Monitoring of Recycled Plastic –
An important Analytical Task in a Circular Economy

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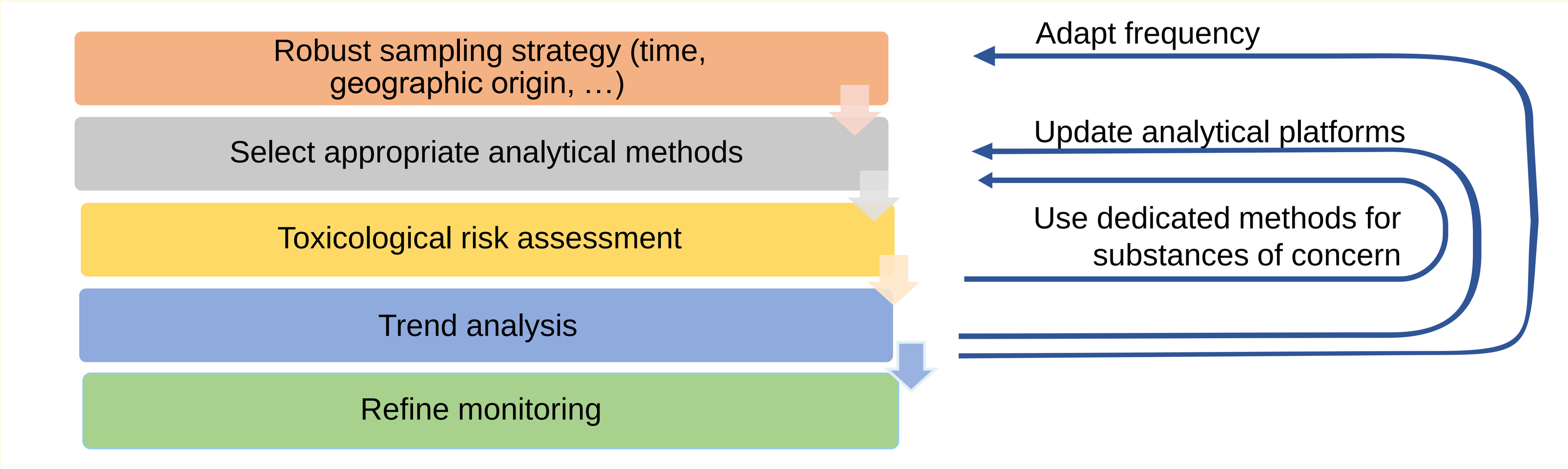
SUMMARY

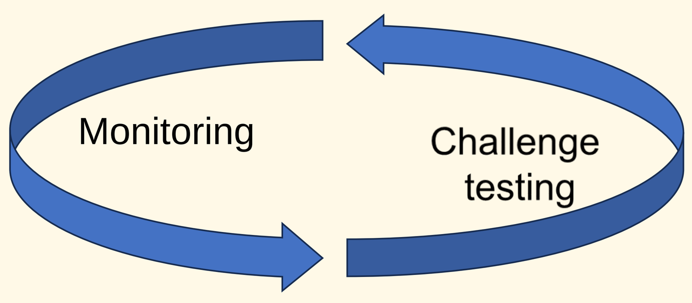
Recycled plastic intended for use as food-contact material must meet the highest safety standards. Therefore, EU 2022/1616 calls for monitoring: the determination of the contamination level before and after recycling. In this case study, real life PET samples were extracted, concentrated and analyzed with GC-MS. Migration modelling and toxicological risk assessment were conducted to conclude that the recycled material was considered safe in view of the intended use. Such a multi-step approach is labor intensive. A screening approach which correlates chromatographic retention to physico-chemical properties, such as OECD 117 for the partition coefficient, may be a future tool to create safety-evaluation data more efficiently. To monitor polyolefin recycling, sample-preparation methods need to be improved to reduce the oligomeric background in GC-MS, or chemometric data interpretation should be applied.

Introduction: Monitoring according to EU 2022/1616

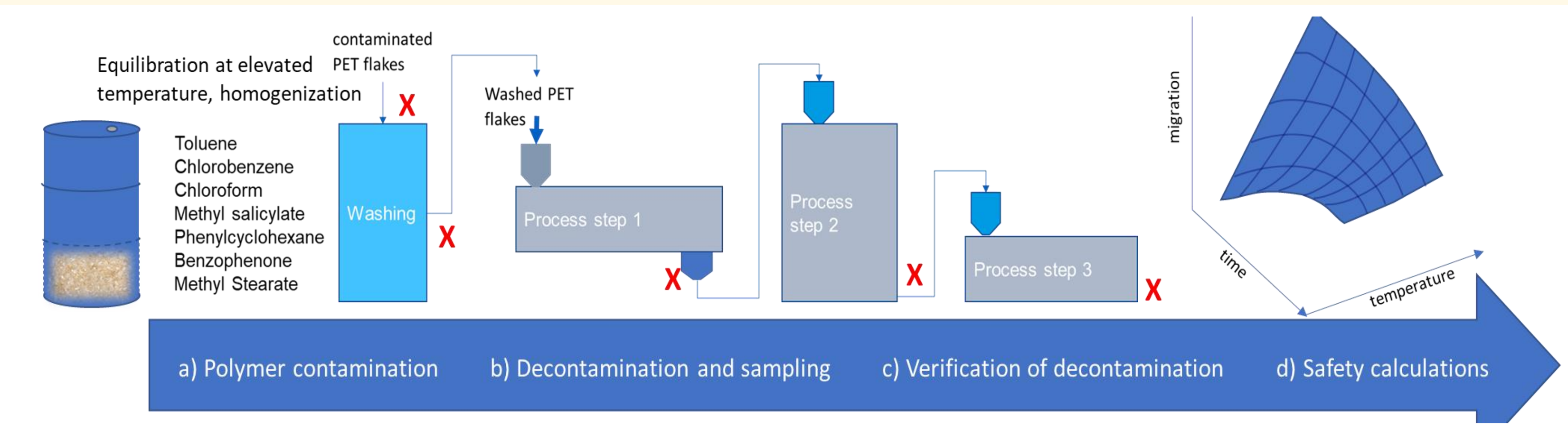
Contamination from previous use may reside in the recycled plastic. Therefore, the contamination level needs to be monitored on a regular basis to assure safe use of the recycled plastic. Regulatory expectations for the monitoring are described in **Article 13 of (EU) 2022/1616** [1]. The steps and decision moments during monitoring are:



The monitoring results may trigger adaptions of, for instance, the sampling strategy and the analytical methods.

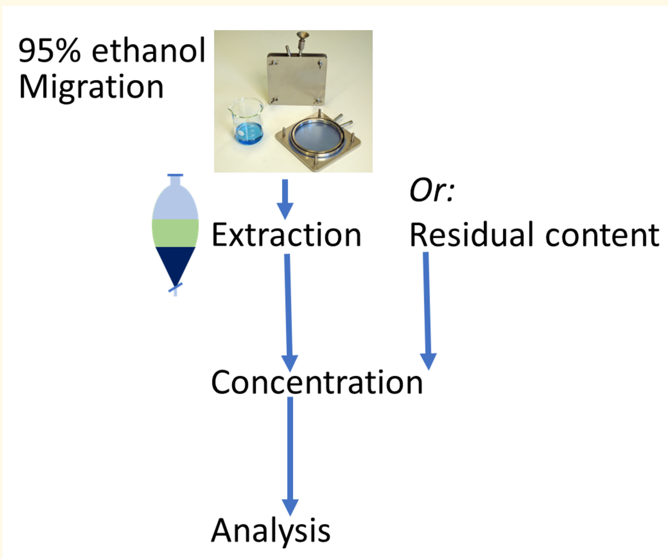


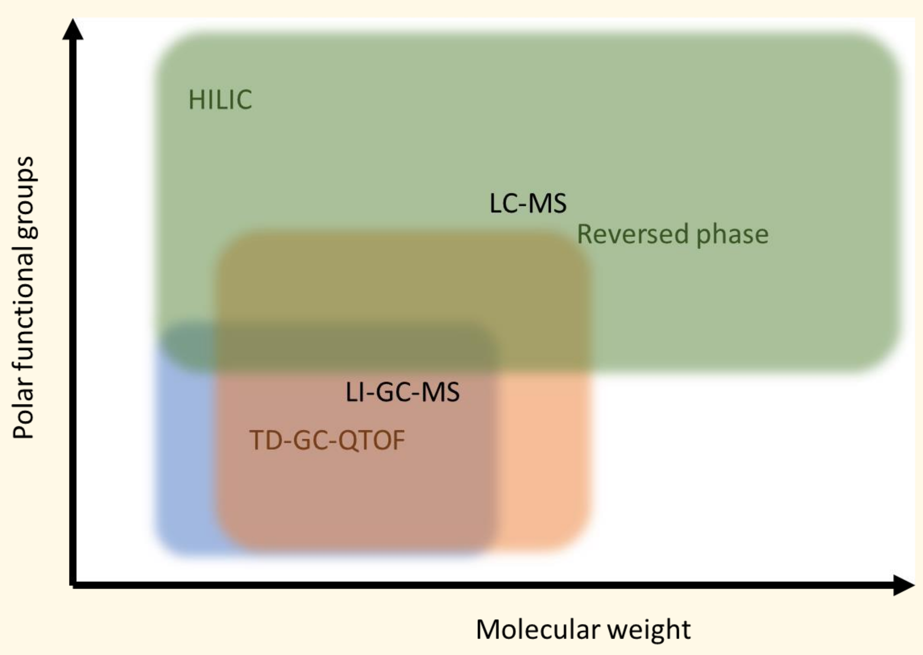
Challenge testing is closely related to monitoring. During a challenge test, Contaminated input material is subjected to the recycling process, and the removal of contaminants is quantified via chemical analysis to determine the **decontamination efficiency** of a recycling process.



Considerations for analytical platforms

A harmonised analytical approach for monitoring is not (yet) available. Ring tests to help the analytical laboratories to align. Monitoring samples may be prepared via **worst-case migration or residual-content**. The physico-chemical properties of the polymer determine suitable solvents. A bigger sample make measurements more representative.





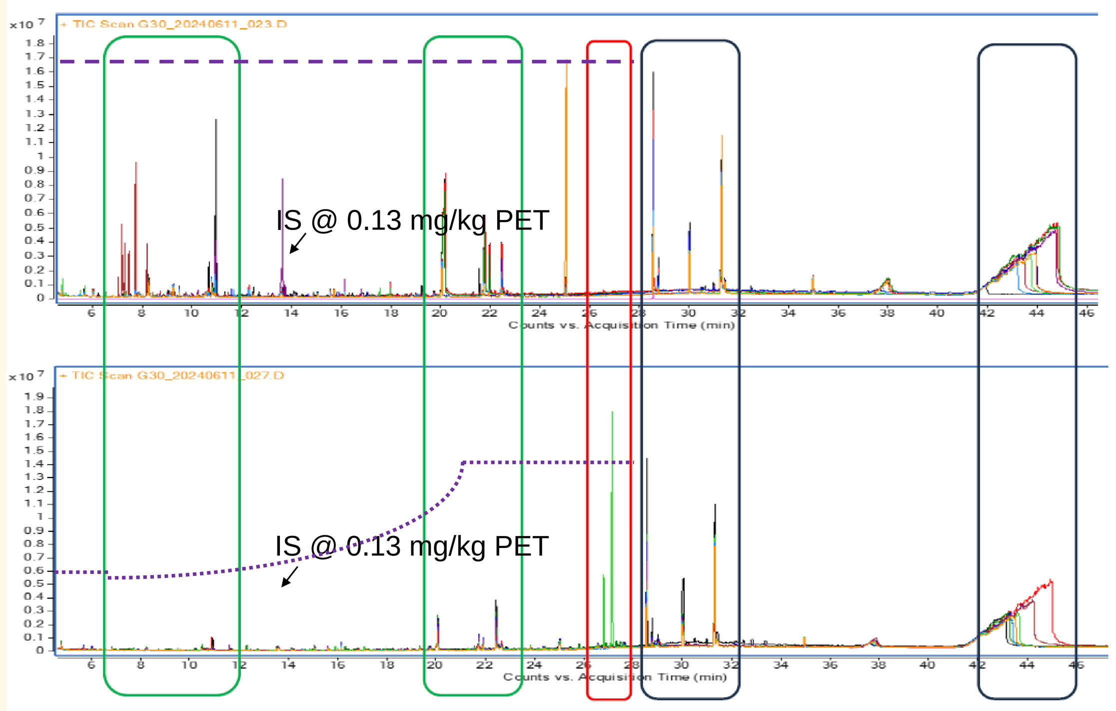
The **diffusion properties** of the polymer define the molecular weight up to which contaminants need to be analysed. Accordingly, GC-MS (with semi-quantified via an internal standard) suffices, and/or LC-MS (with external calibration) have to be applied.

For the monitoring of input material, the decontamination efficiency of the recycling process (i.e. challenge test data) influences the **required sensitivity**. For output material used 100% in food-contact according to the infant scenario, the migration into food needs to be below 0.00962 µg/kg [2]. If migration modelling is applied, c_{mod} as determined by EFSA can be used.

Typical monitoring analysis at Triskelion	
Analytical approach	Residual content
Sample size	20 g
Extraction volume	50 mL
Concentration step	yes, up to 100x
Analytical techique	GC-MS for PET, GC-MS & LC-HRMS for polyolefins

Monitoring of PET: Analysis & Risk assessment

Observations during a **case-study for mechanical recycling of PET**: input and output samples were extracted, concentrated and **analyzed** with GC-MS.



Representative liquid injection-GC-MS chromatograms of extracts from the PET input sample (top) and the PET recycling output samples (bottom).

Purple dashed: indicative upper limit for the contamination in the input, calculated from c_{mod} and challenge test data

Purple dotted: indicative upper limit for the contamination in the output based c_{mod}

Green: After recycling, the most volatile contaminants were not detected. Some contaminants remained with increasing boiling point.

Black: PET oligomers, not affected by decontamination

Red: Phthalates detected in only 1 replicate after recycling (red) point to incidental contamination, for instance with non-food-grade PET.

A reporting limit of 0.1 mg/kg was applied, which was well below the reference value c_{mod} for scenario C (food category 4) for toluene: 0.51 mg/kg PET [2]. The analytical method allowed the detection of signals down to 0.01 mg/kg and below, but low-level impurities were difficult to identify. **Migration modelling** was applied to narrow down the number of contaminants for risk assessment:

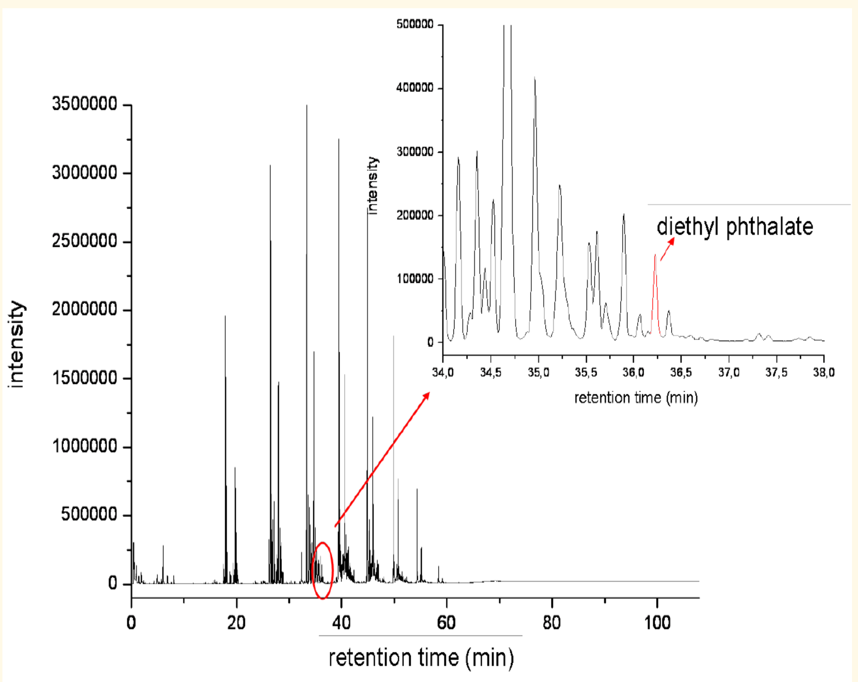
1) Migration modelling using SML (version 5.092, AKTS).
2) Verification that all contaminants had a molecular weight of > 150 g/mol
3) Comparison to the '> 150 g/mol' (modelled-)migration criterion for exposure scenario C: 1.25 µg/kg food [2].

Finally, 3 contaminants were compared with Annex I of 10/2011 or **risk assessed**. In summary, the investigated recycled PET was considered safe in view of the intended use. The steps to reach this conclusion required **expertise in chemical analysis, migration modelling and toxicological risk assessment** which makes monitoring labor intensive. A screening approach which correlates chromatographic retention to physico-chemical properties, such as OECD 117 for the partition coefficient [3], may serve as a future tool to create safety evaluation data more efficiently.

Outlook: From PET to other polymers

Recycling of PET is already well-investigated in terms of typical input contamination levels. Other food-contact materials such as **polyolefins**, however, have been studied less intensively. Their analysis bears several challenges:

- Based on the diffusion characteristics of polyolefins, contaminants with a molecular weight up to 1000 g/mol might be taken up by polyolefins during use. Both **GC-MS and LC-MS** need to be employed for monitoring.
- In GC-MS, polyolefins show a multitude of oligomeric signals. These **oligomers interfere** with the contaminants and make them difficult to recognize. The main oligomer signals are overloaded while contaminant signals require concentration steps.



Representative thermodesorption-GC-MS chromatogram of a PP sample: the contaminant diethylphthalate is difficult to recognize due the oligomer background.

GC-MS data interpretation is easier with **scatter plots** (*i.e.* plots of m/z *versus* retention time). **Chemometrics** is a promising tool to identify the contaminants between the dominant oligomer signals. Alternatively, **sample preparation** techniques may be improved to reduce or remove the oligomers.

References

1. Commission Regulation (EU) 2022/1616 of 15 September 2022 on recycled plastic materials and articles intended to come into contact with foods, and repealing Regulation (EC) No 282/2008
2. EFSA Panel on Food Contact Materials, Enzymes and Processing Aids (CEP), Scientific Guidance on the criteria for the evaluation and on the preparation of applications for the safety assessment of post-consumer mechanical PET recycling processes intended to be used for manufacture of materials and articles in contact with food. EFSA Journal; 22:e8879, 2024.
3. Test No. 117: Partition Coefficient (n-octanol/water), HPLC Method

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