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PFAS in Sewage Sludge

SAFE CUT-OFF VALUES FOR PROTECTION OF FRESHWATER, GROUND WATER, SOIL ECOSYSTEMS AND HUMAN HEALTH

PFAS in Sludge

- The chemical composition of sewage sluge from municipal waste water treatment plants is a mirror of the antropogenic activities in modern society
- No surpise we find PFAS
- The sources are multiple and only vaguely mapped and quantified
- We only monitor a small fraction of all PFAS in sludge
- Precursors are a dominant factor and may lead to higher outlet than inlet concentrations of many PFAS
- Temporary cut-off values are only recently introduced for PFAS

Environmental Threshold Concentrations

Text Box 1.1. Environmental Threshold Concentrations (ETC) or Quality Standards of PFAS in Denmark.

Sewage sludge: 0.4 mg/kg (dw) as sum of PFBS, PFPeS, PFHxS, PFHpS, PFOS, PFNS, PFDS, PFUnS, PFDoS, PFTrS, PFOSA, 6:2 FTS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnDA, PFDoDA and PFTrDA (in this report named $PFAS_{22}$).

Sewage sludge: 0.01 mg/kg (dw) as sum of PFOA, PFOS, PFNA and PFHxS (in this report named $PFAS_4$).

Not risk-based

Soil: 0.4 mg/kg (dw) as $PFAS_{22}$

Soil: 0.01 mg/kg (dw) as $PFAS_4$

Groundwater: 0.1 µg/L as $PFAS_{22}$

Groundwater: 0.002 µg/L as $PFAS_4$

Drinking Water: 0.1 µg/L as $PFAS_{22}$

Drinking Water: 0.002 µg/L as $PFAS_4$

Freshwaters (Annual Average): 6.5×10^{-4} µg PFOS/L

Freshwaters (Maximum): 36 µg PFOS/L

Marine waters (Annual Average): 1.3 x 10-4 µg PFOS/L

Marine waters (Maximum): 7.2 µg PFOS/L

Biota: 9.1 µg PFOS/kg (ww)

PFAS in sludge

TABLE 6.12. Percentiles of the individual PFAS and $PFAS_4$ as measured in 215 Danish sludge samples from 45 different wastewater treatment plants (Appendix C).

µg/kg	$PFAS_4$	PFOS	PFOA	PFNA	PFHxS
MIN	0.36	0.043	0.085	0.07	0.05
10P	3.40	2.4	0.3	0.185	0.137
50P	7.49	4.5	0.85	0.6	0.19
90P	17.83	15	2.5	2.5	2.5
MAX	65.15	55	19	7.4	4.3
N Total	215	215	215	215	215
N > LOQ	215	183	154	99	12

PFAS in Sludge

	$PFAS_4$	$PFAS_{22}$	$PFAS_4$: $PFAS_{22}$	PFOS: $PFAS_4$	PFOA: $PFAS_4$	PFNA: $PFAS_4$	PFHxS: $PFAS_4$
	µg/kg	µg/kg	%	%	%	%	%
MIN	0,36	5,35	2,89	11,85	0,98	0,49	0,39
10P	3,40	12,48	16,53	25,00	5,02	3,37	1,11
50P	7,49	22,94	31,60	73,53	12,14	8,42	3,81
90P	17,83	56,35	56,63	87,63	25,00	25,00	25,00
MAX	65,15	110,15	82,21	98,00	46,84	50,03	34,92
N Total	215	215	215	215	215	215	215

PFAS in sludge is declining in DK

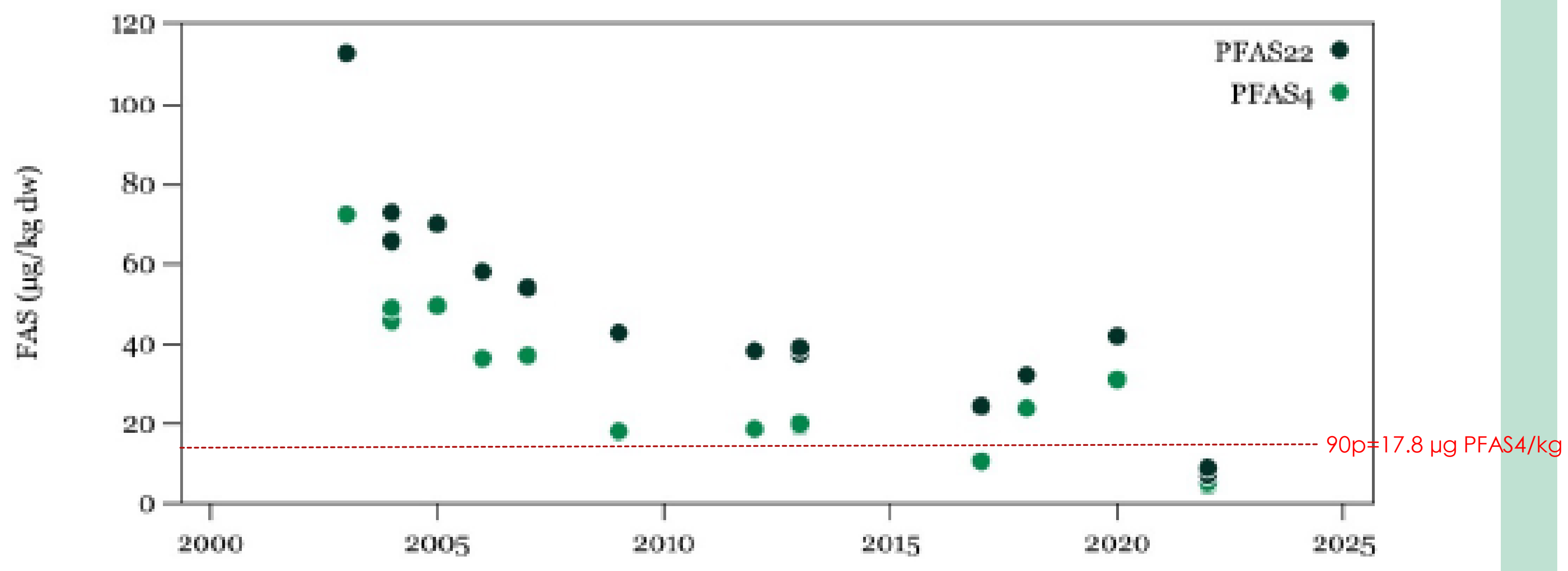


FIGURE 3.1. Measured PFAS (µg/kg dw) in sludge samples covering the period 2003-2022 from Avedøre WWTP used for soil amendment of long-term CRUCIAL research plots (See text). Solid circles are $PFAS_{22}$ and open circles are $PFAS_4$. Reprinted from Draborg and Tsi-tonaki (2023).

Environmental Status

GRUMO. Analyser for PFAS i 2017-2021. GEUS 2023

Stofnavn	DG	KV	Indtag antal			Indtag andel (%)	
	µg/l	µg/l	I alt	≥DG	>KV	≥DG	>KV
Sum 12 PFAS [a)]		0,1	686	124	2	18,1	0,3
Sum 4 PFAS [b)]		0,002	686	95	40	13,8	5,8
PFOS (Perfluoroktansulfonsyre)	0,0003-0,001	0,002	686	60	17	8,7	2,5
PFOA (Perfluoroktansyre)	0,0003-0,001	0,002	686	43	16	6,3	2,3

µg/L	Avg.	50P	10P	90P	% >LoD	LoD	Samples/Stations
Perfluoroctansulfonsyre (PFOS)							
2008-2013	0,0034	<DG	<DG	0,0042	32	0,001	140/12
2014-2019	0,0027	0,0012	<DG	0,0076	75	0,000065-0,065	324/28
Perfluoroctansyre (PFOA)							
2008-2013	0,00080	<DG	<DG	0,003	21	0,002	140/12
2014-2019	0,0064	0,0036	<DG	0,016	66	0,001-0,002	324/28

Data: DCE/AU, Boutrup et al 2021

ETC = 0.00065 µg/L ← Ecotox ETC = 0.023 µg/L

Risk based cut-off values in sludge

- Objective: Quantify the maximum level of PFAS in sludge ensuring a compliance with environmental threshold concentrations
- Methods: Acknowledged kinetic-based functions and equations for exposure calculations used in reverse fashion (backwards) and model, both complex and simplified, predictions
- Protection goals:
  - Soil ecosystem structure and functions
  - Freshwater recipients
  - Ground water
  - Human consumers of agricultural products

Basic Principles

- Acknowledged exposure calculations used in ECHA (Chemicals), EMA (Medicines) and EFSA (Pesticides):
  - Sludge/manure > Soil > Soil pore water > leaching to fresh water / ground water
- Reverse Calculations:
  - ETC (Gw/Fw) > Soil pore water > Soil > Sludge
- Model calculations:
  - No possibility for reverse calculations
  - Fixed PFAS load > ground water concentrations

Key kinetic processes
Soil – Pore water

- The pore water concentration should not exceed the ETCgw (2 ng/L)
  - ETCgw = Cpw

- If the targetted Cpw is known, the the corresponding soil concentration can be calculated knowing the soil-water partitioning coefficient (Ksoil-water) and the density of the soil (RHO)

$$Cpw = \frac{Csoil{-}ss \times RHOsoil\ (dw)}{Ksoil{-}water \times 1000}$$

$$Csoil\text{-}ss = \frac{Cpw \cdot Ksoil{-}water \cdot 1000}{RHOsoil(dw)}$$

Ksoil-water: Use VP, MOLW and **Koc**

Koc

- Distribution coefficient between pore water and organic carbon

- Kd = Koc x foc

- PFAS does not behaviour like most organic pollutants, as they are both hydrophobic as hydrophillic.

$$K_d = \frac{\textit{Concentration in solid phase } (\frac{mg}{kg}\, dw)}{\textit{Concentration in liquid phase } (\frac{mg}{l})}$$

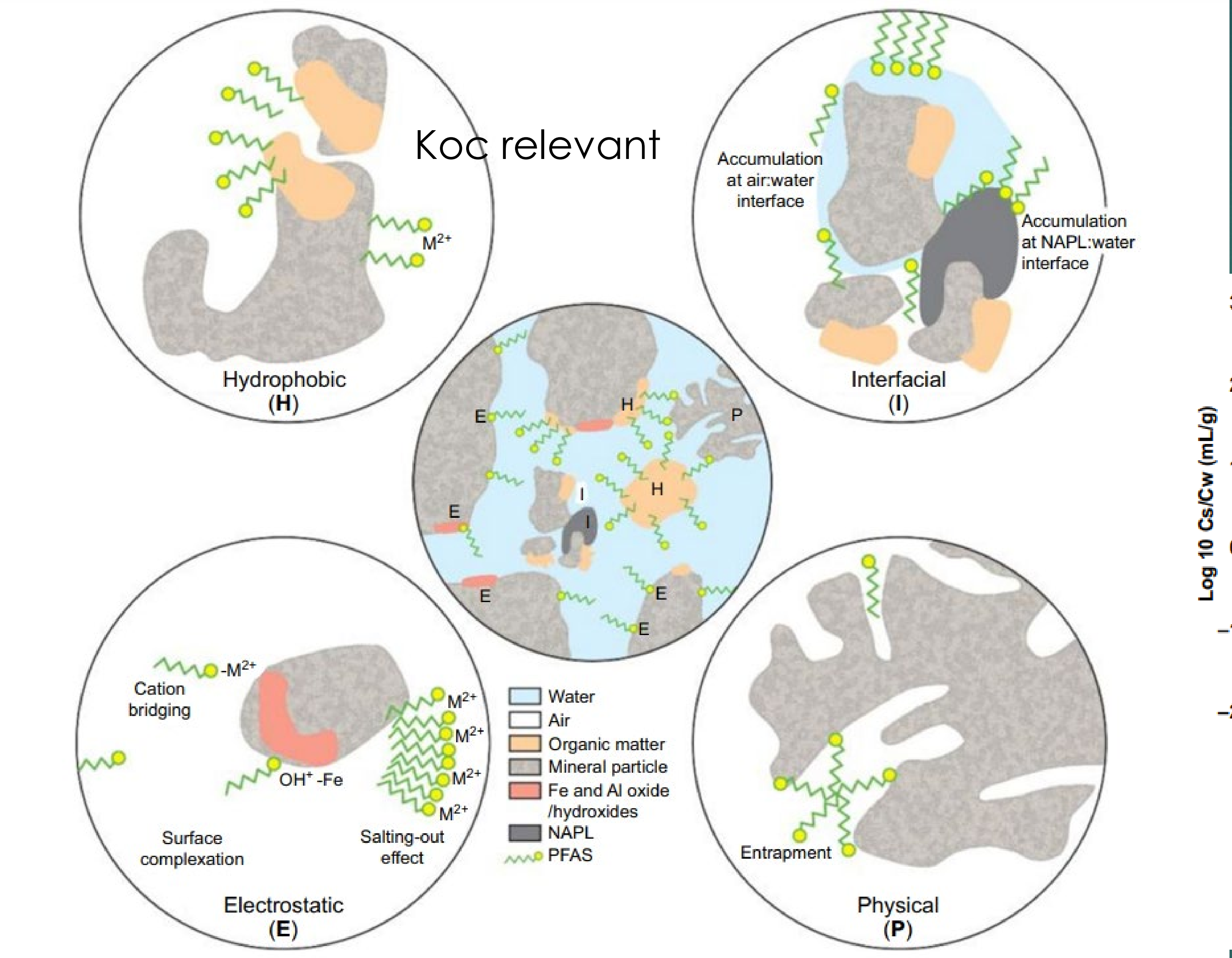
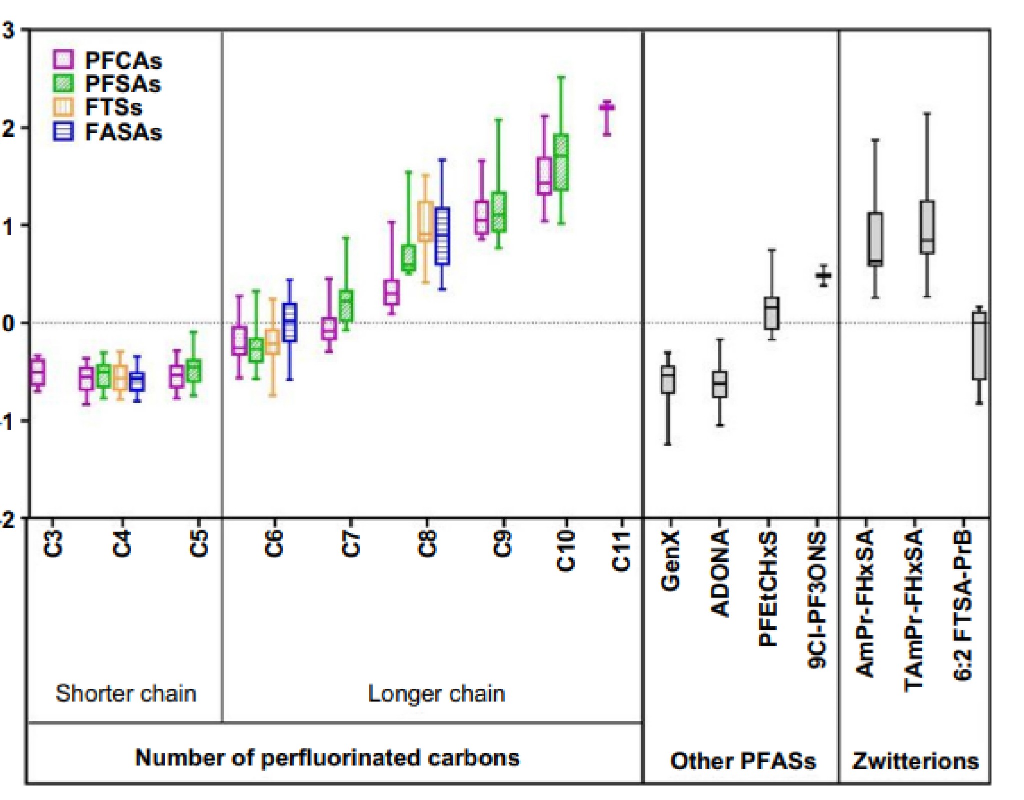


Fig. 1. Various mechanisms contributing to partitioning of PFAS in saturated and unsaturated soils. H, hydrophobic; E, electrostatic interactions; I, interfacial adsorption; and P, physical entrapment.

Kookana RS et al. (2023) Soil Research, 61(2), 107–125.

Kd values



Nguyen et al 2020
Environ. Sci. Technol. 2020, 54, 24, 15883–15892

Koc

- Koc available in soil difffering in:
  - Soil types, OC, pH and anions
- Koc differ accordingly
- Leaching differ accordingly

PFOS	10%	2,84
	50%	3,60
	90%	4,68
	95%	4,80
	N=	83

PFOA	10%	1,77
	50%	2,30
	90%	3,00
	N=	74

	Eq. / Cpt.	Log K_{oc} = 2.84 (10th percentile) (L/kg)	Log K_{oc} = 3.6 (median) (L/kg)	Log K_{oc} = 4.68 (90th percentile) (L/kg)
$K_{soil-water}$ [m^3/m^3]	4.6	20.95	119.6	1436.1
$k_{leaching}$ [d^{-1}]	4.5b	1.15E-04	2.00E-05	1.67E-06
Removal rate by leaching:		5.75	1	0.08

PFAS	# Data (N)	log K_{oc}
PFBS	58	1.80
PFPS	40	1.85
PFHxS	71	2.31
PFHpS	40	2.76
PFOS [Median]	86	3.60
PFOS [10th percentile]	86	2.84
PFNS	40	3.76
PFDS	40	4.23
PFUnS	0	*
PFDoS	0	*
PFTrS	0	*
(P)FOSA	71	4.36
6.2 FTS	40	2.28
PFBA	40	1.90
PFPeA	55	1.38
PFHxA	71	1.50
PFHpA	73	1.91
PFOA	77	2.30
PFNA	74	2.90
PFDA	73	4.00
PFUn(D)A	70	4.30
PFDo(D)A	69	4.77
PFTr(D)A	0	*

*No data

Key kinetic processes
Soil – Pore water

- Pore water must be estimated at the future long term soil concentration when steady state is reached
- When Csoil-ss is known, the soil concentration at year 1can be calculated knowing the annual accumulation rate (Facc)
- The fraction annually accumulating in soil is depending on the total annual removal rate (k-removal [d-1])

$$Facc = e^{-365\ x\ k}$$

$$Csoil - ss = Csoil(0)\ x\ \frac{1}{1-Facc}$$

$$Csoil(0) = Csoil(ss)\ x\ (1 - Facc)$$

Removal rate

$$k = k_{removal} = k_{leaching} + k_{biodegradation} + k_{NER}$$

$$kleaching = \frac{Finf \ x \ RAINrate}{Ksoil{-}water \ x \ DEPTHsoil}$$

$$kbiodegradation = \frac{ln2}{DT50}$$

NB: Removal of PFAS by evaporation/volatilization (k-volat) is assumed to be zero due to lack of suitable data = conservative approach

Removal by plant uptake is neglected, but most likely exceeds k-biodegradation and is shown to be 2-3 orders of magnitude lower than k-leaching

Removal to NER (k-NER)
Non-Extractable Residues

Schäffer A, Kästner M, Trapp S. 2018. A unified approach for including non-extractable resi-dues (NER) of chemicals and pesticides in the assessment of persistence. Environ Sci Eur. 30:51. doi: 10.1186/s12302-018-0181-x.

- **NER Type I:** Are adsorbed or physically entrapped into the matrix, contain the parent sub-stance, transformation products or both. NER Type I have the potential to be remobilized and therefore should be regarded as non-degraded substances when calculating the half-life.
- **NER Type II:** Residues that are strongly bound to the matrix in surface water, soils or sediments and that are considered to have low remobilization rates. Unless there are indications from the available literature or monitoring data regarding their potential remobilization, strongly bound residues may be regarded as irreversibly bound.
- **NER Type III:** NER Type III are incorporated into biomass and result from the anabolic formation of NER. Type III are considered to be of no concern.

Semi-feld verification of NER for PFOS and PFOA

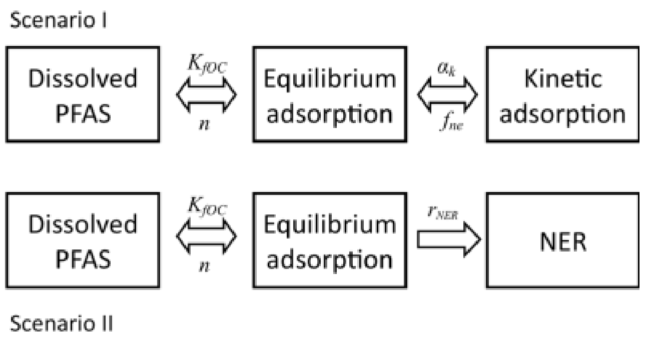
Environmental Science and Pollution Research (2021) 28:2097–2107
https://doi.org/10.1007/s11356-020-10594-6

RESEARCH ARTICLE

Combined leaching and plant uptake simulations of PFOA and PFOS under field conditions

Matthias Gassmann[1] · Eva Weidemann[1] · Thorsten Stahl[2]

- Leaching and plant uptake of PFOS and PFOA were measured for more than a decade in an outdoor lysimeter study
- Study results were compared with model calculations using the EFSA developed FOCUS model MACRO.
- Markedly higher leaching was modelled compared to monitoring data
- Only when including a formation rate of NER, data from model and lysimeter could be aligned.
- K-NER:
  - PFOS: Range 0.0011-00.0016; median 0.0013 d-1
  - PFOA: Range 0.0030-0.0066; median of 0.0047 d-1



NER Pool

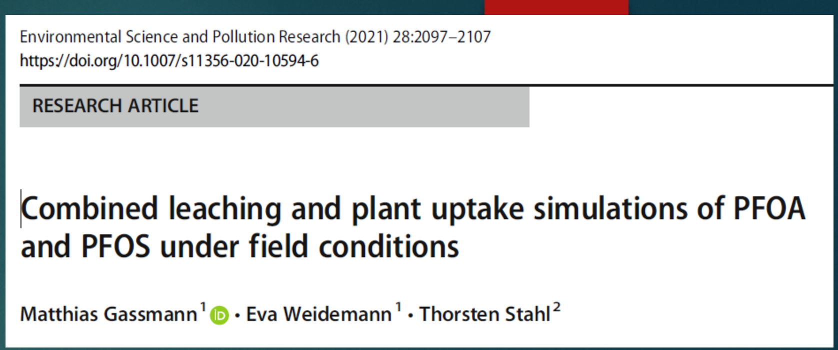

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TABLE 3.1. Simulated and sampled substance balance of PFOA and PFOS from 2007 to 2015. Table re-printed from Gassmann et al. (2021).[6]

	Mass (g/m2)		% of applied	
	PFOA	PFOS	PFOA	PFOS
Leaching mass simulated	4.9–25.5	1.2–3.5	1.4–7.1	0.3–1.0
Leaching mass sampled	13.9	2.7	3.9	0.7
Plant uptake simulated	0.002–0.005	0.016–0.026	0.0006–0.0013	0.004–0.007
Plant uptake sampled	0.005	0.020	0.0013	0.005
Left in Soil (simulated)	334.5–355.1	363.9–366.2	92.9–98.6	99.0–99.7
NER pool	341.8–351.3	335.5–355.3	95.0–97.6	91.3–96.7
Reversible sorption pool	0.0–3.8	8.7–30.7	0.0–1.1	2.4–8.4

From soil to sludge

$$Csoil - ss = Csoil(0)\ x\ \frac{1}{1-Facc}$$

$$Csoil(0) = Csoil(ss)\ x\ (1 - Facc)$$

$$Csoil(0) = \frac{Csludge\ x\ APPLsludge}{DEPTHsoil\ x\ RHOsoil(dw)}$$

$$Csludge = \frac{Csoil(0)\ x\ DEPTHsoil\ x\ RHOsoil(dw)}{APPLsludge}$$

Theoretical max sludge load according to regulation: 7t/ha/yr

Mean sludge load in Denmark due to P regulation: 1.03 t/ha/y

Protection goal: Ecosystems in soils and fresh water

- PFAS is not very toxic to soil dwelling species. ETC is established at 2.0 µg PFOA/kg and 16.0 µg PFOS/kg
- Predicted max Csludge:
  - 134 µg PFOA/kg
  - 110 µg PFOS/kg

No NER; 7.0 t/ha/y

- FW: Assuming a dilution of pore water by 3
- Assuming median NER and Koc and sludge load of 7 t/ha/y
- Predicted max Csludge:
  - 25.8 µg PFOS/kg

Protection goal: Ground water

- PFAS in Pore water = PFAS in Ground water
- Calculations complicated by the fact that the ETCgw is the sum of four PFAS with different chemical-physical properties and hence different leaching potential
- NER has not been identified for PFNA and PFHxS:
  - kNER PFOA = kNER PFHxS = 0.0047 d-1
  - kNER PFOS = kNER PFNA = 0.0013 d-1
- The ETCgw is equally split up, 4 x 0.5 ng/L
- Reverse calculations are made for each of the four PFAS

$\sum C_{max} \approx 65$ µg/kg

TABLE 6.1b. As for Table 6.1a, but with a sludge load (APPLsludge) of 0.103 kg/m^2/y (1.03 t/ha/y).

k_{NER} = Median	PFOA	PFOS	PFNA	PFHxS
C_{sludge} [µg/kg]	**5.07**	**44.9**	**9.43**	**5.19**

Protection goal: Ground water

TABLE 6.1c. As for Table 6.1a and 6.1b, i.e. $APPL_{sludge}$ = 0.103 kg/m²/y (1.03 t/ha/y), but with different input of k_{NER}.

Steady state situation	PFOA	PFOS	PFNA	PFHxS
k_{NER} = minimum	0.0030	0.0011	0.0011	0.0030
C_{sludge} [µg/kg]	**4.40**	**39.5**	**8.38**	**4.36**
k_{NER} = 75% of Min.	0.00225	0.000825	0.000825	0.00225
C_{sludge} [µg/kg]	**3.84**	**31.5**	**6.80**	**3.81**
k_{NER} = 50% of Min.	0.0015	0.00055	0.00055	0.0015
C_{sludge} [µg/kg]	**3.10**	**22.5**	**5.05**	**3.07**
Measured C_{sludge} [µg/kg] (90th Percentile)	2.5	15	2.5	2.5

$\sum C_{max} \approx 35$ µg/kg

Model calculations

- Two models: FOCUS-PELMO + Simplified Box Model
- Input: approximately 90th percentile of PFAS in DK sludge and 7 t/ha/y
- Two soil types from DK (Karup (sand) and Langvad (Clay)
- Box Model: Median NER, simulation until (almost) steady state
- PELMO: No NER, Maximum 20 yr of simulation
- PELMO finds markedly higher leaching of PFOA and PFHxS
- Other shorter PFAS among PFAS22 has higher leaching potential
- Margin of safety (after 20 y) to ETCgw of 0.5 ng/L range from minimum 500 (PFOA) to 10E15 for PFOS.
- At realistic sludge load MoS are 7 times higher, i.e. at least 3500.

PELMO Model

PFAS	DT_{50}	Log K_{oc}	C_{PFAS} Median*	C_{PFAS} Input PELMO	PFAS Load**	C_{gw}	C_{gw}
	Years	kg/L	µg/kg dw	µg/kg dw	kg/ha	µg/L	ng/L
				$PFAS_4$			
PFOS	100	3.6	4,5	16	1.12E-04	1.58E-18	1.58E-15
PFOA	100	2.3	0.85	1.8	1.26E-05	1.04E-06	1.04E-03
PFNA	100	2.9	0.6	0.894	6.26E-06	1.03E-11	1.03E-08
PFHxS	100	2.31	0.19	3.91	2.74E-05	2.13E-06	2.13E-03
				Selected PFAS among the remaining $PFAS_{22}$			
(P)FOSA	100	4.36	0.85	1.73	1.21E-05	<1E-24	<1E-21
6.2 FTS	100	2.28	0.24	3.08	2.16E-05	2.55E-06	2.55E-03
PFBA	100	1.9	0.19	4.65	3.26E-05	1.87E-04	1.87E-01
PFP(e)A	100	1.38	0.24	1.7	1.19E-05	9.30E-04	9.30E-01
PFBS	100	1.8	0.19	3.9	2.73E-05	3.58E-04	3.58E-01
PFDA	100	4	2.4	4.3	3.01E-05	1.25E-24	1.25E-21
PFDoDA	100	4.77	0.85	1.6	1.12E-05	<1E-24	<1E-21

20 years simulation

Sludge load: 7t/ha/y

PFAS Conc: 90% P

Model calculations

- Two models: FOCUS-PELMO + Simplified Box Model
- Input: approximately 90th percentile of PFAS in DK sludge and 7 t/ha/y
- Two soil types from DK (Karup (sand) and Langvad (Clay)
- Box Model: Median NER, simulation until (almost) steady state
- PELMO: No NER, Maximum 20 yr of simulation
- PELMO finds markedly higher leaching of PFOA and PFHxS
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- Margin of safety (after 20 y) to ETCgw of 0.5 ng/L range from minimum 500 (PFOA) to 10E15 for PFOS.
- At realistic sludge load MoS are 7 times higher, i.e. at least 3500.

Box Model – No NER

PFAS	PFAS load	$logK_{oc}$	DT_{50}	$K_{removal}$	C_{gw} (Karup)	C_{gw} (Langvad)	Time to 95% of SS
	kg/ha/y	L/kg	Years	d^{-1}	ng/L	ng/L	Years
PFOS	1.12E-04	3.6	100	1.90E-05	14,7	13,2	200-500
PFOS	1.12E-04	3.6	10	1.90E-04	0,27	0,17	70-80
PFOS	1.12E-04	2.84	100	1.90E-05	61	49,8	200-500
PFOS	3.84E-05	3.6	100	1.90E-05	4,94	4,45	200-500
PFBS	2.73E-05	1.8	100	1.90E-05	66,8	55,4	200-500
PFHxS	2.74E-05	2.31	100	1.90E-05	35,6	28,0	200-500
(P)FOSA	1.21E-05	4.36	100	1.90E-05	0,099	0,067	500-1000
6.2 FTS	2.16E-05	2.28	100	1.90E-05	29,3	23,1	200-500
PFBA	3.26E-05	1.9	100	1.90E-05	72	58,9	200-500
PFP(e)A	1.19E-05	1.38	100	1.90E-05	39,3	34,8	200-500
PFOA	1.26E-05	2.3	100	1.90E-05	16,7	13,1	200-500
PFNA	6.26E-06	2.9	100	1.90E-05	3,07	2,53	200-500
PFDA	3.01E-05	4	100	1.90E-05	1,23	1,03	200-500
PFDoDA	1.12E-05	4.77	100	1.90E-05	0,007	0,004	500-1000

Box Model - NER

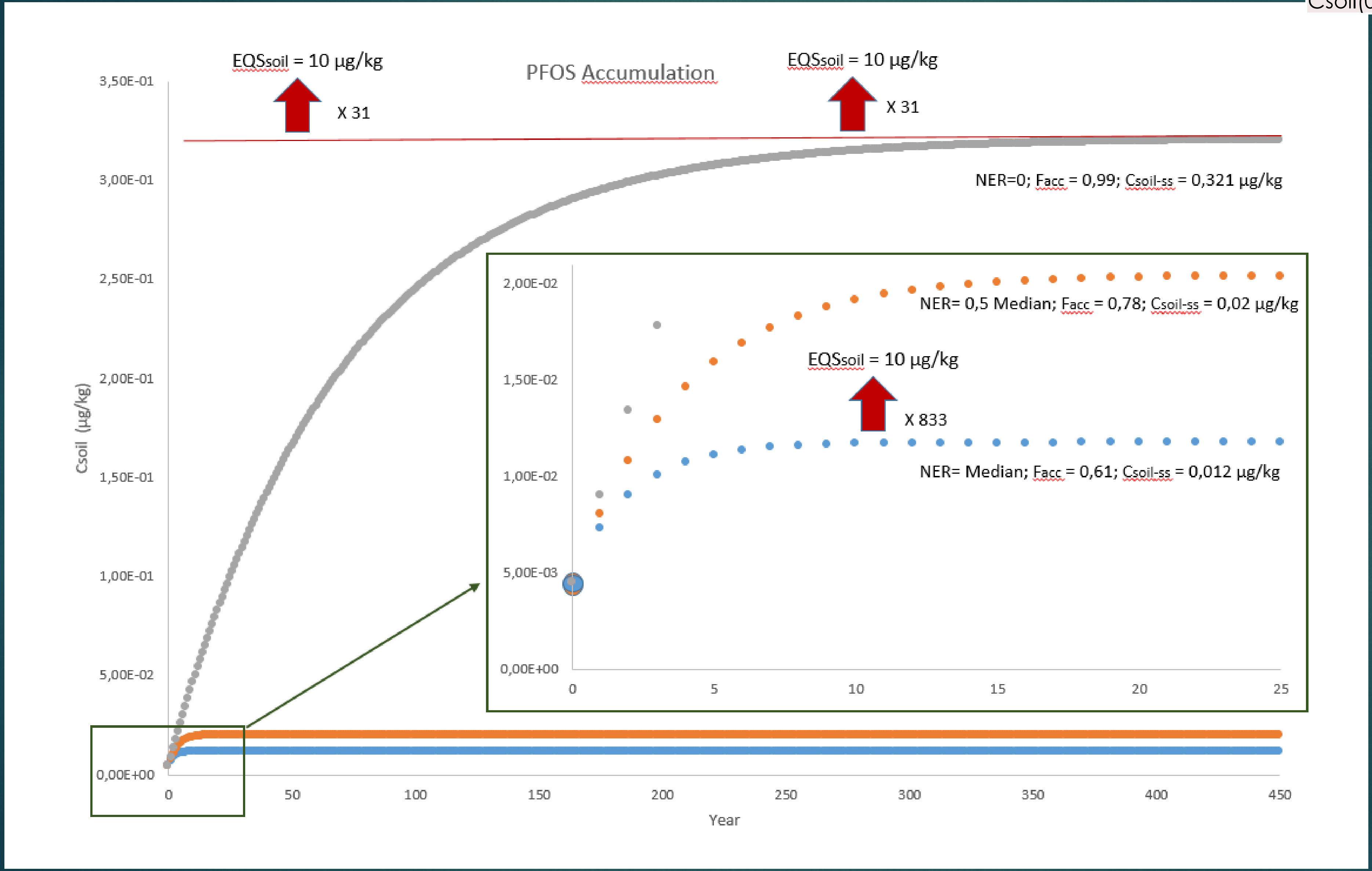
- Steady state reeached within 10-20 years using median NER
- Predicted Cgw is marked below 0.5 ng/L at steady state for all PFAS4 with the kNER reported

PFAS:		PFOS			PFNA			PFOA			PFHxS		
k_{NER} (d^{-1})		0.0011	0.0013	0.0016	0.0011	0.0013	0.0016	0.0030	0.0047	0.0066	0.0030	0.0047	0.0066
Karup	10 years	7,03E-04	4,42E-04	7,94E-05	7,97E-03	5,29E-03	3,01E-03	3,69E-02	1,06E-02	3,67E-03	7,62E-02	2,17E-02	7,51E-03
Karup	50 years	1,02E-03	5,57E-04	8,85E-05	9,32E-03	5,80E-03	3,13E-03	3,70E-02	1,06E-02	3,67E-03	7,62E-02	2,17E-02	7,51E-03
Karup	Steady	<20	<20	<20	<20	<20	<20	<10	<10	<10	<10	<10	<10
Langvad	10 years	3,05E-04	1,91E-04	3,40E-05	4,68E-03	3,05E-03	1,68E-03	2,56E-02	6,76E-03	2,24E-03	5,26E-02	1,38E-02	4,55E-03
Langvad	50 years	4,60E-04	2,46E-04	3,84E-05	5,74E-03	3,45E-03	1,78E-03	2,56E-02	6,76E-03	2,24E-03	5,26E-02	1,38E-02	4,55E-03
Langvad	Steady	<20	<20	<20	<20	<20	<20	<10	<10	<10	<10	<10	<10

Protection Goal: Human Helath

- Not feasible/possible to use reverse calculations in the food-web:
  - Sludge – soil - crop (animal feed) – husbandry (meat/milk) – humans
- When maximum levels in animal feed have been identified, the corresponding sludge concentrations can be calculated on the basis of known bioaccumlation factors from soil to plants
- Instead predicted long term steady state concentrations in sludge amneded soils can be compared to existing toxicological-based soil quality standard protecting humans, including soil ingesting children and peoples gardens and allotments

Csludge	15	µg/kg
APPLsludge	1	t/ha/yr
DEPTHsoil	0,2	m
RHOsoil (ww)	1700	kg/m3
Csoil(0)	4,54E-03	µg/kg



Accumulation in Long term study - CRUCIAL

Boring nr.	B101	B102			B103			B104	B105	B106	B107	B108	B109		Jordkvalitets-kriterium[1]
Dybde (m u.t.)	0,3	0,3	0,5	1,0	0,3	0,5	1,0	0,3	0,3	0,3	0,3	0,3	0,3	0,5	
Type af forsøgs-mark	Slam-be-hand-let.*	Slambehandlet			Slambehandlet-Acc.			Kontrol	Slambehandlet				Slambehandlet-Acc.		
	Værdier i µg/kg TS														
PFOS	0,59	2,6/2,1	0,74/0,26	-/-	3,8/4,1	-/0,33	-/0,18	-/0,11	0,92	1,24	1,76	2,44	3,9	3,6	i.f.
PFOA	-	1,1/1,1	-/0,15	0,06/0,08	1,7/1,9	-/0,23	-/0,10	-/0,09	-	0,72	0,74	1,06	1,3	1,4	i.f.
PFOSA	-	-/-	-/-	-/-	-/0,11	-/-	-/-	-/-	-	-	-	-	-	-	i.f.
PFPeA	-	0,53/0,64	-/-	-/-	0,91/0,81	-/0,13	-/-	-/-	-	-	-	0,66	0,62	0,87	i.f.
PFHxA	-	-/0,3	-/-	-/-	0,54/0,50	-/0,13	-/-	-/-	-	-	0,52	-	-	0,52	i.f.
PFHpA	-	-/0,32	-/-	-/-	0,55/0,53	-/0,12	-/-	-/-	-	-	-	-	-	-	i.f.
PFBA	-	-/ 0,28	-/-	-/-	-/0,30	-/-	-/-	-/-	-	-	-	-	-	0,60	i.f.
PFBS	-	-/-	-/-	-/-	-/0,16	-/0,11	-/-	-/-	-	-	-	-	-	-	i.f.
PFDA	-	0,53/0,46	-/-	-/-	1,1/1,1	-/-	-/-	-/-	-	-	-	0,55	0,79	0,71	i.f.
PFDoDA	-	-/0,12	-/-	-/-	-/0,38	-/-	-/-	-/-	-	-	-	-	-	-	i.f.
PFNA	-	-/0,20	-/-	-/-	-/0,50	-/-	-/-	-/-	-	-	-	-	-	-	i.f.
PFTrDA	-/	-/-	-/-	-/-	-/-	-/-	-/-	-/-	-	-	-	-	0,51	-	i.f.
PFUnDA	-	-/0,12	-/-	-/-	-/0,21	-/-	-/-	-/-	-	-	-	-	-	-	i.f.
Sum af 4 PFAS	0,59	3,6/3,3	0,74/0,41	0,06/0,08	5,5/6,5	-/0,56	-/0,28	-/0,2	0,92	2,0	2,5	3,5	5,3	5,0	10
Sum af 22 PFAS	0,59	4,7/5,5	0,74/0,41	0,06/0,08	8,6/11	-/1,1	-/0,28	-/0,2	0,92	2,0	2,5	4,7	7,2	7,7	400

B101: Stopped 2013

B102, 105-108: 75 y of max sludge load

B103, B109: >200 y of max sludge load

Historical PFAS concentrations >> todays concentrations

> 10 x Csoil-ss; All < ETCsoil og 10µg/kg

Ground water sampling - CRUCIAL

Tabel 5.2: Analyseresultater fra ALS/Eurofins for PFAS i vandprøver fra B101-B110 med fund over detektionsgrænsen. For de øvrige PFAS-forbindelser er der ikke konstateret fund over detektionsgrænsen.

Boring nr.		B107-1	**B107-2**	B108-1	**B108-2**	**B110-1**	Grund-vandskvali-tets-krite-rium[1]
Filtersætning (m u.t.)		12,0-14,0	5,5-6,5	12,0-14,0	4,5-5,5	10,0-12,0	
Type af forsøgsmark		Slambehandlet-høj dosering				Kontrol	
PFOS	ng/l	-	- / -	0,53	1,28 / 0,75	- / -	i.f.
PFOA	ng/l	-	0,38 / 0,40	0,35	1,41 / 1,40	- / -	i.f.
PFPeA	ng/l	-	- / -	-	0,67 / 0,88	- / -	i.f.
PFHxA	ng/l	-	- / -	-	0,68 / 0,62	- / -	i.f.
PFHpA	ng/l	-	- / -	-	0,54 / 0,52	- / -	i.f.
PFBA	ng/l	-	- / -	-	- / 0,71	- / -	i.f.
PFBS	ng/l	-	- / -	-	0,35 / -	- / -	i.f.
Sum af PFOA, PFOS, PFNA og PFHxS	ng/l	-	0,38 / 0,40	0,88	2,69 / 2,15	- / -	2
Sum af 22 PFAS	ng/l	-	0,38 / 0,40	0,88	4,93 / 4,88	- / -	100

Conclusions

- Relativ large margin between calculated cut-off values in sludge and the concentration levels found today
- Large margin between model out-puts and environmental threshold concentrations using input corresponding the maximum PFAS loads in Denmark
- However, large uncertainty with ragard to key paramters like Koc and kNER, significantly influencing the results. This hampers the process of establishing an absolut maximum concentration in sludge
- As a pragmatic approach a cut-off concentration of 15 µg PFAS4/kg dw has insted been suggested as a starting point for setting regulatory cut-off concentrations in Denmark

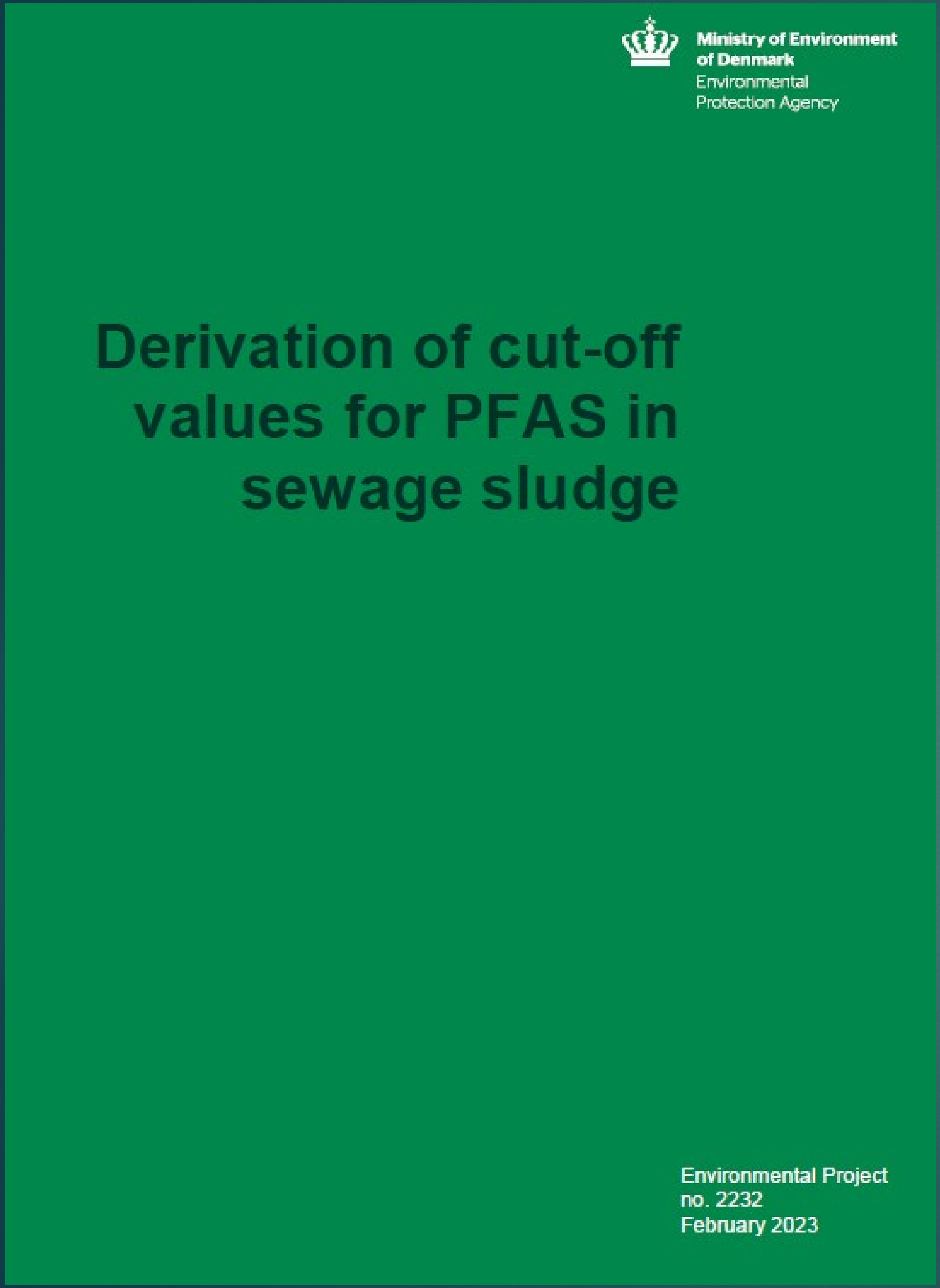
Conclusions

- Under the assumption of normal sludge application rates and median Koc and kNER, is observed that:

- 15 µg $PFAS_4$/kg minimum is a factor of 10 below the predicted maximum concentration in sludge that protects soil dwelling species, soil processes and the terrestrial ecosystem.
- 15 µg $PFAS_4$/kg is markedly below the predicted maximum concentration in sludge protecting groundwater by being in compliance with the ETC_{gw} of 2 ng/L.
- 15 µg $PFAS_4$/kg will as input in the FOCUS model PELMO result in predicted groundwater concentrations several orders of magnitude below the ETC_{gw} of 2 ng/L.
- 15 µg $PFAS_4$/kg is minimum a factor of 10 below the maximum concentration of PFOS in sludge predicted to protect freshwater recipients by being in compliance with the ETC_{fw} of 0.00065 µg/L.
- 15 µg $PFAS_4$/kg in sludge is predicted to result in long-term concentrations in soil pore water below the existing ETC_{fw} of 0.00065 µg/L.
- 15 µg $PFAS_4$/kg in sewage sludge will result in long-term soil concentrations at the steady state situation being at least a factor of 10 below the existing soil quality criteria for $PFAS_4$ of 0.01 mg/kg.

Conclusions

- PFAS is a hazardous group of substances, but yet regulation should be based upon risk assessment approaches
- Data indicate that the majority of sludge production does not pose a risk to environment or human health
- A stronger focus and regulation of PFAS in society will most likely lead to future lower levels of PFAS in sludge
- A potential elimination/reduction on agricultural use of sludge must be compared to the benefit/risk of alternative fertilisers
- The potential extra cost in handling sewage sludge via e.g. incineration should be compared to the impact if used elsewhere for PFAS remediation


Ministry of Environment of Denmark
Environmental Protection Agency

Derivation of cut-off values for PFAS in sewage sludge

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