ANALYSIS OF (MICRO-)PLASTIC-ASSOCIATED CHEMICALS RELEASED INTO MARINE ENVIRONMENTS BY COMPREHENSIVE MULTIDIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Investigating the chemical composition of microplastics and their leachates to better understand microplastic leaching in the marine environment, as well as inform exposure and risk from plastic-associated chemicals.

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Background

Plastic materials contain many different chemicals, which include functional additives as well as trace levels of non-intentionally added substances. Plastic released into the environment acts as a vector for these chemicals, which may cause harm to exposed organisms. The complex mixture of chemical classes and concentrations within plastics is a challenge for analysis, which can be addressed through the use of multidimensional analytical approaches.

Here, the chemical composition of different polymer samples was analysed using comprehensive multidimensional gas chromatography coupled to time-of-flight mass spectrometry. Ultrasonication assisted extractions with solvent represents a 'worse-case-scenario' in relation to environmental leaching, and provides a starting point for non-target analysis of microplastic leaching in marine environments.

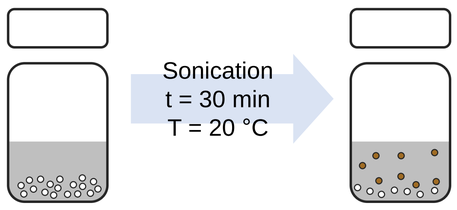
Methods

Polymer Samples

Conventional polymers
- low-density polyethylene (LDPE)
- polypropylene (PP)
- polyvinyl chloride (PVC)
- polyethylene terephthalate (PET)

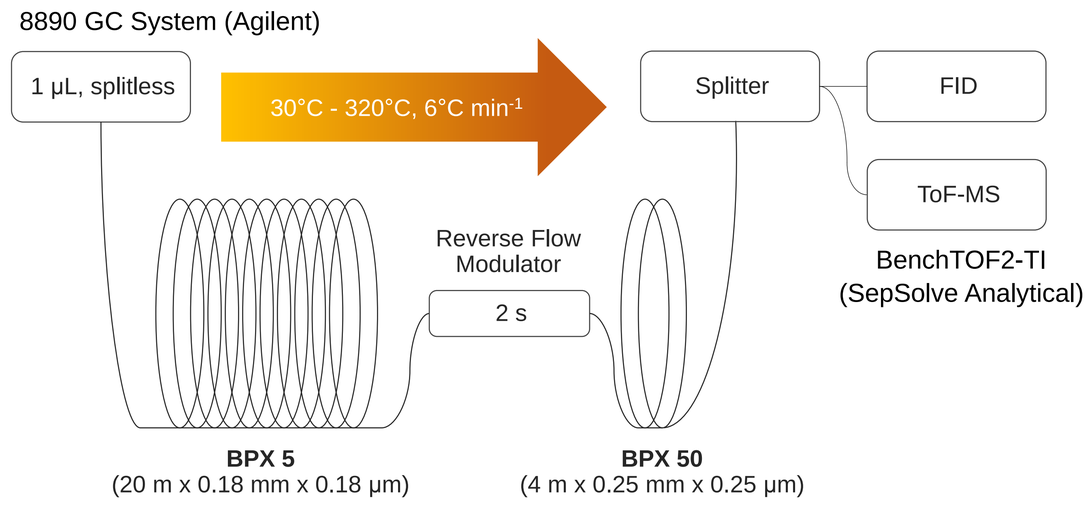
Biopolymers
- polylactic acid (PLA)
- polybutylene succinate (PBS)
- poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)
- polybutylene adipate terephthalate (PBAT)

Organic extractions



Microplastics were generated from virgin polymer pellets. The microplastic samples underwent organic extraction using MeOH, DCM:MeOH (2:1, v/v), Hexane, and EtOAc. The extract was filtered through DCM washed glass wool to remove the plastic, subject to an N_2 blow-down, then made up in DCM for analysis.

GC×GC



Results

All the virgin polymer samples released chemicals under organic extraction. As shown in *Figure 1*, the number of compounds released by each polymer was influenced by the solvent used for the extraction. Additionally, the conventional polymers released a higher number of chemicals than the biopolymers, particularly LDPE and PP.

The high number of compounds released by LDPE and PP is due to the release of polymer-derived alkanes. The use of GC×GC enabled separation and identification of other plastic-associated compounds from the alkane series (see respective chromatograms). In contrast, the other polymers released a range of compound classes. Some of the compounds identified in the extracts, for example phthalates, are detrimental to both human and environmental health.

Below are example chromatograms for the polymer extracts indicated, with compounds of interest shown alongside their application.

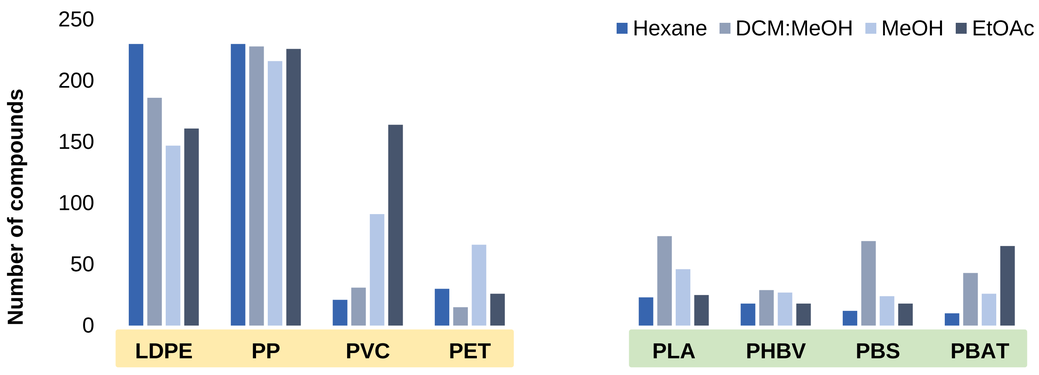
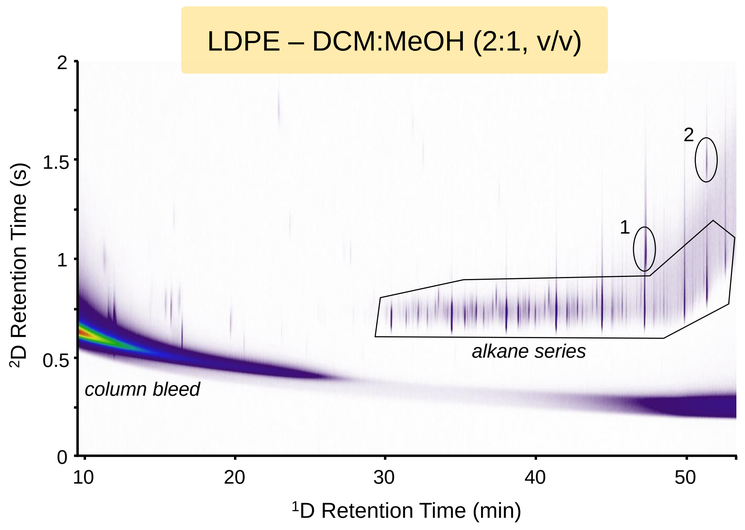
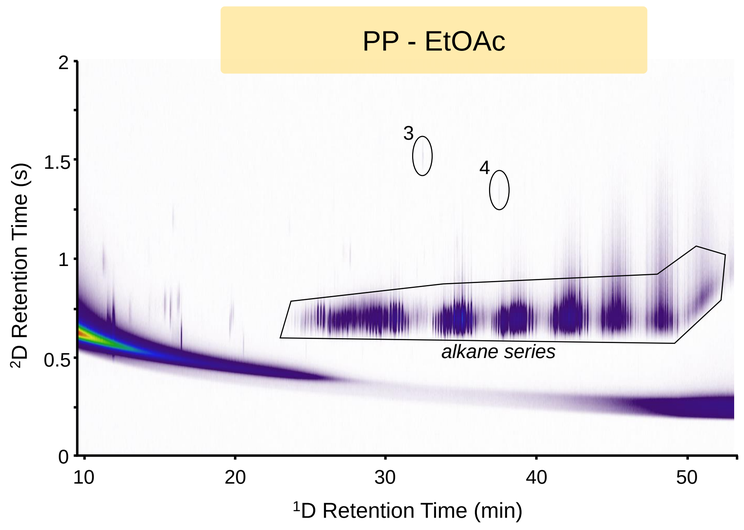
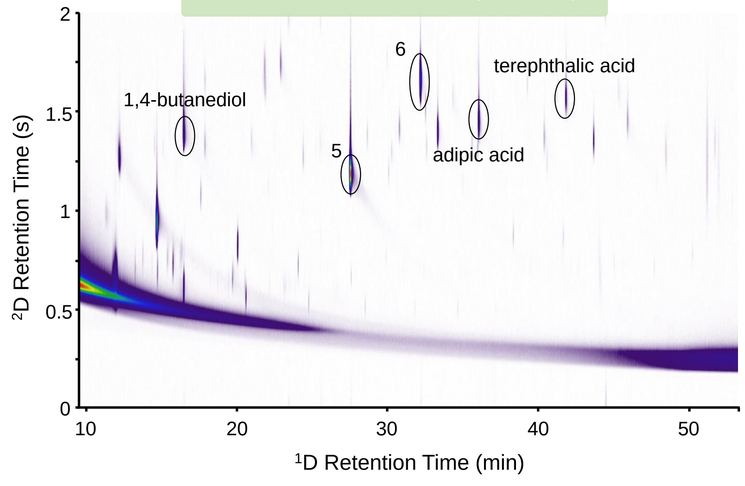
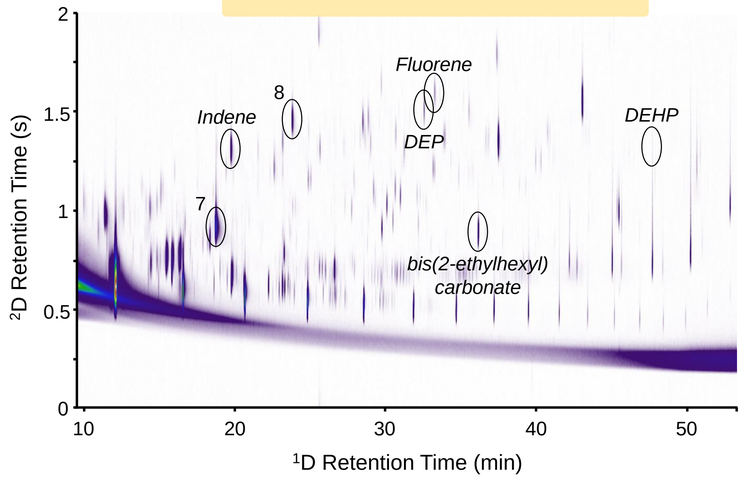


Figure 1: Number of compounds released by each polymer into the different solvents used for extraction



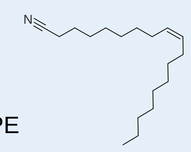






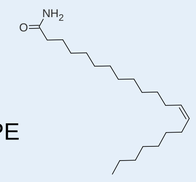
1. Oleonitrile

Lubricant used in production and processing of LDPE



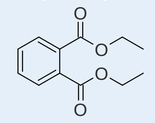
2. Erucamide

Slip agent used in production and processing of LDPE



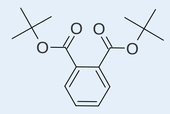
3. Di-ethyl phthalate (DEP)

Common plasticiser



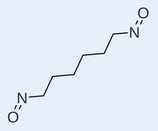
4. Di-tert-butyl phthalate

Common plasticiser



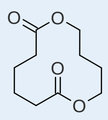
5. 1,6-diisocyanato-hexane

Potentially used as a cross-linking agent or filler



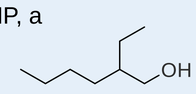
6. 1,6-Dioxacyclododecane-7,12-dione

Plasticiser or breakdown product of PBAT polymer structure



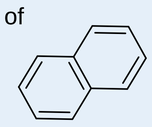
7. 2-ethyl-1-hexanol

Pre-cursor to DEHP, a plasticiser in PVC



8. Naphthalene

Used in manufacture of phthalic anhydride, a pre-cursor to many plasticisers



Conclusion

Chemical extracts from several polymer samples demonstrated that virgin polymer samples contain chemicals which are not chemically bonded to the bulk polymer material – and therefore have potential to be released into the environment. Future leaching studies can be informed by the chemical identifications made, and increase the confidence that those compounds identified in leachates did originate from the respective polymer.

Next Steps

The next steps are to develop a method for analysis of aqueous leachate samples – using the chemical information from the organic extractions. Spiked water samples will be used to develop and optimise an online, direct immersion solid-phase microextraction using SPME Arrows coupled to GC×GC-ToF-MS, after which the method will be used to analyse marine leachate samples which have been prepared with the microplastic samples used here.

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