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.

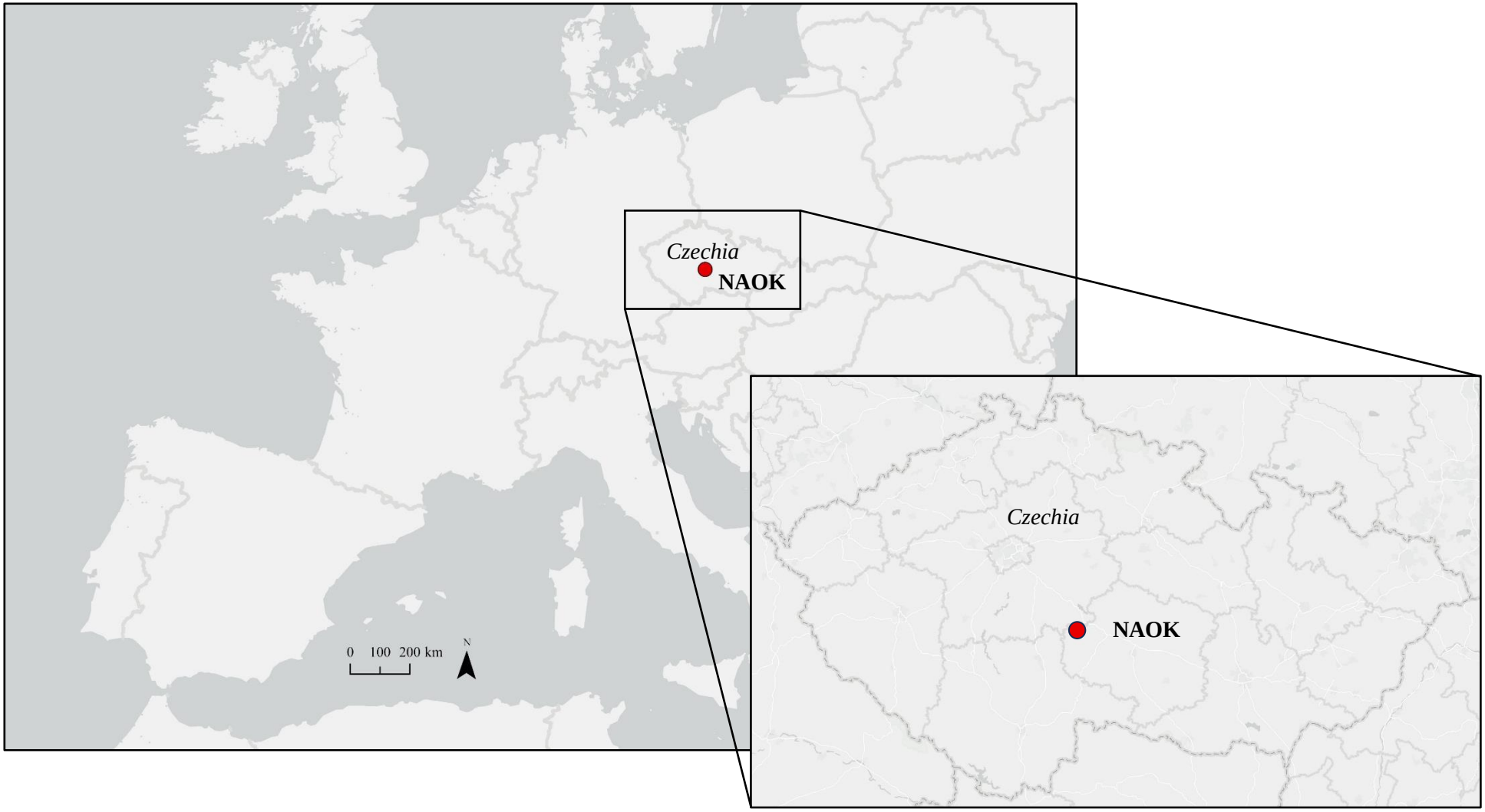

Figure S1. Location of the sampling site.

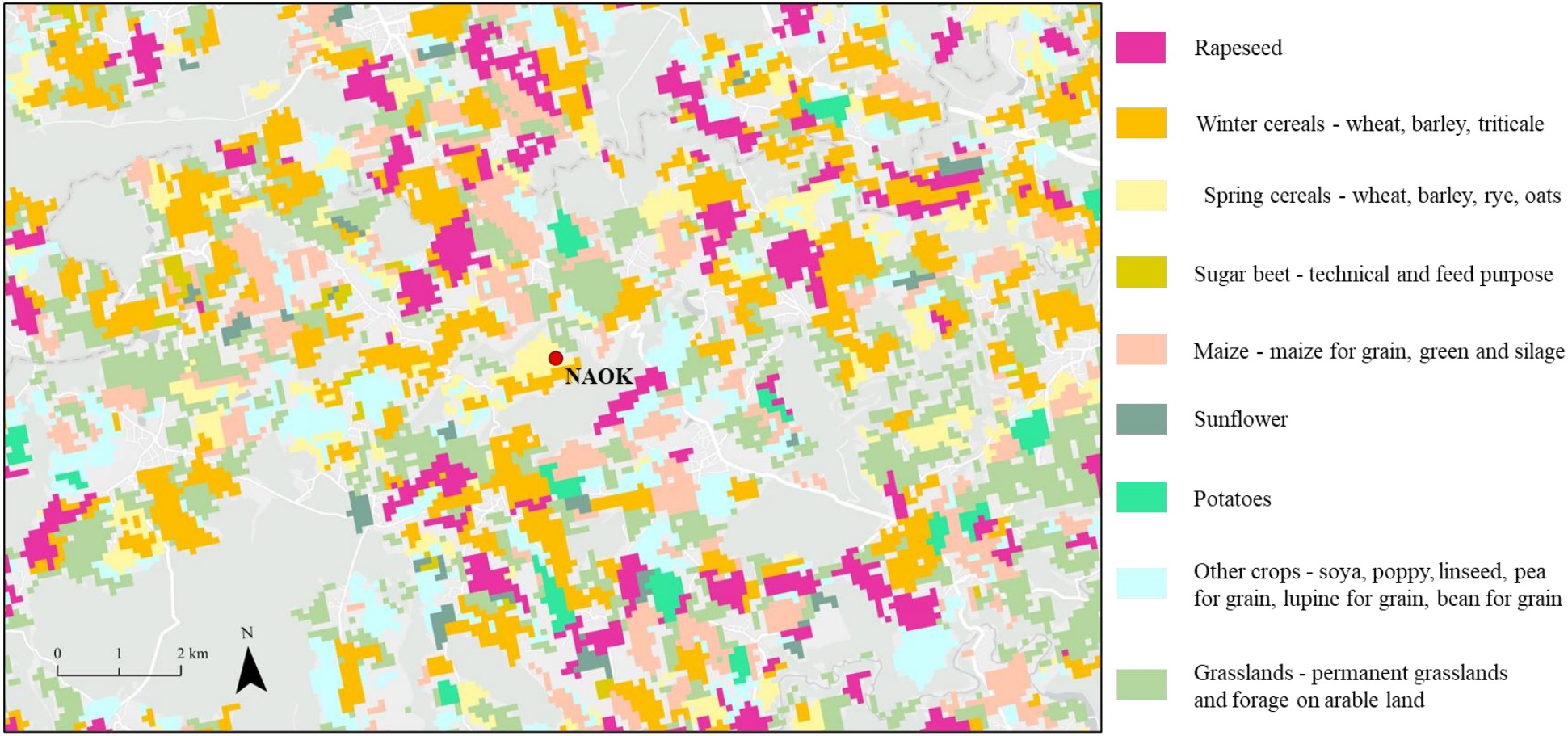

Figure S2. Land-use and crops cultivated in the area of the site during the year 2020. Data from Mapradix s.r.o. Earth Observation services.

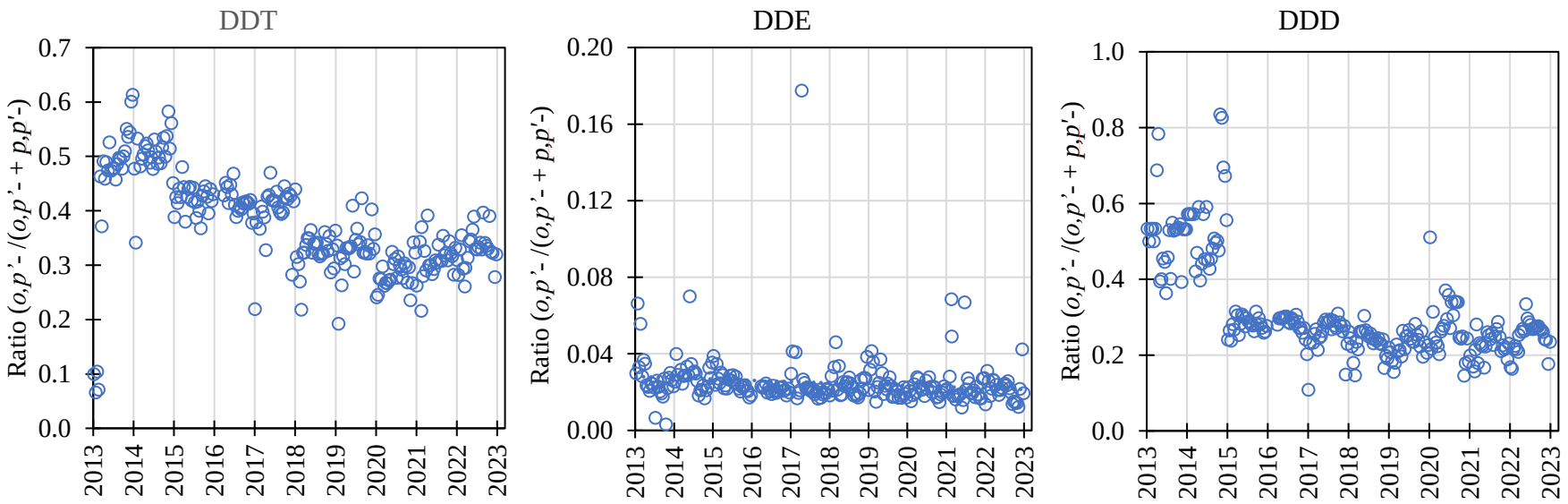

Figure S3. Evolution of the *(o,p'-/(o,p'-+p,p'-)* ratio of for DDX substances over the sampling period.

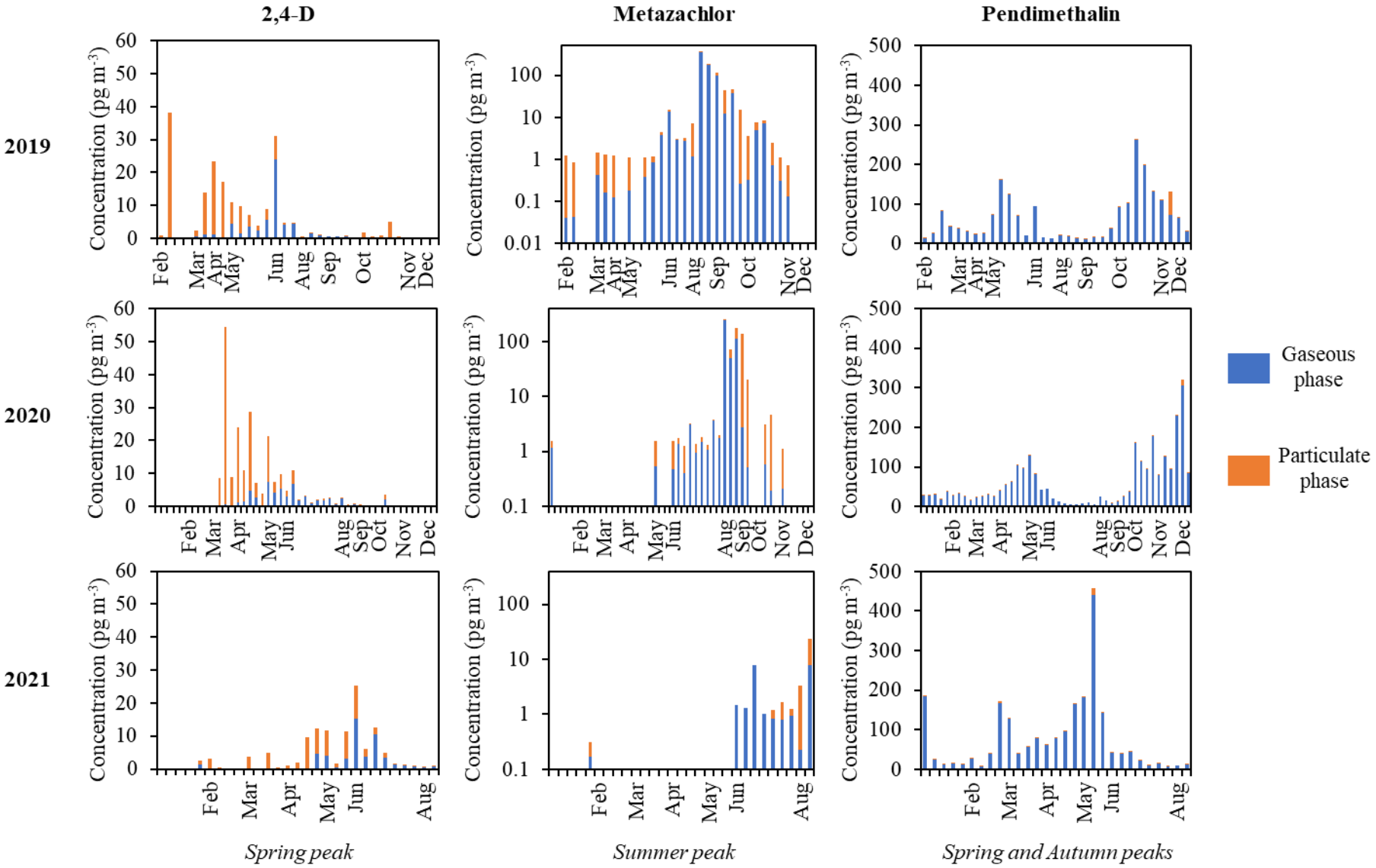

Figure S4. Seasonal variation of selected CUPs with peak concentration during the spring season, during the summer and with two peaks per year.

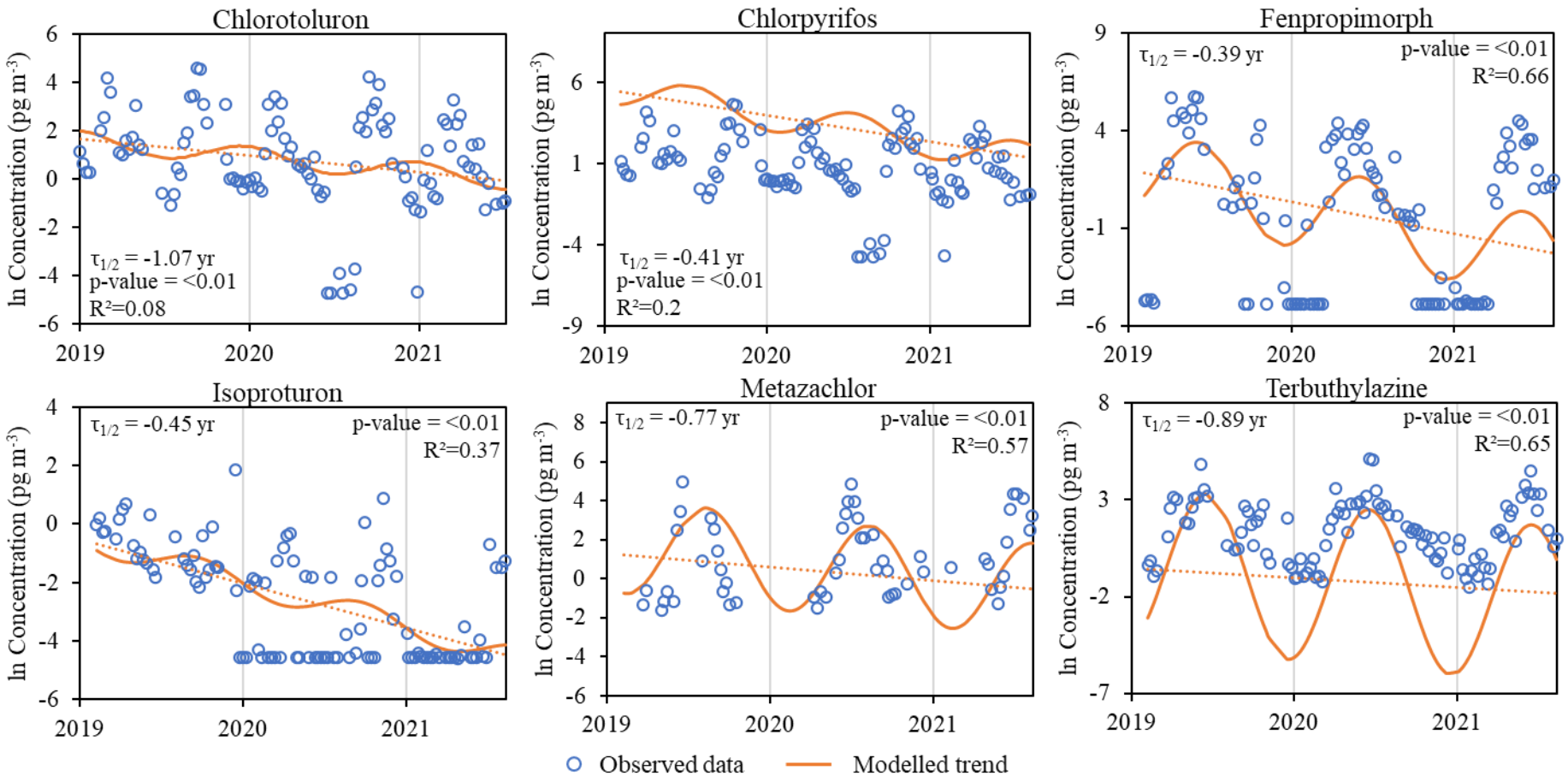

Figure S5. Multi-year variations, using Eq. (1), of selected CUPs with significantly negative trends. Values < MDL were substituted by MDL/2.

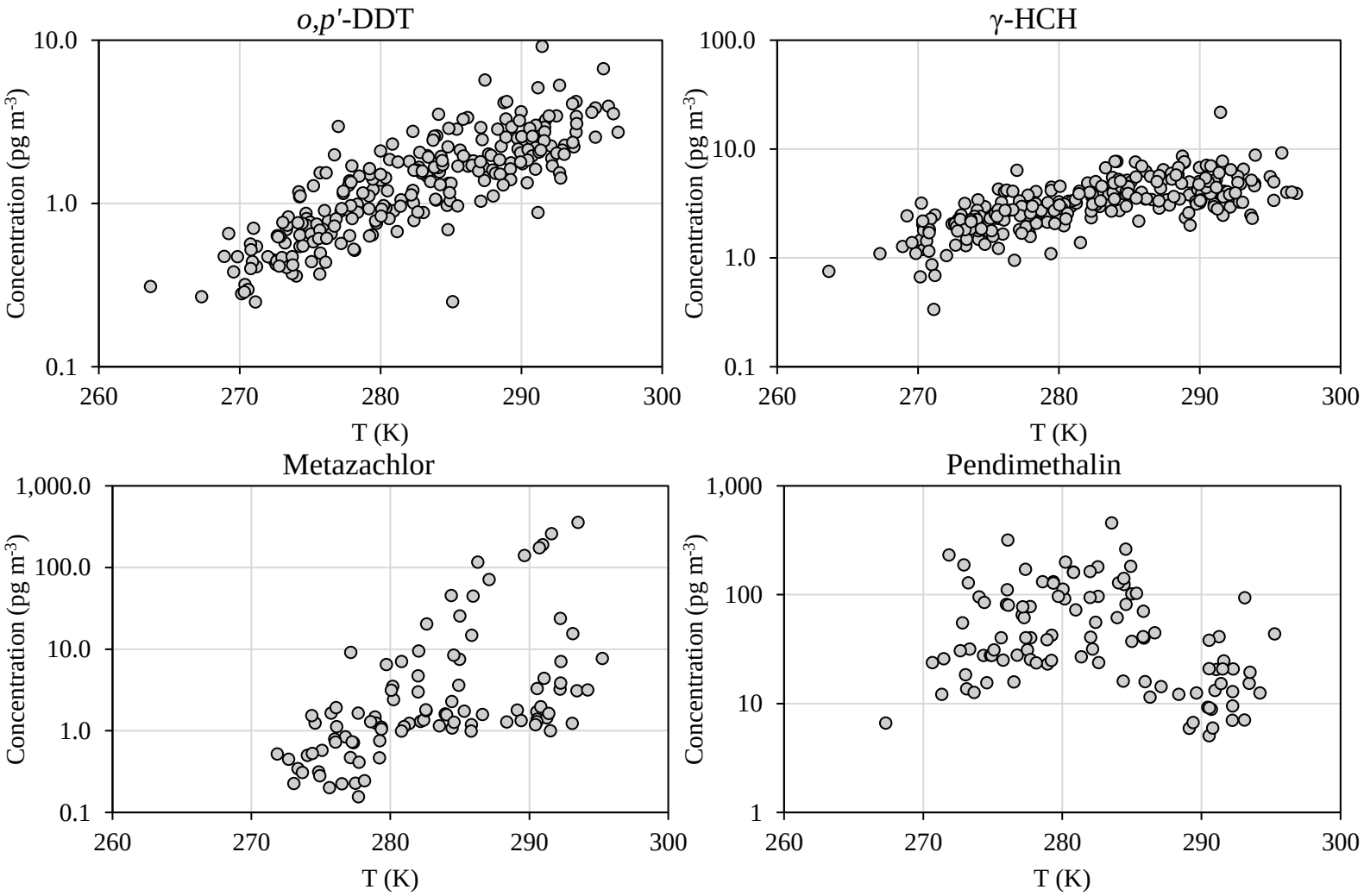

Figure S6. Selected examples of the influence of the temperature on pesticides revolatisation from soils.

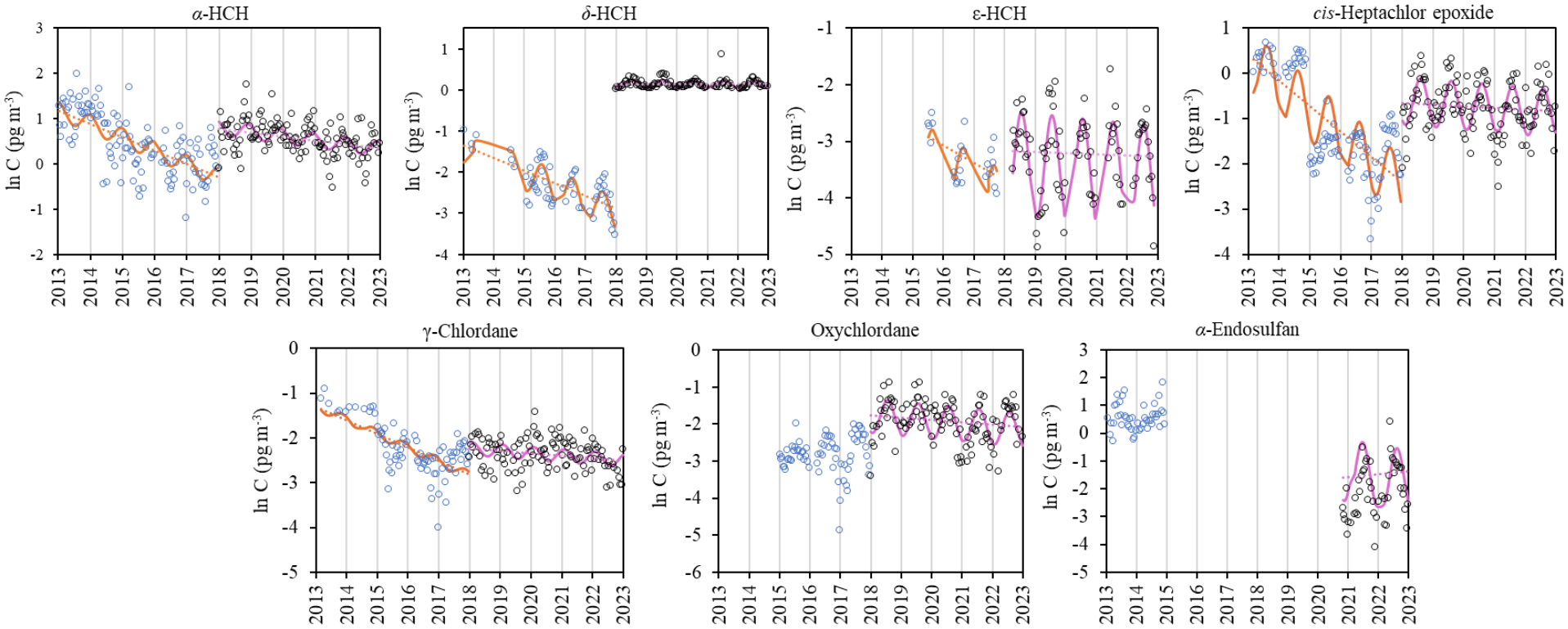

Figure S7. Multi-annual variation of OCP concentrations with significantly negative trends during both time periods (2013-2017 and 2018-2022). Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the modelled variation, whenever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

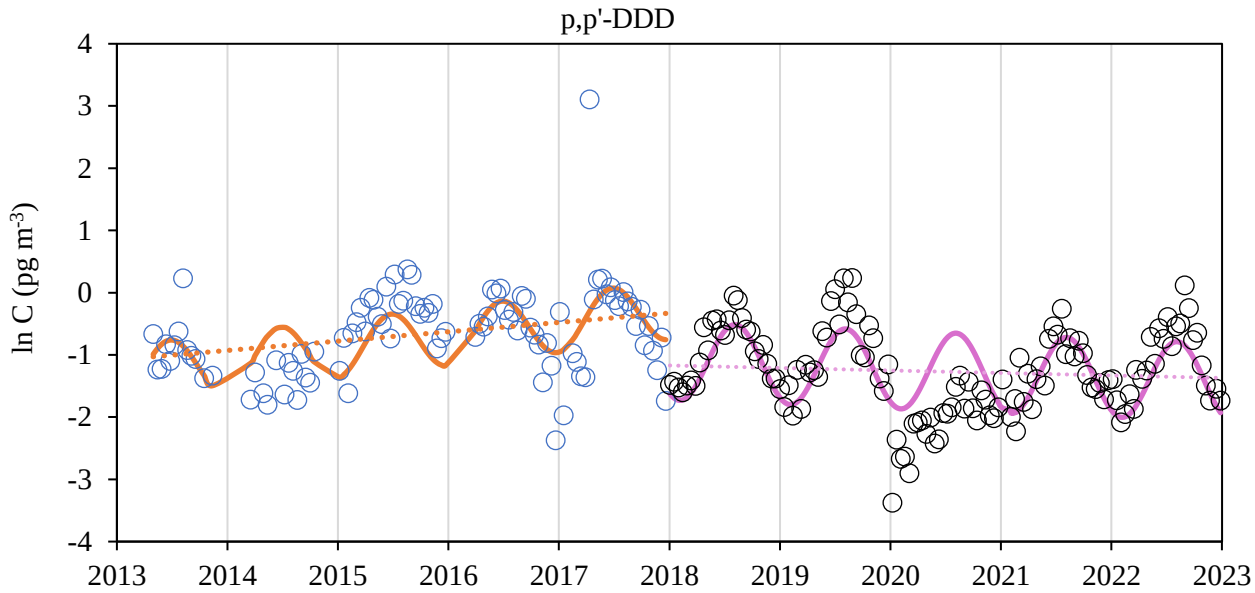

Figure S8. Multi-annual variation of *p,p'*-DDD with significantly positive trend during the 2013-2017 period and significant negative trend during the 2018-2022 period. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the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

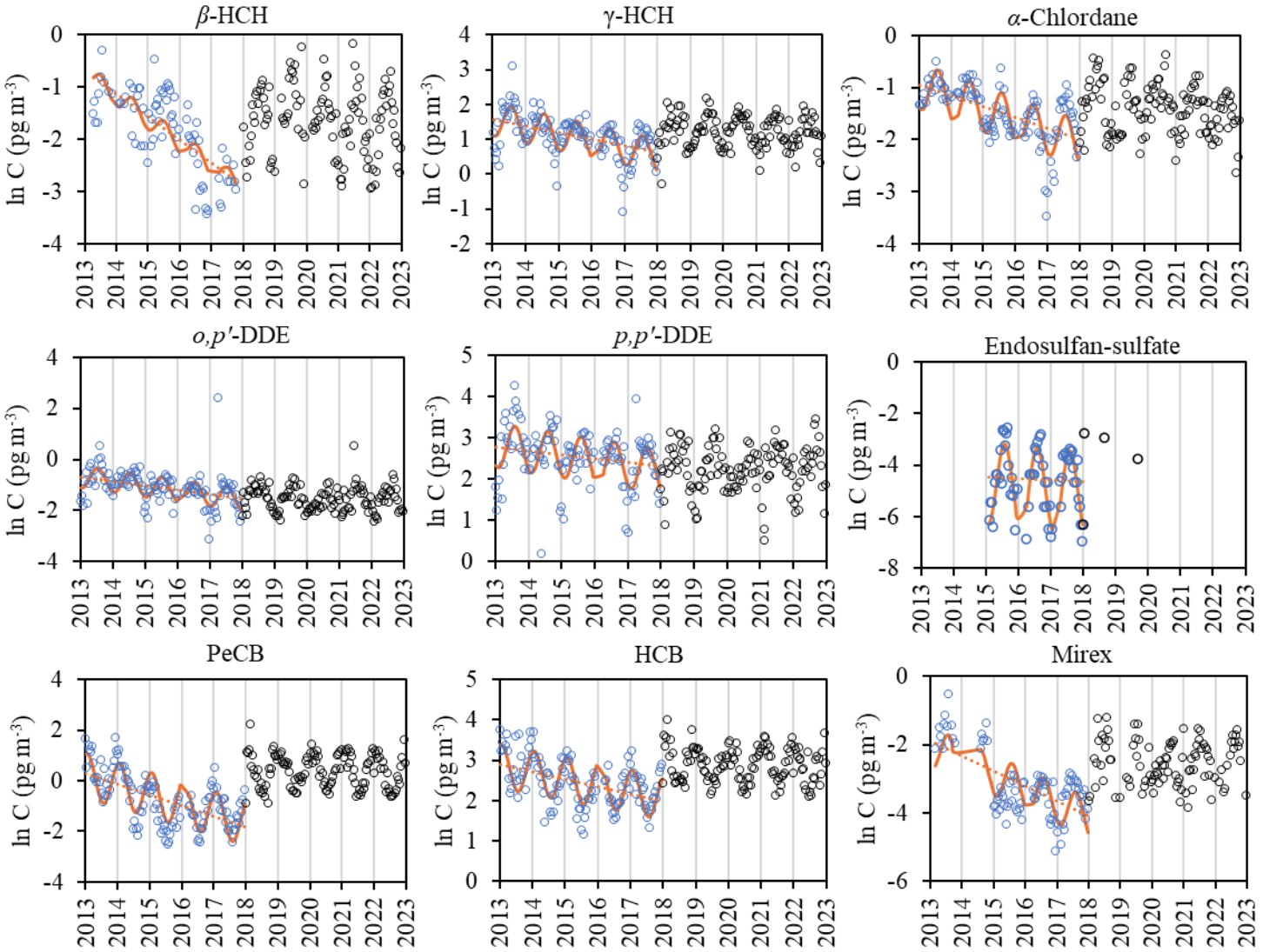

Figure S9. Multi-annual variations of OCP concentrations with significantly negative trends in the time period 2013-2017. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange the significant modelled variation. Values <MDL were not included.

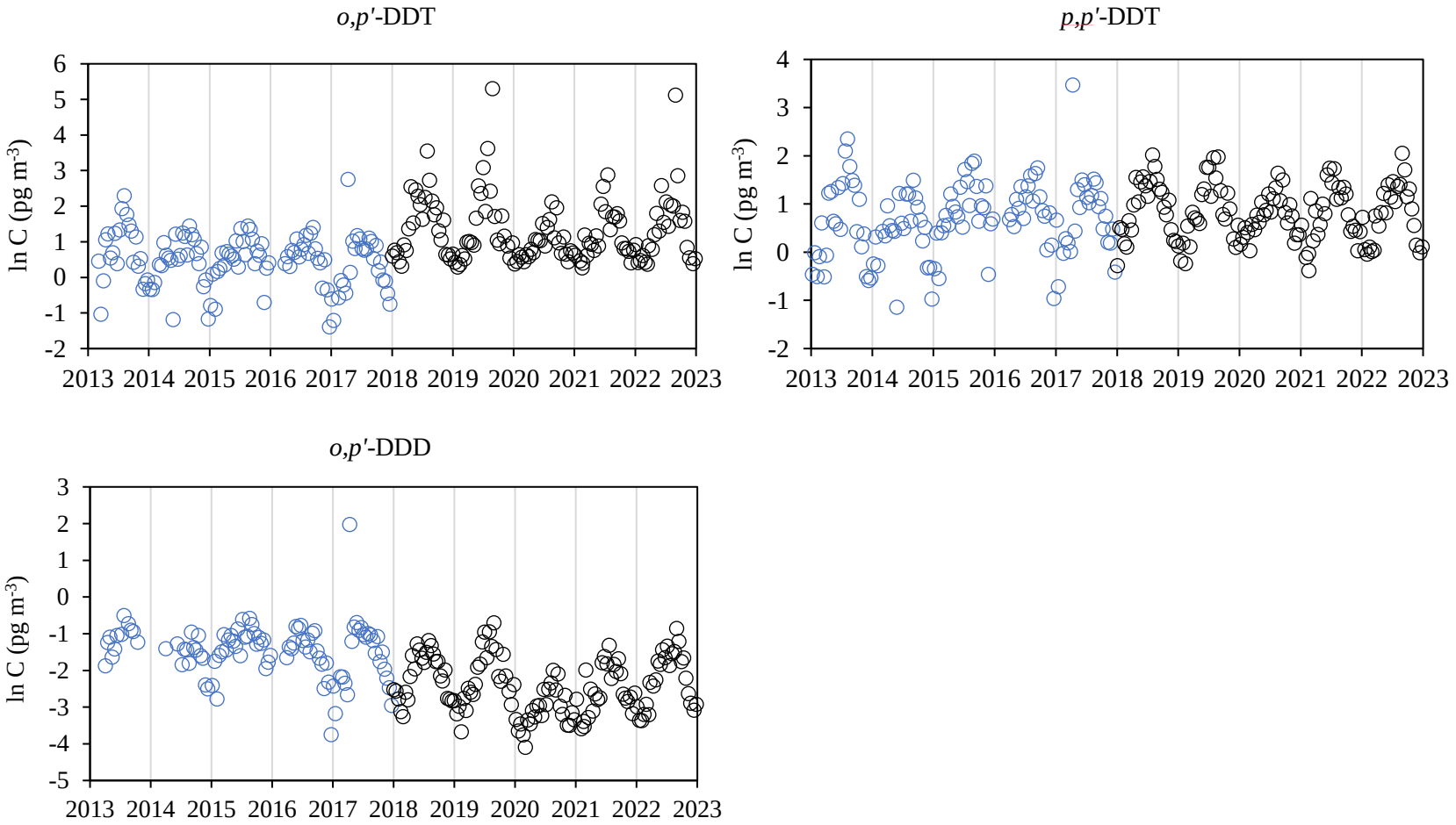

Figure S10. Multi-annual variation of *o,p'*-DDD, DDT and *p,p'*-DDT without significant trends. Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively.

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)

	QFF		PUF-PUF	
OCPs	Average (%)	SD	Average (%)	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 **Use (kg)**	***2020*** **Use (kg)**	***2021*** **Use (kg)**	***2019*** **Use (kg)**	***2020*** **Use (kg)**	***2021*** **Use (kg)**	***2019*** **Use (kg)**	***2020*** **Use (kg)**	***2021*** **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	R^2	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.

CUPs	Approval Status	Detection frequency (%)	Number of Observation	R^2	**Coefficients** Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	**p-value** 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** Intercept (constant)	a_1	cos (a_2*t+a_4)	t (a_3)	a_4	**p-value** 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** Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	**p-value** 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)

OCP	Detection frequency (%)	Number of observations	R^2	Coefficient				p-value	$t_{1/2}$ (years)
				Intercept (constant)	sin (a_1)	cos (a_2)	t (a_3)	t (a_3)	
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	

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