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Test of Two New Adsorbents for Passive Air Sampling of Regulated and Emerging Organic Chemicals in Indoor Environments

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Acknowledgements

Abstract

Persistent organic pollutants (POPs) are chemicals proven as harmful to humans and animals. As the name suggests, those chemicals are persistent in the environment whilst also having the ability to travel long distances by air and accumulating in organic tissues. The chemicals regarded as POPs have

been linked to cancer, endocrine disruption, and developmental issues. The Stockholm convention of 2004 was a global agreement to regulate or ban a list of 12 chemicals groups known as the Dirty Dozen, one of them being Polychlorinated Biphenyls. The list has since been expanded upon and new emerging chemicals of concern are continuously being monitored. Therefore, carrying out measurements of both old and emerging chemicals important to assess the effects of current regulations and to evaluate new ones.

The current methods for sampling and analysis are not suitable for the emerging compounds due to differences in physicochemical properties. The standard sampler used for both passive and active sampling is the Polyurethane Foam (PUF). The challenge with using this sampler is that matrix is co-extracted during sample preparation. This is combated by subjecting the samples to an acid treatment to clean up the sample. However, emerging chemicals such as organophosphorus flame retardants (OPFRs) and chlorinated paraffins (CPs) are too sensitive for this treatment. This thesis will look at the alternative samplers ABN, POCIS and PDMS along with the PUF as passive air samplers. The goal is to find an effective sampler that has minimal matrix issues.

The PUF sampler had generally better results than the alternative samplers, except for certain NBFR and OPFR components where POCIS gave similar or better results. The PUF samples for PCB analysis were unable to analyzed. The sampler had a somewhat linear rate of uptake for the analytes, suggesting that saturation of sampler had not occurred during the sample period.

The ABN in cartridge sampler showed a large amount of matrix throughout the different samples and had quantification issues, indicating an unfitness as a passive air sampler or the need for alternative extraction methods.

Although the POCIS had better results than the ABN in cartridge sampler, it still had some issues with matrix contamination. The results also pointed towards a degradation of CPs on the sampler. The set deployed for 28 days had a contamination of NBFRs. The POCIS had a slight affinity for the lighter PCBs and the OPFR analysis showed a linear rate of uptake for a couple of analytes.

The PDMS also had better results than the ABN, but not as well as the POCIS. The PDMS sampler showed a somewhat linear uptake for each analyte, indicating that the sampler was not saturated during the sampling time.

Looking at the average blank values, the result for which sampler contributes the least changes somewhat with the analyte but is mostly inconclusive. The result here is also marred by unquantifiable samples for PCB on PUF, amongst others.

Sammendrag

Persistente organiske miljøgifter er kjemikalier som er bevist å være skadelige for mennesker og dyr. Som navnet antyder, er disse kjemikaliene persistente i miljøet, samtidig som de har evnen til å reise lange avstander med luft og akkumuleres i organisk vev. Kjemikaliene som anses som POP-er har vært knyttet til kreft, hormonforstyrrelser og utviklingsproblemer. Stockholm-konvensjonen fra 2004 var en global avtale om å regulere eller forby en liste over 12 kjemikalier kjent som «Dirty Dozen», en

av dem er polyklorerte bifenyler. Listen har siden blitt utvidet, og nye kjemikalier som gir bekymring, overvåkes kontinuerlig. Derfor er det viktig å gjennomføre målinger av både gamle og nye kjemikalier for å vurdere effekten av gjeldende regelverk og for å evaluere nye tiltak.

De nåværende metodene for prøvetaking og analyse er ikke egnet for de nye forbindelsene på grunn av forskjeller i fysisk-kjemiske egenskaper. Den standard prøvetakeren som brukes for både passiv og aktiv prøvetaking er polyuretanskum (PUF). Utfordringen med å bruke denne prøvetakeren er at matrisen co-ekstraheres under prøvepreparering. Dette bekjempes ved å utsette prøvene for en syrebehandling for å rense opp i prøven. Imidlertid er nye kjemikalier som organofosfor flammehemmere (OPFR) og klorerte parafiner (CP) følsomme for denne behandlingen. Denne oppgaven vil se på de alternative prøvetakerne ABN, POCIS og PDMS sammen med PUF som passive luftprøvetakere. Målet er å finne en effektiv prøvetaker som har minimale matriseproblemer.

PUF-prøvetakeren hadde generelt bedre resultater enn de alternative prøvetakerne, bortsett fra enkelte NBFR- og OPFR-komponenter der POCIS ga lignende eller bedre resultater. PUF-prøvene for PCB-analyse var ikke i stand til å analysere. Prøvetakeren hadde en noe lineær opptakshastighet for analyttene, noe som tyder på at metning av prøvetakeren ikke hadde skjedd i løpet av prøveperioden.

ABN i hylseprøvetakeren viste en stor mengde matrise gjennom de forskjellige prøvene og hadde kvantifiseringsproblemer, noe som indikerte en uegnethet som passiv luftprøvetaker eller behov for alternative ekstraksjonsmetoder.

Selv om POCIS hadde bedre resultater enn ABN i hylseprøvetakeren, hadde den fortsatt noen problemer med matriseforurensning. Resultatene pekte også mot en degradering av CP på prøvetakeren. Settet som ble utplassert i 28 dager hadde en forurensning av NBFR-er. POCIS hadde en svak affinitet for de lettere PCB-ene og OPFR-analysen viste en lineær opptakshastighet for et par analytter.

PDMS hadde også bedre resultater enn ABN, men ikke så gode som POCIS. PDMS-prøvetakeren viste et noe lineært opptak for hver analytt, noe som indikerer at prøvetakeren ikke var mettet i løpet av prøvetakingstiden.

Ser man på de gjennomsnittlige blindverdiene, endres resultatet for hvilken prøvetaker som bidrar minst noe med analytten, men det er for det meste usikkert. Resultatet her er også skjemmet av ikke-kvantifiserbare prøver for PCB på blant annet PUF.

Abbreviations

ABN – Acid, base neutral

ASE – accelerated solvent extraction

BFR – brominated flame retardant

BTBPE - bis(2,4,6-tribromophenoxy) ethane

CLRTAP – Convention for Long-range Transboundary Air Pollution

CP – chlorinated paraffins

CVMS – cyclic volatile methyl siloxanes

DBDPE - decabromodiphenyl ethane

DCM – dichloromethane

EMEP - European Monitoring and Evaluation Programme

ESI – electrospray ionization

FR – flameretardant

GAPS - Global Atmospheric Passive Sampling

GC-MS – gas chromatography mass spectrometry

HBCD - hexabromocyclododecanes

LRAT – Long rate atmospheric transport

MCCP – medium chain chlorinated paraffins

NBFR – novel brominated flameretardants

NILU – Norsk institutt for Luftforskning

OPFR – organophosphorus flame retardants

PAS – passive air sampling

PBB - polybrominated biphenyls

PBDE - polybrominated diphenyl ethers

PCB – polychlorinated biphenyl

PDMS – polydimethyl siloxane

PE - polyethylene

POCIS – polar organic chemical integrative sampler

POP – persistent organic pollutant

PUF – polyurethane foam

SCCP – short chain chlorinated paraffins

SPE – solid phase extraction

SVOCs – semi volatile organic compounds

TBBP-A - tetrabromobisphenol A

TBBPA-DBPE - tetrabromobisphenol A bis(2,3-dibromopropyl ether)

UPLC - Ultra-High Pressure Liquid Chromatographer

VOCs – volatile organic compounds

XAD - styrene divinyl-benzene copolymer

Contents

1. Introduction

1.1.   Persistent Organic Pollutants (POPs)

Persistent organic pollutants (POPs) are chemicals with properties that make them industrially and or agriculturally useful, but also are of environmental and human concern. POPs are characterized as being persistent in the environment, having the ability to undergo long-range transport, bioaccumulate in organisms and being toxic to organisms. The production and use of these compounds were first regulated in Europe through the 1998 Aarhus Protocol, under the Convention for Long-range Transboundary Air Pollution (CLRTAP). Later, the Stockholm Convention on POPs was signed globally to regulate and ban the production and emission of chemicals that are proven to fulfil the four POP characteristics (Stockholm convention, 2019); being persistent in the environment, having the ability to undergo long-range transport, bioaccumulate in organisms and being toxic to organisms. When the Stockholm Convention entered into force in 2004, twelve compounds (the Dirty Dozen) were originally included, amongst them Polychlorinated Biphenyls. The list has been expanded with new compounds/compound groups over time. Currently 30 compounds/compound groups are included

in the Stockholm Convention. New compounds are continuously being evaluated for inclusion based on findings from the scientific community.

Air is a major pathway for long-range transport (i.e., long-range atmospheric transport, LRAT) of many POPs and new chemicals with POP-like characteristics. POPs can travel over long distances due to their semi-volatile nature and thereby be found in areas far away from their point of release, for example in the Arctic (Hung et al., 2013). While the more volatile POPs can travel with the air masses such as gas, the heavier/less volatile POPs are more likely to be adsorbed to airborne particles.

Measurements of POPs in air are therefore crucial for evaluation of the effectiveness of the regulations. While the European Monitoring and Evaluation Programme (EMEP) measures POPs in air using active air sampling, the Global Atmospheric Passive Sampling (GAPS) monitoring program measures POPs in air using passive air sampling (PAS). The temporal trends of POPs in European air are generally decreasing, reflecting the reduced emissions (EMEP, 2016).

1.1.1.   Polychlorinated Biphenyl

Polychlorinated biphenyls (PCBs) are a group of compounds principally divided by their degree of chlorination. The degree of chlorination and position on the molecule decides their stability. Less stable compounds have less chlorination and a lack of Cl-atoms at the ortho-position. PCBs consist of 209 congeners, where 36 are of interest during environmental sampling (Kimbrough, 1995)

PCBs have been used in a wide variety of functions, most notably as plasticizers, flame retardants, dielectric fluid in transformers and capacitors and as hydraulic fluids (Safe, 1994). The more highly chlorinated compounds have been found to be persistent in the environment and are also capable of LRAT. Their adverse health and environmental effects led to their production ban in the USA (1979) and UK (1981) and to their phase out in the EU (by 1987) (Jepson, 2016).

PCBs are lipophilic and humans are often exposed to them through animal fat. Other significant pathways of exposure are inhalation and dermal contact. Their lipophilic character makes them bioaccumulative, which is alarming due to them being linked to liver disease, cardiovascular disease, and cancer. (Carpenter, 2006).

1.2.   Emerging organic chemicals

While the POPs are regulated under Stockholm Convention and/or other regional/national regulations, new chemicals are constantly produced to replace the regulated chemicals. Others are produced to fulfill new needs. For example, novel brominated flame retardants are replacing the regulated polybrominated diphenyl ethers (PBDEs) (Hou et al., 2021). Many of the new chemicals are produced to be less persistent than the POPs but still many are found in remote areas like the Arctic (Xie et al., 2022). The Arctic is an indicator region for assessing persistence and long-rang transport, and therefore for identifying new POPs. Measurements of non-regulated chemicals on an early stage is crucial to support the regulatory bodies and shorten the time to regulation. And in that way reducing their impact on the environment.

However, air sampling and analyses of new chemicals are challenging. One major issue is that these chemicals are in use and thereby present in many products. This creates a risk of contamination of samples during sampling and analysis and resulting in high and variable background levels. This especially applies for chlorinated paraffins. Also, the chemicals of concern have somewhat different physico-chemical properties compared to the POPs (e.g., less persistent, more volatile, more polar) and the sampling and analytical methods established for POPs are therefore not necessarily applicable

for the new chemicals. For example, novel brominated and phosphorous flame retardants do not survive the commonly used acid clean-up methods. There is therefore a great need for testing new and more robust sampling and analytical methods.

1.2.1. Chlorinated Paraffins

Chlorinated paraffins (CP) are n-alkanes with varying degrees of chlorination. Their general molecular formula is $C_nH_{2n+2-x}Cl_x$. By weight the molecules range from containing 30 to 70 percent Chlorine. CPs with carbon chain length between 10 and 13 are referred to as Short Chain Chlorinated Paraffins (SCCP), whilst those with slightly longer carbon chains, between 14 to 17, are classified as Medium Chain Chlorinated Paraffins (MCCP). The different lengths and degrees of chlorination all affect the physicochemical properties of the molecule (Glüge et al, 2013). These compounds are used flame retardants (FR), plasticizers and pressure additives (UNEP, 2017).

CPs are considered as one the most produced industrial chemicals, due to its production and consumption volumes exceeding 1 000 000 tons in 2013 (ICAIA, 2014). In newer times the production of MCCP is thought to have exceeded the Production of SCCP, as is reflected in environmental samples where MCCPs are more abundant than the SCCPs (Glüge et al, 2016). However, the MCCPs are harder to quantify than SCCPs (Tomy & Stern, 1999) and their persistent, bioaccumulative and toxic properties are not as extensively studied. The short chain CPs have been restricted in the EU since the year 2000 and were listed in Annex A of the Stockholm Convention on persistent organic pollutants in 2017. The list encompasses compounds that are globally banned, but have time- limited exceptions (UNEP, 2017). Both medium chain and short chain are considered to emerging chemicals of concern and MCCPs currently under review as candidates for regulation under the Stockholm convention on POPs (UNEP, 2021).

The log K_{OW} for MCCPs range from 6.77 to 9.85, indicating that MCCPs are more likely to be found in lipid tissues than in aqueous phases (Glüge et al, 2018). The solubility of MCCPs were determined to range from 0.02 μg/L to 40.4 μg/L. With such a wide range the MCCPs are complex to predict in the environment with the available research. Similarly, the SCCP with its 7820 congeners, is quite difficult to give a model to with regards to composition in environmental samples (Chen et al, 2019), but they have been studied more. As a result of these studies the SCCP are found to be more toxic, bioaccumulative and persistent than the MCCP and are therefore more restricted.

1.2.2. Novel brominated flame retardant (NBFR)

Brominated flame retardants (BFRs) were used in textiles, furniture, building materials, electronics and car parts for their efficiency as stopping the spread of fires. These compounds were also found to be highly persistent, bioaccumulative, and capable of LRAT. These older generation BFRs (polybrominated diphenyl ethers and biphenyls (PBDEs and PBBs), hexabromocyclododecanes (HBCDs), and tetrabromobisphenol A (TBBP-A)) were eventually banned (Directive EEC, 2003; California State Assembly, 2003; Renner, 2004; European Court of Justice, 2008) and classified as POPs (Ashton et al., 2009).

To fill the void, another set of BFRs was designed and are often referred to as novel BFRs (NBFRs) or emerging BFRs. Looking at the older generation BFRs, deca-BDE, octa-BDE and TBBP-A their replacements in NBFRs are decabromodiphenyl ethane (DBDPE), bis(2,4,6-tribromophenoxy) ethane (BTBPE), and tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE), respectively (Xiong et al., 2019). These NBFRs have been reported in various environmental matrices, including the Arctic. This means that these compounds also have the ability of LRAT. Sun et al (2018) reported bioaccumulation of NBFRs when studying endocrine disruption in mice. All of these finds point to NBFRs having similar behavior as the BFRs, and that they therefore need to be studied further

1.2.3. Organophosphorus Flame Retardants as replacements for PCB and NBFR

As a result of the bans on PCBs and NBFRs, another emerging group of compounds was produced. The group is called Organophosphorus flame retardants (OPFRs) and are used in similar ways to PCBs and NBFRs (Marklund et al, 2005b). OPFRs are divided into three groups, based on their ester linkage: Chlorinated OPFRs, alkyl-OPFRs and aryl-OPFRs. Studies have pointed out OPFRs potential as endocrine disruptors and having adverse effects on the reproduction system. Aryl OPFRs have been linked to heart toxicity, due to them impeding the expression of transcription regulators in zebrafish (Du et al., 2015). Some chlorinated OPFRs have been proven to be carcinogenic and neurotoxic. OPFRs are easily released into the environment by leaching. Some are easily degraded by sunlight, but chlorinated OPFRs seem to be persistent.

1.3. Air sampling

Measurements of organic chemicals in air can be done using either active or passive air samplers. The active air samplers use a pump to suck air with a controlled flow through a filter and/or a gas-phase adsorbent. The filter collects particles in air and the chemicals associated to those particles. The adsorbent collects the chemicals in gas-phase. Both particles and gas-phase are needed when collecting air samples of semi-volatile organic chemicals like the POPs. The passive air samplers consist of an adsorbent and the air is collected by diffusion which is a natural process and thereby not in need of a pump and electricity. The passive air samplers mainly collects the chemicals in gas-phase, but studies have shown that some passive air samplers also collect particles in air.

The active air samplers have the advantage of a controlled flow (i.e., known air volume) and collection of particles and gas-phase. They are therefore considered the reference methods for POPs. Disadvantages with active air samplers are that they are costly, in need of electricity and trained personnel. In contrast, the passive air samplers are cheap and not in need of electricity and trained personnel and can therefore be used in many places simultaneously and in remote locations. They are also quiet and can therefore easily be used in indoor environments. They are however less accurate than the active air samplers as the volume of air and the concentrations are estimated. A way to control a passive air sampler is to perform an uptake study. This means that the passive air samplers (PAS) are deployed for increasing time periods, for example 1 week, 2 weeks, 3 weeks, 4 weeks, etc. The results should preferably show increasing levels with increasing exposure times following a linear trend.

PAS are efficient at measuring semi volatile organic compounds (SVOCs). PAS perform in two styles, diffuse sampling, and permeation sampling. In diffuse sampling gas-phase compounds spread out through a stagnant boundary layer of air. In permeation sampling the compounds go through a membrane (Zabiegala, 2006). PAS have been in use since the 1850s (Cox, 2003) and were first used to measure ozone concentration on the ground, but have since been innovated to measure volatile organic compounds (VOCs), amongst other things.

For passive air sampling, the analytical reporting limit can be lowered by prolonging the sampling time. This is more convenient and cheaper than cleaning or altering the method of analysis. For indoor air, the reporting limit for most screening levels can be reached with a one-week sampling time (McAlary, 2009)

Examples of commonly used adsorbents in passive and active samplers are polyurethane foam (PUF) and styrene divinyl-benzene copolymer (XAD). PUF and XAD have been developed for measurements of SVOCs in air, but they are mostly optimized for outdoor air sampling (Okeme et al., 2016).

1.3.1. ABN in SPE cartridge

The EVOLUTE® EXPRESS ABN (ABN) has the ability to simultaneously extract acidic, basic and neutral compounds. The ABN medium is a polymer and at the molecular level, ABN has a polar and non-polar interaction optimized for extraction of analytes with a wide range of polarities (Biotage, n.d.).

The ABN sampler has previously been used as an active air sampler. In this thesis the ABN will be explored as a viable option for passive air sampling. The sampler will consist of ABN particulate and a solid phase extraction cartridge. The set up will differ from that described by Al Saify et al. (2021), in that the rings and the filter will not be attached.

1.3.2. Polar Organic Chemical Integrative Sampler

The polar organic chemical integrative sampler (POCIS) was developed for sampling of hydrophilic organic compounds in water. This sampler was designed to gather contaminants (pesticides, industrial chemicals, pharmaceuticals, etc.) from wastewater treatment plants, surface runoff and landfill leachates, that have low levels contamination. Although these compounds are only found at trace levels, their toxicity is still quite significant (European commission, 2012). The POCIS is a passive sampler that has the capacity to give low limits of detection as well as giving a time weighted average concentration of each contaminant.

The POCIS consist of two steel rings with two polyether sulfone filters (pore size 0.1 μm) and in between those filters is the sorbent which in this thesis is ABN (Biotage, Sweden). In previous research, using an 80:20 (wt:wt) sorbent admixture of hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous sorbent (Ambersorb 1500) gave promising results for some polar compounds such as pesticides and hormones (Alvarez, 2004).

1.3.3. Polydimethylsiloxane

The current methods of measuring vapor air intrusion are quite costly, ranging from $250 to $400 per sample, due to the cost of cleaning and renting the active air sampling equipment. Other more conventional samplers also face issues such as bias and variability in measurement and in general a difference of opinion regarding sampling times and sorption issues. In comparison, a passive air sampler will be cheaper, easier to use, and smaller and therefore less invasive.

The membrane to be explored in this thesis is a polydimethylsiloxane (PDMS), which controls uptake of volatile and semi-volatile organic compounds. PDMS consists of a flexible silanol backbone and a methyl side chain, making this compound hydrophobic. The molecule also does not react chemically and presents no bioaccumulative traits. Due to its low glass transition temperature (125 °C), PDMS behaves like rubber under most natural conditions. This ability increases the mobility of compounds in PDMS.

The PDMS is also used in the stationary phase in a gas chromatography-capillary column. The retention time a compound has in a capillary column with PDMS is strongly correlated with its rate of uptake through a PDMS membrane (Zabiegala, 2006). For compounds not previously assessed on PDMS, their uptake can still be estimated fairly well if their retention time is known on a column with PDMS as the stationary phase.

Okeme et al. (2016) found in their study that sampling rates for PDMS were four times that of XAD. When correcting for surface area, the PDMS still outperformed. Although, when looking at the results from a partially covered PUF the outcome was similar and in the case of PBDEs, even better.

1.3.4. Polyurethane foam (PUF)

Polyurethane foam (PUF) is a staple in sampling of the traditional POPs for both active and passive air sampling. The PUF also has the capacity to accumulate analytes from both gas and particle phase (Bohlin et al., 2014; Lévy et al., 2020). However, this sampling medium is not as suitable for new and

emerging compounds of concern due to the required clean-up of the samples. Al Saify found that the PUF will co-extract matrix that will affect the analytical results negatively. To combat this an acid clean-up step is required, but this step will be too harsh for the acid labile compounds. Therefore, a need for new sampling mediums that do not require acid treatment is demanded.

1.4. Objectives of thesis

The purpose of this master thesis study was to test two new adsorbents for passive air sampling of novel brominated flame retardants, chlorinated paraffins and one POP-group (PCBs). The new adsorbents were compared to the commonly used PUF. The adsorbents were evaluated for blank levels and uptake over time.

2. Materials and method

2.1. Chemicals and materials

Table 1 gives an overview of materials, and their productions information, used in this thesis.

Table 1. an overview of the materials used

Item	Producer/origin	Size	Purity grade	Use
ABN	Biotage, Sweden			Sampling material
Acetone Pestinorm	VWR Chemicals	2.5 L	99.7 %	Extraction
Acetone SupraSolv	Merck (Darmstadt, Germany)	2.5 L		Extraction
Acetonitrile Pestinorm	VWR Chemicals	2.5 L	≥99.7%	Extraction
Accelerated Solvent Extraction	Thermos Fisher Scientific			Extraction
Diethyl ether SupraSolv	Merck (Darmstadt, Germany)	1 L		Extraction

Ethyl acetate SupraSolv	Merck (Darmstadt, Germany)	2.5 L		Extraction
Fume hood with laminar flow	Bigneat			Sample extraction and cleanup
Heat mantel	VWR			Soxlet exraction
Isooctane Emsure	Merck (Darmstadt, Germany)	1 L		Solvent used for samples during analysis on GC
n-Hexane Pestinorm	VWR Chemicals		95.0 %	Solvent
n-Hexane SupraSolv	Merck (Darmstadt, Germany)	2.5 L		Cleaning of ABN
NILU PUF	Brødrene Sunde (Norway)			Sampling material
Oven	Electrolux			Drying of sampling material
Precolumn, ISOLUTE® ENV+	Biotage, Sweden			Sample Concentration
Silica gel, 60 Å	Merck (Darmstadt, Germany)	1 kg		Sample cleanup
Anhydrous Sodium sulfate	Merck (Darmstadt, Germany)	1 kg		Sample cleanup
Sulfuric acid Emsure	Merck (Darmstadt, Germany)	1 L		Sample cleanup
TurboVap 500 Concentration Workstation	Biotage / Caliper Lifesciences			Sample concentration
Ultrasonic bath	VWR			Extraction and cleaning of adsorbents, metal and plastic equipment

2.2. Experimental design

The study was done to assess blank levels and uptake over time of two new adsorbents compared to the commonly used PUF-adsorbent for POPs, shown in. The new adsorbents tested were i) ABN powder that previously has been used as an established method for cyclic volatile methyl siloxanes (cVMS) (Werner et al., 2020), and ii) polydimethylsiloxane (PDMS) from Stockholm University, Sweden. The ABN adsorbent was tested in two types of sampler holders; i) the plastic syringe cartridge used for active air sampling of cyclic volatile methyl siloxanes (cVMS) , and ii) the POCIS holder used for sampling of organic chemicals and heavy metals in water. The PDMS-adsorbent was deployed without any sampler housing. The PUF-adsorbent was deployed with the indoor sampler housing. A closer look at the different samplers is given in Figure 1.

Figure 1 This figure shows a close up image of the PUF, ABN in Cartridge, POCIS and PDMS in that order.

The passive air samplers were deployed indoors in an office at the Norwegian Institute for Air Research (NILU) at Kjeller, Norway. The office contains two desktop computers, two office chairs and is in close proximity to two magnet sector mass spectrometers.

The samplers were simultaneously deployed side-by-side in February 2022. The ABN type i) and type i) were deployed in four sets of three samplers each (in total 12 samplers of each type). The PDMS were deployed in four sets of two samplers (in total eight PDMS). The PUFs were deployed in four sets of one sampler (in total four PUFs). Each set was exposed in increasing time periods of 1, 2, 4 and 8 weeks (14.02.2022 – 11.04.2022). Each set consisted of three ABN type i), three ABN type ii), two PDMS, and one PUF. One of the sets is shown in Figure 1. At week 1, 4 and 8 there was also a field blank collected for the POCIS and ABN samplers. For the PUF and PDMS the field blanks were collected at week 1 and 8. In addition, three ABN type i), three ABN type ii), 2 PDMS and 1 PUF were used as laboratory blanks.

Figure 2 Deployment of ABN in cartridge, POCIS, PDMS and PUF. Right side shows the actual deployment, and the left side shows a model deployment.

2.3. Sample preparation

Prior to each extraction procedure, the glass equipment was baked in an oven at 450 °C for 8 hours.

2.3.1. ABN in cartridge (type i) preparation

For the ABN type i), a total number of 18 samplers was prepared and used. Each sampler consisted of a solid phase extraction (SPE) cartridge and two frits. To each of the 18 cartridges, approximately 250 mg ABN was weighed out and sandwiched between an upper and a lower frit. Each cartridge was rinsed with 15 mL Dichloromethane (DCM) followed by 15 mL Hexane. The packed cartridges were then dried under a stream of N_2-gas for 15 minutes. To remove contaminants from the N_2-gass, a precolumn that was rinsed with 5 mL DCM and Hexane was used. The ABN was pressed down using a polyethylene (PE) plunger, and samplers were sealed with a PE stopper and luer tip and wrapped in aluminum foil before deployment.

2.3.2. ABN in POCIS (type ii) preparation

Approximately 4.5 g ABN was weighed out in a Erlen Meyer flask. To that 50 ml of Hexane and 50 ml of DCM were added. The mixture was then sonicated for 15 min in the Ultra Sonic bath. Afterwards the solvent mixture and the ABN was poured out on a piece of foil to dry inside the fume hood. The POCIS sampler was taken apart and the already present adsorbent was exchanged with 250 mg of the sonicated ABN for all 18 samples. The POCIS was then reassembled and wrapped in foil before being deployed.

2.3.3. PUF and PDMS preparation

The polyurethane foam comes pre-cleaned by Soxhlet-extraction using toluene for 24 hours, acetone for 8 hours, and lastly cyclohexane for 8 hours. The PUF is then squeezed dry and placed in an exicator in an oven (80°C, 0.80 kPa). The cleansed PUF comes individually wrapped in foil. The PDMS came pre-cleaned form the University of Stockholm.

2.4. Sample extraction

For every extraction procedure, the glass equipment to be used was baked in an oven at 450 °C for 8 hours. The same goes for the clean-up procedures, where applicable.

2.4.1. Extraction and clean-up of ABN in Cartridge (type i)

To the samples, the internal standards (PFR I (500 pg/μL), CP-DEC I, NyBrom I and PCB I) were added to the upper frit followed by 6 mL of an Acetone and Hexane mixture in a 1:1 ratio at 1 mL intervals.

The extract was vaporized to approximately 600 μL. 1/3 of the extracted sample was transferred to a brown glass vial for OPFR analysis. The remaining 2/3 were transferred to sharp bottomed glass vials. The OPFR samples were solvent exchanged by vaporizing to dryness and then adding 1 ml of Acetonitrile to the vial.

For the clean-up procedure 33% acidified silica and anhydrous sodium sulphate was used. The silica and sodium sulphate were baked at 600∘C overnight. A test-tube rinsed with hexane was filled halfway with sulfuric acid. Two Pasteur pipettes of Hexane were added to the acid before being shaken. When the mixture had reached an equilibrium, the upper layer was removed. This was repeated once more. The cleaned sulfuric acid was added to the silica to make it 33% acid by weight. The acidified silica was shaken several times by hand throughout the course of an hour.

For the clean-up on the SPE-column, some glass wool was packed in the bottom. On top off that approximately.0.7 g of acidified silica and 0.3 g anhydrous sodium sulfate was added. The packed column was then rinsed with 15 mL DCM followed by 20 mL Hexane. A solvent eluent was made consisting of 15% DCM in Hexane. The extracted sample was quantitatively transferred to the solid phase extraction (SPE) column using the 15% DCM solution. 10 mL of the solvent eluent was used to extract the sample through the column in to the test-tube. The sample was then concentrated down to 0.5 mL, the tube was rinsed, and sample was concentrated to 0.5 mL again. Following that, the samples was transferred to a glass vial where 20 μL of the recovery standard PG was added. 20 μL outtakes of each analyte group to be studied (CP, NBFR and PCB) were transferred to a brown vial with insert.

Two additional steps of clean up were carried out on these samples, a sulfuric acid treatment and silica chromatography. For the sulfuric acid treatment, each sample was adjusted to 2 mL with Hexane in a glass test-tube. To the test-tube, 2-6 mL sulfuric acid was added and shaken vigorously. When the separation between acid and hexane had reformed, the hexane layer was transferred to a 500 mL TurboVap-glass. The remaining acid was rinsed twice with 1 mL of Hexane. The extract was the evaporated down to 0.5 mL in a TurboVap instrument.

For the silica chromatography, a glass column with an inner diameter of 15 mm was packed with rinsed cotton followed by 4 to 6 g of activated silica and an upper layer of sodium sulfate. The column was rinsed with 30 mL of Hexane/Diethyl ether 9/1 v/v. The sample was then put on the column and extracted with 30 mL of Hexane/Diethyl ether 9/1 v/v. The extract was then concentrated to 0.5 mL on the TurboVap instrument using a 500 mL TurboVap-glass. The sample was then concentrated further with N_2-gas to 100 μL. For each sample, 20 μL of the recovery standard (PG (2.18.21)) was added and then 20 μL was transferred to a GC-vial with insert.

2.4.2. Extraction of ABN in POCIS (type ii) and clean-up

A glass cartridge with a glass fiber filter in the bottom was rinsed with the Acetone: Hexane mixture. The POCIS sampler was unscrewed, and the contents were transferred to the glass cartridge quantitatively. To each sample 20 μL of each internal standard was added. The samples were then extracted with approx. 5 mL of the Acetone: Hexane mixture. The extract was collected in test-tubes, before being vaporized to 600 μL. 1/3 was transferred to brown glass vials for OPFR analysis. The remaining 2/3 were transferred to sharp bottomed glass vials.

The clean-up was carried out by acidified silica in a glass SPE-column. The column was packed with glass wool and approximately 0.7 g of acidified silica and 0.3 g of anhydrous sodium sulfate. The packed column was then rinsed with 15 mL DCM followed by 20 mL of Hexane. The two solvents were mixed to create the eluent consisting of 15% DCM in Hexane. The extracted sample was transferred quantitatively to the packed SPE-column. The sample was then extracted into a test-tube using 10 mL of the solvent eluent. The sample was then concentrated to 100 μL using N_2-gas before transferring it to a sharp bottomed glass vial. To each sample 20 μL of the recovery standard PG (2.18.21) was added, following that, 20 μL of each sample was transferred to a GC-vial with insert.

2.4.3. Extraction of PUF sampler

After deployment, the PUF disks were extracted according to the NILU-O-2 method for air samples. The PUF disks were extracted on a 250 mL Soxhlet extractor using approximately 300 ml hexane/diethyl ether 9/1 v/v for 8 hours. Prior to the extraction, 20 μL of the internal standards PFR I, PCB I, NyBrom and CP-DEC were added to the disks.

After extraction, a surplus of sodium sulfate is added to remove any water from the extract. The extract was then transferred to a 500 mL TurboVap-glass and evaporated to 0.5 mL on the TurboVap instrument. 150 μL aliquot of the extract was transferred to a brown glass vial, and solvent exchanged to acetonitrile, for OPFR analysis.

The clean-up was carried out in two steps, sulfuric acid treatment and silica chromatography. The sulfuric acid treatment was done in a glass test-tube. The extract was first adjusted to 2 mL using hexane followed by 2-6 mL of concentrated sulfuric acid. The test-tube was shaken vigorously and then put aside until a clear separation between the hexane and acid layer has formed. The hexane layer was transferred, quantitatively, to a new 500 mL TurboVap-glass. The acid was then rinsed with 1 ml of hexane twice, each time transferring the hexane layer to the TurboVap-glass. The extract was again evaporated to 0.5 mL.

For the silica chromatography, a glass column with an inner diameter of 15 mm was used. The bottom opening of the column was plugged with rinsed cotton, before loading the column with 4-6 g of activated silica gel. The column was then packed with roughly 1 g of anhydrous sodium sulfate. The

2.4.4. Extraction of PDMS

The extraction of the polydimethylsiloxane sampler was conducted on an Accelerated Solvent Extraction (ASE) instrument. The samplers were packed in a 10 mL ASE cell with a glass fiber filter on each end. To each sample 20 μL of each internal standard, PFR I (500 pg/μL), NyBrom (09.21), PCB I (1.44.20) and CP-DEC (01.21), was added. The instrument was run in the fixed volume mode with an end volume of 20 mL. The oven temperature was set to 125 °C with a static cycle of 10 minutes. The solvents used for this extraction was Ethyl Acetate and Hexane in a 1:1 ratio.

The samples were then split up for OPFR analysis and CP, PCB and BFR analysis. The OPFR samples had the solvent changed to acetonitrile. The rest of the samples were concentrated to 100 μL using N_2-gass. 20 μL of PG recovery standard (2.18.21) was then added to each of the concentrated samples. Lastly, 20 μL of each sample was transferred to a GC-vial with insert.

2.5. Analysis

2.5.1. PCB

32 PCB congeners were analyzed in each sample using the standard NILU procedure. The instruments used were Gas chromatography- Mass spectrometer (GC-MS) with ionization in EI-mode. The column was a 0,22 mm x 50 m HT-8 column film thickness 0,15 μm. Mobile phase used for PCB analysis was helium. The injection temperature was 280 °C, Gas flow of 1 mL/min. The temperature ramps are shown in table 2.

Table 2. Setting for temperature ramp for PCB analysis.

Temp. 1 [°C]	Time 1 [min]	Ramp 1 [°C/min]	Temp. 2 [°C]	Time 2 [min]	Ramp 2 [°C/min]	Temp. 3 [°C]	Time 3 [min]
90	2	25	170	0	3	300	3

2.5.2. CP

The CP analysis conducted in this thesis focused on SCCP and MCCP. The instrument used here was Agilent GC-TOF with ionization in negative ESI mode. The column was a 15 m Agilent HP-5MS UI 0,25 film thickness and 0,25 inner diameter. Mobile phase used for CP analysis was helium.

2.5.3. NBFR

The samples were analyzed for NBFRs using the Agilent GC coupled with a high-resolution MS from Micromass Autospec. The oven temperature started at 150 °C and was increased to 300 °C. The inlet system was a programmable temperature vaporizing system with injection and interface temperature of 300 °C. The analysis was performed on a Gad Chromatographer coupled to Mass Spectrometer with ionization in EI+ mode and single ion monitoring mode with a temperature of 285°C

2.5.4. OPFR

The OPFR analysis was carried out on a Ultra-High Pressure Liquid Chromatographer (UPLC) coupled with a triple quadrupole mass spectrometer (TSQ Vantage Scientific Inc.). The column used

was a Acquity UPLC BEH Phenyl 1.7 μm 2.1 x 100 mm with a safeguard column of 5 mm (Waters Inc., MA, USA). The oven temperature was held at 40 °C with an injection volume of 10 μL. The mobile phase consisted of 0.1% formic acid in water and 0.1% formic acid in methanol. The flow rate started at 0.3 to 0.4 mL/ minute at 100% mobile phase 0.1% formic acid in methanol.

Electrospray ionization (ESI) in positive mode was used to ionize the analytes. The ESI had a voltage of 3500 V and a temperature of 280 °C using Nitrogen gas as sheath gas and auxiliary gas; 30 Arb and 15 Arb respectively. The capillary temperature was set to 230°C. Argon (1.5 mTorr) was used as a collision gas under the multiple reaction monitoring of the two product ions for each analyte.

A spiked calibration curve with seven levels from 0.1 to 100 ng/mL of organophosphates was used for quantification. Results were processed in Chromeleon (Thermo Scientific Inc.).

3. Results and discussion

3.1. Passive Air Sampling of Chlorinated paraffins

For each sample, the corresponding blank values were subtracted and then divided by the sample volume. The results are presented for each analyte in the following charts.

3.1.1 ABN

The results for ABN in SPE-cartridge were only quantifiable for the MCCP. The results are given in Figure 3. The diagram shows an increase in MCCP with increasing sampling time. Some of the samples had significant amount of matrix present and are therefore more uncertain in their results.
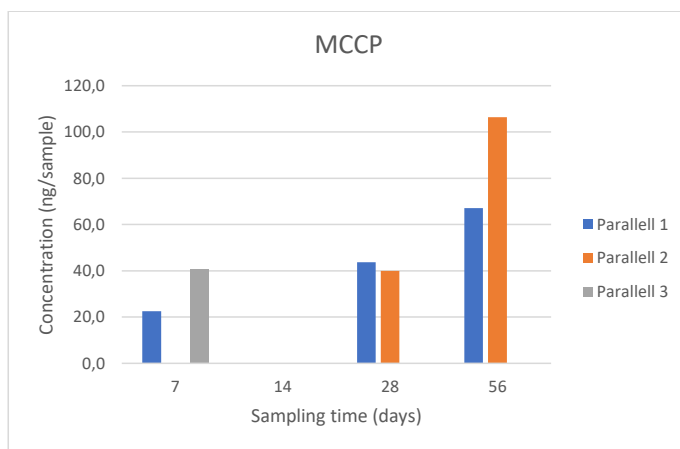
Figure 3 MCCP Concentration (ng/sample) on ABN in cartridge.

3.1.2. POCIS

The results for SCCP and MCCP on POCIS are shown in Figure 4. Here the results show a decline in concentrations for both the MCCP and SCCP. This outcome points to possible degradation of analyte on the sampling medium. However, error in sample preparation might also be the case.

Kommentert [JMV1]: Jeg har ikke lest sample preparation ennå, men kanskje du kan skrive en setning om hva som kanskje kan være feil med preparation.
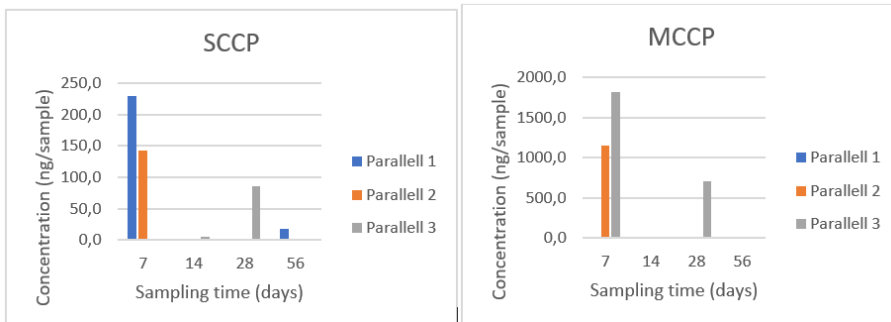
Figure 4 SCCP and MCCP Concentration (ng/sample) on POCIS sampler.

3.1.3. PDMS

The results of PDMS samples analyzed for MCCP and SCCP are presented in Figure 5. The concentrations showed a dip at the 28 days mark (4 weeks) for both CP types. Sample preparation error might be the cause however, since both the parallels at 28 days have this dip in concentration this is unlikely to be the cause.
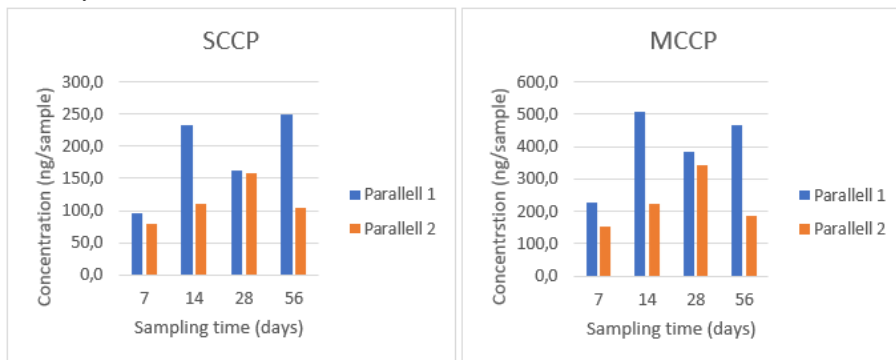
Figure 5 MCCP and SCCP Concentration (ng/sample) on PDMS.

3.1.4. PUF

The results from PUF sampling are shown in Figure 6 for both SCCP and MCCP. The values here show a significant increase between the 28 days sample and the 56 days sample. This sampler only had 1 parallel in each set, any results will therefore be less certain than results from sampling with more parallels.
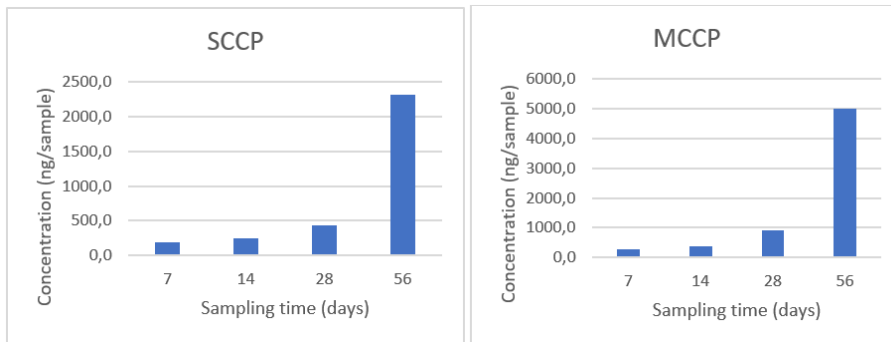
Figure 6 SCCP and MCCP Concentration (ng/sample) on PUF

3.2. Passive Air Sampling of Novel Brominated Flame Retardants

For these samples the results of the field blanks and laboratory blanks were averaged for each analyte and were used as a benchmark. The concentrations determined for each analyte was compared to these benchmarks and the values that exceeded them were used for the diagram. The results are presented for each analyte in the following bar charts.

3.2.1. ABN

The results obtained from ABN sampling are presented as bar charts in Figure 7. The ABN samples suffered from a lot of matrix issues. The technique used to prepare these samples might not have been the most suitable for this sampler. The charts for DPTE, BTBPE, BEHTBP, and DBDPE show characteristics of being contaminated rather than containing analytes from the actual sampling. Compared to the other samplers, ABN is not as efficient with regards to analyte concentration.
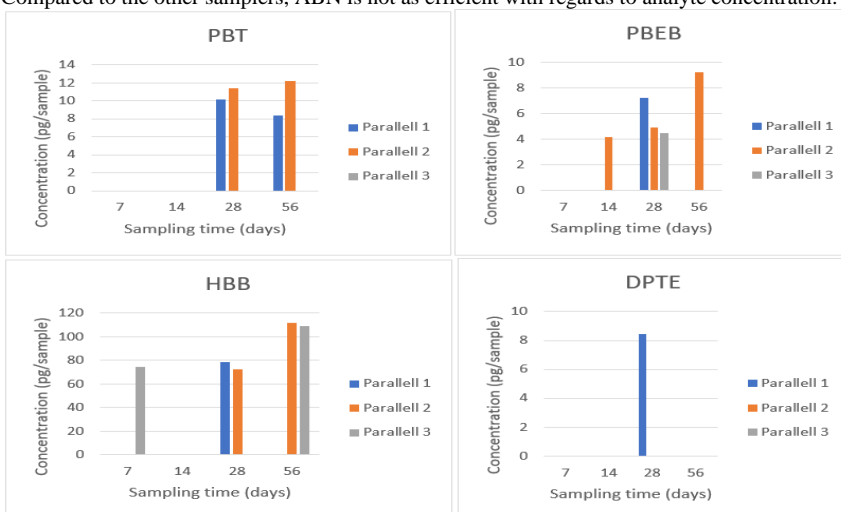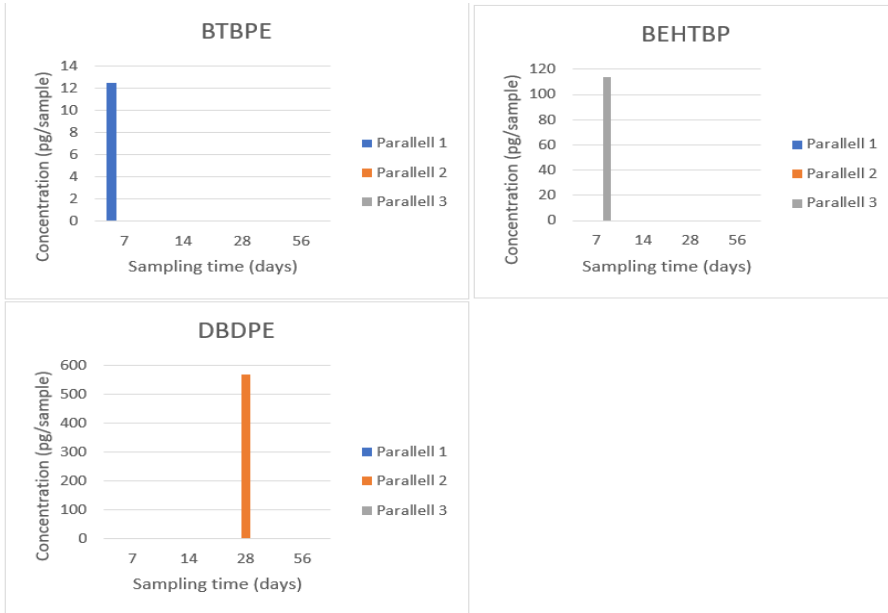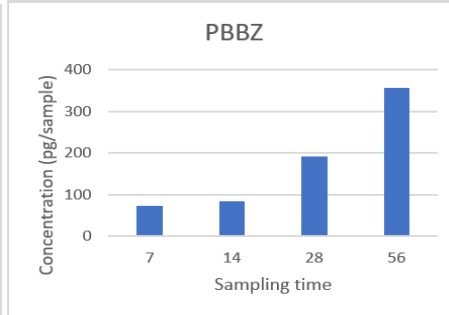
Figure 7 Concentration (pg/sample)of NBFRs on ABN sampler.

3.2.2. POCIS

The concentration of the samples from the 28 days set had exponentially higher values than that of the other sets, therefore these samples are not used for the following diagrams. The values of this set can be found in Figure 18 in the Appendix. The results from the other sets (7, 14 & 56 days) are shown in Figure 8. The significant deviation stems likely from a contamination of the samples. In addition, many samples were affected by high matrix concentrations indicating the need for an adjusted sample preparation method.
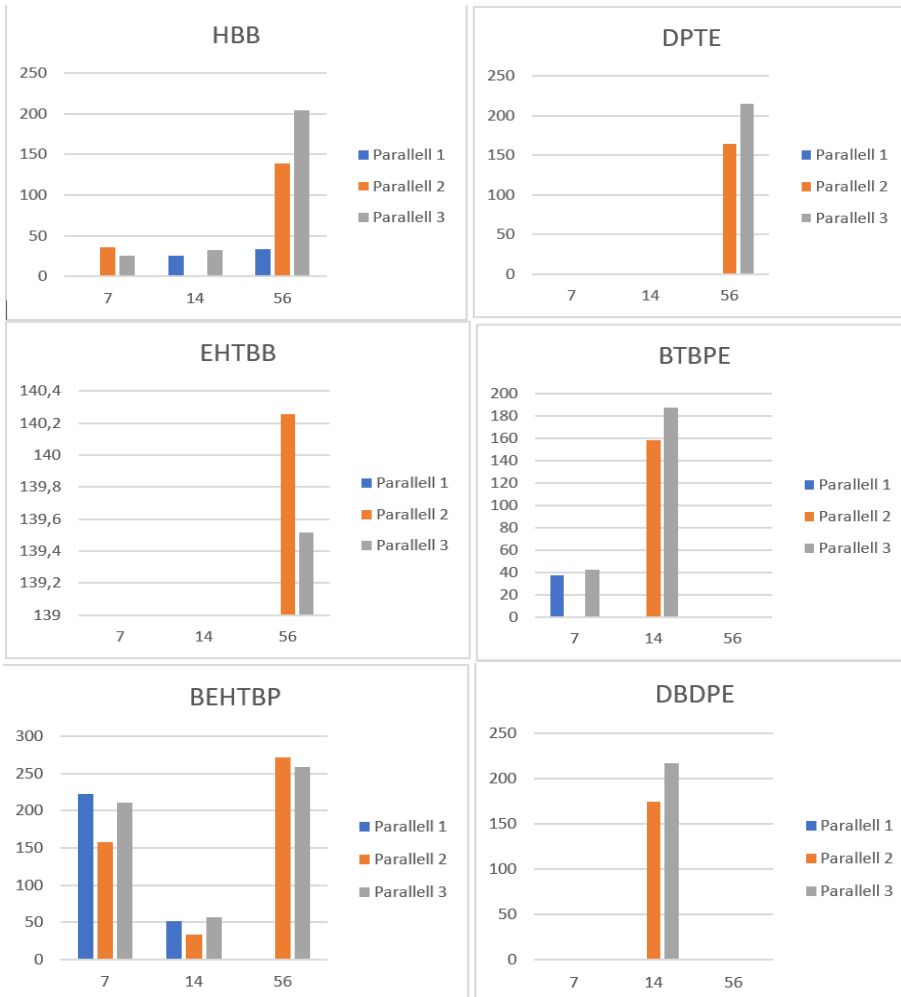
Figure 8 Concentration (pg/sample) of NBFRs on POCIS sampler.

3.2.3. PDMS

The PDMS samples that were analyzed for NBFR compounds are presented in Figure 9. These samples had issues with regards to the internal standard, in that some markers were not present in the sample. Particularly C^{13}-marked BTBPE and DBDPE are the components that are missing. This might lead to an overestimation of the analytes. From the charts of g/d-TBECH and EHTBB, we can conclude that these values most likely stem from contamination.
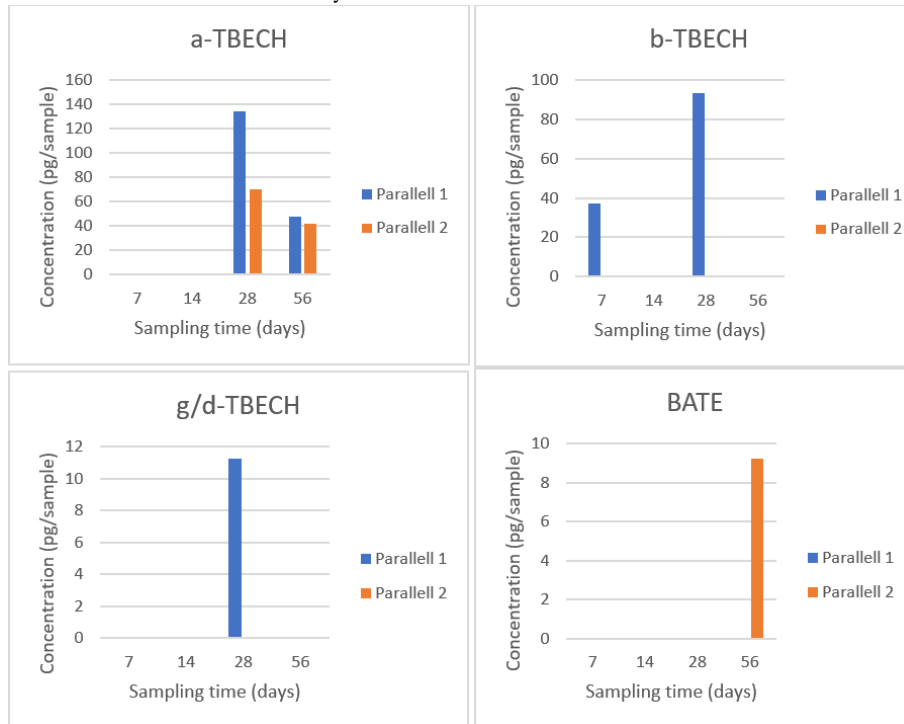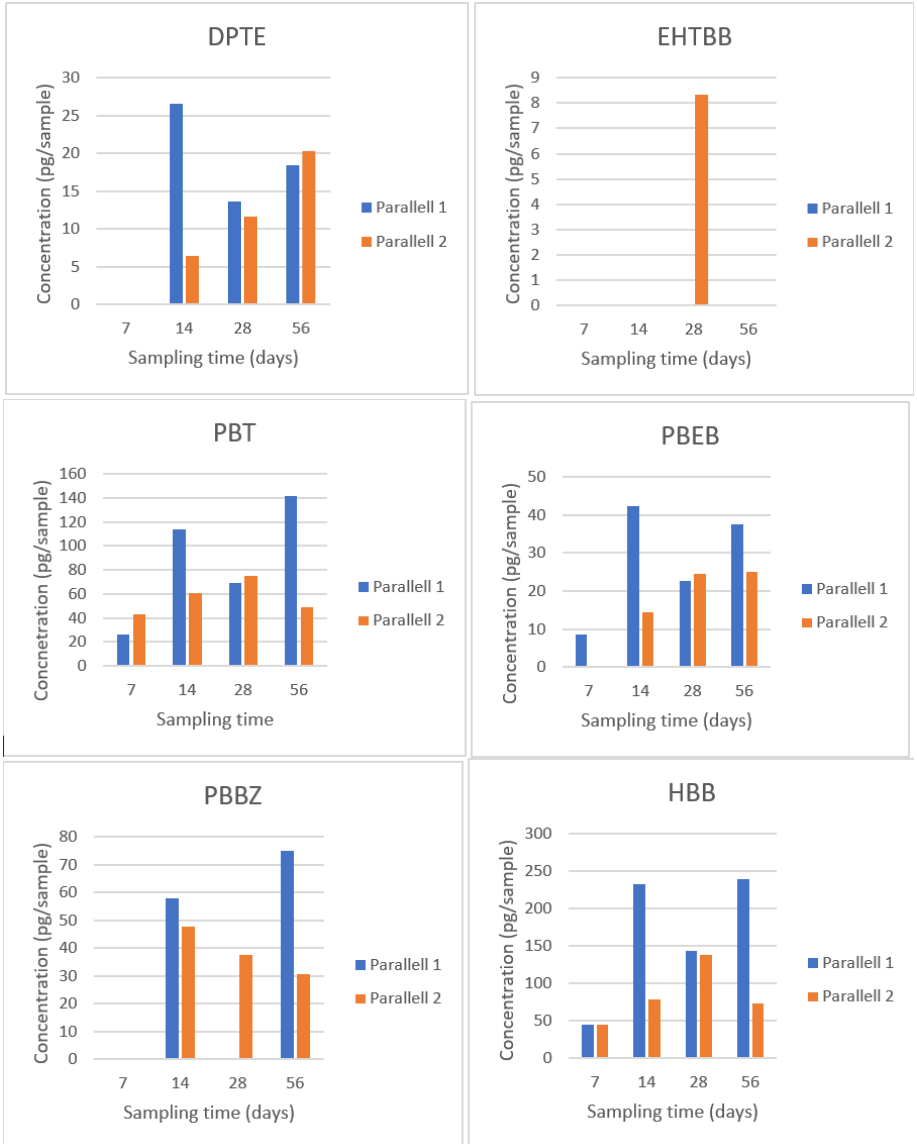
Figure 9 Concentration (pg/sample) of NBFRs on PDMS sampler.

3.2.4. PUF

The PUF sample results are presented in Figure 10. The results from this sampler are also marked by significant amounts of matrices present in the sample as well as some missing internal standard components. The results are also based on 1 parallel for each set, leading to further uncertainties. For certain analytes, the PUF has a tenfold higher concentration than the other samplers.
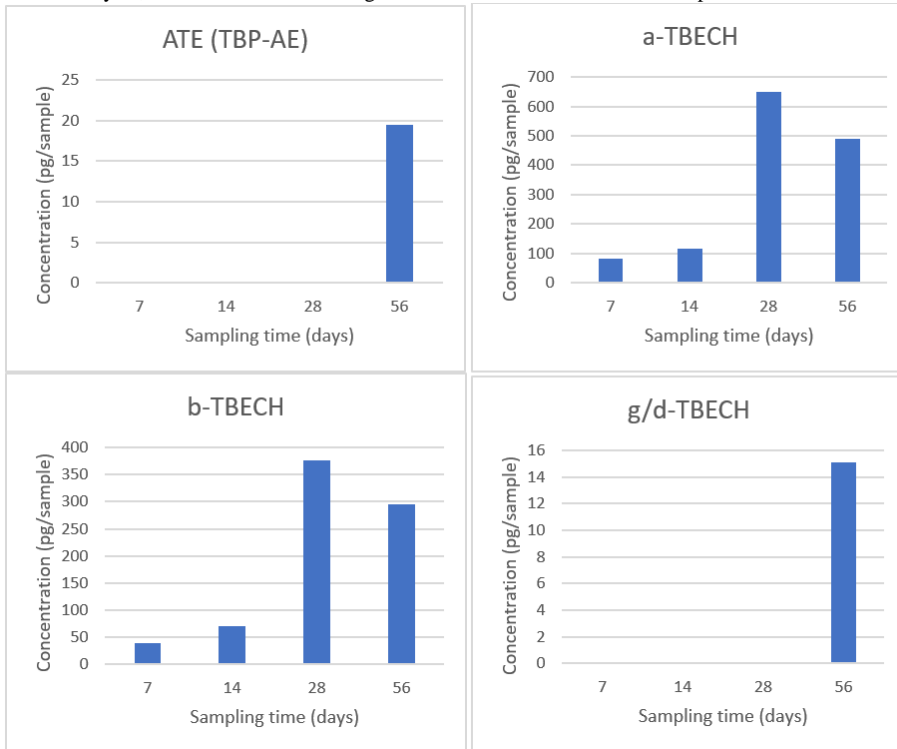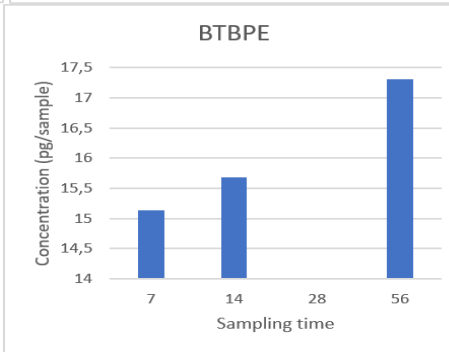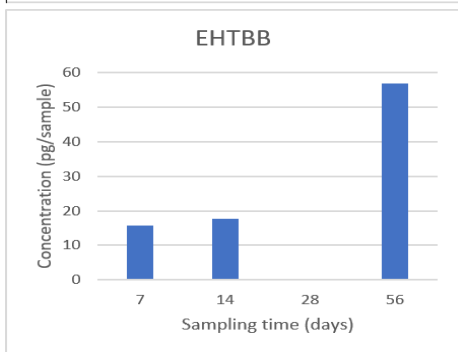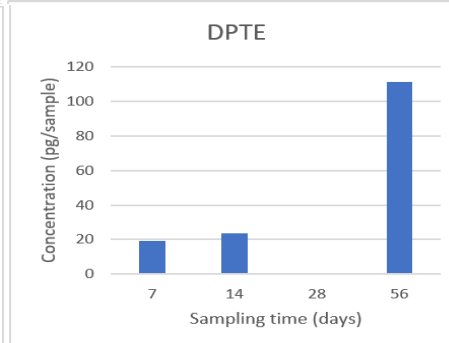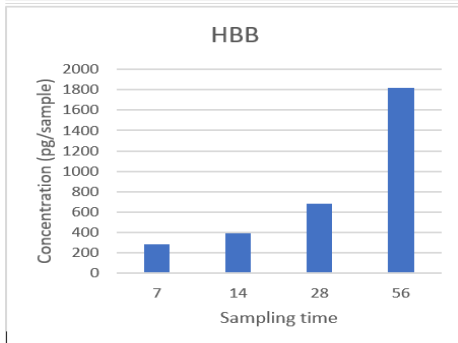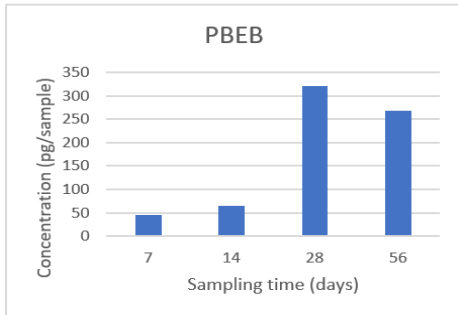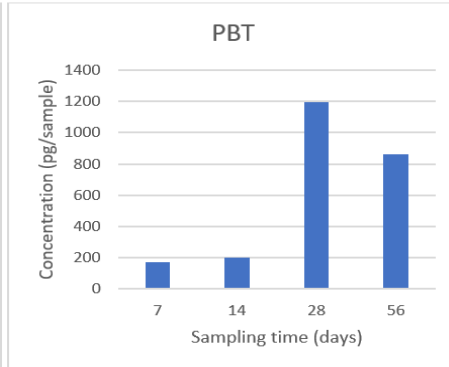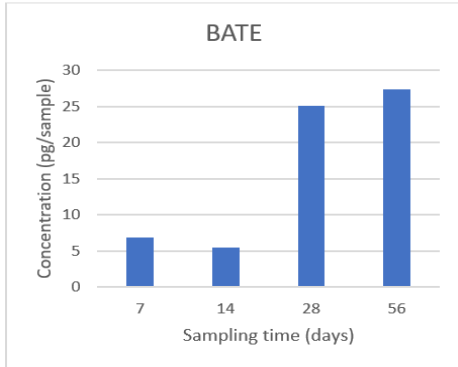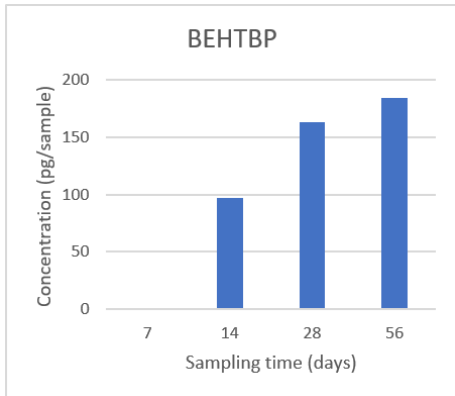
Figure 10 Concentraion (pg/sample) of NBFRs on PUF sampler.

3.3. Passive Air Sampling of Polychlorinated Biphenyls

The average values for the field and laboratory blanks were used as a benchmark for the samples. Values that were below the benchmark were disregarded as background noise in sampling. The results are presented for each analyte in the following bar charts.

3.3.1. ABN

These results showed a lot of matrix contamination in the samples. Many of the parallels were unable to be quantified so the results presented in Figure 11 rely on one, maybe two parallels at best. This could possibly give an inaccurate picture of the actual capabilities of the ABN sampler. The sampler does not seem to show any particular affinity for either the lighter or heavier PCBs. For PCB 37, 74 and 149 the results could stem from contamination, as there are only one sample recorded for each analyte.
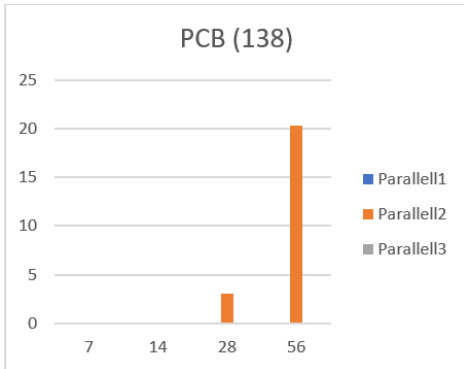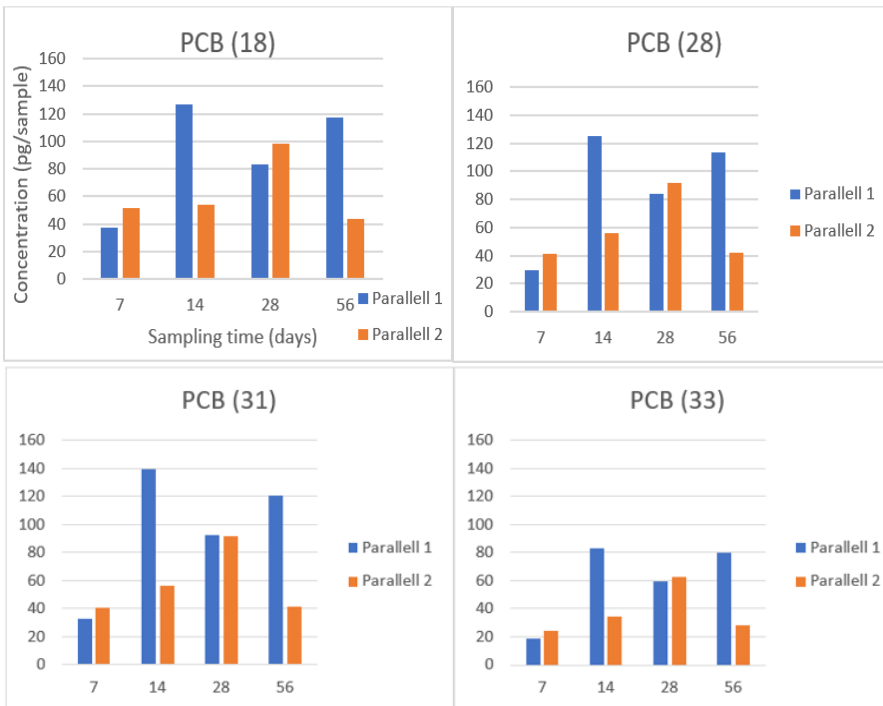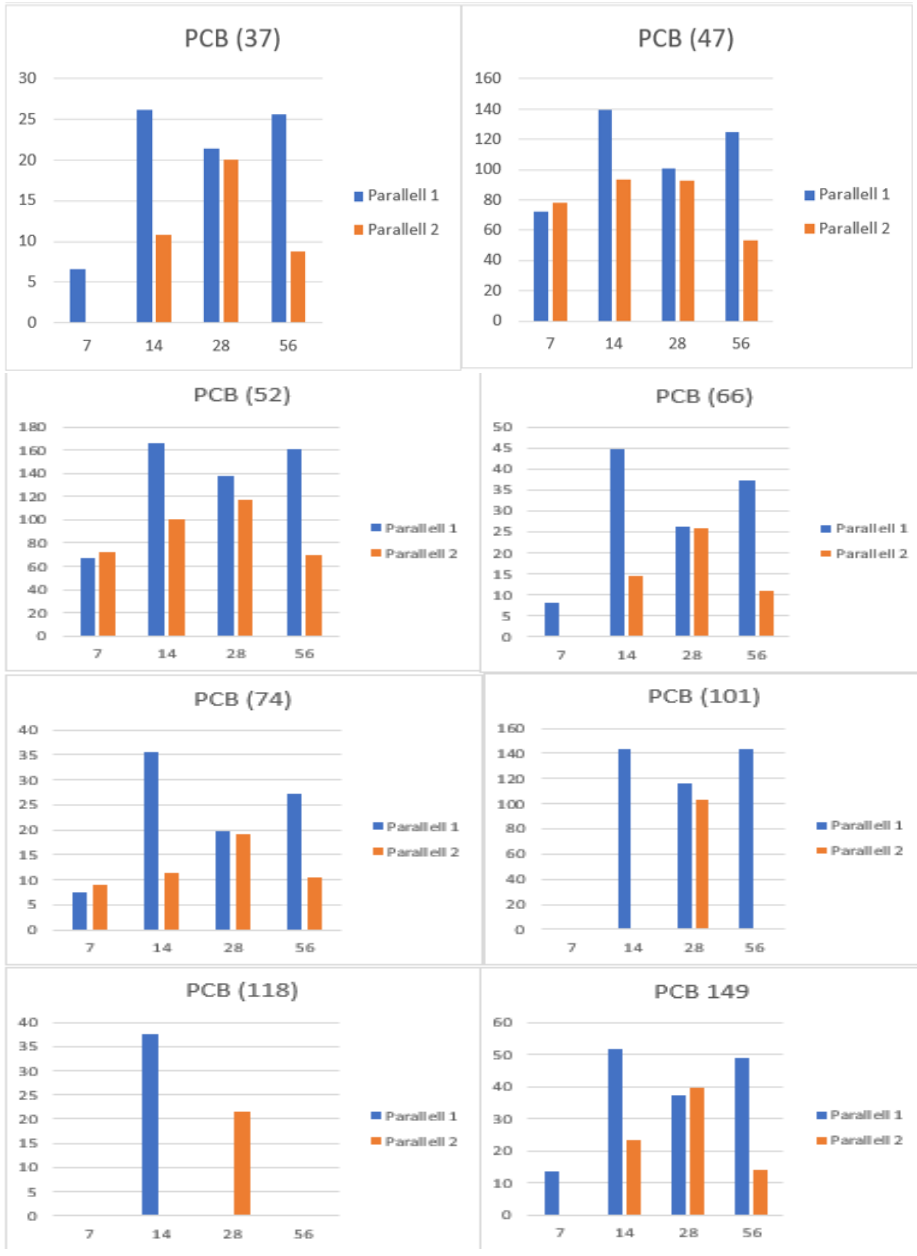
PCB (66)

PCB (74)

PCB (99)

PCB (101)

PCB (105)

PCB (118)

PCB (149)

PCB (153)
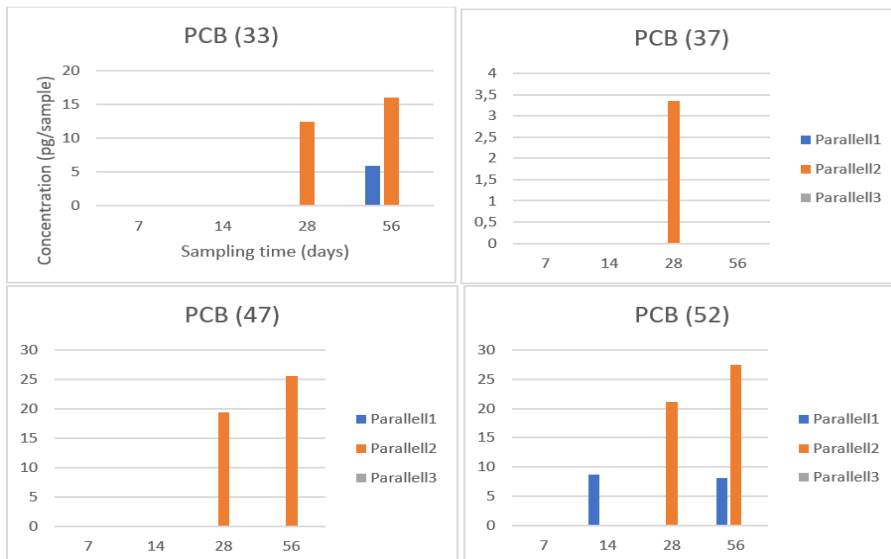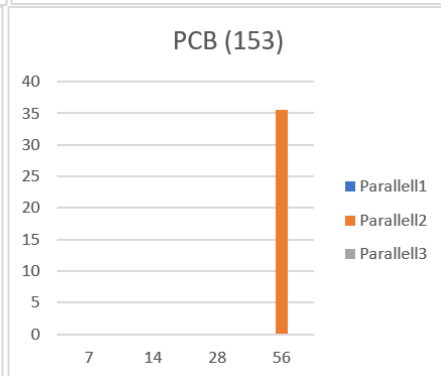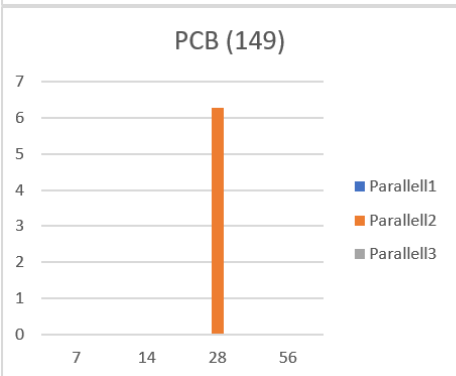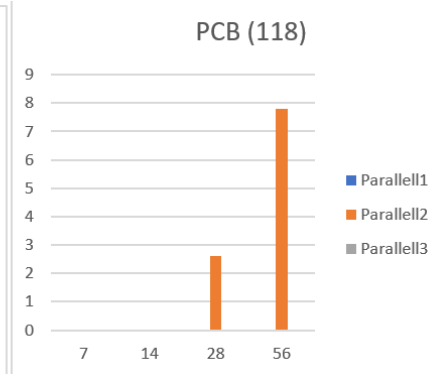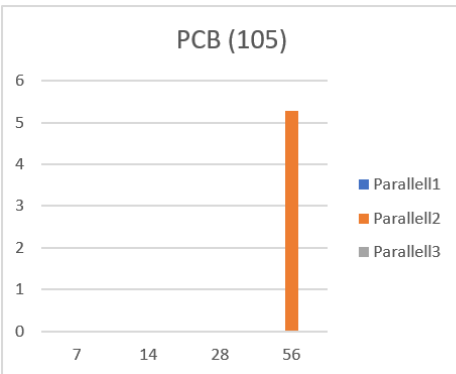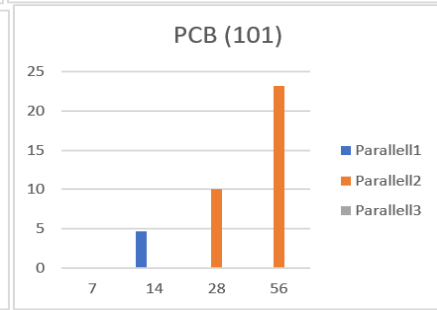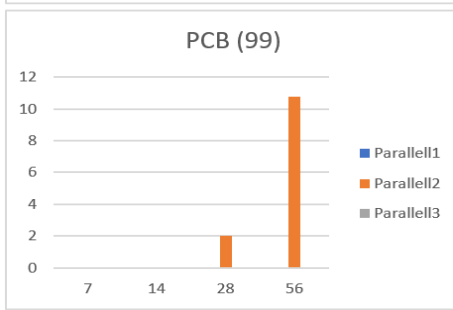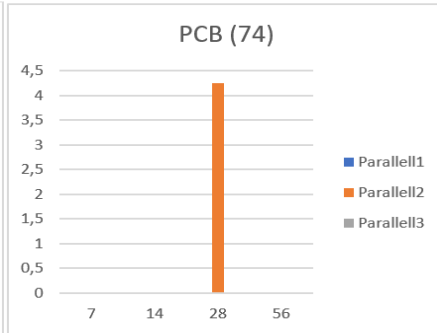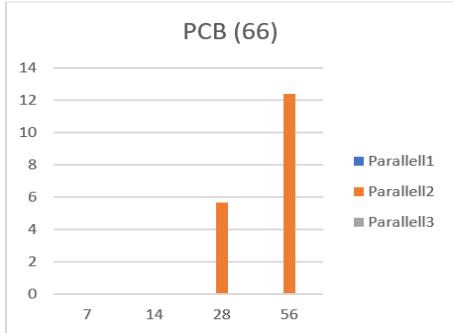
Figure 11 Concentraion (pg/sample) of PCBs in ABN sampler

3.3.2. PDMS

The PDMS sampler results are given in Figure 12. The results are in general higher than the ABN results, but some samples lack a linear uptake of analyte. This sampler shows an affinity for the lighter to mid-range PCBs.
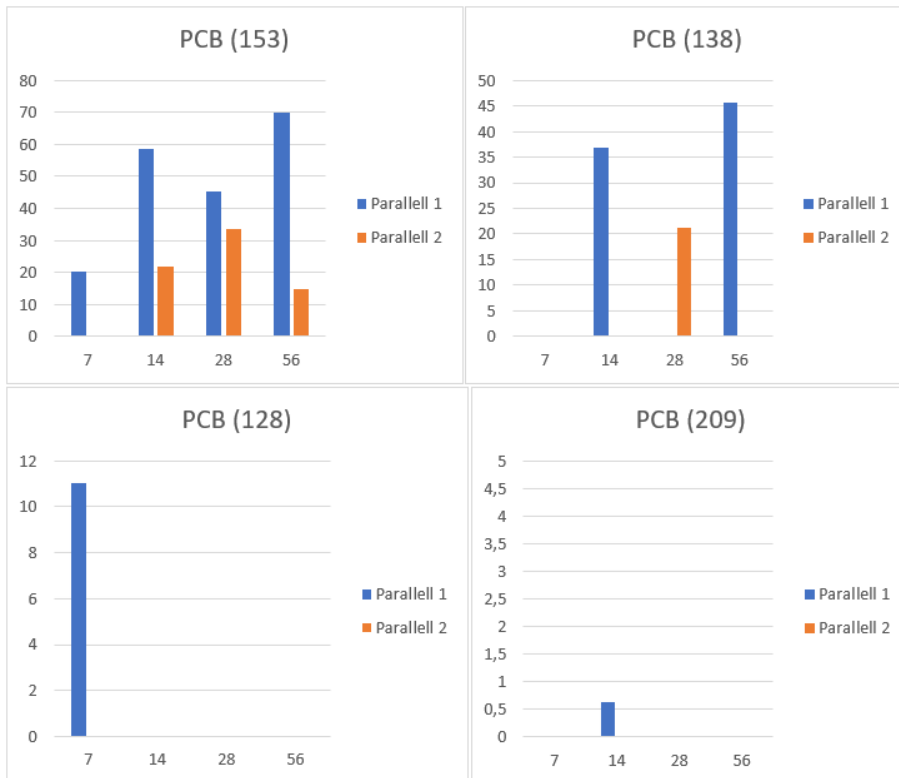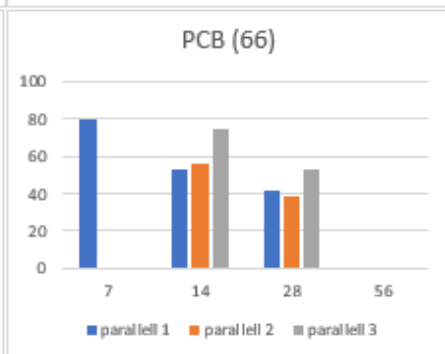
Figure 12 Concentration (pg/sample) of PCBs in PDMS samplers.

3.3.3. POCIS

The results from samples analyzed for PCB's are shown in Figure 13. The Results from the POCIS sampler did not give any definitive answer on the linearity of uptake for this sampler and analyte. The sampler showed an inclination towards lighter PCB's rather than heavier ones. Overall, the POCIS sampler had significantly higher concentration of analyte compared to ABN.

PCB (18)

PCB (28)

PCB (31)

PCB (33)

PCB (37)

PCB (47)

PCB (52)

PCB (66)

PCB (74)

PCB (99)

PCB (101)

PCB (105)

PCB (118)

PCB (141)

PCB (149)

PCB (153)
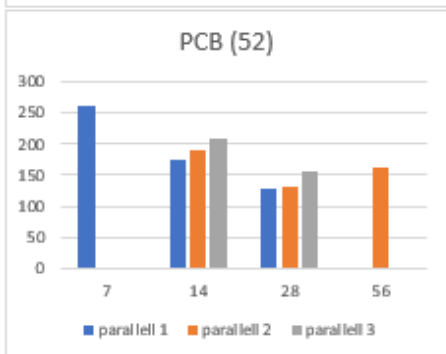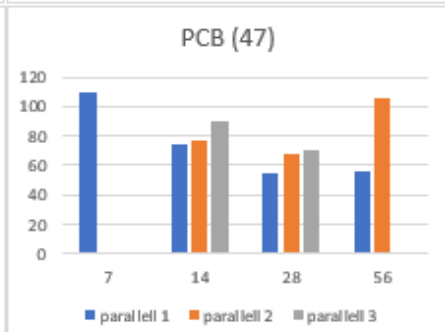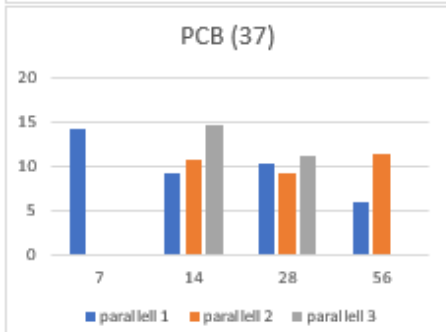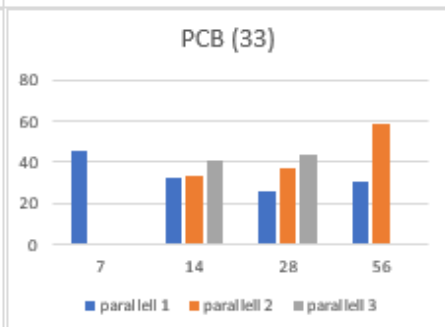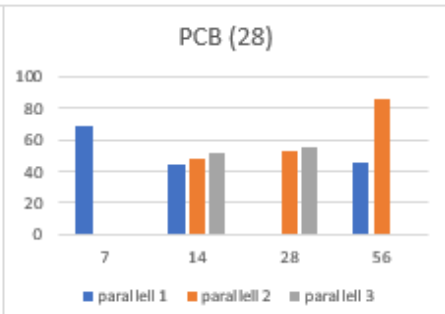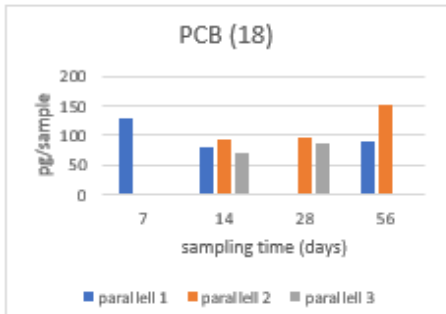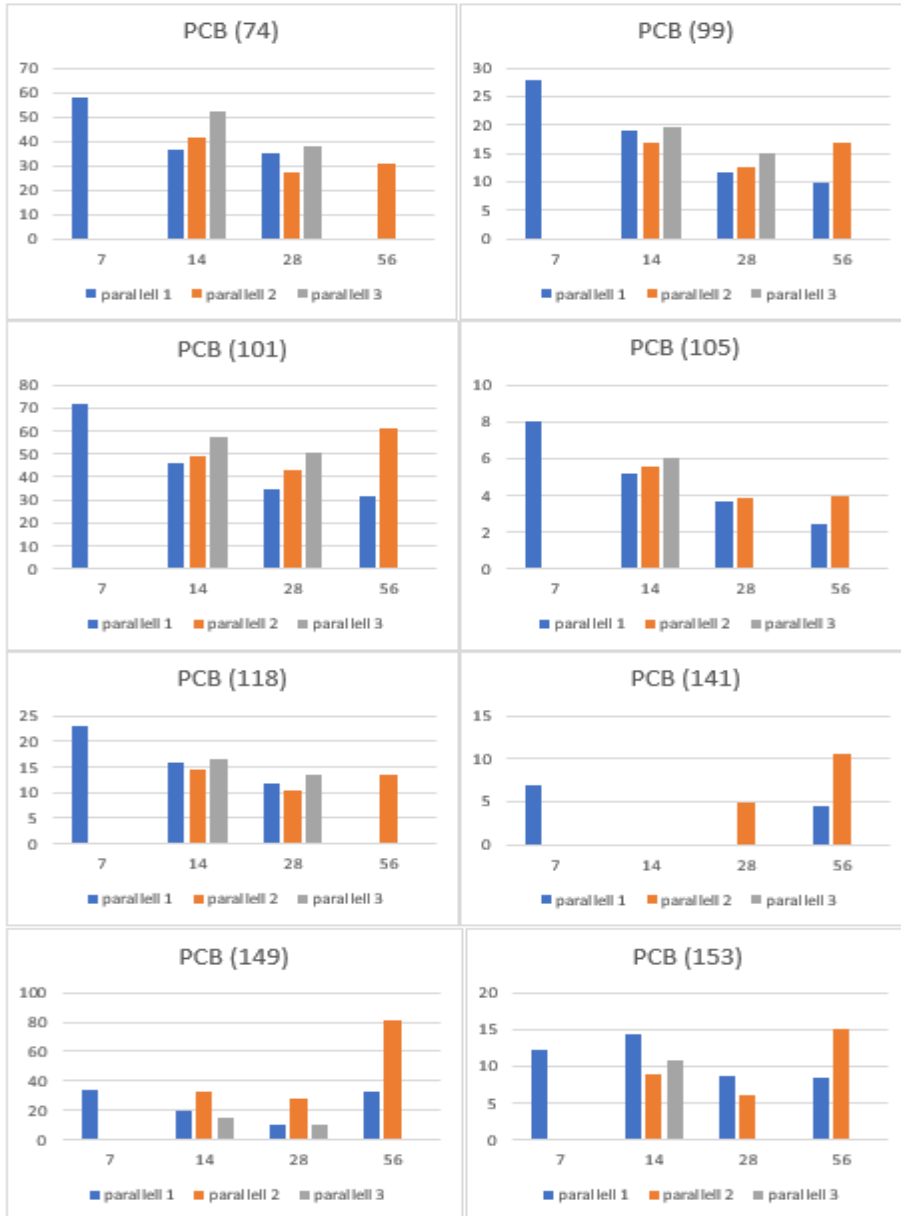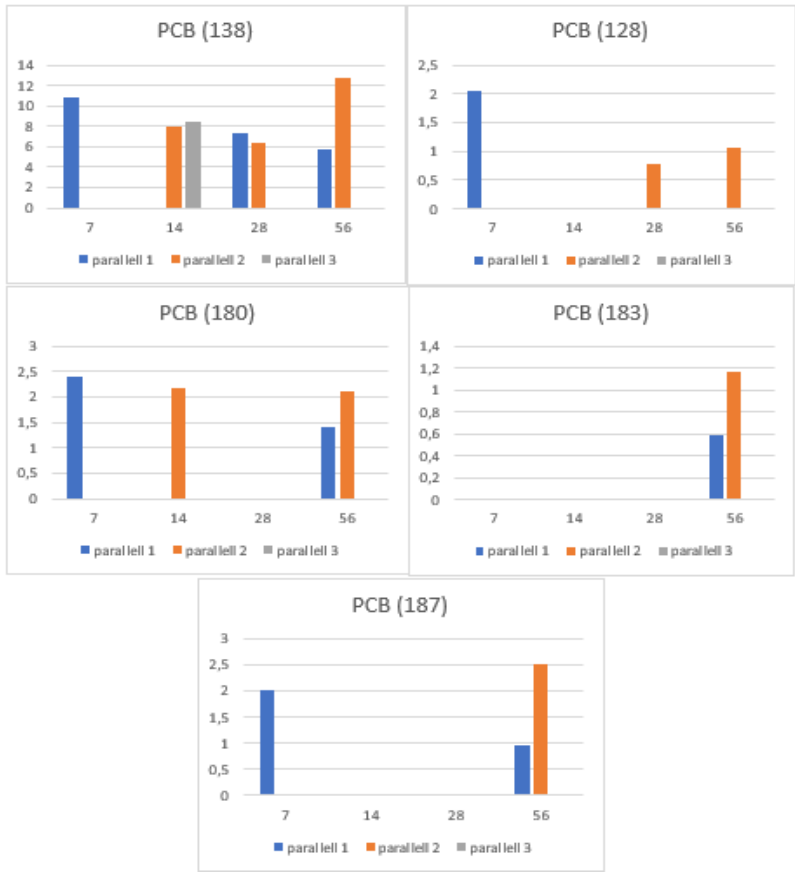
Figure 13 Concentration (pg/sample) of PCBs in POCIS sampler

3.4. Passive Air Sampling of Organophosphorus Flame Retardants

The sample values were compared to the average of both field and laboratory blanks, the sample values that were below that of the average blanks were disregarded as background noise. The results are presented for each analyte in the figures that follow.
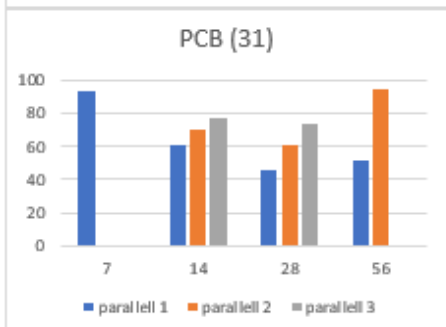
3.4.1. ABN

The results for passive air sampling of OPFRs using ABN are shown Figure 14. For this sampler no analyte showed a clear linear uptake. Certain samples are likely to stem form matrix as the results show a significant decrease or sometimes a lack of analyte from one sampling time to the next. This sampler showed significantly higher values for molecules TCPP and TiBP/TNBP compared to the rest of the analytes.
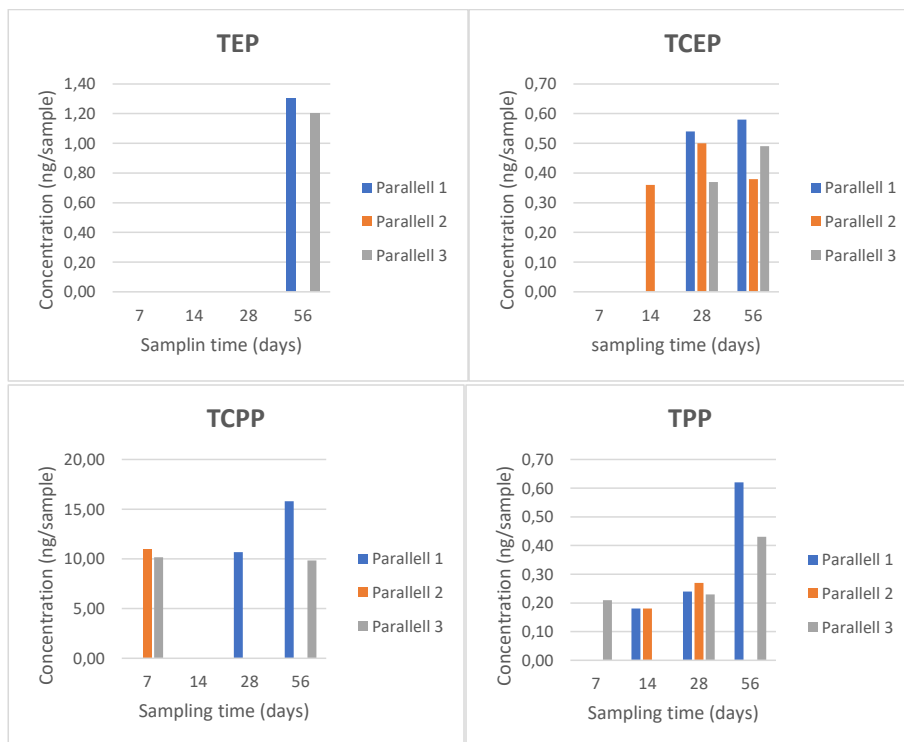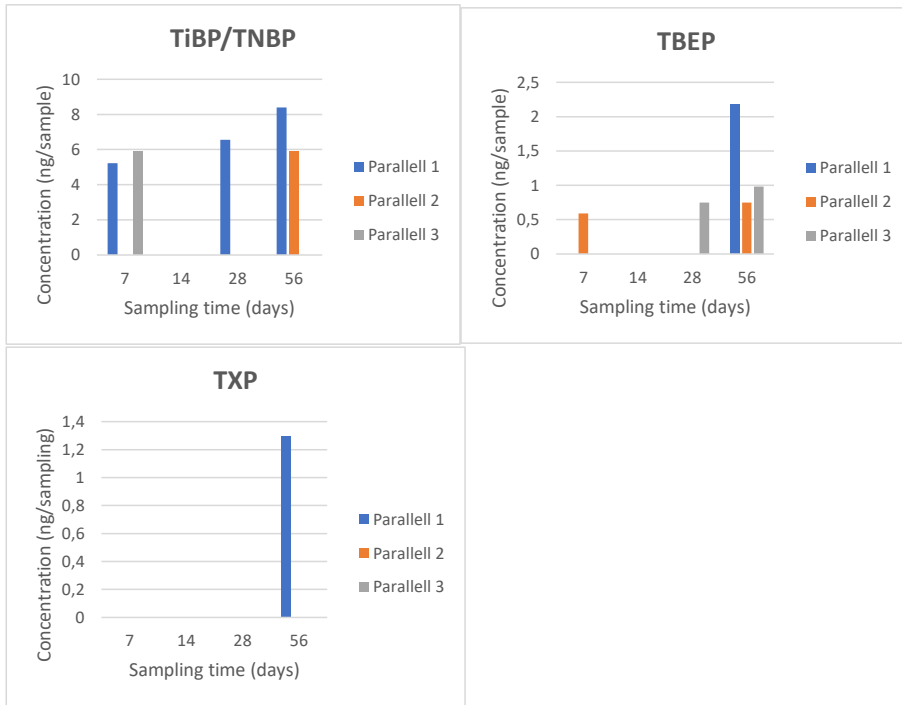
Figure 14 Concentration (ng/sample) of OPFRs on ABN sampler

3.4.2. POCIS

The results for OPFR using POCIS is presented in Figure 15. For the molecules TEP and TCEP there was a slight linear uptake throughout the sampling time. The molecules with the highest concentration on the sampler were TEP, TCPP and TiBP/TNBP with around 10 to 100 times higher concentrations than the rest. The sampler showed possible matrix contamination for the analytes TBEP, TXP and TEHP as some of the previous parallels show higher concentrations than the following.
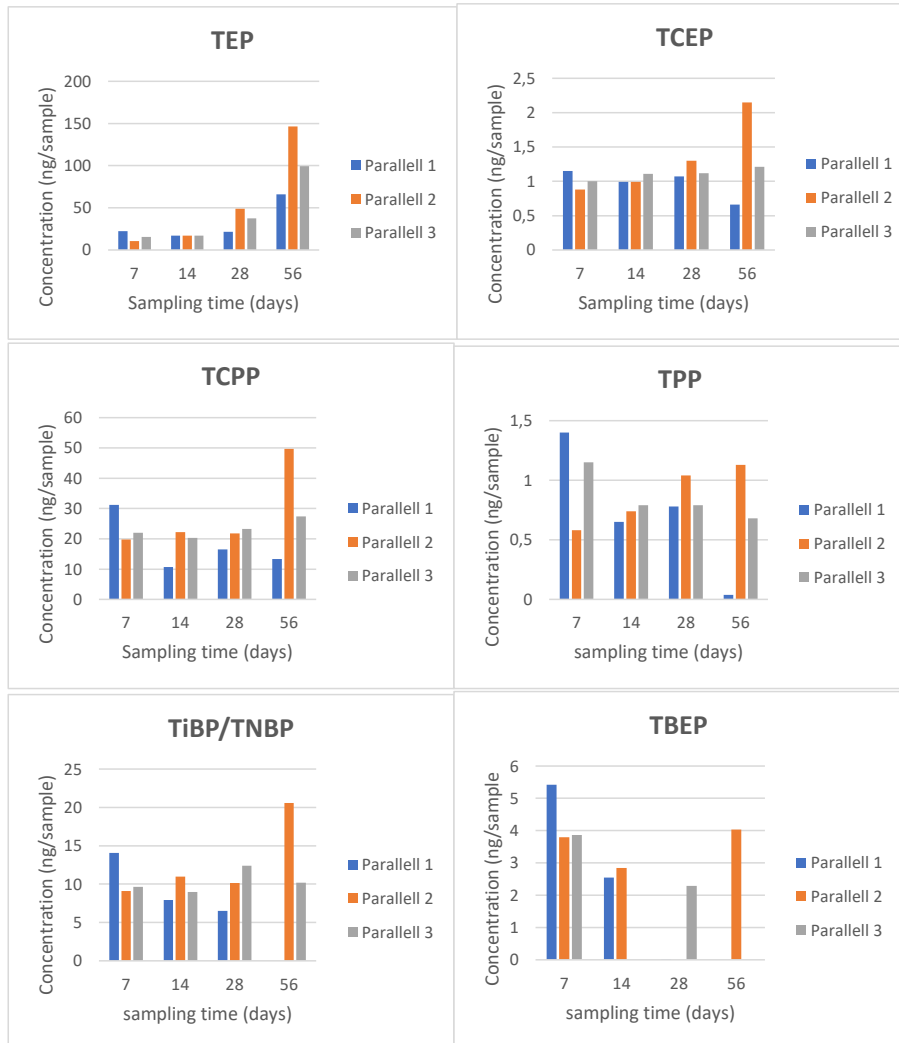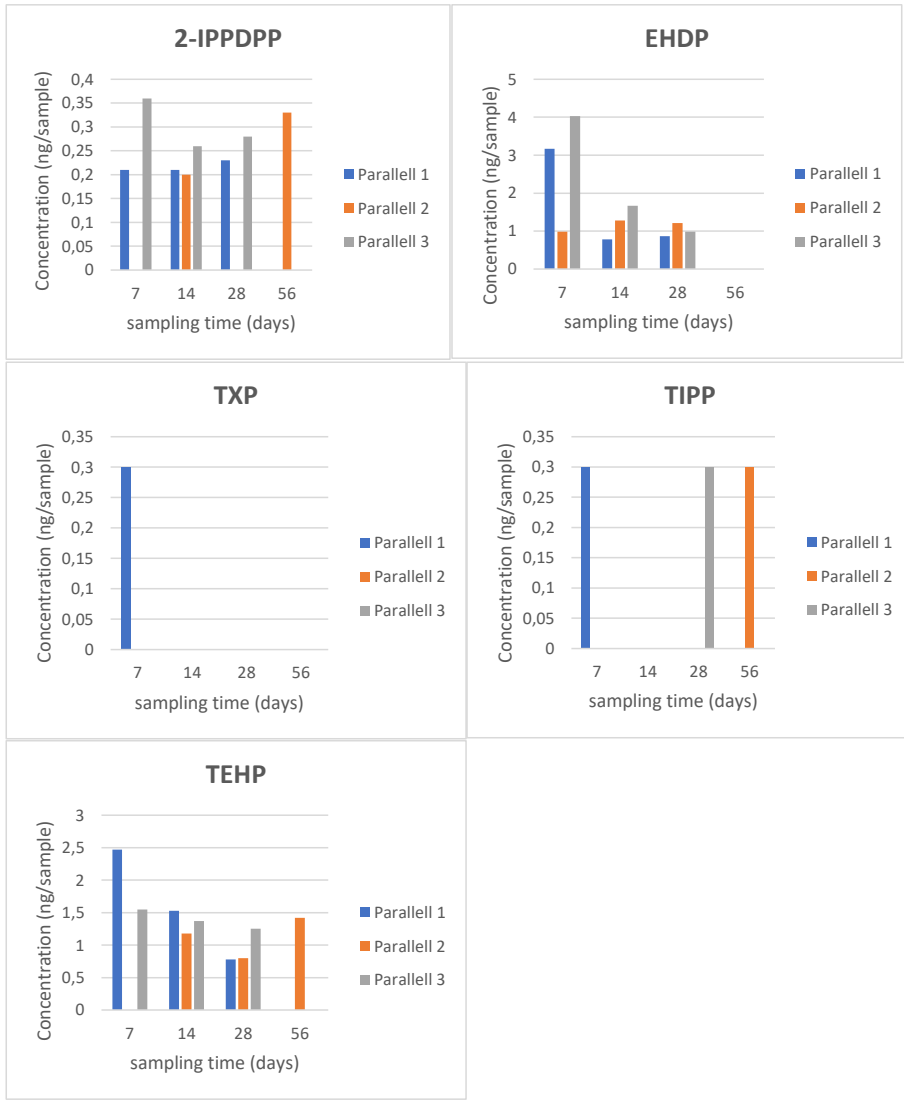
Figure 15 Concentration (ng/sampler) of OPFRs in POCIS sampler

3.4.3. PDMS

For this sampler the results are shown in Figure 16. For this sampler there are several molecules which show a linear uptake, except for one of the parallells taken at 14 days. The molecules with the highest concentration on this sampler are TEP, TCPP, TPP, TiBP/TNBP and TBEP. The parallel at 14 days shows consistently higher values throughout the analytes and is likely a result of contamination.
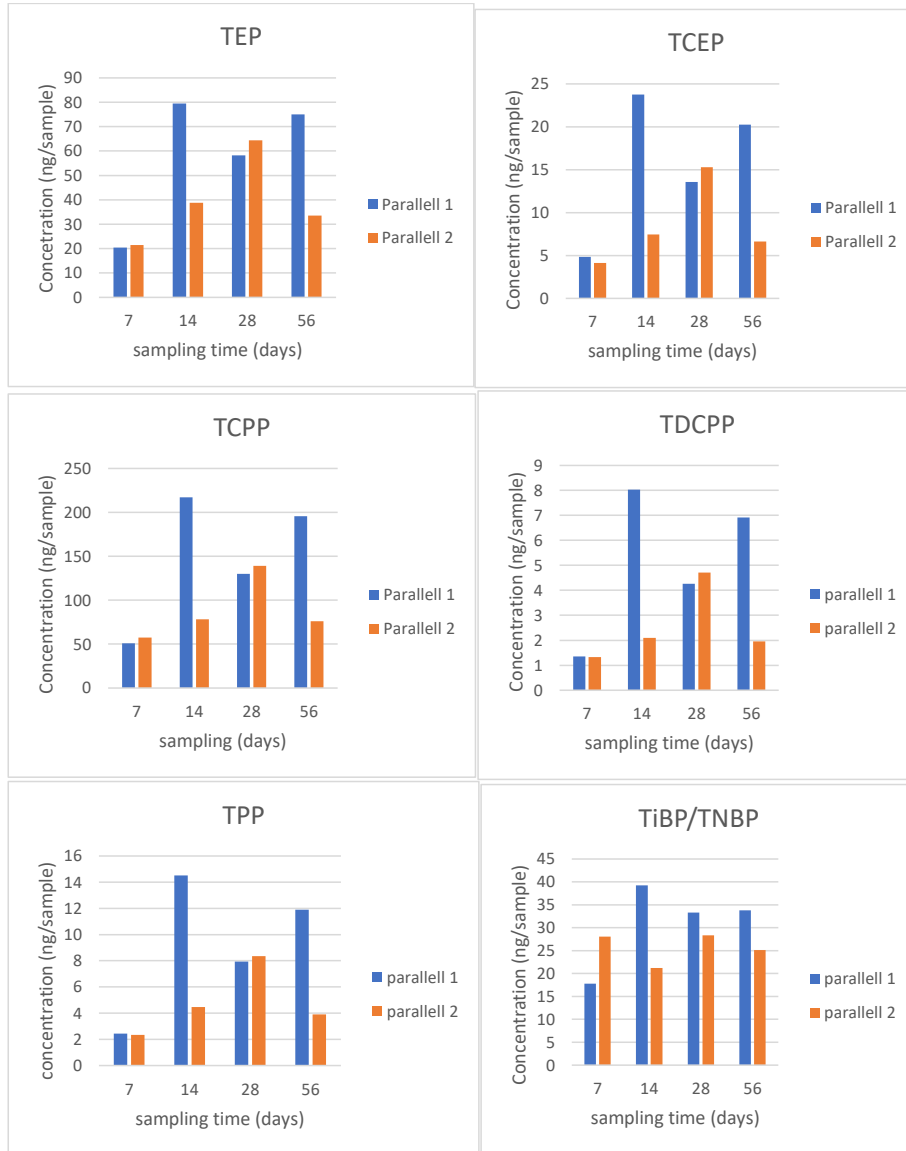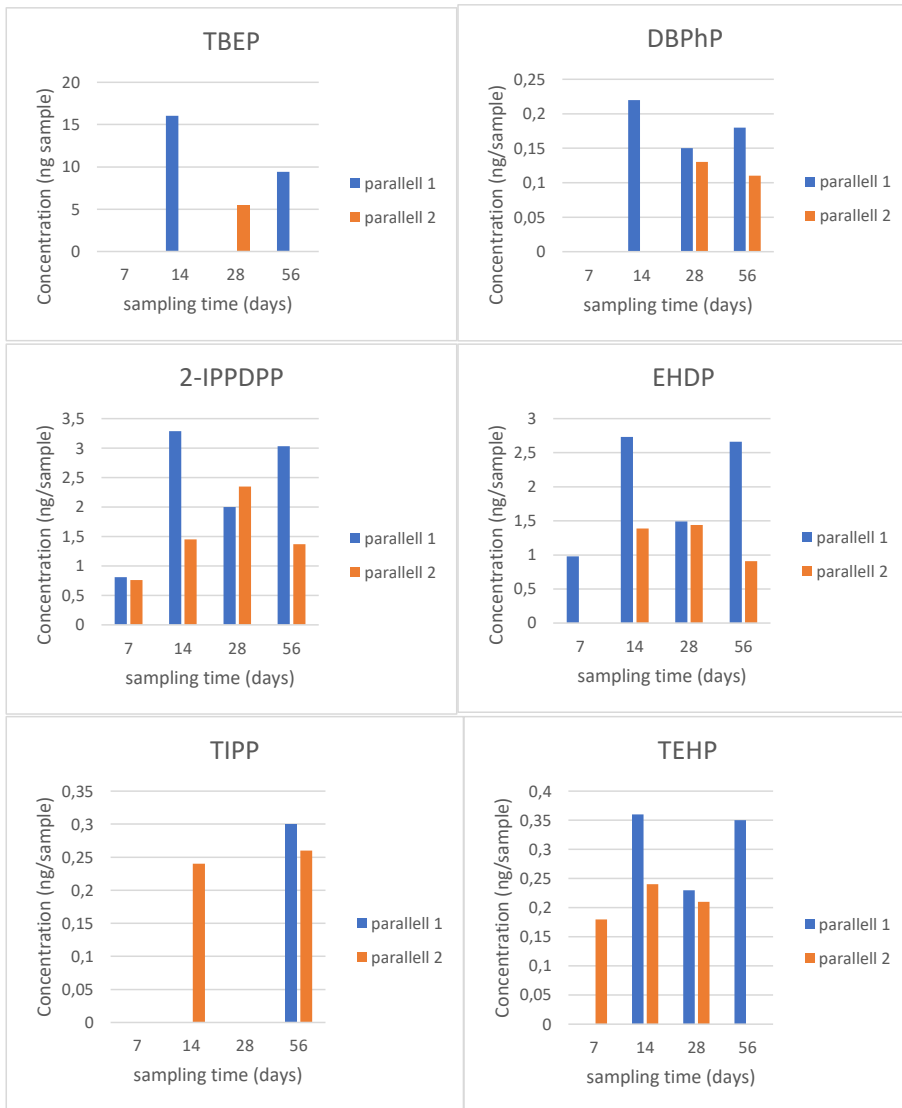
Figure 16 Concentration (ng/sample) of OPFRs in PDMS sampler

3.4.4. PUF

The results of the OPFR analytes found on PUF are presented in Figure 17. This samplers value for 56 days was not included here as the sample was not quantifiable. This leads to a lack of understanding with regards to if there is any saturation of the sampler beyond 28 days. The charts show a mostly linear uptake throughout the analytes. The analyte with the highest concentration was TCPP, reaching a concentration of 361,33 ng/sample at 28 days.
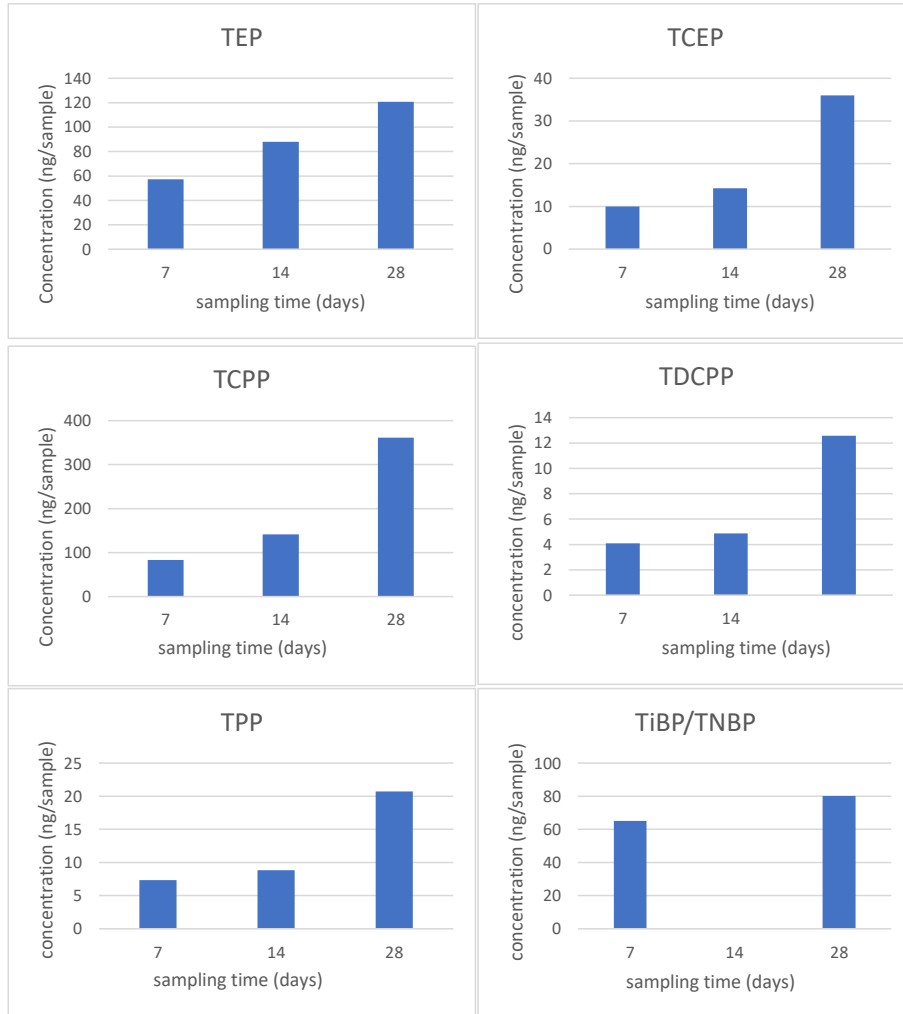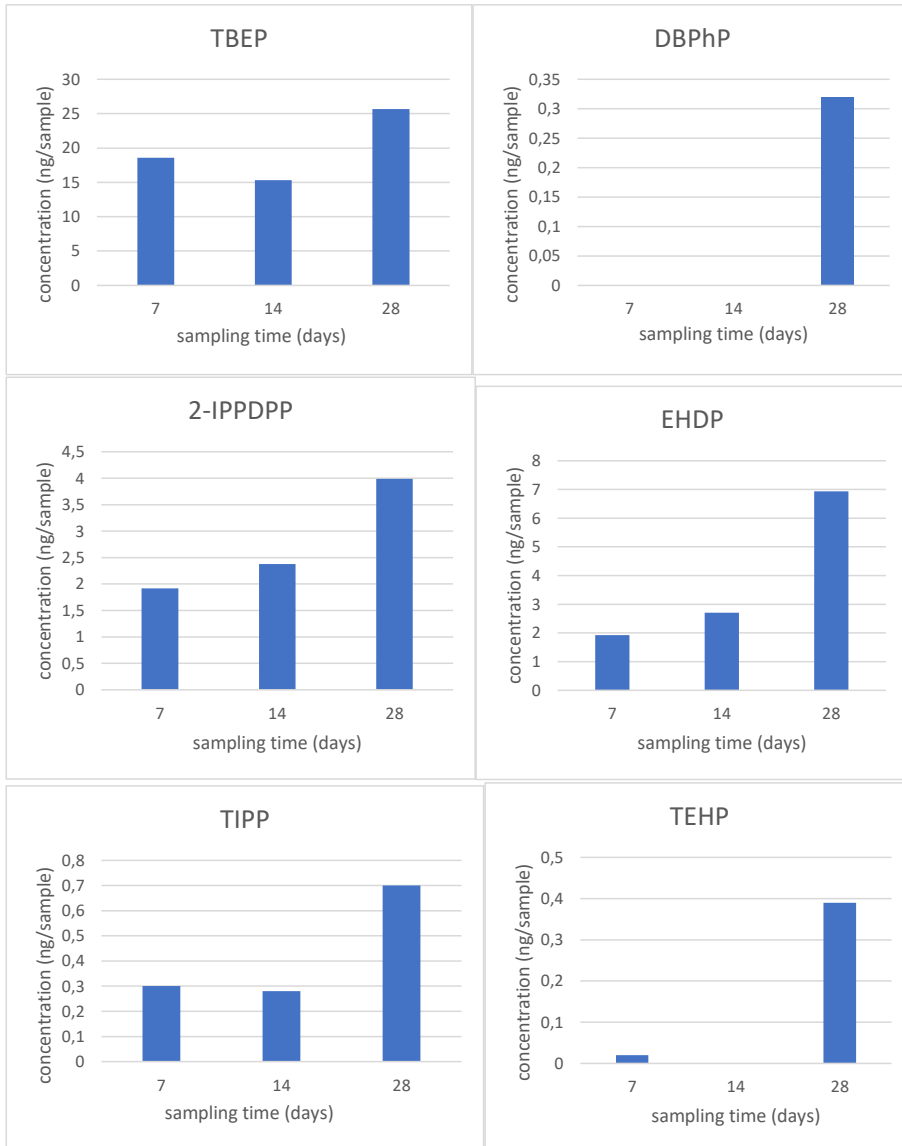
Figure 17 Concentration (ng/sample) of OPFRs in PUF sampler

3.5. Average Blinds of samples

In table 3 the averages of the blank values for each sampler are presented along with the analytes. For PCB the POCIS had the highest average blank values. The PUF sampler did not have any values to compare with for the PCBs. the lowest average blank value is found with the ABN and PDMS, even though some of these samples were not quantifiable. For the NBFRs, there was no clear sampler with the lowest or highest average. The CP analysis resulted in PUF having the highest average blank value and ABN and PDMS with le lowest. The OPFR was also somewhat inconclusive, but it seems that the PDMS and or POCIS had the highest values, depending on which analyte is to be studied.

Table 3. The average blank values for the samplers ABN, PDMS, POCIS and PUF presents along with a graph of the values.

| Analyte	ABN (avg. Blank)	PDMS (avg. Blank)	POCIS (avg. Blank)	PUF (avg. Blank)	Graph
PCB		(pg/sample)			
PCB (18)	9,971	13,604	55,901	-	
PCB (28)	7,448	10,860	31,539	-	
PCB (31)	6,838	8,944	44,020	-	
PCB (33)	5,620	6,202	18,263	-	
PCB (37)	0,000	0,000	0,747	-	
PCB (47)	8,129	69,643	53,974	-	
PCB (52)	7,519	43,566	127,715	-	
PCB (66)	2,575	0,000	43,097	-	
PCB (74)	0,000	4,790	30,270	-	
PCB (99)	1,246	0,000	9,242	-	
PCB (101)	4,526	0,000	23,596	-	
PCB (105)	0,000	0,000	0,462	-	
PCB (114)	0,000	0,000	0,000	-	
PCB (122)	0,000	0,000	0,000	-	
PCB (118)	0,476	0,000	9,822	-	
PCB (123)	0,000	0,000	0,000	-	
PCB (141)	0,000	0,000	0,000	-	
PCB (149)	0,000	0,000	2,944	-	
PCB (153)	2,028	0,000	0,000	-	
PCB (138)	0,000	0,000	0,702	-	
PCB (167)	0,000	0,000	0,000	-	
PCB (128)	0,000	0,000	0,000	-	
PCB (156)	0,000	0,000	0,000	-	
PCB (157)	0,000	0,000	0,000	-	
PCB (170)	0,000	0,000	0,000	-	
PCB (180)	0,000	0,000	0,390	-	
PCB (183)	0,000	0,000	0,000	-	
PCB (187)	0,000	0,000	0,216	-	
PCB (189)	0,000	0,000	0,000	-	
PCB (194)	0,000	0,000	0,000	-	
PCB (206)	0,000	0,000	0,000	-	
PCB (209)	0,000	0,000	0,000	-	
NBFR		(pg/sample)			
ATE (TBP-AE)	0,000	0,000	1,350	0,000	
a-TBECH	0,000	36,958	16,534	0,000	
b-TBECH	0,000	28,539	13,762	0,000	
g/d-TBECH	0,000	6,108	12,714	0,000	
BATE	0,000	5,997	4,676	0,000	
PBT	9,239	9,767	12,295	7,678	
PBEB	3,819	5,923	10,038	2,742	
PBBZ	28,472	0,000	11,102	11,986	
HBB	71,183	19,075	21,963	41,510	
DPTE	4,611	8,048	14,989	8,803	
EHTBB	0,000	0,000	7,221	0,000	
BTBPE	0,000	0,000	21,819	13,518	
BEHTBP	48,831	0,000	33,910	99,908	
DBDPE	0,000	0,000	0,000	0,000	
CP		(ng/sample)			
SCCP	0,000	0,700	6,900	194,567	
MCCP	4,683	6,625	152,783	535,133	
OPFR		(ng/sample)			
TEP	0,000	7,130	1,468	9,820	
TCEP	0,000	0,450	0,245	0,000	
TCPP	9,080	15,223	9,988	19,720	
TPrP	0,000	0,000	0,000	0,000	
TDCPP	0,000	0,000	0,000	0,980	
TPP	0,160	0,448	0,313	1,070	
TiBP/TNBP	5,020	14,270	5,725	59,080	
TBEP	0,580	4,943	2,175	2,820	
DBPhP	0,000	0,000	0,000	0,000	
2-IPPDPP	0,000	0,000	0,037	0,370	
4-IPPDPP	0,000	0,000	0,000	0,000	
TCP	0,000	0,000	0,000	0,000	
BdPhP	0,000	0,000	0,000	0,000	
EHDP	0,000	0,000	0,668	0,000	
B4IPPPP	0,000	0,000	0,000	0,000	
TXP	0,038	0,000	0,000	0,000	
TIPPP	0,000	0,000	0,072	0,000	
TTBPP	0,000	0,000	0,000	0,000	
TEHP	0,195	0,118	0,682	0,210	

4. Conclusion

When looking at ABN as a passive air sampler, the results show a concerning amount of matrix in sample. For the CP analysis the short chain samples were unable to be quantified. The PCB analysis was unable to quantify numerous parallels, giving uncertainty to the overall results. Overall, the sampler showed little to no linearity or affinity for any group of analytes, it is therefore uncertain if there is a saturation of analytes. The sampler could benefit from an alternate method of extraction that takes care to not coextract matrix. Otherwise, the sampler might not be suitable for PAS.

The POCIS sampler outperformed the ABN sampler when looking at PCBs and OPFRs. The POCIS sampler showed an affinity for the lighter PCBs. Although the concentrations were higher for this sampler than for ABN, there similarly was no linearity in the rate of uptake. With regards to CP analysis, the results pointed towards a deterioration of analyte on the sampler. The NBFR analysis indicates that there was a contamination of the set taken down at 28 days. The OPFR analysis showed a slight linear uptake for the molecules TEP and TCEP. The sampler had substantial amounts of matrix for every group of analytes, Therefore, future work should explore different sample preparation procedures. This sampler was extracted on a glass SPE column, whilst the ABN sampler was deployed and directly extracted from a plastic SPE column. A possible solution for the matrix issues with ABN could be to exchange the equipment used during extraction.

The PDMS showed similar concentrations to the POCIS sampler for the SCCP values, but the POCIS outperformed on the MCCP values. This sampler also showed a dip in concentration at 28 days for both SCCP and MCCP. The NBFR values found on PDMS were overall much lower than the POCIS values, but higher than the corresponding ABN concentrations. This sampler had an affinity for the lighter to mid-range PCBs and was also more proficient at accumulating PCBs than ABN but had similar values as POCIS. The OPFRs showed linear uptake for some molecules, except one parallel at 14 days. This implies that a saturation of the sampler has not been reached during the sampling time. The missing internal standards for the NBFR in addition to general matrix issues lead to inaccurate answers for the PDMS sampler.

The SCCP and MCCP concentration on PUF were both significantly higher than the previously mentioned samplers. the Polyurethane foam also has, for the most part, better results when it comes to NBFRs. However, for some NBFR compounds the POCIS is superior. Some components were not quantified due to missing internal standard components. The OPFR values were also mostly higher on the PUF, however PDMS had some similar values to the PUF and POCIS was sometimes better for some components. The OPFR analysis also exhibited linearity throughout. For this sampler, the blanks were not extracted in tandem with the samples, giving room to uncertainty. The PCB values for PUF were unable to be quantified.

Looking at the blank values for each sampler it seems that there are no conclusive samplers which are the most suitable for low blank contribution for each analyte. The best sampler for PCB and OPFR when considering blank contributions, is either ABN or PDMS. For the CP analyte there seems to be several fitting samplers, but there is also the fact that some blanks were not quantified. The NBFRs showed no clear favorable sampler.

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Appendix

NBFRs Week 4

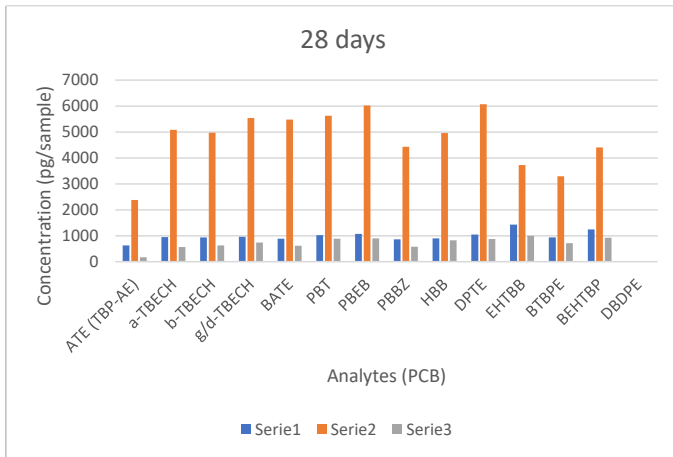Figure 18 presents the values of PCB components on the POCIS sampler exposed for 28 days.

Figure 18. Concentrations of NBFRs on POCIS at 28 days.

Kommentert [JMV2]: Parallell 1,2,3?

Kommentert [JMV3]: (pg/sampke)