

Overall comments

This study presents seasonal and multi-annual trends of organic pesticides at a rural agricultural site in Central Europe and investigates their primary and secondary sources. Over ten years of weekly air monitoring for a wide range of pesticides (48 CUPs and 30 OCPs) has produced a large dataset that enables a comprehensive assessment of atmospheric pesticide contamination in Central Europe and allows for the determination of seasonal and temporal trends with high confidence. The statistical analyses appear sound, and the resulting trends generally align with known usage patterns, regulatory restrictions, and dominant release pathways. However, some statements should be clarified, and the language could be improved for better readability. Detailed comments are provided below.

Detailed comments

The application of two separate equations for OCPs and CUPs is scientifically reasonable, but the manuscript would benefit from a clearer justification of why different models were chosen, especially for readers less familiar with OCP or CUP-specific seasonality patterns.

The authors employed HPLC, GC, and tandem mass spectrometry (MS/MS) to analyze the collected samples and identify OCPs and CUPs. However, both OCPs and CUPs can naturally degrade or transform under specific environmental conditions, potentially forming structurally similar degradation products. Therefore, the authors should discuss how they distinguish between parent compounds and their degradation/metabolic products. Is it possible that the parent compounds could be potentially interfered by their degradation/metabolic products during the analysis?

Title: I am not entirely sure if the modifier “unidentified” is necessary. I think the secondary sources primarily refer to volatilization from land and water surfaces; The “current-use and organochlorine pesticides” can be refined as “legacy and current-use pesticides”.

Consider a refined title of something like “Multi-annual trends of legacy and current-use pesticides in air in Central Europe: primary and secondary sources. “

Line 12, “with revolatilisation from soil apparent in summer.” For OCPs, they can not only be volatilized from soil but also from water bodies, in some cases, e.g. HCH, volatilization from water is more pronounced compared to direct volatilization from soil.

(<https://doi.org/10.1021/acs.est.4c05204>; <https://doi.org/10.1021/es034998k>)

Line 16: “reversal of the direction of air-surface exchange or recent mobilisation from soils, water bodies, or the cryosphere” this sentence is not clear. Reversal from what to what? Convert the direction from surface volatilization to atmospheric deposition? This statement

repeatedly occurs in the manuscript that need to be well clarified. In addition, mobilisation from soil, water bodies, or the cryosphere share the same mechanism as air-surface exchange when regarding the emission to the atmosphere. Therefore, this sentence can be refined.

Line 22, rather than semivolatility, long-range transport ability is more precise accounting for the global cycling.

Section 2.4: To prevent potential breakthrough, PUF/XAD2/PUF sandwich was used for sampling gas-phase CUPs, while only two PUF plugs were used for sampling gaseous OCPs. Why did the author not apply PUF/XAD2/PUF sandwich to OCP sampling? Can the author assure that there is no breakthrough issue for hi-vol sampling of OCPs without XAD? If not, a limitation on this point should be included in the context.

Line 91-92, “100 μ L of MilliQ water were then added to a 100 μ L aliquot of the respective extracts which were finally used for analysis.” This sentence is not clear. 100 μ L water was added to both OCP extracts and CUP extracts? Since n-nonane was previously added in the extracts, water and nonane are immiscible and extracts for OCPs analysis using GC-MS/MS should not contain any water. Please explain this.

Line 95, four different methods were used for CUP analysis. Why did not author combine these methods into one or two since they all are based on LC-MS/MS analysis?

Line 108-114, for the recoveries, were they calculated based on spiked native standards or isotopic standards? If based on the former, a series of recovery tests are required. Then, how many replicates were conducted? Otherwise, recoveries can be calculated for each real sample based on their ratio of labelled spike standards (surrogates) to the injection standards in samples relative to those in the calibration standards. Please clarify.

Line 115, “so was the internal standards for OCPs only.” does it mean that internal standards were changed as well” what dose the “only” refer to?

Line 147, what are the Non-parametric Mann-Whitney tests used for? Test for difference with previous measurements?

Line 160, I believe the Clausius-Clapeyron equation works for gaseous phase only. Please include a reference to support your statement of using total concentrations is more appropriate.

Line 201-202: Can you explain why the low and decreasing (o,p' -/ o,p' -+ p,p' -) ratios ratio indicates that dicofol was not apparently a viable source for presence of DDT in the

atmosphere. To make it understandable, additional information on dicofol and its relationship with DDT and DDT should be included in the context.

Line 207-208, please indicate how to use the ratio $\beta/(\alpha+\gamma)$ HCH to distinguish between HCH isomers, and include a reference for it.

Line 228, how was application of pendimethalin in winter observed? In what cases people apply the pesticide in winter? It's rare to apply pesticides in winter. In fact, it contradicts with the statements in lines 232-233.

Line 240-241: Were the maxima referred to the pre-ban period? If so, the maxima should be higher during the same period in the following years if the legislation works out.

Line 245 255: how did author determine whether the slope is steep or not? One approach is to use the slope of Clausius-Clapeyron plot can derive ΔH_{exp} , and then the ΔH_{exp} can be compared with theoretical ΔH , if derive ΔH_{exp} is close to theoretical ΔH , we assume that local volatilization is dominant. If ΔH_{exp} is much small than theoretical ΔH (shallow slope), the long-range transport is dominant ([DOI:10.1016/j.es034998k](https://doi.org/10.1016/j.es034998k); [DOI:10.1126/sciadv.adi808](https://doi.org/10.1126/sciadv.adi808)).

Line 255-258, how can the “narrow” or “wide” spread be linked to the sources, e.g., soil temperature or secondary sources” Please elaborate.

Line 266-267, a CUP metazachlor, peaked at summer, how can it be distinguished between application in summer and re-volatilization during the warmest period (summer)?

Line 300-301: is there a reason why pp-DDD increased during 2013-2017 while decreased during 2018-2022? Has a similar shift of the trend been reported?

Line 309-310: why this shift of ratio does not indicate any influence of fresh inputs of the pesticide? Because the ratios are both below 1?

Line 314-316, Industrial emissions could be more pronounced compared to the role of being a pesticide for HCB and PeCB. This point can be involved in the discussion in the context rather than being included at the end.

Line 331-332, could consider additionally include the evidence of net HCH volatilization from water to the atmosphere (<https://doi.org/10.1021/acs.est.4c05204>; <https://doi.org/10.1021/es034998k>).

Line 339-342: Despite that gas-particle partition calculation is not available, separate temporal trend analysis for gas- and particle phases is possible. Is there any difference

between the two trends as well as compared with the trend for the total concentrations? It would be worthwhile to bring up this point or a short discussion.

Line 349, if the case for δ - and ε -HCH is the same, why was it separately mentioned rather than being included with other OCPs.

Small things:

Line 15, a comma should be inserted between “mirex” and “levelling off”.

Line 19 For clarity, consider changing “one-year post-ban” to “ one year after the bans”

Line 22-24, consider splitting into two sentences for clarity, rephrase like “Due to their severe health and environmental impacts, OCPs have been restricted in most countries (UNEP, 2001). For compounds like DDT and HCH, this has been consistently reflected in declining air concentrations.”

Line 32, and line 33: inserting a comma between “(CUPs)” and “have”, between “neonicotinoids” and “are”, could make the sentence clearer.

Line 33-34: consider rephrasing the sentence as “are chemically varied and subject to different environmental fates accordingly”

Line 36-39, consider splitting sentence into two for clarity. Something like “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). CUPs can be volatilised from surfaces such as soil, plants and surface water over longer periods of time following application (Bedos et al., 2002), and mobilised through wind erosion of soil particles containing CUPs “

Line 44: “ from a few European countries”

Line 46, “have become “

Line 50-53: consider rephrasing the sentence as: “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, spanning 2013–2022 for OCPs and 2019–2021 for CUPs, allowing for the assessment of seasonal variations and time trends”

Line 82: change “on location until transported to the” to “on site until transport to the”

Line 110: “processed as per samples” sounds wired. It should be “which were then processed as samples” or in a clearer way like “which were processed in the same way as the samples”.

And “with a few exceptions, “

Line 114: “for QFFs and from $49 \% \pm 6$ (PeCB) to $103 \% \pm 10$ (*p,p'*-DDD) for PUFs”

Line 116, suggest use concise and sample expressions for “from 2018 onward”, e.g., “after 2018”, the word “for” in the “for both OCPs and CUPs” can be removed. The sentence can be rephrased as “the concentration of both OCPs and CUPs have been adjusted by the recoveries.”

Line 123, for clarity, here is a rephrased version, “For OCPs, with expected one annual amplitude, Equation (1) was used, which ..”

Line 168, The sentence can be rephrased in a clearer manner. “Eleven CUPs had detection frequencies (DF) greater than 80%, with two CUPs (pendimethalin and tebuconazole) being detected in all samples.”

Line 174, “these CUPs were all quantified in >65% of air samples”

Line 198, “38, 29 and 8.1% of $\Sigma 30$ OCPs, respectively (Figure 1c,d Table S10).”

Line 214, suggest that a revised figure title of “Time series of Σ CUP (a) and Σ OCP (c) concentrations and their relative abundances(b,d) in the atmosphere.

Line 222, change “pointing to” to “aligned with”

Line 239-240, The sentence can be refined as “High concentrations were due to clearly evident application.”

Line 242-243, can be improved as “... with spring being quite broad, ranging from ...”

Line 255: “....suggest that soil temperatures play a significant role in influencing DDD levels at this site...”

Line 274, the sentence can be clarified as “Long-term annual variations in atmospheric concentrations were assessed for 22 CUPs with sufficient concentration data (DF > 20%) using Eq. (2) and Eq. (1) for CUPs and OCPs, respectively.”

Line 285: “one of them” can be removed.

Line 287: The sentence can be refined as “Boscalid was the only in-use CUP in the Czech Republic that was decreasing.”

Line 289-291, The sentences can be rephrased as “...was reported to approach zero or in a low amount in 2021. The observed decline was accelerated from 2020 to 2021 compared to the period during 2019-2020, reflecting the combination of these applications and the degradation in the total environment after ban”

Line 304-307, the sentence is not clear. Please clarify. Doubled period in the end of the sentence.

Line 325, equilibrium rather than equilibria?

Line 328, “which is global” seems not complete. Something like “ which impacts globally” or “which is a global concern”?

Line 329-330, the sentence is not clear. Please clarify.

Line 336, “ have been reported” rather than “have been reporting”

Line 340, the full name of SVOCs should be specified, Semivolatile Organic compounds (SVOCs)

Line 344, the sentence can be refined as “ Overall, this study provided long-term time series data for atmospheric OCPs and CUPs at a Central European site. Consistent with the perception of low degradation rate of many SVOCs in soils, Clausius-Clapeyron analysis results showed that...”

Line 356, “investigating” rather than “investigate” ; “ for the global OCP cycling”?

Line 367, The sentence can be rephrased as “ In addition, we observed that CUPs’ temporal trends are... They were generally negative or insignificant, during which CUPs national use ...”

Line 359, “the decreasing trends were directly related to the revocation of their use authorization. “

Line 360, the sentence can be refined as “...in the atmosphere at detectable levels, suggesting a potential atmospheric persistence. “

Line 362-364, “...highlights... provide sufficient insights into .. and to further develop accurate models to predict key environmental processes such as.. “