Letter

New polymer passive sampler for sensitive biomonitoring of lipid-rich matrices

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New Polymer Passive Sampler for Sensitive Biomonitoring of Lipid-Rich Matrices

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ABSTRACT

The feasibility of passive sampling biological matrices to quantify contaminants has been demonstrated using polydimethylsiloxane (PDMS). PDMS has, however, low sorptive capacity for hydrophobic compounds (with $K_{lipid\text{-}PDMS}$ ~30-40), and increasing the sampler volume and thus chemical mass transfer is not feasible due to concomitant lipid transfer. We therefore developed new polymers by graft polymerization from PDMS substrates, and evaluated the mechanism and kinetics of lipid transfer. $K_{lipid\text{-}polymer}$ was significantly improved to 6.7 ± 0.53 for dioxins and 0.78 ± 0.15 for PCBs using poly(tertiary-butyl methacrylate) (PtBuMA) chain grafts. Consistent with this, PtBuMA solubility of selected dioxins was 6-10 times higher compared to PDMS. Lipid transfer followed a swelling process, which was rapid ($t_{95\%}$=20-72 hours), independent of tissue lipid content and proportional to polymer sampler volume. The new PtBuMA polymer offers new opportunities for sensitive, rapid biomonitoring of PBTs and possibly also less stable neutral hydrophobic compounds in biota and food.

INTRODUCTION

Persistent, bioaccumulative and toxic (PBT) compounds have the potential to accumulate to hazardous levels particularly in long-lived, lipid-rich organisms (e.g. marine mammals, humans) and food (e.g. dairy, seafood).[1] Assessing PBT exposure and associated risks to both the environment and human health relies on information from (bio)monitoring in food, wildlife or humans. In view of the increasingly recognized significance of low-level exposure to complex chemical mixtures, cost-effective approaches that offer high sensitivity and low chemical selectivity are desirable. Traditional (bio)monitoring, however, relies on solvent extraction and extensive cleanup procedures that are costly and inherently selective. This limits the scope of chemical groups that can be evaluated, particularly for biopsies, blood or other low volume biomonitoring matrices.

Polymer-based equilibrium sampling has the potential to address these limitations and has received increasing attention as a possible alternative for quantifying chemical activity and concentration in biological tissues. Studies using polydimethylsiloxane (PDMS) have shown that in complex matrices (e.g., plant and animal oils[2-4], seafood and meats[4-7], other foods[4], invertebrates[3, 8], marine mammal blubber[8, 9], blood[10], human adipose tissue[11]), neutral hydrophobic chemicals partition between lipids (and where relevant, proteins) and the polymer until equal activity in the media is reached. It has also been found that the lipid-PDMS or blood-PDMS partition constants ($K_{lipid\text{-}PDMS}$, $K_{blood\text{-}PDMS}$) are approximately constant across a wide range of octanol-water partition constants (K_{ow}).[7, 9, 10] Thus, lipid normalized PBT concentrations can be easily predicted from their equilibrium concentrations measured in PDMS. Expanding upon these concepts, Allan et al demonstrated the feasibility of implanting PDMS for non-lethal *in-vivo* passive sampling[7] as well as quantifying PBT body burdens from silicone explants[11]. Furthermore, Jin et al.[9, 10, 12] provided proof-of-concept for direct application of lipid-exposed PDMS extracts to cell-based bioassays for effect-based measures, without the need for labor intensive and solvent consuming chemical clean-up. Together, these studies promise exciting opportunities for rapid, and cost-effective (bio)monitoring of PBTs.

Desirable characteristics of a passive sampler include fast diffusive rates, high sorptive capacity and low analytical interferences.[5, 8] Silicone rubbers such as PDMS outperform other available polymers for their high PBT diffusion coefficients.[13] However, their sorptive capacity is relatively low, resulting in low sampling sensitivity. This is illustrated by a relatively high $K_{lipid\text{-}PDMS}$ (approx. ~30-40; corrected for lipid transfer),[6, 7, 9] which means that the PBT concentration in a sample needs to be 300-400 pg g_{lipid}^{-1} to meet an instrument limit of detection of 100 fg (using a 200 mg PDMS sampler, 20 µL extract volume, and 1 µL injection). This is unsuitable for highly toxic PBTs such as dioxins and dioxin-like PCBs, which are typically present (and of concern) in organisms or food at much lower

concentrations.[14] Even for application to sensitive cell-based bioassays such as the CAFLUX assay, which responds to the combined activity of chemicals acting on the aryl hydrocarbon receptor, a TCDD equivalent (TCDD-EQ) of >9-12 pg g_{lipid}^{-1} is required for PDMS-based sampling to meet the assay's LOD (~0.06 $pg_{TCDD-EQ}$ in 100 µL medium).[9]

To reduce the concentration that can be quantified in lipids using PDMS passive samplers, much larger PDMS sampler volumes would be required, which may affect the method's practicality for many applications due to the large size and increased sampling time. In addition, higher sampler volume is expected to sorb more lipids, which can cause analytical interferences and transfer PBTs associated with the lipid fraction.[2, 4, 9] The mechanism or kinetics of this lipid transfer process has not yet been investigated, despite its potential to affect the benefits of passive sampling.[12] Instead of increasing sampler volumes, higher sampler efficiency could also be achieved by changing the sampler's sorptive capacity. Gamma-radiation grafting allows co-polymerization of various monomers onto the PDMS backbone.[15] The resulting custom polymers gain new properties, and grafts with various properties can be selected to alter the PDMS substrate's PBT sorptive capacity compared to unmodified PDMS. This includes, for example, taking advantage of molecular interactions that could be important for most neutral hydrophobic compounds such as van der Waals, electron donor/acceptor, and π-π interactions.

This study investigated both of these avenues by a) developing a library of custom-made polymers grafted to PDMS substrate, and testing these for their potential to achieve lower $K_{lipid\text{-}polymer}$ compared to unmodified PDMS and thus enhanced sampler efficiency, and b) exploring the mechanism and kinetics of lipid transfer to polymers. If the PBT sorptive capacity of polymer-samplers can be significantly enhanced, while controlling for the impact of transferred lipid, passive sampling could become a widely applicable tool for (bio)monitoring of ambient levels of PBTs and other neutral hydrophobic contaminants in lipid containing matrices.

MATERIALS AND METHODS

Polymers

Cross-linked PDMS (density 1.17 g cm^{-3}; Specialty Silicone Products, Ballston, US) served both as reference in its unmodified form, and as solid substrate for grafting. We used six different monomers at different concentrations to generate a series of eleven substrates that had been modified by graft co-polymerization (Supporting Information (SI) Table S1), whereby PDMS was covalently modified with polymer chains of selected properties. The graft polymerization is described in detail elsewhere.[15] Briefly, PDMS sheets (0.5 mm thick) were immersed in a 0.33 or 0.98

M monomer solution and deoxygenated for 5 minutes by purging with nitrogen. The sample mixtures were then placed in a ^{60}Co gamma-source and were irradiated to a total dose of 6 kGy, where interaction of the ionizing radiation with the substrate leads to formation of initiation sites from which the monomer polymerises. After gamma-radiation grafting, free homopolymers and unreacted monomers were removed by washing with dichloromethane, a solvent that maximized solvent-monomer interactions. The monomers polymerize at random sites throughout the PDMS and their concentration and cross-linking affect the overall property of the new co-polymer. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy and confocal Raman micro-spectroscopy was performed on poly(tertiary-butyl methacrylate) (PtBuMA) chain grafts to confirm grafting success on the PDMS surface (2 µm) as well as the bulk of the substrate, respectively (Figures S1 and S2). The level of PtBuMA grafting (4 and 17 wt %) was quantified using thermo-gravimetric analysis (Figure S3), which is described in the SI (Section S1). The polymer grafts exhibit properties ranging from highly hydrophobic (e.g. polyvinyl naphthalene) to hydrophilic (e.g. polyacrylamide) (Table S1). In addition, grafts were selected that were expected to have poor interactions with the analytes, e.g. electron donor/acceptor and hydrogen bond interactions.

After grafting, polymer and PDMS sheets were cut into discs of 6, 9 or 16 mm diameter using a metal punch. Potentially remaining unpolymerised material was removed by sequentially sonicating three times in hexane followed by three times in methanol for 30 minutes each. The weight of all air-dried polymer discs was recorded on a microbalance.

Marine mammal tissue samples

Blubber and hypodermis tissue samples were obtained from three dugongs (*Dugong dugon*) and an Australian humpback dolphin (*Sousa sahulensis*) stranded along the Queensland coast. Further sample details are given in Table S2. Lipid in such tissues is dominated by storage lipids (i.e. mainly triglycerides), and was extracted and quantified gravimetrically, according to a previously described method[9] (see also Section S2).

Lipid transfer experiments

Different sized polymer discs (6 x 0.5, 6 x 1, 9 x 1, 16 x 0.5, 16 x 1 mm; in triplicate) were brought into contact with tissues or lipid extracts for 1 to 216 hours at constant temperature (21 ± 1^{o}C) to determine kinetics, or for 144-288 hours for single point experiments. They were generally placed between sample tissues or immersed in extracts; some tests were carried out where polymers were double stacked on top of samples (see Section S3; Figure S4). After exposure, surface lipid was removed by dipping the polymer briefly into methanol and wiping with lint free tissue. The polymer

was then air-dried and the mass of lipid transferred to the polymer was quantified gravimetrically on a microbalance.

To investigate whether tissue lipid content affects lipid mass transfer, polymer discs (9 x 1 or 6 x 1 mm) were exposed to samples of varying lipid contents, including dugong blubber (ID64-B: 42%, ID14-B: 82%, ID81-B: 91% lipid), dugong hypodermis (ID14-H: 18% lipid) and the respective lipid extracts (100% lipid) of ID64-Bx, ID14-Bx and ID14-Hx, as well as a lipid extract of humpback dolphin blubber (ID39-Bx). A summary of all polymer-sample combinations is given in Table S3.

Partitioning experiments

All partitioning experiments were carried out using dugong blubber (ID81-B; 91% lipid). Polymers (6 x 0.5 or 6 x 1 mm) were spiked with 500 ng PCB 104, PCB 182 and PCB 209, and 400 ng PCB 118. Blubber (200 ± 33.6 mg) was spiked with 400 ng PCDD standard mix containing 2,3,7,8-TCDD; 1,2,3,7,8-PnCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,6,7,8,9-OCDD. Polymers and blubber were left overnight to evaporate all solvent. Spiking directions were previously demonstrated to have no effect on $K_{lipid\text{-}PDMS}$ values for dioxins.[9] We further confirmed this with PCB 118 spiked into either PDMS or blubber, and measured in PDMS at two time points (1 and 15 days) (Figure S5).

The spiked polymer was placed on the spiked blubber sample and left in an incubator at 21 ± 1°C for up to 20 days to confirm previously tested[9] time to equilibrium (time points analysed: 0.75, 1, 2, 5, 8, 12, 13, and 15 or 20 days; Figure S6), or >5-10 days for all subsequent experiments. Although we cannot exclude that some lipid degraded, its effect on $K_{lipid\text{-}polymer}$ was negligible up to day 20 (Figure S6). After exposure, the polymer was removed, weighed on a microbalance (to quantify lipid transfer), immersed in 10 mL n-hexane and extracted for 30 minutes in a sonication bath to desorb PCDDs and PCBs. All custom polymers were tested in at least duplicate at each monomer concentration.

Determination of solubility in PtBuMA and PDMS

Polymer solubility, $S_{polymer}$, of 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD and OCDD was quantified in PDMS and both PtBuMA (0.33 and 0.98 M) polymer discs (2 x 0.5 mm, n=3) following a recently developed method[16] detailed in Section S4. This method is based on equilibrium partitioning between clean polymer discs and PDMS loading sheets that contain solute in excess of saturated concentrations. Equilibrium concentrations of PCDDs measured in the discs therefore equal the polymer solubility. $K_{lipid\text{-}polymer}$ can be calculated as the ratio of the solubility of an analyte in lipid

(S_{lipid}) to that in the polymer ($S_{polymer}$), and thus, the difference in $S_{polymer}$ between samplers is proportional to the change in the analytes' $K_{lipid\text{-}polymer}$.

Analysis

All extracts were concentrated to near dryness and reconstituted in internal standard solution containing 300 pg μL^{-1}, 1,2,3,4,7,8,9-heptachlorodibenzofuran (HpCDF) in toluene. Analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph (30 m × 0.25 mm DB-5 fused silica capillary column) coupled to an electron capture detector (GC-ECD) and is described in more detail elsewhere.[17] Quantification of dioxins and PCBs was carried out using their response relative to that of the internal HpCDF standard against a 5-point calibration series containing all analytes and a constant concentration of HpCDF.

All statistical analyses (t-tests or ANOVA, nonlinear curve and horizontal line fitting, standard error of the mean (±SE)) were carried out in GraphPad Prism 6.0 using a statistical significance of p = 0.05. All $K_{lipid\text{-}polymer}$ values were corrected for the amount of lipid transferred to the polymer using the mass balance equation (1) (see Section S5 for derivation):

$$K_{lipid-polymer} = \frac{m_{polymer}\left(M_{i,spiked}-M_{i,extract}\right)}{m_{lipid-R}\left(M_{i,extract}-\frac{m_{lipid-P}\left(M_{i,spiked}-M_{i,extract}\right)}{m_{lipid-R}}\right)} \quad (1)$$

where $M_{i,spiked}$ and $M_{i,extract}$ (ng) is the mass of analyte (*i*) spiked to the system and extracted from the polymer at equilibrium, respectively; $m_{polymer}$ is the mass of the polymer (mg); $m_{lipid\text{-}R}$ and $m_{lipid\text{-}P}$ (mg) are the equilibrium masses of lipid remaining in the tissue sample and transferred to the polymer, respectively. Note that $M_{i,extract}$ is the sum of chemical masses in the polymer ($M_{i,polymer}$) and $M_{i,lipid\text{-}P}$.

RESULTS AND DISCUSSION

Screening of custom made polymers

Lipid-corrected $K_{lipid\text{-}PDMS}$ for unmodified PDMS averaged 38 ±4.2 for dioxins and 7.7 ±1.7 for PCBs (Figure 1; individual K-values provided in Table S4). Our $K_{lipid\text{-}PDMS}$ values are in agreement with empirical $K_{lipid\text{-}PDMS}$ determined for dioxins by Jin et al.[9, 12] (uncorrected: 31 ±7.3; corrected for lipid uptake: 37), and similar to those estimated for PCBs by Endo et al.[18] based on $K_{lipid\text{-}water}$ and $K_{PDMS\text{-}water}$ (3.9 ±1.9). While $K_{lipid\text{-}PDMS}$ has previously been suggested to be approximately constant across

hydrophobicity, our data suggests this applies only to congeners within a particular compound class as significant differences exist between dioxins and PCBs (Figure 1). This is supported by recent findings of considerably higher PDMS solubility for PCBs than PCDDs with similar K_{OW} (i.e. similar octanol solubility), which was attributed to their different molar volumes.[16] $K_{lipid\text{-}PDMS}$ (and $K_{lipid\text{-}polymer}$ in general) is also expected to differ for other lipid types (e.g. phospholipids, cholesterols) compared to the storage lipids (i.e. consisting mainly of triglycerides) used in this study; however, recent studies have demonstrated relatively small variation in PBT sorptive capacity of extractable organic matter of vastly different origin (e.g., plant oil, muscles, fish, seals, eggs, bacon) and lipid composition.[19] Hence, class-specific K-values should be applied when targeting multiple PBT groups with passive sampling, unless uncertainties associated with a uniform $K_{lipid\text{-}PDMS}$ are acceptable for screening purposes.

Compared to unmodified PDMS, $K_{lipid\text{-}polymer}$ was significantly lower for PCDDs (6.7 ±0.53) and PCBs (0.78 ±0.15) for substrates grafted with poly-tertiary butyl methacrylate using a monomer concentration of 0.98 M (PtBuMA 0.98 M) (Figure 1; Table S4). The higher chemical mass transfer to PtBuMA 0.98 M compared to unmodified PDMS increases the sensitivity of passive sampling by 5.7-9.9 fold. Lower grafted concentrations of PtBuMA (0.33 M) resulted in higher $K_{lipid\text{-}polymer}$ values for both PCDDs and PCBs (Figure 1; Table S4), confirming that PtBuMA affects the sorptive capacity of the substrates. This further suggests that higher monomer concentrations may allow further enhancement of sampler efficiency. In contrast to PtBuMA, the remaining custom polymers mostly resulted in poorer or only slightly enhanced partition constants for PCDDs and PCBs (Figure 1; Table S4). More detailed testing would be necessary to examine relationships between sorptive capacity and the various polymer properties.

Consistent with the results obtained via partition constants, the solubility of HxCDD (110 and 62 ng mg^{-1}), HpCDD (32 and 20 ng mg^{-1}) and OCDD (20 and 13 ng mg^{-1}) was significantly higher in 0.98 M compared to 0.33 M PtBuMA grafts, respectively, and significantly higher compared to unmodified PDMS (HxCDD: 18, HpCDD: 4.8, OCDD: 1.9 ng mg^{-1}) (Figure S7). Based on these solubility data, $K_{lipid\text{-}PtBuMA}$ for the 0.98 M graft is 6.4-10 fold lower, or more efficient, for PCDDs compared to $K_{lipid\text{-}PDMS}$, which is in excellent agreement with the $K_{lipid\text{-}polymer}$ data.

Lipid transfer

Lipid concentrations in exposed PDMS were remarkably consistent (6.8 ±0.17 µg mg_{PDMS}^{-1}), irrespective of PDMS volume, exposure type (see section S3), tissue type (i.e. blubber vs hypodermis), species (i.e. dugong vs dolphin blubber) and tissue lipid content (18-91%) (Figure 2;

Table S5). Furthermore, the mass of lipid transferred was similar for tissues and their respective (100%) lipid extracts (Figure 2; Table S5). Previously reported average lipid concentrations (6-9 µg mg_{PDMS}^{-1}) in PDMS are comparable to these results, and also relatively consistent across a wide range of oils and animal tissues sampled.[2, 4, 9] For most custom made polymers, concentrations of transferred lipid were similar to PDMS, except for the 0.33 and 0.98 M PtBuMA grafts, which contained approximately 2.5-fold (17 ±0.61 µg $mg_{Polymer}^{-1}$) and 4.6-fold (31 ±1.6 µg $mg_{Polymer}^{-1}$) higher lipid concentrations, respectively (Table S5). As for PDMS, however, lipid transfer to PtBuMA grafts was independent of lipid content (Figure 2).

These results indicate that the transfer of lipids to PDMS and custom grafts occurs via a swelling process[20] with swelling equilibrium ($t_{95\%}$) reached within 20-72 hours (Figure 2). Thus, the mass of lipid transferred to these polymers reaches a constant proportion of the polymer mass (0.68% for PDMS; 3.1% for PtBuMA 0.98 M). Accordingly, regardless of polymer-sampler volume or tissue lipid content, 21% of the mass of PCDDs and 5.0% of PCBs in a PDMS sampler were associated with the transferred lipid phase. Despite the higher lipid mass transfer to PtBuMA, its much lower $K_{lipid\text{-}PDMS}$ results in lower fractions of lipid associated PBTs (17% of PCDDs and 2.4% of PCBs for the 0.98 M PtBuMA). The constant lipid-sampler ratio and associated PBT transfer offers a straightforward (albeit PBT class-specific) correction factor in determining C_{lipd} via passive sampling.

Outlook

The PtBuMA polymer designed in the present study considerably enhances the application of polymer-based passive sampling of lipid rich matrices as a quick, simple and cost-effective screening tool. A PtBuMA sampler of 200 mg (e.g. 14.8 x 1 mm) achieves sufficiently high extraction efficiency to detect 7.8 pg_{PCBs} g_{lipid}^{-1} and 67 pg_{PCDDs} g_{lipid}^{-1} (under the same conditions as in the introduction). With such a sampler configuration, the polymer (and thus its extract) contains up to 6.2 mg lipid. In the present study where samples were spiked, cleanup was not required, but selective extraction followed by acid/base- treatment is an option to quantify very low concentrations of particular PBTs. Up-scaling the sampler volume by a factor of 5-10 (e.g. 23-33 x 2 mm) will allow detection of PBTs at typical background concentrations in the low pg g_{lipid}^{-1} range in biota and food. Alternatively, quantification using increasingly more sensitive instruments can decrease the detection limits by a factor of 10-100 at current state-of-the-art technology.[21]

The results from this study provide impetus for future work to optimize $K_{lipid\text{-}PtBuMA}$ while controlling lipid transfer. Based on the present study, we hypothesize that higher PtBuMA graft concentrations can further enhance mass transfer of PBTs, allowing miniature sampler configurations desirable for

minimally invasive *in-vivo* biomonitoring. Furthermore, a high degree of cross-linking of PtBuMA polymer chains (e.g. 10-100 Angstrom pore size) is expected to reduce swelling[20, 22] and thus minimize undesirable transfer of considerably larger storage lipids (mainly neutral triglycerides). Such modification could therefore eliminate chemical cleanup requirements, and provide a universal sampling tool not only for acid-recalcitrant PBTs, but also other, more labile hydrophobic neutral contaminants.

ASSOCIATED CONTENT

Supporting Information

Additional information, tables and figures, as referenced. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest

REFERENCES

1. Kelly, B. C.; Ikonomou, M. G.; Blair, J. D.; Morin, A. E.; Gobas, F. A. P. C., Food Web-Specific Biomagnification of Persistent Organic Pollutants. *Science* **2007,** *317*, (5835), 236-239.
2. Jahnke, A.; McLachlan, M. S.; Mayer, P., Equilibrium sampling: Partitioning of Organochlorine Compounds from Lipids into Polydimethylsiloxane. *Chemosphere* **2008,** *73*, 1575-1581.
3. Mayer, P.; Toräng, L.; Glæsner, N.; Jönsson, J. Å., Silicone Membrane Equilibrator: Measuring Chemical Activity of Nonpolar Chemicals with Poly(dimethylsiloxane) Microtubes Immersed Directly in Tissue and Lipids. *Anal. Chem.* **2009,** *81*, 1536-1542.
4. Jahnke, A.; Mayer, P., Do Complex Matrices Modify the Sorptive Properties of Polydimethylsiloxane (PDMS) for Non-Polar Organic Chemicals? *J. Chromatogr. A* **2010,** *1217*, 4765-4770.
5. Jahnke, A.; Mayer, P.; Broman, D.; McLachlan, M. S., Possibilities and Limitations of Equilibrium Sampling Using Polydimethylsiloxane in Fish Tissue. *Chemosphere* **2009,** *77*, 764-770.
6. Jahnke, A.; Mayer, P.; Adolfsson-Erici, M.; McLachlan, M. S., Equilibrium Sampling of Environmental Pollutants in Fish: Comparison with Lipid-Normalized Concentrations and Homogenization Effects on Chemical Activity. *Environ. Toxicol. Chem.* **2011,** *30*, 1515-1521.
7. Allan, I. J.; Bæk, K.; Haugen, T. O.; Hawley, K. L.; Høgfeldt, A. S.; Lillicrap, A. D., In Vivo Passive Sampling of Nonpolar Contaminants in Brown Trout (Salmo trutta). *Environ. Sci. Technol.* **2013,** *47*, 11660-11667.
8. Ossiander, L.; Reichenberg, F.; McLachlan, M. S.; Mayer, P., Immersed Solid Phase Microextraction to Measure Chemical Activity of Lipophilic Organic Contaminants in Fatty Tissue Samples. *Chemosphere* **2008,** *71*, 1502-1510.
9. Jin, L.; Gaus, C.; van Mourik, L.; Escher, B. I., Applicability of Passive Sampling to Bioanalytical Screening of Bioaccumulative Chemicals in Marine Wildlife. *Environ. Sci. Technol.* **2013,** *47*, 7982-7988.
10. Jin, L.; Escher, B. I.; Limpus, C. J.; Gaus, C., Coupling Passive Sampling with In Vitro Bioassays and Chemical Analysis to Understand Combined Effects of Bioaccumulative Chemicals in Blood of Marine Turtles. *Chemosphere* **2015,** *138*, 292-299.
11. Allan, I. J.; Bæk, K.; Kringstad, A.; Roald, H. E.; Thomas, K. V., Should Silicone Prostheses be Considered for Specimen Banking? A Pilot Study into Their use for Human Biomonitoring. *Environ. Int.* **2013,** *59*, 462-468.
12. Jin, L.; Gaus, C.; Escher, B. I., Adaptive Stress Response Pathways Induced by Environmental Mixtures of Bioaccumulative Chemicals in Dugongs. *Environ. Sci. Technol.* **2015,** *49*, 6963-6973.
13. Rusina, T. P.; Smedes, F.; Klanova, J.; Booij, K.; Holoubek, I., Polymer Selection for Passive Sampling: A Comparison of Critical Properties. *Chemosphere* **2007,** *68*, 1344-1351.
14. EC, Commission Regulation (EU) No 1259/2011 of 2 December 2011 Amending Regulation (EC) No 1881/2006 as Regards Maximum Levels for Dioxins, Dioxin-Like

PCBs and Non Dioxin-Like PCBs in Foodstuffs. *Official Journal of the European Union* **2012,** *L 320/18*, 18-23.

15. Blakey, I.; Day, G.; Girjes, E.; Hunter, D. S.; Rasoul, F., Characterisation of Grafted Supports used for Solid-Phase Synthesis. *Polym. Int.* **2003,** *52*, 1734-1739.
16. Grant, S.; Schacht, V.; Escher, B. I.; Hawker, D.; Gaus, C., An Experimental Solubility Approach to Determine Chemical Activity and PDMS-Water Partition Coefficients. *Environ. Sci. Technol.* **Submitted 2015** (22/09/2015; es-2015-04655x.R1).
17. Grant, S.; Stevenson, G.; Malcolm, D.; Zennegg, M.; Gaus, C., Isomer-Specific Investigation of PCDD/F Mobility and Other Fate Processes in Deep Soil Cores. *Chemosphere* **2015,** *137*, 87-94.
18. Endo, S.; Escher, B. I.; Goss, K.-U., Capacities of Membrane Lipids to Accumulate Neutral Organic Chemicals. *Environ. Sci. Technol.* **2011,** *45*, 5912-5921.
19. Jahnke, A.; Holmbäck, J.; Andersson, R. A.; Kierkegaard, A.; Mayer, P.; MacLeod, M., Differences Between Lipids Extracted from Five Species are not Sufficient to Explain Biomagnification of Nonpolar Organic Chemicals. *Environ. Sci. Technol. Lett.* **2015,** *2*, 193-197.
20. Flory, P. J.; Rehner, J., Statistical Mechanics of Cross-Linked Polymer Networks II. Swelling. *J. Chem. Phys.* **1943,** *11*, 521-526.
21. Patterson Jr, D. G.; Welch, S. M.; Turner, W. E.; Sjödin, A.; Focant, J.-F., Cryogenic Zone Compression for the Measurement of Dioxins in Human Serum by Isotope Dilution at the Attogram Level Using Modulated Gas Chromatography Coupled to High Resolution Magnetic Sector Mass Spectrometry. *J. Chromatogr. A* **2011,** *1218*, 3274-3281.
22. Nielsen, L. E., Cross-Linking–Effect on Physical Properties of Polymers. *J. Macromol. Sci., Polym. Rev.* **1969,** *3*, 69-103.

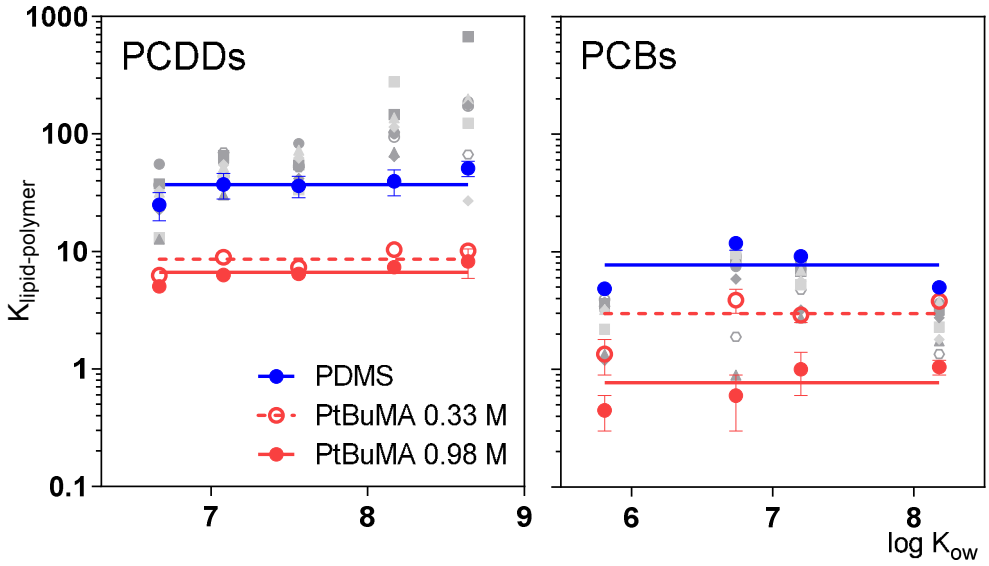

Figure 1. Average $K_{lipid\text{-}polymer}$ for PCDDs (left) and PCBs (right) in unmodified PDMS (blue), 0.98 M and 0.33 M grafted PtBuMA polymers (red), compared to other custom-made polymers tested in this study (grey). Error bars: ±SE for PDMS and PtBuMA (individual K values and ±SE for all polymers are provided in Table S4).

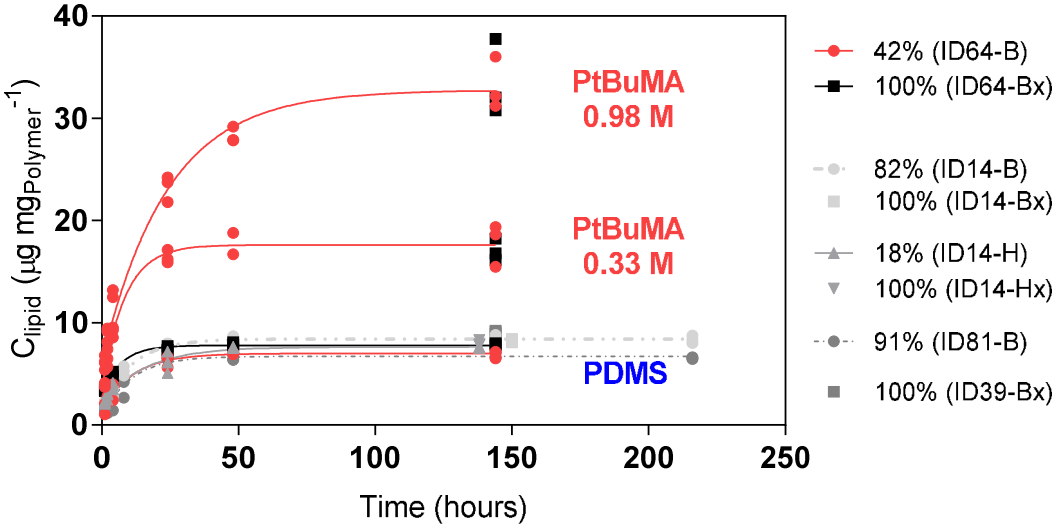

Figure 2. Kinetics of PDMS and PtBuMA (0.33 M and 0.98 M) swelling in tissues of varying lipid contents (18-91%) and lipid extracts (100% lipid), in blubber (B) and hypodermis (H) of dugongs and dolphin. Symbols show individual replicates (n=3) at each time point and lines show a fitted exponential growth model (r^2 = 0.95-0.98). Data plotted at 138-150 hours were all measured at 144 hours (data provided in Table S5).

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TOC ART

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