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Quantitative assessment of multiple pesticides in silicone wristbands of children/guardian pairs living in agricultural areas in South Africa

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HIGHLIGHTS

- Assessed exposure to multiple pesticides in child/guardian pairs in the same household
- Targeted 21 and detected 16 current and past used pesticides on silicon wristbands
- The most frequently detected pesticides (>50%) were: Deltamethrin, chlorpyrifos, boscalid, cypermethrin and *p,p′*-DDT.
- Overall sharing the same household leads to similar exposures to pesticides.
- However, for several pesticides children had higher exposure levels than their guardians.

GRAPHICAL ABSTRACT

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ABSTRACT

Little is known about personal and time-integrated exposure to past and current used pesticides in agricultural areas and within-family exposure similarities. We aimed to assess exposure to pesticides using silicone wristbands in child/guardian pairs living on farms and in villages within two agricultural areas in South Africa.

Using silicone wristbands, we quantified 21 pesticides in child/guardian pairs in 38 households over six days in 2018. Levels (in ng/g wristband) of pesticides and their transformation products (12 current-use pesticides and nine organochlorine pesticides) were measured using GC–MS/MS. We assessed the correlation between pesticide levels and between household members using Spearman correlation coefficients (r_s). Multivariable generalized least squares (GLS) models, using household id as intercept, were used to determine level of agreement between household members, exposure differences between children and guardians and exposure predictors (study area, household location [farm vs. village] and household pesticide use).

We detected 16 pesticides with highest detection frequencies for deltamethrin (89%), chlorpyrifos (78%), boscalid (56%), cypermethrin (55%), and *p,p′*-DDT (48%). Most wristbands (92%) contained two or more pesticides (median seven (range one to 12)). Children had higher concentrations than guardians for four pesticides. Correlation between the pesticide levels were in most cases moderate (*rs* 0.30–0.68) and stronger in children than in guardians. Five pesticides showed moderate to strong correlation between household members, with the strongest correlation for boscalid

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(r_s 0.84). Exposure differences between the two agricultural areas were observed for chlorpyrifos, diazinon, prothiofos, cypermethrin, boscalid, *p,p′*-DDT and *p,p′*-DDE and within areas for cypermethrin.
We showed that for several pesticides children had higher exposure levels than guardians. The positive correlations observed for child/guardian pairs living in the same household suggest non-occupational shared exposure pathways in these communities.

1. Introduction

Living in areas with intensive agriculture production has been shown to result in increased exposure to multiple pesticides (Brouwer et al., 2017) and is linked to adverse health outcomes in farmers, resident populations and their children (English et al., 2012; Gunier et al., 2017). In addition, living in the same household has been suggested to result in similar exposure levels for selected pesticides (Bravo et al., 2020). Most studies on residential pesticide exposure are either based on measurements of short-term urinary biomarkers (Bravo et al., 2020), self-reported pesticide-related activities and behaviors (Chetty-Mhlanga et al., 2020), or land-use-based pesticide exposure estimates (Brouwer et al., 2017). These pesticide exposure assessment methods are limited by several factors: (i) the number of pesticides investigated; (ii) the assessment of short-term exposure windows; (iii) possible reporting bias in the case of self-reported pesticide use from farmers, or misclassification of pesticide use when reported by experts; and (iv) ignoring individual behavior in environmental exposure modeling studies. These limitations are often compounded by practical problems when performing studies in vulnerable populations in remote areas. To overcome some of these limitations, tools such as silicone wristbands have been proposed that enable measurement of time-integrated exposure to multiple chemicals (Doherty et al., 2021; Hammel et al., 2020; Travis et al., 2020; Wise et al., 2020).

In South Africa, more than 3000 pesticide products are registered for agriculture use to control pests (CropLife, 2017; Dabrowski et al., 2014). Previous studies reported the presence of multiple current used pesticides but also legacy pesticides (e.g., organochlorine pesticides (OCPs), which are nowadays banned for agriculture use) in environmental matrices such as water (Curchod et al., 2019; Dalvie et al., 2003; Horak et al., 2021) and air (Degrendele et al., 2021; Fuhrimann et al., 2020; Klánová et al., 2009; Veludo et al., 2021). Other studies investigating human urinary biomarkers indicated that farmers and residents living on farms in the Western Cape in South Africa had higher levels of pyrethroid and organophosphate biomarkers than in other settings (Dalvie et al., 2011; Motsoeneng and Dalvie, 2015; Mwanga et al., 2016). However, there is limited data on cumulative personalized exposure overtime or on pesticide mixtures within and between exposure groups (e.g., at household level and agriculture areas).

We aimed to quantitatively assess exposure to multiple current used and legacy pesticides and their transformation products using silicone wristbands in children and their guardians living in the same household in two areas with intensive agriculture in South Africa. There were three main research questions investigated: (i) are there different exposure profiles in children and guardians?; (ii) is living at the same household resulting in similar pesticide exposure levels?; and (iii) does living in the same agricultural area, sharing the same household location (farm vs. village) or using household pesticide predict pesticides exposure levels?

2. Methods

2.1. Study population

We contacted 40 child/guardian pairs from the Child Agriculture Pesticide Cohort Study in South Africa (CapSA) (Fig. 1a). Households were purposely selected alongside the main urine sampling round of all 1000 children participating in CapSA. This to ensure to have equal numbers of the child/guardian pairs (n = 20) in the two agricultural areas (Grabouw, dominantly pomme fruits (34°09′16.8″S 18°59′56.7″E); and Hex River Valley, dominantly table grape (33°28′34.7″S 19°39′51.9″E)) and to have half of the households on farms (within 50 m from agricultural land use) and half in nearby villages (at least 0.5 km away from the closest agricultural land use). Sampling was conducted during the main pesticide spraying season in Grabouw between 23.10 and 29.10 and in Hex River Valley between 31.10 and 6.11 in 2018.

2.2. Data collection

We administered children and guardians separate structured questionnaires that were developed for the CapSA study (Chetty-Mhlanga et al., 2018). For children, the questionnaire included questions on socio-demographic characteristics (e.g., sex, age, education), activities on the farm (i.e., picking fruits or helping with other tasks), and leisure activities (i.e., swimming in ponds or spending time in agricultural fields). For guardians, the questionnaire included questions on socio-demographic characteristics, occupation and household pesticide use.

In each study site, a child and their guardian each received a silicon wristband to put on their right wrist. Two sizes of uncolored silicone wristbands were used (for children size 1.9 ∗ 11 ∗ 177 mm; guardians' size 1.9 ∗ 11 ∗ 210 mm; MyExposome Inc., Corvallis; US). Participants were asked to wear it for six days constantly (i.e. also during showering and sleeping times). For each study area, one pre-packed wristband was taken along as a field-blank to observe if there was cross-contamination during packing and transportation of the samples. Children were checked every morning at school if they still were wearing their wristbands. After six days, wristbands were collected and stored in the original airtight mylar bag (DS M&T Inc., Fontana, US). The bags were then put in a dark box at room temperature and transported to the laboratory facility at the University of Cape Town within one day, where they were stored at −18 °C. Later they were shipped in a cool box at 0 °C to Wageningen Food Safety Research (WFSR), Wageningen University, the Netherlands, for analysis.

2.3. Selection of target pesticides

A total of 21 pesticides (18 insecticides and three fungicides) were selected for analysis (Table 1). Current used pesticides consisted of eight insecticides (five organophosphates, two pyrethroids, and one insect growth regulator) and three fungicides (two triazoles and one carboxamide). Legacy pesticides, previously used in large amounts in the study areas included two OCP insecticides and their degradation products: the *o,p′* and *p,p′* isomers of dichloro-diphenyl-trichloroethane (DDT) and its degradation products, dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) and alpha and beta isomers of endosulfan and its degradation endosulfan sulfate. Selection of pesticides was motivated by four factors (i) their current use in South Africa in agriculture indicated by a survey with local farmers (Curchod et al., 2019) and a list with currently registered pesticides in South Africa (CropLife, 2017; Curchod et al., 2019); (ii) their past use in agriculture (Dalvie et al., 2009a, 2009b); (iii) their potential use at household level (Tolosana et al., 2009); and (iv) the selection was limited to the analytical capacity of the selected laboratory method.

2.4. Silicone wristband pre-cleaning

Prior sampling, wristbands were conditioned at the MyExposome Inc. (Anderson et al., 2017). In an oven (VacuTherm Vacuum Oven, Thermo Fischer, Type: VT 6060 P) racks at 300 °C for 24 h with Nitrogen purges at

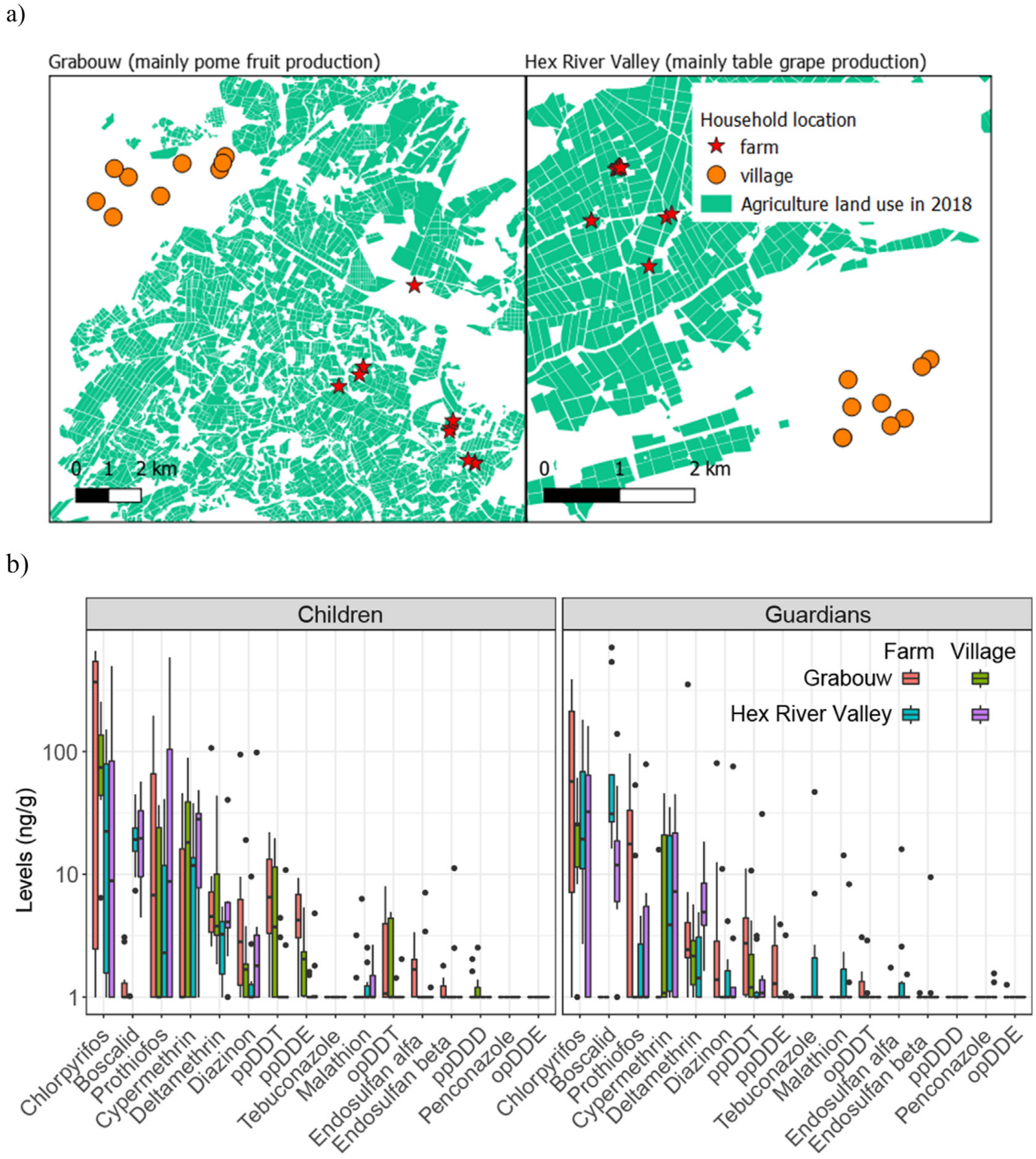

Fig. 1. a) Map showing the two study areas, the enrolled 38 households and the agriculture land use; b) box plots showing levels (ng/g) on log10 scale of all 16 pesticides detected above the limit of quantification. Level 1 = below limit of quantification (LOQ).

15, 30, 45, 60, 120, and 180 min, and every hour after that for 3 h. Once the 24 hour period had elapsed, the chamber was purged with nitrogen, and the oven was turned off to cool (approximately 3 h). Once cooled, wristbands were placed in a pre-cleaned jar and stored at 4 °C. After shipment to South Africa, wristbands were placed in individual ziplock mylar bags (DS M&T Inc., Fontana, US), pre-labeled with a serial number, sizing details, and blank instructions on when to remove the wristband during deployment.

2.5. Silicon wristband extraction

The extraction protocol was based on the methods described by Aerts et al. (2018). Samples were cut into 0.5 cm pieces with a scissor previously cleaned with ethyl alcohol and purified water. After this, each sample was placed into a 50 mL centrifuge tube and 20 mL ethyl acetate was added. The tubes were shaken head-over-head for 1 h. Then extracts were transferred to an evaporation flask and the solvent was evaporated to dryness in a water bath at 40 °C under nitrogen flow. Because ethyl acetate was used for extraction, lipids, squalene and fatty acids from the skin (Pappas, 2009), and thus present on the wristband, are co-extracted. Analysis of lipid-containing extracts may easily deteriorate GC performance (Grob and Kälin, 1991). Therefore, reconstitution was done in acetonitrile (good solubility for pesticides, low solubility for lipids) rather than a non-polar solvent, and a dispersive-solid phase extraction (dSPE) cleanup was performed as known from QuEChERS cleanup approaches (Anastassiades et al., 2003; Perestrelo et al., 2019). Here, C18 was used to remove lipids and squalene, and primary/secondary amine (PSA) to remove free fatty acids. For reconstitution/cleanup, the residue was reconstituted in 1 mL of acetonitrile and transferred to a tube already containing the two sorbents (25 mg of octadecyl silica (C18), 25 mg of PSA) and 150 mg of $MgSO_4$. These tubes were vortexed for 1 min and centrifuged for 5 min. Finally, 495 μL of extract were transferred to autosampler vials followed by the addition of 5 μL of PCB 198 solution (internal instrument standard, 1 μg/mL in acetonitrile) prior to injection into the gas chromatography coupled with tandem mass spectrometry system (GC–MS/MS).

Table 1
Characteristics and summary statistics of the 21 targeted pesticides levels (ng/g wristband) over six-sampling days, stratified by children and their guardians in the Western Cape in South Africa.

Active ingredient[a]	Group[b]	Type[c]	Spray[d]	Total (n = 76)			Children (n = 38)			Guardians (n = 38)		
				Detects[e] n (%)	Median (IQR)[f]	Max[f]	Detects[e] n (%)	Median (IQR)[f]	Max[f]	Detects[e] n (%)	Median (IQR)[f]	Max[f]
Deltamethrin	PYR	I	n/h	69 (90.8)	3.8 (2.9)	352.3	36 (94.7)	4.0 (2.8)	107	33 (86.8)	3.2 (2.9)	352.3
Chlorpyrifos	OP	I	y/h	61 (80.3)	61.1 (131.5)	658.5	29 (76.3)	84.1 (210.2)	658.5	32 (84.2)	29.5 (74.3)	386.1
Boscalid	CAR	F	w	44 (57.9)	18.5 (21.5)	704.6	26 (68.4)	14.0 (17.9)	56.9	18 (47.4)	27.5 (46)	704.6
Cypermethrin	PYR	I	y/h	43 (56.6)	20.2 (21.4)	88.6	24 (63.2)	20.5 (25.4)	88.6	19 (50)	15.9 (20.6)	45.6
p,p′-DDT	OCP	I	b/m	38 (50.0)	4.3 (9.0)	31.0	18 (47.4)	6.7 (9.5)	21.9	20 (52.6)	2.0.6 (3)	31.0
Diazinon	OP	I	n	35 (46.1)	3.0 (6.2)	98.4	22 (57.9)	2.9 (4.5)	98.4	13 (34.2)	3.0 (9.2)	80.5
Prothiofos	OP	I	y	35 (46.1)	28.9 (43.7)	582.6	20 (52.6)	37.1 (55.1)	582.6	15 (39.5)	14.5 (36.5)	96.5
p,p′-DDE	OCP	I	b/m	34 (44.7)	2.3 (2.9)	9.3	22 (57.9)	2.7 (2.9)	9.3	12 (31.6)	1.8 (2.1)	4.6
Endosulfan alfa	OCP	I	b	18 (23.7)	1.7 (1.4)	16	12 (31.6)	1.8 (1.7)	7.1	6 (15.8)	1.6 (1)	16.0
Malathion	OP	I	n	17 (22.4)	1.9 (1.2)	14.3	10 (26.3)	2.2 (1.1)	6.3	7 (18.4)	1.9 (4)	14.3
o,p′-DDT	OCP	I	b	16 (21.1)	3.0 (3.1)	8	10 (26.3)	4.3 (2.5)	8	6 (15.8)	1.5 (1.4)	3.1
Endosulfan beta	OCP	I	b	9 (11.8)	1.4 (1.4)	11.2	5 (13.2)	1.8 (1.1)	11.2	4 (10.5)	1.1 (2.1)	9.5
p,p′-DDD	OCP	I	b/m	5 (6.6)	1.6 (0.7)	2.5	5 (13.2)	1.6 (0.7)	2.5	Not detected		
Tebuconazole	TRI	F	y	4 (5.3)	4.8 (14.7)	46.9	Not detected			4 (10.5)	4.8 (14.7)	46.9
Penconazole	TRI	F	y	2 (2.6)	1.4 (0.1)	1.6	Not detected			2 (5.3)	1.4 (0.1)	1.6
o,p′-DDE	OCP	I	b/m	1 (1.3)	1.3 (0)	1.3	Not detected			1 (2.6)	1.3 (na)	11.3
Buprofezin	UNC	I	n	Not detected								
o,p′-DDD	OCP	I	b/m	Not detected								
Dimethoate	OP	I	n	Not detected								
Endosulfan sulfate	OCP	I	b	Not detected								
Lambda-cyhalothrin	PYR	I	n	Not detected								

IQR = interquartile ran.

[a] DDT = dichloro-diphenyl-trichloroethane; DDE = dichlorodiphenyldichloroethylene; DDD = dichlorodiphenyldichloroethane.

[b] Chemical group: PYR = pyrethroids; OP = organophosphate; CAR = carboxamide; OCP = organochlorine; TRI = triazole; UNC = unclassified.

[c] Type of use: I = insecticide; F = fungicide.

[d] Spray evidence: w = reported on spray record of interviewed farms in the week during the assessment; y = reported on spray record of interviewed farms in the year before the assessment; n = not reported but registered for agriculture use in South Africa; b = banned for agriculture use in South Africa; h = registered as household insecticide; m = registered for malaria control.

[e] n = detects above limit of detection (ng/g wristband).

[f] Levels in ng/g wristband.

2.6. GC–MS/MS analysis of the silicone wristband extracts

Instrumental analysis of the extracts was performed using a Bruker 300-MS GC–MS/MS system. Chromatographic separation was carried out on a Restek RTX CL Pesticides column (30 m × 0.25 mm, Df 0.25 μm). Sample injection (5 μL) was performed in a programmed temperature vaporizing (PTV) injector. The carrier gas used was Helium at a constant flow rate of 1.2 mL min^{-1}. The total run time was 26 min. For each pesticide, two transitions were measured. Identification was based on matching retention time and ion ratios (criteria see EC, 2019), and quantification against multi-level matrix-matched standards, after normalisation of the response to that of the internal standard.

2.7. Validation

Before analysis of the wristbands, the method was validated in line with procedures described in the EU guidance document for pesticide residue analysis (EC, 2019). For this, blank wristbands and spiked wristbands were analysed together with calibration standards. Parameters evaluated included selectivity, linearity of the response, average recovery and repeatability. For validation, single wristbands were cut into pieces as described above, and put into separate 50 mL extraction tubes (pieces of one wristband in one tube). The validation set consisted of 20 tubes/wristbands. Eight were not spiked, of which two were used a blank control, and the others for preparation of matrix-matched calibration standards (see below). The remaining twelve were used for recovery experiments and divided in sets of three, which were spiked at four different levels: 1, 5, 10 and 100 ng/g wristband material (corresponding to 3.8, 19, 38 and 380 ng of each pesticide per wristband). The spiking was done by pipetting a mix-solvent standard onto the wristband pieces in the tubes. The solvent was allowed to evaporate (approx. 30 min). All wristbands/tubes were extracted as described in Section 2.4. For preparation of matrix-matched standards, 485 μL of cleaned extract from the non-spiked wristbands were transferred into six autosampler vials, and 5 μL of internal standard (PCB198) was added. Then 10 μL of different concentrations of mix-calibration standard solutions was added to the autosampler vials to obtain matrix-matched standards of 0.5, 1, 5, 10, 50, and 100 ng/mL.

The non-spiked wristbands were found to be free of pesticides and interferences. Good linearity was observed ($R^2 > 0.994$, back-calculated concentrations mostly within 20% of the actual concentration) for the responses obtained for the matrix-matched calibration standards. The average recoveries at the highest level were in the range of 72%–98% (median 87%). At the lower levels, lower recoveries were obtained, typically in the 60%–70% range. The repeatability (RSD_r) was better than 10% in most cases. For details, see Supplementary information (SI) Table S1. The LOQ was set at the lowest level included in the validation for which good repeatability was observed (i.e. for all pesticides, 1 ng/g wristband (3.8 ng/wristband)).

2.8. Statistical analyses

Descriptive statistics were applied to present the percentage of individuals and combinations of pesticides above LOQ (i.e., quantified) and levels in ng/g on a wristband. The correlation between individual pesticide levels was assessed for all participants and separately in children and guardians using Spearman correlations coefficients (r_s) and was visualized using heatmaps and ciros plots. The correlation between pesticide levels in children and their guardians living in the same household was determined using Spearman correlations coefficients (r_s) and was visualized using scatter plots. Further, all pesticides which were detected (i.e., above LOQ) in 40% of the wristbands were imput. Imputation was done using maximum-likelihood based on log10 transformed pesticide values and area as a predictor, this estimation is accounting for both correlation and distribution of all pesticide data applying the R package "survival" (Lubin et al., 2004). Univariable and multivariable generalized least squares (GLS) models, using household id as intercept, were used to determine the level of agreement between household members (showing unadjusted (un-adj.) and adjusted (adj.) intraclass correlation coefficients (ICC)), exposure differences on the log 10 scale between children and guardians and exposure predictors (study area (Grabouw and Hex River Valley)), household location (farm and village) and household pesticide use (never, last year, last week). With an interaction term, study area and household location were separately looked at for children and guardians. Predictors were a-priori chosen based on findings from previous studies (Chetty-Mhlanga et al., 2020; Molomo et al., 2021). Across all analyses, *p*-values below 0.05 were considered statistically significant. Statistical analyses were done in R (Foundation for Statistical Computing, version 3.5.3, RStudio Version 1.1.4).

2.9. Ethical statement

Written informed consent was obtained from each guardian. The study received ethical clearance from the University of Cape Town's Research Ethics Committee (HREC 637/2018).

3. Results

3.1. Demographics of the study population

Out of 40 contacted households, 38 households (children/guardian pairs) with 76 participants completed the assessments (Table 2). The households paired in: 21 female guardian/male children, 14 female guardian/female children pairs, two male guardians/female child pairs and one male guardian/one male child pair. The households were equally distributed between the two areas (each 19 households), and slightly more households were located on farms (n = 20) than in villages (n = 18).

The children's median age was 12 (IQR two), 22 were males, and 16 were females. Potential pesticide exposure related activities during the week of the assessment were reported by the children as follows: observed any spraying activity (79%), engaging with any pesticide handling activities (55%), swimming in a pond or river (47%), helped to pick fruits (37%) and playing in agriculture field (26%).

Most guardians were women (92%) and the child's mother (82%). About a third of the guardians worked on a farm (37%), while most households had at least one member working on a farm (66%). In about half of the households, working clothes were brought home and washed there (55%), while more than half of the households (55%) used pesticides to control household pests during the sampling period. In total 12 different household pesticide products were obtained at home during the observation, including different pyrethoids (d-phenothrin, prallethrin, imiprothrin, cyphenothrin, d-trans-allethrin, alpha-cypermethrin), a organophospate (dichlorvos) and a carbamate (propoxur). Only alpha-cypermethrin was on our analysis target list and the product was only used by one household.

3.2. Pesticide detection

Out of the 21 targeted pesticides, 16 pesticides were detected above LOQ on the wristbands (Fig. 1b, Table 1). The median [range] number of pesticides detected in children's wristbands was seven [two to 11] and in their guardians five pesticides [one to 12]. Eight pesticides were present in more than 40% of the wristbands (deltamethrin (89%), chlorpyrifos (78%), boscalid (56%), cypermethrin (55%), *p,p′*-DDT (48%), prothiofos (45%), diazinon (44%), and *p,p′*-DDE (44%)). The highest median ng/g wristband [IQR] levels were measured for chlorpyrifos (61.1 [131.5]), followed by prothiofos (28.9 [43.7]) and cypermethrin (20.2 [21.4]) (Table 1, Fig. 1b). In 92% of the wristbands, two or more pesticides were found (Tables 1). Among the pesticides which were detected in more than 40% of wristbands, a mix of the four pesticides boscalid, cypermethrin, chlorpyrifos and deltamethrin was detected in one-quarter of the participants (26%).

3.3. Correlation between detected pesticide levels

Levels of *p,p′*-DDT and *p,p′*-DDE were moderately strong correlated (r_s 0.72) (Fig. 2a), while the correlation between levels of chlorpyrifos, diazinon, malathion and prothiofos were weak to moderate (r_s between 0.27 and 0.58). Levels of *p,p′*-DDT, *p,p′*-DDE and chlorpyrifos were also moderately correlated (r_s between 0.48 and 0.42). Several correlations were different when separately looking at the children and guardian sub-samples (SI Fig. S2b and c). For example, the correlation between *p,p′* and *o,p′* DDT and DDE was stronger in children than in guardians (r_s of 0.81 versus 0.68). On the other hand, guardians had stronger positive correlations for malathion with boscalid (0.56 versus 0.13), chlorpyrifos with deltamethrin (0.35 versus 0.03) and boscalid and chlorpyrifos (r_s 0.16 versus -0.33).

3.4. Correlation of pesticide levels between child and guardian pairs

Correlation between child and guardian pairs were strong for boscalid (*rs* 0.84), while the other seven pesticides showed moderate correlations (0.28–0.58) (Fig. 3). Similarly, the ICCs showed a strong agreement for boscalid within household pairs. However, when adjusted for the relevant

Table 2
Socio-demographic and occupational characteristics of participating children and their guardians stratified by study area the Western Cape in South Africa.

Demographic and exposure variables number per household n (%)			Total	Area Grabouw	Area Hex River Valley
			38 (100)	19 (100)	19 (100)
Place of living		Farm	20 (52.6)	10 (52.6)	10 (52.6)
		Village	18 (47.4)	9 (47.4)	9 (47.4)
Child	Gender	Female	16 (42.1)	7 (36.8)	9 (47.4)
		Male	22 (57.9)	12 (63.2)	10 (52.6)
	Age in years (median, IQR)	years	(12; 2)	(12; 1)	(12; 0.8)
	Observed spraying	Yes	30 (78.9)	16 (84.2)	14 (73.7)
	Swum in a pond or river	Yes	18 (47.4)	9 (47.4)	9 (47.4)
	Played in agriculture field during measurement week	Yes	10 (26.3)	5 (26.3)	5 (26.3)
	Helped to pick fruits during measurement week	Yes	14 (36.8)	7 (36.8)	7 (36.8)
	Engaged with pesticide handling activities during measurement week	Yes	21 (55.3)	10 (52.6)	11 (57.9)
Guardian	Gender	Female	35 (92.1)	18 (94.7)	17 (89.5)
		Male	3 (7.9)	1 (5.3)	2 (10.5)
	Interviewed guardian works on farm	Yes	14 (36.8)	4 (21.1)	10 (52.6)
	Any household member working on a farm	Yes	25 (65.8)	10 (52.6)	15 (78.9)
	Any household member washes working clothes at home	Yes	21 (55.3)	6 (31.6)	15 (78.9)
	Any pesticide sprayed at home during measurement week	No	7 (18.4)	6 (78.9)	1 (5.3)
		Last year	10 (26.3)	6 (31.6)	4 (21.1)
		Last week	21 (55.3)	7 (36.8)	14 (73.7)

IQR = interquartile range.

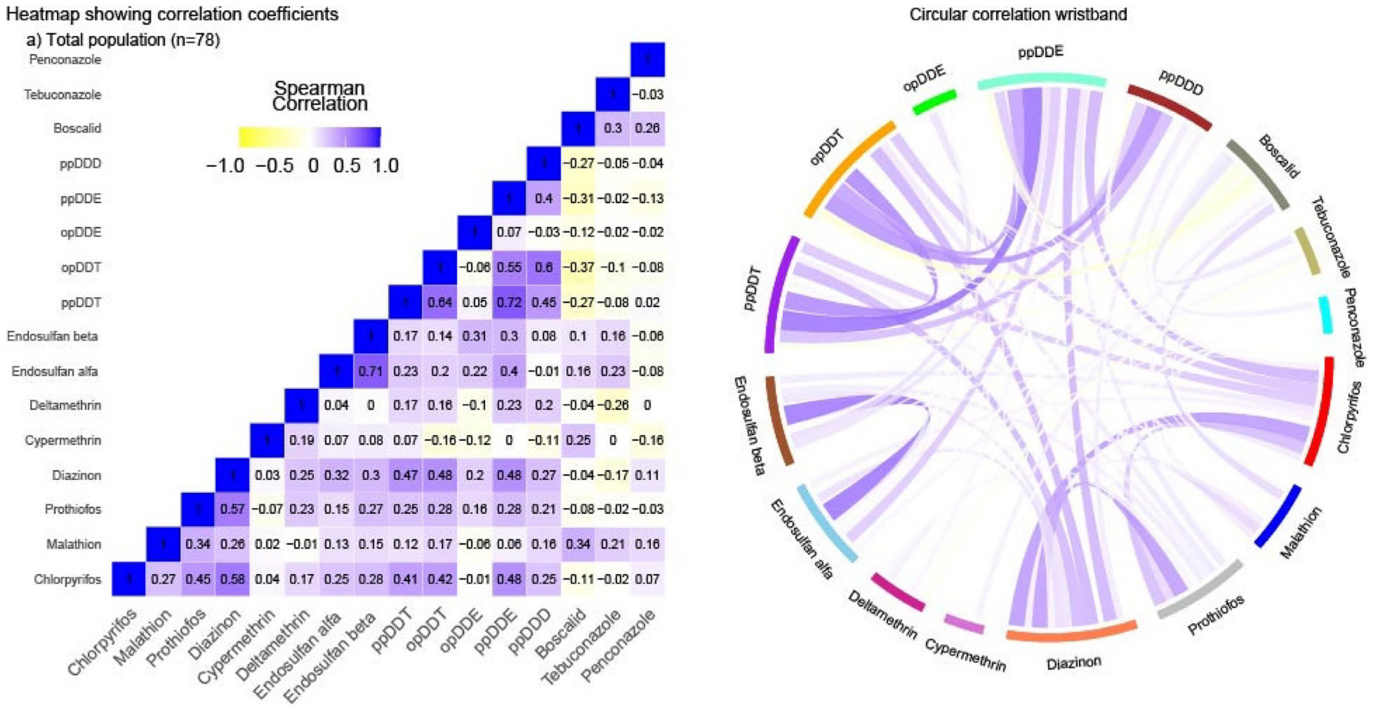

Fig. 2. Heatmap showing Spearman correlation coefficients and circular correlation plot of pesticide levels (ng/g wristband) of the 16 pesticides across all 76 participants.

predictors, the ICCs decreased considerably (unadj. 0.65 and adj. 0.17) (Table S3). Interestingly, the unadjusted and the adjusted ICCs for chlorpyrifos, *p,p′*-DDT, deltamethrin, diazinon were both showing a moderate agreement and only slightly changed due to the adjustment.

3.5. Determinants for the detected pesticide concentrations

GLS identified that children had higher concentrations than guardians for deltamethrin, *p,p′*-DDE, cypermethrin and *p,p′*-DDT (39, 32 29, and three-times higher, respectively) (Fig. 4 and Table S3). For several pesticides, differences between the two areas were found: children and guardians in Hex River Valley had higher levels of boscalid than those in Grabouw (geometric mean ratio (GMR) [95% confidence interval (CI)] of 301 [46; 1,966] and 1,646 [255; 10,632], respectively). Also, for guardians, higher cypermethrin levels (18 [2.6; 120]) were observed in Hex River Valley than in Grabouw (Fig. 4). In contrast, children in Hex River Valley had lower prothiofos (0.1 [0.01; 0.7]), chlorpyriphos (0.2 [0.04; 0.7]), *p,p′*-DDT (0.1 [0.03; 0.2]) and *p,p′*-DDE (0.2 [0.1; 0.3]) than in Grabouw. A difference between farm and village within an area could only be seen for cypermethrin, where guardians living on farms had higher levels (8.8 [1.3; 60.5]) than guardians living in villages. For pesticides used at home last week and last year, no significant different contrast could be observed to participants who never used pesticides at home.

4. Discussion

Using silicone wristbands, we detected 16 out of 21 targeted pesticides in children and their guardians (ten current-use pesticides in agriculture or on household level and six legacy OCPs). We quantified mixtures of current-used pesticides and legacy OCP on wristbands, with higher levels in children than their guardians. We showed that living in the same household can lead to similar exposure levels of individual pesticides, with greater within household similarities for pesticides which were recently applied. Further, for nine pesticides (chlorpyrifos, diazinon, prothiofos, cypermethrin, boscalid, *p,p′*-DDT and *p,p′*-DDE), important exposure differences could be observed for several pesticides between agriculture areas but only for cypermethrin within the areas (farm versus village).

Pesticides belonging to the chemical groups of the organophosphates and pyrethroids were detected in the majority of the participants. This is in line with the observed occurrence of the two chemical groups in resident populations in the study areas (Dalvie et al., 2011; Molomo et al., 2021; Motsoeneng and Dalvie, 2015; Mwanga et al., 2016) and in air (Degrendele et al., 2021; Fuhrimann et al., 2020; Veludo et al., 2021) and water (Curchod et al., 2019; Dalvie et al., 2003). Specifically, the organophosphates chlorpyrifos and prothiofos were detected in high concentrations on the wristbands, likely linked to ongoing use in the areas (recorded use in spray records in September and October 2018 (Curchod et al., 2019) and their long half-lives in the soil of up to a year (Lewis et al., 2016)). The two detected pyrethroids were previously reported to be used in households (deltamethrin; Tolosana et al., 2009) and on farms (cypermethrin; recorded on apple and table grape farm spray records in October 2018; Curchod et al., 2019). However, no association was found in our study between self-reported household pesticide use and deltamethrin, which could be due to the low sample size as a broad set of different pyrethroids insecticides are used in households. Interestingly, also pesticides banned for agricultural use (DDT and endosulfan and their degradation products) were detected in 50% of the wristbands. The detection of both DDT and endosulfan could be the result of historical use and contaminated soils around apple and grape farming areas respectively. Indeed, in the year before this study, our yearly passive air sampling indicated highest DDT levels in Grabouw and higher endosulfan levels in Hex River Valley during the same time of the year (Veludo et al., 2021). The high prevalence of detected DDT could also be explained by the use of obsolete stocks on farmers or leaking buried containers (Dalvie et al., 2006) or long-range transport from other areas in Africa, where it is still used for malaria control (Murray et al., 2018).

Other studies also reported on pesticides detected on wristbands; besides differences in their analysis techniques and pesticide use pattern, there are interesting comparisons to be made as similar pesticides were targeted and detected. Analogous to a study conducted in girls living in agricultural areas in the US with comparable exposure time (seven days) and LOQ (about 1 ng/g), our study showed the same prevalence of cypermethrin (in both studies 57%) (Harley et al., 2019), but a higher prevalence of DDT, deltamethrin and chlorpyrifos. Compared to a study using a

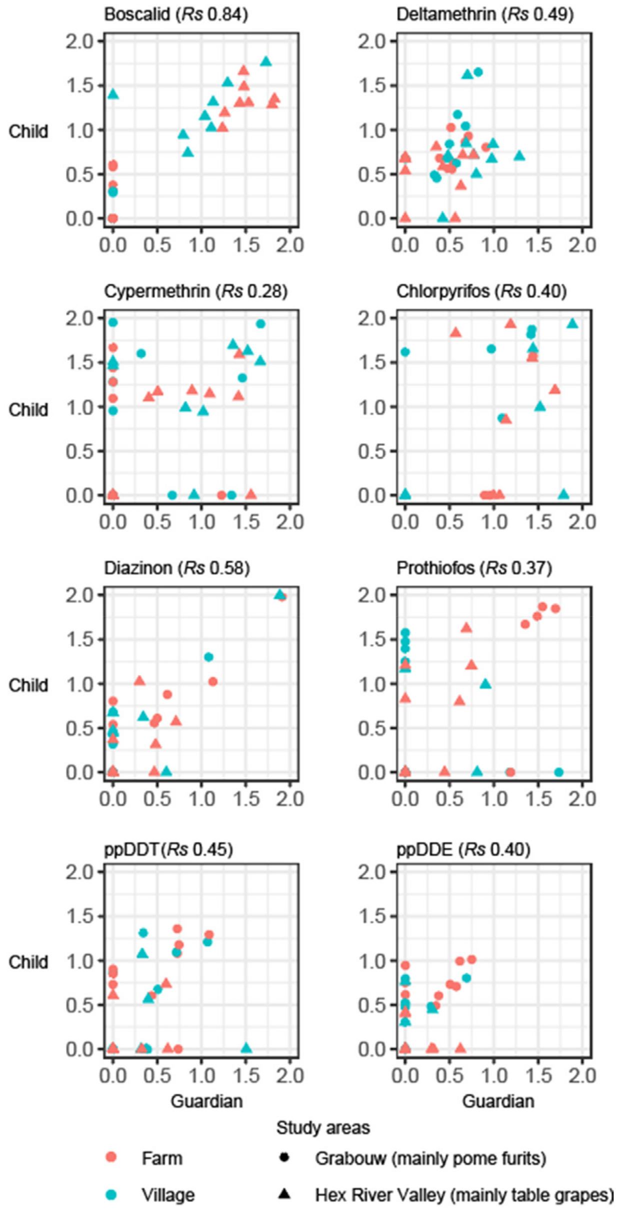

Fig. 3. Scatter plots showing levels (log(ng/g)) of the eight pesticides detected in more than 40% above the limit of detection (LOD) between children and their guardians living in the same household. *Rs* = spearman regression coefficient.

silicone wristband for seven days with 23 children in Uruguay, we detected a lower prevalence of DDE (45% versus 100%) and diazinon (46% versus 95%) (Travis et al., 2020). An explanation for our lower detection could be, next to the differences in farming systems, their considerably lower LOQs (30–100 times lower than in our study). In Belgium, boscalid was detected in lower prevalence than in our study (58% versus 7%) (Aerts et al., 2018), possibly due to a shorter exposure time (5-days and higher LOD 2 ng/g). Chlorpyrifos prevalence was similar to that in a study in Peru (86% versus 80%) even though participants in that study were wearing wristbands for 30 days compared to six days in our study (Bergmann et al., 2017). In a study in among farming families in Senegal, DDE (45% versus 37%) was detected with similar frequencies, while cypermethrin (57% versus 94%) was detected more frequently and chlorpyrifos (80% versus 51%) in lower frequencies than in our study (Donald et al., 2016).

Our comparable pesticide exposure levels between children and guardians living in the same household are pointing to shared non-occupational pathways for exposure. Correlations between mother/child pairs were also seen in urinary pyrethroid and organophosphate biomarkers in a study in Slovenia (Bravo et al., 2020). In our study, several pesticides showed to be different between the areas. In the example of boscalid, this resulted in a high correlation between household members and higher levels in Hex River Valley, where it was reportedly sprayed during the week of the sampling. This might be an indication of direct drift or prolonged evaporation after application. However, with the exception of cypermethrin, we could not see an exposure difference between participants living on a farm or in villages within an area. This contradicts with a study in the Netherlands (Vermeulen, 2019), where air and dust in the households on (<50 m) and in proximity to spraying sites (<250 m) were higher than in households further away (Figueiredo et al., 2021). For several pesticides, higher exposure was observed in children than in their guardians. This could be explained by different exposure pathways (Chetty-Mhlanga et al., 2020). For example, in our questionnaire interviews, children reported helping with pesticide handling, eating crops directly from the field, or playing in agriculture fields.

The pesticide mixtures across all 16 detected pesticides were, in most cases, different (up to 56 different combinations). Indeed, other studies using silicone wristbands also showed highly individualized exposure profiles (Aerts et al., 2018; Dixon et al., 2019). Nevertheless, a quarter of our participants were exposed to a mix including boscalid, cypermethrin, chlorpyrifos, and deltamethrin. Combined exposure to multiple pesticides could be deleterious, especially in vulnerable groups (Fuhrimann et al., 2021; Govarts et al., 2020). Most of these pesticides have known neurotoxic or endocrine disrupting potential and were in the cases of DDT, endosulfan and organophosphates frequently used and also detected in various environments in the two study areas for decades (Dalvie et al., 2006, 2003).

5. Conclusion

Using silicone wristbands in 38 child/guardian pairs, we detected 16 different pesticides over six days during the main spraying season in the Western Cape. This information on personal pesticide exposure to mixtures of 16 pesticides raises concerns for possible cumulative or syngergistic health effects. The magnitude of exposure is even expected to be underestimated as the study was only conducted over a week with a limited pesticide target list, due to methodological limitations not including some of the most sprayed pesticides (e.g., mancozeb, glyphosate and pesticides in the group of neonicotinoids). Finally, for most pesticides, children had higher exposure levels than guardians, while positive correlations were observed for child/guardian pairs living in the same household, suggesting shared (non-occupational) exposure pathways.

CRediT authorship contribution statement

Conceptualization and Methodology: SF, MR, AMD, CD, RV. SF, CD; Investigation: HM, JD: Formal analysis: SF, LP, DF, AH, RV. Visualization: SF; Writing - Original draft: SF: drafting of the manuscript. Writing - Review & editing: All authors.

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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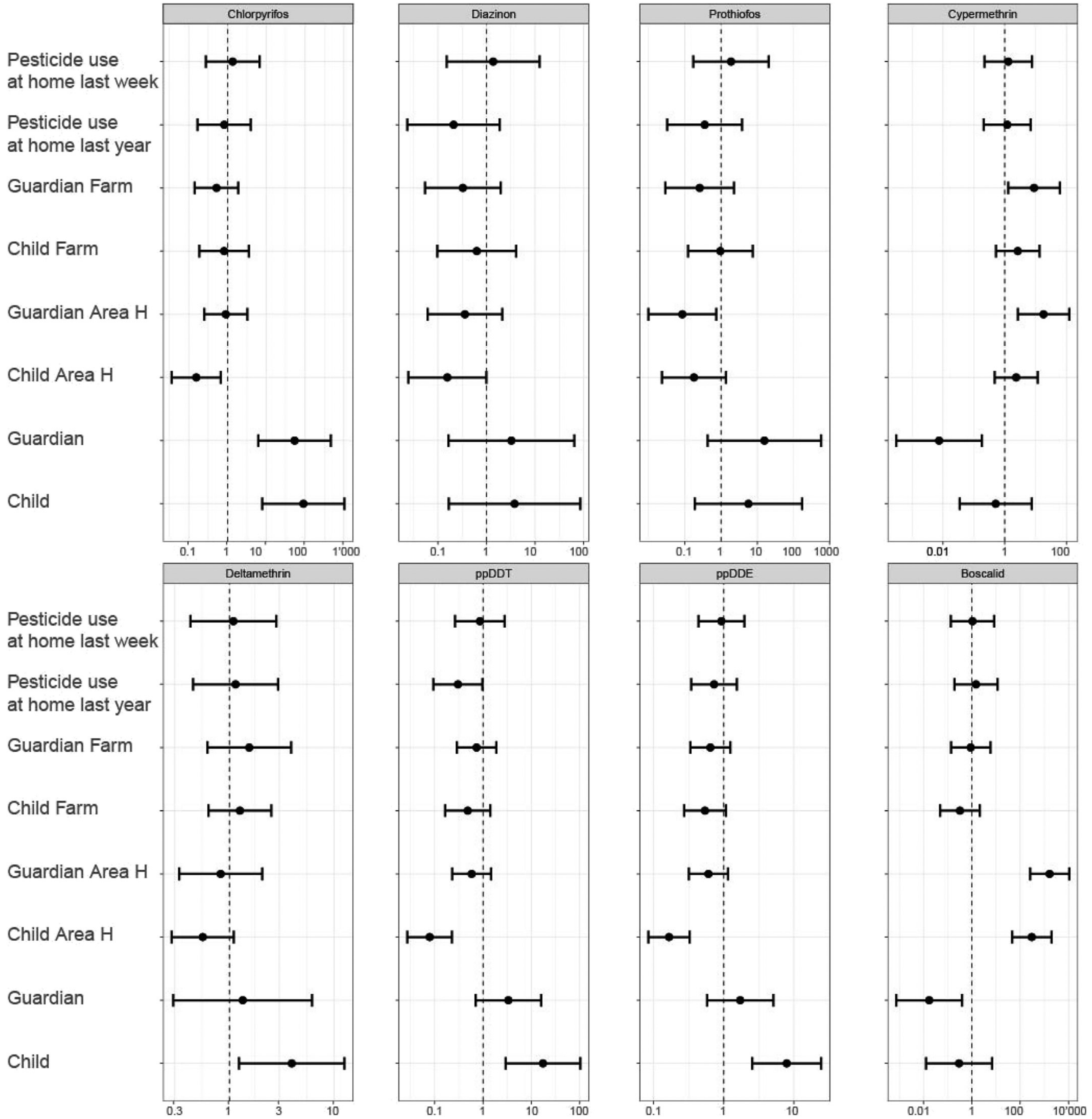

Fig. 4. Adjusted multivariable generalized least square models (GLSM) for the imputed exp(levels (ng/g)) of eight pesticides across all 76 participants. Pesticide use at home (reference (ref) 1: never used); area H: Hex River Valley (ref 1: Grabouw); farm (ref 1: village).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.152330.

References

Aerts, R., Joly, L., Szternfeld, P., Tsilikas, K., De Cremer, K., Castelain, P., Aerts, J.M., Van Orshoven, J., Somers, B., Hendrickx, M., Andjelkovic, M., Van Nieuwenhuyse, A., 2018. Silicone wristband passive samplers yield highly individualized pesticide residue exposure profiles. Environ. Sci. Technol. 52, 298–307. https://doi.org/10.1021/acs.est.7b05039.

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J. AOAC Int. 86, 412–431. https://doi.org/10.1093/jaoac/86.2.412.

Anderson, K.A., Points, G.L., Donald, C.E., Dixon, H.M., Scott, R.P., Wilson, G., Tidwell, L.G., Hoffman, P.D., Herbstman, J.B., O’Connell, S.G., 2017. Preparation and performance features of wristband samplers and considerations for chemical exposure assessment. J. Expo. Sci. Environ. Epidemiol. 27, 551–559. https://doi.org/10.1038/jes.2017.9.

Bergmann, A.J., North, P.E., Vasquez, L., Bello, H., Anderson, K.A., Ruiz, M.del C.G., 2017. Multi-class chemical exposure in rural Peru using silicone wristbands. J. Expo. Sci. Environ. Epidemiol. 27, 560–568. https://doi.org/10.1038/jes.2017.12.

Bravo, N., Grimalt, J.O., Mazej, D., Tratnik, J.S., Sarigiannis, D.A., Horvat, M., 2020. Mother/child organophosphate and pyrethroid distributions. Environ. Int. 134, 105264. https://doi.org/10.1016/j.envint.2019.105264.

Brouwer, M., Kromhout, H., Vermeulen, R., Duyzer, J., Kramer, H., Hazeu, G., de Snoo, G., Huss, A., 2017. Assessment of residential environmental exposure to pesticides from agricultural fields in the Netherlands. J. Expo. Sci. Environ. Epidemiol. 1–9. https://doi.org/10.1038/jes.2017.3.

Chetty-Mhlanga, S., Basera, W., Fuhrimann, S., Probst-Hensch, N., Delport, S., Mugari, M., Van Wyk, J., Roosli, M., Dalvie, M.A., Röösli, M., Dalvie, M.A., 2018. A prospective cohort study of school-going children investigating reproductive and neurobehavioral health effects due to environmental pesticide exposure in the Western cape, South Africa: study protocol. BMC Public Health 18, 857. https://doi.org/10.1186/s12889-018-5783-0.

Chetty-Mhlanga, S., Fuhrimann, S., Basera, W., Eeftens, M., Röösli, M., Dalvie, M., 2020. Association of activities related to pesticide exposure on headache severity and neurodevelopment of school-children in the rural agricultural farmlands of the Western cape of South Africa. Environ. Int. 146. https://doi.org/10.1016/j.envint.2020.106237.

CropLife, 2017. CropLife South Africa agricultural remedies database 2017. CropLife South Africa.

Curchod, L., Oltramare, C., Junghans, M., Stamm, C., Dalvie, M.A., Röösli, M., Fuhrimann, S., 2019. Temporal variation of pesticide mixtures in rivers of three agricultural watersheds during a major drought in the Western Cape, South Africa. Water Res. X 6, 1–12. https://doi.org/10.1016/j.wroa.2019.100039.

Dabrowski, J.M., Shadung, J.M., Wepener, V., 2014. Prioritizing agricultural pesticides used in South Africa based on their environmental mobility and potential human health effects. Environ. Int. 62, 31–40. https://doi.org/10.1016/j.envint.2013.10.001.

Dalvie, A.M., Africa, A., London, L., 2006. Disposal of unwanted pesticides in Stellenbosch, South Africa. Sci. Total Environ. 361, 8–17. https://doi.org/10.1016/j.scitotenv.2005.09.049.

Dalvie, Mohamed Aqiel, Africa, A., Hassan, A., Solomons, A., London, L., Brouwer, D.H., Kromhout, H., Hassan, A., Solomons, A., London, L., Brouwer, D.H., Kromhout, H., 2009. Pesticide exposure and blood endosulfan levels after first season spray amongst farm workers in the Western Cape South Africa. J. Environ. Sci. Health B 44, 271–277. https://doi.org/10.1080/03601230902728351.

Dalvie, Mohamed A., Africa, A., London, L., 2009. Change in the quantity and acute toxicity of pesticides sold in south african crop sectors, 1994–1999. Environ. Int. 35, 683–687. https://doi.org/10.1016/j.envint.2008.12.004.

Dalvie, M.A., Cairncross, E., Solomon, A., London, L., 2003. Contamination of rural surface and ground water by endosulfan in farming areas of the Western Cape, South Africa. Environ. Health 2, 1. https://doi.org/10.1186/1476-069X-2-1.

Dalvie, M.A., Naik, I., Channa, K., London, L., 2011. Urinary dialkyl phosphate levels before and after first season chlorpyrifos spraying amongst farm workers in the Western cape, South Africa. J. Environ. Sci. Health B 46, 163–172. https://doi.org/10.1080/03601234.2011.535384.

Degrendele, C., Klanova, J., Prokes, R., Pribylová, P., Senk, P., Sudoma, M., Röösli, M., Dalvie, M.A., Fuhrimann, S., 2021. Current use pesticides in soil and air from two agricultural sites in South Africa: implications for environmental fate and human exposure. Sci. Total Environ. 150455. https://doi.org/10.1016/j.scitotenv.2021.150455.

Dixon, H.M., Armstrong, G., Barton, M., Bergmann, A.J., Bondy, M., Halbleib, M.L., Hamilton, W., Haynes, E., Herbstman, J., Hoffman, P., Jepson, P., Kile, M.L., Kincl, L., Laurienti, P.J., North, P., Blair Paulik, L., Petrosino, J., Points, G.L., Poutasse, C.M., Rohlman, D., Scott, R.P., Smith, B., Tidwell, L.G., Walker, C., Waters, K.M., Anderson, K.A., 2019. Discovery of common chemical exposures across three continents using silicone wristbands. R. Soc. Open Sci. 6, 181836. https://doi.org/10.1098/rsos.181836.

Doherty, B.T., Koelmel, J.P., Lin, E.Z., Romano, M.E., Godri Pollitt, K.J., 2021. Use of exposomic methods incorporating sensors in environmental epidemiology. Curr. Environ. Health Rep. 8, 34–41. https://doi.org/10.1007/s40572-021-00306-8.

Donald, C.E., Scott, R.P., Blaustein, K.L., Halbleib, M.L., Sarr, M., Jepson, P.C., Anderson, K.A., 2016. Silicone wristbands detect individuals’ pesticide exposures in West Africa. R. Soc. Open Sci. 3, 160433. https://doi.org/10.1098/rsos.160433.

EC, 2019. Analytical quality control and method validation procedures for pesticide residues analysis in food and feed. Document n° SANTE/12682/2019. European Commission, Brussel.

English, R.G., Perry, M., Lee, M.M., Hoffman, E., Delport, S., Dalvie, M.A., 2012. Farm residence and reproductive health among boys in rural South Africa. Environ. Int. 47, 73–79. https://doi.org/10.1016/j.envint.2012.06.006.

Figueiredo, D.M., Duyzer, J., Huss, A., Krop, E.J.M., Gooijer, Y., Vermeulen, R.C.H., 2021. Spatio-temporal variation of outdoor and indoor pesticide air concentrations in homes near agricultural fields. Atmos. Environ. 262, 118612. https://doi.org/10.1016/j.atmosenv.2021.118612.

Fuhrimann, S., Farnham, A., Staudacher, P., Atuhaire, A., Manfioletti, T., Niwagaba, C., Namirembe, S., Mugweri, J., Winkler, M., Portengen, L., Kromhout, H., Mora, A., 2021. Exposure to multiple pesticides and neurobehavioral outcomes among smallholder farmers in Uganda. Environ. Int. 152, 106477. https://doi.org/10.1016/j.envint.2021.106477.

Fuhrimann, S., Klánová, J., Přibylová, P., Kohoutek, J., Dalvie, M.A., Röösli, M., Degrendele, C., 2020. Qualitative assessment of 27 current-use pesticides in air at 20 sampling sites across Africa. Chemosphere 258, 127333. https://doi.org/10.1016/j.chemosphere.2020.127333.

Govarts, E., Portengen, L., Lambrechts, N., Bruckers, L., Den Hond, E., Covaci, A., Nelen, V., Nawrot, T.S., Loots, I., Sioen, I., Baeyens, W., Morrens, B., Schoeters, G., Vermeulen, R., 2020. Early-life exposure to multiple persistent organic pollutants and metals and birth weight: pooled analysis in four flemish birth cohorts. Environ. Int. 145, 106149. https://doi.org/10.1016/j.envint.2020.106149.

Grob, K., Kälin, I., 1991. Towards on-line SEC-GC of pesticide residues? The problem of tailing triglyceride peaks. J. High Resolut. Chromatogr. 14, 451–454. https://doi.org/10.1002/jhrc.1240140706.

Gunier, R.B., Bradman, A., Harley, K.G., Kogut, K., Eskenazi, B., 2017. Prenatal residential proximity to agricultural pesticide use and IQ in 7-year-old children. Environ. Health Perspect. 125. https://doi.org/10.1289/EHP504.

Hammel, S.C., Hoffman, K., Phillips, A.L., Levasseur, J.L., Lorenzo, A.M., Webster, T.F., Stapleton, H.M., 2020. Comparing the use of silicone wristbands, hand wipes, and dust to evaluate Children’s exposure to flame retardants and plasticizers. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.9b07909.

Harley, K.G., Parra, K.L., Camacho, J., Bradman, A., Nolan, J.E.S., Lessard, C., Anderson, K.A., Poutasse, C.M., Scott, R.P., Lazaro, G., Cardoso, E., Gallardo, D., Gunier, R.B., 2019. Determinants of pesticide concentrations in silicone wristbands worn by Latina adolescent girls in a California farmworker community: the COSECHA youth participatory action study. Sci. Total Environ. 652, 1022–1029. https://doi.org/10.1016/j.scitotenv.2018.10.276.

Horak, I., Horn, S., Pieters, R., 2021. Agrochemicals in freshwater systems and their potential as endocrine disrupting chemicals: a South African context. Environ. Pollut. 268, 115718. https://doi.org/10.1016/j.envpol.2020.115718.

Klánová, J., Čupr, P., Holoubek, I., Borůvková, J., Přibylová, P., Kareš, R., Tomšej, T., Ocelka, T., 2009. Monitoring of persistent organic pollutants in Africa. Part 1: passive air sampling across the continent in 2008. J. Environ. Monit. 11, 1952. https://doi.org/10.1039/b913415h.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk. Assess. 22, 1050–1064. https://doi.org/10.1080/10807039.2015.1133242.

Lubin, J.H., Colt, J.S., Camann, D., Davis, S., Cerhan, J.R., Severson, R.K., Bernstein, L., Hartge, P., 2004. Epidemiologic evaluation of measurement data in the presence of detection limits. Environ. Health Perspect. 112, 1691–1696. https://doi.org/10.1289/ehp.7199.

Molomo, R.N., Basera, W., Chetty-Mhlanga, S., Fuhrimann, S., Mugari, M., Wiesner, L., Röösli, M., Dalvie, M.A., 2021. Relation between organophosphate pesticide metabolite concentrations with pesticide exposures, socio-economic factors and lifestyles: A cross-sectional study among school BOYS IN the rural western cape, South Africa. Environ. Pollut. 275, 116660. https://doi.org/10.1016/j.envpol.2021.116660.

Motsoeneng, P.M., Dalvie, M.A., 2015. Relationship between urinary pesticide residue levels and neurotoxic symptoms among women on farms in the Western cape, South Africa. Int. J. Environ. Res. Public Health 12, 6281–6299. https://doi.org/10.3390/ijerph120606281.

Murray, J., Eskenazi, B., Bornman, R., Gaspar, F.W., Crause, M., Obida, M., Chevrier, J., 2018. Exposure to DDT and hypertensive disorders of pregnancy among South African women from an indoor residual spraying region: the VHEMBE study. Environ. Res. 162, 49–54. https://doi.org/10.1016/j.envres.2017.12.006.

Mwanga, H.H., Dalvie, M.A., Singh, T.S., Channa, K., Jeebhay, M.F., 2016. Relationship between pesticide metabolites, cytokine patterns, and asthma-related outcomes in rural women workers. Int. J. Environ. Res. Public Health 13. https://doi.org/10.3390/ijerph13100957.

Pappas, A., 2009. Epidermal surface lipids. Dermatoendocrinology 1, 72–76. https://doi.org/10.4161/derm.1.2.7811.

Perestrelo, R., Silva, P., Porto-Figueira, P., Pereira, J.A.M., Silva, C., Medina, S., Câmara, J.S., 2019. QuEChERS - fundamentals, relevant improvements, applications and future trends. Anal. Chim. Acta 1070, 1–28. https://doi.org/10.1016/j.aca.2019.02.036.

Tolosana, S., Rother, H.-A., London, L., 2009. Child’s play: exposure to household pesticide use among children in rural, urban and informal areas of South Africa. S. Afr. Med. J. 99, 180–184.

Travis, S.C., Aga, D.S., Queirolo, E.I., Olson, J.R., Daleiro, M., Kordas, K., 2020. Catching flame retardants and pesticides in silicone wristbands: evidence of exposure to current and legacy pollutants in Uruguayan children. Sci. Total Environ. 740, 140136. https://doi.org/10.1016/j.scitotenv.2020.140136.

Veludo et al., n.d.Veludo, A., Figueiredo, D., Degrendele, C., Röösli, M., Fuhrimann, F., n.d. Seasonal fluctuation of 25 currently used pesticides (CUPs) and 27 organochlorine pesticides (OCPs) in air across three agricultural areas in South Africa. Under Prep. Chemosph.

Vermeulen, R., 2019. Research on exposure of residents to pesticides in the Netherlands (OBO project). Utrecht University, Utrecht.

Wise, C.F., Wise, C.F., Hammel, S.C., Herkert, N., Ma, J., Ma, J., Motsinger-Reif, A., Stapleton, H.M., Stapleton, H.M., Breen, M., Breen, M., Breen, M., Breen, M., Breen, M., 2020. Comparative exposure assessment using silicone passive samplers indicates that domestic dogs are sentinels to support human health research. Environ. Sci. Technol. 54, 7409–7419. https://doi.org/10.1021/acs.est.9b06605.