

A simple model approach for the desorption of DDT and related compounds from contaminated sediment to plastic polymers

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Abstract

Plastics including microplastic (MP) particles are widely distributed in the environment today. Microcontaminants - especially very persistent organic compounds and trace metals - are also detected to a large extent in the (aquatic) environment, which has led to a growing number of recent studies addressing interactions between organic contaminants and (micro)plastics in the environment. The background of these studies is the presumed function of plastic particles as vectors for biomagnification, leading to negative effects on the ecosystem.

In the present work, interactions between two common plastic polymers, low-density polyethylene (LD-PE) and rigid polyvinyl chloride (H-PVC), and three organic persistent compounds, dichlorodiphenyltrichloroethane (DDT), methoxychlor (DMDT), and dicofol with different log K_{ow} -values, were investigated using a sorption assay and desorption experiments. A new and innovative experimental approach based on a static system resembling burial in deeper sediment layers was investigated. The experimental setup used additive-free plastic containers, resulting in an easy-to-use experiment instead of MP sorption. It is assumed that the basic mechanisms of interaction are evaluated and are material specific.

The present sorption experiment demonstrated adsorption/incorporation of contaminants into the two polymers. Differences between the two polymers are addressed. In the sorption experiments, all target substances were detected in agreement with their hydrophobicity.

In the desorption experiments, diffusion of contaminants from a contaminated sediment to the polymers was detected. As expected, sorption by PE was significantly higher. The differences between the two polymers are based on the different glass transition temperatures (T_g) and polymer structure. A comparison with published data from the Pellet Watch project shows a sorption capacity in the same concentration range.

The simple approach is easy to use and illustrates the limited sorption capacity of the two polymers studied. It eliminates possible sorption effects on glass walls and simulates the ecosystem situation of a multiple aged contaminant mixture, which is usually not represented in laboratory experiments. The same approach is applicable to polystyrene, polypropylene and polyethylene terephthalate beside other polymer containers.

Introduction

First reports on plastic in the environment date back to the 1970s (Carpenter et al. 1972, Colton et al. 1974). Macroplastic degrades into micro- and nanoplastic particles and thus, plastic particles are reported in almost all ecosystem parts, even in deep-sea sediments (van Cauwenberghe et al. 2013, Woodall et al. 2014, Yao et al. 2019, Jung et al. 2021), remote marine gyres (Law et al. 2010, Maximenko et al. 2012, Pan et al. 2019), on remote islands (Crawford 2017, Schönlau et al. 2019) and in biota

(Herzke et al. 2016, Koelmans et al. 2022). Recently, the USA listed the topic (micro)plastic at position 2 of the most warranted research areas (Fairbrother et al. 2019).

Plastic is a general term for a class of materials that is composed of different types of (synthetic) polymers. Such materials contain beside the polymer often different additives at a low content, which optimize or adjust the properties during processing and application.

Plastics are widely used for passive sampling of dissolved or colloidal contaminants in aquatic ecosystems (Booij et al. 2003, Rusina et al. 2010, Ghosh et al. 2014, Rodriguez-Sierra et al. 2019, Taylor et al. 2019, Fuchte et al. 2020), including sediment pore waters (Apell & Gschwend 2014, Lydy et al. 2014, Arp et al. 2015, Katz 2021). In many publications, microplastic was sampled and analysed in general (Bannick et al. 2019, Duemichen et al. 2019) and for additives and contaminants adsorbed to the surface (Rios et al. 2010, Fernandez 2012, Crawford 2017, Camacho et al. 2019, Léon et al. 2019).

For this reason, many scientific papers are already dealing with the interactions between organic contaminants and (micro)plastic in the environment (e.g. Rochman et al. 2019, Laskar et al. 2019, Zhang & Zhu 2022, Prajapati et al. 2022). The background of these investigations is the proposed function of plastic particles as a vector for bio-magnification, resulting in negative ecosystem effects. The applied research concepts and results provide very controversial information. The general approach is the use of microplastic powder/pellets for the distribution experiments (e.g. Bakir et al. 2014, Zhan et al. 2016, Hüffer et al. 2018, Liu et al. 2019). The ad/absorption of POPs such as polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and Dichlorodiphenyltrichloroethane (DDT) is addressed in many scientific papers with the focus on plastic as a transfer vehicle to other ecosystems (Hartmann et al. 2017, Müller et al. 2018, Rochman et al. 2019).

For these experiments, previously manually isolated particles or model experiments on MP particles are performed, which lead to very different results. Due to the unspecific surface morphology and cryo-milling processes test specimen were taken for a better understanding of the model structure. In this case the interface is better defined and the permeation/penetration process is better evaluable.

These particles co-exist with suspended particulate matter, biota and sediments in a roughly calculated ratio of $1:10^7$ - 10^8 (Koelmans et al. 2016). The relative contribution of plastic particles to the total mass of suspended particulate matter is relevant for a realistic assessment of the role of microplastic as a potential vector (Bakir et al. 2016).

However, the range of plastic particles used and the respective shape vary greatly. The organic compounds used in the respective investigations are also subject to a wide range of variations. As far as certain particles are used in water, the recovery of the loaded particles is relatively easy.

In the present study, which examines an anthropogenically contaminated aquatic sediment aged for decades, a different approach was pursued. Basically, it can be assumed that the same processes in organic matter work for the penetration into the free volume in microplastic and larger plastic structures.

An amorphous polymer does not have an organized pattern in its molecular structure, whereas crystalline polymers show a regular line-up polymer molecule and are characterised by an ordered structure.

The concept of free volume is useful for explaining aspects of the chain mobility and permeability of polymers, even though its precise definition is subject to debate. Polymers that trap a large amount of interconnected free volume in the glassy state behave in many respects like microporous materials (Budd et al. 2005).

Permeation generally describes a process of mass transport of a molecule into or through a material (here: polymers). In order to be transported into the interior of polymers at all, the molecules must "dissolve" in the solid. The main mechanism of diffusion within a polymer is the "filling" of the free volume between the individual polymer chains. The "solution" in polymers is a thermodynamic process where the solubility is determined by the change in enthalpy of the solution of the respective molecule in the polymer matrix and the free volume available for occupation. A general assumption is that the surface reaches saturation at the time of exposure and the uptake rate is related to the diffusion rate of molecules adsorbed to the surface into the interior of the material (Duncan et al., 2005).

A new approach is therefore chosen to bring the polymer (here: LD-PE and H-PVC) into contact with the organic compounds (here: DDT, DMDT and dicofol) and to investigate a possible permeation into the polymer and desorption out of the sediment directly into the polymer. The advantage of this approach compared to the use of plastics in powder/pellet form is, for example, that no aggregates or conglomerates can occur in aqueous solution. The complex extraction of the microplastic particles from the sediment is not necessary, which could also have an influence on the distribution.

The distribution is mainly controlled by equilibrium partitioning and molecular diffusion (Mayer et al. 2000, O'Connor et al. 2016, Prajapati et al 2022). The key process is the penetration of contaminants through the boundary layer (biofilm/coating) to the polymer surface and into the "free volume" within the polymer. Three important process parameters are the polarity of the polymer type, including fillers, the pores and voids, the free volume including temperature effects, as well as mechanical stress and possible irreversible absorption of the compound. The compound itself contributes to the processes with its solubility in the surrounding media, size and shape, concentration gradient in the media and degradation in the free volume in addition to the degree of sorption.

A differentiation between adsorption to the surface and absorption into the "free volume" of the polymer is necessary for assessing the short-time (adsorption) and long-time (absorption) release potential. Published boundary layer thicknesses are in the range of 10–100 µm (Berg et al. 1998, Smit et al. 2010, Fernandez et al. 2012, Endo et al. 2013). An actual review paper summarises the most recent research on aging and intermolecular actions (Chandra and Walsh 2024).

In the present work, interactions between two very different polymers (here: polyethylene – LD-PE and polyvinyl chloride - H-PVC) and organic, persistent compounds (here: DDT, DMDT and dicofol) are

investigated. PE is characterised by a glassy transition temperature at -125°C and PVC at ~ 85°C (Pascall et al. 2005; Endo and Koelmans 2016).

DDT and related compounds are examples of hydrophobic organic compounds such as PCBs, PCDD/Fs, modern pesticides and PACs. It is possible to transfer the results to macro plastic and micro plastic particles while applying the same basic mechanisms.

The focus of the study is at first the distribution/permeation of 3 DDX-related compounds (p,p'-DDT, p,p'-DMDT and p,p'-Dicofol) between polymers (LD-PE, H-PVC) and the water phase at their maximum water solubility. These experiments give the maximum "adsorption/distribution" on the surface and in the "free volume" of the polymers in a simple experimental set-up. The experiment was conducted for 3 months along with the second experiment to assure an equilibrium distribution routinely achieved in hours to 10 days (EPA 2012). There was no formation of a biofilm/coating on the surface as indicated by a Raster Electron Microscope analysis (pictures not shown).

The second part of the experiment provides information on the distribution of the compounds in a contaminated sediment compared to polymers. The contaminated sediment was exposed in a static system for up to three months to demonstrate the contribution of polymers to the environmental behaviour of the compounds. The sediment, together with other pharmaceutical production chemicals, solvents and trace metals, was heavily contaminated with pesticide production wastewater for decades. The degradation of the initial effluents is proceeded, indicating a well-adapted microflora. This approach simulates burial in deeper sediment layers with pore water diffusion as a potential release process, besides the turbulence and resuspension caused by commercial shipping/dredging. The selected sediment was demonstrably analytically proven contaminated with all three different compounds used in the permeation experiment. Data for DMDT and metabolites were published in Schwarzbauer et al. (2001) and metabolites of Dicofol were published in Heim et al. (2005) for pore water samples. Dicofol itself was determined in these samples (data M. Ricking 2004, unpublished). All compounds used in the lab experiments were produced at the source.

To the best knowledge, only one publication treats the comparison of the adsorption of POPs (phenanthrene and pyrene) on polymers (PE, PS, PVC) and a sediment sample. The differences in TOC between pure polymers (> 80% TOC) and sediment (10.4% TOC) were addressed (Wang et al. 2019), resulting in a much higher sorption capacity of microplastic relative to the natural sediment. With increasing aqueous concentrations, the distribution coefficients of phenanthrene for the natural sediment decreased, leading to a lower release of the initially sorbed phenanthrene relative to the MP. As far as published, this is the first publication dealing with the desorption from a natural sediment affected by a variety of contaminants.

The presented approach can assist in analysing the desorption from contaminated sediments into plastic polymers as recently recommended by Fred-Ahmadu et al. (2022).

Material and Methods

Chemicals and containers

The PE and PVC containers (1 L) were purchased from Bürkle (Karlsruhe, Germany) and Roth (Karlsruhe, Germany), respectively, and pre-cleaned with demineralised water (aqua demin.) and n-hexane to remove production residues. The polymers contained no additives. All standards were of high purity (> 98–99%; LGC Promochem, Wesel, Germany) and the solvents (ethyl acetate, n-hexane, methanol, acetone) were of picograde quality (LGC Promochem, Wesel, Germany). The average weight of the PE containers without lid is 93.4 g and the weight of the PVC containers is 53.4 g.

Sediment sampling

In total 31 cores were sampled by means of a tube coring system with a stainless-steel liner (Hydrobios, Kiel, Germany) in November 2018 at the Teltow Canal close to the source (Berlin-Chemie) on the right bank at a horizontal distance of approximately 3 m. The sandy surface layer of 20 cm was removed and the deeper layers at a sediment depth of 40–80 cm, containing contaminated sediments, were transported to the lab and stored at 4°C in the dark. The complete sediment (30 L) had been sieved through a 1 mm mesh to remove the large debris prior to the experiments.

Determination of the loss-on-ignition (LOI) and extractable organic matter (EOM)

For homogeneity determination the loss on ignition was analysed in a furnace at 600°C for 4 hours. The TOC has been calculated according to Fringipane et al. (2009) by multiplication of the LOI with a factor of 0.333.

The EOM was determined in duplicate by means of an extraction of 2 g dry sediment with 40 ml acetone/n-hexane (v/v) in an ultrasonic bath for 10 minutes (at 450 W). The residues were filtrated through a 0.45 µm glass fibre filter and evaporated to dryness. The EOM was determined on a microbalance and expressed in µg absolute and in % EOM of the dry sediment.

Determination of the particle size distribution of the sediment samples

The particle size distribution was determined by means of a laser particle analyser (Hoba L960, Retsch, Haan, Germany).

Analysis of the containers by ATR-FTIR

After the termination of the experiments, the pristine and the 3-month PVC- and PE-containers were analysed using ATR-FTIR regarding their polymer composition. A Nicolet iS50 was used (Thermo Fischer,

Dreieich, Germany). An ATR Smart iTX Diamond was used with a DTGS detector. Eight scans were realised with a resolution of 4 cm^{-1} . All spectra were ATR and baseline corrected. for potential differences due to the sorption of contaminants and constituents of the diffusion barrier (biofilm/coating).

Sorption test

The sorption tests with the pure compounds were performed in triplicate in the dark at $\sim 10^{\circ}\text{C}$ without shaking.

Solutions of pre-sterilised aqua demin. have been saturated with $1\text{ }\mu\text{g}$ 4,4'-DDT, $100\text{ }\mu\text{g}$ 4,4'-DMDT and $800\text{ }\mu\text{g}$ 4,4'-Diclofol at the maximum water solubility level and left for 3 months to achieve an equilibrium after mixing for 24 hours. The composition of the solution was checked for possible degradation products through analysing the remaining solution via GC-MS.

Abrasion experiments

Initial tests indicated an abrasion of polymer material on an overhead shaker due to the sandy constituents still included in the sediment.

Based on the experience gained during the abrasion tests, resulting in severe formation of micro polymer particles and the intention to simulate the burial in deeper sediment layers, the static approach is more comparable to the burial in the sediment body.

Desorption experiments

18 containers (9 x PE and 9 x PVC) were filled with the homogenised sediment and incubated in triplicate in the dark for 2 weeks, 4 weeks, and 12 weeks to get information about the principle process to be extrapolated to natural MP particles as no aged reference material was available. The approach was realised in the dark at $\sim 10^{\circ}\text{C}$.

After each time interval the sediment was removed from the containers, these were rinsed twice with 50 ml Aqua demin. and the second rinse was checked for adsorption of contaminants on the surface and dried at 25°C . Immediately, the containers were sequentially extracted with methanol and n-hexane for 24 hours on a horizontal shaker in the dark. The solvent was carefully decanted and reduced to near dryness in a fume hood and re-dissolved in $500\text{ }\mu\text{l}$ ethyl acetate and fortified with $2\text{ ng}/\mu\text{l}$ of the internal standard Dicofol- D_8 and ISM-560 (Acenaphthene- D_{10} , Chrysene- D_{12} , 1,4-Dichlorobenzene- D_4 , Naphthalene- D_8 , Perylene- D_{12} , Phenanthrene- D_{10}) for the analysis. An additional clean-up step was necessary due to high matrix in the extracts, especially for the PE-experiments. Hydrophobic compounds such as alkanes and alkenes were removed by means of a Lichrolut EN™ mini-column (200 mg; Merck, Darmstadt, Germany) conditioned with n-hexane and eluted with n-hexane and ethyl acetate.

The possible sorption effects on glass walls, as mentioned already in the 1970s (Picer et al. 1977) were eliminated by the experimental approach.

GC-MS analysis of the experimental extracts

The GC-MS analysis was performed on an Agilent 6890 GC 5973 MSD (Agilent, Santa Clara, USA).

Starting with a pulsed spitless injection at 270°C including a 2 minutes pulse at 50 psi. The GC-oven was ramped from 60°C (5 min hold) to 300°C at 7°C/min (10 min hold). The pressure was ramped from 14 psi at 0.5 psi/min to 20 psi (30 min hold).

The chromatography was performed on a DB-5-ms column (30 m x 0.25 mm id x 0.25 µm ft; Agilent, Santa Clara, USA). Helium was the carrier gas at a velocity of 45 cm/s. The pressure program was realized at 17 psi constant pressure (2.2 ml/min).

The detection was carried out on an Agilent MSD 5973 in the EI-mode (70 eV). The source temperature was 230°C and the quadrupole was maintained at 150°C. The analysis was performed in the SIM-mode.

The SIM-parameters were (m/z): 139, 143, 250, 251, 258 for Dicofol, Dichlorobenzophenone and Dicofol-d₈; 227, 121, 308, 310, 344 for DMDT and metabolites; 246, 318 for DDE and 235, 237, 165 for DDD and DDMS.

The quantification was performed by means of a 4-point external calibration. The limit of detection (LOD) was 20 pg/g and the limit of quantification (LOQ) was 100 pg/g d.w.

Selected samples were additionally analysed in the SCAN-mode for the identification of degradation products and metabolites in the sorption experiments.

The degradation of DDT, DMDT and Dicofol was checked according to the US-EPA recommendation for the analysis of DDT. The degradation was < 15%.

Procedural blanks of the experiments revealed no contamination by the target compounds.

Additional verification analyses were performed on an Agilent 7890 GC connected to a 5977 B Inert Plus MSD equipped with a Gerstel TDU-2-system (Mühlheim, Germany), applying the micro vial technique. An aliquot of 20 µl was injected spitless at 25°C cryo-focussed in a CIS-system and subsequently after desorption onto the GC-column ramped with a temperature program at 7°C/min to 300°C (10 min hold). The analytical parameters were identical to the above system.

Selected extracts of the desorption experiments were analysed in the SCAN-mode (m/z 40–650) for additional compounds, not targeted in the experiments. Additional information on trace metal and halogenated aromatic (PCBs, PCDD/Fs, HCHs, HCBs, PAHs) levels in sediments collected near the source was published in Ricking et al. (2005).

GC-MS analysis of the sediment sample from the Teltow Canal

The analysis of the original sediment was performed according to Zhu et al. (2019). Briefly, the air-dried sediment has been sequentially extracted with acetone, mixtures of acetone and n-hexane (1:1) and n-hexane via accelerated solvent extraction (Dionex ASE 150, Thermo Fisher Scientific, Waltham, USA) to obtain the solvent extractable fraction (EF). The extracts were dried with anhydrous sodium sulphate and fractionated according to Schwarzbauer et al. (2003). After fortifying with internal standards, the analysis was performed according to Zhu et al. (2019) on a GC-MS system.

Results and Discussion

The experiment revealed a sorption of the compounds and the desorption from the contaminated sediment into the polymer. All target compounds were detected in the sorption experiment while only DDT-related compounds were analysed in the desorption experiments, in accordance with the analysis of the contaminated sediment. Further compounds were identified via SCAN-analysis of the extracts.

Sediment characterisation

The particle size distribution of the sediment reveals a maximum particle size between 90–100 µm with the smallest particles in the range of 10 µm (Fig. 1). 50% of the particles in the sample are ≤ 70 µm, indicating a partially fine-grained sediment composition. A larger number of particles in the range of 50–180 µm was analysed.

The Loss-on-ignition indicated a very homogeneous distribution of the OM throughout the experimental setup ($3.3\% \pm 0.09\%$) (data not shown). To compare the results with earlier investigations, a conversion into TOC was performed by multiplying with a factor of 0.333 according to Frangipane et al. (2009) due to the slightly elevated temperature of 600°C relative to actual recommendations at 475–550°C (DIN 18128:2002-12). The TOC was in the range of a 1.1% in accordance with earlier results at the same location (1.82–2.73% TOC; Ricking et al. 2020).

The extractable organic material (EOM) was determined at 4.8 and 3.7 µg/g d.w., representing an EOM of 0.24 and 0.19%, respectively for sample A and B (mean 0.21%).

In total the sediment is a fine-grained sediment with a low TOC of 1.1%. These two features favour the transfer of contaminants due to an expected low formation of non-extractable residues (NER).

The GC-MS analyses of the contaminated sediment revealed a heavy contamination with DDT-related compounds (DDX) and no DMDT and Dicofol (Table 1). Even the parent compounds p,p'- and o,p'-DDT were detected in accordance with earlier publications (Kucher et al. 2018, Zhu et al. 2019).

Table 1
Concentrations of different DDT-metabolites in the sediment sample used for the desorption experiment (ng/g d.w.).

Name	formula	MW	concentration ng/g
DDM	$C_{13}H_{10}Cl_2$	236	79
DDNU	$C_{14}H_{10}Cl_2$	248	321
DDEt	$C_{14}H_{12}Cl_2$	250	82
DBP	$C_{13}H_8Cl_2O$	250	320
o,p'-/p,p'-DDCN	$C_{14}H_9Cl_2N$	261	13950
DDMU	$C_{14}H_9Cl_3$	282	3281
DDMS	$C_{14}H_{11}Cl_4$	284	22341
o,p'-DDE	$C_{14}H_8Cl_4$	316	55
p,p'-DDE	$C_{14}H_8Cl_4$	316	1328
o,p'-DDD	$C_{14}H_{10}Cl_4$	318	3079
p,p'-DDD	$C_{14}H_{10}Cl_4$	318	12778
o,p'-DDT	$C_{14}H_9Cl_5$	352	26
p,p'-DDT	$C_{14}H_9Cl_5$	352	592

Results of the FTIR-analysis

The composition of the polymeric materials was analysed using ATR-FTIR (Fig. 2). Before the sorption experiments, the materials can be unambiguous determined as PE (characteristic bands at 2920 and 2855 cm^{-1} , 1475 and 1465 cm^{-1} , 731 and 720 cm^{-1}) and PVC (characteristic bands at 700 and 617 cm^{-1}) with a minor part of carbonylic plasticizer (1733 cm^{-1}). After 3 months of incubation in both cases broad bands were added in both spectra between 3700–3000 cm^{-1} , as well as 1700–1500 cm^{-1} and 1200–800 cm^{-1} . Simultaneously the signals of the polymers were reduced. This indicates a surface layer of water-rich biofilm on the containers consisting of hydroxyl groups, aromatic structures and esters, respectively.

Sorption tests with the experimental set-up (only water and the polymers)

This simple approach illustrates the principal distribution between the water phase and the polymer. It ignores the formation of a biofilm/coating and the chosen equilibration time was enough to approach an equilibrium. Compared to data in the literature 12 weeks are enough (EPA 2012, Bakir et al. 2014,

Seidensticker et al. 2017, Hüffer et al. 2018). All three target compounds were detected in the extracts from the containers. A screening of the water phase via a PDMS-Sorbstar™ (IMT Innovative Messtechnik GmbH, Vohenstrau, Germany) revealed a slow degradation of the parent compounds and the detection of traces of metabolites (DDD, DDMS, DDE, MDE and DBP) for DDT, DMDT and Dicofol, respectively. There were no additional metabolites detected in the extracts.

In Fig. 3 the mechanism of sorption/penetration into a polymer sheet is illustrated, not differentiating between adsorption and absorption. The red arrows illustrate the diffusion in and out of the polymer. A biofilm/coating is in green schematically included and the boundary layer is in lighter blue indicated. PE is a partially flexible thermoplastic and semi crystalline and H-PVC is amorphous. The free volume is much lower in the glassy polymers (H-PVC) relative to the flexible polymer structure (PE) (Pascall et al. 2005; Omnexus 2020).

The size of the red arrows visualizes the results of the experiments, which showed a much higher sorption for PE. Differences in the surface properties that determine the sorption properties are in addition caused by the more hydrophilic properties introduced by the chlorine atoms of PVC.

However, there are differences between the two polymers. The results indicate a higher “sorption capacity” for PE relative to PVC (Table 2).

The recovery of the initial target compounds in the solutions extracted from the polymer containers was between 1.97–2.41% for PE and between 0.21–1.46% for PVC in relation to the total mass applied, reflecting the different polymer structure and glassy transition temperature. 4,4′-DBP as transformation product of 4,4′-Dicofol was analysed in a higher concentration in the PE experiments, indicating a higher transformation potential for PE, relative to PVC. The variation in the PVC experiments was much higher than in the PE-experiments. Details are given in the SI.

Table 2

Absolute mass in ng absolute of the three compounds and relative recovery in relation to the initial concentration of 1 µg/L, 100 µg/L and 800 µg/L for DDT, DMDT and Dicofol in the VE-sorption experiment for LD-PE and H-PVC, respectively.

[ng absolute]	4,4'-DDT	4,4'-DMDT	4,4'-DBP	4,4'-Dicofol	Sum
Mean PE	509 ± 63	11794 ± 1013	7309 ± 555	0.00	19612 ± 1630
Mean PVC	203 ± 161	5229 ± 4374	354 ± 22	448 ± 420	6234 ± 4947
Recovery [%]	4,4'-DDT	4,4'-DMDT	4,4'-DBP	4,4'-Dicofol	
LD-PE 1	51.04	11.64	0.90		
LD-PE-2	58.49	13.10	1.01		
LD-PE-3	43.15	10.63	0.84		
H-PVC-1	5.74	1.38	0.05	10.62	
H-PVC-2	42.82	11.35	0.04	0.96	
H-PVC-3	12.42	2.96	0.04	4.70	

The highest relative recovery was determined as a function of water solubility and hydrophobicity for DDT > DMDT > dicofol. The DDT content compared to the other two target compounds was relatively low in relation to data from the Pellet Watch Project (see following chapter). Antagonistic effects are obvious due to the use of a cocktail of compounds with different water solubility.

Desorption experiments

Both polymers accumulated DDT-related compounds according to their polymer structure. The washing extracts (second aqua demin.) indicated no target compounds.

In the two week-samples no compound was detected due to the formation of a diffusion barrier at the polymer surface, as indicated in the chromatograms of the extracts. The fast formation of coatings/biofilms was expected and is in alignment with published data of biofilm formation within minutes to hours (Loeb et al. 1975, Galloway et al. 2017, Rummel et al. 2017, Michels et al. 2018, Li et al. 2019, Miao et al. 2019, Wang et al. 2021). These biofilms turned the polymer into a two-phase domain with an outer organic material shell and an inner polymer core (Endo and Koelmans 2016).

The results for the 1-month (1 M) and 3-month (3 M) experiments are listed in Table 3 and illustrated in Fig. 5. Details are given in the SI.

Table 3
Analysis of the detected compounds of two experimental approaches [ng/container absolute] and calculated relative to the container mass in contact with the contaminated sediment (700 g d.w.).

compound [ng absolute)	DDD	DDE	DBP	DDMS
1 M PVC	495 ± 24	65 ± 65.02	85 ± 38.2	324 ± 24.9
3 M PVC	255 ± 124	62.5 ± 35.7	88 ± 47.7	117 ± 46.5
1 M PE	12671 ± 7656	2367 ± 1362	1236 ± 301	3549 ± 341
3 M PE	8041 ± 1521	1997 ± 194	2282 ± 681	6228 ± 1218

The data clearly depict a desorption of the compounds from the sediment into the polymer. Expected differences for PE and PVC are proven, resulting from the differences in crystallinity. The differences in flexibility at room temperature, related to the glassy transition temperature are obvious (-125°C for PE vs. 67°C for PVC, Omnexus 2020), leading to absorption capacities varying by a factor of ~ 10. The higher capacity of PE is based upon the linear, non-competitive and mostly reversible sorption relative to the nano-pore filling within the PVC polymer (Endo and Koelmans 2016)

A differentiation into the methanolic and n-hexane fraction is shown in the SI. In all cases, the data show for PVC a higher content in the methanolic fraction (first extraction step). All quantified compounds are highly soluble in methanol (Pub Chem 2020). The increased content in the n-hexane fraction of PE indicates a possible diffusion into deeper polymer layers, which could not be extracted with methanol. The stronger sorption within three months (possible formation of non-extractable residues) is illustrated by the reversal of the relative contribution of the methanol and n-hexane fraction for the PE experiments.

A slightly higher content of the total compounds in the three-month samples relates to a non-equilibrium process. The kinetics of the desorption require further attention, especially for the short-time processes.

Tables 2, 3 and Fig. 4 clearly illustrate the differences between the polymers with an expected higher sorption capacity of LD-PE. The additional SCAN-analysis of the extracts revealed tetrachloro- and pentachloro-PCB, fluoranthene, pyrene, benz(a)anthracene and chrysene, beside n-alkanes (C₁₆-C₂₄), in accordance with prior investigations of the sediment (Heim et al. 2005, Ricking et al. 2020). The antagonistic processes for competitive sorption on limited sorption places have to be considered. Differences in contamination are obvious due to an inhomogeneous distribution of the contaminants in the 700 g (d.w.) sediment used for the experiments.

Table 4 and Fig. 5 compares the relative loading of the polymers in the pure sorption experiments and the sediment desorption experiments assuming a relative similarity of the compounds and their physico-chemical characteristics. The loading of PE containers is much higher than that of PVC containers and is in the range of the sorption tests for PE. A somewhat lower degree of desorption is specified for PVC. The analytical details are given in the SI. Figure 5 illustrates the results per g of polymer for the comparison with other data in the literature.

Table 4

Comparison of the relative loading of the sediment desorption experiment for 1 month (1 M) and 3 months (3 M) relative to the sorption experiments.

Sorption experiment [ng/g polymer]	4,4'-DDT	4,4'-DMDT	4,4'-DBP	4,4'- Dicofol	Sum
PE	5.45 ± 0.67	126 ± 10.8	78.3 ± 5.94	0.00	210 ± 17.5
PVC	3.81 ± 3.02	97.9 ± 81.9	6.63 ± 0.41	8.40 ± 7.86	117 ± 93.2
Desorption experiment [ng/g polymer]	4,4-DDD	4,4-DDE	4,4-DBP	4,4-DDMS	Sum
1 M PE	204 ± 123	38.1 ± 21.9	19.9 ± 4.85	57.2 ± 5.49	319 ± 156
3 M PE	130 ± 24.5	32.2 ± 3.12	36.8 ± 11	100 ± 19.6	299 ± 58.2
1 M PVC	15.37 ± 0.74	2.00	2.62 ± 1.18	9.99 ± 0.77	29.9 ± 4.69
3 M PVC	7.86 ± 3.83	1.93 ± 1.10	2.71 ± 1.47	3.60 ± 1.43	16.1 ± 7.84

In comparison with published data for DDX within the International Pellet Watch project (IPW) in the range of n.d. – 198 ng/g S-DDT (Hirai et al. 2011), 1.1–42 ng/g S-DDT (Karapanagioti et al. 2011) and n.d. -140 ng/g S-DDT (Rios et al. 2007) the desorbed and analysed concentrations of DDX in the present study are in the same concentration range but lower than concentrations of 2 locations in California with contents of 1000 and 1100 ng/g S-DDT and two samples from an industrial area in the USA with contents of up to 7100 ng/g S-DDT (Rios et al. 2007).

In a recent publication, the sorption of modern pesticides compared to the ancient POP DDT by microplastics (PE and PVC), charcoal, ash, and river sediments were analyzed in batch equilibrium experiments. Although sorption of DDT by sediments, ash, and charcoal was highest due to hydrophobic interactions, microplastic was the weakest sorbent in the relative order (Fatema & Fahrenhorst 2022).

The different geometry of the experiments (surface of the containers) versus three-dimensional pellets and fragments has to be considered. Information on the absorption in the plastic polymer is currently not available, despite TEM-EDX attempts at the Fritz Haber Institute of the Max Planck Society, Berlin (Dr. Christian Rohner – personal communication 2021).

Differences in exposure (drifting vs. static) and analysis (the potential biofilm is in the Pellet Watch Project co-extracted) have to be considered. Additionally, the Pellet Watch Project analyses unknown aged pellets and fragments relative to the pristine plastic containers applied in the current experiments. The published data reveal an obvious contamination of the marine pellets and fragments by aerobic metabolites of DDT (DDT and DDE) relative to anaerobic metabolites, expected in anoxic sediment samples. Besides, no DDT was analysed in the desorption experiments relative to a detection of DDT in the original sediment sample. The relatively low detection of only a few of the identified and quantified

DDX-metabolites relates to the limited sorption capacity of the polymers, as already stated for the sorption experiments. Differences in $\log K_{ow}$ explain a higher sorption of more hydrophobic compounds. Bakir et al. (2012) experienced the same differences in their kinetic sorption experiments with DDT and phenanthrene on PE and PVC. DDT is more prone to a tighter sorption into the pores of the plastic polymer relative to other compounds (Bakir et al. 2012, Napper et al. 2015).

Due to the diffusion barrier at the surface of the containers (biofilm/coating) no attempt was made to refer the detected concentrations to the total sediment (assuming a homogeneous distribution) and to calculate the sediment layer thickness necessary to deliver the contaminants to the plastic polymer.

Polar metabolites (DDA, DBP, DDCN) are not expected to diffuse onto/into hydrophobic plastic polymer material. Another point is the potential competition for absorption sites with different capacities.

Conclusions

The new approach shows an easy to handle alternative approach for sorption and desorption experiments with LD-PE and H-PVC. The limited sorption/accumulation capacity of pure polymers is shown in the sorption experiments, including antagonistic effects for the compounds, rarely considered in experiments. Within the first week, a diffusion barrier formed on the surface or a biofilm that can act as a sorbent for the substances, so that no compounds could be detected after the first-time interval. The differences in sorption between the 1-month and 3-month analyses give hints to further processes, not yet addressed in lab-experiments.

Differences in polymers are analysed and explained mainly by the glassy transition temperature with subsequent flexibility at room temperature. All three aspects differentiating PE and PVC in polymer structure, polarity and properties, free volume and contaminant behaviour are obvious.

The rapid formation of a biofilm in the sediment limits the sorption capacity, even at the highly contaminated site and compared to pellets and fragments. This approach illustrates a more realistic approach for naturally contaminated systems with a large number of different compounds and possible antagonistic effects on sorption, especially for compounds with varying and high $\log K_{ow}$ -values. The results show a low desorption of contaminants.

- DDT and related compounds are adsorbed on the surface and in the free volume of the polymer
- The maximum diffusion to the polymer is an indicator of the potential accumulation from the water phase
- After saturation of the ad- and absorption capacity, an equilibrium is reached between the surrounding phase and the polymer
- Sedimentary organic matrix is a concurrent sorbent relative to plastic material
- Antagonistic effects occur in multicomponent solutions
- The desorption is limited by the ad- and absorption capacity of the polymeric material

Further experiments on a much wider range of compounds and especially on short-term kinetics are recommended, as well as experiments with a higher TOC-content sediment due to the formation of non-extractable residues (NER) and a much higher expected sorption capacity in the **sedimentary organic matrix (SOM)**.

The very limited sorption capacity of plastic polymers, especially in natural ecosystems with rapid formation of biofilms/coatings, makes their function as transport vehicle/vector for POPs appear low according to publications by Koelmans et al. (2016), Rodrigues et al. (2019) and Shi et al. (2020). The relative contribution of particle-bound transport of contaminants has been researched to a limited extent (e.g. Schwientek et al. 2013, Rügner et al. 2019) and especially flood events, which are the main transport of particulate material, require further research.

Declarations

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- Ethical Approval “Not Applicable”
- Consent to Participate “Not Applicable”
- Consent to Publish “Not Applicable”
- Authors Contributions

All authors contributed to the study conception and design. Material preparation, performance of the experiments and analysis were performed by Mathias Ricking, Alexander Kerndorff and Xiaojing Zhu. The first draft of the manuscript was written by Mathias Ricking and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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- All Data are available on request as part of the Doctoral Thesis

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Figures

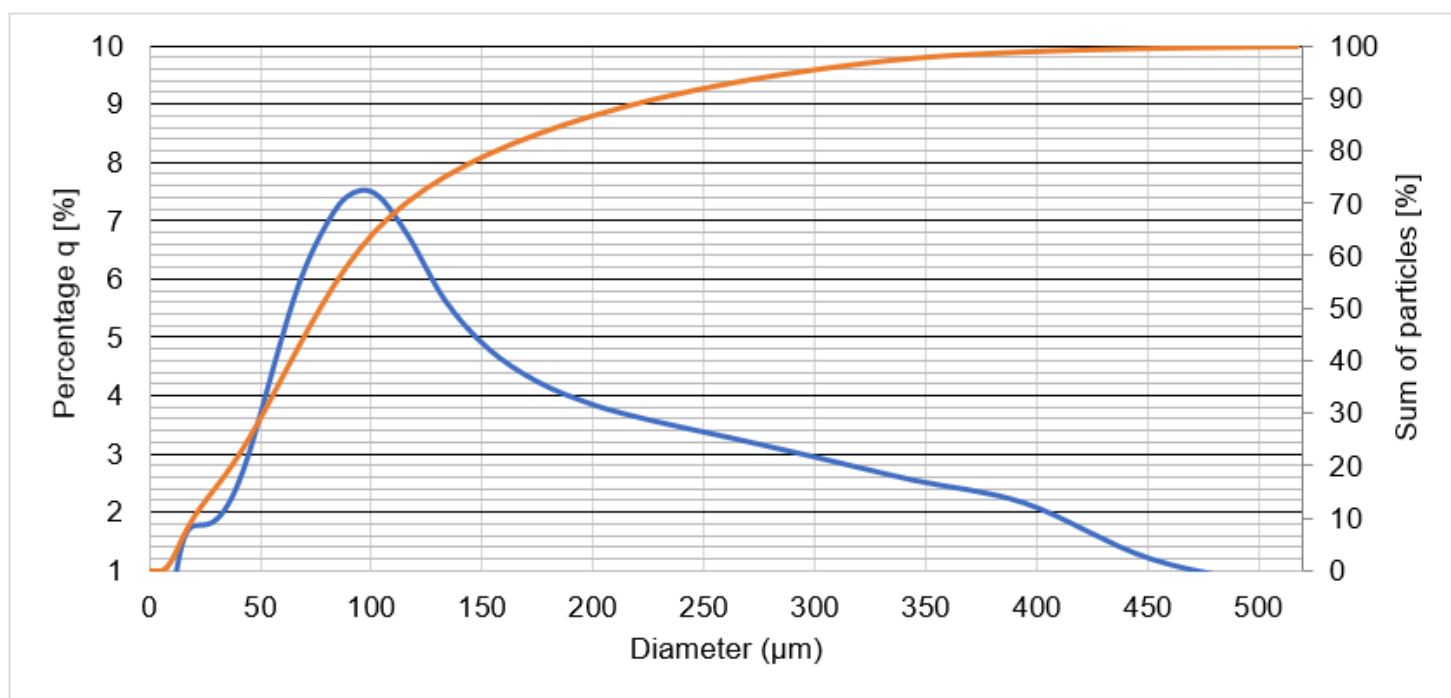


Figure 1

Particle size distribution of the contaminated sediment for the desorption experiment.

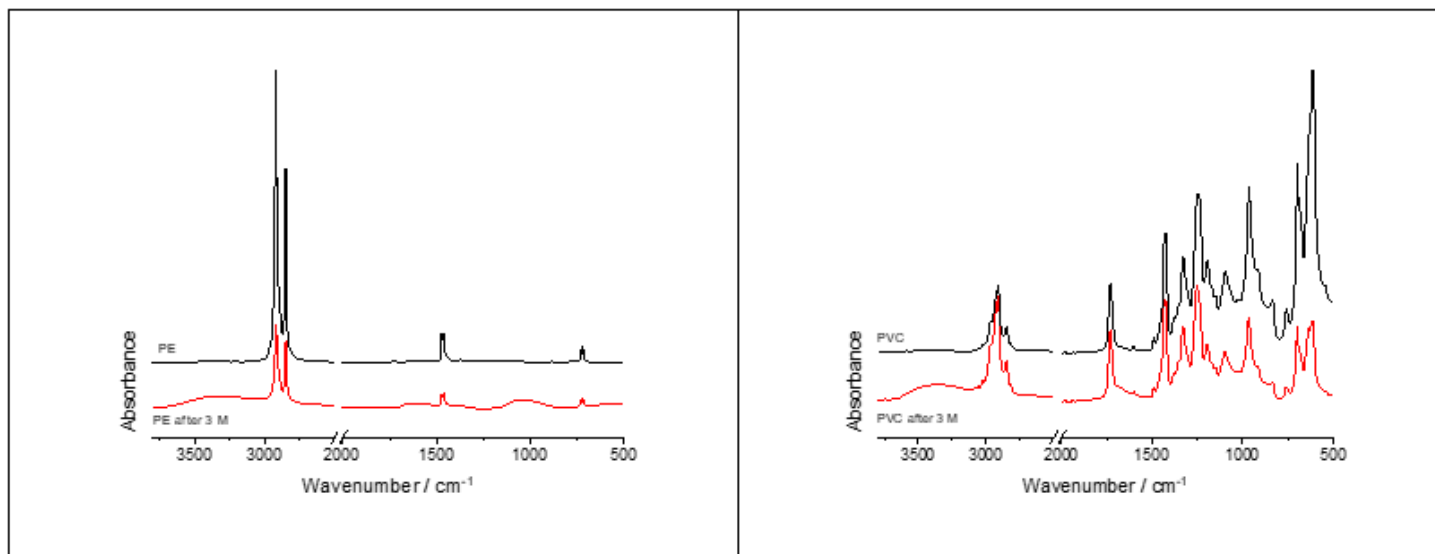
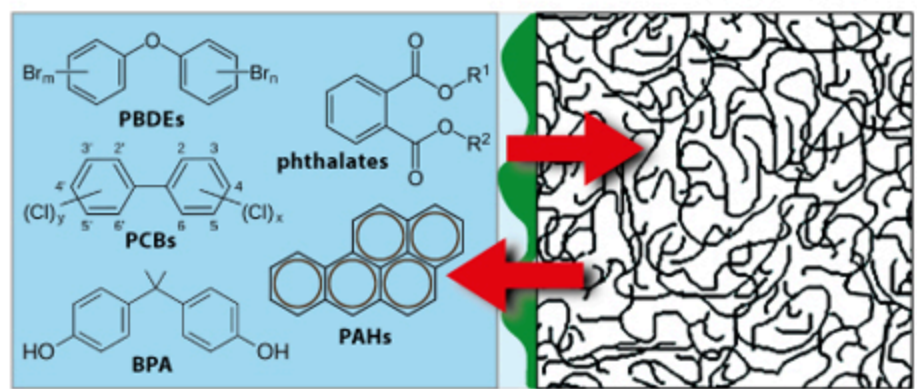
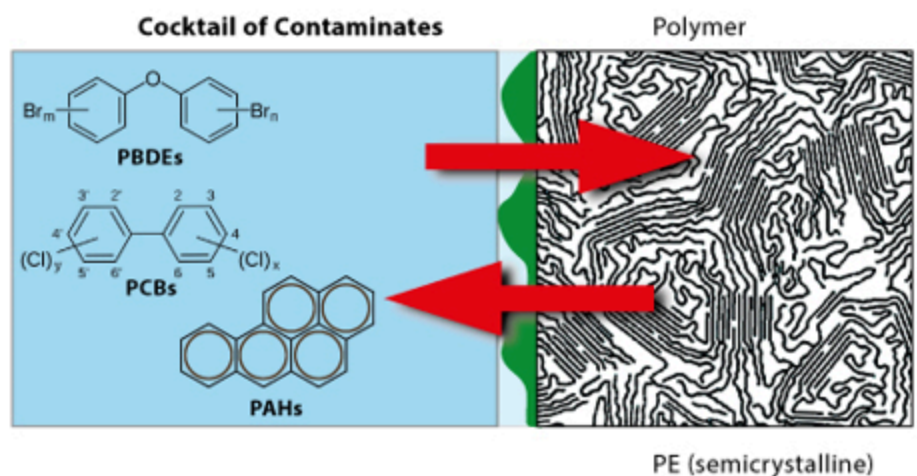


Figure 2

FTIR-spectra [Wavenumber cm^{-1} on the x-axis and Extinction on the y-axis] of the pristine polymer containers before and after the incubation within 3 months.



PE is thermoplast partially flexible (LDPE) semicrystalline

Hard-PVC (amorphous)

PVC is amorphous especially hard-PVC

Figure 3

Schematic illustration of the processes of contaminant transfer into the plastic polymer and the release out of the plastic (graph: J. Evers, FU Berlin). (Abbreviation: PCB = Polychlorinated Biphenyls, PBDE = Polybrominated Diphenyl Ethers, BPA = Bisphenol A, PAH = Polycyclic Aromatic Hydrocarbons)

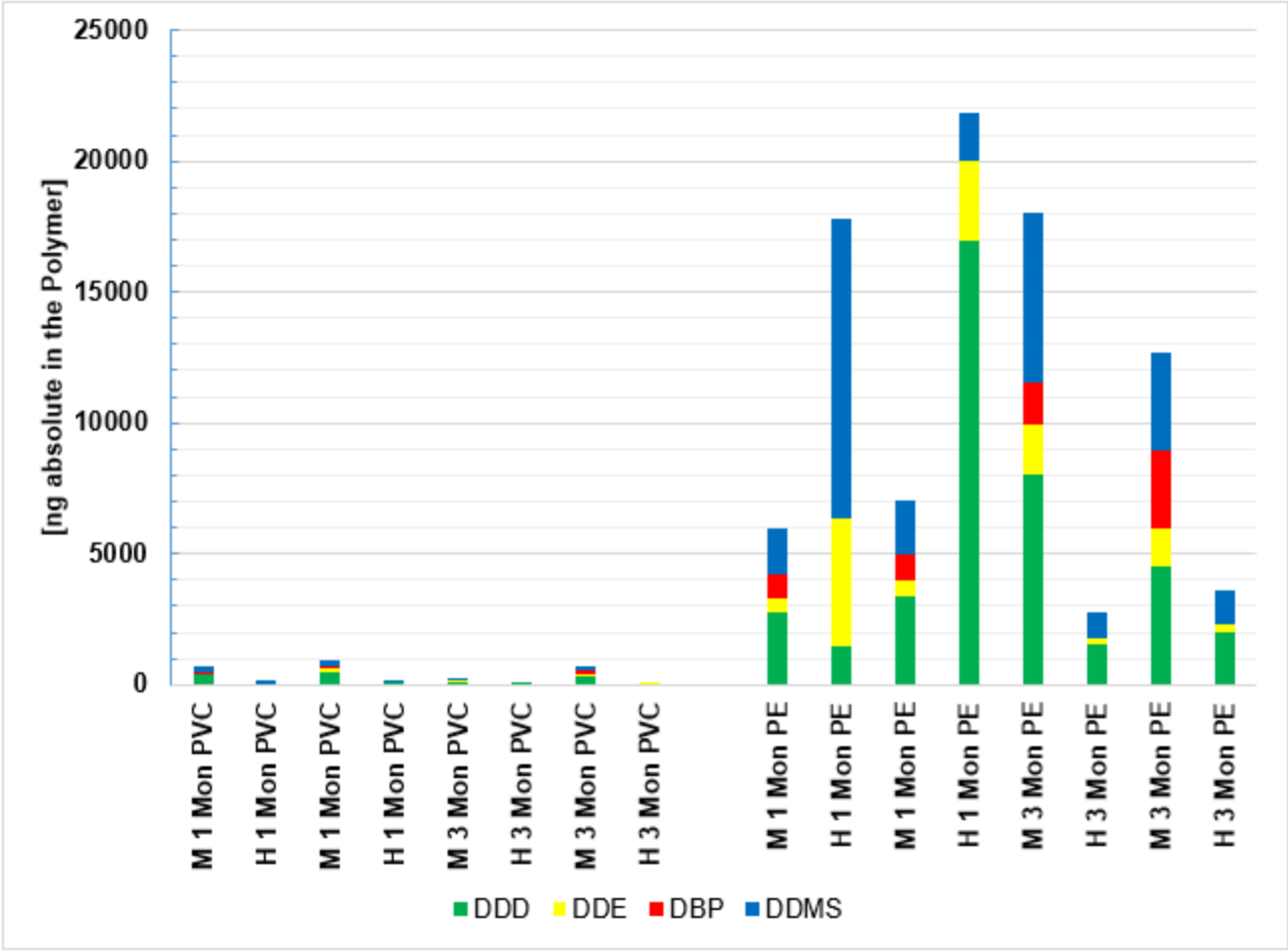


Figure 4

Detection of the selected compounds in the methanolic (M) and n-hexane extracts (H) for 1 and 3 months [ng absolute].

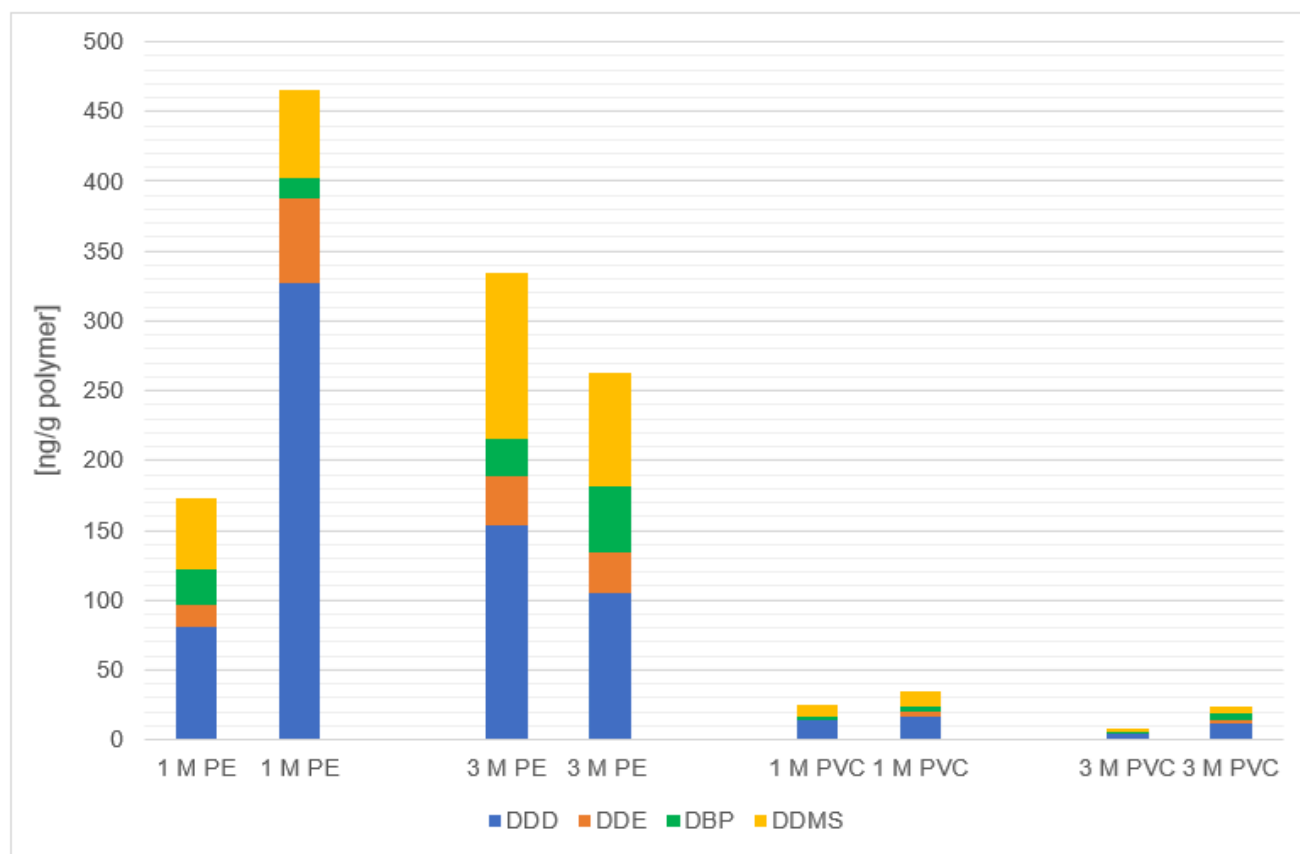
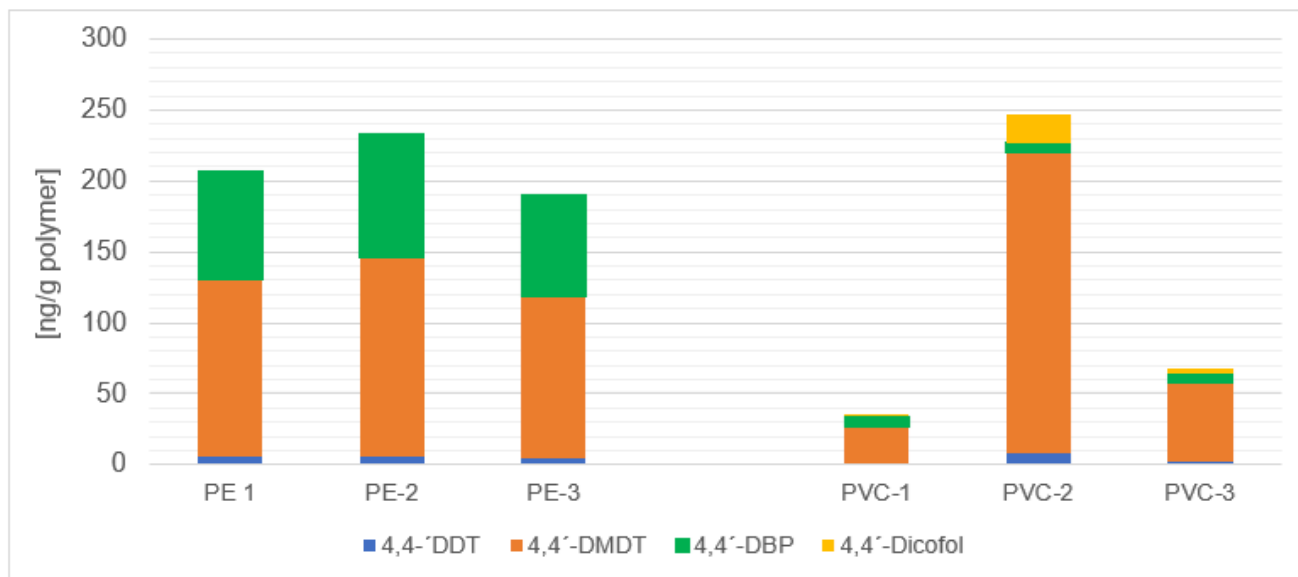


Figure 5

Calculation of the concentrations of the selected compounds [ng/g polymer] for comparison with the literature. Above are the VE-sorption experiments illustrated and below the desorption experiments.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [ESPRTTableSI1.docx](#)
- [ESPRTTableSI2.docx](#)
- [ESPRTTableSI3.docx](#)
- [ESPRTTableSI4.docx](#)