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Incineration of PTFE to evaluate the release of PFAS

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Background

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Greenpeace expedition to Haba Snow Mountain, China, to collect water and snow samples and test them for PFC contamination

Sounding the alarm on PFCs

Since the beginning of its Detox campaign in 2011, Greenpeace has been calling on the clothing industry to eliminate all hazardous chemicals from its supply chain by 2020, highlighting per- and polyfluorinated chemicals (PFCs) as one of the priority hazardous chemical groups to eliminate. PFCs are used in many industrial processes and consumer products, and are well known for their use by the outdoor apparel industry in waterproof and water-repellent finishes.

PFCs are environmentally hazardous substances, which are persistent in the environment.[1] Studies show that some PFCs can accumulate in living organisms such as the livers of polar bears in the Arctic and are also detected in human blood.[2] Animal studies provide evidence that some PFCs cause harm to reproduction, promote the growth of tumours and affect the hormone system.[3]

Source: https://www.greenpeace.org/international/publication/7150/pfc-revolution-in-outdoor-sector, download 24.03.2022

Greenpeace's Detox My Fashion campaign, launched in 2011, challenged the textile industry to remove all hazardous chemicals from their supply chain, highlighting PFCs as one of the priority hazardous chemical groups to eliminate. In 2015, the Detox Outdoor campaign put the spotlight on the outdoor apparel sector, well known for using PFCs in making waterproof membranes and water-repellent coatings. Hundreds of thousands of outdoor enthusiasts from around the world joined the campaign to demand PFC-free gear.

In 2017 Gore Fabrics pledged to eliminate PFCs of Environmental Concern from its general outdoor weatherproofing laminates by the end of 2020 and from its specialized weatherproofing laminates by the end of 2023, exploring both fluorinated and non-fluorinated solutions. Today's announcement means that the first products using the completely PFC-free membrane will be on the market in 2022.

Source: https://www.greenpeace.org/international/press-release/49771/gore-fabrics-announces-major-transition-in-its-product-technology-greenpeace-response/ download 24.03.2022

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Aim of the project

- Incineration of PTFE under standard municipal waste conditions
- Investigation of possible generation of PFAS
- Validation of almost full transformation of PTFE to Fluorine (HF) and trace species in very low concentrations using BAT

PFAS of scope

Abbreviation	CAS Number	Abbreviation	Quantitation limit [µg/m³]
Perfluorobutanoic acid	375-22-4	PFBA [PFC C4]	6.0
Perfluoropentanoic acid	2706-90-3	PFPeA [PFC C5]	0.3
Perfluorohexanoic acid	307-24-4	PFHxA [PFC C6]	0.3
Perfluoroheptanoic acid	375-85-9	PFHpA [PFC C7]	0.3
Perfluorooctanoic acid	335-67-1	PFOA [PFC C8]	0.3
Perfluorononanoic acid	375-95-1	PFNA [PFC C9]	0.3
Perfluorodecanoic acid	335-76-2	PFDA [PFC C10]	0.3
Perfluoroundecanoic acid	2058-94-8	PFUdA [PFC C11]	0.3
Perfluorododecanoic acid	307-55-1	PFDoA [PFC C12]	0.3
Perfluorotridecanoic acid	72629-94-8	PFTrDA [PFC C13]	0.3
Perfluorotetradecanoic acid	376-06-7	PFTeDA [PFC C14]	0.3
Perfluorobutanesulfonic acid	375-73-5	PFBS [PFS C4]	0.3
Perfluorohexanesulfonic acid	355-46-4	PFHxS [PFS C6]	0.3
Perfluoroheptanesulfonic acid	375-92-8	PFHpS [PFS C7]	0.3
Perfluorooctanesulfonic acid	1763-23-1	PFOS [PFS C8]	0.3
Perfluordecanesulfonic acid	335-77-3	PFDS [PFS C10]	0.3
Perfluorooctanesulfonamide	754-91-6	PFOSA	0.3
N-Methyl- Perfluorooctanesulfonamide	31506-32-8	N-Me-FOSA	0.3
N-Ethyl- Perfluorooctanesulfonamide	4151-50-2	N-Et-FOSA	0.3
N-Methyl-Perfluorooctane- sulfon amidoethanol	24448-09-7	N-Me-FOSE alcohol	0.3
N-Ethyl-Perfluorooctane- sulfonamidoethanol	1691-99-2	N-Et-FOSE alcohol	0.3
1H,1H,2H,2H-Perfluoro- octanesulphonic acid	27619-97-2	1H, 1H, 2H, 2H- PFOS	0.3
2H,2H,3H,3H-Perfluoro- undecanoic acid	34598-33-9	4HPFUnA	0.3
Perfluoro-3-7-dimethyl octane carboxylate	-	PF-3,7-DMOA	0.3
7H-Dodecafluoro heptane carboxylate	-	HPFHpA	6.0
2H,2H-Perfluoro decan carboxylate	-	H2PFDA	0.3
1H,1H,2H,2H-Perfluorohexan-1-ol	2043-47-2	4:2 FTOH	24
1H,1H,2H,2H-Perflourooctan-1-ol	647-42-7	6:2 FTOH	24
1H,1H,2H,2H-Perflourodecan-1-ol	678-39-7	8:2 FTOH	24
1H,1H,2H,2H-Perflourododecan-1-ol	865-86-1	10:2 FTOH	24
Trifluoroacetic acid	76-05-1	TFA	0.4

P	er- and Poly-
F	luorinated
A	lkyl
S	ubstances

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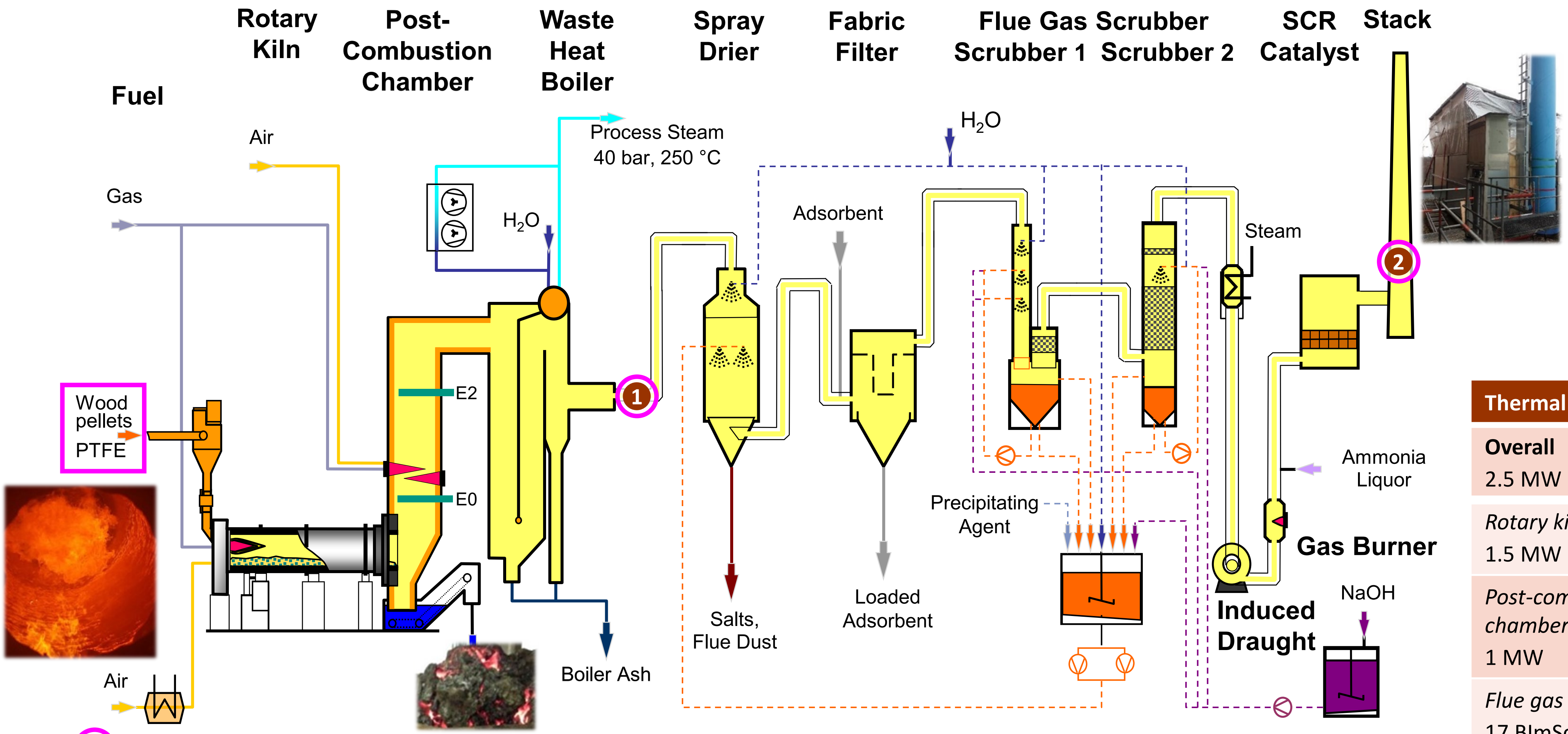
Incineration plant BRENDA



Thermal power
Overall 2.5 MW
Rotary kiln 1.5 MW
Post-combustion chamber 1 MW
Flue gas cleaning 17 BImSchV

② Sampling locations for HF and PFAS, as well as for flue gas composition and flow measurement

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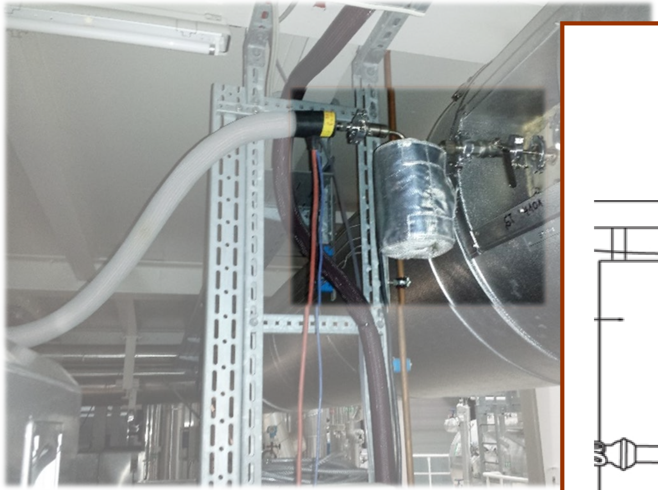
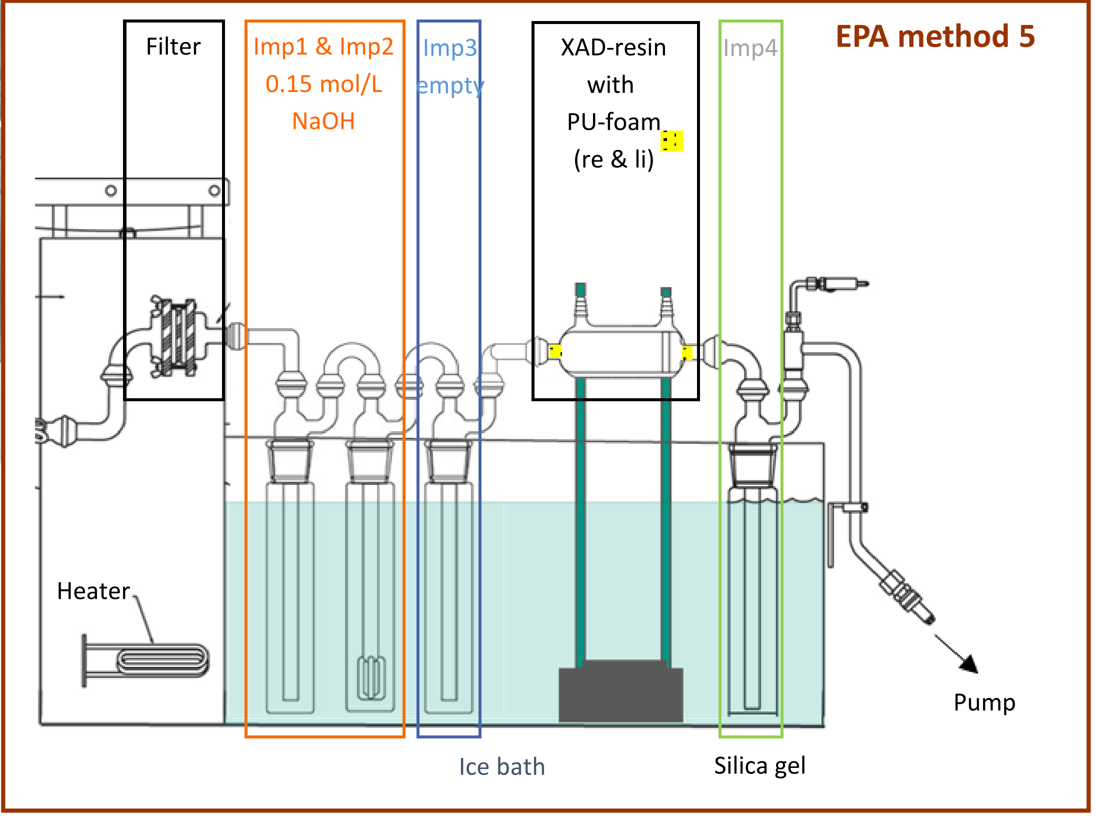
Analytical equipment



PTFE – containing seals & hoses → substitution by rubber, PE & PA

→ "PTFE-noise" elimination



Project preparation

- ✓ **2017 & 2018** → 3 analytics validation campaigns with varying concentrations of chosen species
- ✓ **Lab analytics** → spike-experiments → C8 recovery rate between 70% & 110%
- ✓ **Isokinetic sampling**. Shift every minute across the duct cross section. Duration 60 min.
- ✓ **Retrofitting of 3 Labs at ITC** → *"one-way-road"* mode of operation
- ✓ **Lab staff** → 9 people

- ✓ **LC-MS/MS** → Intertek, SGS Fresenius (3rd party labs)
- ✓ **Fly ash sampling** → VDI 2470
- ✓ **HF – analytics** (from condensate) → **IC** → FM-Lab KIT (internal)

Analytics solid compounds

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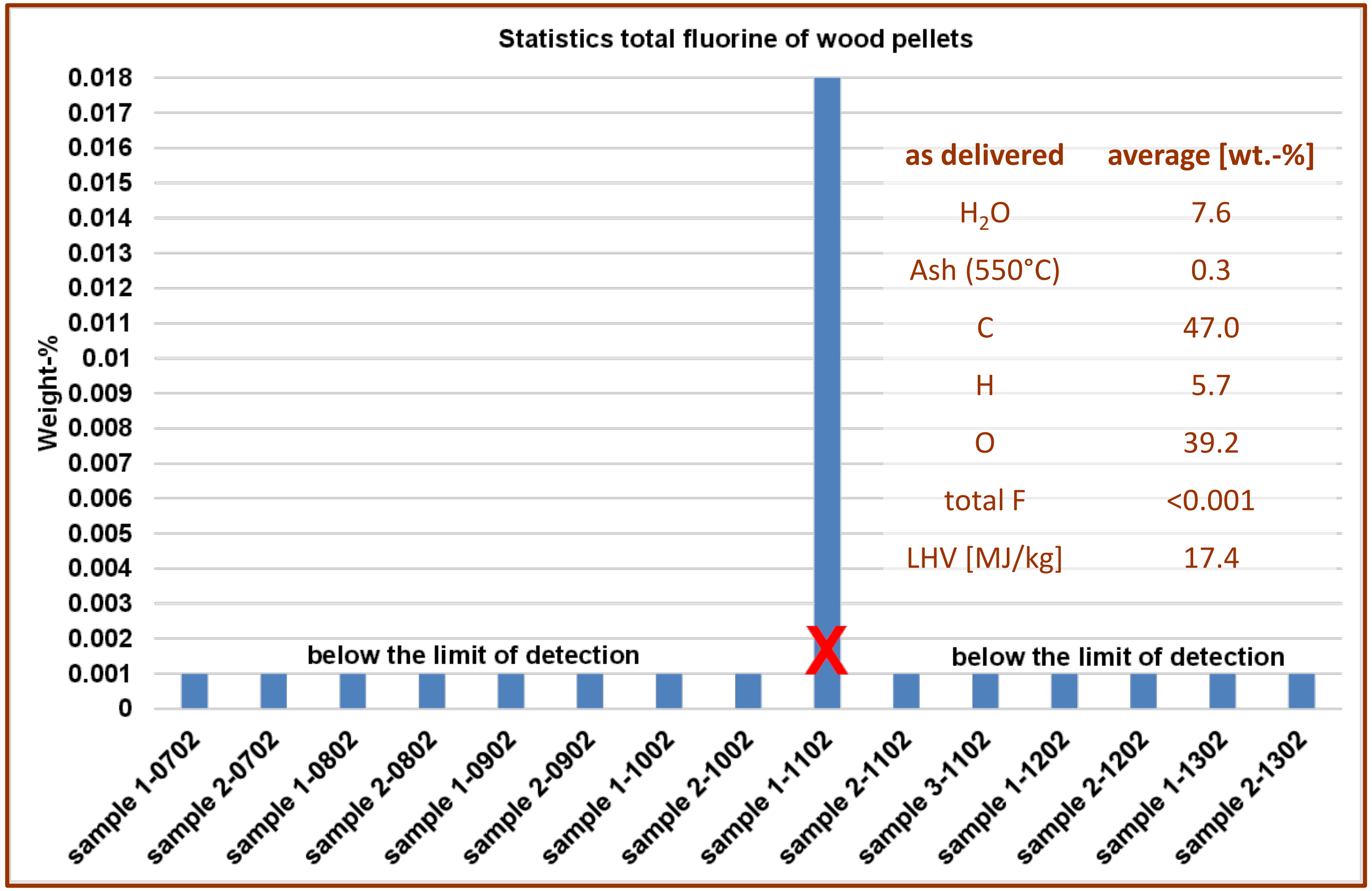

as delivered	average [wt.-%]
H_2O	7.6
Ash (550°C)	0.3
C	47.0
H	5.7
O	39.2
total F	<0.001
LHV [MJ/kg]	17.4

Wood pellets analysis

- ✓ Blended samples
- ✓ Eurofins (external)

- ✓ **F-content filter samples →** IC after high frequency pyrohydrolic separation → H. C. Stark (3rd party lab)
- ✓ **Total Carbon (TC)** filter samples → LUBW, Karlsruhe (3rd party lab)

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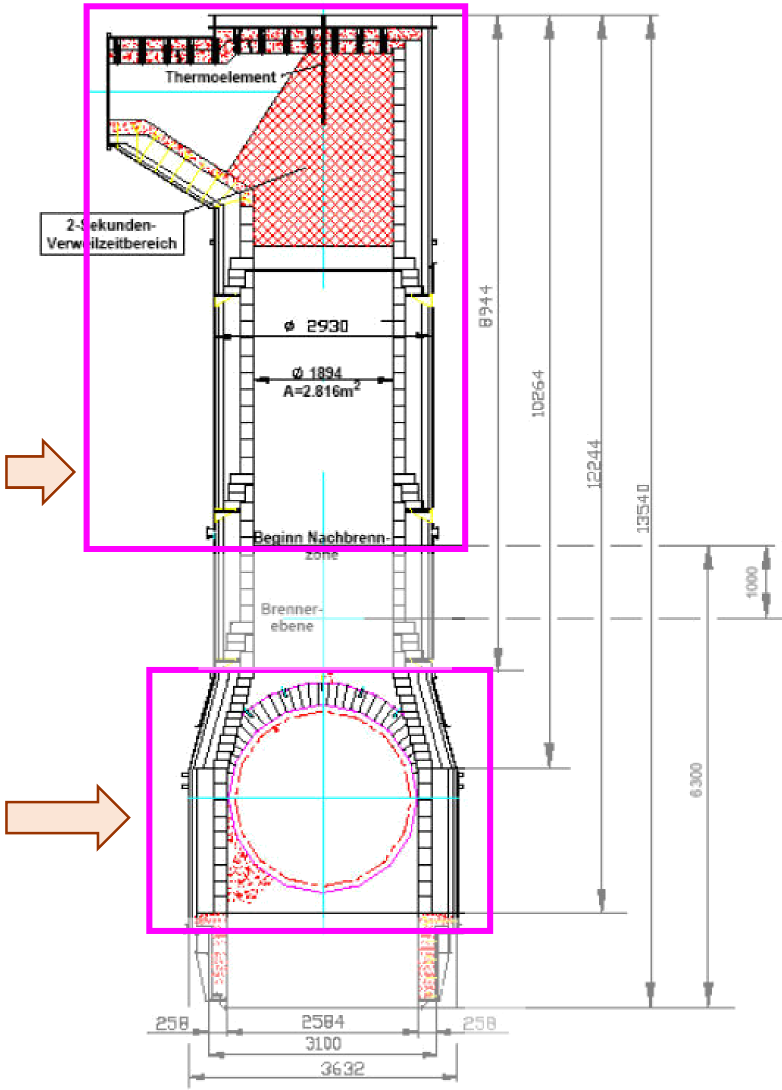
Experimental program

		Unit	setting S1	setting S2
Post – combustion chamber	volume flow natural gas to burner D4.1	m^3_N/h	25	50
	sum of volume flow combustion air to burner D4.1	m^3_N/h	800	1250
	volume flow natural gas to burner D4.2	m^3_N/h	25	50
	sum of volume flow combustion air to burner D4.2	m^3_N/h	800	1250
	residence time	s	4.0	2.7
	temperature flue gas post-combustion chamber outlet (with control)	°C	870	1020
	thermal power	MW	0.5	1
Rotary kiln	mass flow wood pellets	kg/h	100	
	man air	m^3_N/h	800	
	volume flow natural gas to burner D12	m^3_N/h	50	
	volume flow combustion air to burner D12	m^3_N/h	340	
	volume flow cooling air	m^3_N/h	790	
	inclination	°	2	
	rotation speed	rpm	0.6	
	temperature flue gas outlet	°C	800-850	
	thermal power	MW	1	

Gasification natural gas: λ **0.7**; Combustion pellets: λ **2.5**;
Total stoichiometry rotary kiln: λ **1.43**



Optimal operation setting of the rotary kiln

Always paired tests at "setting 1" and "setting 2"

- ✓ Setting 1: 870°C at 4 sec
- ✓ Setting 2: 1020°C at 2.7 sec

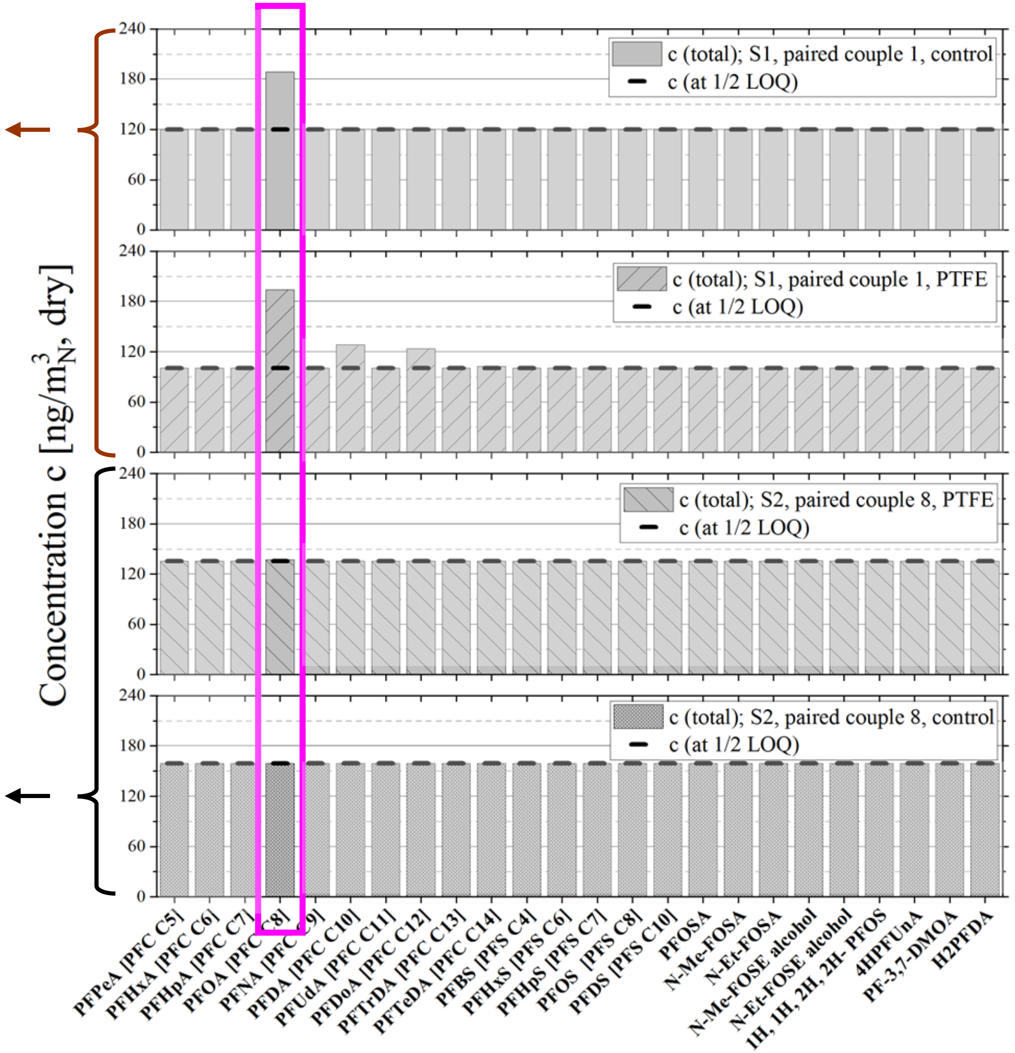
At least 5 samples per setting
(control and with PTFE)

Long-term sampling for fly ash and HF-precipitation
(over night – 8 to 10 hours)

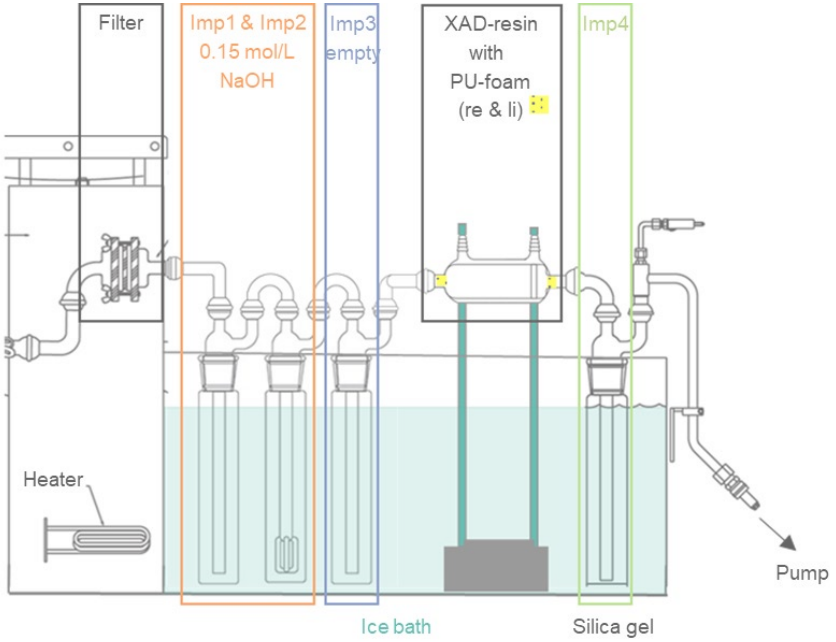
Results - evaluation

Paired couple 1
(Setting S1)
- ✓ Run 1: Control
- ✓ Run 2: with PTFE

Paired couple 8
(Setting S2)
- ✓ Run 1: with PTFE
- ✓ Run 2: Control



Aggregated concentrations from:
- ✓ Quartz filter
- ✓ NaOH
- ✓ MeOH cleaning solution
- ✓ XAD-resin



Results (PFC-C8)

Setting	Paired couple	Type	Concentration [ng/m_N^3 dry]	Difference (PTFE-Control) [ng/m_N^3 dry]	t-value	p-value
S1 (4 sec, 870°C)	1	Control	189	5	-0.624	0.564
		PTFE	194			
	2	PTFE	179	10		
		Control	169			
	3	PTFE	302	70		
		Control	232			
	4	Control	270	84		
		PTFE	354			
	5	Control	723	-539		
		PTFE	184			
S2 (2.7 sec, 1020°C)	6	Control	258	-70	-0.905	0.407
		PTFE	189			
	7	PTFE	644	487		
		Control	157			
	8	PTFE	137	-22		
		Control	159			
	9	Control	2743	-2600		
		PTFE	143			
	10	PTFE	175	32		
		Control	143			
	11	Control	413	-272		
		PTFE	141			

Working hypothesis
If $p > 0.05$ the differences between experiments without and with PTFE do **not** depend from each other

Statistics

- ✓ Average value differences

$$\bar{x} = \frac{1}{n} \cdot \sum x_i$$

- ✓ Standard deviation:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n}}$$

- ✓ t – value:

$$t = \sqrt{n} \cdot \frac{\bar{x}}{s}$$

The **p-value** is obtained from the **t-value** by the means of a statistical distribution

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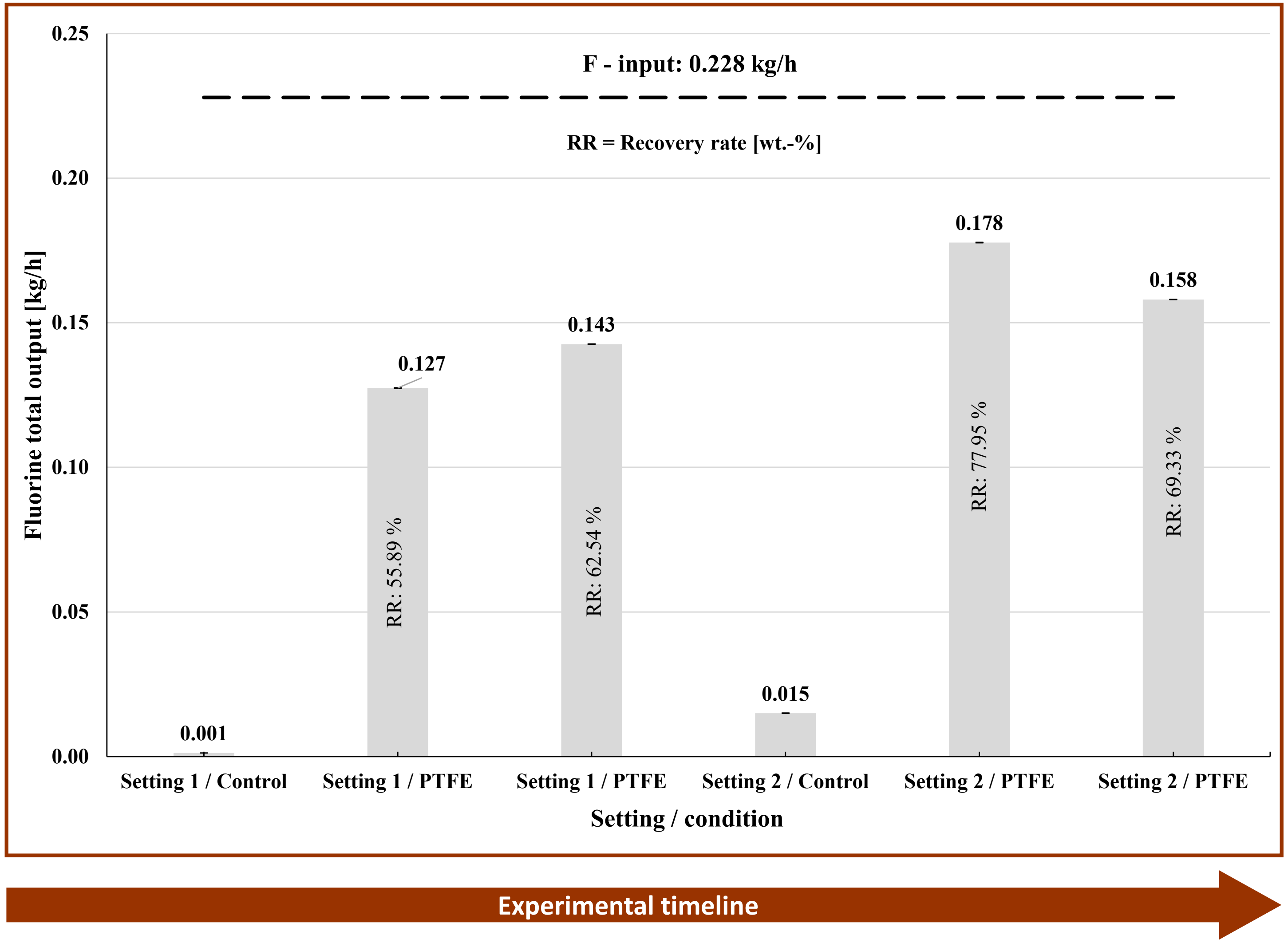
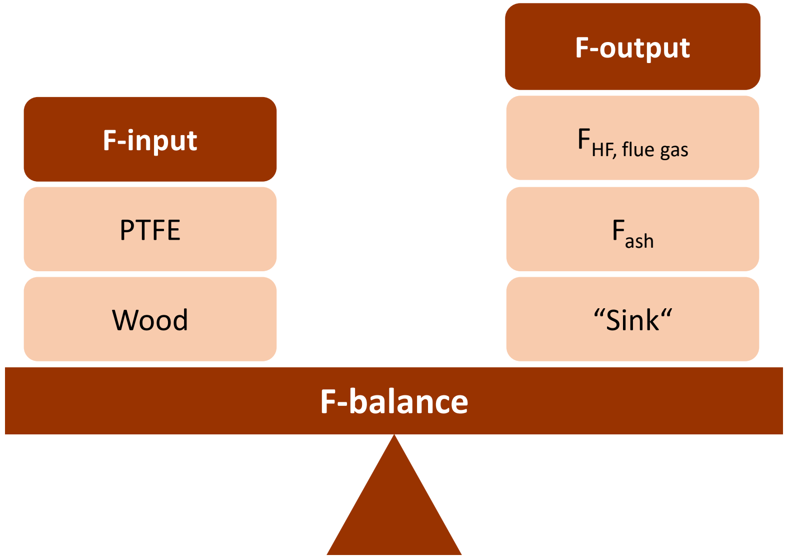
Results (Fluorine – balancing)





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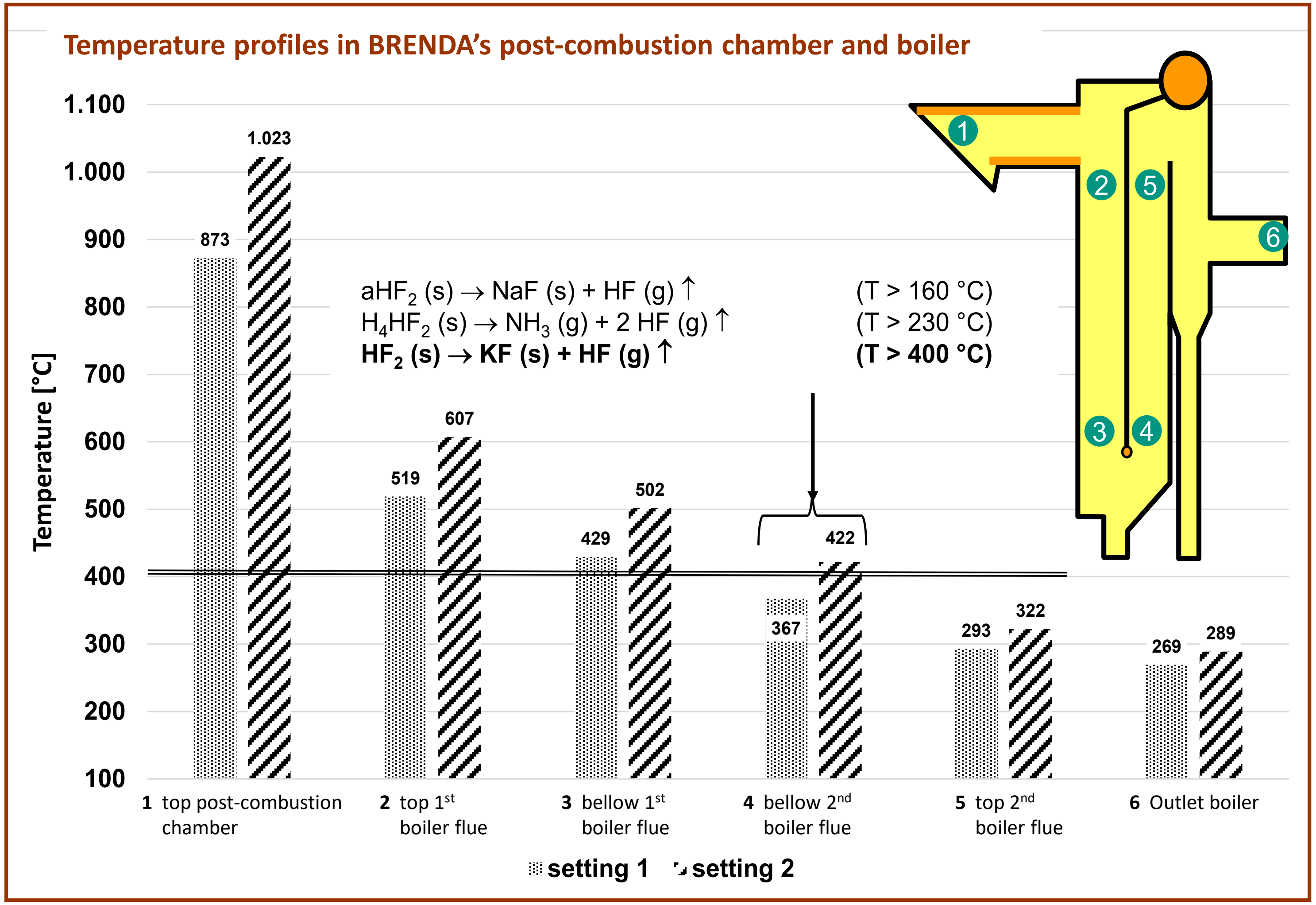
Results (Fluorine – balancing)



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Summary / Outlook

By the incineration of PTFE under operation mode in compliance with the German federal law – 17 BImSchV, the flue gas after the boiler was analyzed for 31 PFAS:

- Thus only **11 PFAS** could be quantified
- For **none** of these 11 PFAS **statistically significant concentration differences** for the case **either with and without PTFE** could be established

✓ **That's why** it is assumed that waste incineration is **no source of PFAS**

- **In progress:** Development of a sampling method for volatile PFAS from flue gases in cooperation with BAM (Project UBA, Start: summer 2022)

Sources:

Gore-Homepage | Paper Chemosphere | Making of

The End

Thank you for your attention!

Back up

Questions for discussion

Question 1:
How did you generate/ calculate the Fluorine balance?

Question 2:
The Fluorine recovery rates are rather low. How can you explain this?

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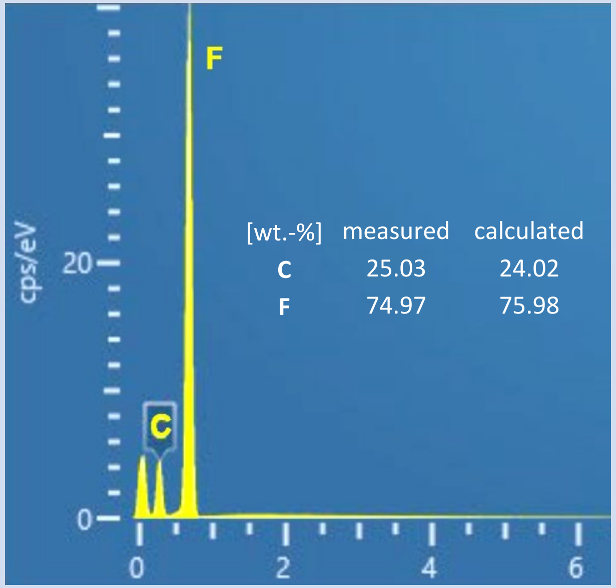
PTFE – characterization

REM-EDX



[wt.-%]	measured	calculated
C	25.03	24.02
F	74.97	75.98

Weber & Leucht GmbH (external)