Advanced HRMS techniques for the screening of organic micropollutants in white-tailed sea eagles through wide-scope target and suspect methodologies

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Georgios Gkotsis[1]; Alexander Badry[2]; Gabriele Treu[3]; Maria-Christina Nika[1]; Nikiforos Alygizakis[1]; Oliver Krone[2]; Carsten Baessmann[4]; Artem Filipenko[5] Nikolaos S. Thomaidis[1]

[1]National and Kapodistrian University of Athens, Athens, Greece; [2]Leibniz Institute for Zoo and Wildlife Research, Department of Wildlife Diseases, Berlin, Germany; [3]Umweltbundesamt, Department Chemicals, Dessau-Rosslau, Germany; [4]Bruker Daltonics GmbH & Co. KG, Bremen, Germany; [5]Bruker Daltonics, Billerica, MA

Introduction

The increasing use of chemicals has shown to result in environmental emissions and wildlife exposures. Thus, the investigation of the distribution of organic micropollutants in top predators is important not only for understanding exposures within food webs, but also for improving risk management in order to contribute to species conservation. White-tailed sea eagles are a powerful sentinel species for environmental studies, due to their high position in food webs, their relatively long lifespan as well as their residency throughout the year, which allows for the spatiotemporal integration of pollutants signals. In this context, 30 liver samples of recently deceased eagles from Northern Germany, were analyzed following state-of-the-art HRMS methodologies.

Methods

A holistic analytical approach was used for the identification of organic micropollutants, combining different and complementary chromatographic techniques (both liquid and gas chromatography) and ionization modes (electrospray and atmospheric pressure chemical ionization, respectively) coupled to High Resolution Mass Spectrometry (QToF, Maxis Impact, Bruker Daltonics, Germany). For this purpose, two different generic sample preparation protocols were applied for broadening the chemical domain accessible to wide-scope target analysis and suspect screening. More polar, less volatile and thermally unstable compounds were extracted with methanol and acetonitrile, whereas hexane and dichloromethane were used for the extraction of more volatile and thermostable compounds. After analysis, all HRMS chromatograms were digitally archived in the NORMAN Digital Sample Freezing Platform for further retrospective suspect screening.

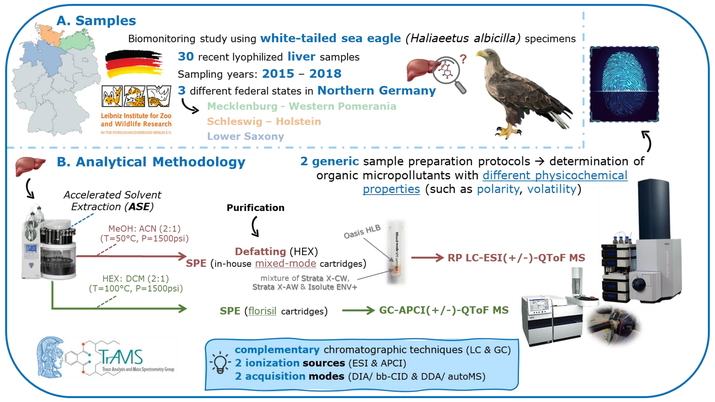

Figure 1: (A) Samples and (B) Analytical methodology for the determination of organic micropollutants by LC- and GC- HRMS.

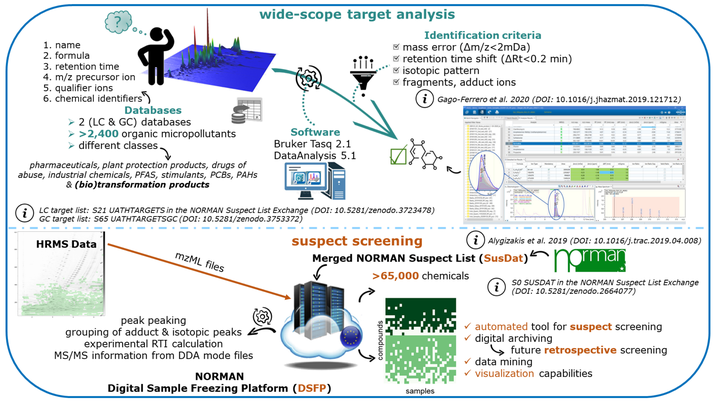

Figure 2: Application of wide-scope target analysis and suspect screening workflows for the determination of known and the identification of unknown organic micropollutants.

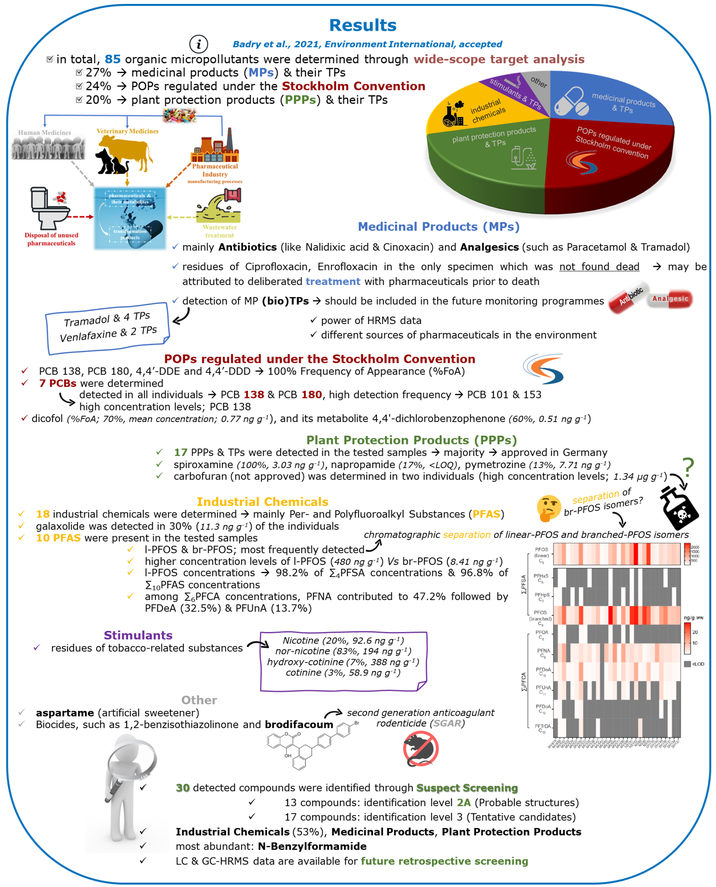

Figure 3: Wide-scope target analysis and suspect screening results.

Results

In total, 85 organic micropollutants were determined through wide-scope target analysis, classified in different categories. The 27% of the detected compounds were medicinal products (MPs) and transformation products (TPs) followed by POPs regulated under the Stockholm Convention (24%) and plant protection products (PPPs) (20%). Among the chemicals regulated under the Stockholm Convention, PCB 138 and PCB 180, as well as 4,4'-DDE and 4,4'-DDD were most frequently detected and show residues in all individuals. Despite their high % Frequency of Appearance (%FoA), the observed concentrations of 4,4'-DDE and PCBs were below the respectively toxicity thresholds. Among the detected PFAS, PFOS showed high concentrations in few individuals (>2.00 μg g^{-1} ww), whereas PFCA concentrations profile indicated, together with the external analysis of stable isotope values a potential biomagnification in the upper trophic levels. Moreover, the detection of numerous TPs in the tested samples underlines the importance of the applied HRMS workflows and indicates that TPs should be included in the future regulatory monitoring programmes.

The suspect screening of more than 65,000 chemicals revealed the presence of 30 additional organic micropollutants. Among them, 13 compounds were identified in level 2A (probable structure), whereas for the rest compounds identification level 3 (tentative candidates) was achieved. The majority of the identified suspect compounds were industrial chemicals, followed by MPs and PPPs.

Conclusions

- The current study demonstrates that white-tailed sea eagles are exposed to a mixture of organic micropollutants.
- Chemical monitoring data from top predators should be included in the risk assessments under the different regulatory frameworks in order to trigger a timely risk management measures before adverse effects in individuals or populations start to manifest
- The chemical fingerprint of apex predators may be revealed by taking full advantage of advanced HRMS techniques and novel workflows.

Environmental: General