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Passive dosing to characterize the sorptive capacities of biota lipids from various trophic levels

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1. Introduction

In a bioaccumulation context, lipids are considered to be the major partitioning phase for hydrophobic organic chemicals. What is referred to as "lipid", however, is a complex matrix consisting of a highly variable mixture of neutral ('storage') and polar ('membrane') lipids. Furthermore, each category comprises lipids with largely different fatty acid compositions. In addition, depending on the organism's fraction of lipids and proteins and the properties of a chemical, other sorptive phases (e.g. proteins) may be particularly important.

The variability of the sorptive capacities of biota lipids has been discussed recently, with some studies showing only minor differences in the sorptive capacities of a range of pure lipids [1,2] while other studies report considerable differences in so-called necroconcentration factors (i.e. whole-body homogenate/water partition ratios), with increasing partitioning into the homogenate of organisms from higher trophic levels [3]. The aim of the present study was to expand our studies of the sorptive capacities of pure lipids into more realistic media, i.e. extractable organic matter obtained by traditional exhaustive lipid extraction of biota from various trophic levels.

2. Materials and methods

We performed traditional solvent-based extraction [4] of tissue homogenates of five different species: whole blue mussels, herring muscle, pork bacon, guillemot egg and seal blubber. The mass of the resulting extract, here denoted extractable organic matter (EOM), is frequently used as a surrogate for the lipid fraction. In this study, we exposed the obtained EOM for 28-214 hours to a range of model chemicals by partitioning via the shared headspace of a closed passive dosing system (Figure 1, [5]). Commercial olive oil served as passive dosing donor and contained the cyclic volatile methyl siloxanes (cVMS) D4, D5, D6, and tri- and tetrachlorobenzene (TriCB and TeCB). Aliquots of non-spiked olive oil were also used as control samples and for characterizing the uptake kinetics.

The following steps were part of the experiment: i) traditional exhaustive extraction to yield EOM [4]; ii) passive dosing of replicates of each EOM sample via a common headspace (Figure 1); iii) sampling of EOM and control olive oil at different time points; iv) purge and trap extraction of the model chemicals from the EOM samples onto ENV+ SPE cartridges, elution and direct GC/MS analysis [6]; v) determination of the fractions of storage and membrane lipids in the EOM samples and the olive oil control via NMR, SPE [7], followed by LC-ELSD and GC-FID.

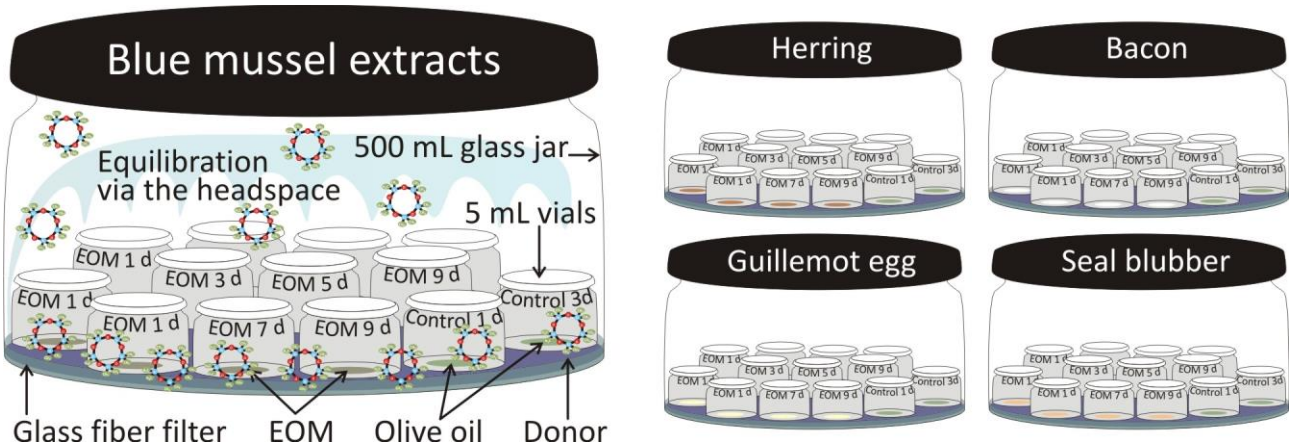

Figure 1: *Passive dosing units for the EOM obtained from tissue homogenate of five different biota samples, illustrated for D5.*

3. Results and discussion

The fraction of EOM extracted from the five biota samples ranged from 1.4% (whole blue mussels) to 95% (seal blubber). The method quantification limits (MQL) were relatively high for the cVMS due to blank contamination (Figure 2); with data <MQL being considered as semi-quantitative. The equilibration between the olive oil donor and the EOM samples and olive oil controls in the passive dosing units was fast for the cVMS, in the range of 1-2 days for D4, 2-4 days for D5 and 4-6 days for D6. The chlorobenzenes approached, but did not fully reach equilibrium, and their equilibrium partitioning concentrations were hence estimated. We observed chemical losses from the repeated opening of the passive dosing jars to remove vials, with the lowest recovery being 83% for the most volatile compound, D4.

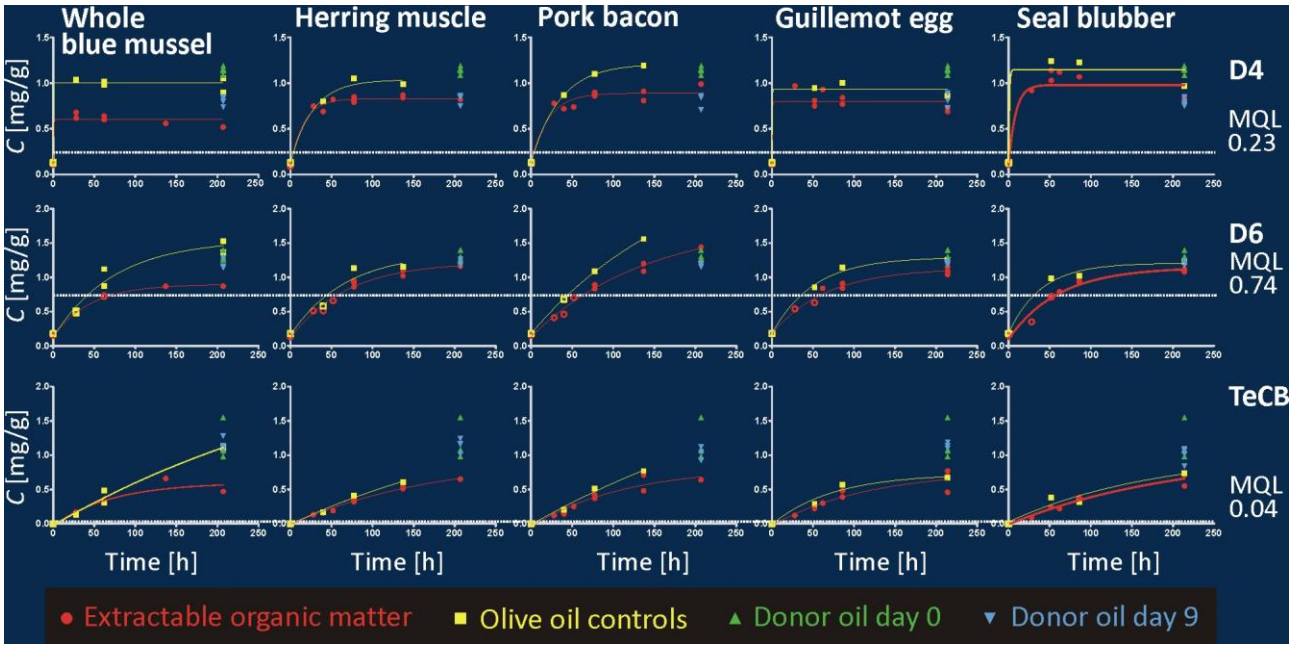

Figure 2: *Uptake kinetics of D4, D6 and TeCB into the EOM samples (red) and olive oil controls (yellow) The concentrations in the donor oils from before the experiment ("day 0", green) and at the end of the dosing experiment ("day 9", blue) are also plotted.*

The obtained results show minor differences of less than a factor of 3 in the sorptive capacities of the EOM obtained from biota of different trophic levels using the protocol *of Jensen et al. (1983)* [4]. The olive oil controls generally showed higher sorptive capacities for the model chemicals than the EOM samples. The partitioning of the model chemicals between EOM and olive oil was not statistically different for EOM originating from bacon and seal blubber, whereas small but statistically significant differences were found for some chemicals in EOM from blue mussels, herring and guillemot egg compared to olive oil. The highest fractions of polar lipids were found in EOM obtained from blue mussels and guillemot egg, which may partly explain the observed differences.

The applied extraction method [4] is known to be particularly suitable for neutral lipids, and even though we found considerable amounts of polar lipids in our extracts, the similarity between the sorptive capacities of the obtained EOM samples and olive oil may in part be explained by a bias as a result of the extraction method. It may hence be advisable to carry out additional experiments in which the EOM is obtained using a more universal extraction protocol.

4. References

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