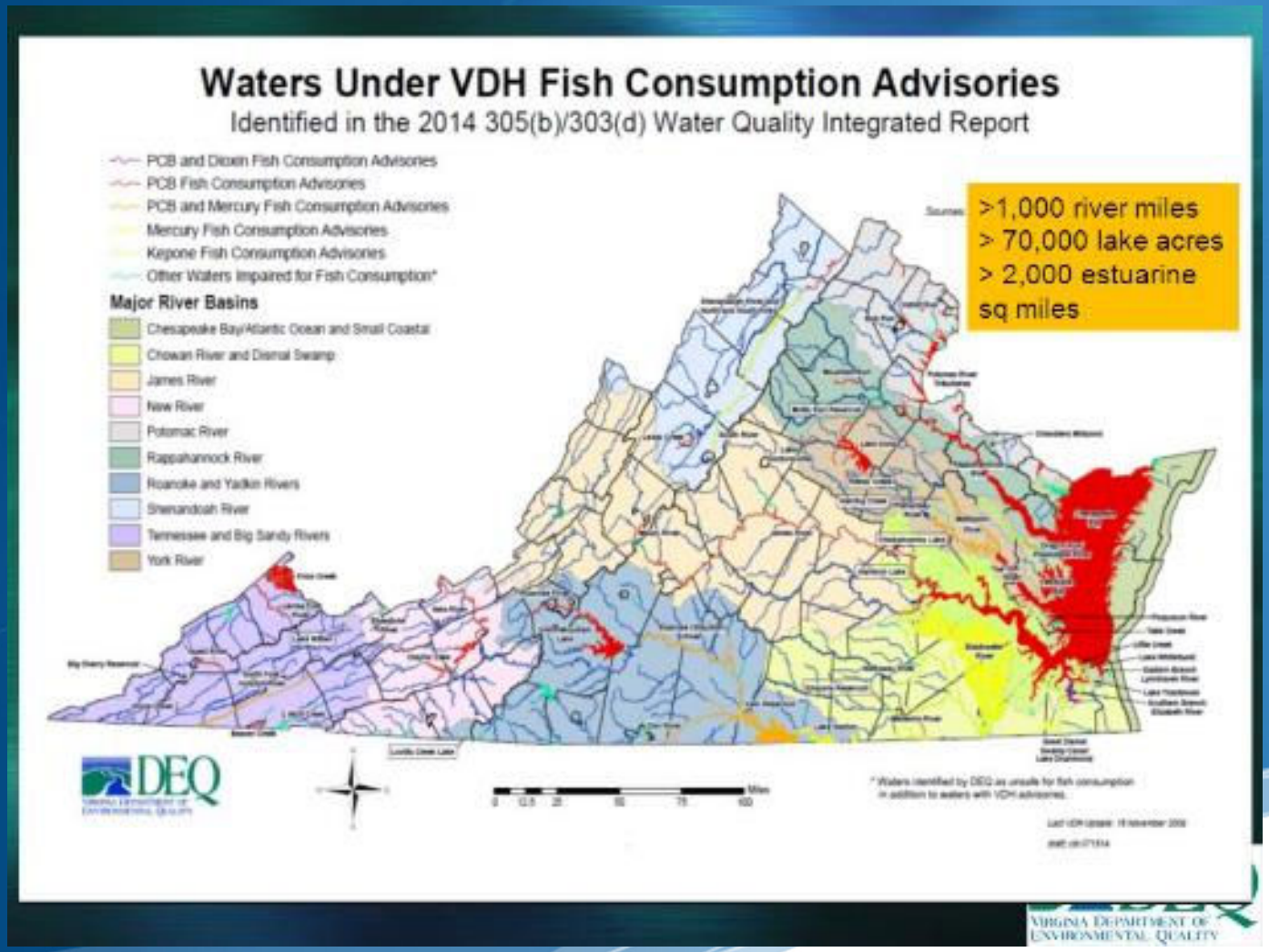
Fast Forward…PCBs in VA fishes…remains an issue today





"Safe" level fish (wet weight) from 2000 to 600 to 50 ug/kg (parts per billion)

https://www.vdh.virginia.gov/environmental-health/public-health-toxicology/fish-consumption-advisory/

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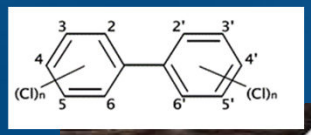
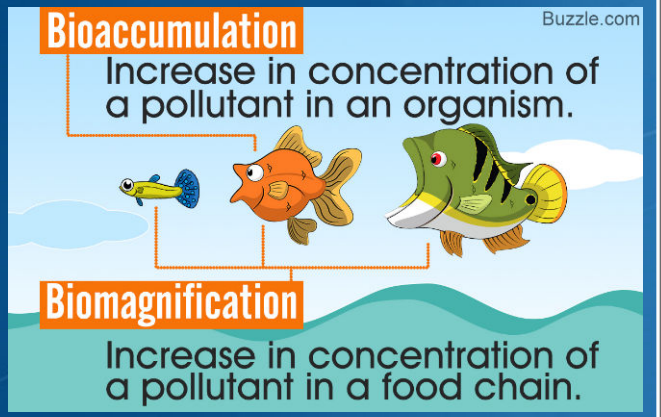




VIRGINIA FISH CONSUMPTION ADVISORY FOR POTOMAC RIVER (GENERAL POPULATION)

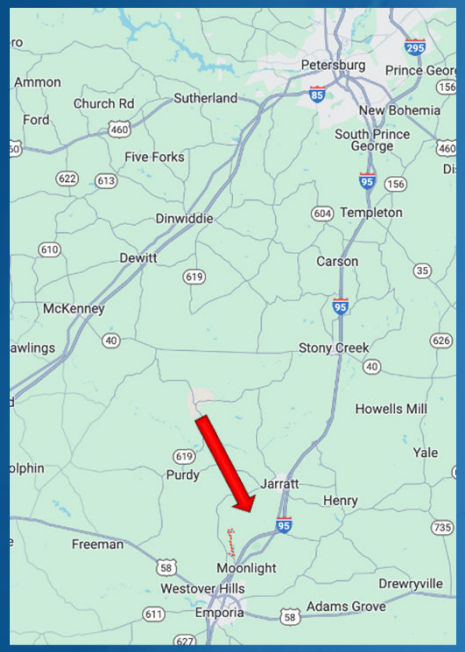
FISH SPECIES	CONTAMINANT	ADVISORY DESCRIPTION	WATERBODY & AFFECTED BOUNDARIES	AFFECTED LOCALATIES
American Eel	PCBs	No more than 2 meals/month	Potomac River Basin	Fairfax Co. & Arlington Co.
Common Carp	PCBs	DO NOT EAT	Potomac River Basin (the tidal portion of the following tributaries and embayments from I395 bridge (above the Woodrow Wilson Bridge) to the Potomac River Bridge at Rt. 301: Four Mile Run, Hunting Creek, Little Hunting Creek, Pohick Creek, Accotink Creek, Occoquan River, Neabsco Creek, Powell Creek, Quantico Creek, Chopawamsic Creek, Aquia Creek, and Potomac Creek. These tributaries comprise ~126 miles)	Arlington Co., Alexandria City, Fairfax Co., Prince William Co., Stafford Co.
American Eel	PCBs	DO NOT EAT		
Channel Catfish ≥ 18in	PCBs	DO NOT EAT		
Channel Catfish ≤ 18in	PCBs	No more than 2 meals/month		
Bullhead Catfish	PCBs			
Largemouth Bass	PCBs			
Anadromous (coastal) Striped Bass	PCBs			
Sunfish species	PCBs			
Smallmouth Bass	PCBs			
White Catfish	PCBs			
White Perch	PCBs			
Gizzard Shad	PCBs			
Yellow Perch	PCBs			

Source: Virgnia Department of Health. For complete information about Fish Consumption Advisories, please refer to Virginia Department of Health website

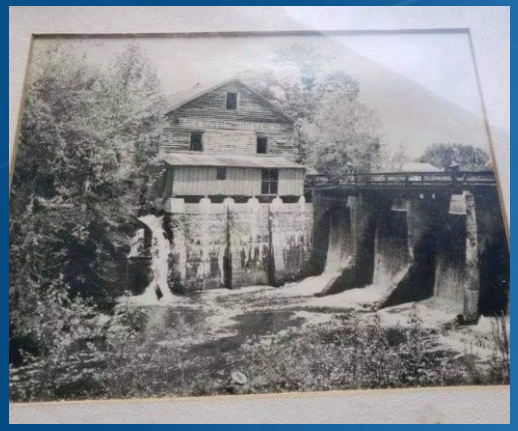
2024 DEQ/VIMS/VDH Survey: "New" PCBs?

Slagle Lake/Three Creek

- American eels: PCBs @ 4982 ug/kg dry wt



Derelict mill PCB source?



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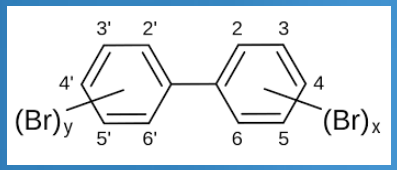
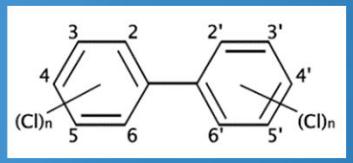
Polybrominated biphenyls (PBBs) flame retardants once used in plastics

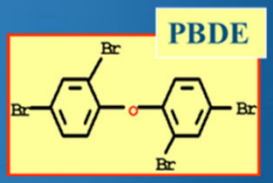
Structural similarities:



PBBs



PCBs



1973 - PBBs accidentally introduced into Michigan livestock feed

>1.5 million farm animal die/killed

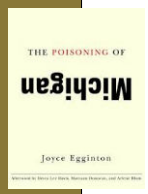
Michigan residents still carry PBB burdens

. $T_{1/2}$ ~10-20 years

PBBs banned in U.S. 1976

Discovery decades later: PBBs accelerates onset of puberty in children

Blanck, H.M. et al. 2002. *Epidemiology* 11:641-647



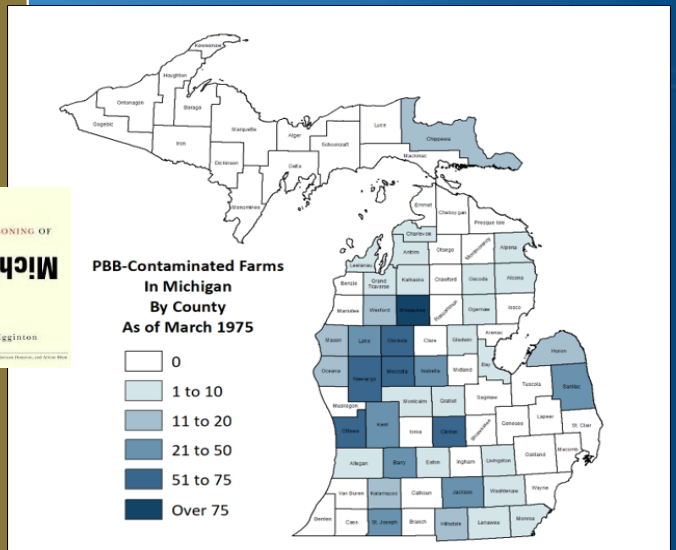


Figure 1: PBB Contaminated Farms in Michigan by County as of March 1975. Adapted from Toxic Substances: Polybrominated Biphenyl (PBB) Contamination in Michigan: Hearings Before the Subcommittee on Science, Technology, and Space of the US Senate Committee on Commerce, Science, and Transportation, 95th Cong. 1st Sess (1977) (testimony of Henry A. Anderson). Table 3

FAST FORWARD

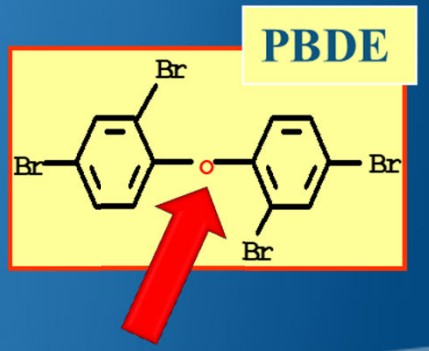
DEQ Virginia Department of Environmental Quality

VDH Virginia Department of Health — Protecting You and Your Environment

1999-2000 Virginia Tributaries PCB Fish Monitoring Project

- Fish collected from different areas annually: DEQ
- Fillets analyzed @ VIMS for PCBs
- Health Advisories issued by VDH

- VIMS detects unknown PBB-like chemicals in all VA fish – **Polybrominated diphenyl ethers (PBDEs)**
  - - discovery scenario similar to 1966 PCB detection by Swedes!



Like PPBs, PBDEs are plastic flame retardants!

- ~20% VA sites had PBDE levels >1000 ppb

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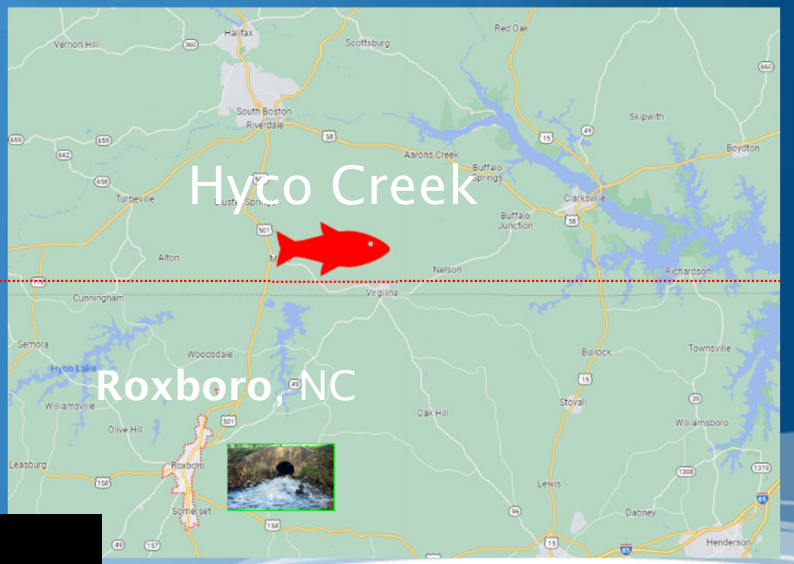
VA PBDE fish level highest in the world!

- 48,000 ug/kg – ironically surpassing an industrialized site in Swedish
- But fish from mouth of small, rural Hyco Creek? (nr South Boston, VA)
- VIMS tracked to NC wastewater treatment plant 20 km upstream - receiving discharges from now-defunct plastics manufacturer in Roxboro.

Roxboro treatment plant

Bales of
Waste plastics



2021: POLYWOOD, a maker of outdoor furniture made from recycled plastics, has announced plans to expand its manufacturing and distribution center located in Roxboro, NC, to include an additional 300 jobs and $61.6 million dollars in capital investment over the next five years.

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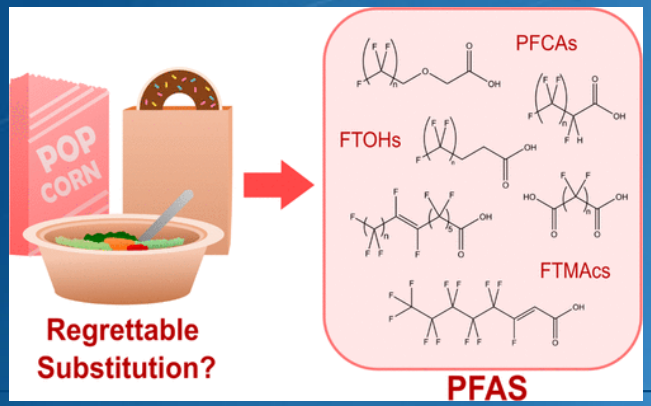
Perfluorinated alkyl substances (PFAS)
Class of F-containing chemicals

~15,000 PFAS compounds?

- Different commercial uses
- Intentional human re-design to reduce negative env. effects?



Class	Molecular Structure	Sources	References
Non-polymers	Chlorinated polyfluorinated ether sulfonate (F53-B)	• Fire Fighting Foams • Chrome Plating Waste	[12,16]
	6:2 Fluorotelomer sulfonamide alkylbetaine (FTAB)	• Fire Fighting Foams • Ceramic Coating	[3,8,9,11]
	6:2 Fluorotelomer sulfonate (FTSA)	• Fire Fighting Foams • Mist Suppressant • Metal Plating • Ink and Toner	[7,11]
	Perfluorooctanesulfonic acid (PFOS)	• Cleaning Products • Metal Plating • Hydraulic Fluids • Fabric Protector	[14,15,17]
	Perfluorooctanoic acid (PFOA)	• Water Filtration • Non-stick Cookware • Stain-resistant Fabrics • Gore-Tex	[13]
Polymers	Polytetrafluoroethylene (PTFE)	• Polymer Gaskets • Chemically Resistant Components • Carpet Coatings	[6,19,20]
Polymers	Viton A/B	• Viton A: General sealing Auto/Aero Fuels Lubricants • Viton B: Gaskets Power-utility seals Chemical Processing	[10,18]

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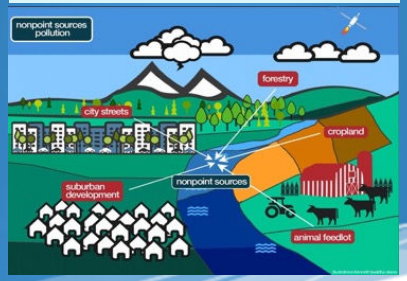
Domestic Sources

Industrial Sources

Fire Fighting Sources

Aqueous Film Forming Foam
AFFF

Nonpoint Sources



2024
EPA Drinking water limit
4-10 parts per trillion

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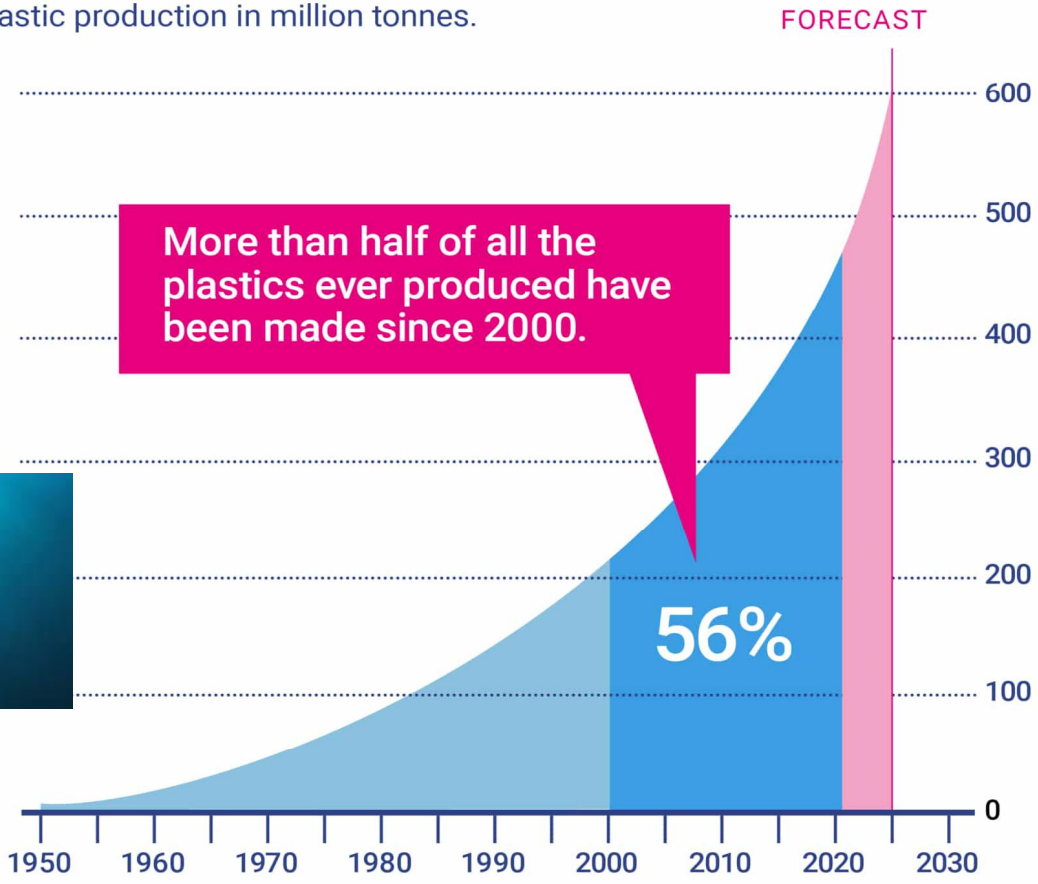
Plastics in the Environment

Modern Society is dependent

PRODUCTION OF PLASTIC

Global annual plastic production in million tonnes.



SOURCE: PLASTIC ATLAS 2019 | © PLASTIC SOUP FOUNDATION

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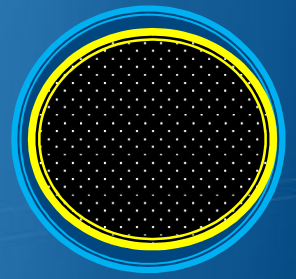
Plastics – complex

Assemblage of material/chemicals

- Differ from "usual" chemical pollutants (e.g., PCBs, DDTs…)
  - **Pollution cluster-bomb: particle & chemical concerns?**

Combination of:

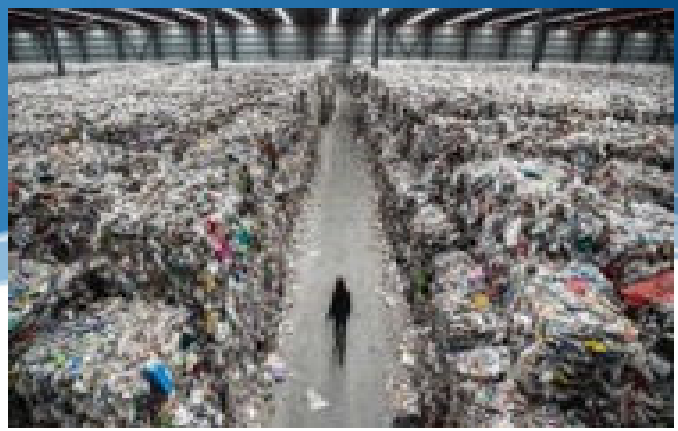
- chemical surface coating
- polymer veneer
- polymer core
- additives, fillers, processing aids…



Understanding composition & uses critical to understanding effects & devising solutions

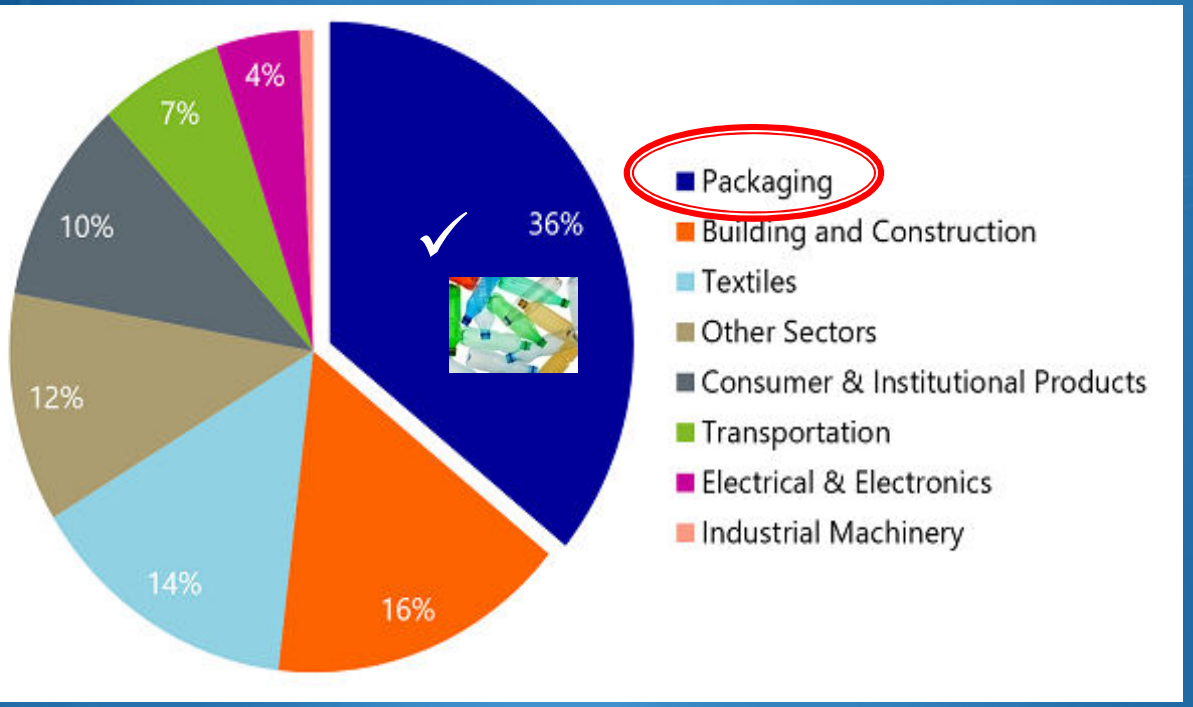
Waste handling formidable challenge

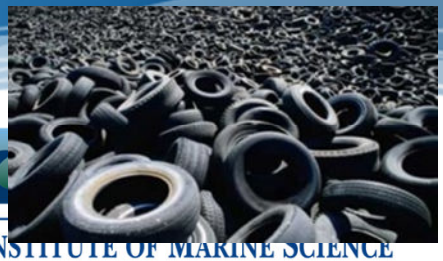
- Recycle, burn, reuse, landfill, litter…
  - **1¢ to make a plastic bag/17¢ to deal with it as waste**



Diverse plastic uses

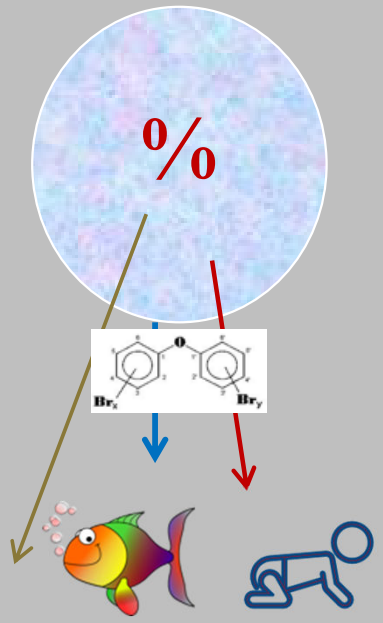
- choose chemical composition
& physical form to meet customer needs





Polymer additives
– modify properties

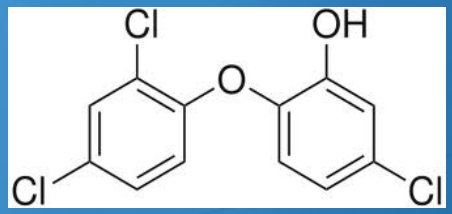
Antimicrobials
Antioxidants
Antistatic Agents
Blowing Agents
External Lubricants
Fillers/Extenders
Flame Retardants
Fragrances
Heat Stabilizers
Impact Modifiers
Lubricants
Light Stabilisers
Pigments
Plasticizers
Process Aids
Reinforcements…



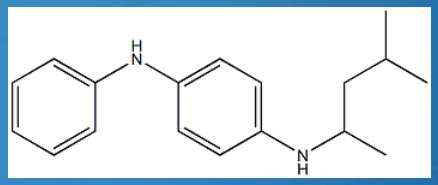
Additives escape?

- Additive properties
- Polymer viscosity
- Distance to "exit"
- Ambient environ. conditions

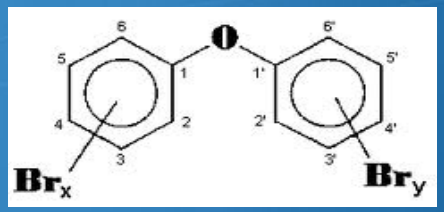
Additive mixtures often *"confidential business information"*



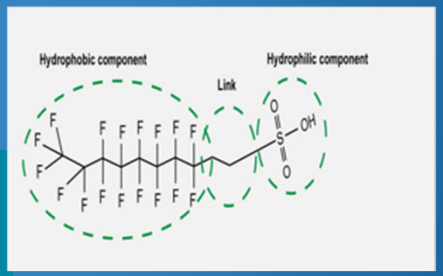
Triclosan



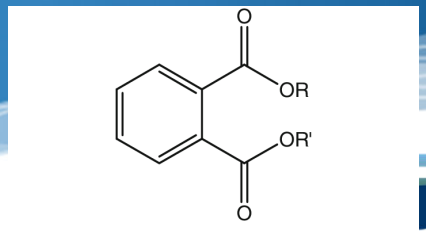
6-PPD



BFRs



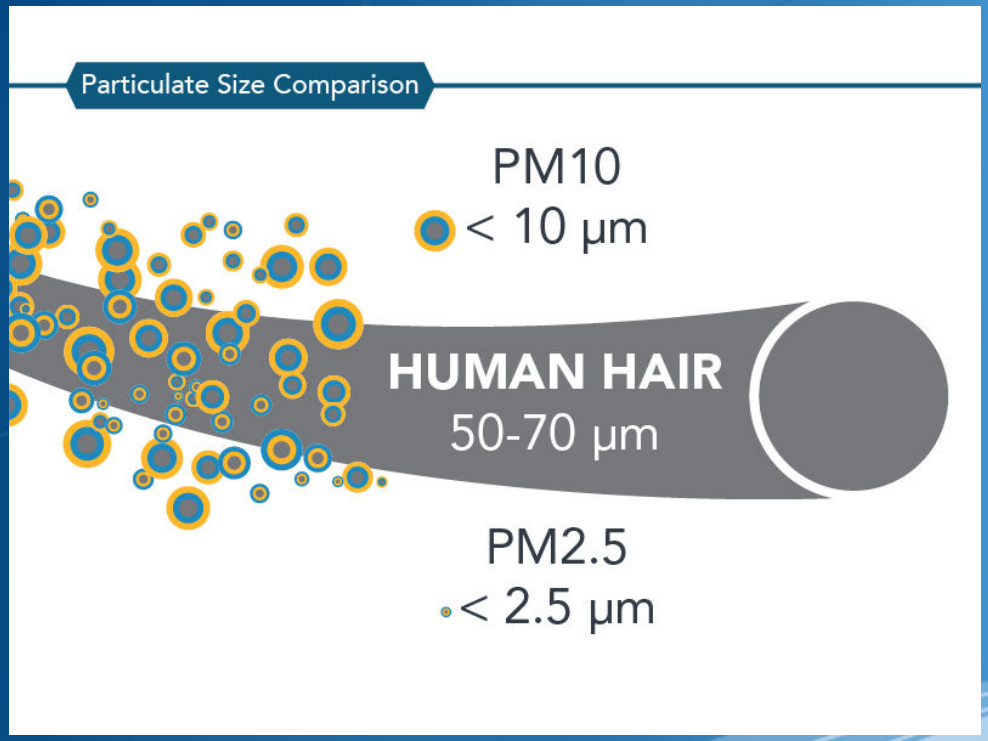
PFAS



Phthalates

Plastics fragment over time

- Macro-plastics >5 mm
- Micro-plastics <5 mm
- Nano-plastics < 1 um
  - Sizes of particles decrease over time



Smaller size increases particle:

- Ease of transport
- Entry into biota
- Relative surface/contact area
- Chemical additive leaching

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Microplastics (MPs) & Wastewater Treatment

- Modern treatment plants: 90-99% MP removal from effluents
  - Surface skimming & sedimentation
  - But MPs concentrate in sludge
    - 60% land-applied as “biosolids”
    - A “new” recycling-derived contaminant?

High PBDEs detected in U.S. “biosolids” in 2001
Hale et al. 2001. Flame retardants: Persistent pollutants in land-applied sludges. Nature 412:141-2.

New EPA/VIMS funded project: Elucidating the occurrence of known and emerging chemical contaminants in wastewater biosolids and the influence of treatment and management processes on their fate, mobility, and bioavailability

Maine & Michigan Farms contaminated by PFAS-containing biosolids

Soil, groundwater, milk, meat

Outcomes reminiscent of Michigan PBB incident from the 1970s

Recent news:

This farmer's (MI) livelihood was ruined by PFAS-contaminated fertilizer that few Midwest states test for

March 11, 2024

These Maine farmers know what PFAS can do to the land — and they want federal help

October 24, 2023

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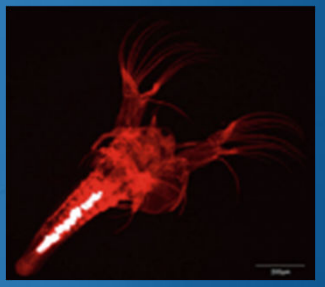
Microplastic Biological effects

The "So What" Question



MP <u>physical effects</u> due to ingestion/entanglement possible for large…but also minute organisms

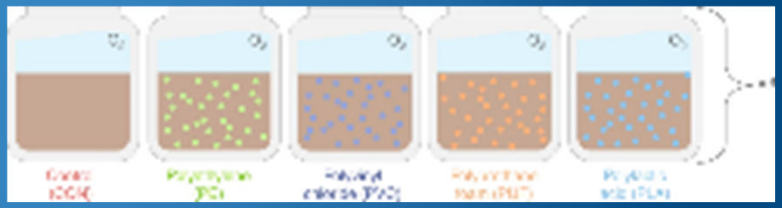
- Gill/gut blockage, feeding satiation, abrasion
- <10 um particles penetrate cell membrane

Exposure/toxicity: leachable MP chemical additives (e.g. phthalates, flame retardants, tire antioxidant degradates

- Tian et al. 2021. *Science* 371(6525), 185-189

MP presence alters microbial community species composition & N cycling in marine sediments

- Seeley et al., 2020. *Nature Comm*. 11, 2372



Interactions of plastics & infectious disease on host health/survival (postulated for coral diseases by Lamb et al. 2018. *Science* 359 (6374), 460-462

Microplastics in the Real World - Multiple-stressors

VIMS Study – Does microplastic/virus co-exposure increase mortalities/disease susceptibility in a commercial salmonid species?

funded by NOAA Marine Debris Program

Fish: rainbow trout (*Oncorhynchus mykiss*)

Disease: *Infectious hematopoietic necrosis virus* (IHNV): major disease/mortality in salmonid fishes

Seeley et al. 2023. Microplastics exacerbate virus-mediated mortality in fish. *Sci. Total Environ.* 866. 161191

doi.org/10.1016/j.scitotenv.2022.161191

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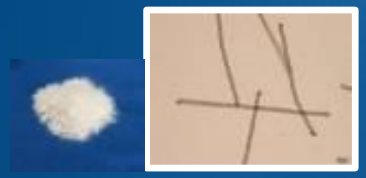
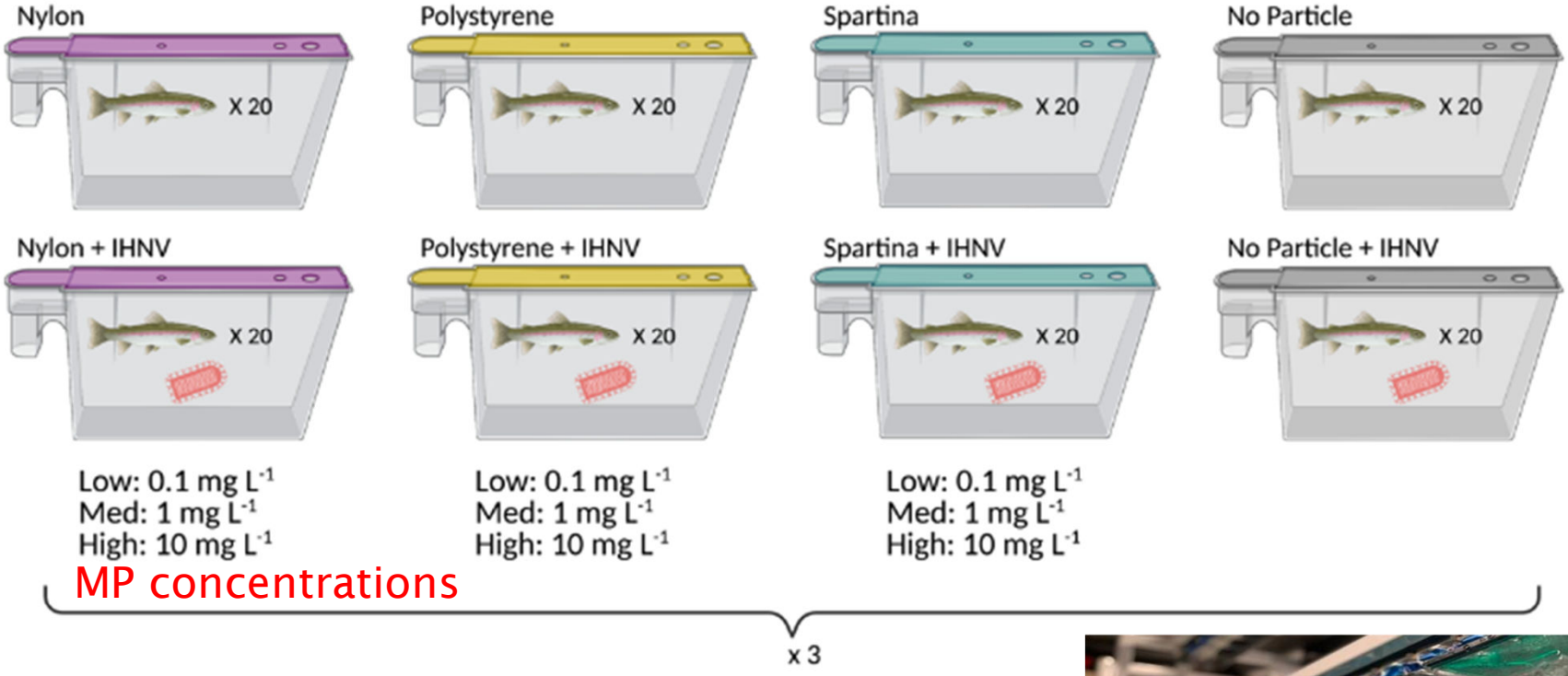
In-vivo Experimental Design: fish, MP, virus



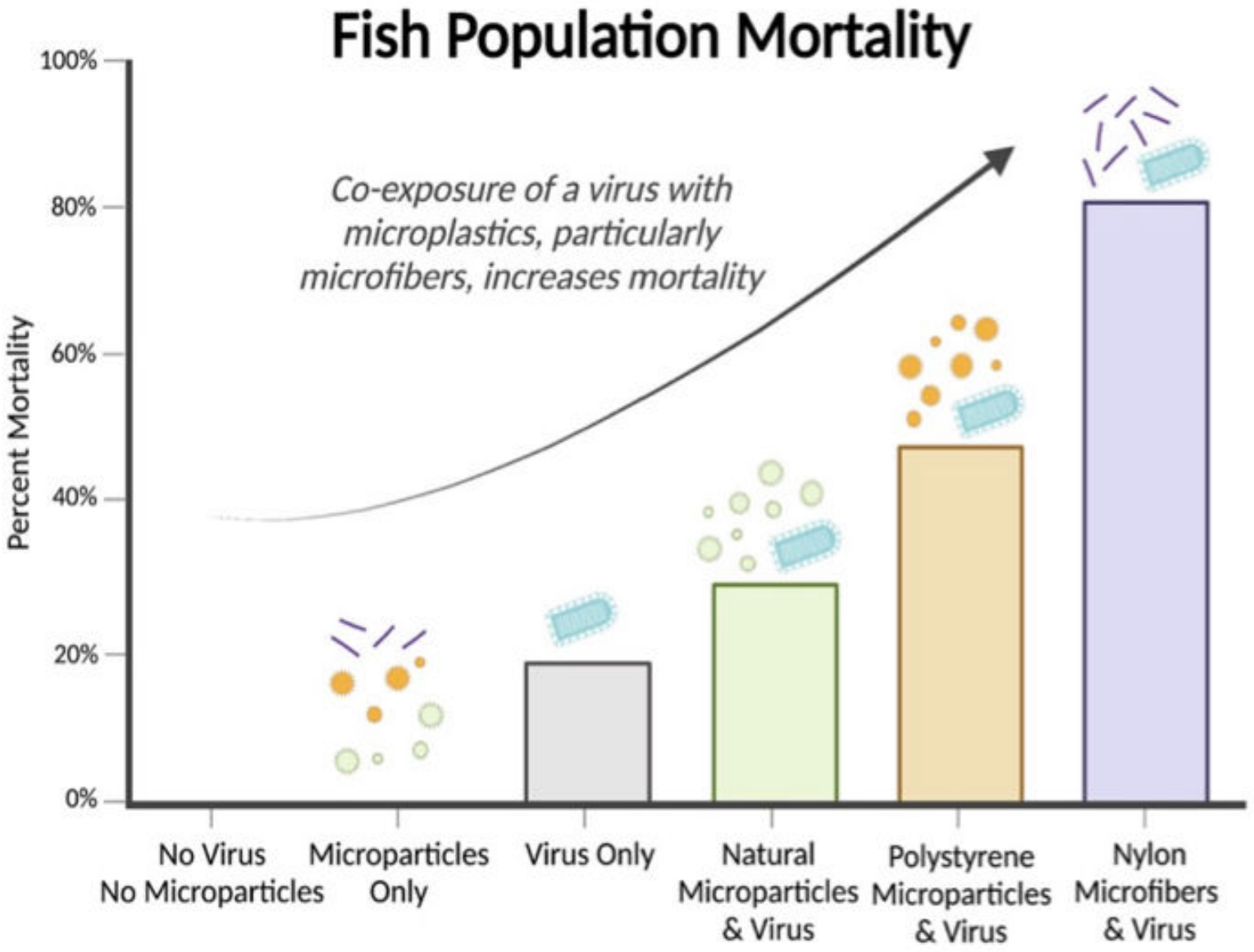
none

IHNV



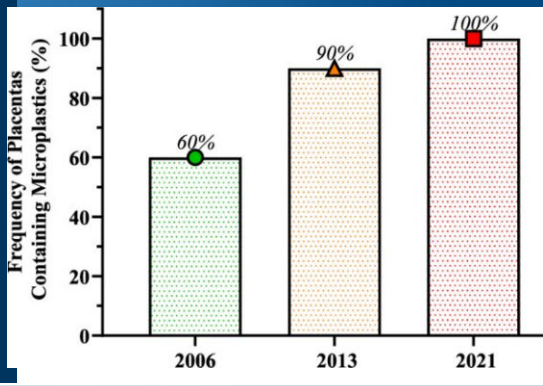
68 tanks and 1340 fish total

Fish Mortalities following exposure to microplastics, IHN virus or both together?



Exposure: Microplastics Indoors? An important issue

- **We spend 90% of our lives indoors**
  - **Surrounded by plastics, with recirculated air**
- **Lung disease from occupational inhalation of nylon fibers**
  - ***DOI: 10.1101/2021.01.25.428144***
- **Additives: U.S. human exposure to PBDE polymer additives dominated by dust ingestion**
  - ***Environ. Sci. Technol. 2007, 41, 5, 1584–1589***
- **Microplastics used in cosmetics, some contain PFAS**
- **Laundering/drying of clothes an indoor source**
- **2023: Temporal trends in microplastic accumulation in placentas from pregnancies in Hawai'i**
  - **DOI: 10.1016/j.envint.2023.108220**



Concluding thoughts

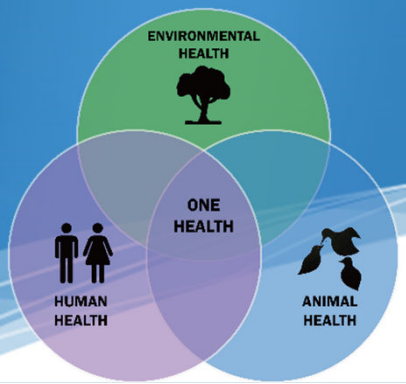
Most synthetic chemicals (+ impurities, degradates…) go untracked in the environment - thus are future "emerging contaminants", depending on their properties

Chemicals with PBT properties (often containing Cl, Br or F) may be most problematic

Recycling recirculates the good (e.g., nutrients) & the bad (e.g., banned polymer additives)

Chemicals exist in products & the environment as mixtures.
These include microplastics
Organisms (including us) are exposed to "combinations"

Yes, I still eat fish!



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REDUCE EXPOSURE

- PCB's **accumulate in the fatty tissue** of the fish. You need to clean and cook the fish in ways that **reduce fat**. Don't know where to find the fat in the fish? See the image below.
- Mercury **builds up in the muscle tissue** of the fish, so you can NOT reduce your exposure by following specific preparation or cooking instructions…so follow the advisories!

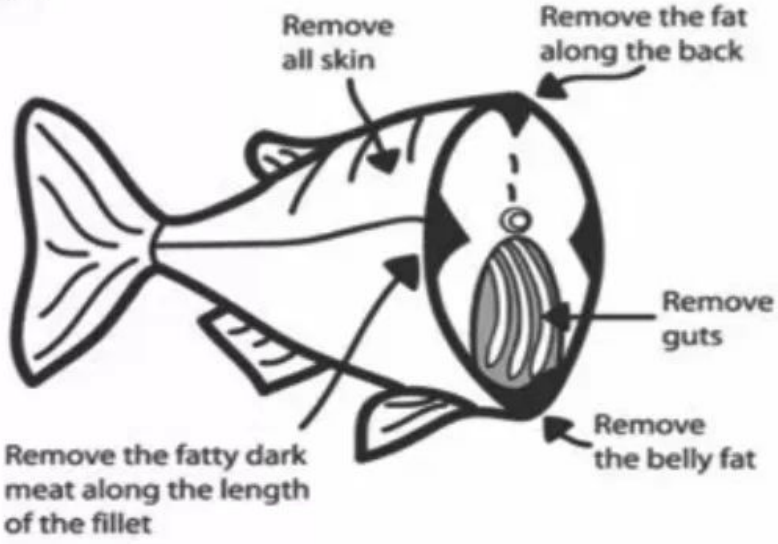

Image Courtesy of AL Dept. of Public Health

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