Ollscoil na Gaillimhe
University of Galway

Chemical Pollution: Assessing Human Exposure and Unravelling Exposure Pathways

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Construct Innovate

Centre for One Health
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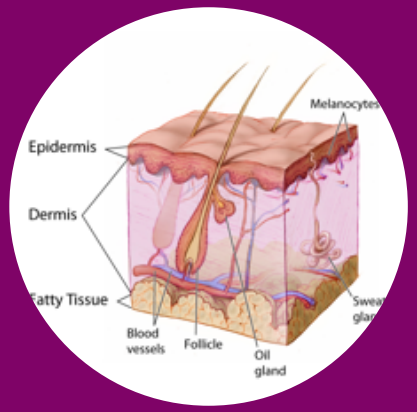
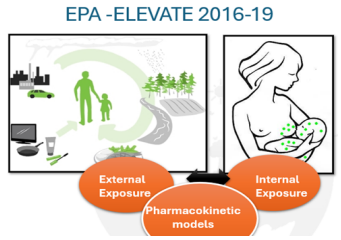


Assessing human exposure and exposure pathways

- Inhalation
  - *exposure level in air inhaled,*
  - *Particulate matter, radon, flame retardants, silica…*
- Dermal
  - *concentration on skin, area of skin exposed*
  - *Flame retardants, pesticides*
- Ingestion – inadvertent
  - *mass of chemical being swallowed*
  - *Flame retardants, pesticides*



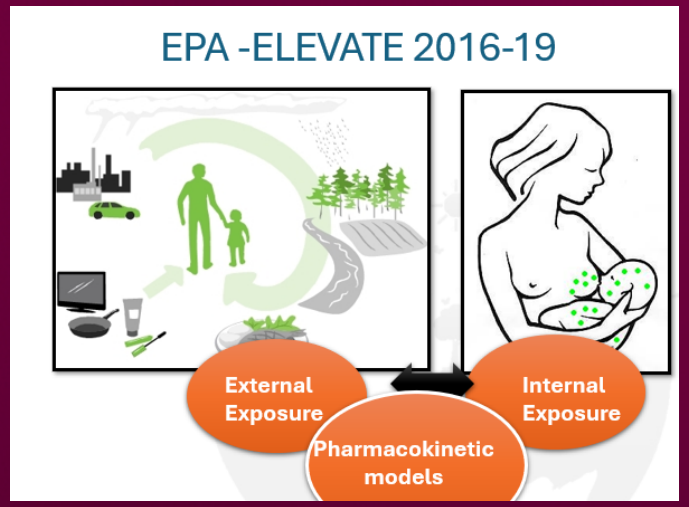
ELEVATE → Human impact → Flame retardants (FRs) & PFAS

IMAGE → Human impact → Pesticides

TERRACHEM → Environmental Impact → Antibiotics, biocides, FRs etc

ARDEN/HAVEN/ Be-Vent → Human impact → PM2.5, Formaldehyde, BTEX

Exposure monitoring is key to understanding the impact on human health and the environment (risk assessment)



2022 - 2025

TERRAChem
CHEMICALS POLLUTANTS SOILS AND SEDIMENTS

Dr Nina Wemken, Dr Martin Sharkey, Dr Mark Healy (University of Galway) and Prof Stuart Harrad University of Birmingham

epa Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

ELEVATE -Elucidating Levels and Pathways of Human Exposure in Ireland to POP-BFRs and PFAS 2016-19

Internal Exposure

External Exposure

Pharmacokinetic models

Environmental Protection Agency
An Ghníomhaireacht um Chaomhnú Comhshaoil

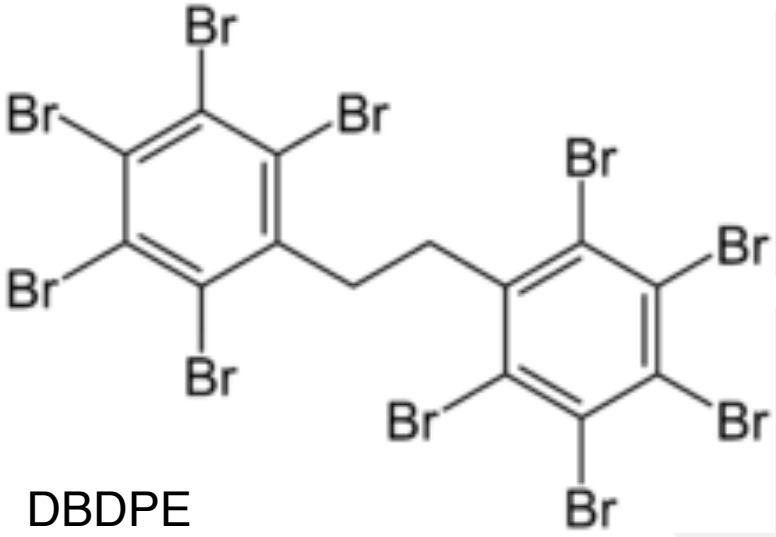
Legacy Brominated Flame retardants (X13)

Hexabromocyclododecane (HBCDD)

Polybrominated diphenyl ethers (PBDEs)

Stockholm Convention
Penta & Octa-BDE
Deca-BDE

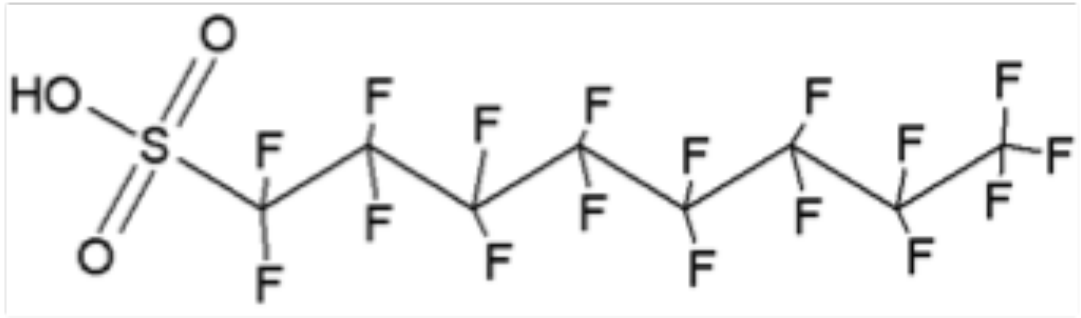
Replacement BFR- Decabromodiphenyl ethane (DBDPE)



DBDPE

Applications:

Per- and polyfluoroalkyl substances (PFAS) x10



Stockholm Convention
PFOS, -2009
PFHxS, PFOA, PFOS, – 2019

ELEVATE - Human Biomonitoring 2016-18

- Recruit 110 primiparas from two Irish maternity hospitals
- PBDEs, HBCDD, DBDPE, (PFASs) in 16 pools
- Compare to previous Irish Studies (2010)* and global trends

**Pratt et al., 2013;*

Exposure pathways – inhalation/ingestion

Air & dust
BFRs

PFASs water
concentrations

Microenvironment	
30 Homes	
30 Cars	
30 Offices	
30 Schools	

Sampling period Aug 2016 – Jan

Human Biomonitoring – (median) concentrations (ng/g lipid, DF)

BDE-28	BDE-47	BDE-100	BDE-99	BDE-154	BDE-153	BDE-183	BDE-209
<0.06 (0%)	0.5 (100%)	<0.2 (0%)	<0.2 (0%)	<0.12 (0%)	0.71 (100%)	<0.3 (8%)	1.4 (81%)

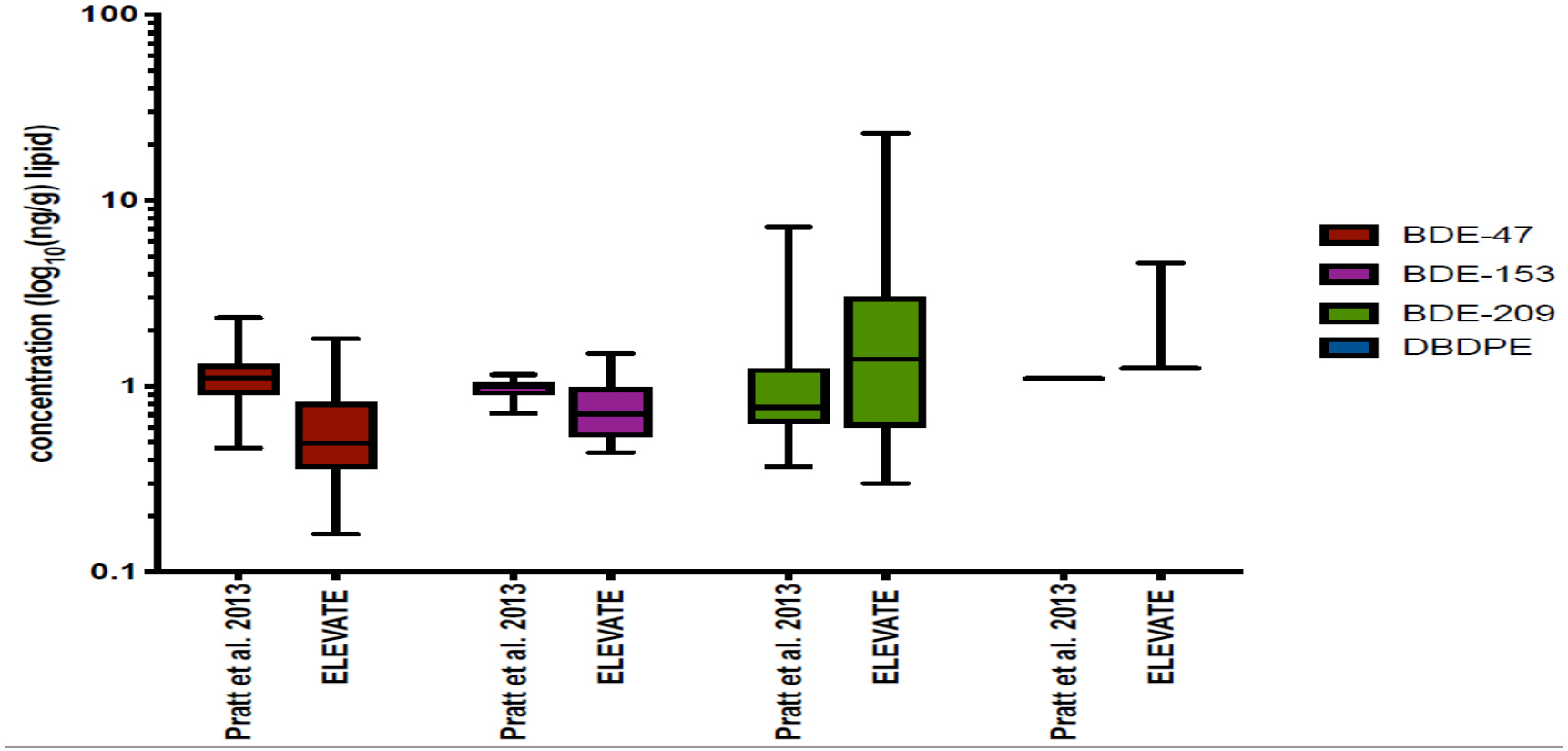
DBDPE	α-HBCDD	β-HBCDD	γ-HBCDD
<2.5 (19%)	1.4 (100%)	0.19 (88%)	0.16 (81%)

PFOA	PFNA	PFHxS	MeFOSE	PFOS	PFBS	PFNA	FOSA	EtFOSA	MeFOSA
0.10 100%	0%	<0.04 31%	0%	0.0536 2%	0%	0.034 69%	**0%**	**0%**	**0%**

Comparing 2016 – 2010 data - BFRs

BDE-47 & 153

(*p< 0.05*)



HBM PFOS & PFOA

- EFSA proposed TWIs for PFOA and PFOS in 2018 = 6 & 13 ng/Kg bw/week
    - Direct comparisons not possible for infants PFOA
    - PFOS - Breast feeding scenarios (EFSA) no health concern at concentrations measured in milk samples
- 2020 EFSA NEW TWI

Results-Dust PBDEs & PFAS

- Order of highest dust concentrations for PBDE congeners:
  BDE-209>BDE-99>BDE-47>BDE-183

- PFBS>PFOS>PFOA

- **Detection frequency (df)**
  - BDE-209 in 100% of samples
  - BDE-183 in76% of samples
  - BDE-99 in 73% of samples
  - BDE-47 in 98% of samples
  - DBDPE in 98% of samples

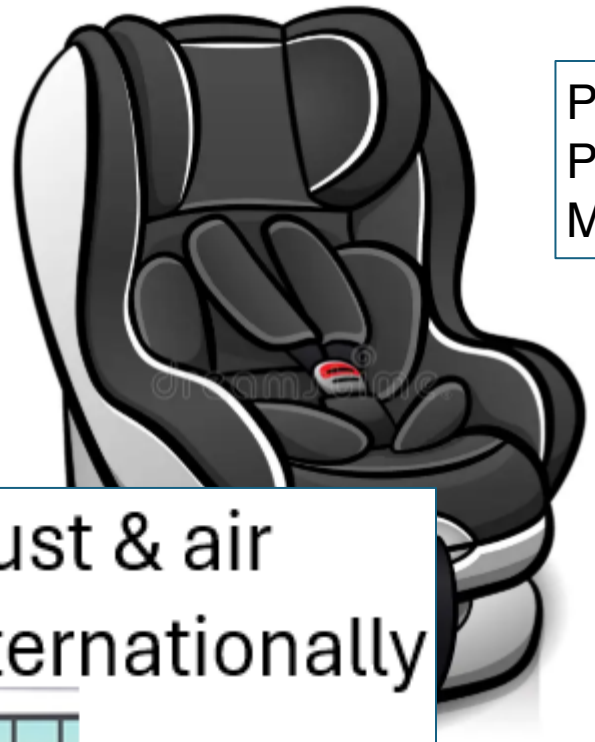
(df)

PFBS – 81%
PFOA – 66%
PFOS – 63%
PFHxS – 47%

Results-AIR PBDEs & PFAS

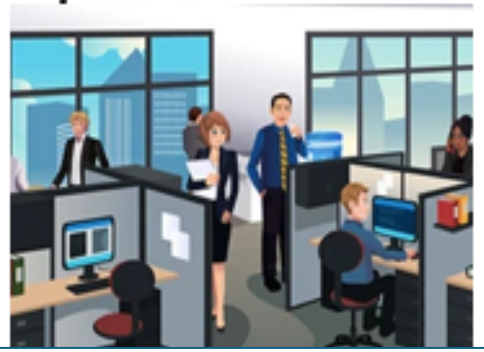
- Order of air concentrations for PBDE congeners analysed:
  BDE-209>BDE-99>BDE-47>BDE-183
- PFOA>PFOS>PFBS

- **Detection frequency (df)**
  - BDE-209 in 97% of samples
  - BDE-183 in 8% of samples
  - BDE-99 in 93% of samples



PFOA
PFNA
MeFOSE

Median concentrations of DPDPE in dust & air exceed significantly those reported internationally



Exposure pathways - PFASs

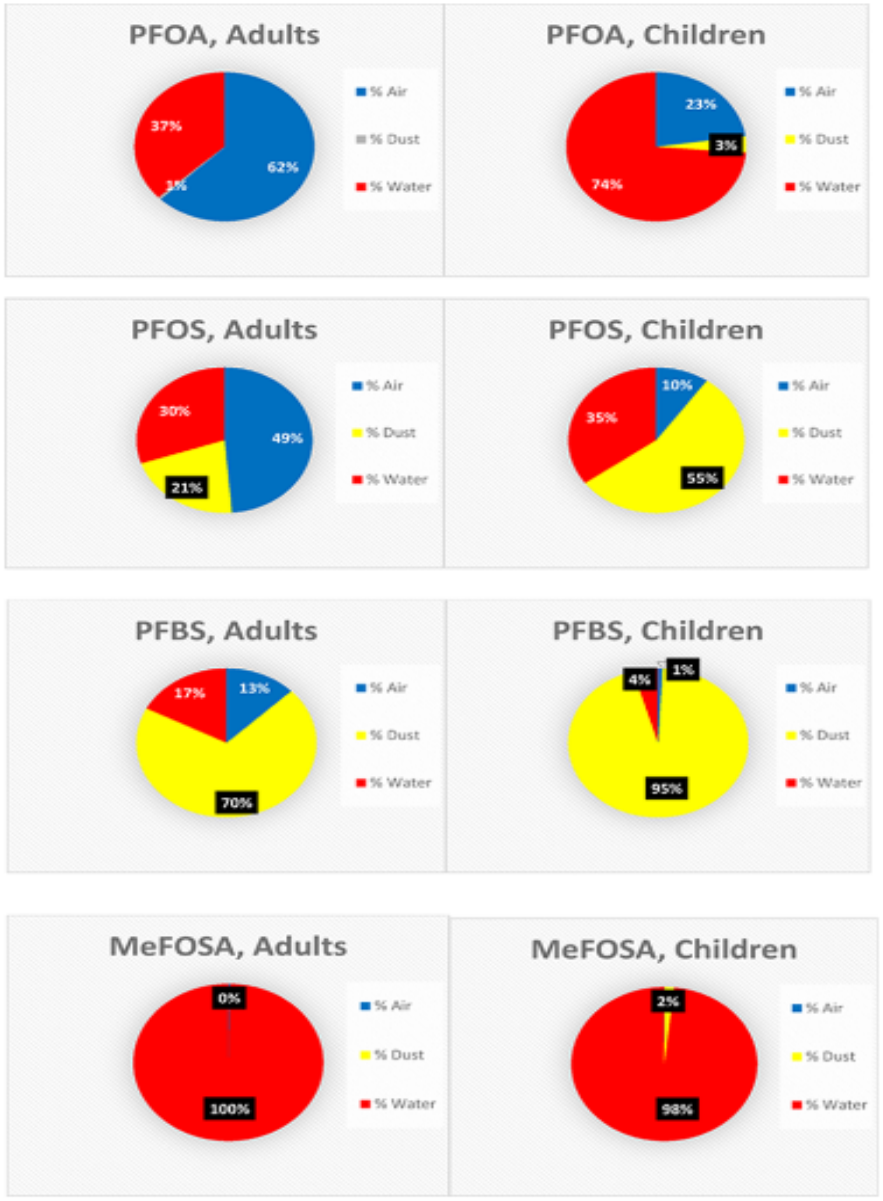


Figure 1. Relative contribution (expressed as %) of different target PFASs to the overall daily exposure (ng/day) of Irish toddlers and adults via drinking water, inhalation, and dust ingestion under typical exposure scenarios.

- Drinking water is an important exposure pathway for children e.g. PFOA
- Dust also and important contributor for PFBS
- **When combined with dietary < 10% of total**
- Non dietary exposures < EFSA TWI PFOA and PFOS

Take home messages ELEVATE

- Evidence of reduction in exposure to banned/restricted BFRs

- Suggest substantial use of Deca BDE in Ireland leading to exposure via
  - **Air & Dust > dietary exposure** (median 13,000 ng/g dust in Irish homes– Wemken et al., 2019)
  - Food (*Garcia Lopez et al., 2018)* *DIET?*

- Given DBDPE concentrations in Irish dust ~ those of BDE-209 (Wemken et al., 2019), hypothesise body burdens of DBDPE will increase over next few years

- PFAS
  - Not detected in previous studies. Concentrations within the range of those reported globally. Levels do not suggest any health concern in 2018 –
    - TWI has since changed
    - Impact of restrictions and bans

Further reading

Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 9826−9836

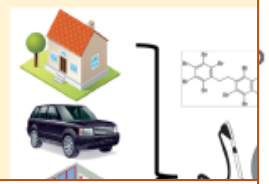
pubs.acs.org/est

Concentrations of Brominated Flame Retardants in Indoor Air and Dust from Ireland Reveal Elevated Exposure to Decabromodiphenyl Ethane

Nina Wemken,[†] Daniel Simon Drage,[‡] Moh
and Marie Ann Coggins[*,†]

[†]School of Physics and the Ryan Institute, National Univ
[‡]School of Geography, Earth & Environmental Sciences,

Supporting Information



Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. 2019, 53, 13449−13457

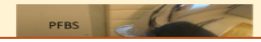
pubs.acs.org/est

Perfluoroalkyl Substances in Drinking Water, Indoor Air and Dust from Ireland: Implications for Human Exposure

Stuart Harrad,*[,†] Nina Wemken,[‡] Daniel Simon Drage,[†] Mohamed Abou-Elwafa Abdallah,[†] and Ann-Marie Coggins[‡]

[†]School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham B15 2TT, U.K.
y of Ireland, Galway H91TK33, Ireland

easured in air and dust from cars,
th drinking water from homes and



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journal homepage: www.elsevier.com/locate/chemosphere

Concentrations of perfluoroalkyl substances in human milk from Ireland: Implications for adult and nursing infant exposure

Mohamed Abou-Elwafa Abdallah [a], Nina Wemken [b], Daniel Simon Drage [a], Christina Tlustos [c], Claire Cellarius [d], Kathy Cleere [e], John J. Morrison [d], Sean Daly [e], Marie Ann Coggins [b], Stuart Harrad [a,*]

Environmental Research 180 (2020) 108805

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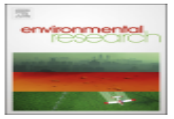

Emerging and legacy brominated flame retardants in the breast milk of first time Irish mothers suggest positive response to restrictions on use of HBCDD and Penta- and Octa-BDE formulations

Nina Wemken[a], Daniel Simon Drage[b], Claire Cellarius[c], Kathy Cleere[d], Jo
Sean Daly[d], Mohamed Abou-Elwafa Abdallah[b], Christina Tlustos[e], Stuart
Marie Ann Coggins[a,*]

[a] School of Physics and the Ryan Institute, National University of Ireland, Galway, H91TK33, Ireland
[b] School of Geography, Earth & Environmental Sciences, University of Birmingham, Birmingham, B15 2TT, UK
[c] Obstetrics & Gynaecology, University Hospital Galway, Galway, H91 YR71, Ireland

Houlihan et al. J Environ Expo Assess 2021;1:2
DOI: 10.20517/jeea.2021.02

Journal of Environmental Exposure Assessment

Research Article

Open Access

Concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in human milk from Ireland: temporal trends and implications for nursing infant exposure

Margarete Houlihan[1], Nina Wemken[2], Myra Keogh[1], Colman O'Riordain[1], Conor Noone[1], Julie Tierney[1], Claire Cellarius[3], Kathy Cleere[4], John J. Morrison[3], Sean Daly[4], Stuart Harrad[5], Christina Tlustos[6], Marie Ann Coggins[2]

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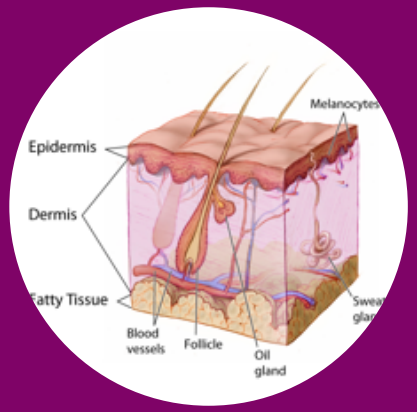
[2]School of Physics and the Ryan Institute, National University of Ireland, Galway H91TK33, Ireland.
[3]Department of Obstetrics & Gynaecology, National University of Ireland, Galway H91TK33, Ireland.



Assessing human exposure and exposure pathways

- Inhalation
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- Dermal
  - *concentration on skin, area of skin exposed*
  - *Flame retardants, pesticides*
- Ingestion – inadvertent
  - *mass of chemical being swallowed*
  - *Flame retardants, pesticides*
- *Diet*
  - *Chemical contamination in food*
  - *PFAS, flame retardants, PCBs*

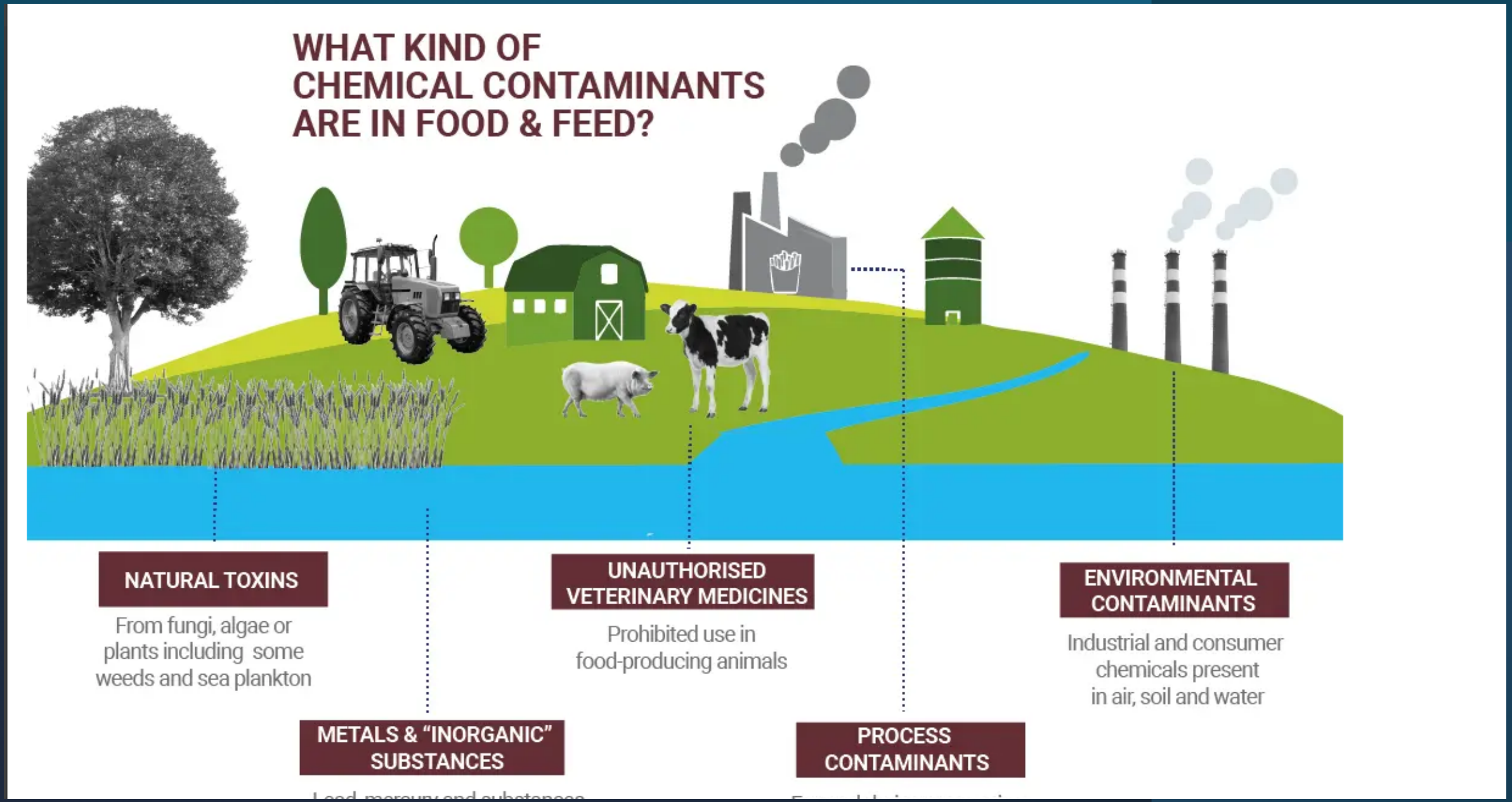


Image credit EFSA, 2025

Assessment of the Environmental Contamination of Sediments and WWTP derived biosolids with Hazardous Chemicals

--- TERRAChem ---

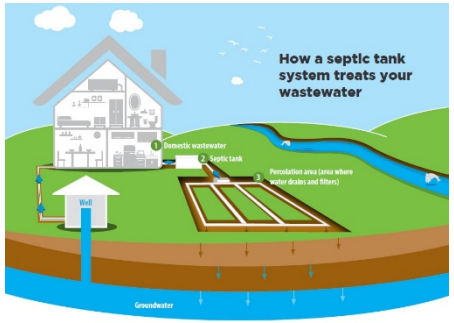
Marie Coggins, Martin Sharkey, Mark Healy, Stuart Harrad, William Stubbings

Contaminants in waste…

Agriculture (Livestock)
Antibiotic, Antiparasitic

Agriculture (Crops), Horticulture
Pyrethroid
PFAS, BFR, PCB,
Antibiotic, Antiparasitic,
SSA/UVF

Landfill (General, C&D, Industrial)
PFAS, BFR, PCB
Antibiotic, UVF



Domestic Wastewater
Antibiotic, UVF,
PFAS, Antiparasitic

Industrial Wastewater
PCB, BFR, PFAS

SOLID WASTE

WASTEWATER TREATMENT PLANT

The TERRAChem Project 2022-25

Persistent Organic Pollutants (POPs), WFD Watch list, emerging chemical of concern (Norman Network)

Nationwide screening of sediments (N=81), and WWTP-derived biosolids (N=21) to determine degree of environmental contamination.

TERRAChem a dataset presenting the concentrations 91 chemicals!

Legacy and emerging Flame retardants

Antibiotics

Pyrethroids & anthelmintics

PFASs

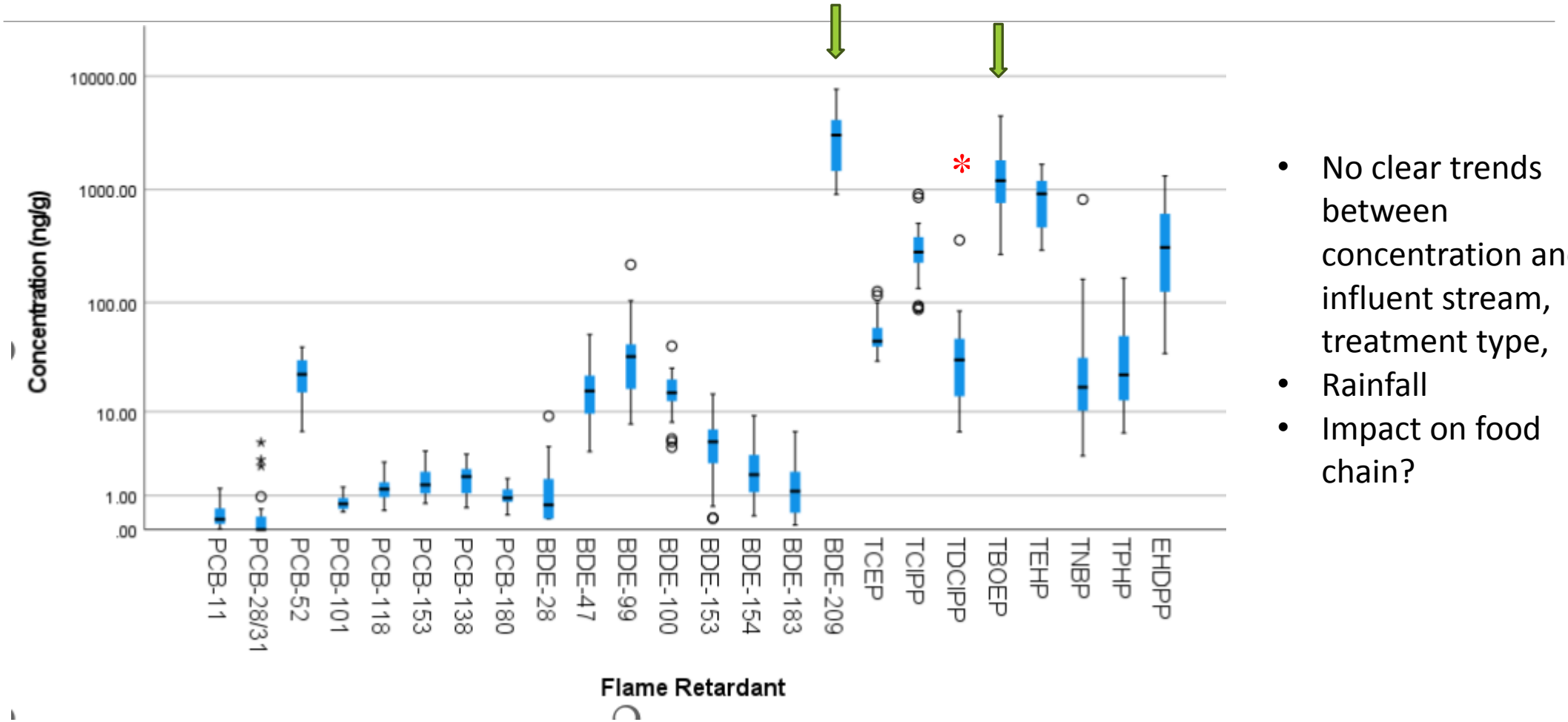
Sunscreen agents/UV Filters

PFASs	PFUnDA	PCBs	Antibiotics	Flame Retardants
PFBS	PFDoDA	PCB-11	Trimethoprim	BDE-28
PFPS	PFTrDA	PCB-28	Azithromycin	BDE-47
PFHxS	**SSAs/UVFs**	PBC-52	Roxithromycin	BDE-99
PFHpS	2-ethylhexyl-4-methocycinnamate	PCB-101	Doxycycline	BDE-100
PFOS	Benzophenone	PCB-118	Sulfamethoxazole	BDE-153
PFNS	Homosalate	PCB-138	Trimethoprim	BDE-154
PFDS	Octocrylene	PCB-153	Clarithromycin	BDE-183
PFUnDS	4-methylbenzylidene camphor	PCB-180	Lincomycin	BDE-209
PFDoDS	**Pyrethroids**	**Antiparasitics**	Sulfadiazine	α-,β-,γ-HBCDD
PFTrDS	Bifenthrin	Ivermectin	Erythromycin	TBBP-A
PFBA	Cyfluthrin	Doramectin	Difloxacin	TTBP-TAZ
PFPA	λ-cyhalothrin	Eprinomectin	Enrofloxacin	TCEP
PFHxA	Esfenvalerate	Moxidectin	Norfloxacin	TCIPP
PFHpA	Permethrin	Emamectin Benzoate	Ofloxacin	TDCIPP
PFOA	Resmethrin	Diflubenzuron	Levofloxacin	
PFNA	Deltamethrin	Teflubenzuron	Ciprofloxacin	
PFDA	Cypermethrin			

WWTP Site Reference #	Population Equivalent (PE) Band	Output Flow Band (m^3/day)	Types of Biosolids Treatment
WWTP 1	> 100,000	> 30,000	Advanced AD
WWTP 2	> 100,000	> 30,000	AD, TD
WWTP 3	> 100,000	> 30,000	AD, TD
WWTP 4	>100,000	>30,000	THP, AD
WWTP 5	2,000 - 50,000	1,000 - 10,000	AD, P
WWTP 6	2,000 - 50,000	1,000 - 10,000	AD, TD
WWTP 7	50,000-100,000	10,000 - 30,000	LS

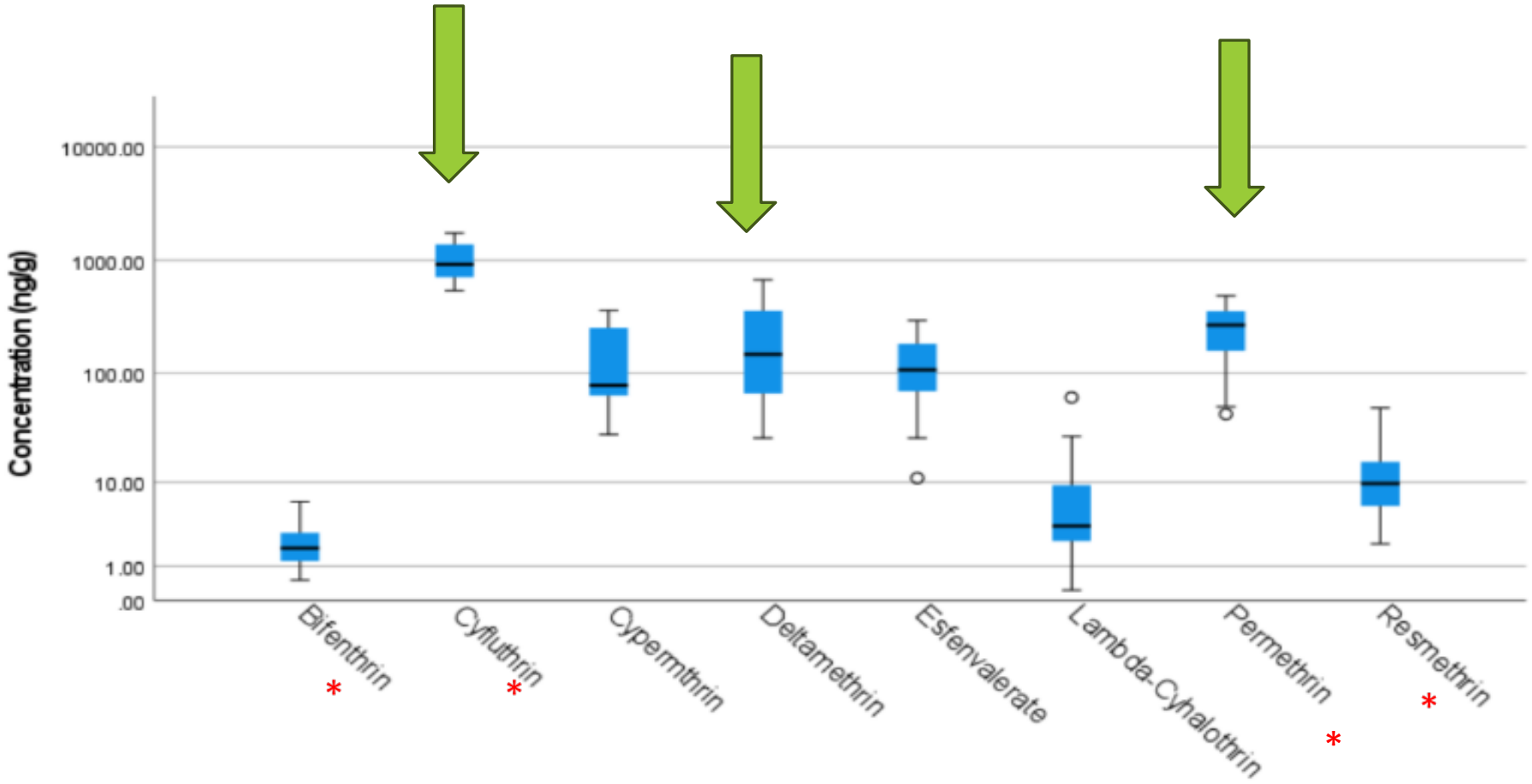
Table 1 - Available metadata for biosolid samples collected from 7 WWTP's in Ireland. AD = Anaerobic Digestion; TD = Thermal Drying; THP = Thermal Hydrolysis Processing; P = Pasteurization; LS = Lime Stabilisation.

Concentrations of target PCB, PBDEs, CL-OPEs in biosolids



- No clear trends between concentration and influent stream, treatment type,
- Rainfall
- Impact on food chain?

Concentrations of target pyrethroids in biosolids (ng/g)



- Cyfluthrin 57%, permethrin 15%, deltamethrin 12% of Σ_8 Pyre
- No significant correlation with rainfall
- Higher PE and FB associated with higher concentrations

Further Findings from TERRAChem

ELSEVIER

Science of The Total Environment

Volume 954, 1 December 2024, 176582

Legacy and emerging flame retardants in sediments and wastewater treatment plant-derived biosolids

Martin Sharkey [a], Shijie Wang [b], Stuart Harra
Mark G. Healy [c], Jingxi Jin [b], Ann Marie Coggins [a]

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ELSEVIER

Chemosphere

Volume 369, December 2024, 143793

Antibiotics residues in inland and transitional sediments

Martin Sharkey [a], William A. Stubbings [b], Stuart Harrad [b], Mark G. Healy
Shijie Wang [b], Jingxi Jin [b], Ann Marie Coggins [a]

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ELSEVIER

Science of The Total Environment

Volume 979, 1 June 2025, 179380

Concentrations of perfluoroalkyl substances in sediments and wastewater treatment plant-derived biosolids from Ireland

Yulong Ma [a], Martin Sharkey [b], Ann Marie Coggins [b], Will Stubbings [a],
Mark G. Healy [c], Stuart Harrad [a]

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Take home messages TERRACHEM

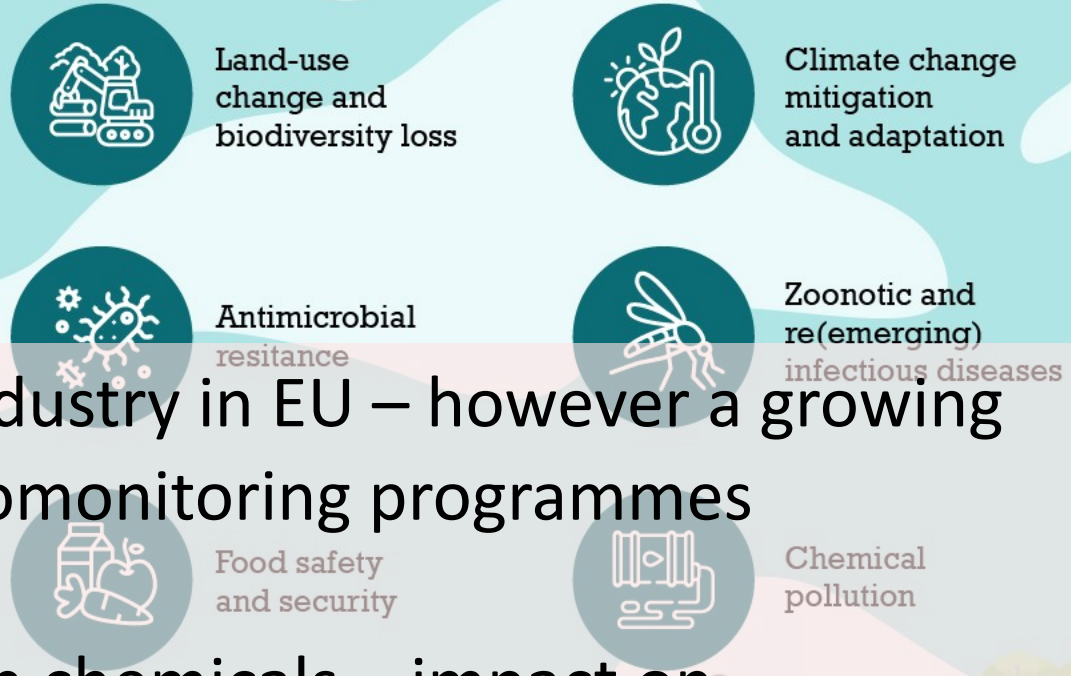
First baseline assessment (WWTP derived biosolids & sediment) of legacy and chemicals of emerging concern

Chemicals detected in both biosolids and sediment – chemicals present in use in Ireland and finding their way into our environment

Follow up study needed to assess soil concentrations and also impact on food crops and grazing animals – long term impact on land spreading

FINAL REPORT available via EPA late 2025

ENVIRONMENT and HEALTH



Chemical manufacturing is the 4th largest industry in EU – however a growing number of chemicals detected in human biomonitoring programmes

Continue to improve our knowledge base on chemicals – impact on environment and health

Monitoring presence in our environment and in humans key to understanding impact and risk

Raise awareness of POPs and other chemicals of concern

Ollscoil na Gaillimhe
University of Galway

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ELEVATE, *Dr Christina Tlustos FSAI, Prof. John Morrison*
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Prof Stuart Harrad, Dr Dan Drage, Dr Mohammed Abdallah (UoB) Wemken (University of Galway)

TERRAChem Martin Sharkey, Mark Healy, Stuart Harrad, Mark Healy, William Stubbings

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epa Environmental Protection Agency
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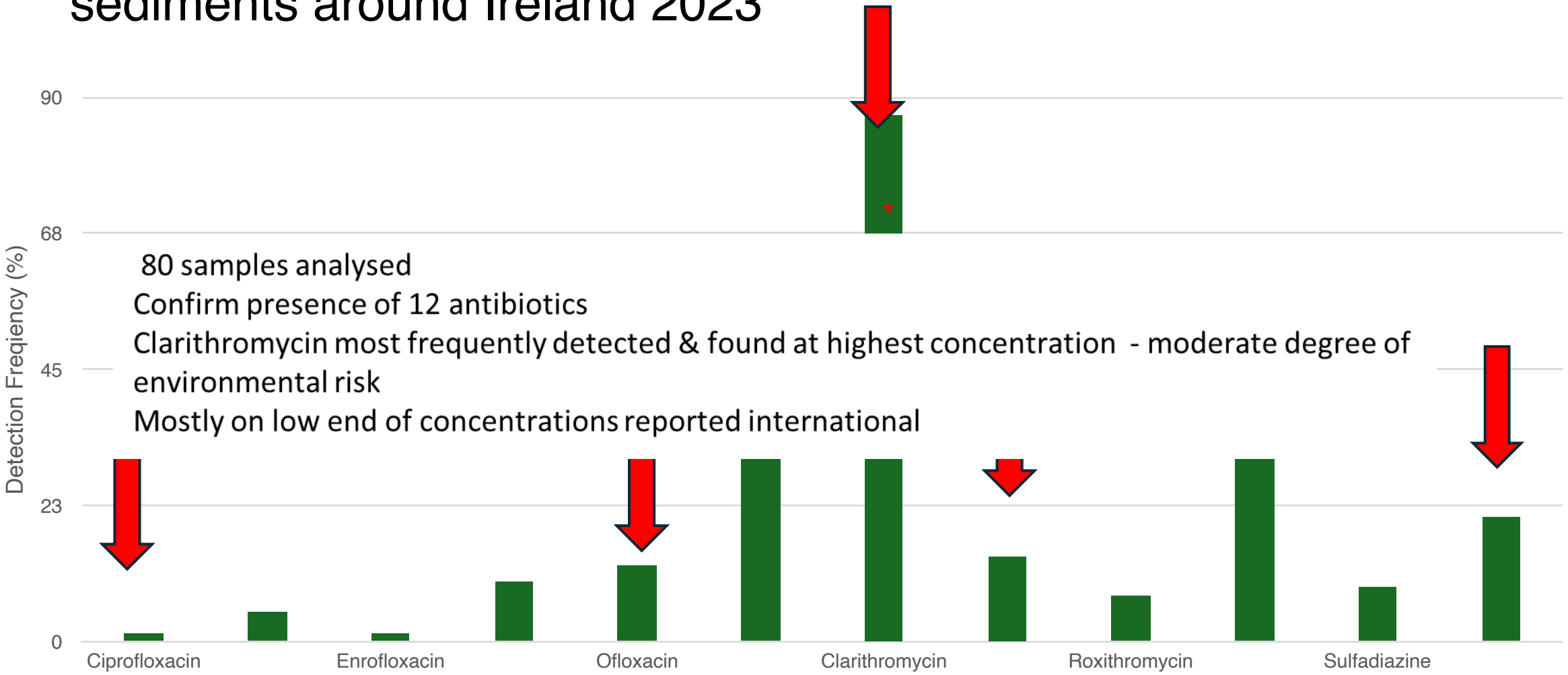
Antibiotic detection frequency in inland and transitional sediments around Ireland 2023



Proximity to Wastewater Discharge Point

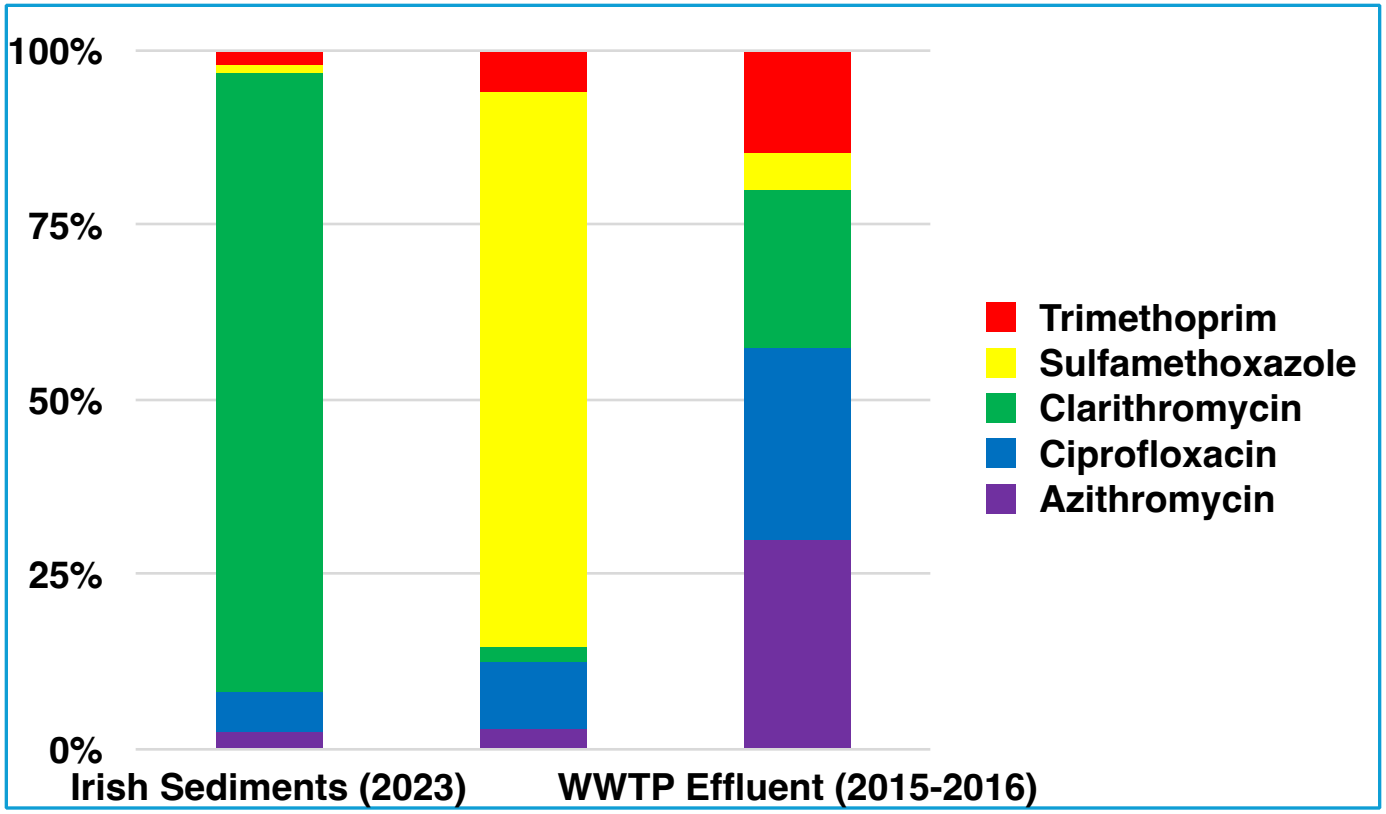
Distance from Emission Point (km)	Conc. ± Std. Dev. (ng/g)
< 0.1	49.3 ± 24.7
0.1 – 5.0	9.0 ± 9.7
> 5.0	4.7 ± 3.8

Two notable exceptions showed ∑antibiotics above 10 ng/g

Both samples directly traceable to high pressure agricultural/ aquaculture zones

Higher concentrations in this “mid-range” were also shown to coincide with either high population densities, or agriculture/ aquaculture pressure zones.

Antibiotics in Different Environmental Compartments

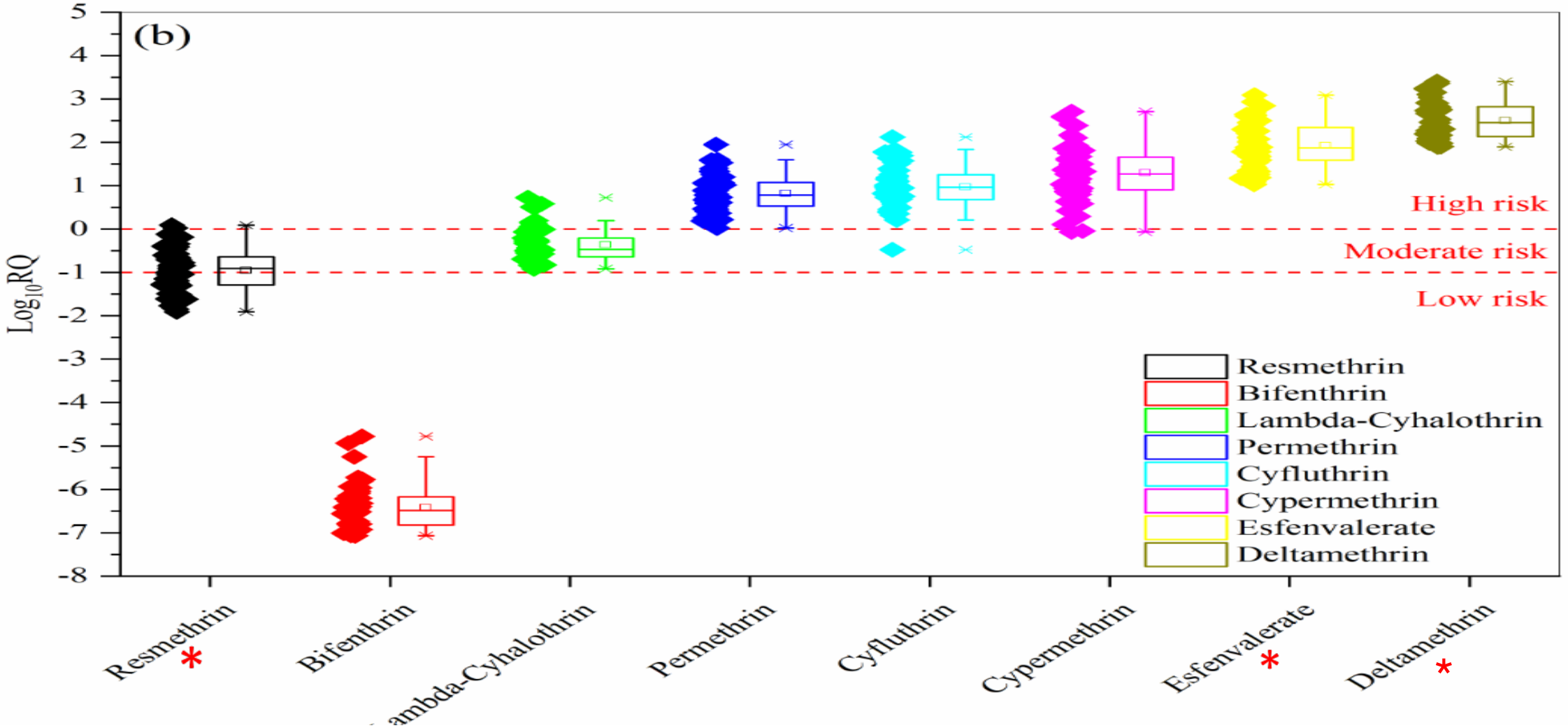


Antibiotics in WWTP effluent broadly conforms to reported usage in Ireland.

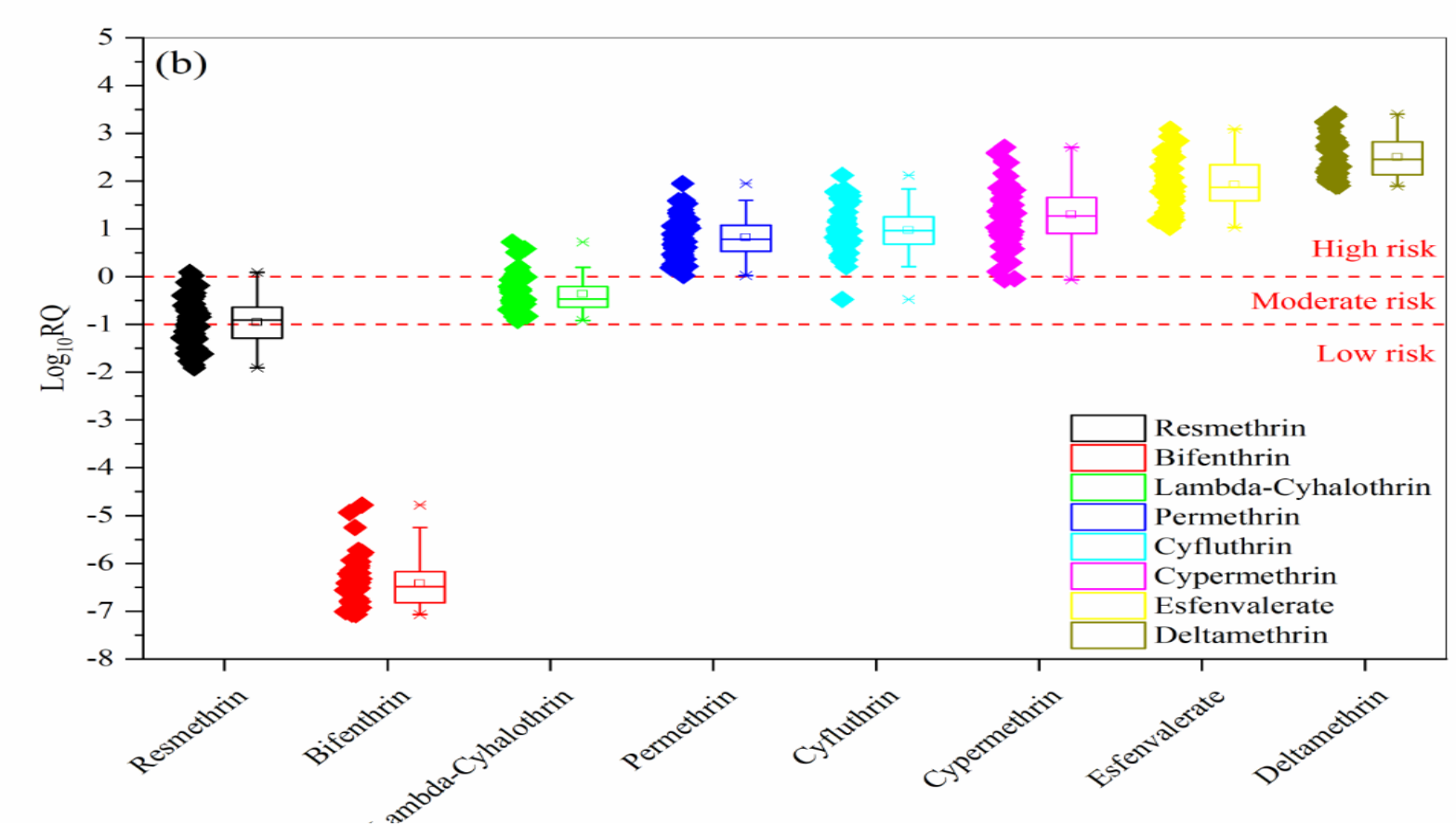
Notable differences in uptake to different environmental compartments: SME in water vs CLA in sediment.

Therefore, low ecotox. risk in sediments may not necessarily translate to low risk in other environmental compartments.

Concentrations of target Pyrethroids in sediments



Concentrations of target Pyrethroids in sediments



Plant protection products Resmethrin, bifenthrin, permethrin, cyfluthrin, – not approved

Lambda – Cyhalothrin – candidate for substitution Cypermethrin-

Esfenvalerate & deltamethrin – due for renewal 2026

Deltamethrin used in agri – lice/ flee treatment

Exposure pathways - total body burden

Table 3. Predicted daily intakes of PFOS and PFOA (pg/kgbw/day) required to support observed concentrations in Irish human milk.

PFAS	Human milk concentration (ng/mL)	Predicted total intake[a]	Non-dietary intake[b]	Predicted additional intake[c]	EFSA "TDI"[d]
PFOS	Average	245	1.6	244	1857
	Median	136	2.0	134	1857
	Minimum	67	0.6	66	1857
	Maximum	799	71	728	1857
PFOA	Average	591	30	561	857
	Median	474	30	444	857
	Minimum	73	1.4	72	857
	Maximum	1610	132	1478	857

EFSA TDI 2020 4.4 ng/Kg bw/week = 628 pg/Kgbw/day
Σ PFOA,PFOS, PFNA, PFHxS