Determination of emerging contaminants in apex predators and their prey from European Specimen Banks & Natural History Museums by High Resolution Mass Spectrometry Techniques

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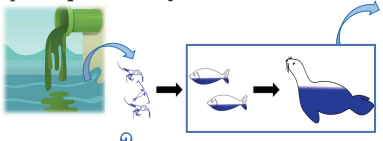
Introduction

...end up to **aquatic ecosystem**...

ECs & PPs...



...and are being **bioaccumulated** through the food chain.

Emerging Contaminants: ECs
Priority Pollutants: PPs
(Bio)Transformation Products: (bio)TPs

LIFE APEX focuses on the analysis of ***apex predators*** due to their unique characteristics:

- ✓ top of food webs
- ✓ long lifespan
- ✓ exposure over time & areas
- ✓ quantification & monitoring of populations

Aim of Tier 1

Data from ***AP & P*** for the presence of ECs in the environment

Wide-Scope Target Analysis

Prioritization of target substances by frequency of appearance

Predominant chemical mixtures

Tier 2: Temporal Trend Analysis

*Sampling Years: **1996-2019!!!***

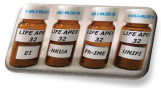
Tier 3: AP & P samples from ***different European*** countries

LIFE APEX Samples

67 *Samples (Tier 1)*

4 *countries (**UK**, **DE**, **NL** & **SE**) – different locations*

Same *species of AP&P*



Livers *(individuals & pooled)**:***

Common Buzzards (12)

Eurasian Otters (20)

Harbour & Grey Seals (11) / *Harbour Porpoise* (5)

Muscles *(individuals & pooled)**:***

freshwater fish: Breams (6) / Roaches (5)

marine fish: Eelpouts (3) / Herrings (3)

Eggs:

Herring Gull (2)

Fraunhofer IME · Centre for Ecology & Hydrology · Umwelt Bundesamt · Naturalis Biodiversity Center · Naturhistoriska riksmuseet

Materials & Methods

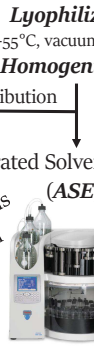
Lyophilization

(T: -55°C, vacuum: 0.05 mbar)

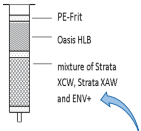
Homogenization

distribution

Accelerated Solvent Extraction (***ASE***)



Generic protocols of extraction



MeOH:ACN → ***SPE*** (mixed-mode cartridge)

HEX:DCM → ***SPE*** (florisil cartridge)

determination of analytes with ***different physicochemical properties***

Database
>2,400 *ECs, PPs & (bio)TPs*

RP LC-ESI(+/-)-qToF MS

GC-APCI (+/-)-qToF MS

Results - Discussion

>18 ***Plant Protection Products*** & ***(bio)TPs***
(in all tested countries, >10 in ***DE*** !)

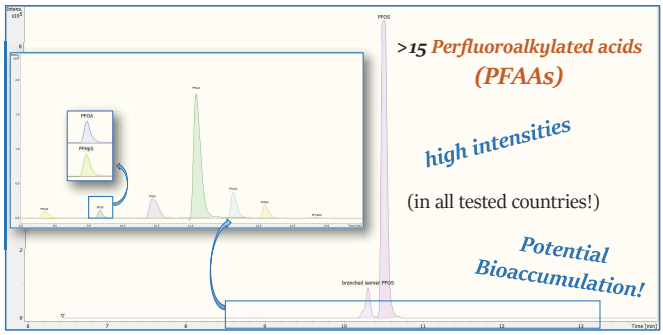
- ***herbicides*** (e.g. Diuron, Alachlor-ESA, Simazine, Dinoterb)
- ***pesticides*** (e.g. 2,6-Dichlorobenzamide (BAM), Fenuron)
- ***insecticides*** (e.g. Aldicarb-sulfoxide, Thiacloprid)
- ***fungicides*** (e.g. Myclobutanil)

Wide-scope Target Screening

Identification Thresholds:

1. Mass Accuracy (Δm/z <2 mDa)
2. Retention Time shift (ΔT_r <0.40 min)
3. Isotope fitting (mSigma <100)
4. Characteristic fragments
5. Adduct Ions

BRUKER TASQ™



>15 ***Perfluoroalkylated acids (PFAAs)***

high intensities

(in all tested countries!)

Potential Bioaccumulation!

Nor-Nicotine, Cotinine, Hydroxy-Cotinine (nicotine's ***metabolites***)

Stimulants, such as ***Nicotine*** & ***Caffeine*** (***UK, NL, DE***)

Theophylline, Theobromine (caffeine's ***metabolites***)

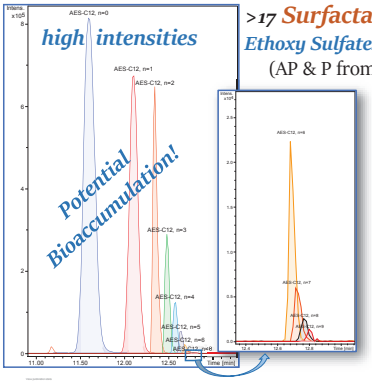
Antipsychotic & Antidepressant drugs
(e.g. ***Sertraline, Quetiapine, Citalopram, Venlafaxine*** it's metabolite ***Desvenlafaxine***)
(AP & P from ***UK***, ***SE*** and ***DE***).

>17 ***Pharmaceuticals*** and ***(bio)TPs***
(in all tested countries!)

- ***Antiepileptics*** (e.g. Levetiracetam)
- ***Antifungal medication*** (e.g. Terbinafine)
- ***Anti-arrhythmics*** (e.g. Mexiletine)
- ***Antibiotics*** (e.g. Sulfadiazine)
- ***Medication to treat pain*** (e.g. Paracetamol, Dihydro-Codeine , Tramadol)

4 Tramadol's ***metabolites*** in ***AP*** (Harbour Porpoise)

N-bisdesmethyl-tramadol
N-desmethyl-tramadol
O-desmethyldinor-tramadol
O-desmethylnor-tramadol



high intensities

Potential Bioaccumulation!

>17 ***Surfactants***, such as ***Alcohol Ethoxy Sulfates (AES)***
(AP & P from ***DE*** & ***UK***).

Other classes of detected compounds:

- ***Industrial Chemicals*** (e.g. 1-H-Benzotriazole, Tolytriazole)
- ***Amphetamine and amphetamine derivatives*** (e.g. 3,4-Methylenedioxyamphetamine (MDA))
- ***Sweeteners*** (e.g. Saccharine)
- ***PAHs*** (e.g. Anthracene, Naphthalene)
- ***OCPs*** (e.g. 4,4-DDE)
- ***PCBs*** (e.g. PCB 101, PCB 138)

Acknowledgments

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