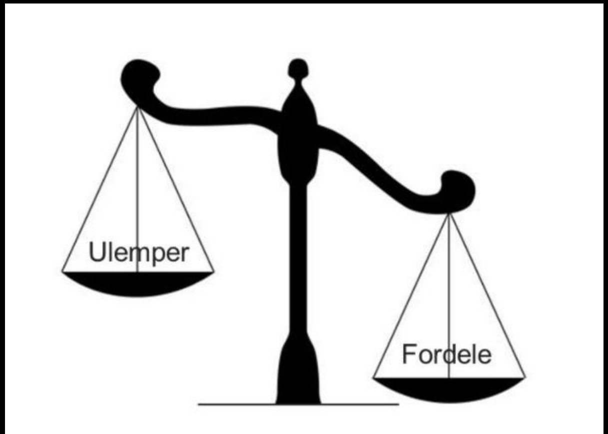
PFAS i Spildevandsslam



En uønsket stofgruppe i en værdifuld resource

Hvordan vægter man fordele og ulemper?

John Jensen, AU

Vi har været her før

EU er ikke bekymret

The EFSA Journal (2005) 284, 1 - 137

OPINION OF THE SCIENTIFIC PANEL ON CONTAMINANTS IN THE FOOD CHAIN ON A REQUEST FROM THE COMMISSION RELATED TO THE PRESENCE OF NON DIOXIN-LIKE POLYCHLORINATED BIPHENYLS (PCB) IN FEED AND FOOD

(Question N° EFSA-Q-2003-114)

Adopted on 8 November 2005

EU rapport på 262 sider om tilstedeværelsen af PCB i fødevarer.

Spildevandsslam er ikke nævnt én eneste gang

EU er ikke bekymret

The Joint Research Centre under den Euro-pæiske Kommission konkluderede i 2001 at:

"OCs [organic contaminants] in sludge are not expected to pose major health problems to the human population when sludge is re-used for agricultural purposes". Samt;

›"...it does not make much sense to include PCDD/Fs, PCBs and PAHs in routine monitoring programmes, but occasionally it may be motivated with respect to the origin of the sludge.".

(Erhardt & Prüeß 2001)

Lad mig slå fast:

- Jeg anser mange stoffer fra gruppen af PFAS som stærkt problematiske qua deres stabilitet i miljøet og deres dokumenteret potentiale for skader på mennesker og pattedyr i den øverste del af fødekæden
- Den igangsatte udfasning af mange PFAS bør fortsætte
- Jeg er stor fortaler for at forurenede grunde bliver bedre kortlagt generelt (V1>V2) og specifikt for PFOS/PFAS
- Spildevandsslam bør generelt kun recirkuleres/bruges i det omfang det ikke udgør en uacceptabel **risiko** for mennesker, dyr og planter
- Alt kommer med en pris – også en restriktion (forbud) i anvendelsen af spildevandslam

Definition af uacceptabel bør ideelt set være risikobaseret og langtidssikret

Slam kvalitetskrav for PFAS…….

- …bør sikre, at der ikke sker irreversible skader på jordbundsdyr og planter (jordkvalitet)
- …bør sikre, at der ikke sker nedsivning til grundvand i uacceptable mængder
- …bør sikre, at der ikke sker overflade- eller drænafstrømning til recipienter i uacceptable mængder
- …bør sikre, at der ikke sker optag i foderafgrøder, som kan afstedkomme ophobning i animalske fødevare i uacceptable mængder

- …burde ikke tage hensyn til scenarier, som indebærer muligheden for direkte indtag af jordpartikler spist af husdyr eller mennesker (børn)
- …burde ikke tage hensyn til scenarier som indebærer muligheden for optag i grøntsager og andre vegetabilske fødevare

PFAS i slam


Miljøministeriet
Miljøstyrelsen

Risikoevaluering af fem miljøfremmede stofgrupper i spildevandsslam udbragt på landbrugsjord

Miljøprojekt nr. 1405 2012

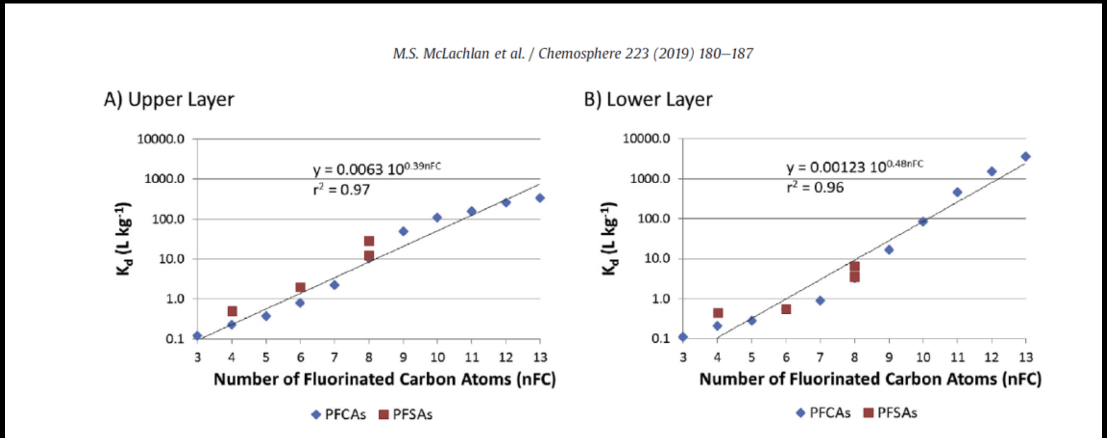
- Midlertidige krav fastsat på baggrund af JKK
- Nye krav bør (modsat PCB) blive risikobaseret
- Slam bør ikke fjerne fokus fra hovedproblemet = PFAS fra forurenede grund som f.eks. Brandøvelsespladser og flyvestationer

PFOS og andre polyfluorerede stoffer er dog meget svært nedbrydelige i jordmiljøet, og den beregnede koncentration i markjorden efter gentagne Slambehandlinger* ligger derfor en faktor 33 under den koncentration, der på baggrund af den eksisterende viden kan anses for at være sikker for planter og jordbundsdyr. Denne sikkerhedsmargin er marginalt lavere end den faktor på 50, som EU anbefaler i risikovurderingen af kemikalier under REACH programmet.

* International worst case

Environmental fate

- C-F bindingen er nærmest unedbrydelig af mikroorgansimer
- Adsorption til jord af PFAS er possitivt korreleret til kulstofkædens længde
- Primære adsorptionsmateriale er OC
- Kd værdier fra 15.8 to 47.1 L/kg i tre jordtyper (Beach et al. 2006)
- Dissipation skyldes stort set ikke nedbrydning, men NER og/eller leaching



Kd målt i lysimeter (PFOS-29; PFOA-2.2)

Fate:Non-Extractable Residues (NER)

- Stahl et al 2013: Aqueous solutions of PFOA and PFOS applied to 25 mg/kg soil in four lysimeter soil plots. After 5 years, 96.88% of the PFOA and 99.98% of the PFOS originally applied to the soil were still in the lysimeter. These values were obtained by subtracting the rounded off amounts lost to plant uptake (PFOA, 0.001%; PFOS, 0.004%) and to leachate (PFOA, 3.12%; PFOS, 0.013%)

Table 2 Simulated and sampled substance balance of PFOA und PFOS from 2007 to 2015 (scenario II)

	mass (g/m^2)		% 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

Gosmann et al 2021

Environmental fate

Mclachlan: Five different PFAS contamination levels: background concentrations (unspiked), 0.1 mg/kg, 1 mg/kg, 5 mg/kg, and 10 mg/kg of each PFAS; Stahl: 25 mg/kg

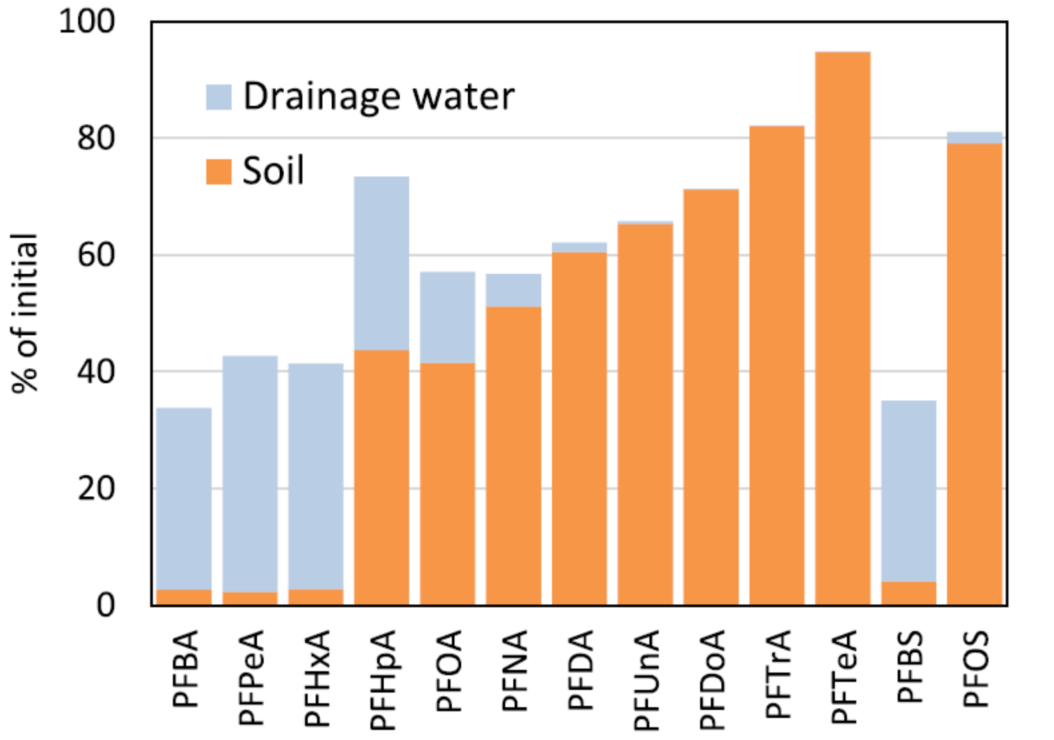


Fig. 2. Quantity of PFAA in soil at harvest and in the accumulated leachate for the level 1 lysimeter planted with lettuce. The results are expressed as a percentage of the initial quantity of PFAA in the lysimeter.

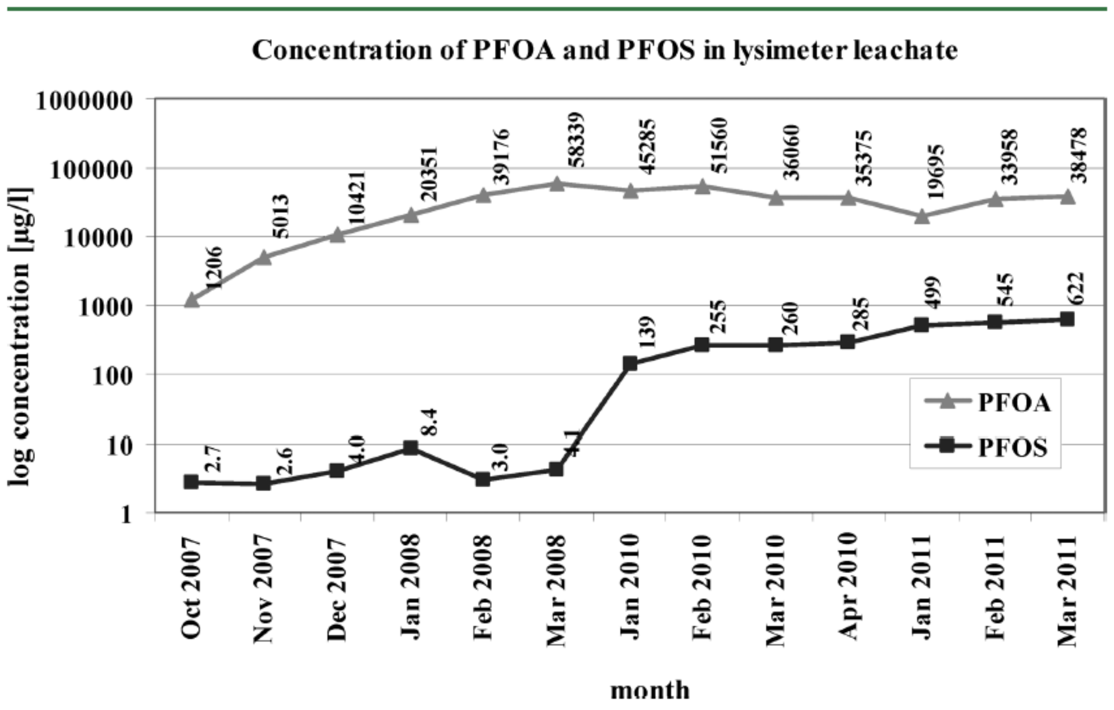


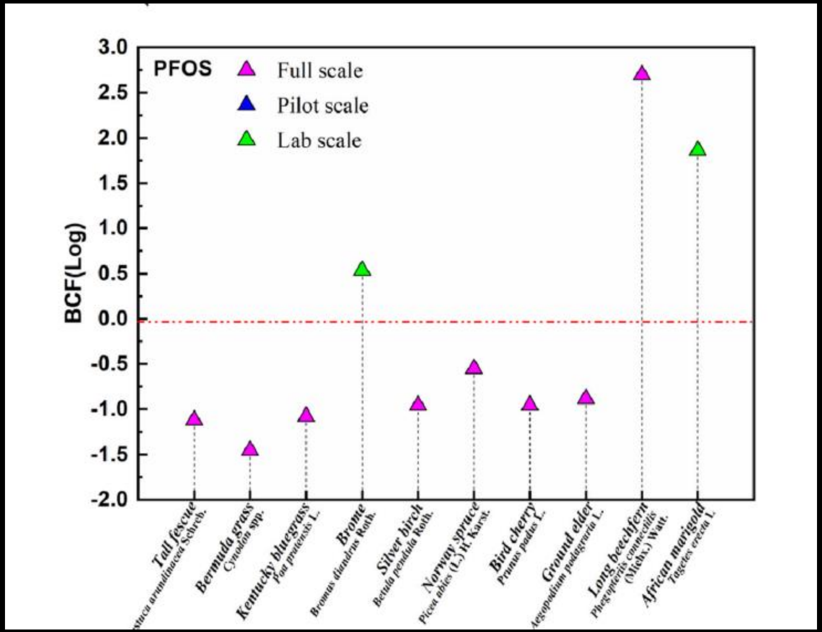
Figure 5. Concentrations of PFOA and PFOS in lysimeter leachate 2007–2011.

McLachlan et al 2019

Stahl et al 2013

Plant uptake

Environmental Science and Pollution Research (2021) 28:30459–30470
https://doi.org/10.1007/s11356-021-14069-0



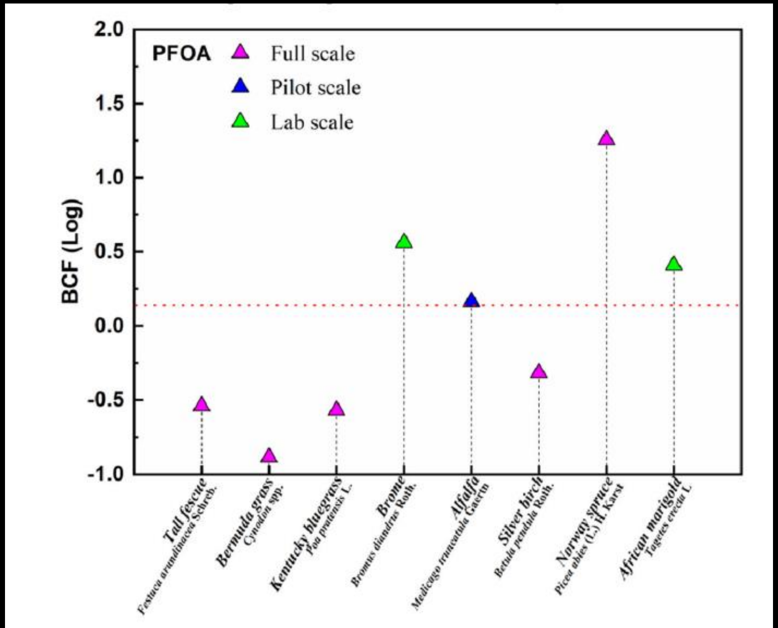
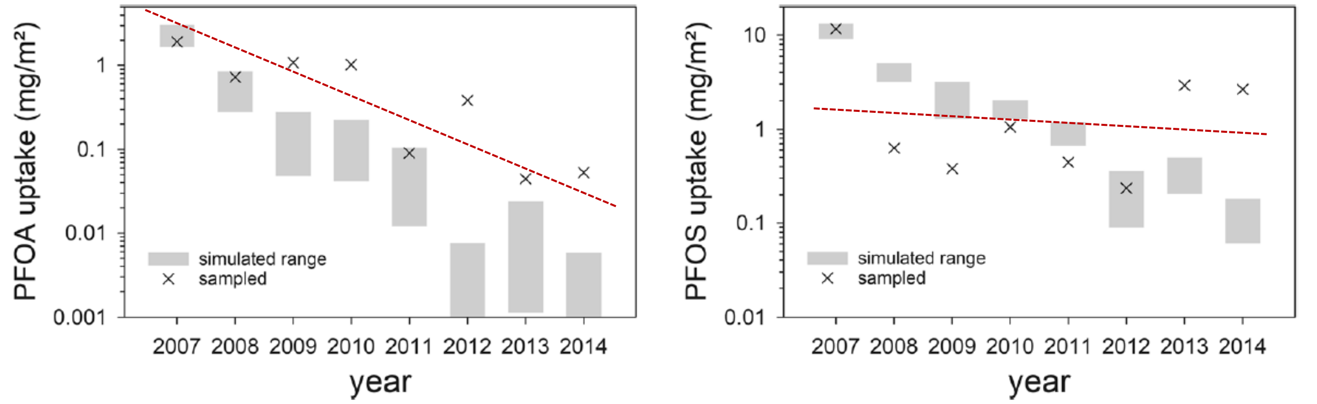


Fig. 2 Comparison of terrestrial plant BCF(Log) values based on a calculated average line (data from Table 2)

Fig. 3 Simulated and observed plant uptake of PFOA and PFOS (scenario II)



Plant Uptake

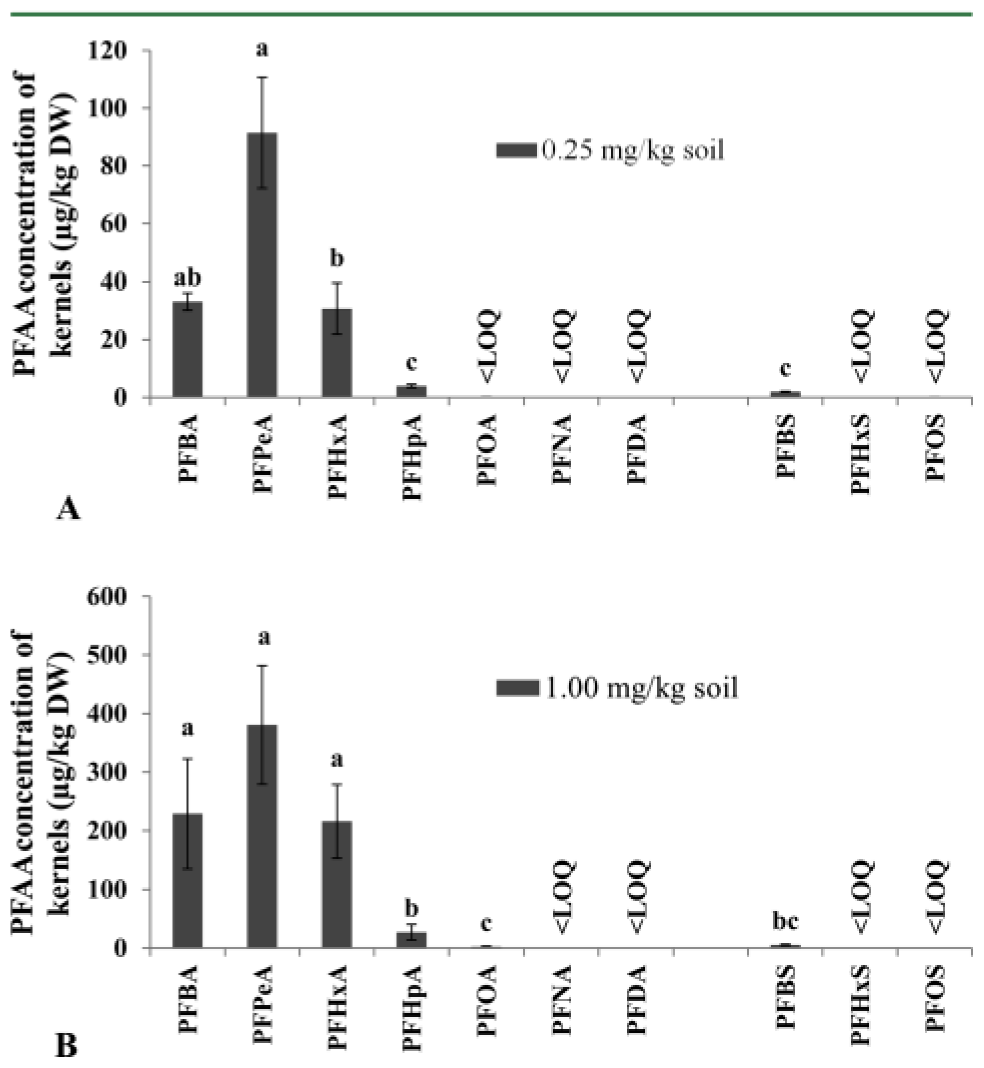


Figure 2. PFCA and PFSA concentrations of maize kernels. PFCA and

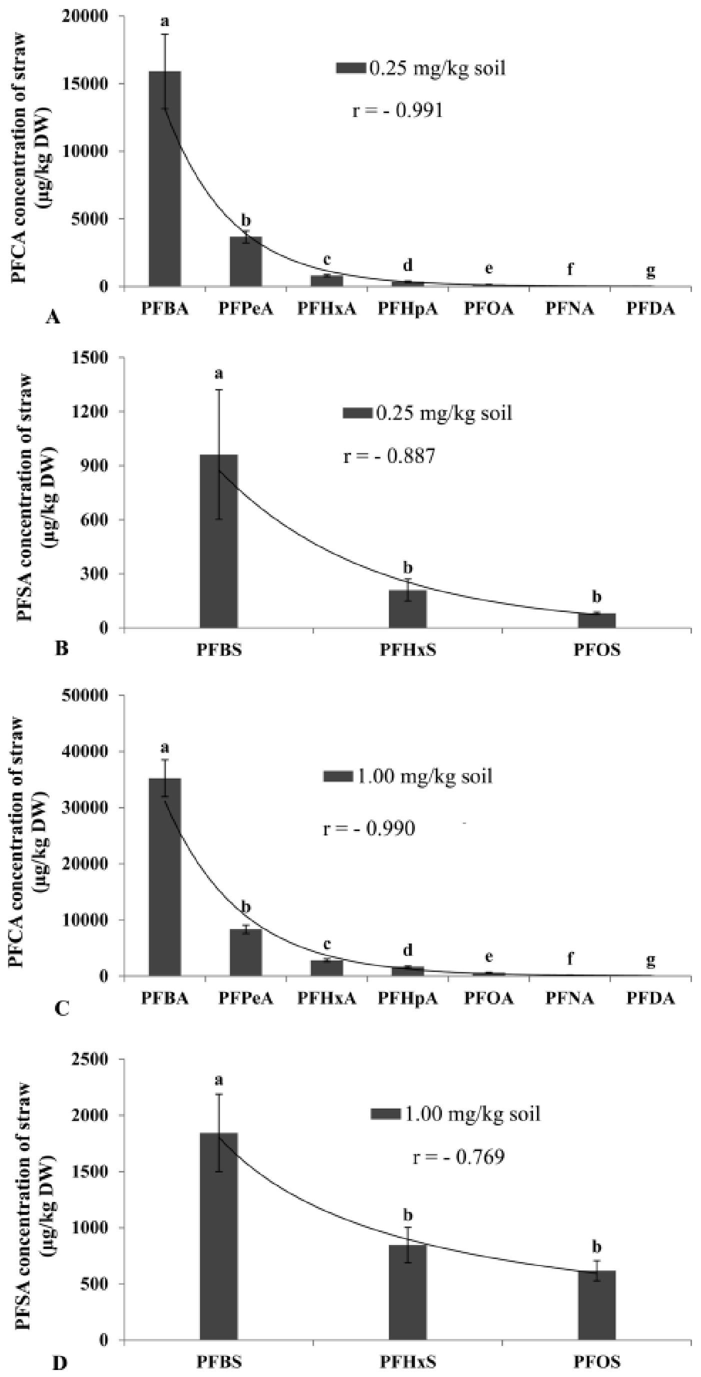


Figure 1. PFCA and PFSA concentrations of maize straw. PFCA (A)

Bioconcentration / soil-plant transfer

$$TF_{straw} = \frac{\text{PFAA concentration in straw (mg/kg dry weight)}}{\text{PFAA concentration in soil (mg/kg dry weight)}} \quad (1)$$

$$TF_{kernels} = \frac{\text{PFAA concentration in kernels (mg/kg dry weight)}}{\text{PFAA concentration in soil (mg/kg dry weight)}} \quad (2)$$

Journal of Agricultural and Food Chemistry

Table 2. Transfer Factors of PFCAs and PFSAs in Maize Straw[a]

treatment	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFBS	PFHxS	PFOS
0.25 mg/kg	63.64 a	14.68 a	3.19 a	1.41 a	0.56 a	0.12 a	0.03 a	3.85 a	0.84 a	0.32 a
1.00 mg/kg	35.23 b	8.33 b	2.82 a	1.67 a	0.65 a	0.16 a	0.04 a	1.84 a	0.85 a	0.62 b
transfer ratio*	0.55	0.57	0.88	1.18	1.16	1.33	1.33	0.48	1.01	1.94

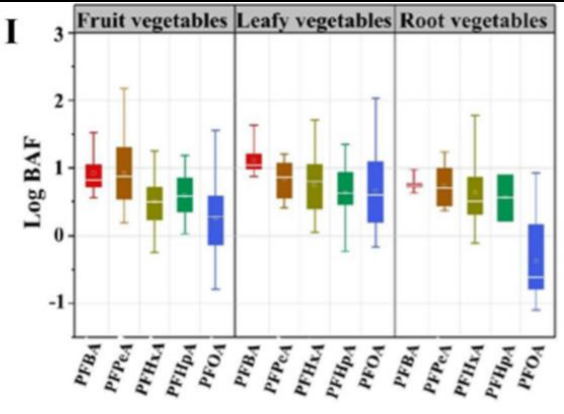
[a]Transfer factors for PFAAs in maize straw after spiking the soil with 0.25 mg and 1.00 mg of the individual substances/kg soil. Comparison of means (*t* test), $p \leq 0.05$; mean value ($n = 4$). Letters (a, b) indicate significant differences between transfer factors after spiking with two different concentrations. *The relationship of the transfer factors of PFAAs after spiking with 1.00 mg and transfer factors after spiking with 0.25 mg are represented (transfer ratio = PFAA concentration$_{1.00mg}$/PFAA concentration$_{0.25mg}$); LOQ = limit of quantification (1 μg/kg).

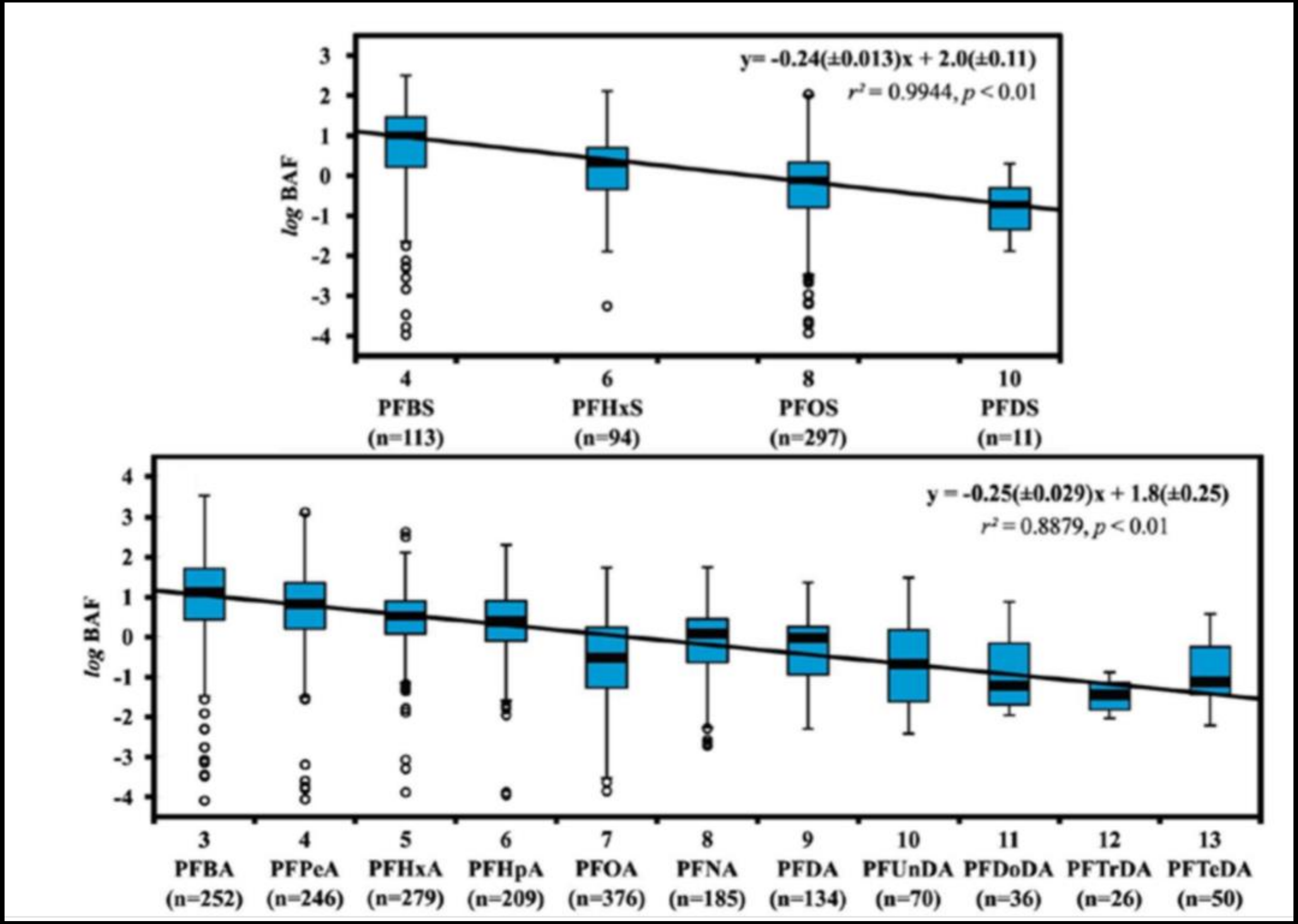
Table 3. Transfer Factors of PFCAs and PFSAs in Maize Kernels[a]

treatment	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFOA	PFBS	PFHxS	PFOS
0.25 mg/kg	0.133 a	0.366 a	0.123 a	0.016 a	<LOQ	<LOQ	<LOQ	0.008 a	<LOQ	<LOQ
1.00 mg/kg	0.229 a	0.380 a	0.216 a	0.027 a	0.002	<LOQ	<LOQ	0.005 a	<LOQ	<LOQ
transfer ratio*	1.72	1.04	1.76	1.69				0.63		

Plant uptake

Log BCF/BAF > 3 = Potentielt kritisk





Many highly polluted soils
Effluents etc.

Environment International 158 (2022) 106891

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

ELSEVIER

Exposure routes, bioaccumulation and toxic effects of per- and polyfluoroalkyl substances (PFASs) on plants: A critical review

Jiuyi Li [a], Jing Sun [a], Pengyang Li [a,b,*]

Bioaccumuation earthworms

Table S2.- Concentrations (ng/g d.w.) of PFASs and HFRs in the four biosolids selected (n=3; mean ± SD) for MS-3 experiment.

	W-1	W-2	W-3	W-4
PFBS	N.D.	N.D.	N.D.	2.05 ± 0.36
PFOS	14.6 ± 5.25*	28.2 ± 2.19*	64.4 ± 7.87*	0.65 ± 0.30*
PFDS	N.D.	N.D.	N.D.	N.D.
PFBA	N.D.	34.3 ± 10.2	N.D.	5.74 ± 0.89
PFPeA	2.03 ± 0.70	2.11 ± 0.11	3.35 ± 1.11	2.29 ± 0.41
PFHxA	0.92 ± 0.65*	4.77 ± 0.37*	5.34 ± 0.25*	1.78 ± 0.32*
PFHpA	0.64 ± 0.12*	0.85 ± 0.14*	1.44 ± 0.33*	0.80 ± 0.04*
PFOA	3.65 ± 0.35*	8.90 ± 0.13*	9.37 ± 0.19*	2.52 ± 0.24*
PFNA	0.55 ± 0.02*	2.58 ± 1.03*	1.25 ± 0.27*	0.73 ± 0.21*
PFDA	3.46 ± 0.67*	19.0 ± 0.61*	7.55 ± 0.62*	0.64 ± 0.02*
PFUdA	0.58 ± 0.05*	2.57 ± 0.37*	0.99 ± 0.17*	0.17 ± 0.05*
PFDoA	0.66 ± 0.12	2.20 ± 0.53*	0.92 ± 0.37	0.17 ± 0.08*
PFTrDA	0.21 ± 0.08	1.22 ± 0.37	N.D.	N.D.
PFTeDA	N.D.	5.97 ± 3.90	2.20 ± 0.11	N.D.
PFHxDA	N.D.	4.74 ± 2.94	N.D.	N.D.
PFODA	N.D.	2.64 ± 1.89	N.D.	N.D.
Σ PFASs	27.31 ± 5.41*	120.02 ± 15.86*	96.82 ± 8.66*	17.55 ± 1.11*

Environmental Research 149 (2016) 32–39

Contents lists available at ScienceDirect

ELSEVIER

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Bioaccumulation of emerging organic compounds (perfluoroalkyl substances and halogenated flame retardants) by earthworm in biosolid amended soils

CrossMark

Irene Navarro[a,*], Adrián de la Torre[a], Paloma Sanz[a], Javier Pro[b], Gregoria Carbonell[b], María de los Ángeles Martínez[a]

[a] Persistent Organic Pollutants Group. Department of Environment, CIEMAT, Avda. Complutense 40, 28040 Madrid, Spain
[b] Laboratory for Ecotoxicology. Department of the Environment, INIA, Crta. La Coruña km 7.5, 28040 Madrid, Spain

Bioaccumulation earthworms

BCF/BAF > 1000 = Potentielt kritisk

ng/g	PFBS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	Σ PFASs
Control													
Soil t=0	N.D.	N.D.	N.D.	0.22	N.D.	0.52	0.19	0.04	N.D.	N.D.	N.D.	N.D.	0.97
Soil t=final	N.D.	0.16	N.D.	N.D.	0.05	N.D.	0.17	0.17	0.03	0.02	N.D.	N.D.	0.59
Earthworm	N.D.	1.33	N.D.	N.D.	N.D.	N.D.	0.43	N.D.	N.D.	N.D.	N.D.	N.D.	1.76
BAF	---	8.55	---	---	---	---	2.39	---	---	---	---	---	2.25
Treatment-1													
Soil t=0	N.D.	0.38	N.D.	N.D.	N.D.	0.47	0.41	0.15	N.D.	0.05	N.D.	N.D.	1.47
Soil t=final	0.17	0.31	0.22	N.D.	0.10	0.06	0.32	0.27	0.03	0.05	N.D.	N.D.	1.54
Earthworm	N.D.	10.6	N.D.	N.D.	N.D.	N.D.	0.43	1.89	1.68	8.54	4.74	9.86	37.71
BAF	---	30.3	---	---	---	---	1.17	8.95	50.5	171	---	---	25.07
Treatment-2													
Soil t=0	N.D.	0.55	0.13	0.05	0.06	0.11	0.27	0.21	0.04	N.D.	N.D.	N.D.	1.42
Soil t=final	N.D.	0.65	0.31	0.21	0.35	0.09	1.42	0.47	0.06	0.06	N.D.	N.D.	3.63
Earthworm	N.D.	16.8	N.D.	N.D.	N.D.	N.D.	2.44	7.92	6.46	26.0	17.8	22.5	99.86
BAF	---	28.1	---	---	---	---	2.89	23.3	123	402	---	---	39.56
Treatment-3													
Soil t=0	N.D.	0.55	0.82	0.15	N.D.	0.27	0.21	0.06	0.06	0.04	N.D.	N.D.	2.16
Soil t=final	0.14	0.61	N.D.	N.D.	0.08	0.06	0.33	0.21	0.06	0.03	N.D.	N.D.	1.49
Earthworm	N.D.	14.5	N.D.	N.D.	N.D.	N.D.	N.D.	0.63	N.D.	2.93	N.D.	3.82	21.84
BAF	---	24.9	---	---	---	---	---	4.76	---	82.9	---	---	11.97
Treatment-4													
Soil t=0	N.D.	0.32	0.90	0.11	N.D.	0.41	0.23	0.06	N.D.	N.D.	N.D.	N.D.	2.04
Soil t=final	0.19	0.21	N.D.	0.08	0.09	0.04	0.22	0.14	0.01	0.02	N.D.	N.D.	0.99
Earthworm	N.D.	2.85	N.D.	N.D.	N.D.	N.D.	N.D.	0.93	N.D.	2.46	1.34	2.29	9.88
BAF	---	10.7	---	---	---	---	---	9.21	---	138	---	---	6.53

Bioaccumulation Earthworms

Chemosphere 118 (2015) 361–366

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

ELSEVIER

Bioavailability of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in biosolids-amended soils to earthworms (*Eisenia fetida*)

Bei Wen[a,*], Hongna Zhang[a], Longfei Li[a], Xiaoyu Hu[b], Yu Liu[a], Xiao-quan Shan[a], Shuzhen Zhang[a]

- Bioavailability of PFOS and PFOA by earthworm in biosolids-amended soils was studied.
- The bioaccumulation factors (BAFs) of PFOS and PFOA ranged 1.54–4.12 and 0.52–1.34, respectively.
- The BAFs decreased with increasing concentrations of PFOS and PFOA in soils.
- The exposure concentrations of PFOS and PFOA, and organic matter (OM) contents in soils explained 87.2% and 91.3% of the variation in bioavailable PFOS and PFOA, respectively.
- Soil pH and clay contents played relatively unimportant role in PFOS and PFOA bioavailability.

Rå risikobetragtninger

PFOS	Scenarios	Scenario	APPL-sludge	APPL-sludge	Csludge	DEPTHsoil	RHOsoil	PEC soil
			ton/ha/y	kg/m2/y	mg/kg	m	kg/m3	mg/kg
	10% P	Median sludge load	10,00	1,00	0,4	0,2	1500	0,001333
					Slam-max			

$$PECsoil = \frac{Csludge \times APPLsludge}{Depth \times Density}$$

Where

Csludge=	Concentration in dry sewage sludge	[mg kg^{-1}]
APPLsludge=	Dry sludge application rate	[kg.m^{-2} y^{-1}]
Depth=	Mixing depth of soil	[m]
Density=	Bulk density of soil	[kg m^{-3}]
PECsoil=	Concentration in soil due to sludge in first year at t=0	[mg kg^{-1}]

RQ=PEC/PNEC

PNEC = Jensen 2012

PEC	NOEL	RQ	MoS
0,001333	1	0,001333333	750

PNEC = JKK MST 2021

PEC	PNEC	RQ	MoS
0,001333	0,4	0,003333333	300

OBS: Ikke baseret på opdateret viden > 2012!

Jordkvalitet - opmærksomhedspunkter

- Ingen langtidseffekter på (foder)afgrøder og andre planter
- Ingen langtidseffekter på jordlevende invertebrater
- Ingen langtidseffekter på mikroorganismer og jordbundsprocesser
- Ingen effekter på fugle og pattedyr, som spiser insekter, orme og frø
- Ingen uacceptabel ophobning i jorden

Åbne spørgsmål

- Hvordan sikrer man sig en opdateret og relevant slamregulering?
- Skal denne være risikobaseret kræver det opdateret jordkvalitetskriterier
- Hvordan balancerer man fordele og ulember (risk:benefit) ved udbringning af spildevandsslam
- Kræver man kombinerer bæredygtighedsprincipper, LCA og risikovurdereinger = sammneligner pærer og baner.
- En gennemsigtig og tværgående weight-of-evidence tilgang er nødvendig, som kræver en vægtning og skalering af de elementer som skal indgå.
- Hvordan styrer man risiko-kommunikation i en verden styret af irrationalitet og høj grad af kemofobi?
- Hvordan kombinerer man handlekraft med is i maven?

Risk:Benefit

- Hvordan balancerer man fordele og ulember (risk:benefit) ved udbringning af biosolids
- Risiko og fordele (LCA baseret) beregnes og præsenteres på forskellig måde, i forskellige måleenheder og fortolkes af forskelligt fagpersonale
- Et fravalg er slam som gødning er i udgangspunktet de facto et tilvalg af andre gødningstyper hvilket bør indgå i Risk:Benefit
- Hvordan vægtes potential risiko ved PFOS i slam med risiko af f.eks. Cadmium i handelsgødning

- Vi plæderer for et vidensbaseret og datastyret beslutningsstøttesystem, der transparent indrager risiko, bæredygtighed og økonomi
-