Ministry of Environment of Denmark
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Sources of PFAS and their exchange between sediment and surface water in the lakes Furesø, Bagsværd sø, Lyngby sø and the river Mølleåen

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1. Dansk Sammenfatning

Dette studies overordnede formål var at undersøge, om det er sandsynligt at fund af PFOS fundet i Mølleåens vand og i de forbundne søer (Furesøen, Bagsværd sø og Lyngby sø) stammer fra nuværende punkt-forureninger eller skyldes historiske udledninger frigjort fra sedimentet. Derudover giver det nogle forslag til hvilke PFAS det kunne være relevant at måle for i hvilke matricer i fremtidige studier. Studiet viser, at PFOS og deres precursors (prePFOS) forekom i meget højere niveauer i sedimentet end i vand, hvilket indikerer at historiske anvendelser fortsat frigives fra sedimentet til å-systemet. Derudover blev der fundet en lang række andre PFAS, hvoraf tilstedeværelsen af især de kortkædede og meget vandopløselige PFAS som fx 6:2 FTS (en precursor til PFHxA og PFHpA) tyder på at PFAS stadig bruges og udledes til Mølleås systemet.

PFOS niveauerne i vand og sediment blev sammenlignet og en fordelingskoefficient K_D blev udregnet for alle syv lokationer. En $\log K_{D,\,PFOS} = 2.3 \pm 0.6$ blev beregnet og konfirmerede, at PFOS også i dette akvatiske system fordeler sig til sediment, i overensstemmelse med tidligere studier. Punkt-kilder kunne observeres som outliers fra gennemsnitsværdien. Mere forfinede modeller findes, men vil kræve ekstra testning af sediment strukturer, porestørrelser, organisk carbon og porevand for hver lokalitet som input til modellerne.

Til en start blev information indhentet vedr. nuværende og historiske industrielle og andre aktiviteter nær Mølleåen og søerne, som potentielt kunne have anvendt PFAS. Informationerne omfattede også sted positionen af emissionspunkterne (spildevand, bække og evt. run-off fra overflader), samt eksisterende analysedata i vand, jord og spildevand foretaget af Region Hovedstanden og kommunerne Furesø, Rudersdal, Gladsaxe, Lyngby-Taarbæk kommune og tilgængelige på Miljøportalen. Der blev også indhentet informationer fra nyere og ældre avis nyhedsartikler på internettet, fra kemikalie producenters beskrivelser af typiske anvendelser og udfasning af PFAS produktion, og fra lokale foreninger (Birkerød Sejlklub, Bagsværd roklub og Dansk Naturfredningsforening).

Adskillelsen af ansvarsområderne mellem kommuner og regioner, og ikke-forbundne databaser gjorde det både besværligt og tidskrævende at indsamle relevant information - på trods af stor hjælpsomhed fra Regionen og kommunerne for at skaffe os data. En lettere adgang til sådan information, samt også øget koordinering af regionale og kommunale myndigheders studier såsom studie-designs og hvilke PFAS der bliver målt i hvilke medier, vil kunne lette og forbedre kvaliteten af fremtidige studier.

På baggrund af den indsamlede information blev prøvetagningen designet både ifht. lokationer, prøveudtagnings-medier, hvilke PFAS der skulle måles for og med hvilken følsomhed. Til eksempel blev 6:2 FTS tilføjet til måleprogrammet og følsomheden af PFAS i sediment-analyserne estimeret. Det blev også vurderet, at de kommercielle PFAS Total (ved EOF-CIC) analyser ikke var tilstrækkeligt følsomme for PFAS i sediment og analysen blev derfor ikke gennemført. Syv prøvetagningsteder blev udvalgt, heraf seks nær kendte eller mistænkte forureningskilder, samt et referencepunkt væk fra kendte punktkilder (Furesøen - Nørreskov). Vand og sediment prøver blev udtaget, men ikke fisk da de grundet årstiden (vinter) forventes at opholde sig på dybt vand, og dermed ikke nær de lave prøvetagningssteder. I fremtiden vil det være højst relevant at analysere både for PFAS Total ved laboratorier med tilstrækkeligt lave detektionsgrænser i sediment samt i biota.

En suspect screening analyse metode blev udviklet til at kunne måle primært for anioniske PFAS i sedimentet ved brug af væske kromatografi koblet til nøjagtig massespektrometri (LC-MS), for

33 PFAS (med reference standarder) og 28 PFAS (uden reference standarder) og med fokus på PFOS precursors og andre perfluoroalkyl syrer.

Vandprøverne blev opsamlet over 4 uger fra november til december 2022 ved brug af Sorbiceller, der sampler aktivt og dermed giver gennemsnitskoncentrationer over opsamlingsperioden. Sedimentet blev udtaget i december 2022. Både sediment og vand prøver blev sendt til et kommercielt akkrediteret laboratorium til analyse for 22 PFAS ($PFAS_{22}$). Sedimentet blev derudover analyseret for mere end 50 PFAS ved suspect screening (LC-QTOF MSMS) på Københavns universitet.
Resultaterne i dette studie, kan ikke anvendes til at udtale sig om den generelle tilstand i vandområderne, men er et udtryk for hvordan indholdet og fordelingen af de forskellige undersøgte PFAS i vand og sediment har været i undersøgelsesperioden.

Vandanalyserne indikerede, at der udover den menneskeskabte PFAS baggrundsforurening er PFAS punktkilde emissioner. Sandsynlige kilder er udledninger fra rensningsanlæg som modtager spildevand fra mindre industrier (fx metal forkromning), forskningsinstitutioner og husholdninger. Især 6:2 FTS – som bl.a. anvendes i elektronik, metal, forkromnings, kemisk, malings, gummi og plast, renserier og brandsluknings-industrier som erstatning for PFOS og andre PFAS – blev fundet i høje mængder. Fortolkningen af data blev imidlertid begrænset af, at 6:2 FTS også blev fundet i blind-prøverne. Opfølgende undersøgelser af kommunen viste at 6:2 FTS ikke var tilstede i Birkerød Sejlklubs vandhanevand (som var blevet brugt til forberedelse af Sorbicellerne), og heller ikke forekom i prøveudtagningsbeholderne, eller i det kommercielle laboratorium. En potentiel kilde kunne have været luft eller støv fra imprægnerede sejl i Sejlklubbens lokale. På den baggrund er der blevet givet forslag til fremtidige prøveudtagnings-forberedelser generelt og specifikt for Sorbiceller for at undgå PFAS blindværdier. Dette understreger vigtigheden af *altid* at inkludere mindst to *prøveudtagnings*-blindprøver, særligt i studier der anvendes til beslutningstagning af myndigheder.

For at kunne vurdere hvilke PFAS der kunne være relevante at medtage i fremtidige måleprogrammer, blev der set på hvilke PFAS der indgår i gældende reguleringer, og hvilke der med sandsynlighed vil komme til at indgå i kommende reguleringer af relevans for Danmark og det akvatiske miljø. De akkrediterede $PFAS_{22}$ niveauer var 6-19 gange over $EQS_{ferskvand}$ for PFOS og derivater (prePFOS) på 0.65 ng/L. Overskridelserne skyldes alene PFOS, eftersom prePFOS ikke blev målt i vand. I forhold til den (*i 2022 foreslåede*) $PFAS_{24}$ sum-værdi, lå summen af $PFAS_{22}$ 2.7-7 gange over de 4.4 ng/Lfor $EQS_{ferskvand}$, målt i PFOA-ekvivalenter. Omregningen til PFOA-ækvivalenter bruger såkaldte 'Relative Potens Faktorer' (RPF) og inkluderer *ikke* 6:2 FTS. $EQS_{freshwater}$ (4.4 ng/L). For de syv PFAS hvor RPF er givet i et interval, er den højeste RPF anvendt. De højeste niveauer blev fundet nær rensningsanlæg og et tidligere metal forkromningsanlæg. Generelt, hvis PFAS er tilstede i vandmiljøet, vil det være mindre sandsynligt at vand vil overskride $EQS_{ferskvand}$ for $PFAS_{24}$, da vandopløselige, kortkædede PFAS typisk har RPFs <1, Sediment og biota vil omvendt have en større risiko for at overskride grænseværdierne for $PFAS_{24}$, da disse medier ophober lang-kædede PFAS, som typisk har RPF >1.

Sediment analyserne for $PFAS_{22}$ (eksklusiv prePFOS) målt med target analyser af det kommercielle laboratorium fandt kun PFOS over detektionsgrænsen. EQSsediment (13500 ng PFOS og derivater/kg dw) blev ikke overskredet for nogen lokationer, men var meget tæt på ved Bagsværd rostadion.

Suspect screeningen for mere end 50 PFAS foretaget at Københavns Universitet fandt imidlertid høje værdier af prePFOS og af andre PFAA og prePFAA på flere lokationer. Sumværdien for $PFAS_{24}$ (i PFOA-ækvivalenter og som ww) blev sammenlignet med EQS_{biota} (77 ng/kg ww). På alle lokationer var PFOA-ækvivalenterne over EQS_{biota} (3-33 gange over). Hvis prePFOS var blevet inkluderet i PFOA-ækvivalenterne ville det have resulteret i markant højere niveauer over $EQS_{biota.}$ Igen blev de højeste niveauer fundet ved Bagsværd Rostadion, hvor N-Me-FOSAA og

N-Et-FOSAA (transformationsprodukter af N-Me/Et-FOSE) dominerede, men kilden kunne ikke endeligt fastslåes. Høje niveauer blev også fundet af især langkædede PFAAere ved Mortonsvej (tidligere metal forkromningsvirksomhed) og ved Dybendal renseanlæg, der modtager spildevand fra små-industri, Danmarks Tekniske Universitet (DTU) og husholdninger. Isomer mønstrene for PFSAerne og deres derivater, indikerer at stofferne er fremstillet ved elektrokemisk fluorinering (ECF), som man som oftest tilskriver historiske kilder før 2002 hvor PFOS og derivater blev fremstillet af 3M. Imidlertid er ECF produktionen de sidste årtier flyttet til bl.a. Kina og Indien, så nuværende emissioner ville kunne forekomme på trods af PFOS restriktionen, hvis virksomheder lovligt (undtagelser fra restriktionerne) eller ulovligt anvender PFOS og derivater købt i fx Kina eller Indien. Desuden kan de anvende PFAS som endnu ikke er omfattet af restriktioner, eller hvis branchen ikke falder under industri emissionslovgivningen.

I fremtidige undersøgelser vil følgende tiltag kunne bidrage til at få overblik og derved kunne mindske risiciene ved PFOS, og PFAS generelt:

- **analyse af PFOS precursorerne (prePFOS) i sediment og biota** - det gældende EU vandrammedirektiv omfatter 'PFOS og derivater', men er trods deres historiske store anvendelse og forekomst p.t. ikke inkluderet i monitoreringsprogrammerne. En simpel sum af koncentrationerne (RPF=1) ville kunne anvendes.
- **information om hvilke PFAS, herunder prePFOS, som er undtaget af REACH forbud og stadig lovligt kan anvendes i hvilke processer** – anvendeligt for myndigheder som udgangspunkt for tildeling og kontrol med virksomheders miljøgodkendelser, samt krav til planlægning af monitoreringsprogrammer.
- **monitorering af flere af de (grupper af) PFAS, hvis anvendelser er ved at blive begrænset/forbudt** – af REACH, EFSA og i Danmark, herunder PFAS total analyser. Dette ville kunne guide virksomheder til en omstilling til PFAS-fri produktion, og dermed reducere den samlede belastning og behov for fremtidig oprensning af bevidste PFAS udledninger.
- **prioritering af monitorering af de PFAS der hyppigst forekommer i et medie:** Det er økonomisk og praktisk umuligt at måle for alle PFAS, så det er nødvendigt at prioritere hvilke PFAS man vil måle for. .PFAS total kan anvendes til screeninger og til kontrol af grænseværdier sat for PFAS Total. Man ville også kunne vælge hvillke PFAS det er mest sandsynligt forekommer og derfor er mest relevante at måle efter i forskellige medier. Kort-kædede PFAS forekommer oftest i vand hvorfra de optages i planter; lang-kædede PFAS forekommer oftest i sediment og i biota (dyr). PFAS håndbogens anbefalinger (Danish Regions, 2022) har allerede foreslået en del relevante stoffer, og dette studie foreslår yderligere PFAS der ville kunne understøtte fremtidige kildeopsporinger og risikovurderinger af PFAS i vand.
- **regelmæssig opdatering af PFAS monitoreringslister**: PFAS reguleringen udvikler sig hastigt, og i forskellige tempi på tværs af reguleringerne som fx vandrammedirektivet, REACH eller industri emissions direktivet. Reguleringerne kan derfor ikke forventes at være harmoniserede i EU eller nationalt. Det gælder både hvilke PFAS der er inkluderet, hvilke brancher der er opfattet af en regulering, og hvilke anvendelser der kan være omfattet af udfasning eller forbud – og evt. bliver erstattet af andre PFAS. En national opdateringsfrekvens på 3-5 år vil være hensigtsmæssigt, og evt. koblet til data fra overvågning og early warning screeningsprogrammer.

En særlig tak for det gode samarbejde til Birkerød Sejlklub for brug af lokaler, samt Bagsværd roklub for tilladelse til at opbevare sejlbåd, til Københavns Kommune for lån af sejlbåd, til Eurofins for at hjælpe med at udsætte Sorbicellerne, til Bo Svensmark (emeritus på Københavns Universitet) for at transportere båden og være vores kaptajn. Også en stor tak til Region Hovedstaden for indgående indføring i data og problemstillinger, og til kommunerne omkring Mølleåen og søerne for samarbejdet.

2. Background and aims

2.1 Environmental monitoring and aims of the study

In Denmark, environmental monitoring is performed by different authorities. Municipalities provide environmental permits to industries/activities, whereby they have information on regulated chemicals used by that activity, and checks that emissions going into the environment from permitted activities are compliant with the issued permits. The Danish EPA surveys pollution *in the environment* (through the NOVANA program), where seven PFAS[1] currently are monitored in biota (fish) (FT, 2023). In case that a non-compliant pollution is *detected* in the monitoring, the municipality has the responsibility to locate the source of the pollution and take risk management measures, such as giving an injunction or remediation. Regions survey that soil pollution, does not pose a risk to groundwater, surface water, nature or human health. Their planning is based on which activities that are likely to cause pollution, and may remediate polluted soils and water when the pollution is of high concern to society, and the polluter no longer exist or can pay.
More information on the roles of authorities can be found in the PFAS Handbook (Danish Regions, 2022).

In this project a case study of ‘Furesøen, Bagsværd sø, Lyngby sø and Mølleåen was selected, since PFOS and other PFAS had been detected in the waters, but sources were not fully accounted for. A recommendation not to fish had consequently been put in place, and is still upheld. The Municipalities and the Regions had wished for a survey of whether the sediment of the waterbody could partially or fully explain the PFOS levels found in the water.

The Danish EPA specified the following aims of this study:

1) Survey of possible historic and current point-sources of PFAS pollution emitted to Mølleåen.
2) Set-up of a method for suspect screening for PFOS and PFOS precursors in sediment, water and fish.
3) Assess whether, and to which extent, it is possible PFOS and other PFAS in the sediment can be exchanged to water and fish, and thereby be the cause – partly or fully – of the high levels found in water and fish both in Mølleåen, and in general.
4) Assess if it is reasonable that the DK EPA recommends to analyse for PFOS (or other PFOS) in the sediment in case of exceedance of the PFOS EQS (or detection of high concentrations of other PFAS) in surface waters and/or biota.

The following sections provide an overview of the special characteristics of the large family of PFAS, their uses, how some PFAS may transform to form other PFAS, analytical approaches in source-tracking, and regulation of PFAS in Danish freshwater systems.

2.2 PFAS properties

This section only gives a brief background on PFAS properties, since information on uses, characteristics, environmental contamination, health concerns and current regulations and regulatory developments on PFAS is summarised elsewhere (EEA, 2019), in ‘PFAS håndbogen’ (Danish Regions 2022) and at the IRTC website (IRTC 2022).

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[1] PFHxS, PFOS, PFOSA, PFOA, PFNA, PFDA, PFUnDA.

Per- and polyfluorinated alkyl substances (PFAS, in Danish called ‘fluorstoffer’) is a large group of substances consisting of more than 10,000 commonly used chemicals, which can be divided into sub-categories as shown in Figure 1. PFOS belongs to the group of so-called perfluoroalkyl sulfonic acids (PFSAs), while PFOA belongs to the group of perfluorocarboxylic acids (PFCAs), and PFSAs and PFCAs belong to the larger group of perfluoroalkyl acids (PFAAs). The PFAAs are very persistent, because all the carbon atoms are bound to flour instead of hydrogen, and the flour-carbon bonding is the strongest binding known. The fluorocarbon chain is therefore very resistant to heat, chemicals and physical stresses. Because the fluorocarbon chains do not form bonds, they also repel both water, oil and dirt. In addition to the *per*-fluorinated PFAS there are *poly*-fluorinated PFAS, which have both fluorine and hydrogen atoms bound to the carbon chain. The hydrocarbon part of the molecule can as other organic materials be degraded, but the remaining fluorocarbon hardly degrades. Larger PFAS compounds are called precursors of perfluoroalkyl acids (PFAA), because they may break down to PFAAs. According to the 2021 OECD definition (Wang, 2021) a PFAS is a chemical with one $–CF_2–$ unit, whereas other definitions (incl. the OECD 2018 definition) may require more than one unit.

The special physical-chemical characteristics of PFAS, has resulted in their use in a broad variety of products and processes. More than 200 use categories exist for just 1400 PFAS (Glüge et al., 2020, with reference to PFAS according to the OECD 2018 definition), across industries and in consumer products. Several studies on PFAS uses have been made in Denmark, as well as in the Nordic countries and further abroad (Danish Regions 2022). A key use of PFAS released to the open environment are as surfactants, used for instance as aqueous film forming agents (AFFF) in firefighting foams and in hard chrome plating batch, as emulsifiers in creams and polymers, as coatings on metal, stone, wood, paper, plastic, textiles and leather and as spreading agents in paints, detergents and pesticides. The widespread uses, has led to a global contamination of the environment and of people.

Due to their poor degradability PFAS accumulate in the environment and in people. The larger ‘long-chain PFAS, from around C6 and up in PFAAs, tend to accumulate in biota (proteins), sediment and soil. The smaller ‘short-chain’ polar PFAS will accumulate in water, and the short-chain non-polar will accumulate in air (e.g. F-gases). In recent years multiple lines of evidence have shown that PFAS have multiple hazards, though they differ in their toxicities due to their varied structures. Hazards and observed effects on humans and biota include immunotoxicity, metabolic diseases (such as increase in cholesterol), kidney/liver/testicular cancers and endocrine disruption. F-gases, used as refrigerants and as feedstock for other PFAS or formed as by-products/degradation products during synthesis or incineration, are very potent greenhouse gases contributing to climate change and thereby harm Earth systems. Further information on uses, characteristics, environmental contamination, health concerns and current regulations and regulatory developments on PFAS is summarised elsewhere (EEA, 2019).

Until recently large quantities of PFAAs, such as PFOA and PFOS, were used directly, that is by addition of PFOA as an emulsifier (dispersion agent) during fluoropolymer production of Teflon, or use of PFOS in hard chromeplating and in firefighting foams. Releases from such activities, as well as the manufacturing of fluoropolymers into products, have resulted in hot-spot polluted sites everywhere, including in Denmark. Impurities of PFAAs in products containing precursors of PFAAs, are also considered direct sources.

Indirect sources of PFAAs, relate to the degradation of PFAA precursors. Examples are PFOS derivatives also called prePFOS, and more generally PFSA derivatives, which in Figure 1 are called PASF-based substances. Typical uses are Scotchban used for various types of coating of e.g. paper and textiles. Studies from Vancouver Bay and Tyrifjord (Norway) found that the PFOS-precursor concentrations then were much higher than PFOS (10x or more). Another example is fluorotelomer sulfonates (FTS) and their derivatives, which have replaced many of the PFSA derivaties – and which degrade to PFCAs.

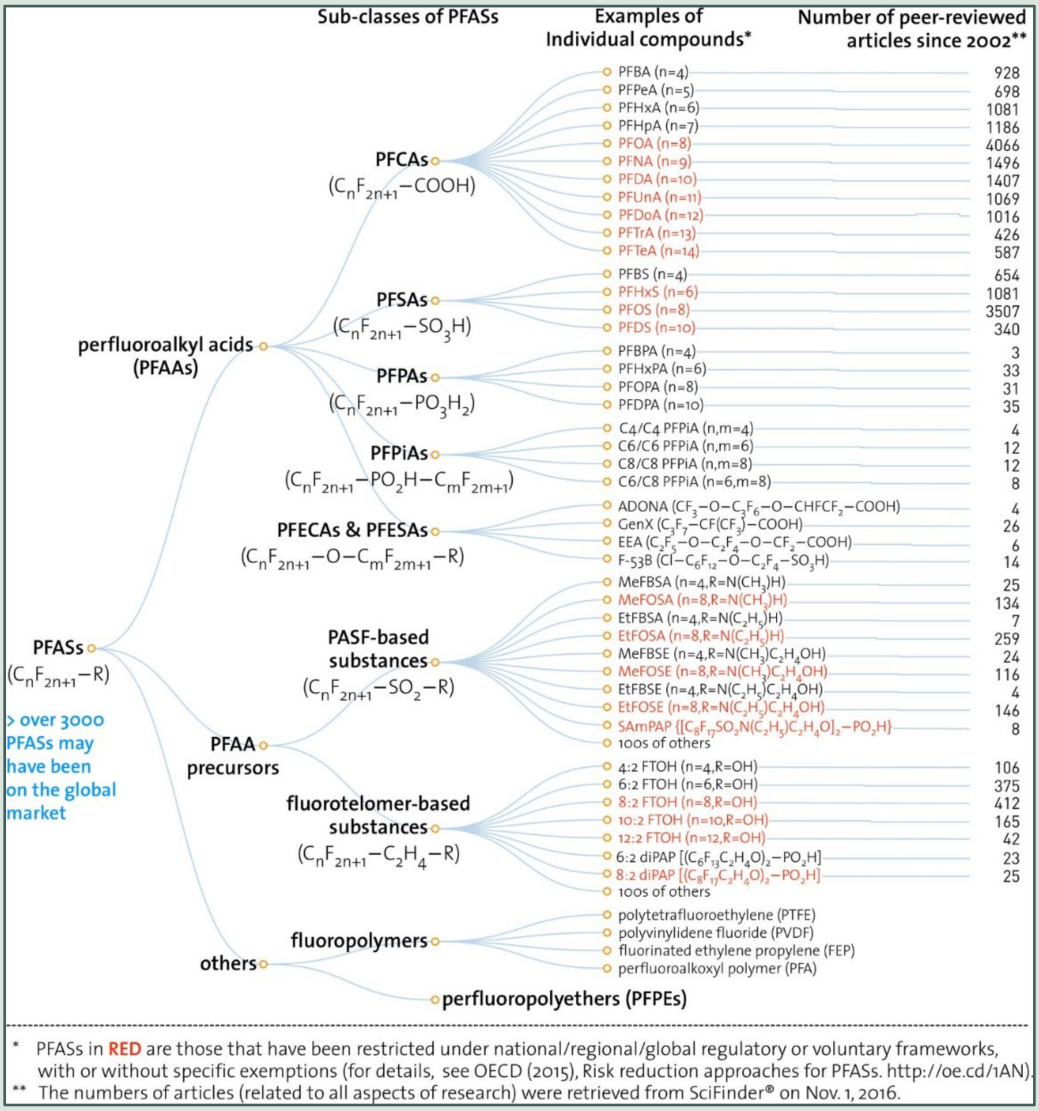

FIGURE 1. Overview of some of the most studied PFAS, categorised into family trees (Wang et al. 2016).

2.3 PFAS analysed in this study and their significance in source identification

In this study, more than 40 PFAS chemical reference standards were included in the method validation to enable the identification and quantification of PFAS in sediments. However, for the majority of PFAS neither the native (pure) chemical reference standards, nor technical blends used by industry are commercially available. Native internal standards (IS) were used when available. If native IS were not available, resembling PFAS IS which eluted nearby were used (Pieke et al. 2017). For some PFAS a chemical reference standard was not available, and they were quantified against another closely eluting PFAS and are shown in a different colour in Table 1. While this introduces uncertainty both in the identification and in the quantification, it should be balanced against the greater inaccuracy of not measuring and hence assessing PFAS present in the environment.

TABLE 2.1. PFAS analysed in this study. Calibration and Internal standards marked in the colour yellow where quantified with other structures than the target analyte. PrePFCAs and prePFSA can degrade to the PFCA or PFSA respectively with the same number of fluorinated carbon atoms. 6:2 FTS may hence degrade to PFHpA (and PFHxA), and Me-FOSAA may degrade to PFOS. Precursors of PFBS are denoted by 'B', PFHxS by 'Hx' and PFOS by 'O'. RPFs are taken from the SCHEER 2022 report (DK EPA, 2023) which are used to calculate the PFOA equivalents for each PFAS. PFAS marked in green were quantified, PFAS marked in blue were quantified against other PFAS or other internal standards, and PFAS marked in purple were not quantified. PFHxDA, PFODA, diPAPs$_{x+y=12,14,16}$ and S- diPAPs$_{x+y=12,14,16}$, mono-PAPs, di-PAPs and SamPAPS were not quantified because the identification was uncertain (retention times could not be established, due to lack of chemical standards and overlapping *m/z*'s from organohalogen compounds). Gen-X, ADONA and F53Ba/b were analysed, but due to lack of time they were not quantified.

Substance group	Full name	Abbreviation(s)	No.C_F in alkyl backbone	CAS No.	Analyte structure	Calibration std	Internal std (IS)	Relative Potency Factor (RPF)
PFCA	Perflurobutanoic acid	PFBA	3	375-22-4	C3F7•COOH	PFBA	PFBA-IS	0.05
	Perfluoropentanoic acid	PFPeA	4	2706-90-3	C4F9•COOH	PFPA	PFPeA-IS	0.03
	Perfluorohexanoic acid	PFHxA	5	307-24-4	C5F11•COOH	PFHxA	PFHxA-IS	0.01
	Perfluoroheptanoic acid	PFHpA	6	375-85-9	C6F13•COOH	PFHpA	PFHpA-IS	0.505
	Perfluorooctanoic acid	PFOA	7	335-67-1	C7F15•COOH	PFOA	PFOA-IS	1
	Perfluorononanoic acid	PFNA	8	375-95-1	C8F17•COOH	PFNA	PFNA-IS	10
	Perfluorodecanoic acid	PFDA	9	335-76-2	C9F19•COOH	PFDA	PFDA-IS	7
	Perfluoroundecanoic acid	PFUnDA	10	2058-94-8	C10F21•COOH	PFUnDA	PFUnDA-IS	4
	Perfluorododecanoic acid	PFDoDA	11	307-55-1	C11F23•COOH	PFDoDA	PFDoDA-IS	3
	Perfluorotridecanoic acid	PFTrDA	12	72629-94-8	C12F25•COOH	PFTrDA	PFDoDA-IS	1.65
	Perfluorotetradecanoic acid	PFTeDA	13	376-06-7	C13F27•COOH	PFTeDA	PFTeDA-IS	0.3
	Perfluorohexadecanoic acid	PFHxDA	15	67905-19-5	C15F31•COOH	-	-	0.02
	Perfluorooctadecanoic acid	PFODA	17	16517-11-6	C17F35•COOH	-	-	0.02
prePFCA	4:2 Fluorotelomer sulfonate acid	4:2 FTS 4:2 FTSA	4	757124-72-4	C4F9•C2H4•SO3H	4:2 FTS	4:2 FTS-IS	-
	6:2 Fluorotelomer sulfonate acid	6:2 FTS 6:2 FTSA	6	27619-97-2	C6F13•C2H4•SO3H	6:2 FTS	6:2 FTS-IS	-
	8:2 Fluorotelomer sulfonate acid	8:2 FTS 8:2 FTSA	8	39108-34-4	C8F17•C2H4•SO3H	8:2 FTS	8:2 FTS-IS	-
	10:2 Fluorotelomer sulfonate acid	10:2 FTS 10:2 FTSA	10	120226-60-0	C10F21•C2H4•SO3H	8:2 FTS	8:2 FTS-IS	-
Substance group	**Full name**	**Abbreviation(s)**	**No.C_F in alkyl backbone**	**CAS No.**	**Analyte structure**	**Calibration std**	**Internal std (IS)**	**Relative Potency Factor (RPF)**

Substance group	Full name	Abbreviation(s)	No.C_F in alkyl backbone	CAS No.	Analyte structure	Calibration std	Internal std (IS)	Relative Potency Factor (RPF)
	12:2 Fluorotelomer sulfonate acid	12:2 FTS 12:2 FTSA	12	149246-64-0	C12F25•C2H4•SO3H	8:2 FTS	8:2 FTS-IS	-
	6:2 Fluorotelomer alcohol	6:2 FTOH	6	647-42-7	C6F13•C2H4•OH	-	-	0.02
	8:2 Fluorotelomer alcohol	8:2 FTOH	8	678-39-7	C8F17•C2H4•OH	-	-	0.04
	HFPO-DA or Gen X (Ammonium perfluoro (2-methyl-3-oxahexanoate)	GenX		62037-80-3	CF3•O•CF(CF3)•COOH	-	-	0.06
	ADONA (Ammonium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy)propanoate)	ADONA		958445-44-8	CF3•O•C3F6•O•CHF•CF2•COOH			0.03
	C6O4 (Acetic acid / 2,2-difluoro-2-((2,2,4,5-tetrafluoro-5-(trifluoromethoxy)-1,3-dioxolan-4-yl)oxy)-)	C6O4		1190931-41-9	CF3•O•(cyclic CF•O•CF2•OC3F6•O•CHF) •CF2•COOH			0.06
PFSA	Perfluorobutane sulfonic acid	PFBS	4	375-73-5	C4F9•SO3H	PFBS	PFBS-IS	0.001
	Perfluoropentane sulfonic acid	PFPeS	5	2706-91-4	C5F11•SO3H	PFPeS	PFBS-IS	0.3005
	Perfluorohexane sulfonic acid	PFHxS-lin PFHxS-br	6	355-46-4	C6F13•SO3H	PFHxS-lin PFHxS-br	PFHxS-lin-IS PFHxS-lin-IS	0.6
	Perfluoroheptane sulfonic acid	PFHpS	7	375-92-8	C7F15•SO3H	PFHpS	PFHxS-lin-IS	1.3
	Perfluorooctane sulfonic acid	PFOS-lin PFOS-br	8	335-67-1	C8F17•SO3H	PFOS-lin PFOS-br	PFOS-lin-IS PFOS-lin-IS	2
	Perfluorononane sulfonic acid	PFNS	9	474511-07-4	C9F19•SO3H	PFNS	PFOS-lin-IS	-
	Perfluorodecane sulfonic acid	PFDS	10	335-77-3	C10F21•SO3H	PFDS	PFOS-lin-IS	2
prePFSA		Me-F**B**SE	4	34454-97-2		?	N-Me-F**O**SE-IS	-
		Me-F**Hx**SE	6	?		?	N-Me-F**O**SE-IS	-
		F**O**SA PFOSA	8	754-91-6	C8F17•SO2•NH2	F**O**SA	FOSA-IS	-
		F**O**SAA PFOSAA	8	2806-24-8	C8F17•SO2•NH•(CH2•CO2H)	?		-
		N-Me-F**O**SA me-FOSAA	8	31506-32-8	C8F17•SO2•NH•(CH3)	?		-

Substance group	Full name	Abbreviation(s)	No.C_F in alkyl backbone	CAS No.	Analyte structure	Calibration std	Internal std (IS)	Relative Potency Factor (RPF)
Substance group	**Full name**	**Abbreviation(s)**	**No.C_F in alkyl backbone**	**CAS No.**	**Analyte structure**	**Calibration std**	**Internal std (IS)**	**Relative Potency Factor (RPF)**
		N-Me-F**O**SAA	8	2355-31-9	C8F17•SO2•N(CH3)•CH2•COOH	N-Me-F**O**SAA	N-Me-FOSAA-IS	-
		N-Et-F**O**SAA et-PFOSAA	8	2991-50-6	C8F17•SO2•N(C2H5)•CH2•COOH	N-Et-F**O**SAA	N-Et-FOSAA-IS	-
		N-Me-F**O**SE	8	24448-09-7	C8F17•SO2•N(CH3)•C2H4•OH	N-Me-F**O**SE	N-Et-FOSAA-IS	-
		N-Et-F**O**SE et-PFOSE	8	1691-99-2	C8F17•SO2•N(C2H5)•C2H5•OH	N-Et-F**O**SE	N-Et-FOSAA-IS	-
		di-SAm-PAPS di-SN-PAPS	2*6 = 12		[C6 F 13 •SO2 •N•(C2H5)•C2 H4 •O]2•PO2H	N-Et-FOSAA	N-Et-FOSAA-IS	-
		di-SAm-PAPS di-SN-PAPS	2*7 = 14		[C7 F 15 •SO2 •N•(C2H5)•C2 H4 •O]2•PO2H	N-Et-FOSAA	N-Et-FOSAA-IS	-
		di-SAm-PAPS di-SN-PAPS	2*8 = 16	2965-52-8	[C8 F 17 •SO2 •N•(C2H5)•C2 H4 •O]2•PO2H	N-Et-FOSAA	N-Et-FOSAA-IS	-

2.3.1 Perfluoroalkyl sulfonic acids (PFSA)

Perfluoroalkyl sulfonic acids (PFSA) are a class of substances with fully fluorinated carbon backbone of varying length, and a sulfonic acid (-SO_2H)"tail". The most studied chemical is perfluorooctane sulphonic acid (PFOS), with eight carbon atoms. PFOS has been listed under annex B in the Stockholm convention since 2009, due to its adverse environmental effects. The production and use of this substance is therefore restricted. Perfluorohexane sulphonic acid (PFHxS), with a six carbon backbone, has recently been given more attention. PFBS is less likely to bioaccumulate than its long-chain analogues but is very mobile and as persistent as other PFAS. A literature study of 80 articles performed by NGI for the Norwegian Environmental Agency showed that PFBS is found in 88 % of all water samples reported in these articles (NGI/NIVA, 2019).

Before 2002, the typical PFSA synthesis was by electrochemical fluorination of carboxylic acids which can be made with even or un-even numbers of carbon-chain lengths. Most often only with one chain-length is present, but with both linear (-lin) and branched (-br) PFSAs which is a signature of electrochemical fluorination. The branched PFSAs can somewhat degrade, and will therefore become less prevalent over time compared to the linear PFSAs. The spatial gradient from a source has also been used to determine a likely source where the branched PFSAs will be more prevalent. This was used in a Norwegian study of PFOS sources in Tyrifjorden both for PFSA and PFSA-precursors (Sam-PAPS) (NGI/NIVA, 2019). Since the degradation depends on the ecosystems degradation capacity it is however not possible to tell the age of a contamination just based on the ratio of branched to linear PFSA. While the prevalence of branched PFSAs may indicate an older source of PFSAs and/or precursors, the continued electrochemical production of PFSAs in other parts of the world (e.g. in China), means that a newer sources/uses cannot be ruled out when branched PFSAs are found.

Before 2002, PFOS derivatives (i.e. prePFOS) were widely used. Upon degradation in the environment and in biota and humans prePFOS can form PFOS (Benskin 2013). Other PFSA derivatives with shorter chain lengths have since been produced. On Nov 30th 2023 IARC listed PFOA and PFOS as suspected carcinogens for humans (Rahm, 2023). ECHA has recommended that the EU Commission also restricts use of PFCA with longer chain lengths than PFOA (C9-C14).

Concentrations of both linear and branched PFOS (br-PFOS) were quantified, and linear and branched isomers were summed, cf. the SCHEER 2022 report supporting the EQS stating, that *'All PFAS isomers (linear and branched) should be measured as remarked by the experts and the results presented as the sum of all isomers. Compliance should be checked against the sum of all isomers'* (DK EPA, 2023).

2.3.2 Perfluoroalkyl carboxylic acids (PFCA)

Perfluoroalkyl carboxyl acids (PFCA) are a class of substances with a fully fluorinated carbon backbone of varying length, and a carboxylic acid (-COOH)"tail". The most studied of these substances is perfluorooctanoic acid (PFOA) with a backbone of eight carbon atoms, of which seven are fully fluorinated. PFOA has been restricted in production and use in the Western world (included as a candidate of substance of very high concern (SVHC) by the European Chemical Agency (ECHA) and is also on the recommended list under review for the Stockholm convention. On Nov 30th 2023 IARC listed PFOA and PFOS as suspected carcinogens for humans (Rahm, 2023). ECHA has recommended that the EU Commission also restricts use of PFCA with longer chain lengths than PFOA (C9-C14).

Some PFCAs e.g. PFOA (C8) and PFNA (C9) have been and are still being used directly as dispersion agents (emulsifiers) in the polymerisation of fluoropolymers such as Teflon. This is a significant source of pollution globally from fluoropolymer production sites, and manufacturing of fluoropolymer containing products. They also occur as impurities in other PFAS chemicals, that can degrade to PFCAs. Historically PFCAs were used as starting/intermediate chemicals for other PFAS (e.g. PFOS), and may still be in countries where the so-called electrochemical fluorination is being used (e.g. in China).

2.3.3 Precursors of perfluoroalkyl sulfonic acids (PFSAs) and perflouroalkyl carboxylic acids (PFCAs)

Polyfluorinated PFAS, may contain both one or several perfluorinated alkyl chains, as well as hydrocarbon moieties and typically other chemical moieties. Common for all of these PFCA and PFSA derivatives is that the part that is not fluorinated can degrade, and ultimately only the fluorinated chain remains in the form of PFSAs or PFCAs. The precursors may be non-polymeric or polymeric and even include aromatic substances to which fluorinated chains are attached. Figure 2 shows the various degradation routes being biotic (by living organisms) and abiotic (by physical/chemical mechanisms e.g. oxidation/reduction and heat) for a PFCA precursor.

Before 2002, many of the non-polymeric PFAS were PFOS-derivatives such as Scotchban and Scotchguard, were widely used, with an examples being perfluoroalkane sulfonylamidoethanols phosphate esters (SAmPAP also called SN-diPAPs by Trier). This group of surfactants were introduced by 3M in 1974, for use in food contact paper and packaging (Begley, 2005) and accurate MS spectra were produced by Trier et al. (2011a). These may form PFOS upon degradation and have been found in the sediments of Vancouver Bay (Benskin, 2012) and Tyrifjord (Arp, 2014; NGI/NIVA 2019). Since 2002 PFSA derivatives with shorter chain lengths (e.g. PFBS and PFHxS derivatives) have been produced and are still marketed under the brand of ‘Scotch’. 3M recently compiled a long list of current uses of PFAS for the state of Maine (3M 2022).

After 2002 there was a shift in the western world towards PFAS chemistries not relying on PFOS which mainly had been , and a synthesis process called *fluoro-telomerisation* was for a while the dominant PFAS synthesis that replaced the electrochemical fluorination synthesis of PFSA including PFOS and its derivatives. Many of these are made from the so-called fluorotelomers (FT), which contain an even-numbered linear fluorocarbon chain (with n fluorinated carbons) that is attached to two hydrocarbons (CH_2CH_2). This is attached to a hetero-atom X (X= oxygen, sulfur, nitrogen, phosphorous etc.), which finally is attached to some other chemical group (R). R may be non-fluorinated or fluorinated.

$$F(CF_2)_n - CH_2CH_2 - X - R$$

Typical examples of fluorotelomers are the fluorotelomer alcohols (n:2 FTOH) which have an alcohol (-OH) ‘tail’, and fluorotelomer sulfonate acids (n:2 FTS, also called FTSA) which have a sulfonic acid ($-SO_2H$) ‘tail’. The first number denotes the number of fluorinated carbon atoms, while the other two are not fluorinated. FTOHs may be used *directly* e.g. as water and grease repellents on paper and board and textiles and FTS as replacement for PFOS and other PFSA used in firefighting foams and in metal plating.

Fluorotelomers are also used to build larger molecules, such as various types of polyfluorinated alkyl phosphate substances (PAPS), e.g. mono- and di-PAPS, SdiPAPs (also called FTMAPs) and Lodyne2000. In the Norwegian Tyrifjord study they hence found 6:2-12:2 FTS which had been used for paper and board after they ceased using the PFOS-derivative SAmPAPs. Fluorotelomers can also be attached onto (non-fluorinated) polymers such as acrylates, that are commonly used for surface treatment of e.g. carpets, textiles, paper, stone and leather. These are referred to as fluorinated sidechain polymers or fluorotelomer sidechain polymers, sometimes referred to as FT-polymers.

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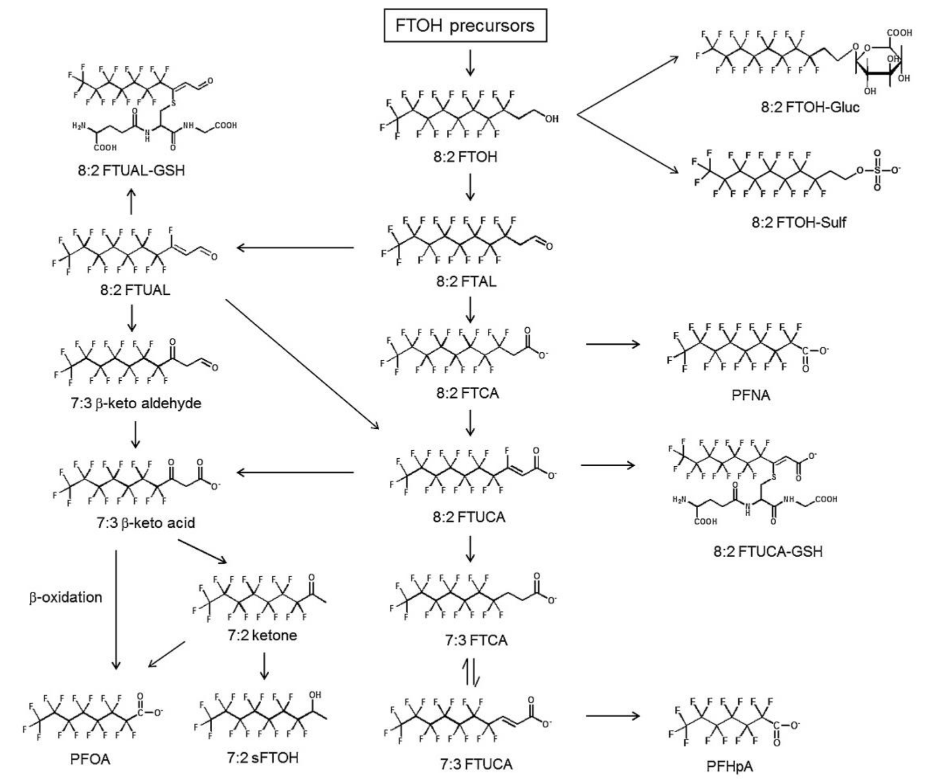

Figure 6. 8:2 Fluorotelomer alcohol (FTOH) biotransformation pathway in rainbow trout as proposed by Butt et al. [33]. "FTOH Precursors" refers to fluorotelomer-based compounds that degrade to the 8:2 FTOH. Adapted from Butt et al. [33]. See Table 1 for definition of abbreviations.

FIGURE 2. Biotic and abiotic degradation pathways of PFCA precursors, here shown for 8:2 FTOH. Note how PFCAs of various chain lengths are formed with PFNA>PFOA >>PFHpA. Taken from Butt et al. (2014).

2.4 Regulation of PFAS

This section only gives a brief and non-exhaustive overview on current regulations at EU and national, Danish level to inform the design of the studies (choice of media, which PFAS to monitor, at which sensitivity) and for future guidance on which PFAS to monitor for in which media, of relevance to enforcement and risk assessment. A more comprehensive summary on the development in regulations at Danish and EU levels has recently been produced by Regionernes Videnscenter for Miljø og Ressourcer in their PFAS Handbook (Håndbog om undersøgelse og afværge af forurening med PFAS-forbindelser) (Danish Regions, 2022).

Many of the PFAAs and their precursors are either already regulated or intended to be regulated in the EU under REACH, and for PFOA and PFOS (since 2009) also under UNEPs Stockholm Convention. Currently the EU water framework directive (WFD) only has an Environmental quality status (EQS) limit set for 'PFOS *and its derivatives',* at 0.65 ng/L to protect humans eating fish.

In 2020 EFSA re-evaluated their opinion on the safe human intake limits for PFAS, and set the tolerable weekly intake (TW) for the sum of the concentrations of four PFAS (PFOA, PFNA, PFHxS and PFOS) at 4.4 ng PFAS/kg bw/*week* (EFSA, 2020). The values were 81-1700 times lower than the previous levels for PFOA and PFOS. This has influenced the new values for PFOS in the Groundwater and surface water directive, which the Scientific Committee on Health, Environmental and Emerging Risks (SCHEER) in July 2022 set for the Sum of 24 PFAS at

4.4ng/L in water (SCHEER, 2022). On 26 October 2022 the European Commission put an official legal proposal for the revision of the WFD (COM (2022) 540 final) and the annex is currently out for consultation. In June 2023 the Danish EPA translated the SCHEER (JRC, 2022) document to Danish (DK EPA, 2023), and this is now the regulation in force in Denmark on PFAS water quality criteria in surface, fresh-, ground- and coastal waters.

The sum of the 24 PFAS is calculated in PFOA equivalents for the individual PFAS by multiplying the RPFs with the measured concentrations. RPFs are a measure for the toxicity of the individual PFAS compared to PFOA, and are shown in Table 1. The sum of these 24 individual PFOA-equivalents should be compared to the limit values in Table 2. As described in DK EPA (2023, p.130),

PFOA-equivalents $= \mathrm{PFAS}_{\mathrm{individual}} * \mathrm{RPF}_{\mathrm{individual\ PFAS}}$, for PFAS listed in DK EPA, 2023
Sum of PFAS_{24} in PFOA-eq. $= \Sigma\,(\mathrm{PFAS}_{\mathrm{individual}} * \mathrm{RPF}_{\mathrm{individual\ PFAS}})$, for PFAS listed in DK EPA, 2023

The RPFs are generally below 1 for the short-chain PFAS water soluble compounds, since these compounds are *less* bioaccumulable and therefore are of lower risk to animals at the top levels of the food chain, including humans. In contrast the long chain PFAS which bioaccumulate have higher RPFs. Long-chain PFAS also tend to distribute to sediment and biota, which therefore is more likely to exceed the PFAS EQS values. From a regulatory point of view, it may therefore be more relevant to sample where there is the highest risk of exceedances, which would be in the sediment and biota, rather than water.

It is noteworthy that

- for some of the RPFs they are given in ranges. The principle of the WFD is that if in doubt to use the most protective approach, and by consequence the highest RPF should be used (PC, 2024).
- both 'PFOS derivatives' and 'PFNS' are missing from the SCHEER document, particularly because these have been heavily used. In Denmark N-MeFOSE (prePFOS) and PFNS were reported to be amongst the top 8 most used PFAS from 2007-2016 according to the Danish product registry (DK EPA, 2014). The EC (DG ENV) confirms that from their perspective PFOS precursors are still covered (and expects that the text will be updated) – but it will depend on the Member states, and for now the RPFs are not known (PC, 2024). If PFAS beyond the 24 (e.g. PFOS derivatives = prePFOS) were to be added to the sum, a question would be how to deal with substances that currently have no RPF. An option could be to take the approach taken by EFSA for the sum of PFAS_4, being a simple concentration addition that corresponds to use an RPF of 1.

The proposal contains EQS for 24 PFAS in various matrices. The EQS relevant for this study are shown in Table 2, together with the current limit values for PFOS in the aquatic surface water environment.

Currently $\mathrm{EQS}_{\mathrm{sediment}}$ are not set for PFAS in the SCHEER 2022 report, and hence not in DK EPA (2023), but biota limits may be used if they are as protective as the sediment values (PC, 2023). Since the $\mathrm{EQS}_{\mathrm{biota}}$ = 77 ng/kg ww (human intake) is much lower than the current $\mathrm{EQS}_{\mathrm{sediment}}$ = 13500 ng/kg dw, the $\mathrm{EQS}_{\mathrm{biota}}$ = 77 ng/kg ww is more protective and can be used. To compare with the $\mathrm{EQS}_{\mathrm{biota}}$ the measured sediment Total PFAS-equivalents have been calculated in ww:

Sum of detected PFAS ww (PFOA eq.) = Sum of detected PFAS dw (PFOA eq.) * % dry matter
, assumption: density of sediment ~ density of biota

It should be noted that dry matter (dm) and dry weight (dw) are interchangeably used here.
If sediment values will be included in the future EQS, these can be expected to be lower than the $\mathrm{EQS}_{\mathrm{biota}}$ (77 ng/kg ww), to protect against bioaccumulation from the sediment to biota.

With concentration factors of 50-120, a level around or below 1 ng/kg ww can be expected. This concentration is so low, that it possibly would be easier to detect the higher PFAS levels accumulated in biota and compare them detected with the higher biota limit values.

TABLE 2.2. Regulatory limit values that may be relevant to compare PFAS levels in water, sediment and biota sampled from freshwater bodies. Units for sediment are given in dry weight (dw) and in biota in wet weight (ww). Limit values are taken from the latest update (DK EPA, 15 december 2023).
* or 270.000 ug/kg dw x fOC .
** The list of 24 PFAS is from the implemented draft of the updated EU WFD, which is under negotiation. The list of PFAS may hence be updated in the forthcoming EU WFD, where suggestions to include e.g. PFNS, PFOS derivatives (as in the current legislation on PFOS and derivatives) and PFAS Total have been proposed by member states. PFAS total methods can be useful to screen which samples have the highest PFAS levels in them. In sediment and soil the EOF-CIC and LC-HRMS methods have been shown to correlate well (Zweigle, 2024).

Media limit applies to	**Legal status**	**Protection goal**	**Value**	**Unit**	**PFAS**
Freshwater – EU WFD (EQS)	Legislation in force since 2017	Environment/ humans	0.65	ng/L	PFOS and derivatives
Inland freshwater	Legislation in force in Denmark since 2023	Environment/ humans	4,4	ng/L	For 24 PFAS calculated as PFOA equivalents**
Sediment	Legislation in force in Denmark since 2023	Environment/ humans	13500	ng/kg **dw** (5%OC)*	PFOS
Biota	Legislation in force since 2017	Environment/ humans	9100	ng/kg **ww**	PFOS and derivatives
Biota	Legislation in force in Denmark since 2023	Environment/ humans	22300 (fish) 6200 (mussels) 77 (for human consumption)	ng/kg **ww** ng/kg **ww** ng/kg **ww**	24 PFAS calculated as PFOA equivalents **

When assessing the chemical pressure on an ecosystem, combined exposures to chemical mixtures have an effect. Such mixture effects are not considered here, and would require broader chemical or effect based screening methods. However, the EQS values for specific chemicals, are complemented by good quality status of the ecosystems, meaning that if pollution e.g. near emission points, should not damage eco-systems (less thriving vegetation, bio-diversity and population densities) compared to the surroundings.

In addition to these chemical limit values in environmental media, regulations are in place on industrial emissions of chemicals to the environment. The EU E-PRTR and the Industrial Emissions Directive currently have limits for PFOS and its derivatives and some specific F-gases, but in the recent revision it has become possible to add new substances when there is evidence of risk. It is therefore likely that more limit values will be set across industrial sectors for PFAS, and possibly also for the sum of PFAS. In parallel, in the EU many initiatives are underway to regulated PFAS as a result of the Chemicals Strategy for Sustainability (EC, 2020a), and its supporting staff working document on PFAS (EC, 2020b). In February 2023 five countries (Denmark, Germany, Norway, Sweden and The Netherlands) put forward a broad restriction of PFAS as a class, and are now processing more than 5600 comments received during the consultation which ended in September 2023 (ECHA, 2024). As a result it is likely that more PFAS will be added to the list of restricted substances, and that new PFAS will be added to the environmental regulations.

A pro-active approach could therefore be to include the specific PFAS and groups of PFAS which already now are intended for regulation into the monitoring.

3. Mapping of potential PFAS sources

3.1 Sites with current or historic activities using PFAS

Given that there are such a variety of PFAS, and varied uses for each group source tracking calls for an informed approach whereby typical industrial activities are mapped against PFAS patterns. This may also help to prioritise a monitoring strategy to focus on the most likely polluting activities where samples first would be taken. In Denmark several mappings have taken place, primarily of the industrial activities in which PFAS are used (DK EPA, 2014). In 2014 approximately 80 sites were identified based on mapping of 1000 PFAS and the Nordic Product Registry (DK EPA, 2014). In 2022 Danish Regions did a follow-up study, whereby 14700 sites (0.7% of all Danish plots) where PFAS potentially had been used were identified, and therefore potentially could be contaminated (Danish Regions, 2024). Similar activities have taken place in the US, e.g. in the state of Michigan, and in Europe (Forever chemicals project, 2023) – which did not include the most updated Danish Regions study. In the literature the approach and the underlying tools have been described in Glüge et al (2020) and in a recent publication by Sima et al. (2021): *Presumptive Contamination: A New Approach to PFAS Contamination Based on Likely Sources*. In their paper they argue that in the absence of high-quality testing data, PFAS contamination can be presumed around three types of facilities: (1) fluorinated aqueous film-forming foam (AFFF) discharge sites, (2) certain industrial facilities, and (3) sites related to PFAS-containing waste.

For this study we sought information from the following sources

- Literature study on which PFAS have previously been found in surface and marine waters and sediments, and which sources have they been attributed to – with focus on PFOS precursors.
- Literature study on known uses of PFAS by different types of industry – with a focus on PFOS. Please also refer to Danish Regions (2022) for a further description of PFAS uses.
    - Firefighting training areas
    - Areas where there have been larger fires
    - Metal plating – especially hard chrome plating
    - Painting companies
    - Wax manufacturers or users of (a lot of) wax – impregnation of racing boats, skis, restauration (at museums), internal or external wood structures etc.
    - Lubrication oils – manufacturers and users
    - Leather manufacturers (surface coating)
    - Paper manufactures and handling of wastes
    - Textile producers (surface coating)
    - Wood manufacturers (impregnated/surface coated wood)
    - Concrete and stone maintenance (coating of concreate and removal of graphitti)
    - Dry cleaning – stain removers and the PFAS from cleansed textiles
    - Electronic manufacturers, e.g. microchips
    - Research institutions
    - Elderly homes and hospices (from medicine wastewater)
    - Handling of chemicals and gases
    - Waste deposits/landfills

- A shortlist of potentially polluted sites was produced which was discussed with authorities, see Appendix 1-Sampling.
- Meetings with authorities and review of existing data, some of which were not published.
- Searched the internet (e.g. the Danish Environmental Portal (Miljøportalen) containing published data) for investigated/identified polluted sites by a variety of industrial activities, including historic pictures, environmental permit reports and description of the historic activities.

3.1.1 Involved authorities

Initial meetings with the municipalities, the Region and the DK EPA provided a lot of information. The municipalities and the Regions have different purposes for their investigations, and refer to different legislations. Since no authority is tasked with collecting and assessing data across investigations, an overview lacked and data were not always publically available.

In our case four municipalities (Farum/Rudersdal, Gladsaxe, Lyngby, Bagsværd), and one Region (Region Hovedstaden) covered the investigated areas. One contact point was allocated for the 4 municipalities, but we had to get information from at least one other municipality.

3.1.2 Possible sources of PFAS based on historic activities at the sites

A primary investigation was made into historic uses of PFAS, environmental permits around the sampling sites, pipes/point of emissions and previously measured PFAS in environmental monitoring. These were considered as potential sources of PFAS in the inland lakes and streams fresh water and sediment.

1) **Furesøen – Nørreskoven**

   This is the reference point with no known point sources. PFAS concentrations may come from general mixing in Furesøen, run-off from uses on land and from aerial deposition by rain and dust. In Furesøen the main source may be Stavnsholt WWTP (2)

2) **Furesøen - Stavnsholt WWTP**

   This site was of interest since higher and varying levels of 6:2 FTS had been observed, with more 6:2 FTS during industrial operational days and less on holidays. Investigation of the current factories showed that three potential metal coating places are in operation, one of which had a remark in their environmental permit that they should make an effort to reduce the use of PFAS. PFAS has therefore likely been used historically and may continue to be so. A challenge was that the end of the WWTP pipe is situated at 9 m depth, which was too deep for the sediment sampling equipment and at an almost too high pressure for the Sorbicells. It was therefore decided to sample closer to the coast in the predominant downstream direction. When we collected the sorbicells the cells had been moved about 50 m penpendicular/up-stream to the waste water pipe, presumably by a very strong winter storm, but in the direction of the WWTP emission point. This adds some uncertainty to the interpretation of the results, mainly that the sampling was not at the waste water pipe emission point. Given that Furesøen (reference point/no known sources) is upstream from Stavnsholt WWTP the main expected PFAS sources are:

   a) The WWTP with its mix of industrial metal plating and household sources

3) **Bagsværd sø – Bagsværd rowing stadium**

   At this location an international rowing stadium is located, with a wooden bridge structure. Above the stadium there is a larger restaurant and smaller buildings. The first building was constructed in 1952 and the second yellow brick building was added in 1963. It was not possible to identify activities that for certain could have used PFAS, but the following potential sources were considered:

a) PFAS waxes, such as 3M's Scotchban PFOS-based wax, may potentially have been used for boats (mixed into the pap-mache casing?) since they were marketed in the about 1960's.
b) PFAS coatings on the boats to reduce the water friction for competitions, e.g. PFOS-based historically used, or newer fluorosilicones which also are used for larger ships. There are however no historic accounts of prepping the boats with such waxes, but it may come with the buying of the boats. Boats are waxed about one time/year with products from a common car-shop. Some may contain 'Teflon', but not records could be found of them being PFOS-based.
c) firefighting foam from a fire incident, or from firefighting foams having been used at fairs (as it previously was common practice in Denmark, and in kindergardens as well)
d) impregnation/coating of the wooden bridge and/or the buildings to prevent algae growth/dirt
e) cleaning/polishing wood or stone in the restaurant
f) a (historic) wastewater eluent pipe that has been led into the lake?
g) dumping of waste or waste water?

4) Bagsværd sø - Nybrovej

This site is next to a former dry cleaning site, and PFOS has been found by the Regions groundwater sampling. Nybrovej is downstream from Bagsværd rowing stadium and the boats have their rowing lanes situated nearby but this also means that sediment has been dug out and removed to deepen the lake for the boats. The support boat often waits near this site.

The suspected point-sources are:

a) The dry-cleaning
b) Downstream pollution from Bagsværd rowing stadium

5) **Lyngby sø – Mortonsvej**

At this location several types of industries had been active, including metal plating of plastics and storage/burning of paper and board. The Region had measured high levels of PFOS (2800 ng/L) in sludge under the floor in one of the buildings, and in a groundwater drilling. Emissions may have occurred via wastewater being led to the lake via a little stream, been emitted via air/smoke emissions, via dust during the demolishment of the industrial building/construction of new buildings shown in Figure 3 below, or seeped in from underneath with the groundwater. The suspected point-sources are:

a) Hard chrome-plating of metal onto plastic or metal products. PFOS and other PFSAs until about 2006, and since FTS replacements may have been used.
b) PFAS coatings used in paper and board can have been released via direct leaching, smoke/dust and leaching from the ashes. Since this activity stopped in the 1960's (early days of PFAS) it is less likely the major source – but it is relevant to look for PFOS precursors such as SAmPAPs and other types of paper coatings (FOSEs and various PAPs).

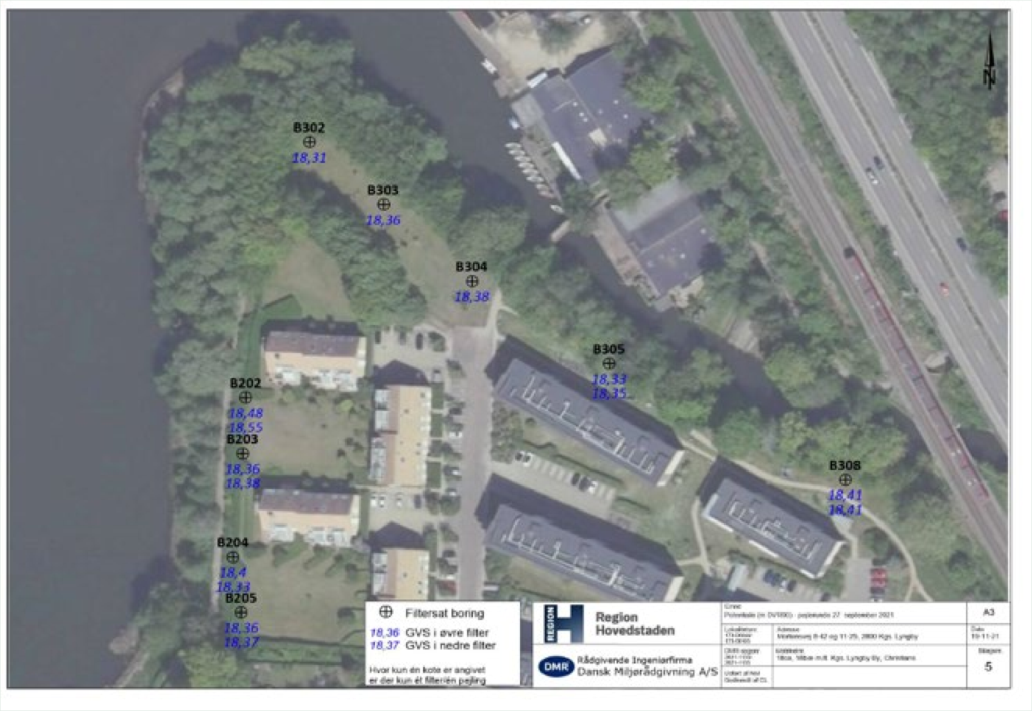

FIGURE 3. Example of a report by the Region Hovedstaden for the former industrial site at Mortonsvej, which informed the sampling plan.

6) **Mølleåen - Dybendal WWTP**

   This site is downstream from lakes that contain PFAS, and about 20 m downstream from the Dybendal wastewater treatment plant (WTTP), which receives waste water from amongst others the Technical University of Denmark (DTU). At DTU various PFAS have over the years been used for research in coatings of polymers, drug research, in instruments, when monitoring, and likely in a variety of other uses related to coatings etc. The suspected sources are:

   a) PFAS from the upstream water
   b) The waste water treatment plant, from households and activities leading to the Dybendal WWTP such as the university, DTU.

7) **Mølleåen - Kulsviervej**

   The sampling point was situated where two streams connected (the major feeding from the upstream lake, the minor passing in through the adjacent buildings). At Kulsviervej there has been textile activities from 1938-1974, and a dry cleaning facility. PFAS may have been used to impregnate the textiles (e.g. various types of PFOS based or PAPs type coatings), or may have come off in the dry cleaning of e.g. carpets, curtains and other textiles. PFAS have also been used for spot-removal. Previous studies done by the Region had monitored and found chlorinated solvents used for dry cleaning. Other sources may be PFAS containing paints or ‘anti-grafitti’/ growth/dirt coatinngs (sometimes used to protect the surfaces of historic buildings).

   The potential sources are therefore not very conclusive but could include

   a) PFAS coatings used for textiles
   b) Dry cleaning releasing PFAS containing fibres or from spot cleaning
   c) Sources from upstream from the lakes

4. Sampling of PFAS

4.1 Purpose of monitoring

The sampling design depends on the purpose of analyses. If the purpose is to track the source, samples will be taken near the suspected PFAS activity, e.g. upsteam or downstream. In contrast, if the purpose is to get data for human or environmental risk assessment, the samples would typically be taken more evenly to get a distribution of occurrence or exposure.

The analysis strategy of what to monitor and in which media will also depend on what the data will be used for. If the monitoring is to check for compliance with legislation, the method performance requirements are typically high, to ensure low uncertainty on quantification and identification of the chemicals. This will allow authorities to determine if a concentration is above or below limit values. Very certain data are also needed to feed indicators showing trends, since the lower the uncertainty, the smaller variations can be observed. For these purposes, so-called ‘targeted analysis’ are typically used.

For source tracking a more broad screening may be used, e.g. by suspect screening or non-targeted screening that can provide fingerprints. A fundamental principle in public management is to ensure division between those designing studies, monitoring and assessing the risks, and those who will manage the risk.

4.2 Choice of sampling locations

Appendix 1 on Sampling contains the details of the sampling of water and sediment. In addition to the samples taken for the DK EPA, some samples were taken for a B.Sc. project (extra reference points and foam samples) which are not reported here.

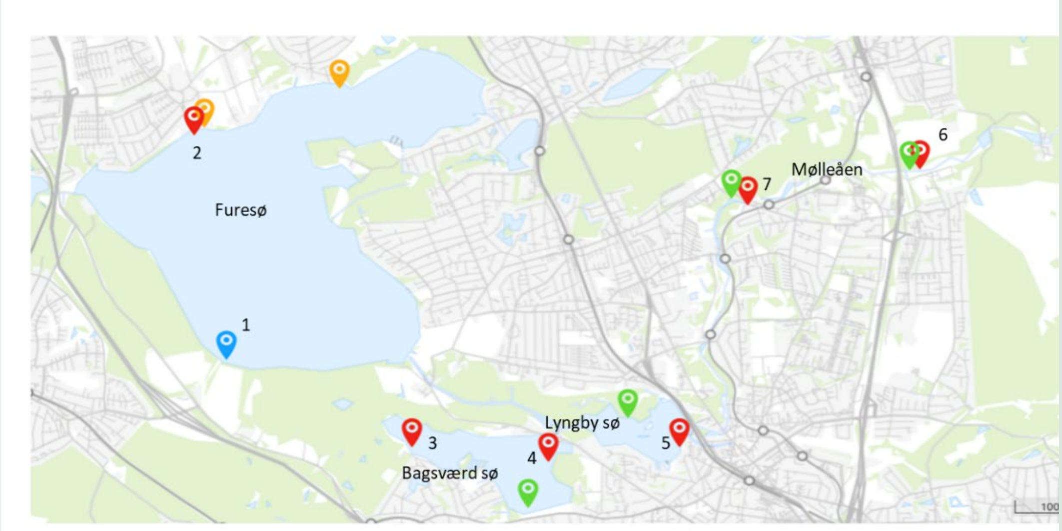

FIGURE 4. Map of Furesø, Bagsværd sø, Lyngby sø and Mølleåen. Sampling sites are 1: Nørreskoven (Furesø, ref point), 2: Stavnsholt WWTP, 3: Bagsværd Rowing Stadium (aka Rostadion) (Bagsværd sø), 4: Nybrovej (Bagsværd sø), 5: Mortonsvej (Lyngby sø), 6: Dybendal WWPT (Mølleåen), 7: Kulsviervej (Mølleåen). Red sites: Hotspot (sediment+Sorbicells), Green: Reference (sediment taken for UCPH), Blue: Reference for MST (sediment and Sobicell), Orange: Foam (taken for UCPH Bsc.).

Hotspot locations:

Hotspot locations shown in Figure 4 were chosen based on the information gathered from the existing data as described above. The considerations included:

- Concentrations above the apparent 'general' concentration level of ca. 20-30 ng/L. So far 'typical numbers' lack for the anthropocenic background PFAS concentrations surface waters in Denmark, but will soon be published based on the Regions data; the frequency of detection of 12 PFAS in streams and lakes range from 0-90% (Thomsen N, 2023). In the NOVANA surveillance program, average concentrations of PFAS in in rainwater run-off are not yet measured, but PFAA levels in overflow of waste water range from 0.8-2.2 ng/L (DK EPA, 2022). In rainwater in the Lyngby area, the concentration is 1.5 ng/L.
- Different patterns in the distribution of the individual PFAS
- Proximity to an activity using PFAS
- Different types of activities using different PFAS
- Sampling was done downstream from prevalent wind and streams and at sites where sediment was expected to accumulate

Reference locations:

For the DK EPA study one reference was included (Furesøen – Nørreskoven), where no apparent potential PFAS using activities could be found. The sample was taken at a deeper and less 'disturbed' location, based on a depth map of the lakes, see Figure 5 with the example of Furesøen.

Biota samples:

Due to the time of year, fish had moved away from specific locations towards deeper locations why it was decided not to sample fish. A few mussels were collected from location 2 where they had stuck to the cages but were not analysed as it would require extra method optimisation/validation.

Mussels are site specific and contain fewer enzymes that can metabolise poly-PFAS, e.g. FTS to PFCAs (Langberg, 2019). In the future mussels/invertebrates could therefore be relevant to investigate hot-spot pollution and sources. Fish on the other hand are relevant for human consumption and may contain higher levels due to bioaccumulation in predator fish. A combination of both mussels and fish would be good to sample for surveys, and mussels/shell-fish to search for sources of hot-spot pollution.

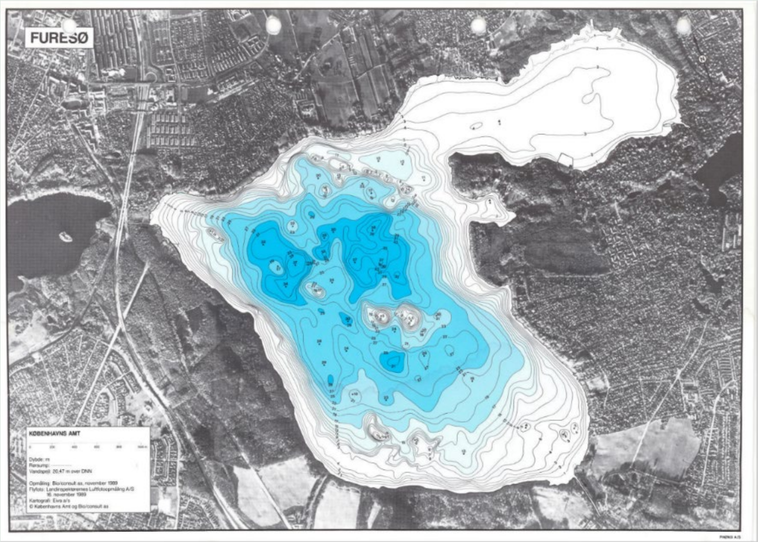

FIGURE 5. Example of a depth map of Furesø, used to determine where to take samples.

4.3 Sampling of water and sediment

With reference to the aims of the study, water and sediment were sampled.

Water was sampled over 4 weeks (8-9 November 2022 to 5-6 December 2022) by a device called Sorbicells, through which water is slowly sucked

Collection of water samples

by a hydraulic pressure, through a solid-phase filter over the time that the Sorbicells are left. This allows to estimate average concentrations of PFAS in water. Different sorbent materials are used to trap contaminants, and the 'PFA' sorbent (aimed at PFAS) was used. Depending on the depth (i.e. sampling pressure) two different tubes, with 'PFA' sorbents of different permeability were used to control the flow-rate. The tubes were pre-wetted with tap-water prior to sampling. Two tubes were placed for about a month, at each site, and the temperature was recorded. Upon collection, the volume of water that had run through the cells was determined, by weighing of the collected water inside the device.. One tube was capped and sent to Eurofins (A tubes) for targeted analyses of 22 PFAS). A 'blank' was collected by passing 5 mL of tap-water from Birkerød sejlklub through an unused tubes and sent to Eurofins. The 'B' tubes were kept for UCPH (B tubes) for non-targeted/suspect screening analyses, and they were stored at -20C until analyses. Appendix 1 contains the principles and the description of how to utilise the Sorbicells.

Sediments were sampled by inspiration of the sampling guide for marine sediment sampling developed for NOVANA (DMU, 2004), on 5-6 December 2022. In summary at each location two cores (sub-samples) of approximately 5 cm length were taken with a kayak sampler. The two sub-samples were combined into one composite sample with a metal spoon (a new spoon was used every time) in Birkerød sailing club. White plastic containers with lids were supplied by Eurofins on the day of sampling (so no rinsing in ethanol was possible), and no extra containers were available for blank analysis).

Preparation of sediment samples for analysis

5. Analyses of PFAS

This section describes the targeted analyses from previous studies, targeted LC-MS analyses of water and sediment (by Eurofins), and suspect screening LC-QTOF MS analyses of sediment (by UCPH).

5.1 Existing data from municipal and regional studies

To decide on where to sample, we collected data from previous investigations from the river, the lakes, groundwater, soil and waste water effluents from the Region, the municipalities and the Danish environmental portal (Danish Miljøportal, 2024). The preciously monitored river and lake water had PFAS at all sites, with a typical concentration of 20 ng/L for the sum of PFAS most often observed at sites, and a fairly constant distribution of PFAS. Since some data are confidential they are not shared here. Further information were sought for sites with levels above 30 ng/L. A few sites stood out: At Mortonsvej PFOS had been found up to 2800 ng/L in water from a drilling under a former metal plating site. At Stavnsholt WWTP up to 1100 ng/L 6:2 FTS had been measured in a wastewater pipe, with levels being high during working days and low during days off. Three metal plating facilities are leading wastewater to the WWTP, and that the environmental permit on one factory said that it should 'minimise its use of PFAS as much as possible'. 6:2 FTS was therefore included in the study. Bagsværd rowing stadium had only slightly elevated concentrations (38 ng/L) but had a different pattern of PFAS indicating a different source.

5.2 Eurofins targeted analyses of 22 PFAS (PFAS$_{22}$)

5.2.1 Targeted analyses of PFAS in water sampled by Sorbicells

Analyses by Eurofins included 22 PFAS as listed in the tables with the results for water below. In addition to the standard package of PFAS, 6:2 FTS was analysed by the accredited method called 'DIN 38414-14 mod. LC-MS/MS'. The sample preparation and analyses of Sorbicells and sediment done by Eurofins is not described in this report. One set of the Sorbicells sampled at each site, was sent to Eurofins for analyses, and one was kept at UCPH for future suspect screening. Discussions on how blanks were handled in the laboratory elucidated that the laboratory had corrected for blanks of e.g. 6:2 FTS, but that no representative method blank had been included as this is not part of the standard analysis program.

5.2.2 Targeted analyses of PFAS in sediment

One set of sediment, combined and well mixed duplicate samples was weighed and sent to Eurofins for analyses of 22 PFAS and for dry matter determination (dm).

5.3 Suspect screening of PFAS in sediment by LC-ESI$^-$-QTOF-MSMS

Sediments were screened by UCPH for a total of 33 PFSAs and precursors, and 28 PFCAs and precursors, as described in section 2.2.

5.3.1 Sampling

Details are provided on the Sampling in Appendix 1, and in the Technical report.

5.3.2 Materials and chemicals and Sample pre-treatment

Details on Chemicals and materials/Sample pre-treatment are provided in the Technical report. Care was taken to wash all plastic equipment in ethanol before analyses (and dry it before use) to minimise blank carry-over.

In summary the principle of the sample treatment was a slightly modified method by Langberg et al. (2021), where subsamples were weighed out, porewater centrifuged, internal standard (IS) added, twice acetonitrile was added followed by ultrasonification/shaking/centrifuging, decanting of acetonitrile, evaporation to 5 mL, filtration, evaporation to 100 uL, and recombination to 700 uL of 1:1 water:methanol.

5.3.3 Quantification by LC-ESI$^-$- QTOF MS analyses

Details on Analyses by suspect/non-targeted screening by UCPH, and on Method performance (calibration curves etc.) are provided in the Technical report. The use of internal standards (IS) spiked to the sediments from the beginning resulted in rather good/repeatable calibration curves. Blanks were also included and were automatically used to correct for blanks in the quantification. Detection limits were not very low, but comparable to those from Eurofins. The variation was in most cases good, so the issue is more blanks for some of the compounds. A challenge for the quantification is that internal standards have small impurities of the ‘target’ PFAS (eg. PFOS-IS may have a bit of PFOS in it), and also the FOSE/FOSA/FOSAA standards. While these in principle may be corrected for this is rather complicated and time-consuming so typically they will add to the ‘blank’ value. Isotopically labelled standards may also have degradation products that are identical to the product ions of the PFAS, which means that quantification ions have to be selected *very* carefully – and sometimes the most intense product ion cannot be used, which hampers the LOD. It is therefore key always to have at least one subsample to which no internal standards are added, and to analyse this at least twice to lower the uncertainty.

Variation in the areas of the internal standards was also observed to affect the quantification. Of several possible explanations investigated, two possible contributing factors were found:
a) Matrix effects lowering the ionisation efficiency could explain some but not all the variance,
d) Matrix effects due to subsamples material composition could explain the variance. This was particularly observed for the long-chain PFAS (such as PFTeDA) which partition strongly to organic matter, and the reason may be that the extraction is not 100%. In the future at least double extraction should be done to ensure high recoveries for the long-chain PFAS. The Technical report provides further information on this.

5.3.4 Identification by LC-ESI$^-$- QTOF MS analyses

For some PFAS the identification of the peaks and their respective retention times were not certain enough so these were not included in the reported PFAS. This was in part because many of the PFAS have the same product ions, which complicated the annotation of peaks. Another issue was that the larger and stable prePFOS such as SAmPAPs were not sufficiently fragmented to produce enough product ions used for the identification. In the future the collision energy ramp used (10-60 eV) should go to 100 eV. Shifts in retention times also made it difficult to assign peaks with high certainty. This is likely due to a very high LC backpressure. Here the IS’s helped annotation, since the distances between the retention times of the analyte peaks and the IS’s were rather constant. In the future changing the solvent to acetonitrile/water, potential use of a shorter column and use of pre-columns may solve such issues.

As mentioned the issue using IS are the presence of small impurities of the PFAS (eg. PFOS-IS may have a bit of PFOS in it), and in some cases Also standards such as the FOSEs had impurities of PFOS.

The lack of certainty on retention times, and the lack of product ions for confirmation meant that rather large retention time spans had to be used in the search for e.g. SAm-PAPS. Another issue was the presence of high levels of organo-chlorine/bromine contaminants, which have negative mass defects similar to the PFAS. These organohalogens were spotted due to their characteristic isotopic patterns – e.g. at Mortonsvej (5) and Kulsviervej (6)) but also because the ion ratios of the precursor vs. the product ions did not match the standards. As a result, the accurate masses of the stable precursor ions did not provide sufficient certainty to identify other prePFOS such as SAm-PAPS, and data were not reported. The Technical report provides further information on this.

In the Technical report, more detailed explanations and suggestions are given of how analyses in the future may be improved to increase the certainty of identification of PFAS and the sensitivity of the PFAS analyses, including

- *Sample pre-treatment:* higher extraction efficiency of long chain PFAS, use of SPE, measurement of organic carbon.
- *Quantification*: include more prePFAA standards, increase fragmentation of long chain PFAS, prediction of retention times and MS patterns, increase stability of retention times by lowering of the LC backpressure, use of on-line SPE, and run all the samples twice with and without IS.
- *Identification of suspect/unknown PFAS by accurate mass spectrometry:* use Data Dependent Acquisition (DDA) mode to ensure generation of clean product ion spectra, prediction of retention times, use libraries such as FluoroMatch to search for PFAS, explore if presence of impurities and homologous series from known synthesis routes can be used as additional identification points, use typical adduct ions to identify PFAS for which there are no pure reference standards, use series of $C_3F_7^-$ (m/z of 168.9894 Da) to search for PFCAs and precursors, and SO_3^- (m/z of 79.9568 Da) to search for PFSAs and precursors – and **always include sampling blanks** to ensure that signal is not from contaminated equipment.

6. Occurrence of PFAS in water

This section contains the results of PFAS in water measured by Sorbicells (by Eurofins).

6.1 PFAS levels in water

Table 6 shows the mass of PFAS measured on the tubes. It is remarkable that also the blank (Blin(8)) has a rather high content of 6:2 FTS (29 ng/tube). Further analyses were taken to investigate if the blank could come from the tap-water of Birkerød Sejlklub or from the materials or the laboratory, but both these sources were both ruled out. The remaining suspected source is dust or vapours in the sailing club from textile sails that may be coated with a 6:2 FTS precursor. Since it is unknown if this blind has equally affected all samples, the samples were not corrected for this blank value. This points towards the high importance, that a blank always be included in all analyses, and as part of the laboratories standard analyses. For comparison 6:2 FTS had been detected in 2 of 10 lakes in Denmark and Sweden and in 4% (of 55) streams and rivers (Thomsen, 2023).

TABLE 6.1. PFAS in water sampled by Sorbicells (ng/tube). Mølle (6) = Mølleåen - Dybendal WWTP. Values above the detection limit are shown in red, and are shown with two significant digits. Numbers are not corrected for blanks.

PFAS	Unit	Nørr (1)	Stav (2)	Bags (3)	Nybr (4)	Mort (5)	Møll (6)	Kuls (7)	Blin (8)
Water	*L*	*0,297*	*0,501*	*0,0532*	*0,0527*	*0,115*	*0,357*	*0,293*	*< 0,05*
PFBA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFBS	ng/tube	1,0	1,0	0,29	<0,25	0,32	0,56	0,64	<0,25
PFPeA	ng/tube	0,71	0,65	<0,25	<0,25	0,31	0,41	0,47	<0,25
PFPeS	µg/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFHxA	ng/tube	1,2	1,0	0,48	<0,25	0,5	0,73	0,85	<0,25
PFHxS	ng/tube	0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFHpA	ng/tube	1,1	0,94	0,32	<0,25	0,37	0,67	0,68	<0,25
PFHpS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFOA	ng/tube	1,1	0,94	0,43	0,33	0,43	0,80	0,71	<0,25
PFOS	ng/tube	3,3	2,7	0,53	0,32	0,78	2,0	2,0	<0,25
6:2 FTS	ng/tube	1,8	1,5	140	5,9	84	68	160	29
PFOSA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFNA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFNS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFDA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFDS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFUdA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFUnDS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFDoA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFDoS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25
PFTrA	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25

PFTrDS	ng/tube	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25	<0,25

Table 5 shows the water concentrations after dividing the ng by the water volume (L) that ran through the Sorbicells. The low volume of water that was put through the blind (approximately 5 mL) did not allow for the concentration to be reported, so numbers are not corrected for sample blanks.

The pattern of PFAS across the sites shows is a variety of PFAS, and mainly of short-chain (water-soluble) PFCAs and PFSAs plus 6:2 FTS. Long chain PFAS remain absent in the water, which is in line with their very low water solubility. In the future it could be considered to focus the water measurements on the most water soluble PFAS (4:2 FTS, 8:2 FTS, GenX and other mobile PFAS), and potentially if such water soluble PFAS could replace the poorly water soluble long-chain PFAS (from C11 and above). Such long-chain PFAS are more likely to partition to and be found in sediment or biota.

The uneven PFCAs (C5, C7) could indicate biotic or abiotic degradation of longer chain polyfluorinated PFAS (Butt et al. 2014). The presence of both PFSAs (PFOS, PFHxS, PFBS) and 6:2 FTS is similar to the pattern in Figure 17 found by Langberg et al. (2021) which indicates a common source, such as metal-plating or firefighting foam.

TABLE 6.2. PFAS in water sampled by Sorbicells (ug/L). Mølle (6) = Dybendal WWTP. Values above the detection limit are shown in red, and are shown with two significant digits. The detection limits vary due to the different amounts of sampled water. Numbers are not corrected for blanks.

PFAS	**Unit**	**Nørr (1)**	**Stav (2)**	**Bags (3)**	**Nybr (4)**	**Mort (5)**	**Møll (6)**	**Kuls (7)**	**Blin (8)**
Water	*L*	*0,297*	*0,501*	*0,0532*	*0,0527*	*0,115*	*0,357*	*0,293*	*< 0,05*
PFBA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFBS	ng/L	3,7	4,3	2,8	< 3	3,4	1,6	2,4	-
PFPeA	ng/L	2,6	2,8	< 2	< 3	3,3	1,2	1,8	-
PFPeS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFHxA	ng/L	4,4	4,3	4,7	< 3	5,3	2,1	3,2	-
PFHxS	ng/L	0,92	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFHpA	ng/L	4,1	4,1	3,1	< 3	3,9	2,0	2,5	-
PFHpS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFOA	ng/L	4,1	4,1	4,2	4,0	4,5	2,3	2,7	-
PFOS	ng/L	12	12	5,2	3,9	8,2	5,8	7,5	-
6:2 FTS	ng/L	6,6	6,5	1400	72	880	200	600	-
PFOSA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFNA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFNS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFDA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFDS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFUdA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFUnDS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFDoA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFDoS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFTrA	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-
PFTrDS	ng/L	< 0,9	< 1	< 2	< 3	< 3	< 0,7	< 0,9	-

PFAS	Unit	Nørr (1)	Stav (2)	Bags (3)	Nybr (4)	Mort (5)	Møll (6)	Kuls (7)	Blin (8)
Sum of PFAS$_4$	ng/L	17	16	9,4	7,9	13	8,1	10	-
Sum of PFAS$_{22}$	ng/L	38	38	1400	80	910	220	620	-

An overview of the concentrations of PFAS water concentrations at the sites is shown in Figure 6. Bagsværd Rostadion, Mortonsvej and Kulsviervej have significantly higher levels, which is mainly due to 6:2 FTS (at 1400 ng/L at Bagsværd Rowing Stadium). PFOS levels are rather low compared to 6:2 FTS. The reference point Nørreskoven is low as expected, and Nybrovej has also low levels. It is however surprising that Stavnsholt has so low concentrations compared to the analyses done by the municipality at the emission point. Perhaps it could be due to the fact that the sampling cages had been moved East by the wind, and therefore was not sufficiently close to the downstream 'plume' from the wastewater plant.

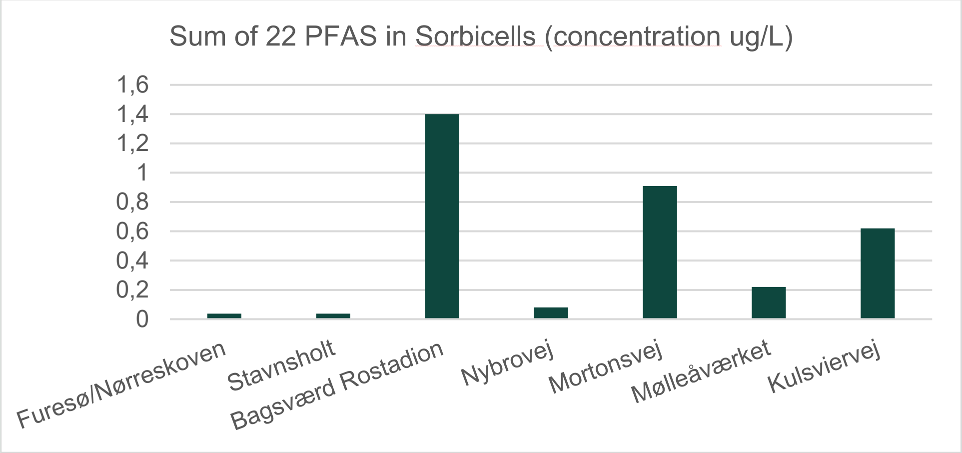

FIGURE 6. Sum of 22 PFAS in water (ug/L). Mølleåværket = 6-Dybendal WWTP. Bagsværd Rostadion = Bagsværd Rowing Stadium.

6.2 Comparison with of water levels with Danish and EU regulations and guidance value

Table 6 shows the extent to which the PFAS water concentrations are above Danish and EU limit and guidance values for water, listed in Table 1a. For PFOS and derivatives the levels are 6-19 times higher than the 0.65 ng/L; this is caused solely by PFOS because prePFOS were not measured in water. Compared to the proposed EU value at 4.4 ng/L PFOA equivalents (excluding 6:2 FTS), levels were 2.7 -7.0 times above. The proposed EU value is since 2023 a Danish guidance value, but was not in force at the time of sampling.

TABLE 6.3. Comparison of PFAS levels in water vs. limit and guidance values. Note, that in water only PFOS derivatives were not measured, so the factor above is caused by PFOS alone. Sum of 22 PFAS (PFAS22) was calculated as sum of PFOA equivalents = RPF * Concentration (ng/L), and compared against the proposed EQS for water.

Water	Furesøen - Nørreskov (1)	Furesøen - Stavnsholt WWTP (2)	Bagsværd - Rowing Stadium (3)	Bagsværd - Nybrovej (4)	Lyngby sø - Mortonsvej (5)	Mølleåen - Dybendal (6)	Mølleåen - Kulsviervej (7)
PFOS and derivatives (ng/L) –*only PFOS*	12	12	5.2	3.9	8.2	5.8	7.5
Factor above 0.65 ng/L for PFOS & derivatives	**19**	**19**	**8**	**6**	**13**	**9**	**12**
Sum of PFAS$_{22}$ (ng/L)	38	38	1400	80	910	220	620
Sum of PFAS$_{22}$ in PFOA eq. (RPF * ng/L)	31	30	14	12	23	15	19

Water	Furesøen - Nørreskov (1)	Furesøen - Stavnsholt WWTP (2)	Bagsværd - Rowing Stadium (3)	Bagsværd - Nybrovej (4)	Lyngby sø - Mortonsvej (5)	Mølleåen - Dybendal (6)	Mølleåen - Kulsviervej (7)
Factor that sum of $PFAS_{22}$ (in PFOA eq.) is above proposed EQS (water) 4.4 ng/L	**7.0**	**6.9**	**3.2**	**2.7**	**5.2**	**3.4**	**4.3**

The differences in how much the factors are above, of 'PFOS and derivatives' vs. the sum of $PFAS_{24}$ can be explained by: 1) how low the value is (0.65 ng/L is very low), 2) which PFAS are included in the sums 3) if weighting factors are multiplied onto the concentration levels.

Interestingly, the 'reference' site (Furesøen – Nørreskov) had the highest sum of $PFAS_{22}$ (in PFOA equivalents) which mainly was caused by PFOS. 6:2 FTS was not added to the sum, because it is one of the 24 PFAS in $PFAS_{24}$. However, had 6:2 FTS been included (using a RPF set to 1), the site with the highest value would have been Bagsværd Rowing Stadium.

7. Occurrence of PFAS in sediment

This section contains the results from the analyses of 22 PFAS ($PFAS_{22}$) in sediment (by Eurofins), and identification and quantification of a broader range of PFAS in sediment (by UCPH). The values have been compared with different regulatory limits and guidances to illustrate how much it influences conclusions of of the monitoring, whether different PFAS are included in the sum values, and which environmental compartments (water and sediment) that have been sampled.

7.1 Occurrence levels of $PFAS_{22}$ in sediment by Eurofins

Table 7 (Eurofins data) shows that only PFOS was found but in levels significantly higher than in water. This is to be expected since PFOS has a $logK_D \sim 2$ and consequently will distribute to sediment. That no other PFAS were detected can be explained by a number of reasons: Short-chain and polar PFAS such as 6:2 FTS have high affinity towards water, but low affinity towards sediment, meaning that very low amounts will bind to the sediment. Another situation is that commercial methods are often optimised to test near regulatory limits. In this case the current limit for PFOS and derivatives is at 13500 ng/kg dw, so the method has likely been optimised around this limit value, and not optimised to achieve a the lowest possible detection limit – to the method could be further optimised if needed. Another observation is that only one PFOS precursor (prePFOS) namely PFOSA, is measured routinely in water or sediment. This is somewhat surprising given that the current EQS limit is set for 'PFOS and its derivatives'. While this does not explain the differences between water and sediment in the commercial analysis, it does explain why the higher PFAS levels found in the UPCH where more prePFOS were analysed (see below).

In sediment, *PFOS* concentrations declined in the following order: (3) Bagsværd rowing stadium >> (5) Mortonsvej > (6) Mølleåen (Dybendal) = (2) Stavnsholt > (7) Kulsviervej = (4) Nybrovej = (1) Nørreskoven, as depicted in Figure 7.

TABLE 7.1. PFAS in sediment (ng/kg dm), calculated as the measured levels (ng/L) multiplied by the fraction dry matter (%dm/100%). Levels above the detection limit are shown in red. Note that the detection limits vary between sites, depending on the % drymatter in the samples, and also vary between PFAS. Only PFOS contributed to the sum. Mølle (6) = Dybendal WWTP.

PFAS	Unit	Nørr (1)	Stav (2)	Bags (3)	Nybr (4)	Mort (5)	Møll (6)	Kuls (7)	DL
Drymatter	*%*	*68*	*49*	*6,9*	*63*	*23*	*9,6*	*26*	*0,25*
PFBA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFBS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFPeA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFPeS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFHxA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFHxS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFHpA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFHpS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100

PFAS	Unit	Nørr (1)	Stav (2)	Bags (3)	Nybr (4)	Mort (5)	Møll (6)	Kuls (7)	DL
PFOA	ng/kg dm	< 50	< 62	< 440	< 50	< 140	< 320	< 120	50
PFOS	ng/kg dm	540	1300	12000	430	2900	1300	350	50
6:2 FTS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFOSA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFNA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFNS	ng/kg dm	< 200	< 250	< 1800	< 200	< 530	< 1300	< 470	200
PFDA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFDS	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFUdA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFUnDS	ng/kg dm	< 1000	< 1300	< 8700	< 1000	< 2700	< 6300	< 2400	1000
PFDoA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFDoS	ng/kg dm	< 1000	< 1300	< 8700	< 1000	< 2700	< 6300	< 2400	1000
PFTrA	ng/kg dm	< 100	< 130	< 870	< 100	< 270	< 630	< 240	100
PFTrDS	ng/kg dm	< 1000	< 1300	< 8700	< 1000	< 2700	< 6300	< 2400	1000
Sum of $PFAS_4$	ng/kg dm	540	1300	12000	430	2900	1300	350	
Sum of $PFAS_{22}$	ng/kg dm	540	1300	12000	430	2900	1300	350	

Figure 7 shows the occurrence levels of sum of $PFAS_{22}$ in sediment.

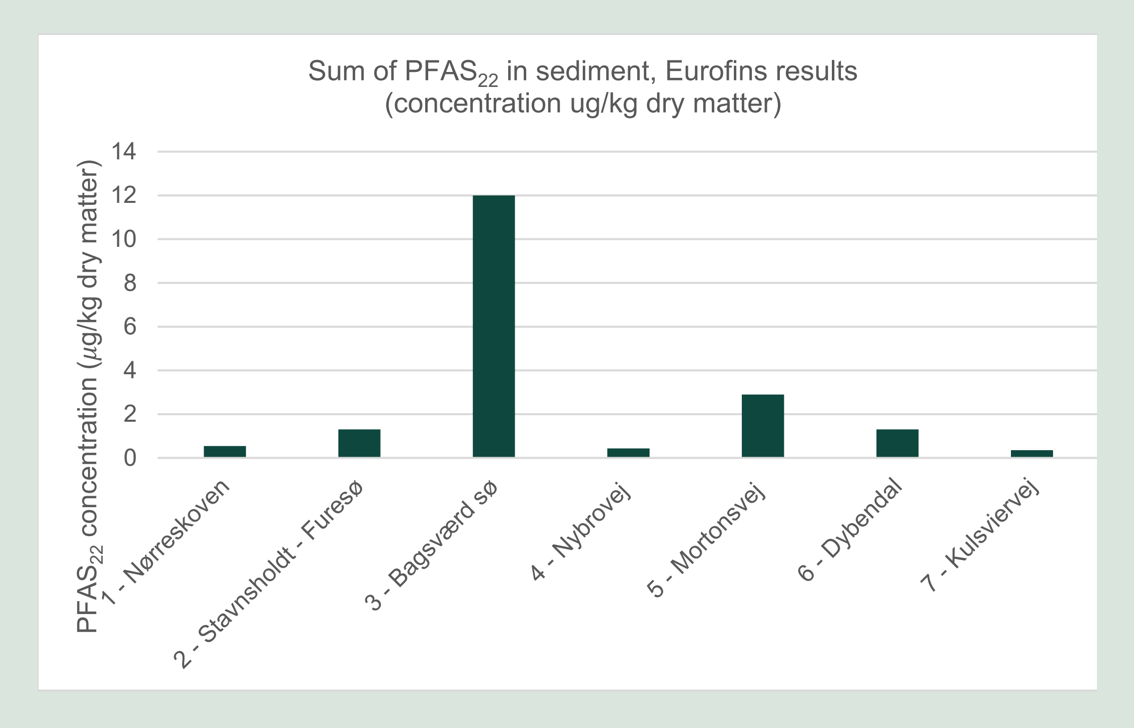

FIGURE 7. Sum of 22 PFAS ($PFAS_{22}$) in sediment (ug/kg dm). Only PFOS contributed to the sum.

7.2 Occurrence levels of PFAS in sediment by suspect screening

The results are shown in table 8 below, while the Figures 8, 9 and 10 show the data for the 'Sum of all detected PFAS' (ng/g dm); the 'PFCAs and precursors' and the 'PFSAs and precursors' for PFAS that were detected.

TABLE 7.2. Sum of all detected PFAS in sediment measured by suspect screening. In (parenthesis) PFAS that were seen but were below the limit of detection are shown, because they provide additional information on the patterns of PFAS. LOD (ng/kg) = V (mL)* Conc (ng/mL)/dw(kg). Numbers are shown with two significant figures. Numbers marked in green are below the EQS for PFOS+derivatives, while numbers in red are above the EQS for $PFAS_{24}$ (in PFOA equivalents). $PFAS_{lin}$ = $PFAS_{linear}$, and $PFAS_{br}$ = $PFAS_{branched}$.
* 13500 ng/kg (for 5% organic content) was used since organic matter data lacked for the individual samples. PFAS total ww (PFOA eq.) = PFAS total dw (PFOA eq.) * % dry matter, and under the assumption that comparison of sediment with biota values are at least as protective.

PFAS (ng/kg dm)	Furesøen – Nørreskov (1)	Furesøen - Stavnsholt WWTP (2)	Bagsværd Rowing Stadium (3)	Bagsværd - Nybrovej (4)	Lyngby sø - Mortonsvej (5)	Mølleå – Dybendal (6)	Mølleå - Kulsviervej (7)	LOD (ng/mL)
Dry weight (g)	*3.90*	*3.42*	*0.59*	*3.93*	*3.32*	*0.44*	*2.99*	-
PFHxA	< 26	< 29	200	140	160	370	39	100
PFHpA	< 26	< 29	79	< 25	< 30	< 230	< 33	100
PFOA	42	68	400	36	70	320	39	50
PFNA	24	27	320	36	42	(53)	< 33	50
PFDA	36	55	360	42	77	(210)	(16)	100
PFUnDA	(18)	41	440	42	84	320	(8)	100
PFDoDA	(18)	34	200	(18)	98	1900	78	100
PFTrDA *	< 26	< 29	(79)	< 25	< 30	< 230	(31)	100
PFTeDA	54	< 29	< 170	140	443	< 230	450	100
6:2 FTS	(24)	(27)	(120)	(18)	< 30	(110)	(16)	100
8:2 FTS	< 26	< 29	< 170	< 25	< 30	160	< 33	100
10:2 FTS *	< 26	< 29	< 170	< 25	< 30	580	< 33	100
12:2 FTS *	< 26	(20)	200	< 25	< 30	1500	94	100
PFBS	(6)	(14)	(160)	(18)	(21)	< 230	< 33	100
PFHxS - lin	(18)	34	200	(18)	(21)	320	< 33	100
PFHxS - br1+br2 *	< 26	(7)	< 170	< 25	(7)	(53)	< 33	100
PFHpS *	(18)	(14)	(120)	(18)	(21)	< 230	< 33	100
PFOS - lin	840	1600	5500	470	1300	3200	94	50
PFOS - br1+br2	160	410	1900	110	370	480	31	100
PFNS - lin+br *	< 13	< 15	< 85	< 13	< 15	580	< 15	50
PFDS – lin *	(18)	41	(120)	(18)	56	850	(23)	100
FOSAA	< 26	(14)	(120)	(6)	(21)	(210)	(16)	100
FOSA	12	(27)	< 170	(12)	49	320	(8)	100
N-Me-FOSAA	12	41	240	(18)	63	2000	(8)	100
N-Et-FOSAA	72	280	990	54	180	5500	47	100
Simple sum (ng/kg)	*1200*	*2600*	*11000*	*1100*	*3000*	*18400*	*870*	-
PFOS and derivatives (ng/kg)	*1200*	*2500*	*9400*	*750*	*2100*	*13000*	*230*	-
*Level above PFOS and derivatives of 13500 ng/kg dw **	*0.09*	*0.18*	*0.69*	*0.055*	*0.16*	*0.96*	*0.017*	-
Sum of $PFAS_{24}$ in PFOA eq. (ng/kg)	*2700*	*5200*	*24000*	*2200*	*5300*	*18500*	*890*	-
Dry matter	68	49	6.9	63	23	9.6	26	%
Sum of $PFAS_{24}$ ww (in PFOA eq.) above EQS_{sed} (humans) 77 ng/kg ww	***24***	***33***	***21***	***18***	***16***	***23***	***3.0***	

The ratio between PFOS-lin/PFOS-br is very consistent, and the presence of impurities is typical of electrochemical fluorination. This was typically used before 2006, but may still be present if other PFOS-derivatives are imported from e.g. China where electrochemical fluorination still is used. A higher ratio, could signify an older contamination since the branched PFOS degrade faster upon biotic degradation (e.g. fish). Langberg et al. (2021) hence found that the distribution between linear PFOS and branched PFOS was higher in pore water, than in fish livers – likely since branched PFAS in the fish livers are more easily enzymatically metabolised, than the linear PFOS.

It is also clear that some use of prePFOS sulfonamides (presence of FOSA, N-Me/Et-FOSA), possibly as the N-Me/Et-FOSEs, which were included in the method, are non-polar an in this (anionic) LC-MS method had very low sensitivity and therefore also uncertain identification. They were therefore not reported, but it would be relevant to search for such non-ionic PFAS, as well as for cationic PFAS (e.g. 6:2 and 8:2 FTAB used in firefighting foams), in future studies using methods optimized for such compounds. The presence of sulfonamide compounds, often abbreviated to FASA (fluorinated alkyl sulfonamides), correlates well with these substances being amongst the top 8 (tonnes/yr) imported PFAS in Denmark (DK EPA, 2016 p.7). Concerns of the potential hazard of N-Me-FOSE has led the US EPA to issue a test order on the substance (US EPA, 2024). Recent data also show that even <C6 FASAs bioaccumulate in fish and contribute significantly to the sum of PFAS (Pickard, 2024). The prePFOS sulfonamides are typically used as surfactants for surface coatings to provide oil, water and dirt-repellency, and have also been used in firefighting foams. Until recently the main chemical provider was 3M but in the past 10-15 years other vendors mainly from China and India have entered the market. In the Danish list of PFAS EQS (DK EPA (2023) which is a translation of the draft WFD and its EQS) these prePFAS are not listed and hence no RPFs are available. These prePFOS are therefore not included in the Sum of $PFAS_{24}$. Given that the simple sum of prePFOS is about the same level as the PFOA-equivalents for all the other PFAS, shows that had prePFOS been included (using an RPF=1, see section on Regulation) the EQS would have been exceeded. Furthermore since the prePFOS are taken up in the food chain and transformed in biota such as hens and pigs (Numata, 2014 and Kowalczyk, 2020) and in fish (Pickard, 2024) it is likely that the (future) RPFs would be at least as high as for PFOS. If prePFOS in the future will be included in the list of PFAS, it therefore increases the likelihood that the PFOA-equivalents will be above the EQS. Since prePFOS accumulate in sediment and biota, it is relevant to investigate if current uses exist and can be prevented.

Other PFAS screened for but not found by this method were: PFCA and precursors category: PFBA, PFPeA, 4:2 FTS, diPAPs (n=12,14,16), S-diPAPs, and in the PFSA and precursors calegory: PFPeS, N-Me-FOSA, N-Et-FOSA, N-Me-FBSE, N-Me-FHxSE, N-Me-FOSE, N-Et-FOSE, SAmPAPs (n=12,14,16). All the PFAS that were detected had native standards that were used for calibration. As described in the Analyses section, substances that have their own native internal standards, have higher identification and quantification certainty than the PFAS marked with *, which did not have either native standards and/or internal standards.

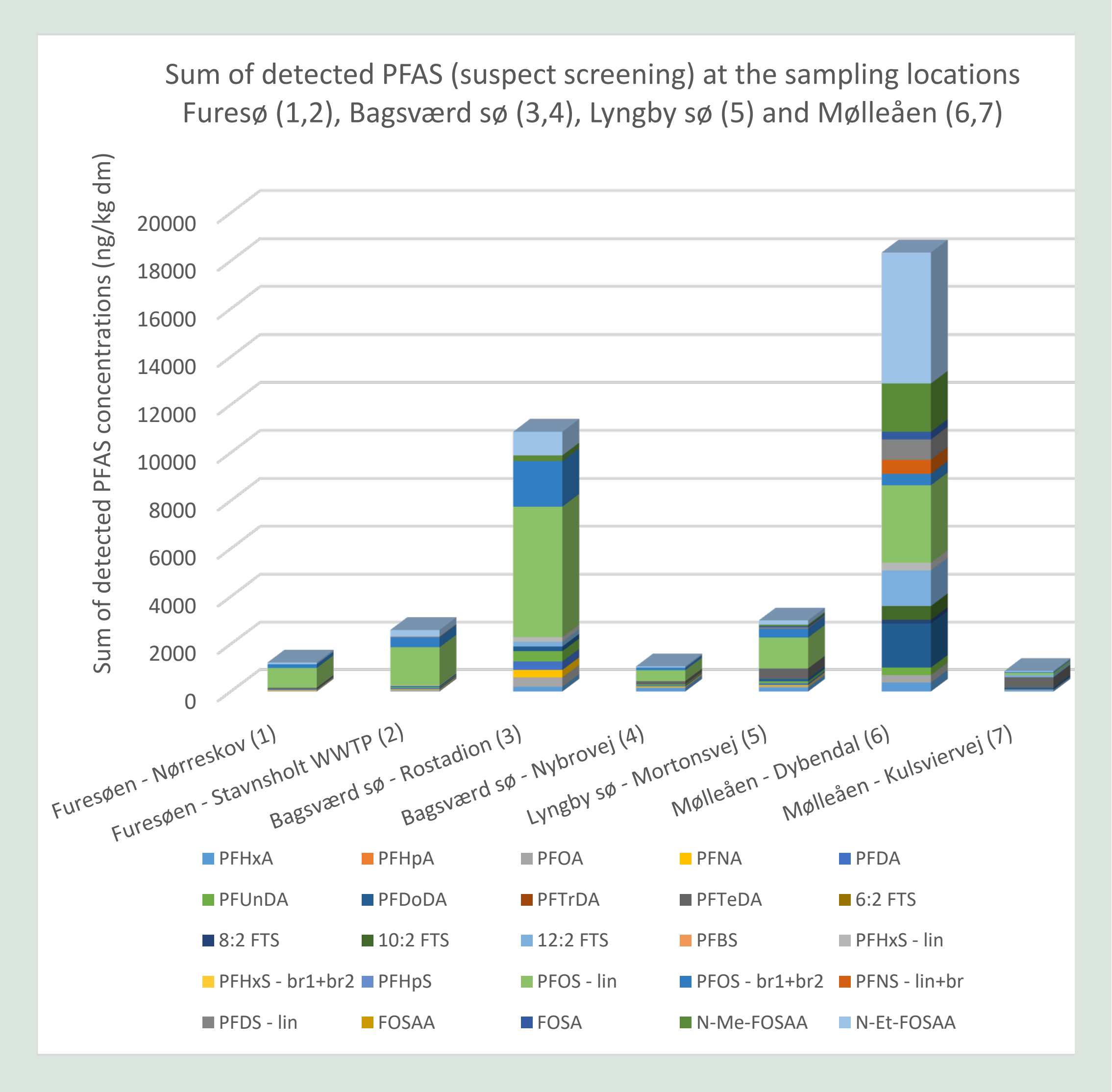

FIGURE 8. Shows the ‘Sum of detected PFAS’ by LC-MS suspect screening at the sampling locations.

The sites near the wastewater treatment plants have more varied PFAS patterns, with higher presence of PFCAs and long chained 10:2 and 12:2 FTS (which are PFCA precursors). The levels of N-Me/Et-FOSAAs are particularly high. This could point towards mixed sources of pollution, from both households, industry and possibly research institutions leading waste water to the site. Historic as well as current uses of PFAS are likely based on the patterns.

The samples taken from Bagsværd Rowing Stadium (3) and Dybendal WWTP (6) were very watery, with low dry matter (dm). When transforming from ng/mL to ng/kg (concentration (ng/kg dm) = concentration (ng/mL) * volume (mL)/weight (g dm), the concentration will be divided by a small number – which means that uncertainties also will be magnified. There is also an uncertainty that the sediment samples are not homogenous, since in lakes there can be a mixture of small pieces of branches, leaves, stones etc. that are (and cannot) be fully homogenized. This means that a sample taken for analysis (of x g) does not exactly contain the same organic matter or dry matter weight as the subsamples that were taken for dry matter weight determination. However, since duplicates were taken for dry matter determination some variation can be expected to have been accounted for.
To further enable comparison with $EQS_{sediment}$ values, future sediment studies would benefit from measuring not only the dry matter, but also the organic carbon.

Nørreskoven – Furesøen is situated away from known sources of direct PFAS emissions, and have lower levels in the sediment. However, there is still a pattern of predominantly PFSA contamination, which could point towards older PFSA contamination that via water and particulate matter has spread over the lake.

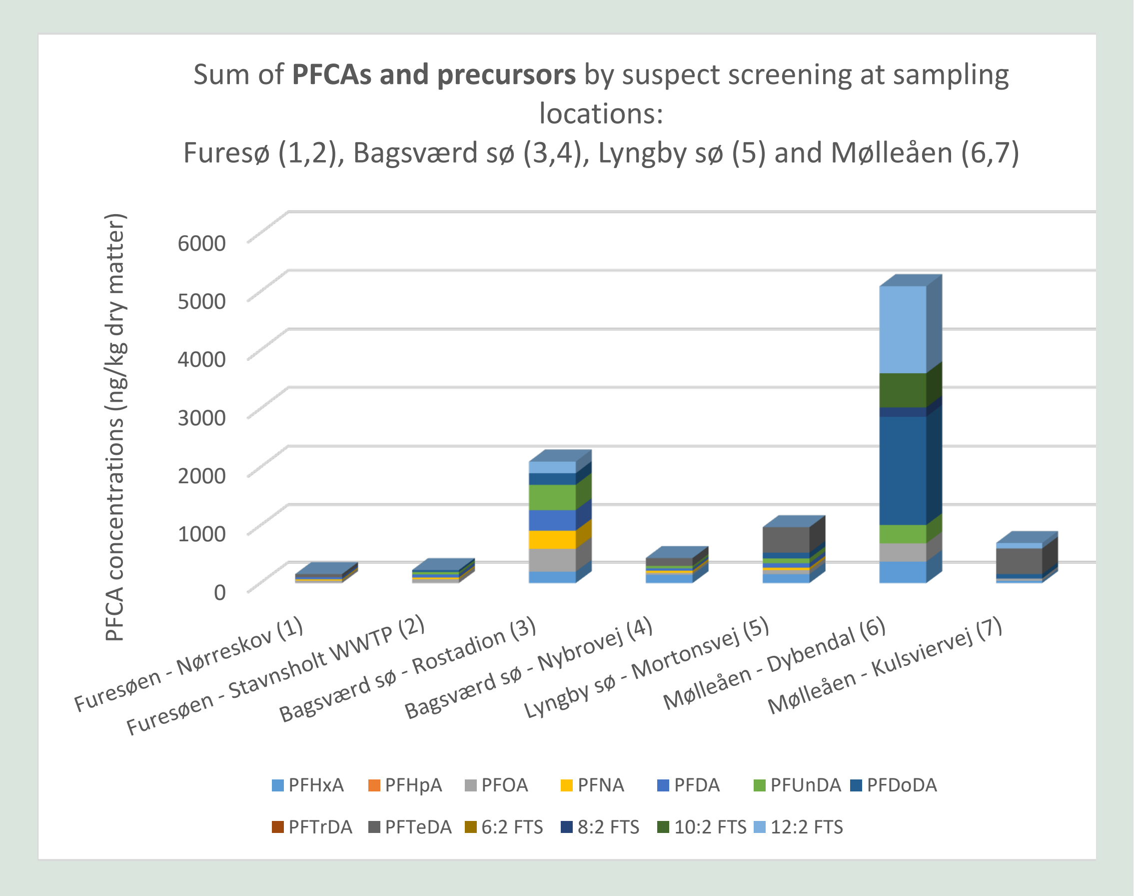

FIGURE 9. Shows the detected **PFCAs and precursors** at the sampling locations

Dybendal (6) has a specific pattern of x:2 FTS, from 6:2 to 12:2 FTS, with increasing levels with increasing chain length which correlates with their distribution towards the sediment. This is in line with the previous findings of 6:2 FTS in the effluent waste water and also 6:2 FTS in the water. It also correlates with the pattern in Figure 11 from Langberg et al. (2021). The metal plating industries may be using the non-restricted FTS in their production.

High levels of long chain FTS can also explain the sediments higher levels of long chain PFCAs (PFDA, PFUnDA and PFDoDA), which are degradation products of the FTS's cf. Figure 2. Since the long chain PFCAs have rather high relative potency factors (RPFs) the continued use of FTS will contribute to a higher risk level for the sum of PFAS, for biota and for human consumption of fish and wildlife.

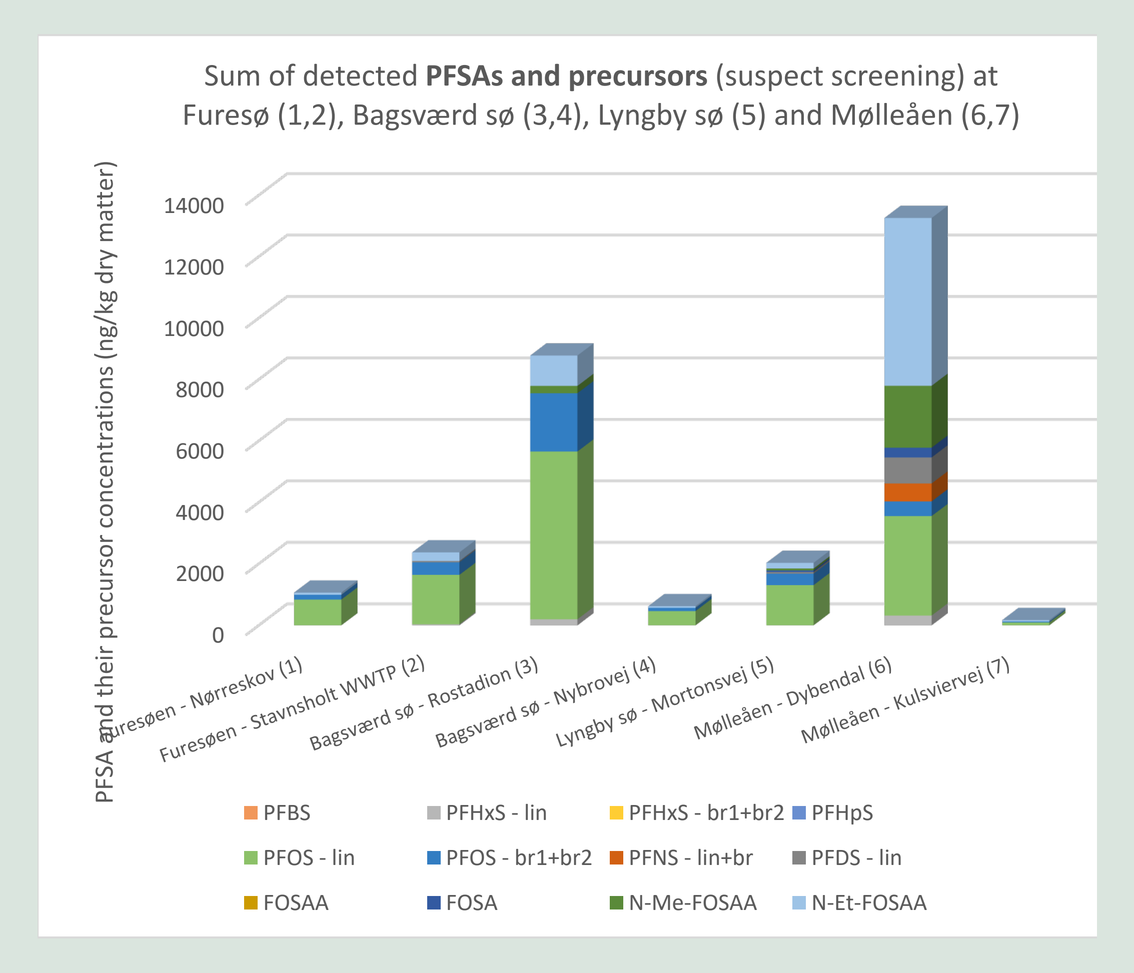

FIGURE 10. Shows the Sum of detected **PFSAs and precursors** (suspect screening) at the sampling locations. In this figure the isomers of PFHxS and PFOS are shown separately for the linear (lin) and the branched (br1+br2). For PFNS the sum of linear and branched are shown ($PFNS_{lin+br}$) and for PFDS only the linear ($PFDS_{lin}$) is shown, since the branched PFDS was not detected. For N-Me-FOSAA and N-Et-FOSAA both linear and branched isomers were detected and added to the sum. Rostadion = Rowing Stadium.

The sites Mølleåen – Dybendal WWTP (6) and Bagsværd – Rowing Stadium (3) have remarkably high levels of PFOS precursors (FASAs, here N-Me/Et-FOSAAs), which are degradation products of N-Me/Et-FOSEs. The presence of more than one from this group of prePFOS strengthens the identification. It may be that N-Me/Et-FOSEs also were present but this would require further investigation since these non-ionic substances have low sensitivity in LC-MS analyses. The 'FOSA' pattern correlates well with the findings of Langberg et al. which shows that the patterns of PFAS are somewhat correlated to their source, in the plot shown in Figure 11.

Bagsværd Rowing Stadium's PFOS and precursor pattern points towards that some surface coating of e.g. wood, textile, leather or paper, e.g. Scotchban (by 3M) has been used or emitted near the Rowing Stadium.
Mølleåen – Dybendal WWTP has additional PFSAs, namely PFHxS, PFNS and PFDS that contribute to the sum. It is worth noting that PFNS is not included in the $PFAS_{24}$ EQS, but is relevant to include since it is both toxic and occur in environmental media.

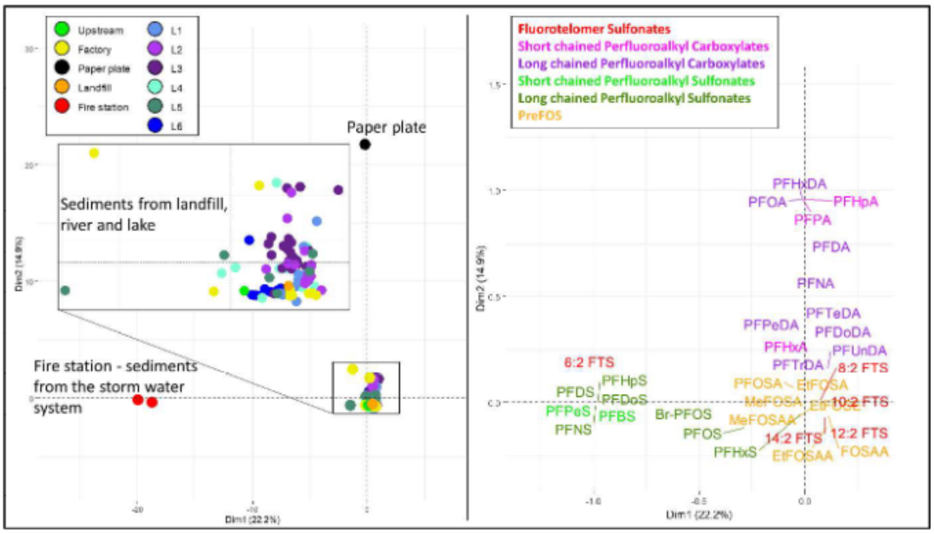

Figure S13. Principal Component Analysis (PCA) for sediment samples and the product from the factory (paper plate). In the score plot (left), sediments from the factory area, landfill, and the lake grouped together close to the centre (0,0), while sediments from the storm water system at the fire station grouped towards the left. In the loading plot (right), FTS longer than 6:2 FTS and preFOS grouped close to the centre (0,0), while PFCA were plotted along the y-axis. PFSA and 6:2 FTS grouped towards the left. Concentrations below the LOQ were treated as 0.

FIGURE 11. Typical PFAS patterns from various industrial activities. From Langberg et al. (2021)

In the future it could be highly relevant to test sediment and biota for PFAS that accumulate here, such as long-chain (>C7$_F$) and FASAs (<C6) and non-ionic PFAS. This information would be relevant to assess PFAS levels in benthic organisms such as invertebrates (shellfish, mussels, worms) (Yeong ,2022) which from the lower level of the food web are a source of PFAS that accumulate in fish and wildlife consumed by humans. An initial prioritization of which PFAS to include in the screening could be based on frequently detected PFAS (Danish Regions (2022)), as well as knowledge of PFAS used in high volumes such as perfluoropolyethers (PFPEs), cf. the Danish product registry (DK EPA, 2016), and complemented by a broadening of the PFAS monitoring to methods that can detect non-ionic, cationic and side-chain polymer PFAS. Since the product registry does not cover all Danish uses of PFAS, and because the types of PFAS depends both on the industry and whether some PFAS are restricted and replaced by other PFAS, such lists would have to be updated regularly, e.g. every 3-5 years.

To complement the target and suspect screening analyses, PFAS Total methods could be used to identify sites or matrices with high levels of PFAS. A PFAS Total limit value has been set in the revised EU Drinking Water Directive, and in the ongoing negotiation of the EU WFD (EQS values), countries have proposed ot include a PFAS Total EQS for surface water as well. A variety of 'PFAS Total' methods exist, with Extractable Organic Fluorine – Combustion Ion Chromatography (EOF-CIC), Total Oxidizable Precursor Assay (TOPA), non-targeted high resolution mass spectrometry (NTS HRMS), Proton Induced Gamma Emission spectroscopy (PIGE) and 19F NMR being the more commonly used techniques. Common to all of these are that though they detect more than target analyses do, they still only detect a fraction of the totality of PFAS, why they are referred to as Total Assessed PFAS, or proxy for PFAS Total. Methods have been reviewed by the Nordic Council of Ministers (NCM, 2022) but methods improve rapidly due to the high interest in assessing a higher fraction of class of PFAS. Recent studies by Zweigle et al. (2024) have shown, that there is a good correlation between the EOF-CIC and NTS (by LC-MS using FindPFAS) for soil, sediment and ashes, and that short-chain PFAS do not contribute significantly to the sum. For screening purposes, the cheaper and faster EOF-CIC may therefore be sufficient to use to prioritize samples.

8. Exchange of PFAS between sediment and water

8.1 Exchange model

Benskin (2012) found, that PFOS precursors were present in significantly higher concentration in marine sediment than in water, where mostly PFOS was detected. This means that sediment can release PFOS upon degradation of prePFOS. It is therefore of key interest to examine the distribution of PFAS between sediment and water.

To describe how emissions of PFAS may have resulted in pollution in a lake Langberg *et al*. (2021) used a two-box water sediment model. The exchange of PFAS between sediment, water, biota and air has been described in Arp et al. (2014), and is here shown as a two-box linear water-sediment model in Figure 12.

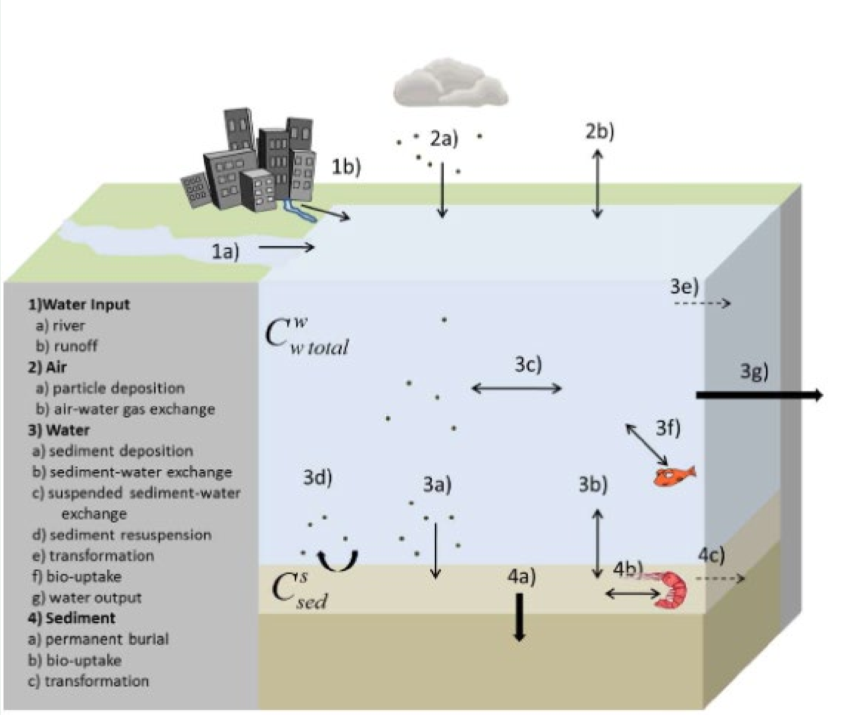

FIGURE 12. Distribution of PFAS between environmental compartments. From Langberg et al. (2021)

The model can in principle be used for 'systems' as lakes, fjords etc. and for different pollutants, provided that necessary data inputs are available. As reviewed by Sima and Jaffé (2021), data inputs include sedimentation rates, physical properties (e.g. temperature, convection i.e. 'mixing' of the system which is affected by wind and currents), chemical properties (such as pH, salinity and sediment composition such as total organic carbon (TOC)) and PFAS concentrations. Particularly the TOC influences the partitioning of PFAS to sediment. TOC is in turn linked to the sediment deposition rate, which is affected by currents. The current also influences the thickness of the still layer above the surface, which is a diffusion limited step in the exchange of PFAS between sediment and the bulk water. The concentrations of pollutants in the still layer are typically measured as the pore water.

However, when steady state conditions apply, the thickness of the pore water (slowing down release of PFAS from the sediment to the bulk of water) is not affecting the measured concentration in the bulk water. Steady state may be assumed when there are no major changes in the PFAS influx or outflux of the system, when the temperatures are fairly stable, and when sampling times exceed the time it takes for PFAS concentrations to equilibrate between sediment and the bulk of water. The model hence applies if the pollution stems from historic uses, or if the current emissions are small compared to the amount of PFAS already present in the system.

For this study, the influx conditions are generally fulfilled (historic emissions), with a potential exemption near waste water treatment sites where the current influx may exceed the outflux. With regards to physical parameters the assumptions are also acceptable, since the water temperatures were fairly constant (5-11 °C) and sampling took place over approximately 4 weeks (with Sorbicells). Based on this a steady state can be assumed, and it was therefore sufficient to measure PFAS in the bulk water and not pore water. On the other hand, limits to costs and complexity, meant that the study design did not include all the types and numbers of samples to properly estimate the different compartment and fluxes. A simplified steady state model similar to Benskin (2012), (Figure 13) was therefore used in this study.

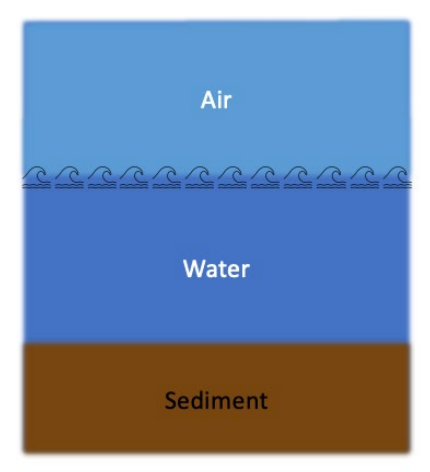

FIGURE 13. Model used to describe sediment-water distribution coefficient

The sediment-water distribution coefficient, $\mathrm{K_D}$ (L/kg dm) with ‘dm’ being dry matter, was calculated by dividing the concentration in sediment by the concentration in water:

$$K_D = \frac{c_{sediment}}{c_{water}}$$

, where:

$\mathrm{c_{sediment}}$ is the concentration measured in sediment $(\mathrm{ng/kg\ dm})$

$\mathrm{c_{water}}$ is the concentration measured in surface water $(\mathrm{ng/L})$ by Sorbicells.

The determined $\mathrm{K_D}$ value is applicable to the area where the sample was taken, and we assumed that during the sampling there would be no significant transport in space (vertically or horizontally) or in time. We also assumed a limited exchange with/from air (including arial deposition). It is also assumed that the c_{water} is constant, which is a fair estimate, given the concentration represent an average of the approximately 4 weeks the water was sampled with the Sorbicell.

In the case that K_D values were found to be constant it would mean that the $c_{sediment}$ were constant across the sampling areas. In the case that the sediment had a very homogenous composition this could indicate one common and well-distributed source, e.g. rain. However, as the sediment in lakes and rivers is rather inhomogeneous with very different TOC in it, it is expected that the K_D and concentration in sediment can vary as it is dependent on the sedimentation rate, current, temperature etc. Also, in the case that there are PFAS point-sources in e.g. at the end of a waste-water pipe or where a creak runs out from a PFAS polluted area, differences in the K_D will between highly polluted and less impacted sites.

The ratios between sediment and water were calculated for PFOS (Table 9), which was the predominant PFAS in the sediment and the only substance detected in water (by Eurofins). The distribution coefficient is also presented as a logarithmic (base 10) value for easier comparison.

It seems that the PFOS levels double going from Kulsviervej to Nørreskoven (our ‘background’ reference point, upstream in Furesøen) and to Stavnsholt, (logK_D =1.5-1.8-2.1). Nybrovej, Mortonsvej and Mølleåen/Dybendal WTTP are about the same levels (logK_D =2.4-2.6), while Bagsværd rowing stadium is significantly higher (logK_D =3.3).

TABLE 8.1. Preferential partioning of PFOS to sediment vs. water

PFAS	**Unit**	**Nørr (1)**	**Stav (2)**	**Bags (3)**	**Nybr (4)**	**Mort (5)**	**Møll (6)**	**Kuls (7)**	**Average**
PFOS-sed-Eurofins	ng/kg dm	540	1300	12000	430	2900	1300	350	
PFOS-sed-UCHP		990	2000	7400	570	1700	3700	130	
PFOS-sed- average		765	1650	9700	1000	2300	2500	240	
PFOS - water	µg/L	12	12	5.2	3.9	8.2	5.8	7.5	
$K_{D\ average}$ (sediment/ water)		**64**	**138**	**1870**	**256**	**281**	**431**	**32**	
log K_D		**1.8**	**2.1**	**3.3**	**2.4**	**2.6**	**2.6**	**1.51**	**2.3 ± 0.6**

At Nybrovej, Mortonsvej and Mølleåen/Dybendal WTTP there could be specific PFAS sources. At these three locations the sediments were all very humus rich (high TOC). A local PFOS source is therefore likely near Bagsværd Rowing Stadium. The sediment is likely a sink of prePFOS (and other PFAS that distribute to the sediment) which upon degradation releases PFOS.

The values are in accordance with previous studies of logK_D’s for PFSAs. Benskin (2012) hence reported logK_D for PFSAs of 2.5 ± 0.12, which is within the range of this study’s finding of Log$K_{D,\ PFOS}$ = 2.3 ± 0.6 (n =7). Other studies have reported $\log K_D$ values for China (2.88-3.67), The Netherlands (2.35), and France (2.4). For the PFAS of varying chain lengths, it is expected that log K_D increases as the number of CF_2-units increases or when other hydrocarbon moieties are attached. Such as distribution pattern can also be observed in reversed phase liquid chromatography (e.g. C18 column) where long chain PFAS and those with more hydrocarbon moieties have longer retention times, e.g. for SN-diPAPs, S-diPAPs, SAmPAPS etc. (Trier et al. 2011a).

8.2 Historic patterns from sediment cores

Langberg et al. (2021) used a (very approximate) Koc model, and estimated that PFOS based Scotch ban should have peaked in the top 1 cm sediment and water around 1985, whereas FTS should have peaked around 2005, see Figure 14.

In our study the sampling equipment (handheld Kayak sampler) did not allow for the dissection of very precise 1 cm layers. Likewise will a van der Veen grab not give a precise layered core, but rather such sampling requires hydraulic equipment available at ships for marine waters.

Often the lake and river sediment were so water-rich that water/sediment layers were not distinguishable. We could therefore not make a historic line of concentrations down through the sediment.

Another approach to determine time trends, without depending on machinery that may not be accessible, is to monitor the same spot on a yearly basis.

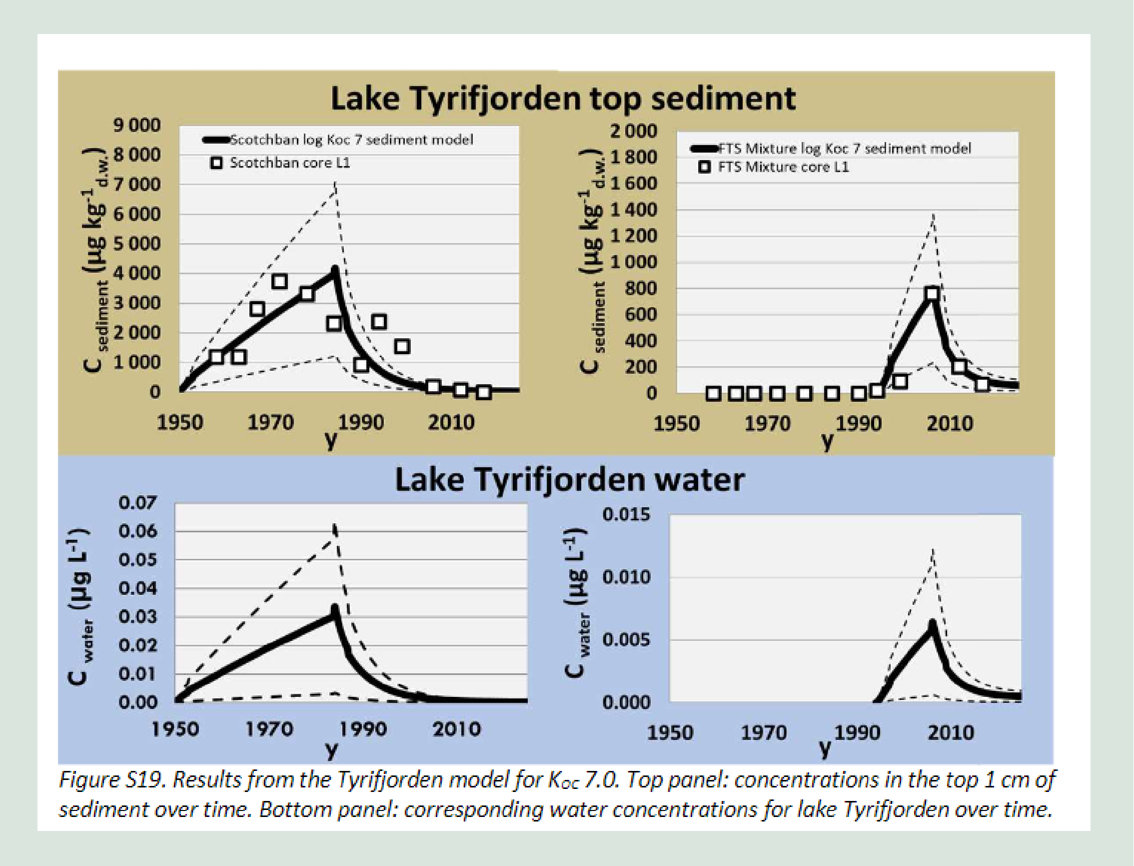

Figure S19. Results from the Tyrifjorden model for K_{OC} 7.0. Top panel: concentrations in the top 1 cm of sediment over time. Bottom panel: corresponding water concentrations for lake Tyrifjorden over time.

FIGURE 14. An example of modelled emission patterns of PFOS, taken from Langberg et al. (2021)

9. Outlook on future surveys for PFAS in surface waters

9.1 Sampling strategy and source tracking

The sampling strategy and where to sample, fully depends on the purpose of the analysis, and needs to be clarified from the beginning. The different purposes also influence which PFAS that are measured. Examples of different purposes include
a) checking compliance with environmental limit values
b) risk assessment in relation to intake of food from polluted areas
c) source tracking to determine who the polluter(s) is/are
d) long term surveillance.

The sampling strategy should ideally be based on the knowledge of existing pollution levels and on potential emitters current and historic activities likely to have used specific PFAS. A list over activities that are likely to use PFAS in Denmark can be found in the 'PFAS handbook' (Danish Regions, 2022).

Different aims of the different regulations and their related authorities (Regions and municipalities) means that sampling and monitoring strategies currently are not harmonised. A stronger coordination mechanism and data-sharing and -collection between the involved institutions may help to effectively design monitoring strategies, that will make it possible to get a more complete picture of the contamination patterns. This will in turn provide evidence to support decision-making and risk reduction measures. It may be useful to extend collaboration and build on experiences of neighbouring countries such as Norway, Sweden and Germany who have conducted research, monitoring and managed environmental risks of PFAS for more than 10 years.

Sampling water from the lake

Knowledge of existing pollution levels and current or historic activities, will increase the certainty in the identifications of pollutants and thereby support the source identification (Salvatore, 2022). This may require that information from municipalities/regions on both environmental permits and monitoring made by the authorities or the industry are made readily accessible to investigators. When tracking sources, it is important to chose matrices that are site specific and consider if the pollution is current or historic – and if the PFAS are most likely to be found in water or sediment/biota. For long-chain PFAS sediment sampled close to emission points can give information both on current and historic emissions. Typically there is also a lower rate of transformation of precursors so the original PFAS is more likely to be found, than if measured in e.g. fish that enzymatically transforms prePFAA to PFAA. Biota that only have limited enzymatic degradation of the precursors may also be good species for source tracking, such as invertebrates (shellfish, crabs, mussels) (Langberg et al. 2019) and in general benthic organisms living in or near the sediment have high levels of PFAS in them (Young 2022).
For water soluble PFAS, measurement of water sampled up- or down-stream to a suspected source may be useful, and has been used by the US EPA as evidence of polluters.

It would be most important to ensure that 'baselines' or 'reference points' of 'background anthropogenic pollution' levels are established to support the evidence of a point-source pollution, for cases where the polluter is required to pay or take action. It is also absolutely critical to always collect at least duplicate sampling blanks, to avoid that PFAS blanks (which are common and particularly relevant at ng/L concentrations) lead to false positives, or increase the limits of detection.

For the source tracking by use of suspect or non-target screening, it would be important to prioritise to look for PFAS that have been used in high amounts (DK EPA, 2016), for PFAS that are restricted or are intended to be restricted PFAS, and also to look for legacy PFAS. If high levels are found for PFAS not yet covered by the EQS, such PFAS could be flagged for attention to the municipalities who are in contact with industries. If considered a substantial risk, the municipality has the option to ask the industry to measure and provide the data. Other options are to include the PFAS in the monitoring surveillance programs, and potentially making national legislation on them.

Table 10 below shows how the different matrices will influence various parameters relevant for the study design and interpretation.

TABLE 9.1. Parameter affected by the matrix sampled

Parameter affected by the matrix sampled	Water	Sediment	Biota
Easy to sample	Yes	Partially	No
Sample homogeneity is high (lower uncertainty)	Yes	No	No
Short chain PFAS (with low RPFs)	Yes	No	Somewhat
Site specific (point sources)	Partially	Yes	Yes (mussels/shellfish) No (fish)
Historic use pattern	Partially	Yes	Somewhat
Long chain PFAS incl. precursors (with high RPFs)	No	Yes	Yes (mussels/shellfish) Somewhat (fish)

9.2 Sampling

Depending on what the purpose of the analyses is, there are several options to further improve the study design and the data generation.

Better understanding of the degree of contamination in a water body:

1) Measure at more sites to get a more representative sampling of the area of the lake/rivers
2) Take duplicate samples as a minimum, but triplicate measurements are better
3) Take measures to avoid contamination, and correct for blank values to ensure that levels do not come from the handling or laboratory solvents or equipment (cf ‘high’ 6:2 FTS blanks)
    a) Clean equipment (including plastic-ware, Sorbicells etc.) with alcohol (ethanol) if possible. For Sorbicells that need to be ‘wetted’ with water, supply clean lab-water or prewet them so on-site water does not need to be used
    b) Always take field blanks that follow through the method

Understand in which compartments which PFAS are most prevalent

Table 11 below provides and overview of which PFAS are more likely to be found in different media, and the pros and cons of their relevance and of sampling them.

TABLE 9.2. Choice of sampling media – pros and cons

Sampling media	Relevance	Note
Bulk water	Sampled between the surface layer and the sediment is generally homogenous and relatively simple to sample and analyse. Fluctuations over time can be evened out by use of 4 weeks sampling with Sorbicells tested in this study. Mainly the short-chain, water soluble PFAS will be present in the water. In contrast the long chain (incl. prePFOS precursors) do not distribute to water, and will mainly be present in the water column bound to suspended particulate matter. Since the short-chain PFAS are considered less toxic than the long-chain PFAS (cf. their relative response factors), the PFAS in the bulk water will likely not be the main risk drivers in the lake and river systems. PFAS in bulk water is can mainly provide information on compliance with environmental limits current emissions of water soluble PFAS.	Bulk water is not useful to test for long-chain precursors and for legacy PFAS contamination. At different locations different Sorbicells will sample varying volumes, resulting in different LODs.
Top layer water and foams	Will contain the *l*ess water soluble (long-chain) *surfactant* PFAS that distribute to interfaces such as water-air, and have concentrations up to hundred folds higher than the bulk water. Natural foams blown to the shore and in-lands can contaminate the terrestrial ecosystems. Top-layer water and foams are therefore likely risk drivers, for water surface-dwelling biota, and is highly relevant to sample.	Top layer water and foams are currently not included in sampling guidelines
Pore water in sediment	Measurement of PFAS in pore water will be needed to further refine exchange models, but may not be necessary for routine sampling.	
Sediment	Sediment is a key source of exposure for smaller sediment-dwelling animals (e.g. benthic and worms) at the bottom of the food chain, and other animals, such as bottom-dwelling fish that feed of the sediment. Sediment will preferentially contain the long-chain PFAS (such as PFAA precursors) which are more toxic (higher RFPs). Sediment is therefore likely to be the risk driver in a water body. Sediment is more site-specific than both water and biota like fish and birds. PFAS concentrations in sediment can provide information on Point sources Sinks of PFAS and precursors in the sediment Historic patterns	Is much more inhomogeneous and is more difficult to sample than water, especially in lakes and rivers where ships with drilling equipment cannot enter. Getting the top 2-5 cm of *undisturbed* sample may therefore be difficult. Large variations between levels at sampling locations are common, and even between replicates.
Biota	Biota will typically bioaccumulate (animals, long chain PFAS) or biocentrate (plants, short chain PFAS) making it easier to detect PFAS. Fish may be good to sample to assess human risks particularly for PFAAs. The fish species, age and feeding patterns will influence their PFAS levels, where particularly top-predator fish feeding on bottom-dwelling fish can be expected to have highest PFAS levels. Biota with less enzymes (e.g. shellfish and mussels) and which are more site-specific, are better indicator species to detect the original PFAS (precursors of PFAAs) such as such as FTS (Langberg et al. 2019, and hence to track sources of PFAS pollution. Wildlife, such as ducks and other birds and terrestrial animals living and hunted near surface waters (mice, boars, dears) could be sampled to assess risks from human intake and effects on terrestrial ecosystems. Algae/water plants at the water surface may theoretically have relatively high PFAS, from PFAS residing at the water surface. PFAS in biota can provide information on Point sources Precursors of PFAS (biota without enzymes) PFAA loads (biota with enzymes) and risk from human intake	Is more difficult to sample. Fish are not ideal for source identification, because their enzymes degrade precursors of PFAAs to PFAAs, and because they may migrate in winter to avoid frozen areas

9.3 Analyses

Which PFAS to look for in which levels depends on the aims of the study and hence what the data will be used for. Exploratory and pre-assessment analyses are typically used to discover a broad array of PFAS (and other chemicals) present in the sampled medium. This may be also be used to look for potential sources and typically non target or suspect screening analyses are used, potentially in combination with Total PFAS methods as an initial screening. Here the semi-quantification may be acceptable. Table 12 below shows some pros and cons in the choice of different target, suspect screening and group-based PFAS analysis methods.

TABLE 9.3. Choice of analytical methods for different purpose of analysis

Purpose of analysis	Target analysis (confirmatory)	Suspect screening (exploratory)	Group-based methods (exploratory)
Compliance testing	Yes, gives accurate data for the selected PFAS in the method	Possible, but time consuming. Mainly useful for authorities to demonstrate a concern of non-compliance, which can be used to ask the suspected polluter to provide more evidence. Can be used to identify sources of pollution. Sensitivity and speed of analysis could be increased by use of online SPE.	Yes, if the limit values are set for PFAS Total, as for drinking water (EU) and for food contact materials of paper and board (DK). Sufficient instrument capacity and LOD of methods (in DK) due to blanks are currently a challenge.
Input to risk assessment	Yes, gives accurate data for the selected PFAS in the method	Good for the PFAS not included in the target analyses. Sensitivity and speed of analysis could be increased by use of online SPE.	If the method has information on the substances, it can be used – e.g. for 19F NMR, for Total Oxidizable Precursor Assay (TOPA) that measures the degraded PFAAs (but works only for PFAS that are prePFAAs and PFAAs). Total fluorine (EOF-CIC) methods that lack substance information cannot be used.
Screenings	Not ideal since it has a limited chemical scope (few PFAS measured)	Yes, has a broader chemical scope than target methods – but depends on the method and if both non-polar, and if (an/cat) ionic PFAS are measured	Yes, gives a broader chemical scope, particularly for EOF-CIC methods and depending on the sample preparation also for 19F NMR. TOPA can measure for typically only (an)ionic prePFAAs and PFAAs.
Surveillance	Yes, gives accurate data for the selected PFAS in the method	Detection frequency of substances may be a useful trend to monitor. To assess concentration trends, the (semi-)quantification will have to stay constant.	Yes, to measure trends in Total PFAS
Further improvement needs	For target analyses, better use of monitoring resources could be achieved by prioritizing to measure the PFAS present in the matrix – e.g. short chain PFAS in water, and long chain PFAS in sediment. Methods need to be expanded to analyse for neutral and cationic PFAS which are used, but seldomly included in PFAS analysis packages. Further work to reduce surface area in contact with the sample and chosing materials to avoid adhesion of PFAS – and blanks. Washing of all materials in ethanol to avoid blanks.	Suspect screening are costly and time-consuming, mainly on the data-interpretation side. Increasing the automisation of the identification is key to speed up analysis and lowering costs. MS acquisition method (such as Data dependent analysis, DDA) that are interoperable with commercial softwares such as FluoroMatch could be explored in the future. They can therefore be prioritised for use as i) (early warning) screenings ii) to get further information if screening analysis points towards significant PFAS pollution iii) to identify the polluter. Prediction tools such as fragmentation patterns, retention times, chemical synthesis patterns and presumptive contamination patterns may further enhance the certainty of identification. Lowering the LOD (and increasing extraction efficiency) will increase identification certainty of substances. Intercalibration of the methods between laboratories will increase the robustness, expertise and trust in the methods when used in decision making	Screening of PFAS total could in the future be a good starting point, to base prioritisation of locations to further analyse. Currently PFAS Total analyses works best for water followed by biota and sediment. It is least costly if sampling for all potential ‘analysis packages’ is done at one time.

Table 13 summarised which PFAS that may be relevant to monitor in different media in future studies.

TABLE 9.4. Suggested *specific* PFAS in various aquatic media

Sampling media	**Relevance**
Bulk water	Short-chain water soluble <C7 PFAS such as 4:2 FTS, 6:2 and 8:2 FTS and their FTCA degradation products, as well as short-chain PFAS (e.g. 6:2, 8:2 FTAB) as well as PFECHS and TFA which increasingly are being found in water, would be relevant to include in future studies. *Surface (top-layer) water and foams* would be relevant to investigate for long-chain >C6 (an- cat- and non-ionic) PFCAs and PFSAs.
Top layer water and foams	Relevant to investigate for long-chain >C6 (an- cat- and non-ionic) PFCAs and PFSA
Pore water in sediment	Same PFAS as for the bulk water – but if used for modelling experiments, then also the long chain PFAS likely to distribute to soils need to be measured.
Sediment	Long-chain PFAS with Kow>1, including >C6 PFCAs and PFSAs and their derivatives: N-Me-FOSE and N-Et-FOSE and their impurities/degradation products (FOSA, Me-FOSA, Et-FOSA, Me-FOSAA, Et-FOSAA) and PFNS which have major PFAS uses in Denmark (DK EPA, 2016), and their replacement chemicals: E.g. derivatives of PFBS, PFHxS, 6:2FTS, 8:2 FTS og 10:2 FTS. In sediment addi-tionally long-chain PFCAs (C10-C14), PFSAs (C10-C12) and their precursors, such as fluorinated al-kylated phosphate esters (PAPs) and long-chain fluorinated carboxylates (FTCAs, which are degrada-tion products of FTOHs and FTSs and fluorinated sidechain polymers) and long-chain cationic PFAS such as FTABs and other (acrylic) betaines used as coatings of paper, textiles and building products. Also the an-/kat-/non-ionic perfluoropolyethers (PFPEs) have been used in high production volumes in Denmark (DK EPA, 2016), and the non-ionic FTOHs can be expected to occur in sediment near emis-sion points.
Biota	Relevant and may be easier to detect PFAS that accumulate; harder to sample and analyse. Fish: to assess intake to humans and the fish themselves; top predators and bottom-dwellers are most likely to accumulate long chain PFAS. Fish are not ideal for source-tracking, since they migrate and have enzymes that degrade polyfluorinated PFAS to PFAAs. Shellfish/mussels: good for source tracking as they are fairly site specific, exposed to PFAS in sediment, accumulate PFAS and have limited enzymatic degradation of precursors to PFAAs. Wildlife (ducks, boars, dears): feeding or drinking from surfaces of polluted freshwater (potentially containing sediement/soil) could be relevant to test for PFAS. Plants: Algae with high surface area and rich in sugars/proteins may adsorb long chain PFAS well; other plants may bio-concentrate short chain PFAS, particularly leafy plants from which water evaporates.

9.4 PFAS accumulation and distribution between sediment and water

As long as PFAS is emitted, PFAS will accumulate as the original PFAS used or as PFAS degradation products, such as PFAAs. Since PFAS are emitted to an already polluted environment, it will over time be more and more difficult to stay within compliance of the environmental quality standards set. In other words, there is less space left to pollute in, before the risks exceed tolerable limits. As mentioned in the section on regulation, the situation is closely linked to the lack of coordination between industrial and environmental regulations, both at EU and national levels.

In any case, in the future it may be increasingly important to establish whether PFAS originates from current emissions or from historic pollution, in order to establish who is the responsible authority and the responsible polluter. For this purpose, it may be useful to achieve a better understanding of exchange of PFAS between phases such as sediment-water. Some suggestions for studies could be to

a) Measure at different depths of the sediment. This requires specialized sampling boats that can take undisturbed cores, and access to inland lakes or rivers.
b) In addition to temperatures and dry-weight, it would be important to measure organic carbon content (TOC), pH, salinity, and pore-sizes which influence K_D.
c) As input to more refined exchange models, measurements of PFAS in pore-water would be needed.

10. Conclusions

The overarching purpose of this study was to investigate if PFOS found to exceed the water environmental quality standard ($EQS_{freshwater}$) in a river and lake system, and more generally if PFAS pollution, is likely to be cause by current point source emissions or due to legacy pollution released from the sediment. In addition it suggests which PFAS it could be relevant to monitor in which media in future studies. This study finds that it is likely that legacy pollution continue to pollute the river and lake system with PFOS, since much higher levels of PFOS and precursors (prePFOS) were found in the sedient than in the water. In addtition a number of other PFAS were found, e.g. the highly water-soluble 6:2 FTS, which points towards a combination of legacy and current activities emitting PFAS into the waterbody.

The PFOS levels measured by the Eurofins in water and in sediment were compared, and partition coefficients K_D were calculated for all 7 sites. The $LogK_{D, PFOS} = 2.3 \pm 0.6$ confirmed that PFOS also in this aquatic system distributes to sediment, and in the expected range seen from other studies. Outliers showed presence of suspected hot-spot polluted sites. More refined models exist but would require additional data, and hence additional testing of sediment structures, pore-sizes, organic carbon and of pore water at each site.

Methodology: Initially information was assembled on current and past activities potentially using PFAS near the river Mølleåen and the connected lakes (Furesø, Bagsværd sø and Lyngby sø), position of emission points (of sewage and run-off water) to the water bodies, and previously monitored data on PFAS in water, soil and waste water was gathered beforehand from several resources: The responsible Region (Hovedstaden), the municipalities (Furesø, Rudersdal, Gladsaxe, Lyngby-Taarbæk), the Danish Miljøportal (data and environmental permits), historic (news) articles on the internet, from chemical vendors and from contact with local stakeholders (Birkerød Sailing Club, Bagsværd Rowing Club, the Danish Nature Conservation).

The division of responsibilities, storage of data and information, made it somewhat difficult and time consuming to locate and retrieve the right information, despite all stakeholders being very helpful. Future studies would greatly benefit from easier access to such information, and ideally also further coordination between municipal and regional authorities with regards to the access to existing studies and planning of study designs including which PFAS to monitor for in which media. In future studies it will be highly relevant to include PFAS Total in sediment and biota, using methods and laboratories that have sufficiently low detection limits compared to the regulatory limit values.

This knowledge was instructive for the sampling design and to prioritize where to sample, in which media, for which PFAS and at which expected concentration levels. 6:2 FTS was hence added to the standard water analysis, done by a commercial laboratory, and the needed sensitivity of the sediment analyses was estimated. Seven sampling points were chosen, with six being close to various types of known or suspected point-sources plus one reference point away from suspected or know point-sources (Furesøen) were chosen. Water and sediment were sampled, but biota were not sampled because fish were not expected near the sites in the winter time.

An analytical suspect screening monitoring method was developed to detect mainly anionic PFAS in sediment, by liquid chromatography – electrospray ionisation – quadrupole time-of-flight mass spectrometry. The method was set up for 33 PFAS (with standards) and 28 PFAS (without standards), with a focus on precursors to PFOS and other perfluoroalkyl acids.

Water samples were collected in December 2022 from seven sites, one being a reference site, where the water was sampled over 4 weeks using Sorbicells (active sampling) to get average water concentrations. Sediment samples were taken in December 2022. Sediment and water samples were sent to a commercial laboratory for accredited target analysis for 22 PFAS ($PFAS_{22}$). Sediment was additionally analysed by the in-house developed suspect screening method (LC-QTOF MSMS) for more than 50 PFAS at University of Copenhagen.
The results in this study cannot be used to assess the general condition in Danish water bodies, but reflects the levels and distributions of the various PFAS in water and sediment during the investigation period.

The water analyses, indicated that current PFAS point-source emissions may exist, with likely sources being wastewater treatment plants receiving effluents from smaller industries (e.g. chrome plating), research institutions and households. Particularly the PFOS replacement chemical, 6:2 FTS (used in industries such as electronics, metal, chromepaling, chemical, paint, rubber and plastics, dry-cleaning and in fire-fighting) was found in high levels. The assessment of sources was however challenged by the presence of 6:2 FTS also in the blanks. Follow-up tests by the municipality showed that 6:S FTS is not present in the tap-water from Birkerød Sailing Club, which had been used in the sample preparation of the Sorbicells. Tests by the commercial laboratory found that 6:2 FTS neither was present in the containers. A potential source, could have been the air and dust in the Sailing club, if sails had been coated with 6:2 FTS or derivatives thereof. Suggestions for future preparation of Sorbicells, was provided. This example underlines the importance to always include minimum duplicate *field* blanks in studies, used for authority decision making.

To assess which PFAS that could be relevant to include in future monitoring programs, the PFAS listed in current regulations and those foreseen to be included in future regulations of relevance to Denmark and the aquatic environment were reviewed. The accredited $PFAS_{22}$ levels were 6-19 times above the $EQS_{freshwater}$ for PFOS and precursors (0.65 ng/L), which was caused solely by PFOS (precursors were not measured in water). For the sum of 24 PFAS (calculated as PFOA-equivalents and not including 6:2 FTS) levels were 2.7-7 times above the (*in 2022 proposed*) $EQS_{freshwater}$ (4.4 ng/L). The calculation of PFOA-equivalents is a sum of the individual 24 PFAS concentrations multiplied by so-called relative potency factors (RPFs). For the seven PFAS for which a range of RPFs are given, the highest RPF was used. $PFAS_{24}$ does not include 6:2 FTS. Highest levels were found near the wastewater treatment plants, and near a former metal plating site.
In general, if PFAS is present in a water body, water is less likely to cause exceedances of the $EQS_{freshwater}$ for $PFAS_{24}$, since water soluble PFAS have RPFs <1. Sediment and biota are on the other hand more likely to exceed limit $PFAS_{24}$, since they accumulate long-chain PFAS with RPFs >1.

The sediment analyses for $PFAS_{22}$ measured by *target analyses* (by Eurofins) did not exceed the $EQS_{sediment}$ (13500 ng PFOS and derivatives/kg dw). $PFAS_{22}$ only included PFOS and the precursor PFOSA.

However, the suspect screening of more than 50 PFAS in sediment by UCPH found high levels of prePFOS (PFOS derivatives) and of other precursors of perfluoroalkyl acids (PFAAs, such as perfluorocarboxylic acids PFCAs) at several locations. The sum of PFOS and derivatives was calcated with the additional prePFOS included, and at no sites the value was exceed; at Bagsværd Rowing Stadium the level was very close to the limit.

The Sums of $PFAS_{24}$ in PFOA-equivalents (in ww) were compared with the EQS_{biota} (77 ng/kg ww). In all cases concentrations were above the EQS_{biota} (3-33 times above). Had the prePFOS been included (using an RPF=1), levels would significantly have exceeded the EQS. Higher levels of both PFOS, prePFOS and of other PFSAs and PFCAs, were found particularly at

Bagsværd rowing stadium (source unknown), where N-Me-FOSAA and N-Et-FOSAA, which are transformation products of N-Me- and N-Et-FOSE. High levels of particulary long-chain PFAAs were also found at Mortonsvej (a former metal plating site) and Dybendal wastewater treatment plant (receiving wastewater from metal and plastic coatings, a research institution and households). Based on the isomer patterns of linear and branched PFSAs, the prePFOS likely stem from electrochemical fluorination, which historically were produced by 3M, but still are produced in countries like China. If current emissions exist, they may therefore stem from activities where PFOS precursors are exempted from the restrictions, and from PFAS not yet restricted or regulated by industrial emissions legislations.

In future surveys, a number of measures could be taken with the aim to improve the overview of the pollution spread, and thereby help to prioritize actions to reduce risks from PFAS:

- **analyse PFOS precursors in sediment and potentially also in biota** – the WFD on PFOS and derivates (still is in force) already requires to measure *PFOS and derivatives* (ie prePFOS), but prePFOS are despite their widespread uses and occurrence currently included in the monitoring. A simple concentration addition (RPF=1) could be used.
- **seek information on which PFOS precursors (and PFAS substitutes) for which uses, that are exempted from the REACH restriction on PFOS and derivatives**, which can be used to guide checks of environmental permits of industries for these PFAS and to guide monitoring programs.
- **monitor for a wider set of (groups of) PFAS for which restrictions are in the process or have been agreed** – by REACH, EFSA and in Denmark, including PFAS Total analyses. This could guide industries to transition towards a PFAS-free production. In turn, this would reduce further emissions of PFAS into water bodies and potential need for future remediation, while it would make it easier to stay below PFAS sum limit values.
- **prioritise to monitor PFAS in the media they most likely are present in**: Since it is not economically or practically feasible to monitor for all PFAS, some prioritisation of substances is needed. PFAS Total methods can be used for screening but also for enforcement of PFAS Total limits. A choice of which PFAS to monitor for in which media could be made, based on their likely occurrence: Short-chain PFAS predominates in water and in plants (uptake via the water), and long-chain PFAS in sediment and animals (biota). The PFAS handbook has recommended some PFAS to be added to the monitoring (Danish Regions, 2022), and this study suggests a number of specific PFAS that in the future could support source tracking and risk assessment of PFAS in aquatic environments.
- **update monitoring lists regularly:** The PFAS legislation is rapidly evolving, and coherence may therefore lack across legislations such as REACH, the WFD and the Industrial Emissions Directive. In addition the product registry does not cover all Danish uses of PFAS, and which PFAS are used depends both on the industry and whether some PFAS are restricted and replaced by other PFAS. For these reasons monitoring lists should be updated regularly, e.g. every 3-5 years, potentially as a combination of a surveillance program and early warning screening programs.

11. References

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Appendix 1. Sampling

Appendix 1.1 Shortlist of potential sampling sites discussed with authorities

Locality	Matrikel No.	Municipality	Where	Chosen	Reason
Strandmøllen	3bi	Lyngby-Taarbæk		No	Less certain use, no PFAS measured
Raadvad	1ag 1ah 2d	Lyngby-Taarbæk	Hovedløb	No	Stopped manufacturing before 1960's, 'average' levels)
Rensningsanlæg Dybendalsvej				Yes	Also receives wastewater from DTU
Haldor-Topsøe - Not screened by neither municipality nor Region	8e 8n 4df	Lyngby-Taarbæk		No	Wastewater not emitted to Mølleåen, only 'overløbsvand'. Unlikely that they have production on site, and no permits for PFAS found)
Dry cleaning	9e	Lyngby-Taarbæk	230-20000 (file no.)	No	
Firestation next to Lyngby waterworks		Lyngby-Taarbæk		?	?
Waterwork in Lyngby	33e	Lyngby-Taarbæk	Historical data	?	?
Unknown		Lyngby-Taarbæk	173-00090 No PFAS on site – in the river it is about the same level as in the waterbody (20ng/L)	No	
River is not prioritized for protection (not 'målsat')	37a	Lyngby-Taarbæk	Is cleaned up about every 10 years. Sediment can be of interest	No	
Metal Plating (Mortonsvej)		Lyngby-Taarbæk	173-00105 PFOS found on site.	Yes	High risk, High levels of PFAS in a drilling on site. Previous storage and burning of paper and cardboard.
Technical School (Mortonsvej)		Lyngby-Taarbæk	173-00044 The municipality has taken samples of the lake. Take sample by 209	Yes	Same as above
Metal product business Nybrovej	11s	Gladsaxe	159-03247 PFAS in drilling	Yes	PFAS in drilling
Eldercare centre	11m	Gladsaxe	Emissions due to medicine?	No	
Waste water treatment plant	74a	Gladsaxe	From industri and the city. Bagsværd sø (lake) is very polluted	?	?
Bagsværd Rostadion (Rowing Stadium)		Gladsaxe	Different PFAS pattern. Competition rowing – PFAS wax coatings?	Yes	Different pattern of PFAS, relatively high level – PFAS used in race rowing boat coatings?
Falck station	2n			Yes?	Stavnsholt?
Dry cleaning (Akacietorvet)	9an	Farum	207-00128	No	Have included Nybrovej

			370 m to the lake. Is there a stream towards the lake?		
Dry cleaning (Farum hovedgade)		Farum		No	Have included Nybrovej
Refrigiator factory, electronics etc.			By Søllerød Sø (lake) 181-00014	No	Less certain use, no PFAS measured

Appendix 1.2 Sampling of water by Sorbicells

The temperature was about 10-11 C when cages were set out in November, and about 5-6 C when collected in December 2022.

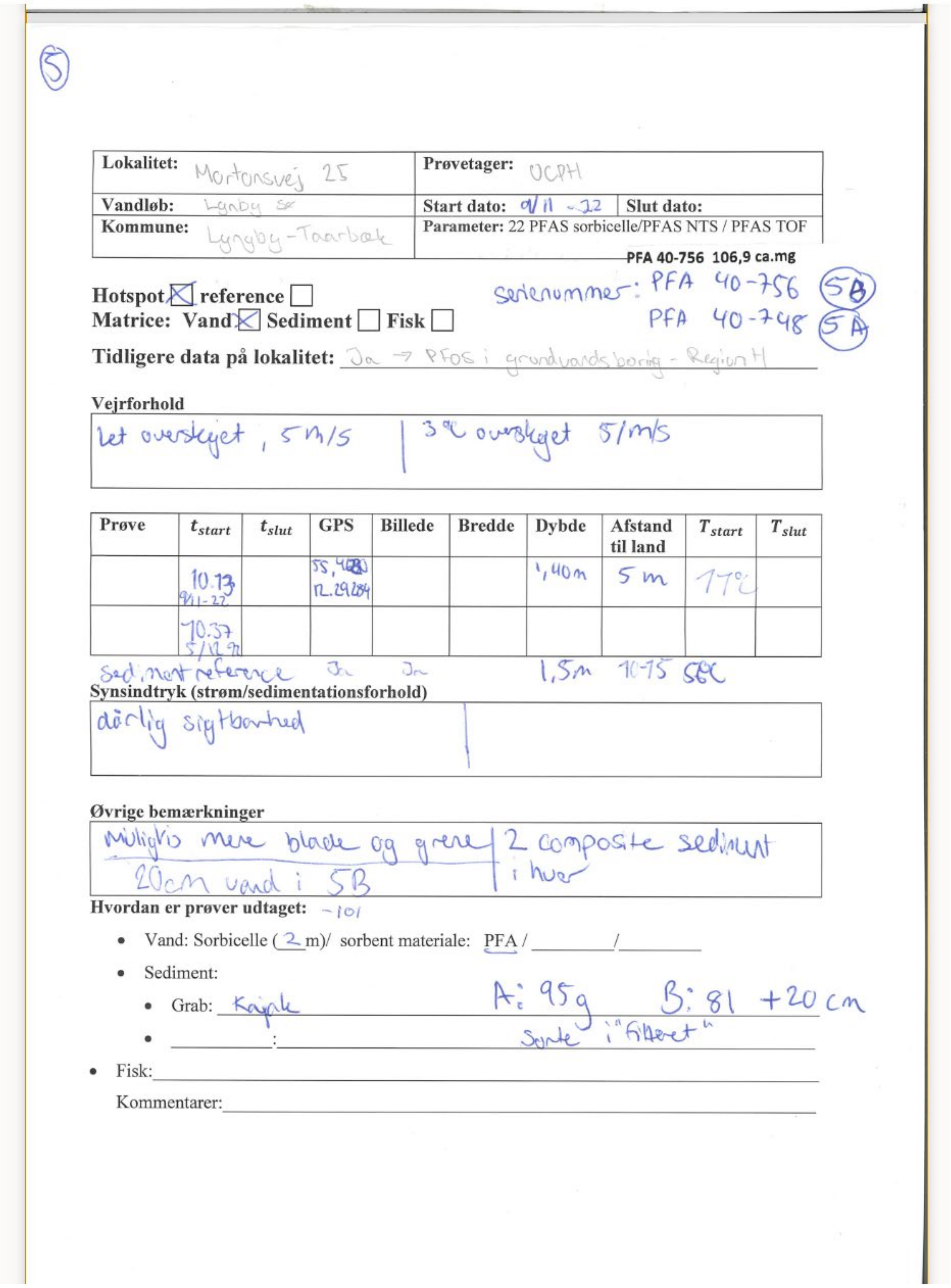
Water sampled by sorbicells								
No	Site	Sampled	GIS location	Tube type	Sampling depth	Tube A (g water collected)	Tube B (g water collected)	Comment
1	Nørreskoven	8/11-5/12-22	55.80367/ 12.40846	102	4.02 m	271 g	301 g	
2	Stavnsholt WWTP	8/11-5/12-22	55.80957/ 12.40856	102	2.90 – 3.10 m	231 g	244 g	Cage moved about 100 m East by wind
3	Bagsværd Rostadion	8/11-5/12-22	55.77272/ 12.44247	101	1.50 m	101 g	102 g	Very dirty at the top
4	Nybrovej	9/11-5/12-22	55.77136/ 12.46791	101	1.20 m	82 g	90 g	Dirty at the top
5	Mortonsvej	9/11-5/12-22	55.46230/ 12.29284	101	1.40 m	95 g	81 g + 20 cm	Black at the “filter”
6	Dybendal WWTP	9/11-6/12-22	55.80272/ 12.53664		0.5 m	342 g	461 g	
7	Kulsviervej	9/11-6/12-22	55.80197/ 12.95873	101	0.56 m	257 g	135 g	

Appendix 1.3 Sampling of sediment

Sediments									
No	Site	Sampled	Mass-A (g)	Mass-B (g)	Total mass (g)	Eurofins mass (g)	Eurofins %dw	UCPH mass (g)	UCPH %dw
1	Nørreskoven	5/12-2022	188	150	338		68		77
2	Stavnsholt WWTP	5/12-2022	80	98	178		49		66
3	Bagsværd Rostadion	5/12-2022	109	98	207		6.9		17
4	Nybrovej	5/12-2022	93	86	179		63		77
5	Mortonsvej	5/12-2022	107	104	211		23		62
6	Dybendal WWTP	6/12-2022	103	100	203		9.6		68
7	Kulsviervej	6/12-2022	107	112	219		26		49

Appendix 1.4 Example of a field journal

Example of Field journal for sampling of water by Sorbicells. Weight of water for sub-sample A is 95 g and subsample B is 81 g, plus 20 cm in the tubing.



⑤

Lokalitet: Mortonsvej 25	**Prøvetager:** UCPH
Vandløb: Lyngby Sø	**Start dato:** 9/11 -22 **Slut dato:**
Kommune: Lyngby-Taarbæk	**Parameter:** 22 PFAS sorbicelle/PFAS NTS / PFAS TOF

PFA 40-756 106,9 ca.mg

Hotspot ☒ **reference** ☐

Matrice: Vand ☒ **Sediment** ☐ **Fisk** ☐

Serienummer: PFA 40-756 (5B)

PFA 40-748 (5A)

Tidligere data på lokalitet: Ja → PFOS i grundvandsboring - Region H

Vejrforhold

let overskyet, 5 m/s | 3 °C overskyet 5/m/s

Prøve	t_{start}	t_{slut}	**GPS**	**Billede**	**Bredde**	**Dybde**	**Afstand til land**	T_{start}	T_{slut}
	10.13 9/11-22		55,40[illegible] 12.29284			1,40m	5 m	17°C	
	10.37 5/12-22								

Sediment reference Ja Ja 1,5m 10-15 SEC

Synsindtryk (strøm/sedimentationsforhold)

dårlig sigtbarhed |

Øvrige bemærkninger

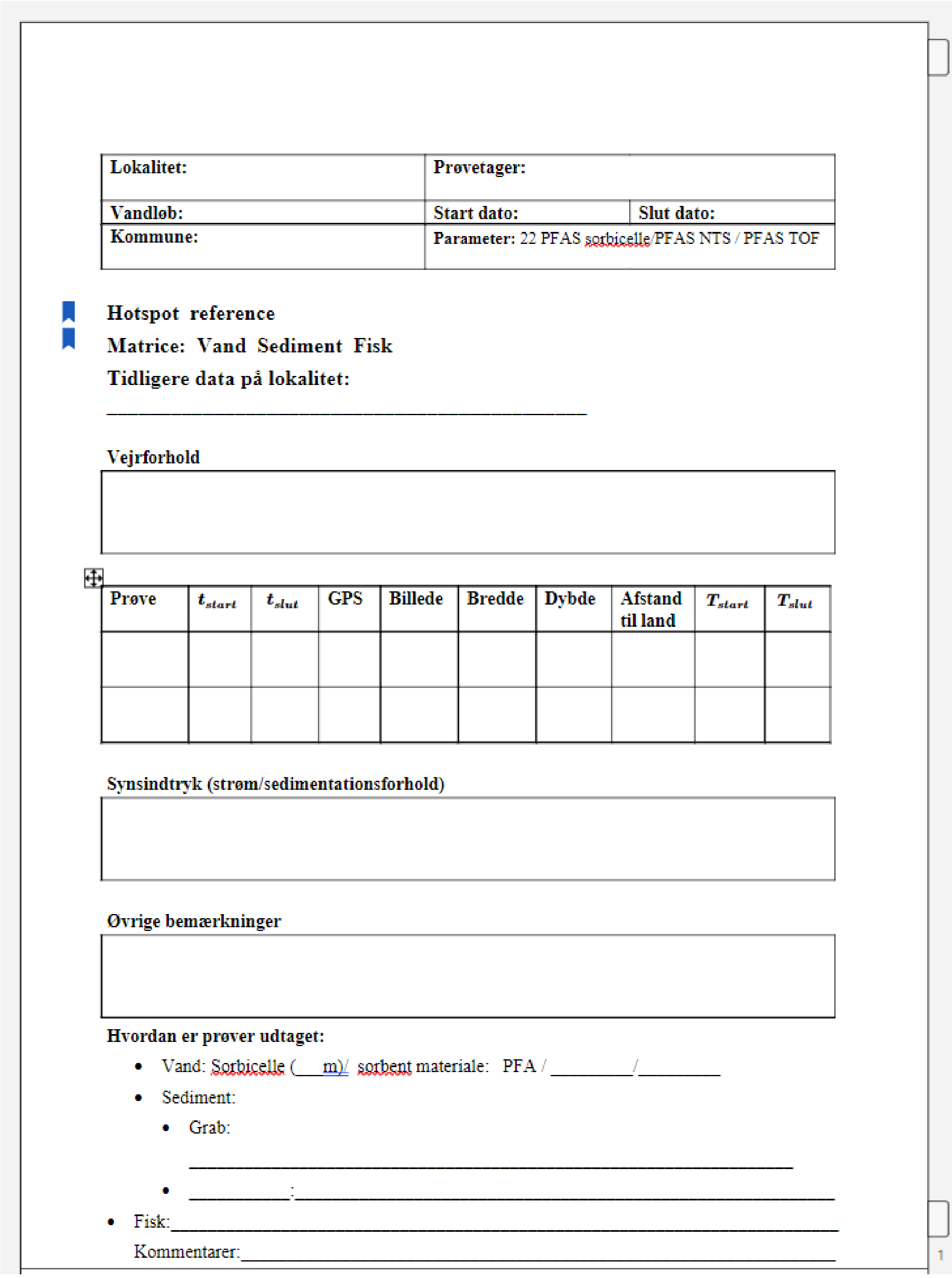
Muligvis mere blade og grene | 2 composite sediment i hver

20cm vand i 5B

Hvordan er prøver udtaget: -101

- Vand: Sorbicelle (2 m)/ sorbent materiale: PFA / ________ / ________
- Sediment:
  - Grab: Kajak A: 95g B: 81 +20 cm
  - ________: Sorte i "filteret"
- Fisk: ________

Kommentarer: ________



Lokalitet:	**Prøvetager:**	
Vandløb:	**Start dato:**	**Slut dato:**
Kommune:	**Parameter:** 22 PFAS sorbicelle/PFAS NTS / PFAS TOF	

Hotspot reference

Matrice: Vand Sediment Fisk

Tidligere data på lokalitet:

____

Vejrforhold

Prøve	**t_{start}**	**t_{slut}**	**GPS**	**Billede**	**Bredde**	**Dybde**	**Afstand til land**	**T_{start}**	**T_{slut}**

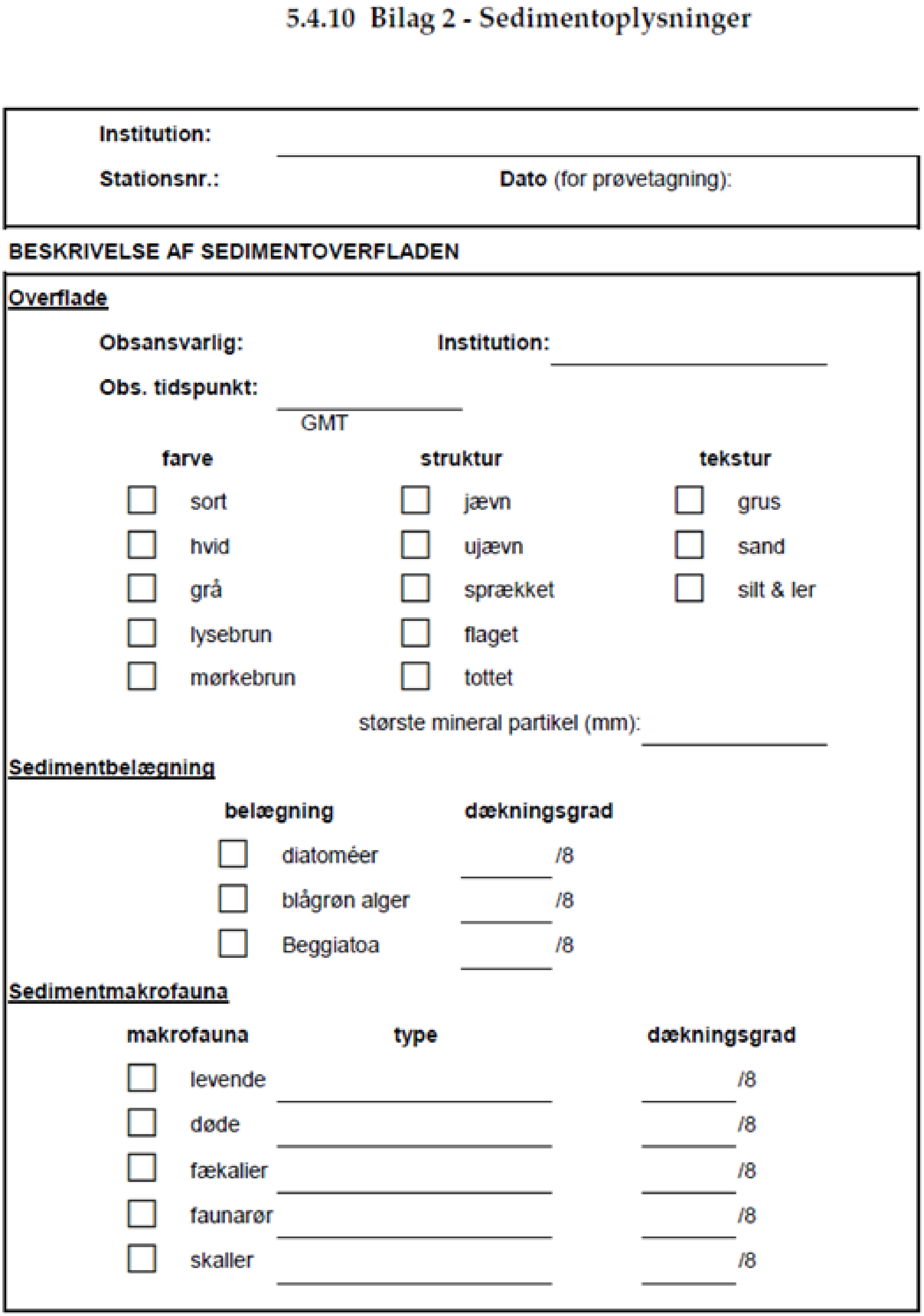
Synsindtryk (strøm/sedimentationsforhold)

Øvrige bemærkninger

Hvordan er prøver udtaget:

- Vand: Sorbicelle (___m)/ sorbent materiale: PFA / _________/_________
- Sediment:
  - Grab:
    ____
  - ___________:____
- Fisk:____

Kommentarer:____



5.4.10 Bilag 2 - Sedimentoplysninger

Institution: ____________________

Stationsnr.: ____________________ **Dato** (for prøvetagning):

BESKRIVELSE AF SEDIMENTOVERFLADEN

Overflade

Obsansvarlig: **Institution:** ____________________

Obs. tidspunkt: ____________ GMT

farve	**struktur**	**tekstur**
☐ sort	☐ jævn	☐ grus
☐ hvid	☐ ujævn	☐ sand
☐ grå	☐ sprækket	☐ silt & ler
☐ lysebrun	☐ flaget	
☐ mørkebrun	☐ tottet	

største mineral partikel (mm): ____________

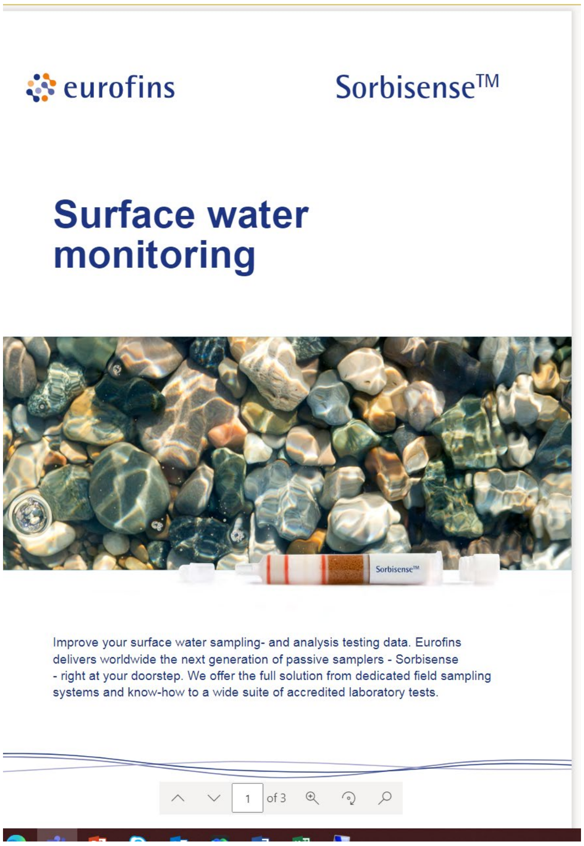
Sedimentbelægning

belægning	**dækningsgrad**
☐ diatoméer	______ /8
☐ blågrøn alger	______ /8
☐ Beggiatoa	______ /8

Sedimentmakrofauna

makrofauna	**type**	**dækningsgrad**
☐ levende	____________	______ /8
☐ døde	____________	______ /8
☐ fækalier	____________	______ /8
☐ faunarør	____________	______ /8
☐ skaller	____________	______ /8

Appendix 1.5 Sorbicells /Sorbisense description of principle and use



Surface water monitoring

Improve your surface water sampling- and analysis testing data. Eurofins delivers worldwide the next generation of passive samplers - Sorbisense - right at your doorstep. We offer the full solution from dedicated field sampling systems and know-how to a wide suite of accredited laboratory tests.

Figure 1 Pictures of SorbiCell VOC. Left picture, from left to right: unexposed as purchased in transportation tube and pre wetted in demineralized water; exposed, fitted with protection caps to prevent drying; exposed Sorbicells with about [illegible]% salt depletion. Picture right shows field mounting units WW-50 (TOP) and GWS-40 (BOTTOM)

Background

The regulation on surface water quality is one of the important corner stones for protection of aquatic eco systems as well as production of drinking water. Overlooking periodic run-off events can bring about serious consequences. Also, finding the source of pollutions in surface waters can be a difficult task due to the dynamic nature of natural runoff sources contributing to the various tributaries.

Traditional surface water sampling methods are either based on "spot sampling" or done with the help of expensive water sampling stations. Therefore, monitoring with SorbiCell™ can greatly improve the efficiency of surface water sampling. With documented capital savings up to [illegible]% on field infrastructure investments, there is no need to compromise on data quality, while at the sames time major total project cost reductions can be achieved.

Typical problems related to traditional methods are.

- Traditional water samples represent a snapshot value, while solute concentrations in rivers and streams may vary strongly over time
- Permanent sampling station are capital intensive, need electricity and frequent servicing
- Over time, water sample quality may be compromised e.g. due to volatilization of compounds
- Liquid sampling handling with pumps and tubing is tedious, may require filtrations steps, and is prone to loss by volatilization or sorption to tubing.
- Fast transport to the laboratory is critical due to poor conservation of bulky water samples

Benefits of Sorbisense method

Sorbisense solves these problems while maintaining high data quality and sample-integrity:

- The sampling process occurs over a longer time period (typically 1-4 weeks), averaging out short time fluctuations
- Easy field procedure, typically under [illegible] minutes per station
- No electricity, sample tubing, or other infrastructure required
- The method is well-suited for both small streams and channels, as well as rivers and lakes
- No need for liquid sampling handling
- Sorbicell requires very little space and is well conserved for storage and transport

Field sampling procedure

Two basic components together enable monitoring in surface water. SorbiCell™ is a small, 3 ml passive sampling unit for on-site sampling and pre-concentration of organic or inorganic substances. The Sorbicell is clicked onto a surface water sampler (WW-50 Sorbisystem)

unit, and then installed in the river or stream. The unit is either placed on the bottom of the stream, or fixed with a wire to a fixed point or floating object (e.g. a buoy). Once submerged under the water table, a small subsample of the passing surface water slowly flows through the Sorbicell at a controlled flow rate until the WW-50 unit is filled (see pictogram BELOW and pictures of non-exposed and exposed Sorbicells LEFT). The required sample volume is 0.1-0.5 L, and once the WW-50 unit is emptied it is ready for re-use. The Sorbicell is removed, placed back in transportation tube and send to the laboratory in a regular plastic bubble envelope. For deep surface water sampling (>10 m sampling depth) we recommend the pressure rated GWS-40 unit (see picture LEFT).

Laboratory analysis

The SorbiCell cartridge is analysed with standard accredited laboratory methods for quantification of solutes. The accumulated mass of solutes, is thus quantified and likewise, the depletion of salt is measured and related to sample volume. The analysis results are reported as the time-weighted average concentration during the installation period for each contaminant (e.g., 10 µg/L of vinyl chloride).

Figure 2. Schematic of installation in surface water

SorbiCell PFAS;
Per- and polyfluoralkyl substances

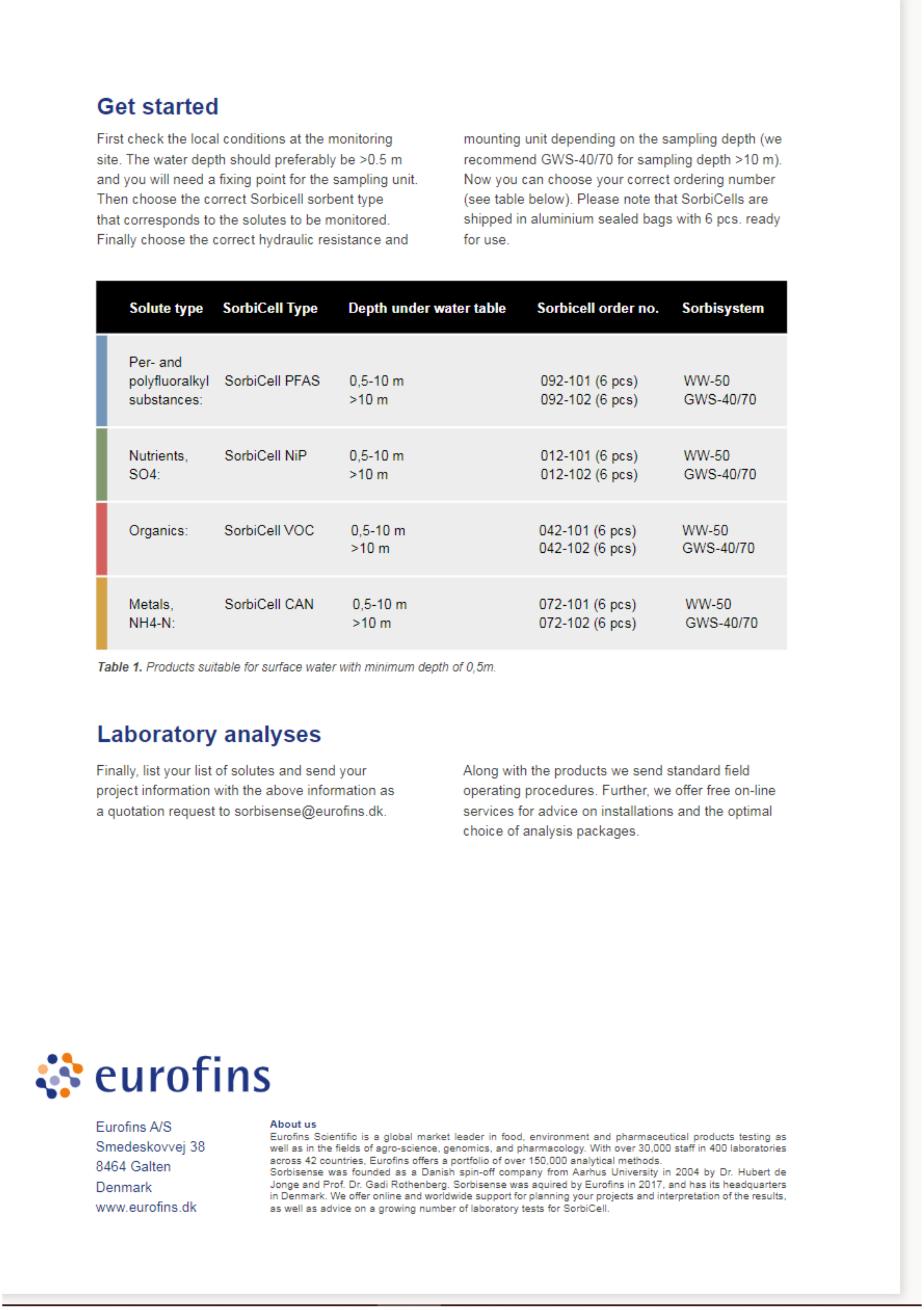
SorbiCell N,P
- Nutrients (NO3-N, PO_4, SO_4)

SorbiCell VOC
- Aromatics (BTEXM)
- Chlorinated solvents and metabolites
- Fuels, Oil
- PAHs
- PCBs
- Phenols
- Pesticides (200)
- Pharmaceuticals (1[illegible]0)

SorbiCell CAN
- Metals (e.g. Cd, Cr, Pb, Hg, Ni)
- NH_4-Nitrogen

Choose the right Sorbicell for your application

Four generic types of SorbiCells are available with different sorbents that are suitable for chemical groups of solutes (see ABOVE). The range of analytes is continuously expanding, please contact us for a quotation for your application



Get started

First check the local conditions at the monitoring site. The water depth should preferably be >0.5 m and you will need a fixing point for the sampling unit. Then choose the correct Sorbicell sorbent type that corresponds to the solutes to be monitored. Finally choose the correct hydraulic resistance and mounting unit depending on the sampling depth (we recommend GWS-40/70 for sampling depth >10 m). Now you can choose your correct ordering number (see table below). Please note that SorbiCells are shipped in aluminium sealed bags with 6 pcs. ready for use.

Solute type	SorbiCell Type	Depth under water table	Sorbicell order no.	Sorbisystem
Per- and polyfluoralkyl substances:	SorbiCell PFAS	0,5-10 m >10 m	092-101 (6 pcs) 092-102 (6 pcs)	WW-50 GWS-40/70
Nutrients, SO4:	SorbiCell NiP	0,5-10 m >10 m	012-101 (6 pcs) 012-102 (6 pcs)	WW-50 GWS-40/70
Organics:	SorbiCell VOC	0,5-10 m >10 m	042-101 (6 pcs) 042-102 (6 pcs)	WW-50 GWS-40/70
Metals, NH4-N:	SorbiCell CAN	0,5-10 m >10 m	072-101 (6 pcs) 072-102 (6 pcs)	WW-50 GWS-40/70

Table 1. Products suitable for surface water with minimum depth of 0,5m.

Laboratory analyses

Finally, list your list of solutes and send your project information with the above information as a quotation request to sorbisense@eurofins.dk.

Along with the products we send standard field operating procedures. Further, we offer free on-line services for advice on installations and the optimal choice of analysis packages.

eurofins

Eurofins A/S
Smedeskovvej 38
8464 Galten
Denmark
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About us

Eurofins Scientific is a global market leader in food, environment and pharmaceutical products testing as well as in the fields of agro-science, genomics, and pharmacology. With over 30,000 staff in 400 laboratories across 42 countries, Eurofins offers a portfolio of over 150,000 analytical methods.

Sorbisense was founded as a Danish spin-off company from Aarhus University in 2004 by Dr. Hubert de Jonge and Prof. Dr. Gadi Rothenberg. Sorbisense was aquired by Eurofins in 2017, and has its headquarters in Denmark. We offer online and worldwide support for planning your projects and interpretation of the results, as well as advice on a growing number of laboratory tests for SorbiCell.

b.pdf

Feltvejledning Sorbisense WW-50 i vandløb.

Hubert de Jonge, Eurofins Miljø. 2022.

Udstyr og værktøj

- Sorbicells og feltprotokoller, transportrør (ved optagning)
- Værktøj: målestok, skævbider eller kniv, skruetrækker med lige kærv, strips, hammer
- Målebæger eller målecylinderglas til opsamling af feltvolumen.
- Reserveslang PE 6x8 mm og gummipropper (Eurofins Sorbisense)

Feltprotokol, opsætning prøvetagning

1. Tjek og mål vanddybde.
2. Montér luftslangen på beholdere ca. 1,5 m længde. Tjek at luftslangen sidder helt fast.
3. Montér SorbiCellen i beholderen og tryk fast med transportrør af Sorbicell. Sorbicell VOC/POL kan monteres direkte efter aftagning af bund- og top-propper. Ved anvendelse af Sorbicell PFA/NiP/CAN skal der ske en opfugtning af cellen før montering med vand fra målested eller evt. demineraliseret vand. Skriv type og serienr. af Sorbicells på feltprotokol. Bevar transportrør til optagning og transport. OBS til WW-50 montage bruges hydraulisk modstand der passer med måledybde **–** for overfladevand type "101", for regnvand med periodiske tørperioder anvendes type "090". Hydraulisk modstand kan ses på etiketten på poserne, ligesom udløbsdato og serienummer er angivet på emballagen:

SorbiCell™ produktinfo på emballage:

- På posen fremgår endvidere:
  Varenummer (OBS hydraulisk modstand og montage):
  - 998 montage i kugle ("Instream")
  - 090 regnvandsbrønd
  - 101 overfladevand 115-0072-101
  - 102 grundvand
- Produktions- og holdbarhedsdato ; best before 24-06-2022
- Unik serienummer der skal fremgår på rekvisitionen: CAN 31-605..
- Sorbicellerne kan sendes i transportrør, og i en plast-

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4. På hver målested installeres antal 1,2 eller flere montage systemer efter behov. Ved flere montagesystemer, kan de beholdere evt. strippes "løst sammen" og sættes i en metal kurve, se billede herunder.
5. Øverste kurve sættes på som låg, og luftslanger samles og trækkes igennem låget. Kurver befæstes med strips.
6. Ved enden af luftslanger laves viklinger for at forhindre at fx regnvand kan trænge ind.

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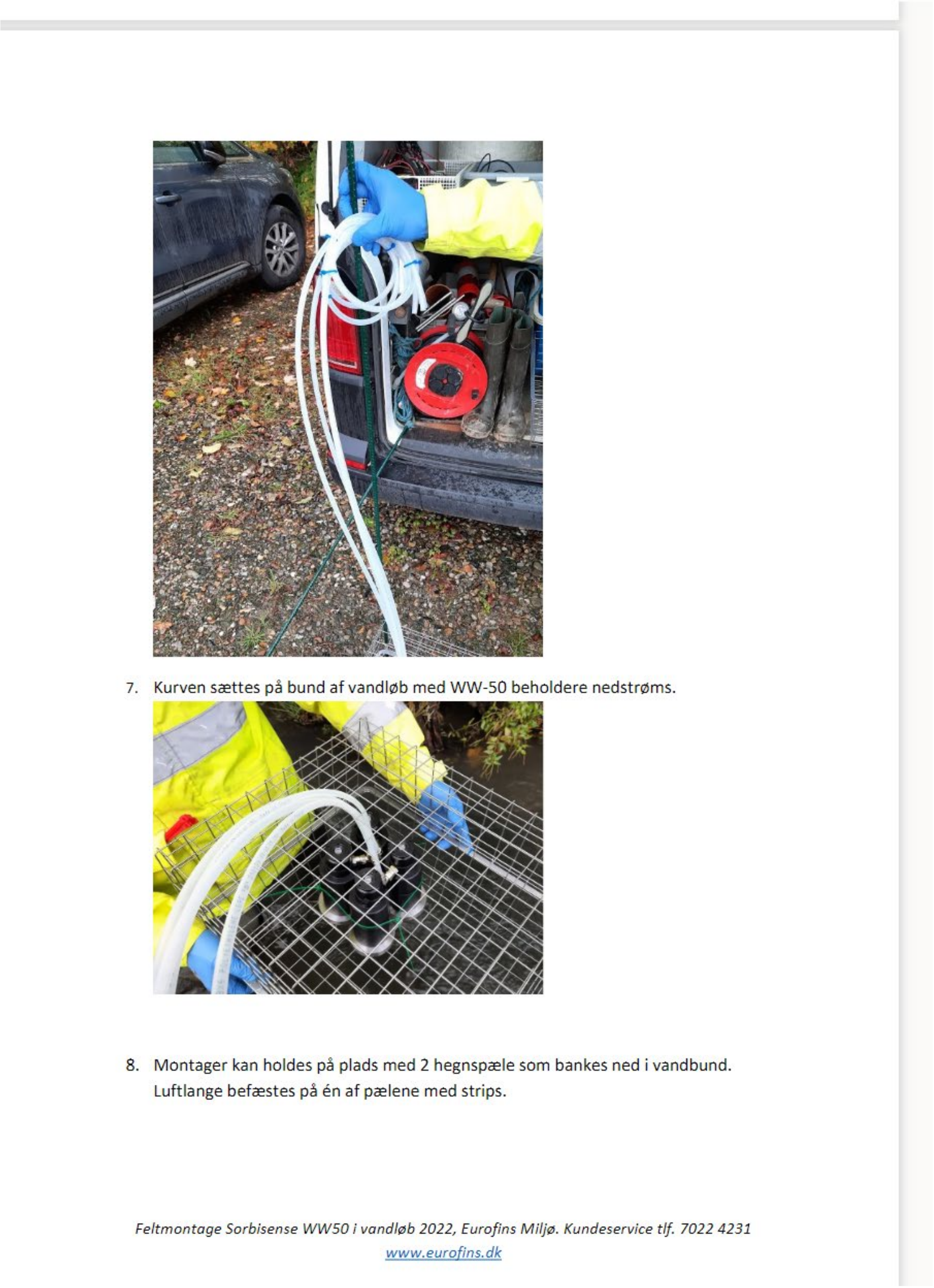

7. Kurven sættes på bund af vandløb med WW-50 beholdere nedstrøms.

8. Montager kan holdes på plads med 2 hegnspæle som bankes ned i vandbund. Luftlange befæstes på én af pælene med strips.

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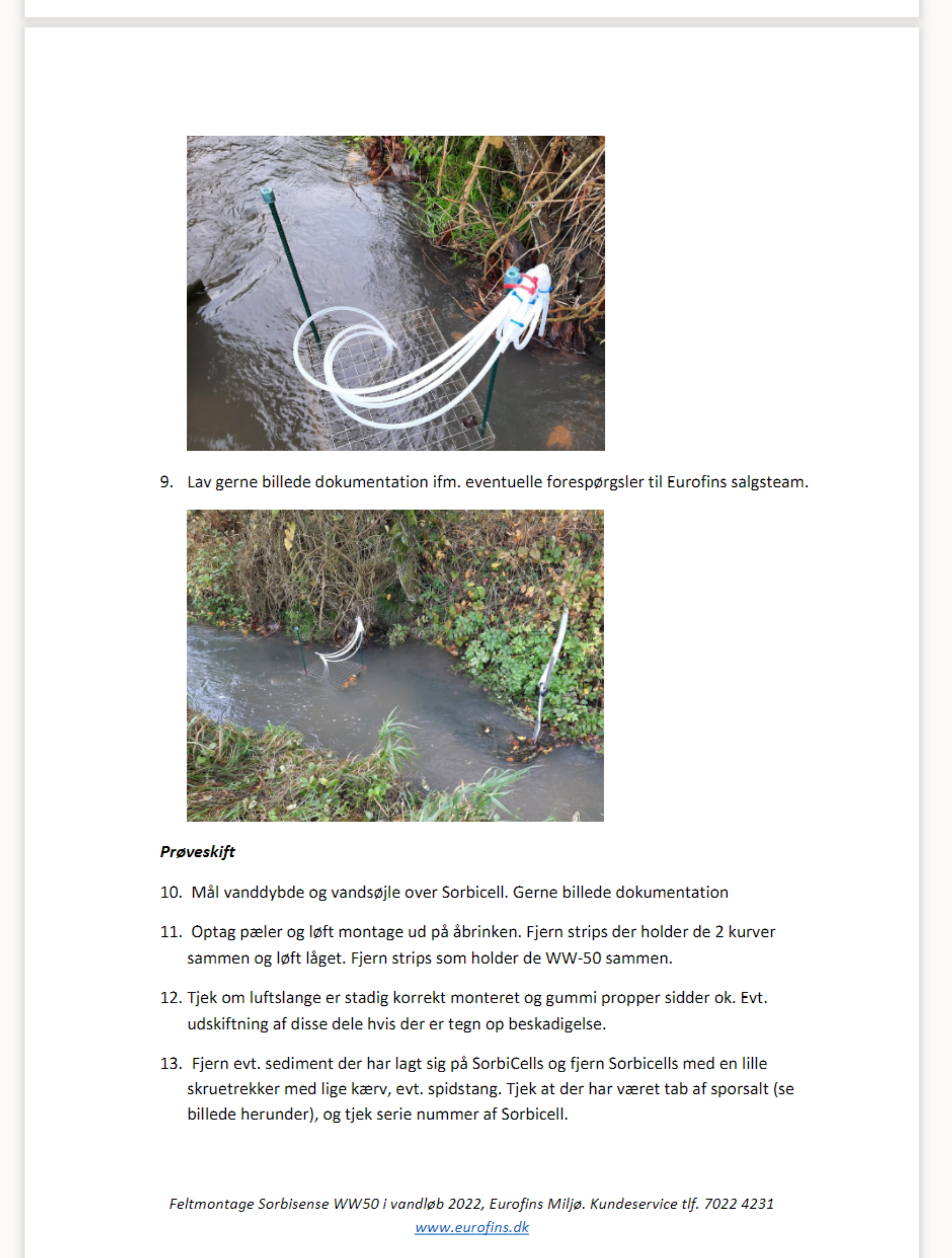

9. Lav gerne billede dokumentation ifm. eventuelle forespørgsler til Eurofins salgsteam.

Prøveskift

10. Mål vanddybde og vandsøjle over Sorbicell. Gerne billede dokumentation

11. Optag pæler og løft montage ud på åbrinken. Fjern strips der holder de 2 kurver sammen og løft låget. Fjern strips som holder de WW-50 sammen.

12. Tjek om luftslange er stadig korrekt monteret og gummi propper sidder ok. Evt. udskiftning af disse dele hvis der er tegn op beskadigelse.

13. Fjern evt. sediment der har lagt sig på SorbiCells og fjern Sorbicells med en lille skruetrekker med lige kærv, evt. spidstang. Tjek at der har været tab af sporsalt (se billede herunder), og tjek serie nummer af Sorbicell.

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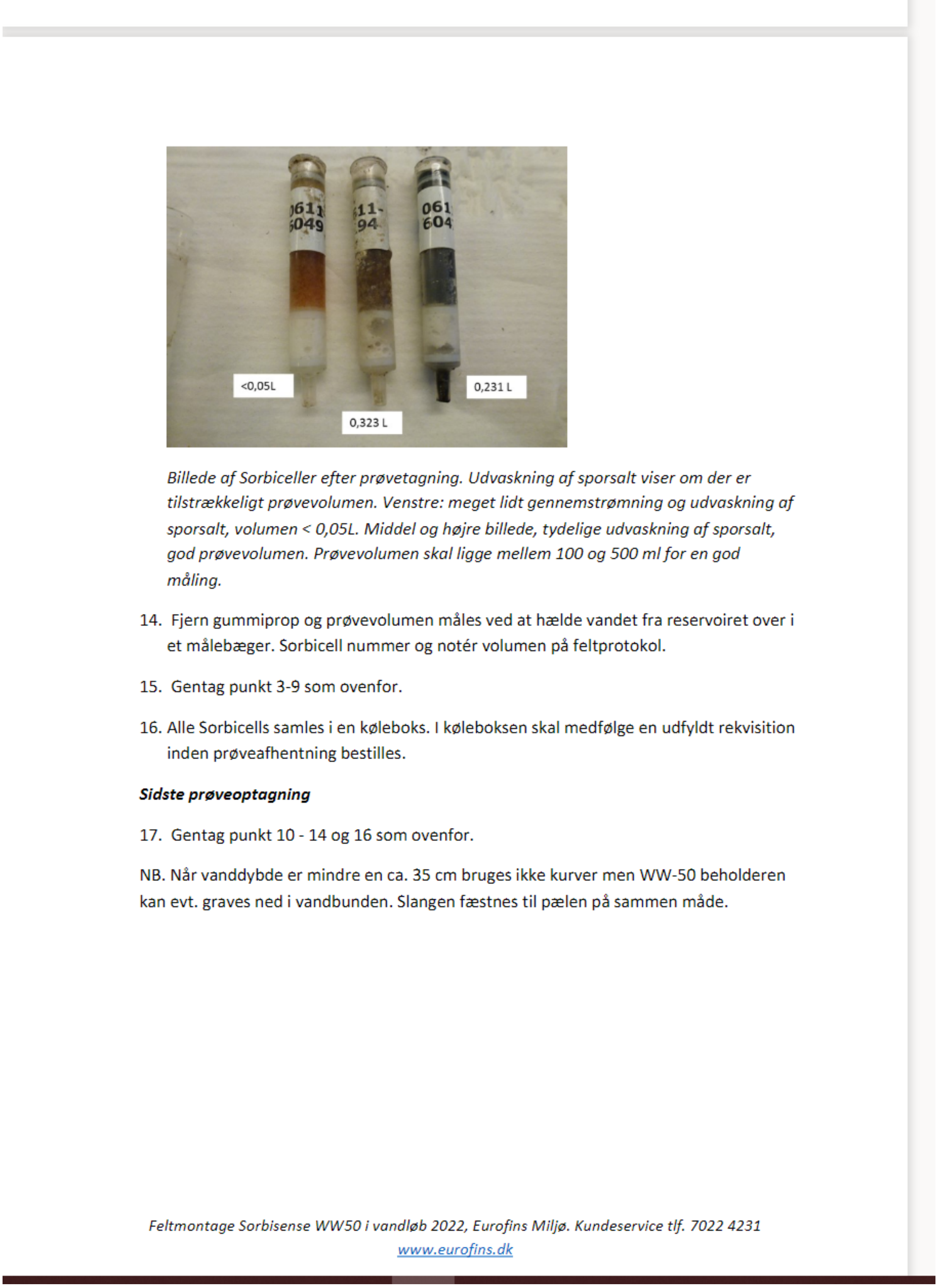

Billede af Sorbiceller efter prøvetagning. Udvaskning af sporsalt viser om der er tilstrækkeligt prøvevolumen. Venstre: meget lidt gennemstrømning og udvaskning af sporsalt, volumen < 0,05L. Middel og højre billede, tydelige udvaskning af sporsalt, god prøvevolumen. Prøvevolumen skal ligge mellem 100 og 500 ml for en god måling.

14. Fjern gummiprop og prøvevolumen måles ved at hælde vandet fra reservoiret over i et målebæger. Sorbicell nummer og notér volumen på feltprotokol.
15. Gentag punkt 3-9 som ovenfor.
16. Alle Sorbicells samles i en køleboks. I køleboksen skal medfølge en udfyldt rekvisition inden prøveafhentning bestilles.

Sidste prøveoptagning

17. Gentag punkt 10 - 14 og 16 som ovenfor.

NB. Når vanddybde er mindre en ca. 35 cm bruges ikke kurver men WW-50 beholderen kan evt. graves ned i vandbunden. Slangen fæstnes til pælen på sammen måde.

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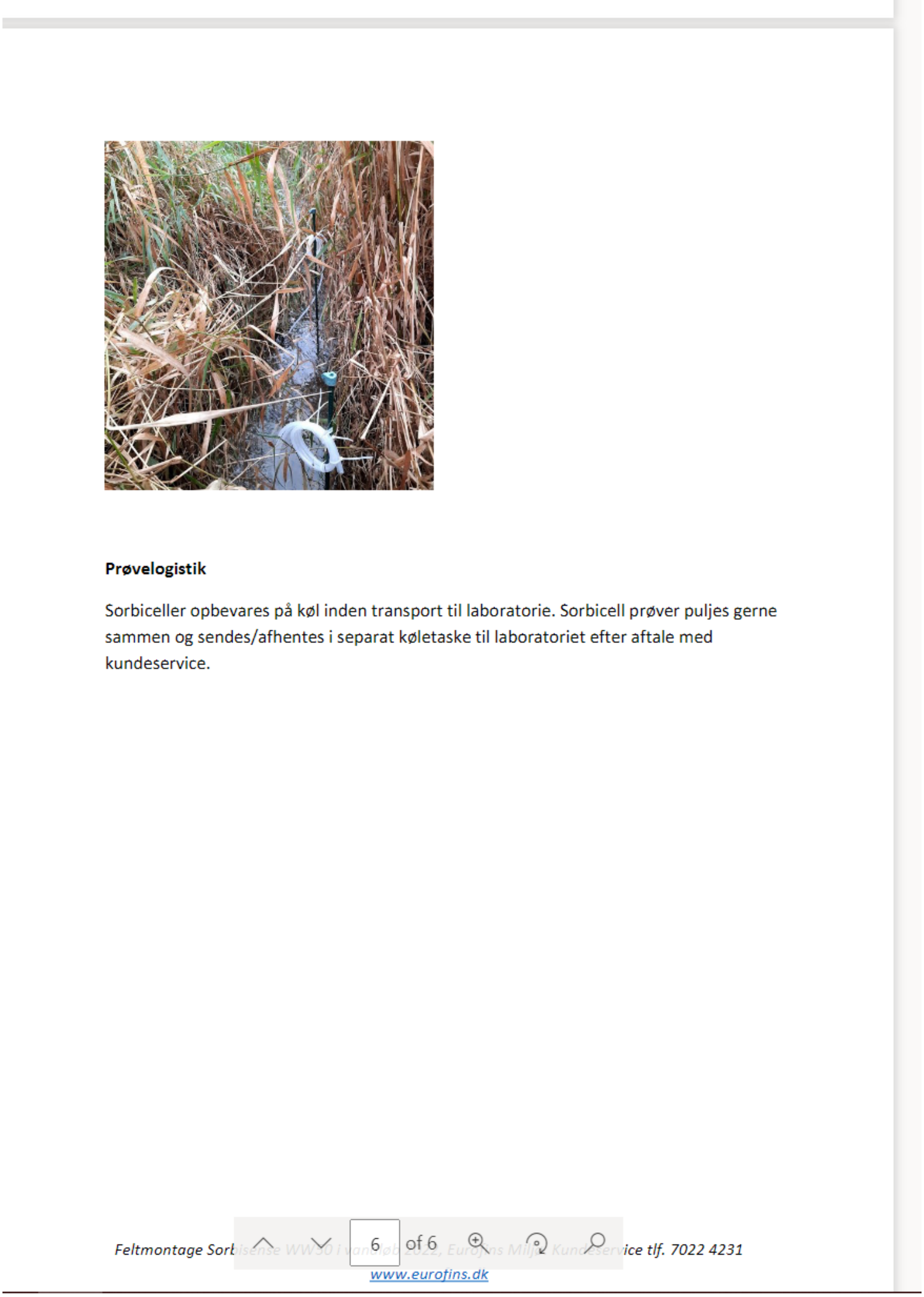

Prøvelogistik

Sorbiceller opbevares på køl inden transport til laboratorie. Sorbicell prøver puljes gerne sammen og sendes/afhentes i separat køletaske til laboratoriet efter aftale med kundeservice.

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Appendix 2. Acronyms

Please note that all the abbreviations for the PFAS are in found in Table 1.

AFFF	aqueous film-forming foam
AOF	adsorbable organic fluorine
bw	body weight
C	carbon
C8	historical name for PFOA
CAS	Chemical Abstracts Service
COOH	carboxylic acid functional group
dw (or dm)	dry weight (or dry matter)
DWD	drinking water directive (EU)
EEA	European Environment Agency
ECHA	European Chemicals Agency
ESI^{-}	electrospray ionisation, negative mode
EQS	Environmental Quality Standard
EU	European Union
F	fluorine
FASA	perfluoroalkane sulfonamide
FASE	perfluoroalkane sulfonamido ethanol (var: perfluoroalkane sulfonamide ethanol)
FASAA	perfluoroalkane sulfonamido acetic acid (var: perfluoroalkane sulfonamide acetic acid)
FCM	food contact materials
foc	fraction of organic carbon
FOSA (PFOSA)	perfluorooctane sulfonamide
FOSE	perfluorooctane sulfonamido ethanol (var: perfluorooctane sulfonamide ethanol)
FOSAA	perfluorooctane sulfonamido acetic acid (var: perfluorooctane sulfonamide acetic acid)
FTCA	fluorotelomer carboxylic acid
FTOH	fluorotelomer alcohol
FTS (or FTSA)	fluorotelomer sulfonate (or fluorotelomer sulfonic acid)
GC	gas chromatography
HRMS	high-resolution mass spectrometry
IARC	International Agency for Research on Cancer
ITRC	Interstate Technology and Regulatory Council
Kd	bulk partitioning coefficient
Koc	organic carbon partitioning coefficent
LC	liquid chromatography
LC/MS/MS	liquid chromatography/mass spectrometry/mass spectrometry
LDPE	low-density polyethylene
LOD	limit of detection
LOQ	limit of quantitation
MeFASA	N-methyl perfluoroalkane sulfonamide
MeFASE	N-methyl perfluoroalkane sulfonamido ethanol (var: N-methyl perfluoroalkane sulfonamide ethanol)
MeFASAA	N-methyl perfluoroalkane sulfonamido acetic acid (var: N-methyl perfluoroalkane sulfonamide acetic acid)
MeFOSA	N-methyl perfluorooctane sulfonamide
MS	mass spectrometry
MST	Miljøstyrelsen (Danish EPA)
N-EtFOSA	N-ethyl perfluorooctane sulfonamide
NMeFOSAA	N-Methylperfluorooctane sulfonamidoacetic acid
NOVANA	The Danish national surveillance for water environment and nature
OECD	Organisation for Economic Co-operation and Development
PFAS	per- and polyfluoroalkyl substances
PFCA	perfluoroalkyl carboxylate, perfluoroalkyl carboxylic acid
PFS	perfluoroalkyl sulfonate, perfluoroalkane sulfonic acid
pH	negative log of hydrogen ion concentration (measure of acidity)
QTOF	quadrupole time-of-flight
REACH	European Chemicals Regulation
SPE	solid-phase extraction

TOC	total organic carbon
TOP (A)	total oxidizable precursor (analysis or assay)
ug/kg	micrograms per kilogram
ww	wet weight
WWTP	wastewater treatment plant

Resumé

The overarching purpose of this study was to investigate if PFOS found to exceed the water environmental quality standard (EQSfreshwater) in a river and lake system, and more generally if PFAS pollution, is likely to be cause by current point source emissions or due to legacy pollution released from the sediment. In addition it suggests which PFAS it could be relevant to monitor in which media in future studies. This study finds that it is likely that legacy pollution continue to pollute the river and lake system with PFOS, since much higher levels of PFOS and precursors (prePFOS) were found in the sedient than in the water. In addtition a number of other PFAS were found, e.g. the highly water-soluble 6:2 FTS, which points to-wards a combination of legacy and current activities emitting PFAS into the water-body.

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