

PFAS Soil and Groundwater Threshold Limits in Europe

What should we do when PFAS are not regulated?

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Agenda

- 01 Background & Scope of Work
- 02 Approach
- 03 Leaching Test Results & Modelling Approach – Case Studies
- 04 Existing Frameworks
- 05 Comparison
- 06 Conclusions

01

Background & Scope of Work

Background

- **Threshold limit values** for soil and groundwater are **not always defined** in some European countries, and PFAS specific regulatory frameworks are missing or have been recently elaborated.
- **EU Directive 2020/2184: PFAS in drinking water.** In some EU countries these values have been **adopted as groundwater threshold values.**
- **US-EPA (2024)** has recently published enforceable **MCLs**. This standard will reduce exposure **drinking water** to the lowest effective implementation.
- **Leaching test** are gradually incorporated in **Regulatory Frameworks** (for example: Germany, Flanders (Belgium))

EU Directive

100 ng/l Σ 20 PFAS

500 ng/l Total PFAS

US-EPA

Maximum Contaminant Levels

PFOA 4 ng/L

PFOS 4 ng/L

PFHxS 10 ng/L

GenX 10 ng/L

PFNA 10 ng/L

PFNA, PFHxS, PFBS, GenX

Hazard Index < 1

Scope of Work & Objective

When dealing with a potentially contaminated site or during a site assessment in the context of a due diligence for a site acquisition shall we, as part of the industry, look at the presence of PFAS? No “formal” liabilities if compared to the regulatory requirements could be recognized, however **how a potential impact** of these constituents **can be quantified**?

The **absence of specific threshold concentrations** for at least some selected PFAS in groundwater, but **mostly in soil**, needs to be addressed as the public awareness for the presence of these recalcitrant compounds is now recognized as widespread in the environment.

The objective of this work is to provide a **perspective for the assessment of PFAS in the environmental matrices in the absence of specific regulations**, focusing on **leaching test** as a tool to project groundwater by comparing lab results to Regulatory Threshold values.

02

Approach

Approach

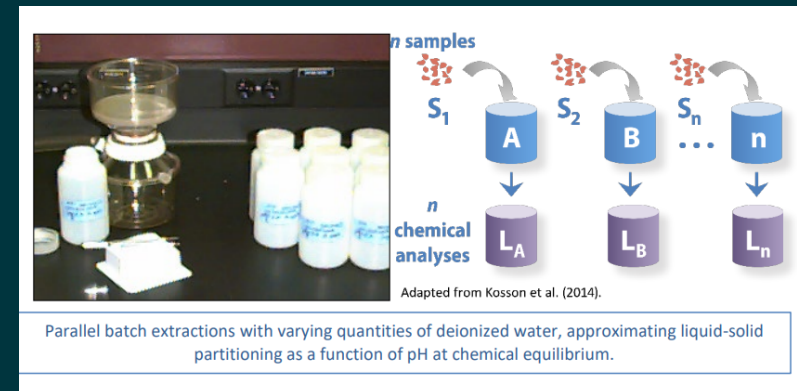
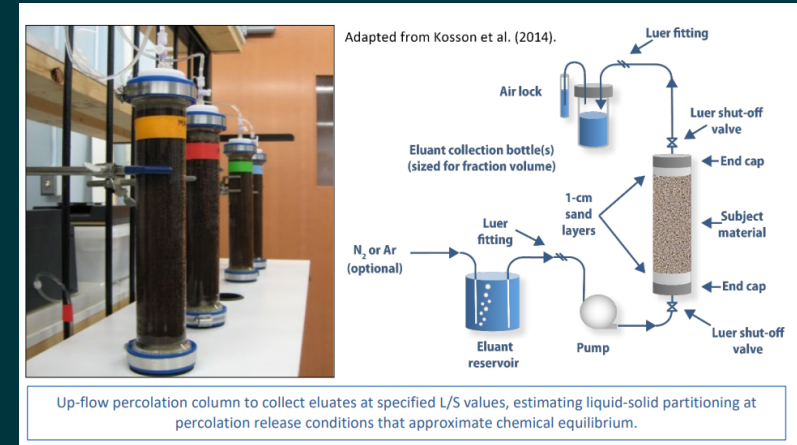
- **Derive Site Specific Soil Concentrations** based on Leaching tests according to the LEAF protocol for a site in Italy and Switzerland
- **Screening** existing **Regulatory Threshold Limit values** that have been derived in some European Countries (such as, Belgium and the Netherlands) and in various EU States
- **Comparison** of the Site Specific Derived Soil Concentrations to existing Regulatory Threshold Values focusing on groundwater protection

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Leaching Test Results & Modelling approach

Application of LEAF protocol

- Application of **Leaching Environmental Assessment Framework** (LEAF), developed by the US Environmental Protection Agency (EPA), including laboratory **column tests** (which better represent the infiltration process through the unsaturated part of the soil), and the **static test** with different L/S
- As an example of adopting site-specific approaches, in the absence of soil threshold concentrations were requested in Switzerland and Italy, and it is believed that will be useful for developing improved soil target concentrations that can be used to enhance site investigations and management for PFAS-impacted sites.
- Collection of **soil samples** for **site specific** properties and soil analyses



Leachate tests



Figure 1. Column equipment for dynamic leaching test.

- EPA method 1314 (**column test**): (which better represent the infiltration process through the unsaturated part of the soil), production of eluates by dynamic leaching, starting from soil samples, by liquid-solid partitioning, as a function of the time-varying L/S ratio.
- EPA method 1316 (**static test**) production of eluates, starting from soil samples, by liquid-solid partitioning, according to the variation of the L/S ratio. The method in question is used to monitor the quantity of inorganic and organic non-volatile substances PFAS contained in soil samples.

Leaching test results and modelling approach

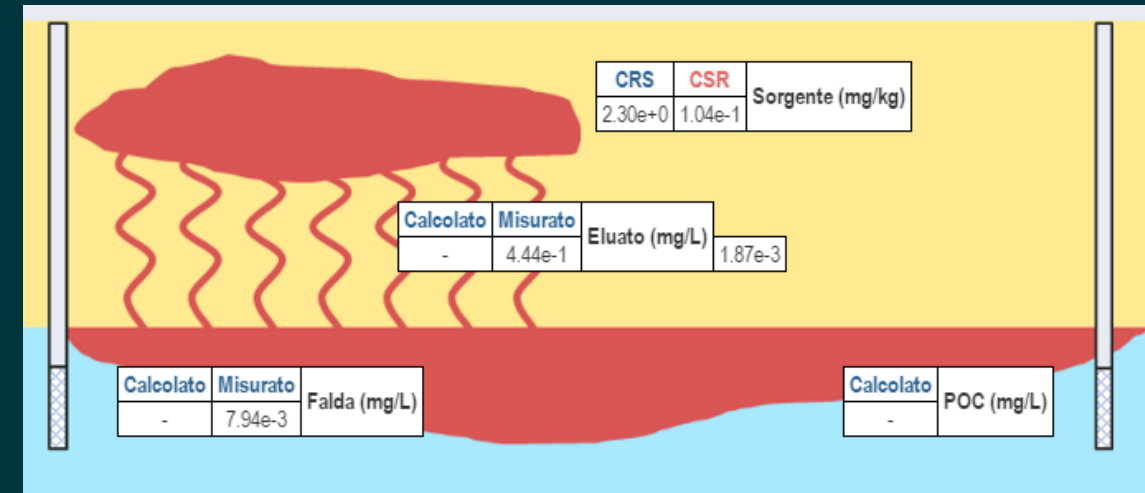
- Source
 - Complex chemistry
 - Interactions with soil geochemistry
 - Vadose Zone
 - Sorption and retardations
 - Precursor transformations
 - Groundwater
 - Sorption and retardations
 - Precursor transformations
- 
- Nature of release
 - Extent
 - Duration
 - Soil type
 - Permeability
 - Clay content
 - Organic content
 - Hydrogeology
 - Advective transport
 - Geochemistry

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Leaching Test results and modelling approach – CASE STUDY 1

CASE STUDY 1 - Leaching test results and modelling approach

- Analysis of leaching test results, with identification of the most significant constituent of the mixture (PFOS)
- Calculation of site-specific partition coefficient
- Application of unsaturated transport model to groundwater and calibration with groundwater quality at monitoring well located below the source area
- Application of the migration pathway transport analytical model to the Point of Compliance (POC) at the site downgradient boundary
- Validation of the modelled concentration at the POC with the numerical model calibrated in 2021 for Area 1.
- Validation of the site-specific PFOS Log k_{oc} value with other experimental values reported in the literature
- Calculation of target concentrations in the source area both in the leachate and in soil (dry matter) with site specific partitioning coefficient



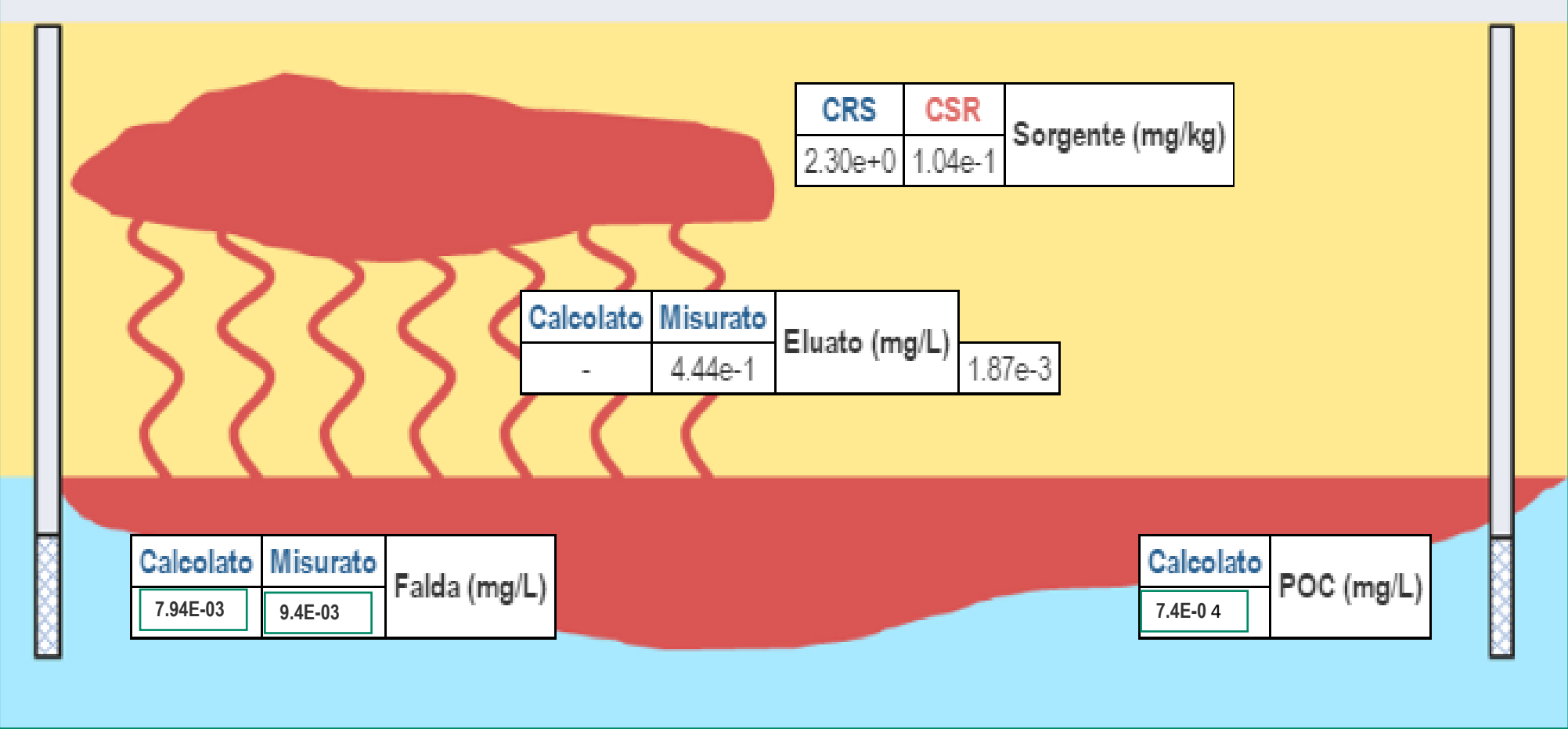
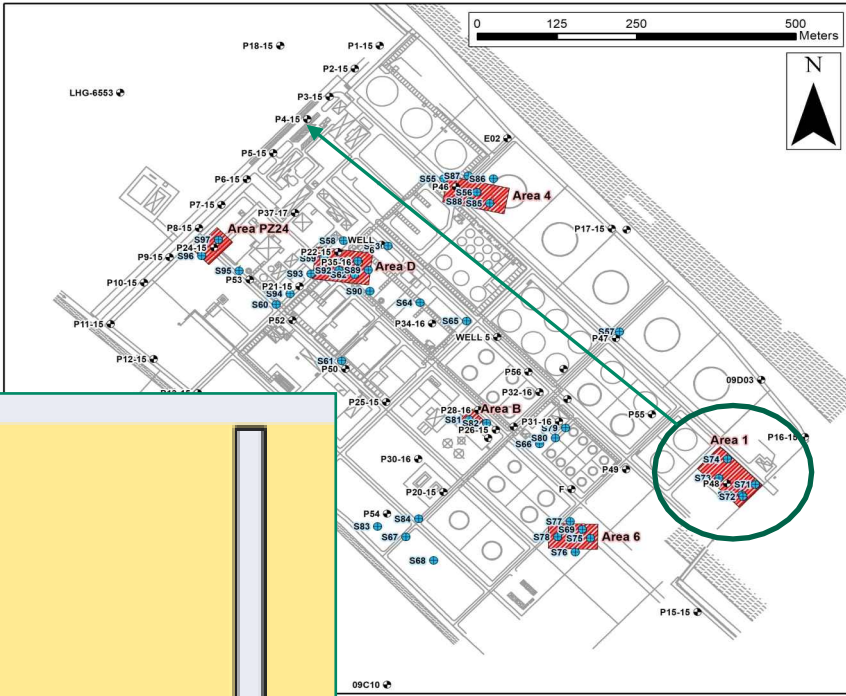


Area 1

	Concentration in soil mg/kg	Concentration in soil mg/kg	Leaching test 2:1 mg/l	Leaching test - Dynamic - EPA 1314 sum of concentrations T1÷T9 mg/l	Leaching test - Static - EPA 1316 maximum concentration T1÷T5 mg/l	GW concentration POC=0 mg/l			GW concentration POC>0 mg/l			
	S74 (0-1 m) - raw material	S113 (0-1 m)	S74 (0-1 m)	S113 (0-1 m)	S113 (0-1 m)	P-48			P-3			
	May-21	Aug-22	May-21	Aug-22	Aug-22	10/2/2020	5/27/2021	3/28/2022	1/22/2020	9/30/2020	5/27/2021	3/29/2022
PFBA	0.00056	<0,00093	0.00023	0.001238	0.0012	0.00011	0.00043	0.00014	0.000032	0.000037	0.00004	0.000046
PFBS	0.000036	0.00116	0.000017	0.002278	0.00199	0.000022	0.000021	0.0000061	0.000017	0.00002	0.0000094	0.0000059
PFHpA	0.0017	0.0044	0.00072	0.014884	0.008	0.000064	0.0011	0.00018	0.000044	0.000051	0.000074	0.000067
PFHxA	0.0038	0.0034	0.00077	0.009026	0.0072	0.00018	0.00086	0.00031	0.000078	0.00012	0.000085	0.00012
PFHxS	0.0122	0.045	0.0036	0.21234	0.095	0.00016	0.0015	0.00024	0.00014	0.00027	0.0002	0.00024
PFNA	0.004	0.00212	0.00049	0.004163	0.00147	0.000007	0.000051	0.000015	0.0000013	<0,00001	0.0000017	0.0000024
PFOA	0.034	0.045	0.016	0.19803	0.101	0.00009	0.0029	0.00015	0.00011	0.00018	0.00016	0.00019
PFOS	2	2.3	0.69	3.0872	0.444	0.0004	0.0094	0.00085	0.0003	0.00043	0.00049	0.00064
PFPeA	0.00146	0.00208	0.00075	0.004231	0.0038	0.00029	0.0012	0.00052	0.0001	0.00015	0.00014	0.00017

Area 1

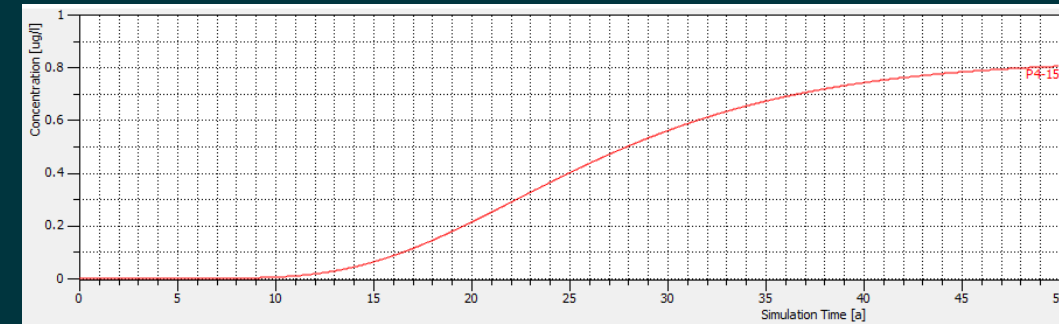
- [Area 1.xlsx](#)
- EPA 1316



Validation of the modelled concentration at the POC with the numerical model calibrated in 2021 for Area 1

- The concentration of PFOS modelled at the POC was validated with the use of a finite elements numerical model (Feeflow® code), calibrated with 2021 groundwater concentrations
- **50 years** simulation time
- Area 1 PFOS mass-flux (2nd-kind) BC as from calibrated 2021 numerical model (i.e. $1.7\text{E-}04$ g/m²/d), corresponding to a flux deriving from leachate concentration of **0.444 mg/l (leachate test EPA 1316 results)**
- Numerical model simulated PFOS concentrations at POC of **$8.0\text{E-}04$ mg/l**
- Analytical model simulated PFOS concentrations at POC of **$7.4\text{E-}04$ mg/l**
- Average measured (Jan and Oct 2020, May 2021) PFOS concentration at POC of **$6.7\text{E-}04$ mg/l**

POC simulated PFOS concentrations



Validation of the site-specific Log Koc value for PFOS - Area 1

$$K_{ws} = \frac{C_{sol}}{C_{tot}} = \frac{\rho_s}{(K_d \cdot \rho_s + \theta_w + H \cdot \theta_a)}$$

$$K_d = K_{oc} \times f_{oc}$$

$$k_{oc} = \frac{\rho_s - k_{ws}\theta_w - k_{ws}H\theta_a}{\rho_s * k_{ws} * f_{oc}}$$

INPUT	
Csol (mg/l):	0.444
Ctot (mg/kg)	2.3
ρs (g/cm3)	1.7
θw (-)	0.288
θa (-)	0.057
H (-)	1.81E-05
foc (-)	0.01052

OUTPUT	
Kws	0.193043
Kd	5.01E+00
Koc	4.76E+02
log Koc	2.7

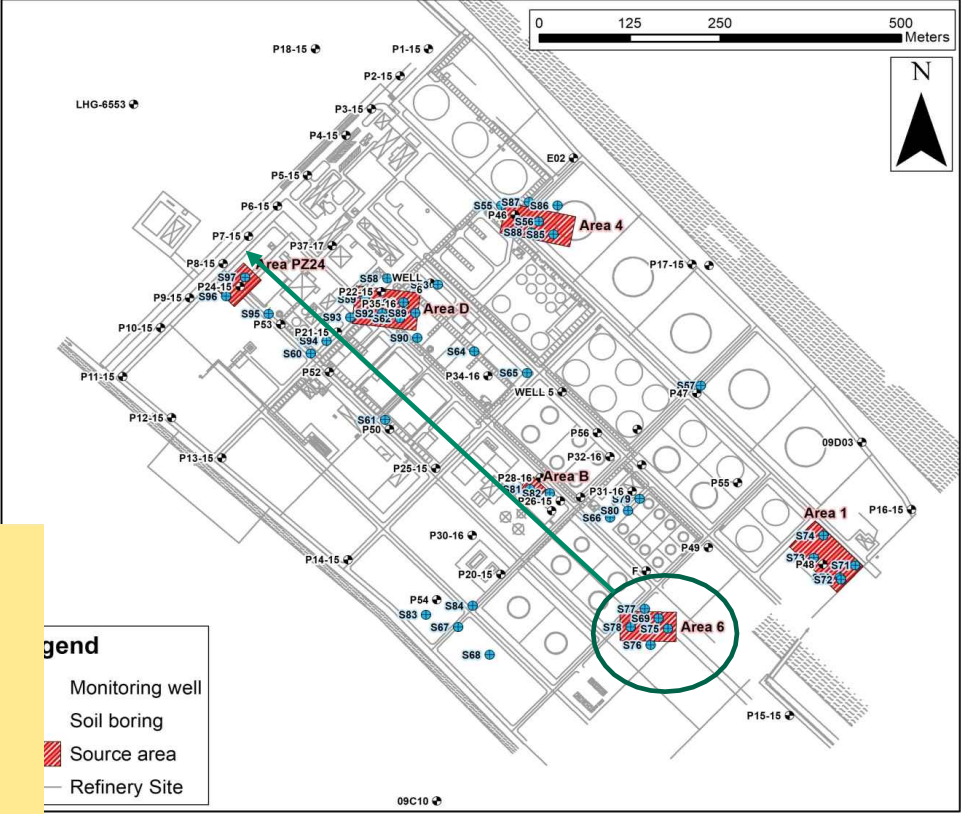
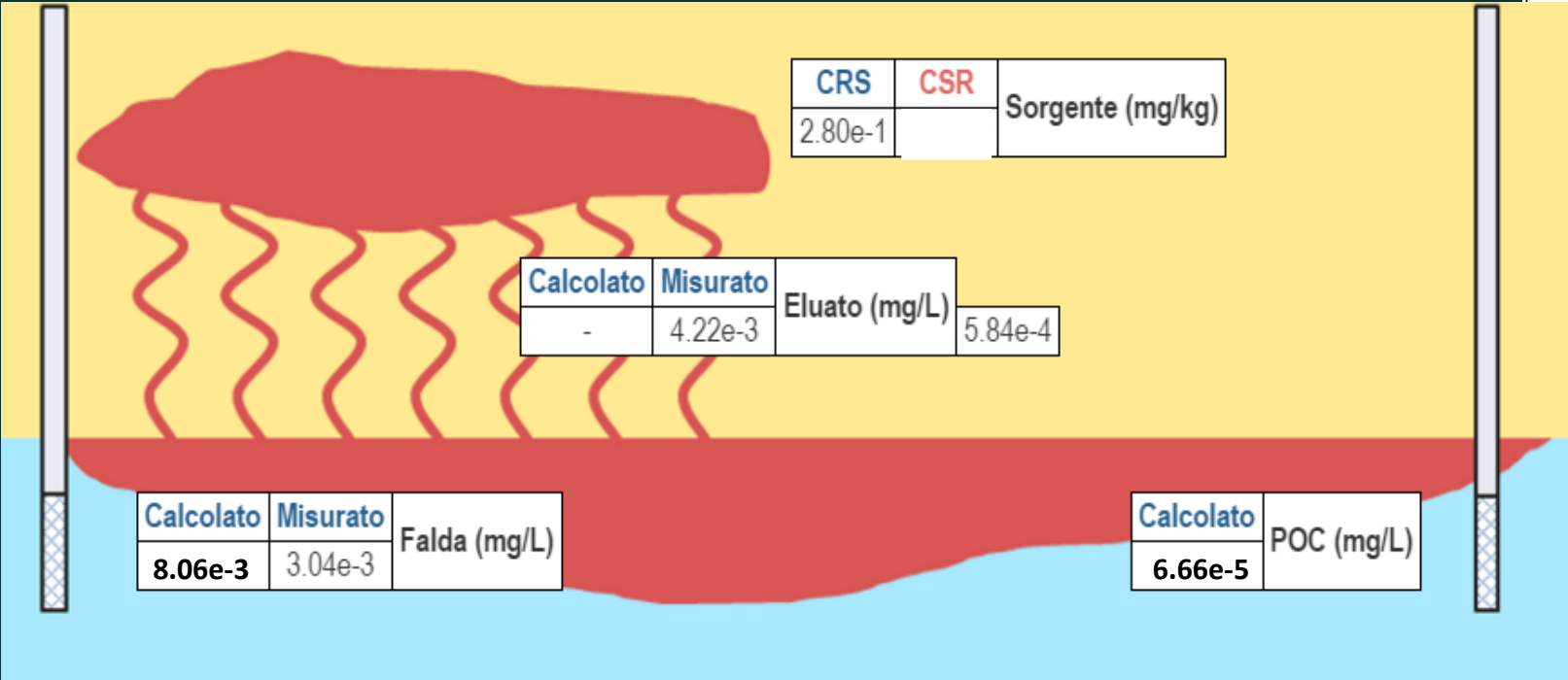
Table 1

Published distribution coefficients derived from laboratory sorption experiments (logK_d, logK_{oc}).

Sample	log K _d (log l kg ⁻¹)	log K _{oc}	References
PFOS			
Five sediments with C _{org} of 0.56–9.66%, dithionite–citrate–bicarbonate extractable iron of 116–1025 μmol/g	–	2.7	Higgins and Luthy (2006)
Ottawa sand standard	2.81	–	Johnson et al. (2007)
Kaolinite	5.31	2.4	Johnson et al. (2007)
Goethite	7.88	–	Johnson et al. (2007)
High iron sand standard	8.90	–	Johnson et al. (2007)
Lake Michigan sediment	7.52	2.4–2.6	Johnson et al. (2007)
Clay	18.3	2.8	3 M corp. cited in Johnson et al. (2007)
Clay loam	9.72	2.6	3 M corp. cited in Johnson et al. (2007)
Sandy loam	35.3	3.1	3 M corp. cited in Johnson et al. (2007)
River sediment	7.42	2.8	3 M corp. cited in Johnson et al. (2007)
Water treatment sludge	120	2.5	3 M corp. cited in Johnson et al. (2007)
Paddy soil (0.91% C _{org}) at c(water) = 5.0 μg l ⁻¹	–	3.3	Chen et al. (2009)
Crude oil spiked to soil	–	4.2–4.4	Chen et al. (2009)
Oil-derived black carbon (diesel soot), c(water) = 5–50 μg l ⁻¹ at pH = 5.05	–	3.0–3.1	Chen et al. (2009)
Aquifer sediment Washington County, USA (t = 0)	0.1	2.5	Ferrey et al. (2009)
Aquifer sediment Washington County (t = 574 d)	–0.7	2.8	Ferrey et al. (2009)
Taihu Lake	–	2.9 ± 0.6	Yang et al. (2011)
Sediment 1	1.2	4.7	Ahrens et al. (2011)
Sediment 2	1.2	3.0	Ahrens et al. (2011)
Sediment 3	1.9	3.8	Ahrens et al. (2011)
Average PFOS (log l kg ⁻¹)		3.0	
Standard deviation PFOS (log l kg ⁻¹)		0.7	
Coefficient of variation PFOS (%)		21	
Median PFOS (log l kg ⁻¹)		2.8	

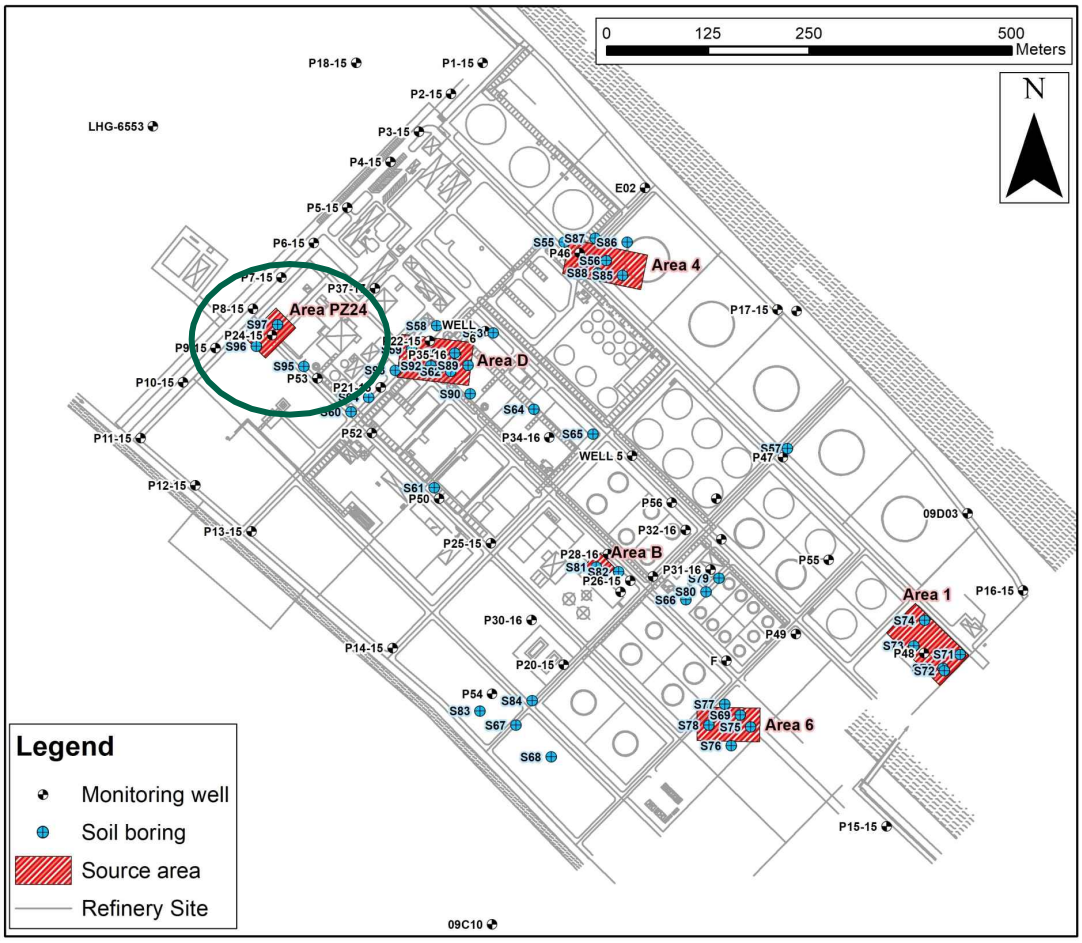
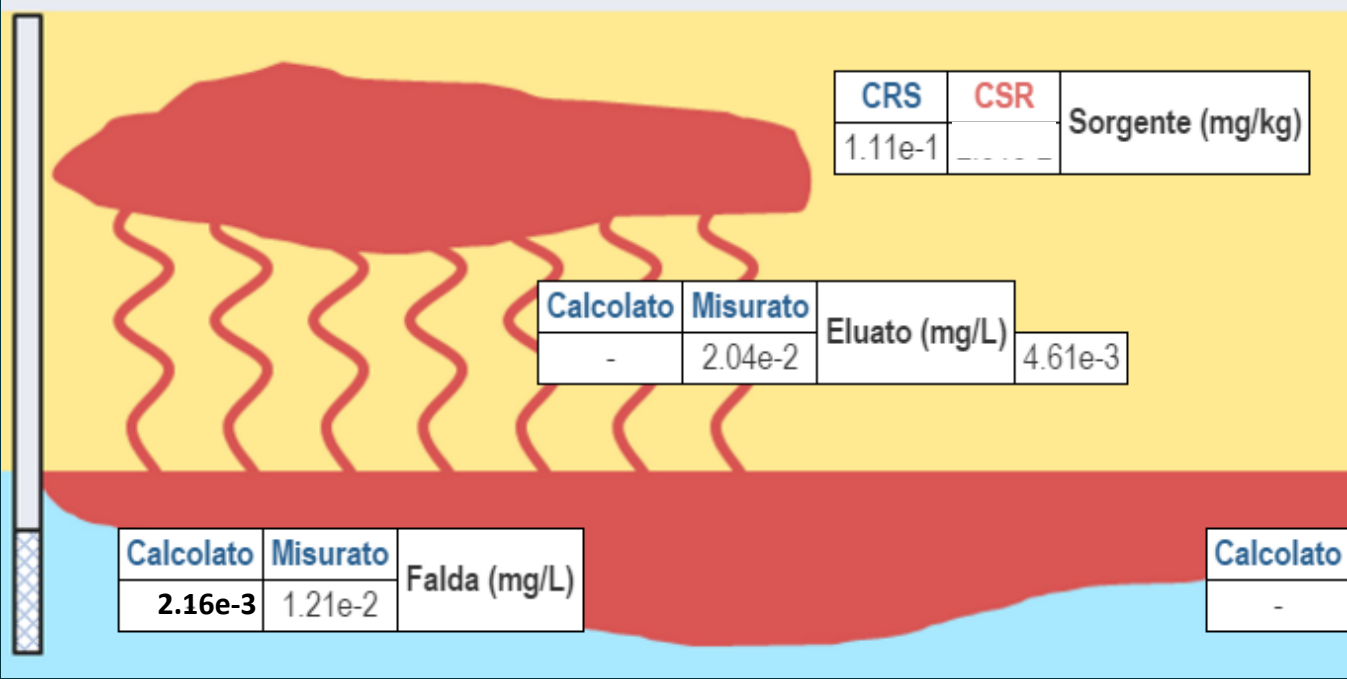
Area 6

- [Area 6.xlsx](#)
- EPA 1314
- P28-16, located at approximately 150 m from source



Area PZ24

- [Area PZ24.xlsx](#)
- EPA 1314
- POC = site downgradient boundary, likely getting impact from other sources located upgradient



7.40E-04

Conclusions

- Significant differences in leaching test results conducted with 2:1 L/S with results obtained from EPA 1314 and 1316 were recorded in Area 1. For Area 6 and PZ24 results of EPA 1314 and 2:1 L/S were similar.
- The work has been performed only on 3 source areas; additional validation of the method applied may be required
- PFOS site-specific concentrations associated with protection of groundwater ranged 0.0024-1.44 mg/kg

Nice to have

- Comparison with PFAS partitioning model (Brusseau et al , 2019, 2022)
- Collect lysimeters samples for comparison

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Leaching Test results and modelling approach – CASE STUDY 2

CASE STUDY 2 - Leaching test results applied for the calculation of site-specific organic carbon partition coefficients

- Analysis of soil samples
- Analysis of leaching test results (PFOA, PFOS, HFPO-DA_GenX)
- Calculation of site-specific organic carbon partition coefficients (K_{oc})
- Calculation of risk-based target concentrations in the soil of the source area using the site-specific organic carbon partition coefficients

Collected samples and leaching tests

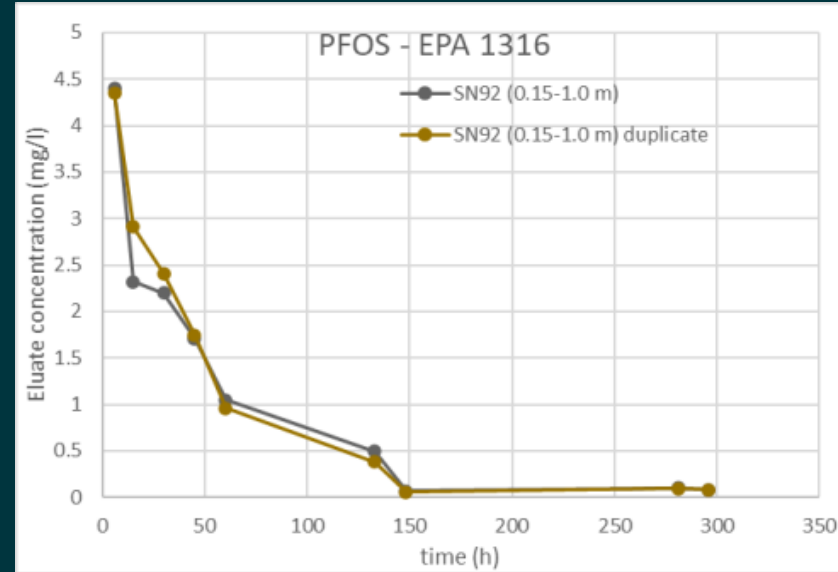
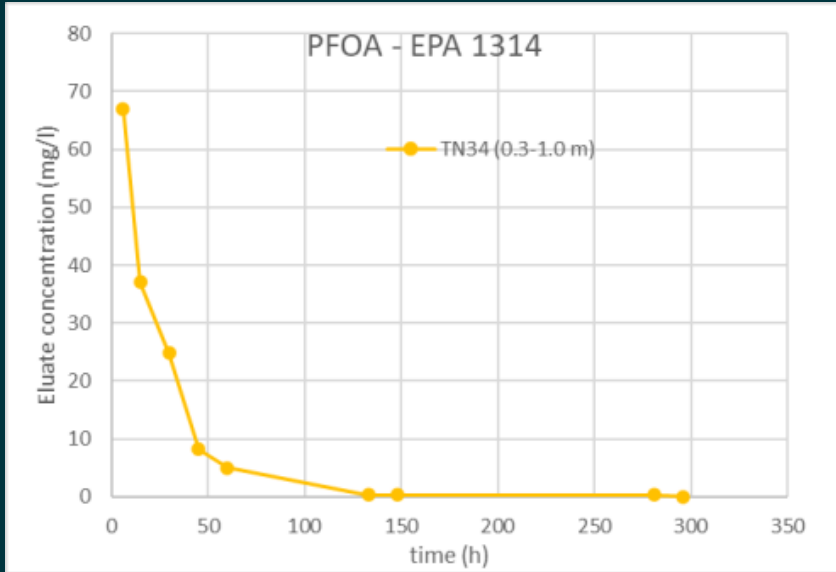
- n. 8 soil samples
- n. 3 duplicates (verification analysis)
- n. 8 leaching tests 2:1 (APAT – ISS)
- n. 8 leaching tests – Dynamic EPA 1314
- n. 8 leaching tests – Static EPA 1316

→ insufficient data for statistical calculations

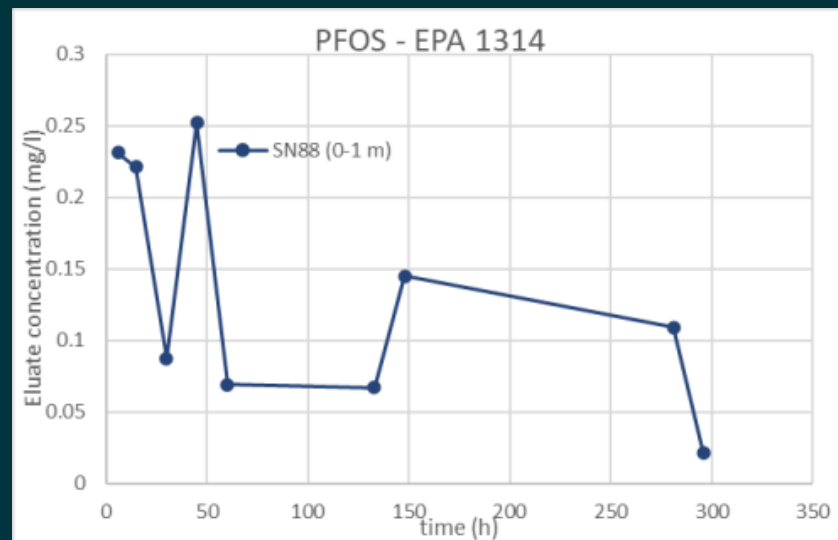
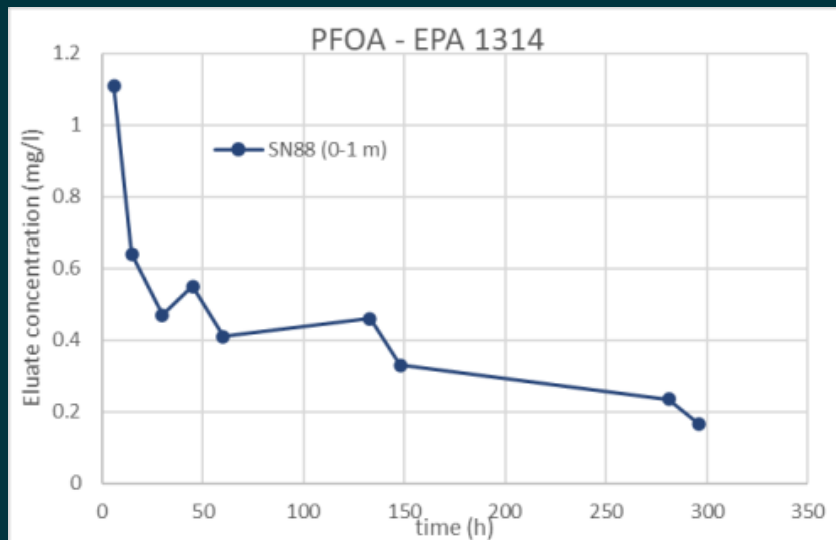


Soil sample	Duplicate	Analytes	GenX	C6O4	Leaching test 2:1	EPA 1314	EPA 1316
SN41 (4-5 m)		BTF			X	X	X
SN41 (4-5 m)	X	BTF					X
TN34 (0.3-1.0 m)		PFAS	X	X	X	X	X
TN34 (0.3-1.0 m) duplicate	X	PFAS	X	X			X
SN44 (1-2 m)		GenX	X		X	X	X
SN88 (0-1 m)		PFAS			X	X	X
SN89 (0.75-1 m)		C6O4		X	X	X	X
TN93 (1-1.4 m)		BTF			X	X	X
SN92 (0.15-1.0 m)		BTF, PFAS	X	X	X	X	
SN92 (0.15-1.0 m) duplicate	X	BTF, PFAS	X	X	X	X	

Assessing the representativeness of the obtained results



Valid test



Non-representative test

Results

- site-specific organic carbon partition (Koc) values
- higher Koc values from 2:1 L/S (APAT) test compared to those from EPA 1314-1316
- replicability of the results (validation through duplicate tests)

PFOA

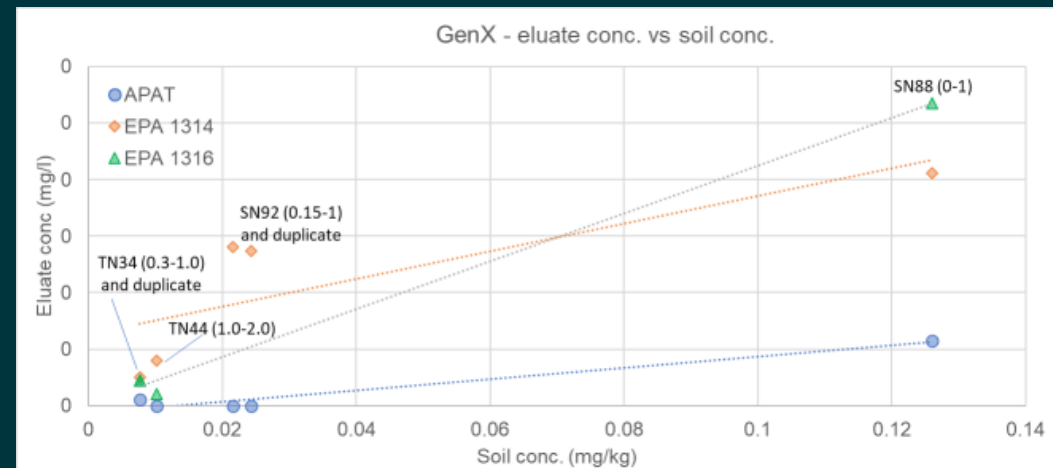
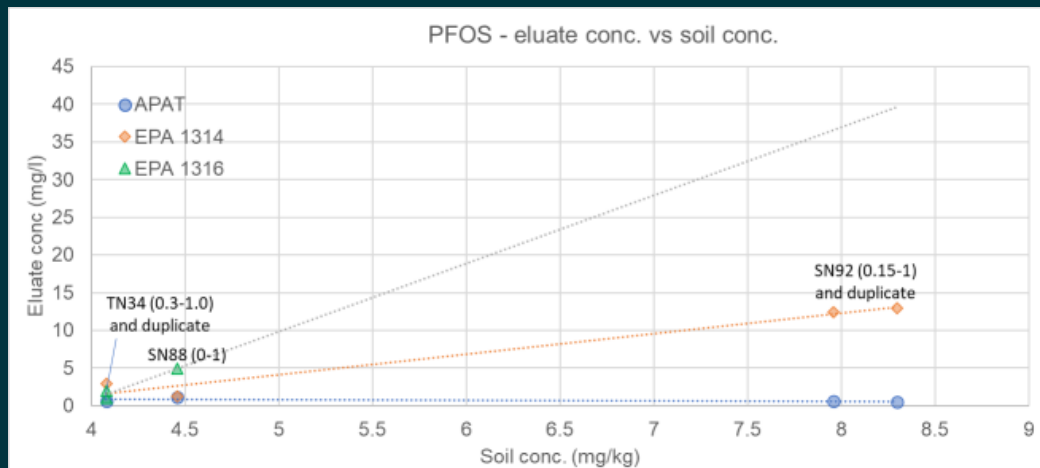
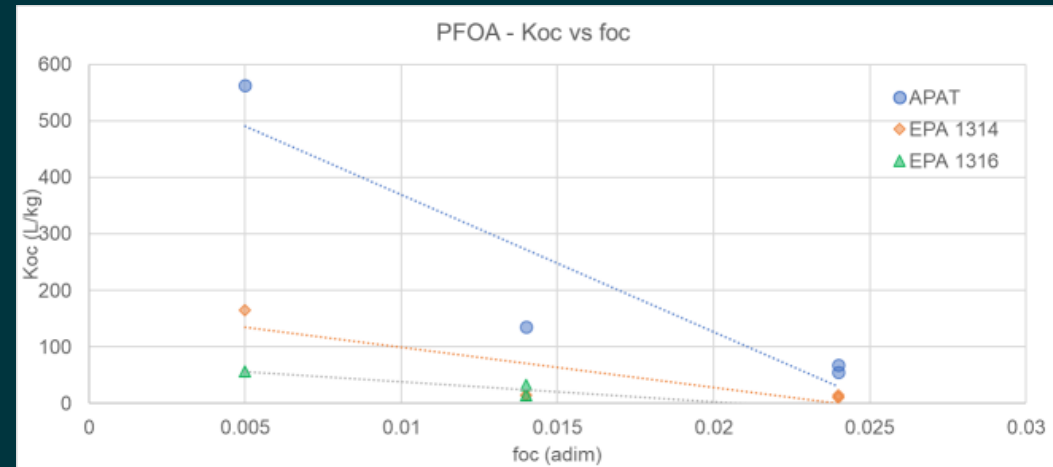
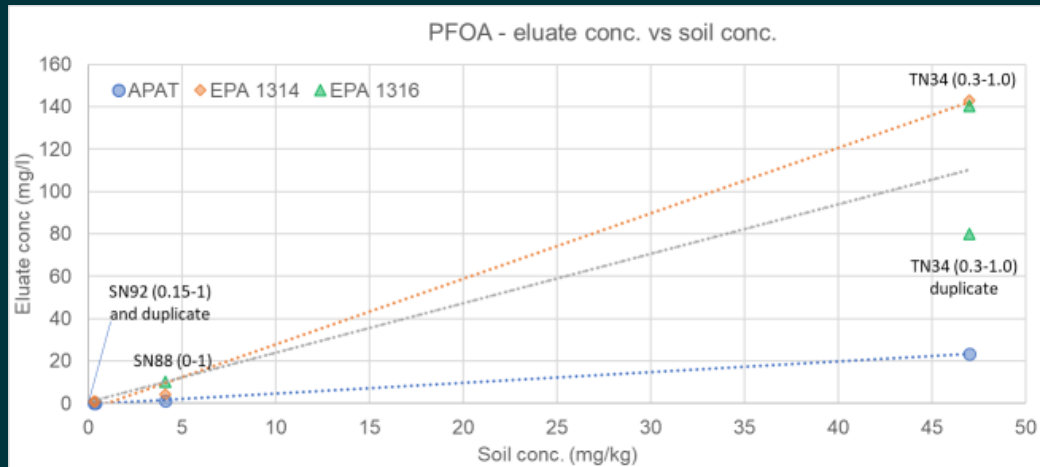
Sample ID	foc	clay (%)	Soil conc. (mg/kg)	TEST	Eluate conc. (mg/l)	Koc (L/kg)
TN34 (0.3-1.0 m)	0.014	15.3	47	APAT	23.30	135.13
				EPA 1314	142.85	14.55
				EPA 1316	140.40	14.96
TN34 (0.3-1.0 m) - d	0.014	15.3	47	EPA 1316	80.00	33.01
SN92 (0.15-1 m)	0.024	9.8	0.35	APAT	0.20	68.16
				EPA 1314	0.74	14.93
SN92 (0.15-1 m) - d	0.024	9.8	0.28	APAT	0.19	55.69
				EPA 1314	0.75	10.84

PFOS

Sample ID	foc	clay (%)	Soil conc. (mg/kg)	TEST	Eluate conc. (mg/l)	Koc (L/kg)
TN34 (0.3-1.0 m)	0.014	15.3	4.08	APAT	0.59	488.37
				EPA 1314	2.94	90.28
				EPA 1316	1.95	140.19
TN34 (0.3-1.0 m) - d	0.014	15.3	4.08	EPA 1316	1.09	258.42
SN92 (0.15-1 m)	0.024	9.8	7.96	APAT	0.60	547.10
				EPA 1314	12.43	21.93
SN92 (0.15-1 m) - d	0.024	9.8	8.3	APAT	0.50	681.42
				EPA 1314	13.00	21.85

Results

- PFOA-PFOS-GenX: direct correlation between concentration in soil and in the leachate
- PFOA: inverse correlation between organic carbon fraction (foc) and organic carbon partition coefficient (Koc)



Results

- Range of the derived site-specific levels for the protection of groundwater

Analyte	Italian Soil Threshold Values (mg/kg)		Risk-based Soil Values for the protection of groundwater (mg/kg)	
	Residential use	Industrial use	min	max
HFPO_GenX	0.00007	0.00007	0.00052	9.68
PFOA	0.96	15	0.0154	11.4
PFOS	0.96	15	0.0789	1.83

Conclusions

- Significant differences in leaching test results conducted with 2:1 L/S with results obtained from EPA 1314 and 1316
- Insufficient data for statistical calculations
- PFOA: inverse correlation between organic carbon fraction (foc) and organic carbon partition coefficient (Koc)
- Risk-based levels for the protection of groundwater:
 - wide variability (1 to 4 orders of magnitude)
 - significant differences (higher or lower) compared to regulatory values

Nice to have

- Many more samples to perform leaching tests on
- Collect lysimeters samples for comparison

04

Existing Regulatory Threshold Values & Frameworks

Regulatory Frameworks with focus on protection groundwater (Selection)

- Flanders (Belgium)

- New temporary framework (potentially applicable as of Q4 2024)
- Threshold values related to actual use (does not take protection of groundwater into account)
- Diffuse pollution – reuse of soils
 - Specific Threshold values for free reuse of soils above groundwater table
 - Leaching test (static) mandatory as soon as PFAS are detected and soils are applied under groundwater table
 - Leaching test (static) mandatory in case Free Reuse Threshold values are exceeded but soils are not applied under groundwater table

- The Netherlands

- Stand still principal
- Tool: Region specific PFAS background maps (for example Port of Rotterdam versus rural area)
- No specific leaching tests required

- Germany

- Mantelverordnung
- Leaching tests required when applying PFAS containing soils
- Leaching tests for risk assessments

- USA (US-EPA)

- Specific SSL for protection of groundwater

PFAS Leaching tests are starting to get incorporated into Regulatory Frameworks

Selection of Soil Threshold Values

PFAS	Soil Threshold Values [mg/kg]					
	Agricultural Land Use		Residential Land Use	Green/Recreational Land use	Commercial/industrial Land use	
	Belgium (Flanders)	The Netherlands	Belgium (Flanders)		Belgium (Flanders)	The Netherlands
PFOS	0,0038	0,086	0,0049	0,11	0,268	0,059
PFOA	0,0025		0,0079	0,632	0,303	0,06
HFPO-DA_GenX						0,057

PFAS	Soil Quality Values [mg/kg]		
	UK	Sweden	Norway
PFOS	0,013	0,003	0,1
PFOA	0,019	-	-

PFAS	US EPA SSLs [mg/kg]		
	Screening Levels		Protection of Groundwater SSLs
	Resident Soil (mg/kg)	Industrial Soil (mg/kg)	Risk-based SSL (mg/kg)
PFOS	0,13	1,6	0,00031
PFOA	0,19	2,5	0,00091
HFPO-DA_GenX	0,23	3,5	0,000015

05

Comparison

Comparison

- Derived site-specific levels versus relevant Regulatory Threshold Values

	Derived Risk-based Soil Values for the protection of groundwater		Threshold values to protect groundwater		Regulatory Soil Threshold Values based on actual use, regardless of protection of groundwater					
			US EPA SSLs groundwater protection	Flanders (free reuse of soils) ⁽¹⁾	Italy		Belgium (Flanders)		USA	
	min	max			Residential	Industrial	Residential	Industrial	Residential	Industrial
HFPO_GenX	0.00052	9.68	0.000015	/	0.00007	0.00007	/	/	0.23	3.5
PFOA	0.0154	11.4	0.00091	0.003	0.96	15	0.0079	0.303	0.19	2.5
PFOS	0.0789	1.83	0.00031	0.003	0.96	15	0.0049	0.268	0.13	1.6
Sum PFAS	/	/	/	0.008	/	/	/	/	/	/

All values in mg/kg.dm unless stated otherwise

(1) New more strict leaching conditions not taken into account

Comparison to USA & Flanders

- Derived Threshold Values

- **Minimum and Maximum values** are higher compared to the most strict Regulatory Threshold values to protect the groundwater
- **Minimum and Maximum values** are higher compared to the Residential Threshold values in Flanders

- Regulatory Threshold values to Protect the Groundwater

- Too conservative?
- Low range Derived Site Specific Threshold Values a better pragmatic alternative?
- High range Derived Site Specific Threshold Values not conservative enough?

- Derived Threshold values as stand still principle

06

Conclusions

Conclusions

- Leaching Tests are gradually being incorporated into Regulatory Frameworks
- Derived Site Specific Threshold values based on Leaching Tests and/or modeling:
 - are useful in case regulatory Frameworks are missing
 - also an added in case generic Frameworks are in place.
- Additional research required

THANK YOU

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