Biocide monitoring in Swiss surface waters

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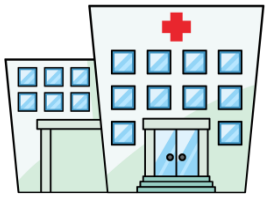
Environmental Chemistry, Eawag

Many exposure pathways for biocides

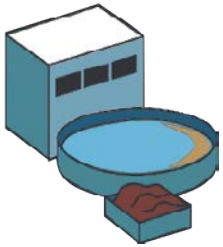


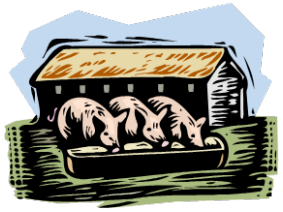
Hospital

Household

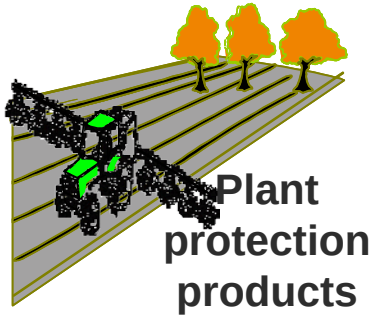
Urban areas

Industry

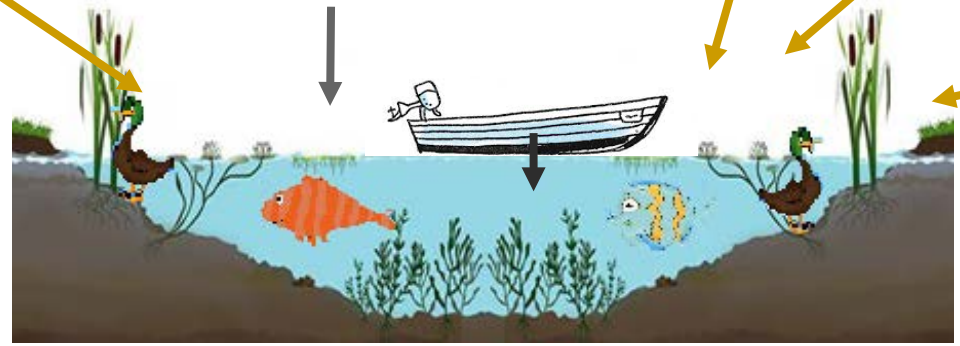




Stables



Plant protection products (PPP)



Content

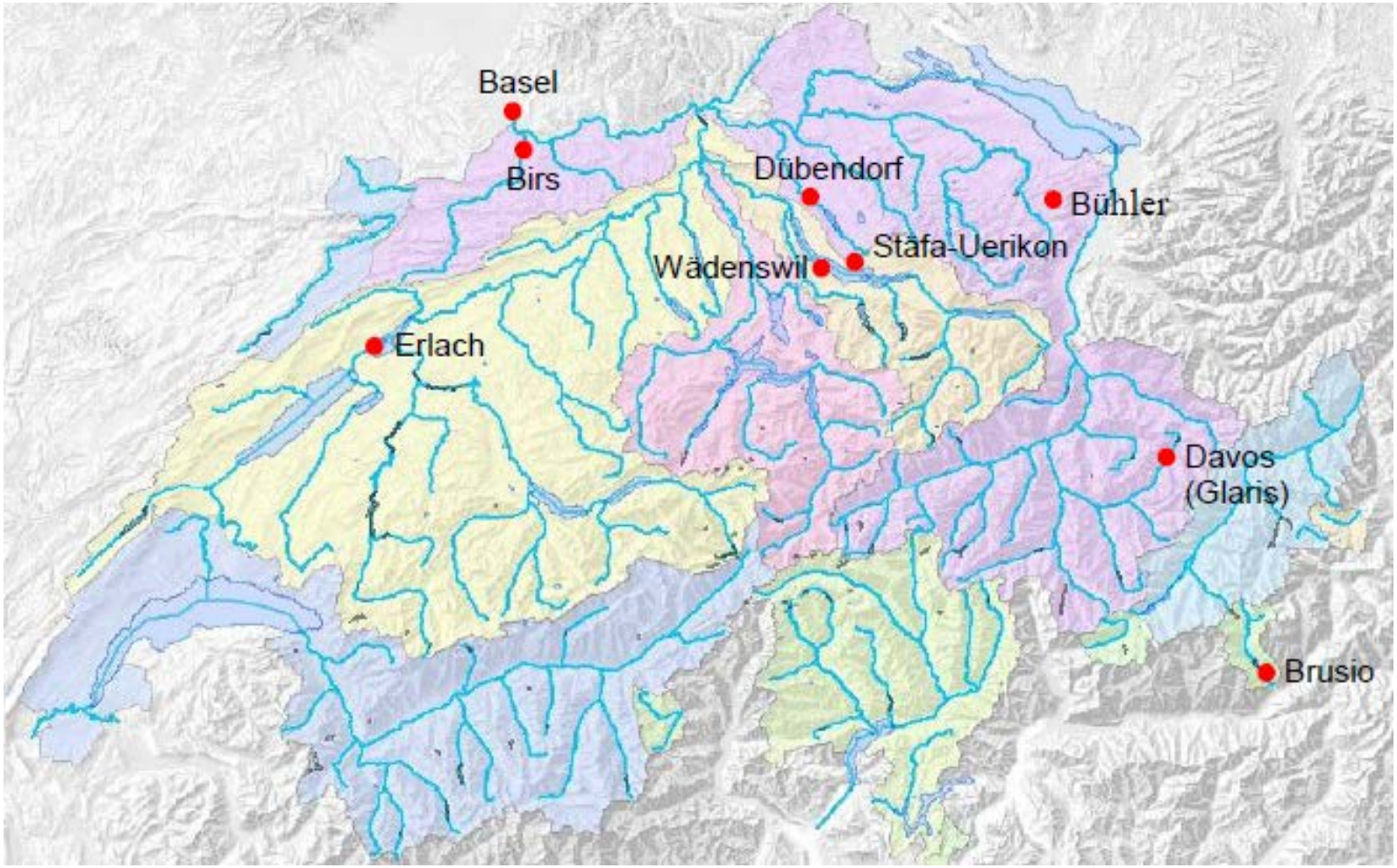
Monitoring studies from 2007-2014

- **Sources:**
  wastewater, run-off, industry
- **Surface waters**
  high-frequent sampling
  composite sampling
- **Lake sediment** as sink

- in Switzerland about **400 biocides** for all non-plant protection purposes notified
- Broad range of structures with **different physical-chemical properties**

Screening in 9 wastewater treatment plants (WWTP)

72h-flow proportional sampling of influent & effluent in summer 2013



Results of WWTP screening

- Screening using LC coupled to high resolution mass spectrometry after solid phase extraction & quantification
- 10 of 15 biocides & 1 of 4 biocide metabolites detected

Highest effluent concentrations

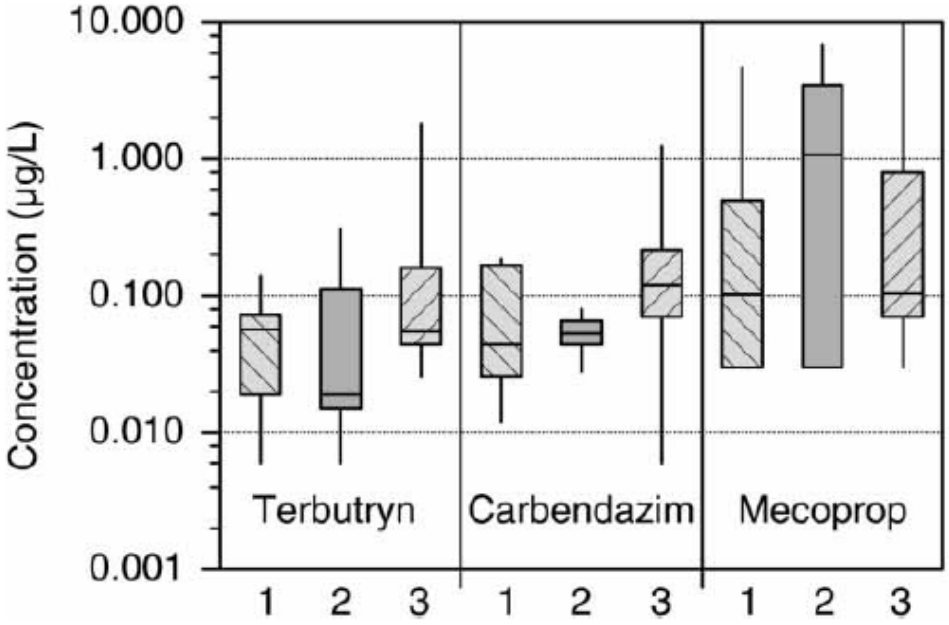
Substance	Class	Concentration range (ng/L)
Carbendazim[P]	fungicide	20-100
Diuron[P]	herbicide	20-100
DEET	repellent	up to 8000
Diazinon[PX] (not longer permitted)	insecticide	< 8 - 990
Mecoprop[P]	herbicide	7 – 1500
Triclosan	disinfectant	< 40 - 500

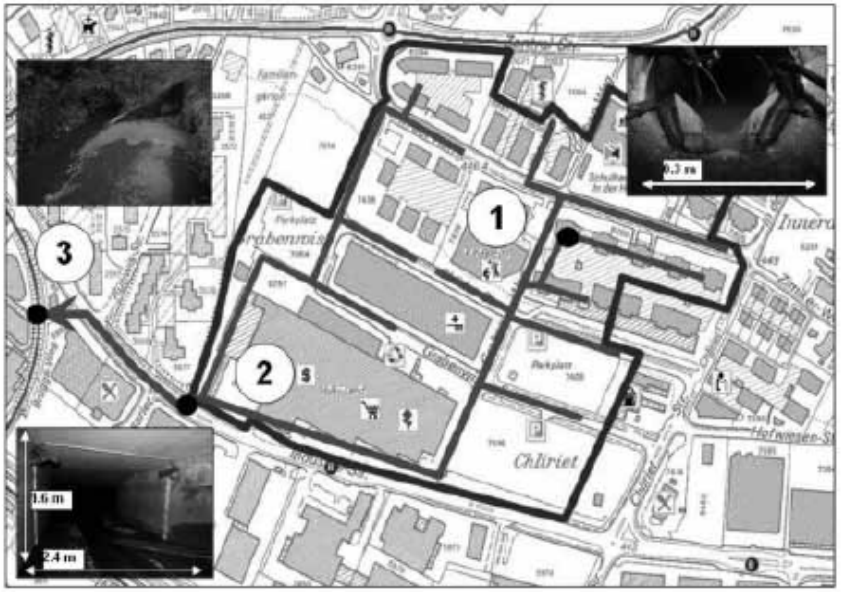
[P] also plant protection product, [X] not longer permitted

- Highly fluctuating concentrations from < LOQ to µg/L
  ⇒ elimination efficiency difficult to assess

Leaching from facades and roofs during rain events

Run-off from new buildings

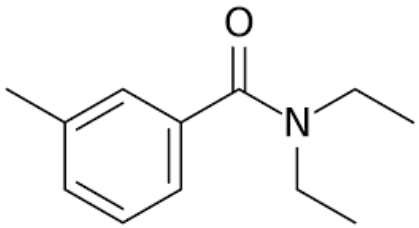




Burkhart et al., 2011. Wat. Sci. Technol. 63: 1974-1982

Industrial input

Daily load of the insect repellent DEET in 2013/14
at the Rhine monitoring station in Basel



Load [kg/day]

cumulative load [kg]

Discharge (no scale)

0 2 4 6 8 10 12 14 16 18

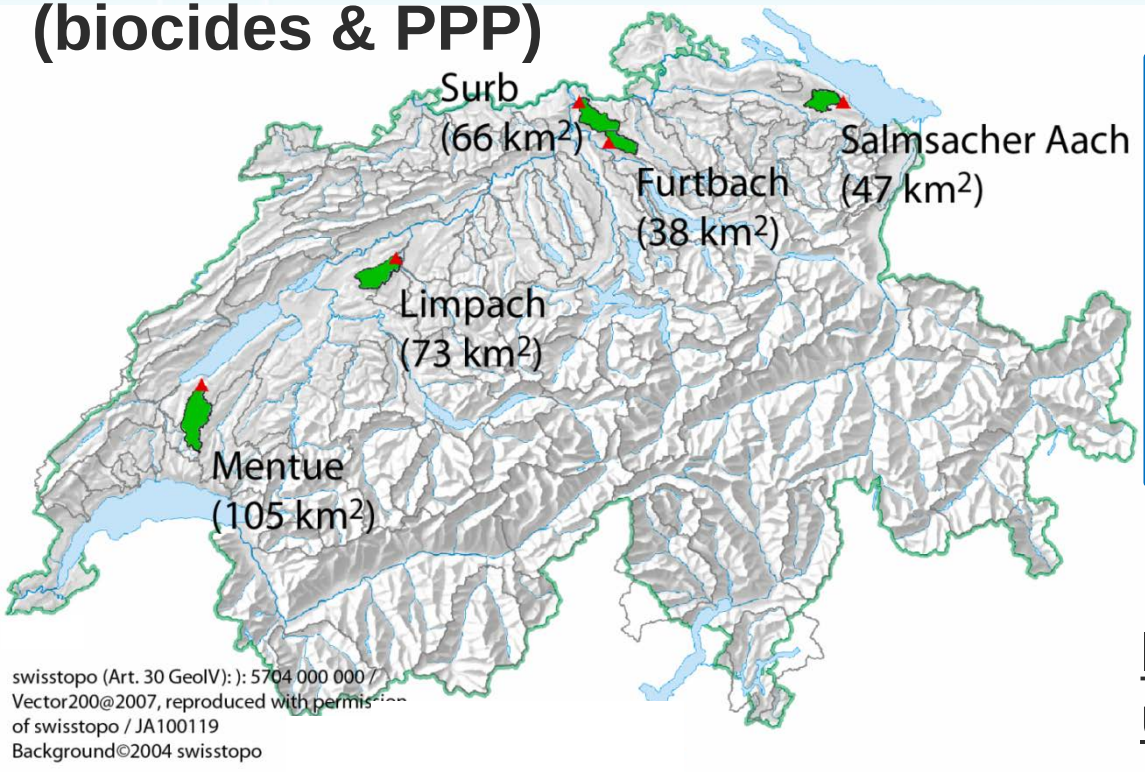
0 150 300 450 600 750 900 1050 1200 1350

Jan Apr Jul Okt Jan Apr Jul Okt

2013 Time 2014

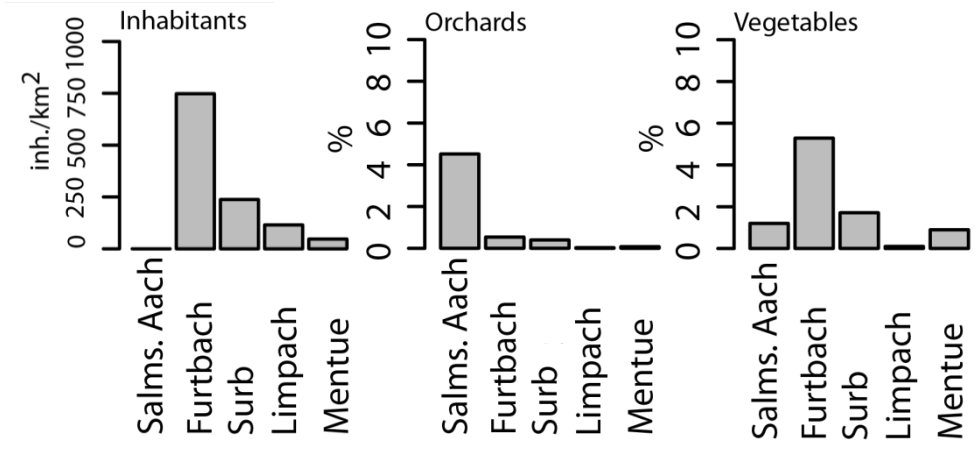
Data: Rhine monitoring, AUE Basel-City

Field study 2012: Screening of all registered pesticides (biocides & PPP)



Limpach

Surb



<u>large differences in land use:</u>

- differences in urban area and waste water amount
- high densities of arable crops
- 1-2 special crops in each catchment

Sampling

9 continuous bi-weekly samples per site
March - July 2012

Water samples
time-proportional using an automatic sampler (e.g. ISCO)
LC-HRMS/MS analysis after SPE
Moschet et al., Anal. Chem. 2013, 85(21): 10312-10320

Passive sampling with chemcatcher (SDB)
LC-HRMS/MS analysis
(Moschet et al., Wat. Res. 2015, 71: 306-317)

Passive sampling with silicone rubbers (PDMS)
GC-MS/MS analysis after pressurized liquid extraction & purification
(Moschet et al., Wat. Res. 2014, 66: 411-422)

Categorisation of biocides in Switzerland

Number of compounds that are :

notified (2012) — **381**

pest control, repellent, disinfectant

.. **registered** at least in 1 product (75%) + synthetic organic (66%) + no polymer — **142**

wood preservation

environmental relevance

annual **consumption** — **???**

film or process preservation

Input likely…
(stable in water, logKow < 5) — **99**

ad hoc **EQS** < 0.1 µg/L
(mainly pyrethroides) — **10**

antifouling agent,

Target & suspect screening of water samples

Sample preparation & chromatography
- Solid phase extraction (mixed mode cartridge)
- Reverse phase chromatography

Detection: HRMS/MS (Qexactive)
- Electrospray ionization (pos/neg)
- HR scan (R=140000) with data dep. MSMS-scans (17500)

- logKow<5
- ionizable in electrospray

target screening
with reference standard available in advance

- high sales numbers
- low Koc
- high DT50 in soil
- high DT50 in water

suspect screening
(remaining compounds)
search for exact mass
→ reference standard for positive detects

190 pesticides + TPs

quantification

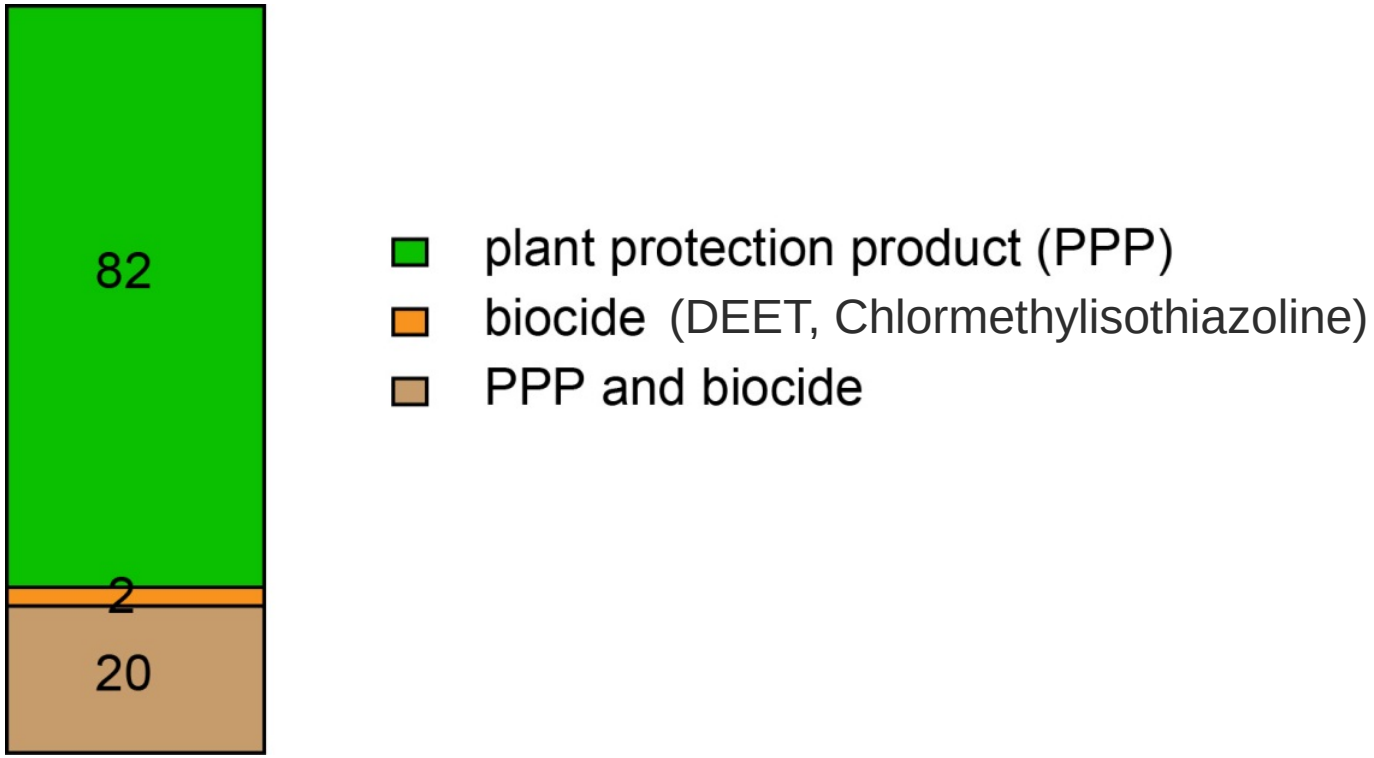
235 pesticides + TPs

86 % of all organic pesticides

Organic, synthetic biocides (without alcohols, strongly sorbing, readily degradable compounds) **88 of 109 compounds covered (27 target analysis)**

Number of plant protection products and biocides detected

104 pesticides detected (30-50 per sample)



+ 8 non-polar insecticides detected in silicon rubber passive sampler extracts (6 biocides and PPP)

Most relevant biocides in the five Swiss rivers

Compounds	Use	Frequency [> 5 ng/L]	Max. conc. [ng/L]	Number of sites	Number > EQS
Terbutylazine	P, **BX**	62%	630	5	6
Isoproturon	P, B	67%	350	5	1
Diuron	P, B	60%	52	5	**13**
CMI	**B**	9%	510	2	2
Mecoprop	P, (B)	98%	470	5	0
DEET	**B**	87%	520	5	0
Diazinon	**PX**, **BX**	47%	43	5	8
Thiacloprid	P, B	22%	65	4	**6**
Carbendazim	P, B	69%	65	5	0
Cypermethrin	P, B	0%	0.2	4	**7**
Deltamethrin	P, B	0%	0.5	2	**10**
Tebuconazole	P, B	50%	86	5	0

P: PPP, B: biocide, PX, BX: today no longer allowed

Wittmer et al. (2014), AQUA & GAS 3: 32-43
Moschet et al. (2015), AQUA & GAS 4: 54-65

11 biocides as selected indicator compounds for Swiss monitoring of diffuse pollution (=RBSP)

also indicators for urban point pollution

DEET	→ Insect repellent (MEC_{95} > 107 ng/l)	*(PT 19)*
Mecoprop[P]	→ Bitumen sheets, garden and agriculture (cereals)	*(not officially)*
Diuron[P W]	→ Facades and fruits	*(PT 7,10)*
Carbendazim[P]	→ Film preservatives and agriculture (fruit, cereal, rape)	*(PT 7,9,10)*
Diazinon[Px]	→ No longer registered as biocide or plant protection agent, only as veterinary pharmaceutical	*(forbidden)*
Triclosan	→ Disinfectant, human hygiene	*(PT 1,2,7,9)*
Cypermethrin[P W]	→ Wood protection, pest control and agriculture	*(PT 8,18)*
Tebuconazol[P]	→ Wood protection and agriculture	*(PT 7,8,9,10)*
Terbutryn[W]	→ Film preservative	*(PT 7,9,10)*
Irgarol/Cybutrin[W]	→ Antifouling	(PT 21)
Isoproturon[P]	→ Facades but main use rather in agriculture	*(PT 7,10)*

P: also registered as plant protection product, x not longer permitted [W] WFD priority compound

Wittmer et al. Beurteilungskonzept, 2014

Monitoring of hydrophobic biocides

Sampling of lake sediment (2010 and 2012)
integrative for contamination within the catchment

www.eures.ch

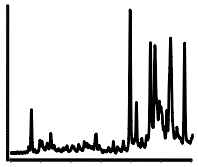
Lake Greifensee: 8.17 km² , 34 m
Lake Lugano: 48.67 km², 288 m

Analytical procedure

Lake sediment cores

Freeze-drying & homogenization

Pressurized liquid extraction & purification using liquid-liquid extraction (Quechers)



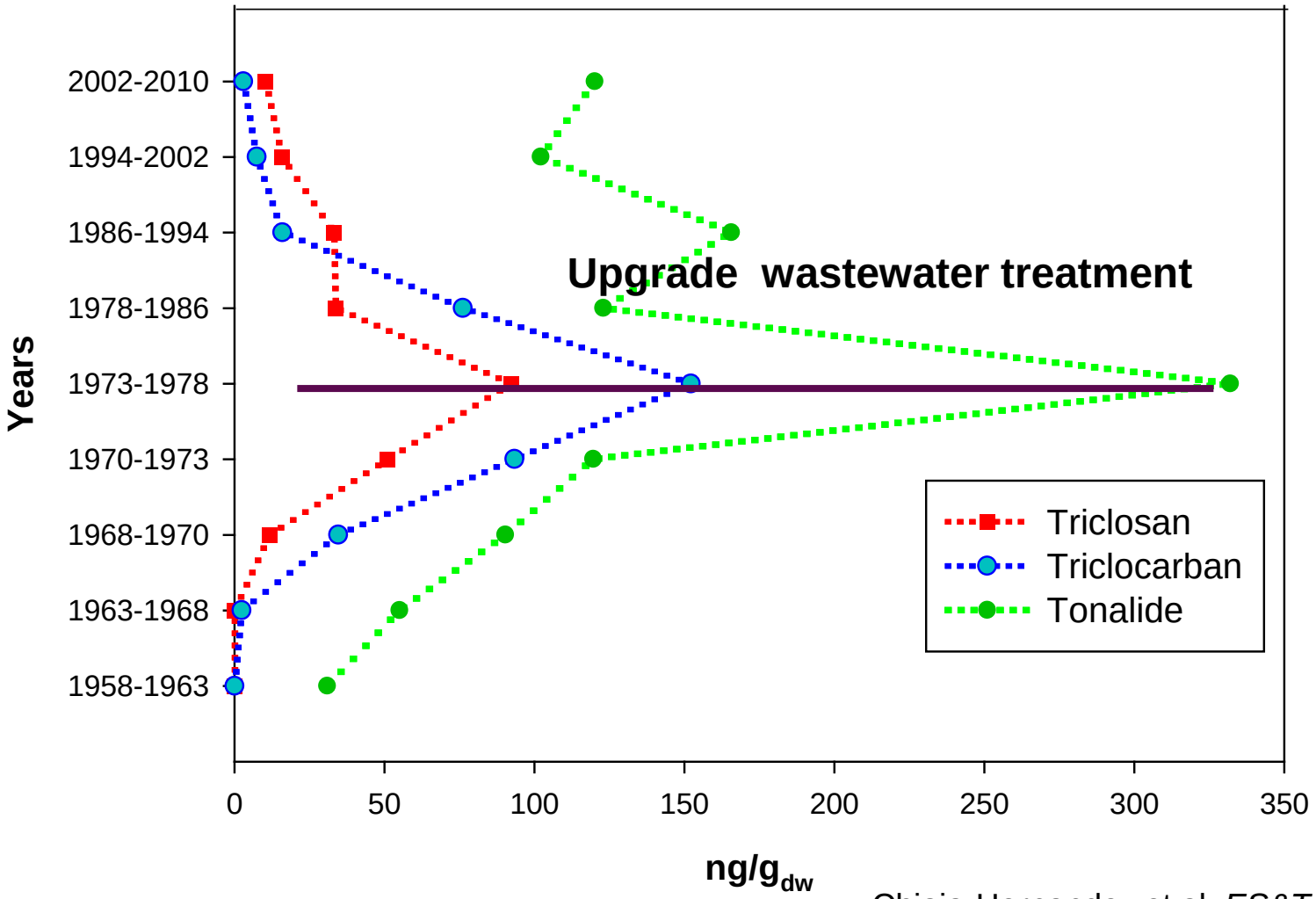
RP chromatography (Xbridge)
ESI +/-
Orbitrap-HRMS/MS

- 180 targets (21 biocides)

Chiaia-Hernandez et al. *ES&T* 2013, 47(2) pp. 976-986

Temporal pollution pattern

Time series of personal care products in sediment cores from Lake Greifensee

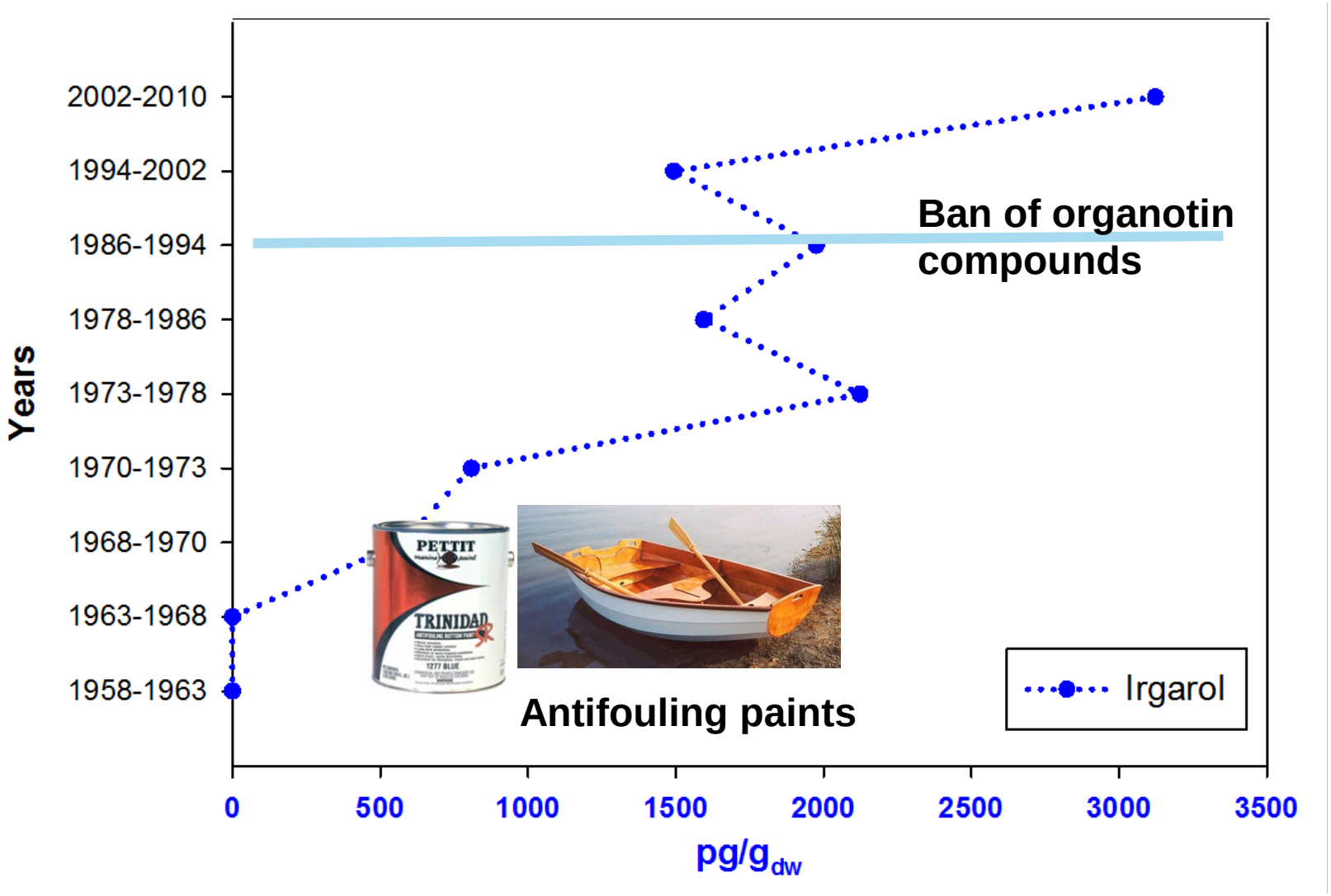


Triclosan / Triclocarban

Chiaia-Hernandez et al. *ES&T* 2013, 47(2) pp. 976-986

Temporal pollution pattern

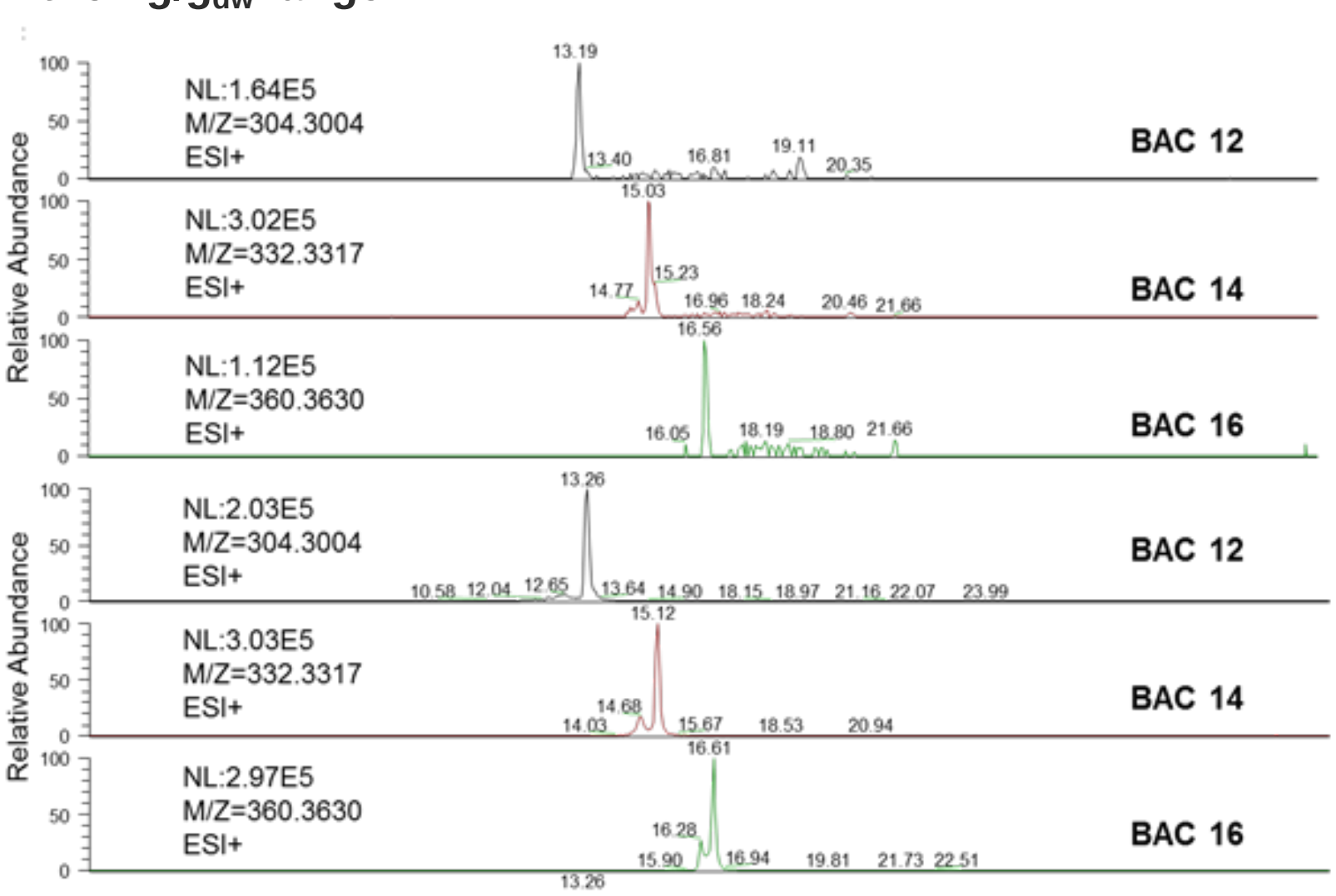
Time series of the pesticide irgarol in sediment cores from Lake Greifensee



Chiaia-Hernandez et al. *ES&T* 2013, 47(2) pp. 976-986

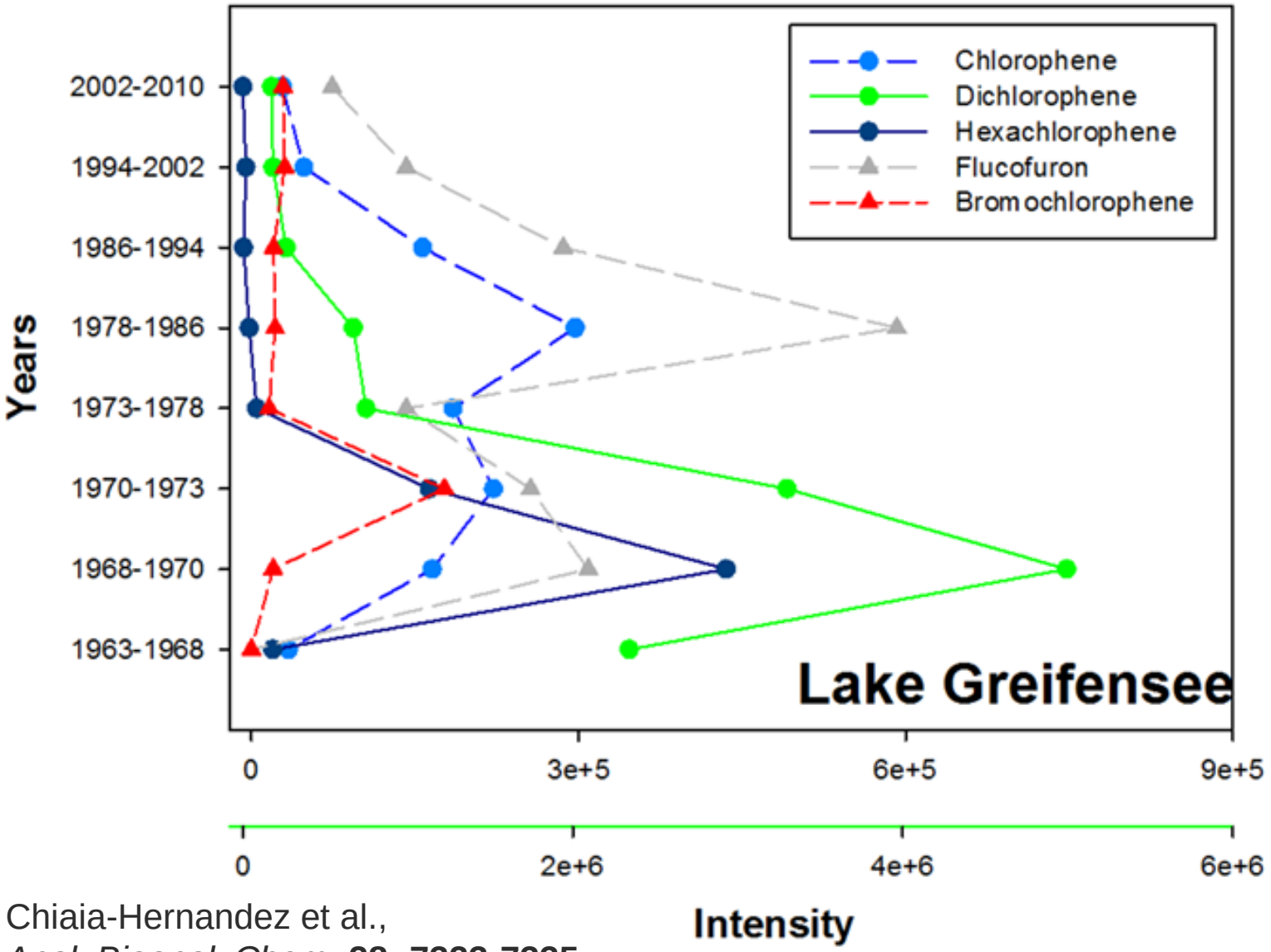
Suspect screening of quarternary ammonium surfactants

Benzyldimethylammonium compounds (BAC) in the ng/g_{dw} range



Chiaia-Hernandez et al. *ES&T* 2013, 47(2) pp. 976-986

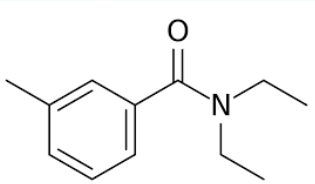
Temporal pattern of suspects & non-targets



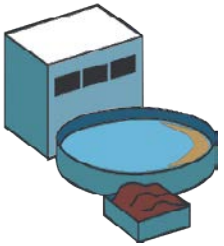
Chiaia-Hernandez et al.,
Anal. Bioanal. Chem. **28: 7323-7335**

Conclusions

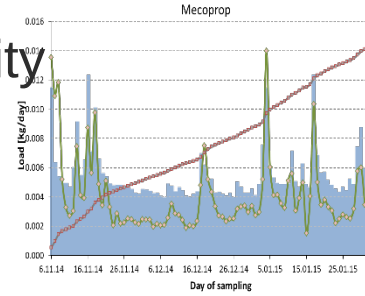
Variety of biocides
broad range of physical chemical properties & persistence
detected compounds often used also in plant protection products



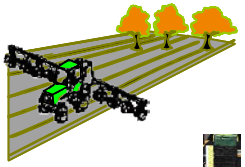
Various input pathway
WWTPs, combined sewer overflow, urban surface run-off
often triggered by rain events



Complex concentration dynamics
⇒ high resolved sampling for max. concentrations & acute toxicity
⇒ time-proportional sampling or passive sampling (14d)
for mean concentrations & chronic toxicity



Surface water: in ***agriculturally influenced water bodies***
pesticides mostly more relevant with regard
to concentrations & compound numbers



Sediment/WWTP sludge: sink for some relevant hydrophobic biocides

Thank you! Questions?

Acknowledgement

- Funding: Federal Office for the Environment (FOEN), Swiss National Science Foundation
- Cantonal Authorities (Thurgau, Aargau, Zürich, Solothurn, Waadt) for sampling.
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