Supplementary material for

Current-use and organochlorine pesticides' multi-annual trends in air in Central Europe: primary and unidentified secondary sources

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S1. Methodology

S1.1. Analytical method and QA/QC of OCPs

S1.1.1. 2013 to 2017

Samples collected from 2013 to 2014 were analysed on a 7000B GC (Agilent, USA) coupled to triple quadrupole mass spectrometers for 13 OCP compounds/isomers (i.e., PeCB, HCB, *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, *ε*-HCH, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT). Detailed information regarding the analytical methods have previously been described (Degrendele et al., 2016). For samples collected from 2015 to 2017, OCPs were analysed on 7890A GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 µm Rxi-5Sil-MS column (Restek, FR) coupled to a triple quadrupole 7000B MS (Agilent, USA) from 2015-2017. The temperature program for GC oven started at 80 °C (1.5 min hold), then continued with 40 °C min^{-1} to 200 °C (18 min hold) and lastly 5 °C/min to 305 °C (no hold). The inlet temperature was 280 °C. Injection volume was 3 µL in pulsed-splitless mode. The carrier gas was helium with a flow rate of 1.5 mL min^{-1}. The temperature of the GC-MS transfer line was 310 °C. Ion source was heated to 250 °C. Mass spectrometer was operating in multiple reaction monitoring (MRM) mode with nitrogen as collision gas with flow of 1.5 mL min^{-1}. Compound quantification was done with the MassHunter Workstation B.06.00 software. For those samples OCPs were quantified using external eight-point linear calibration curve with native compound concentrations ranging from 1 ng mL^{-1} to 1000 ng mL^{-1} and PCB 30 and PCB 185 internal standards with concentrations of 10 ng mL^{-1} across all calibration levels. Instrumental limits of quantification (iLOQ) were calculated from the lowest calibration point as an amount producing a signal-to-noise ratio of 10. OCP concentrations in the samples were not recovery corrected.

Additionally, samples from 2013 to 2015 were analyzed for 17 additional OCPs (i.e., heptachlor, *cis*-heptachlor-epoxide, *trans*-heptachlor-epoxide, aldrin, dieldrin, endrin, endrin-aldehyde, endrin-ketone, isodrin, *α*-chlordane, *γ*-chlordane, oxychlordane, *α*-endosulfan, *β*-endosulfan, endosulfan sulfate methoxychlor and mirex) using gas chromatography with electron ionization tandem quadrupole mass spectrometry (GC-EI-MS/MS) on a 6890N GC (Agilent, USA) coupled to Quattro Micro GC (Waters, UK). The GC was fitted with a 30m × 0.25mm × 0.25 um Rxi-5Sil MS column (Restek, USA). The injection was splitless at 250 °C. He was used as carrier gas at a constant flow of 1.5 mL min^{-1}. The oven temperature programme was 90 °C (1 min hold), then 40 °C min^{-1} to 200 °C, followed by 2 °C min^{-1} to 240 °C, and finally 40 °C min^{-1} to 310 °C (3.5 min hold). OCPs were quantified using internal standards (^{12}C PCB 121). For this second set of OCPs, QA/QC was checked by running spiked reference samples. LOQs were determined for each compound and for each batch of samples by the quantification software (MassLynx TargetLynx 4.1®) and were defined as concentration for a peak with the signal-to-noise ratio of 9:1 in the respective chromatograms of the sample and analyte.

S1.1.2. 2018 to 2022

OCP samples for 13 OCP compounds/isomers (i.e., PeCB, HCB, *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, *ε*-HCH, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT), collected from 2018 to 2022 were analysed on an 8890 GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 µm Rxi-5Sil-MS column (Restek, FR) coupled to a triple quadrupole 7000D MS (Agilent, USA). The GC temperature programme was 80 °C (1.5 min hold), then 40 °C min^{-1} to 200 °C (18 min hold), and finally 5 °C/min to 305 °C. Inlet temperature was 280 °C. Injection volume was 3 µL in pulsed-splitless mode. Carrier gas was helium with flow rate of 1.5 mL min^{-1}. Temperature of the transfer line was 310 °C and 250 °C of the ion source. The mass spectrometer was operating in multiple reaction monitoring (MRM) mode with nitrogen as collision gas with flow rate of 1.5 mL min^{-1}. Compound quantification was done using the MassHunter Workstation 10.1 software. These samples were quantified for OCPs by isotopic dilution method, using an external eight-point linear calibration curve with native compounds concentrations ranging from 1 ng mL^{-1} to 1000 ng mL^{-1} and isotopically labeled compounds with concentration of 10 ng/mL across all calibration levels. iLOQ were calculated from the lowest calibration point as an amount producing a signal to noise ratio of 10. OCP concentrations in the samples were recovery-corrected using ^{13}C labeled surrogate compounds.

Furthermore, samples for the 17 additional OCPs (i.e., heptachlor, *cis*-heptachlor-epoxide, *trans*-heptachlor-epoxide, aldrin, dieldrin, endrin, endrin-aldehyde, endrin-ketone, isodrin, *α*-chlordane, *γ*-chlordane, oxychlordane, *α*-endosulfan, *β*-endosulfan, endosulfan sulfate methoxychlor and mirex) from 2016 onwards were analysed by gas chromatography atmospheric pressure chemical ionization tandem mass spectrometry (GC-APCI-MS/MS) on a Waters Xevo TQ-S MS coupled to Agilent 7890 GC. The MS was operated under dry source conditions in MRM. The GC was fitted with a 30m × 0.25mm × 0.25 um Rxi-5Sil MS column (Restek, USA). The injection was splitless at 250 °C. He was used as carrier gas at a constant flow of 1.5 mL min^{-1}. The oven temperature programme was 90 °C (1 min hold), then 40 °C min^{-1} to 200 °C, followed by 2 °C min^{-1} to 240 °C, and finally 40 °C min^{-1} to 310 °C (3.5 min hold). OCPs were quantified using internal standards (^{13}C PCB 95). For this second set of OCPs, during the 2016-2022 period, ^{13}C *α*- and *β*-endosulfan were used as internal standards for OCPs quantification. LOQs were determined for each compound and for each batch of samples by the quantification software (MassLynx TargetLynx 4.1®) and were defined as concentration for a peak with the signal-to-noise ratio of 9:1 in the respective chromatograms of the sample and analyte.

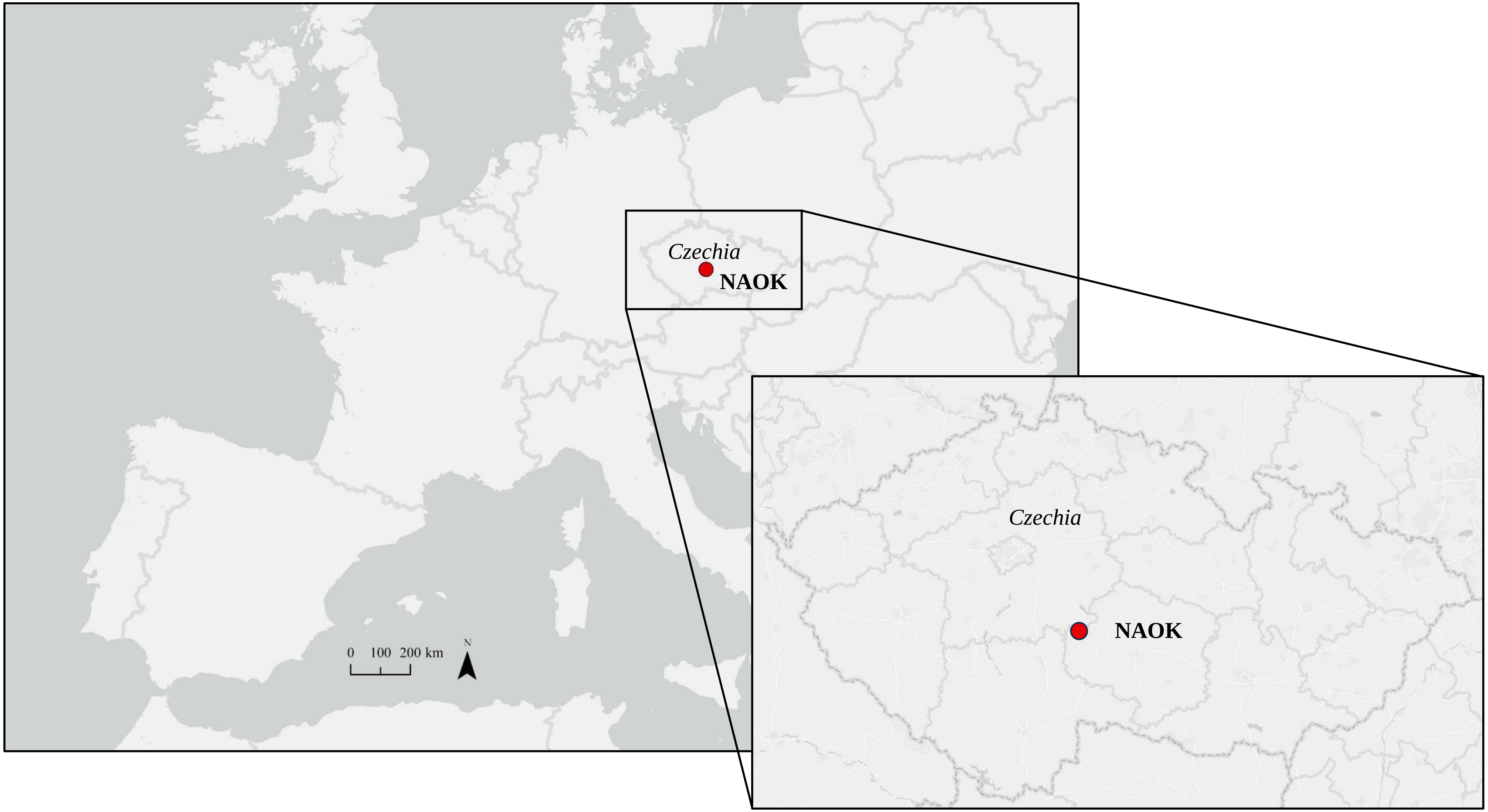

Figure S1. Location of the sampling site.

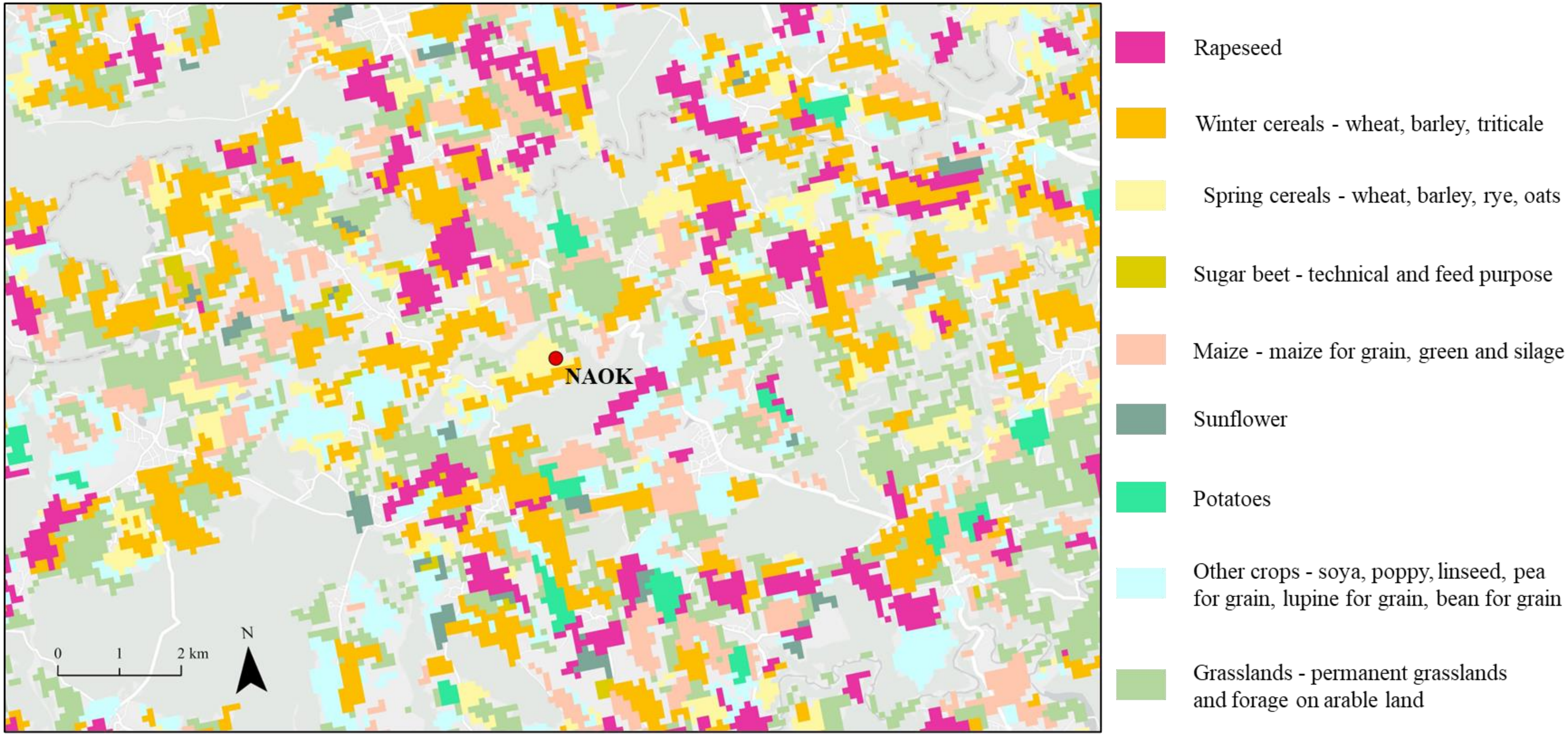

Figure S2. Land-use and crops cultivated in the area of the site during the year 2020. Data from Mapradix s.r.o. Earth Observation services.

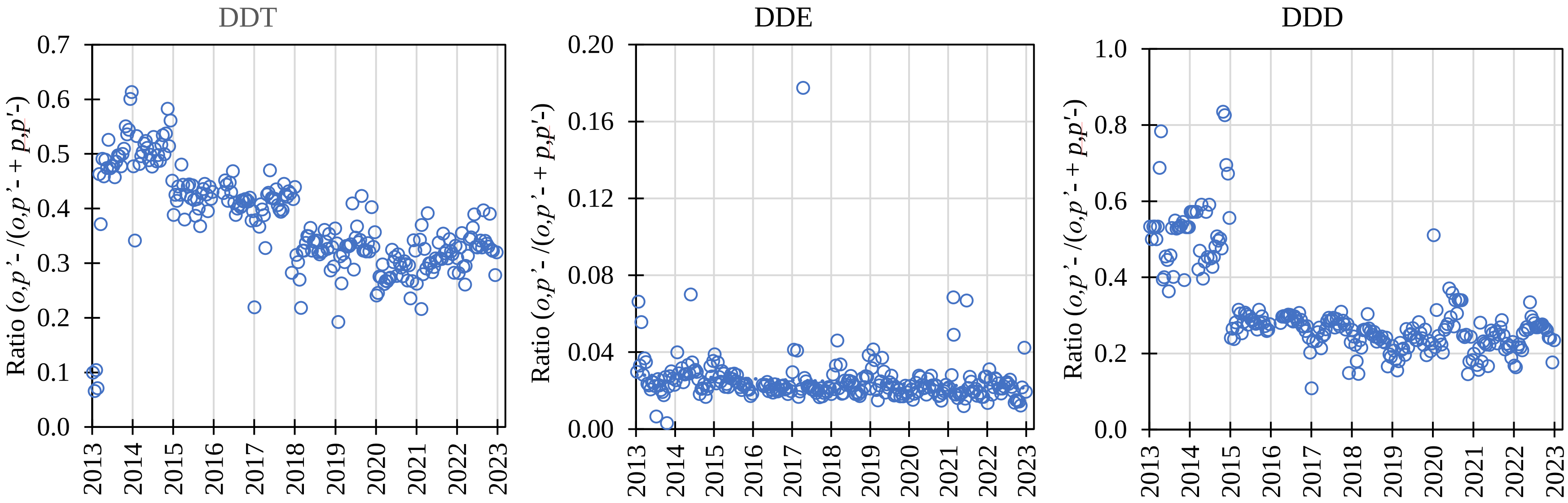

Figure S3. Evolution of the *(o,p’-/(o,p’-+p,p’-)* ratio of for DDX substances over the sampling period.

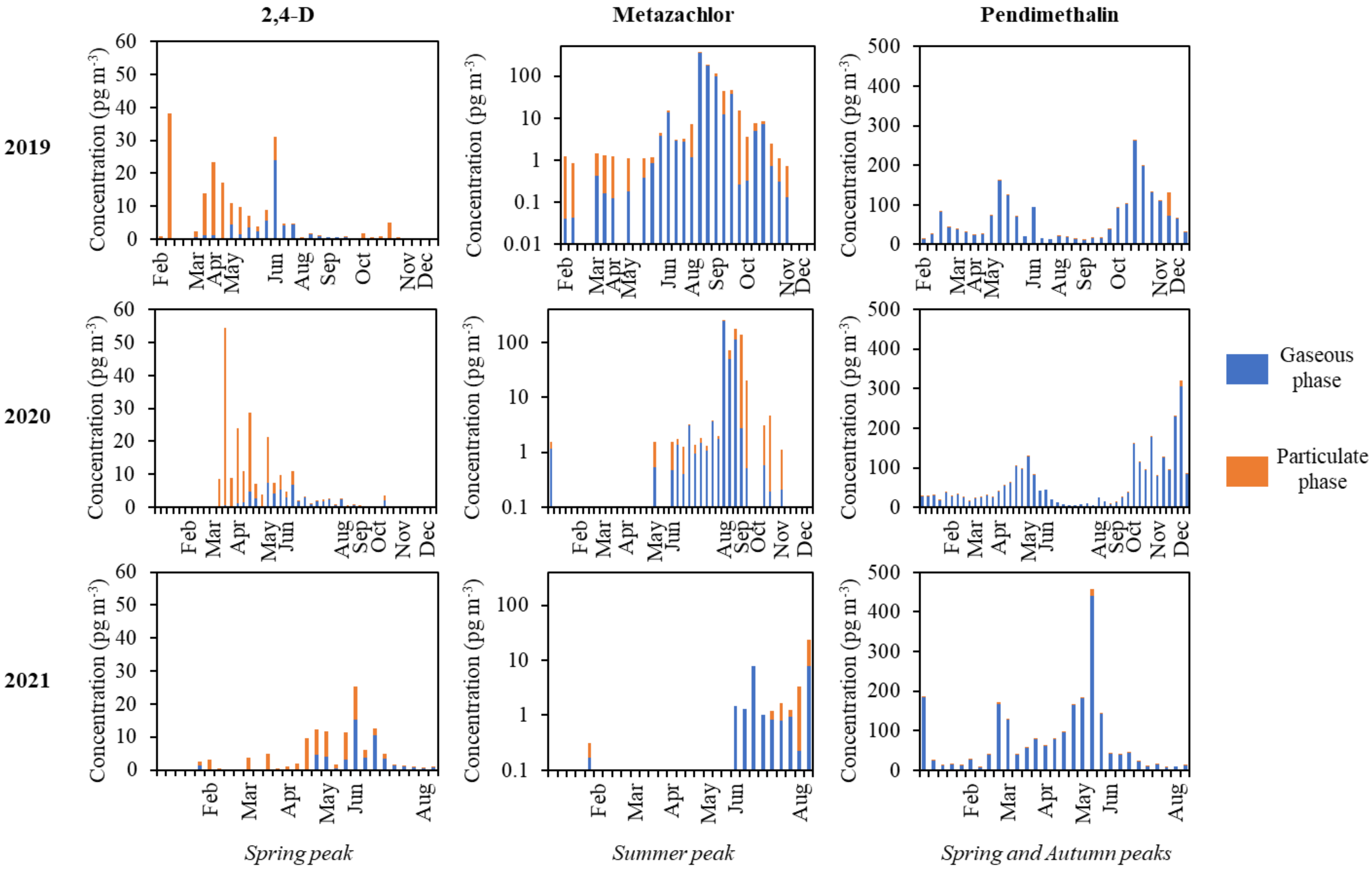

Figure S4. Seasonal variation of selected CUPs with peak concentration during the spring season, during the summer and with two peaks per year.

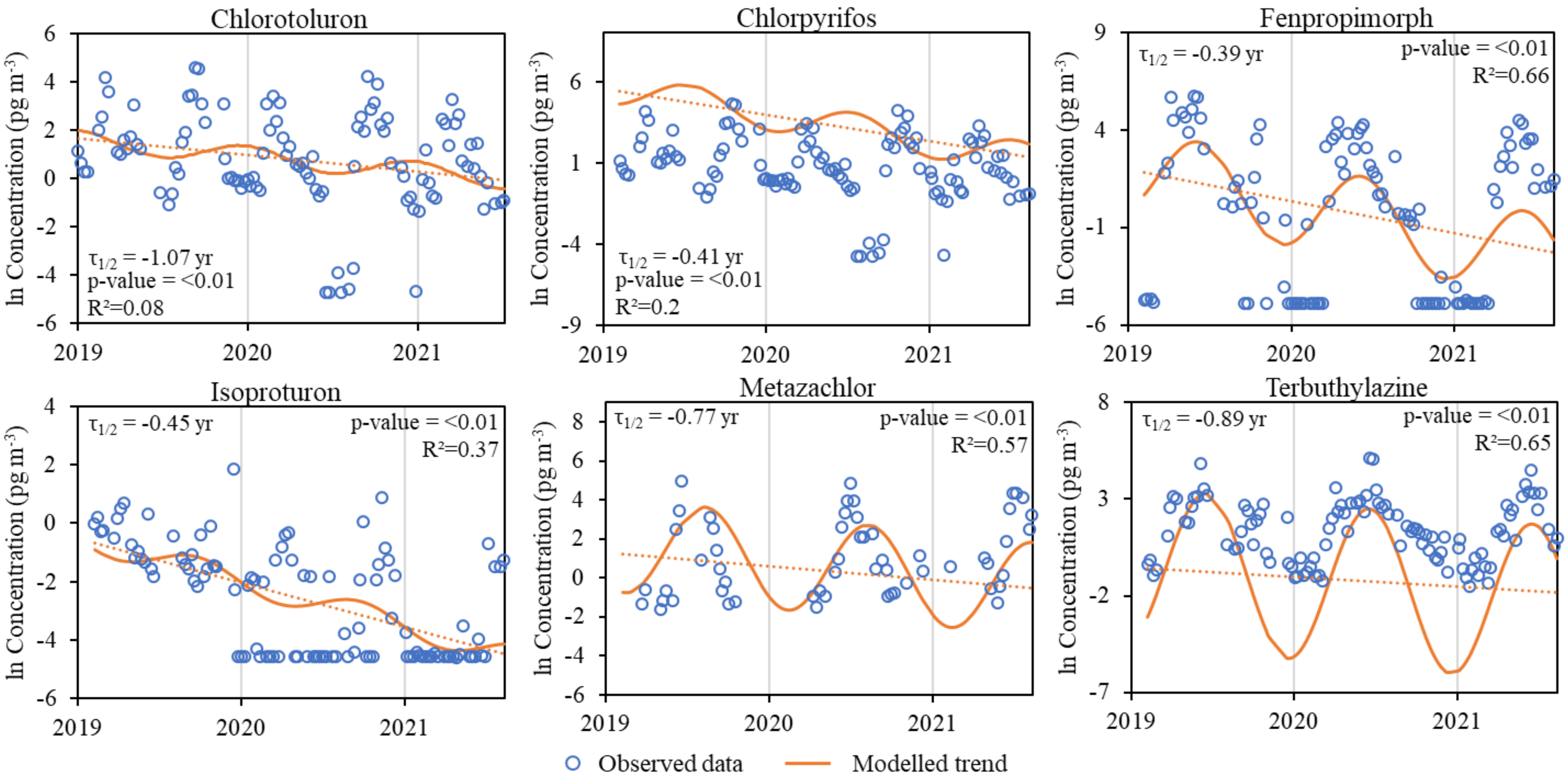

Figure S5. Multi-year variations, using Eq. (1), of selected CUPs with significantly negative trends. Values < MDL were substituted by MDL/2.

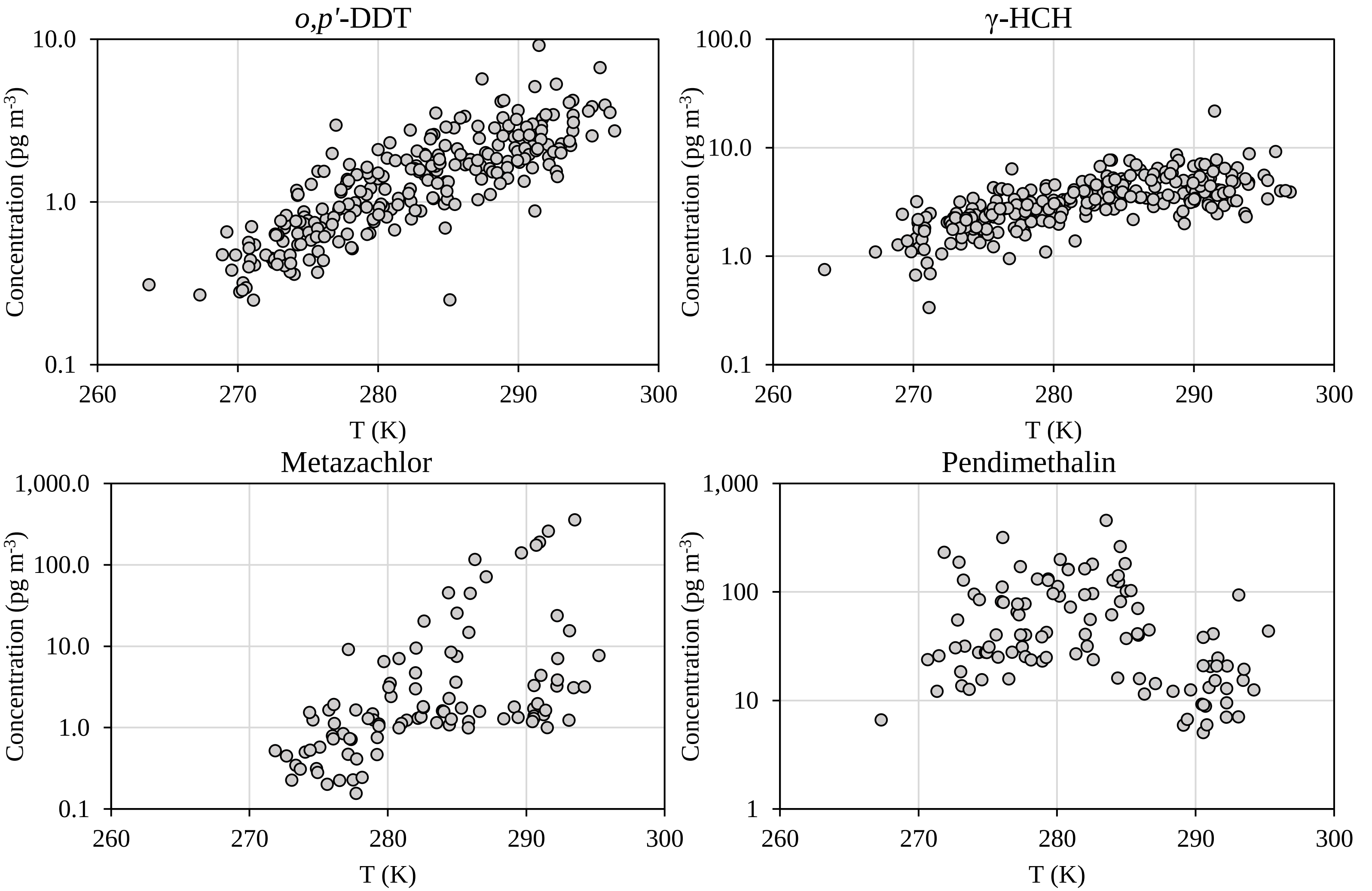

Figure S6. Selected examples of the influence of the temperature on pesticides revolatisation from soils.

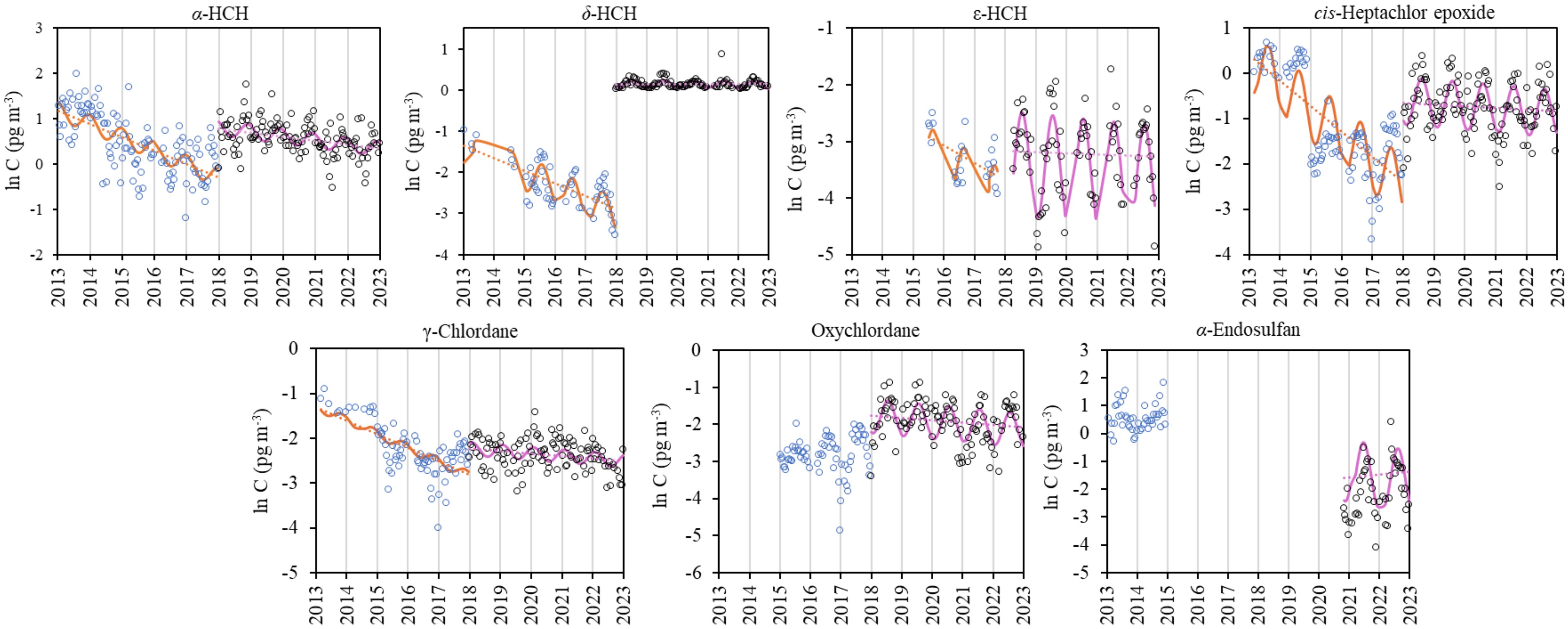

Figure S7. Multi-annual variation of OCP concentrations with significantly negative trends during both time periods (2013-2017 and 2018-2022). Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the modelled variation, whenever the trend was significant. Values <MDL were not included.

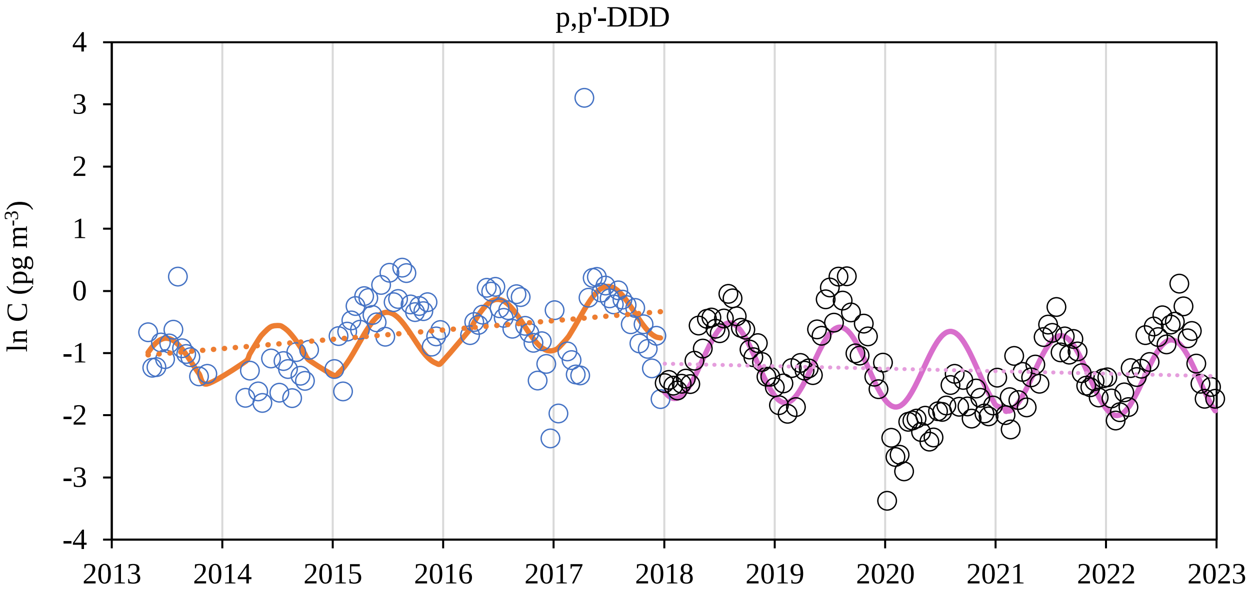

Figure S8. Multi-annual variation of *p,p'*-DDD with significantly positive trend during the 2013-2017 period and significant negative trend during the 2018-2022 period. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the modelled variation, whenever the trend was significant. Values <MDL were not included.

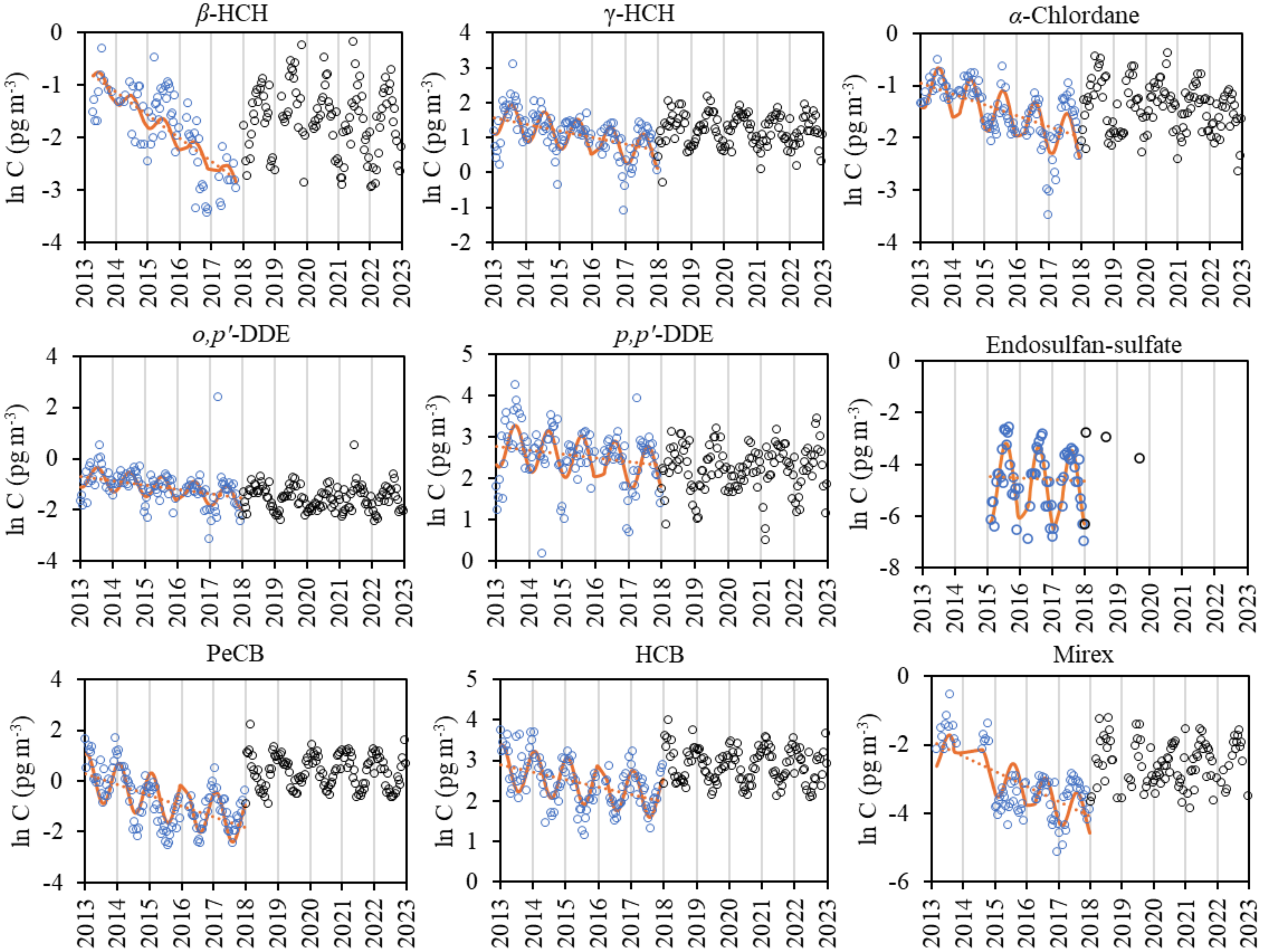

Figure S9. Multi-annual variations of OCP concentrations with significantly negative trends in the time period 2013-2017. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange the significant modelled variation. Values <MDL were not included.

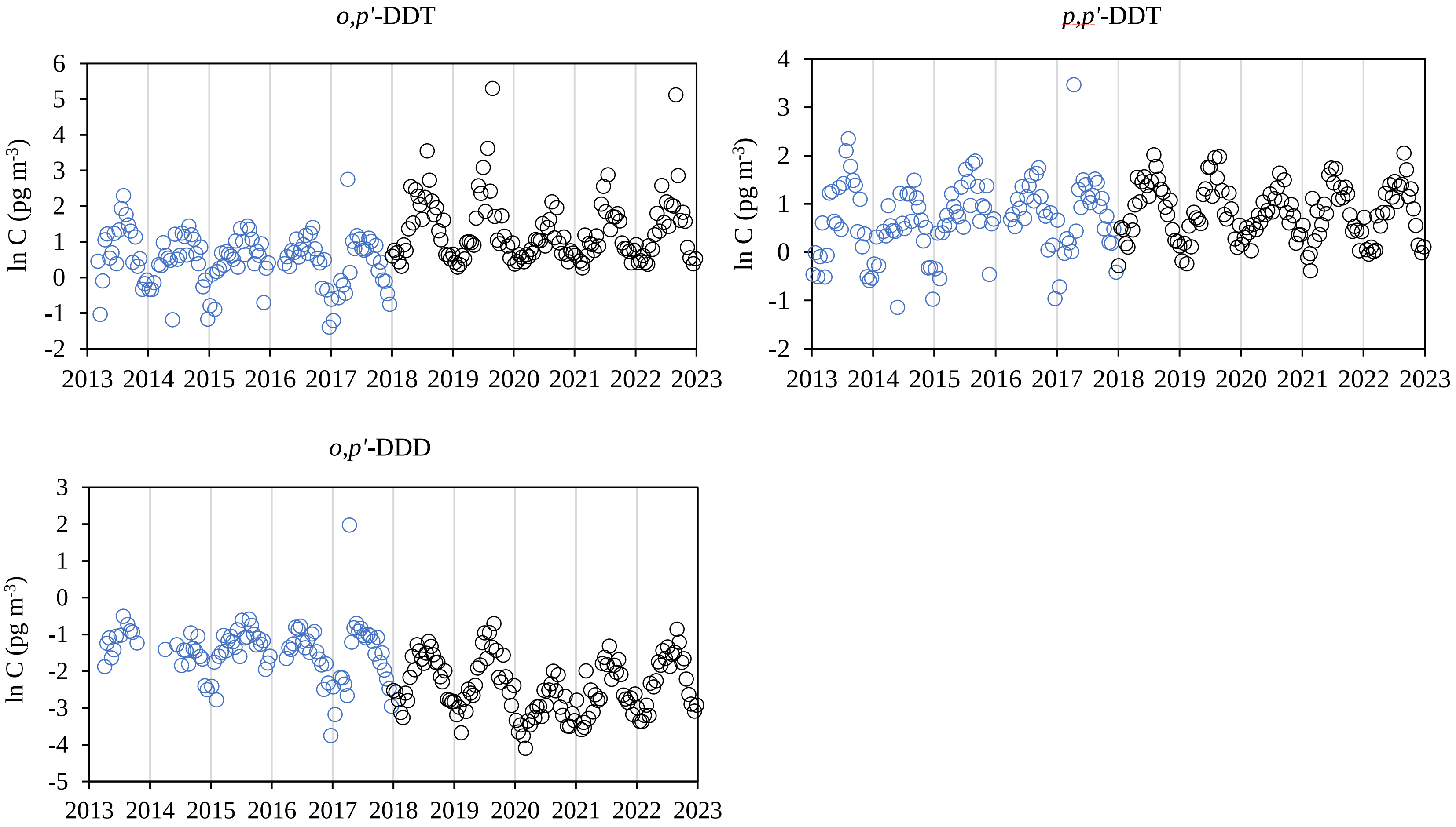

Figure S10. Multi-annual variation of *o,p'*-DDD, DDT and *p,p'*-DDT without significant trends. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively.

Table S1. Information on the current-use pesticides in this study, herbicide (a), insecticides (b) and fungicide (c)

(a)

Herbicide	**CAS number**[a]	**Chemical class**[a]	**Status under Reg. (EC) No 1107/2009**[b]	**Date of approval**[b]	**Expiration of approval**[b]	**In use in Czech Republic during the sampling period?**[c]
2,4-D	94-75-7 4	Alkychlorophenoxy	Approved	01/01/2016	31/12/2030	Yes
Acetochlor	34256-82-1	Chloroacetamide	Not approved			No
Alachlor	15972-60-8	Chloroacetamide	Not approved			No
Atrazine	1912-24-9	Triazine	Not approved			No
Chloridazon	1698-60-8	Pyridazinone	Not approved		31/12/2018	Yes
Chlorotoluron	15545-48-9	Urea	Not approved	01/01/2010	31/12/2019	Yes
Chlorsulfuron	15545-48-9	Urea	Not approved	01/01/2010	31/12/2019	Yes
Dimethachlor	50563-36-5	Chloroacetamide	Approved	01/01/2010	31/12/2022	Yes
Diuron	330-54-1	Phenylamide	Not approved	01/10/2008	30/09/2020	No
Fluroxypyr	69377-81-7	Pyridine	Approved	01/01/2012	31/12/2024	No
Isoproturon	34123-59-6	Urea	Not approved		30/06/2016	No
Mecoprop	7085-19-0	Aryloxyalkanoic acid	Not approved	01/06/2004	31/01/2017	Yes
Metamitron	41394-05-2	Triazinone	Approved	01/09/2009	31/08/2022	Yes
Metazachlor	67129-08-2	Chloroacetamide	Approved	01/08/2009	31/07/2022	Yes
Metribuzin	21087-64-9	Triazinone	Approved	01/10/2007	31/07/2022	Yes
Pendimethalin	40487-42-1	Dinitroaniline	Approved	01/09/2017	30/11/2024	Yes
Prosulfocarb	52888-80-9	Thiocarbamate	Approved	01/11/2009	31/10/2022	Yes
Quizalofop ethyl	76578-14-8	Aryloxyphenoxypropionate	Approved	01/12/2009	30/11/2022	Yes
Simazine	122-34-9	Triazine	Not approved			No
S-Metolachlor	87392-12-9	Chloroacetamide	Approved	01/04/2005	31/07/2022	Yes
Terbuthylazine	5915-41-3	Triazine	Approved	01/01/2012	31/12/2024	Yes

[a] = Lewis et al., 2016; [b] = EU pesticides database; [c] = UZKUZ Central Institute for Supervising and Testing in Agriculture, 2024

(b)

Insecticide	**CAS number[a]**	**Chemical class[a]**	**Status under Reg. (EC) No 1107/2009[b]**	**Date of approval[b]**	**Expiration of approval[b]**	**In use in Czech Republic during the sampling period?[c]**
Acetamiprid	135410-20-7	Neonicotinoid	Approved	01/03/2018	28/02/2033	Yes
Azinphos methyl	86-50-0	Organophosphate	Not approved			No
Carbaryl	63-25-2	Carbamate	Not approved			No
Carbofuran	1563-66-2	Carbamate	Not approved			No
Chlorpyrifos	2921-88-2	Organophosphate	Not approved	01/02/2005	08/07/2019	Yes
Diazinon	333-41-5	Organophosphate	Not approved			No
Dimethoate	60-51-5	Organophosphate	Not approved	01/10/2007	30/06/2019	Yes
Esfenvalerate	66230-04-4	Pyrethroid	Approved			Yes
Fenitrothion	122-14-5	Organophosphate	Not approved			No
Fonofos	944-22-9	Organophosphate	Not approved			No
Parathion methyl	298-00-0	Organophosphate	Not approved			No
Phosalone	2310-17-0	Organophosphate	Not approved			No
Pirimicarb	23103-98-2	Carbamate	Approved	01/02/2007	30/04/2023	Yes
Temephos	3383-96-8	Organophosphate	Not approved			No
Terbufos	13071-79-9	Organophosphate	Not approved			No
Thiacloprid	111988-49-9	Neonicotinoid	Not approved	01/01/2005	03/02/2020	Yes

[a] = Lewis et al., 2016; b = EU pesticides database; [c] = UZKUZ Central Institute for Supervising and Testing in Agriculture, 2024

(c)

Fungicide	CAS number[a]	Chemical class[a]	Status under Reg. (EC) No 1107/2009[b]	Date of approval[b]	Expiration of approval[b]	In use in Czech Republic during the sampling period?[c]
Boscalid	188425-85-6	Carboxamide	Approved	01/08/2008	31/07/2022	Yes
Cyprodinil	121552-61-2	Anilinopyrimidine	Approved	01/05/2007	30/04/2023	Yes
Fenpropidin	67306-00-7	Morpholine	Approved	01/01/2009	31/12/2022	Yes
Fenpropimorph	67564-91-4	Morpholine	Not approved	01/05/2009	30/04/2019	Yes
Iprovalicarb	140923-17-7	Carbamate	Approved	01/04/2016	31/03/2031	Yes
Kresoxim-methyl	143390-89-0	Strobilurin	Approved	01/01/2012	31/12/2024	Yes
Metalaxyl	57837-19-1	Phenylamide	Approved	01/07/2010	30/06/2023	Yes
Prochloraz	67747-09-5	Imidazole	Approved	01/01/2012	31/12/2021	Yes
Propiconazole	60207-90-1	Triazole	Not approved	01/06/2004	19/12/2018	Yes
Spiroxamine	118134-30-8	Morpholine	Approved	01/01/2012	31/12/2023	Yes
Tebuconazole	107534-96-3	Triazole	Approved	01/09/2009	31/08/2022	Yes

[a] = Lewis et al., 2016; [b] = EU pesticides database; [c] = UZKUZ Central Institute for Supervising and Testing in Agriculture, 2024

Table S2. Information on the organochlorine insecticides analysed in this study.

Pesticide	CAS number[a]	Initially listed under the Stockholm Convention on Persistent Organic Pollutants in 2004?[b]	Added in the later revisions?[c]
α-HCH	319-84-6		2009
β-HCH	319-85-7		2009
γ-HCH	58-89-9		2009
δ-HCH	319-86-8		
ε-HCH	6108-10-7		
o,p'-DDE	3424-82-6	Yes	
p,p'-DDE	72-55-9	Yes	
o,p'-DDD	53-19-0	Yes	
p,p'-DDD	72-54-8	Yes	
o,p'-DDT	789-02-6	Yes	
p,p'-DDT	50-29-3	Yes	
PeCB	608-93-5		2009
HCB	118-74-1	Yes	
Heptachlor	76-44-8	Yes	
cis-Heptachlor epoxide	1024-57-3		
trans-Heptachlor epoxide	28044-83-9		
Aldrin	309-00-2	Yes	
Dieldrin	60-57-1	Yes	
Endrin	72-20-8	Yes	
Endrin aldehyde	7421-93-4		
Endrin ketone	53494-70-5		
Isodrin	465-73-6		
Oxychlordane	27304-13-8		
α-Chlordane	5103-71-9	Yes	
γ-Chlordane	5103-74-2	Yes	
α-Endosulfan	959-98-8		2011
β-Endosulfan	33213-65-9		2011
Endosulfan-sulfate	1031-07-8		
Methoxychlor	72-43-5		
Mirex	2385-85-5	Yes	

[a] = Lewis et al., 2016; [b] = UNEP, 2001; [c] = UNEP, 2014

Table S3. Information on the chemical analysis performed on CUPs, for individual herbicides (a), insecticides (b) and fungicides (c).

(a)

Herbicide	Native standard used	Internal standard
2,4-D	Neochema (Germany)	2,4-D-13C6[a]
Acetochlor	Neochema (Germany)	Acetochlor-D11[b]
Alachlor	Neochema (Germany)	Alachlor-D13[b]
Atrazine	Chromservis (Czech Republic)	Atrazine-D5[c]
Chloridazon	Chromservis (Czech Republic)	Pyrazon-D5[b]
Chlorotoluron	Neochema (Germany)	Chlorotoluron-D6[b]
Chlorsulfuron	Neochema (Germany)	Metamitron-D5[d]
Dimethachlor	Chromservis (Czech Republic)	Diuron-D6[c]
Diuron	Chromservis (Czech Republic)	Diuron-D6[c]
Fluroxypyr	Neochema (Germany)	Metribuzin-D3[d]
Isoproturon	Chromservis (Czech Republic)	Isoproturon-D3[d]
Mecoprop	Neochema (Germany)	Mecoprop-D6[d]
Metamitron	Chromservis (Czech Republic)	Metamitron-D5[d]
Metazachlor	Neochema (Germany)	Metazachlor-D6[e]
Metribuzin	Chromservis (Czech Republic)	Metribuzin-D3[d]
Pendimethalin	Chromservis (Czech Republic)	Pendimethalin-D5[d]
Prosulfocarb	Neochema (Germany)	Prosulfocarb-D7[f]
Quizalofop ethyl	Neochema (Germany)	Quizalofop ethyl-D3[g]
Simazine	Chromservis (Czech Republic)	Simazine-D10[d]
S-Metolachlor	Neochema (Germany)	Metolachlor-D6[b]
Terbuthylazine	Chromservis (Czech Republic)	Terbuthylazine-D5[b]

HPLC-MS/MS = Agilent 1290 (Agilent Technologies, Palo, Alto, California, USA), Mass spectrometer: QTRAP 5500 (AB Sciex, Foster City, California, USA); [a] Toronto Research Chemicals Inc. (Canada); [b] LGC Dr. Ehrenstorfer (Germany); [c] Restek (United States); [d] HPC Standards GmbH (Germany); [e] Chiron AS (Norway); [f] ASCA GmbH (Germany); [g] Cambridge Isotope Laboratories, Inc. (United States)

(b)

Insecticide	Native standard used	Internal standard
Acetamiprid	Neochema (Germany)	Acetamiprid-D3[a]
Azinphos methyl	Chromservis (Czech Republic)	Fenitrothion-D6[b]
Carbaryl	Neochema (Germany)	Diuron-D6[c]
Carbofuran	Neochema (Germany)	Carbofuran-D3[d]
Chlorpyrifos	Chromservis (Czech Republic)	Chlorpyrifos-D10[b]
Diazinon	Chromservis (Czech Republic)	Diuron-D6[c]
Dimethoate	Neochema (Germany)	Dimethoate-D6[a]
Esfenvalerate	Neochema (Germany)	Fenpropathrin-D5[a]
Fenitrothion	Neochema (Germany)	Fenitrothion-D6[b]
Fonofos	Chromservis (Czech Republic)	Diuron-D6[c]
Imidacloprid	Neochema (Germany)	Imidacloprid-D4[e]
Parathion methyl	Chromservis (Czech Republic)	Fenitrothion-D6[b]
Phosalone	Neochema (Germany)	Phosalone-D10[b]
Pirimicarb	Neochema (Germany)	Diuron-D6[c]
Temephos	Neochema (Germany)	Chlorpyrifos-D10[b]
Thiacloprid	Neochema (Germany)	Thiacloprid-D4[d]

[a] Toronto Research Chemicals Inc. (Canada); [b] HPC Standards GmbH (Germany); [c] Restek (United States); [d] LGC Dr. Ehrenstorfer (Germany); [e] Chiron AS (Norway)

(c)

Fungicide	Native standard used	Internal standard
Boscalid	Neochema (Germany)	Boscalid-D4[a]
Cyprodinil	Neochema (Germany)	Cyprodinil-D5[a]
Fenpropidin	Neochema (Germany)	Fenpropidin-D10[a]
Fenpropimorph	Chromservis (Czech Republic)	Diuron-D6[b]
Iprovalicarb	Neochema (Germany)	Aldicarb-D3[a]
Kresoxim-methyl	Neochema (Germany)	Kresoxim-methyl-D7[a]
Metalaxyl	Neochema (Germany)	Metalaxyl-D6[a]
Prochloraz	Chromservis (Czech Republic)	Prochloraz-D7[c]
Propiconazole	Neochema (Germany)	Propiconazole-D5[c]
Spiroxamine	Neochema (Germany)	Spiroxamine-D4[a]
Tebuconazole	Chromservis (Czech Republic)	Tebuconazole-D6[c]

[a] Toronto Research Chemicals Inc. (Canada); [b] Restek (United States); [c] LGC Dr. Ehrenstorfer (Germany)

Table S4. Selected HPLC-MS/MS experimental parameters for CUPs analysis, instrumental limits of detection (iLODs) and instrumental limits of quantification (iLOQs).

Analyte	**Precursor ion** (m/z)	**Product ion 1** (m/z)	**Product ion 2** (m/z)	**R_t** (min)	**iLOD** (ng/mL)	**iLOQ** (ng/mL)
2,4-D	218.8	160.9	124.9	2.4	0.02	0.06
Acetamiprid	222.9	142.0	*N.A.*	3.2	0.08	0.29
Acetochlor	270.1	224.2	148.1	4.9	0.1	0.25
Alachlor	270.1	238.1	162.1	5.0	0.1	0.25
Atrazine	216.1	174.2	68.0	3.8	0.01	0.03
Azinphos methyl	318.0	130.0	160.0	4.1	0.03	0.1
Boscalid	343.2	307.1	140.1	5.9	0.12	0.4
Carbaryl	201.9	145.0	127.1	3.0	0.1	0.3
Carbendazim	192.0	160.0	131.9	1.2	0.03	0.05
Carbofuran	222.1	165.1	123.0	5.0	0.04	0.13
Chloridazon	222.0	104.0	77.0	2.3	0.06	0.12
Chlorotoluron	213.1	72.2	46.2	3.7	0.1	0.3
Chlorpyrifos	349.9	197.9	96.9	6.7	0.01	0.03
Chlorsulfuron	357.9	141.0	167.0	3.0	0.01	0.03
Cyprodinil	226.0	93.1	108.1	5.8	0.11	0.36
Diazinon	305.0	169.0	153.1	5.4	0.01	0.03
Dimethachlor	256.1	224.0	148.1	4.0	0.03	0.1
Dimethoate	230.0	198.9	124.9	2.2	0.03	0.1
Diuron	232.9	71.8	46.1	4.0	0.1	0.25
Esfenvalerate	437.0	420.1	167.0	4.2	0.46	1.55
Fenitrothion	277.9	125.1	109.0	4.7	0.3	1
Fenpropidin	274.1	147.1	86.1	5.5	0.1	0.34
Fenpropimorph	304.1	147.1	117.1	2.4	0.01	0.03
Fluroxypyr	255.0	180.9	208.9	2.7	1	3
Fonofos	246.9	109.0	137.0	5.4	0.1	0.25
Iprovalicarb	321.0	119.0	203.0	6.1	0.1	0.32
Isoproturon	207.2	72.1	46.1	3.9	0.01	0.03
Kresoxim methyl	314.0	116.1	131.1	6.3	0.22	0.74
Mecoprop	212.9	141.0	71.1	2.5	0.02	0.07
Metalaxyl	280.0	220.1	192.0	5.5	0.12	0.41
Metamitron	203.0	175.1	104.0	2.2	0.25	0.5
Metazachlor	278.2	134.2	210.2	3.7	0.03	0.05
Metribuzin	215.1	187.1	84.0	3.3	0.03	0.1
Parathion methyl	264.0	125.0	232.0	4.0	0.5	0.1
Pendimethalin	282.2	212.0	194.2	6.4	0.01	0.04
Phosalone	367.9	111.0	181.9	6.4	0.07	0.25
Pirimicarb	239.0	72.0	182.1	2.1	0.01	0.03
Prochloraz	376.0	308.0	70.0	4.9	0.01	0.03
Propiconazole	342.0	159.0	69.0	5.0	0.03	0.1
Prosulfocarb	252.0	91.1	128.1	6.6	0.06	0.21
Quizalofop ethyl	273.0	299.0	271.0	6.6	0.03	0.1
Simazine	202.0	132.0	124.0	3.3	0.01	0.03
S-Metolachlor	284.1	252.2	176.1	4.9	0.01	0.03
Spiroxamine	298.1	144.2	100.0	5.6	0.09	0.29
Tebuconazole	308.1	70.0	125.0	4.9	0.01	0.03
Temephos	466.9	419.0	124.9	6.3	0.03	0.05
Terbuthylazine	230.0	174.0	96.0	4.5	0.01	0.03
Thiacloprid	252.9	126.0	90.0	4.4	0.04	0.14

R_t = retention time

Table S5. Information on the chemical analysis performed on OCPs, selected experimental parameters, instrumental limits of detection (iLOD) and quantification (iLOQ) from 2018 onward.

Compound	**Instrument**	**Native standard**	**Internal standard**	**Precursor m/z**	**Product m/z**	**R_t min**	**iLOQ 2015-2017 ng/mL**	**iLOQ 2018-2022 ng/mL**
PeCB	a	LGC Standards (United Kingdom)	^{13}C6 PeCB^{c}	250	215	8.96	0.389	0.03
HCB	a	LGC Standards	^{13}C6 HCB^{c}	283.8	248.9	11.6	0.632	0.09
α-HCH	a	LGC Standards	^{13}C6 *γ*-HCH^{c}	181	145	11.3	0.735	0.24
β-HCH	a	LGC Standards	^{13}C6 *γ*-HCH^{c}	181	145	12.1	0.463	0.38
γ-HCH	a	LGC Standards	^{13}C6 *γ*-HCH^{c}	181	145	12.6	0.269	0.31
δ-HCH	a	LGC Standards	^{13}C6 *γ*-HCH^{c}	181	145	13.6	0.667	0.53
ε-HCH	a	LGC Standards	^{13}C6 *γ*-HCH^{c}	181	145	14.2	0.471	0.34
o,p'-DDE	a	LGC Standards	^{13}C12 *p,p'*-DDE^{c}	246	176	25.5	0.374	0.16
p,p'-DDE	a	LGC Standards	^{13}C12 *p,p'*-DDE^{c}	246	176	28.1	0.466	0.19
o,p'-DDD	a	LGC Standards	^{13}C12 *p,p'*-DDD^{c}	235	165	28.6	0.352	0.33
p,p'-DDD	a	LGC Standards	^{13}C12 *p,p'*-DDD^{c}	235	165	31	0.446	0.43
o,p'-DDT	a	LGC Standards	^{13}C12 *p,p'*-DDT^{c}	235	165	31.2	0.529	0.71
p,p'-DDT	a	LGC Standards	^{13}C12 *p,p'*-DDT^{c}	235	165	33.3	0.43	0.83
Heptachlor	b	Supelco (United States)	^{13}C endosulfan^{c}	336.7	265.8	7.96		
cis-Heptachlor epoxide	b	Supelco	^{13}C endosulfan^{c}	352.7	252.8	9.96		
trans-Heptachlor epoxide	b	Supelco	^{13}C endosulfan^{c}	352.7	252.8	10.1		
Aldrin	b	Supelco	^{13}C endosulfan^{c}	262.7	227.8	8.87		
Dieldrin	b	Supelco	^{13}C endosulfan^{c}	382.7	278.8	12.2		
Endrin	b	Supelco	^{13}C endosulfan^{c}	381.7	280.9	13.1		
Endrin aldehyde	b	Supelco	^{13}C endosulfan^{c}	380.7	280.8	14.2		
Endrin ketone	b	Supelco	^{13}C endosulfan^{c}	380.7	244.8	17.8		
Isodrin	b	Dr Ehrenstorfer (Germany)	^{13}C endosulfan^{c}	365.7	195	9.69		
Oxychlordane	b	Dr Ehrenstorfer	^{13}C endosulfan^{c}	388.7	288.8	9.97		
α-Chlordane	b	Supelco	^{13}C endosulfan^{c}	374.7	265.8	11.2		
γ-Chlordane	b	Supelco	^{13}C endosulfan^{c}	374.7	265.8	10.7		
α-Endosulfan	b	Supelco	^{13}C endosulfan^{c}	407.8	252.8	11.2		
β-Endosulfan	b	Supelco	^{13}C endosulfan^{c}	407.8	252.8	13.5		
Endosulfan-sulfate	b	Supelco	^{13}C endosulfan^{c}	421.8	228.8	15.4		
Methoxychlor	b	Supelco	^{13}C endosulfan^{c}	228	169	18.9		
Mirex	b	Dr Ehrenstorfer	^{13}C endosulfan^{c}	271.8	236.8	21.5		

a = 7890A GC coupled to a triple quadrupole 7000B MS for 2015-2017 samples then 8890 GC coupled to a triple quadrupole 7000D MS for 2018-2022 samples; b = GC-APCI-MS/MS on a Waters Xevo TQ-S MS coupled to Agilent 7890 GC. For those, LOQs are computed for each sample and not shown in this table. [c] Cambridge Isotope Laboratories, Inc. (United States)

Table S6. Concentrations of individual pesticides (in pg m^{-3}) observed in field blanks (FB) on quartz fibre filter (F) and on PUF-XAD-2-PUF sandwich configuration (G) for CUPs (a) and OCPs (b). The average sampled volume of 3124 m^3 for CUPs and 5167 m^3 for OCPs were used to estimate the concentrations.

(a)

	FB-F-1	**FB-F-2**	**FB-F-3**	**FB-F-4**	**FB-F-5**	**FB-F-6**	**FB-F-7**	**FB-F-8**	**FB-F-9**	**FB-F-10**
2,4-D	<MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Chlorpyrifos	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Metalaxyl	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	0.179	<MDL
Metazachlor	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Pendimethalin	0.154	0.154	0.154	0.154	0.154	<iLOD	0.154	0.154	0.154	0.189
Prosulfocarb	0.077	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.144
S-metolachlor	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	0.243	<MDL
Tebuconazole	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	0.035	<MDL
Terbuthylazine	< MDL	< MDL	< MDL	< MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

	FB-G-1	**FB-G-2**	**FB-G-3**	**FB-G-4**	**FB-G-5**	**FB-G-6**	**FB-G-7**	**FB-G-8**	**FB-G-9**
2,4-D	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Chlorpyrifos	0.112	0.109	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Metalaxyl	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.035
Metazachlor	<MDL	0.109	0.083	0.077	0.099	0.074	<MDL	0.077	<MDL
Pendimethalin	0.208	0.154	0.432	0.154	0.160	0.186	0.154	0.237	0.198
Prosulfocarb	0.077	0.077	0.141	<MDL	<MDL	<MDL	<MDL	0.282	0.077
S-metolachlor	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Tebuconazole	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Terbuthylazine	0.061	0.054	0.029	0.032	0.026	0.032	0.038	0.026	0.042

(b)

	PeCB	**HCB**	**_γ_-HCH**	**_p,p′_-DDE**	**_p,p′_-DDT**	**_trans_-heptachlor epoxide**	**_γ_-Chlordane**	**_α_-Chlordane**	**_β_-Endosulfan**	**Endosulfan-sulfate**
FB-F-2015-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0040	<MDL	<MDL	<MDL
FB-F-2015-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0020	<MDL	<MDL	<MDL
FB-F-2015-3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0020	<MDL	<MDL	<MDL
FB-F-2016-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0020	<MDL	<MDL	<MDL
FB-F-2016-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2017-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2017-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2017-3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2018-1	<MDL	0.0065	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2018-2	<MDL	0.0061	<MDL	0.0043	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2018-3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.1800
FB-F-2019-1	<MDL	0.0073	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2019-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2019-3	<MDL	0.0061	<MDL	3.6900	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2020-1	<MDL	0.0091	<MDL	0.0122	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2020-2	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2020-3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2021-1	<MDL	0.0146	0.0297	0.0084	<MDL	0.0691	<MDL	<MDL	<MDL	<MDL
FB-F-2021-2	0.0031	0.0082	0.0219	0.0070	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2021-3	<MDL	0.0103	0.0338	0.0046	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2022-1	<MDL	0.0064	0.0354	0.0060	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2022-2	<MDL	0.0089	0.0198	0.0092	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-F-2022-3	<MDL	0.0054	0.0261	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

	PeCB	**HCB**	***γ*-HCH**	***p,p′*-DDE**	***p,p′*-DDT**	***trans*-heptachlor epoxide**	***γ*-Chlordane**	***α*-Chlordane**	***β*-Endosulfan**	**Endosulfan-sulfate**
FB-G-2015-1	0.0188	0.1090	0.0553	0.0325	<MDL	<MDL	0.0060	0.0020	<MDL	<MDL
FB-G-2015-2	0.0225	0.1210	0.0570	0.0480	<MDL	<MDL	0.0060	0.0040	<MDL	<MDL
FB-G-2015-3	0.0203	0.1180	<MDL	0.0591	0.0211	<MDL	0.0060	0.0040	<MDL	<MDL
FB-G-2016-1	<MDL	0.0361	<MDL	0.0235	<MDL	<MDL	0.0020	<MDL	<MDL	<MDL
FB-G-2016-2	<MDL	0.0375	<MDL	0.0250	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2017-1	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.0020	<MDL	<MDL	<MDL
FB-G-2017-2	0.0239	0.0626	<MDL	<MDL	<MDL	<MDL	0.0020	0.0020	<MDL	0.0020
FB-G-2017-3	0.0463	0.0855	<MDL	<MDL	<MDL	<MDL	0.0040	0.0040	<MDL	<MDL
FB-G-2018-1	0.0419	0.0969	0.0155	0.0194	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2018-2	0.0168	0.0605	0.0085	0.0126	0.0236	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2018-3	0.0217	0.1000	<MDL	0.0142	<MDL	0.0836	<MDL	<MDL	<MDL	<MDL
FB-G-2019-1	0.0141	0.0391	<MDL	0.0260	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2019-2	0.0142	0.0387	<MDL	0.0123	<MDL	<MDL	<MDL	<MDL	0.0764	<MDL
FB-G-2019-3	0.0116	0.0308	<MDL	0.0090	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2020-1	0.0103	0.0301	<MDL	0.0249	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2020-2	0.0226	0.0395	0.0636	0.0154	0.0781	0.0364	<MDL	<MDL	<MDL	<MDL
FB-G-2020-3	0.0124	0.0460	<MDL	0.0093	<MDL	0.0582	<MDL	<MDL	<MDL	<MDL
FB-G-2021-1	0.0241	0.0595	<MDL	0.0282	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2021-2	0.0207	0.0442	<MDL	0.0127	<MDL	0.0545	<MDL	<MDL	<MDL	<MDL
FB-G-2021-3	0.0209	0.0636	<MDL	0.0179	<MDL	0.0891	<MDL	<MDL	<MDL	<MDL
FB-G-2022-1	0.0184	0.0654	0.0129	0.0179	0.0167	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2022-2	0.0326	0.0680	<MDL	0.0091	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
FB-G-2022-3	0.0131	0.0473	0.0113	0.0209	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL

Table S7. Recoveries (in %) and standard deviations (SD) of CUPs (a) and OCPs (b) determined from spike recovery tests of air sampling media (QFFs and PUF-XAD2-PUF sandwiches, n=5 each)

(a)

CUPs	QFF		PUF-XAD-2-PUF		CUPs	QFF		PUF-XAD-2-PUF	
	Average (%)	SD	Average (%)	SD		Average (%)	SD	Average (%)	SD
2,4-D	102	3.8	98.7	4.6	Fonofos	85	7.1	118	15
Acetamiprid	95.8	5.5	99.1	4.5	Iprovalicarb	153	22	132	9.8
Acetochlor	96.2	5.9	88.6	9.9	Isoproturon	75.5	6	96	4.8
Alachlor	101	8.9	102	5.7	Kresoxim-methyl	72.8	3.4	61.1	2.9
Atrazine	91.3	5.5	102	3.8	Mecoprop	88.9	3.1	101	2.7
Azinphos-methyl	77.3	8.8	109	6.2	Metalaxyl	103	6.4	98.3	3.4
Boscalid	147	26	90.5	7.8	Metamitron	89.9	3.8	104	3.0
Carbaryl	67.6	14	83.6	4.0	Metazachlor	100	15	104	4.2
Carbendazim	102	14	90.2	3.8	Metribuzin	86	9.6	98.4	4.0
Carbofuran	102	7.6	84.1	5.8	Parathion-methyl	96.4	15	93.3	11
Chloridazon	80.4	9.1	105	4.1	Pendimethalin	103	15	102	7.1
Chlorotoluron	92.8	10	117	7.1	Phosalone	109	3.9	99.7	4.0
Chlorpyrifos	87.7	4.8	80.2	6.2	Pirimicarb	79.5	15	68.6	4.6
Chlorsulfuron	96.6	10	92.2	2.8	Prochloraz	106	17	94.4	5.1
Cyprodinil	99.6	6.5	96.5	1.7	Propiconazole	88.4	7.6	103	4.3
Diazinon	61.4	16	34.1	13	Prosulfocarb	106	4.4	104	4.3
Dimethachlor	83.6	6.5	96.3	5.8	Quizalofop ethyl	100	1.7	94.5	4.3
Dimethoate	111	3.8	104	5.3	Simazine	94.8	12	103	4.0
Diuron	100	18	86.7	3.9	S-Metolachlor	74.4	2.5	97.8	2.2
Esfenvalerate	77.7	13	62.3	19	Spiroxamine	102	3.9	96.7	2.6
Fenitrothion	95.1	18	93.2	7.9	Tebuconazole	74.2	7	80.8	5.9
Fenpropidin	102	4	96.7	3.7	Temephos	99.9	13	83.1	13
Fenpropimorph	153	20	113	24	Terbuthylazine	98.1	11	86	2.4
Fluroxypyr	85.1	9	119	7.8	Thiacloprid	103	4.5	100	2.4

(b)

OCPs	QFF Average (%)	QFF SD	PUF-PUF Average (%)	PUF-PUF SD
PeCB	46.8	8.0	49.1	6.0
HCB	50.2	7.3	50.9	4.6
γ-HCH	65.0	11	72.6	12
p,p'-DDT	80.1	15	87.1	20
p,p'-DDD	100	8.9	104	9.1
p,p'-DDE	97.6	5.2	99.0	8.7
Endosulfan	112	27.7	73.3	22.5

Table S8. Detection frequency (DF, in %) of CUPs (a) and OCPs (b) in the particulate, gaseous phase and total during the sampling period.

(a)

	Detection frequencies (%)		
	Particulate phase	Gaseous phase	Total
2,4-D	70.1	69.2	80.4
Acetamiprid	22.4	0	22.4
Acetochlor	0.93	0	0.93
Alachlor	0	0	0
Atrazine	3.74	0	3.74
Azinphos methyl	0	0	0
Boscalid	26.2	0	26.2
Carbaryl	8.41	0	8.41
Carbendazim	0	0	0
Carbofuran	0	0	0
Chloridazon	0	0	0
Chlorotoluron	92.5	15.0	93.5
Chlorpyrifos	16.8	93.5	93.5
Chlorsulfuron	0	0	0
Cyprodinil	29.0	0	29.0
Diazinon	4.67	0	4.67
Dimethachlor	9.35	14.0	17.8
Dimethoate	0	0	0
Diuron	4.67	0	4.67
Esfenvalerate	0	0	0
Fenitrothion	0	0	0
Fenpropidin	62.6	4.67	62.6
Fenpropimorph	72.0	3.74	72.0
Fluroxypyr	0	0	0
Fonofos	0	0	0
Iprovalicarb	23.4	0.9	23.4
Isoproturon	51.4	0	51.4
Kresoxim methyl	0	0	0
Mecoprop	0	1.87	1.87
Metalaxyl	50.5	26.2	52.3
Metamitron	2.80	0	2.80
Metazachlor	87.9	50.5	91.6
Metribuzin	0	0.93	0.93
Parathion methyl	0	0	0
Pendimethalin	84.1	100	100
Phosalone	0	0	0
Pirimicarb	81.3	15.0	81.3
Prochloraz	79.4	0	79.4
Propiconazole	85.0	0	85.0
Prosulfocarb	33.6	89.7	90.7
Quizalofop ethyl	4.67	0	4.67
Simazine	0	0	0
S-metolachlor	59.8	83.2	89.7
Spiroxamine	99.1	5.61	99.1
Tebuconazole	100	19.6	100
Temephos	0	0	0
Terbuthylazine	62.6	17.8	66.4
Thiacloprid	26.2	0	26.2

(b)

	Detection frequencies (%)		
	Particulate phase	Gaseous phase	Total
α-HCH	0	100	100
β-HCH	0	77.8	77.8
γ-HCH	3.17	100	100
δ-HCH	0	69.8	69.8
ε-HCH	0	44.0	44.0
o,p'-DDE	17.5	98.8	98.8
p,p'-DDE	95.6	100	100
o,p'-DDD	10.7	90.1	90.1
p,p'-DDD	63.1	89.7	90.1
o,p'-DDT	51.2	98.4	98.4
p,p'-DDT	84.9	100	100
PeCB	51.2	100	100
HCB	65.9	100	100
Heptachlor	0.40	9.92	10.3
cis-Heptachlor epoxide	0	91.7	91.7
trans-Heptachlor epoxide	2.38	7.14	9.1
Aldrin	0.40	1.2	1.6
Dieldrin	0	17.1	17.1
Endrin	0	0.40	0.4
Endrin aldehyde	3.17	1.59	3.6
Endrin ketone	0.40	0.40	0.8
Isodrin	1.19	0.79	2.0
Oxychlordane	0.40	72.2	72.2
α-Chlordane	8.78	75.6	78.6
γ-Chlordane	8.37	90.5	94.4
α-Endosulfan	0.38	63.3	66.3
β-Endosulfan	0.40	6.0	6.3
Endosulfan-sulfate	12.3	24.6	26.2
Methoxychlor	1.98	0	2.0
Mirex	0.79	75.4	75.4

Table S9. Czech use of CUPs as PPP during the sampling period (ÚKZÚZ; 2024).

	National use			**Regional use**			**District use**		
	2019	***2020***	***2021***	***2019***	***2020***	***2021***	***2019***	***2020***	***2021***
	Use (kg)	**Use (kg)**	**Use (kg)**	**Use (kg)**	**Use (kg)**	**Use (kg)**	**Use (kg)**	**Use (kg)**	**Use (kg)**
2,4-D	33489	29808	33406	1796	1754	2264	391	315	409
Acetamiprid	5234	5108	16125	307	340	1273	106	127	370
Boscalid	23585	21924	17758	2676	2497	1982	454	453	469
Chloridazon	30114	12253	0	14	3	0	0	0	0
Chlorotoluron	158710	112684	156983	12956	8285	12168	2486	1670	2208
Chlorpyrifos	125953	73435	0	16052	7559	0	2134	1207	0
Chlorsulfuron	1586	1800	22	140	146	1	32	44	0
Cyprodinil	2033	4081	6268	127	326	307	47	76	7
Dimethachlor	16563	12694	11937	804	581	789	1	0	62
Dimethoate	7849	1867	0	289	30	0	63	0	0
Esfenvalerate	894	1013	1525	52	71	121	11	7	20
Fenpropidin	42568	17395	18130	1611	844	1241	475	30	106
Fenpropimorph	36647	23491	2284	3684	2336	259	388	186	4
Fluroxypyr	20145	19519	20971	1301	1435	1832	338	290	320
Iprovalicarb	1649	2157	1995	0	0	0	0	0	0
Kresoxim-methyl	2347	2326	832	203	291	116	49	51	16
Mecoprop	473	499	630	0	9	76	0	8	13
Metalaxyl	1808	2191	2564	232	255	383	121	132	190
Metamitron	76459	61141	55858	431	179	150	0	0	0
Metazachlor	138013	131923	132788	12701	11842	13540	2255	2214	2451
Metribuzin	7752	8415	8843	1870	1949	1960	815	752	674
Pendimethalin	85918	77303	86165	6640	6023	6383	830	586	563
Pirimicarb	842	1073	1102	0	8	10	0	0	1
Prochloraz	104991	64374	69286	6922	3636	4752	1087	481	397
Propiconazole	26681	1514	0	1323	114	0	241	8	0
Prosulfocarb	33829	35487	48311	5132	6436	7731	2427	3244	3181
Quizalofop ethyl	8626	8139	10645	0	0	0	0	0	0
S-Metolachlor	49173	50195	47415	4076	3533	4088	753	469	405
Spiroxamine	64755	64854	69881	4696	4167	5656	1190	1131	1445
Tebuconazole	158762	159782	159994	12198	11064	13239	2722	2396	2520
Terbuthylazine	71722	71600	68129	10517	10516	10184	1178	964	1183
Thiacloprid	35146	41440	33	3094	4209	0	681	784	0

Table S10. Summary total atmospheric concentrations (pg m^{-3}) for CUPs (a) and OCPs (b) during the 2019-2021 and 2013-2022 periods, respectively.

(a)

CUPs	Median	Average	Min.	Max.
2,4-D	2.41	6.26	0.04	54.5
Acetamiprid	0.52	0.91	0.16	4.38
Acetochlor	3.19	3.19	3.19	3.19
Atrazine	0.74	0.70	0.34	0.97
Boscalid	4.51	5.85	1.34	22.4
Carbaryl	0.22	0.39	0.15	1.68
Chlorotoluron	2.54	9.66	0.26	101
Chlorpyrifos	54.6	116	1.53	891
Cyprodinil	1.98	3.65	0.46	16.3
Diazinon	0.11	0.13	0.07	0.21
Dimethachlor	5.19	21.3	0.95	84.0
Diuron	0.54	0.54	0.39	0.75
Fenpropidin	9.19	38.7	0.42	307
Fenpropimorph	1.35	14.5	0.14	345
Iprovalicarb	1.78	3.07	0.86	13.7
Isoproturon	0.29	0.60	0.10	6.38
Mecoprop	7.75	7.75	1.03	14.5
Metalaxyl	1.92	15.6	0.20	146
Metamitron	7.58	9.60	3.67	17.5
Metazachlor	1.51	17.1	0.16	358
Metribuzin	22.0	22.0	22.0	22.0
Pendimethalin	38.4	65.4	5.07	459
Pirimicarb	0.46	3.09	0.05	60.4
Prochloraz	0.52	2.01	0.12	50.4
Propiconazole	0.85	2.60	0.40	50.5
Prosulfocarb	4.50	79.7	0.10	1631
Quizalofop ethyl	1.25	1.08	0.60	1.40
S-metolachlor	10.5	115	0.06	5025
Spiroxamine	1.16	40.6	0.06	546
Tebuconazole	3.76	12.7	0.23	166
Terbuthylazine	2.34	13.1	0.13	180
Thiacloprid	1.26	1.97	0.31	6.19

(b)

OCPs	**Median**	**Average**	**Min.**	**Max.**
α-HCH	1.54	1.65	0.30	5.79
β-HCH	0.18	0.21	0.03	0.84
γ-HCH	3.19	3.36	0.34	8.78
δ-HCH	0.10	0.13	0.03	0.88
ε-HCH	0.04	0.05	0.01	0.18
o,p'-DDE	0.24	0.31	0.04	11.1
p,p'-DDE	11.0	11.6	1.65	51.3
o,p'-DDD	0.13	0.20	0.02	7.24
p,p'-DDD	1.30	1.55	0.25	15.6
o,p'-DDT	0.39	0.57	0.03	22.3
p,p'-DDT	2.26	2.78	0.38	32.1
PeCB	0.84	1.27	0.08	9.45
HCB	13.8	16.1	3.17	54.5
Heptachlor	0.01	0.04	0.00	0.22
cis-Heptachlor epoxide	0.35	0.42	0.03	1.46
trans-Heptachlor epoxide	0.07	0.08	0.03	0.21
Aldrin	0.15	0.17	0.10	0.29
Dieldrin	2.18	2.09	0.05	3.37
Endrin	0.12	0.12	0.10	0.14
Endrin ketone	0.01	0.07	0.01	0.20
Isodrin	0.01	0.02	0.00	0.06
Oxychlordane	0.10	0.13	0.01	0.42
α-Chlordane	0.22	0.24	0.03	0.68
γ-Chlordane	0.09	0.10	0.02	0.24
α-Endosulfan	0.18	0.29	0.02	1.67
β-Endosulfan	0.06	0.09	0.02	0.53
Endosulfan-sulfate	0.04	0.04	0.00	0.20
Methoxychlor	9.94	14.2	1.58	30.1
Mirex	0.05	0.07	0.01	0.30

Table S11. Mann-Whitney nonparametric test result comparing CUPs concentration between sampling period in this study and the 2012-2013 period (Degrendele et al., 2016).

CUPs	p-value	Highest concentration period
Chlorotoluron	0.01	2019-2021
Chlorpyrifos	<0.01	2019-2021
Fenpropimorph	0.26	
Isoproturon	0.01	2012-2013
Metazachlor	<0.01	2012-2013
Prochloraz	<0.01	2019-2021
S-metolachlor	<0.01	2019-2021
Terbuthylazine	0.10	

Table S12. CUP atmospheric concentration seasonal peak(s). Spring defined as April to June; Summer as July and August; Autumn as September to November; Winter as December to March.

CUPs	Atmospheric concentration peak season	Simulated centre date(s) the application(s)[a]
2,4-D	Spring	28th April
Acetamiprid	Spring	1st August
Boscalid	Spring	30th November
Chlorotoluron	Spring and autumn	3rd July and 30th October
Chlorpyrifos	Spring and autumn	22nd June and 20th October
Cyprodinil	Spring	11th October
Fenpropidin	Spring	22nd July
Fenpropimorph	Spring	18th October
Iprovalicarb	Spring	1st November
Isoproturon	Spring and autumn	23rd June and 1st October
Metalaxyl	Spring	29th June
Metazachlor	Summer	6th October
Pendimethalin	Winter/spring and autumn	12th March and 3rd November
Pirimicarb	Spring	21st March
Prochloraz	Spring	24th August
Propiconazole	Spring	22nd June
Prosulfocarb	Spring and autumn	4th September and 14th November
S-metolachlor	Spring	25th February
Spiroxamine	Spring	23rd October
Tebuconazole	Spring	5th November
Terbuthylazine	Spring	17th May
Thiacloprid	Spring	6th March

[a] Date derived based on the maximum of the simulated function (Eq. (2))

Table S13. Clausius-Clapeyron equation parameters slope (m) and constant (b), coefficient of determination (R^2) and confidence level (p) for CUPs (a) and OCPs (b).

(a)

CUPs	**m**	***b***	**R^2**	**p-value**	**Number of observations**	**Detection frequency (%)**
2,4-D	-15567	29.6	0.25	<0.01	86	80
Acetamiprid	-4515	-13.3	0.04	0.04	24	22
Boscalid	-11980	14.3	0.17	<0.01	28	26
Chlorotoluron	3330	-36.3	0.02	0.14	100	93
Chlorpyrifos	-9200	10.2	0.07	0.01	100	93
Cyprodinil	-5366	-8.91	0.04	0.04	31	29
Fenpropidin	-29092	77.3	0.44	<0.01	67	62
Fenpropimorph	-12487	18.4	0.21	<0.01	77	72
Iprovalicarb	-21280	45.9	0.47	<0.01	25	23
Isoproturon	-2207	-20.1	0.01	0.30	55	51
Metalaxyl	-39217	110.8	0.62	<0.01	56	52
Metazachlor	-18873	41.8	0.47	<0.01	98	91
Pendimethalin	3493	-34.2	0.08	<0.01	107	100
Pirimicarb	-17542	35.7	0.55	<0.01	87	81
Prochloraz	-9576	6.76	0.12	<0.01	85	79
Propiconazole	-2870	-16.0	0.02	0.15	91	85
Prosulfocarb	-8140	4.81	0.05	0.03	97	90
S-metolachlor	-24486	62.9	0.56	<0.01	96	89
Spiroxamine	-20446	47.9	0.38	<0.01	106	99
Tebuconazole	-13457	23.5	0.51	<0.01	107	100
Terbuthylazine	-26999	69.2	0.43	<0.01	71	66
Thiacloprid	-4749	-12.2	0.03	0.08	28	26

(b)

OCPs	**m**	**b**	**R²**	**p-value**	**Number of observations**	**Detection frequency (%)**
α-HCH	991.6	-28.55	0.03	<0.01	252	100
β-HCH	-6899	-3.211	0.26	<0.01	197	78
γ-HCH	-4160	-9.641	0.51	<0.01	252	100
δ-HCH	-6819	-3.772	0.34	<0.01	172	68
ε-HCH	-7768	-1.661	0.28	<0.01	108	43
o,p'-DDE	-3809	-13.48	0.32	<0.01	249	99
p,p'-DDE	-4746	-6.419	0.46	<0.01	252	100
o,p'-DDD	-6175	-5.764	0.44	<0.01	228	90
p,p'-DDD	-5559	-7.092	0.34	<0.01	228	90
o,p'-DDT	-7221	0.072	0.65	<0.01	248	98
p,p'-DDT	-6112	-3.324	0.68	<0.01	252	100
PeCB	6513	-48.65	0.36	<0.01	252	100
HCB	3880	-36.61	0.46	<0.01	252	100
Oxychlordane	-3302	-15.94	0.06	<0.01	184	73
γ-Chlordane	-31.43	-28.06	0.00	0.93	199	79
α-Chlordane	-3694	-14.27	0.42	<0.01	238	95
α-Endosulfan	-4878	-10.45	0.08	<0.01	163	65
Endosulfan-sulfate	-2879	-18.39	0.02	0.04	68	27
cis-Heptachlor epoxide	-4198	-11.85	0.22	<0.01	231	92
Mirex	-5429	-9.884	0.32	<0.01	191	76

Table S14. Summary of CUP time trends analysed using Eq. (1). Positive and negative trends indicated by red and green cells, respectively. CUPs with detection frequency > 20% shown only. R^2 = coefficient of determination from the multiple linear regression. In bold significant variation (p-value <0.05). For the analysis, data <MDL were substituted by MDL/2 values.

					Coefficients				**p-value**	
CUPs	Approval Status	Detection frequency (%)	Number of Observation	R^2	Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	t (a_3)	$\tau_{1/2}$ ***(years)***
2,4-D	Approved	80.4	86	0.57	68.08	1.03	-2.66	-1.6E-03	**1.9E-02**	**-1.22**
Acetamiprid	Approved	22.4	24	0.33	-58.20	1.15	-0.98	1.2E-03	**4.4E-02**	**1.55**
Boscalid	Approved	26.2	28	0.29	19.85	0.77	-1.75	-5.1E-04	5.1E-01	
Chlorotoluron	Not approved	93.5	100	0.08	78.66	0.22	0.34	-1.8E-03	**1.7E-02**	**-1.07**
Chlorpyrifos	Not approved	93.5	100	0.20	207.10	-0.25	-0.95	-4.6E-03	**1.2E-05**	**-0.41**
Cyprodinil	Approved	29.0	31	0.49	54.78	1.78	-1.44	-1.3E-03	**4.1E-02**	**-1.45**
Fenpropidin	Approved	62.6	67	0.70	109.56	0.92	-4.38	-2.5E-03	**1.7E-03**	**-0.76**
Fenpropimorph	Not approved	72.0	77	0.66	212.07	0.78	-2.03	-4.8E-03	**1.4E-15**	**-0.39**
Iprovalicarb	Approved	23.4	25	0.43	-47.25	-0.49	-2.38	9.9E-04	1.9E-01	
Isoproturon	Not approved	51.4	55	0.37	181.91	-0.43	-0.03	-4.2E-03	**1.5E-11**	**-0.45**
Metalaxyl	Approved	52.3	56	0.67	-37.82	-1.73	-4.61	8.0E-04	3.9E-01	
Metazachlor	Approved	91.6	98	0.57	108.34	-1.59	-1.80	-2.5E-03	**5.4E-05**	**-0.77**
Pendimethalin	Approved	100.0	107	0.08	-3.99	0.11	0.41	1.7E-04	6.4E-01	
Pirimicarb	Approved	81.3	87	0.56	103.97	-1.00	-1.74	-2.4E-03	**5.9E-06**	**-0.79**
Prochloraz	Approved	79.4	85	0.25	109.12	0.56	-1.32	-2.5E-03	**1.3E-03**	**-0.75**
Propiconazole	Not approved	85.0	91	0.39	173.50	0.29	-0.51	-4.0E-03	**1.5E-11**	**-0.48**
Prosulfocarb	Approved	90.7	97	0.07	-16.19	-0.44	-1.15	4.0E-04	7.3E-01	
S-metolachlor	Approved	89.7	96	0.62	76.88	-0.28	-3.13	-1.7E-03	**1.0E-02**	**-1.11**
Spiroxamine	Approved	99.1	106	0.72	33.88	1.35	-3.20	-7.6E-04	1.8E-01	
Tebuconazole	Approved	100.0	107	0.63	28.94	0.04	-1.82	-6.3E-04	9.0E-02	
Terbuthylazine	Approved	66.4	71	0.65	92.70	0.87	-3.96	-2.1E-03	**7.5E-03**	**-0.89**
Thiacloprid	Not approved	26.2	28	0.39	87.04	1.63	-1.15	-2.1E-03	**4.4E-03**	**-0.92**

Table S15. Summary of CUP time trends analysed using Eq. (2). Positive and negative trends indicated by red and green cells, respectively. CUPs with detection frequency > 20% shown only. R^2 = coefficient of determination from the non-linear regression. In bold significant variation (p-value <0.05). For the analysis, data <MDL were substituted by MDL/2 values.

CUPs	Approval Status	Detection frequency (%)	Number of Observation	R^2	**Coefficients**					**p-value**	
					Intercept (constant)	a_1	cos (a_2*t+a_4)	t (a_3)	a_4	t (a_3)	***τ1/2 (years)***
2,4-D	Approved	80	86	0.57	67.6	2.85	1.7E-02	-1.5E-03	4.22	**0.03**	**-1.22**
Acetamiprid	Approved	22	24	0.33	-56.0	1.53	1.8E-02	1.2E-03	-9.96	0.06	
Boscalid	Approved	26	28	0.30	7.3	1.92	1.7E-02	-2.3E-04	31.9	0.72	
Chlorotoluron	Not approved	93	100	0.55	63.4	2.01	3.4E-02	-1.4E-03	34.5	**< 0.01**	**-1.33**
Chlorpyrifos	Not approved	93	100	0.37	176	1.98	3.4E-02	-3.9E-03	41.0	**< 0.01**	**-0.48**
Cyprodinil	Approved	29	31	0.50	58.0	2.34	1.8E-02	-1.4E-03	-17.5	**0.03**	**-1.37**
Fenpropidin	Approved	63	67	0.70	110	4.47	1.7E-02	-2.5E-03	2.76	**< 0.01**	**-0.75**
Fenpropimorph	Not approved	72	77	0.67	221.9	2.22	1.8E-02	-5.1E-03	-17.6	**< 0.01**	**-0.38**
Iprovalicarb	Approved	23	25	0.50	-104	2.65	1.6E-02	2.3E-03	63.8	**< 0.01**	**0.83**
Isoproturon	Not approved	51	55	0.45	175	0.84	3.0E-02	-4.0E-03	198.0	**< 0.01**	**-0.47**
Metalaxyl	Approved	52	56	0.67	-72.0	4.98	1.7E-02	1.6E-02	22.0	0.14	
Metazachlor	Approved	92	98	0.59	136	2.42	1.8E-02	-3.1E-03	-36.2	**< 0.01**	**-0.62**
Pendimethalin	Approved	100	107	0.48	-7.2	1.01	3.5E-02	2.5E-04	-7.53	0.40	
Pirimicarb	Approved	81	87	0.58	73.2	2.10	1.6E-02	-1.7E-03	42.6	**< 0.01**	**-1.12**
Prochloraz	Approved	79	85	0.26	97.5	1.45	1.6E-02	-2.3E-03	39.9	**0.01**	**-0.84**
Propiconazole	Not approved	85	91	0.39	176	0.61	1.8E-02	-4.0E-03	-28.1	**< 0.01**	**-0.47**
Prosulfocarb	Approved	91	97	0.51	-20.6	3.24	3.4E-02	5.0E-04	2.01	0.57	
S-metolachlor	Approved	90	96	0.62	80.9	3.14	1.7E-02	-1.8E-03	-0.98	**0.02**	**-1.05**
Spiroxamine	Approved	99	106	0.73	20.9	3.46	1.7E-02	-4.6E-04	20.0	0.43	
Tebuconazole	Approved	100	107	0.63	26.6	1.82	1.7E-01	-5.8E-04	7.22	0.16	
Terbuthylazine	Approved	66	71	0.65	78.0	4.05	1.7E-02	-1.8E-03	16.5	**0.04**	**-1.05**
Thiacloprid	Not approved	26	28	0.39	87.4	2.01	1.7E-01	-2.1E-03	-1.15	**< 0.01**	**-0.91**

Table S16. Summary of OCP time trends. Positive and negative trends indicated by red and green cells, respectively, for the 2013-2017 period (a) and 2018-2022 period (b). OCPs with detection frequency > 20% shown only. R^2 = coefficient of determination from the multiple linear regression. In bold significant variation (p-value <0.05). For the analysis, data <MDL were substituted by MDL/2 values.

(a)

OCP	Detection frequency (%)	Number of observations	R^2	**Coefficient**				**p-value**
				Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	t (a_3)
α-HCH	100	122	0.49	34.5	-0.02	0.19	-8.1E-04	**3.0E-17**
β-HCH	63.9	78	0.54	49.1	-0.02	-0.19	-1.2E-03	**1.8E-13**
γ-HCH	100	122	0.54	25.2	-0.16	-0.45	-5.7E-04	**2.2E-13**
δ-HCH	49.2	60	0.72	35.9	-0.19	-0.36	-9.0E-04	**2.6E-14**
ε-HCH	19.7	24	0.52	33.1	-0.42	-0.28	-8.6E-04	**2.0E-03**
o,p'-DDE	97.5	119	0.35	19.8	-0.10	-0.42	-5.0E-04	**5.8E-07**
p,p'-DDE	100	122	0.34	17.2	-0.30	-0.44	-3.5E-04	**3.5E-04**
o,p'-DDD	79.5	97	0.41	0.53	-0.06	-0.66	-4.9E-05	6.8E-01
p,p'-DDD	79.5	97	0.27	-24.9	0.04	-0.46	5.7E-04	**2.7E-05**
o,p'-DDT	96.7	118	0.50	7.71	-0.28	-0.69	-1.7E-04	6.8E-02
p,p'-DDT	100	122	0.48	-5.50	-0.23	-0.69	1.5E-04	1.2E-01
PeCB	100	122	0.72	42.8	0.40	0.80	-1.0E-03	**2.2E-19**
HCB	100	122	0.61	20.6	0.19	0.51	-4.3E-04	**4.6E-10**
cis-Heptachlor epoxide	82.8	101	0.72	64.4	-0.50	-0.44	-1.6E-03	**5.9E-24**
Oxychlordane	58.2	71	0.51	-3.3	-0.30	-0.43	9.8E-06	9.4E-01
α-Chlordane	91.0	111	0.64	23.9	-0.23	-0.38	-6.0E-04	**9.1E-18**
γ-chlordane	68.9	84	0.45	34.0	-0.07	0.06	-8.6E-04	**7.2E-12**
α-Endosulfan	37.7	46	0.18	-7.86	-0.08	-0.26	2.0E-04	5.6E-01
Endosulfan-sulfate	58.2	71	0.75	11.1	-0.76	-1.39	-3.8E-04	1.4E-01
Mirex	73.0	89	0.61	45.0	-0.30	-0.50	-1.1E-03	**5.9E-14**

(b)

				Coefficient				p-value	
OCP	Detection frequency (%)	Number of observations	R^2	Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	t (a_3)	***$t_{1/2}$ (years)***
α-HCH	100	130	0.22	11.7	-0.09	0.13	-2.5E-04	**7.3E-06**	**-7.5**
β-HCH	90.8	118	0.53	-12.7	-0.66	-1.11	2.4E-04	1.01E-01	
γ-HCH	100	130	0.56	4.9	-0.18	-0.43	-8.5E-05	9.4E-02	
δ-HCH	89.2	116	0.52	19.7	-0.36	-1.05	-5.0E-04	**2.6E-04**	**-3.8**
ε-HCH	66.9	87	0.72	9.3	-0.90	-1.28	-3.0E-04	**1.1E-02**	**-6.3**
o,p'-DDE	100	130	0.48	3.1	-0.23	-0.39	-1.1E-04	6.6E-02	
p,p’-DDE	100	130	0.46	3.4	-0.34	-0.41	-2.6E-05	7.1E-01	
o,p'-DDD	100	130	0.59	4.2	-0.41	-0.69	-1.5E-04	6.3E-02	
p,p’-DDD	100	130	0.43	7.0	-0.36	-0.51	-1.9E-04	**3.3E-02**	**-10.1**
o,p'-DDT	100	130	0.72	4.6	-0.35	-0.69	-1.0E-04	8.0E-02	
p,p’-DDT	100	130	0.74	4.9	-0.29	-0.63	-9.2E-05	6.3E-02	
PeCB	100	130	0.71	1.1	0.35	0.67	-1.6E-05	7.8E-01	
HCB	100	130	0.63	4.7	0.13	0.45	-4.2E-05	3.3E-01	
cis-Heptachlor epoxide	100	130	0.46	6.2	-0.30	-0.43	-1.6E-04	**2.6E-02**	**-12.1**
Oxychlordane	85.4	111	0.39	5.9	-0.27	-0.49	-1.8E-04	**3.4E-02**	**-10.5**
α-Chlordane	97.7	127	0.35	3.8	-0.17	-0.37	-1.2E-04	8.1E-02	
γ-Chlordane	87.7	114	0.14	4.0	0.08	0.17	-1.5E-04	**3.5E-02**	**-13.0**
α-Endosulfan	93.1	121	0.57	24.4	-0.29	-1.07	-6.0E-04	**3.6E-06**	**-3.2**
Endosulfan-sulfate	2.3	3	0.03	3.6	0.02	-0.08	-1.5E-04	1.1E-01	
Mirex	100	130	0.45	-5.3	-0.22	-0.81	5.4E-05	6.3E-01	

Supplementary references

Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukučka, P., Audy, O., Kohoutek, J., Čupr, P., and Klánová, J.: Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides, Atmos. Chem. Phys., 16, 1531–1544, 2016.

EU: European Union Pesticides Database - Active substances: https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/start/screen/active-substances (last accessed: 21 November 2024), 2024.

Lewis, K. A., Tzilivakis, J., Warner, D. J., and Green, A.: An international database for pesticide risk assessments and management, Hum. Ecol. Risk Assess.: Int. J., 22, 1050–1064, 2016.

ÚZKÚZ: Consumption of plant protection products per individual years. 2024. Central Institute for Supervising and Testing in Agriculture (ÚZKÚZ), Prague, Czech Republic, https://eagri.cz/public/portal/ukzuz/pripravky-na-or/ucinne-latky-v-por-statistika-spotreba/spotreba-pripravku-na-or/spotreba-v-jednotlivych-letech, (last accessed online: 20 June 2024).

UNEP: Stockholm Convention on Persistent Organic Pollutants (POPs), United Nations Environment Programme, http://chm.pops.int/tabid/208/Default.aspx, (last accessed online, 5 Dec. 2024), 2001.

UNEP: The 16 new POPs. United Nations Environment Programme, https://www.pops.int/TheConvention/ThePOPs/TheNewPOPs/tabid/2511/Default.aspx (Last accessed online, 5 Dec. 2024), 2017.

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Current-use and organochlorine pesticides' multi-annual trends in air in Central Europe: primary and unidentified secondary sources

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Abstract. This study investigated 48 current-use pesticides (CUPs) and 30 organochlorine pesticides (OCPs) in ambient air at a rural-agricultural site in the Czech Republic, with biweekly sampling over three and 10 years, respectively. Despite being banned decades ago, OCPs persist in the atmosphere, with revolatilisation from soils apparent in summer . Temporal trend analysis revealed decreasing atmospheric concentrations for several OCPs, which indicate diminishing reservoirs in environmental compartments especially soil over the years. For *β*- and *γ*-HCH, *o,p'*- and *p,p'*-DDE, *o,p'*-DDD, *o,p'*- and *p,p'*-DDT, *α*-chlordane, and mirex levelling off is observed, which points to recently enhanced secondary sources in the region or beyond i.e., reversal of the direction of air-surface exchange or recent mobilisation from soils, water bodies, or the cryosphere. CUP concentrations peaked during application seasons, with multi-annual trends either insignificant or declining. For compounds like chlorpyrifos and fenpropimorph, declining trends aligned with regulatory bans, though their presence in the atmosphere was evident one-year post-ban, suggesting persistence.

1 Introduction

The wide use of organochlorine pesticides (OCPs) started in the 1940s for agricultural and vector disease control purposes. Because of persistence and semivolatility, these substances cycle globally. Due to their severe health and environmental effects, OCPs have been restricted in most countries (UNEP, 2001), which for DDT and HCH has been consistently reflected in declining concentrations in air (UNEP, 2003; Becker et al., 2008; Gao et al., 2010; Venier and Hites, 2010; Shunthirasingham et al., 2016; Wöhrnschimmel et al., 2016). Without primary emissions, re-volatilisation from soils and surface waters, triggered by the reversal of the direction of air-surface exchange under declining levels in air (Bidleman et al., 1995; Lakaschus et al., 2002; Semeena et al., 2006; Stemmler and Lammel, 2009; Wöhrnschimmel et al., 2012, 2016; O'Driscoll, 2014; Lammel et al., 2018; Li et al., 2020) should be the only remaining source for banned OCPs in air (Salamova et al., 2015; Wong et al., 2021). Most of the total environmental burdens of OCPs is stored in surface compartments, while only a minor fraction is cycling in air (Semeena et al., 2006; Wöhrnschimmel et al., 2012; 2013; Mackay and Parnis, 2020).

Newer types of pesticides, called current-use pesticides (CUPs) have since been developed and have been extensively used worldwide (Alexandratos and Bruinsma, 2012; Sharma et al., 2019; FAOSTAT, 2024). CUPs, including more than 30 substance class such as organophosphates, pyrethroids, and neonicotinoids are chemically very different and subject to accordingly diverse environmental fate (van Pul et al., 1999; Lewis et al., 2016; Carvalho, 2017). CUPs have been detected in many environmental matrices worldwide (Tang et al., 2021) and are capable of long-range transport (Balmer et al., 2019; Mayer et al., 2024). CUPs can enter the atmosphere during application, where up to 90% of the mass applied can be released directly into the atmosphere (van den Berg et al., 1999), can volatilise from surfaces such as soil, plants and surface water over longer periods of time following application (Bedos et al., 2002), and can be mobilised through wind erosion of soil particles containing CUPs (Glotfelty et al., 1989). Moreover, alike OCPs, CUPs can also be re-volatilised from soils and surface waters . Application vs. re-volatilisation (and resuspension) sources of CUPs can be distinguished by an examination of time trends, as well as comparison with OCP time-trends. OCP sources and atmospheric concentrations have been monitored for decades at continental sites (Bidleman, 1999; Sofuoglu et al., 2004; Holoubek et al., 2007; Cindoruk, 2011; Salamova et al., 2015; White et al., 2021; Kalina et al., 2022; Hites and Venier, 2023) and remote sites (Hung et al., 2005, 2010, 2016; Wong et al., 2021). Monitoring of CUPs in air has been reported from few European countries (Duyzer, 2003; Coscollà et al., 2010, 2017; Degrendele et al., 2016; Villiot et al., 2018; LCSQA, 2019; IVL, 2021; Kruse-Plaß et al., 2021; Debler et al., 2024; Habran et al., 2024), and CUP regional distributions became an increasing focus of research in recent years (Wang et al., 2021; Mayer et al., 2024).

Multi-annual observations of these compounds are essential not only for assessing the effectiveness of policy decisions (e.g., the immediate effects of banning certain pesticides) and evaluating the overall atmospheric pesticide load, but also for identifying their sources in the atmospheric environment. In this study, biweekly samples of OCPs and CUPs were collected in both the gas and particulate phases at a rural site in an agricultural region of Central Europe. Sampling spanned 2013 to 2022 for OCPs and 2019 to 2021 for CUPs, allowing for the assessment of seasonal variations and time trends.

2 Methodology

2.1 Pesticide selection

Forty-eight CUPs (21 herbicides, 16 insecticides and 11 fungicides) encompassing 24 chemical classes were selected (Table S1) based on previous studies (Degrendele et al., 2016; Désert et al., 2018; Mayer et al., 2024), national and global pesticides usage trends (Maggi et al., 2019; ÚKZÚZ, 2024) and their potentially harmful effects on the environment and human health (Jepson et al., 2020; Hulin et al., 2021). In addition, 30 OCPs and related metabolites were also measured (Table S2).

2.2 Site location

The National Atmospheric Observatory Košetice, Czech Republic (NAOK), is a regional background site of the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP), Global

Atmosphere Watch (GAW) and Integrated Carbon Observation System (ICOS) networks, and contributes to the Aerosols, Clouds and Trace Gases (ACTRIS) research infrastructure (Holoubek et al., 2007; Lammel et al., 2010; Váňa et al., 2020). However, as this site is located in an agricultural area (Figure S1) and in close vicinity to fields (samplers distanced <20 m from fields; Figure S2), the site is a rural site and not representing background conditions with regards to emissions from agriculture.

2.3 Sample collection

A high-volume air sampler (Digitel DH77; Digitel, Volketswil, Switzerland), equipped with a PM10 pre-separator sampling head, was used to collect week-long samples every second week from January 2013 to December 2022 for OCPs alongside another high-volume air sampler (Baghirra, Baghirra s.r.o., Prague, Czech Republic) and from February 2019 to August 2021 for CUPs. For OCPs, the sampling volume was on average 5167 ± 518 m^3, while it was 3124 ± 491 m^3 for CUPs. Particles were collected on quartz fibre filters (QFFs) (QM-A, 150 mm, Whatman, UK) for both OCPs and CUPs, while gaseous OCPs were collected on polyurethane foam (PUF) plugs (two in sequence, T3037, 110×50 mm, 0.030 g cm^{-3}, Molitan, Břeclav, Czech Republic) and gaseous CUPs on a sandwich sorbent consisting of a PUF plug, a layer of XAD resin (Supelpak-2, Merck, Darmstadt, Germany), and another PUF plug, separated by cotton wool (i.e., PUF/XAD2/PUF sandwich). This configuration has been shown to be the most efficient for the collection of gaseous CUPs (López et al., 2018). Prior to sampling, PUFs used for OCP sampling were precleaned via Soxhlet extraction with acetone and dichloromethane for 8 hours each, and both PUFs and XAD2 used for CUP collection were precleaned via Soxhlet extraction with acetone and methanol for 8 hours each.

In total, 252 air samples were collected for OCP analysis, while 107 samples were collected for CUP analysis. Six samples from early January to March 2016 were removed from the dataset due to road reconstruction in the vicinity of the sampling, which prompted a strong resuspension of soil particles. After collection, samples were wrapped in aluminium foil, sealed in a plastic bag, stored at -18 °C on location until transported to the RECETOX Trace Analytical Laboratories, and stored at -18 °C until extraction and analysis.

2.4 Sample preparation and analysis

Air samples were first spiked with isotopically-labelled standards (Table S3) and then underwent extraction using an automated extractor (E-800, Büchi Extraction System, Flawil, Switzerland), with 150 mL of methanol and 5 mM of ammonium acetate for CUPs and 150 mL of dichloromethane for OCPs. CUPs extract clean-up was done by filtration through a 0.22 µm pore size cellulose acetate membrane (Corning Costar Spin-X, United States). OCPs extracts were transferred to a glass column (30 mm i.d.) filled with 0.5 g of activated silica, 30 g of H_2SO_4 modified activated silica and 1 g of non-activated silica and were eluted with 40 mL of DCM:hexane (1:1). 50 µL of n-nonane was added as a keeper solvent and then both extracts were then concentrated under a gentle stream of nitrogen to a final volume of 500 µL. 100 µL of MilliQ water were then added to a 100 µL aliquot of the respective extracts which were finally used for analysis.

CUPs were analysed using a high-performance liquid chromatograph (HPLC, Agilent 1290, Agilent, Santa Clara, USA) coupled to a mass spectrometer (QTRAP 5500, AB Sciex, Framingham, USA) using four different methods previously developed and described (Mayer et al., 2024). The precursor to product ions were monitored in scheduled multiple reaction monitoring mode (MRM) (Table S4). The identification of individual pesticides was based on the comparison of intensity ratios of ions and retention times with standards and quantification was done using internal calibration with isotopically labelled standards (Table S4).

OCPs were analysed by gas chromatography-mass spectrometry (GC-MS/MS). Detailed information on the methods employed is available in the Supplementary Information (SI Methodology and Table S5).

2.5 Quality assurance and quality control

Twenty-three and eight field blanks were collected and treated alongside the collected samples for OCPs and CUPs, respectively. They were placed in the sampler without pumping air for several seconds (Table S6). Instrumental limits of detection (iLODs) and quantification (iLOQs) were determined by distinguishing the intensity of analytes with a signal-to-noise ratio of 3:1 and 10:1, respectively. Field blanks were used to determine method detection limits (MDLs) based on the average of the analyte concentrations in field blanks plus three times their standard deviation. If field blanks levels were below iLOQ, then iLOQs were used as MDL.

The recoveries of individual pesticides were assessed by spiking sampling media (i.e., QFFs and PUF/XAD2/PUF sandwiches for CUPs and PUFs for OCPs) with the native standards and their corresponding isotopically-labelled standards, which were then processed as per samples. With few exceptions, most analytes recoveries were in the range of 60–120 % and had standard deviations lower than 20 %. For the 48 CUPs analysed using the HPLC-MS/MS, the method recoveries of individual analytes ranged from 68 % ± 14 (carbaryl) to 153 % ± 22 (iprovalicarb) for QFFs and from 61 % ± 3 (kresoxim-methyl) to 132 % ± 10 (iprovalicarb) for sandwiches (Table S7), while for OCPs, recoveries ranged from 47 % ± 8 (PeCB) to 100 % ± 9 (*p,p'*-DDD) for QFFs and from 49 % ± 6 (PeCB) to 103 % ± 10 (*p,p'*-DDD).

In 2018, the analytical instrument was changed and so was the internal standards for OCPs only. As a consequence, the chromatographic results from 2018 onward, for both OCPs and CUPs have been adjusted for sample recoveries (SI S1.1.2.), while results for OCPs prior to 2018 were not recovery corrected (SI S1.1.1.). Therefore, the time trends are done separately for the two periods: (1) from 2013 to 2017 and (2) from 2018 to 2022. The different treatment of recoveries is clearly visible in some of the OCPs time series (e.g., PeCB, HCB and HCHs).

2.6 Data processing and statistical analysis

As our objective is to link atmospheric levels with sources, the data analysed are the total (particulate + gaseous) concentrations. Individual pesticide temporal trends were investigated using a multiple regression equation accounting for seasonalities. For OCPs, with expectedly one annual amplitude Equation (1) is used, which has been widely applied for trend analysis of OCPs (Venier et al., 2012; Wang et al., 2018), as well as for other semivolatile air pollutants which are dominated

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by secondary emissions, such as polychlorinated biphenyls (Degrendele et al., 2020) and polybrominated diphenyl ethers (Ma et al., 2013; Li et al., 2016; Degrendele et al., 2018), halogenated flame retardants (Liu et al., 2016), per- and polyfluoroalkyl substances (Paragot et al., 2020) and organophosphate ester (Wang et al., 2020).

$$\ln C_{air} = a_0 + a_1 \sin(zt) + a_2 \cos(zt) + a_3 t \qquad (1)$$

where C_{air} equals the total (particulate + gaseous) concentration of a compound (pg m^{-3}), t is the time (in years) when the samples were collected; z equals (2π/365.25) to fix the periodicity to a year; a_0 is an intercept to rectify the units, a_1 and a_2 are harmonic coefficients describing seasonal variations, and a_3 is a first-order rate constant and the long-term exponential component (yr^{-1}). The parametric F-test was used in order to assess the significance of each of these coefficients, while the coefficient of determination R^2 reflects the fit of equation (1).

Long-term trends of primary emitted pesticides (CUPs), with one or more application seasons were analysed using Eq. (2), which captures up to two annual amplitudes and their timing.

$$ln\ C_{air} = a_0 + a_1 \cos(a_2 zt + a_4) + a_3 t \qquad (2)$$

with a_1 being a harmonic coefficient describing seasonal variation, a_2 allowing for other periods than one year, a_3 is the long-term exponential component (yr^{-1}) and a_4 defining a phase shift deviating from the seasons. The initial guess for the value of a_4 was chosen according to the recommended timing of application (e.g., 2.32 in units of 2π for mid of May) and was later fine-tuned during the regression.

For both equations (1) and (2), the coefficient a_3 is used to calculate the halving (< 0) or doubling time (> 0) for a given compound as according to Equation 3:

$$\tau_{1/2} = \left(\frac{\ln(2)}{a_3}\right)/365.25 \qquad (3)$$

The apparent halving or doubling time (τ; in years) describes the time for concentrations of a compound to decrease by 50% or to increase by 100%. These halving or doubling times should not be confused with half-lives associated with degradation processes.

Non-parametric Mann-Whitney tests were applied to compare atmospheric concentrations of CUP previous measurements conducted at the same site in 2012-2013 (Degrendele et al., 2016).

2.7 Clausius-Clapeyron equation

The influence of the near-ground air temperature on volatilization from soil of pesticides can be represented using the Clausius-Clapeyron equation (Hoff et al., 1998; Equation 4):

$$\ln p = (\Delta H_{exp}/R)\ (1/T_a) + constant \qquad (4)$$

with partial pressure p (Pa), near-ground air temperature T_a (K), experimentally-based enthalpy of the soil-air exchange ΔH_{exp} (kJ mol^{-1}) and the universal gas constant R (8.314 Pa m^3 K^{-1} mol^{-1}). Firstly, the partial pressures of individual pesticides were calculated as Equation 5,

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$$p = (c_{tot}\, R\, T_a)/M_g \tag{5}$$

Using total (sum of gas and particulate phases) concentrations c_{tot} (in g m^{-3}) for OCPs and CUPs as deemed more appropriate than using only gaseous phase, since for long-lived substances, we expect rapid phase equilibrium, the ideal gas law, air temperature and M_g as the molecular weight of the compound (g mol^{-1}). The pesticide vapour pressures were expressed as linear regressions of the natural logarithm of partial pressure versus inverse temperature (Hoff et al., 1998; Equation 6):

$$\ln p = \frac{m}{T_a} + b \tag{6}$$

where m and b correspond to the slope and intercept of the linear regression, respectively.

3. Results & Discussion

3.1 Pesticides detection frequencies

Overall, 32 of the targeted 48 CUPs were observed in at least one sample. Eleven CUPs had detection frequencies (DF) ranging from 80% to 100%, including two CUPs, pendimethalin and tebuconazole, that were present in all samples. Six CUPs had DF from 50% to < 80%, five CUPs from 20% to < 50%, while 10 CUPs had DF < 20% (Table S8). The CUPs included in this study represented 22%, 30% and 28% of all the pesticides used in agriculture in the Czech Republic during the years 2019, 2020 and 2021, respectively (Table S9). Among them, chlorotoluron, chlorpyrifos, metamitron, metazachlor, pendimethalin, prochloraz, spiroxamine, tebuconazole and terbuthylazine were used in the largest amount (> 50 t of active substances per year), and these CUPs were all quantified > 65 % air samples, except for metamitron (2.8 % DF). Most of the CUPs quantified during the sampling period were applied as plant protection products in Czech Republic, however six compounds, acetochlor, atrazine, carbaryl, diazinon, isoproturon and mecoprop, had DFs ranging from 0.9% to 51 % and had no documented use. Cyprodinil and diuron were approved, but no use was reported in the Czech Republic, while the other compounds were prohibited for use in Europe.

During the 2013 to 2022 period, all targeted legacy OCPs and metabolites were detected in at least one sample. Six compounds were present in every sample, emphasizing their persistence in the environment: pentachlorobenzene (PeCB); hexachlorobenzene (HCB); two stereoisomers of hexachlorocyclohexane (HCH): *α*-HCH and *γ*-HCH; *p,p'*-dichlorodiphenyltrichloroethane (*p,p'*-DDT), as well as one of its associated metabolites *p,p'*-dichlorodiphenyldichloroethane (*p,p'*-DDE) (Table S8). Twelve additional compounds were present in more than 50% of the samples, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *α*-chlordane, *γ*-chlordane and associated metabolite oxychlordane, *β*-HCH, *δ*-HCH, *cis*-heptachlor epoxide, *α*-endosulfan, and mirex. Aldrin, dieldrin, *β*-endosulfan, endrin, endrin aldehyde, endrin ketone, heptachlor, *trans*-heptachlor epoxide, isodrin and methoxychlor were all detected in less than 25% of the samples (Table S8).

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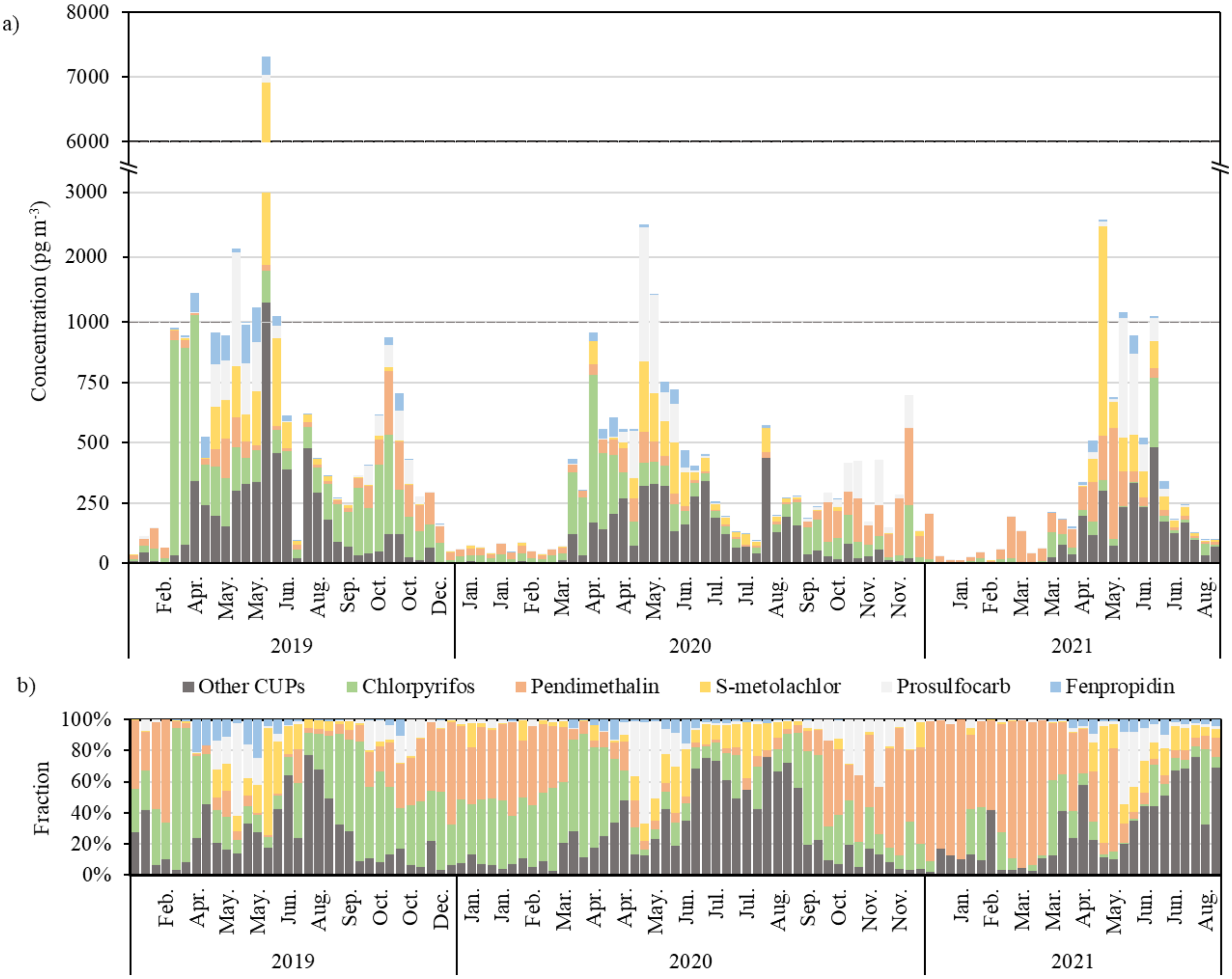
3.2 Total concentrations

The concentrations of individual CUPs ranged over five orders of magnitude, from 40 fg m^{-3} (2,4-D) to 5 ng m^{-3} (s-metolachlor). Chlorpyrifos, fenpropidin, fenpropimorph, metalaxyl, metazachlor, pendimethalin, prosulfocarb, s-metolachlor, spiroxamine, tebuconazole and terbuthylazine were the only CUPs with total concentrations exceeding 100 pg m^{-3} on multiple occasions, while chlorotoluron exceeded that concentration only once during the sampling period (Figure 1a, b, Table S10). High concentrations of chlorpyrifos, s-metolachlor, and pendimethalin (average concentrations of 116, 115, and 65.4 pg m^{-3}, respectively) have been reported in rural environments (Debler et al., 2024; Habran et al., 2024; Mayer et al., 2024; Ni et al., 2024). Similarly, elevated levels of fenpropidin (0.42-307 pg m^{-3}), prosulfocarb (0.1-1631 pg m^{-3}), and s-metolachlor (0.06-5025 pg m^{-3}) have been observed previously, in various European countries, including Germany, France, Belgium, and the Netherlands (Villiot et al., 2018; Kruse-Plaß et al., 2021; Debler et al., 2024; Habran et al., 2024) (Fig. 1a,b; Table S10).

The average weekly concentration of Σ_{30}OCPs was 44.3 pg m^{-3}, with HCB, *p,p'*-DDE and *γ*-HCH accounting on average for 38, 29 and 8 .1% of Σ_{30}OCPs (Figure 1c,d Table S10). The ratio of (*p,p'*-DDT)/(*p,p'*-DDE + *p,p'*-DDD) can be used as an indicator of aged technical DDT. A lower ratio is indicative of aged DDT, while a ratio > 1 implies fresh application (Sari et al., 2020). In this study, the ratio ranged from 0.03 to 0.53, indicating aged DDT, as would be expected considering Czechoslovak restrictions on DDT in the 1970s. Moreover, the (*o,p'*-/(*o,p'*-+*p,p'*-) ratios for each DDX substance were compared (Figure S3). For both DDT and DDD, this ratio decreased over time and remained low (0.37 and 0.31 for DDT and DDD, respectively), indicating that dicofol was seemingly not a viable source for presence of DDT in the atmosphere, not during years of declining concentration nor later (Ricking and Schwarzbauer, 2012). For DDE however, the ratio remained stable and low (i.e., average ratio = 0.02) indicating great environmental persistence, as the more stable *p,p'*-DDE isomer predominates, leading to prolonged contamination and potential bioaccumulation in ecosystems.

Additionally, the ratio *β*-/(*α*-+*γ*-) HCH can be used to distinguish between technical HCH and lindane as sources of environmental contamination, which in this case was 0.01-0.16 . The overall low level of *β*-HCH and the *β*-/(*α*-+*γ*-) HCH ratios confirm the use of lindane, which was banned more recently (1995), as the dominant HCH source (Sari et al., 2020). Similar results have been recently observed in Turkey, Peru, South Korea and Argentina (Sari et al., 2020; Miglioranza et al., 2021; Lee et al., 2022).


a)
8000
7000
6000
3000
2000
1000
750
500
250
0
Concentration (pg m⁻³)
Feb.
Apr.
May.
May.
Jun.
Aug.
Sep.
Oct.
Oct.
Dec.
Jan.
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2020
2021
b)
Other CUPs
Chlorpyrifos
Pendimethalin
S-metolachlor
Prosulfocarb
Fenpropidin
100%
80%
60%
40%
20%
0%
Fraction
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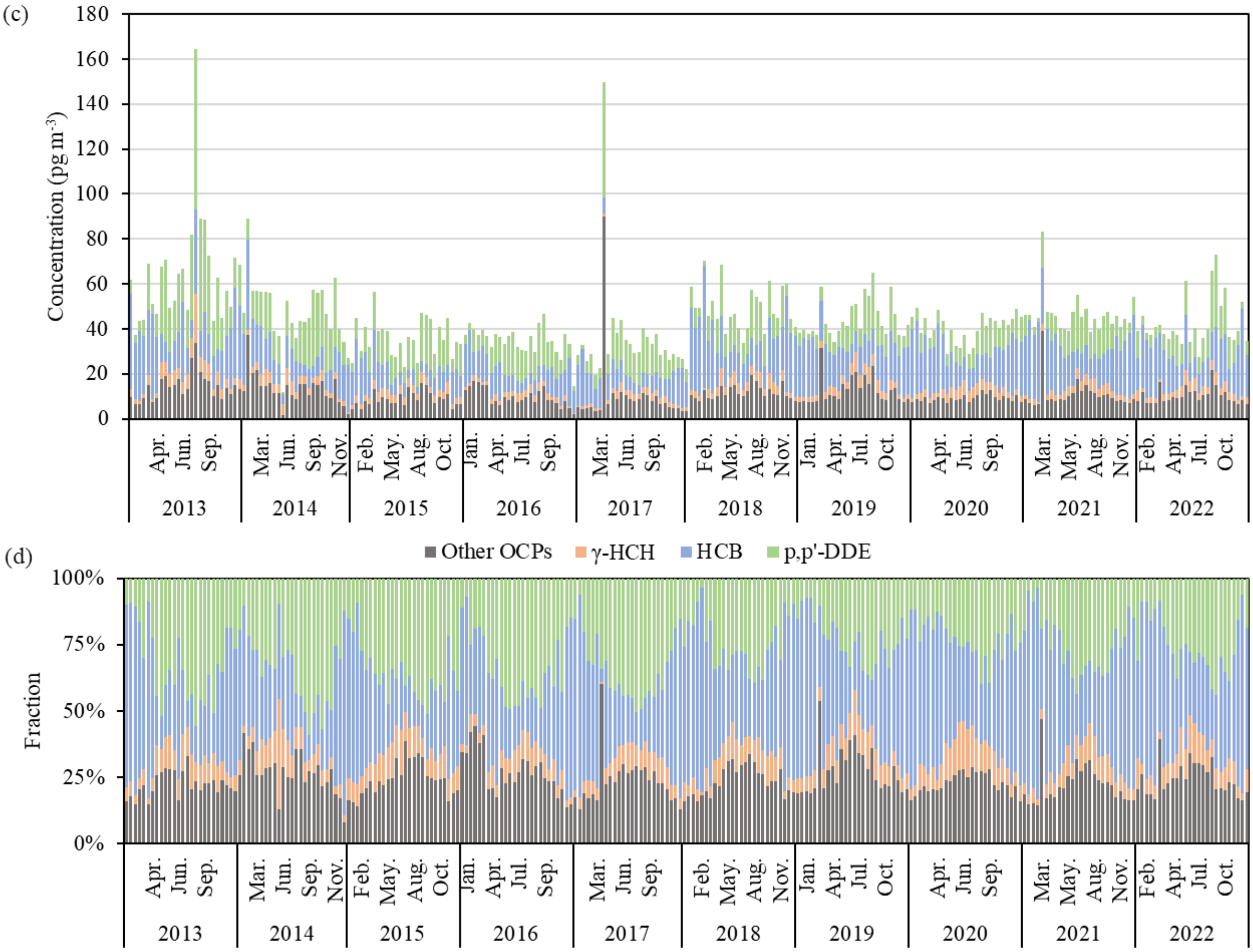

Figure 1. Times series of CUP (a,b) and OCP (c,d) absolute (a,c) and relative (b,d) total atmospheric concentrations.

CUPs have previously been monitored at this site from 2012 to 2013 (Degrendele et al., 2016). Total concentrations were compared for compounds with sufficient data (DF>20%) in both this study and the previous one. Overall, eight CUPs were compared. The 2019-2021 concentrations were significantly higher for chlorotoluron, chlorpyrifos, prochloraz and s-metolachlor, for which approvals existed during the entire study period, 2012-2021. The 2012-2013 concentrations were higher for isoproturon, banned as a plant protection product since 2016, and metazachlor, approved during the entire study period. No significant differences were observed for fenpropimorph and terbuthylazine (Table S11).

3.3 Seasonal variations

Out of the 22 CUPs with DF > 20%, total atmospheric concentration for 16 peaked in spring (Table S12), pointing to the application season. The typical shape of applications during an application season is reflected as a fast increase in concentration followed by a slow decrease. Similar patterns have been previously observed for CUPs such as chlorpyrifos, fenpropidin, metazachlor, prosulfocarb and pendimethalin (Hayward et al., 2010; Degrendele et al., 2016; Carratalá et al., 2017; Villiot et al., 2018; Wang et al., 2021) . Five CUPs, i.e., chlorotoluron, chlorpyrifos, isoproturon, pendimethalin and prosulfocarb, had atmospheric concentrations that peaked in both spring and autumn (Figure S4; Table S12). For pendimethalin, as a pre-emergence herbicide, a winter application is also seen 2019-2020. The autumn peak is likely due to direct application of pesticides for winter cereals (Garthwaite et al., 2014; Degrendele et al., 2016). However, it is also possible that volatilisation from surfaces such as soil, plants and pre-treated seed (Nuyttens et al., 2013) as well as tillage practices (Alletto et al., 2010) occurring at this time may contribute to the levels in air (Alletto et al., 2010). This is most likely the case for isoproturon, which has been banned since 2016, and therefore, application is unlikely. During winter months, without any expected pesticide application, CUPs occurrence in ambient air indicates low degradability. During December to February, chlorpyrifos, isoproturon, and prosulfocarb were the dominant CUPs (with atmospheric concentrations > 100 pg m^{-3}), which have been indicated to be persistent previously (Debler et al., 2024; Mayer et al., 2024). Lastly, metazachlor peaked in the summer (Table S12, Figure S4). This summer peak can be explained by the fact that metazachlor is most used for seed oil plants and is usually applied during the summer period for weed control of winter cereals. This has previously been observed (Mai et al., 2013; Degrendele et al., 2016). Bans on chlorotoluron, chlorpyrifos, fenpropimorph, propiconazole and thiacloprid became effective during the sampling period and an indication of these bans was apparent in the data; during 2019, high concentrations due to application were evident, but these maxima were six times lower during the same period in the following years, highlighting the immediate effect of the legislation (Figure 1). In addition, based on the simulated concentrations distribution encountered derived from Eq. (2) (Table S12), we found that pesticide application was done from February until November, with the spring are mostly around quite broad as it ranged from mid-March to end of June, while the autumn one ranged from mid-October to end of October.

3.4 Influence of temperature on pesticide revolatilisation

The influence of local secondary emissions of pesticides via re-volatilization from soils was examined using the Clausius-Clapeyron equation (Table S13) (Hoff et al., 1998).

A statistically significant correlation between the natural logarithm of partial pressure and the inverse ambient temperature was found for all OCPs with DF > 20%, except γ-chlordane (Table S13b). In addition, slopes were negative for 17 OCPs (Table S13b) and ranged from -7768 (ε-HCH) to -2879 (endosulfan sulfate). This indicates that those pesticides' atmospheric concentration increased with increasing air temperature (Figure S6). Previous studies noted that a steep slope and high R² values (> 0.6) are synonymous with temperature-controlled air–surface cycling and the significant influence of short-range transport on the ambient concentrations (Hoff et al., 1998; Wania et al., 1998; Degrendele et al., 2016). This was observed for two OCPs: *o,p'*-DDT and *p,p'*-DDT, , with respective slopes ranging of -7221 and -6112, while respective R² values were 0.65 and 0.68 (Table S13b). The results from the Clausius-Clapeyron analysis suggest at this site that soil temperatures play a significant role in influencing DDD levels, as indicated by the narrower spread of the scatter plot for DDD (R² = 0.34). In contrast, the scatter plot for DDE (Figure S7-S9) shows a wider spread (R² = 0.46), suggesting that DDE is more likely influenced by secondary sources located far from the sampling area (Ricking and Schwarzbauer, 2012).

In general, the Clausius-Clapeyron relationships suggest that atmospheric concentrations of most OCPs in this study were controlled by the exchange between soil and air and therefore, by revolatilisation from surfaces close to the sampling site. This observation agrees with other studies (Cabrerizo et al., 2011; Degrendele et al., 2016; Zhan et al., 2017). For the less temperature-dependent compounds, it is suggested that atmospheric concentrations were more influenced by long-range atmospheric transport (LRAT; Table S13b).

According to the Clausius-Clapeyron relationship, 18 CUPs were found to be temperature dependent (Table S13a; p-value < 0.05). Previously, terbuthylazine and s-metolachlor have been found to have significant temperature dependency (Degrendele et al., 2016). Unlike for OCPs, CUP maximum concentrations were not encountered during the warmest period (summer) but during their application periods (Figure S6 and Table S11).

The overall results emphasize the differences between OCPs and CUPs. For OCPs, temperature dependent volatilization is the main influence on OCP atmospheric concentration. For authorised CUPs, atmospheric concentrations were mainly influenced by application, while temperature-dependent resuspension and LRAT influenced CUPs atmospheric levels for banned compounds.

3.5 Multi-annual variations

Long-term annual variations in atmospheric concentrations were assessed for 22 CUPs which had sufficient data for total atmospheric concentrations (DF > 20%) using Eq. (2), while Eq. (1) was used for OCPs. Values below MDL were substituted by MDL/2. Eq. (1) was tested for CUPs trends, too, which led to lower R² values as compared to using Eq.(2) (Tables S15-S16), not only for CUPs with 2 concentration maxima per year, but also for CUPs with only one.

A decrease of total atmospheric concentrations is found for 14 CUPs over the period 2019-2021 (Eq. 2, Table S15). Nine of these were approved pesticides: 2,4-D, chlorotoluron, cyprodinil, fenpropidin, metazachlor, pirimicarb, prochloraz, s-metolachlor and terbuthylazine. National usage of these pesticides in the Czech Republic was almost constant during 2019-2021, except for fenpropidin and prochloraz, which annual amounts decreased by approximately 40% during this period. Decreasing trends were also observed for recently banned pesticides (chlorpyrifos, fenpropimorph, and thiacloprid), as well as the earlier banned CUPs isoproturon and propiconazole. This reflects the immediate and long-term effects of legislation. Generally, for the CUPs with decreasing concentrations, the estimated halving times $\tau_{1/2}$ ranged from 0.62 to 1.37 yr for the approved pesticides while for the banned pesticides halving times were expectedly lower (i.e., $\tau_{1/2} \approx$ 0.38-0.48 yr), except for one of them, thiacloprid ($\tau_{1/2} \approx$ 0.91 yr) (Figure 2; Table S15). Seven CUPs showed no significant change of their atmospheric concentration over time. These compounds are all approved for use and applied in the Czech Republic with stable or increasing usage. Boscalid was the only CUP which usage in the Czech Republic was decreasing (ÚKZÚZ, 2024).

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For chlorpyrifos and fenpropimorph, the usage was reduced by 30-50% from 2019 to 2020 in the Czech Republic and was reported zero or very low amount in 2021 (Table S9). The observed decline which was accelerated from 2020 to 2021 as compared from 2019 to 2020 reflect the combination of these applications and the degradation in the total environment after ban (total environmental residence time $\tau_{overall}$ up to many months, BCPC, 2012).

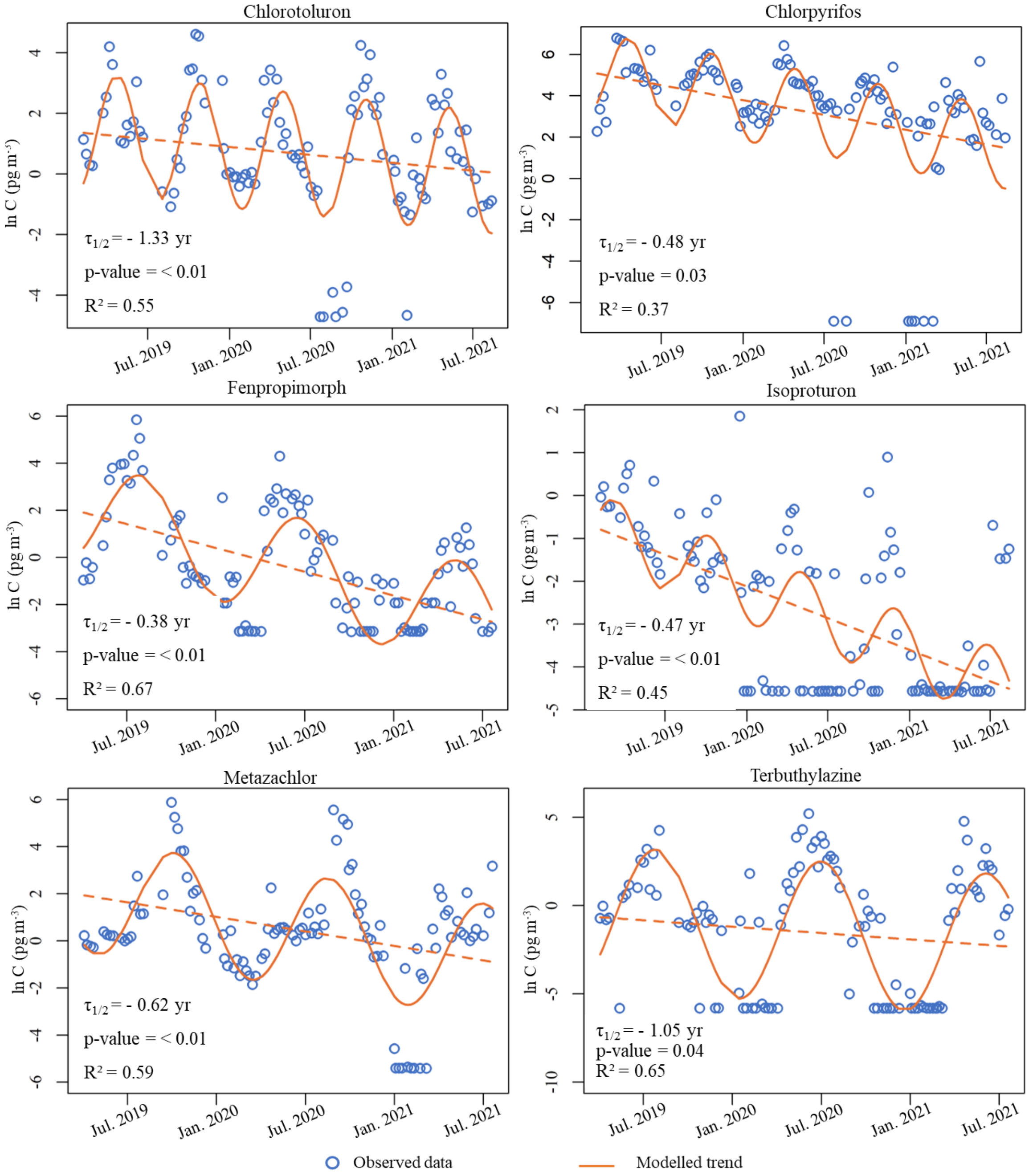

Figure 2. Multi-annual variations of selected CUPs with significantly negative trends. Values < MDL were substituted by MDL/2.

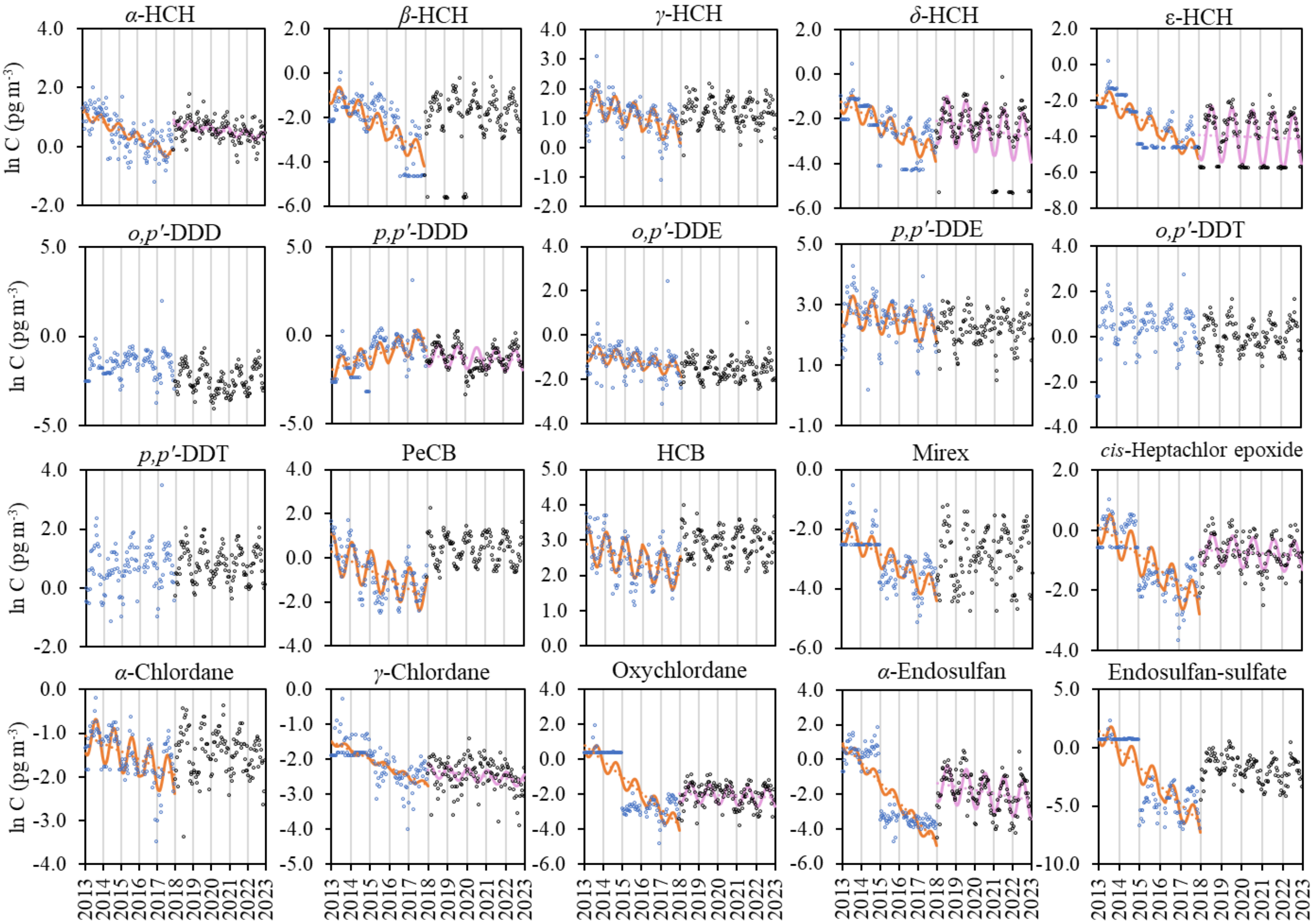

Figure 3. Multi-annual variations of OCPs (DF > 20%). Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the modelled variation, whenever the trend was significant. Values < MDL were substituted by MDL/2.

The time trend analyses of the OCPs were assessed separately for the time periods 2013-2017 and 2018-2022 (Eq. (1), Table S16). A significant decrease in total atmospheric concentration is observed in both periods for *α*-, *δ*- and ε-HCH, *cis*-heptachlor epoxide, *γ*-chlordane, oxychlordane, and *α*-endosulfan (Figures 3 and S6). *p,p'*-DDD shows an increasing trend in the 2013-2017 period, but a decreasing one in the 2018-2022 period (Figures 3 and S7, Table S16). The decreasing trends in 2018-2022 range -7.29% ± 5.15% yr^{-1}, with the steepest slope, -16.7% yr^{-1}, found for *α*-endosulfan. Consistently, this steepest slope of *α*-endosulfan corresponds with the shortest time period passed since ban (2013) among these eight OCPs (Alarcón et al., 2023). Twelve OCPs i.e., PeCB, HCB, *β*- and *γ*-HCH, *o,p'*- and *p,p'*-DDE, *o,p'*-DDD, *o,p'*- and *p,p'*-DDT, *α*-chlordane, mirex and endosulfan sulfate show insignificant trends in the 2018-2022 period (Figures 3 and S8, Table S16b) after significantly decreasing (8 substances) or insignificant trends (4 substances, namely *o,p'*-DDD, *o,p'*- and *p,p'*-DDT, *α*-chlordane, mirex and endosulfan sulfate) in the 2013-2017 period (Figures 3 and S8, Table S16a). . The trend of these 12 substances suggests that the total environmental burdens cycling across environmental compartments have been levelling off in the region in recent years. For DDT compounds, the ratio of the pesticide over its metabolites, DDT/(DDE+DDD), shifted from ≈0.27 during 2013-2017 to ≈ 0.34 during 2018-2022, which does not indicate any influence of fresh inputs of the pesticide. For chlordane, the isomeric ratio shifted from $\alpha/\gamma \approx 2.2$ during 2013-2017 to $\alpha/\gamma \approx 2.8$ during 2018-2022. With α/γ <1 indicating fresh inputs (Liu et al., 2009), this observed trend indicates that eventually recently enforced sources are from old storage of the pollutant. The negative trends found are consistent with trends reported from the region for the years 1996-2023 (UNEP, 2023; EMEP, 2024), namely for chlordane, α-, β- and γ-HCH, DDT and DDE. For HCB, a long-term increase was reported in European background air for the years 2016 to 2019 compared to the previous decade (Fiedler et al., 2023; Lunder Halvorsen et al., 2023). However, for Iceland, Germany, Norway and Sweden decreasing HCB was reported during 2016-23 (EMEP, 2024). For PeCB both negative as well as insignificant trends were reported in the region (UNEP, 2023). Levelling off of HCB, α-, β- and γ-HCH, *o,p'*- and *p,p'*-DDE, and α-chlordane concentrations has not been observed before, but declining levels of these pollutants have been reported until 2023 for α-, β- and γ-HCH, PeCB, α-chlordane, and DDX substances in the region (central and eastern Europe; UNEP, 2023), for DDX substances, α- and γ-HCH in Germany, Denmark, Finland, Sweden, Norway and Iceland, and for β-HCH in Denmark and Iceland (EMEP, 2024). Levelling off of α- and γ-HCH, *p,p'*-DDE, *p,p'*-DDT and α- and γ-chlordane since ≈ 2014 has been reported in some but not all Arctic air monitoring stations, including in the European Arctic ($\tau_{1/2} \gtrsim 10$ yr; Wong et al., 2021). No mirex monitoring data were recently reported in Europe.

In general, the atmospheric levels of banned OCPs previous declining in air could be sustained by reversal of the direction of air-surface exchanges driven by chemical equilibria (Bidleman et al., 1995; Mackay and Parnis, 2020) or mobilisation from surface compartments by climate events, such as melting of glaciers, permafrost soils or polar ice, flooding or heating of soils by wildfires (Holoubek et al., 2007; Bogdal et al., 2009; Nadal et al., 2015). For the recent years, the influence of such events on OCP cycling is not evident but cannot be excluded, regarding on-going climate change and the spatial scale, which is global. Reversal of air-surface exchange of banned OCPs is an implication of their chemodynamics, occurring at a point in time determined by the compartmental distribution and the physico-chemical properties. Long-term chemodynamics and air-surface exchange of OCPs has been addressed in only few large-scale multicompartment modelling studies. Based on global multicompartment modelling, net volatilisation of DDT and β-HCH from soils of the region are expected since at least the early 2000s (Stemmler and Lammel, 2009; Wöhrnschimmel et al., 2012). PeCB and HCB are out-phased from agricultural usage since long, but are unintentionally released by industries and combustion processes, such as waste incineration (Thomsen et al., 2009; UNEP 2024). Unlike for the other OCPs, influence of recent primary emissions cannot be excluded for DDT, as India and some African countries have been reporting DDT applications throughout the last decade for vector disease control purposes (van den Berg et al., 2017; UNEP, 2024). In the case of endosulfan sulfate, lack of significant trends is inconclusive due to low detection frequency (Figure S9).

One aspect that was not investigated in this study is determining the CUP gas-particle partitioning (GPP) and related temporal trends. GPP models tested successfully for other SVOCs (e.g., polycyclic aromatic compounds and PBDEs; Shahpoury et al., 2016; Qin et al., 2021) could not yet be adopted for testing CUPs’ GPP, because of lack of field (PM chemical composition) and laboratory data (GPP model parameters).

4 Conclusions

Overall, this study provided long-term data series for OCPs and CUPs at a Central European site. Consistent with the perception of semivolatiles slowly degrading in soils, Clausius-Clapeyron analysis showed that revolatilisation is a source for OCPs (all targeted) and CUPs (most) in air in summer in rural central Europe.

Although OCPs were banned decades ago, their occurrence in the rural atmosphere demonstrates their persistence in the environment. For the OCPs α-HCH, *cis*-heptachlor epoxide, γ-chlordane, oxychlordane, and α-endosulfan significant negative trends are found until 2023, consistent with previous findings in the region, the same for δ- and ε-HCH. However, the trends during 2018-2023 are no longer significantly negative for PeCB, HCB, β- and γ-HCH, *o,p’*- and *p,p’*-DDE, *o,p’*-DDD, *o,p’*- and *p,p’*-DDT, α-chlordane, and mirex. This suggests levelling off of these pollutants’ levels in air in the region and possibly beyond. Except for PeCB and HCB, which atmospheric levels may be sustained by unintended releases, the levelling off of these OCPs results from enhanced secondary sources i.e., reversal of the direction of air-surface exchange or recent mobilisation of their reservoirs in soils, water bodies or the cryosphere. Longer time trends, experimental verification of the direction of air surface exchange and large-scale multicompartment model simulations are needed for comprehensively investigate the chemodynamics of the globally cycling OCPs.

In addition, our observations of CUPs’ temporal trends are dominated by applications. They were generally negative or insignificant, while at the same time CUPs national use in the Czech Republic increased for most of the compounds. For pesticides such as chlorpyrifos and fenpropimorph, the decreasing trends were directly related to their use authorisation being revoked. However, one year after their ban, these compounds were still present in the atmosphere detectable concentration, seemingly bringing evidence about a potential atmospheric persistence.

The long-term data presented in this study highlight the importance of continued research on these compounds to generate sufficient insights into their atmospheric fate and to furthermore develop accurate models predicting key processes such as transport, deposition, and gas-particle partitioning.

Author contributions

Ludovic Mayer: Investigation, Data Curation, Writing – Original Draft. Lisa Melymuk: Data Curation. Adela Holubová Šmejkalová: Investigation. Jiři Kalina: Methodology. Petr Kukučka: Validation. Jakub Martiník: Validation. Petra Přibylová: Validation. Pourya Shahpoury: Data Curation. Gerhard Lammel: Data Curation. All authors: Writing – Review & Editing, Approval of final manuscript.

Competing interest

The authors declare that they have no conflict of interest.

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References

Alarcón, P. C., Kitanovski, Z., Padervand, M., Pöschl, U., Lammel, G., and Zetzsch, C.: Atmospheric hydroxyl radical reaction rate coefficient and total environmental lifetime of α-endosulfan, Environ. Sci. Technol., 57, 15999–16005, 2023.

Alexandratos, N. and Bruinsma, J.: World Agriculture towards 2030/2050: the 2012 revision, Food and Agriculture Organization (FAO), Rome, Italy, www.fao.org /docrep/016/ap106e/ap106e.pdf (last accessed online: 15 Nov 2023).

Alletto, L., Coquet, Y., Benoit, P., Heddadj, D., and Barriuso, E.: Tillage management effects on pesticide fate in soils. A review, Agron. Sustain. Dev., 30, 367–400, 2010.

Balmer, J. E., Morris, A. D., Hung, H., Jantunen, L., Vorkamp, K., Rigét, F., Evans, M., Houde, M., and Muir, D. C. G.: Levels and trends of current-use pesticides (CUPs) in the arctic: An updated review, 2010–2018, Emerg. Contam., 5, 70–88, 2019.

Becker, S., Halsall, C. J., Tych, W., Kallenborn, R., Su, Y., and Hung, H.: Long-term trends in atmospheric concentrations of α- and γ-HCH in the Arctic provide insight into the effects of legislation and climatic fluctuations on contaminant levels, Atmos. Environ., 42, 8225–8233, 2008.

Bedos, C., Cellier, P., Calvet, R., Barriuso, E., and Gabrielle, B.: Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: Overview, Agronomie, 22, 21–33, 2002.

Bidleman, T. F., Jantunen, L. M., Falconer, R. L., Barrie, L. A., and Fellin, P.: Decline of hexachlorocyclohexane in the Arctic atmosphere and reversal of air-sea gas exchange, Geophys. Res. Lett., 22, 219–222, 1995.

Bidleman, T. F.: Atmospheric transport and air-surface exchange of pesticides, in: Fate of Pesticides in the Atmosphere: Implications for Environmental Risk Assessment (van Dijk, H. F. G., van Pul, W. A. J., and de Voogt, P., eds.), Springer, Dordrecht, Netherlands, pp. 115–166, 1999.

BCPC: British Crop Protection Council.: The pesticide manual : A world compendium., 16th ed., MacBean, C. ed., BCPC Publications, Alton, United Kingdom, 2012.

Bogdal, C., Schmid, P., Zennegg, M., Anselmetti, F. S., Scheringer, M., and Hungerbühler, K.: Blast from the past: Melting glaciers as a relevant source for persistent organic pollutants, Environ. Sci. Technol., 43, 8173–8177, 2009.

Cabrerizo, A., Dachs, J., Jones, K. C., and Barceló, D.: Soil-air exchange controls on background atmospheric concentrations of organochlorine pesticides, Atmos. Chem. Phys., 11, 12799–12811, 2011.

Carratalá, A., Moreno-González, R., and León, V. M.: Occurrence and seasonal distribution of polycyclic aromatic hydrocarbons and legacy and current-use pesticides in air from a Mediterranean coastal lagoon (Mar Menor, SE Spain), Chemosphere, 167, 382–395, 2017.

Carvalho, F. P.: Pesticides, environment, and food safety, Food Energy Secur., 6, 48–60, 2017.

Cindoruk, S. S.: Atmospheric organochlorine pesticide (OCP) levels in a metropolitan city in Turkey, Chemosphere, 82, 78–87, 2011.

Coscollà, C., Colin, P., Yahyaoui, A., Petrique, O., Yusà, V., Mellouki, A., and Pastor, A.: Occurrence of currently used pesticides in ambient air of Centre Region (France), Atmos. Environ., 44, 3915–3925, 2010.

Coscollà, C., López, A., Yahyaoui, A., Colin, P., Robin, C., Poinsignon, Q., and Yusà, V.: Human exposure and risk assessment to airborne pesticides in a rural French community, Sci. Total Environ., 584–585, 856–868, 2017.

Debler, F., Abrantes, N., Harkes, P., Campos, I., and Gandrass, J.: Occurrence and distribution of pesticides and transformation products in ambient air in two European agricultural areas, Sci. Total Environ., 940, 173705, 2024.

Degrendele, C., Okonski, K., Melymuk, L., Landlová, L., Kukučka, P., Audy, O., Kohoutek, J., Čupr, P., and Klánová, J.: Pesticides in the atmosphere: a comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides, Atmos. Chem. Phys., 16, 1531–1544, 2016.

Degrendele, C., Wilson, J., Kukučka, P., Klánová, J., and Lammel, G.: Are atmospheric PBDE levels declining in central Europe? Examination of the seasonal and semi-long-term variations, gas-particle partitioning and implications for long-range atmospheric transport, Atmos. Chem. Phys., 18, 12877–12890, 2018.

Degrendele, C., Fiedler, H., Kočan, A., Kukučka, P., Přibylová, P., Prokeš, R., Klánová, J., and Lammel, G.: Multiyear levels of PCDD/Fs, dl-PCBs and PAHs in background air in central Europe and implications for deposition, Chemosphere, 240, 2020.

Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., Pochet, G., Savelli, J. L., Wortham, H., and Quivet, E.: Spatial and temporal distribution of current-use pesticides in ambient air of Provence-Alpes-Côte-d'Azur Region and Corsica, France, Atmos. Environ., 192, 241–256, 2018.

Duyzer, J.: Pesticides in Perspective Pesticide concentrations in air and precipitation in the Netherlands, J. Environ. Monit., 5, 77N-80N, 2003.

EMEP: EMEP 2024 database, Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe, URL: https://ebas.nilu.no/data-access/ (last accessed online 13 Dec. 2024), 2024.

FAOSTAT: Pesticides use. UN Food and Agriculture Organisation (FAO), http://www.fao.org/faostat/en/#data/RP (last accessed online 21/03/2024).

Fiedler, H., Abad, E., and de Boer, J.: Preliminary trends over ten years of persistent organic pollutants in air - Comparison of two sets of data in the same countries, Chemosphere, 324, 138299, 2023.

Gao, H., Ma, J., Cao, Z., Dove, A., and Zhang, L.: Trend and climate signals in seasonal air concentration of organochlorine pesticides over the Great Lakes, J. Geophys. Res., 115, 2010.

Garthwaite, D. G., Hudson, S., Barker, I., Parrish, G., Smith, L., and Pietravalle, S.: Pesticide usage survey report 250: Arable crops in the United Kingdom 2012 (including aerial applications 2012), Food and Environment Research Agency, York, UK, https://pusstats.fera.co.uk/upload/kxZtSlyLVGQl5Wj0oFpHmPtX3PI3i6ZOF7L8Ep8Q.pdf (last accessed online 3 Jan. 2025), 2012.

Glotfelty, D. E., Leech, M. M., Jersey, J., and Taylor, A. W.: Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor and toxaphene, J. Agric. Food Chem., 37, 546–551, 1989.

Habran, S., Giusti, A., Galloy, A., Gérard, G., Delvaux, A., Pigeon, O., and Remy, S.: Spatial and temporal variations of currently used pesticides (CUPs) concentrations in ambient air in Wallonia, Belgium, Chemosphere, 351, 141241, 2024.

Hayward, S. J., Gouin, T., and Wania, F.: Comparison of four active and passive sampling techniques for pesticides in air, Environ. Sci. Technol., 44, 3410–3416, 2010.

Hites, R. A. and Venier, M.: Good news: Some insecticides have been virtually eliminated in air near the Great Lakes, Environ. Sci. Technol., 57, 2199–2204, 2023.

Hoff, R. M., Brice, K. A., and Halsall, C. J.: Nonlinearity in the slopes of Clausius−Clapeyron plots for SVOCs, Environ. Sci. Technol., 32, 1793–1798, 1998.

Holoubek, I., Klánová, J., Jarkovský, J., and Kohoutek, J.: Trends in background levels of persistent organic pollutants at Kosetice observatory, Czech Republic. Part I. Ambient air and wet deposition 1996-2005, J. Environ. Monit., 9, 557–563, 2007.

Hulin, M., Leroux, C., Mathieu, A., Gouzy, A., Berthet, A., Boivin, A., Bonicelli, B., Chubilleau, C., Hulin, A., Leoz Garziandia, E., Mamy, L., Millet, M., Pernot, P., Quivet, E., Scelo, A. L., Merlo, M., Ruelle, B., and Bedos, C.: Monitoring of pesticides in ambient air: Prioritization of substances, Sci. Total Environ., 753, 141722, 2021.

Hung, H., Blanchard, P., Halsall, C. J., Bidleman, T. F., Stern, G. A., Fellin, P., Muir, D. C. G., Barrie, L. A., Jantunen, L. M., Helm, P. A., Ma, J., and Konoplev, A.: Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring, Sci. Total Environ., 342, 119–144, 2005.

Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J. M., Leppänen, S., Bossi, R., Skov, H., Manø, S., Patton, G. W., Stern, G., Sverko, E., and Fellin, P.: Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993-2006, Sci. Total Environ., 408, 2854–2873, 2010.

Hung, H., Katsoyiannis, A. A., Brorström-Lundén, E., Olafsdottir, K., Aas, W., Breivik, K., Bohlin-Nizzetto, P., Sigurdsson, A., Hakola, H., Bossi, R., Skov, H., Sverko, E., Barresi, E., Fellin, P., and Wilson, S.: Temporal trends of Persistent Organic Pollutants (POPs) in Arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP), Environ. Pollut., 217, 52–61, 2016.

Jepson, P. C., Murray, K., Bach, O., Bonilla, M. A., and Neumeister, L.: Selection of pesticides to reduce human and environmental health risks: a global guideline and minimum pesticides list, The Lancet Planet. Health, 4, e56–e63, 2020.

Kalina, J., White, K. B., Scheringer, M., Přibylová, P., Kukučka, P., Audy, O., Martiník, J., and Klánová, J.: Comparability of semivolatile organic compound concentrations from co-located active and passive air monitoring networks in Europe, Environ. Sci.: Processes and Impacts, 24, 898–909, 2022.

Kruse-Plaß, M., Hofmann, F., Wosniok, W., Schlechtriemen, U., and Kohlschütter, N.: Pesticides and pesticide-related products in ambient air in Germany, Environ. Sci. Eur., 33, 114, 2021.

Lakaschus, S., Weber, K., Wania, F., Bruhn, R., and Schrems, O.: The air−sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica, Environ. Sci. Technol., 36, 138–145, 2002.

Lee, M., Lee, S., Noh, S., Park, K.-S., Yu, S. M., Lee, S., Do, Y.-S., Kim, Y. H., Kwon, M., Kim, H., and Park, M.-K.: Assessment of organochlorine pesticides in the atmosphere of South Korea: spatial distribution, seasonal variation, and sources, Environ. Monit. Assess., 194, 754, 2022.

Lammel, G., Novák, J., Landlová, L., Dvorská, A., Klánová, J., Čupr, P., Kohoutek, J., Reimer, E., and Škrdlíková, L.: Sources and distributions of polycyclic aromatic hydrocarbons and toxicity of polluted atmosphere aerosols, in: Environ. Sci. Eng., Springer Science and Business Media Deutschland GmbH, 39–62, 2010.

Lammel, G., Degrendele, C., Gunthe, S. S., Mu, Q., Muthalagu, A., Audy, O., Biju, C. V., Kukučka, P., Mulder, M. D., Octaviani, M., Příbylová, P., Shahpoury, P., Stemmler, I., and Valsan, A. E.: Revolatilisation of soil-accumulated pollutants triggered by the summer monsoon in India, Atmos. Chem. Phys., 18, 11031–11040, 2018.

LCSQA: Résultats de la campagne nationale exploratoire de mesure des résidus de pesticides dans l'air ambiant (2018-2019), 2019.

Lee, M., Lee, S., Noh, S., Park, K.-S., Yu, S. M., Lee, S., Do, Y.-S., Kim, Y. H., Kwon, M., Kim, H., and Park, M.-K.: Assessment of organochlorine pesticides in the atmosphere of South Korea: spatial distribution, seasonal variation, and sources, Environ. Monit. Assess., 194, 754, 2022.

Lewis, K. A., Tzilivakis, J., Warner, D. J., and Green, A.: An international database for pesticide risk assessments and management, Hum. Ecol. Risk Assess.: Int. J., 22, 1050–1064, 2016.

Li, W. L., Huo, C. Y., Liu, L. Y., Song, W. W., Zhang, Z. F., Ma, W. L., Qiao, L. N., and Li, Y. F.: Multi-year air monitoring of legacy and current-use brominated flame retardants in an urban center in northeastern China, Sci. Total Environ., 571, 633–642, 2016.

Li, Y., Lohmann, R., Zou, X., Wang, C., and Zhang, L.: Air-water exchange and distribution pattern of organochlorine pesticides in the atmosphere and surface water of the open Pacific Ocean, Environ. Pollut., 265, 2020.

Liu, X., Zhang, G., Li, J., Yu, L.-L., Xu, Y., Li, X.-D., Kobara, Y., and Jones, K. C.: Seasonal patterns and current sources of DDTs, chlordanes, hexachlorobenzene, and endosulfan in the atmosphere of 37 Chinese cities, Environ. Sci. Technol., 43, 1316–1321, 2009.

Liu, L. Y., Salamova, A., Venier, M., and Hites, R. A.: Trends in the levels of halogenated flame retardants in the Great Lakes atmosphere over the period 2005-2013, Environ. Int., 92–93, 442–449, 2016.

López, A., Coscollà, C., and Yusà, V.: Evaluation of sampling adsorbents and validation of a LC-HRMS method for determination of 28 airborne pesticides, Talanta, 189, 211–219, 2018.

Lunder Halvorsen, H., Bohlin-Nizzetto, P., Eckhardt, S., Gusev, A., Moeckel, C., Shatalov, V., Skogeng, L. P., and Breivik, K.: Spatial variability and temporal changes of POPs in European background air, Atmos. Environ., 299, 2023.

Ma, Y., Salamova, A., Venier, M., and Hites, R. A.: Has the phase-out of PBDEs affected their atmospheric levels? Trends of PBDEs and their replacements in the Great Lakes atmosphere, Environ. Sci. Technol., 47, 11457–11464, 2013.

Mackay, D. and Parnis, J. M.: Multimedia environmental models: The fugacity approach, 3rd edition, CRC Press: Boca Raton, FL, USA., CRC press., 2020.

Maggi, F., Tang, F. H. M., la Cecilia, D., and McBratney, A.: PEST-CHEMGRIDS, global gridded maps of the top 20 crop-specific pesticide application rates from 2015 to 2025, Sci. Dat., 6, 170–190, 2019.

Mai, C., Theobald, N., Lammel, G., and Hühnerfuss, H.: Spatial, seasonal and vertical distributions of currently-used pesticides in the marine boundary layer of the North Sea, Atmos. Environ., 75, 92–102, 2013.

Mayer, L., Degrendele, C., Šenk, P., Kohoutek, J., Přibylová, P., Kukučka, P., Melymuk, L., Durand, A., Ravier, S., Alastuey, A., Baker, A. R., Baltensperger, U., Baumann-Stanzer, K., Biermann, T., Bohlin-Nizzetto, P., Ceburnis, D., Conil, S., Couret, C., Degórska, A., Diapouli, E., Eckhardt, S., Eleftheriadis, K., Forster, G. L., Freier, K., Gheusi, F., Gini, M. I., Hellén, H., Henne, S., Herrmann, H., Holubová Šmejkalová, A., Hõrrak, U., Hüglin, C., Junninen, H., Kristensson, A., Langrene, L., Levula, J., Lothon, M., Ludewig, E., Makkonen, U., Matejovičová, J., Mihalopoulos, N., Mináriková, V., Moche, W., Noe, S. M., Pérez, N., Petäjä, T., Pont, V., Poulain, L., Quivet, E., Ratz, G., Rehm, T., Reimann, S., Simmons, I., Sonke, J. E., Sorribas, M., Spoor, R., Swart, D. P. J., Vasilatou, V., Wortham, H., Yela, M., Zarmpas, P., Zellweger Fäsi, C., Tørseth, K., Laj, P., Klánová, J., and Lammel, G.: Widespread pesticide distribution in the European atmosphere questions their degradability in air, Environ. Sci. Technol., 58, 3342–3352, 2024.

Miglioranza, K. S. B., Ondarza, P. M., Costa, P. G., de Azevedo, A., Gonzalez, M., Shimabukuro, V. M., Grondona, S. I., Mitton, F. M., Barra, R. O., Wania, F., and Fillmann, G.: Spatial and temporal distribution of Persistent Organic Pollutants and current use pesticides in the atmosphere of Argentinean Patagonia, Chemosphere, 266, 129015, 2021.

Nadal, M., Marquès, M., Mari, M., and Domingo, J. L.: Climate change and environmental concentrations of POPs: A review, Environ. Res., 143, 177-185, 2015.

Ni, J., Cai, M., Lin, Y. J., Li, T., and Ma, J.: Occurrence, seasonal variations, and spatial distributions of current-use organoamine pesticides in the atmosphere of Shanghai, China, Atmos. Pollut. Res., 15, 102187, 2024.

Nuyttens, D., Devarrewaere, W., Verboven, P., and Foqué, D.: Pesticide-laden dust emission and drift from treated seeds during seed drilling: A review, Pest Manag. Sci., 69, 564–575, 2013.

O'Driscoll, K.: Air-sea exchange of legacy POPs in the North Sea based on results of fate and transport, and shelf-sea hydrodynamic ocean models, Atmosphere, 5, 156–177, 2014.

Paragot, N., Bečanová, J., Karásková, P., Prokeš, R., Klánová, J., Lammel, G., and Degrendele, C.: Multi-year atmospheric concentrations of per- and polyfluoroalkyl substances (PFASs) at a background site in central Europe, Environ. Pollut., 265, 114851, 2020.

Qin, M., Yang, P.-F., Hu, P.-T., Hao, S., Macdonald, R. W., and Li, Y.-F.: Particle/gas partitioning for semi-volatile organic compounds (SVOCs) in level III multimedia fugacity models: Both gaseous and particulate emissions, Sci. Total Environ., 790, 148012, 2021.

Ricking, M. and Schwarzbauer, J.: DDT isomers and metabolites in the environment: an overview, Environ. Chem. Lett., 10, 317–323, 2012.

Salamova, A., Venier, M., and Hites, R. A.: Revised temporal trends of persistent organic pollutant concentrations in air around the Great Lakes, Environ. Sci. Technol. Lett., 2, 20–25, 2015.

Sari, M. F., Córdova Del Águila, D. A., Tasdemir, Y., and Esen, F.: Atmospheric concentration, source identification, and health risk assessment of persistent organic pollutants (POPs) in two countries: Peru and Turkey, Environ. Monit. Assess., 192, 655, 2020.

Semeena, V. S., Feichter, J., and Lammel, G.: Impact of the regional climate and substance properties on the fate and atmospheric long-range transport of persistent organic pollutants-examples of DDT and γ-HCH, Atmos. Chem. Phys, 6, 1231–1248, 2006.

Shahpoury, P., Lammel, G., Albinet, A., Sofuoğlu, A., Dumanoğlu, Y., Sofuoğlu, S. C., Wagner, Z., and Zdimal, V.: Evaluation of a conceptual model for gas-particle partitioning of polycyclic aromatic hydrocarbons using polyparameter linear free energy relationships, Environ. Sci. Technol., 50, 12312–12319, 2016.

Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G. P. S., Handa, N., Kohli, S. K., Yadav, P., Bali, A. S., Parihar, R. D., Dar, O. I., Singh, K., Jasrotia, S., Bakshi, P., Ramakrishnan, M., Kumar, S., Bhardwaj, R., and Thukral, A. K.: Worldwide pesticide usage and its impacts on ecosystem, SN, Appl. Sci., 1, 1446, 2019.

Shunthirasingham, C., Gawor, A., Hung, H., Brice, K. A., Su, K., Alexandrou, N., Dryfhout-Clark, H., Backus, S., Sverko, E., Shin, C., Park, R., and Noronha, R.: Atmospheric concentrations and loadings of organochlorine pesticides and polychlorinated biphenyls in the Canadian Great Lakes Basin (GLB): Spatial and temporal analysis (1992–2012), Environ. Pollut., 217, 124–133, 2016.

Sofuoglu, A., Cetin, E., Bozacioglu, S. S., Sener, G. D., and Odabasi, M.: Short-term variation in ambient concentrations and gas/particle partitioning of organochlorine pesticides in Izmir, Turkey, Atmos. Environ., 38, 4483–4493, 2004.

Stemmler, I. and Lammel, G.: Cycling of DDT in the global environment 1950–2002: World Ocean returns the pollutant, Geophys. Res. Lett., 36, 2009.

Tang, F. H. M., Lenzen, M., McBratney, A., and Maggi, F.: Risk of pesticide pollution at the global scale, Nat Geosci, 14, 206–210, 2021.

Thomsen, M., Nielsen, O.-K., & Illerup, J. B.: Unintentional formation and emission of the persistent organic pollutants HCB and PCBs in the Nordic countries: Documentation of existing information regarding sources and emissions to air, water and soil, with focus on reporting obligations according to the Stockholm Convention, the UNECE POP protocol, and PRTR registers. Nordic Council of Ministers. TemaNord No. 518. http://norden.diva-portal.org/smash/get/diva2:700932/FULLTEXT01.pdf (last accessed online 5 Dec. 2024), 2009.

UNEP: United Nations Environment Programme (UNEP), Regionally Based Assessment of Persistent Toxic Substances, Global Rep. 2003, 211 pp., Geneva, Switzerland, 2003.

UNEP: Stockholm Convention on Persistent Organic Pollutants (POPs), United Nations Environment Programme, http://chm.pops.int/tabid/208/Default.aspx, (last accessed online, 5 Dec. 2024).

UNEP: United Nations Environment Programme (UNEP), Regionally Based Assessment of Persistent Toxic Substances, Global Rep., 211 pp., Geneva, Switzerland, 2003.

UNEP: Third global monitoring report. Global monitoring plan for persistent organic pollutants under the Stockholm Convention Article 16 on effectiveness evaluation. Secretariat of the Basel, Rotterdam and Stockholm conventions, United Nations Environment Programme, Geneva., 2023.

ÚZKÚZ: Consumption of plant protection products per individual years. 2024. Central Institute for Supervising and Testing in Agriculture (ÚZKÚZ), Prague, Czech Republic, https://eagri.cz/public/portal/ukzuz/pripravky-na-or/ucinne-latky-v-por-statistika-spotreba/spotreba-pripravku-na-or/spotreba-v-jednotlivych-letech, (last accessed online: 20 June 2024).

van den Berg, F., Kubiak, R., Benjey, W. G., Majewski, M. S., Yates, S. R., Reeves, G. L., Smelt, J. H., and Van der Linden, A. M. A.: Emission of pesticides into the air, Water, Air, Soil Pollut., 195–218, 1999.

van den Berg, H., Manuweera, G., and Konradsen, F.: Global trends in the production and use of DDT for control of malaria and other vector-borne diseases, Malar. J., 16, 401, 2017.

van Pul, W. A. J., Bidleman, T. F., Brorström-Lunden, E., Builtjes, P. J. H., Dutchak, S., Duyzer, J. H., Gryning, S.-E., Jones, K. C., van Dijk, H. F. G., and Vann Jaarsveld, J. A.: Atmospheric transport and deposition of pesticide: an assessment of current knowledge, Water, Air Soil Pollut., 115, 245–256, 1999.

Váňa, M., Smejkalová, A. H., Svobodová, J., and Machálek, P.: Long-term trends of air pollution at national atmospheric observatory Košetice (ACTRIS, EMEP, GAW), Atmosphere (Basel), 11, 537, 2020.

Venier, M. and Hites, R. A.: Time trend analysis of atmospheric POPs concentrations in the Great Lakes region since 1990, Environ. Sci. Technol., 44, 8050–8055, 2010.

Venier, M. and Hites, R. A.: DDT and HCH, two discontinued organochlorine insecticides in the Great Lakes region: Isomer trends and sources, Environ. Int., 69, 159–165, 2014.

Venier, M., Hung, H., Tych, W., and Hites, R. A.: Temporal trends of persistent organic pollutants: A comparison of different time series models, Environ. Sci. Technol., 46, 3928–3934, 2012.

Villiot, A., Chrétien, E., Drab-Sommesous, E., Rivière, E., Chakir, A., and Roth, E.: Temporal and seasonal variation of atmospheric concentrations of currently used pesticides in Champagne in the centre of Reims from 2012 to 2015, Atmos. Environ., 174, 82–91, 2018.

Wang, C., Wang, X., Gong, P., and Yao, T.: Long-term trends of atmospheric organochlorine pollutants and polycyclic aromatic hydrocarbons over the southeastern Tibetan Plateau, Sci. Total Environ., 624, 241–249, 2018.

Wang, C., Wang, P., Zhao, J., Fu, M., Zhang, L., Li, Y., Yang, R., Zhu, Y., Fu, J., Zhang, Q., and Jiang, G.: Atmospheric organophosphate esters in the Western Antarctic Peninsula over 2014–2018: Occurrence, temporal trend and source implication, Environ. Pollut., 267, 2020.

Wang, S., Salamova, A., and Venier, M.: Occurrence, spatial, and seasonal variations, and gas-particle partitioning of atmospheric current-use pesticides (CUPs) in the Great Lakes Basin, Environ. Sci. Technol., 55, 3539–3548, 2021.

Wania, F., Haugen, J.-E., Lei, Y. D., and Mackay, D.: Temperature dependence of atmospheric concentrations of semivolatile organic compounds, Environ. Sci. Technol., 32, 1013–1021, 1998.

White, K. B., Kalina, J., Scheringer, M., Přibylová, P., Kukučka, P., Kohoutek, J., Prokeš, R., and Klánová, J.: Temporal trends of persistent organic pollutants across Africa after a decade of MONET passive air sampling, Environ. Sci. Technol., 55, 9413–9424, 2021.

Wöhrnschimmel, H., Tay, P., von Waldow, H., Hung, H., Li, Y.-F., MacLeod, M., and Hungerbühler, K.: Comparative assessment of the global fate of α- and β-hexachlorocyclohexane before and after phase-Out, Environ. Sci. Technol., 46, 2047–2054, 2012.

Wöhrnschimmel, H., MacLeod, M., and Hungerbühler, K.: Emissions, fate and transport of persistent organic pollutants to the Arctic in a changing global climate, Environ. Sci. Technol., 47, 2323–2330, 2013.

Wöhrnschimmel, H., Scheringer, M., Bogdal, C., Hung, H., Salamova, A., Venier, M., Katsoyiannis, A., Hites, R. A., Hungerbühler, K., and Fiedler, H.: Ten years after entry into force of the Stockholm Convention: What do air monitoring data tell about its effectiveness? Environ. Pollut., 217, 149–158, 2016.

Wong, F., Hung, H., Dryfhout-Clark, H., Aas, W., Bohlin-Nizzetto, P., Breivik, K., Mastromonaco, M. N., Lundén, E. B., Ólafsdóttir, K., Sigurðsson, Á., Vorkamp, K., Bossi, R., Skov, H., Hakola, H., Barresi, E., Sverko, E., Fellin, P., Li, H., Vlasenko, A., Zapevalov, M., Samsonov, D., and Wilson, S.: Time trends of Persistent Organic Pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEAC) in Arctic air from 25 years of monitoring, Sci. Total Environ., 775, 145109, 2021.

Zhan, L., Lin, T., Wang, Z., Cheng, Z., Zhang, G., Lyu, X., and Cheng, H.: Occurrence and air–soil exchange of organochlorine pesticides and polychlorinated biphenyls at a CAWNET background site in central China: Implications for influencing factors and fate, Chemosphere, 186, 475–487, 2017.