Influence of microplastics in the bioconcentration and depuration of organic pollutants in European eels

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Abstract. Despite high levels of organic pollutants (OPs) have been found in ecosystems considered as the habitats of European eels, there is scarce information about the bioconcentration and depuration kinetics of such OPs, and only few research has reported them in different eels' tissues. In this research, the bioconcentration and depuration kinetics of a cocktail of 22 OPs in muscle, liver tissue and plasma of silver European eel were studied through a laboratory approach. Eels were distributed in three groups: control, exposed to OPs, and exposed to OPs and microplastics (MPs). The study was carried out for 58 days separated in two stages (i) exposure during days 0–28, and (ii) depuration during days 29–58. OPs in eels' muscle and liver samples were extracted by QuEChERS and dispersive solid phase extraction (dSPE) whereas plasma was extracted by SPE. Then, extracts were analysed via UHPLC-MS/MS. OPs showed increasing concentrations in the three tissues (PFDA, PFOS, PFOA, chlorpyrifos, and terbuthylazine), or in some of them. PFASs' bioconcentration followed the trend plasma > liver tissue > muscle. Two tendencies were observed in the depuration phase. One with OPs concentrations that tended to decrease (chlorpyrifos and terbuthylazine; in all tissues), another one, with concentration values that were similar or even tended to be higher than at the exposure phase (PFDA, PFOS, and PFOA; in all tissues). The presence of MPs seemed to affect the bioconcentration and depuration of OPs in eels' tissues (increased kinetic bioconcentration factor BCF_k). Pollutants are believed to be a key issue in understanding the reasons for the eels' stock decrease and therefore, further research about PFASs, PPCPs and pesticides accumulation, depuration and toxicity on eels is imperative as this may be of great interest for human risk assessment of this widely consumed fish.

1. Introduction

Pollutants of anthropogenic origin are widespread in groundwater and surface water globally including pharmaceuticals and personal care products (PPCPs), per- and polyfluoroalkl substances (PFASs), pesticides, microplastics (MPs), and so on. In this study, the European eel (*Anguilla Anguilla Linnaeus*, 1758) was selected to study the bioconcentration of OPs, given its physiological and behavioural characteristics, which make it vulnerable and sensitive to the presence of these substances (1). Furthermore, in 2007, it was placed on the International Union for Conservation of Nature's Red List of Endangered Species, listed as "critically endangered" (2). Overfishing, water barriers hindering migration, climate change, parasitic diseases, habitat reduction and chemical pollution, among others, can be defined as main causes of the drastic reduction of its population since 1970 (1). Up to our knowledge, there are no studies covering cocktails of emerging OPs, belonging to different families, in which bioconcentration and depuration are assessed in different eel's tissues. Consequently, the general aim of this research was to study the bioconcentration and depuration kinetics of a mixture of 22 OPs in muscle, liver tissue and plasma of European eel, and to evaluate the influence of MPs in them.

2. Materials & Methods

The OPs included 10 PPCPs, 5 pesticides, 5 PFASs and 2 illicit drugs, which were inoculated through water or food, depending on their chemical properties (such as solubility). The compounds of the former group are acetaminophen, atenolol, bentazone, bufotenine, caffeine, diclofenac, etoricoxib, ibuprofen, imazalil, naproxen, perfluorobutane sulfonate (PFBS), perfluorodecanoic acid (PFDA), perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluoropentanoic acid (PFPeA), salicylic acid, terbuthylazine, and vildagliptin (n=18). The compounds that were supplied through food include (n=4): chlorfenvinphos, chlorpyrifos, triclosan and 4-methoxyphencyclidine (4-MeO-PCP). The experimental study lasted 58 days including: (a) an exposure stage between days 0 and 28, in which the mixture of OPs and MPs was administered through water (10 µg/L of OPs and 0.04 g MPs per specimen), and through food (20 ng per eel/day); and (b) a depuration phase, between days 29 and 58, in which the water from aquariums was renewed (clean water without pollutants). OPs in eels' muscle and liver samples were extracted by QuEChERS and dispersive solid phase extraction (dSPE) whereas plasma was extracted by SPE (3). Then, extracts were analysed via UHPLC-MS/MS. Water samples were analysed every day during the exposure stage to verify the real concentration of OPs.

3. Results & Discussion

The exposure through water of diclofenac, etoricoxib, imazalil, PFDA, PFOA, PFOS, terbuthylazine, and through food of chlorpyrifos, at the tested concentrations, seemed to cause their bioconcentration in the three eels' tissues (with and without MPs). Other pollutants appeared to show a preferential tissue bioconcentration as caffeine, chlorfenvinphos (muscle),

naproxen (liver), bufotenine and PFBS (plasma), triclosan (muscle, liver), and 4-MeO-PCP (liver, plasma). During the exposure stage, two different trends were observed. A first group of OPs with increasing concentrations in the three tissues (PFDA, PFOS, PFOA, chlorpyrifos, and terbuthylazine), or in some of them, and a second group with less clear or erratic trends. PFASs concentrations followed the trend plasma > liver tissue > muscle. The occurrence of MPs seemed to play an important role in the bioconcentration kinetic of the OPs analysed here. Some recent research have proved that MPs can act as vectors of pollutants in the aqueous environment (4). During the depuration stage, the OPs described two trends. In the first one, concentrations tended to decrease (chlorpyrifos, terbuthylazine), and in the second one, concentrations were similar or even tended to be higher than were those measured at the exposure phase (PFDA, PFOS, PFOA). In relation to the occurrence of MPs, concentrations reached at the end of the depuration phase tended to be higher at the group with MPs than at group without them in muscle and liver tissue, but lower in the group without them in plasma.

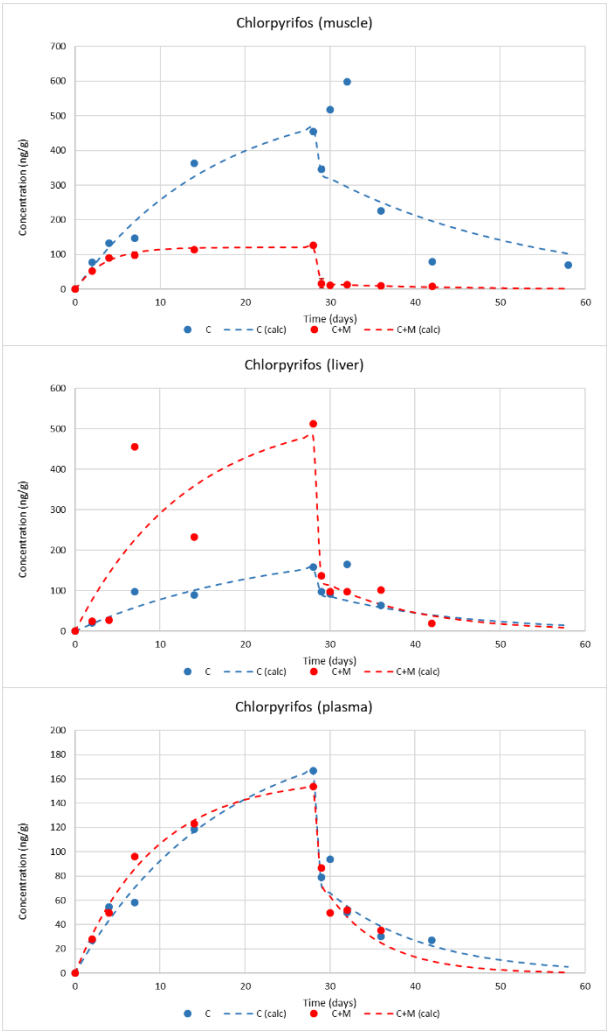

Fig 1. Toxico-kinetic curves obtained from the modelling in both groups (C: OPs, C+M: OPs + MPs) for chlorpyrifos.

From the 22 compounds initially considered, chlorpyrifos, PFDA, PFOA, PFOS, and terbuthylazine were modelled in the three matrices (Fig. 1). Kinetic bioconcentration factors (BCF_k) presented similar ranges in the three eels' tissues studied but some differences were observed between OPs and between groups. PFAS's BCF_k values were related to their lipophilicity, describing the trend PFDA > PFOA ≈ PFOS > PFBS. The kinetic factors of terbuthylazine and chlorpyrifos tended to be higher in muscle than in liver tissue (or plasma). The occurrence of MPs seemed to increase the BCF_k of PFASs in liver and plasma while in muscle appeared to decrease. Chlorpyrifos' BCF_k seemed to increase in their presence in liver but to decrease in muscle and plasma whereas terbuthylazine seemed to augment with MPs in muscle and plasma.

4. Conclusions

Many pollutants are widespread and measured concentrations are at a level that more than likely is causing ecotoxicological effects in European eels. Legacy substances such as PCBs and heavy metals are relatively well studied, however the impact on the eel of emerging compounds (e.g. PPCPs, PFASs, illicit drugs, etc.) which are known to pose serious and increasing problems in aquatic ecosystems, is poorly understood. Compared to other fish species, eels are challenging to study and to protect due to their catadromous and semelparous lifecycle. We have proved that pollutants are not distributed evenly among eels' tissues and that higher concentrations can be found in plasma and liver than in muscle. Bioconcentration and depuration of OPs in eels seemed to be highly determined by the type of pollutant, and by different processes related to the combination of a mixture of chemicals including the presence of MPs. Further research is needed to clearly understand the effects and toxicity, singly and cumulatively, of multiple and different pollutants in target organs of (wild) eels, and to assess their partitioning and distribution among eel tissues. Studying the role of pollution in eel population dynamics and health is crucial, and quantifying the magnitude and the level at which one or more emerging pollutants may affect immune and reproductive systems is critically important.

References

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