How Applicable are Existing Methods for the Determination of Adsorption/Desorption of Polymers – Application and Comparison of Test Guidelines OECD 106 and OECD 121

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Background

The ecological hazard and risk for small molecules and products thereof are assessed among other things with the help of several physico-chemical properties. With the upcoming developments and growing concerns regarding the use of polymers also the demand for these data for polymers are rising.

There are analytical methods described in technical guidance documents (e.g. OECD TG 100 series), which were developed for small molecules, but have not yet been tested for applicability or extended for the analysis of polymers.

Scope

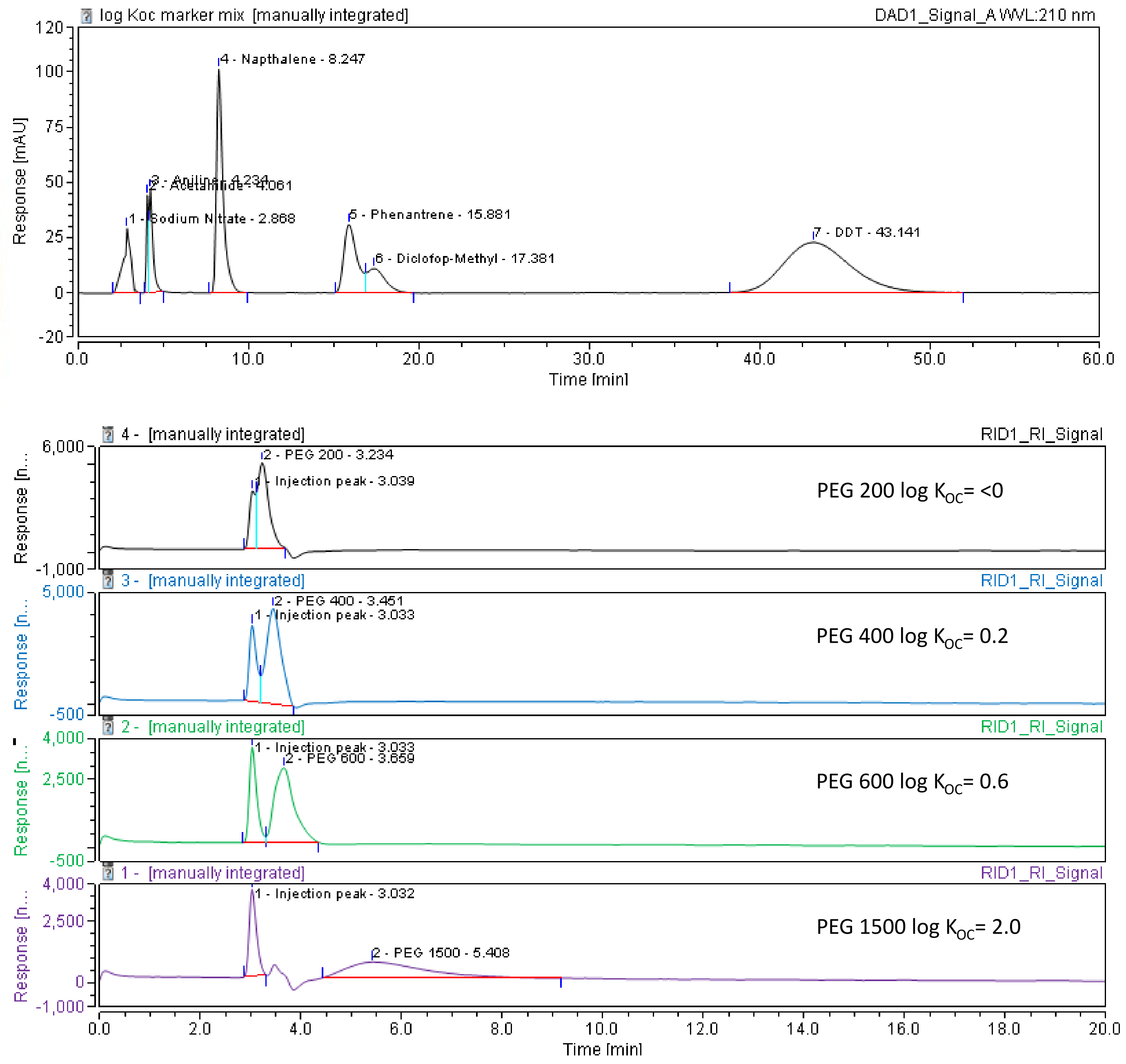
One of the relevant properties is the adsorption and desorption to soil or sludge, which is used e.g. to estimate the behavior in wastewater treatment plants or accumulation in ground in the environment.

The project's objective is to compare OECD tests 106 and 121 using well-defined polymer samples, focusing on their applicability and potential limitations. Differences in feasibility and outcomes were evaluated using both test guidelines.

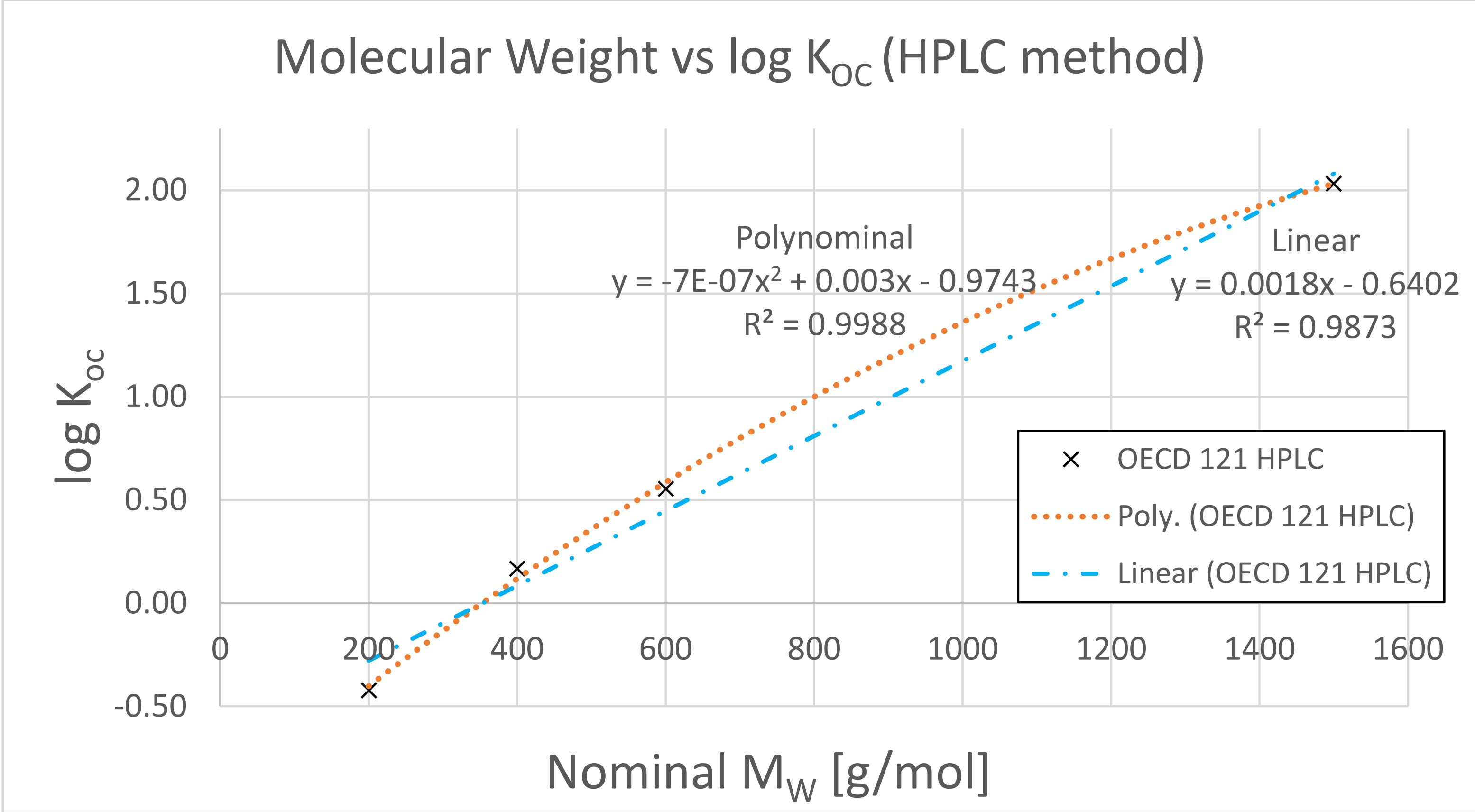
OECD 121 (HPLC-Method)

Method summary:

- ➢ Retention time of dissolved polymer is determined via HPLC-UV-RID using standardized cyanopropyl stationary phase and methanol / water isocratic eluent
- ➢ Calibration of retention time vs log K_{OC} via marker with known log K_{OC} value
- ➢ Similar design as OECD 117 (Partition Coefficient HPLC)



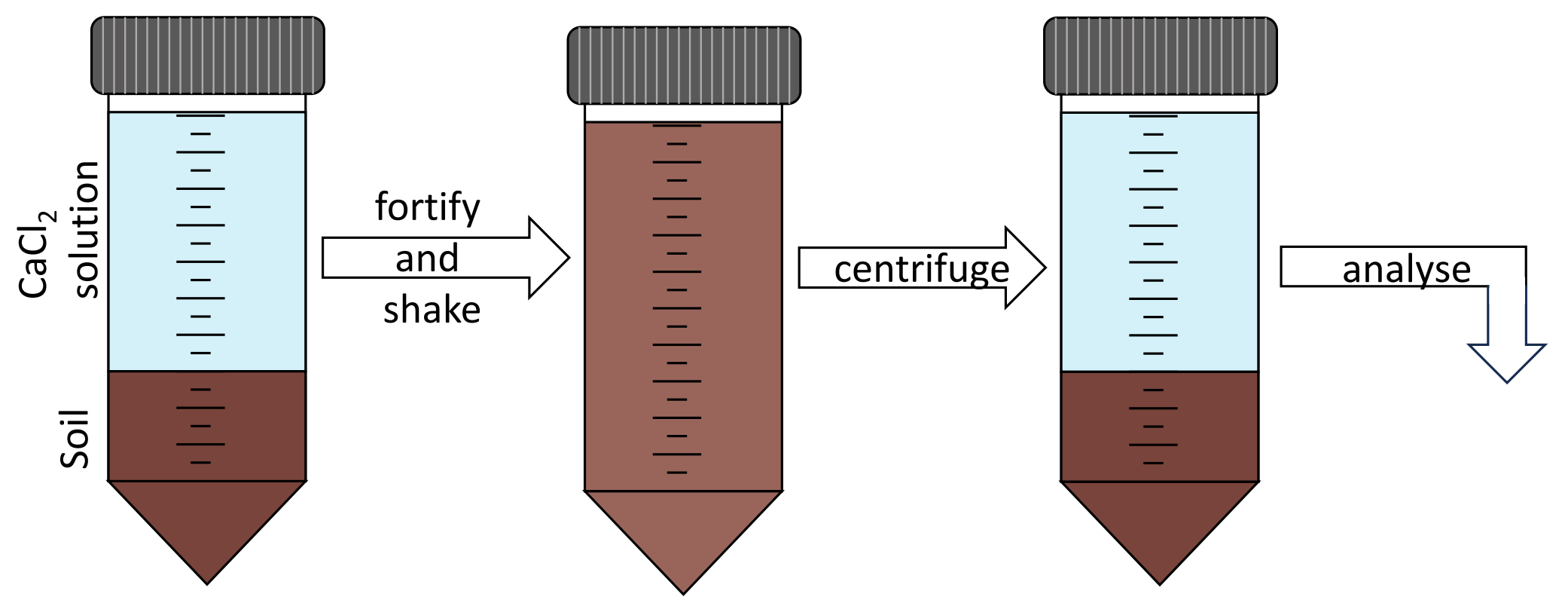
Retention times of markers with known log K_{OC} values were determined via HPLC-UV, whereas retention times for the PEG polymers was determined via HPLC-RID due to low detector response at given wavelength. After calibration values between < 0 and 2.0 were obtained for the polyethylene glycols (PEG).

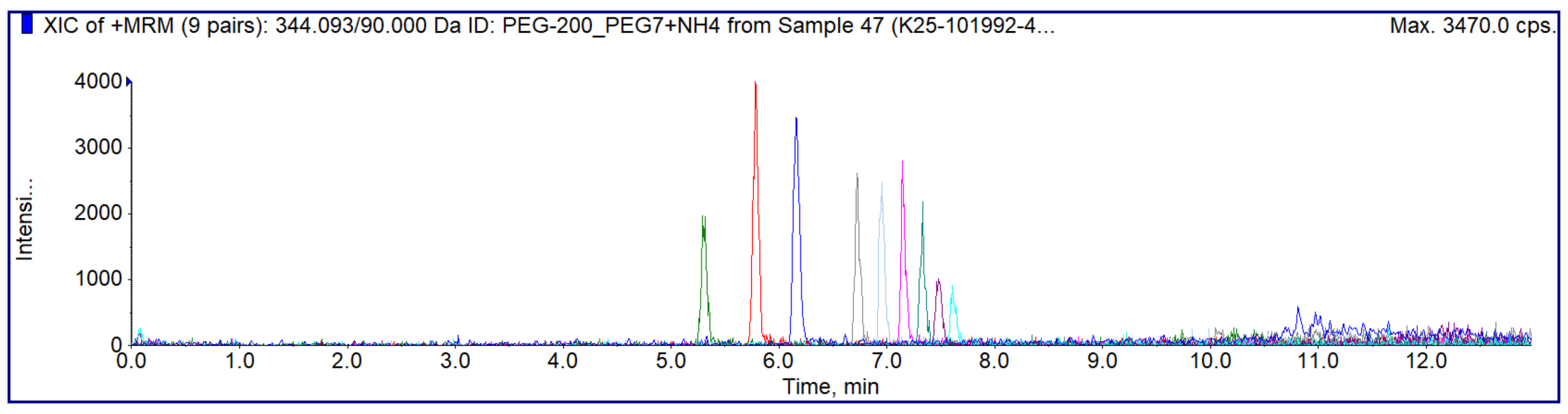


OECD 106 (Batch Equilibrium Method)

Method summary:

- ➢ Distribution of dissolved polymer in standardized soil / calcium chloride system
- ➢ Analysis of concentration in each phase and calculation of log K_{OC}
- ➢ Similar design to OECD 107 (Partition Coefficient Shake-Flask)





For each tested PEG three species with varying chain length were evaluated. From left to right: PEG 200 (n=5/6/7), PEG 400 (n=9/10/11), PEG 600 (n=12/13/14) Close to 100% of the fortified PEG was found in the aqueous phase resulting in a low log K_{OC} value. The analysis was carried out using an HPLC coupled to a triple quadrupole mass spectrometer.

Comparison

Various water-soluble PEG species (PEG 200, PEG 400, PEG 600 and PEG 1500) were analysed using both methods resulting in a similar log K_{OC}, showing feasibility of application to small polymers. The quick and easy HPLC method can give a rough estimation needed for further risk assessments. The batch equilibrium method can analyse individual polymer molecules and separate by mass-to-charge ratio (m/z) using LC-MS/MS.

Challenges and Limitations

The HPLC method does not separate individual polymer species with only little variation in chain length, therefore only a ranging value can be given for a polymer with broad molecular mass distribution, which then may not represent the whole sample.

Polymers that are poorly soluble in water may not be analysed without modification of the fortification process (for the batch equilibrium method) or may not show sufficient detector response.

LC-MS/MS analysis of intact polymers may either be outside of the quadrupole mass range or multiple charged signals may result in complex overlay.

Especially for more complex polymers such as poorly characterized biopolymers (UVCB), highly functionalized polymers or surfactants the methods may have limitations.

Outlook

Future research will focus on evaluating the applicability of these methods to more complex polymers, such as those with functionalized head groups. Advancements in LC-MS(/MS) acquisition techniques will enable the analysis of larger polymers, providing access to more comprehensive data. Additionally, comparing OECD 106 and 121 with the method outlined in OECD guideline 312 (Leaching in Soil Columns) will offer a deeper understanding of their effectiveness and limitations.

Contact

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