

Top-down and bottom-up approaches to identify organic contaminants in soils

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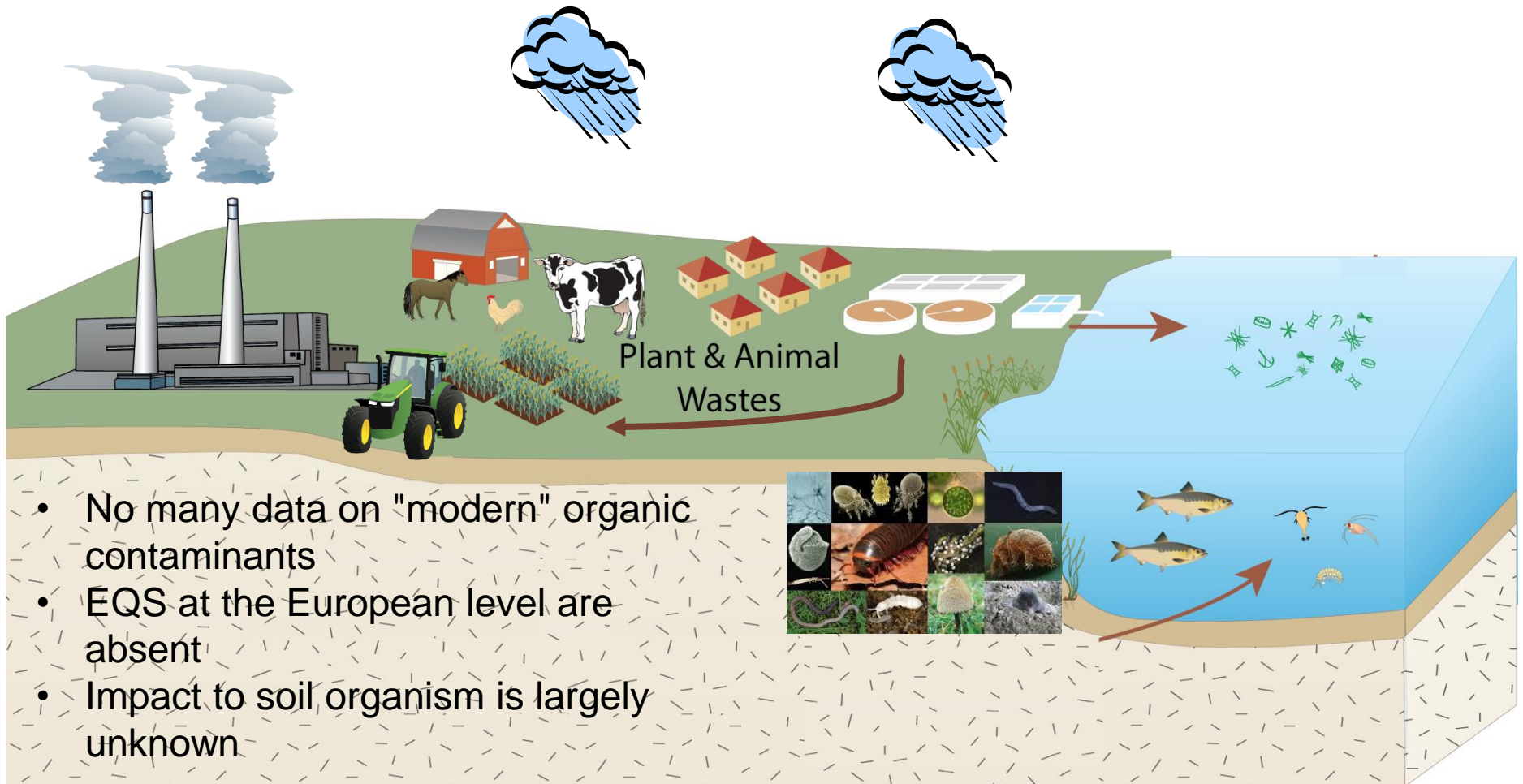
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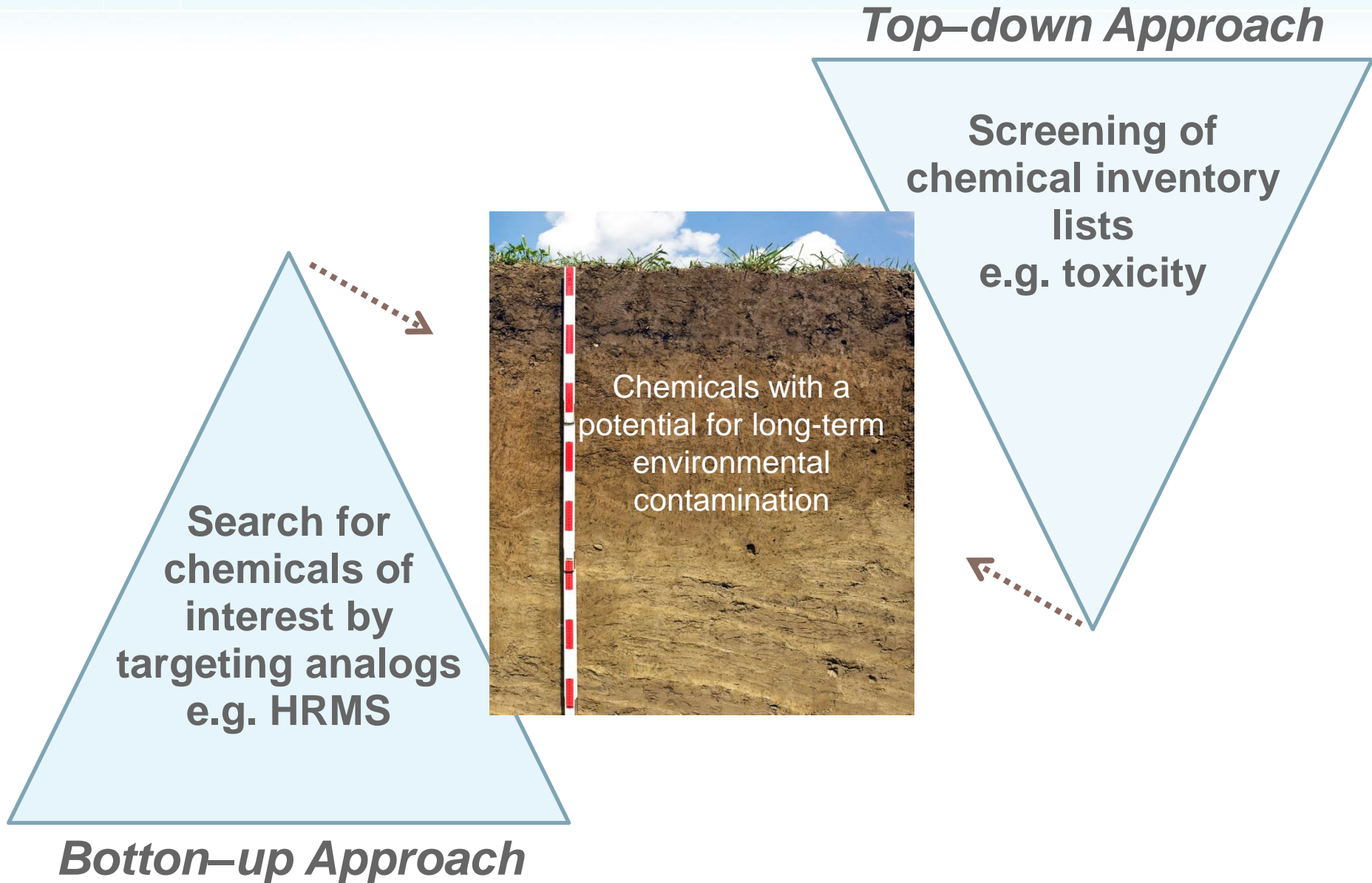
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Soils as Archive of Pollution



How can we identified organic contaminants in soils?

Top-down and bottom-up approaches

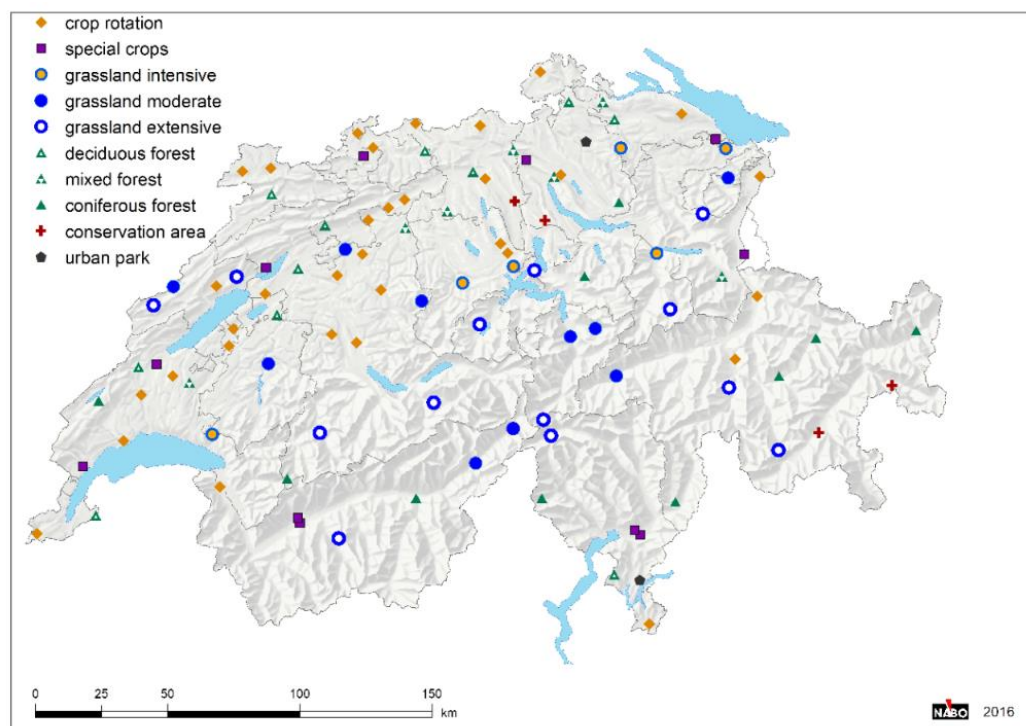


Sampling Campaign

- Swiss Soil Monitoring Network (**NABO**)
 - Long-term monitoring sites since 1985
- Comprises 105 observation sites across Switzerland,
 - Diverse geology, soil types, land use and climate conditions

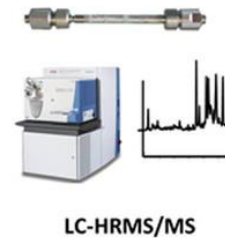


Agroscope



Long-Term Persistence of Organic Contaminants and TPs in Archived Soils

- 1. Asses the persistence of pesticides with known application under real agricultural practice



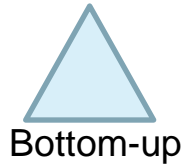
Persistence of pesticides with known application

- 1. Comparison with pesticide application

Top-down



Screening of 80 pesticides based on application data between 1995 and 2008



Bottom-up

Additional pesticides and TP of applied pesticides (>90)

- Pilot study: Selection of 29 archived samples (1995-2008) from 14 agricultural sites

Arable cropping



7 sites (12 samples)

Orchards



3 orchards (7 samples)

Vineyards



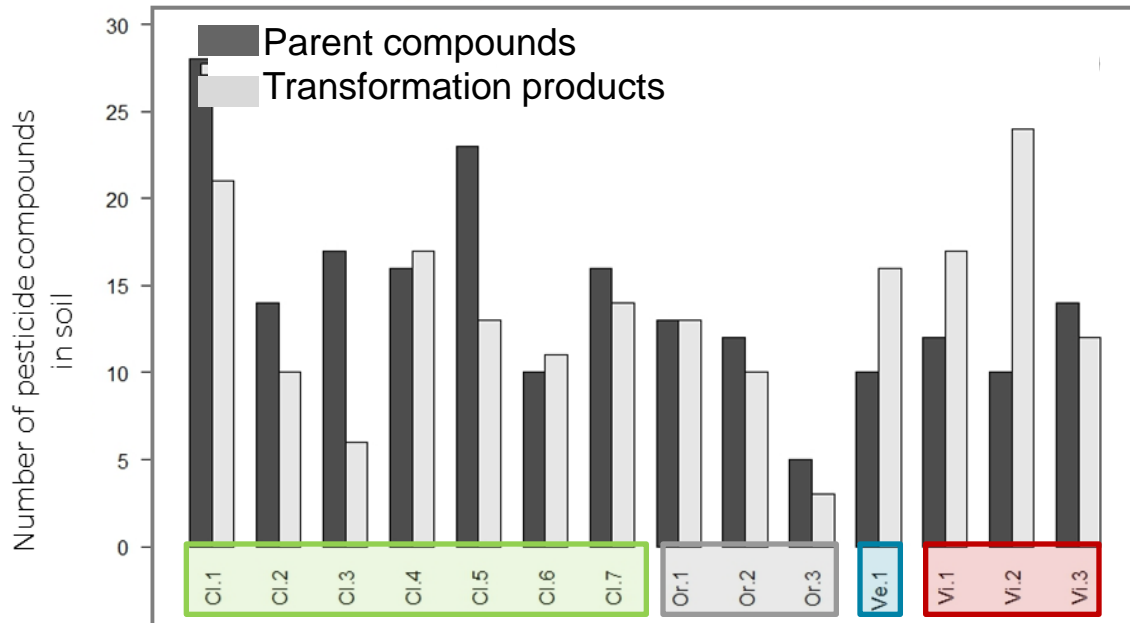
3 vineyards (8 samples)

Vegetables



1 vegetable growing

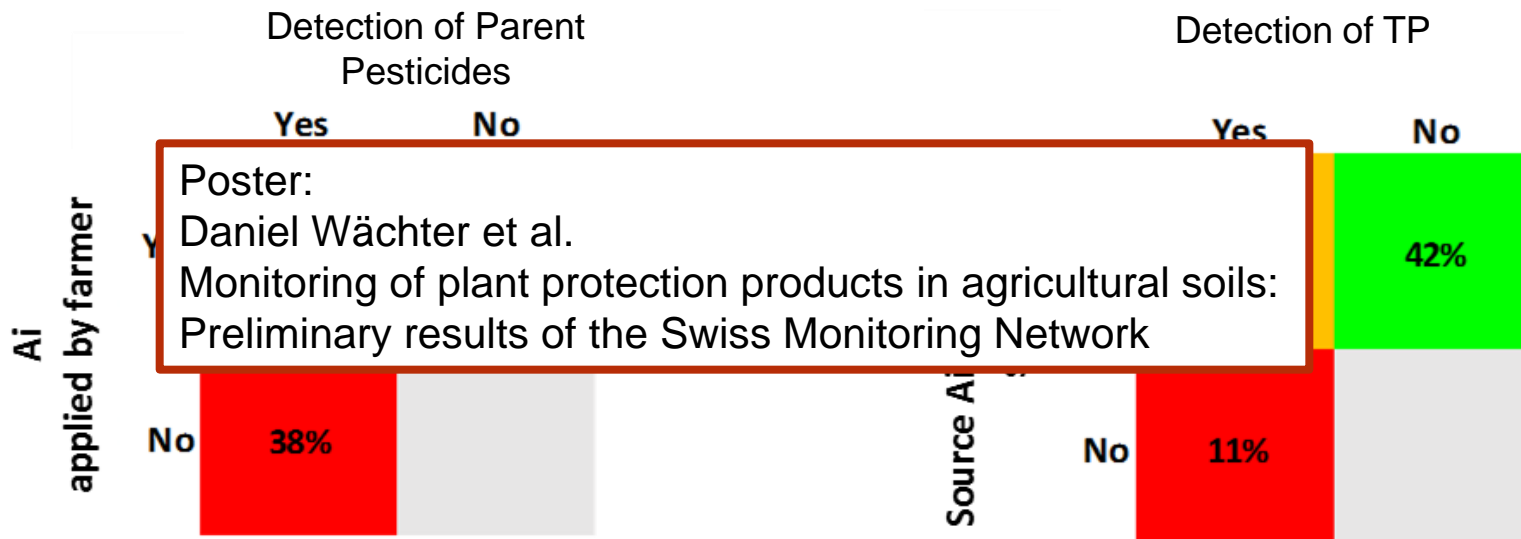
Persistence of pesticides with known application



- High variation between crop type and field sites
- Detection frequency was in good agreement with farmers but higher in crop soils
- Pesticide per site range between 5 and 30 (ave. 12) compounds/soil
- TPs were detected for 75% of the pesticides measured
 - 1-15 TP/site

Persistence of pesticides with known application

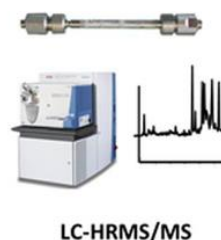
- 1. Comparison of pesticide residues with application data



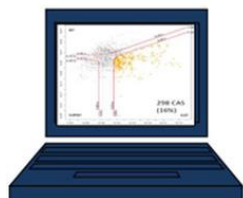
Applied pesticides may be present in soils up to decades after application

Long-Term Persistence of Organic Contaminants and TPs in Archived Soils

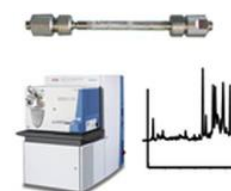
- 1. Persistence of pesticides with known application



- 2. Combination of modelling and screening tools



Computer-based
screening and multimedia
fate model

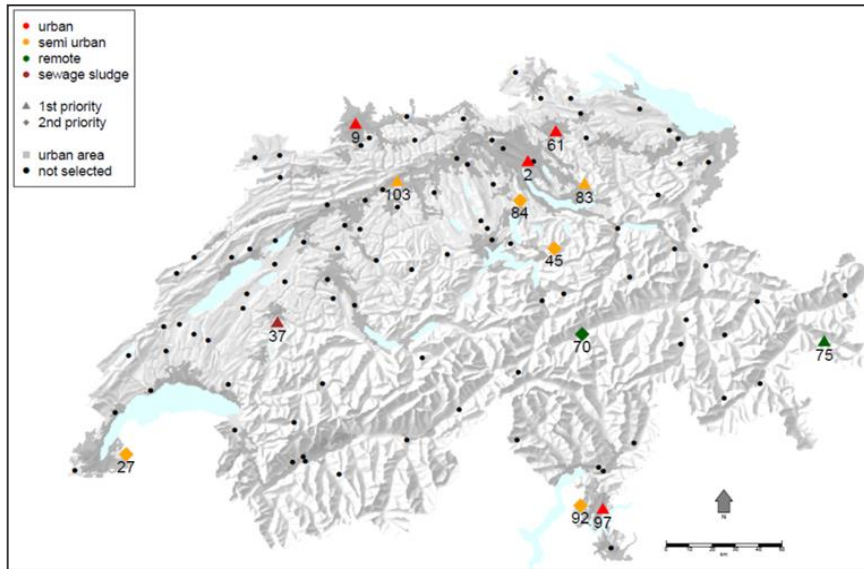


LC-HRMS/MS

Long-term Persistence of Organic Contaminants and TPs in Archived Soils

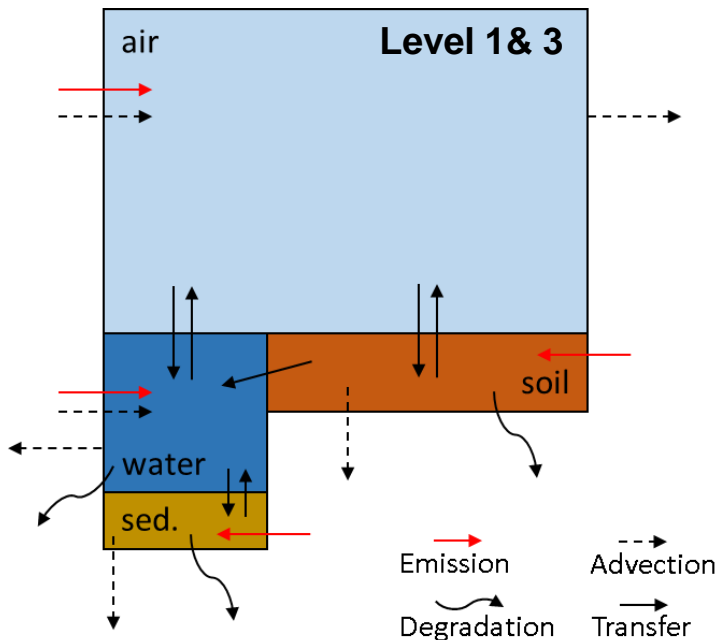
- 2. Combination of modelling and screening tools

● 13 locations sampled



Prioritizing organic contaminants in Soils

- 2. Combination of modelling and screening tools
 - Inventory of Chemicals in the Swiss Market
 - Level 1 and 3 model



- Scope: Chemicals on the Swiss Market
 - >18,000 individual substances identified
 - Estimate fractions in > 90% in soil for >1,400
 - >520 Halogenated compounds

Long-term Persistence of Organic Contaminants and TPs in Archived Soils

2. Combination of modelling and screening tools

Top-down

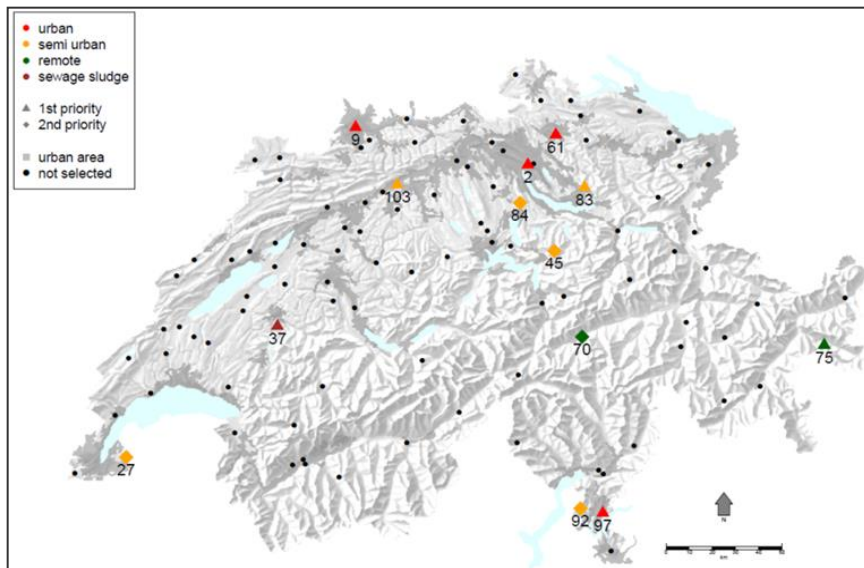


Screening of > 520 halogenated substances from the Swiss market base on modeling results



Bottom-up

In-house screening of ~1000 compounds



13 locations sampled



Model Approach

- Confirmation of **3%** (16) compounds out of 520 candidates
 - Pesticides, antimicrobials, industrial chemical and personal care products
- Tentatively identified **~3%** (15) compounds

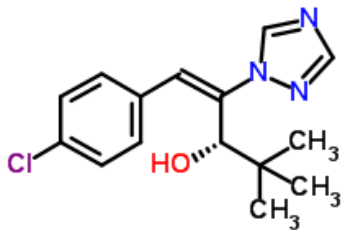
6%

Type	Industrail chemical	Personal Care Product (PCP)			PCP and Pesticide	Pesticide						
	PFOS	Bromochlorophen	Triclocarban	Triclosan	Hexachlorophene	Atrazine	Difeconazole	Diflufenican	Diuron	Fluazinam	Fludioxonil	Propiconazole
Agriculture		Green	Yellow	Orange	Yellow	Yellow	Red	Red	Red	Green	Orange	Orange
Agriculture		Green	Orange	Orange	Yellow	Orange	Green	Green	Green	Green	Yellow	Green
City Park		Green	Yellow	Orange	Yellow	Yellow	Green	Green	Green	Yellow	Yellow	Yellow
City Park		Yellow	Yellow	Orange	Yellow	Green	Green	Green	Green	Green	Yellow	Red
forest		Green	Green	Green	Yellow	Green	Green	Green	Green	Green	Green	Green
forest		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Deciduous forest		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Deciduous forest		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Grasslands		Green	Orange	Orange	Yellow	Yellow	Green	Green	Green	Green	Green	Green
Grasslands		Green	Yellow	Yellow	Green	Green	Green	Green	Green	Green	Green	Green
Mixed forest		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Protection site		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green
Protection site		Green	Green	Green	Green	Green	Green	Green	Green	Green	Green	Green



In-house Screening

- Confirmation of 20 additional compounds
 - 16 compounds overlap (total 36 compounds)
 - Mostly pesticides
 - Exception: plant growth retardant uniconazole
 - 7 halogenated compounds were not predicted by the model



- Additional Screening with GC-MS/MS
 - +10 compounds
 - Additives, personal care products and pesticides

Conclusions

- Soils have memory
- Combination of large-scale screening techniques and screening tools is essential to detect the next generation of organic contaminants
- Further investigation is needed on the persistence of organic contaminants in soil and the ecotoxicology effects of organic contaminants mixtures

Thank You!

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Long-term Persistence of Pesticides and TPs in Archived Agricultural Soil Samples

- Comparison with pesticide application

Rank	Name	CAS No.	Type	No. of Samples Detected ²	% of Detected Samples	Concentration Range (µg/kg _{dw})
1	Simazine	122-34-9	Herbicide	28	97	1 - 80
2	Atrazine	1912-24-9	Herbicide	25	86	2 - 250
3	Tebutam	35256-85-0	Herbicide	23	79	1 - 20
4	Carbendazim	10605-21-7	Fungicide & TP ¹	21	72	1 - 60
5	Terbuthylazine	5915-41-3	Herbicide	18	62	1 - 9
6	Dinoseb	88-85-7	Herbicide	17	59	2 - 320
7	Metolachlor	51218-45-2	Herbicide	16	55	2 - 25
8	Alachlor	15972-60-8	Herbicide	15	52	1 - 40
9	Cyprodinil	121552-61-2	Fungicide	14	48	1 - 30
10	Diuron	330-54-1	Herbicide	14	48	2 - 330
11	Linuron	330-55-2	Herbicide	14	48	2 - 190
12	Pendimethalin	40487-42-1	Herbicide	14	48	2 - 160
13	Chlortoluron	15545-48-9	Herbicide	12	41	3 - 6
14	Ethofumesate	26225-79-6	Herbicide	12	41	2 - 80
15	Fludioxonil	131341-86-1	Fungicide	12	41	2 - 330
16	Isoproturon	34123-59-6	Herbicide	12	41	2 - 4
17	Mecoprop	7085-19-0	Herbicide	11	38	4 - 20
18	Metamitron	41394-05-2	Herbicide	11	38	6 - 140
19	Propiconazole	60207-90-1	Fungicide	11	38	1 - 5
20	Fenpropidin	67306-00-7	Fungicide	10	34	1 - 14

Long-term Persistence of Pesticides and TPs in Archived Agricultural Soil Samples

● Comparison with pesticide application

Rank	Parent Compound	Type	Transformation Product (TP)	TP Type	No. Of Samples Detected ²	Concentration Range (µg/kg _{dw})
1	Atrazine	Herbicide	Atrazine-2-hydroxy	Major	29	2 - 220*
2	Simazine	Herbicide	Simazine-2-hydroxy + Terbutylazine-desethyl-2-hydroxy	Major	27	2 - 680*
3	Terbutylazine	Herbicide	Terbutylazine-desethyl	Major	26	1 - 2*
4	Atrazine	Herbicide	Atrazine-desisopropyl	Major	25	1 - 9*
5	Diuron	Herbicide	Diuron-desmonomethyl	Major	22	2 - 130*
6	Chlorothalonil	Fungicide	Chlorothalonil-hydroxy	Major	19	D
7	Terbutylazine	Herbicide	Terbutylazine-hydroxy	Major	16	D
8	Chlorpyrifos	Insecticide	3,5,6-Trichloro-2-pyridinol	Major	15	6 - 70*
9	Diuron	Herbicide	Diuron-desdimethyl	Major	15	2 - 30*
10	Chlorothalonil	Fungicide	3-cyano-6-hydroxy-2,4,5-trichlorobenzamide / 3-cyano-4-hydroxy-2,5,6-trichlorobenzamide	Major	14	D
11	Terbutylazine	Herbicide	Terbutylazine-desethyl-hydroxy	Minor	14	D
12	Atrazine	Herbicide	Atrazine-desethyl	Major	12	3 - 9*
13	Carbendazim	Fungicide & TP ¹	2-Aminobenzimidazole	Major	12	2 - 3*
14	Pendimethalin	Herbicide	Pendimethalin-benzimidazole	Major	12	D
15	Metamitron	Herbicide	Metamitron-desamino	Major	11	2 - 20*
16	Isoproturon	Herbicide	Isoproturon-monodemethyl	Major	10	1 - 5*
17	Difenoconazole	Fungicide	1-[2-chloro-4-(4-chlorophenoxy)phenyl]-2-(1H-1,2,4-triazol-1-yl)ethanol	Major	9	D
18	Azoxystrobin	Fungicide	Azoxystrobin acid	Major	8	D
19	Dinoseb	Acaricide	Acetyl-dinoseb-6-amino	Unknown	8	D
20	Dinoseb	Acaricide	Dinoseb-6-amino	Unknown	8	D

Step 2: Analytical Methods



Preservation and Storage



Extraction and Enrichment

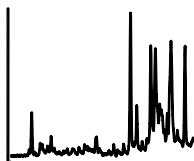


Chromatography



**Orbitrap-MS
HR Chromatogram**

1. Target
2. Suspect
3. Non-target



- **Generic method**
- **Non-compound class specific**

Long-term Persistence of Pesticides and TPs in Archived Agricultural Soil Samples

● Comparison with Pesticide Application

Pilot study: Selection of 29 archived samples (1995-2008)
from 14 agricultural sites with known pesticide application patterns

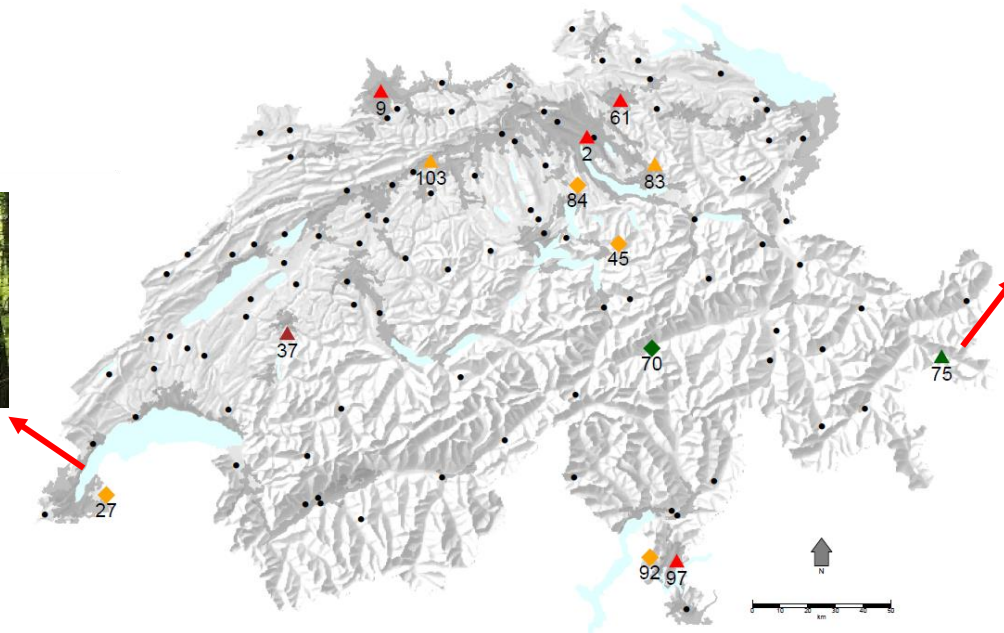
Arable cropping :
7 sites (12 samples)

Specialized cropping:
3 vineyards (8 samples)
1 vegetable growing (2 samples)
3 orchards (7 samples)



Combination of modelling and screening tools

Type Use	Industrial chemical	Personal Care Product (PCP)			PCP and Pesticide	Pesticide							
		PFOS	Bromochlorophen	Triclocarban		Triclosan	Hexachlorophene	Atrazine	Difeconazole	Diflufenican	Diuron	Fluazinam	Fludioxonil
9 Agriculture													
103 Agriculture													
61 City Park													
97 City Park													
83 forest													
45 forest													
27 Deciduous forest													
92 Deciduous forest													
37 Grasslands													
70 Grasslands													
2 Mixed forest													
84 Protection site													
75 Protection site													



Model Approach

