AN EXPLORATORY STUDY ON CEC IN THE FLEMISH SOIL

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GENERAL KNOWLEDGE ON CEC

Widespread in the environment ➔ found in soil, sediments & groundwater

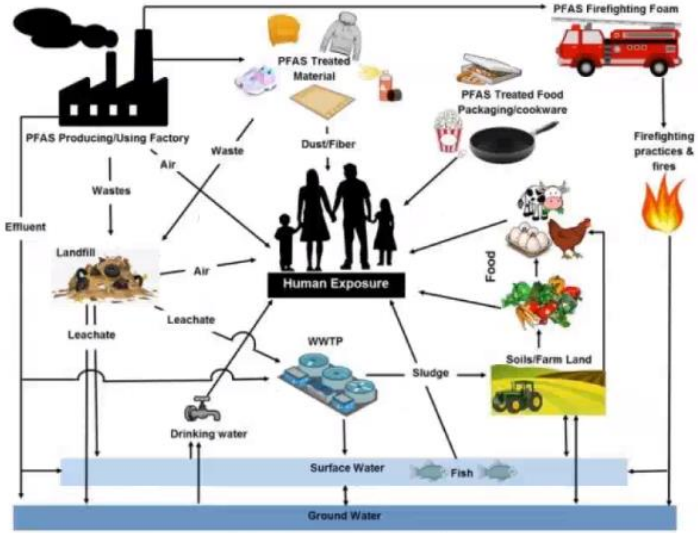
- wide application
- industrial emissions
- incidents
- dissolve well in water & absorb little to soil particles
- are resistant to biological & chemical degradation

Pose risk to human health & the environment

- their toxicity
- their persistence

Monitoring

- **Pesticides in surface water & groundwater (VMM)**
- **Soils = ?**



Human Exposure and sources of PFAS
Image: DWP, adapted from Oliaei et al. 2013.

➔ **EU soils** (Hvězdová et al. 2018; Silva et al. 2019)
pesticides in most of the soils studied

➔ **PFAS in soils** – Background levels versus contaminated sites (Brusseau, 2020)
present in soils across the globe & soil is a significant reservoir for PFAS

OBJECTIVES OF THE STUDY

➢ **2020 – study to derive background values for PFAS and some other CECs**

2 OBJECTIVES

1. **Deriving background values for PFAS**
2. **Research into the occurrence of a selected number of CECs in soils in Flanders**

Objective 1 – deriving background values for PFAS – is part of the

- **OVAM policy** ➔ SRS & limit values for re-use of soils/sediments
- **Flemish PFAS action plan** ➔ to identify sources and health effects to limit human exposure

Objective 2 – occurrence of a selected number of CECs in soil – is part of the

- **OVAM policy** ➔ identifying 'new' CECs and drawing up policy advice

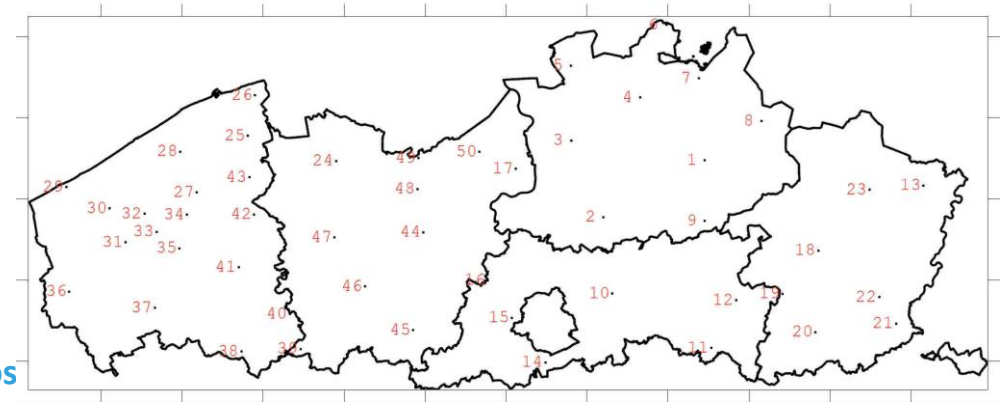
PFAS IN SOILS – LITERATURE REVIEW

Source	Location	PFAS	Range min. – max. (µg/kg dm)	Background values (µg/kg dm)
Rankin et al. (2016)	**Worldwide** (6 EU countries) 10 locations/12 PFAS	**PFOS** **PFOA**	<LOQ - **3,1** 0,015 - **2,7**	-
Vedagiri et al. (2018)	**US & Canada**	**PFOS** **PFOA**	0,02 – **1,95** 0,06 – **1,77**	-
Kikuchi et al. (2018)	**Sweden** 28 locations/15 PFAS	**PFOS** **PFOA**	<LOQ - **1,7** <LOQ - **0,57**	-
Wintersen et al. (2020)	**Netherlands** 100 locations/29 PFAS	**PFOS** **PFOA**	- -	1,4 (P95) 1,9 (P95)
OVAM (2020) ➔ **this study**	**Flanders** 50 locations/39 PFAS	**PFOS** **PFOA**	0,21 – **2,10** 0,19 – **2,20**	1,5 (P90) 1,0 (P90)

FIELD WORK – SET UP

Background values for PFAS in Flanders

- 50 unpolluted topsoil samples (0-0,2 m)
- 39 PFAS-compounds



➔ **starting point: 45 locations**

background values heavy metals (2006)

representative for PFAS ?

digital land use map, soil map & aerial photos

➔ **Selection = absence of**

PFAS production sites (3M & DuPont)

PFAS processing industry (paint industry, textile industry, paper industry, galvanic industry)

Firefighter areas, water treatment plants & landfills

Traffic roads, railways & residential areas

➔ **50 locations** = 1 location per 6 municipalities (1 per 275 km²)

STATISTICAL ANALYSIS FOR 39 PFAS

No outliers

PFBA, PFOS & PFOA ➔ sufficient data to derive background values

PFBA 100 %
PFOS 94 %
PFOA 72 %

	# > LOQ	min	max	Average	Geom. mean	Parameter	# > LOQ	Parameter	# > LOQ
PFBA	**50**	**0.35**	**2.60**	**0.762**	**0.688**	PFDoA	0	10:2 FTS	0
PFOS	**47**	**0.21**	**2.10**	**0.775**	**0.641**	PFTrDA	0	FOSA	0
PFOA	**36**	**0.19**	**2.20**	**0.558**	**0.469**	PFTeDA	0	MeFOSA	0
6:2 FTS	**27**	**0.21**	**1.00**	**0.407**	**0.377**	PFHxDA	0	EtFOSA	0
PFPeA	11	0.20	0.36	0.265	0.260	PFODA	0	FOSAA	0
PFHpA	5	0.21	0.27	0.238	0.237	PFPeS	0	MeFOSAA	0
6:2 PAP	5	0.31	1.60	0.942	0.833	PFHxS	0	EtFOSAA	0
PFHxA	2	0.26	0.39	0.325	0.318	PFHpS	0	8:2 PAP	0
PFBS	2	0.20	0.30	0.250	0.245	PFNS	0	6:2 diPAP	0
PFNA	1	0.24	0.24	0.240	0.240	PFDS	0	6:2/8:2diPAP	0
PFDA	1	0.21	0.21	0.210	0.210	PFDoS	0	HFPO-DA	0
8:2 diPAP	1	0.70	0.70	0.700	0.700	4:2 FTS	0	ADONA	0
PFUdA	0	0	0			8:2 FTS	0	PFECHS	0

OCCURRENCE OF PFAS IN FLANDERS

- **PFOS, PFOA & PFBA** structurally found ➔ **ubiquitous in the top layer**
- **P90-value = background value**

Descriptive statistics (µg/kg dm)								
Parameter	Valid N	Geomean	Minimum	Maximum	Per_5	Per_10	**Per_90**	Per_95
PFBA	50	0.688	0.350	2.600	0.390	0.415	**1.250**	1.500
PFOA	36	0.469	0.190	2.200	0.200	0.250	**0.960**	1.400
PFOS	47	0.641	0.210	2.100	0.240	0.270	**1.500**	1.700

The Netherlands (P95-value)

PFOS = 1,4 µg/kg dm
PFOA = 1,9 µg/kg dm

- **6:2 FTS** in **27/50** soil samples

SELECTION OF 52 CECS – CANDIDATE PESTICIDES

Occurrence of CECs in Flanders

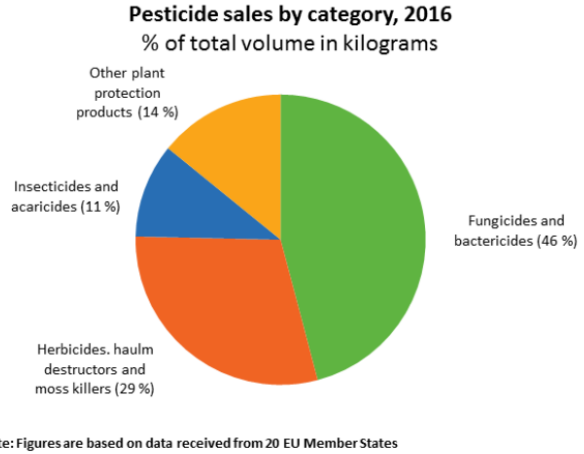
- same 50 topsoil samples
- pesticides, flame retardants, plastic components & medicines

➢ Selection of candidate pesticides

Crop protection products, biocides & degradation products
Research into *glyphosate* (herbicide) also includes *AMPA*

- **Pesticide use (EU & B)**
  - ➔ **EU** fungicides + bactericides (50%) > herbicides (30%) >> insecticides (10%)
  - ➔ **B** herbicides (37%) ~ fungicides + bactericides (35%) >> insecticides (7%)
- **Fytoweb**
- **Literature** - Silva (2019), Hvezdova (2018), Chiaia-Hernandez (2017)
- **Degradation rate:** DT50 > 30 days
- **Soil adsorption coefficient:** Koc > 1000

Pesticide use in Europe (Source: Eurostat)



Note: Figures are based on data received from 20 EU Member States

SELECTION OF 52 CECS – OTHER CECS

➢ Selection other CECs is based on literature

- *'Environmental pollutants in the terrestrial and urban environment'* (Herzke et al., 2019)
  study on behalf of the NEA (Norwegian Environmental Agency)
  monitoring of ambient air, soil and biota for the occurrence of common pollutants as **CECs**

- CECs in the **water compartment**
  ➔ **pharmaceuticals** (veterinary drugs) - **sulfamethoxazole** & **flubendazole** (Snow et al., 2017)
  ➔ **benzotriazoles** & **benzothiazoles** (anti-corrosion agents; e.g. on vehicles)
  ➔ **1,3-diphenylguanidine, hexa (methoxymethyl) melamine** & **1,3-dicylohexylurea** (traffic; rubber)

➢ RESULT = LIST of 52 CECs

OCCURRENCE OF 52 CECS IN FLANDERS - TABLE

*** AM (Analytical Methods)**
(1) GC-MS
(2) LC-ESI(+)MS/MS
(3) LC-ESI(-)MS/MS
(4) LC-MS/MS

N: # samples C > LOQ
H: # samples C > geom. mean

PFAS
6:2 FTS **27/14**

Insecticides (10)	N/H	AM*
op'-DDT	**33/16**	(1)
pp'-DDT	**45/18**	(1)
o,p'-DDE	0	(1)
p,p'-DDE	**43/18**	(1)
o,p'-DDD	6	(1)
p,p'-DDD	**27/12**	(1)
Chlorpyrifos	2	(1)
Chlorpyrifos-ethyl	5	(1)
Gamma-HCH (lindane)	3	(1)
Imidacloprid	2	(2)
Flame retardants (7)	N/H	AM*
PBDE's		
BDE-47	4	(1)
BDE-99	6	(1)
BDE-209	**20/9**	(1)
Hexabromobenzene	0	(1)
BTBPE	1	(1)
OPFR's		
Tricresylfosfaat (TCP)	4	(1)
EHDPP	3	(2)

Phenols (5)	N/H	AM*
Octylphenol	0	(3)
Nonylphenol	3	(3)
Bisphenol A	**18/6**	(3)
Bisphenol S	1	(3)
Bisphenol F	**16/6**	(3)
Fungiciden (15)	N/H	AM*
Boscalid	**15/8**	(2)
Epoxiconazole	5	(2)
Tebuconazole	5	(2)
Fluazinam	0	(2)
Chlorothalonil	0	(2)
Prothioconazole	0	(2)
Tebuconazole	5	(2)
Dimethomorph	3	(2)
Dodine	0	(2)
Hexachlorobenzene	**14/7**	(1)
Fenpropidin	0	(2)
Fenpropimorph	3	(2)
Difenoconazole	6	(2)
Mandipropamid	4	(2)
Prochlozar	0	(2)

Herbicides (11)	N/H	AM*
Glyphosate	**9/4**	(4)
AMPA	**29/15**	(4)
Terbutylazine	6	(2)
Aclonifen	3	(2)
Prosulfocarb	0	(2)
Flufenacet	7	(2)
Diflufenican	**9/4**	(2)
Benfluralin	2	(2)
Tri-allate	0	(2)
Pendimethalin	0	(2)
Phenmedipham	3	(2)

Farmaceuticals (2)	N/H	AM*
Flubendazole	0	(2)
Sulfametoxozole	0	(2)

Anti corrosion (2)	N/H	AM*
Benzotriazole	0	(2)
5-methyl-1H-benzotriazole	0	(2)

MONITORING IN FLANDERS

➢ Flemish human biomonitoring program (started in 2002) <> HBM4EU (European HBM)

- Monitoring human exposure to CECs in Flanders by measurements in blood & urine samples
- NO identification of the sources of exposure
- Useful information about the effectiveness of protective measures
- **Fact sheets*** for 11 of the 13 CECs (not for Boscalid en Diflufenican)

HBM4EU science and policy for a healthy future

➢ Monitoring of the water system by the Flanders Environment Agency (VMM)

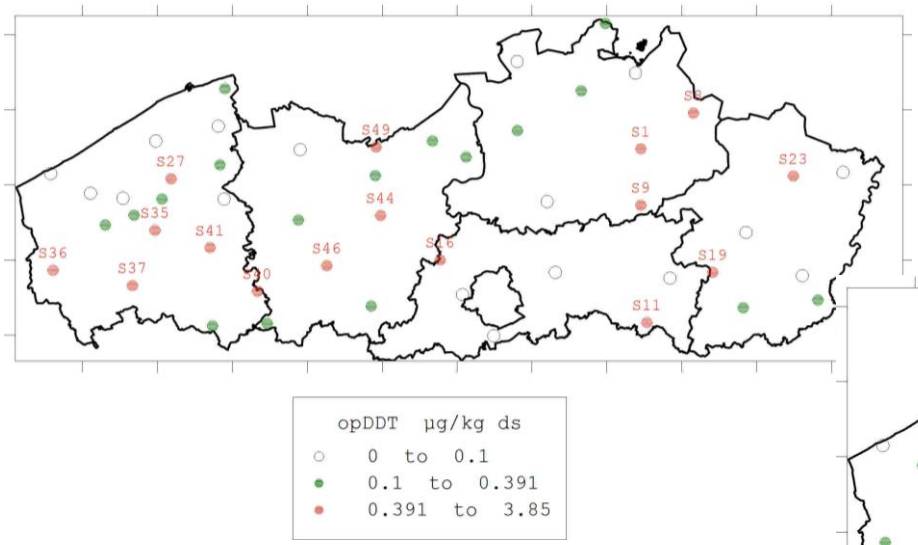
- Pesticides in surface water (VMM; 2017)
- Pesticides in groundwater (VMM, 2012)
- Monitoring the quality of sediments (VMM, 2016)
- Measuring pollutants in biota (started in 2015)

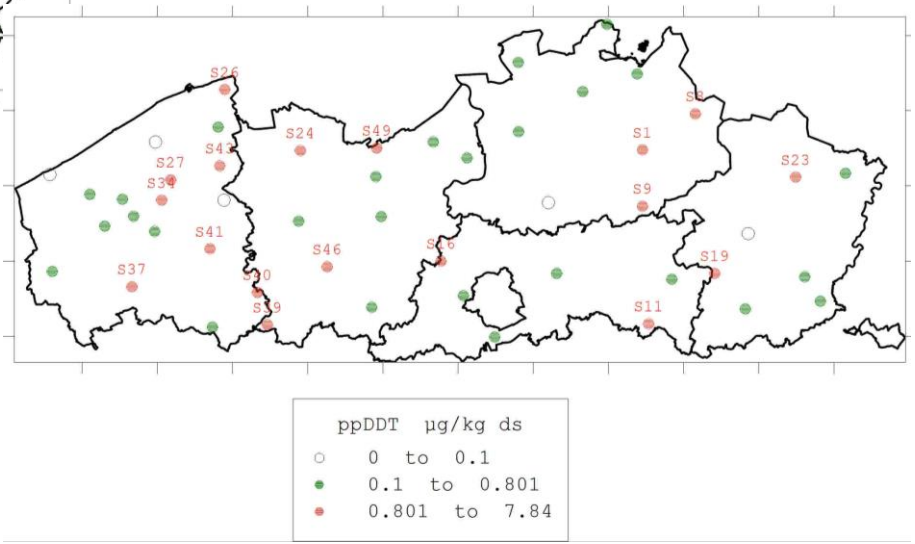
➢ Flemish Eel pollutant monitoring network (1994 – 2001)

- Institute of Forestry and Wildlife Management
- levels of pollutants (PCBs, organochlorine pesticides, heavy metals, …) in eels

* http://www.milieu-en-gezondheid.be/nl/wat-meten-we-factsheets

OCCURRENCE IN SOIL – OP-DDT (33/16) & PP-DDT (45/18)





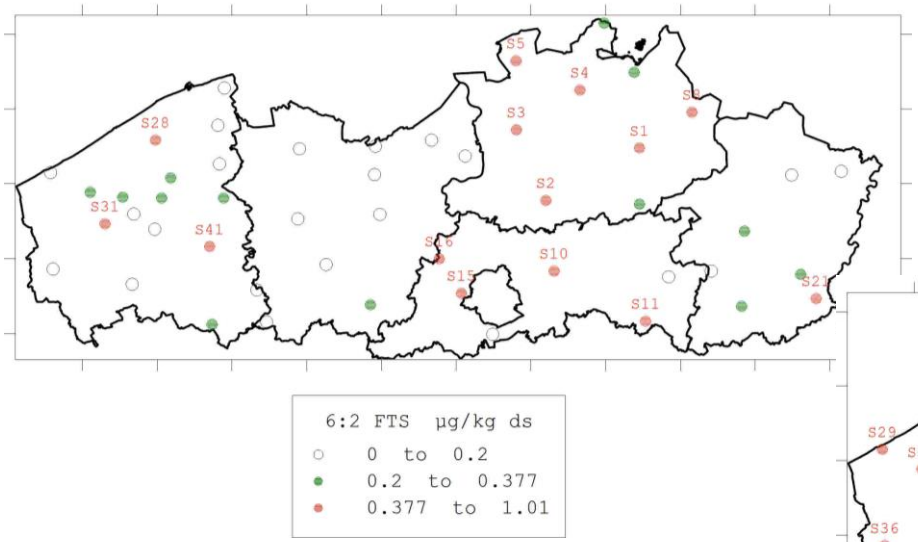
INFORMATION ON DDT & METABOLITES IN FLANDERS

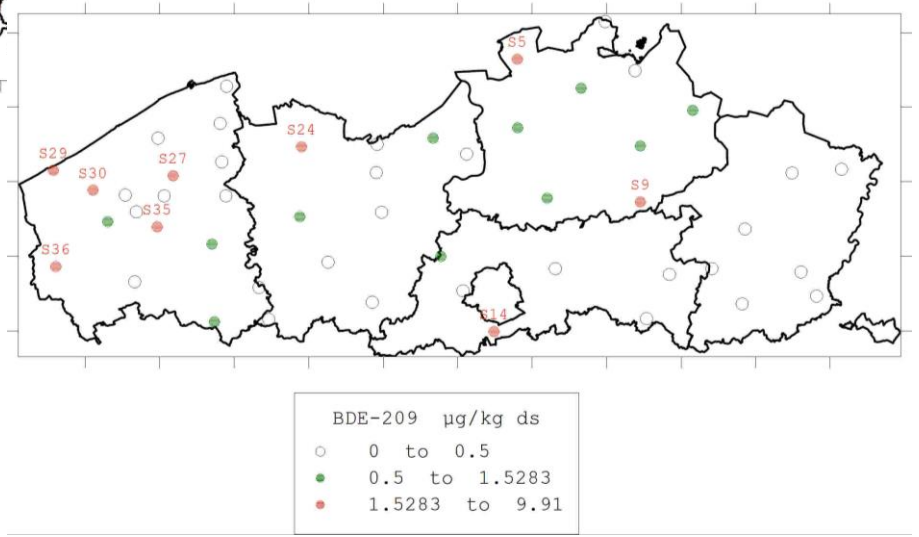
- **Banned** ➔ for agricultural applications in 1974
  ➔ for other applications in 1976
- **HBM** ➔ DDT metabolites continue to decline compared to previous campaigns
- **Water** ➔ DDT in surface water slightly increase compared to previous campaigns
- **Eel** ➔ pp-DDT appeared to decrease between 1994-2001, but increased again since 2002 (old stocks ?)
- **Soil** ➔ frequently measured
  ➔ concentrations up to 8 µg/kg dm

CONCLUSION

Traces of DDT and its metabolites are still present = 'historical' pollution

OCCURRENCE IN SOIL – 6:2 FTS (27/14) & BDE-209 (20/9)





INFORMATION ON 6:2 FTS IN FLANDERS

- **Limiting production** of PFOS/PFOA (EU directives)
  - ➔ substitutes such as 6:2 FTS are produced
  - ➔ **little scientific information on the PFAS precursor !**
- **HBM**
  - **12 PFAS**: PFOS, PFOA, PFHxS, PFNA, PFDA, PFUnDA, PFHxA, PFHpS, PFDoDA, PFHpA, PFBS & PFPeA
    - ➔ **6:2 FTS not included**
  - 10 of the 12 PFAS are detected in young people
- **Soil**
  - ➔ frequently measured above LOQ (27/50 samples)
  - ➔ concentrations for 6:2 FTS are low: 0.2 to 1.0 µg/kg dm

CONCLUSION

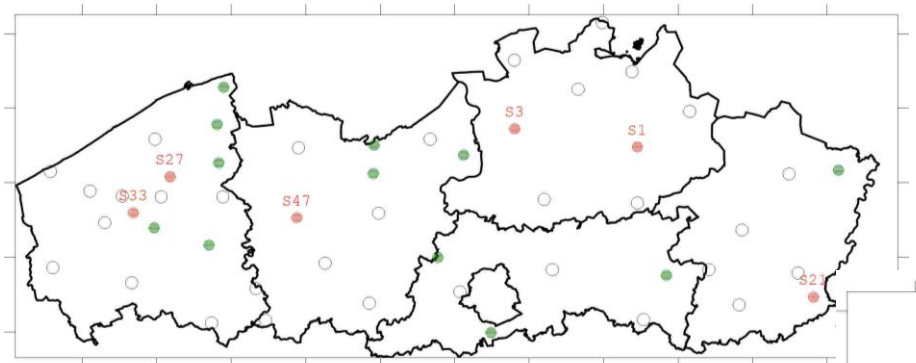
Since it is a substitute for PFOS and PFOA the parameter requires **attention in the future!**

➔ **Flemish PFAS action plan**

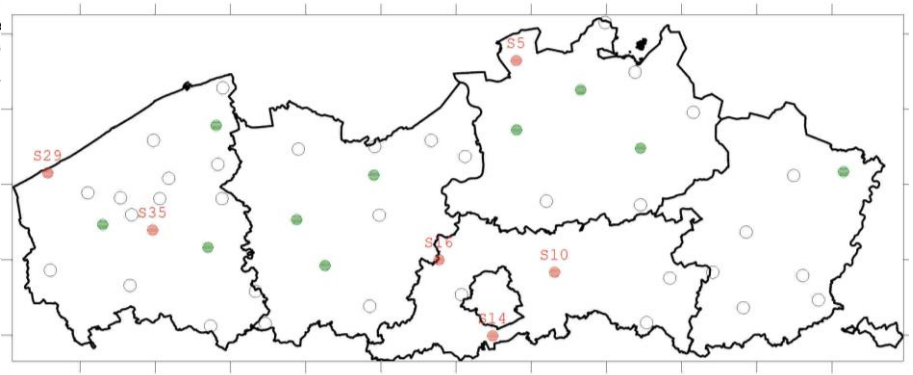
INFORMATION ON BDE-209 IN FLANDERS

- **Limited use**
  - ➔ added to the Stockholm Convention in 2017
- **HBM**
  - ➔ only BDE 47, 99, 153 & 154 are still measured in the blood samples of young people (latest campaign)
  - ➔ **BDE 209 was not included**
- **Soil**
  - ➔ frequently measured above LOQ (20/50 samples)
  - ➔ only in 9 soil samples above geom. mean
- **Sediment** ➔ frequently detected

OCCURRENCE IN SOIL – BISPHENOL A (18/6) EN F (16/6)



Bisphenol A µg/kg ds
- 0 to 0.2
- 0.2 to 0.578
- 0.578 to 3.483

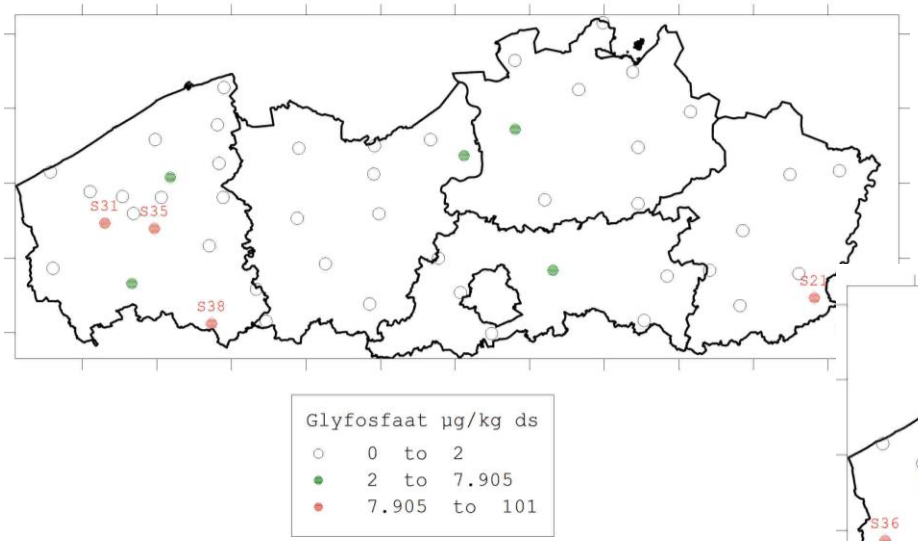


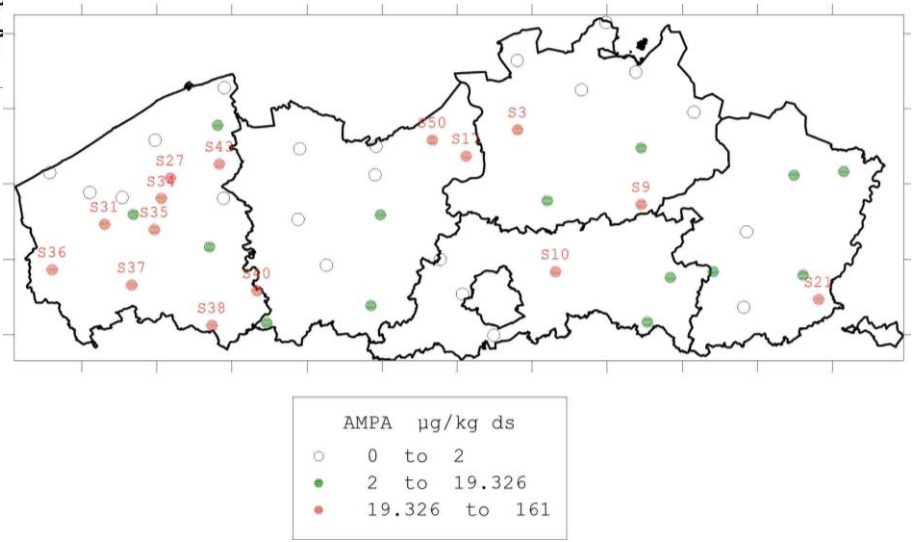
Bisphenol F µg/kg ds
- 0 to 0.2
- 0.2 to 0.526
- 0.526 to 3.947

INFORMATION ON BISPHENOL A & F IN FLANDERS

- **BPA partially banned**
  - ➔ in plastic feeding bottles since 2011 (EU)
  - ➔ in all food packaging for children under 3 years old since 2012 (B)
  - ➔ in thermal paper since 2020 (EU)
  - ➔ **BPA** was identified as **endocrine disrupting substance** in **2017** (ECHA)
  - ➔ substitutes such as **bisphenol S** and **bisphenol F** are used
    little scientific information on toxicity ➔ similar health effects ?
- **HBM** ➔ lower BPA levels in urine (young people) compared to previous campaigns
  - ➔ bisphenol F, S, B, Z and AF were also analyzed
  - ➔ BPA detected in 86%, BPF in 97% and BPS in 83% of the young people
- **Soil** ➔ BPA in 18/50 soil samples and BPF in 16/50 soil samples (<> BPS in 1/50)
- **wastewater** ➔ BPA enters the environment through wastewater

OCCURRENCE IN SOIL – GLYPHOSATE (9/4) & AMPA (29/15)





INFORMATION ON GLYPHOSATE & AMPA IN FLANDERS

- **Limited use**
  - ➔ 2017: the use by private individuals is banned (Flanders)
  - ➔ 2018: the use for non-professional users & private individuals are banned (BE)
  - ➔ exception: professionals with a phytolicense
- **HBM** ➔ glyphosate detected in 42% and AMPA in 56% of the young people
- **Water**
  - ➔ average concentration of glyphosate and AMPA in surface water ~ constant
  - ➔ concentrations in groundwater of glyphosate and AMPA: highest in 'de Polders'
  - ➔ AMPA is frequently detected in groundwater in the south of East and West Flanders
- **Soil**
  - ➔ glyphosate only in 9 of 50 soil samples, but AMPA in 29 soil samples
  - ➔ concentrations AMPA up to 160 µg/kg dm

KNOWN PREVENTION CAMPAIGNS AND ACTION PLANS

➢ Prevention campaigns

- Tips to reduce use and to limit exposure (professionals & general population)
- **HBM** ➔ fact sheets on website of 'Steunpunt Milieu en Gezondheid'
  ➔ raising awareness via local health consultation & health professionals
- **Campaigns**
  'KGA' ➔ against small and hazardous waste via intermunicipal companies & municipalities
  'Gezond uit eigen grond' (healthy gardening)
  'Zonder is gezonder' (Without is healthier) ➔ against (banned) pesticides

➢ Action plans

- **NAPAN** - Belgian national action plan for the reduction of pesticides (2012/2013)
- **Flemish PFAS action plan** (2020)
- **NAPED** - National action plan for endocrine disruptors ➔ 2021

napan pesticide
Nationaal Actie **Plan** d'Action National

POLICY RECOMMONDATIONS

- **residues from former activities** (DDT) **<> result of a recent application** (Glyphosate & AMPA)
- **close follow-up of the reuse of soil and waste flows = no recirculation**
  - Leachate from landfills & effluents from WWTPs
  - Re-use of soil and (sewage) sludge (e.g. on agricultural land)
  - Irrigation with 'reclaimed' wastewater
- **diffuse soil pollution -** traffic and agriculture are almost everywhere in Flanders
  - get a better idea of the general exposure of the population
  - blood & urine samples (HBM) combined with samples from the garden, indoor dust, air, vegetables, …
- **harmonized monitoring networks**
  - by adding environmental compartments such as soil & air
  - by analyzing 'new' CECs (e.g. PFAS, bisphenols, …)
  - by improving the exchange and visualization of data between different monitoring networks
    ➔ **geopunt, DOV (database subsurface Flanders), sediment explorer**

STATE OF AFFAIRS REGARDING DIFFUSE SOIL POLLUTION

➢ **Inventory of data sources** (2020, Arcadis on behalf of OVAM)

- list of primary sources of diffuse pollution in Flanders (8 categories)

transport	agriculture
infrastructure and building materials	households
industry	energy
waste	other

- distribution routes from source tot soil (atmospheric deposition, run-off, …)
- secondary sources such as reuse of soil/sediment, drift, run-off, …

➢ **Further research into 'how' to prioritize and manage research into diffuse soil pollution**

Maps indicating areas with a high risk of diffuse contamination (GIS-layers, …)

➔ to avoid further spreading by the reuse of soil

➔ to be consulted by soil experts (soil decree) or by public/citizens

➔ used by policymakers to develop prevention campaigns for CECs - 'healthy' soils

➔ used to select locations for monitoring or to derive background values