

PFC CONTAMINATION IN DANISH GROUNDWATER, LESSONS LEARNT FROM A TREATMENT UNIT AND A (BRIEF) REVIEW OF ALTERNATIVE TREATMENT OPTIONS

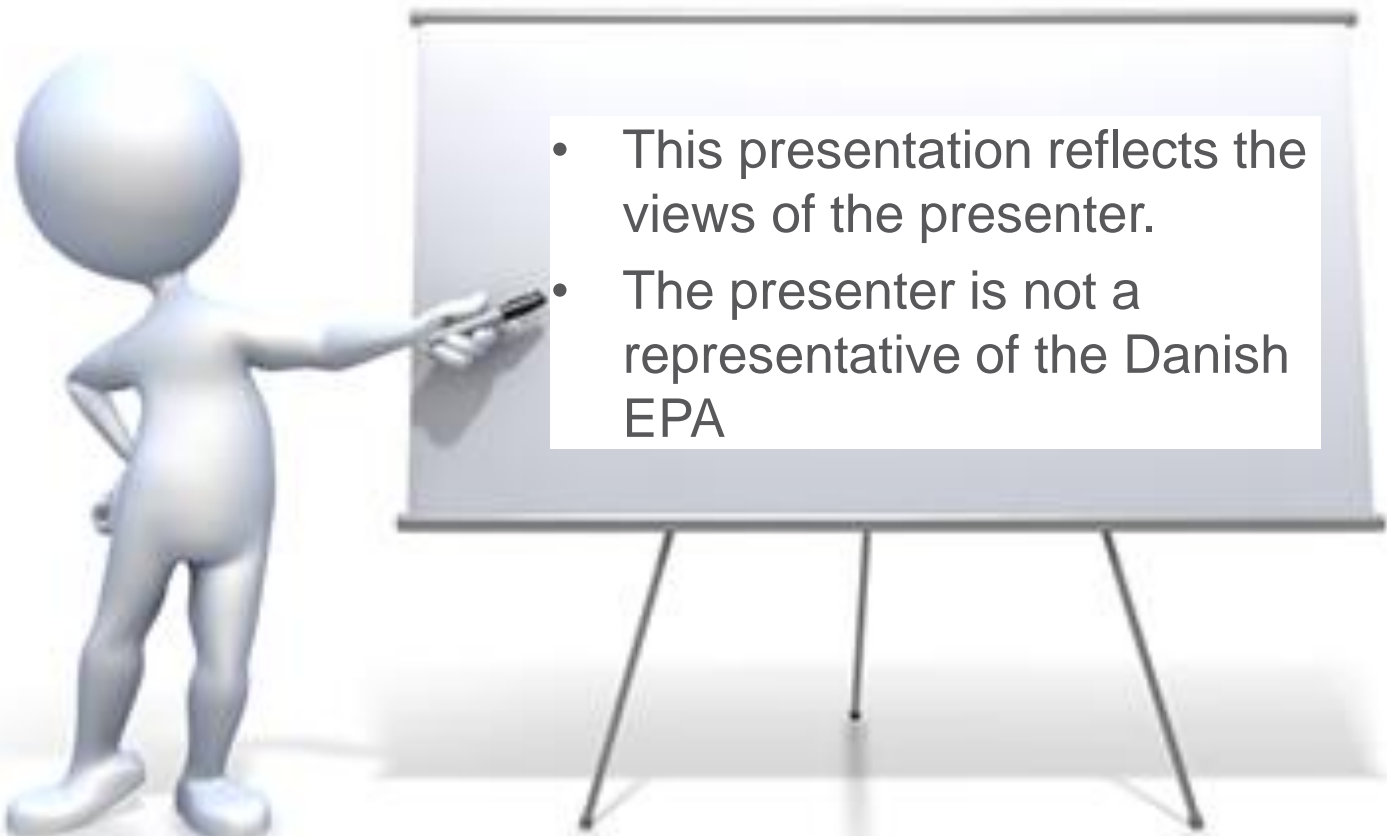


NICOLE WORKING GROUP ON EMERGING CONTAMINANTS

Manchester, June 24th 2015

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- This presentation reflects the views of the presenter.
 - The presenter is not a representative of the Danish EPA

A bit of history for PFCs in Scandinavia

- 1949 – 3M begins production in the US
- 1966-2000: Use of PFAS is widespread
- 2000: 3M announces phase out of PFAS
- 2002: PFAS (especially PFOS use drops significantly).
- 2006: EU regulation on use of PFAS.
- 2008: first finds of PFAS in Sweden at Arlanda airport.
- 2010: First finds in Denmark, at an airport
- 2011: Swedavia investigates all large Swedish airports
- 2013: The Danish EPA initiates the first project on mapping PFAS contamination
- 2014-2015: The Danish Defence investigates all their relevant sites
- May 2015: Danish criteria for groundwater and soil are set

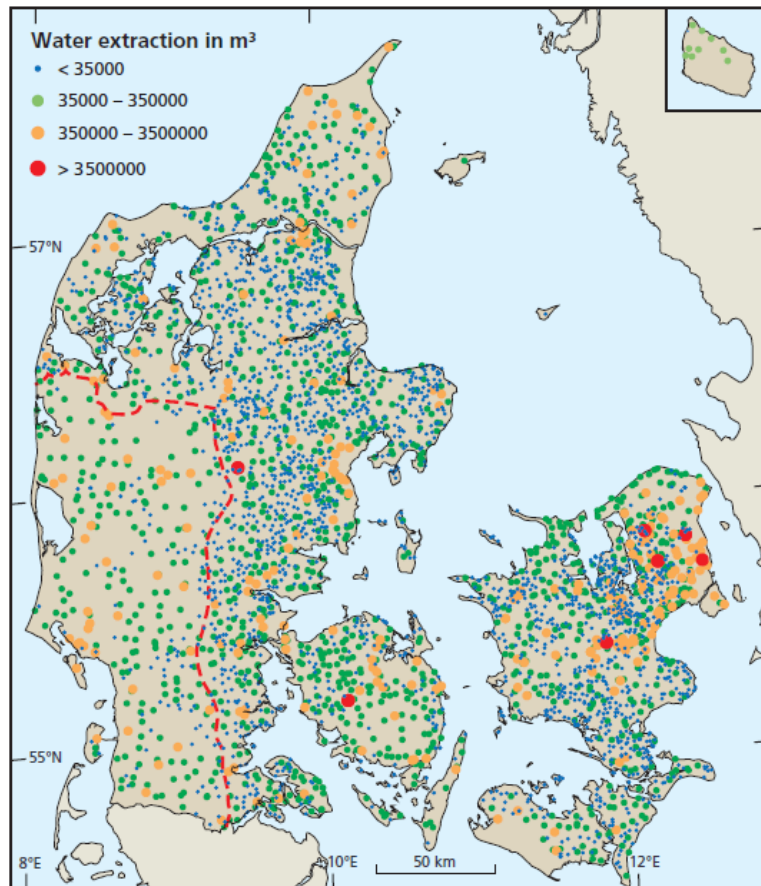
Danish EPA study on the occurrence of PFAS in groundwater



Forsvaret
Forsvarets Bygnings- & Etablissementstjeneste

Motivation for mapping PFC contamination

- The drinking water supply in DK is entirely based on



Drinking water should be based on pure groundwater which only needs simple treatment with aeration, pH adjustment and filtration before it is distributed to the consumers. Groundwater quality in deeper aquifers in Denmark is generally good, thus obviating the need for complex and expensive water purification. Except for Copenhagen, with long transmission networks, **the drinking water is not chlorinated and the quality of tap water is even better than bottle water.**

PFC in Danish media

FORBRUGERKEMI 9. SEP. 2010 KL. 15.45

Stof i pizzabakker mistænkt for at øge dit kolesteroltal

Højt kolesteroltal kan hænge sammen med et stof, der findes i emballage og mad

Ingeniøren

Nyheder | Blogs | Debat | Jobfinder | Avisen | Kursusguide | Ingeniøren+

Sektioner: Biotek Byggeri Elektronik Energi & miljø Forskning Fødevarer It Karriere Produktion Rumfart Tra

De såkaldt miljøvenlige alternativer rendyrket hokuspokus

Industrien bruger alternativer til fluorstoffer, der enten er lige så skadelige eller b nedbrudt til de selvsamme forbudte fluorstoffer, viser kinesisk forskning.

Af [Thomas Djursing](#) 8. nov 2013 kl. 11:21

Alternativer til de forhadte perfluorerede stoffer som PFOS og PFOA findes i rigelige mængder i produkter i dag – men undersøgelser foretaget af kinesiske forskere viser, at alternativerne er lige så skadelige for både mennesker og miljø.

Ofte tilføjer industrien blot et oxygenmolekyle eller en amidgruppe til det langkædede perfluorerede stof, og undersøgelserne viser, at de modificerede stoffer f.eks. blot kobler amidgruppen af under nedbrydning, så det perfluorerede stof bliver reaktiveret. I andre tilfælde – som med alternativet F35B der har været brugt i årtier i Kina – opfører stoffet sig fuldstændig ligesom det oprindelige PFOA.

»Fisk d
ved at b
som PF

Do Perfluoroalkyl Compounds Impair Human Semen Quality?

Ulla Nordström Joensen,¹ Rossana Bossi,² Henrik Leffers,¹ Allan Astrup Jensen,³ Niels E. Skakkebak,¹ and Niels Jørgensen¹

¹University Department of Growth and Reproduction, Rigshospitalet, Copenhagen, Denmark; ²National Environmental Research Institute, University of Aarhus, Roskilde, Denmark; ³FORCE Technology, Brøndby, Denmark

FORBRUGERKEMI 25. OKT. 2013 KL. 22.30

Norge har forbudt hormonforstyrrende stof - i Danmark er det lovligt

Forbrugerrådet vil have det hormonforstyrrende stof PFOA forbudt.



Q SLIP-LET. Det i stegepander. - Fot

DEL

Teflonbelægnin
sko kan indeho

Norge har forbu
stoffet.

LES OGSÅ Såda

Perfluorooctans
vand- og smuds

Ingeniøren

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Sektioner: Biotek Byggeri Elektronik Energi & miljø Forskning Fødevarer It Karriere Produktion Rumfart Tra

Farlige fluorstoffer vælter ind fra Kina

Efter et forbud i Vesten mod de farligste fluorstoffer har Kina øget produktionen. Forskere advarer nu om, at stofferne ender her gennem produkter og fødekæder.

Af [Thomas Djursing](#) 8. nov 2013 kl. 05:03

Hos os er det forbudt – men i Kina er produktionen af et af de mest frygtede perfluorerede stoffer, PFOS, de seneste år steget voldsomt. Det kan måles direkte i luften i Beijing, hvor koncentrationen af perfluorerede stoffer er 14-doblet fra 2004-2010. Og herfra spredes stofferne til Vesten gennem produkter og fødekæder:

»Vi skal være meget bekymrede for det, som sker i Kina for tiden. Vi vælter os i kinesiske perfluorstoffer, som når hertil med produkter som jakker, sko, potter og pander. De kommer ind over grænsen gennem produkter og gennem fødekæderne i havet, og vi har slet ikke styr på det,« siger centerleder og professor ved Institut for Folkesundhed på Aarhus Universitet Eva Cecilie Bonefeld-Jørgensen.

Bevisbyrden mod de perfluorerede stoffer er vokset de seneste år, og sammenhænge er fundet

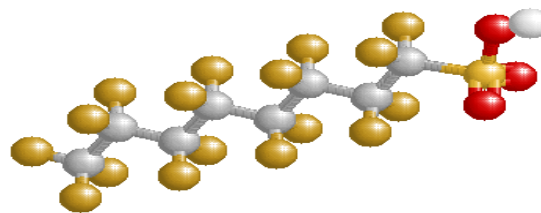
me.

ar set en sammenhæng
t. Og når stofferne har
et fra Eva Cecilie

day, July 03,
2015

6

Project aim



- to **identify potential point sources of groundwater pollution** with PFC and perform investigations at relevant sites
- **A first step** in mapping PFC contamination in Danish groundwater.
- The project is an initiative under the Danish EPAs risk management strategy for PFOS and PFOA.
- PFOS, PFOA and 7 other PFCs were investigated (6 long chained and 1 short chained)

Navn	Group	Carbon chain length	Abbreviation	CAS nr.	Classification
Perfluoro-n-heptanoic acid	PFCA	C7	PFHpA	375-85-9	no classification available
Perfluorooctanoic acid	PFCA	C8	PFOA	335-67-1	R22 R34 R52/53, S26 S36/37/39 S45
Perfluoro-n-nonanoic acid	PFCA	C9	PFNA	375-95-1	no classification available
Perfluorobutanesulfonic acid	PFSA	C4	PFBS	375-73-5	no classification available
Perfluorohexanesulfonic acid	PFSA	C6	PFHxS	355-46-4	no classification available
Perfluorooctane sulfonic acid	PFSA	C8	PFOS	1763-23-1	Carc. Cat. 3; R40, Repr. Cat. 2; R61, T; R48/25, Xn; R20/22, R64, N; R51-53
Heneicosafuoro-1-decanesulfonic acid	PFSA	C10	PFDS	335-77-3	no classification available
Perfluorooctanesulfonamide	FASAs	C8	PFOSA	754-91-6	no classification available
Perfluorohexanoic acid	PFCAs	C6	PFHxA	307-24-4	no classification available

PFC applications in Denmark



Consumption in Denmark 9-16 tons per year until 2005

- 1 % used in firefighting foam for fuel fires
- 50 % used in impregnation of textiles leather and paper
- Moreover used in paints, cleaning agents
- Still used in hard chromium plating

There can be other sources than firefighting foams/fire drill sites



Project approach

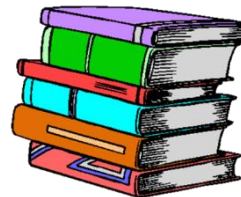
Phase 1

The project's first phase comprised a review of industries where PFCs have been used and could potentially result in the pollution of soil and groundwater.

- Literature review
- Interviews with industry representatives

Phase 2

Site investigations (groundwater sampling) were performed/data was collected from 17 sites for PFOS, PFOA and seven other PFCs.



Results of phase 1

The following industries/site uses were highlighted as potential sources of PFC contamination in groundwater as PFC's have been used in there industries:

- Fire drill sites for fuel-fires, PFC used up to 2011
- Chromium plating,
- Carpet manufacturing,
- Paint manufacturing,
- Landfill sites for construction waste and older municipal waste landfills.

Criteria

- Amount of PFCs used
- Processes that are likely to cause a leak to soil and groundwater

Phase 2: Overview of investigated sites



We performed investigations at existing wells at

- 8 fire drill sites*
- 2 chromium plating sites
- 4 landfill sites
- 1 carpet industry
- 1 paint industry

*At 2 sites we drilled new investigation wells

Site selection based on

- accessibility
- availability of suitable monitoring wells
- Previous knowledge of contamination with other contaminants



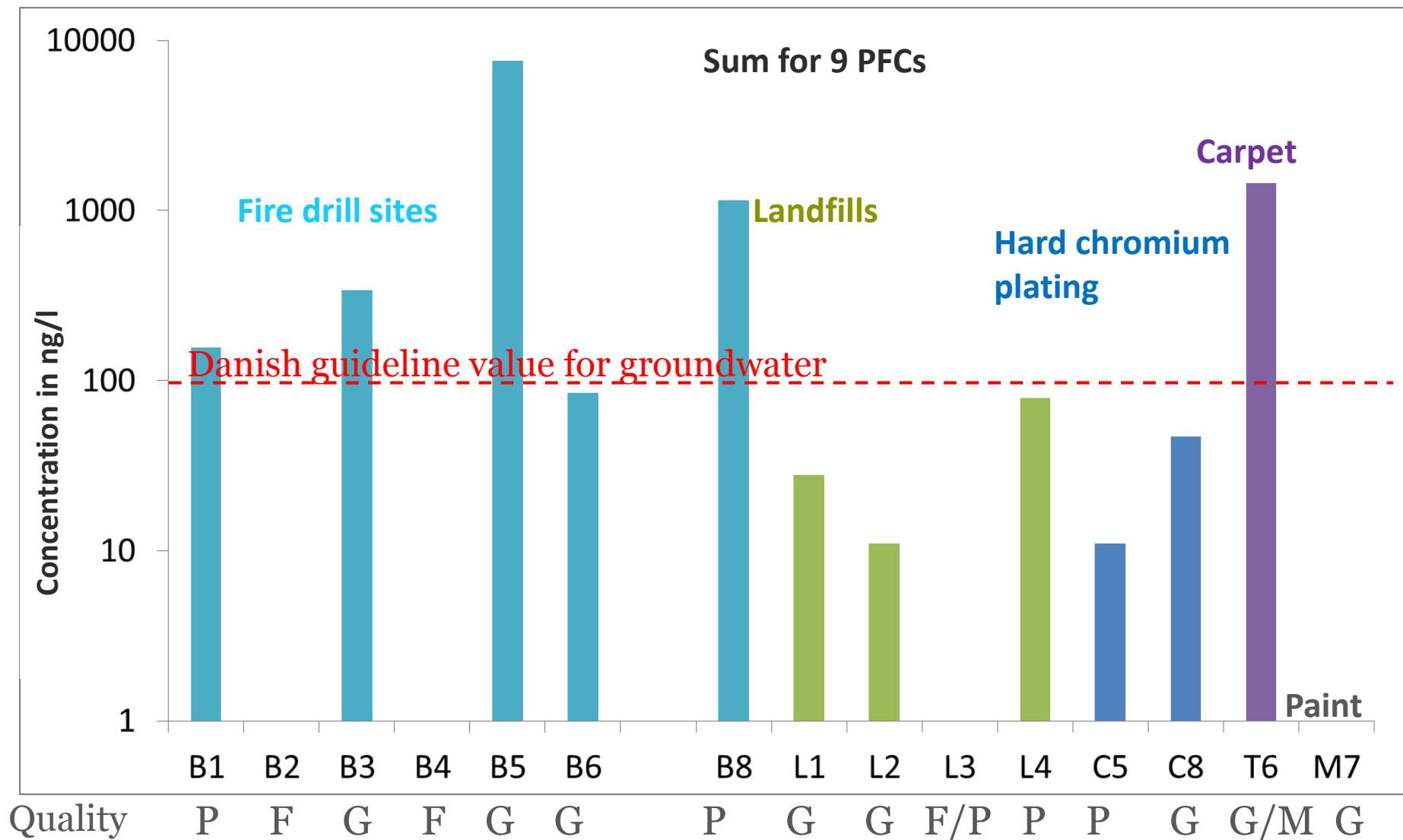
Quality of site investigations

Poor: <2 wells not necessarily at or down gradient PFC application area

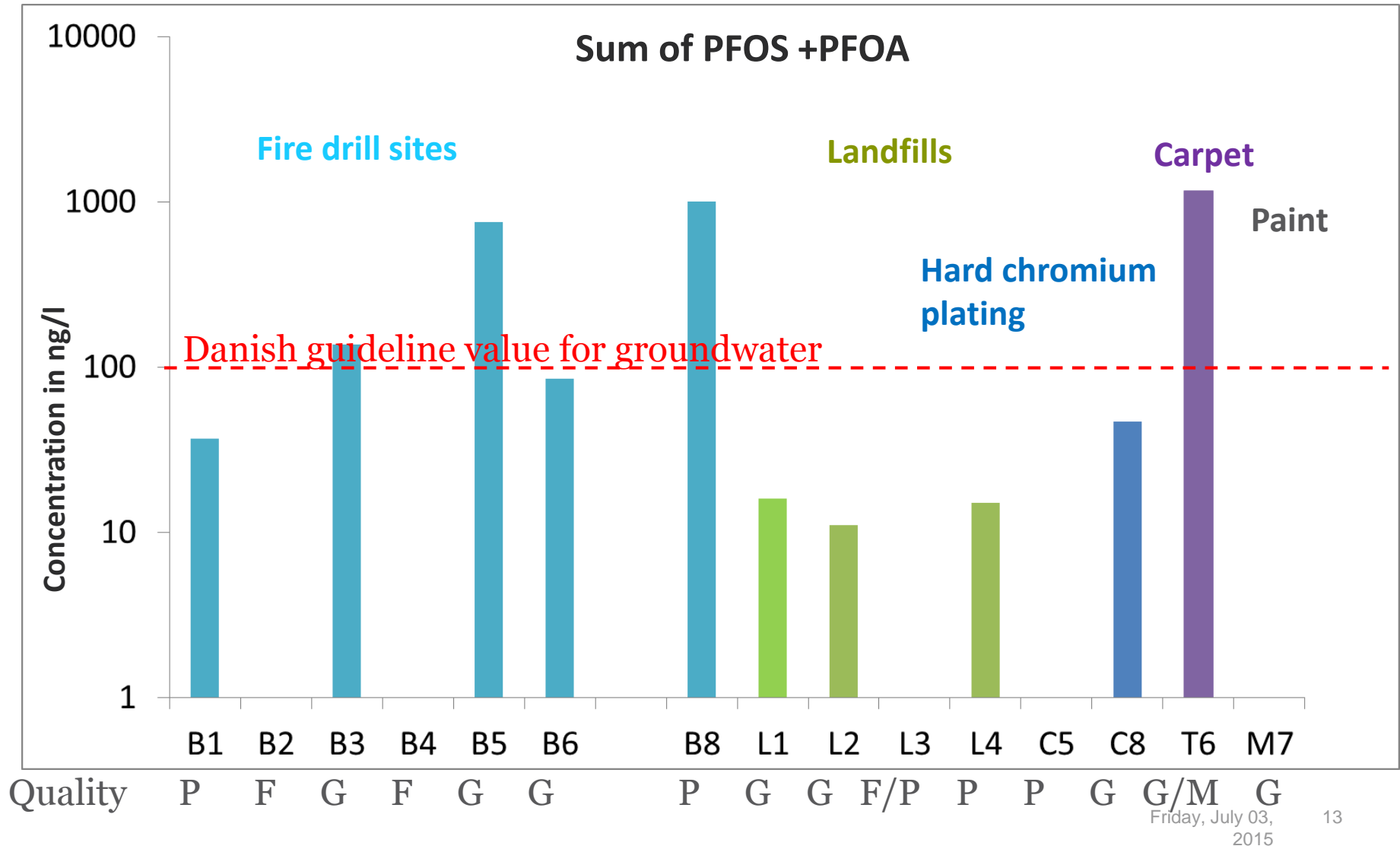
Fair: <2 wells situated at or directly down gradient PFC application area

Good: >2 wells situated at or directly down gradient PFC application area or a deeper pumping well

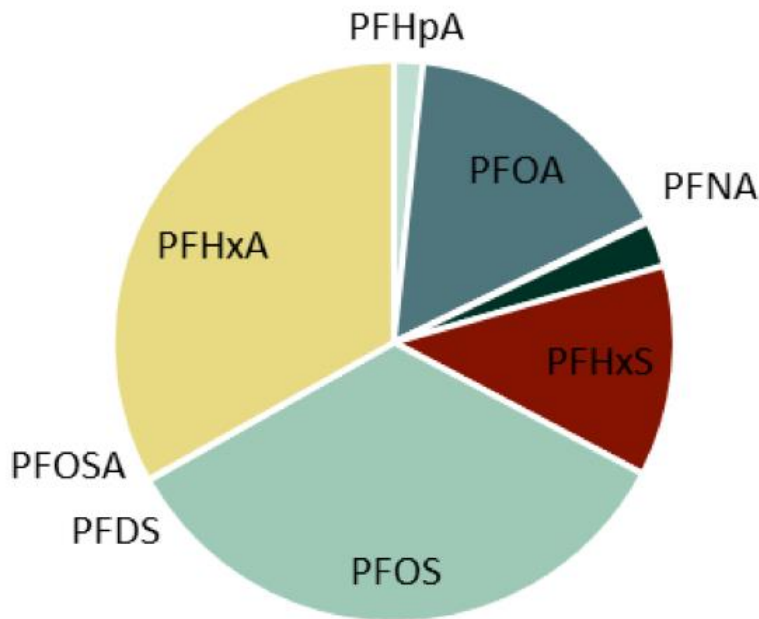
Results of site investigations



Results of site investigations



Composition of PFAS found at fire drill sites



There could be others
The Danish defense find a
higher content of PFHeA

FIGUR 6.3 FORDELINGEN AF PFAS MELLEM DE 9 FOKUSSTOFFER FOR SUMMEN AF PÅVISTE STOFFER PÅ BRANDØVELSESPLADSER

Conclusion and perspectives: Fire drill sites

PFC found in 5/8 fire drill sites

- 2 sites with levels over 1,000 ng/l
- 2 sites with levels over 100 ng/l
- Detailed investigations → PFC found
- Less detailed investigated sites → little or no PFC
- 27 other candidate sites



Conclusions and perspectives-Other industries

- Landfills and paint industry: No sign of significant PFC contamination but only few sites have been investigated
- Chromium plating- Possible source of PFC pollution
- Carpet industry- Likely source of PFC pollution but limited number of sites





The press had fun...



Kronik: Fluor-sagen viser behov for systematisk overvågning af vand

30. okt 2014 6



Rapport anbefaler: Tjek alle brandøvelsespladser for giftige fluorstoffer

Danske brandøvelsespladser er så afgørende en kilde til forurening af grundvandet med fluorstoffer, at de bør undersøges for en bred vifte af stoffer, fastslår ventet rapport.

22. okt 2014 1



Hver tredje svensker drikker vand med skadelige fluorstoffer

Sundhedsskadelige fluorstoffer er så udbredte i drikkevand, at 3,6 millioner svenskere dagligt indtager dem i små koncentrationer, viser en svensk undersøgelse. Der er ingen planer om en tilsvarende kortlægning herhjemme.

9. okt 2014 6



Minister sætter styrelser på plads: I skal sikre drikkevand uden fluorstoffer

Et halvt år er alt for lang tid at sidde på viden om giftige fluorstoffer i grundvandet uden at undersøge drikkevandet, mener miljøminister Kirsten Brosbøl. Nu beordrer hun myndighederne til flere undersøgelser.

23. sep 2014 3



Fluorstoffer: Tag med Ingeniøren gennem myndighedernes uendelige telefonkæde

Hvem har ansvaret for at garantere danskerne drikkevand uden fluorstoffer? Det simple spørgsmål fik myndighederne til at sende Ingeniøren rundt og rundt mellem hinanden. Gør turen med os i denne artikel.

19. sep 2014 4

Danish PFCs Guidelines for groundwater set after this project



- 0,1 µg/l for the sum of 12 PFCs in groundwater and drinking water and 400 µg/kg for the sum of 12 PFCs in soil



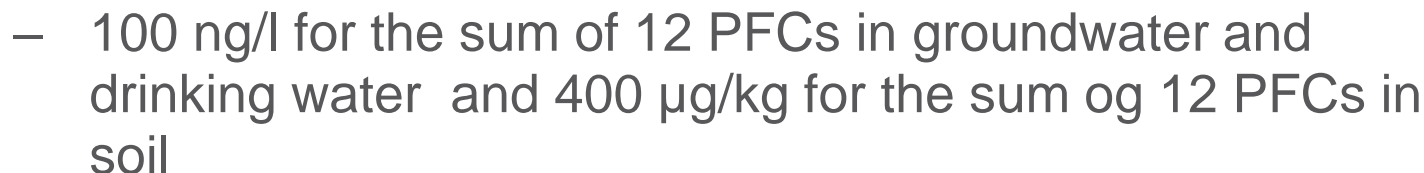
- Suggested MCL of 0,1 µg/l for PFOS +PFOA in Germany



- 0,3 µg/l for PFOS og 10 µg/l for PFOA in drinking water in Great Britain



- EPA provisional health advisory (200 ng/l for PFOS and 400 ng/l for PFOA), NJ 40 ng/l for PFOA

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A Case study

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Remediation options



What I am keeping an eye on

- Activated Persulfate oxidation (High temperature, ozone, UV, iron)
 - Positive results for PFOS decomposition at 80 C (Pardo et al., 2015)
 - Mixed results (Dr. Lee, Purdue University, Dr. McIndoe, University of Victoria)
 - Most promising for PFOA and short chained (Dr. Lee, Purdue)
 - Need for careful experimental design to avoid false positives
 - Need for proof of actual decomposition
 - Perozox® to be applied at Schiphol
- Bioremediation with fungi (Dr. Mahendra, UCLA)
 - Experimental, very promising results for precursors
- Electrodialysis (With g-Irradiation University of Arizona)
- Ion Exchange Resins
- Reverse Osmosis (Used at POU treatment)
- Immobilisation (eg. Matcare™ , or RemBind™)
- PRB with GAC and ECOHR (SERDP project)

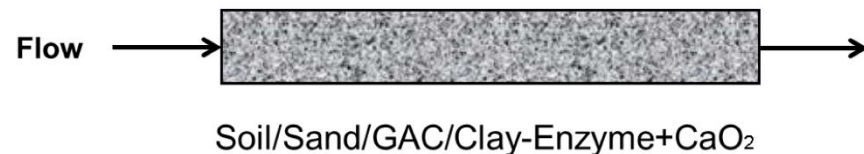


Figure 14. Conceptual model of an ECHOR barrier