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Unveiling the occurrence of organic micropollutants in different species of terrestrial mesocarnivores utilizing HRMS techniques

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ABSTRACT

The introduction of organic micropollutants in terrestrial and aquatic ecosystems, which mainly originate from anthropogenic activities, is supported by overwhelming evidence from global studies conducted as early as the turn of the 20th century. A fraction of these xenobiotics, the regulated "Persistent Organic Pollutants (POPs)", are constantly monitored due to their thoroughly studied persistent, bioaccumulative, and toxic (PBT) properties. Although the occurrence of POPs in the various environmental compartments is well-studied, there are chemicals, which are not systematically subjected to examination, the so-called "Emerging Contaminants (ECs)". These contaminants are not subjected to marketing restrictions or regulatory investigations but are candidates for future regulation, due to their frequent detection in environmental matrices and their potential toxic properties (Gkotsis et al; 2023, Thomaidis et al; 2012, Badry et al; 2022). The partitioning of organic micropollutants through the ecosystems and their subsequent bioaccumulation and biomagnification in the upper trophic levels necessitate the systematic investigation of their presence in this group of organisms. (Badea et al., 2020; Riget et al., 2016). Subsequently, biomonitoring and risk assessment studies that target apex predators benefit from certain characteristics of their trophic position in the ecosystem, such as their relatively long lifespan over which bioaccumulation occurs, the incorporation of spatial and temporal exposure, and the relative ease of quantifying their populations (Movalli et al; 2022, Malarvannan et al; 2020). Even though there are many biomonitoring data concerning the presence of xenobiotics in marine organisms, the respective data on terrestrial predators are scarce.

The aim of the current biomonitoring study is to reveal the chemical fingerprint of terrestrial mesocarnivores gathered from Germany by utilizing complementary chromatographic techniques coupled with High-Resolution Mass Spectrometry (HRMS). In this framework, 23 mesocarnivore liver samples collected in Baden-Württemberg state, Germany between 1993 and 2021, were analyzed following wide-scope target screening methodologies, in order to investigate the presence of organic micropollutants. Different species were analyzed, including European polecats, beech martens, and European pine martens.

Briefly, the analytes were extracted from lyophilized liver samples through generic sample preparation protocols using Accelerated Solvent Extraction (ASE), followed by a purification step using Solid Phase Extraction (SPE). The cartridges used for the SPE step were in-house mixed-mode and Florisil, for LC and GC analysis, respectively. The final extracts were analyzed by Liquid Chromatography (LC) with Electrospray Ionization (ESI) and Gas Chromatography (GC) with Atmospheric Pressure Chemical Ionization (APCI) as ion sources, coupled with HRMS, to broaden the chemical domain accessible to wide-scope target analysis.

The acquired HR-MS data were screened for the presence of more than 2,400 organic micropollutants, included in the target lists of the National and Kapodistrian University of Athens (NKUA). Compounds of different classes (such as pharmaceuticals, personal care products, illicit drugs, plant protection products, stimulants, industrial chemicals, sweeteners, plasticizers, surfactants, flame retardants, and phthalates), as well as their Transformation products (TPs) and metabolites, are included in the NKUA datasets, which are updated regularly. The LC and GC target lists are available as data sets in Zenodo((DOI: 10.5281/zenodo.3723478, and GC database DOI:10.5281/zenodo.3753372, respectively). The data treatment protocols applied during the target screening utilized the strict identification thresholds of mass accuracy (<2mDa), retention time shift (<0.20min), isotopic pattern fitting (mSigma<100), and fragmentation pattern match. The standard addition method was used for the quantification of the analytes (Gago-Ferrero et al;2020).

The results yielded by the LC & GC HRMS analysis reveal the presence of numerous organic pollutants in the tested samples, classified under several different chemical categories, such as pharmaceuticals (including venlafaxine, gabapentin, oxfendazole), plant protection products (like jasmolin, propoxur, and tralkoxydim), personal care products (for instance the parabens butylparaben, ethylparaben, methylparaben). Furthermore, several industrial chemicals were detected comprising of 4 Polychlorinated Biphenyls (PCBs), 6 Polycyclic Aromatic Hydrocarbons (PAHs) and 14 Per- and Polyfluoroalkyl Substances (PFAS). In addition to the parent compounds, multiple TPs of pharmaceuticals, plant protection products, as well as coffee and tobacco-related compounds were detected in the terrestrial mesocarnivore liver samples. Moreover, the most abundant and frequently detected xenobiotic compound was PFOS, affirming its persistent and bioaccumulative properties already reported in the literature (Rupp et al; 2023). The persistence of these analytes may cause potentially harmful effects on the environment and eventually on human health and therefore should be thoroughly investigated in environmental studies. Overall, the previously indicated findings highlight the importance of HRMS wide-scope target screening methodologies in biomonitoring studies.

KEYWORDS: Organic Micropollutants; High Resolution Mass Spectrometry; Biomonitoring; Terrestrial Ecosystem; Mesocarnivores.

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