Ulisses

UNIVERSITY OF LISBON
INTERDISCIPLINARY STUDIES
ON SUSTAINABLE ENVIRONMENT AND SEAS

Contaminants of emerging concern

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Contaminants of emerging concern

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Contaminants of emerging concern

Learning Objectives

- Impacts or threats to the ocean
- Noise pollution
- Contamination *versus* pollution
- Contaminants of emerging concern (CECs): terminology
- Contaminants of emerging concern: old and new problems
- Endocrine disruptor compounds
- Marine impact of CECs: case studies

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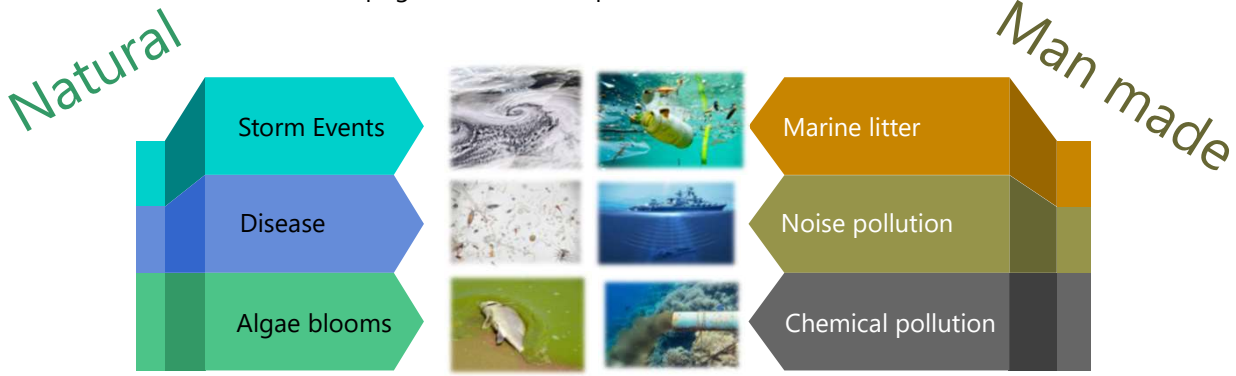
Impacts or threats to the ocean

There are many kinds of impacts or threats to the ocean. Some are natural, like storms, and some are from the anthropogenic source, like pollution.



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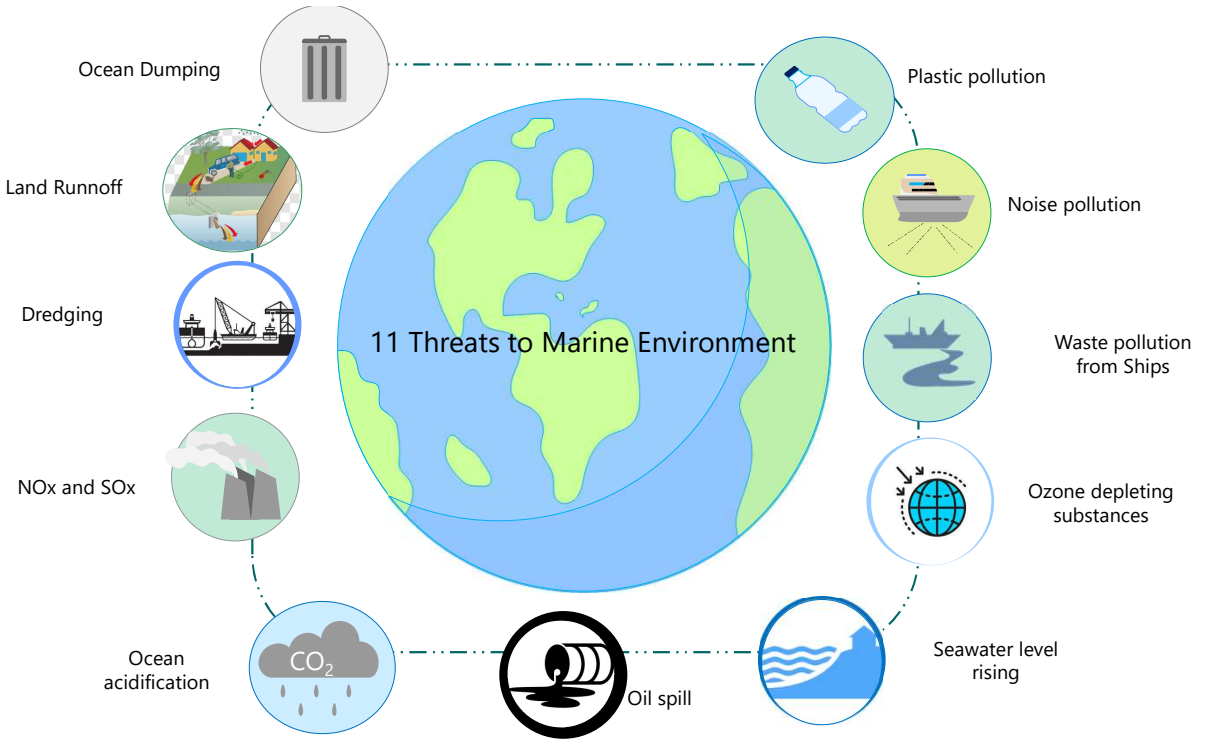

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Noise pollution

Underwater sounds travel five times faster and 60 times further than sound travels through air.

Ambient noise levels are predicted to continue increasing in both coastal and deep ocean areas.

Major contributors of man-made sources of sound

- Commercial ships and recreational watercraft
- Oil and gas exploration
- Sonar
- Marine pile driving
- Underground explosions

Natural sources of sound

- Earthquakes
- Wave action
- Wind
- Rain
- Sounds produced by marine animals

https://www.boem.gov/sites/default/files/oil-and-gas-energy-program/GOMR/Marine-Mammals-And-Noise-Fact-Sheet.pdf

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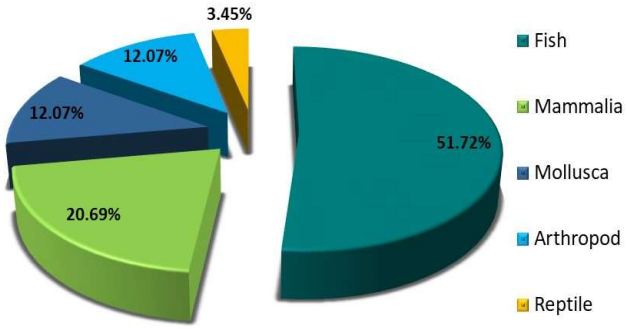
Noise pollution

Noise pollution is any man-made noise that might be louder than the natural sounds in the ocean !!!

Marine animals, use sound for:

- feeding
- navigation
- predator avoidance
- reproduction

Noise may cause stress in animals, increase the risk of mortality by unbalancing predator-prey interaction, and interfere with sound-based orientation and communication, especially in reproductive contexts.



Chao *et al*, Noise in the Sea and Its Impacts on Marine Organisms, Int J Environ Res Public Health, 2015, 12(10): 12304–12323.

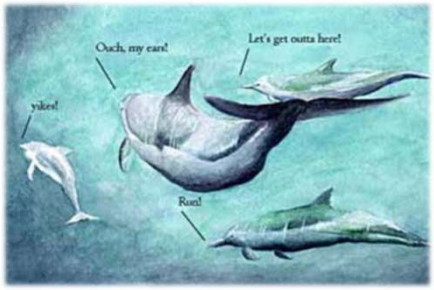
Noise pollution

Whale stranding!

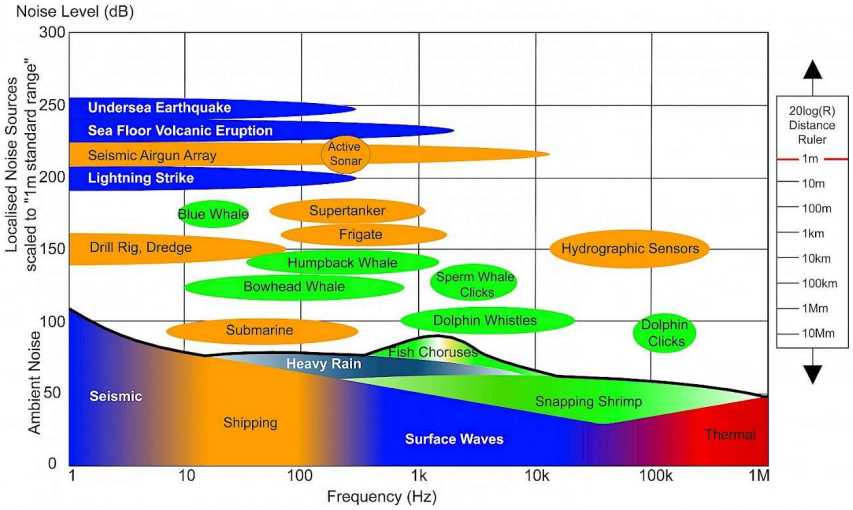
https://www.oceancare.org/en/our-work/ocean-conservation/underwater-noise/underwater-noise-consequences/

Dead whales lie on the beach at Farewell Spit on New Zealand's South Island December 28, 2009. More than 100 pilot whales died after being stranded at Farewell Spit, according to local media. The beached whales were discovered by a tourist plane on Saturday. Photo: New Zealand Department of Conservation/Handout via Reuters.

Noise pollution



https://sciencenotes.ucsc.edu/9601/Ocean Noise/00Intro.html



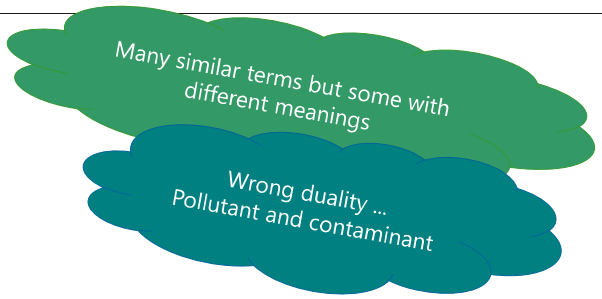
https://www.ospar.org/work-areas/eiha/noise

Contaminants of emerging concern

- Emerging contaminants (ECs)
- Compounds of emerging concern (CECs)
- Contaminants of emerging concern (CECs)
- Emerging pollutants (EPs)
- Emerging substances (ESs)
- Emerging organic contaminants (EOCs)
- Emerging environmental contaminants (EECs)
- Trace organic contaminants (TOrCs)
- New contaminants

- Pharmaceutically active compounds (PhACs)
- Pharmaceutical compounds (PhCs)
- Pharmaceuticals and personal care products (PPCPs)

- Endocrine disrupting compounds (EDCs)
- Hormonally active agents (HAAs)



European Comission, Science for Environment Policy

http://ec.europa.eu/environment/integration/research/newsalert/archive/chemicals.htm

EPA, USEPA
United States Environmental Protection Agency
https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=311604

Contamination *versus* pollution

Increase of any substance ou microorganism

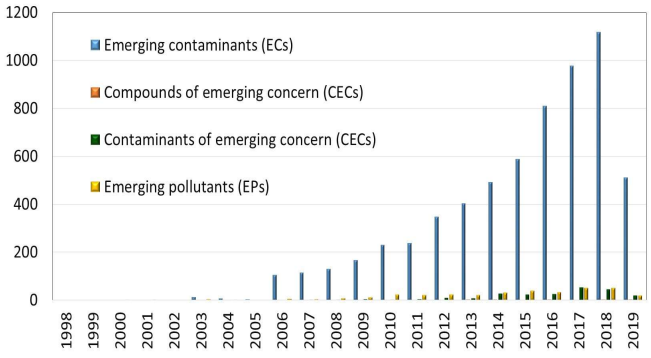
Contamination	Pollution
Transmission of substances or microorganisms harmful to health by water. The presence of a pathogenic organism does not mean that the aquatic environment is ecologically unbalanced. Pollutants may be introduced on time (domestic and / or industrial sewage) or diffuse (agricultural fields and / or urban drainage).	Alteration of its characteristics by any actions or interferences, natural or antropogenic, producing aesthetic, physiological or ecological impacts. The concept of pollution must be associated with water usage.

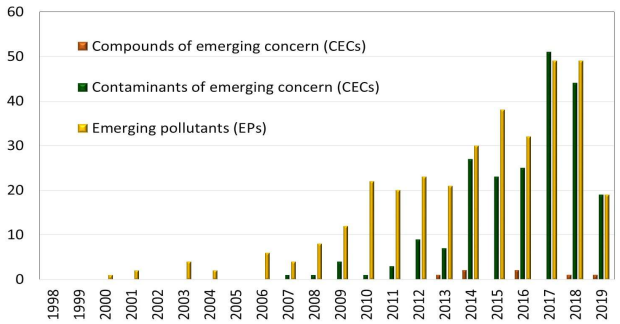
Contamination ≠ Pollution

Contaminants of emerging concern

Nº Publications/year with the designation"_____" título

PubMed, Web of Science Core Collection, 02-05-2019





What is the correct designation?

Emergent contaminants ?

Contaminants of emerging concern?

What is emergent ?

The qualification of what is "emerging" is relative in time !

Emergent contaminants ?

Contaminants that have recently appeared.

Contaminants of emerging concern ?

Contaminants that have been in the environment for some time, but whose concerns are relatively recent

Emergent questions ?

New data or information that presents a new perspective or approach to problems related to contaminants, already well known or more traditional

Contaminants of emerging concern (CECs)

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Contaminants of emerging concern

Definition

Unregulated contaminants, which can become candidates for future regulations, depending on the results of studies on their toxicity and/or harmful effect on the environment and human and animal health and monitoring data related to their occurrence in the environment.

3 Meanings / 3 Approaches

I. Compounds recently introduced into the environment (for example, medicines recently approved by the competent authorities and which, due to their use, start to enter the environment) or compounds that have been present in the environment for some time but whose presence has only recently been detected.

II. Contaminants or unregulated pollutants may become candidates for future regulations, depending on the results of studies on their toxicity and/or harmful effect on the environment and human and animal health, and monitoring data related to their occurrence in the environment.

III. Conventional pollutant already legislated, but due to new data regarding their occurrence, fate or adverse effects, it has become a new focus of attention.

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Contaminants of emerging concern

...and emerging terminology, too!

Acronym	Definition
EC	**Emerging Contaminants**
ECC	**Emerging Contaminants of Concern**
CEC	**Contaminants of Emerging Concern**
OWC	**Organic Wastewater Contaminants (Chemicals/Compounds)**
PPCP	**Pharmaceuticals & Personal Care Products**
PAC	**Pharmaceutically Active Chemicals (or Compounds)**
PIE	**Pharmaceuticals in the Environment**
EDC	**Endocrine Disrupting Compounds (or Chemicals)**
EAC	**Endocrine Active Compounds**
EAS	**Endocrine Active Substances**
MC	**Microconstituents**
AOC	**Anthropogenic Organic Compounds**
AWI	**Anthropogenic Waste Indicators**
TOrC	**Trace Organic Compound**
POP	**Persistent Organic Compounds**

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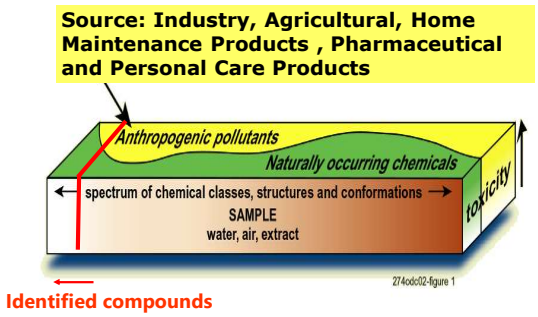
Contaminants of emerging concern (CECs)

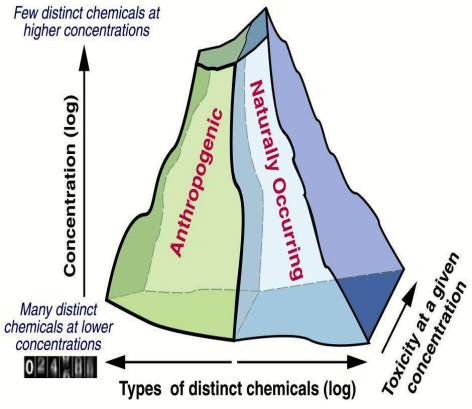
Is it a new problem or phenomena?



No. The problem has existed since the products started to be commercialized. It is a current problem due to the new methodologies of analysis, which allow quantifying these compounds in the order of ppb and even of ppt.

C.G. Daughton

US EPA July 2002



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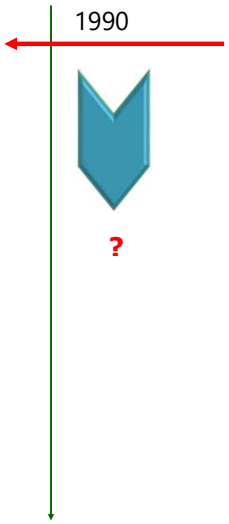
Contaminants of emerging concern

- Algae and cyanotoxins
- Brominated flame retardants (BFRs)
- Disinfection by-products
- Gasoline additives
- Hormones and other compounds with endocrine disrupting action (EDCs, "Endocrin Disruptors Compounds"
- Organometallic compounds
- Organophosphate flame retardants and plasticizers
- Human and veterinary medicines, their metabolites and degradation products
- Pharmaceuticals and Personal care products (PPCP)
- Polar pesticides and their degradation/transformation products
- Surfactants and their metabolites



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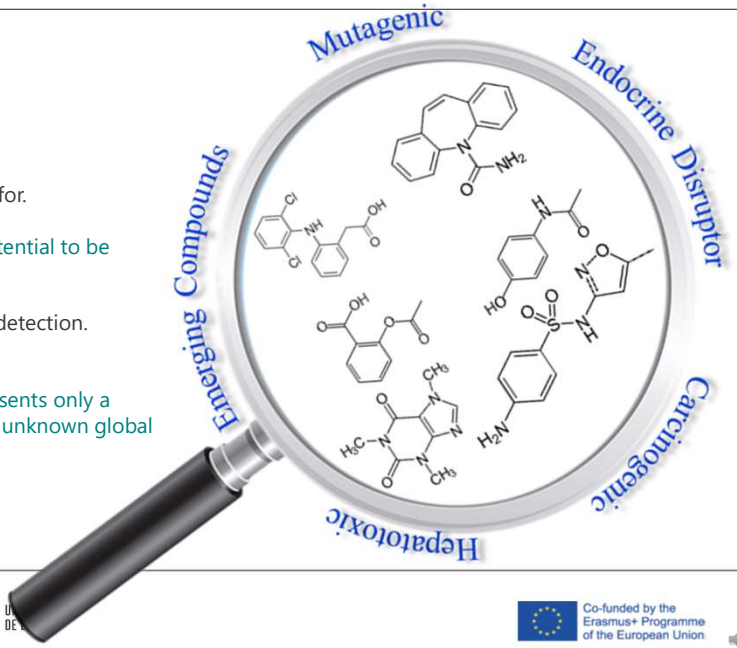
Descriptor 8: Contaminants

- What we find usually depends on what we are looking for.
- In monitoring, only the target compounds have the potential to be identified and quantified.
- All other non-target compounds will elude or confuse detection.
- The spectrum of pollutants identified in a sample represents only a portion of those present in that sample, which have an unknown global risk.



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Contaminants of emerging concern

Sensitivity of analytical method

g/L	1 g/L	Titrimetric
mg/L	10^{-3} g/L	Spectrophotometric
µg/L	10^{-6} g/L	HPLC-DAD
ng/L	10^{-9} g/L	GC/MS (full scan mode)
pg/L	10^{-12} g/L	GC/MS (SIM mode)
fg/L	10^{-15} g/L	GC-MS/MS; UPLC-MS/MS
ag/L	10^{-18} g/L	
zg/L	10^{-21} g/L	
yg/L	10^{-24} g/L	

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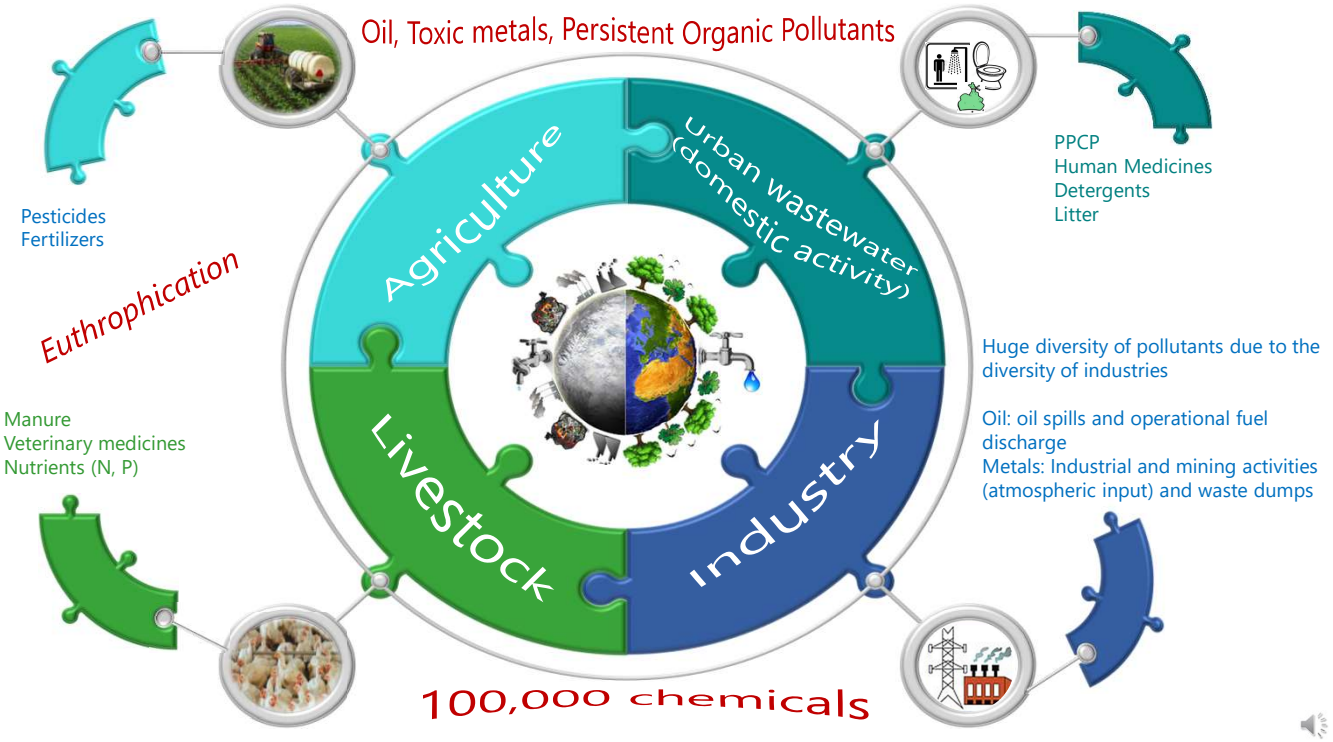

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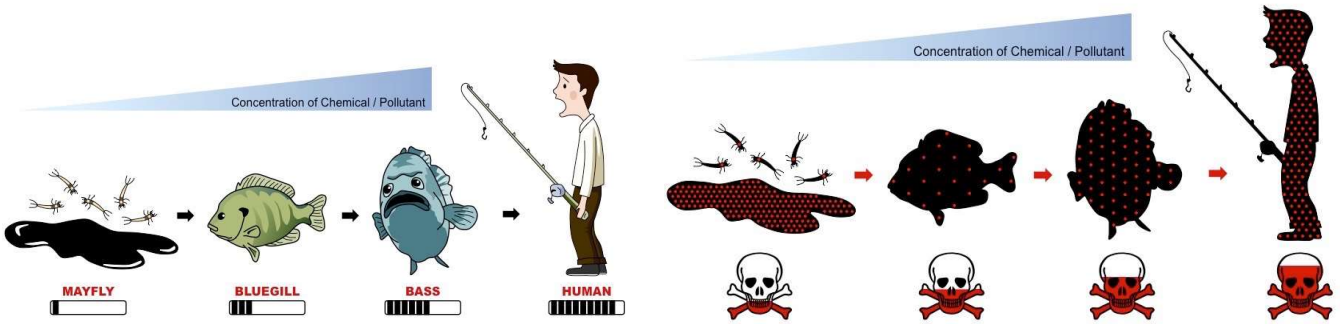
Contaminants of emerging concern



Biomagnification

Any concentration of a toxic compound in the tissues of tolerant organisms at successively higher levels in a food chain

https://ib.bioninja.com.au/options/option-c-ecology-and-conser/c3-impacts-of-humans-on/biomagnification.html

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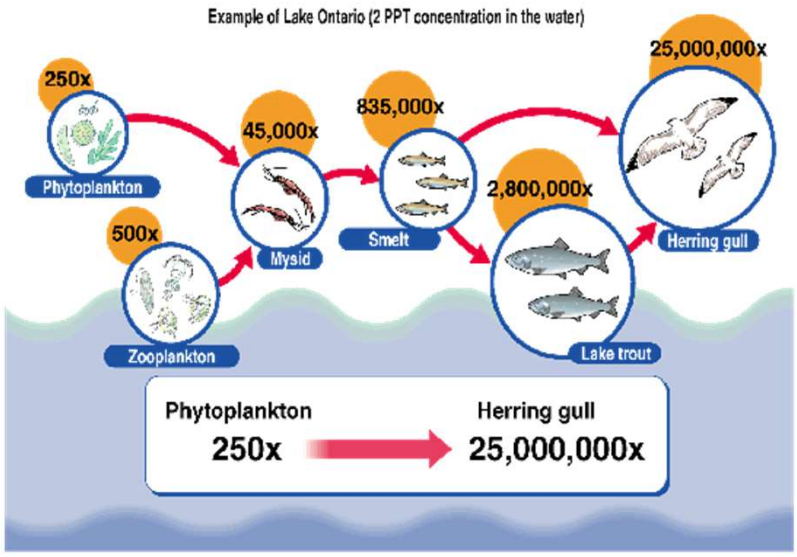
Food Web Biomagnification of PCBs



http://www.af-info.or.jp/eng/honor/gif/2000/img002.gif

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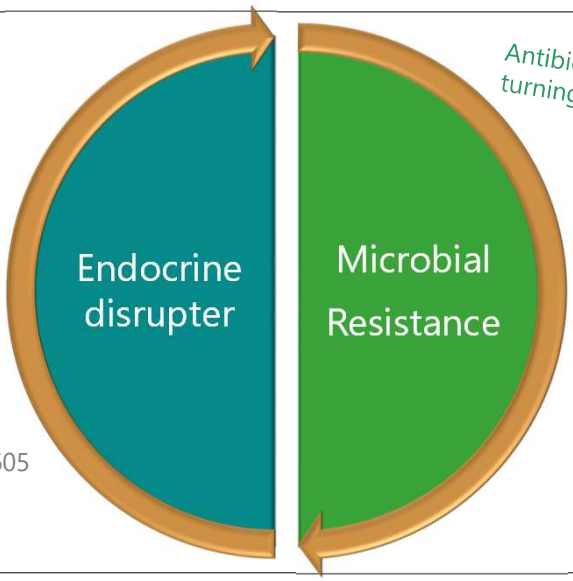
Contaminants of emerging concern

In 2019, new regulations relating to endocrine-disrupting chemicals in Europe were introduced; that require plant protection products and biocides to be assessed for endocrine activity

Biocidal Products Regulation (BPR, EU 2017/2100)

Commission Regulation (EU) no 2018/605 for plant protection products).



Antibiotic-Resistant Bacteria are turning up in Marine Life

Harbor seal

Contaminants of emerging concern

Endocrine disrupter compounds (EDCs)

"An endocrine disruptor is an exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub)populations"

"Exogenous substance or compound that alters one or more functions of the endocrine system and has adverse effects on health in an intact organism, its progeny or (sub) populations".

Feminization of male foetuses, reproductive disfunctions, behavioral changes and development problems

Commission of the European Communities, On Implementation of the Community Strategy for Endocrine Disrupters - a Range of Substances Suspected of Interfering with the Hormone Systems of Humans and Wildlife, Progress Report, COM 706, 1999.

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Natural hormones

- Human and animal sex hormones and phytoestrogens

Synthetic substances

- Synthesis hormones.
- Compounds used or disposed of by the industry.
- Compounds used in agriculture.
- Personal care products.

Mechanism of action
Imitates the hormone's action;
It blocks hormone receptors;
Changes the synthesis, transport, metabolism and excretion of hormones, changing their concentration.

Growth
Development
Reproduction
Behavior

Pharmaceutical active compounds ?!

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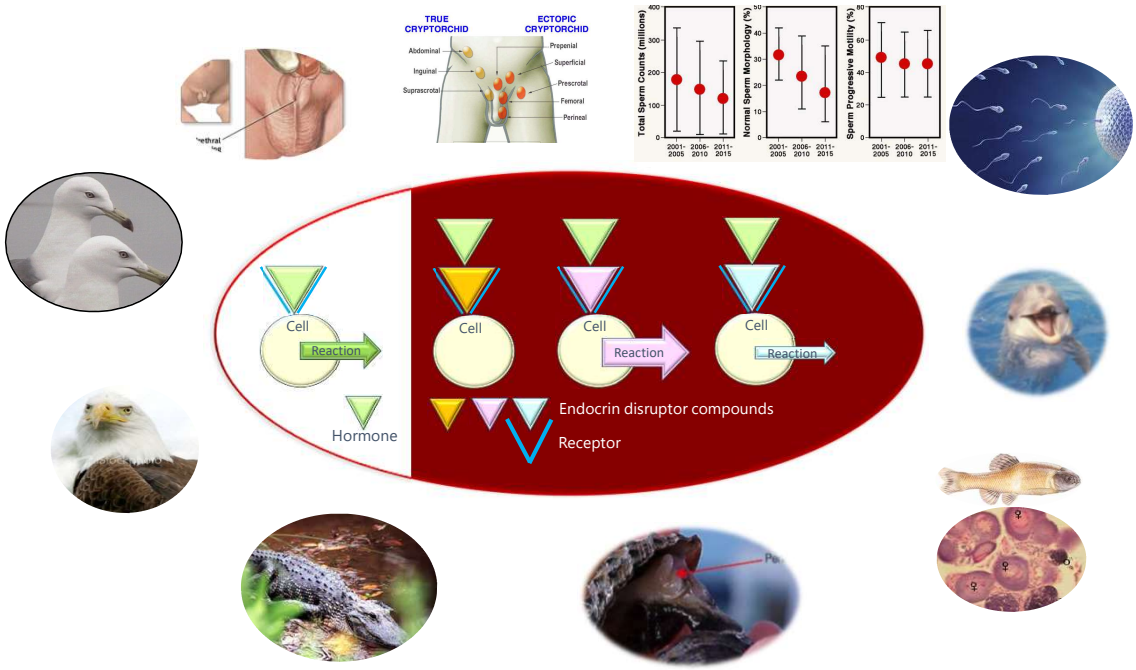

Declines in wildlife populations and loss of species as well as increasing incidences of hormone-related diseases in human

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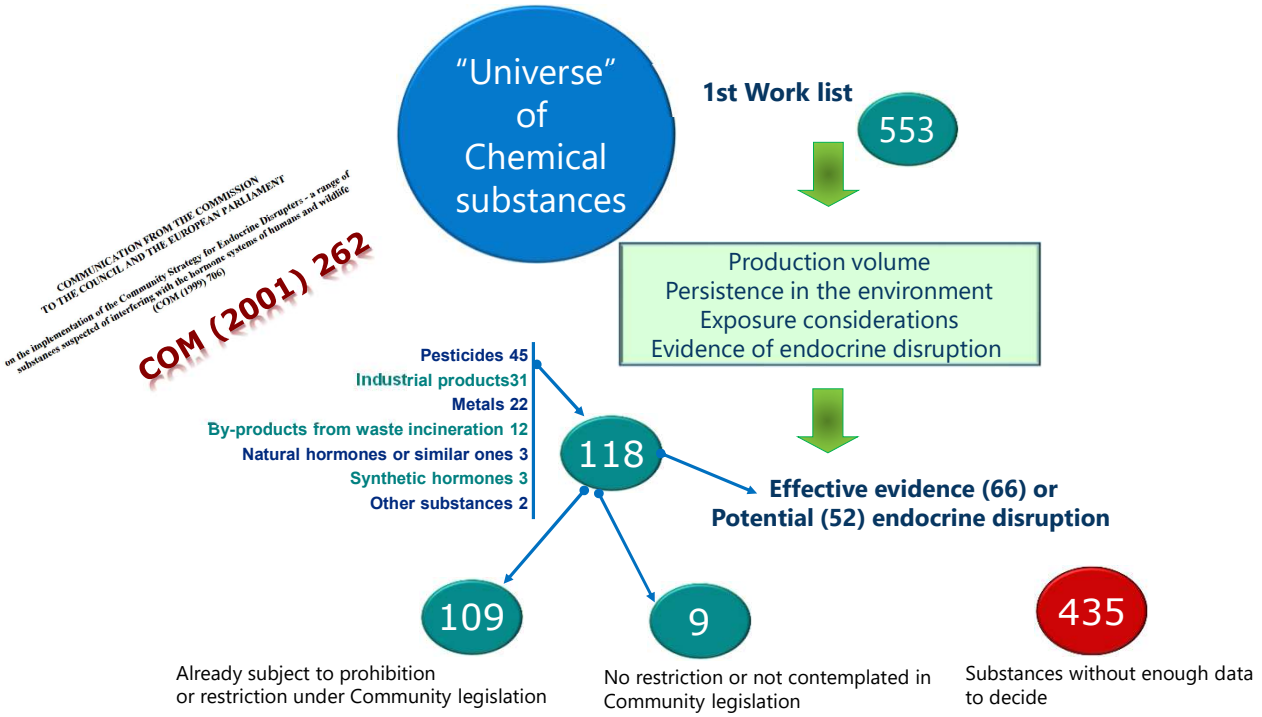

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Pesticides

1. Vinclozolin
2. Manebe
3. Sodium metam
4. Tirame
5. Zinebe
6. Lindane
7. Linuron
8. Amitrol
9. Atrazine
10. Acetochlor
11. Alachlor
12. 2,4-Dichlorophenoxyacetic acid
13. N-propyl-N- [2- (2,4,6-trichlorophenoxy) ethyl] -1H-imidazole-1-carboxamide
14. Dicofol
15. Iprodione
16. Zirame
17. Diuron
18. Diazinon
19. Dimetoato
20. Malathion
21. Methyl parathion
22. Paration
23. Simazine
24. Triadimefon
25. Bromomethane
26. Propanil
27. Carbendazine
28. Endosulfan (alpha and beta)

Industrial products

1. Styrene
2. PCB (polychlorinated biphenyls)
3. Phthalates
   - Benzyl and butyl phthalate
   - Bis (2-ethylhexyl) phthalate
   - Dibutyl phthalate
4. Bromodiphenyl (BDF)
   - DecaBDF
   - OctaBDF
   - PentaBDF
5. Phenols
   - 4-chloro-cresol
   - 4-ter-butylphenol
   - Nonylphenol
   - Bisphenol A

By-products from waste incineration

1. 1,2,3,7,8-pentachlorobenzodioxin
2. 2,3,7,8-Tetrachlorodibenzo-p-dioxin
3. Pentabromodibenzofuran
4. Tetrabromodibenzofuran
5. Chlorodibenzofuran (CDF)
   - TeCDF
   - PeCDF

Natural hormones

1. 17b-estradiol
2. Progesterone
3. Testosterone

Synthetic hormones

4. Melengestrol acetate
5. Trenbolone
6. Zeranol

Other substances

1. 3,4-Dichloroaniline
2. Tetrachlorethylene

Metals

Tributyltin derivatives

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Contaminants of emerging concern

DIRECTIVES

DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 12 August 2013

amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy

(Text with EEA relevance)

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Contaminants of emerging concern

Priority Substances

- Alachlor, Atrazine, Simazine, Aclonifene, Bifenox, Terbutrin (Herbicides)
- Clorfenvinfos, Chlorpyrifos, Cypermethrin, Dichlorphos (Insecticides)
- Diuron, Isoproturon (Herbicides)
- Cybutrin (Algicide)
- Benzene, 1,2-dichloroethane
- Dichloromethane, Chloroform
- Fluoranthene, Naphthalene
- Octylphenols (4-tert-octylphenol), Pentachlorophenol
- Trichlorobenzenes

Directive 2013/39/EU

Priority Hazardous Substances

- Trifluralin (Herbicide), Dicofol (Insecticide), Quinoxyfen (Fungicide)
- DEHP (Di(2-ethylhexyl) phthlate)
- PBDEs, C10-C13 Chloroalkanes, Pentachlorobenzene
- Endosulfan, HCB, HCH, Hexachlorobutadiene, Heptachlor and Heptachlor epoxide
- Nonylphenols (4-nonylphenol and isomers)
- Polyciclic Aromatic Hidrocarbons (PAHs) (5), Anthracene
- Tributyltin Compounds
- PFOS (Perfluorooctanesulfonic acid) and derivatives (surfactants)
- Dioxins
- Hexabromocyclododecans (HBCDD)

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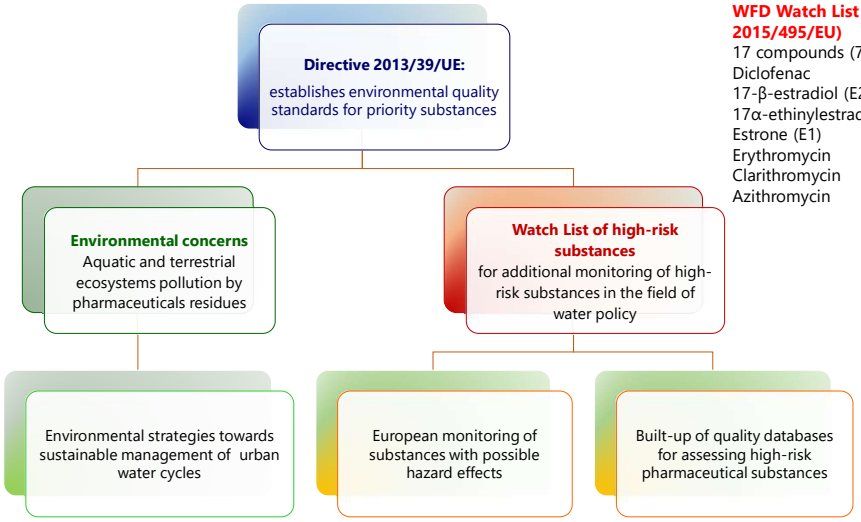
European legal framework



Pharmaceuticals in the 1st WFD Watch List (Decision 2015/495/EU)
17 compounds (7 PhCs)
Diclofenac
17-β-estradiol (E2)
17α-ethinylestradiol (EE2)
Estrone (E1)
Erythromycin
Clarithromycin
Azithromycin

Pharmaceuticals in the 2nd WFD Watch List (Decision 2018/840/EU)
15 compounds (9 PhCs)
Diclofenac
17-β-estradiol (E2)
17α-ethinylestradiol (EE2)
Estrone (E1)
Erythromycin
Clarithromycin
Azithromycin
Amoxicilin
Ciprofloxacin

Pharmaceuticals in the 3rd WFD Watch List (Decision 2020/1161/EU)
27 compounds (12 PhCs)
Erythromycin
Clarithromycin
Azithromycin
Amoxicilin
Ciprofloxacin
Trimethoprim
Sulfamethoxazol
Clotrimazol
Fluconazol
Miconazol
Venlafaxine
O-desmethylvenlafaxine

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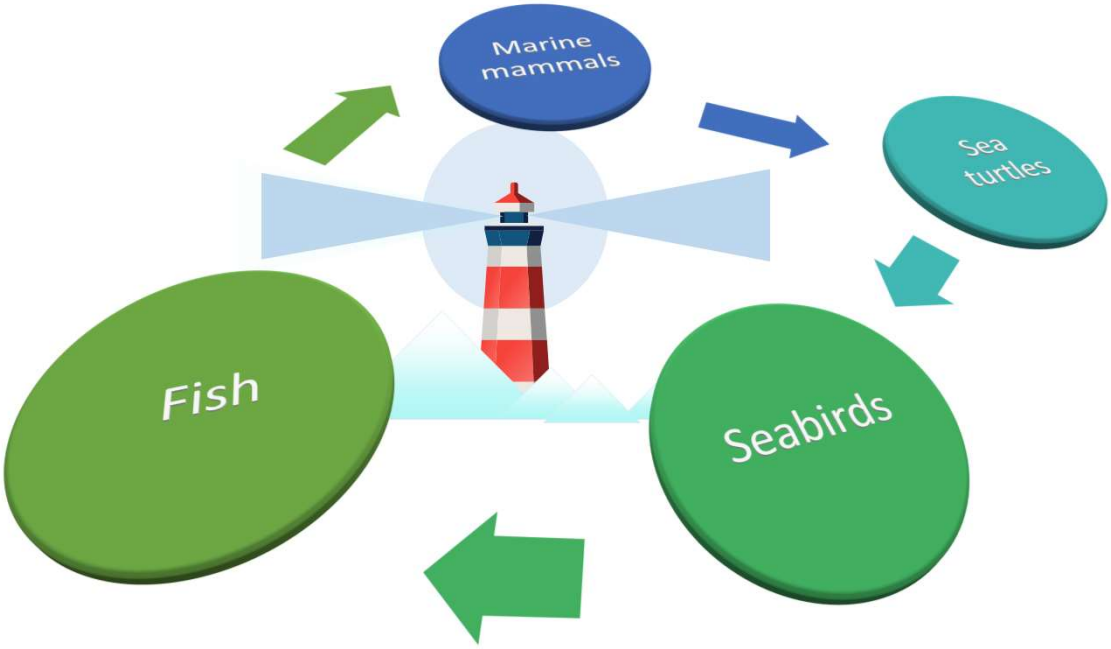

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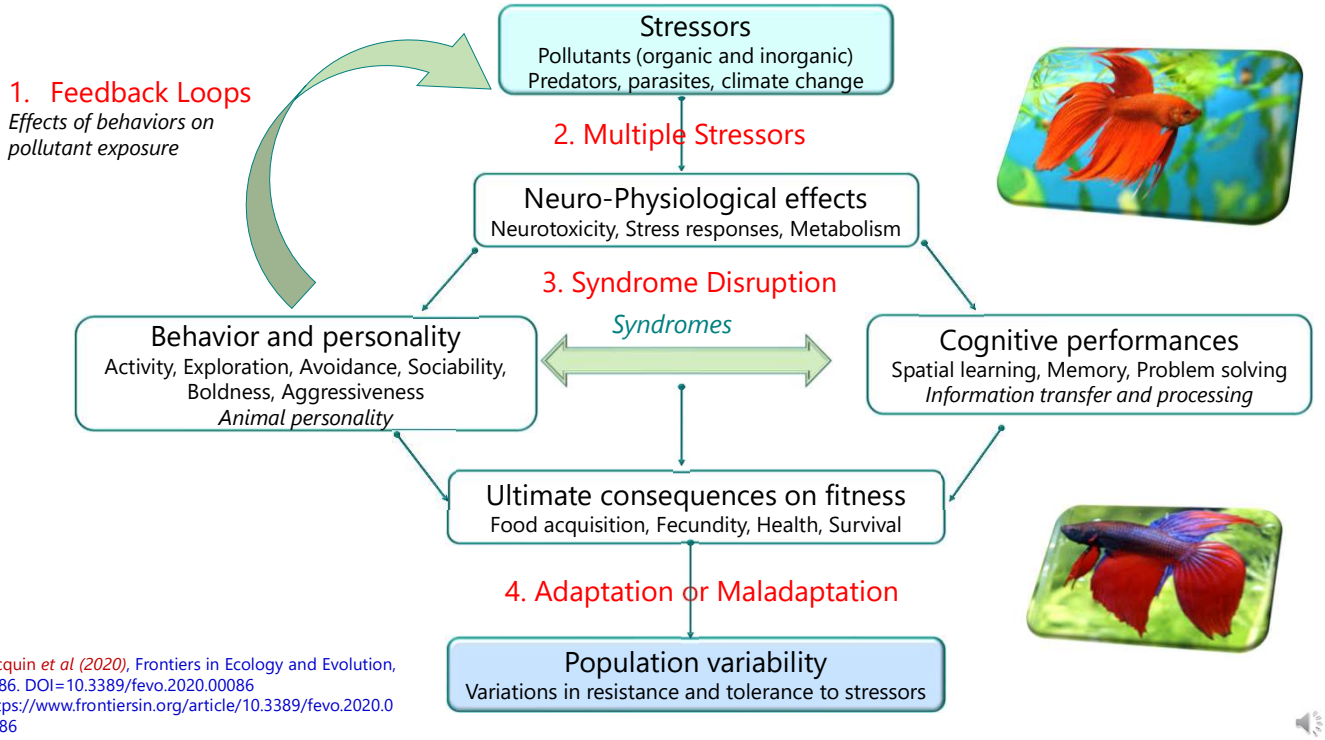

Jacquin *et al (2020)*, Frontiers in Ecology and Evolution, 8, 86. DOI=10.3389/fevo.2020.00086 https://www.frontiersin.org/article/10.3389/fevo.2020.00086

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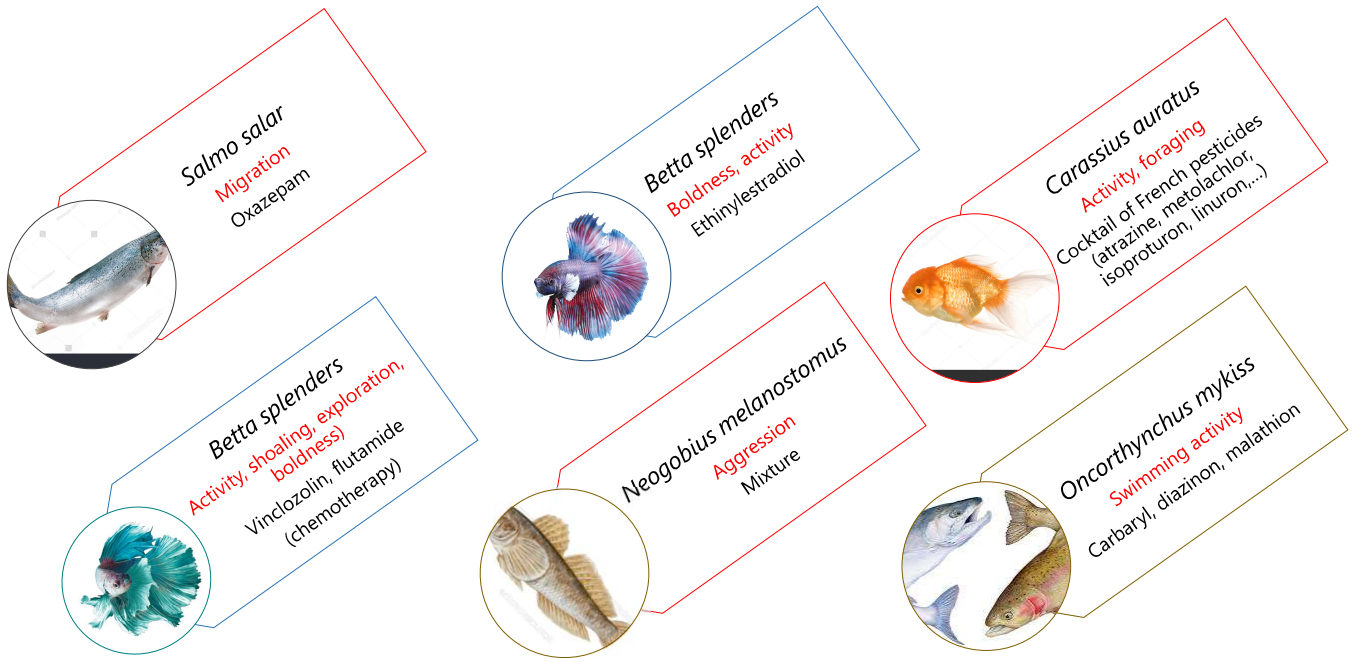

Jacquin et al (2020), *Frontiers in Ecology and Evolution*, 8, 86. DOI=10.3389/fevo.2020.00086 https://www.frontiersin.org/article/10.3389/fevo.2020.00086

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Jacquin et al (2020), *Frontiers in Ecology and Evolution*, 8, 86.

Contaminant	Ecological relevance	Fish species	Behavioral traits
Plastics			
Microplastics	Yes	*Bathygobius krefftii*	Boldness, exploration
Microplastics	Yes	*Acanthochromis polyacanthus*	Activity, feeding, aggression
Nanoplastics	Yes	*Carassius carassius*	Activity, feeding, exploration
Pharmaceuticals			
Oxazepam	Yes	*Perca fluviatilis*	Activity, boldness, sociality, feeding rate
Vinclozolin, flutamide (chemotherapy)	Yes	*Betta splendens*	Activity, shoaling, exploration, boldness
Ethinylestradiol	Yes	*Betta splendens*	Boldness, activity
Ethinylestradiol	Yes	*Poecilia reticulata*	Sexual behaviors
Fluoxetine	Yes	*Several species*	Antipredator behavior, boldness, aggression, associative learning
Various psychiatric drugs	Yes	*Several species*	Boldness, aggression, activity, feeding, anxiety
Oxazepam	Yes	*Salmo salar*	Migration

Contaminant	Ecological relevance	Fish species	Behavioral traits
Pesticides			
Cocktail of French pesticides (atrazine, metolachlor, isoproturon, linuron…)	Yes	*Carassius auratus*	Activity, foraging
Vinclozolin (fungicide), DDE (DDT metabolite)	NA	*Poecilia reticulata*	Sexual behaviors
Carbaryl, chlordane, 2,4 DMA, DEF, methyl parathion, pentachlorophenol	Yes	*Oncorhynchus mykiss*	Activity, feeding
Chlorpyryfos		*Danio rerio*	Spatial learning
Glyphosate	Yes	*Piaractus mesopotamicus*	Feeding
Glyphosate	Yes	*Danio rerio*	Exploration, locomotion, aggression, memory
Atrazine, linuron, metolachlor	Yes	*Oncorhynchus mykiss*	Aggression, locomotion
Ethoprofos	Yes	*Astyanax aeneus*	Avoidance, escape behavior
Carbofuran	Yes	*Dicentrarchus labrax*	Swimming activity
Carbaryl, diazinon, malathion	Yes	*Oncorhynchus mykiss*	Swimming activity
Other Organic Pollutants			
PCB, PoBDE	Yes	*Fundulus heteroclitus*	Activity, feeding

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Jacquin et al (2020), *Frontiers in Ecology and Evolution*, 8, 86.

Contaminant	Ecological relevance	Fish species	Behavioral traits
Nonylphenol (industrial surfactant)	Yes	*Fundulus diaphanus*	Shoaling, recognition
Metals			
Mercury		*Danio rerio*	Activity, escape
Methylmercury MeHg		*Danio rerio*	Anxiety, locomotion
MeHg	Yes	*Fundulus heteroclitus*	Activity, feeding
Metal mixture	Yes	*Pimephales promelas*	Swimming performance
MeHg	Yes	*Fundulus heteroclitus*	Sociality
MeHg	No	*Danio rerio*	Spatial learning
Several metals (Cu, Zn,…)	No	*Several species*	Avoidance, activity
Ag	Yes	*Danio rerio*	Avoidance, swimming, spatial learning
Cd	Yes	*Oncorhynchus mykiss*	Sociality
PCBs and PAHs	Yes	*Ameiurus nebulosus*	Aggression, activity, escape response
Trenbolone (agricultural pollution)	Yes	*Poecilia reticulata*	Reproductive behaviors
PAHs Polycyclic aromatic hydrocarbons	NA	*Poecilia reticulata*	Exploration, activity, sociality
Benzo[a]pyrene	NA	*Oncorhynchus kisutch*	Territoriality
PAHs	Yes	*Neogobius melanostomus*	Competition

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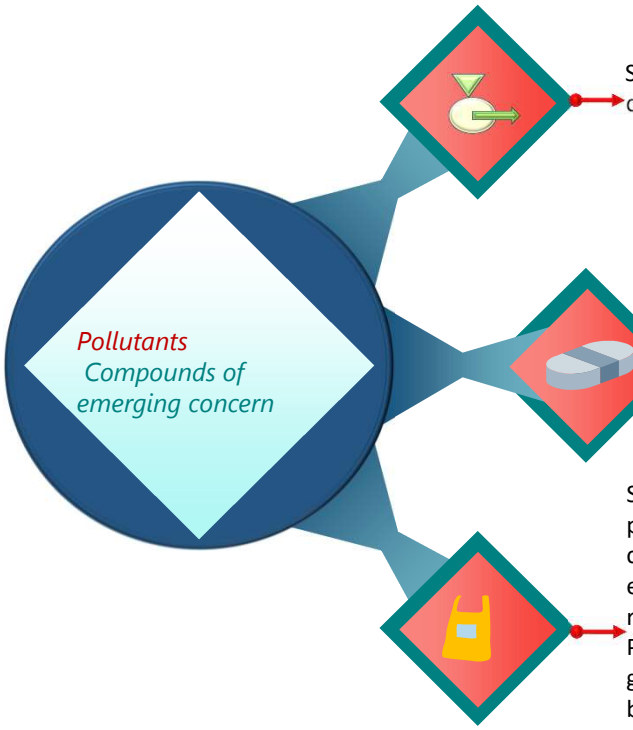

Some of these changes are underpinned by alterations of cholinesterase activity, neurotransmitter or hormone levels

Other behavioral changes could be indirectly due to changes in energetic balance, due to the costs of detoxification and stress responses

Some emerging pollutants such as new pesticides, pharmaceuticals, plastics, and nanoparticles are new chemicals that fish have never encountered in their environment in the past, so that polluted environments might represent evolutionary novel conditions.
Pollution-induced behavioral changes could thus potentially generate maladaptive effects and generate evolutionary traps, but this hypothesis remains to be tested.

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1- Feeding
2- Exploration
3- Migration
4- Activity
5- Locomotion
6- Antipredator behavior
7- Boldness
8- Shoaling
9- Associative learning
10- Swimming activity
11- Reproductive behaviour

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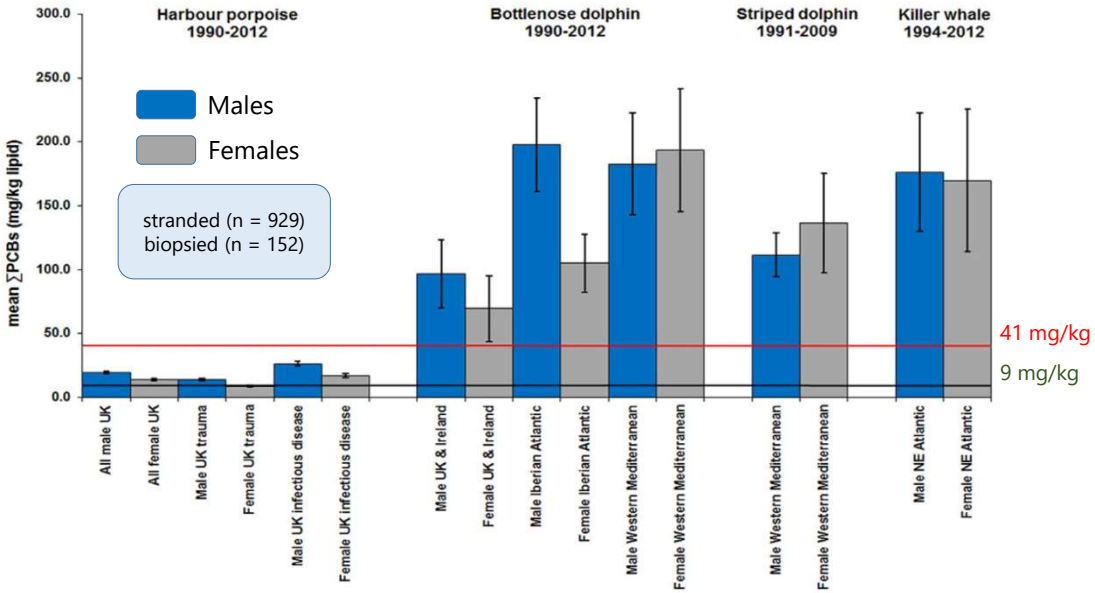
Four species; all ages




PCB (polychlorinated biphenyls)



Jepson *et al*, PCB pollution continues to impact populations of orcas and other dolphins in European waters, Scientific Reports 2016, 6: 18573

9.0 mg ΣPCBs/kg lipid for onset of physiological effects in experimental marine mammal studies.
41.0 mg ΣPCBs/kg lipid for the highest PCB toxicity threshold published for marine mammals based on marked reproductive impairment in ringed seals in the Baltic Sea

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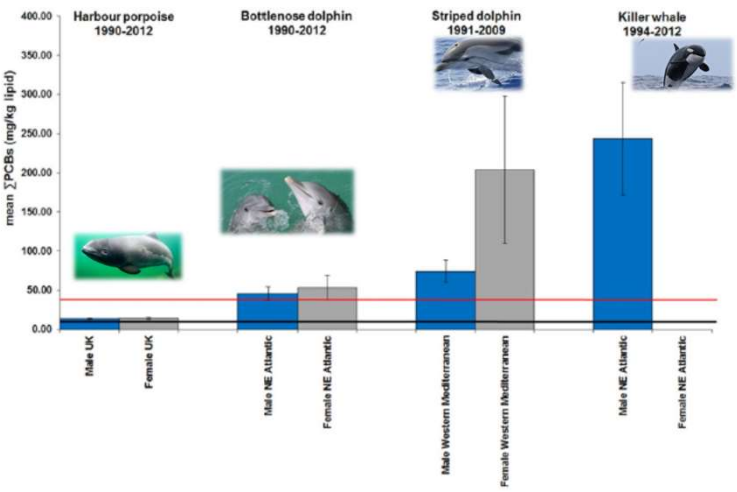
Jepson *et al*, PCB pollution continues to impact populations of orcas and other dolphins in European waters, Scientific Reports 2016, 6: 18573

Four species; juveniles only

PCB (polychlorinated biphenyls)



Immunosuppression and increased susceptibility to disease

- macro-parasitic and bacterial pneumonias
- high lung and gastric macro-parasite burdens
- generalised bacterial infections (septicaemias).
- Cetacean morbillivirus (CeMV) infection was frequently seen.
- Multiple dental infections leading to large mandibular abscesses

High ΣPCB contamination can cause immunosuppression and may be a significant contributing factor in the death of many of the stranded individuals that had fatal infectious diseases on necropsy.

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Rotander *et al*, Polybrominated diphenyl ethers (PBDEs) in marine mammals from Arctic and North Atlantic regions, 1986–2009, Environment International 40 (2012) 102–109

Brominated flame retardants (BFRs)

Polybrominated diphenyl ethers (PBDE)

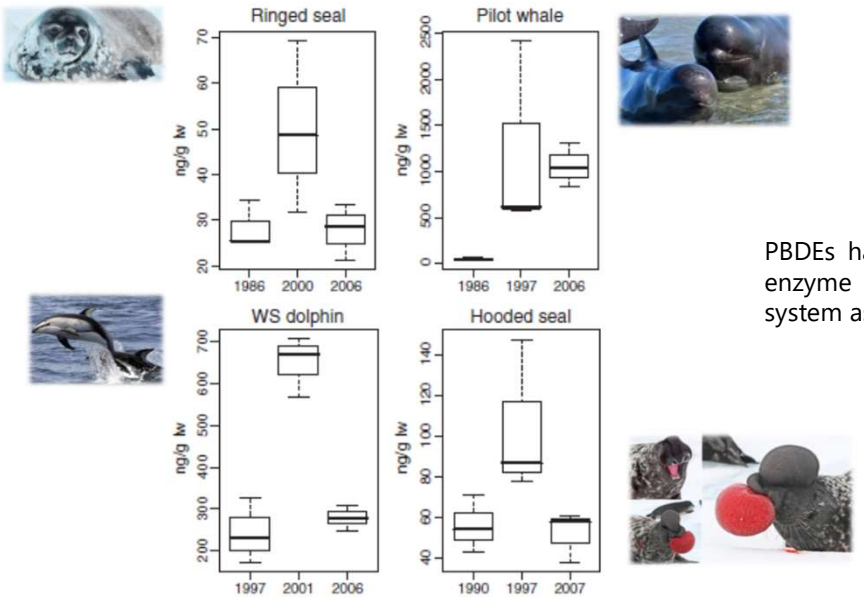

Fig. 2. ΣPBDE concentrations (ng/g l.w.) in pooled blubber samples of ringed seals, pilot whales, Atlantic white-sided dolphins and hooded seals (n = 3). Solid bars indicate median concentrations and max and min values are shown by whiskers.

PBDEs have a potential to interfere with liver enzyme production and the thyroid hormone system as well as induce immunotoxicity

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Rotander *et al*, Polybrominated diphenyl ethers (PBDEs) in marine mammals from Arctic and North Atlantic regions, 1986–2009, Environment International 40 (2012) 102–109

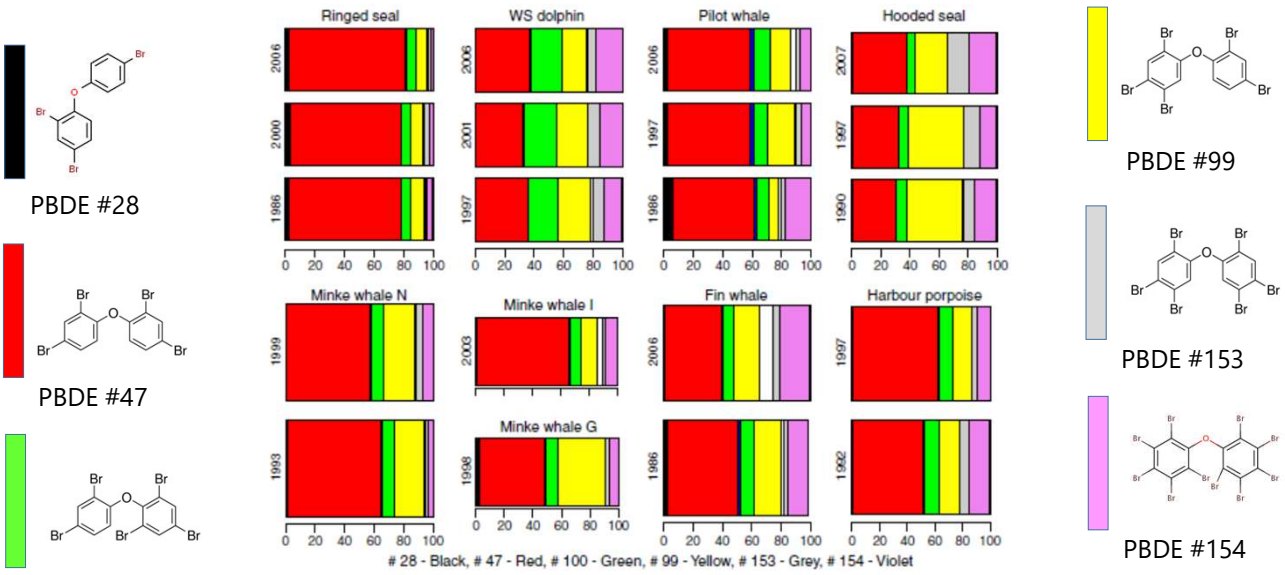

Fig. 4. Congener distribution in percentage of ∑ PBDE for BDE #28, #47, #100, #99, #153 and #154 indicated by colors. N = Norway, I = Iceland and G = Greenland.

doi:10.1016/j.envint.2011.07.001

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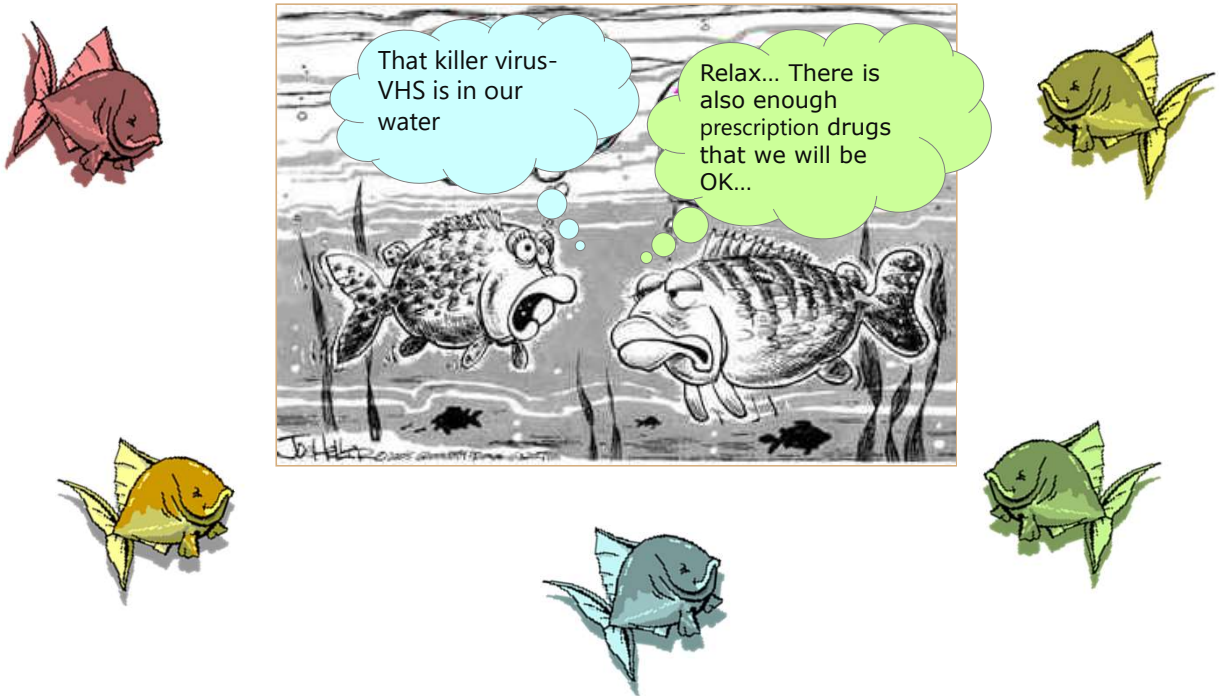
That killer virus-VHS is in our water
Relax… There is also enough prescription drugs that we will be OK…

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