Indhold

UNDERSTANDING PFASS

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Poly and perfluorinated substances (PFAS) are used in a wide range of industrial applications and commercial products due to their unique surface tension/levelling properties. These include textile stain guards, grease-proof paper, fluoropolymer manufacture, coatings, and aqueous film-forming foams. Relevant to the refining industry is the use of PFAS in class B (flammable liquid) fire-fighting foams, including Aqueous Film Forming Foam (AFFF), Fluoroprotein (FP) and Film Forming Fluoroprotein Foam (FFFP). At sites where fire-fighting foams have been used, PFAS source zones may include fire-fighting training areas, areas where large fires have occurred historically, foam storage and dispensing locations and locations where AFFF has been repeatedly used for flammable vapour suppression during 'hot work'.

Concern around the environmental effects of PFAS use began in the late 1990s when it was realised that, due to their resistance to biodegradation, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), two of the most abundant PFAS, were ubiquitous in various biological and environmental matrices, and could biomagnify. Simultaneously, it became clear that they could have effects on human health and the (aquatic) environment.

In 2009, PFOS was added to Annex B of the Stockholm Convention on Persistent Organic Pollutants (POPs), meaning that measures must be taken to restrict its production and use. With global restrictions now in place for PFOS, further regulation is proposed in Europe and elsewhere to restrict the manufacture and use of any PFAS substance that contains a C7 or C8 perfluorocarbon moiety in its molecular structure. The use of legacy firefighting- foam products containing >0.001wt% PFOS has been banned in the EU since 27th June 2011.

The degree of biomagnification is proportional to perfluorocarbon chain length and so the regulations to restrict the manufacture and use of PFAS substances generally focus on the long chained PFAS. As there is a growing understanding of the properties of PFAS via increased academic research, it is clear that further information on their persistence, bioaccumulation potentialand toxicity, is required to further define which specific PFAS compounds pose a potential for risk to human health and the environment.

In 2013, PFOS and its derivatives were included in the Directive on "Environmental Quality Standards" (EQSD). The EU annual average environmental quality standard (AA-EQS) for PFOS in surface freshwater is set at a very low criterion of 0,00065 µg/l, based on the potential for secondary poisoning in humans due to fish consumption. The AA-EQS of 0,00065 µg/l is derived from starting points that are considered by many as very conservative, and is lower than background levels typically recorded in surface waters. It is also lower than the limit of quantitation (LOQ) typically achieved by commercial laboratories. The date set for EU-wide compliance with the AA-EQS is 22nd December 2027, with member states required to submit to the Commission a supplementary monitoring programme and a preliminary programme of measures to achieve compliance by 22nd December 2018.

Toxicity
Available data on PFAS toxicity is dominated by PFOS, PFOA and also perfluorohexane sulfonate (PFHxS) due to the widespread detection of these compounds in humans and the environment, and concern that these could biomagnify to a level whereby humans consuming fish may be adversely affected. Much less data is available on the toxicology of other PFAS, and this is often inconsistent and fragmentary. For the less investigated polyfluorinated chemicals, toxicology is often estimated based on structure- activity relationships, or structural homologues.

Human exposure to PFAS is mainly by ingestion of contaminated food or water. These compounds are not metabolised, bind to proteins (not to fats) and are mainly detected in blood, liver and kidneys. Elimination of PFOS, PFHxS and PFOA from the human body takes some years, whereas elimination of shorter chain PFAS is in the range of days. The half-life of PFOS and PFOA in rodents is in the range of months which differs significantly from humans and can cause extrapolation issues in tests. There is significant data available on the impact of (sub)chronic PFOS and PFOA exposure on reproductive and/or developmental and other types of effects in both humans and animals. However, the results from epidemiological studies are not always consistent.

Environmental fate and effects
Perfluoroalkyl sulphonic and carboxylic acids (PFSAs (e.g. PFOS) and PFCAs (e.g. PFOA)) are widely distributed in the global environment due to their high solubility in water, low/moderate sorption to soils and sediments and resistance to biological and chemical degradation. While many studies have been published on environmental concentrations of PFSAs and PFCAs, little data is available for precursor substances due to the difficulty inherent in their identification and analysis. Many types of PFAS precursors have been shown to be transformed through a variety of pathways. In many situations PFOS, PFOA or other PFSAs and PFCAs are the endpoint of biotransformation. Photolysis of PFOS and PFOA under natural circumstances is unlikely. Bio- and abiotic transformations of PFAS can be associated with substantial changes in the physicochemical properties of the compounds.

The PFAS group of compounds consists of both perfluorinated compounds or perfluoroalkyl acids (PFAAs), where all carbons are saturated with F atoms, and polyfluorinated compounds, where both fluorine saturated carbons and carbons with hydrogen bonds are present. Polyfluorinated “precursor” compounds biotransform to produce PFAAs as dead end extremely persistent daughter products. The understanding of the fate and transport of these compounds in the environment is complex and challenging and will be discussed. The concepts of in situ generation of perfluroalkyl acids (PFAAs) via precursor biotransformation will be used to explain how significant PFAS mass remains hidden in source areas in an analogous manner to NAPL residuals for hydrocarbon or chlorinated solvents.

PFAA precursors are so named because they transform slowly over time through abiotic and biological processes to the PFAAs. There is a natural “biological funneling” in which a whole host of PFAA precursor compounds containing a range of perfluorinated alkyl chain lengths and functional groups, aerobically biotransform to persistent PFAA products.

Fire-fighting foam formulations and many fluorochemicals used across multiple industries are composed of many PFAS that are PFAA precursors. Unlike the PFAAs, these species are not strictly anionic, as some contain multiple charges (zwitterionic) and some are positively charged (cationic). These zwitterionic and cationic PFAA precursors are currently undetected

by conventional analytical tools but can be quantified using more advanced approaches such as the Total Oxidizeable Precursor (TOP) assay. A significant mass of PFAA precursors in addition to the PFAAs have been detected in both fire-fighting foam-impacted soil and groundwater. A conceptual site model describing PFAS fate and transport at a firefighter training area is hypothesized and will be presented, as described below.

The precursors are not accounted for by the U.S. EPA analytical method 537 (LC-MS/MS). Additional analytical challenges are associated with the required low reporting limits/detection limits and sampling protocols, which need to consider other cross contamination.

ARCADIS have implemented the use of multiple analytical methods to quantify the total mass of precursors and qualitatively assess the nature of individual precursors.

PFAS I LABORATORIET
- HVILKE UDFORDRINGER OG MULIGHEDER ER DER?

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Baggrund og formål

- Gennemgang af mulighederne mht analyse af PFAS i laboratoriet
- GC/LC. Hvilken type ekstraktion og hvorfor?
- Kig på resultater for prøvetagningsemballage, plast/glas
- ”Total screening” for PFAS
- Sorbiceller, alternativ prøveudtagning

Metode, teknik

- LCMSMS
- Ekstraktion
- Sorbiceller

Resultater

- Robust metode, kan udvides med flere stoffer
- LC er nødvendigt
- Glas som emballage ok under bestemte forudsætninger
- Total screening findes på markedet

HVAD FINDER VI I FORBINDELSE MED FORURENINGSUNDERSØGELSER AF PFAS

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Regionerne undersøger for PFAS i forbindelser med forureningsundersøgelser, hvor man vurderer, at det er relevant. Der er efterhånden samlet en betydelig mængde data. Formålet med præsentationen er at vise de vigtigste trends omkring stoffer og brancher.

Baggrund og formål

Præsentationen giver et overblik over, hvilke stoffer der analyseres for og i forbindelse med hvilke brancher.

Metode

Datagrundlaget er de 5 regioners forureningsundersøgelser af PFAS forureninger. Data er samlet af VMR i anledning af dette møde, og representerer således et øjebliksbillede fra efteråret 2017. Data er analyseret for relevante trends, som vises i præsentationen.

Resultater

Undersøgelsen representerer en status for efteråret 2017 og er et oplæg til diskussion af, hvordan opgaven kan løses fremadrettet. Der er udpeget 5 branhcer: Brandøvelsespladser, forkromningsindustri, tæppeindustri, malingsindustri og fyldpladser. Oplægget giver på baggrund af opdateret viden en mulighed for at diskutere, hvor mange brancher, det er relevant at udføre forureningsundersøgelser for PFAS på.

HVAD ANBEFALES I VMR´S NYE HÅNDBOG?

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VMR og Regionerne har i 2016 iværksat arbejde om en håndbog om undersøgelse og afværge af forureninger med PFAS-forbindelser. Håndbogen er udarbejdet af NIRAS og Rambøll i samarbejde med regionernes følgegruppe og forventes udgivet i slutning af 2017.

Baggrund og formål

PFAS-forbindelser er en gruppebetegnelse for et stor antal persistente og problematiske stoffer, der betegnes som **P**er**F**luoro**A**lkyl og **P**oly**F**luor**A**lkyl forbindelser. Formålet med håndbogen er at beskrive bedste praksis for undersøgelser og afværge af PFAS-forureninger i jord og grundvand, således at medarbejdere i regionerne og deres rådgivere har et godt grundlag for at planlægge/tilrettelægge, udføre og evaluere sådanne projekter.

Metode

Håndbogen har fokuseret på de særlige egenskaber ved PFAS-forureninger, som adskiller sig fra almindelige forhold ved traditionelle undersøgelser af jord og grundvand. Håndbogen omfatter ikke detaljerede beskrivelser af standard undersøgelsesteknikker. Den fokuserer på de aspekter og problemstillinger, som er væsentlige for forståelse af den konceptuelle model og for at tilrettelægge, gennemføre og evaluere forureningsundersøgelser.

Håndbogen indeholder mange informationer, idet PFAS-forbindelser udgør en meget stor og kompliceret stofgruppe. Mange af disse oplysninger er ikke nødvendige for at gennemføre en standardundersøgelse, med giver læseren mulighed for at finde oplysninger og litteraturhenvisninger, og dermed en dybere forståelse af forureningsforhold.

Resultater

Håndbogen repræsenterer status for viden i foråret 2017 og samler baggrundsoplysninger om PFAS-forbindelser herunder stofbetegnelser, brancheanvendelser, miljø og sundhedsmæssige konsekvenser samt grænseværdier i jord, grundvand og biota. De dansk kvalitetskriterier for jord, drikkevand og grundvand er baseret på et administrativt sumkriterium for 12 specifikke PFAS-forbindelser, men der findes over 6.000 forskellige PFAS-forbindelser. Derfor er der udarbejdet forslag til en udvidet liste af 32 stoffer som kan være relevante ved udførelse af miljøundersøgelser, dog bør ny viden eller konkret kendskab til anvendelse af et PFAS-holdigt produkt inddrages i undersøgelsesstrategien.

Blandt andet er der foretaget en vurdering af stoffernes fysiske –kemiske egenskaber og spredning/fordeling i luft, jord, grundvand og overfladevand og udviklet 3 konceptuelle modeller baseret på typiske forureningsscenarier. Udover undersøgelsesstrategier er de analytiske redskaber og mulige afværgeforanstaltninger er skitseret.

A REVIEW OF CONTAMINATION OF SURFACE-, GROUND-, RAW AND DRINKING WATER IN SWEDEN BY PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFAS)

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Perfluoroalkyl and polyfluoroalkyl substances (PFASs) are a wide group of man-made chemicals. PFAS are used in wide range of industrial and consumer applications such as: electronics, cosmetics, impregnation of garment, leather goods, food packaging materials, hydraulic oils and as tension lowering agents in aqueous film forming foams (AFFF) among others. Most of these products are used in everyday life. During their life-cycle PFAS are leaking out from the products, either when they are used or during the end of their life-cycle as they are disposed to landfills (Schellenberger., 2016). Industrial applications, such as hydraulic oils or use of AFFFs in firefighting practice ultimately lead to point source contamination of soil, ground water and surface water that are close to well defined areas such as industries, mechanical workshops and firefighting practice sites. Circulation of PFASs in the environment is illustrated in Figure 1 below.

Figure1: The Fate of the good deed. (Andreas Ekoutsidis®).

The most well studied perfluorinated alkyl acids (PFAAs) are perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which are ubiquitously detected in the aquatic environment, wildlife and humans worldwide. In Sweden, PFAS have been analyzed since the early 2000s (Banzhaf, Filipovic, Lewis, et al., 2017). Since these first observations of PFAS in the Swedish environment, numerous follow-up studies have been conducted in order to analyze the fate and transport of PFAS in the environment. In Sweden, there are

more than 2000 identified and potential point sources of PFAS, including 28 firefighting training sites in the vicinity of airports, >300 municipal firefighting training sites, industries and landfills. From these point sources PFAS can mitigate and contaminate surface water and groundwater.

This review presents the current occurrence of PFAAs in the surface water, ground water, raw and drinking water in Sweden. Monitoring studies show the omnipresence of PFAS in the Swedish aqueous environment, PFAS are frequently being detected at (ng/L to µg/L concentrations in groundwater and surface water). Currently, PFAAs are not removed during conventional waste water treatment or during production of drinking water, and therefore pose a severe threat (Filipovic and Berger., 2015).

Although, first detections of PFAAs were reported in the early 2000s, PFASs only recently attracted significant media attention raising public concern. In Sweden, for instance, several public water works needed to be closed due to high PFASs concentrations in drinking water. Moreover, threshold values for drinking water are under discussion and a first preliminary guideline value for PFOS in ground water was recently presented (Pettersson et al., 2015).

The Swedish guideline values for PFASs in drinking water do not include the possible presence of precursor compounds. As identifying and quantifying the numerous known and unknown PFASs in the environment remains problematic, novel approaches to address these issues have been developed. The first approach is the so-called total precursor assay (TOP-assay), where oxidizing agents are used to degrade all potential PFAA precursors to form PFAAs as end products (Houtz and Sedlak., 2012).

A TOP-assay on a surface water sample from Lake Mälaren in Stockholm demonstrated an increase of shorter chained PFAAs of up to 57%. A second approach is to measure the total organic fluorine in environmental samples. This method can be done with combustion ion chromatography (CIC) (Weiner et al., 2013). Both of these methods have been applied on various types of samples indicating the presence of PFAS and PFAS precursors in the Swedish environment.

This work describes potential sources for PFASs to enter the ground and surface water supply in Sweden and compares different occurrences of PFASs in raw and drinking water in the country. The study is concluded with an analysis of future challenges and the way forward.

Litteraturhenvisning

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DANSKE OG SVENSKE LOSSEPLADSER – FORSKELLE I PFAS INDHOLD?

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Baggrund og formål

De senere år er der fundet en række PFAS i dansk grundvand. En af kilderne til PFAS forurening kan være deponering af PFAS-holdigt affald på gamle losse- og fyldpladser og på deponier.

Formålet med indlægget er at belyse indholdet af PFAS i danske og svenske lossepladser og at diskutere, hvorfor der er forskelle i påviste indhold.

Metode, teknik

Data for indhold af PFAS i perkolat fra og grundvand under danske og svenske lossepladser er indsamlet fra danske miljøprojekter og svenske rapporter. Resultaternes oprindelse og sammenlignelighed diskuteres. PFAS-sammensætning og forureningsstyrker sammenlignes med henblik på at belyse forskelle, der bl.a. kan skyldes måden at håndtere og bortskaffe affald på, og forskelle i anvendelse og håndtering af PFAS i produktionen.

Resultater

Resultater fra danske og svenske lossepladsundersøgelser gennemgås med fokus på koncentrationer og sammensætning af PFAS. Desuden belyses, hvorvidt resultaterne kan sammenlignes pga. forskelle i prøvetagningssteder, analysepakker mm.

Konklusion og perspektivering

På basis af tilgængelige data viser sammenligningen, at der tilsyneladende udvaskes mindre mængder PFAS fra danske lossepladser i forhold til svenske lossepladser/deponier. Dette vurderes bl.a. at skyldes, at der ikke er produceret PFAS i Danmark, og at der i Sverige er mange flere og større virksomheder, der anvender og har anvendt PFAS til f.eks. overfladebehandling af diverse produkter. Datagrundlaget i Danmark er lille, men viser, at PFAS kan forventes at findes i perkolat og at PFAS fortsat bør indgå i analyseprogrammer ved losseplads-undersøgelser. Dette understøttes af de svenske data.

Litteraturhenvisning

MP 1933/2017 Nye forureningsstoffer i perkolat fra lossepladser
MP 1892/2016 Spredning og sammensætning i grundvand ved PFAS-forureninger
MP 1905/2016 Kortlægning af brancher, der anvender PFAS
MP 1600/2014 Screeningsundersøgelse af udvalgte PFAS-forbindelser som jord- og grundvandsforurening i forbindelse med punktkilder
IVL 1827/2016 Sammanställning av befintlig kunskap om föroreningskällor til PFAS-ämnen i svensk miljö
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CASE FRA FORSVARSMINISTERIETS EJENDOMSSTYRELSE

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Nærværende case omhandler forureningsundersøgelser for PFAS på Forsvarsministeriets arealer med brandøvelsespladser. Her specifikt om de undersøgelser som er foretaget på Beredskabsstyrelsen Hedehusene, som er Beredskabsstyrelsens frivilligcenter.

Baggrund og formål

I de omkringliggende lande har forsvaret stor fokus på forekomsten af PFAS-forbindelser i grundvandet som følge af anvendelsen af PFAS til brandslukning og brandslukningsøvelser. På baggrund af fund af PFAS-forbindelser i grundvandet i bl.a. Norge og Sverige er der også i Forsvarsministeriet i Danmark kommet fokus på anvendelsen af disse stoffer og den miljømæssige påvirkning heraf.

Forsvarsministeriets Ejendomsstyrelse foretog de første PFAS-undersøgelser i 2012 og 2013, hvilket leder frem til, at der i 2015 udføres en screening for indhold af PFAS i jord- og grundvandsprøver udtaget på Forsvarsministeriets arealer. Ved screeningen blev der udtaget prøver flere steder i landet, bl.a. ved Beredskabsstyrelsen Hedehusene.
Screeningen viste forhøjede værdier i den prøve, som blev udtaget på Beredskabsstyrelsen Hedehusene ved en brandøvelsesplads for træning af tankvognbrand.

Metode, teknik,

Beredskabsstyrelsen Hedehusene er beliggende i OSD, hvorfor der i 2015 blev udarbejdet en revideret miljøhistorisk redegørelse til brug for kortlægning på vidensniveau 1 efter jordforureningsloven. Miljøhistorikken identificerede flere potentielle kilder til forurening med PFAS-forbindelser. Forsvarsministeriets Ejendomsstyrelse udarbejdede i 2015 endvidere sin egen interne indsatsplan for grundvandsbeskyttelse for etablissementet.

Som følge heraf blev der i 2015, som en del af screeningsundersøgelsen for PFAS, udført en DTH boring til det primære grundvand 14 m u.t. Der blev ikke påvist sekundært grundvand i området. Det efterfølgende år blev der udført GeoProbe boringer til yderligere analyser af vandprøver for kulbrinter, chlorerede stoffer og PFAS-forbindelser. PFAS-analyserne er udført som analyser for de 12 stoffer, som er en del af Miljøstyrelsens kvalitetskriterium.

Resultater

Der er ved både screeningsundersøgelsen og ved de efterfølgende GeoProbe undersøgelser konstateret indhold af PFAS-forbindelser i det primære magasin på lokaliteten. I et område omkring brandøvelsespladserne træffes der indhold af PFAS op til 14 gange over Miljøstyrelses grundvandskvalitetskriterier. Nedstrøms etablissementet er der ligeledes konstateret indhold af PFAS i grundvandsprøver med et lignende indhold af PFAS-forbindelser.

Konklusion og perspektivering
Fremadrettet planlægges der udført moniteringsboringer med filtre i to dybder, samt udtaget vandprøver til analyse fra boringer placeret nedstrøms etablissementet. Det ønskes endvidere undersøgt, hvorvidt noget af PFAS- indholdet kan stamme fra aktiviteter opstrøms etablissementet, da der generelt ses et indhold af PFAS i grundvandet i området.

Forsvarsministeriets Ejendomsstyrelse er endvidere blevet opmærksom på udfordringer med at finde et brandøvelsesskum uden indhold af PFAS. De grænseværdier der er for hvornår producenterne skal angive tilstedeværelsen af PFAS i deres produkt, ligger over grænseværdierne for PFAS i grundvandet. Forsvarsministeriets Ejendomsstyrelse vil derfor få foretaget analyser af forskelligt brandslukningsskum, og forsøge at belyse hvilke typer skum, der kan anvendes uden risiko for udledning af PFAS til miljøet.

Notater

Notater

Notater

Notater