

SLUDGEFFECT: Enabling a circular economy for sludge through source control and thermal treatment methods

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SLUDGEFFECT: primary objective



Identify how thermal treatments can be optimized for removing hazardous substances in sludge and e-waste plastic for increasing recycling and sustainability



"Pyrolysis solves the issue with organic contaminants in sewage sludge"¹

Boiling points deciding factor \rightarrow volatilized or decomposed²

> Figure: Buss (2021) ACS Sust Chem. Eng. https://doi.org/10.1021/acssuschemeng.1c03651

Is this really true for PFAS and other persistent contaminants?

1) Buss (2021) ACS Sust Chem. Eng. https://doi.org/10.1021/acssuschemeng.1c03651

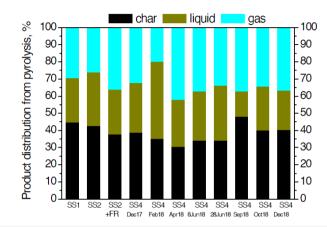
NG 2) Moško et al (2021) Chemos <u>https://doi.org/10.1016/j.chemosphere.2020.129082</u>

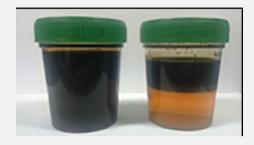
Variation in fertilizer from dry pyrolysis



Sludge biochar fertilizer (30-50%)

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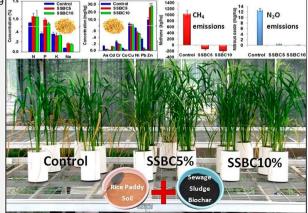


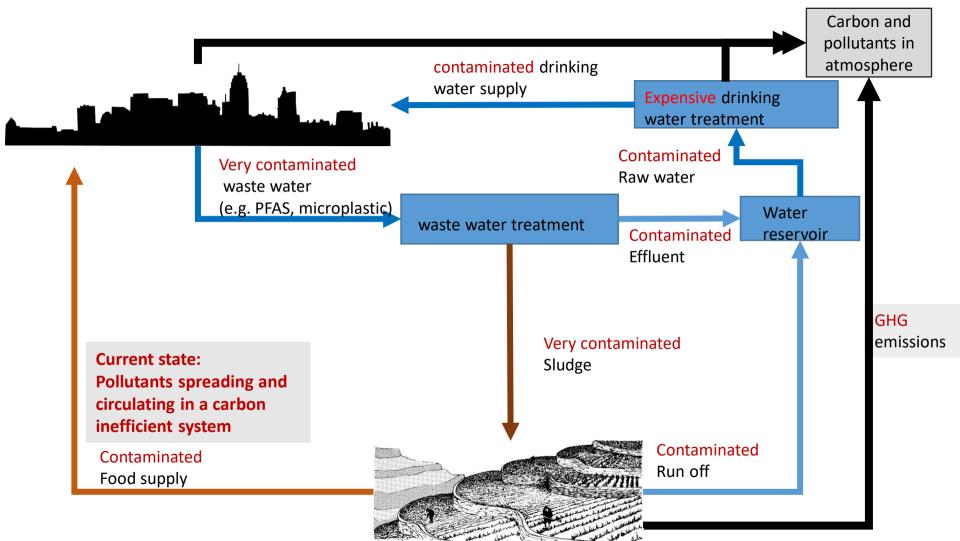


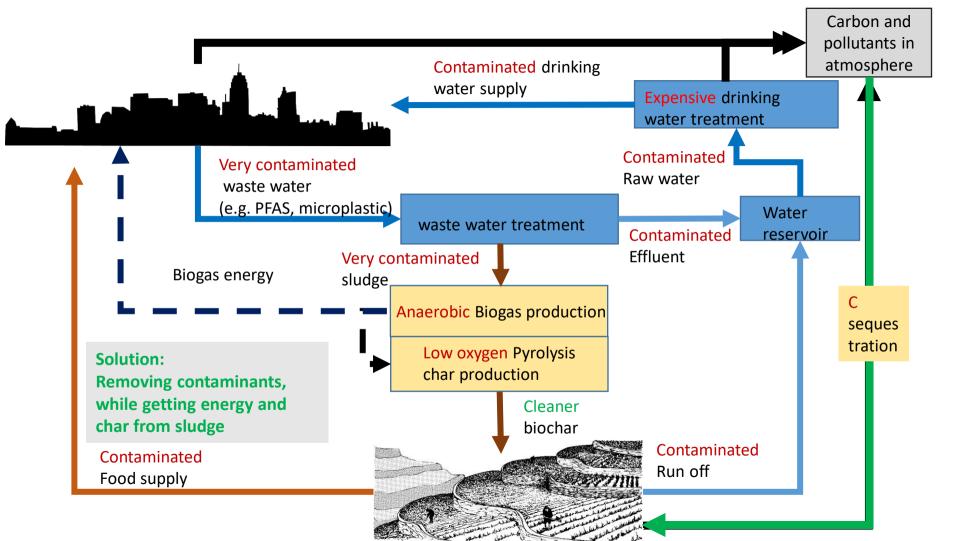
Pyrolysis condensates (complex) (20-40%), best for producing energy on-site, e.g. providing heat to pyrolyzer/co-incineration

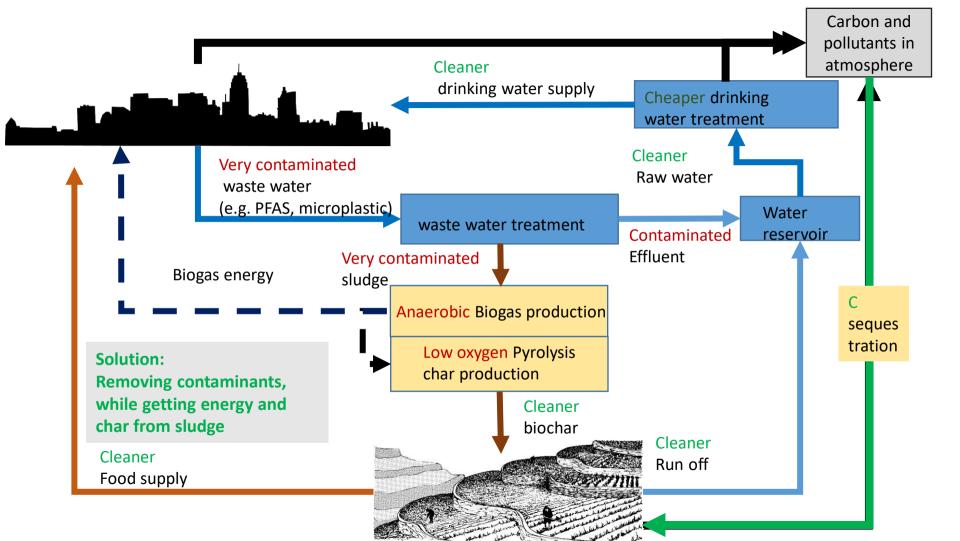
Kwapinska, M., Agar, D. A., Bonsall, B., & Leahy, J. J. (2020) Valorisation of Composted Organic Fines and Sewage Sludge Using

Bioavailable phosphorous – Phosphorous is retained. The best studies indicated a doubling in soil fertility from sludge to sludge chare, due to diverse properties (e.g. alkalinity, water retention) (e.g. Khan et al. ES&T 2012)

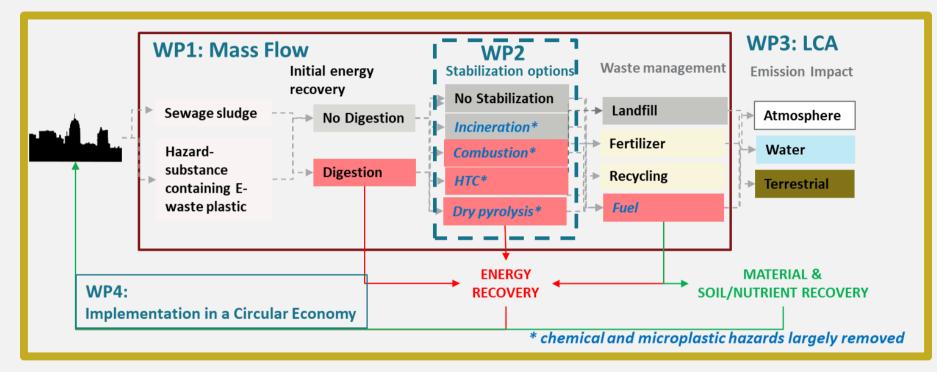








SLUDGEFFECT



Life cycle effects from removing hazardous substances in sludge and plastic through thermal treatment.

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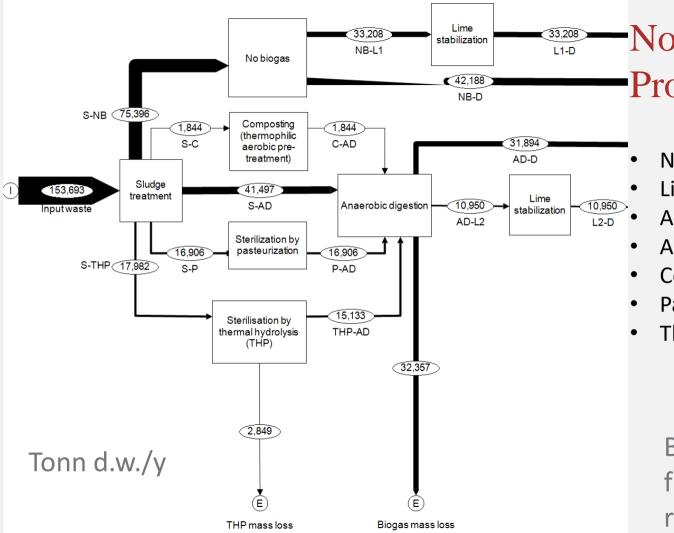
Sludge management in Norway compared to the EU

Figure	Norway (2018)	EU-27 (2019)
Population	5.3 million	447.7 million
Total sludge produced	118 kton/y (22 kg/capita)	8300 kton/y (19 kg/capita/y)
% used for biogas production	49%	<pre>?? (no data, but expected to grow)</pre>
% agriculture/soil	82%	40%
% incinerated	1%	27%
% landfilled (+ composted/other)	5% (+ 12%)	11% (+10%)



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Sources: SSB Norway, Collivignarelli et al., 2019 Preliminary SLUDGEFFECT results (biogas)



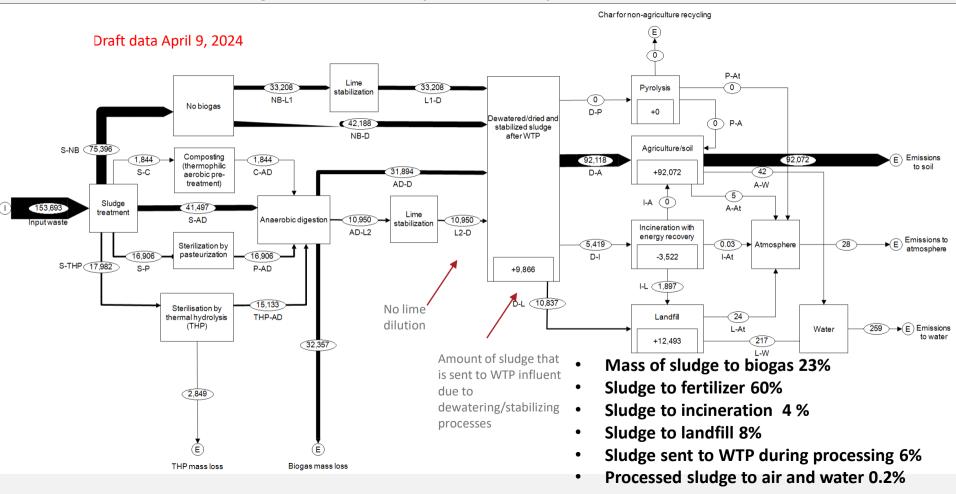
Norwegian Sludge Processing in 2020

No treatment 22%

- Lime stabilization 27%
- Aerobic digestion (AD) 21%
- AD + lime stabilization **7%**
- Composting + AD 1%
- Pasteurization + AD 11%
- Thermal hydrolysis + AD 12%

Basert på data samlet fra SSB, Norskvann og renseanlegger

Mass flow of sludge in all Norway (tonn dw/y) (2020)



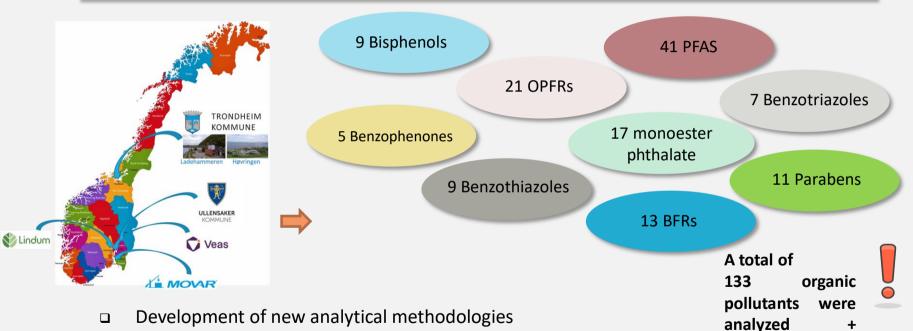
What about the flow of contaminants in Norwegian sludge?



Target Analytes



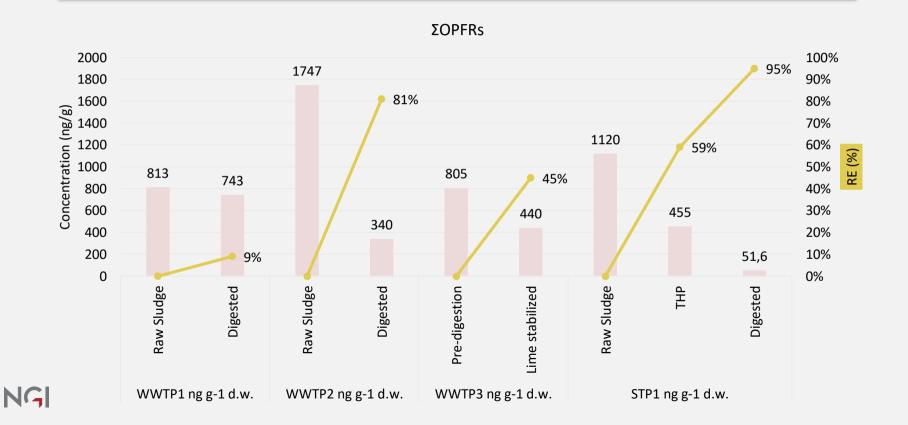
hazardous metals



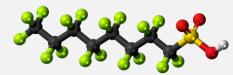
- Analysis of 87 sludge samples
- **Quantification of several families of emerging pollutants and metals**

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Removal Efficiency of OPFRs in the WWTPs



Removal Efficiency of PFAS in the WWTPs



Concentration ng/g

		Raw sludge	Post-pasteurization	Digested	Lime stabilized	Anaerobic transformation (%)
	∑Uncategorized	0.16	0.33	9.53	-	-98%
	ΣFTS	5.51	5.02	0.66	-	88%
	ΣΡϜϹΑ	4.58	18.53	93.07	-	-95%
	Long-chain PFCA	3.73	4.82	2.59	-	31%
WWTP1	Short-chain PFCA	0.86	13.71	90.48	-	-99%
WWTP2	ΣPFSA	25.65	17.49	2.09	-	92%
	Long-chain PFSA	2.90	1.81	0.86	-	70%
	Short-chain PFSA	22.75	15.68	1.23	-	95%
	<u>Σ</u> Pr <u>eFOS</u>	n. <u>d.</u>	<u> </u>	<u>n.</u> d.		n <u>.d</u> .
	ΣΡϜΑS	35.90	42.47	105.35		-66%
	∑Uncategorized	3.56		13.02	n.d.	100%
	ΣFTS	7.93	-	1.29	102.58	-92%
	ΣΡϜϹΑ	437.28	-	824.39	308.11	30%
	Long-chain PFCA	17.92	-	14.85	308.11	-94%
WWTP3	Short-chain PFCA	419.36	-	809.54	0.00	100%
WW IP5	ΣPFSA	90.21	-	32.25	36.60	59%
	Long-chain PFSA	0.00	-	n.d.	0.00	n.d.
	Short-chain PFSA	90.21	-	32.25	36.60	59%
	ΣPreFOS	79.13		2.11	11.45	86%
	ΣΡϜΑS	618.11		873.06	458.74	26%

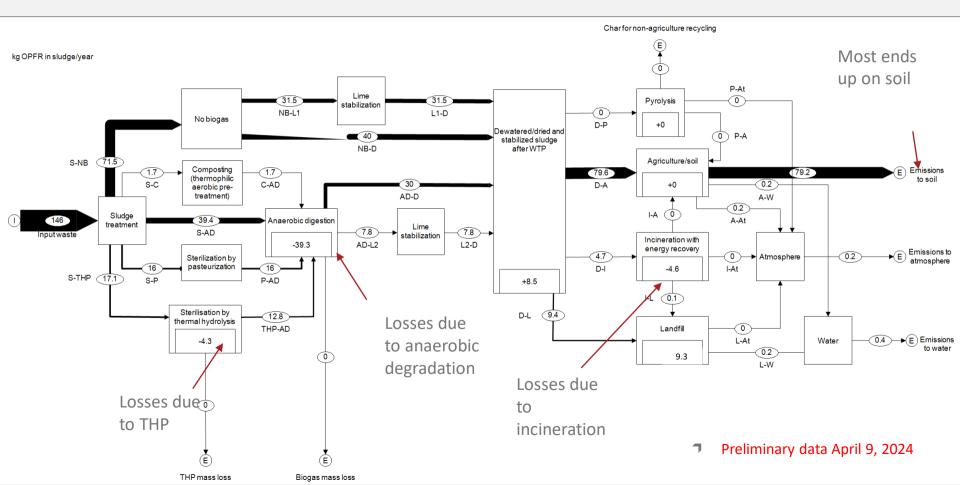
Anerobic digestion of PFAS

- Anaerobic digestion in WWTP1 leads to the transformation of precursors into short-chain PFCAs.
- The combination of primary treatment and subsequent hygienization with lime removed the <u>26%</u> of the total PFAS concentration, favouring the transformation from the precursors and PFSA into longchain PFCAs (94% transformation).

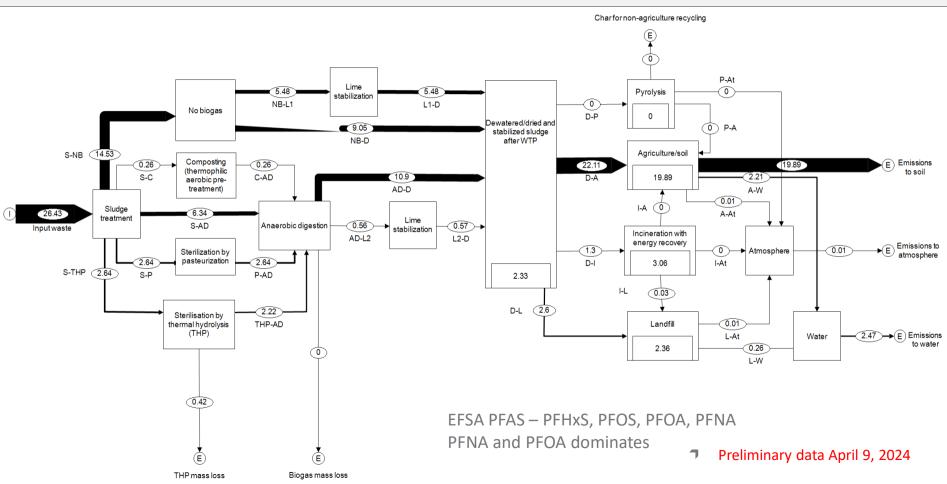
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E. Sørmo et al. (2023). The decomposition and emission factors of a wide range of PFAS in diverse, contaminated organic waste fractions undergoing dry pyrolysis. Journal of Hazardous Materials 454, 131447.

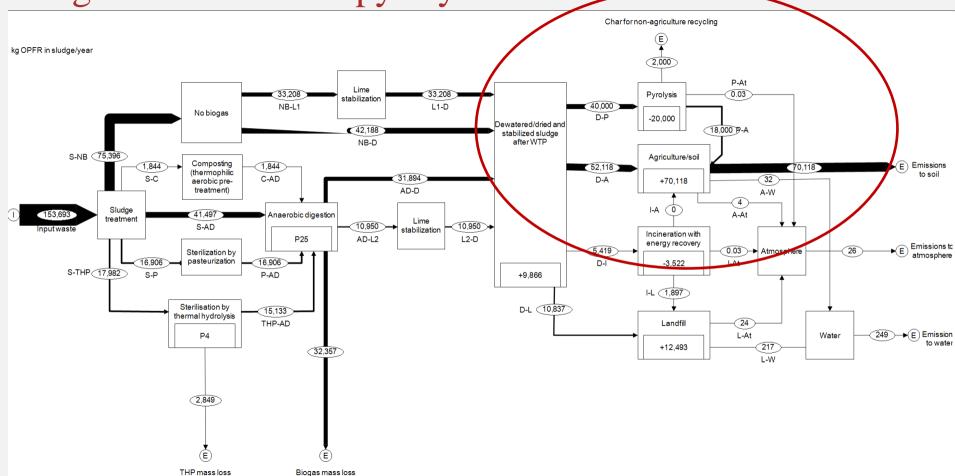
Mass flow of OPFRs in Norway (kg d.w./y)



Mass Flow of EFSA PFAS in Norway (kg d.w./y)



Imagine a future with pyrolysis ...

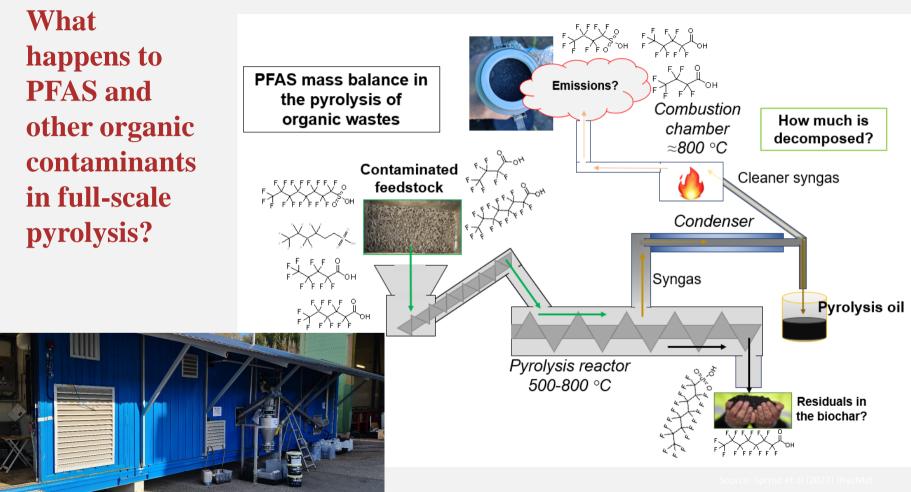


Biogreen by ETIA Ecosolutions (VOW ASA)

- Full-scale relevant, medium size (2-5 kg biochar/hr)
- Electrically heated Spirajoule[®] (up to ≈850 °C)
- Condensation of pyrolysis oils
- Pyrolysis gas combustion in simple "torch" (700-900 °C)





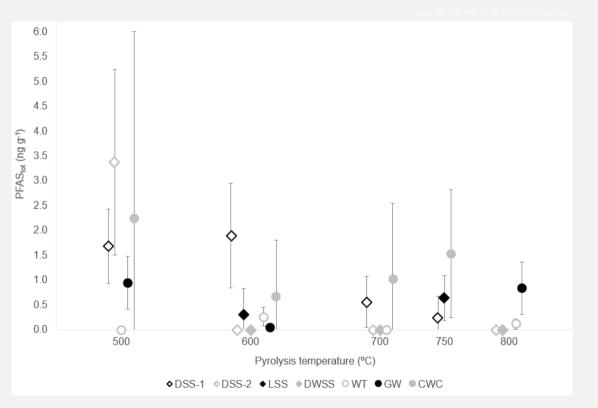


PFAS-residuals were found in the biochar

- PFAS decreased by factors of 10 – 1000, more loss with increasing temp dependence
- 60-100% fewer congeners

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 Shift towards long chain PFAS (>6xCF₂)



Digested sewage sludge (DSS-1 and DSS-2), limed sewage sludge (LSS), de-watered sewage sludge (DWSS), food waste reject (FWR), waste timber (WT), garden waste (GW), & wood chips from forestry (CWC)

PFAS Emissions from pyrolysis to air (without a scrubber)

		DSS-1		DSS-2				LSS		
		500	600	700	500	600	700	800	600	750
Emission con	.c. (ng m⁻³)	59 ± 23	217 ± 110	96 ± 62	0.6 ± 0.8	27 ± 23	7.4 ± 0.5	20 ± 1	9.6 ± 0.5	12 ± 2
EF (mg tonne	e ⁻¹)	0.2 ± 0.1	3.1 ± 1.6	1.2 ± 0.8	0.01 ± 0.02	0.9 ± 0.8	0.32 ± 0.02	0.7 ± 0.1	0.0010 ± 0.0005	0.9 ± 0.2
Fractions	Gaseous (%)	97	94	88	0	87	0	55	0	0
	Particles (%)	3	6	12	100	13	100	45	100	100

Digested sewage sludge (DSS-1 and DSS-2) & limed sewage sludge (LSS)

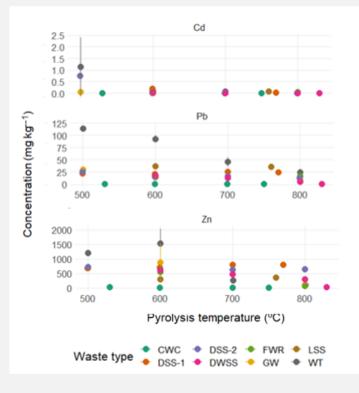
- Some PFAS are emitted
 - 0.01 to 3.1 mg tonne-1 of biochar produced
 - Account for up to 2.8 % of analysed PFAS total mass
 - Dominated by short chain PFAS

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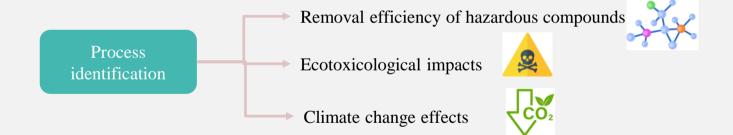
Heavy metal concentrations in biochars reduced by increasing pyrolysis temperature

- Cd most easily volatilized
 - <0.2 mg kg⁻¹ left in biochar made at ≥600 °C
- Volatilization of Pb and Zn at \geq 700°C
 - Matrix dependent

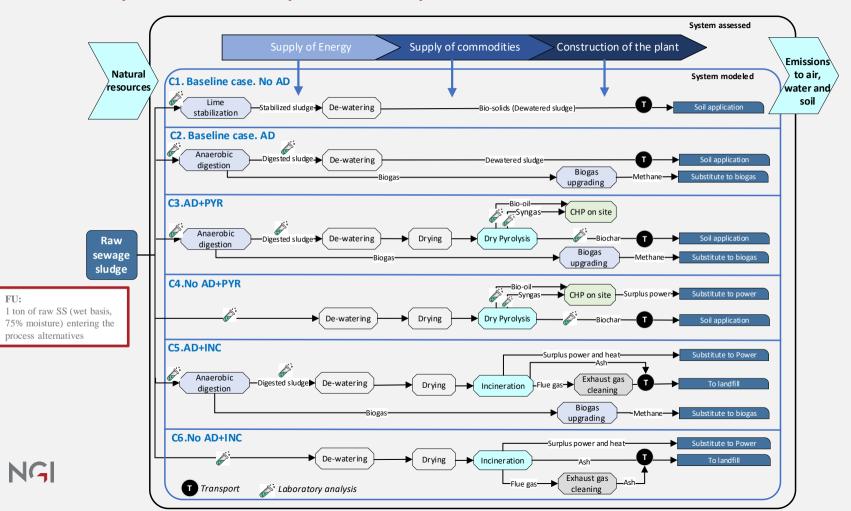
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Toxicological, Ecotoxicological and Climate change impacts of thermal treatments



Life Cycle Assessment System Boundary and Functional unit



Hazardous Organic compounds (HOCs) and Heavy metals evaluated in the LCA

Abbreviation

CAS-number

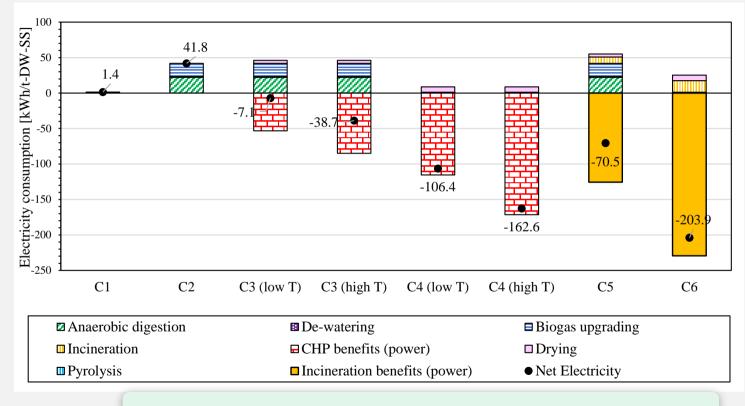
	 OPFRs (Organophosphate flame retardants) 		
	Trimethyl phosphate	TMP	000512-56-1
(Triethyl phosphate	TEP	000078-40-0
	Tripropyl phosphate	TnPP	000513-08-6
	Tributyl phosphate	TnBP	000126-73-8
	Triisobutyl phosphate	TiBP	000126-71-6
	Tris(2-chloroethyl) phosphate	TCEP	000115-96-8
	Tris(1-chloro-2-propyl) phosphate	TCiPP	013674-84-5
	Triphenyl phosphate	TPhP	000115-86-6
	Diphenyl methylphosphonate	DPMP	007526-26-3
OPFRs	bis(2-butoxyethyl) 2-hydroxyethyl phosphate	BBOEHEP	1477494-86-2
	Trimethylolpropane phosphate	TMPP	001005-93-2
(Organosphosphate flame	2-Ethylhexyl diphenyl phosphate	EHDP	001241-94-7
retardants)	Isodecyl diphenyl phosphate	IDPhP	029761-21-5
ictatualits)	Tris(2-butoxyethyl) phosphate	TBOEP	000078-51-3
21 OPFRs included	Bis(2-butoxyethyl) 3-hydroxyl-2-butoxyethyl	3OH-TBOFP	1477494-87-3
	phosphate	SOIFIBOLE	14//454-07-5
	Tris(1,3-dichloro-2-propyl) phosphate	TDCIPP	013674-87-8
	TriS(2-ethylhexyl)phosphate	TEHP	000078-42-2
	Tris(4-tert-butylphenyl) phosphate	TTBPP	000078-33-1
	Rersorcinol bis(diphenylphosphate)	RDP	057583-54-7
	Commercial products of 2,2-bis(chloromethyl)	V6	038051-10-4
	 trimethylene bis[bis(2 chloroethyl) phosphate] 	10	050051 10 4
Bisphenols	Bisphenol A bis(diphenyl phosphate)	BPA-BDPP	005945-33-5
Displicitois	Bisphenols	_	
1 Bisphenol included	Bisphenol A	BPA	000080-05-7
i Displicitor included	PFAs (Poly-and perfluoroalkylated substances)		
DEAG	Fluorotelomer sulfonates	∑FTS	-
PFAS	Perfluoroalkyl carboxylates	∑PFCA	-
(Doly and norfly proplated	Perfluoroalkane sulfonates	∑PFSA	-
(Poly-and perfluoroalkylated	Perfluorooctane sulfonate precursors	∑PreFOS	-
substances)	Heavy metal content	_	
,	Arsenic	As	-
41 PFAs included	Barium	Ba	-
	Cadmium	Cd	-
	Cobalt	Со	-
HMs (Heavy metals)	Chromium	Cr	-
12 HMs included	Copper	Cu	-
	Molybdenum	Mo	-
	Nickel	Ni	-
	Lead	Pb	-
	Strontium	Sr	-
	 Vanadium 	V	-

IUPAC name

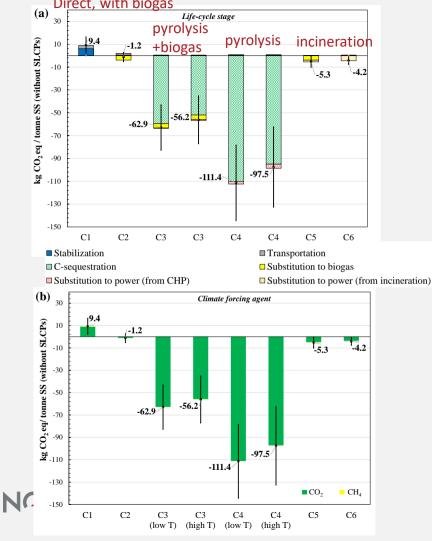
	Abbreviation	IUPAC name	CAS-number
	Gen-X	2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate	62037-80-3
	SAmPAP Di	bis[2-(N-ethylperfluorooctane-1-sulfonamido)ethyl] phosphate	30381-98-7
Uncategorized	F53B	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	73606-19-6
	NaDONA	dodecafluoro-3H-4,8-dioxanonanoate	958445-44-8
	DecaS	Sodium 1- decanesulfonate	13419-61-9
	4:2 FTS	1H,2H-Perfluorohexan sulfonate (4:2)	757124-72-4
FTS	6:2 FTS	1H,2H-Perfluorooctane sulfonate (6:2)	27619-97-2
-15	8:2 FTS	1H,2H-Perfluorodecan sulfonate (8:2)	39108-34-4
	10:2 FTS	1H,2H-Perfluorododecan sulfonate (10:2)	120226-60-0
	PFBA	Perfluorobutanoic acid	375-22-4
	PFPeA	Perfluoropentanoic acid	2706-90-3
	PFHxA	Perfluorohexanoic acid	307-24-4
	PFHpA	Perfluoroheptanoic acid	375-85-9
	PFOA	Perfluorooctanoic acid	335-67-1
	PFNA	Perfluorononanoic acid	375-95-1
	PFDA	Perfluorodecanoic acid	335-76-2
PFCA	PFUnDA	Perfluoroundecanoic acid	2058-94-8
	PFDoDA	Perfluorododecanoic acid	307-55-1
	PFTrDA	Perfluorotridecanoic acid	72629-94-8
	PFTeDA	Perfluorotetradecanoic acid	376-06-7
	PEHxDA	Perfluoro-n-hexadecanoic acid	67905-19-5
	PFOcDA	Perfluorooctadecanoic acid	16517-11-6
	7H-PFHpA	7H-Dodecafluoroheptanoic Acid	1546-95-8
	PF-3,7-DMOA	Perfluoro-3,7-dimethyloctanoic acid	172155-07-6
	PEBS	Perfluorobutanoic acid sulfonate	108427-52-7
	PEPeS	Perfluoropentane sulfonic acid	2706-91-4
	PFHxS	Perfluorohexane sulfonic acid	355-46-4
	PFHpS	Perfluoro-1-heptanesulfonate	146689-46-5
PFSA	PFOS	Perfluorooctano sulfonic acid	1763-23-1
	PFNS	Perfluorononane sulfonic acid	68259-12-1
	PEDS	Perfluorodecane sulfonic acid	335-77-3
	PEDoDS	Perfluorododecane sulfonic acid	79780-39-5
	PFECHS	Perfluoroethylcyclohexane sulfonic acid	335-24-0
	PFOSA	Perfluorooctane sulfonamide	754-91-6
	MeEOSA	N-methylPerfluoro-1-octanesulfonamide	31506-32-8
	EtFOSA	Sulfluramid	4151-50-2
	MeFOSE	N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide	24448-09-7
PreFOS	EtFOSE	N-ethyl-N-(2-hydroxyethyl)-N-methylperfluorooctane sulfonamide	1691-99-2
	FOSAA	Perfluoro-1-octanesulfonamidoacetic acid	2806-24-8
	MeFOSAA	2-(N-methylPerfluoro-1-octansulfonamido)acetic acid	2355-31-9
	EtFOSAA	N-ethylPerfluoro-1-octanesulfonamide acetic acid	1336-61-4



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Thermal treatments (Pyrolysis and Incineration) result on power benefits.



Climate change (GWP100)

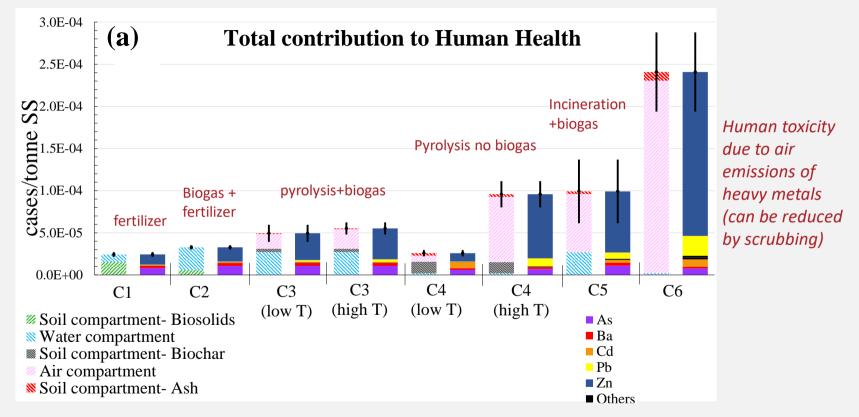
Pyrolisis benefits

- ✓ Negative climate change effects.
- ✓ Climate change benefits from:
 - ✓ Biochar: carbon capture and storage
 - ✓ Energetic products: power and biogas substitution.

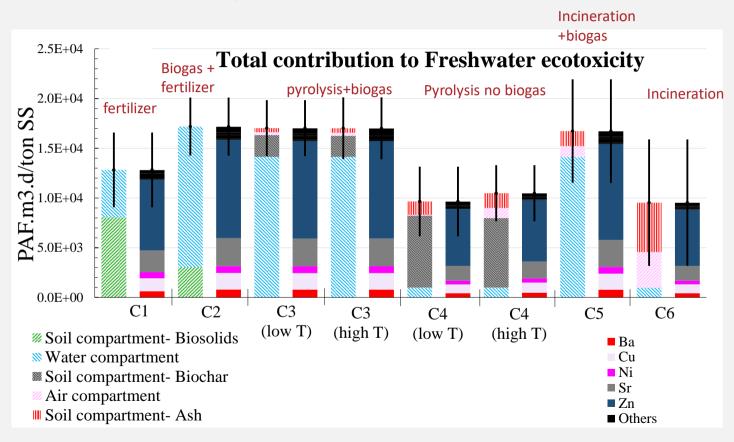
Black dots represent the net GWP100 impacts, and the whiskers show uncertainty range from Monte-Carlo analysis (± Standard deviation).

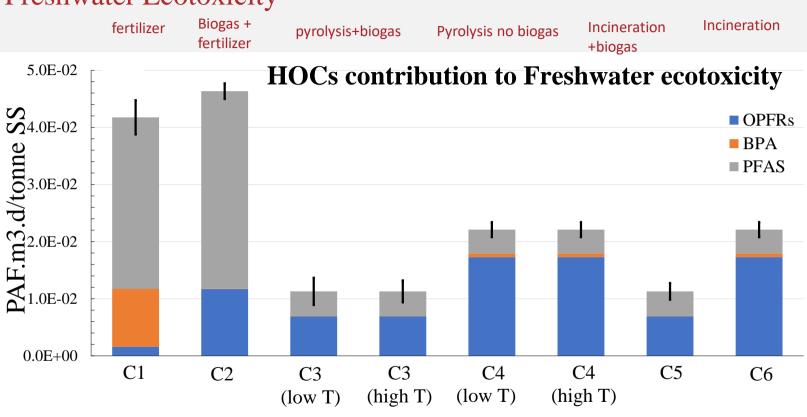
Toxicity to Human Health (non-cancer effects)

Incineration



Freshwater Ecotoxicity





Freshwater Ecotoxicity

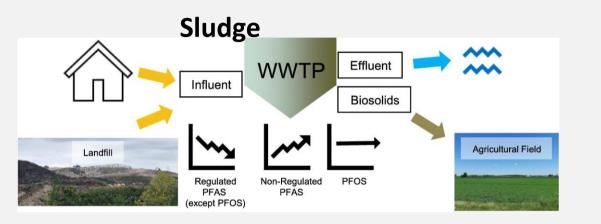
Key findings on climate change and toxicity impacts



- Pyrolysis without AD represents the most eco-friendly treatment for sewage sludge
 - Negative climate change impacts.
 - C-storage (Biochar)
 - Energy benefits
 - Reduce contaminants and ecotoxicological impacts.
- However burden shifting from hazardous metals releases to air (recommend to use a air scrubber, pyrolyse outside urban centers)

Sludge in a circular economy

Source control matters

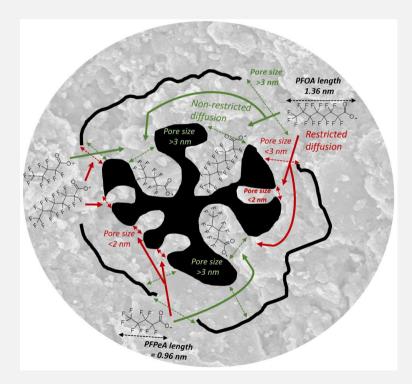


- Gewurtz et al STOTEN 2024
- Decreasing trends for other persistent pollutants in Zennegg, Environ. Int. 60, 202–208. https://doi.org/10.1016/j.envint.2013.08.020

- Chemicals that become regulated tend to decrease in sludge over time
- New contaminants introduced to the market increase over time
- Hazardous metals and persistent organic substances are a chronic issue

Several markets for pyrolysed sludge in a circular economy

- Fertilizer (phosphorous retention)
- As a PFAS sorbent at PFAS polluted sites/WWTP
- Replacement for coal in cement or metallurgy



Recommendations

The best solution is local, and depends on contaminants in the sludge, need for phosphorous, climate mitigation targets, goals towards zero pollution and ability for innovation. New thermal technologies can have a role.

Recommendations inspired by EurEau (2021) are:

- 1. Control at source (prevent pollution from entering sludge, e.g. PFAS restriction) *is the most important part* of sludge management (see: REVAQ system in Sweden)
- 2. Biosolids have a role, as do pyrolyzed biosolids, for agriculture and land reclamation in a climate mitigating way (particularly if chemical risks are low)
- 3. Risk assessment for chemicals is important
- 4. Incineration / co-combustion only in extreme situations: if chemical risks are unacceptable, phosphorous not needed locally, land application not feasible, etc.
- 5. Innovation towards zero pollution should not be hindered by over-complex/contradicting regulation



SLUDGEFFECT in a nut shell

- Reduce pollutants upstream
- Pyrolyse more (with gas scrubing) for climate benefits and diverse uses of sludge-char in a circular economy
- Areas affected by contaminants will receive most benefit from generating sludge char (e.g. removal of PFAS, use of char for PFAS remediation or other markets)
- Lots of potential for green investment but needs regulatory clarity



Thank-you!

Researchers

- NGI: Hans Peter H. Arp (PI), Sarah Hale, Gerard Cornelissen, Erlend Sørmo, Heidi Knutsen, Mari Løseth
- NTNU: Hans Peter H. Arp, Alexandros Asimakopoulos, Gabriela Castro, Otavio Cavalett, Francesco Cherubini, Junjie Zhang, Marjorie Morales + over 20 MSc students ⁽²⁾
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- REVAC Kay Riksfjord
- Waste water sector
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Science and TecMology



Lindum











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Thank you!





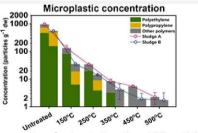
Contaminants and thermal treatment

Contaminant	Reaction to sludge incineration/pyrolsis	Ref
PAHs / dioxins	Formed to a varying degrees. High temperature and long times tends to give less PAHs/dioxins, low temperature processes (e.g. gasification) tend to produce more. Often strongly sorbed to chars/soots (limited bioavailability).	Hale et al. ES&T 2012
Heavy metals	Some lost to flue gas, remainder is enriched in the ash/char. Bioavailability tends to decrease though treatment dependant (incineration -> insoluble oxides, pyrolysis increases pH to insoluble oxidation states)	Kahn et al. ES&T 2012
Microplastics	Converted to volatiles (e.g. monomers) or mineralized by 500 °C given enough time (more efficient at higher temp)	Ni et al. ES&T lett. 2021
PFAS	Converted to volatiles or mineralized to CO_2 /chars starting at 600 °C given enough time (more efficient at higher temp)	Simon & Kaminsky (1998)
Other organic contaminants	Converted to volatiles (e.g. monomers) or mineralized by 500 °C given enough time (more efficient at higher temp)	SLUDGEFFECT







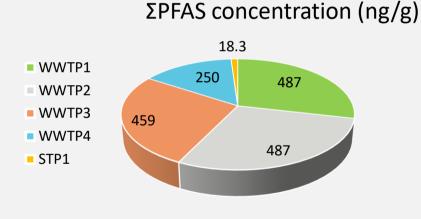


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Per- and polyfluoroalkyl substances (PFAS)

Occurrence of PFAS in Norwegian digested sludge



Median WWTP1-WWTP2	Concentration (ng/g)	
Analyte	This study	PFAS in the nordic sludge 2017
PFOA	10.56	1.18-1.29
PFBA	0.75	<0.04
PFPeA	1.84	<0.04
PFNA	79.67	0.56-0.67
PFDoDA	5.23	n.d 1.10
PFOS	0.90	2.60-2.82
PFPeS	0.86	<0.04
Gen-X	9.47	NA
6:2 FTS	0.01	0.06-0.1

100% DF for FTS (4:2, 6:2, 8:2, 10:2), PFHpS and PFOS in digested sludge.

Higher concentrations were detected in the WWTPs with

primary treatment (WWTP1 and WWTP2).

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Overview of thermal treatment recycling technology categories

Thermal treatment Description category		Recycling Negatives 😕	Recycling Positives	
Monovalent Incineration	Dedicated sewage sludge incinerators	Carbon is lost, ash and flue gas management, air emissions*	energy recycling, P can be extracted (struvite)	
Co-combustion	Combusting sludge with e.g. coal, municipal waste, cement kilns	Carbon is lost, fertilizer is lost, air emissions,* ash management unless cement	energy recycling, cement raw material	
Wet-pyrolysis/ gasification	Heating wet sludge with no oxygen	Fertilizer is lost?, ash and flue gas management, air emissions	efficient for energy recapture (e.g. syngas & liquid fuel)	
Dry-pyrolysis	Heating dry sludge with no oxygen	Heavy metals concentrate in fertilizer, air emissions	C-sequestration, fuel, bioavailable P concentrates	

* Incinerators and co-combusters (also pyrolyzers?) need to fulfill air emission regulations, such as Directive 2010/75/EU and Directive 2001/80/EC

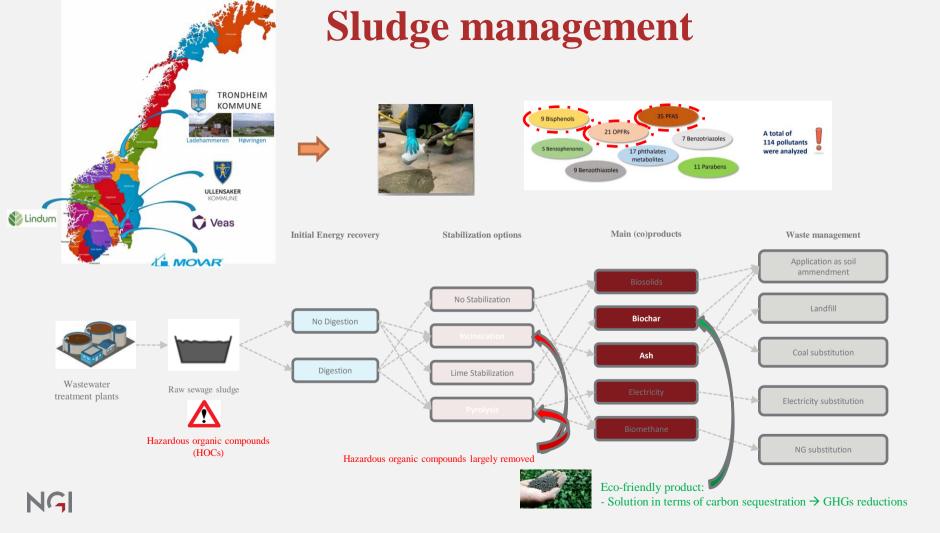


Further reading:

<u>https://www.umweltbundesamt.de/en/publikationen/technical-guide-on-the-treatment-recycling-0</u> https://www.eureau.org/resources/news/545-key-to-a-circular-future

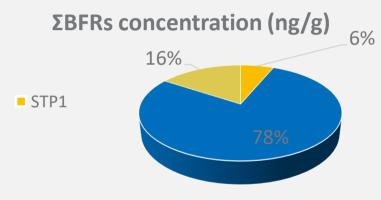
Summary – several benefits for pyrolysis to pursue

	Direct soil application	Incineration	нтс	Pyrolysis
Energy recovery	None	High	Medium	Medium
Carbon storage	Low	None	Medium?	High
Fertilizer/soil improvement	High/high	None	Medium/medium	Low/medium
Other benefits	-	None	Sorbents, fuel	Sorbents, coal substitute, fillers
Destruction of contaminants	None	High	Medium?	High
Emissions to soil	High	Low	Low	Low
Emissions to air	Low	High/medium	Low?	Medium
Emissions to water	High	Medium	Medium/low?	Low

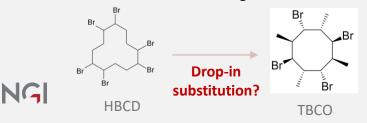


Brominated flame retardants (BFRs)

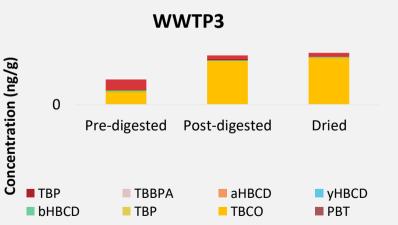
Occurrence of BFRs in Norwegian digested sludge

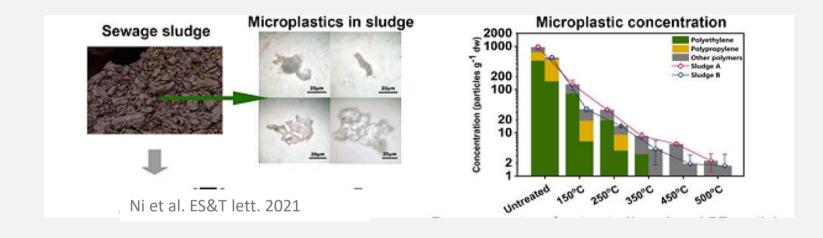


100% DF for HBB in digested sludge. TBCO was found in the highest concentrations.









Proposed upper limits for contaminants in sluge in Norway

7 EU (2022)		7 Cowi 2018		7	NIBIO 2019		
Contaminants included		Non-adjusted ML values ¹ (mg/kg dw)			Adjusted ML values ² (mg/kg dw)		
DEHP	Y		50			50	
PFOS	Y		0.1	.1 0.1			
PFOA ³	Y		0.1	0.1			
SCCP	Y		0.9	2			
HHCB	Ν		0.5	10			
AHTN	N		0.6	10			
OTNE	Ν		n.s.	n.s.			
BDE-20)9 N (a	andre BDE)	0.5	0.5			
PCB 7	N (kun dioksin PCB)	0.004	0.02			
NP + N	PE Y		4	10			
¹ Median	¹ Median WWTP1-WWTP2			Concentration (m		(mg/kg)	tet al.,
1		Analyte		This study	PI	FAS in the nordic sludge 2017	
	PFOA			0.011 0.001		Ū.	
	PFOS			0.01	0.01 0.003		

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https://www.miljodirektoratet.no/publikasjoner/2019/november-2019/maximum-limit-values-for-selected-hazardous-organic-contaminants-hocs-in-secondary-raw-materials-used-in-fertilisers-and-soil-products/





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