

NEWSLETTER

LIFE APEX



ISSUE NO. 5 | DECEMBER 2020

 **YouTube** <https://youtu.be/7y3zDawHDck>



LifeAPEX - Project video

Telegram

- +++New Life Apex project video is available on [Youtube](https://youtu.be/7y3zDawHDck)+++
- Novel analytical techniques for PFAS were developed
- Results for Tier 2 time-trend analysis (2000-2018) are available
- Detection of novel compounds that have not been reported in Tier 1
- Many PFAS show declining trends in otters from the UK and harbour seals from Germany
- Similar trends were observed for mercury in bream (Germany).
 - However, levels were above the environmental quality standard (20 µg/kg wet weight)

- BDEs were declining in otters (UK) and bream (Germany) as well
- 64 Buzzard samples were shipped to the University of Florence for assessing the impact and effectiveness of risk management measures for legacy pollutants at national and European scale
- Sample selection across Europe (Tier 3) has been finalized
 - Wide spatial coverage of available samples

The Life APEX-Team wishes you Merry Christmas and a Happy New Year!



TOPIC 01

- Presentation of novel analytical techniques
- Tier 2 time-trend results

TOPIC 02

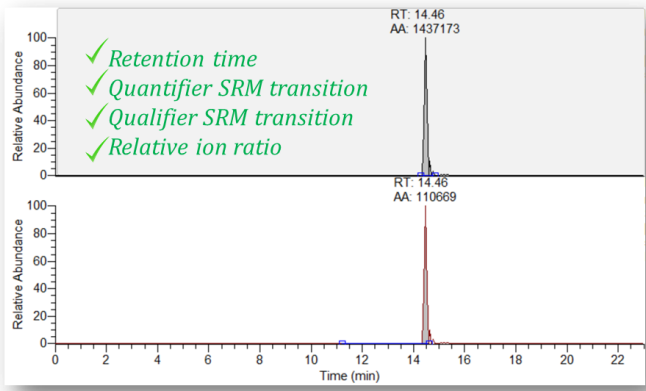
- Demonstrator 3 (Common Buzzard)

TOPIC 03

- Virtual project meeting in June, 2020
- Sample selection for Tier 3
- Networking activities

01: DEVELOPMENT OF NOVEL ANALYTICAL TECHNIQUES FOR PFAS

LC-ESI-MS/MS (QqQ) multiresidue method for the determination of 56 PFAS from 16 classes



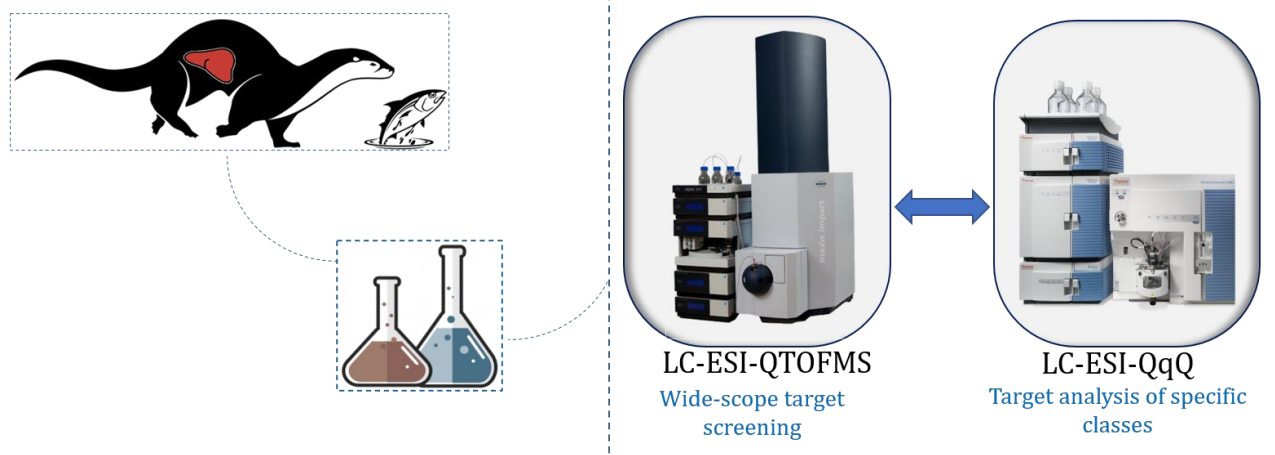
- High sensitivity → low detection limits
- Increased selectivity → reduced interferences
- Confident identification & confirmation (t_R , MRMs, ion ratio)

- Perfluoroalkyl carboxylic acids (PFCAs)
- Perfluoroalkyl sulphonic acids (PFSA's)
- Perfluorooctane sulfonamides (FOSAs)
- Perfluoroalkylphosphonic acids (PFAPAs)
- Perfluoroalkylphosphinic acids (PFPI's)
- Telomer alcohols (FTOHs)
- Mono-substituted polyfluorinated phosphate esters (PAPs)
- Di-substituted polyfluorinated phosphate esters (diPAPs)
- Saturated fluorotelomer acids (FTAS)
- Unsaturated fluorotelomer acids (FTUAs)
- N-Alkyl perfluorooctane sulfonamidoethanols (FOSEs)
- Fluorotelomer sulphonic acids (FTSAs)
- Perfluoroether carboxylic acids (PFECAs)
- Chlorinated perfluoroether sulphonic acid (Cl-PFESA)
- and 32 isotopically labeled compounds

Robust quantification

- LIFE APEX samples were analyzed for the presence of legacy and emerging PFASs, employing a highly sensitive liquid chromatography electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS). The method currently includes 56 PFAS from 16 classes.

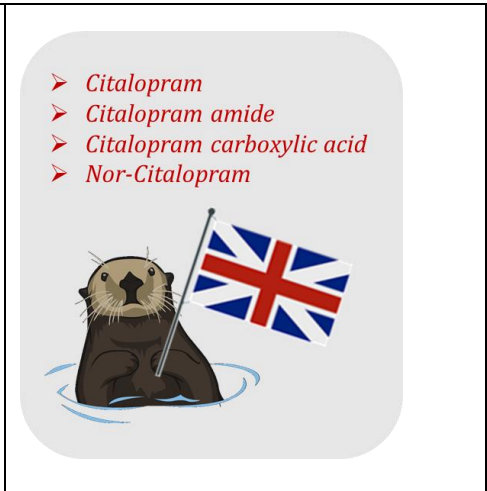
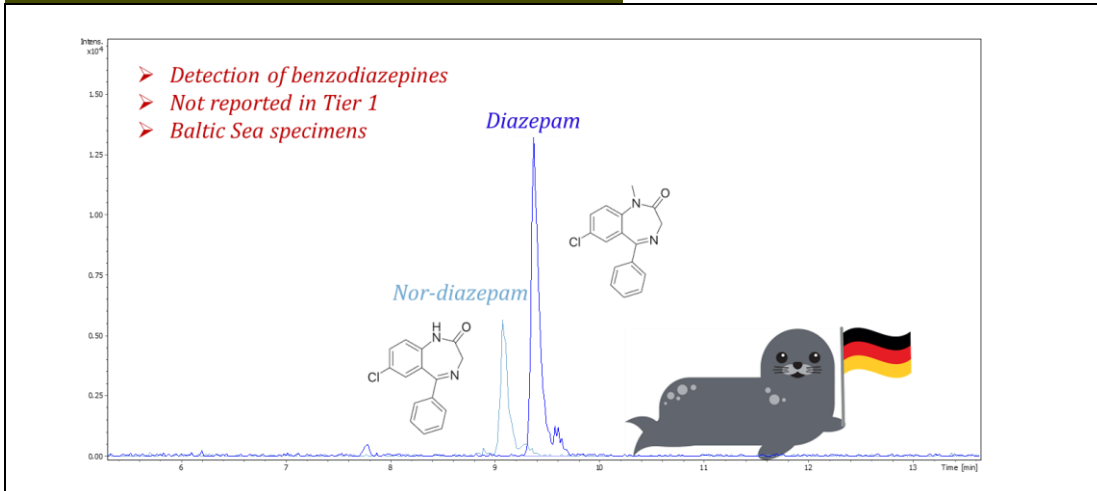
Use of complimentary analytical techniques to fully exploit their detection capabilities



Detection of **additional** PFASs and emerging PFOS alternatives at **trace levels** in AP&P samples (Tier 1):

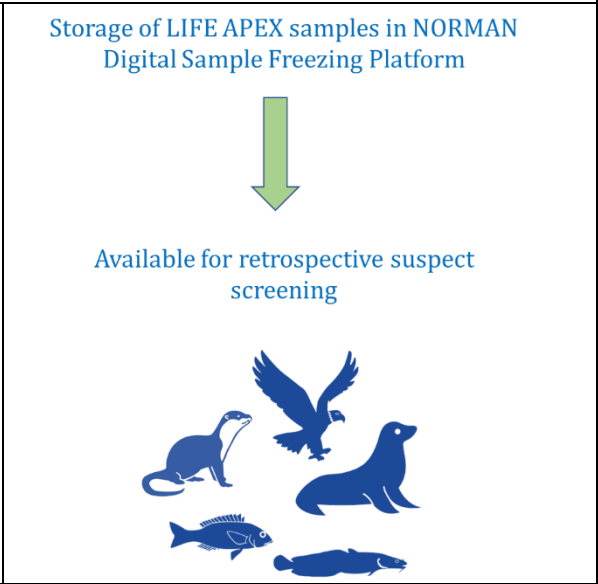
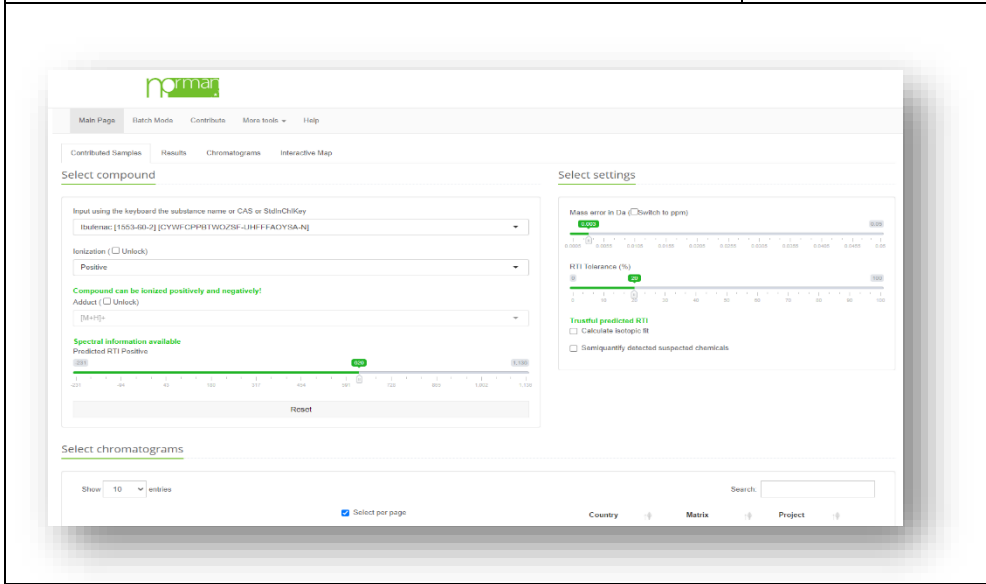
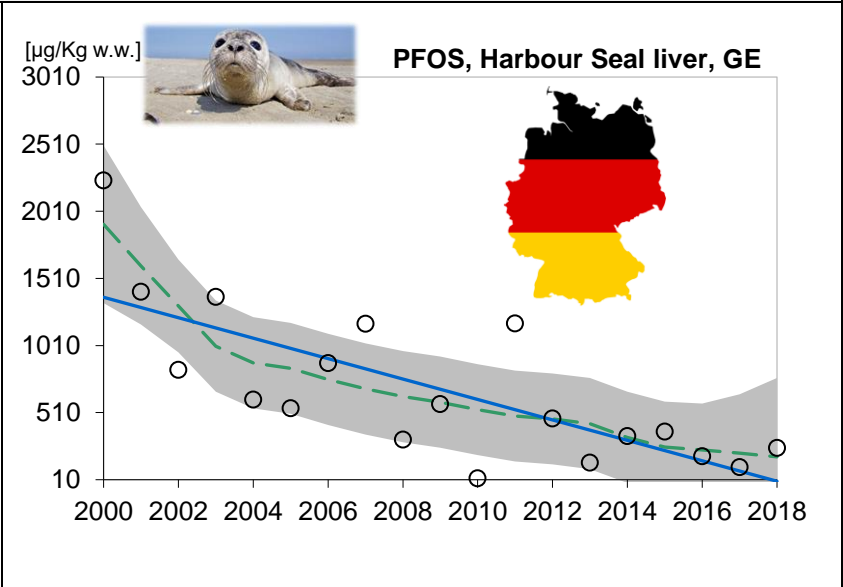
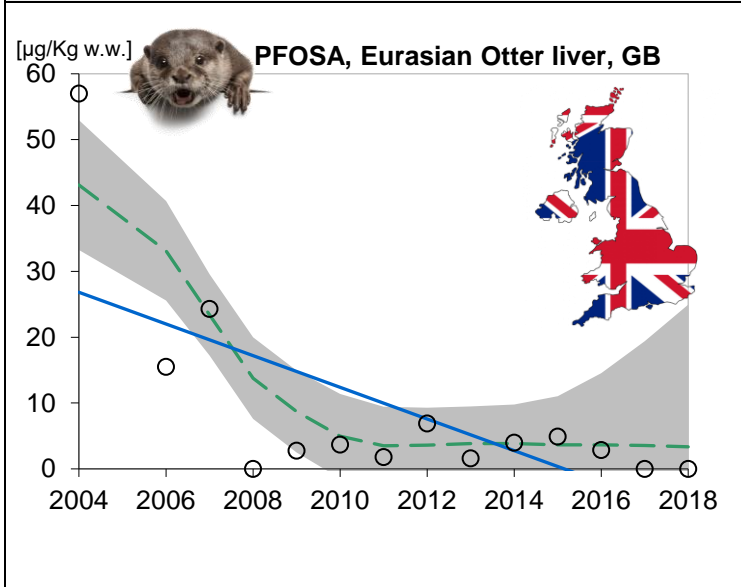
- Long-chain and hyper-long-chain PFCAs (PFTeDA (C14) and PFHxDA (C16), respectively)
- 6:2 & 8:2 FTS
- 6:2 & 8:2 PAPs
- N-EtFOSE and F-53B
- 6:6, 6:8 and 8:8 PFPI's

01: TIER 2: WIDE SCOPE TARGET SCREENING AT UNIVERSITY OF ATHENS



➤ Most of the detected compounds have already been reported in Tier 1 apex predators

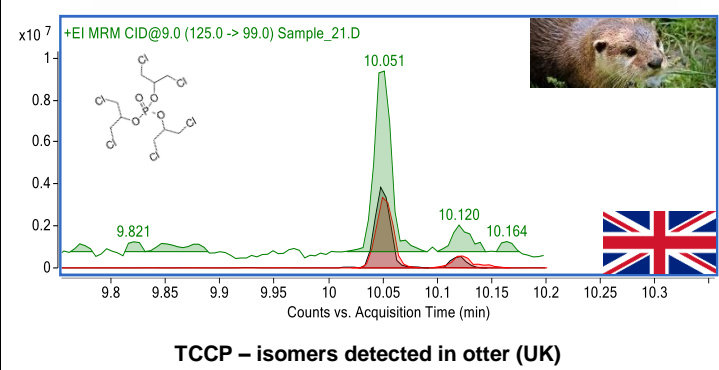
Trend-analysis of the detected emerging contaminants



01: TARGET SCREENING AT ENVIRONMENTAL INSTITUTE

Novel organophosphorus flame retardants – GC-MS/MS

- **TIBP** (Tri-iso-butyl phosphate)
 - 0.36-2.08 ng/g ww – Otter – Groningen, NL
- **TCEP** (Tris(2-chloroethyl) phosphate)
 - 0.15-2.68 ng/g ww – Eelpout – North Sea Varel Mellum, DE
- **TCPP** (Tris(2-chloroethyl) phosphate)
 - 0.11-1.16 ng/g ww – Otter– Solent and South Downs, UK)
- **TDCIPP** (Tris (1,3-dichloropropyl) phosphate)
 - 1.31 ng/g ww – Buzzard – Lower Saxony, DE
- **TPHP** (Triphenyl phosphate)
 - 5.85 ng/g ww – Buzzard – Baden-Württemberg, DE
- **EHDP** (2-ethylhexyl diphenyl phosphate)
 - 0.09-0.45 ng/g ww – Harbour seal – Öresund, SE)
- **TEHP** (Tris(2-ethylhexyl) phosphate)
 - 0.06-3.07 ng/g ww – Harbour seal – Noord-Holland, NL)
- **TBP** (Triphenyl phosphate)
 - 0.12- 5.31 ng/g ww – Harbour seal – Noord-Holland, NL)



01: NON-TARGET SCREENING AT ENVIRONMENTAL INSTITUTE

Samples measured by GC-MS in (Electron Impact/Positive Chemical Ionisation/Negative Chemical Ionisation) SCAN mode

Chromatogram evaluation:

- **Manually**
- **AMDIS** search
- *GC-Digital Sample Freezing Platform in progress*

Manual (example: harbour porpoise, UK):

- Number of determined compounds in total **38**
- Tentatively identified - **22**

AMDIS search (example: harbour porpoise, UK):

- Number of determined compounds in total 300
- Tentatively identified - **63** using APEX library (3200 compounds)

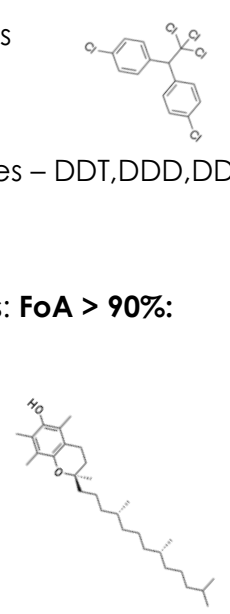
Common overlap of identified compounds: **86%**

Anthropogenic compounds: **FoA > 70%:**

- Polychlorinated biphenyls
- Hexachlorobenzene
- Organochlorine pesticides – DDT,DDD,DDE

Naturally occurring compounds: **FoA > 90%:**

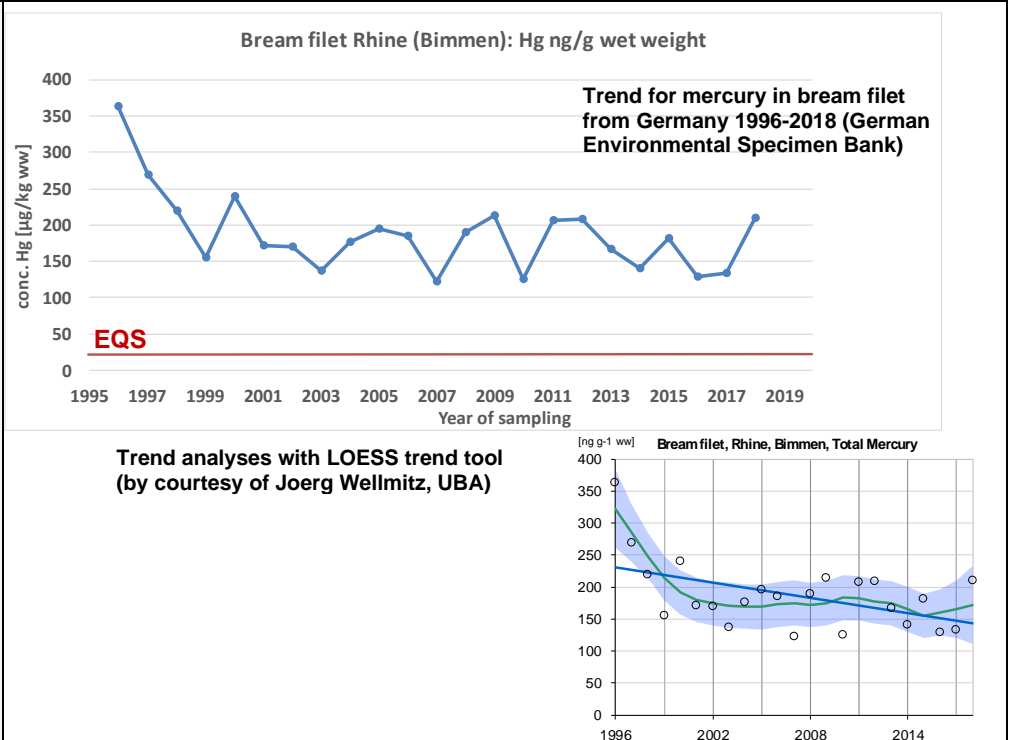
- Steroids
- Alkanes, alkenes
- Alcohols
- Vitamins
- Higher fatty acids



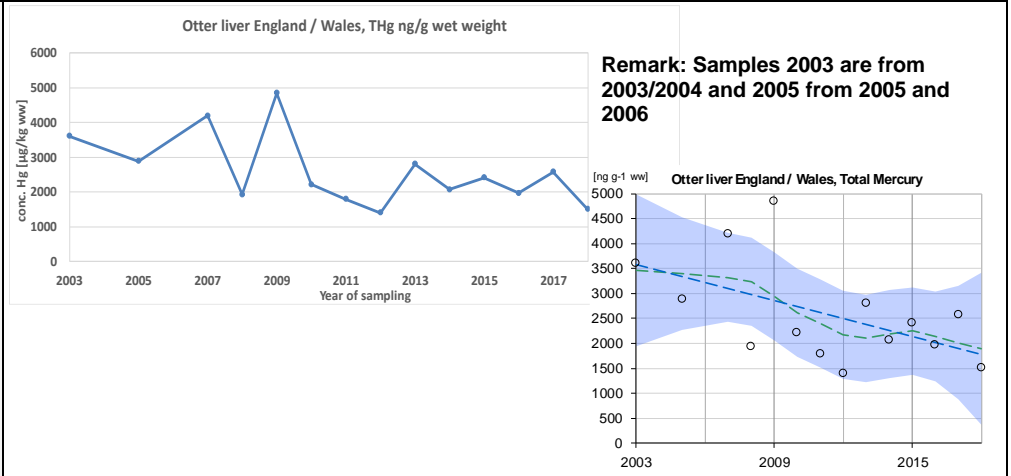
01: TIER 2: MERCURY ANALYSIS AT FRAUNHOFER IME

Mercury is an element of special concern due to its global distribution caused mainly by anthropogenic activities. Therefore, as in Tier 1 (spatial study), mercury was also analyzed in Tier 2 samples (temporal study). Measurements of total mercury were performed with the same methodology as in Tier 1 to assure comparability of the results. A minor part of samples was measured as a solid material by combustion (DMA 80; thermal decomposition, amalgamation, and atomic absorption spectrometry). The majority of samples were digested by a microwave induced acid digestion and measured by CV-AAS/AFS (Cold vapor - atomic absorption/atomic fluorescence spectrometry). The different procedures were necessary because of the high concentration differences among samples as already observed in Tier 1.

- Bream filet Germany:**
- Total mercury concentrations in fish fillet samples are **above** the environmental quality standard (EQS) of the Water Framework Directive (> 20 µg/kg wet weight, ww)
 - Significant linear **decreasing trend** for mercury in bream from sampling site Bimmen (Rhine, Germany)
 - -4.0 ng/g mercury p.a.; last 7 years: -0.8 ng/g mercury p.a.
 - Contrast of samples from **1996 to 2018** (smoother):
 - **-44%**, significant p=0.01 (p.a. - per year)

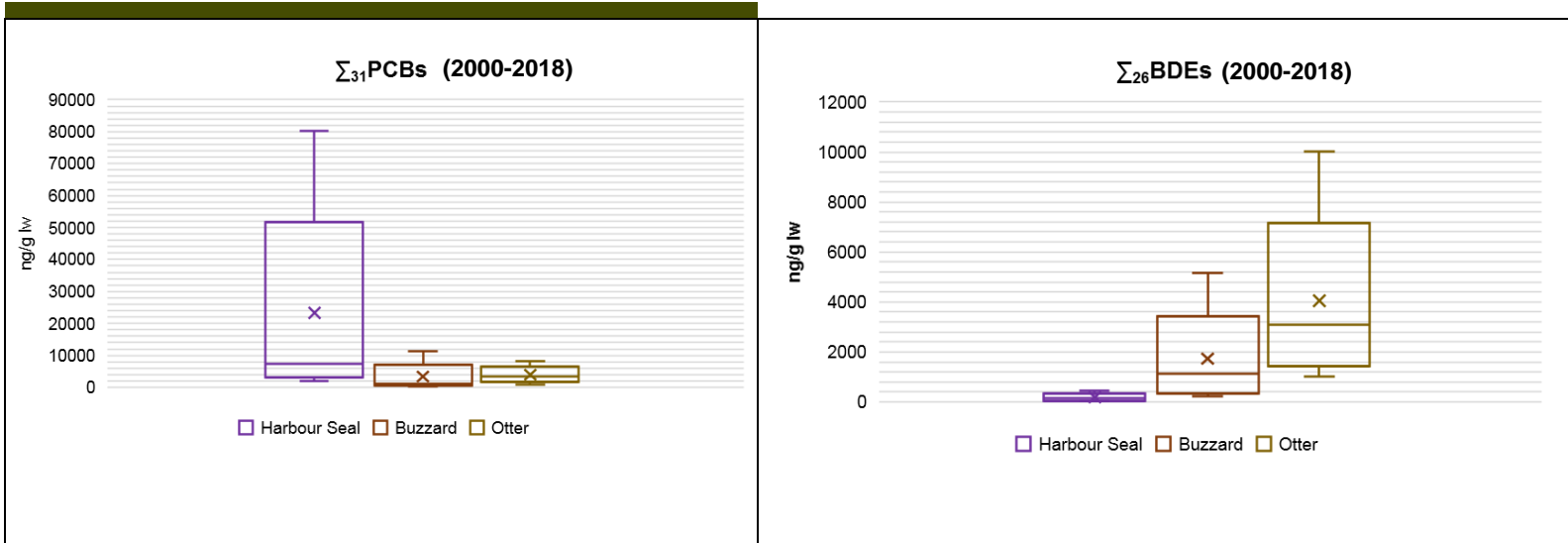


- Otter liver England:**
- No significant linear **decreasing trend** for mercury in Otter liver from England/Wales
 - -120 ng/g mercury p.a.; last 7 years -46.5 ng/g mercury p.a.
 - Contrast of samples from **2003 to 2018** (smoother):
 - **-45%**, not significant p=0.13

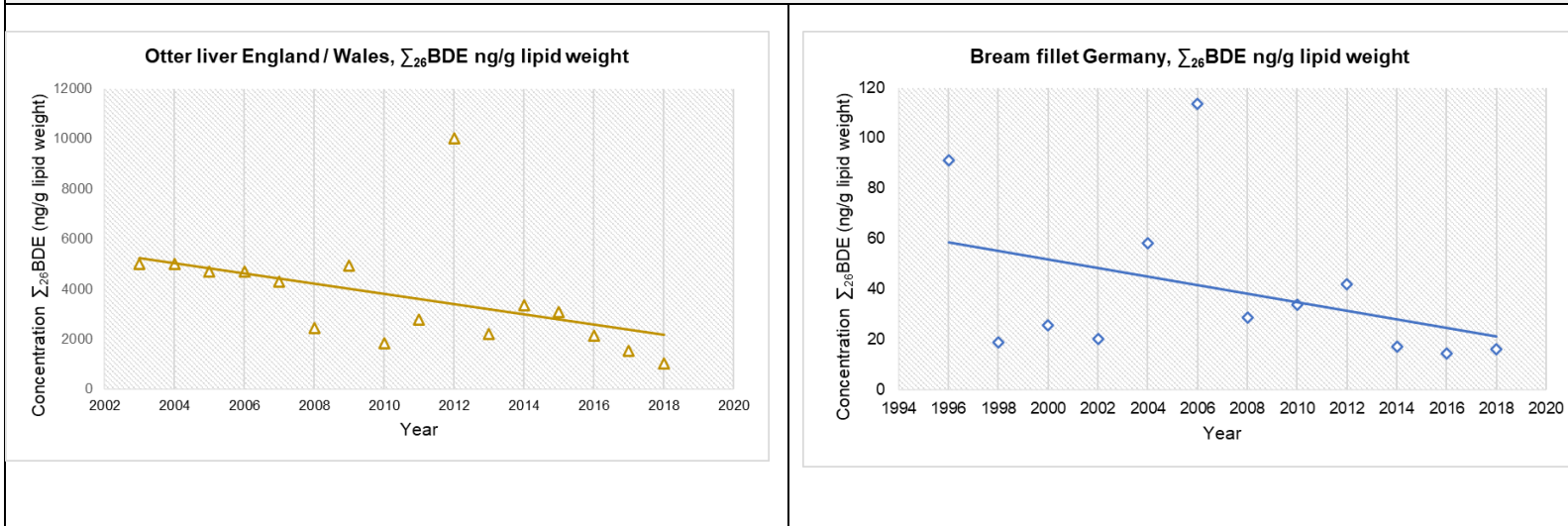


Further Life Apex Tier 2 samples are currently analyzed: one time series of buzzard liver samples from England (UK; 2001-2018) and one set of harbor seal liver samples (Germany; North Sea, 2000-2018). While the first results of the buzzard samples reveal no large temporal variation, the harbor seal mercury data seem to vary without a clear trend.

01: TIER 2: ANALYSIS OF LEGACY POLLUTANTS AT UNIFI



- DioxinLike-PCBs (77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167, 189) are 2.2% (harbour seal), 11.4% (buzzard) and 15.1% (otter) of $\Sigma_{31}\text{PCBs}$.
- Penta-BDEs (28, 47, 100, 99, 153, 154) are 66.3% (harbour seal), 68.4% (buzzard) and 84.1% (otter) of $\Sigma_{26}\text{BDEs}$
- PCB-153 is the most abundant congener in the samples, followed by PCB-138.



- Trend for $\Sigma_{26}\text{BDE}$ in bream fillet from Germany 1996-2018 and Otter liver from South West England, South Central England and South East Wales.

02: DEMONSTRATOR 3 (COMMON BUZZARD)

Use of raptor chemical monitoring data to assess impact and effectiveness of risk management measures at national and European scale

- Work is now well advanced on the **national scale study** for The Netherlands and the UK. Sixty-four buzzard liver samples were shipped from The Netherlands in early October to the University of Florence and are now undergoing analysis for PCBs, PDBEs and Dechlorane Plus (DP) (which have been subject to chemical management measures the last few decades). Second Generation Anticoagulant Rodenticide (SGAR) analysis has started for the UK, where these biocides are subject to a stewardship initiative aiming to reduce exposure in wildlife. Mercury (Hg) analysis will follow the SGAR analysis in the new year, Hg is subject to the international Minamata convention which aims to reduce the levels of Hg in our environment.
- Work has also started on the **European scale study**. A joint survey carried out with the COST Action European Raptor Biomonitoring Facility has located over 1300 buzzard specimens in collections' freezers around Europe. Work is currently under way to select and ship over 70 pooled buzzard liver samples from 10+ countries across Europe to the University of Florence and to the UK Centre for Ecology & Hydrology for analysis.
- Results from the national scale study will be used to simulate the impact that within-year pooling of samples has on the provision of representative country-scale data for the detection of changes, over time, in average residue concentrations, with a view to assessing the power of monitoring with pooled samples. Knowledge on the power of monitoring with pooled samples has the potential to inform the design of cost-effective monitoring (with raptors) of the effectiveness of chemical management measures.

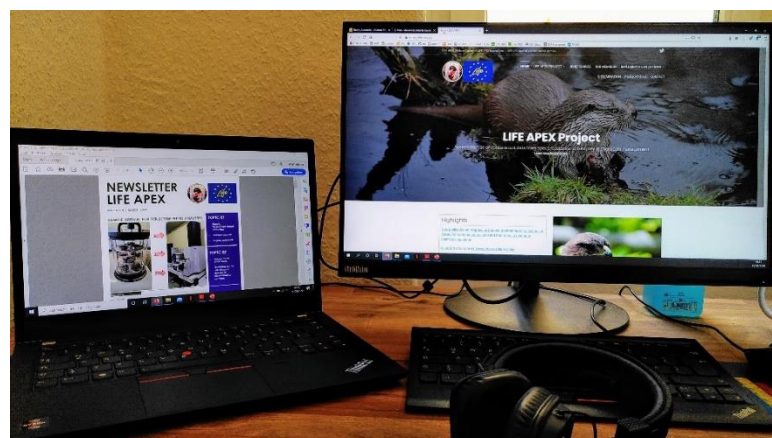
Sourcing of raptor samples across Europe for Tier 3 studies

- Using the results of the above-mentioned survey, work has also begun to select and ship 20 pooled buzzard liver samples in early 2021 from 10 countries to the University of Athens for wide-scope target analyses and non-target screening as part of the Tier 3 studies under Demonstrator 1.

03: VIRTUAL PROJECT MEETING IN JUNE, 2020

Discussion of adjustments to COVID19

- Adjusting laboratory schedules in accordance with national and regional regulations
- Presentation and discussion of Life APEX Tier 2 results
- Proceeding with the development of online data base systems and digital sample freezing platform
- Discussion of sample collection for Tier 3 (wider-European scale)



03: SAMPLE SELECTION FOR TIER 3

Eurasian Otter:

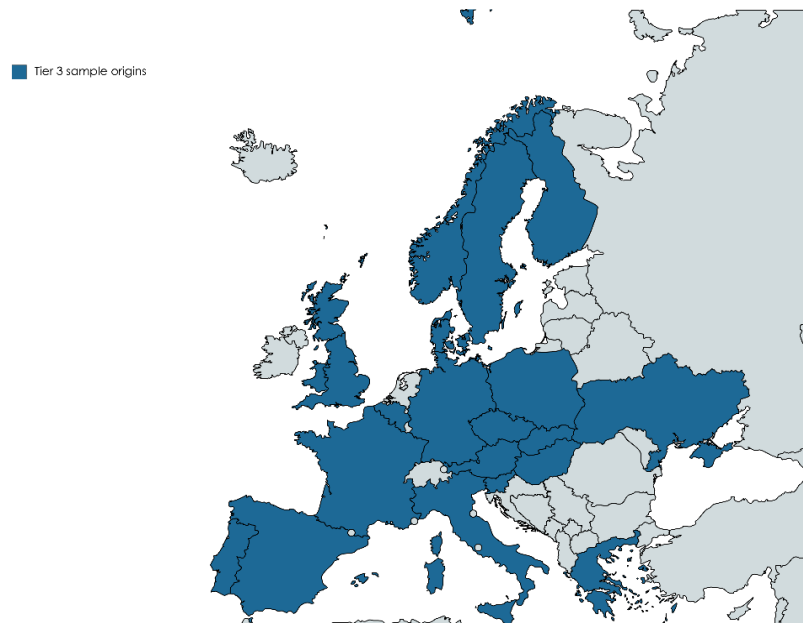
- Italy, France, Austria, England, Wales, Denmark, Czech Republic, Hungary

Marine mammals:

- Grey seal:
 - Germany, Scotland, Belgium, Poland
- Ringed seal & bearded seal
 - Norway (Svalbard)
- Harbour porpoise
 - Ukraine, Scotland, Norway
- Common dolphin
 - Spain, Scotland
- Bottlenose dolphin
 - Spain, Italy
- Striped dolphin
 - Spain
- White-beaked dolphin
 - Scotland

Common Buzzard:

- Slovakia, Greece, Germany, Spain, Portugal, Finland, France, Italy, Sweden, Slovenia




03: ONGOING NETWORKING ACTIVITIES

- Check out the [LIFE APEX Twitter account](#) as well as www.lifeapex.eu for regular project updates
- Life Apex presentations at **regulatory forums**:
 - ECHA PBT Expert Group: EU LIFE APEX Project: *Prioritization of chemicals for PBT-Assessment*
- Life Apex presented at **scientific forums**:
 - AK Umweltmonitoring: *Prioritization of substances of concern with the JANUS tool and assessment of the applicability of such monitoring data for PBT assessment in the European regulatory context*
 - Poster SETAC 2020: *LIFE APEX - Improving the systematic use of contaminant data from apex predators and their prey in chemicals management*



Project Partners

 <p>Environmental Institute</p>	 <p>German Environment Agency</p>	 <p>Naturalis Biodiversity Center</p>	 <p>National and Kapodistrian University of Athens</p>
 <p>Fraunhofer Institute for Molecular Biology and Applied Ecology IME</p>	 <p>UK Centre for Ecology & Hydrology</p>	 <p>Università degli Studi di Firenze</p>	

IMPRINT

Project Coordinator

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Project Manager

Natalia Glowacka is the project manager of LIFE APEX. She got her PhD degree in environmental management. She has more than five years of experience in the field of administration and management of national and international environmental projects in Environmental Institute.



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Alexander Badry is an early career researcher in the field of environmental toxicology. He is working as research assistant at the German Environment Agency and is doing his Doctorate at the Leibniz Institute for Zoo and Wildlife Research on contaminants in birds of prey.



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