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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 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).

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

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.

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

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:

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

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):

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

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,

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

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).

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).

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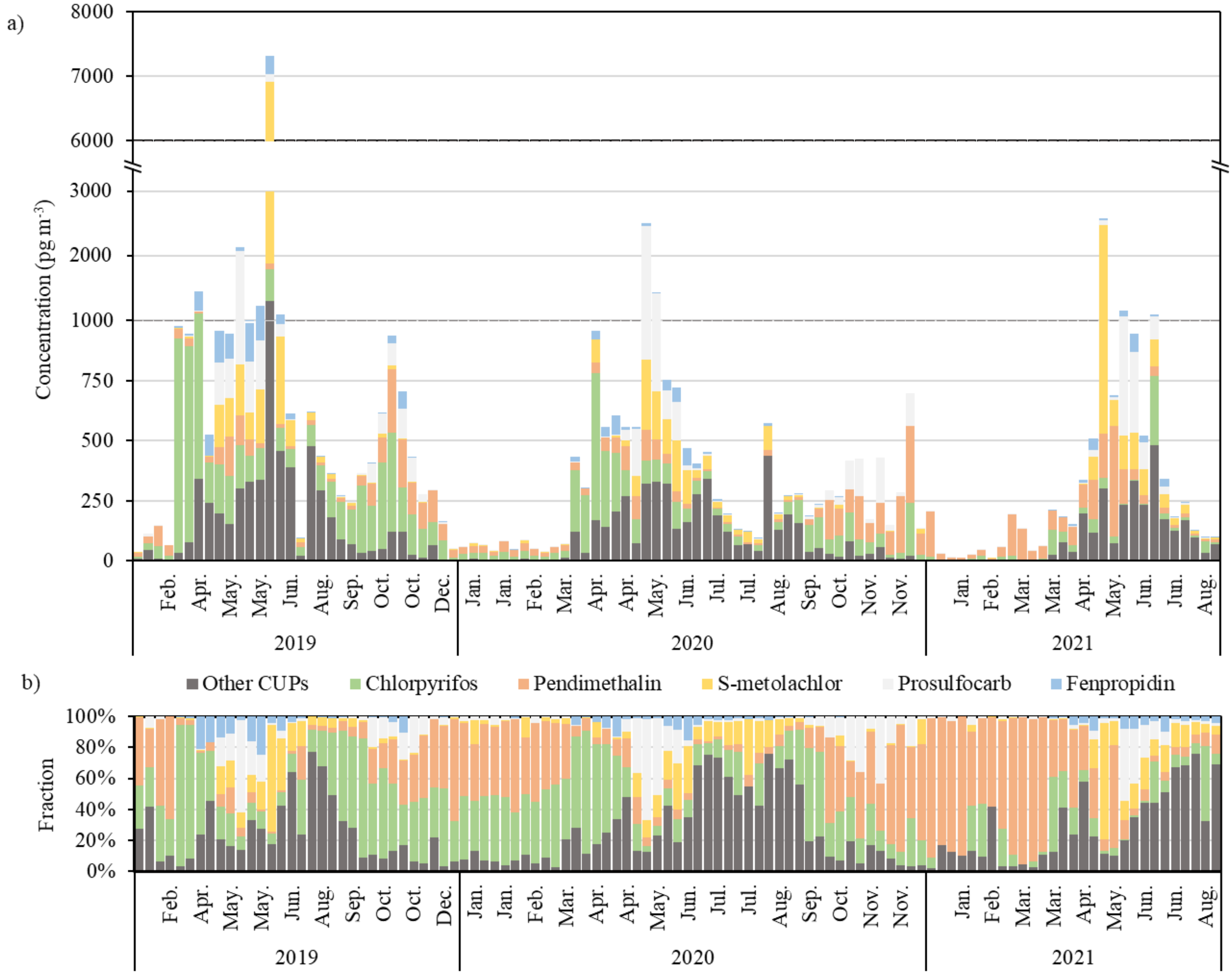

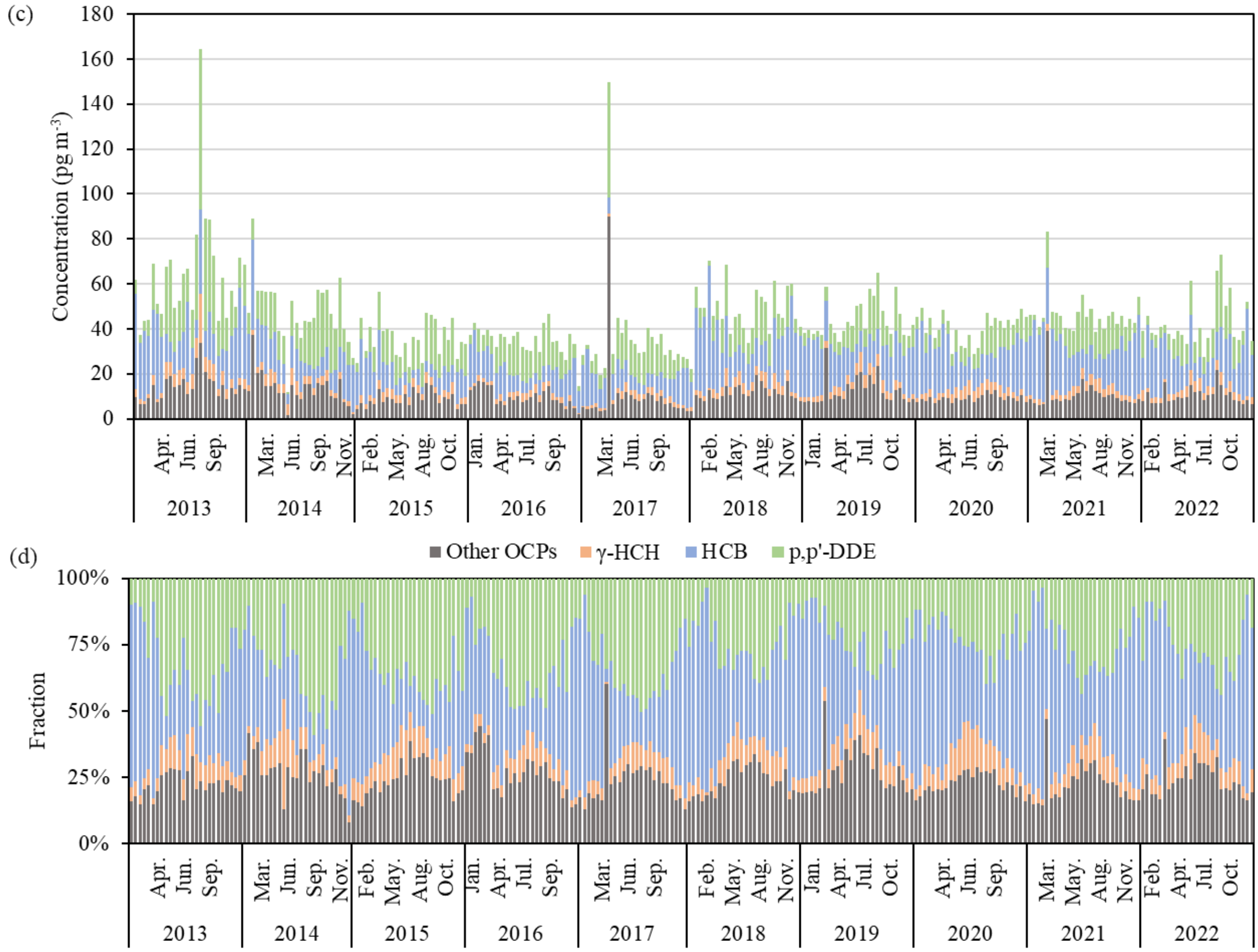

Figure 1. Times series of CUP (a,b) and OCP (c,d) absolute (a,c) and relative (b,d) total atmospheric concentrations.

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

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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 R^2 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 R^2 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 (R^2 = 0.34). In contrast, the scatter plot for DDE (Figure S7-S9) shows a wider spread (R^2 = 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 R^2 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).

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).

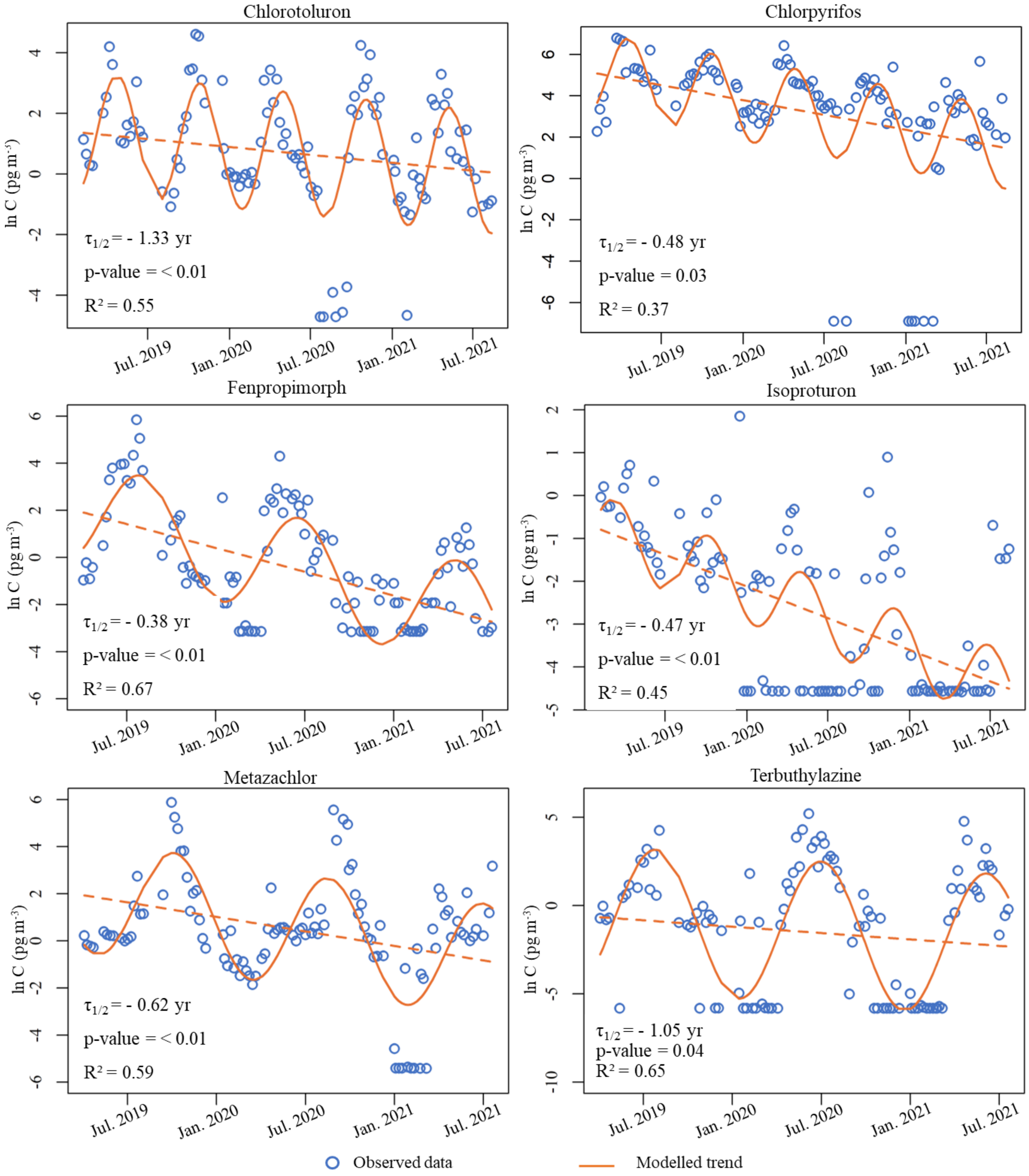

Figure 2. Multi-annual variations of selected CUPs with significantly negative trends. Values < MDL were substituted by MDL/2.

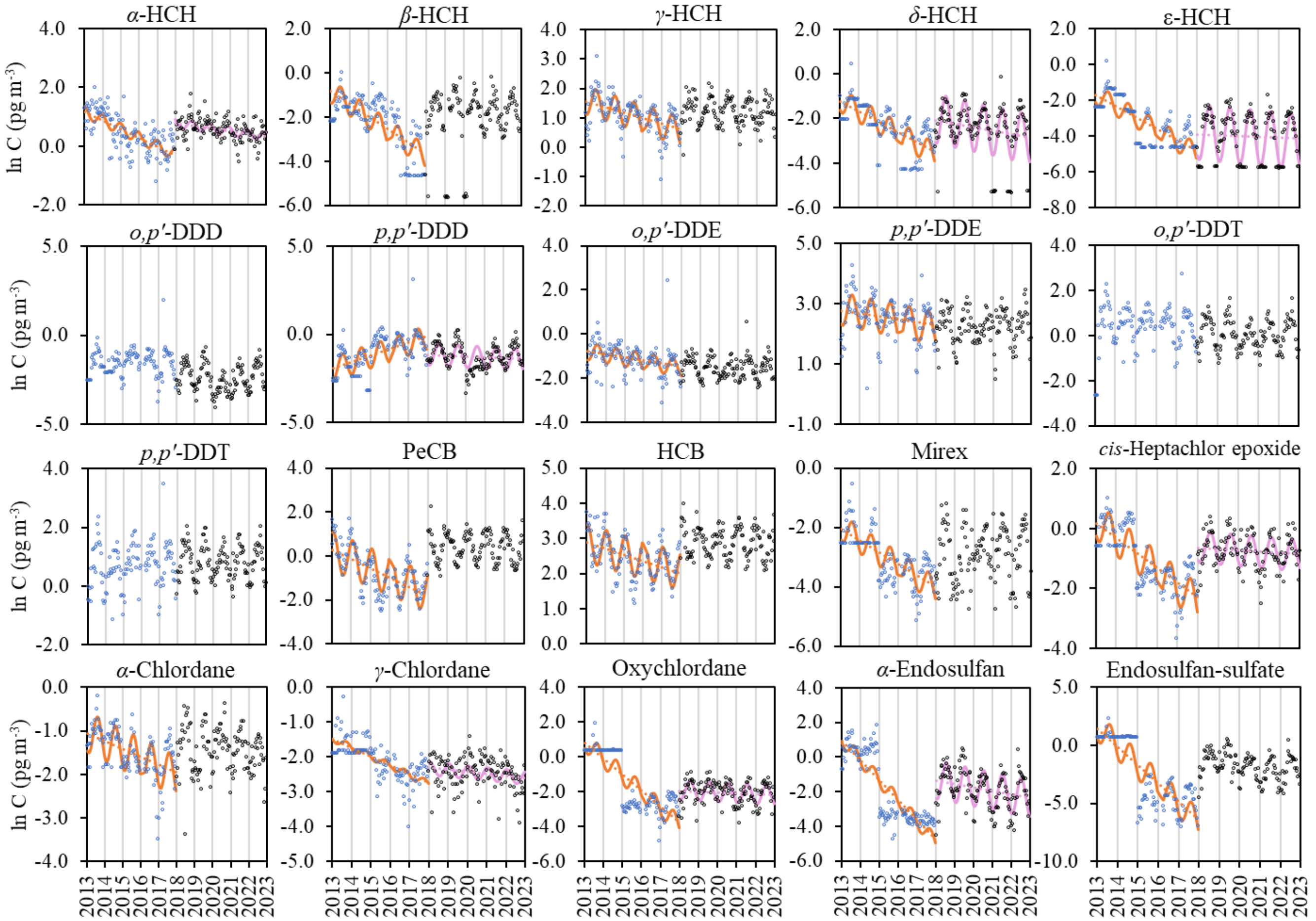

Figure 3. Multi-annual variations of OCPs (DF > 20%). Blue and black dots represent data from the 2013-2017 and 2018-2022 periods, respectively. The orange and purple lines represent the modelled variation, whenever the trend was significant. Values < MDL were substituted by MDL/2.

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

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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 $\alpha/\gamma < 1$ 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.,

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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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