Master's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

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The presence and sorption of bisphenols and benzophenones in plastic-containing electronic waste and vehicle fluff from Norwegian waste handling facilities

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Supervisor: Hans Peter H. Arp, Alexandros G. Asimakopoulos
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Abstract

E-waste and vehicle fluff can be described as complex mixtures of inhomogeneous materials containing arrays of both valuable resources and hazardous substances. As part of the ambition in transitioning towards a circular economy in Europe, there is a growing interest in developing technology and processes for recycling all raw materials in waste, not only the metals and metalloids, but also the plastics.

Bisphenol A (BPA) is a compound frequently used as an additive in polymers. BPA is being phased out due to its endocrine effects on biological systems, and other bisphenols are replacing BPA. However, it is still not clear what the best BPA alternatives are when considering recycling, human exposure and environmental exposure. An ideal BPA alternative should have a low risk of environmental exposure and be easy to recycle. The desired sorption property of an additive depends on the approach of the recycling process; whether the objective is to contain the additive within the material or extract it.

This study concerns BPA alternatives and benzophenones found in E-waste and vehicle fluff. The concentrations of nine bisphenols and five benzophenones were measured in twelve samples from five different waste handling facilities in Norway. Moreover, a passive sampling method using polyoxymethylene (POM) was developed for use in lab-scaled batch experiments for bisphenols and benzophenones. The POM method was developed in order to understand the leachability and sorption of these substances in the E-waste and vehicle fluff samples. A set of waste-water partition coefficients (K_{waste}) of the bisphenols and benzophenones in the plastic-containing waste were established using POM.

The substances measured to have the largest concentrations were BPA, bisphenol F and bisphenol S with maximum concentrations determined to 246000, 42400 and 332 ng/g, respectively. POM reached equilibrium concentrations with bisphenols and benzophenones within 14 days of shaking. POM-water sorption isotherms showed very good correlations for the different bisphenols and benzophenones (from $R^2 = 0.83$ to 0.99), and POM-water partition coefficients (K_{POM}) showed good correlations with octanol-water partition coefficients (K_{ow}): $R^2 = 0.82$. Bisphenol S and benzophenone-2 showed the lowest log K_{waste} values (1.63 ± 0.32 and 1.71 ± 0.16, respectively) in addition to the highest leaching percentages, 83 and 62%, respectively. For this purpose, POM was considered suitable for measuring freely-dissolved concentrations, as the correlation between log K_{waste} and log K_{POM} was very good ($R^2 = 0.84$). The correlation between log K_{waste} and log K_{ow} resulted in $R^2 = 0.67$. This indicates that POM may be a better fitting reference sorption phase for E-waste and vehicle fluff samples.

Sammendrag

EE-avfall og fluff fra kjøretøy kan bli beskrevet som komplekse blandinger av inhomogene materialer bestående av både verdifulle ressurser og farlige stoffer. Som del av ambisjonen om overgang til en sirkulær økonomi i Europa er det en økende interesse for utvikling av teknologi og prosesser for å gjenvinne alle råvarer i avfall, ikke bare metaller og halvmetaller, men også plastmaterialer.

Bisfenol A (BPA) er en forbindelse mye brukt som et tilsetningsstoff i polymerer. BPA blir faset ut ettersom stoffet har hormonforstyrrende effekter på biologiske systemer, og dermed erstattes BPA med andre bisfenoler. Det er imidlertid fortsatt ikke kjent hva som er det beste BPA-alternativet med tanke på gjenvinning, menneskelig eksponering og miljøpåvirkning. Et ideelt BPA-alternativ bør være forbundet med lav risiko for miljøutslipp og være enkel å gjenvinne. Ønskelige sorpsjonsegenskaper for et tilsetningsstoff er avhengig av hvordan resirkuleringsprosessen foregår; hvorvidt målet er å beholde tilsetningsstoffet inni materialet eller ekstrahere det.

Denne studien omfatter BPA-alternativer og benzofenoner funnet i EE-avfall og fluff fra kjøretøy. Konsentrasjonene av ni bisfenoler og fem benzofenoner ble målt i tolv prøver fra fem ulike avfallshåndteringsanlegg i Norge. Videre ble en metode for passiv prøvetaking ved bruk av polyoksymetylen (POM) utviklet for bruk i batch-eksperimenter i labskala for bisfenolene og benzofenonene. POM-metoden ble utviklet for å forstå sorpsjonen og hvordan disse stoffene utlekkes fra prøver av EE-avfall og fluff fra kjøretøy. Et sett med avfall-vann fordelingskoeffisienter (K_{waste}) for bisfenolene og benzofenonene i avfallet ble etablert ved bruk av POM.

Stoffene som ble målt til å ha de høyeste konsentrasjonene var BPA, bisfenol F og bisfenol S med maksimale konsentrasjoner bestemt til henholdsvis 246000, 42400 og 332 ng/g. POM nådde likevektskonsentrasjoner med bisfenoler og benzofenoner i løpet av 14 dagers risting. Sorpsjonsisotermer for POM-vann viste veldig gode korrelasjoner for de ulike bisfenolene og benzofenonene (fra $R^2 = 0.83$ til 0.99), og fordelingskoeffisienter for POM-vann (K_{POM}) viste gode korrelasjoner med fordelingskoeffisienter for oktanol-vann (K_{ow}): R^2=0.82. Bisfenol S og benzofenon-2 viste de laveste log K_{waste}-verdiene

(henholdsvis 1.6 ± 0.3 og 1.7 ± 0.2) i tillegg til de høyeste utlekkingsprosentene, henholdsvis 83 og 62%. Til dette formålet ble POM ansett som egnet for måling av fritt oppløste konsentrasjoner, siden korrelasjonen mellom log K_{waste} og log K_{POM} var veldig god ($R^2 = 0.84$). Log K_{waste} og log K_{ow} resulterte i $R^2 = 0.67$. Dette indikerer at POM kan være en sorpsjonsfase som er bedre egnet som referanse for prøver av EE-avfall og fluff fra kjøretøy.

Preface

This thesis is completing my Master's degree in Analytical Chemistry at the Department of Chemistry at Norwegian University of Science and Technology (NTNU) in Trondheim. The work has been carried out during spring 2019.

I would like to thank my supervisor Hans Peter H. Arp for inspiring and helpful guidance and thorough feedback, as well as for providing me samples to analyze. It was very motivating spending some days at the environmental laboratory at NGI in Oslo to get a practical introduction to the subject and some hands-on experience.

I would also like to thank my co-supervisor Alexandros G. Asimakopoulos for his enthusiasm and for sharing his knowledge. I have really appreciated his problem-solving "don't you worry"-mindset. Moreover, I would like to thank Kristine Vike-Jonas for laboratory assistance and in the use of the LC-MS/MS instrument.

Special thanks to Jonas, family and friends for moral support and encouragement. Finally, I would like to thank my classmates Caroline and Torstein for motivational quotes and homemade cakes.

Contents

Abbreviations

API	Atmospheric Pressure Ionization
APCI	Atmospheric Pressure Chemical Ionization
APPI	Atmospheric Pressure Photoionization
ASR	Automotive Shredder Residue
Avg.	Average
BPs	Bisphenols
BzPs	Benzophenones
DOC	Dissolved Organic Carbon
EDC	Endocrine Disruptive Chemical
ESI	Electrospray Ionization
HPLC	High Pressure Liquid Chromatography
EE-avfall	Elektrisk og elektronisk avfall
EPS	Equilibrium Passive Samplers
E-waste	Electronic waste
IS	Internal Standard
LC	Liquid Chromatography
LOD	Limit Of Detection
LLOQ	Lower Limit Of Quantitation
Max.	Maximum
Min.	Minimum
MRM	Multiple Reaction Monitoring
MS	Mass Spectrometry
m/z	mass-to-charge
MW	Molecular weight

POM	Polyoxymethylene
QA	Quality Assurance
QC	Quality Control
R^2	Coefficient of Determination
rpm	Rotations per minute
RT	Retention Time
RRT	Relative Retention Time
SD	Standard Deviation
ToF	Time-of-Flight
UHPLC	Ultra High Performance Liquid Chromatography
UHPLC-MS/MS	Ultra High Performance Liquid Chromatography tandem Mass Spectrometry
UV	Ultraviolet
WEEE	Waste Electrical and Electronic Equipment

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1 Introduction

Waste Electronic and Electrical Equipment (WEEE), also called E-waste, comprises a complex array of materials, plastics, metals, metalloids and chemicals. Automotive Shredder Residue (ASR) refers to all non-metallic, non-easily removable parts of a car such as plastics, textiles, dirt and a variety of other materials. In the recycling industry the term "vehicle fluff" is often used. [1] E-waste and vehicle fluff often include bisphenols and benzophenones showing endocrine disruptive effects. [2][3][4]

The use of additives in polymers generates materials suitable for several applications in the plastic market, but it also makes the plastic material more complex, and thus complicates recycling. In many cases, the cost of recycling exceeds the revenue recovered from materials, especially in countries with strict environmental regulations. [5]

A study from 2015 reported high concentrations of bisphenol A (BPA) in E-waste and vehicle fluff samples collected at different sites in the eastern part of Norway, as well as showing E-waste and vehicle fluff fractions contributing to BPA leachate concentrations at waste facilities. [6] Due to the growing restrictions on the use of BPA, several other bisphenols are gaining importance as substitutes for BPA in a variety of applications. [7] Bisphenol F (BPF) and bisphenol S (BPS) as well as BPA have previously been found in surface waters in Japan, Korea, China and India. [8] It remains unclear to what extent other bisphenols as well as benzophenones have an impact on the environment and human health, and which BPA substitute is the best considering human exposure, environmental exposure and recycling.

The shift towards a circular economy in Europe favors minimization of waste and aims at making the most out of resources. [9] Applying suitable recycling processes is an important part of taking advantage of already existing products. However, currently it is a topic under discussion how to best manage recycling of mixed-materials containing hazardous substances like BPA. Further, it is also uncertain if BPA alternatives would be easier to manage, both technologically and in terms of risk during material recycling. Knowing the sorption properties of alternative BPA additives is useful in this regard, as this will impact the emissions and exposure under different recycling processes, as well as have relevance to the identifying of the best alternatives in a circular economy with strict environmental regulations.

Comparing the leachability of bisphenols and benzophenones from waste, i.e. the sorption, can give an indication of the ability of the substitutes to dissolve from waste and potentially enter the surroundings when in an aqueous environment. This can be undesirable if the aim is to carry out a recycling process while keeping the additive within the material. However, if the aim is to separate the additive from the material during a recycling process, a high leachability is desirable.

The objectives of this study are to: i) Measure concentrations of BPA, BPA alternatives and benzophenones present in plastic-containing E-waste and vehicle fluff, ii) Develop a method for measuring free-phase concentrations of BPA alternatives and benzophenones in water using a polyoxymethylene (POM) passive sampler and quantifying POM-water partition coefficients for these substances, and iii) Measure and describe the partitioning behaviour of BPA, BPA alternatives and benzophenones of plastic-containing E-waste and vehicle fluff.

2 Background

2.1 E-waste, vehicle fluff and recycling

Growth in industrial activity, emissions to environment, solid waste generation and landfill disposal have led to a rising consumption of natural resources. [10] A circular economy favors activities such as reuse, remanufacturing and recycling over waste disposal, to create a regenerative closed loop with limited resource input and waste. [9] However, both E-waste and vehicle fluff are not only consisting of complex materials, but also contain a lot of hazardous chemicals. Developing recycling processes is very challenging as the different parts can be hard to separate.

In bulk manufacturing of commercial polymers, a combination of additives is usually introduced to obtain the desired properties of the material, and thereby add its commercial value. The additives can be categorized as e.g. plasticizers, stabilizers, lubricants, pigments, UV absorbers, flame retardants or fillers, among others, depending on the properties they introduce to the material. [11] To approach the circularity concept, the use of additives in polymer products should be considered. At least the use of different alternatives regarding human exposure, environmental exposure and recycling should be assessed.

E-waste and vehicle fluff facilities can also be environmental emission sources of hazardous substances themselves. [1] When materials containing plastics are stored on landfills or at recycling facilities, small fragments tend to emit with time. [12] It is reasonable to assume that additives from plastic-containing material may end up as more or less free molecules or within secondary microplastics in the landfill, and that they might be transported by air and leachate out of the landfill.

2.2 Endocrine Disruptive Compounds (EDC)

An Endocrine Disruptive Compound (EDC) is a chemical that may interfere with the hormonal system and lead to harmful disturbances in humans and other biological organisms. The endocrine system of organisms works as a chemical messenger system between the nervous system and different functions such as growth and development, metabolism, immunity, reproduction and behaviour. [13] EDCs can mimic or partly mimic naturally occurring hormones, block a receptor by binding to it, or interfere or block the way natural hormones or their receptors are controlled or made. This may result in a disturbed signal response. [**?**]

2.3 Bisphenols and benzophenones

Bisphenol A (BPA) is an additive with endocrine disruptive properties that has been extensively used in the manufacturing of consumer products containing polycarbonate plastics and epoxy resins. [2] Examples of such products are toys, food containers, liquid containers, inner lining of metal cans, DVDs, CDs, thermal paper and circuit boards. As the BPA-containing materials are employed in a wide variety of applications, the human exposure to this chemical has been widespread. Due to the growing restrictions on the use of BPA, several other bisphenols are gaining importance as substitutes for BPA in a variety of applications. [7] It is still not clear what impact these BPA substitutes have on the environment and on human health.

Benzophenones (BzPs) is a group of additives used in plastic manufacturing reported having endocrine disruptive effects on animals. [3][4] Benzophenones are added to some plastics such as polypropylene as a UV filter to prevent degradation of the plastic product through photo-oxidation. [14] Another use is as an agent in sunscreen. [15]

BPA and eight other bisphenols (BPs) that possibly are used as substitutes, as well as five benzophenones are listed in Table 2.1. The properties include abbreviation, full name, molecular weight (MW), logarithmic octanol-water partition coefficient (K_{ow}) and CAS-number. The octanol-water partition coefficient is used as a parameter to study the hydrophobic properties of a compound. The structures of the bisphenols and benzophenones included in the study are presented in Figure 2.1 and Figure 2.2.

Table 2.1: Properties of nine bisphenols and five benzophenones included in this study.

Abbreviation	**Full name**	**MW [g/mol]**	**log K_{ow}**	**CAS-number**
BPA	2,2-Bis(4-hydroxyphenyl)propane	228.3	4.04[7]	80-05-7
BPAF	2,2-Bis(4-hydroxyphenyl)hexafluoropropane	336.2	4.77[7]	1478-61-1
BPAP	4,4'-(1-Phenylethylidene)bisphenol	290.4	5.18[7]	1571-75-1
BPB	2,2-Bis(4-hydroxyphenyl)butane	242.3	4.49[7]	77-40-7
BPF	4,4'-Methylenediphenol	200.2	3.46[7]	620-92-8
BPM	4,4'-(1,3-Phenylenediisopropylidene)bisphenol	346.5	n/a	13595-25-0
BPP	4,4'-(1,4-Phenylenediisopropylidene)bisphenol	346.5	6.72[7]	2167-51-3
BPS	4,4'-Sulfonyldiphenol	250.3	2.32[7]	80-09-1
BPZ	4,4'-Cyclohexylidenebisphenol	268.4	4.91[7]	843-55-0
BzP-1	2,4-Dihydroxybenzophenone	214.2	3.17[16]	131-56-6
BzP-2	2,2',4,4'-Tetrahydroxybenzophenone	246.2	3.16[16]	131-55-5
BzP-3	Oxybenzone	228.2	3.79[16]	131-57-7
BzP-8	Dioxybenzone	244.2	3.93[16]	131-53-3
4-OH-BzP	4-Hydroxybenziphenone	198.2	3.07[17]	1137-42-4

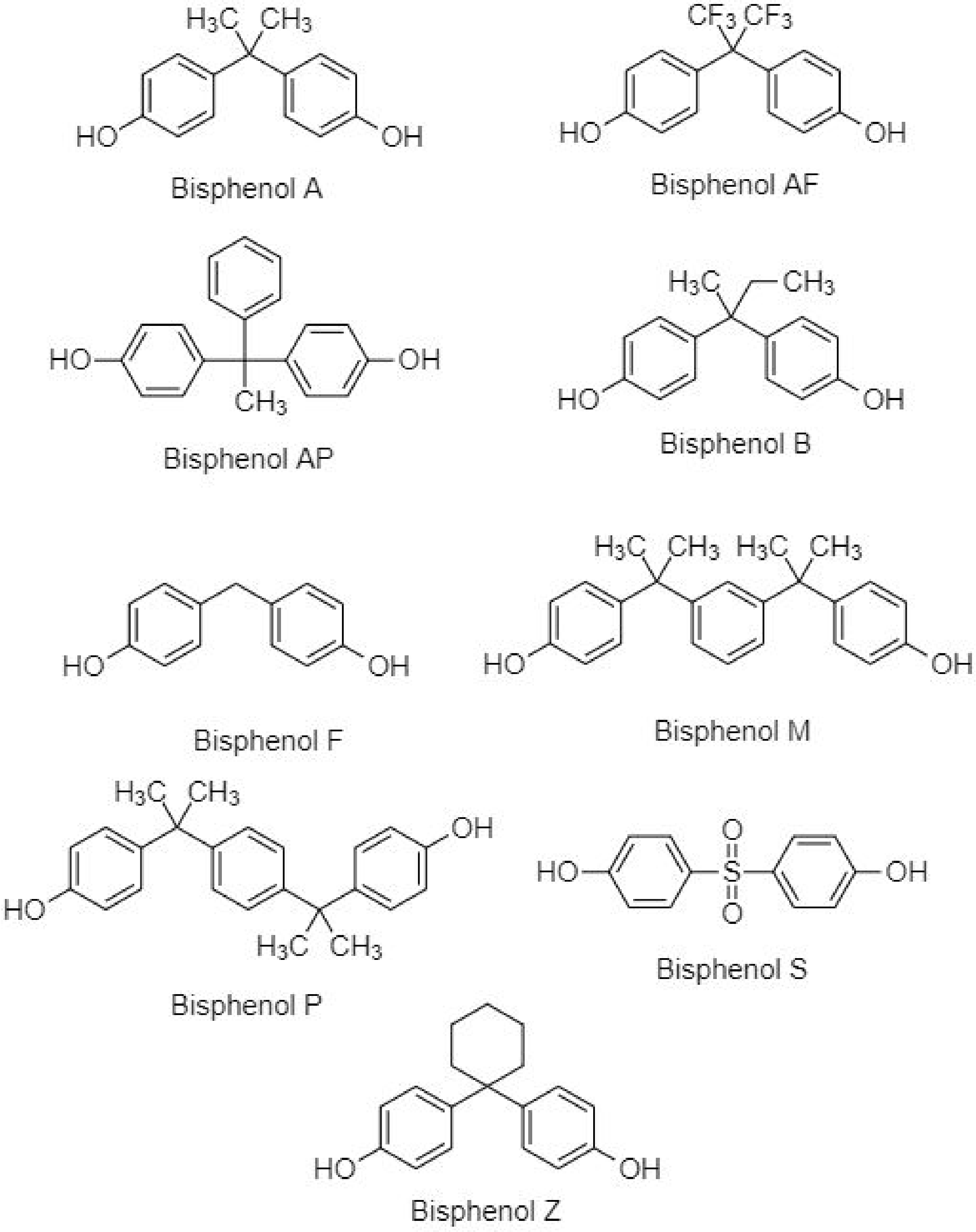
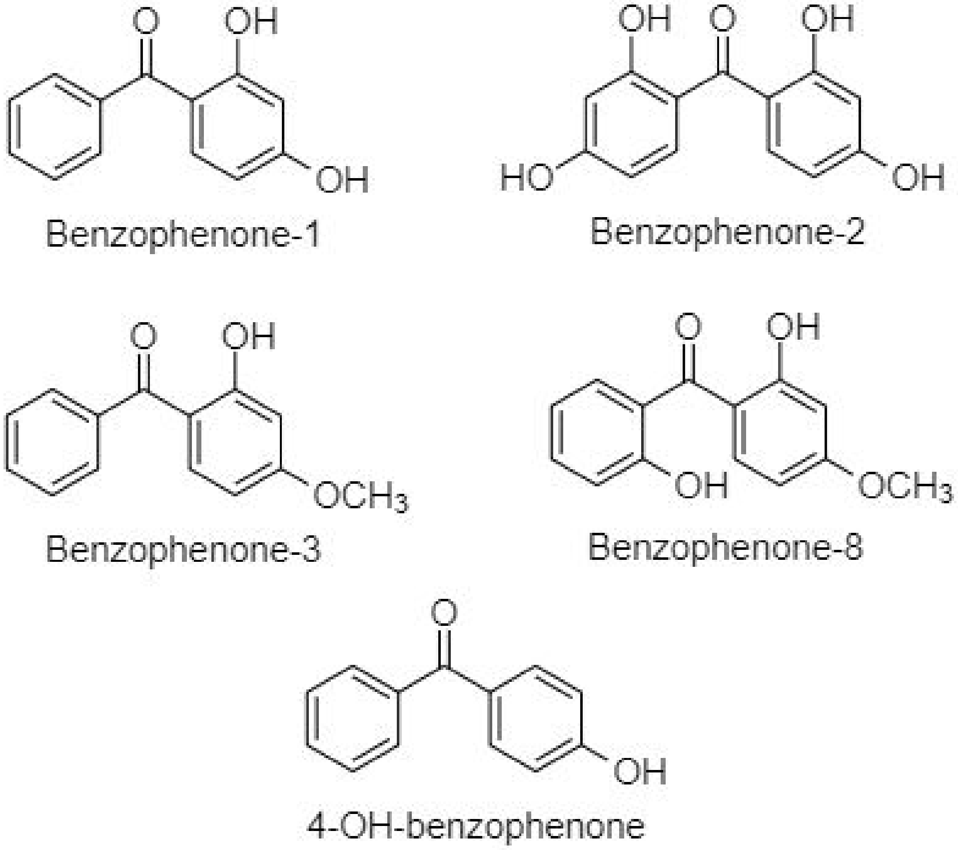


Figure 2.1: Structures of bisphenols included in this study.



Benzophenone-1

Benzophenone-2

Benzophenone-3

Benzophenone-8

4-OH-benzophenone

Figure 2.2: Structures of benzophenones included in this study.

2.4 Partition coefficients

Equilibrium ratio or a partition coefficient (K) of a system is useful to give an indication on how a substance behaves between two phases. Equation 2.1 gives the concentration ratio between an organic phase and water phase. [18]

$$\mathrm{K} = \frac{\mathrm{C}_{\text{organic phase}}}{\mathrm{C}_{\text{water phase}}} \tag{2.1}$$

K is the sorption coefficient, $C_{organic\ phase}$ is the concentration of substance in organic phase at equilibrium and $C_{water\ phase}$ is the concentration of substance in water phase at equilibrium. From Equation 2.1 it can be interpreted that a large value of K means that the substance not easily dissolves in water. Most of the analyte is still bound to the organic phase. A small value of K suggests a very water soluble substance. Hence, the partition coefficient describes how hydrophobic or hydrophilic a compound is. This gives further indications as to whether the compound easily can be taken up in an aqueous environment and in turn possible pollute the surroundings. Knowledge of the nature of these compounds can be used to predict the mobility in aqueous environment. [19]

The coefficient can be used to study general sorption properties of a substance as well as the tendency to migrate from one part of the environment to another. This makes it possible to determine expected environmental distribution patterns of substances. [20]

2.5 Polyoxymethylene (POM) samplers

To derive a K-value, a sorption isotherm can be employed. A sorption isotherm describes the relation between the equilibrium concentration of the sorptive and the quantity of sorbate on the surface at constant temperature. This can be visualized by plotting the concentration of sorbate over the concentration of sorptive for different spiked or naturally occurring concentrations.

Equilibrium Passive Samplers (EPS) based on polyoxymethylene (POM) have been used to achieve a sensitive determination of freely dissolved water concentrations of hydrophobic organic compounds in the environment. In other words, substances not bound to colloids or Dissolved Organic Carbon (DOC). The use of these passive samplers gives less artifacts from water quantitation as interference from colloids and DOC is minimized. In addition, several studies have found that freely dissolved concentrations give better correlations with ecotoxicological and toxicological endpoints than whole water samples. [6] [21] POMs are slightly polar which make them appropriate as passive sampler for bisphenols and benzophenones. An advantage of POM compared to other passive samplers used for the same purpose, is that the material is easy to handle due to a hard and smooth surface with an excellent physical and chemical stability. [22]

The working principle of the POM passive sampler is as following: when a clean POM strip is exposed to a suitable analyte, the strip accumulates the contaminants until equilibrium is reached. Therefore, in order to use POM as passive samplers, a reliable understanding of the uptake kinetics is required, as well as the equilibrium concentrations of the compounds in water. Uptake kinetics can be studied by preparing a solution of a known concentration of desired analytes and shaking vials containing POM passive sampler and solution for a different number of days. The amount of time needed to reach equilibrium can then be measured.

Passive sampler measurements can be used to establish partitioning coefficients for concentration ratios. The ratio between equilibrium concentration of a compound in the POM phase ($\mathrm{C_{POM}}$) and equilibrium freely dissolved concentration in water ($\mathrm{C_{water}}$) gives the partition coefficient $\mathrm{K_{POM}}$, see Equation 2.2.

$$\mathrm{K_{POM}} = \frac{\mathrm{C_{POM}}}{\mathrm{C_{water}}} \tag{2.2}$$

Waste-water partition coefficient (K_{waste}) and POM-waste partition coefficient ($K_{\text{POM,waste}}$) are defined in Equation 2.3 and Equation 2.4. C_{POM} is the equilibrium concentration of target analyte in POM passive sampler, C_{water} is the equilibrium concentration of target analyte in water and C_{waste} is the equilibrium concentration of target analyte in waste.

$$K_{\text{waste}} = \frac{C_{\text{waste}}}{C_{\text{water}}} \tag{2.3}$$

$$K_{\text{POM,waste}} = \frac{C_{\text{POM}}}{C_{\text{waste}}} \tag{2.4}$$

When studying waste samples using a passive sampler, a three-phase system can be created between K_{POM}, K_{waste} and $K_{\text{POM,waste}}$. The analytes can transfer between the phases as visualized in Figure 2.3.

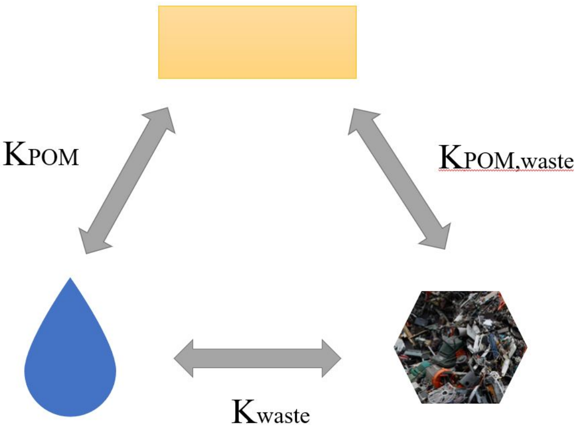


Figure 2.3: Equilibrium relationship between K_{POM}, K_{waste} and $K_{\text{POM,waste}}$. From the top, clockwise; POM phase, waste phase and water phase.

To quantify K_{POM} over a concentration range, bisphenol and benzophenone solutions with different concentrations can be prepared. The solutions can be shaken with POM strips, and C_{POM} and C_{water} can be measured when equilibrium is reached. Previous research shows that K_{POM} gives a linear isotherm over an environmentally relevant concentration range. [6][21]

2.6 Environmental leaching

The natural extraction process by which water-soluble substances such as hydrophilic organic substances are washed out from waste disposal areas is called leaching. Thus, leaching is a process where organic contaminants are released from the solid phase into the water phase by different mechanisms such as sorption and dissolution, and may cause pollution of surrounding surface and subsurface waters. [19] To calculate the leachable concentration of a compound from a matrix, Equation 2.5 can be used. [6] $C_{leachable}$ is the concentration of the leachable compound [μg/kg dry weight], and $\frac{L}{S}$ is the liquid-to-solid ratio [μg/kg dry weight].

$$\mathrm{C}_{\mathrm{leachable}} = \mathrm{C}_{\mathrm{water}} \cdot \frac{L}{S} \tag{2.5}$$

2.7 Solid waste preparation

When analyzing organic compounds bound in a solid matrix, sample preparation is required before performing the extraction process. If possible, a high degree of homogeneity should be obtained. This can be achieved by grinding solid samples. Water miscible solvents can be used to break up the sample matrix and dissolve the more polar analytes. Contact between the matrix and and the extracting solvents must be as complete as possible for extraction to occur efficiently and reproducibly. [23] In some cases a suitable salt can be added to push target analytes into the organic phase, via the salting-out effect. The salting-out effect can improve the extraction power by decreasing the solubility of analytes in the aqueous phase and promotes the transfer of the analytes towards the organic solvent. [24]

2.8 Instrumentation

2.8.1 Liquid Chromatography (LC)

To isolate individual analytes from a mixture, column chromatography can be applied. The principle of chromatography is based on different compounds having different affinity to the column for a given liquid phase, which results in separate retention times. Several techniques of Liquid Chromatography (LC) exist, and among the most modern techniques are High Performance Liquid Chromatography (HPLC) and Ultra High Performance Liquid Chromatography (UHPLC). HPLC was introduced in the 1970s and includes smaller particles in the column, thus more surface area, and a mobile phase pumped through the system at higher pressures. This made the LC technique more convenient by providing higher efficiency and higher resolution, as well as requiring shorter columns. UHPLC is even more efficient as even smaller particles are used and thus the pressure is higher. The method is also faster. However, higher pressure requires a more robust system and the instrument cost is usually higher. [23] [25]

Environmental analysis in one of the most important application areas of Liquid Chromatography Mass Spectroscopy (LC-MS). The method has been used widely in environmental monitoring as it requires short analysis time and can analyze a large range of polar compounds in ng/mL levels even in complex matrices. [26]

2.8.2 Atmospheric Pressure Ionization (API) probes

Several Atmospheric Pressure Ionization (API) probes can be applied at the interface of the liquid chromatography and the mass spectrometer, including Electrospray Ionization (ESI), Atmospheric Pressure Chemical Ionization (APCI) and Atmospheric Pressure Photoionization (APPI). Their aim is to ionize the molecules before inserting them into the mass analyzer. Polarity and size of the target analytes are important factors when choosing a suitable interface. Some difficults may be faced when coupling the LC equipment to the mass spectrometer as the former operates with liquids under high pressure, while the latter in vacuum. [25]

Electrospray Ionization (ESI) is suitable for compounds with polar groups, and is carried out at atmospheric pressure. Neutral compounds either accept or donate protons under given conditions, yielding positive or negative ions. The ions can be detected in either positive or negative mode. A high voltage, typically -5 kV or 5 kV, is applied to a capillary where the mobile phase containing target analytes is introduced. Droplets form with the help of a nebulizing gas introduced into the flow, e.g. N_2. A counterflowing gas decreases the size of the highly charged droplets as the surface tension of the droplets breaks. An advantage of the ESI technique is that it can be used on neutral, acidic and basic compounds.

Atmospheric Pressure Chemical Ionization (APCI) is a different ionization mode that can be used on less polar compounds. The mobile phase is heated up in order to vaporize all solvents and solutes before mixing the vapour with N_2. A high potential is applied on a needle creating a plasma of ions. After a series of reactions, ionized compounds are generated.

Atmospheric Pressure Photoionization (APPI) can be applied when the target analytes are even less polar. As in APCI, the mobile phase is heated and vaporized, but in this case a UV lamp causes ionization through energy transfer. Dopant molecules can be introduced to increase the ionization efficiency.

2.8.3 Mass analyzers in Mass Spectrometry (MS)

Mass Spectroscopy (MS) is an instrument that is based on counting ion fragments according to their mass to charge ratio (m/z). When entering the mass spectrometer, the analytes pass a series of lenses and different compartments separated by skimmers to gradually lower the pressure until vacuum is obtained. Multiple Reaction Monitoring (MRM) is a mode analyzing several fragments.

Several mass analyzers with the same aim of separating fragments exist, such as the quadrupole mass analyzer, the ion trap analyzer and Time-of-Flight (ToF) analyzer. [25] The generated ions carry an electric charge, which means they will also be affected by an electrical field. The quadrupole mass analyzer uses this property to separate ions according to their m/z, as the ions pass along the central axis of four parallel equidistant rods. Ions with an unstable trajectory will not be detected as they collide with one of the quadrupoles. The advantages of quadrupole mass analyzer are that the system is robust, relatively inexpensive and has a high sensitivity. The method is suitable for multi-analytic target analyses.

The ion trap technique also takes advantage of the effect the electrical field has on the ions generated. The ions are introduced into a ring electrode with an applied electrical field before they get cooled down by helium at low pressure. By varying the potential, the ions are allowed to leave the trap, and can thus be detected. As voltage is increased, the lighter ions leave first and the heavier ions last. Ion trap is a common method when analyzing a few samples with higher concentrations of target analytes.

The ToF analyzer is based on the velocity of ions travelling through a field-free tube being inversely proportional to their m/z. Ions enter a field-free drift tube, and a pulse of high potential difference is introduced to give the ions similar kinetic energy. This causes them to move along the tube. As the lighter ions have shorter time of flight, it is possible to detect the ions depending on time used through the tube. ToF is commonly used for research purposes when a lot of information is requested. Among the advantages of this system is its very good quantitation ability as well as being able to acquire full range of mass spectra. However, the instrument has higher vacuum requirements which makes it more expensive.

2.8.4 Ultra High Performance Liquid Chromatography coupled to Mass Spectrometer (UHPLC-MS/MS)

Ultra High Performance Liquid Chromatography coupled to a tandem Mass Spectrometer (UHPLC-MS/MS) is a technique with high selectivity and sensitivity that combines the separation ability of liquid chromatography with the mass analysis capability of mass spectrometry. MS/MS demonstrates good suppression of noise and matrix interferences. This is because only molecules with the correct molecular ion filtered in the first quadruple and the correct product ion generated in the collision cell and filtered in the third quadruple reach the detector. Both qualitative and quantitative information can be obtained, which makes the combination of UHPLC and MS useful. Additionally, the short time required for performing an analysis is a valuable advantage of the instrument.

2.9 Quantitation

2.9.1 Retention Time (RT) and Relative Retention Time (RRT)

The Retention Time (RT) of a compound is defined as the time between the sample introduction and the elution of the compound. [25] Elution time is dependant on several factors such as injection technique, flow rate and column temperature. Thus, the value will not be fixed for different chromatographic systems. To correct for that, a Relative Retention Time (RRT) can be calculated, see Equation 2.6. This equation gives the ratio between the RT of the analyte and the internal standard. This should give an universal number when analyzing the same compound under same conditions (same internal standard, mobile phase and solid phase), even though the mass flow or system dimension have minor variations.

$$RRT = \frac{RT_{analyte}}{RT_{IS}} \tag{2.6}$$

In Equation 2.6 RRT is the relative retention time, $RT_{analyte}$ is the retention time of the analyte of interest and RT_{IS} is the retention time of the internal standard.

2.9.2 Lower Limit Of Quantitation (LLOQ) and Limit Of Detection (LOD)

Lower Limit Of Quantitation (LLOQ) is defined as the lowest concentration of an analyte in a sample that can be determined with an acceptable precision and accuracy and is therefore used as the lowest value used for quantitation. Limit Of Detection (LOD) is defined as the lowest concentration of an analyte in a sample that can be detected, but not necessarily quantified.

There are several ways to establish these parameters, depending on the analytical method used and the matrix itself. The LLOQs for the analytes were estimated as the lowest concentration level that could be reliably quantified based on the signal/noise ratio of 10 in the calibration standard solution of every compound. The LODs were estimated from the respective LLOQs as shown in Equation 2.7, where LOD is the concentration limit of detection and $LLOQ$ is the limit of quantitation. [27] [28]

$$LOD = \frac{LLOQ}{3} \tag{2.7}$$

2.9.3 Internal standard method

In order to infer concentrations from chromatographic data, a relation between chromatographic response and analyte mass needs to be established. Calibration curves can be created using known concentrations of standard solutions and their signals obtained with the MS. The number of standard solutions needed depends on the type of experiment. A good calibration should provide a good Coefficient of Determination (R^2), see Equation 2.8. y_i is a value from the data set, f_i is the respective value of the fitted model, and $\bar{y}$ is the mean value of the observed data.

$$\mathrm{R}^2 = 1 - \frac{\sum (\mathrm{y_i} - \mathrm{f_i})^2}{\sum (\mathrm{y_i} - \bar{y})^2} \tag{2.8}$$

R^2 can be a good indicator whether the regression is a good representation of the data set or not. The closer to 1, the better the correlation.

An internal standard can be used to quantify the target analytes, as loss of compound at different steps and disturbances are effectively compensated during sample processing. The internal standard should have properties and chemical behaviour as similar as possible to the analytes of interest, but not be present in the sample initially.

An isotope-labelled compound has near-identical chemical and physical behaviour as the corresponding non-labeled compound, including the same behaviour concerning mechanisms leading to loss. This makes it nearly an ideal internal standard as long as the detection method can differentiate between isotopes. Examples of isotope-labelled internal standards include deuterated and ^{13}C-containing compounds. These compounds have a slightly different retention time than the corresponding target analyte, but are behaving in a similar manner as the non-labelled compounds.

In cases where the MS gives several fragment spectra of m/z of the compounds, quantifiers need to be determined. Quantifiers can be chosen by studying the R^2-value of every calibration curve, in combination with determining which m/z that shows the most abundant and stable signals. A more abundant mass fragment gives higher selectivity, and the chosen quantifier for every compound can be used for quantitation.

The *area ratio* between analyte and internal standard signal can be calculated using Equation 2.9 to include the signals of the internal standard (IS). $area_{sample}$ is the signal area of the analyte of interest in the sample, and $area_{IS}$ is the signal area of the internal standard of the analyte of interest. The blank signal is subtracted from the signals to obtain corrected ratios.

$$area\ ratio = \frac{area_{sample}}{area_{IS}} \tag{2.9}$$

The relation between the area ratio and the known concentration in one of the standard solutions can be used to calculate the unknown concentrations of the analytes in the samples, see Equation 2.10. C_{sample} is the concentration of analyte of interest in a sample, $area\ ratio_{sample}$ is the signal area ratio in the sample, C_{std} is the known concentration of a point in the calibration curve and $area\ ratio_{std}$ is the signal area ratio of the standard concentration.

$$C_{sample} = \frac{area\ ratio_{sample} \times C_{std}}{area\ ratio_{std}} \tag{2.10}$$

Depending on the circumstances, a method recovery blank can also be used to calculate concentrations, see Equation 2.11. C_{sample} is the concentration of analyte of interest in a sample, $area_{sample}$ is the signal area in the sample, $C_{method\ recovery\ blank}$ is the known concentration of the method recovery blank and $area_{method\ recovery\ blank}$ is the signal area of the method recovery blank.

$$\mathrm{C_{sample}} = \frac{\mathrm{area_{sample}} \times \mathrm{C_{method\ recovery\ blank}}}{\mathrm{area_{method\ recovery\ blank}}} \tag{2.11}$$

2.9.4 Standard Deviation (SD) and Detection Rate (DR)

Standard Deviation (SD) is a measurement of the variation in a given data set. The calculation of SD is shown in Equation 2.12, and can be used to study the scatter of the data as it expresses how much the values vary from the mean value. SD is the standard deviation, n is the total number of data, x_i are the data points in the data set and $\bar{x}$ is the mean value of the data set.

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}} \tag{2.12}$$

Detection Rate (DR) is defined as in Equation 2.13, where n is the number of samples where the concentrations were detected, and N is the total number of samples.

$$DR = \frac{n}{N} \times 100 \tag{2.13}$$

2.10 Quality Assurance and Quality Control (QA/QC)

Quality Assurance (QA) refers to the overall measures to ensure and monitor quality from an experimental data set. Quality Control (QC) is a key element to ensure reliable results and involves the use of blanks, duplicate samples and calibration standards among others. The QC criteria depends on the analytical problem to be solved, including elements that needs to be considered such as volume of work, costs and availability. [29]

The use of internal standards can account for variations throughout an experiment such as mass loss during sample preparation or differences in volume injection. A frequent use of procedural blanks is a way of evaluating contamination arising from sample preparations. [28] To check for carryover of target analytes between samples, solvents blanks can be injected frequently. By injecting calibration check standards regularly during analysis, any drift in the instrument sensitivity can be observed. [30]

To provide reliable results, it should be considered whether a correction for mass loss should be conducted or not. Correction for mass loss can be employed using Equation 2.14.

$$\mathrm{C_{corrected}} = \frac{\mathrm{C_{measured}}}{\text{mass fraction recovered}} \tag{2.14}$$

In this study, the actions done to provide reliable results are described in detail in Section 3.9.

3 Methods

3.1 Chemicals

Standards of Bisphenol A (BPA, $\geq$ 99%), Bisphenol AF (BPAF, $\geq$ 99%), Bisphenol AP (BPAP, $\geq$ 99%), Bisphenol B (BPB, $\geq$ 98%), Bisphenol F (BPF, $\geq$ 98%), Bisphenol M (BPM, $\geq$ 99%), Bisphenol P (BPP, $\geq$ 99%), Bisphenol S (BPS, $\geq$ 98%), Bisphenol Z (BPZ, $\geq$ 99%), Benzophenone-1 (BzP-1, , $\geq$ 99%), Benzophenone-2 (BzP-2, $\geq$ 97%), Benzophenone-3 (BzP-3, $\geq$ 98%), Benzophenone-8 (BzP-8, $\geq$ 98%), 4-Hydroxybenzophenone (4-OH BzP, $\geq$ 98%) were purchased from Sigma-Aldrich (St. Louis MO, USA). ^{13}C-isotope of Bisphenol A (BPA-13C12, $\geq$ 99%), ^{13}C-isotope of Bisphenol AF (BPAF-13C12, $\geq$ 99%), ^{13}C-isotope of Bisphenol B (BPB-13C12, $\geq$ 99%), ^{13}C-isotope of Bisphenol F (BPF-13C12, $\geq$ 99%) and ^{13}C-isotope of Bisphenol S (BPS-13C12, $\geq$ 98%) were purchased from Cambridge Isotope Laboratories (Andover MA, USA). Complete compound names are listed in Table 2.1 and Table 3.1.

Internal standards	
BPA-13C12	2,2-Bis(4-hydroxyphenyl)propane 13C12
BPAF-13C12	2,2-Bis(4-hydroxyphenyl)hexafluoropropane 13C12
BPB-13C12	2,2-Bis(4-hydroxyphenyl)butane 13C12
BPF-13C12	4,4'-Methylenediphenol 13C12
BPS-13C12	4,4'-Sulfonyldiphenol 13C12

Table 3.1: List of bisphenol internal standards.

Methanol (MeOH, hypergrade for LC-MS) was obtained from Merck (Billerica MA, USA). Milli-Q water was delivered by Millipore Water Purification System (Millipore, Burlingon MA, USA). Ethyl acetate from VWR Chemicals (Rue Carnot, Fontenay-sous-Bois, France) was used as a solvent. In the LC-MS instrument, ammonium hydroxide solution from Sigma Aldrich (St. Louis MO, USA) was used in the mobile phase. Sodium azide (Sigma Aldrich, USA) was added to water samples to prevent microbial degradation.

Nine standard working solutions were prepared from standard stock solutions of the 14 target analytes and the internal standard. The concentrations of the solutions were 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 ng/mL. The concentration of internal standards in the calibration curve was 20 ng/mL.

3.2 E-waste and vehicle fluff samples

Several kilograms of E-waste samples from recycling and waste handling facilities in the eastern part of Norway were collected during a previous study. [6] These samples were obtained from various locations in the facility to be visually representative of materials that were found there. The samples used in this experiment were representative subsamples from 12 of the samples taken from Morin et al. [6], and all samples were ground until they could pass through a 4 mm sieve. Thereby, the plastic materials within this plastic-containing waste would conform to the definition of microplastic of less than 5 mm [31], though several other debris may have been included in this matrix. The content of the subsamples was visually heterogeneous, and in each bag one or several kinds of materials were present. This could be plastic granulates, powder, plastics, small objects, cable residues, recycled metals among others. A list and description of the samples taken to further analysis is shown in Table B.1. Exact location of the sampling are anonymized as requested by the site owners.

3.3 Extraction of solid waste samples

The samples were spiked with a mixture of five internal standards: BPA-13C12, BPAF-13C12, BPB-13C12, BPF-13C12 and BPS-13C12 (10 µL, 1 µg/mL). A solution of ammonium acetate ($C_2H_7NO_2$, 0.3 mL, 1M) was added to all 12 samples, in order to push the target analytes into the organic phase due to the salting-out effect.

As a beginning step in the extraction process, ethyl acetate ($C_4H_8O_2$, 3 mL) was added as a solvent to each ammonium acetate-moistened sample. Moderate turning of the extraction tubes was done manually to mix the solid samples with the solvent. The tubes were then put into an ultrasonic bath for 45 minutes and preserved in the refrigerator overnight. Samples were centrifuged before the supernatant was extracted. The process was repeated twice, such that a total of three supernatant of each sample were gathered, which made a volume of 6 to 9 mL of each sample.

Prior to analysis, samples were washed by adding distilled water (2 mL), centrifuging, and withdrawing the supernatant, before being evaporated to $\approx 0.25\,\mathrm{mL}$ using N_2. Once the samples were put in LC vials and washed out with droplets of methanol, a solution of methanol and distilled water (CH_3OH, H_2O; 1:1, v:v) was added until a final volume of 1 mL was reached.

3.4 Preparation of POM passive samplers

A passive sampler method was previously developed to specifically target freely dissolved concentrations of BPA in water. [6] This method was further developed in this study for the first time to target freely dissolved concentrations of other bisphenols and benzophenones in lab-scaled sorption batch experiments. Cleaning of POM passive samplers was done in a clean room, and the procedure was nearly as described in the previous study. POM (76 µm thickness, CS Hyde USA) were cut into pieces weighing approximately 0.1 g each before being pre-rinsed using an orbital shaker at 60 rpm. The POM strips were immersed in acetone:hexane (1:1, v/v) and shaken for 24 hours. Then, there was a solvent exchange to methanol followed by another 24 hours shaking. Methanol was replaced with Milli-Q water and shaken once again for 24 hours. The Milli-Q water was replaced three times, before storing POMs in the third replacement rinse. Before use, the POM strips were allowed to dry on aluminium foil in room temperature overnight, before put into clean and labelled amber vials.

3.5 Kinetic uptake of BPA alternatives and benzophenones in POM

A kinetic experiment was designed to obtain a reliable understanding of bisphenol and benzophenones uptake kinetics into POM passive samplers. A cocktail solution containing nine bisphenols; BPA, BPAF, BPAP, BPB, BPF, BPM, BPP, BPS and BPZ (100 ng/mL), five benzophenones; BzP-1, BzP-2, BzP-3, BzP-8 and 4-OH BzP (100 ng/mL), five internal standards; BPA-13C12, BPAF-13C12, BPB-13C12, BPF-13C12 and BPS-13C12 (10 ng/mL), NaN_3 (1 g/L) and Milli-Q water were prepared. Sodium azide was added to minimize microbioal activity.

33 mL of the solution (BP, BzP: 100 ng/mL) was transferred to 18 amber vials, where 15 of the vials contained a POM strip (0.1 g). The vials were set to shake in the dark in an orbital shaker at 60 rpm in triplicate for 3, 7, 14, 21 and 28 days respectively. The three vials without POM strips were shaken in the dark for 28 days. An overview of the kinetic experiment showing vial number, concentration of target analyte, amount of POM and shaking time is presented in Table 3.2.

Table 3.2: Experiment information of kinetic uptake of BPA alternatives in POM; vial number, concentration of target analytes [ng/mL], amount of POM [g] and shaking time.

Vial no.	**Conc. of target analytes [ng/mL]**	**Amount of POM [g]**	**Shaking time [days]**
1	100	0.0951	3
2	100	0.1008	3
3	100	0.0994	3
4	100	0.0937	7
5	100	0.0933	7
6	100	0.0973	7
7	100	0.1044	14
8	100	0.0956	14
9	100	0.1068	14
10	100	0.0993	21
11	100	0.0879	21
12	100	0.1031	21
13	100	0.1064	28
14	100	0.1162	28
15	100	0.1047	28
16	100	-	28
17	100	-	28
18	100	-	28

After shaking, a water sample (0.5 mL) was withdrawn from the vial into an LC vial with methanol (0.5 mL), and the respective POM strips were put into test tubes with ethyl acetate (10 mL) before being cold extracted. Cold extraction was done in the dark using an orbital shaker at 60 rpm for 7 days. Further, the POM was removed, and the content was evaporated until about 10 µL. 1 mL methanol was added to the vials, and the samples were then transferred to LC vials. Due to cloudy appearance, the samples were diluted with methanol (0.25 mL sample, 0.75 mL methanol) before being analyzed by LC-MS/MS.

3.6 POM-water partition coefficients of BPA alternatives and benzophenones

An equilibrium experiment was designed to determine the POM-water partitioning coefficients (K_{POM}, see Equation 2.2) for a concentration range. Three cocktail solutions with different concentrations of nine bisphenols (BPA, BPAF, BPAP, BPB, BPF, BPM, BPP, BPS and BPZ) and five benzophenones (BzP-1, BzP-2, BzP-3, BzP-8 and 4-OH BzP) were prepared; 1 ng/mL, 10 ng/mL and 20 ng/mL. The solutions did also contain five internal standards; BPA-13C, BPAF-13C, BPB-13C, BPF-13C and BPS-13C 10 ng/mL, NaN_3 1 g/L) and Milli-Q water. Sodium azide was added to minimize microbial activity.

33 mL of the three solutions (1 ng/mL, 10 ng/mL and 20 ng/mL) were transferred in triplicate to nine amber vials, each containing a POM strip ($\approx$ 0.1 g). The vials were set to shake in the dark in an orbital shaker at 60 rpm for 21 days. Samples containing 100 ng/mL shaken for 21 days from the kinetic experiment were also used to get a broader range of concentrations. An overview of the equilibrium experiment showing vial number, concentration of target analyte, amount of POM and shaking time is presented in Table 3.3.

Table 3.3: Experiment information to establish POM-water partition coefficients of BPA alternatives; vial number, concentration of target analytes [ng/mL], amount of POM [g] and shaking time.

Vial no.	**Conc. of target analytes [ppb]**	**Amount of POM [g]**	**Shaking time [days]**
19	1	0.1165	21
20	1	0.0998	21
21	1	0.1159	21
22	10	0.1065	21
23	10	0.1061	21
24	10	0.0938	21
25	20	0.1109	21
26	20	0.1330	21
27	20	0.0879	21
10	100	0.1031	21
11	100	0.1165	21
12	100	0.1159	21

After shaking, a water sample (0.5 mL) was withdrawn from the vial into an LC vial with methanol (0.5 mL), and the respective POM strips were put into test tubes with ethyl acetate (10 mL) before being cold extracted. Cold extraction was done in the dark using an orbital shaker at 60 rpm for 7 days. Further, the POM was removed, and the content was evaporated until about 10 µL. 1 mL methanol was added to the vials, and the samples were then transferred to LC vials. Due to cloudy appearance, the samples were diluted with methanol (0.25 mL sample, 0.75 mL methanol) before being analyzed by LC-MS/MS.

3.7 Waste-water partition coefficients of BPA alternatives and benzophenones

A lab-scaled batch experiment of leaching was developed to determine waste-water partition coefficients (K_{waste}, see Equation 2.3) and measure the leachability for a selection of the E-waste and vehicle fluff samples. Four of the samples that were found to have the highest concentrations of bisphenols and benzophenones with more or less different origin were chosen as representative samples. Three of the chosen samples were plastic residues from E-waste processing (sample 3, 5 and 12), whereas sample 7 was vehicle fluff. Table 3.4 lists the numbering of the samples, the amount of waste, the amount of POM and shaking time. Waste samples (1 g) was added into triplicate clean amber vials containing POM strips (0.1 g). A solution of five internal standards; BPA-13C, BPAF-13C, BPB-13C, BPF-13C and BPS-13C (10 ng/mL), NaN_3 (1 g/L) and Milli-Q water were prepared. Sodium azide was added to minimize microbial activity. The solution (33 mL) was transferred to 12 amber vials in addition to a blank control, keeping some air headspace to allow mixing. Samples were put on an orbital shaker in dark conditions for 21 days, 60 rpm. A manual shake was given on a daily basis in order to avoid cluster of lumps and to allow proper mixing.

Table 3.4: Sample information of the samples chosen to determine K_{waste} partition coefficients; vial number, sample number in this study, amount of waste, amount of POM and shaking time.

Vial no.	**Sample no.**	**Amount of waste [g]**	**Amount of POM [g]**	**Shaking time [days]**
28	3	1.0642	0.0789	21
29	3	1.0055	0.0925	21
30	3	1.0245	0.0933	21
31	5	1.0213	0.0917	21
32	5	1.0236	0.1001	21
33	5	1.0774	0.1000	21
34	7	1.0845	0.1165	21
35	7	1.0927	0.1018	21
36	7	1.0771	0.0993	21
37	12	1.0145	0.0974	21
38	12	1.0759	0.0919	21
39	12	1.0687	0.1085	21
40	-	0.0000	0.0000	21

After shaking, the POM strips were removed and put into test tubes with ethyl acetate (10 mL) before being cold extracted. Cold extraction was done in the dark using an orbital shaker at 60 rpm for 7 days. After cold extraction the POM was removed and a washing procedure was conducted to get rid of waste particles. 2 mL of Milli-Q water was added, then the vials were centrifuged, and the organic phase was pipetted into a new vial. Following, the content was evaporated until about 10 µL. 1 mL methanol was added to the vials, and the samples were then centrifuged before being transferred to LC vials.

A selection of waste from each of the four chosen waste samples was taken out of the sample vials after shaking. Waste was dried in an oven at 37 °C for 60 minutes, before being left in room temperature overnight. 0.1 gram of the four samples were put in vials followed by an extraction process. Ammonium acetate (0.3 mL, 1M) and ethyl acetate (3 mL) was added into the vials and gently mixed before sonication bath for 60 minutes. Centrifugation was done (3500 rpm, 10 minutes) and the supernatant was taken out and another 3 mL ethyl acetate was added to the vial. The procedure was repeated until a total of three supernatants were gathered from each sample, which lead to about 8-9 mL final volume. Then, the samples were washed with Milli-Q water (2 mL) and centrifuged before withdrawing the organic phase (without water or particles) into new vials. Samples were evaporated to approximately 10 µL. Methanol (1 mL) was added and samples centrifuged, and samples were withdrawn into LC vials.

0.5 mL of the blank sample (sample 40) was put into a vial together with methanol (0.5 mL). The samples were then analyzed by LC-MS/MS.

3.8 LC-MS/MS analysis

Chromatographic separation was carried out using Acquity UHPLC Thermo system (Waters, Milford, U.S.). Instrumental settings are listed in Table A.1. Before analysis, the cone was run for 1 hour with acetone blanks to clean the system, followed by 20 injections of 10 ng/mL target analytes to saturate the cone. Analysis was performed in negative mode (ESI-). The column used was a Kinetex C18 column (50 x 2.1 mm, 1.3 µm, 100Å, Phenomenex) serially connected to a Phenomenex guard column (C18, recommended for 2.1 mm ID columns). Organic phase (A) consisted of water with 0.1% v/v ammonium hydroxide, water phase (B) was methanol (hypergrade for LC-MS, Merck). Mobile phase gradient used are listed in Table A.2. The injection volume was set to 4 µL with a flow rate of 300 µL/min. Tandem mass spectrometric system was a Xevo TQ-S, Triple Quadrupole Mass analyser (QqQ), with a ZSpray ESI function (Waters, Milford, U.S.).

The method used for quantitation of bisphenols and benzophenones was modified from a previous study. [32] Concentrations of the bisphenols and benzophenones were determined using the internal standard method, using five different ^{13}C-labelled compounds as internal standards. A list of RT values and RRT values is given in Table A.3. Area ratios corresponding to a concentration of 50 ng/mL of every target analyte were used in the calculations of the solid waste concentrations.

Bisphenols and benzophenones spiked into blank control flask (no POM added, 100 ng/mL spike, 28 days of shaking in triplicate) were used to determine concentrations in the kinetic uptake experiment and deriving K_{POM} values. This was done by relating signal areas of the samples to the area of the 100 ng/mL method recovery blank, as shown in Equation 2.11.

3.9 QA/QC

Glassware used in this study was rinsed using soap and tap water, Milli-Q water and methanol. All stock solutions and internal standards were prepared from pure analyte powder dissolved in LC-grade methanol and stored at -22 °C. Before shaking, water samples were spiked with sodium azide to prevent microbial degradation.

Internal standards were employed together with external standards in the determination of solid waste concentrations in order to account for any mass loss during sample preparation and extraction process.

Two reagent blank samples were prepared simultaneously as the solid waste samples to control if there were any contamination from solid sample preparation or from extraction process. Any signal was subtracted from the sample signals as it could be assumed to be contamination valid for all samples in the solid waste batch experiment.

Analyzing solvent blanks (pure solvent) regularly in between the samples was done to check for any potential cross contamination or sample carryover during LC-MS analysis. Calibration standard solution of 20 ng/mL was regularly analyzed to take into account the possibility of signal drifting with time.

Bisphenols and benzophenones spiked into blank control flask (no POM added, 100 ng/mL spike, 28 days of shaking in triplicate) were used as a method recovery blank to correct for mass loss and other related artefacts that differed from the calibration vials such as sorption to glass and needle. The same test was used as a comparison to mass losses with POM; Average mass loss of bisphenols and benzophenones in the kinetic uptake experiment were determined by proceeding a shake test (with POM, 100 ng/mL, 28 days of shaking in triplicate). The effect of mass loss was considered when establishing K_{waste}-values when the mass recovery was less than 60%. This was done by calculating corrected concentrations in POM ($C_{\mathrm{POM,corrected}}$) using Equation 2.14.

3.10 Data treatment

Data from LC-MS/MS were acquired and integration of peaks was carried out using the MassLynx and TargetLynx software packages (version 4.1, Waters Corporation, Milford MA, USA). Data was processed in a spreadsheet (Excel, 2016). Chosen quantifiers and qualifiers are listed in Tables A.4 and A.5.

4 Results and discussion

4.1 Bisphenols and benzophenones in E-waste and vehicle fluff samples

LLOQ and LOD for the target analytes are shown in Table 4.1. Concentrations that were below the limit of detection were removed from the data set.

Table 4.1: LLOQ and LOD given in ng/mL for bisphenols and benzophenones target analytes.

Compound	**LLOQ [ng/mL]**	**LOD [ng/mL]**
BPA	0.10	0.03
BPAF	0.10	0.03
BPAP	0.10	0.03
BPB	0.20	0.07
BPF	0.20	0.07
BPM	0.10	0.03
BPP	0.10	0.03
BPS	0.10	0.03
BPZ	0.10	0.03
BzP-1	0.10	0.03
BzP-2	0.10	0.03
BzP-3	0.10	0.03
BzP-8	0.10	0.03
4-OH BzP	0.10	0.03

The limit of detection value were 0.07 ng/mL for BPB and BPF, and 0.03 ng/mL for the remaining twelve compounds. This indicates a sensitive method that can detect very low concentrations.

BPA, BPAF, BPB, BPF and BPS had ^{13}C-labelled compounds as internal standards, which gave RRT values close to 1, see Table A.3. For the calculations of the rest of the compounds, the internal standard with the closest retention time and most stable signal was chosen, see Table A.5. In general it could be expected that the results are more accurate for the compounds having an isotope as the internal standard, but as the internal standards offered steady and reliable signals they are expected to be good standards also for compounds with similar structure, including the remaining bisphenols as well as for the benzophenones.

The average, median, minimum and maximum concentrations of bisphenols and benzophenones in E-waste and vehicle fluff samples are listed in Table 4.2. Additionally, standard deviation of the data set and the detection rates for every compound are shown. Twelve samples were analyzed to determine the presence of bisphenols and benzophenones. Waste origin and description of the samples are shown in Table B.1. A complete list of the measured concentrations in the E-waste and vehicle fluff samples are presented in Tables B.2 and B.3.

Table 4.2: Concentrations of bisphenols and benzophenones in the E-waste and vehicle fluff samples. Average concentration (Avg. [ng/g]), median concentration (Med. [ng/g]), minimum concentration above LOD (Min. [ng/g]), maximum concentration (Max. [ng/g]), standard deviation (SD) and detection rate (DR [%]). Total number of samples evaluated: n = 12.

Compound	**Avg. [ng/g]**	**Med. [ng/g]**	**Min. [ng/g]**	**Max. [ng/g]**	**SD**	**DR [%]**
BPA	33231	10348	858	245682	68274	100
BPAF	2.85	1.69	0.38	15.9	4.3	100
BPAP	18.6	3.51	0.55	150	43	100
BPB	16.0	4.35	0.78	91.7	33	58
BPF	9141	2850	82.2	42432	13715	75
BPM	2.37	2.45	0.44	4.85	1.4	100
BPP	8.19	4.20	0.61	31.8	9.7	100
BPS	66.1	12.2	1.36	332	119	100
BPZ	6.66	7.36	0.85	13.7	5.6	42
BzP-1	48.0	15.4	1.54	155	59	100
BzP-2	3.12	2.65	0.68	8.05	2.5	67
BzP-3	53.9	20.3	0.30	285	80	100
BzP-8	4.06	2.49	1.10	13.3	4.6	50
4-OH BzP	10.4	5.36	0.28	35.4	11	92

The maximum concentrations measured were as following: BPA (245682 ng/g) > BPF (42432 ng/g) > BPS (332 ng/g) > BzP-3 (285 ng/g) > BzP-1 (155 ng/g) > BPAP (150 ng/g) > BPB (91.7 ng/g) > 4-OH-BzP (35.4 ng/g) > BPP (31.8 ng/g) > BPAF (15.9 ng/g) > BPZ (13.7 ng/g) > BzP-8 (13.3 ng/g) > BzP-2 (8.05 ng/g) > BPM (4.85 ng/g).

The twelve solid waste samples could be divided into two categories; E-waste and vehicle fluff. Samples 2, 3, 4, 5, 11 and 12 were samples from E-waste, and samples 1, 6, 7, 8, 9 and 10 were taken from vehicle fluff.

The average, median, minimum and maximum concentrations of bisphenols and benzophenones in the E-waste samples are presented in Table 4.3. Additionally, standard deviations and detection rates for every compound are shown. A total of six E-waste samples were investigated.

Table 4.3: Concentrations of bisphenols and benzophenones in the E-waste samples. Average concentration (Avg. [ng/g]), median concentration (Med. [ng/g]), minimum concentration above LOD (Min. [ng/g]), maximum concentration (Max [ng/g]), standard deviation (SD) and detection rate (DR [%]). Total number of samples investigated: n = 6.

Compound	**Avg. [ng/g]**	**Med. [ng/g]**	**Min. [ng/g]**	**Max. [ng/g]**	**SD**	**DR [%]**
BPA	59442	22022	10180	245682	92306	100
BPAF	2.03	1.73	0.50	4.66	1.43	100
BPAP	10.4	4.70	2.08	38.3	14.0	100
BPB	32.9	6.13	0.78	91.7	51.0	50
BPF	7517	7426	82.2	15136	7193	67
BPM	2.84	3.02	0.93	4.85	1.57	100
BPP	7.53	4.20	2.89	23.9	8.14	100
BPS	66.0	9.06	1.36	332	131	100
BPZ	8.11	8.80	1.19	13.7	5.29	67
BzP-1	7.94	6.55	1.54	19.5	6.70	100
BzP-2	2.37	1.98	0.68	4.83	1.94	67
BzP-3	74.2	27.6	0.30	285	108	100
BzP-8	6.10	3.36	1.68	13.3	6.26	50
4-OH BzP	6.14	4.21	0.28	15.2	6.49	83

The average, median, minimum and maximum concentrations of bisphenols and benzophenones in the vehicle fluff samples are presented in Table 4.4. Additionally, standard deviations and detection rates for every compound are shown. A total of six vehicle fluff samples were investigated.

Table 4.4: Concentrations of bisphenols and benzophenones in the vehicle fluff samples. Average concentration (Avg. [ng/g]), median concentration (Med. [ng/g]), minimum concentration above LOD (Min. [ng/g]), maximum concentration (Max [ng/g]), standard deviation (SD) and detection rate (DR [%]). Total number of samples investigated: n = 6.

Compound	**Avg. [ng/g]**	**Med. [ng/g]**	**Min. [ng/g]**	**Max. [ng/g]**	**SD**	**DR [%]**
BPA	7020	2727	858	24632	9264	100
BPAF	3.66	1.46	0.38	15.9	6.07	100
BPAP	26.8	1.15	0.55	150	60.4	100
BPB	3.34	3.56	1.77	4.47	1.30	67
BPF	10439	653	107	42432	18238	83
BPM	1.90	1.97	0.44	3.49	1.26	100
BPP	8.84	5.54	0.61	31.8	11.7	100
BPS	66.2	18.1	2.25	306	119	100
BPZ	0.85	0.85	0.85	0.85	0	17
BzP-1	88.0	104	2.71	155	61.3	100
BzP-2	3.88	3.20	1.06	8.05	3.05	67
BzP-3	33.7	20.3	1.48	110	40.4	100
BzP-8	2.03	2.25	1.10	2.72	0.83	50
4-OH BzP	14.0	7.32	1.66	35.4	13.8	100

The average concentrations of bisphenols and benzophenones for the two waste categories E-waste and vehicle fluff given with error bars are shown in Figure 4.1.

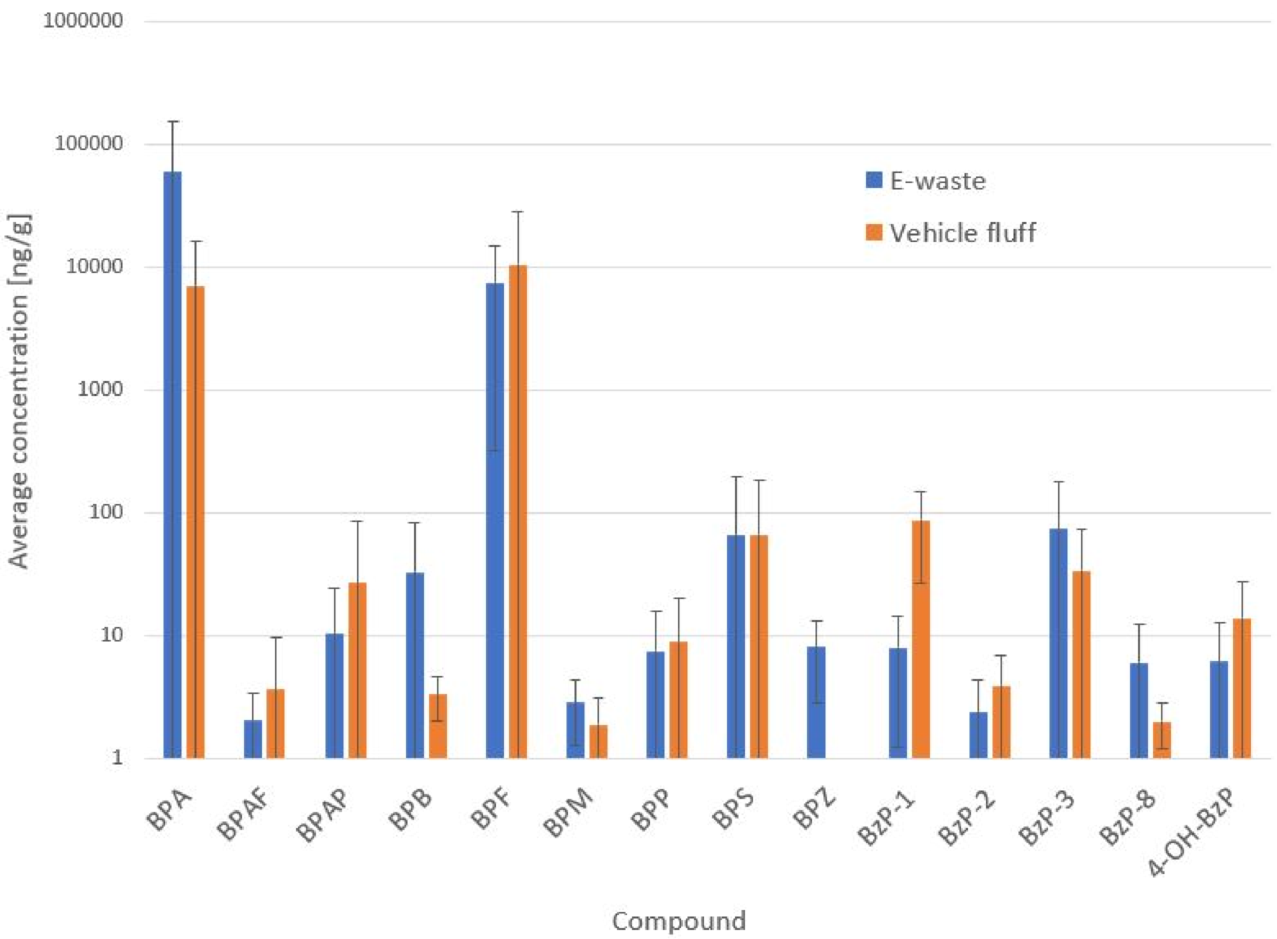


Figure 4.1: Average concentrations [ng/g] of bisphenols and benzophenones in E-waste and vehicle fluff samples given with standard deviation error bars. Number of E-waste: n = 6, number of vehicle fluff: n = 6, total number of samples: n = 12.

As the concentrations of bisphenols and benzophenones in some of the E-waste and vehicle fluff sample extracts were higher than the calibration curve having 50 ng/mL as the highest concentration, the higher concentrations contain a higher degree of uncertainty. This could have been limited by diluting some of the samples with the highest presence of bisphenols and benzophenones. On the other hand, a dilution step would introduce an extra degree of uncertainty, so this was not done.

Tables 4.2 to 4.4 and Figure 4.1 indicate there is a substantial presence of the different bisphenols and benzophenones in the E-waste and vehicle fluff samples. From Figure 4.1, the waste category with the largest average concentration of BPA, BPB, BPM, BPZ, BzP-3 and BzP-8 was E-waste. vehicle fluff had the largest average concentrations of BPAF, BPAP, BPF, BPP, BzP-1, BzP-2 and 4-OH-BzP, whereas BPS was measured to have similar average concentrations in the two waste categories. The presence of these various bisphenols and benzophenones implies an increased use of BPA alternatives and benzophenones in materials ending up being E-waste and vehicle fluff.

4.2 Kinetic uptake of BPA alternatives and benzophenones in POM

Table 4.5 shows the mass recovery for bisphenols and benzophenones (with POM, 100 ng/mL) after 28 days of shaking.

Table 4.5: Mass recovery obtained from kinetic experiment after 28 days of shaking for the different compounds given with standard deviations.

Compound	**Mass recovery [%] (± SD)**
BPA	85 (± 4)
BPAF	75 (± 6)
BPAP	67 (± 4)
BPB	83 (± 2)
BPF	87 (± 8)
BPM	76 (± 8)
BPP	84 (± 9)
BPS	93 (± 2)
BPZ	52 (± 3)
BzP-1	76 (± 4)
BzP-2	87 (± 4)
BzP-3	38 (± 2)
BzP-8	53 (± 5)
4-OH BzP	87 (± 5)

The mass losses were accounted for in the calculations of the kinetic uptake and for the determination of partition coefficients by always measuring both C_{water} and C_{POM}. However, as BPZ, BzP-3 and BzP-8 showed a mass recovery less than 60%, this was corrected for in the determination of K_{waste} using Equation 2.14.

Plots of the log C_{POM}/C_{water} for the different bisphenols as a function of shaking time are provided in Figure 4.2. Standard deviation error bars for C_{POM}/C_{water} are shown but are mostly smaller than the markers. Values and standard deviations are presented in Table C.1. It could be observed that 14 days of shaking was enough to ensure equilibrium.

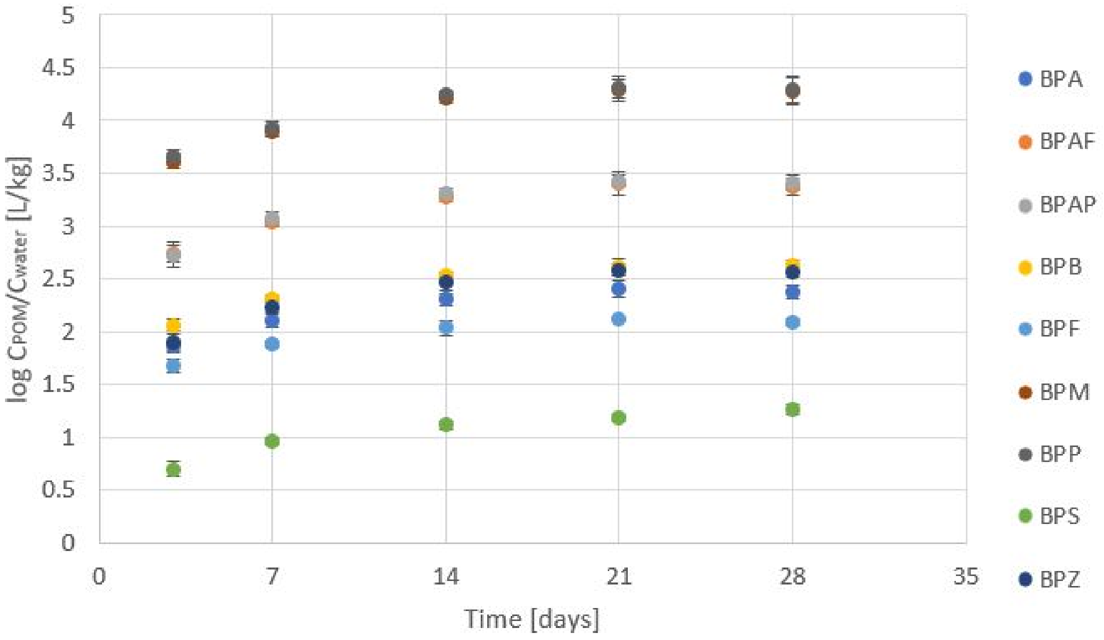


Figure 4.2: Changes in log C_{POM}/C_{water} for bisphenols with standard deviation error bars as a function of shaking time.

Plots of the log C_{POM}/C_{water} for the different benzophenones as a function of shaking time are provided in Figure 4.3. Standard deviation error bars for C_{POM}/C_{water} are shown but are mostly smaller than the markers. Values and standard deviations are presented in Table C.2. It could be observed that 14 days of shaking was enough to ensure equilibrium.

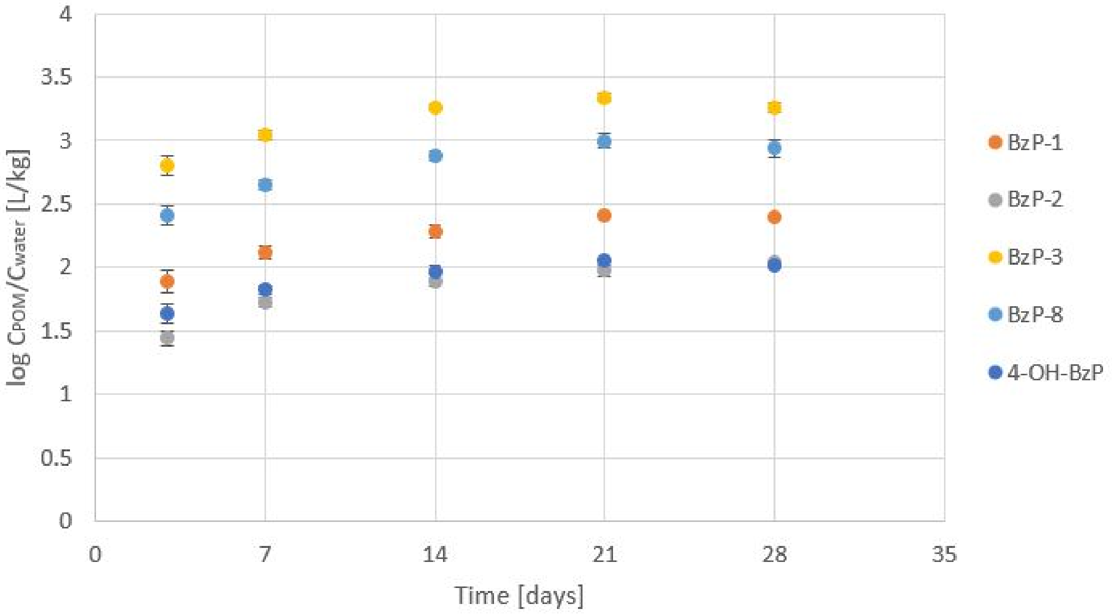


Figure 4.3: Changes in log C_{POM}/C_{water} for benzophenones with standard deviation error bars as a function of shaking time.

In the previous study end-over-end shaking at 13 rpm was used when performing shaking experiments. [6] In this study, due to availability, an orbital shaker at 60 rpm was used for the kinetic, equilibrium and K_{waste} experiments. This could have lead to lack of proper shaking and therefore an inadequate sorption study. On the other hand, orbital shaking could simulate a more realistic sorption process in natural surroundings, and the sorption isotherms show that equilibrium was reached after 14 days. The reason for the different amount of days required can be seen in context with different type of shaker as well as vials used, as Morin et al. [6] used 500 mL glass flasks instead of 40 ml amber vials.

The POM samples in the kinetic and the equilibrium experiments appeared cloudy when put into LC vials. This may have been avoided by centrifuging and pipetting out the solution. Instead, the samples were diluted with methanol. The influence of the cloudy vials on the data uncertainty was not tested.

4.3 POM-water partition coefficients of BPA alternatives and benzophenones

Sorption isotherms with standard deviation error bars for the different compounds are shown in Figures 4.4 to 4.9. Log C_{POM} and log C_{water} for the different concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL) are presented with standard deviations in Tables D.1 to D.4.

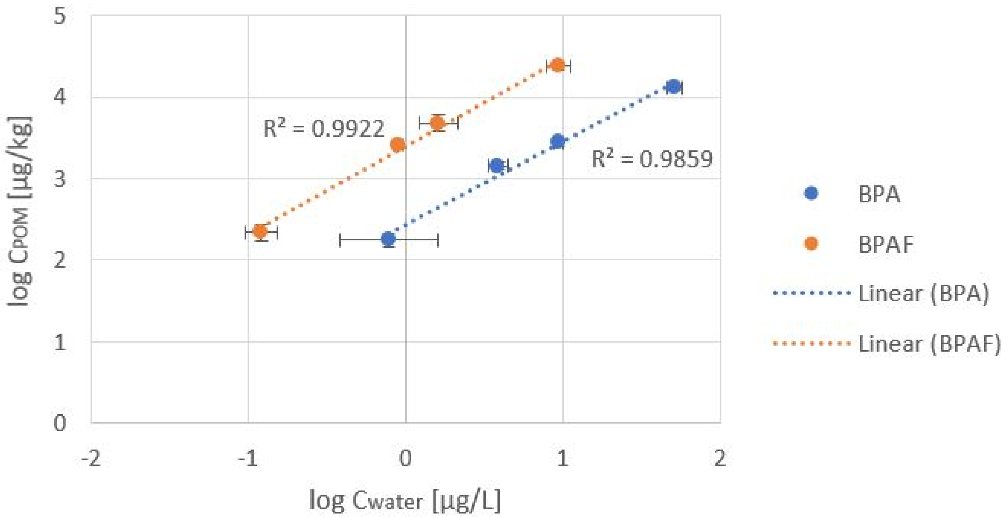


Figure 4.4: POM-water sorption isotherms for BPA and BPAF with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

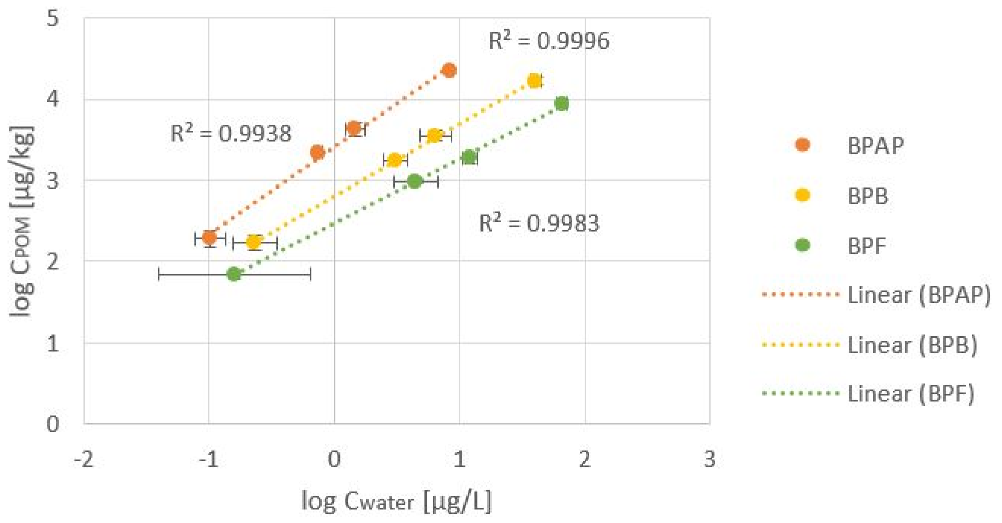


Figure 4.5: POM-water sorption isotherms for BPAP, BPB and BPF with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

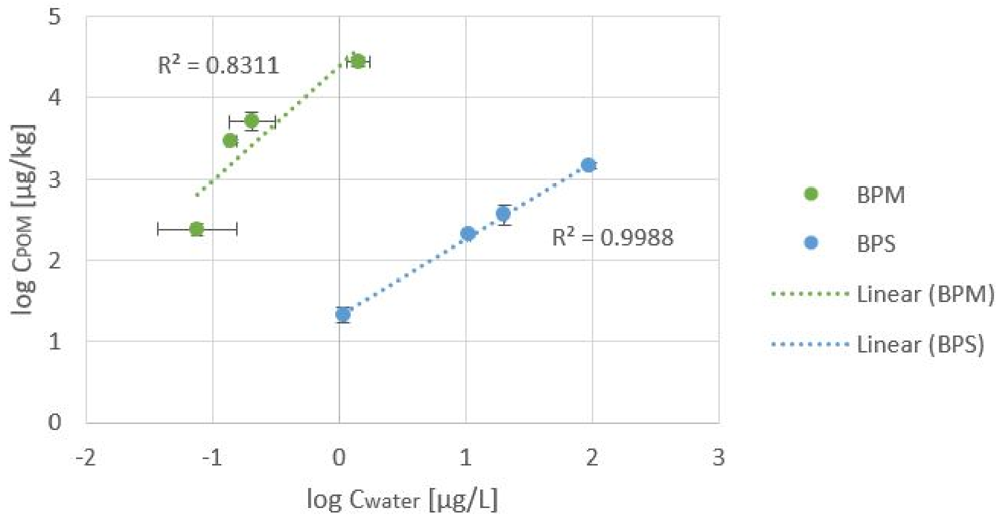


Figure 4.6: POM-water sorption isotherms for BPM and BPS with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

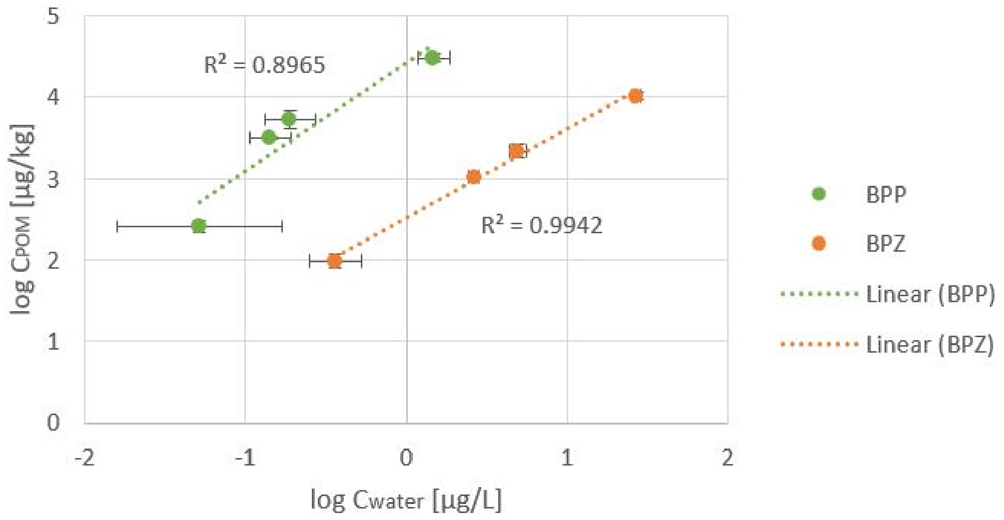


Figure 4.7: POM-water sorption isotherms for BPP and BPZ with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

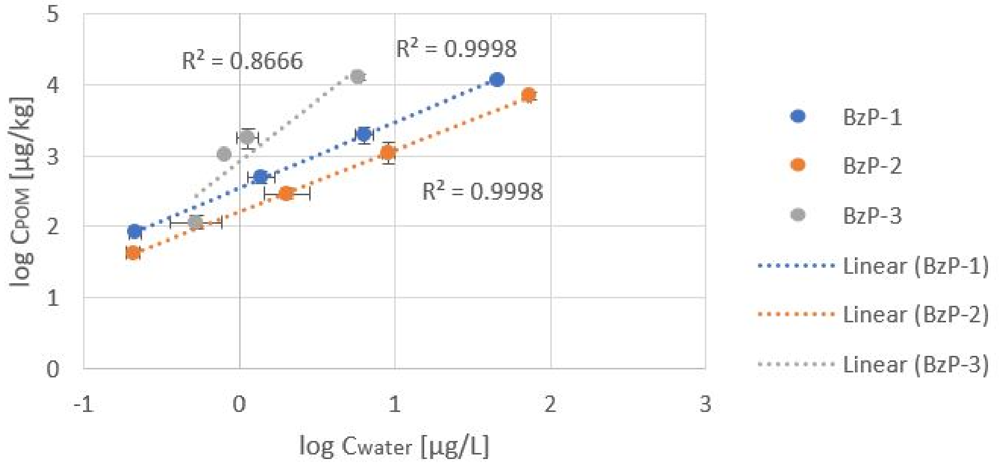


Figure 4.8: POM-water sorption isotherms for BzP-1, BzP-2 and BzP-3 with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

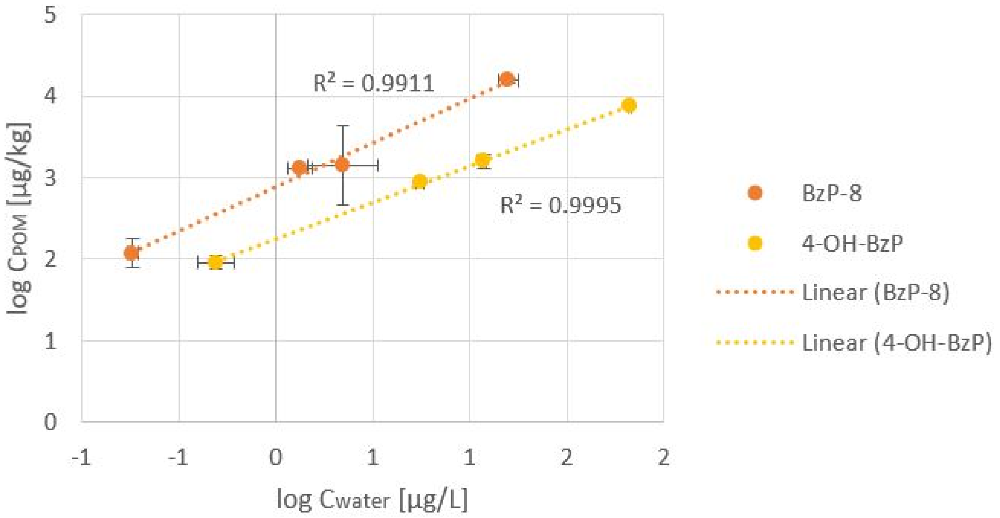


Figure 4.9: POM-water sorption isotherms for BzP-8 and 4-OH-BzP with standards deviation error bars. Different spiked concentrations (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

Resulting values of log K_{POM} with standard deviation, R^2 for the corresponding sorption isotherm and predicted log K_{POM} are listed in Table 4.6. K_{POM} with standards deviations are given in Table D.5. The predicted log K_{POM} are values from a sorption prediction model based on Linear Solvation Energy Relationships via the UFZ-LSER data base, based on the approach in Endo et al. [21] [33]

Table 4.6: Log K_{POM} given with standard deviation, R^2 values for the sorption isotherms and predicted log K_{POM} (from UFZ-LSER data base) of every compound.

Compound	**log K_{POM} (± SD)**	**R^2 POM-water sorption isotherm**	**Predicted log K_{POM}[33]**
BPA	2.45 (± 0.16)	0.99	2.17
BPAF	3.40 (± 0.12)	0.99	n/a
BPAP	3.41 (± 0.10)	0.99	n/a
BPB	2.74 (± 0.16)	0.99	n/a
BPF	2.32 (± 0.33)	0.99	n/a
BPM	4.13 (± 0.40)	0.83	n/a
BPP	4.20 (± 0.38)	0.90	n/a
BPS	1.25 (± 0.08)	0.99	n/a
BPZ	2.57 (± 0.14)	0.99	n/a
BzP-1	2.51 (± 0.09)	0.99	n/a
BzP-2	2.13 (± 0.15)	0.99	n/a
BzP-3	3.00 (± 0.42)	0.87	3.44
BzP-8	2.90 (± 0.23)	0.99	n/a
4-OH BzP	2.16 (± 0.10)	0.99	2.65

As evident from the error bars in Figures 4.4 to 4.9 and corresponding raw data in Tables D.1 to D.4, the largest standard deviations were linked to the lowest concentrations in the equilibrium experiment. This is reasonable as more uncertainty is expected for low concentrations as the signals from 100 ng/mL were used to calculate the concentrations.

Eleven of the 14 POM-water isotherm curves showed an excellent correlation giving R^2 values equal to 0.99. Even though there were only four measured points it is a very good indication of K_{POM} being a linearly increasing ratio. The isotherms for the analytes BPM, BPP and BzP-3 resulted in R^2 values of 0.83, 0.90 and 0.87 which also indicate good correlations. In all three cases it could be observed that the point that differed the most from the rest was the point at the smallest concentration. Additionally, these relatively poorer correlations may be due to the stability of the substances. As presented in Table 4.5, these substances showed either the largest standard deviations in terms of mass loss such as BPM and BPP, or the lowest recovery such as BPZ, BzP-3 and BzP-8.

Correlation between log K_{POM} and log K_{ow} is presented in Figure 4.10.

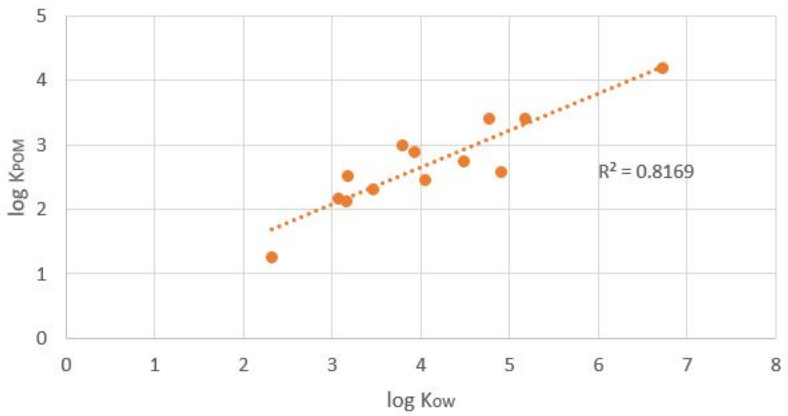


Figure 4.10: Correlation between log K_{POM} and log K_{ow}.

Linear correlation with $R^2 = 0.82$ indicates a good correlation for the 13 data points in Figure 4.10. Deviations are mainly caused by POM and octanol being different sorption phases. Furthermore, the quality of the K_{ow} values from literature can be a reason for not giving a coefficient of determination closer to 1. Data points of log K_{POM}, predicted log K_{POM} and log K_{ow} (as well as log K_{waste}) for the bisphenols and benzophenones target analytes are shown in Table E.1.

As only three data points were available, the correlation between log K_{POM} and predicted log K_{POM} from UFZ-LSER data base could not give a representative description of all the 14 substances. In increasing order, the available predicted log K_{POM} values were as following: BPA (2.17) < 4-OH BzP (2.65) < BzP-3 (3.44). The corresponding experimental log K_{POM} values were BPA (2.45 ± 0.16), 4-OH BzP (2.16 ± 0.10) and BzP-3 (3.00 ± 0.42). Some correlation can be observed, but additional data points are required to give a more reliable relation between the data sets.

4.4 Waste-water partition coefficients of BPA alternatives and benzophenones

From the kinetic experiment, the mass recoveries for the compounds were found. To ensure good data quality the mass loss was corrected in the calculations of K_{waste} when the total recovery (POM + water) was less than 60%. Equation 2.14 was used to calculate corrected concentrations of C_{POM}.

Log K_{waste} with standard deviations, percentage of analyte leached and total number of samples with signal above LOD are listed in Table 4.7. The solid waste samples analyzed were sample 3, 5, 7 and 12, and the $\frac{L}{S}$ ratio was 31 L/kg. Log C_{waste}, K_{waste} and leachable concentrations in solid waste samples 3, 5, 7 and 12 are listed with standard deviations in Table E.2.

Table 4.7: Log K_{waste} given with standard deviations, % of bisphenols and benzophenones leached, and total number of samples with signal above LOD (n).

Compound	**log K_{waste}**	**% leached**	**n**
BPA	2.57 (± 0.12)	7.6	4
BPAF	3.25 (± 0.72)	3.5	4
BPAP	3.46 (± 0.00)	0.5	1
BPB	< LOD	-	0
BPF	3.30 (± 0.37)	1.1	4
BPM	4.03 (± 0.63)	0.4	2
BPP	4.24 (± 0.48)	0.1	2
BPS	1.63 (± 0.32)	83	4
BPZ	2.39 (± 0.17)	18	2
BzP-1	2.55 (± 0.50)	7.8	4
BzP-2	1.71 (± 0.16)	62	3
BzP-3	2.97 (± 0.53)	2.2	3
BzP-8	< LOD	-	0
4-OH BzP	2.29 (± 0.20)	14	4

There can be observed some inconsistency between the increasing order of K_{waste} and log K_{waste} for the different compounds, due to a difference between arithmetic averages and geometric averages. The logarithmic values were determined for each K_{waste} before taking the average of these logarithmic values. By doing this, standard deviations leading to negative numbers were avoided, such as negative concentrations and negative partition coefficients.

Even though the K_{waste} values were calculated for only four of the total twelve waste samples, it can be said to be a good approach to study the possible partitioning and leaching behaviour of the E-waste and vehicle fluff samples. A great range in standard deviations supports a collection of representative samples. Despite the effort to homogenize them, the samples were very heterogeneous, particularly when considering that subsamples of 1 g were analyzed. When determining the concentrations in the waste, only one of the triplicates were chosen and let to dry, which gives an indication of the leaching despite to few data points.

The compounds that showed the highest percentage leached were BPS (83%) > BzP-2 (62%) > BzP-1 (18%) > 4-OH-BzP (14%) > BzP-1 (7.8%) > BPA (7.6%). In these samples, BPS and BPA were observed to be the compounds most likely to be emitted into the environment, which corresponds to the relatively low log K_{waste} values; 1.63 (± 0.3) and 2.57 (± 0.1), respectively.

Correlation between log K_{waste} and log K_{ow} is presented in Figure 4.11.

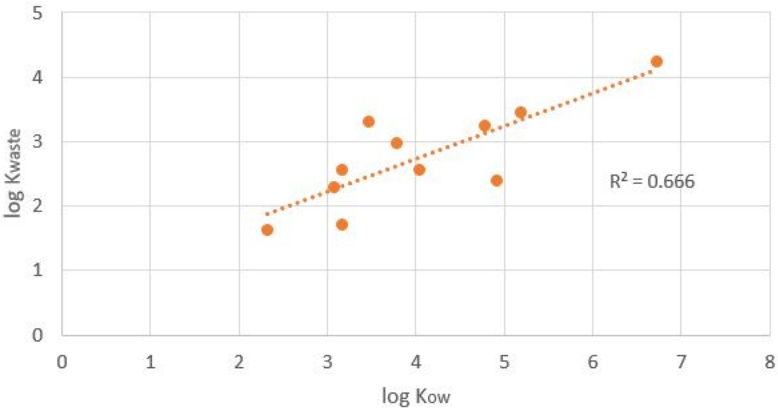


Figure 4.11: Correlation between log K_{waste} and log K_{ow}.

Linear correlation with $R^2 = 0.67$ in Figure 4.11 indicates a good correlation between the eleven data points. Data points of log K_{waste}, log K_{ow}, log K_{POM} as well as predicted log K_{POM} for the bisphenols and benzophenones target analytes are presented in Table E.1.

As K_{ow} describes the hydrophobic property of a compound, this can be interpreted further to describe the polarity of a compound. The lower the value, the more polar the compound, as the compound is more present in the polar water phase. K_{POM} values were smaller for more polar compounds such as BPA, BPS, BzP-2 and 4-OH-BzP, where the K_{POM} were below 300. Likewise, the highest K_{POM} values corresponded to the least polar compound, such as BPP, BPM, BPAP, BPAF and BzP-3. The log K_{POM} value for BPA was established to be 2.45 ± 0.16 which corresponds perfectly to Morin et al. (2.45 ± 0.12) [6], and is similar to Endo et al. (2.63 ± 0) [21].

Correlation between log K_{waste} and log K_{POM} is presented in Figure 4.12.

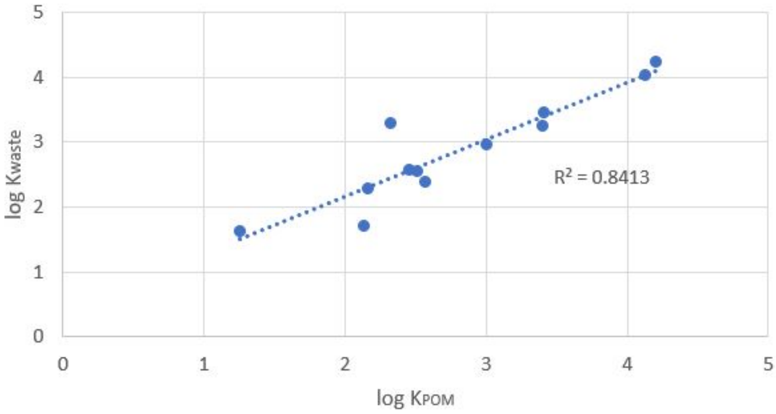


Figure 4.12: Correlation between log K_{waste} and log K_{POM}.

Linear correlation with $R^2 = 0.84$ in Figure 4.12 indicates a very good correlation between the twelve data points. This correlation is stronger than the correlation between K_{waste} and log K_{ow} which indicates that POM may be a better reference sorption phase for E-waste and vehicle fluff than octanol.

4.5 Partition coefficients and recycling approaches

In terms of a circular economy where it is desirable to minimize waste and conduct recycling processes, the desired sorption property depends on the approach. If the aim is to reuse and recycle as much as possible of the material, including the bisphenols or benzophenones that were initially implemented, it can be desirable having a substance with a high K_{waste} value. This leads to a substance more likely to stay within the product, and preferably obtain the initial purpose of the additive when being reused or recycled.

On the other hand, if the approach of the recycling process is to remove the bisphenols or benzophenones to achieve a purer product, a low K_{waste} value would be beneficial. This way the substance would be easier to remove and may even be reused for its initial purpose. The disadvantage of waste containing substances with low K_{waste} values is the potential to leach into the aqueous surroundings and be more mobile in the aqueous environment. If waste is stored at a landfill over a period of time prior to recycling, the potential of environmental emission and human exposure in the short term may increase. In a landfill all bisphenols and benzophenones will eventually leach at time infinity, but substances with the lower K_{waste} will leach first.

In addition to K_{waste}, there are many other factors that have to be considered regarding recycling and the use of bisphenols and benzophenones. Toxicity, bio-accumulation and persistency in the environment are particularly important. The most suitable bisphenol or benzophenone in a circular economy has low cost, low risk for emission, is easy to recycle and has predictable sorption properties.

5 Conclusions

The BPA alternatives and benzophenones measured to have the largest concentrations in the E-waste and vehicle fluff samples were BPF and BPS with maximum concentrations determined to 42400 and 332 ng/g, respectively. Maximum concentration of BPA was measured to 246000 ng/g. BzP-3, BzP-1 and BPAP were also found in considerable amounts (maximum concentrations determined to 285, 155 and 150 ng/g, respectively). The presence of the various BPA alternatives and benzophenones implies an increased use of these substances in products ending up being E-waste and vehicle fluff.

A method was developed using POM passive sampler for measuring free-phase concentrations of BPA alternatives and benzophenones. POM-water sorption isotherms showed very good correlations (from $R^2 = 0.83$ to 0.99) and achieved equilibrium in less than 14 days with the method used. Log K_{POM} showed good correlations with log K_{ow}: $R^2 = 0.82$. Thus, POM was observed to be a very convenient passive sampler method for measuring partition behaviour of studied bisphenols and benzophenones in analyzed waste samples to a polar environment. The POM strips were easy to handle and the correlation between log K_{waste} and log K_{POM} was very good ($R^2 = 0.84$), whereas the correlation between log K_{waste} and log K_{ow} resulted in $R^2 = 0.67$. This indicates that POM may be a better reference sorption phase for E-waste and vehicle fluff samples.

As indicated by their larger K_{ow}, the K_{POM} and K_{waste} were in general largest for the compounds BPP, BPM, BPAP and BPAF (log $K_{waste} = 4.24 \pm 0.48$, 4.03 ± 0.63, 3.46 ± 0.00 and 3.25 ± 0.72, respectively). Similarly, K_{POM} and K_{waste} were smallest for the compounds having smaller K_{ow} such as BPS, BzP-2, 4-OH-BzP and BPA (log $K_{waste} = 1.63 \pm 0.32$, 1.71 ± 0.16, 2.29 ± 0.20 and 2.57 ± 0.12, respectively). This was supported by the latter compounds having highest percentages leached from the samples; 83, 62, 14 and 7.6%, respectively.

Whether a high or low sorption coefficient of a BPA alternative or benzophenone is favorable depends on the desired recycling process. If the approach is to keep the substance within the material, an additive such as BPP, BPM, BPAP and BPAF could be appropriate, whereas an additive such as BPS, BzP-2 or 4-OH-BzP could be more suitable if the aim is extract it. However, a further assessment on the risks regarding toxicity and environmental hazard of the compounds should be considered within a holistic assessment of relevant recycling and reuse processes.

References

[1] H. P. H. Arp, N. A. O. Morin, S. E. Hale, G. Okkenhaug, K. Breivik, and M. Sparrevik. The mass flow and proposed management of bisphenol A in selected Norwegian waste streams. *Waste Management*, 60:775–785, 2 2017.

[2] B. S. Rubin. Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects. *Journal of Steroid Biochemistry and Molecular Biology*, 127(1-2): 27–34, 2011.

[3] K. L. Kinnberg, G. I. Petersen, M. Albrektsen, M. Minghlani, S. M. Awad, B. F. Holbech, J. W. Green, P. Bjerregaard, and H. Holbech. Endocrine-disrupting effect of the ultraviolet filter benzophenone-3 in zebrafish, Danio rerio. *Environmental Toxicology and Chemistry*, 34(12):2833–2840, 2015.

[4] H. Jarry, J. Christoffel, G. Rimoldi, L. Koch, and W. Wuttke. Multi-organic endocrine disrupting activity of the UV screen benzophenone 2 (BP2) in ovariectomized adult rats after 5 days treatment. *Toxicology*, 205(1-2 SPEC. ISS.):87–93, 2004.

[5] M. K. S. Bhutta, A. Omar, and X. Yang. Electronic Waste: A Growing Concern in Today's Environment. *Economics Research International*, 2011:1–8, 2011.

[6] N. Morin, H. P. H. Arp, and S. E. Hale. Bisphenol A in Solid Waste Materials, Leachate Water, and Air Particles from Norwegian Waste-Handling Facilities: Presence and Partitioning Behavior. *Environmental Science and Technology*, 49 (13):7675–7683, 7 2015.

[7] J. Regueiro, A. Breidbach, and T. Wenzl. Derivatization of bisphenol A and its analogues with pyridine-3-sulfonyl chloride: Multivariate optimization and fragmentation patterns by liquid chromatography/Orbitrap mass spectrometry. *Rapid Communications in Mass Spectrometry*, 29(16):1473–1484, 2015.

[8] E. Yamazaki, N. Yamashita, S. Taniyasu, J. Lam, P. K. S. Lam, H. B. Moon, Y. Jeong, P. Kannan, H. Achyuthan, N. Munuswamy, and K. Kannan. Bisphenol

A and other bisphenol analogues including BPS and BPF in surface water samples from Japan, China, Korea and India. *Ecotoxicology and Environmental Safety*, 2015.

[9] M. Geissdoerfer, P. Savaget, N. M. P. Bocken, and E. J. Hultink. The Circular Economy – A new sustainability paradigm? *Journal of Cleaner Production*, 143: 757–768, 2017.

[10] M. Lieder and A. Rashid. Towards circular economy implementation: A comprehensive review in context of manufacturing industry. *Journal of Cleaner Production*, 115:36–51, 2016.

[11] A. Kumar and R. K. Gupta. *Fundamentals of Polymer Engineering.* Marcel Dekker, Inc., New York, 2nd edition, 2003.

[12] I. M. Steensgaard, K. Syberg, S. Rist, N. B. Hartmann, A. Boldrin, and S. F. Hansen. From macro- to microplastics - Analysis of EU regulation along the life cycle of plastic bags. *Environmental Pollution*, 224:289–299, 5 2017.

[13] N. Andersson, M. Arena, D. Auteri, S. Barmaz, E. Grignard, A. Kienzler, P. Lepper, A. M. Lostia, S. Munn, J. M. Parra Morte, F. Pellizzato, J. Tarazona, A. Terron, and S. Van der Linden. Guidance for the identification of endocrine disruptors in the context of Regulations (EU) No 528/2012 and (EC) No 1107/2009. *EFSA Journal*, 16(6), 6 2018.

[14] C. Maier and T. Calafut. Additives. In *Polypropylene*, pages 27–47. William Andrew Publishing, 1st edition, 1 1998.

[15] A. G. Asimakopoulos, M. Elangovan, and K. Kannan. Migration of parabens, bisphenols, benzophenone-type UV filters, triclosan, and triclocarban from teethers and its implications for infant exposure. *Environmental Science and Technology*, 50(24):13539–13547, 2016.

[16] N. Negreira, I. Rodríguez, M. Ramil, E. Rubí, and R. Cela. Solid-phase extraction followed by liquid chromatography-tandem mass spectrometry for the determina-

tion of hydroxylated benzophenone UV absorbers in environmental water samples. *Analytica Chimica Acta*, 654(2):162–170, 2009.

[17] H. K. Jeon, Y. Chung, and J. C. Ryu. Simultaneous determination of benzophenone-type UV filters in water and soil by gas chromatography-mass spectrometry. *Journal of Chromatography A*, 1131(1-2):192–202, 2006.

[18] A. Leo, C. Hansch, and D. Elkins. Partition coefficients and their uses. *Chemical Reviews*, 71(6):525–616, 1971.

[19] J. G. Speight. *Introduction Into the Environment.* Number 1. 2017.

[20] P. J. McCall, D. A. Laskowski, R. L. Swann, and H. J. Dishburger. Estimation of environmental partitioning of organic chemicals in model ecosystems. In Francis A Gunther and Jane Davies Gunther, editors, *Residue Reviews*, pages 231–244, New York, NY, 2012. Springer New York.

[21] S. Endo, S. E. Hale, K. U. Goss, and H. P. H. Arp. Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices. *Environmental Science and Technology*, 45(23): 10124–10132, 2011.

[22] M. Jonker and A. A. Koelmans. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. *Environmental Science and Technology*, 35(18):3742–3748, 2001.

[23] F. W. Fifield and P. J. Haines. *Environmental Analytical Chemistry.* Blackwell Science Ltd, 2nd edition, 2000.

[24] J. Regueiro, M. Llompart, C. Garcia-Jares, J. C. Garcia-Monteagudo, and R. Cela. Ultrasound-assisted emulsification-microextraction of emergent contaminants and pesticides in environmental waters. *Journal of Chromatography A*, 1190:27–38, 2008.

[25] E. Lundanes, L. Reubsaet, and T. Greibrokk. *Chromatography: Basic Principles, Sample Preparations and Related Methods.* Wiley-VCH Verlag GmbH & Co. KGaA, 1st edition, 2014.

[26] V. Pérez-Fernández, L. M. Rocca, P. Tomai, S. Fanali, and A. Gentili. Recent advancements and future trends in environmental analysis: Sample preparation, liquid chromatography and mass spectrometry. *Analytica Chimica Acta*, 983: 9–41, 2017.

[27] A. Shrivastava and V. B. Gupta. Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chronicles of Young Scientists*, 2(1):21, 2011.

[28] A. G. Asimakopoulos, L. Wang, N. S. Thomaidis, and K. Kannan. A multi-class bioanalytical methodology for the determination of bisphenol A diglycidyl ethers, p-hydroxybenzoic acid esters, benzophenone-type ultraviolet filters, triclosan, and triclocarban in human urine by liquid chromatography-tandem mass spectromet. *Journal of Chromatography A*, 1324:141–148, 2014.

[29] J. L. M. Vidal, A. G. Frenich, and F. J. E. González. Internal quality-control criteria for environmental monitoring of organic micro-contaminants in water. *TrAC - Trends in Analytical Chemistry*, 22(1):34–40, 2003.

[30] A. G. Asimakopoulos, L. Wang, N. S. Thomaidis, and K. Kannan. Benzotriazoles and benzothiazoles in human urine from several countries: A perspective on occurrence, biotransformation, and human exposure. 2013.

[31] K. Law and R. C. Thompson. Microplastics in the seas - Concern is rising about widespread contamination of the marine environment by microplastics. *Science*, 345(6193):144–145, 2014.

[32] A. G. Asimakopoulos, J. Xue, B. Pereira De Carvalho, A. Iyer, K. O. Abualnaja, S. S. Yaghmoor, T. A. Kumosani, and K. Kannan. Urinary biomarkers of exposure to 57 xenobiotics and its association with oxidative stress in a population in Jeddah, Saudi Arabia. *Environmental Research*, 150:573–581, 2016.

[33] Helmholtz Centre for Environmental Research UFZ. UFZ-LSER database. Last visited 03/06/2019. URL `https://www.ufz.de/index.php?en=31698&contentonly=1&m=0&lserd_data%5Bmvc%5D=Public/start`.

[34] H. P. H. Arp, N. Morin, G. Okkenhaug, S. Hale, G. Breedveld, M. Sparrevik, Å. Almås, P. Andersson, F. Wania, and K. Breivik. WASTEFFECT – Life Cycle Effects of Emerging Contaminants in Waste – Final Report. (20120445), 2016.

Appendices

A. LC-MS/MS analysis of bisphenols and benzophenones

Table A.1: Settings for LC-MS/MS instrument during analysis of bisphenols and benzophenones.

Settings	
Capillary	1.5 kV
Cone	50 V
Source offset	30 V
Source temperature	150 °C
Desolvation temperature	350 °C
Cone gas flow	150 L/hour
Desolvation gas flow	650 L/hour
Collision gas flow	0.15 mL/min
Nebulizer gas flow	7.0 bar

Table A.2: Mobile phase gradient used during LC-MS/MS procedure. *A* is the organic phase, *B* is the water phase.

Time [min]	**Flow [mL/min]**	**%A**	**%B**	**Step**
Initialized	0.25	75	25	Initialized
0.1	0.25	75	25	6
3.6	0.25	25	75	5
3.7	0.25	1	99	6
4.2	0.25	1	99	1
4.3	0.25	75	25	3
4.4	0.25	75	25	6

Table A.3: RT and RRT for analysis of bisphenols and benzophenones.

Compound	**RT [min]**	**RRT**
BPA	2.34	1.00
BPAF	1.95	1.00
BPAP	2.85	1.05
BPB	2.70	1.00
BPF	1.76	1.00
BPM	3.96	1.47
BPP	3.97	1.47
BPS	0.39	0.99
BPZ	3.10	1.15
BzP-1	0.48	1.22
BzP-2	0.39	1.00
BzP-3	3.21	1.19
BzP-8	1.86	1.06
4-OH BzP	0.48	1.23

Table A.4: m/z transitions of internal standards used to study bisphenols and benzophenones.

Internal standard	**Quantitation ion [m/z]**	**Confirmation ion [m/z]**
BPA-13C12	239 > 224	239 > 224
BPAF-13C12	347 > 277	347 > 208
BPB-13C12	253 > 224	253 > 217
BPF-13C12	211 > 111	211 > 99
BPS-13C12	261 > 114	161 > 162

Table A.5: m/z transitions of the bisphenols and benzophenones studied as well as internal standard used for every analyte.

Compound	**Quantitation ion [m/z]**	**Confirmation ion [m/z]**	**Internal standard**
BPA	227 > 212	227 > 133	BPA-13C12
BPAF	335 > 265	335 > 177	BPAF-13C12
BPAP	289 > 274	289 > 195	BPB-13C12
BPB	241 > 212	241 > 212	BPB-13C12
BPF	199 > 93	199 > 105	BPF-13C12
BPM	345 > 133	345 > 133	BPB-13C12
BPP	345 > 330	345 > 330	BPB-13C12
BPS	249 > 108	249 > 156	BPS-13C12
BPZ	267 > 173	267 > 145	BPB-13C12
BzP-1	213 > 135	213 > 91	BPS-13C12
BzP-2	245 > 135	245 > 109	BPS-13C12
BzP-3	227 > 211	227 > 183	BPB-13C12
BzP-8	243 > 123	243 > 93	BPF-13C12
4-OH BzP	197 > 92	197 > 120	BPS-13C12

B. Data from determination of bisphenols and benzophenones in solid waste samples

Table B.1: Sample number, waste origin, description of the selection and weight of subsamples. The waste origin is listed as in the WASTEFFECT[34] project.

Sample	**Waste origin**	**Description**	**Weight** [g]
1	Vehicle	Fine particles, fluff.	0.1188
2	Cable	Plastic granulates, fine particles.	0.1143
3	Cable	Fine particles.	0.1165
4	Cable	Plastic granulates, fine particles.	0.1191
5	Plastic	Powder.	0.1232
6	Vehicle	Some powder, fluff.	0.1033
7	Vehicle	Medium-sized particles, fluff.	0.1039
8	Combustible	Fine particles, fluff.	0.1311
9	Combustible	Medium-sized particles, fluff.	0.1027
10	Vehicle	Small amounts of powder, fluff.	0.1223
11	Plastic	Larger, dense particles.	0.1382
12	Plastic	Larger, dense particles.	0.1198

Table B.2: Concentrations of bisphenols and benzophenones in E-waste and vehicle fluff samples given in ng/g: Samples 1 to 6.

Compound	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
BPA	10007	46230	10517	245682	10180	3430
BPAF	2.23	2.05	4.66	0.50	1.27	0.49
BPAP	1.17	10.4	4.63	4.77	38.3	0.67
BPB	2.76	0.78	91.7	< LOD	6.13	4.35
BPF	653	< LOD	82.2	< LOD	12002	42432
BPM	3.49	1.13	4.10	0.93	3.19	0.44
BPP	31.8	2.97	23.9	2.89	3.82	1.16
BPS	10.8	1.36	42.3	2.67	13.6	306
BPZ	< LOD	< LOD	13.7	10.2	7.36	< LOD
BzP-1	92.1	19.5	11.3	2.17	1.54	2.71
BzP-2	2.28	< LOD	3.01	< LOD	0.96	1.06
BzP-3	110	17.2	38.0	0.30	89.0	20.2
BzP-8	2.25	3.36	1.68	< LOD	13.3	< LOD
4-OH BzP	5.09	0.61	15.2	< LOD	10.4	9.28

Table B.3: Concentrations of bisphenols and benzophenones in E-waste and vehicle fluff samples given in ng/g: Samples 7 to 12.

Compound	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**
BPA	24632	858	1171	2024	14238	29806
BPAF	1.96	0.97	0.38	15.9	1.42	2.30
BPAP	1.12	0.55	150	7.20	2.39	2.08
BPB	4.47	< LOD	< LOD	1.77	< LOD	< LOD
BPF	8621	384	< LOD	107	15136	2850
BPM	2.06	0.50	3.04	1.89	4.85	2.84
BPP	0.61	3.01	8.06	8.41	7.08	4.58
BPS	47.8	2.25	25.4	5.46	332	4.47
BPZ	0.85	< LOD	< LOD	< LOD	< LOD	1.19
BzP-1	116	25.5	155	137	7.39	5.72
BzP-2	8.05	< LOD	4.13	< LOD	4.83	0.68
BzP-3	44.0	1.48	20.3	5.77	15.9	285
BzP-8	2.72	< LOD	1.10	< LOD	< LOD	< LOD
4-OH BzP	27.0	1.66	5.36	35.4	4.21	0.28

C. Data from kinetic uptake of BPA alternatives and benzophenones in POM

Table C.1: POM-water uptake kinetics information for bisphenols used for plotting uptake kinetics plots: log K_{POM} (± SD).

Compound	**log K_{POM} (± SD) after shaking [days]**				
	3	**7**	**14**	**21**	**28**
BPA	1.86 (± 0.04)	2.11 (± 0.07)	2.30 (± 0.06)	2.41 (± 0.08)	2.37 (± 0.06)
BPAF	2.74 (± 0.08)	3.03 (± 0.04)	3.28 (± 0.04)	3.41 (± 0.11)	3.38 (± 0.07)
BPAP	2.73 (± 0.12)	3.07 (± 0.06)	3.31 (± 0.05)	3.42 (± 0.05)	3.41 (± 0.07)
BPB	2.05 (± 0.07)	2.31 (± 0.04)	2.54 (± 0.02)	2.62 (± 0.08)	2.62 (± 0.06)
BPF	1.68 (± 0.07)	1.88 (± 0.03)	2.04 (± 0.07)	2.12 (± 0.02)	2.09 (± 0.03)
BPM	3.62 (± 0.07)	3.90 (± 0.04)	4.21 (± 0.05)	4.29 (± 0.10)	4.28 (± 0.12)
BPP	3.65 (± 0.08)	3.92 (± 0.07)	4.24 (± 0.03)	4.31 (± 0.10)	4.29 (± 0.14)
BPS	0.70 (± 0.08)	0.96 (± 0.03)	1.11 (± 0.04)	1.19 (± 0.04)	1.26 (± 0.05)
BPZ	1.90 (± 0.10)	2.23 (± 0.06)	2.47 (± 0.07)	2.58 (± 0.06)	2.57 (± 0.05)

Table C.2: POM-water uptake kinetics information for benzophenones used for plotting uptake kinetics plots: log K_{POM} (± SD).

Compound	**log K_{POM} (± SD) after shaking [days]**				
	3	**7**	**14**	**21**	**28**
BzP-1	1.90 (± 0.09)	2.12 (± 0.05)	2.28 (± 0.05)	2.41 (± 0.01)	2.40 (± 0.02)
BzP-2	1.44 (± 0.06)	1.72 (± 0.04)	1.89 (± 0.04)	1.97 (± 0.05)	2.04 (± 0.01)
BzP-3	2.80 (± 0.07)	3.05 (± 0.04)	3.26 (± 0.02)	3.34 (± 0.03)	3.26 (± 0.04)
BzP-8	2.41 (± 0.07)	2.65 (± 0.04)	2.88 (± 0.03)	2.99 (± 0.06)	2.94 (± 0.07)
4-OH BzP	1.63 (± 0.07)	1.82 (± 0.03)	1.96 (± 0.05)	2.05 (± 0.02)	2.02 (± 0.03)

D. Data from POM-water partition coefficients of BPA alternatives and benzophenones

Table D.1: POM-water isotherm values used for plotting isotherm figures for bisphenols: log C_{POM} (± SD). Values are determined at equilibrium for different initial concentrations of bisphenols (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

Compound	**log C_{water} (± SD)**			
	1 ng/mL	**10 ng/mL**	**20 ng/mL**	**100 ng/mL**
BPA	-0.11 (± 0.31)	0.59 (± 0.06)	0.97 (± 0.03)	1.71 (± 0.05)
BPAF	-0.92 (± 0.10)	-0.05 (± 0.03)	0.21 (± 0.12)	0.97 (± 0.07)
BPAP	-0.99 (± 0.12)	-0.13 (± 0.04)	0.16 (± 0.08)	0.92 (± 0.03)
BPB	-0.64 (± 0.18)	0.49 (± 0.09)	0.81 (± 0.13)	1.61 (± 0.05)
BPF	-0.80 (± 0.61)	0.65 (± 0.18)	1.08 (± 0.07)	1.82 (± 0.04)
BPM	-1.12 (± 0.31)	-0.85 (± 0.05)	-0.69 (± 0.18)	0.15 (± 0.09)
BPP	-1.29 (± 0.52)	-0.85 (± 0.13)	-0.72 (± 0.15)	0.17 (± 0.10)
BPS	0.03 (± 0.01)	1.02 (± 0.01)	1.31 (± 0.01)	1.98 (± 0.01)
BPZ	-0.44 (± 0.16)	0.42 (± 0.03)	0.69 (± 0.05)	1.43 (± 0.03)

Table D.2: POM-water isotherm values used for plotting isotherm figures for bisphenols: log C_{water} (± SD). Values are determined at equilibrium for different initial concentrations of bisphenols (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

Compound	**log C_{POM} (± SD)**			
	1 ng/mL	**10 ng/mL**	**20 ng/mL**	**100 ng/mL**
BPA	2.24 (± 0.09)	3.15 (± 0.04)	3.44 (± 0.05)	4.12 (± 0.04)
BPAF	2.34 (± 0.11)	3.41 (± 0.01)	3.68 (± 0.11)	4.38 (± 0.04)
BPAP	2.28 (± 0.10)	3.34 (± 0.02)	3.63 (± 0.09)	4.35 (± 0.04)
BPB	2.23 (± 0.09)	3.25 (± 0.02)	3.55 (± 0.06)	4.23 (± 0.04)
BPF	1.84 (± 0.06)	2.98 (± 0.02)	3.27 (± 0.07)	3.94 (± 0.04)
BPM	2.38 (± 0.07)	3.47 (± 0.02)	3.70 (± 0.12)	4.44 (± 0.06)
BPP	2.41 (± 0.07)	3.50 (± 0.01)	3.73 (± 0.11)	4.48 (± 0.05)
BPS	1.32 (± 0.10)	2.32 (± 0.03)	2.56 (± 0.13)	3.17 (± 0.04)
BPZ	1.99 (± 0.08)	3.02 (± 0.00)	3.34 (± 0.08)	4.02 (± 0.05)

Table D.3: POM-water isotherm values used for plotting isotherm figures for benzophenones: log C_{POM} (± SD). Values are given determined at equilibrium for different initial concentrations of benzophenones (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

Compound	**log C_{water} (± SD)**			
	1 ng/mL	**10 ng/mL**	**20 ng/mL**	**100 ng/mL**
BzP-1	-0.67 (± 0.04)	0.14 (± 0.09)	0.80 (± 0.06)	1.66 (± 0.01)
BzP-2	-0.68 (± 0.04)	0.31 (± 0.15)	0.96 (± 0.04)	1.87 (± 0.01)
BzP-3	-0.28 (± 0.17)	-0.09 (± 0.01)	0.06 (± 0.07)	0.77 (± 0.02)
BzP-8	-0.74 (± 0.02)	0.12 (± 0.06)	0.34 (± 0.18)	1.20 (± 0.05)
4-OH BzP	-0.31 (± 0.09)	0.74 (± 0.02)	1.07 (± 0.02)	1.82 (± 0.01)

Table D.4: POM-water isotherm values used for plotting isotherm figures for benzophenones: log C_{water} (± SD). Values are given determined at equilibrium for different initial concentrations of benzophenones (1 ng/mL, 10 ng/mL, 20 ng/mL and 100 ng/mL).

Compound	**log C_{POM} (± SD)**			
	1 ng/mL	**10 ng/mL**	**20 ng/mL**	**100 ng/mL**
BzP-1	1.92 (± 0.04)	2.70 (± 0.09)	3.29 (± 0.12)	4.07 (± 0.02)
BzP-2	1.63 (± 0.03)	2.47 (± 0.07)	3.03 (± 0.16)	3.84 (± 0.05)
BzP-3	2.06 (± 0.10)	3.02 (± 0.02)	3.25 (± 0.14)	4.11 (± 0.04)
BzP-8	2.07 (± 0.17)	3.11 (± 0.01)	3.15 (± 0.48)	4.19 (± 0.03)
4-OH BzP	1.96 (± 0.09)	2.94 (± 0.01)	3.20 (± 0.08)	3.88 (± 0.02)

Table D.5: K_{POM} given with standard deviation of every compound.

Compound	$\mathbf{K_{POM}}$ **[L/kg] (± SD)**
BPA	296 (± 30)
BPAF	2593 (± 27)
BPAP	2615 (± 20)
BPB	588 (± 43)
BPF	326 (± 154)
BPM	17316 (± 52)
BPP	19948 (± 49)
BPS	18 (± 19)
BPZ	382 (± 25)
BzP-1	330 (± 20)
BzP-2	143 (± 34)
BzP-3	1332 (± 58)
BzP-8	873 (± 38)
4-OH BzP	148 (± 25)

E. Data from waste-water partition coefficients of BPA alternatives and benzophenones

Table E.1: Log K_{waste}, log K_{POM}, predicted log K_{POM} and log K_{ow} for bisphenols and benzophenones.

Compound	**log K_{waste}**	**log K_{POM}**	**Predicted log K_{POM}**	**log K_{ow}**
BPA	2.57 (± 0.12)	2.45 (± 0.16)	2.17	4.04
BPAF	3.25 (± 0.72)	3.40 (± 0.12)	n/a	4.77
BPAP	3.46 (± 0.00)	3.41 (± 0.10)	n/a	5.18
BPB	< LOD	2.74 (± 0.16)	n/a	4.49
BPF	3.30 (± 0.37)	2.32 (± 0.33)	n/a	3.46
BPM	4.03 (± 0.63)	4.13 (± 0.40)	n/a	n/a
BPP	4.24 (± 0.48)	4.20 (± 0.38)	n/a	6.72
BPS	1.63 (± 0.32)	1.25 (± 0.08)	n/a	2.32
BPZ	2.39 (± 0.17)	2.57 (± 0.14)	n/a	4.91
BzP-1	2.55 (± 0.50)	2.51 (± 0.09)	n/a	3.17
BzP-2	1.71 (± 0.16)	2.13 (± 0.15)	n/a	3.16
BzP-3	2.97 (± 0.53)	3.00 (± 0.42)	3.44	3.79
BzP-8	< LOD	2.90 (± 0.23)	n/a	3.93
4-OH BzP	2.29 (± 0.20)	2.16 (± 0.10)	2.65	3.07

Table E.2: Concentrations of bisphenols and benzophenones in waste (C_{waste} (± SD)), waste-water partition coefficients (K_{waste} (±SD)), leachable concentration for bisphenols and benzophenones ($C_{leachable}$ (± SD)) and total number of samples with signal above LOD (n).

Compound	$\mathbf{C_{waste}}$ [μ**g/kg**]	$\mathbf{K_{waste}}$ **[L/kg]**	$\mathbf{C_{leachable}}$ [μ**g/kg**]	**n**
BPA	10812 (± 6970)	381 (± 110)	826 (± 330)	4
BPAF	2.9 (± 1.4)	3577 (± 3884)	0.1 (± 0.1)	4
BPAP	2.5 (± 2.8)	2863 (± 0)	0 (± 0.)	1
BPB	< LOD	< LOD	< LOD	0
BPF	6927 (± 8266)	2567 (± 1878)	78 (± 61)	4
BPM	0.4 (± 0.4)	16725 (± 18294)	0 (± 0)	2
BPP	0.9 (± 0.9)	23026 (± 21139)	0 (± 0)	2
BPS	34 (± 18)	53 (± 42)	28 (± 20)	4
BPZ	2.7 (± 2.8)	257 (± 99)	0.5 (± 0.4)	2
BzP-1	41 (± 30)	576 (± 654)	3.2 (± 2.5)	4
BzP-2	1.6 (± 0.6)	53 (± 19)	1 (± 0.6)	3
BzP-3	103 (± 150)	1518 (± 1714)	2.2 (± 1.4)	3
BzP-8	< LOD	< LOD	< LOD	0
4-OH BzP	26 (± 22)	210 (± 92)	3.6 (± 2.8)	4

Kristin Runde

The presence and sorption of bisphenols and benzophenones in plastic-containing electronic waste and vehicle fluff

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