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Seasonal variations in air concentrations of 27 organochlorine pesticides (OCPs) and 25 current-use pesticides (CUPs) across three agricultural areas of South Africa

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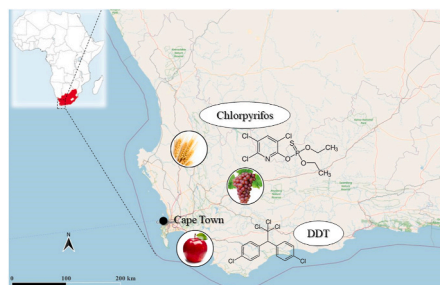
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HIGHLIGHTS

- Overall, 21 organochlorine (OCPs) and 16 current-use pesticides (CUPs) were detected.
- A median of 16 OCPs and 10 CUPs were detected per sample.
- In total, 11 OCPs and 24 CUPs different combinations were observed.
- *p,p'*-DDE and chlorpyrifos had the highest concentrations in air.
- Air concentrations of pesticides varied according to farming area and seasons.

GRAPHICAL ABSTRACT



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ABSTRACT

For decades pesticides have been used in agriculture, however, the occurrence of legacy organochlorine pesticides (OCPs) and current-use pesticides (CUPs) is poorly understood in Africa. This study investigates air concentrations of OCPs and CUPs in three South African agricultural areas, their spatial/seasonal variations and mixture profiles.

Between 2017 and 2018, 54 polyurethane foam-disks passive air-samplers (PUF-PAS) were positioned in three agricultural areas of the Western Cape, producing mainly apples, table grapes and wheat. Within areas, 25 CUPs were measured at two sites (farm and village), and 27 OCPs at one site (farm). Kruskal-Wallis tests investigated area differences in OCPs concentrations, and linear mixed-effect models studied differences in CUPs concentrations between areas, sites and sampling rounds.

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In total, 20 OCPs and 16 CUPs were detected. A median of 16 OCPs and 10 CUPs were detected per sample, making a total of 11 OCPs and 24 CUPs combinations. Eight OCPs (*trans*-chlordane, *o,p'*-/*p,p'*-dichlorodiphenyldichloroethylene (DDE)/dichlorodiphenyltrichloroethane (DDT), endosulfan sulfate, γ -hexachlorocyclohexane and mirex) and two CUPs (carbaryl and chlorpyrifos) were quantified in all samples. *p,p'*-DDE (median 0.14 ng/m³) and chlorpyrifos (median 0.70 ng/m³) showed the highest concentrations throughout the study. Several OCPs and CUPs showed different concentrations between areas and seasons, although CUPs concentrations did not differ between sites. OCPs ratios suggest ongoing chlordane use in the region, while DDT and endosulfan contamination result from past-use.

Our study revealed spatial and seasonal variations of different OCPs and CUPs combinations detected in air. Further studies are needed to investigate the potential cumulative or synergistic risks of the detected pesticides.

1. Introduction

Pesticides are applied to protect crops from undesirable pests in agriculture (e.g., insects, fungal diseases or weeds) and to control disease vectors or household pests (Rother, 2016; van den Berg et al., 2012). Currently, about three billion kg of insecticides, fungicides and herbicides are applied annually in agriculture worldwide (Sharma et al., 2020). In the coming years, estimations foresee an increase in the use of pesticides resulting from the intensification of agriculture production, the appearance of new pest resistance (Busi et al., 2019) or changes in pest patterns (Sharma et al., 2019).

Over time, the use of active ingredients (the biologically active component of a pesticide) changed considerably. Pesticides are often divided between the organochlorine pesticides (OCPs), which were used for agricultural purposes in the past, and the current-use pesticides (CUPs). OCPs are highly efficient insecticides introduced in the 1940s. They have been widely used in agriculture throughout the globe (Meeker and Boas, 2011) and are still used in some countries for disease vector control (Bouwman and Kylin, 2011; Eskenazi et al., 2019). However, OCPs are highly persistent in the environment (e.g., up to several decades in soil, Thompson et al., 2017) and are associated with endocrine, neurologic, reproductive and carcinogenic effects in humans (Jayaraj et al., 2016; Taiwo, 2019). Consequently, OCPs were banned for agricultural uses and included in the list of persistent organic pollutants (POPs), regulated by the Stockholm Convention (Townson, 1992; UNEP, 2009). As an alternative, other insecticides in the group of CUPs (e.g., organophosphates and carbamates) emerged (Taiwo, 2019; Wandiga, 2001). CUPs, englobing several insecticides, herbicides and fungicides, are thought to be less persistent, more water-soluble and to have a lower bioaccumulative potential than OCPs (Climent et al., 2019; Degrendele et al., 2016a). Nevertheless, some CUPs are also highly toxic and have been associated with considerable morbidities and mortality amongst applicators (Motsoeneng and Dalvie, 2015; Ndlovu et al., 2014; Ohlander et al., 2020), further affecting residents and their children living in the proximity of agricultural sites (Butz, 2017; Chetty-Mhlanga et al., 2021; Raheison et al., 2019).

Air is a key medium by which pesticides travel from the application site to non-target areas (i.e., spray drift; Figueiredo et al., 2021). Wind erosion of particles or volatilization from soils, water or vegetation, can further lead to pesticides in air (Coscollà et al., 2014; Degrendele et al., 2016a; Mamy et al., 2021; Taylor et al., 2020). Air monitoring studies revealed the presence of several OCPs (Hao et al., 2019) and CUPs (Balmer et al., 2019) far away from application sites (up to the Arctic region). Hence, the past and current-use of pesticides result in a complex mixture of active ingredients, potentially threatening environmental and public health (Mackay et al., 2014; Taiwo, 2019).

South Africa is the leading pesticide user in Africa due to the continuous expansion of agricultural areas and intensification of cropping systems (OECD-FAO, 2016). About 26,000 tonnes of pesticides are used in agriculture every year and over 3,000 pesticide products are available on the market (AVCASA, 2017). Some of the CUPs reported to be used in South Africa (e.g., atrazine, chlorpyrifos or carbaryl) have been banned from agricultural use in the European Union due to their

adverse environmental and public health effects. Additionally, certain OCPs – like dichlorodiphenyltrichloroethane (DDT) – are still encouraged for indoor residual spraying (IRS) in malaria-endemic areas of South Africa (Bouwman and Kylin, 2011; Eskenazi et al., 2019). Despite recent efforts to study the environmental fate of pesticides in Africa (Arinaitwe et al., 2016; Dalvie et al., 2014a, 2014b; Degrendele et al., 2021; Fuhrmann et al., 2020; Isogai et al., 2018; Lisouza et al., 2020), longitudinal data on spatial and seasonal variations of CUPs and OCPs are rare. If available, data cover only a few selected (mostly OCP) pesticides (Batterman et al., 2008; Isogai et al., 2018; Klánová et al., 2009; Lisouza et al., 2020; White et al., 2020) or show qualitative information (presence/absence) of CUPs (Fuhrmann et al., 2020). Yet, specific information on air concentrations of CUPs is lacking. Also, comparisons between air concentrations of OCPs and CUPs have never been performed in Africa. Understanding seasonal and spatial variations of pesticide mixtures can further provide insights on factors driving their concentrations in air, while identifying possible crop-specific pesticide profiles and critical exposure windows.

This study aims to investigate the presence and concentrations of several legacy OCPs and CUPs in air by studying their spatial and seasonal variations and the occurrence of pesticide mixtures in three different agricultural regions of the Western Cape, South Africa. Three objectives were studied as follows: (i) to determine the pesticide occurrence and their concentrations; (ii) to investigate seasonal and spatial differences within and between agricultural areas; and (iii) to assess the correlation between individual pesticides and identify their mixtures.

2. Materials and methods

2.1. Study design and area

This study is part of the ongoing “Child health Agricultural Pesticide cohort study in South Africa” (CapSA) project, which aim is to determine the association between agricultural pesticide exposure and its consequent health effects on 1,000 children (Chetty-Mhlanga et al., 2018). Passive air sampling (PAS) was conducted over one year in six sampling rounds (SR) of two-months at three different agricultural areas in the Western Cape, South Africa, between the July 10, 2017 and June 15, 2018 (Fig. 1). Information on the specific spraying season for each of our study areas, crop types and amounts of the different active ingredients applied, among other information, was gathered from baseline and in follow-up interviews with farmers from 57 different farms. The results were analysed and described in a parallel study (see Curchod et al. (2020)) which measured the concentrations of different pesticides in three watersheds, each located in one of our study areas. The study areas were selected based on their different crop-specific profiles: Grabouw (GRB) (pome fruits 81% of the agricultural land use); Hex River Valley (HRV) (table grapes 98% of the agricultural land use); and Piketberg (PKT) (cereals 56% of the agricultural land use). In fruit growing areas (GRB and HRV), pesticide spraying is most intense between September and December (spring season in South Africa), whereas in wheat-growing areas (PKT), pesticides are mainly applied between June

and July (Curchod et al., 2020).

A total of 54 PAS were collected: 36 PAS measured the concentrations of CUPs and 18 measured the concentrations of OCPs. To study spatial variations within small scale distances, in each study area, air sampling was conducted at two sampling sites: at “farm” (within 100 m to agriculture land use) and at “village” (>1 km away from agriculture land use and where most households are located). Because the use of OCPs has been banned for decades, spatial variations within small scale distances (i.e., “farm” vs “village”) were not expected to occur. Thus, for OCPs, sampling was only performed at the “farm” site. Sampling locations were located as follows: “village” GRB (34°09′18.4″S, 19°00′11.8″E) and “farm” GRB (34°08′39.6″S, 19°02′46.2″E); “village” HRV (33°28′51.8″S, 19°40′46.3″E) and “farm” HRV (33°28′13.9″S, 19°40′26.7″E); “village” PKT (32°53′57.0″S, 18°45′39.6″E) and “farm” PKT (32°47′20.4″S, 18°48′31.2″E) (Fig. 1).

2.2. Air sampling

PAS was conducted using polyurethane foam (PUF) disks (15 cm diameter, 1.5 cm thickness). Prior to the sampling, PUF disks were Soxhlet pre-cleaned at the RECETOX Centre (in acetone and methanol for CUPs and in acetone and dichloromethane for OCPs for 8 h in each solvent), wrapped in two layers of aluminium foil, packed in ziplock bags and stored at $-20\text{ }^{\circ}\text{C}$ until they were sent to the partner laboratories for deployment. Prior and after sampling, the samples were transported in a cooling box at $5\text{ }^{\circ}\text{C}$ to the partner laboratory, where they were maintained in a freezer at $-18\text{ }^{\circ}\text{C}$ until the shipment to the RECETOX Centre. At the sampling site, PUFs were placed between two stainless steel bowls forming a chamber allowing the air to blow freely between the bowls and protecting the PUF disks from precipitation or sunlight at a height of 1.5–3 m above the ground (Poizo et al., 2006; Poizo

et al., 2009a, 2009b). At each SR, at least one field blank PUF disk was taken along for quality control (prepared and sampled in the same way as the remaining PUFs). The exact deployment time (days) for each of our study areas and SR can be found in the Supplementary Information (SI, Table S1a/b).

2.3. Sample preparation and analysis

2.3.1. OCPs

Prior extraction, all PUF samples were spiked with internal standards (i.e., PCB 30 and 185, Absolute Standards Inc., USA). PUF disks were Soxhlet-extracted (Büchi Extraction System B-811, Switzerland) using 150 mL of dichloromethane (DCM), 40 min of warm Soxhlet and 20 min of solvent rinsing. DCM extracts were then concentrated using a gentle stream of nitrogen. Samples were cleaned-up using a silica column consisting of 1 g of anhydrous sodium sulfate and 5 g of activated silica gel deactivated by 10% Milli-Q water and eluted with 10 mL of hexane and 50 mL of DCM. The eluate volume was reduced by a stream of nitrogen in a TurboVap II (Caliper LifeSciences, USA) concentrator unit. All samples were transferred into GC vials in which 50 μL of nonane was added. Syringe standard PCB 121 (Absolute Standards Inc., Hamden, USA) was added prior the analysis of the cyclodien OCPs (i.e., aldrin, chlordane, chlordecone, dieldrin, endosulfan, endrin, heptachlor and mirex). Then, the samples were cleaned on sulfuric acid modified silica (44% w/w) columns (8 g) eluted with 30 mL of *n*-hexane: DCM (1:1). The eluate volume was reduced by a stream of nitrogen in a TurboVap II concentrator unit and transferred into GC vials, where samples were concentrated under a gentle stream of nitrogen to a final volume of approximately 50 μL . Syringe standard (i.e. $^{13}\text{C}^{12}$ PCB 162, Wellington Laboratories Inc., Canada) was added prior the analysis of the remaining OCPs (i.e., *o,p'*-dichlorodiphenyldichloroethane (DDD), *p,p'*-DDD, *o,p'*-

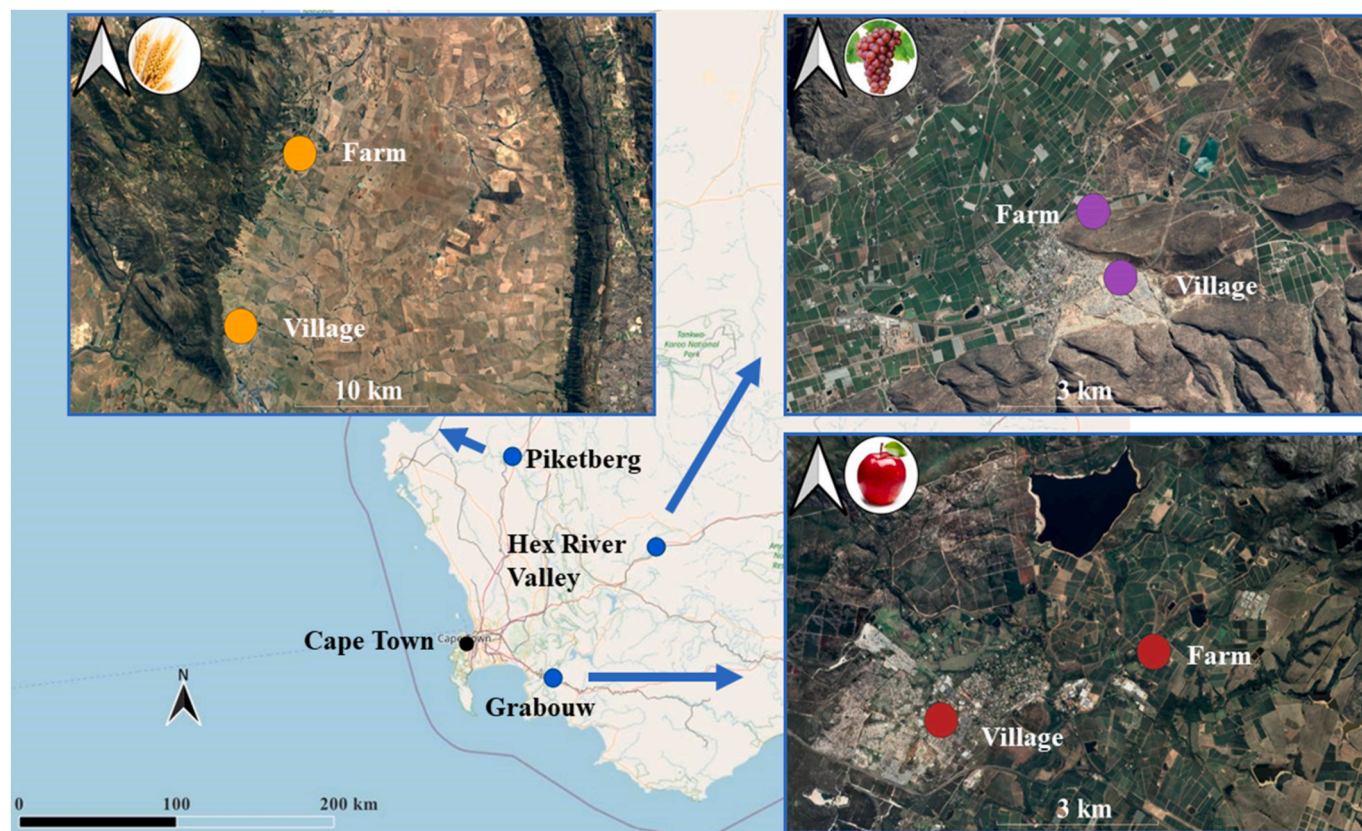


Fig. 1. Map of the Western Cape, South Africa showing the three study areas: Grabouw (pome fruits), Hex River Valley (table grapes) and Piketberg (wheat). Within each study area air samples were collected at “farm” (OCPs $n = 6$; CUPs $n = 6$) and “village” (CUPs $n = 6$). (IN COLOUR; SINGLE IMAGE). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dichlorodiphenyldichloroethylene (DDE), *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, α -hexachlorocyclohexane (HCH), β -HCH, δ -HCH and γ -HCH).

Cyclodien pesticides were analysed by gas chromatography atmospheric pressure chemical ionization tandem mass spectrometry (GC-APCI-MS/MS) on a Waters Xevo TQ-S MS (USA) coupled to Agilent 7890 GC (USA). The MS was operated under dry source conditions (N_2 at constant pressure 40 psi) in multiple reactions monitoring (MRM) mode. The GC was equipped with a $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ Rxi-5Sil MS column (Restek, USA). The injection was splitless at $250\text{ }^\circ\text{C}$. Helium was used as carrier gas at constant flow of 1.5 mL min^{-1} . The oven temperature programme was $90\text{ }^\circ\text{C}$ (1 min hold), then $40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ until $200\text{ }^\circ\text{C}$, followed by $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ until $240\text{ }^\circ\text{C}$, and $40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ until $310\text{ }^\circ\text{C}$ (5 min hold).

The remaining OCPs were analysed on a 7890A GC (Agilent, USA) equipped with a $60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ Rxi-5Sil-MS column (Restek, FR) coupled to a 7000B MS (Agilent, USA). The temperature program for GC started at $80\text{ }^\circ\text{C}$ (1.5 min hold), then $40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $200\text{ }^\circ\text{C}$ and finally $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ to $305\text{ }^\circ\text{C}$ (no hold). The inlet temperature was $280\text{ }^\circ\text{C}$. Injection volume was $3\text{ }\mu\text{L}$ in pulsed-splitless mode. The carrier gas was helium with a flow rate of 1.5 mL min^{-1} . The temperatures of the transfer line and the ion source were $310\text{ }^\circ\text{C}$ and $250\text{ }^\circ\text{C}$, respectively. The mass spectrometer was operating in MRM mode with nitrogen as collision gas with a flow of 1.5 mL min^{-1} .

2.3.2. CUPs

PUF samples were extracted by methanol for CUP analysis using an automated warm Soxhlet extractor (same as above) for three cycles, each consisting of 60 min of warm Soxhlet and 30 min of solvent rinsing. The extracts were concentrated using a gentle stream of nitrogen. After extraction, CUP extracts were passed through syringe filters (nylon membrane, 25 mm diameter, pore size of $0.45\text{ }\mu\text{m}$), transferred to LC vial and nitrogen concentrated for analysis.

CUPs were analysed using an Agilent 1290 high-performance liquid chromatography (HPLC, Agilent Technologies, Waldbronn, Germany) with a Luna® C18 (2) endcapped analytical column ($100\text{ mm} \times 2.0\text{ mm} \times 3\text{ }\mu\text{m}$, Phenomenex, Torrance, CA, USA). Analyte detection was performed by tandem mass spectrometry using an AB Sciex Qtrap 5500 (AB Sciex, Concord, ON, Canada) operating in positive electrospray ionization (ESI+).

Identification was based on a comparison of ion ratios and retention times with corresponding isotopically labelled standards and quantification via internal standards available at the time of analysis: acetochlor-d11, alachlor-d13, atrazine-d5, carbendazim-d4, dimethoate-d6, diuron-d6, fenitrothion-d6, chloridazon-d5, chlorotoluron-d6, chlorpyrifos-d10, isoproturon-d6, metatitron-d5, metazachlor-d6, S-metolachlor-d6, metribuzine-d3, phosmet-d6, prochloraz-d7, propiconazole-d5, simazine-d10, tebuconazole-d6 and terbuthylazine-d5 (Toronto Research Chemicals, Canada; Dr. Ehrenstorfer LGC Standards, UK; Chiron AS, Norway; and Neochema, Germany). The instrumental limits of detection and quantification (LODs and LOQs, respectively) were estimated as the quantity of analytes with a signal to noise ratio of 3:1 and 10:1, respectively. Additional information on analytical parameters is available elsewhere (Degrendele et al., 2016a).

2.4. Quality assurance-quality control

In total, nine field blanks (five for OCPs and four for CUPs) were prepared, taken along to the field site and analysed as per samples. Most of the target analytes were not detected in the field blanks or had low concentrations (SI, Table S1a/b), suggesting minor contamination during sampling, transport and sample preparation. The concentrations reported here were blank-corrected by subtracting the average concentrations found in the field blanks separately for each batch of samples. LOQs were derived from the field blanks, using the average concentrations in the blanks plus three times their standard deviations. The recoveries of individual OCPs and CUPs were determined from

spike-recovery tests of PUF disks (SI, Table S1a/b) and ranged from $38.2\% \pm 12.7$ – $148\% \pm 6.86$ for OCPs and from $59.3\% \pm 17.5$ – $170\% \pm 19.8$ for all CUPs, except diazinon. For diazinon, its recoveries were lower (i.e., $5.4\% \pm 2.0$), which leads to higher uncertainties. Nevertheless, given that this is a relevant pesticide in environmental studies, results are also presented for diazinon but should be taken with caution. OCPs data were not recovery-corrected and for those individual OCPs which have recoveries lower than 50%, higher uncertainties are associated with the reported concentrations. For CUPs, the reported concentrations were recovery-corrected as isotope dilution method was used.

2.5. Meteorological data

Data on the daily maximum and minimum temperatures, daily rainfall and daily windspeed were accessed from the three closest weather stations in our study areas in GRB ($34^\circ 08' 42.0''\text{S}$, $19^\circ 01' 26.4''\text{E}$), HRV ($33^\circ 28' 26.4''\text{S}$, $19^\circ 39' 54.0''\text{E}$) and PKT ($32^\circ 54' 21.6''\text{S}$, $18^\circ 45' 14.4''\text{E}$) at a distance of 4, 4 and 14 km, respectively, from the farms (EAD, 2018). Information on the meteorological data per study area can be found in SI, Table S2.

2.6. Calculation of pesticide concentration in the air (ng/m^3)

Air concentrations (ng/m^3) of both OCPs and CUPs were obtained dividing PUF-PAS concentrations (C_{PUF}) by the effective air volume (V_{AIR} , m^3) in each SR, derived from the sampling rate (R) and the number of days sampled ((Francisco et al., 2017; Harner, 2020). For OCPs, concentrations were obtained using a standard template estimating R (Harner, 2020) (SI, Table S3a). For CUPs, a standard R of $4\text{ m}^3\cdot\text{day}^{-1}$ was used, which is considered adequate given the wind speed registered in our SR (up to 4 m s^{-1} ; SI, Table S2) (Gouin et al., 2008; Pozo et al., 2009a, 2009b; Tuduri et al., 2006). As a complement, a sensitivity analysis using $R = 2\text{ m}^3\cdot\text{day}^{-1}$ (lower limit) and $R = 6\text{ m}^3\cdot\text{day}^{-1}$ (upper limit) was performed for CUPs (SI, Table S3b). More information on the calculations performed is presented in Supplementary Information.

2.7. Imputation of data below the limit of quantification

To select the best method to attribute values to the left-censored data (i.e., data $<$ LOQ), histograms were performed on the normal and log-transformed data for better visualization of their distribution (SI, Figs. S1–S2). For most OCPs, the observations followed a non-linear distribution. Therefore, substitutions were performed on the left-censored values using a fixed value of $\frac{1}{2}$ LOQ for those showing at least 40% of data $>$ LOQ. Out of the 27 targeted OCPs, 17 met this criterion and were selected for further analysis (Table 1).

For CUPs, which followed a normal-like distribution, left-censored values were imputed based on the maximum likelihood estimation, using area and site as predictors. In this method a log-likelihood function, for each estimated parameter, is created using all records in the dataset. Imputations are carried out using bootstrap random selected values from a log-normal distribution of the estimated parameters. Detailed information on this method has been described elsewhere (Lubin et al., 2004). Imputations were performed on CUPs showing 40% of data $>$ LOQ. Out of the 25 measured CUPs, ten met this criterion and were selected for further analysis (Table 1).

2.8. Data visualization and analyses

2.8.1. Data visualization

Descriptive information on the quantification frequency and range of concentrations (ng/m^3) is presented for the 17 OCPs and ten CUPs quantified in at least 40% of samples. To observe seasonal variations across the areas, heat maps were produced for all OCPs and CUPs

Table 1

Quantification frequency and air concentrations (ng/m³) of the targeted organochlorine (OCPs) and current-use (CUPs) pesticides in South Africa between 2017 and 2018.

Pesticide category	Pesticide type	Active ingredient *	Chemical group**	Vapor Pressure (Pa) ^a	DT ₅₀ in soil (days) ^{a, b}	Quantification freq. (%) ^{***}	Median (IQR) ng/m ³	Max ng/m ³	
Legacy organochlorine pesticides (OCPs)	Insecticides	<i>cis</i> -Chlordane ^c	OCP	1.4 × 10 ⁻³	Chlordane: 365	94.4	1.4 × 10 ⁻³ (4.5 × 10 ⁻³)	0.01	
		<i>trans</i> -Chlordane ^c	OCP	1.2 × 10 ⁻³	Chlordane: 365	100	2.6 × 10 ⁻³ (5.2 × 10 ⁻³)	0.02	
		Oxychlordane ^c	OCP	2.8 × 10 ⁻⁴	Chlordane: 365	88.9	1.5 × 10 ⁻⁴ (1.3 × 10 ⁻⁴)	4.8 × 10 ⁻⁴	
		<i>o,p'</i> -DDD ^c	OCP	NA	DDD: 1000	88.9	1.3 × 10 ⁻³ (4.7 × 10 ⁻³)	0.01	
		<i>p,p'</i> -DDD ^c	OCP	5.2 × 10 ⁻⁴	DDD: 1000	88.9	3.7 × 10 ⁻³ (9.4 × 10 ⁻³)	0.02	
		<i>o,p'</i> -DDE	OCP	8.3 × 10 ⁻⁴	DDE: 5000	100	3.8 × 10 ⁻³ (7 × 10 ⁻³)	0.02	
		<i>p,p'</i> -DDE	OCP	8.6 × 10 ⁻⁴	DDE: 5000	100	0.14 (0.56)	1.2	
		<i>o,p'</i> -DDT	OCP	3.1 × 10 ⁻⁴	DDT: 6200	100	9.9 × 10 ⁻³ (3 × 10 ⁻²)	0.06	
		<i>p,p'</i> -DDT	OCP	1.5 × 10 ⁻⁴	DDT: 6200	100	0.02 (0.05)	0.1	
		Dieldrin	OCP	2.4 × 10 ⁻⁵	1400	38.9	9.9 × 10 ⁻³ (4.1 × 10 ⁻²)	0.08	
		Endosulfan 1 ^c	OCP	3.8 × 10 ⁻⁵	Endosulfan: 50	44.4	8.6 × 10 ⁻⁴ (3.9 × 10 ⁻³)	0.1	
		Endosulfan 2	OCP	NA	Endosulfan: 50	33.3	2.2 × 10 ⁻³ (2.7 × 10 ⁻²)	0.06	
		Endosulfan sulfate	OCP	4.9 × 10 ⁻⁵	Endosulfan: 50	100	3.9 × 10 ⁻⁴ (4.6 × 10 ⁻³)	7.1 × 10 ⁻³	
		α-HCH ^c	OCP	4.9 × 10 ⁻¹	175	94.4	2.3 × 10 ⁻³ (1.5 × 10 ⁻³)	5.8 × 10 ⁻³	
		β-HCH ^c	OCP	NA	NA	83.3	9.8 × 10 ⁻⁴ (6 × 10 ⁻⁴)	2.7 × 10 ⁻³	
		δ-HCH	OCP	NA	NA	5.6	5 × 10 ⁻⁴ (0)	5 × 10 ⁻⁴	
		γ-HCH ^c	OCP	9.1 × 10 ⁻¹	980	100	0.02 (0.02)	0.06	
		Heptachlor ^c	OCP	2 × 10 ⁻²	285	94.4	1.2 × 10 ⁻⁴ (2.1 × 10 ⁻⁴)	1.5 × 10 ⁻³	
		Heptachlor epoxide ^c	OCP	1.1 × 10 ⁻³	NA	94.4	1.4 × 10 ⁻⁴ (1.7 × 10 ⁻⁴)	6.5 × 10 ⁻⁴	
		Mirex	OCP	1.1 × 10 ⁻⁴	300	100	1.4 × 10 ⁻⁴ (1.3 × 10 ⁻⁴)	1.3 × 10 ⁻⁴	
Current-use pesticides (CUPs)	Herbicides	Carbaryl	CAR	4.16 × 10 ⁻⁵	16	100	0.02 (0.24)	1.3	
		Azinfos-methyl	OPH	5 × 10 ⁻⁷	10	0.03	0.03 (0)	0.03	
		Chlorpyrifos	OPH	1.4 × 10 ⁻³	386	100	0.70 (1.30)	16.20	
		Diazinon ^c	OPH	1.2 × 10 ⁻²	9.1	97.2	0.03 (0.06)	1.4	
		Dimethoate	OPH	2.4 × 10 ⁻²	2.5	33.3	0.01 (0.01)	0.19	
		Malathion ^c	OPH	3.1 × 10 ⁻³	0.2	66.7	6.4 × 10 ⁻³ (0.02)	0.20	
		Metazachlor ^c	ACM	9 × 10 ⁻⁵	8.6	58.3	9.8 × 10 ⁻⁴ (2.7 × 10 ⁻³)	9.2 × 10 ⁻³	
		S-metolachlor ^c	CAM	3.7 × 10 ⁻³	52	97.2	0.02 (0.04)	0.29	
		Atrazine ^c	TZI	3.9 × 10 ⁻⁵	75	72.2	2.3 × 10 ⁻³ (6.6 × 10 ⁻³)	0.04	
		Simazine ^c	TZI	8.1 × 10 ⁻⁷	60	72.2	0.02 (0.04)	0.88	
		Terbuthylazine ^c	TZI	1.5 × 10 ⁻⁴	72	97.2	0.05 (0.16)	0.79	
		Metribuzin	TZN	1.2 × 10 ⁻⁴	7	33.3	0.01 (0.02)	0.03	
		Diuron	URE	1.2 × 10 ⁻⁶	147	19.4	0.01 (0.02)	0.12	
		Fungicides	Prochloraz	IMI	1.5 × 10 ⁻⁴	120	13.9	4.8 × 10 ⁻³ (3.8 × 10 ⁻³)	5.4 × 10 ⁻³
		Propiconazole	TZL	5.6 × 10 ⁻⁵	72	27.8	0.03 (0.06)	0.08	
Tebuconazole ^c	TZL	1.3 × 10 ⁻⁶	63	97.8	0.03 (0.07)	0.43			

* Active ingredient: the following active ingredients were never detected – aldrin, endrin, endrin aldehyde, endrin ketone, isodrin, methoxychlor, *trans-endo*-heptachlor epoxide, acetochlor, carbendazim, chlorotoluron, chloresulfuron, dimetachlor, isoproturon, metamitron, pirimicarb and pyrazon.

** Chemical group: OCP = organochlorines, CAR = carbamates, OPH = organophosphates, ACM = acetamides, CAM = chloracetamides, TZI = triazines, TZN = triazinones, URE = ureas, IMI = imidazoles, TZL = triazoles.

*** Quantification frequency: the quantification frequency was based on the total number of samples (OCP n = 18; remaining groups n = 36).

^a <http://sitem.herts.ac.uk/aeru/ppdb/>, NA – not available.

^b DT₅₀ typical in soils: for the isomers where half-life is not available, the half-life of the technical mixture is provided.

^c Pesticides where substitution/imputation of left-censored values was performed – for these, the median and interquartile range (IQR) were obtained including those values.

quantified at least once (Fig. 2). For CUPs showing two values per area (“farm” or “village”), the highest value was plotted. To visualize differences in CUPs concentrations between sites (“farm” and “village”), line graphs were created, including also the maximum daily temperature to provide insight on temperature patterns throughout the sampling year (Fig. 3; SI, Figs. S3–S11).

To investigate mixtures amongst the detected OCPs, CUPs and between chemical groups, UpSet plots were created (in overall samples and individual study areas) (SI, Figs. S12–S15). Lastly, correlation plots using Spearman’s correlation coefficients (r_s), further studied the strength and direction of the correlation between pesticide concentrations (Fig. 4; SI, Figs. S13–S15). All graphs were built using R (Foundation for Statistical Computing, version 3.5.3, RStudio Version 1.1.4).

2.8.2. Statistical analyses

For the 17 OCPs where substitution of left-censored data was performed, Kruskal-Wallis tests were used to assess differences in the concentrations between the three study areas.

For the ten imputed CUPs, the log 10-transformed concentrations were modeled using a linear mixed-effect model (LME) according to (fixed effects): area (GRB, HRV and PKT), site (“farm” and “village”),

and SR. The SR was also accounted for as a random effect. By including the SR as a fixed and as a random effect, we are accounting for seasonal events that occurred throughout the study year (e.g., fluctuations in temperature/rainfall or pesticide application period). Z-proportion test additionally studied if the proportion of <LOQ vs >LOQ was significantly different between “farm” and “village”. Across all analyses, p-values <0.05 were considered statistically significant.

2.8.3. OCPs isomer ratio

OCPs ratios have been widely used to identify the source of these compounds in environmental matrices (Li et al., 2007; Liu et al., 2009; Park et al., 2011; Qiu et al., 2005; Venier and Hites, 2014). The ratio of DDT, chlordane and endosulfan isomers was calculated to understand if air concentrations derived from past or ongoing use of these OCPs in the region (Kim et al., 2020; Park et al., 2011; Qiu et al., 2005). Moreover, the *o,p'*-DDT/*p,p'*-DDT and α-HCH/γ-HCH ratios were used to understand if the source of DDT and HCH contamination is a result of the use of the technical mixtures (i.e., a mixture sold by a manufacturer, with a given name of the main component present) or other mixtures where the isomers are also present in high amounts (e.g., dicofol-type-DDT and lindane as source of HCHs) (Liu et al., 2009; Park et al., 2011; Ullah

et al., 2019; Venier and Hites, 2014). Information on the ratio calculations and threshold levels above which the aforementioned OCPs are considered to be result of ongoing application (or application of the technical mixtures) is described in supplementary information. The average yearly ratio was calculated for the overall samples and individual areas, with the exception of endosulfan which was only calculated for HRV as it was not detected in the remaining areas.

3. Results

3.1. OCPs

3.1.1. Quantification frequency and air concentrations (ng/m^3)

Among the 27 targeted OCPs, 20 were quantified in at least one sample (Table 1, Fig. 2a). Eight OCPs (*trans*-chlordane, *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, endosulfan sulfate, γ -HCH and mirex) were quantified in 100% of the samples, followed by *cis*-chlordane, α -HCH, heptachlor and heptachlor epoxide, quantified in 94.4% of the samples (Table 1). *p,p'*-DDE showed the highest concentrations (median of 0.14 ng/m^3 ; IQR 0.56 ng/m^3), with higher concentrations in GRB. This was followed by *p,p'*-DDT, (median of 0.02 ng/m^3 ; IQR 0.05 ng/m^3), γ -HCH (0.02 ng/m^3 ; IQR 0.02 ng/m^3) and *trans*-chlordane (0.003 ng/m^3 ; IQR 0.01 ng/m^3) (Table 1).

3.1.2. Seasonal variations across the sampling periods

For most OCPs, no clear variations were observed throughout the SRs. However, for some compounds (e.g., *o,p'*-/*p,p'*-DDE or β -HCH), we observe a slight increase in air concentrations during the warmer months (i.e., November–February 2018) (Fig. 2a).

3.1.3. Spatial variations across study areas

In general, most OCPs show higher concentrations in HRV, followed by GRB and PKT (Fig. 2a; SI, Table S4). In total, 13 OCPs showed significantly different concentrations between study areas. For instance, chlordane (*cis*-/*trans*-chlordane, oxychlordane and heptachlor) and endosulfan (endosulfan 1 and endosulfan sulfate) were found in higher concentrations in HRV. DDT isomers and γ -HCH, on the other hand, showed higher concentrations in GRB compared to the remaining areas.

3.1.4. OCPs isomer ratio

OCPs isomer ratios are presented in Supplementary Information (SI, Table S6). The ratio of DDT isomers and its metabolites infer that the DDTs present in air results from historical use ($(\text{DDE} + \text{DDD})/\sum \text{DDT} > 1$) of the technical mixture of DDT (*o,p'*-DDT/*p,p'*-DDT between 0.42 and 0.75). Also, for endosulfan, the ratio in HRV (endosulfan 1/endosulfan 2 between 1.49 and 2.41) suggests past use of the pesticide in the region. For HCHs (α -HCH/ γ -HCH between 0.03 and 0.54), the results suggest that the source of environmental contamination is likely to be related to the use of lindane other than the technical mixture of HCH. The results from the ratio between *trans*-/*cis*-chlordane (range 1.20–13.44) suggest the ongoing application of technical chlordane in the region, more evident in PKT.

3.2. CUPs

3.2.1. Quantification frequency and air concentrations (ng/m^3)

Among the 25 targeted CUPs, 16 were quantified at least once (Fig. 2b; Table 1). Carbaryl and chlorpyrifos were the only CUPs quantified in all the samples (100%), followed by diazinon, S-metolachlor and terbuthylazine (quantified in 97.2% of the samples) and tebuconazole (91.7%).

Chlorpyrifos showed the highest concentrations (median concentration of 0.70 ng/m^3 ; IQR 1.30 ng/m^3), with higher concentrations detected in GRB, followed by PKT and HRV (Fig. 3). Carbaryl had the second highest concentrations (median concentration of 0.02 ng/m^3 ; IQR 0.24 ng/m^3) followed by terbuthylazine (0.05 ng/m^3 ; IQR 0.16 ng/m^3)

and tebuconazole (0.03 ng/m^3 ; IQR 0.07 ng/m^3) (Table 1). The median concentrations in the individual areas can be found in SI, Table S4.

3.2.2. Seasonal variations across the sampling period

The seasonal variations of CUPs presented in this study were similar across areas. Higher concentrations are generally observed during the most active spraying season in each area (SR 1–2 in GRB and HRV; SR 1 and 6 in PKT), remaining steady throughout the warm summer months (SR 3–4). A decrease is observed mainly in the last SR in GRB and HRV, corresponding to the colder months and heaviest rainfall period, where most concentrations fall below LOQ (Fig. 2b; SI, Figs. S3–S12).

3.2.3. Spatial variations across study areas and sites

Looking at the individual study areas, median concentrations of CUPs are generally higher in PKT, followed by GRB and HRV (SI, Table S4). The results from the LME model further show significant differences for carbaryl, diazinon, malathion, metazachlor, simazine and tebuconazole, with higher concentrations detected in PKT when compared to GRB (Table 2). On the other hand, no differences were found between “farm” and “village” for any of the targeted pesticides. This is further emphasized by the results from the Z-proportion test that show no significant differences between the proportion of >LOQ observed in “farm” and in “village”.

3.3. Occurrence of pesticide mixtures across study areas

From the 18 PUF disks used to measure OCPs in air, a median of 16 [IQR 2] OCPs were detected per sample throughout the study period, making a total of 11 different OCPs combinations. On the other hand, from the 36 PUF disks used for CUPs, a median of 10 [IQR 5] pesticides were detected with a total of 24 CUPs combinations. The two most frequent OCP mixtures (1 - DDT isomers, $\alpha/\beta/\gamma$ -HCH, chlordane isomers, oxychlordane, heptachlor, heptachlor epoxide and mirex; 2 - same as 1 plus endosulfan 1/2) appeared in four samples, whereas the CUP mixture more frequently detected (carbaryl, chlorpyrifos, terbuthylazine, S-metolachlor, diazinon, tebuconazole) appeared in five samples (SI, Fig. S12).

Looking only at the “farm” sites, where both OCPs and CUPs were measured, OCPs, triazoles, triazines, organophosphates, carbamates and chloracetamides were frequently detected together (33% of samples, SI, Fig. S16). Positive correlations between four pesticide clusters were also identified (Fig. 4). The first shows a moderate to strong positive correlation (r_s 0.51–0.98) between DDT isomers, diazinon and γ -HCH; the second is a moderate to strong correlation (r_s 0.56–0.88) between chlordane isomers and metabolites (*trans*-/*cis*-chlordane, heptachlor, heptachlor epoxide and oxychlordane), endosulfan 1 and endosulfan sulfate; also a moderate correlation was found between atrazine, simazine, chlorpyrifos and S-metolachlor (r_s 0.51–0.67), with the triazine herbicides (atrazine, simazine and terbuthylazine) further correlating positivity between each other (r_s 0.54–0.70); and the last corresponds to a moderate to strong correlation (r_s 0.53–0.92) between tebuconazole, malathion, metazachlor, α - and β -HCH. UpSet plots and clusters for the study areas can be found in SI, Figs. S12–S15.

4. Discussion

We detected 20 legacy OCPs and 16 CUPs, while we identified in median 16 OCPs and 10 CUPs per sample. This resulted in a total of 11 OCP and 24 CUP different combinations/mixtures. We showed that pesticide occurrence varies between areas with different crop production systems, although CUPs' concentrations did not differ between “farm” and “village”. Finally, we observed that CUPs' air concentrations fluctuated throughout the year whereas OCPs generally remained at steady levels.

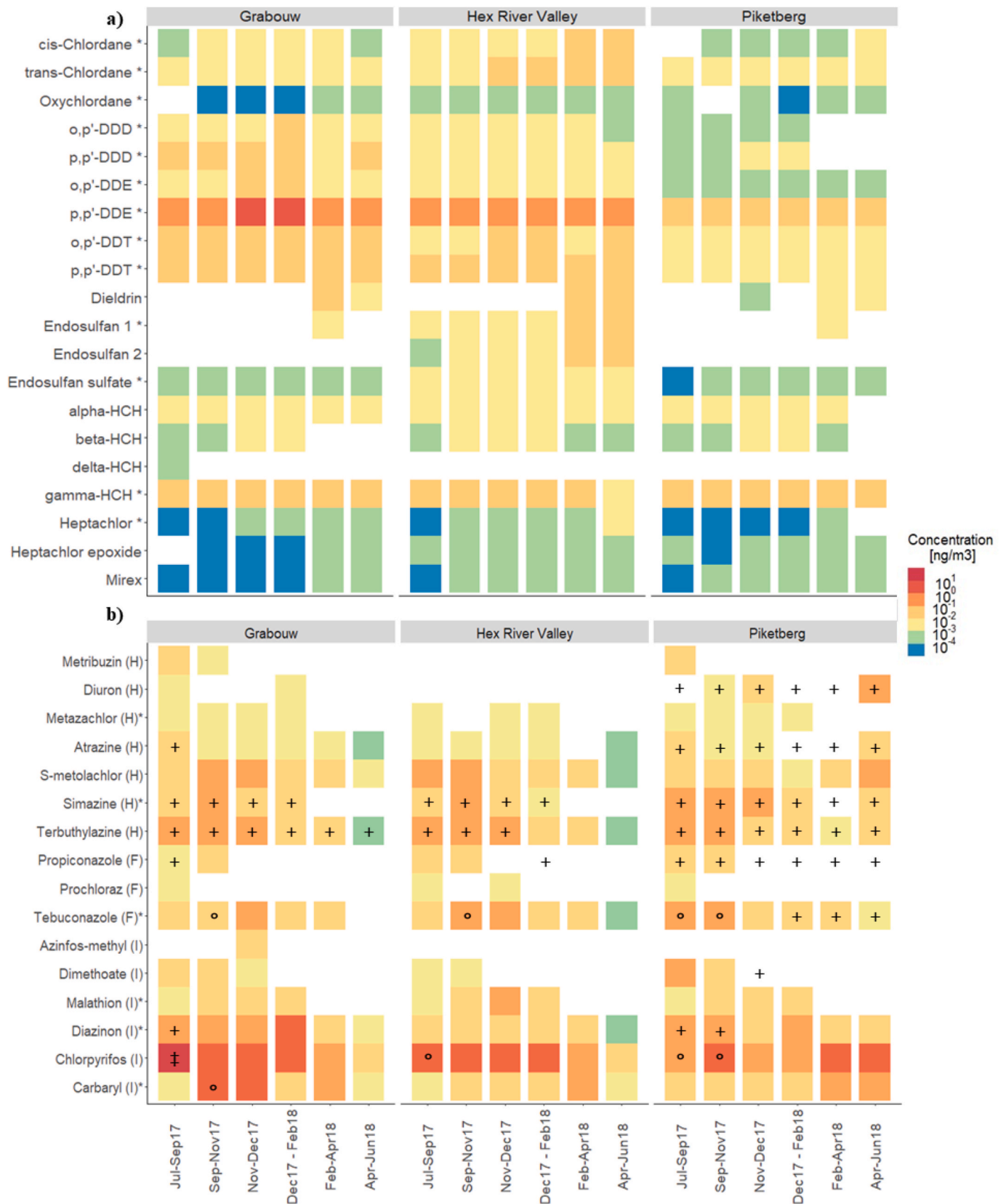


Fig. 2. Heat maps representing two-months sampling periods for the a) 20 quantified OCPs; and b) 16 quantified CUPs (F – fungicide; H – Herbicide; I – insecticide). For CUPs, the highest concentration detected in each period was plotted, independently of the site. Blank space indicates concentrations < LOQ. * indicates significant differences between areas. + indicates sampling rounds where pesticides were detected in water. ° indicates spraying record of the active ingredient. ‡ indicates spraying activity and detection in water (Curchod et al., 2020) (IN COLOUR; SINGLE IMAGE). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

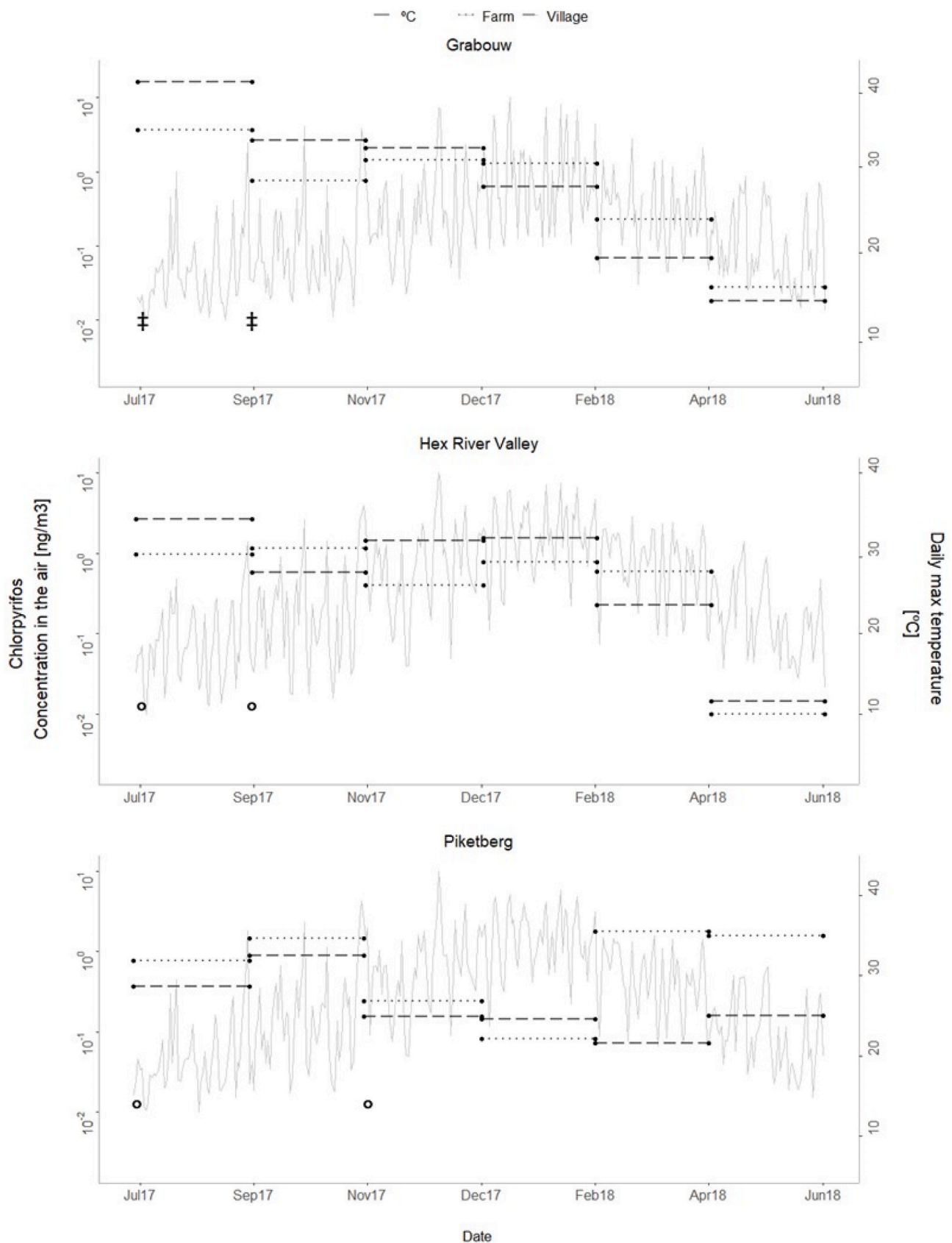


Fig. 3. Atmospheric concentrations (ng/m³) of chlorpyrifos in each area, site, sampling round (indicated by the dashed lines) and daily maximum temperature (indicated by solid lines). ° indicates period of spraying activity. † indicates period of spraying activity and detection in water (Curchod et al., 2020). For the remaining imputed CUPS, the line graphs can be found in Supplementary Information. (SINGLE IMAGE).

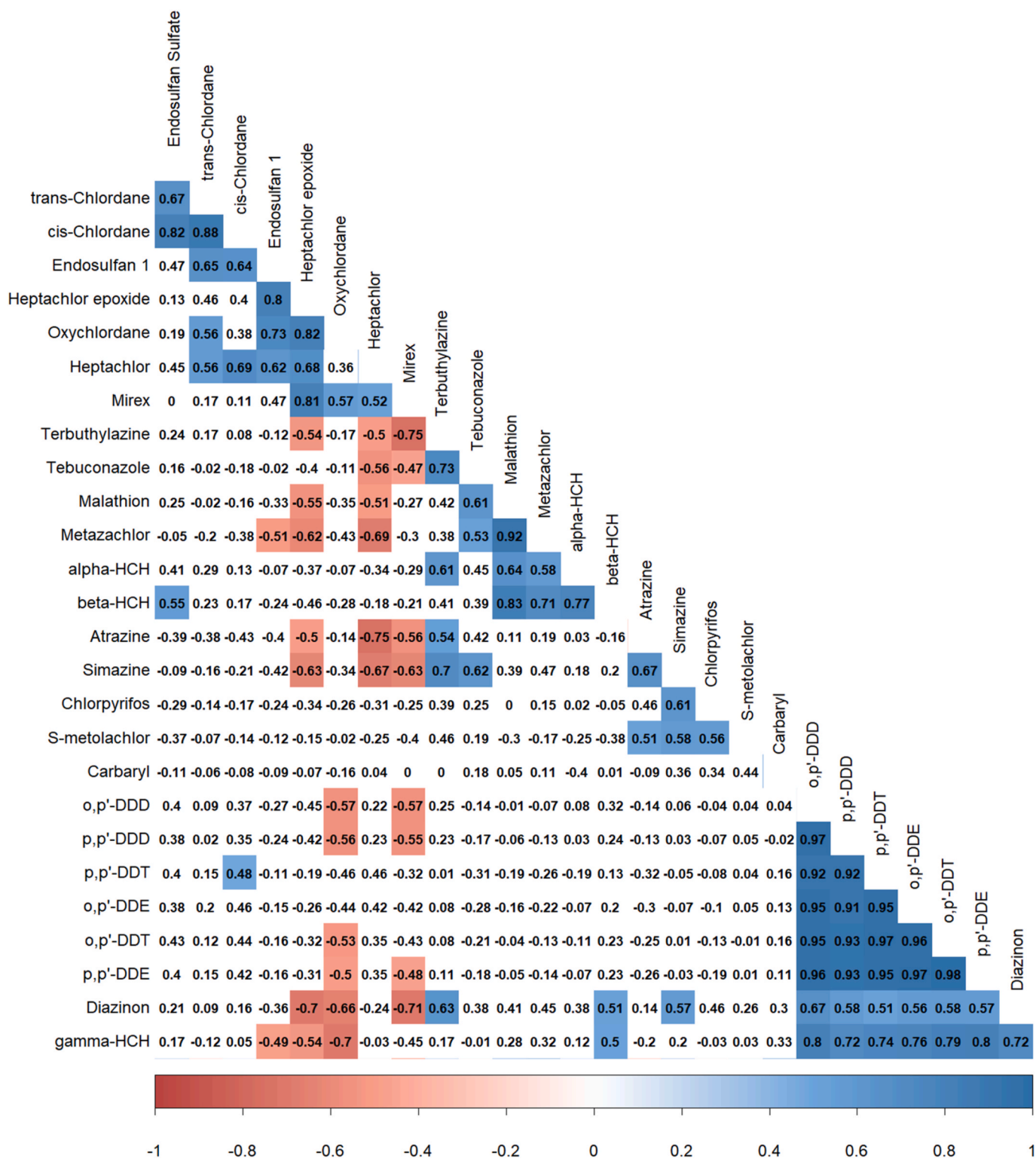


Fig. 4. Correlation plot using the Spearman’s correlation for targeted organochlorine (OCPs) and current-use (CUPs) pesticides structured by hierarchical clustering. Only concentrations detected at the “farm” site were used. White squares indicated that the correlations were not statistically significant. (IN COLOUR; SINGLE IMAGE). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

4.1. OCPs

Eight OCPs were constantly detected in concentrations that had little variation over the six SRs. Despite the OCP ban for agricultural purposes, these compounds were intensively used in the past and are highly persistent in the environment (e.g., half-life in soil for investigated OCPs

range between 150 days and 17 years) (PPDB, 2014). Therefore, reoccurring volatilization from soils can be accountable for the observed presence of the OCPs in air (Degrendele et al., 2016b; Mackay et al., 2014). The differences in concentration detected between the three areas are likely due to the type of crops grown in each area, and hence, to the past use of individual OCPs. For instance, the high concentrations

Table 2

Results from the linear mixed-effect model used to assess the influence of site, area and sampling round (used also as random effect and not here presented) on the log₁₀ concentrations of the ten imputed CUPs. Only results for the pesticides showing significant results are here presented.

Pesticide	Covariates	β-estimate	95% CI
		n = 36	
Carbaryl	Site ^a : Village	-0.0002	[-0.41; 0.41]
	Area ^b : HRV	-0.54 ^c	[-1.03; -0.05]
	PKT	-0.18	[-0.67; 0.31]
Diazinon	Site: Village	-0.26	[-0.67; 0.15]
	Area: HRV	-0.69 ^c	[-1.2; -0.18]
	PKT	-0.10	[-0.59; 0.39]
Malathion	Site: Village	-0.04	[-0.39; 0.31]
	Area: HRV	0.70 ^d	[0.07; 0.81]
	PKT	0.38	[-0.05; 0.71]
Metazachlor	Site: Village	-0.22	[-0.49; 0.05]
	Area: HRV	0.10	[-0.25; 0.45]
	PKT	0.71 ^e	[0.36; 1.06]
Simazine	Site: Village	0.14	[-0.55; 0.83]
	Area: HRV	-0.09	[-0.95; 0.78]
	PKT	1.20 ^c	[0.34; 2.06]
Tebuconazole	Site: Village	-0.07	[-0.34; 0.20]
	Area: HRV	0.41 ^c	[0.08; 0.74]
	PKT	0.47 ^c	[0.14; 0.80]

^a Farm was taken as the reference group.

^b GRB was taken as the reference group.

^c Indicates a p-value ≤ 0.05.

^d Indicates a p-value ≤ 0.01.

^e Indicates a p-value ≤ 0.001.

and detection frequencies of OCPs in HRV and GRB, is in line with the main crops that have been farmed for decades in those areas (table grapes and pome fruits, respectively) alongside the intensive use of insecticides (London and Myers, 1995; Raine et al., 1999). *p,p'*-DDE, a DDT metabolite, was the OCP measured in highest concentrations across all study areas, followed by *p,p'*-DDT (almost ten-times lower than *p,p'*-DDE). In Durban (South Africa) nonetheless, higher concentrations for *p,p'*-DDT (average 0.04 ng/m³) have been reported compared to *p,p'*-DDE (average 0.01 ng/m³) (Batterman et al., 2008). Differences between studies can be related to ongoing IRS of DDT in areas close to Durban (e.g., KwaZulu-Natal and Mpumalanga) (Eskenazi et al., 2019; Maharaj et al., 2019). Also, this can be a result from environmental degradation of DDT into DDE in the ten years separating studies, further emphasized by DDT isomers ratio (4.92, yearly average of (DDE + DDD)/∑DDT) suggesting DDT contamination in the region to be originated from past use of DDT technical mixture. Lower concentrations were observed for technical HCH and endosulfan, compared to previous studies (Dalvie et al., 2014b; Pozo et al., 2009a, 2009b). Pozo et al. (2009a, 2009b) reported in De Aar, South Africa, maximum concentrations almost 100-times higher for α-HCH and endosulfan 1 (0.12 ng/m³ and 0.33 ng/m³, respectively) than our results. Although banned in 1983 (DAFF, 2017), α/β-HCH were being unintentionally produced during the production of lindane (mainly composed by γ-HCH, but also contains traces of α/β-HCH). Lindane restriction in 2009 (DAFF, 2017) might have resulted in a decrease of environmental HCHs throughout the years. This is also in line with White et al. (2020), who reported a general decrease in OCPs concentrations (e.g., DDT, HCHs and endosulfan) over ten years in African countries. Chlordane isomers concentrations were, nonetheless, the exception. We detected concentrations almost ten times higher than those described previously by Batterman et al. (2008) and by Pozo et al. (2009a, 2009b). Also, the chlordane isomers ratio suggests ongoing use close to the sampling sites (3.46, yearly average of trans/cis-chlordane). Though banned in 2005 (DAFF, 2017), there are concerns that illegal trading and contamination/use of old stocks of several OCPs are still ongoing in countries such as South Africa (Dalvie et al., 2006; Klánová et al., 2009). This could explain the rather high concentrations of chlordane isomers detected throughout

the course of the study.

4.2. CUPs

Tebuconazole, terbuthylazine, S-metolachlor, diazinon, carbaryl and chlorpyrifos were the pesticides the most frequently quantified in this study (>95% of samples). Tebuconazole showed its highest concentrations in HRV (median 0.03 ng/m³). This fungicide is widely used on grapes (main crop in HRV) to control fungal infections (Herrero-Hernández et al., 2011). It is moderately persistent in the soil (half-life between 26 and 92 days), explaining its maintenance in air during the study (PPDB, 2014). Terbuthylazine was the herbicide showing the highest air concentrations in HRV and GRB. Our measured terbuthylazine concentrations (max 0.79 ng/m³ in HRV) are almost ten times higher than concentrations reported using active air samplers by Degrendele et al. (2016) in Czech Republic, and by Carratalá et al. (2017) in Spain. Indeed, terbuthylazine has been reported as a frequently used CUP in South Africa (Dabrowski et al., 2014). For most herbicides, nevertheless, we detected higher concentrations at PKT (SI, Table S4), with metazachlor and simazine showing higher concentrations, compared to a pome fruit region like GRB (Table 2). This is likely due to crop differences between areas, with herbicides being heavily used in wheat crops for decades (Curchod et al., 2020; Dalvie et al., 2009; London and Myers, 1995). The highest concentrations of the insecticides diazinon, carbaryl and chlorpyrifos were detected in GRB compared to the other two areas (SI, Table S4). Chlorpyrifos concentrations here reported were, in some SRs, almost 20-times higher than in previous studies using also PUF-PAS devices – e.g., Estellano et al. (2015) reported a max of 0.58 ng/m³ in Italy, and Koblizkova et al. (2012) a max of 0.36 ng/m³ in Czech Republic – but in the same order of magnitude of concentrations reported in Chilean agricultural areas (max of 14.62 ng/m³) (Cortes et al., 2020). Although banned in the EU in 2019, chlorpyrifos is still widely used in agriculture, in households and for disease vector control in many African countries, including South Africa (Fuhriemann et al., 2020; Dalvie et al., 2014a, 2014b). Interestingly, no significant differences were found between the concentrations measured at “farm” and “village” for any of our measured pesticides. We hypothesize that the concentrations registered at the “village” may be a result from close proximity to nearby farms (Fig. 1), with spray drift and atmospheric transport playing a major role in these findings. Also, the domestic use of organophosphates (e.g., chlorpyrifos) has been reported in South Africa (Dabrowski et al., 2014; Dalvie et al., 2014a, 2014b). This could additionally explain the concentrations measured at the “village” site, where in some occasions were even higher than those measured at the “farm” site (Fig. 3; SI, Figs. S3–S11).

Although the spraying records were only collected from a small percentage of the actual number of farms present in each study area (Curchod et al., 2020), it is possible to observe that for most targeted CUPs (e.g., chlorpyrifos, tebuconazole or carbaryl), higher concentrations are mainly related to the spraying events in each area (i.e., SR 1–2 in GRB and HRV; SR 1 and 6 in PKT) (Fig. 2b). It has been shown that following application, up to 30% of the amounts sprayed never reach their final target due to spray drift, ending up entering the atmosphere (van den Berg et al., 1999). Therefore, higher concentrations in air are expected during these seasons (Figueiredo et al., 2021). A decrease is then observed throughout the SRs following application, with lower values coinciding with the period further from the application season in addition to the peak of rainfall events (SR 5–6), that could lead to wash-off of pesticides from air (Mackay et al., 2014) (Fig. 2b; SI, Table S2, Figs. S3–S11). This is not so evident in Piketberg, where SR 6 also corresponds to spraying activity (e.g., growing of wheat and other cereals). Some CUPs, nevertheless, (e.g., chlorpyrifos, terbuthylazine or tebuconazole) can still remain at high concentrations throughout the summer months (SR 3–4), which possibly is a result of volatilization from soils. Out of the 16 CUPs detected in air, nine had previously been reported to be present also in the respective rivers of each study area

(Fig. 2b; Curchod et al., 2020). This emphasizes the wide environmental contamination by these compounds and the importance for future studies combining different environmental matrices for further risk assessment studies.

4.3. Occurrence of pesticide mixtures across study areas

From the 20 OCPs and 16 CUPs detected here, only 11 OCPs and 24 CUPs combinations were detected across study areas. This highlights the low variability of both OCPs and CUPs combinations in air. For OCPs, for instance, this is likely a result of the substantial past use of specific OCPs (e.g., chlordane, heptachlor, endosulfan or DDT) (Dalvie and London, 2001; Dalvie et al., 2006) across agricultural areas, which are still nowadays heavily contaminated with these compounds. Some OCPs showing strong positive correlations (e.g., DDT isomers or γ -HCH), were even detected in concentrations in the same order of magnitude than CUPs. This not only highlights the heavy use of technical DDT and lindane in the past, but further emphasizes the still considerable contamination in the region. For CUPs, the low variability of combinations can be related to the different parameters affecting the presence of CUPs in air (e.g., different half-lives in soils and air, or different likelihood to undergo volatilization), which are not all well understood (Das et al., 2020; Socorro et al., 2016). Notwithstanding, from the detected combinations, positive correlations were found between triazine herbicides (atrazine, simazine and terbuthylazine), S-metolachlor (chloracetamide) and tebuconazole (triazole). Studies have shown that applying pesticide mixtures can delay pests' resistance to active ingredients, while increasing the target pest range of commercial products (Busi et al., 2019). Indeed, in South Africa, some products on the market (mainly herbicides) are already a combination of different active ingredients, either within the same chemical group (e.g., combinations of triazines), or different chemical groups (e.g., triazines and chloracetamides) (AVCASA, 2017), which corroborates the positive correlations found between these compounds. Notwithstanding, having in mind that the atmospheric residency time might be different amongst active ingredients, there might be an underrepresentation of CUPs mixtures in air compared to those found in commercial products. The main concern of pesticide mixtures (either OCPs/organophosphates or other CUP mixtures) is their potential deleterious cumulative and synergistic effects on accidental targets (such as humans), which is so far poorly understood (Lewis et al., 2016; Zhou et al., 2020).

5. Strengths and limitations

Our study had three main strengths: (i) this is the first study that provides joint insights on the air concentrations of several OCPs and CUPs across different agricultural regions in South Africa; (ii) the use of PUF-PAS showed to be a powerful tool, allowing to assess seasonal variations of several pesticides in air, over a consecutive year; and (iii) all the data are available on the Global ENvironmental ASsessment Information System (GENASIS, <https://www.genasis.cz/>), which provides information on air concentrations of CUPs and other chemicals (e.g., OCPs, flame retardants, dioxins and furans).

Further, there are two noteworthy limitations: (i) PUF-PAS only provides semi-quantitative measurements. Hence, the atmospheric concentrations, the presence/absence of pesticides, and OCPs ratios require a careful interpretation due to the unknown particle collection efficiency (Melymuk et al., 2014); (ii) this study did not target some other commonly used CUPs reported by farmers (e.g., mancozeb, glyphosate or neonicotinoids) (Curchod et al., 2020).

6. Conclusion

Our results show different spatial and seasonal patterns for 20 OCPs and 16 CUPs over one year. Concentrations of OCPs are likely to be deriving from volatilization from environmental matrices due to past

use. CUPs concentrations seem mainly driven by spraying seasons over the year. Similar concentrations detected at "farm" and "village" might result from atmospheric transport of pesticides from nearby farms. Finally, the joint and persistent detection of multiple pesticides in the group of OCPs, organophosphates, carbamates, triazines, chloracetamides and triazoles raise concerns for potential cumulative and synergistic health effects of these mixtures and should be further evaluated.

Author contributions

Samuel Fuhrimann, Mohamed Aqiel Dalvie, Martin Röösl, Lindile Masinyana, Lou Curchod, Céline Degrendele, Jana Klánová; were responsible for conception and planning. Samuel Fuhrimann, Mohamed Aqiel Dalvie, Lindile Masinyana and Lou Curchod were responsible for site selection and collection of data. Céline Degrendele, Petr Kukučka, Jakub Martíník, Petra Příbylová; were responsible for laboratory analysis and QA-QC. Adriana Fernandes Veludo, Samuel Fuhrimann and Daniel Martins Figueiredo were responsible for the analysis and interpretation of data. Adriana Fernandes Veludo, Samuel Fuhrimann, Daniel Martins Figueiredo and Céline Degrendele were responsible for the drafting of the manuscript. All authors participated in editing the final version of the manuscript.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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