Atmospheric pesticides monitoring for three years (2019-2021) at the National Atmospheric Observatory Košetice (CZ)

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Ludovic Mayer

RECETOX, Masaryk University, Faculty of Science, Brno, CZ

Airborne pesticides…

Currently-used pesticides

- Large number of substances (>1000)
  e.g., chlorpyrifos, pendimethalin, …

Atmospheric fate information exist only for a selected few

Poorly studied and poorly understood

Organochlorine pest. (OCPs)

- Persistent organic pollutants (POPs)
  e.g., DDT, Endosulfan, …

Banned since 1960s/70s and globally 2001

Well studied and well understood

Currently, in the European Union:

- Pesticides levels in other environment are monitored with thresholds set
  - **Water** (European Water framework directive)
  - **Food** (EFSA)

Nothing currently exist in regards to atmospheric levels of pesticides

National Atmospheric Observatory Košetice

- Established in 1988
- Long-term air quality monitoring and research at the background scale

Adapted from: 10.3390/atmos10110687

https://actris.cz/web/fotogalery/

emep

ACTRiS Exploring the Atmosphere

ICOS Integrated Carbon Observation System

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National Atmospheric Observatory Košetice

Land-use analysis (%; 10 km radius CORINE LC 2018)	NAOK
Agricultural areas	65
Forest	29
Artificial surfaces with possible pesticides uses	3
Shrub and/or herbaceous vegetation	3

Adapted from Mayer et al., 2023/4 (under review)

https://actris.cz/web/fotogalery/

- NAOK: located in free area outside of towns and direct sources of pollution…
  … except for pesticides

National Atmospheric Observatory Košetice

- **<u>POPs monitoring: since 1988</u>**
  - Legacy organochlorine pesticides (OCPs; n=12)

α-HCH	*o, p'–DDT*
β-HCH	*p, p'–DDT*
γ-HCH	*o, p'–DDE*
δ-HCH	*p, p'–DDE*
HCB	*o, p'–DDD*
PeCB	*p, p'–DDD*

- Current-use pesticides (CUPs) monitoring since 2012
  - n=27 until 2014
  - n= 48 from 2019 to 2021

National Atmospheric Observatory Košetice

Sampling of OCPs and CUPs:

- High-volume air samplers (Digitel DH-77; Switzerland)
- Alternating weekly sample: one-week OCP, following week CUPs, …
- Average sampling volume: 4310 m^3
- **OCPs: daily sample (HV, ≈ 700 m^3)**

Sampler configuration:

- OCPs and CUPs: Quartz fiber filter (Whatman QFF; UK)
- OCPs: Polyurethane foam (PUF)
- CUPs: Sandwich (PUF – XAD-2 – PUF)

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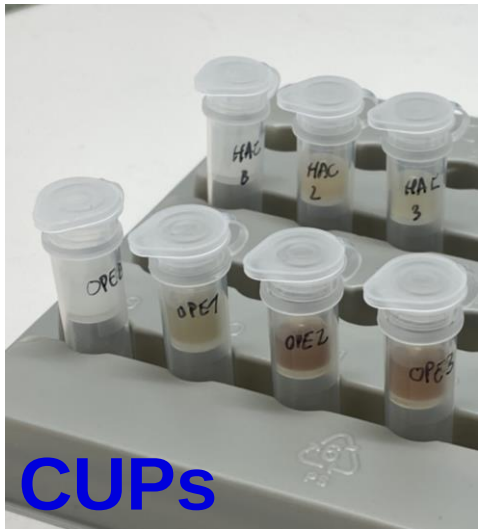
Samples extraction

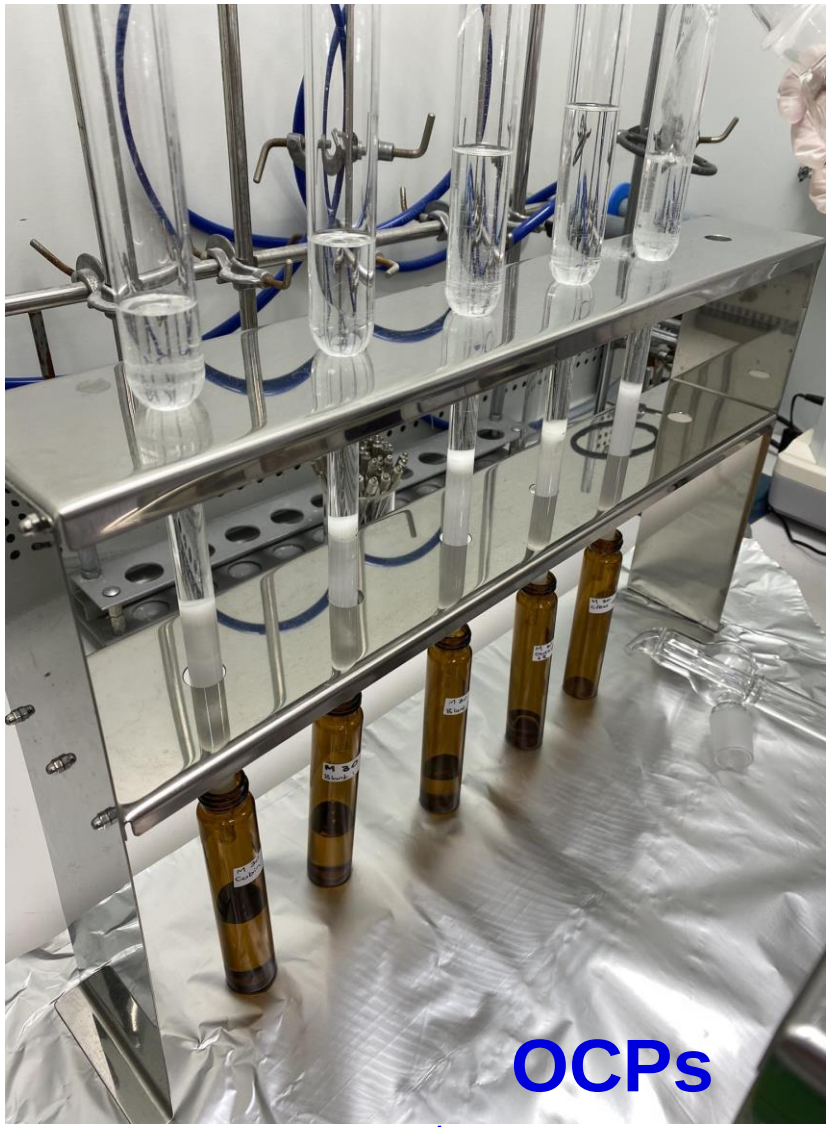
OCPs

- DCM Sohxlet extraction
- Sillica gel + H_2SO_4 deact. clean-up

CUPs

- Methanol Sohxlet extraction
- Filtration through cellulose acetate membrane (0.22 µm diameter)





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Sample analysis

OCPs

GC coupled to a tandem MS/MS

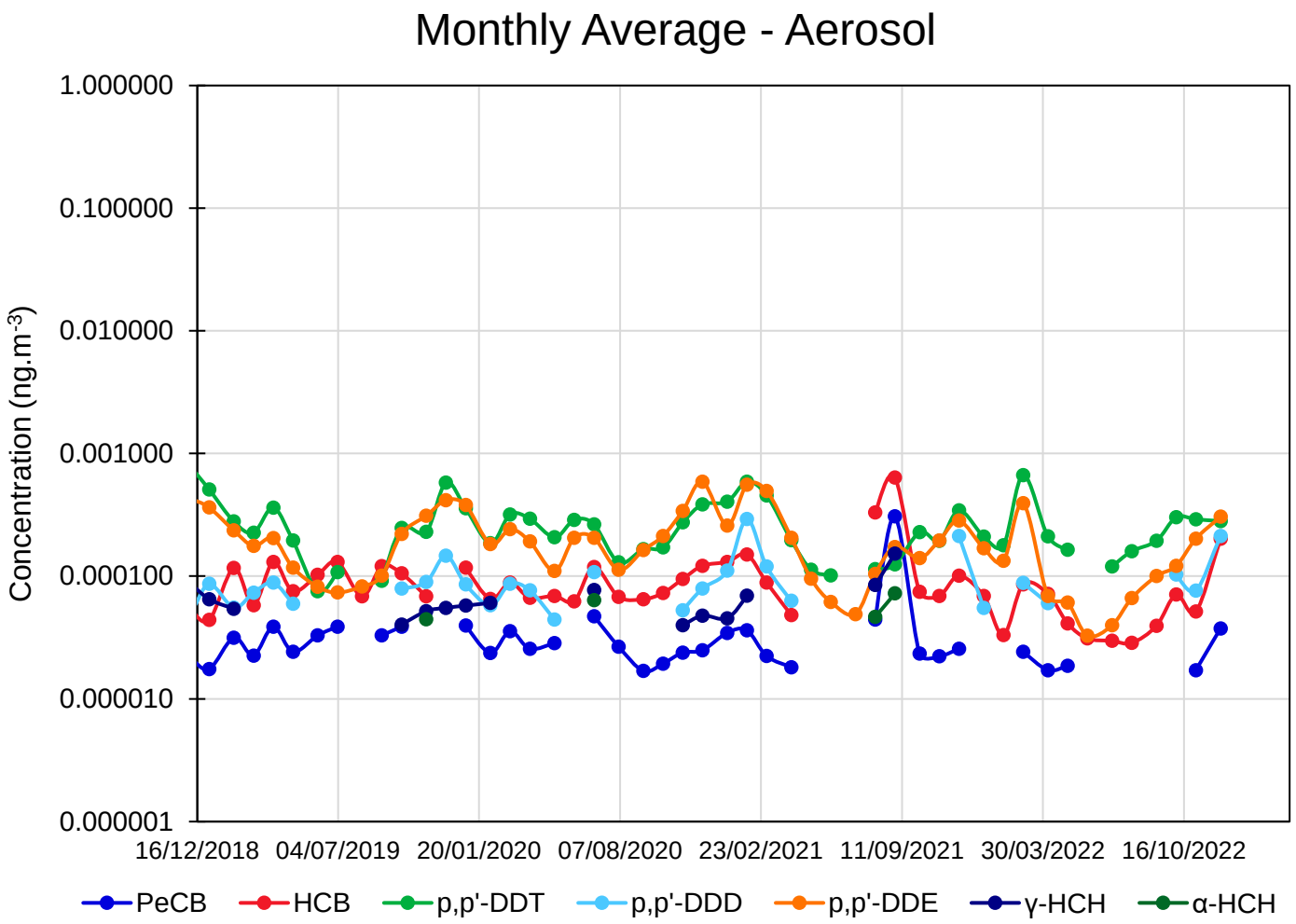
- Agilent 8890A GC (Agilent Technologies, USA)
- 60 m × 0.25 mm × 0.25 µm Rxi-5Sil-MS capillary column (Restek, Inc., France),
- triple quadrupole Agilent 7000D MS (Agilent Technologies, USA).

CUPs analysis:

HPLC coupled to a tandem MS/MS

- HPLC: Agilent 1290 (Agilent Technologies, USA)
- Columns:
  - Phenomenex Synergi Fusion C-18 column (n = 28 CUPs)
  - Acquity UPLC BEH C18 column (1.7 µm, 100 × 2.1 mm) (n= 20 CUPs).
- MS: QTRAP 5500 (AB Sciex, USA).

OCPs (2019-2021)



- Median [OCPs] = 0.08 pg m^{-3}
- No decrease over time
- $[OCPs]_{winter} > [OCPs]_{summer}$

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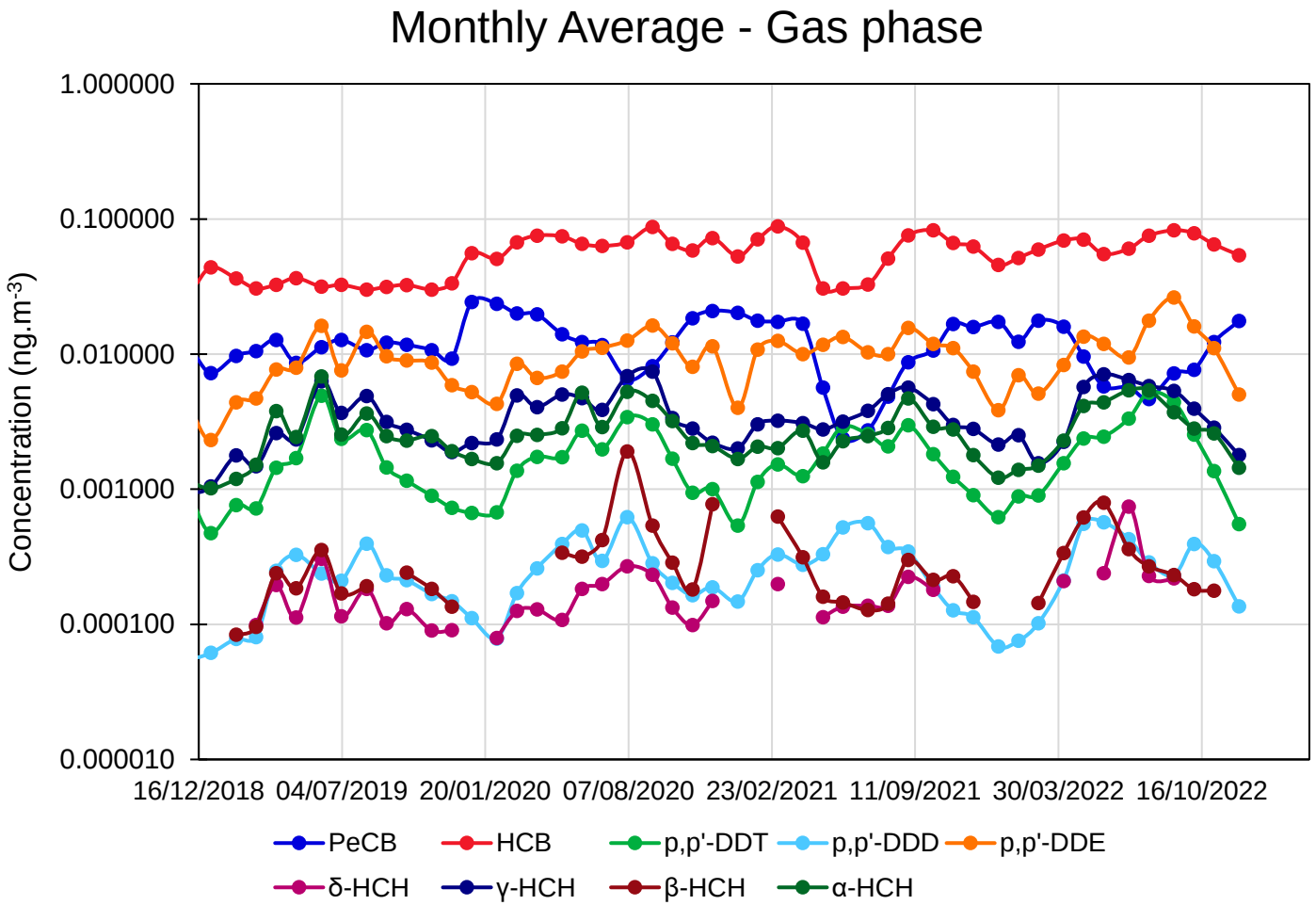
OCPs (2019-2021)



- Median [OCPs] = 3 pg m^{-3}
- No decrease over time
- $[OCPs]_{summer} > [OCPs]_{winter}$

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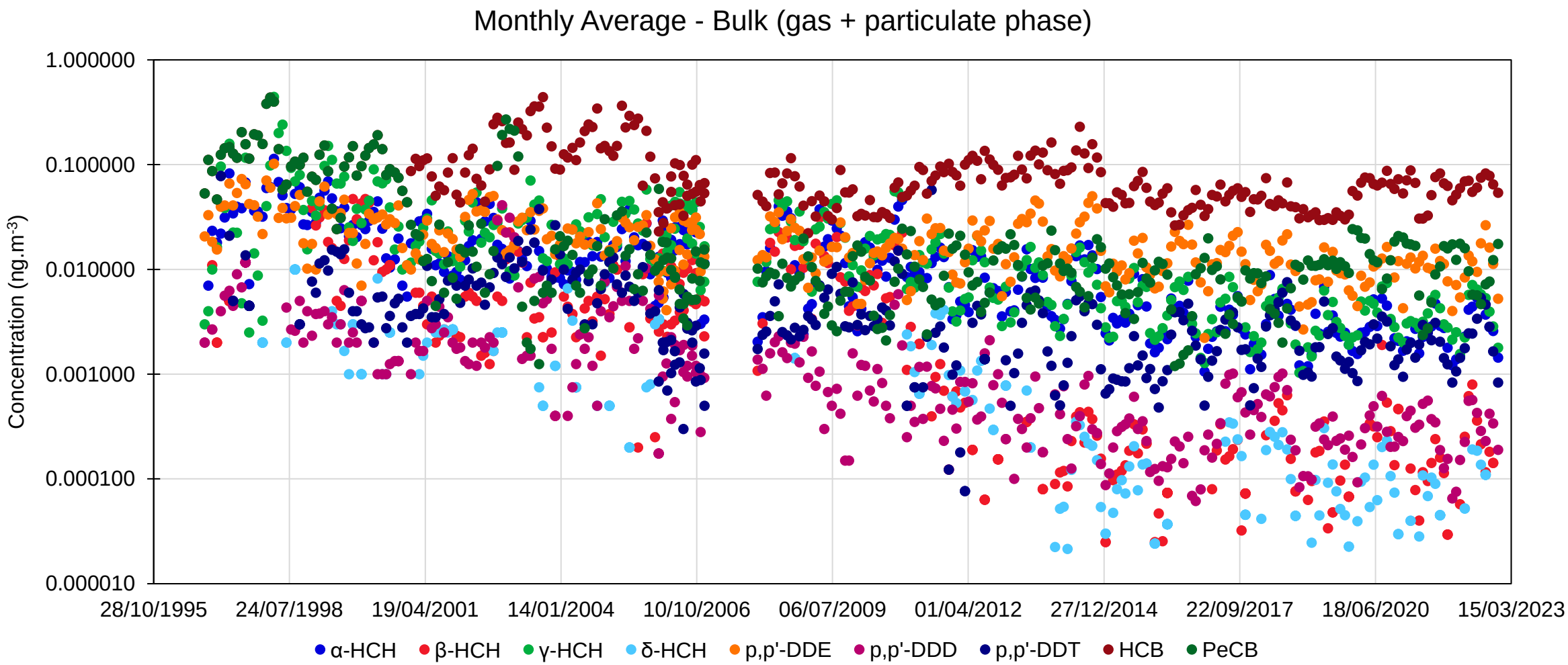
OCPs (1996 – 2022)



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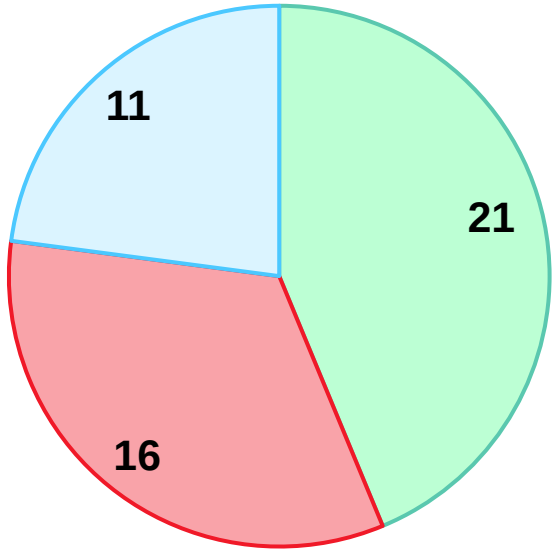
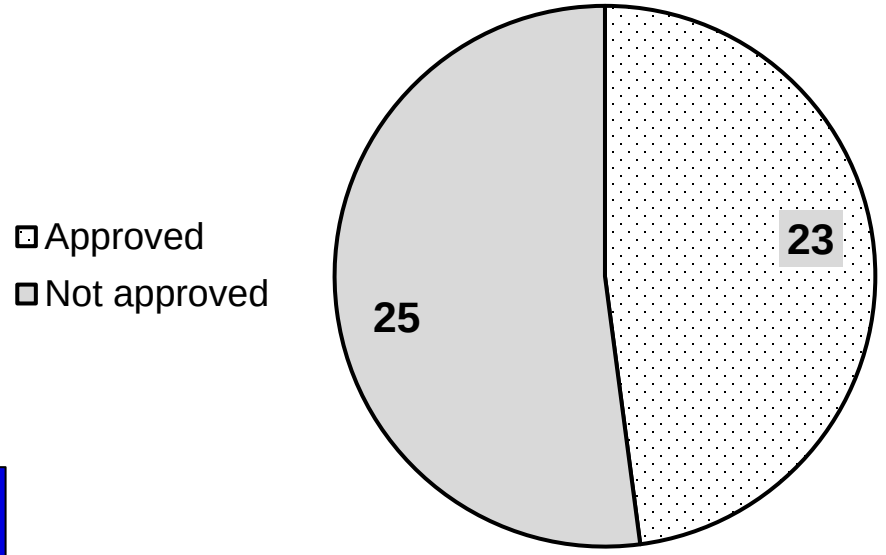
Analysed currently-used pesticides

Chosen according to:

- Previous research and monitoring studies
- Potential harmful effect to environmental and human health
- Usage of individual substances





Total: 48 CUPs

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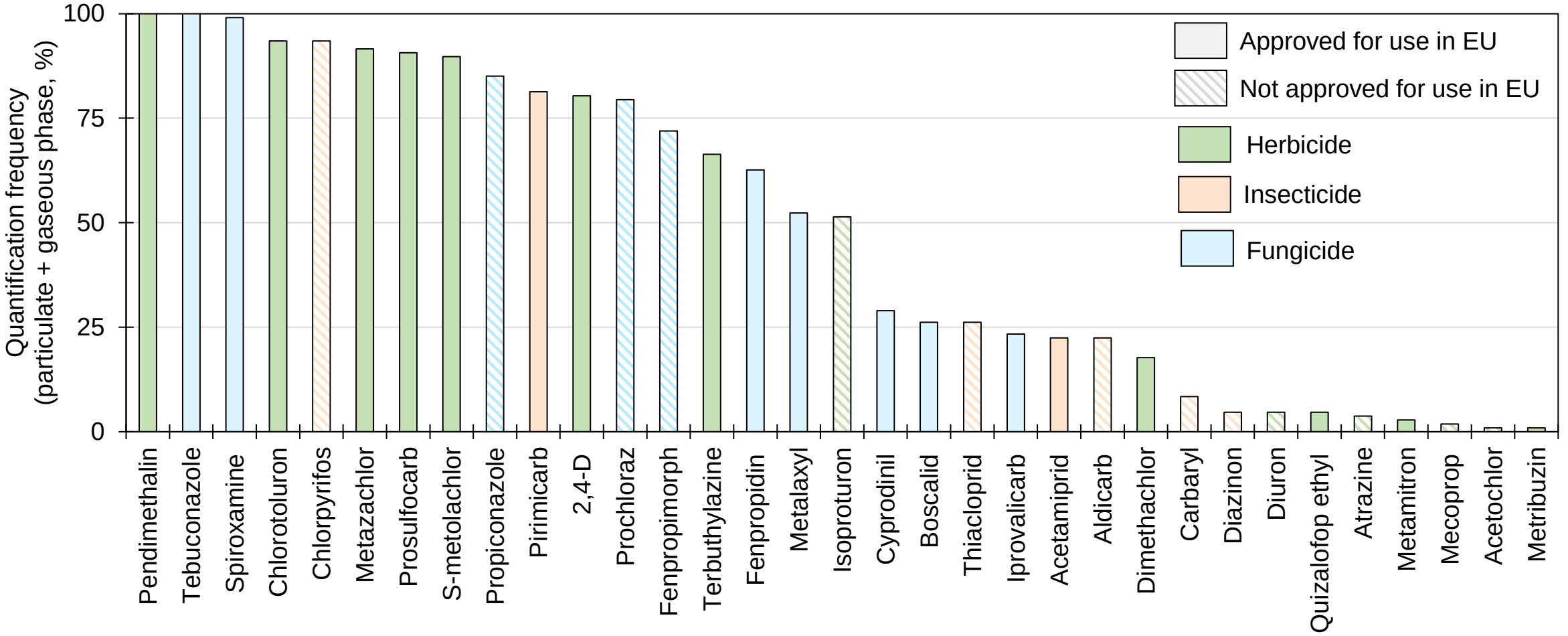
CUPs (2019-2021)



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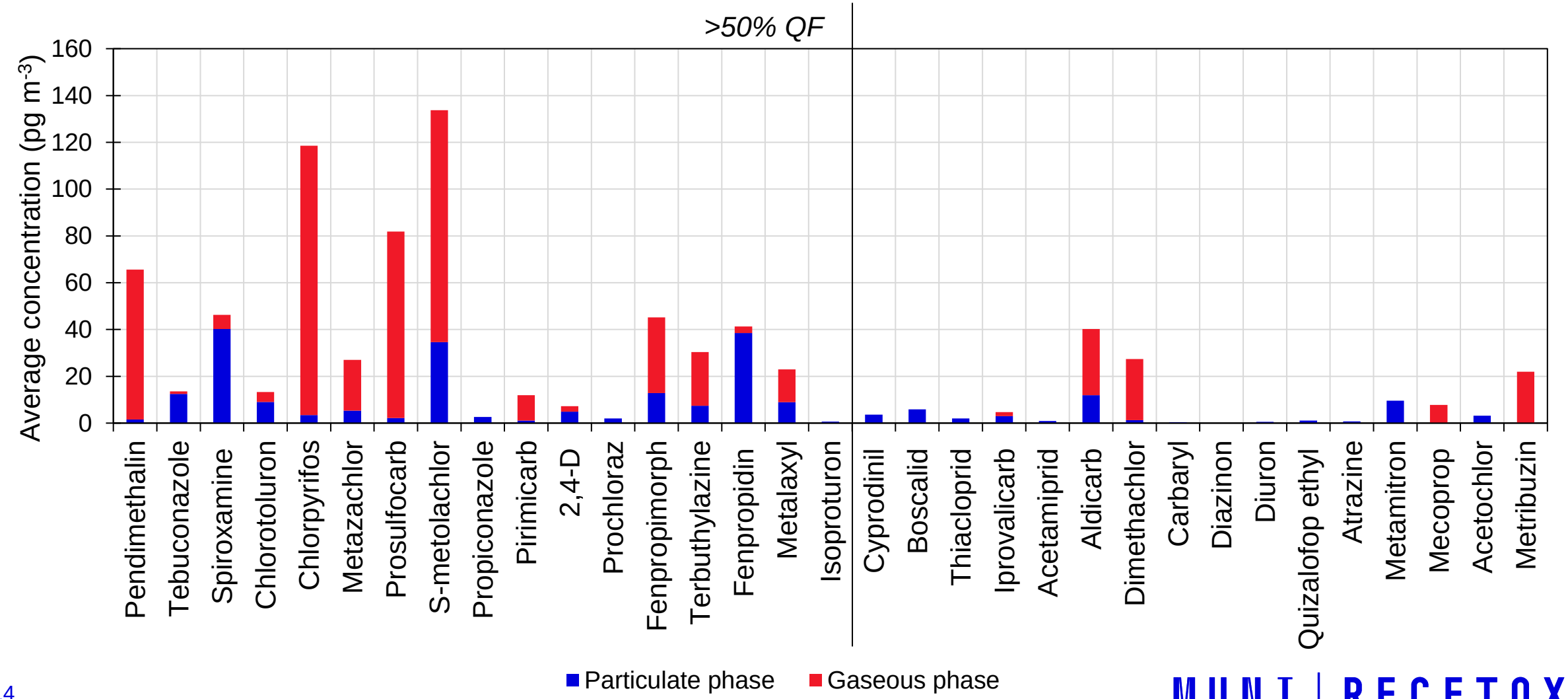
CUPs (2019-2021)



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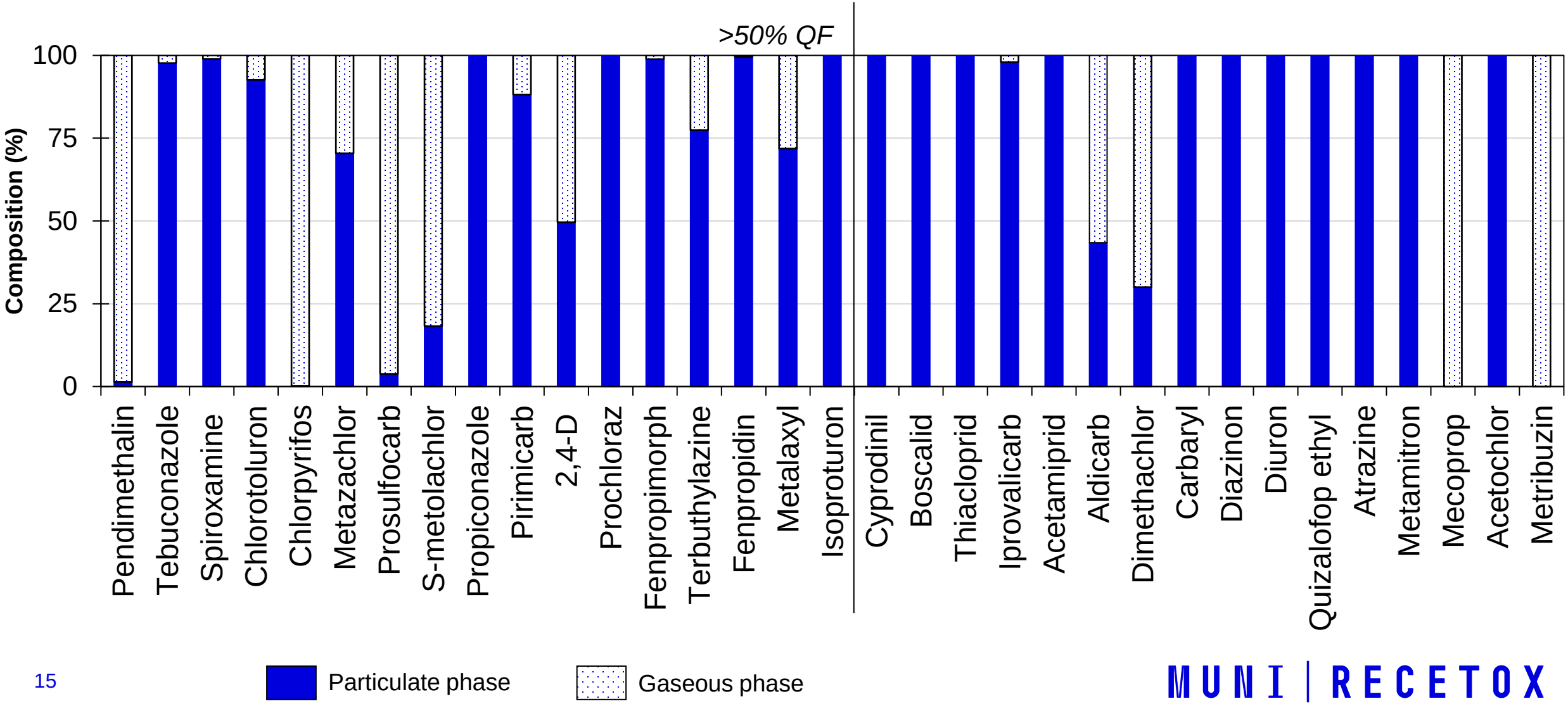
CUPs (2019-2021)



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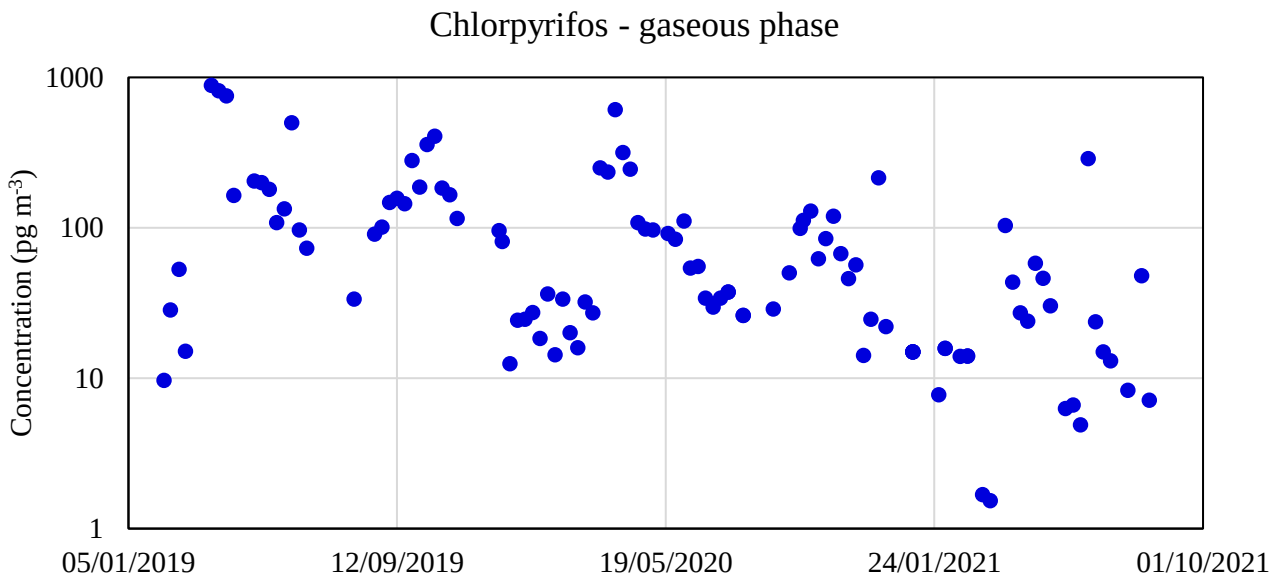
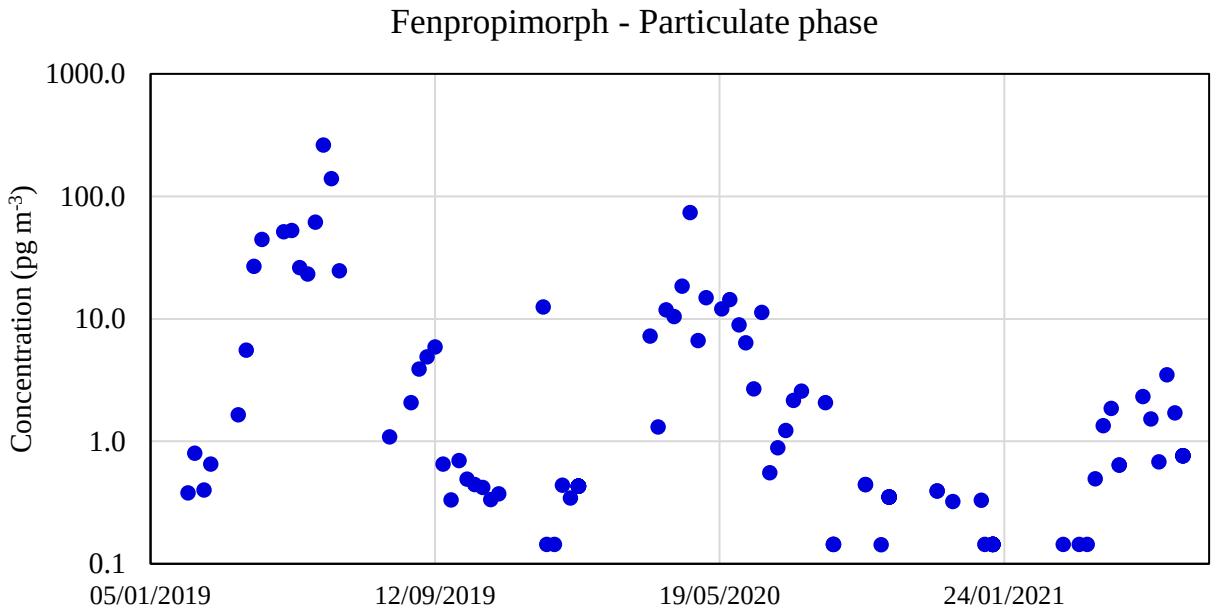
CUPs (2019-2021)

Long term trends

(Venier et al., 2012; DOI:10.1021/es204527q)

Particulate phase		*Gaseous phase*	
Pesticide	***$T_{1/2}$ (years)***	***Pesticide***	***$T_{1/2}$ (years)***
2,4-D	1.7	**Chlorpyrifos**	**0.7**
Chlorotoluron	1.7	Metazachlor	1.0
Fenpropidin	0.9	S-metolachlor	1.3
Fenpropimorph	**0.5**	Tebuconazole	0.9
Metalaxyl	1.2		
Pirimicarb	1.8		
Propiconazole	**1.0**		





Conclusions

- Evolution of OCPs atmospheric levels

  → persistence

- Generate the lacking data regarding CUPs atmospheric levels

- Immediate effect of legislation on CUPs atmospheric levels (e.g., chlorpyrifos)

Acknowledgments

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Thank you for your attention