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Current use pesticides in soil and air from two agricultural sites in South Africa: Implications for environmental fate and human exposure

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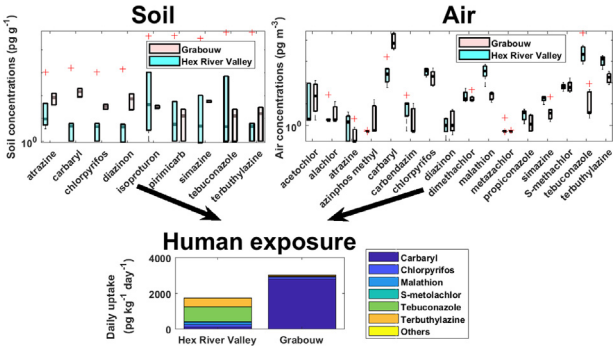
HIGHLIGHTS

- The levels of CUPs in African air and soils were reported for the first time.
- Out of 30 CUPs targeted, nine and 16 CUPs were found in soil and air, respectively.
- For chlorpyrifos, intake via soil ingestion could exceed the one from inhalation.
- Pesticide environmental exposure was influenced by the type of crop cultivated.
- The hazard risks via inhalation and soil ingestion of pesticides were negligible.

GRAPHICAL ABSTRACT



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ABSTRACT

Concerns about the possible negative impacts of current use pesticides (CUPs) for both the environment and human health have increased worldwide. However, the knowledge on the occurrence of CUPs in soil and air and the related human exposure in Africa is limited. This study investigated the presence of 30 CUPs in soil and air at two distinct agricultural sites in South Africa and estimated the human exposure and related risks to rural residents via soil ingestion and inhalation (using hazard quotients, hazard index and relative potency factors). We collected 12 soil and 14 air samples over seven days during the main pesticide application season in 2018. All samples were extracted, purified and analyzed by high-performance liquid chromatography coupled with tandem mass spectrometry. In soils, nine CUPs were found, with chlorpyrifos, carbaryl and tebuconazole having the highest concentrations (up to 63.6, 1.10 and 0.212 ng g^{-1}, respectively). In air, 16 CUPs were found, with carbaryl, tebuconazole and terbuthylazine having the highest levels (up to 25.0, 22.2 and 1.94 pg m^{-3}, respectively). Spatial differences were observed between the two sites for seven CUPs in air and two in soils. A large dominance towards the particulate phase was found for almost all CUPs, which could be related to mass transport kinetics limitations (non-equilibrium) following pesticide application. The estimated daily intake via soil ingestion and inhalation of individual pesticides ranged from 0.126 fg kg^{-1} day^{-1} (isoproturon) to 14.7 ng kg^{-1} day^{-1} (chlorpyrifos). Except for chlorpyrifos, soil ingestion generally represented a minor exposure pathway compared

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to inhalation (i.e. <5%). The pesticide environmental exposure largely differed between the residents of the two distinct agricultural sites in terms of levels and composition. The estimated human health risks due to soil ingestion and inhalation of pesticides were negligible although future studies should explore other relevant pathways.

1. Introduction

The global agricultural use of pesticides, or so-called plant protection products, has significantly increased from 2.3 million tonnes in 1990 to 4.1 million tonnes in 2018 (FAO, 2021) and this growth is expected to continue during the next decade (OECD, FAO, 2018). Consequently, concerns about their possible negative impacts on both the environment and human health have increased worldwide (Landrigan et al., 2017). Indeed, it has been recently estimated that more than 70% of global agricultural land was at ecological risk of pesticide pollution (Tang et al., 2021) and contain multiple pesticide residues (Tang and Maggi, 2021). Moreover, the presence of many pesticides (e.g. chlorpyrifos, diazinon) in remote locations (AMAP, 2017; Balmer et al., 2019; Gao et al., 2019; Hageman et al., 2006; Jantunen et al., 2015) suggests some are persistent enough to undergo long-range atmospheric transport. In addition, the frequent detection of pesticides in various matrices such as air (Coscollà et al., 2014; Désert et al., 2018; Yao et al., 2008), waters (Bradley et al., 2017; Mai et al., 2013), soils (Hvezdova et al., 2018; Silva et al., 2019), biota (Köhler and Triebskorn, 2013) or even human urine (Bravo et al., 2020; Fišerová et al., 2021) all over the world suggest their ubiquitous presence in the environment and subsequent exposure of biota and humans. Indeed, pesticide contamination has been related to declines in bees (Stanley et al., 2015; Woodcock et al., 2017) and insectivorous birds (Hallmann et al., 2014). In particular, the new generation of pesticides is associated with a considerable increase in toxicity to aquatic invertebrates and pollinators (Schulz et al., 2021). At the global level, exposure by pesticides has been considered as one of the main chemical threats on human health (Landrigan et al., 2017) as several CUPs (e.g. chlorpyrifos, carbaryl, terbuthylazine) are known to be carcinogenic, neurotoxic or are associated with adverse growth effects, disruption of the endocrine system and respiratory problems (FAO and WHO, 2016; Kim et al., 2017; Mamane et al., 2015; Mostafalou and Abdollahi, 2017; Zhang et al., 2018). Therefore, the potential risks of pesticides for the environment and human health exist and need to be assessed.

Pesticides on the market are chemically diverse and have been referred as the current use pesticides (CUPs), even though some are not anymore authorized for use at national or regional scales (e.g. atrazine, carbaryl or chlorpyrifos in Europe). CUPs used in crop farming can be coated on the seeds in order to protect the plant at its earlier growth phase (Lentola et al., 2020) or applied to the target crops via spraying techniques (Das et al., 2020; Perine et al., 2021). Upon emission, CUPs reach, in addition to the target crops, the agricultural soils where they can alter soil quality, soil biodiversity and transport of contaminants via water or wind erosion (Silva et al., 2019; Tang and Maggi, 2021). For example, the widespread presence of tebuconazole and terbuthylazine has been found in agricultural soils at the European scale (Hvezdova et al., 2018; Silva et al., 2019) but never studied in Africa. Besides soils, pesticides also represent a significant threat to the atmosphere as up to 2% and 30% of the pesticides will directly enter the air during seed planting (Lentola et al., 2020) and spraying (Van den Berg et al., 1999), respectively. In addition, days or weeks after agricultural activities, pesticides (e.g. metribuzin) can reach the atmosphere via revolatilisation from soils and vegetation (Davie-Martin et al., 2015; Degrendele et al., 2016a; Mamy et al., 2021; Taylor et al., 2020) or via wind erosion of soil particles on which pesticides (e.g. alachlor, simazine) are sorbed (Glotfelty et al., 1989). Once in the air, CUPs will partition between the gaseous and the particulate phases. This process is crucial regarding their environmental fate as it will influence their removal from the atmosphere (via photolysis, degradation or wet and dry deposition) (Feigenbrugel et al., 2006; Socorro et al., 2016; Wania et al., 1998; Zhang et al., 2013), and therefore, their mobility and their potential for long-range atmospheric transport. Because of their polarity, the gas-particle partitioning of CUPs differs from legacy pesticides (i.e. organochlorine pesticides) (Arp et al., 2008a, 2008b; Arp and Goss, 2009; Degrendele et al., 2016b; Götz et al., 2007), although the amount of field data remains largely limited for CUPs (Li et al., 2014; Sadiki and Poissant, 2008; Sauret et al., 2008; Schummer et al., 2010; Yao et al., 2008), particularly in Africa where it has never been studied. Previous studies have shown the presence of pesticide mixtures in air at agricultural, urban or remote locations in Europe (Coscollà et al., 2017; Degrendele et al., 2016b; Mai et al., 2013), North and South America (Nascimento et al., 2017; Wang et al., 2018), Asia (Li et al., 2014; Zhou et al., 2020) or Africa (Fuhrimann et al., 2020), but a quantitative assessment of atmospheric levels of multiple pesticides has never been done in Africa. CUPs present in soil and air contribute to human exposure via soil ingestion and inhalation (Coscollà et al., 2017; Doan et al., 2021; Hulin et al., 2021; Li et al., 2014; Morgan et al., 2014) and possible risks exist (López et al., 2017b), particularly for agricultural residents who are more likely to be exposed to higher levels of CUPs than the general population (Ohlander et al., 2019). However, these exposure pathways have never been assessed in Africa. In addition, the influence of the type of crops cultivated on the environmental exposure to pesticides has never been studied.

South Africa plays an important role in global agriculture and is one of the ten largest producers of various crops such as grapefruit, pears or green maize (FAO, 2021). As a consequence of its intensive farming, South Africa has registered about 700 different active ingredients for agricultural use (AVCASA, 2017), and is, therefore, the largest consumer of pesticides in Africa (Dabrowski et al., 2014; Gwenzi and Chaukura, 2018), contributing about one-third of all pesticides used on this continent (FAO, 2021). Subsequently, South Africa, with its semi-arid climate and high biodiversity, has been recently included among the top 30 countries susceptible to high pesticide pollution risk (Tang et al., 2021). Indeed, several studies already highlighted the presence of several CUPs in air (Dalvie et al., 2014; Fuhrimann et al., 2020), water (Curchod et al., 2020; Dabrowski and Balderacchi, 2013; Ojemaye et al., 2020), fish and food (Mutengwe et al., 2016; Rimayi et al., 2018) or human samples (Dalvie et al., 2014; Fišerová et al., 2021; Molomo et al., 2021). However, the knowledge on the potential risks of CUPs in South Africa for both the environment and human health is extremely limited. Previous studies have shown that chlorpyrifos levels in South African rivers exceeded the environmental quality standards (Curchod et al., 2020) while those of prochloraz in mangoes and permethrin in wheat exceeded the maximum residue limits (Dalvie and London, 2009; Mutengwe et al., 2016). In addition, a recent study has shown for South African children an association between pesticide exposure (e.g. working with pesticides or eating fruits) and several neurobehavioral outcomes (Chetty-Mhlanga et al., 2021). However, to the best of our knowledge, the human risks related to pesticide uptake via inhalation and soil ingestion have never been assessed for South African or even African citizens.

In order to fill these gaps, a field campaign took place in two agricultural areas where distinct crops are cultivated in Western Cape, South Africa, during the main season of pesticide application in 2018 where samples of soil and air (gas and particles) were collected. This study

took part within the larger project "Child health Agricultural Pesticide cohort study in South Africa" (CapSA), which is assessing the health impacts of pesticide exposure of 1000 children in South Africa (Chetty-Mhlanga et al., 2018). The aims of this specific study were to (i) characterize the occurrence of 30 CUPs in soil and air, (ii) assess the gas-particle partitioning of these CUPs at agricultural sites, (iii) compare the human exposure to these CUPs via soil ingestion and inhalation between the two sampling sites, and (iv) evaluate the health hazards via soil ingestion and inhalation related to these CUPs.

2. Methodology

2.1. Collection of soil and air samples

The sampling campaign took place in two different agricultural sites located in Western Cape, South Africa: Hex River Valley (33°28′S;19°38′E) and Grabouw (34°12′S;19°5′E) (Fig. S1 in the Supplementary Information). Each sampling site consisted of a small village (up to 30,000 habitants) surrounded by mountains within an agricultural area characterized by intensive monoculture. These two sampling sites, located about 110 km from each other (Fig. S1), were selected as they exhibited distinct crop-specific profiles with 98% of the agricultural lands used for table grapes in Hex River Valley and 81% for pome fruits in Grabouw (Curchod et al., 2020). The sampling campaign took place during the main season of pesticide application from the 22nd to the 29th of October 2018 in Hex River Valley and from 30th of October to 6th of November 2018 in Grabouw. At Hex River Valley, the weather was warm (i.e. minimum and maximum daily temperature of 11.6 °C and 38.5 °C) and dry (no precipitation), while at Grabouw, the weather was usually colder (i.e. minimum and maximum daily temperature of 4.4 °C and 31.1 °C) and precipitation events occurred on 30/10/18 (Day 1, 2.2 mm), 04/11/18 (Day 6, 12.2 mm) and 05/11/18 (Day 7, 16.6 mm).

Air was collected in the close vicinity (<20 m) of agricultural fields. At each site, seven consecutive daily samples were collected at the height of 91 cm above ground level using a medium volume air sampler (flow rate of 2.3 $m^3\ h^{-1}$, Leckel MVS6, PM_{10} inlet) collecting gaseous and particulate phases. The sampling duration ranged from 21 to 25 h, leading to a collected volume of 48.8–57.5 m^3. Particles were collected on quartz microfiber filters (QFFs, QMA, 47 mm, Whatmann, UK). Gaseous phase was collected on a PUF/XAD/PUF sandwich consisting of a layer of polyurethane foam (PUF, Molitan a.s., CZ, density 0.030 g. cm^{-3}, 5.5 cm diameter, 5 cm depth in total), a layer of XAD resin (Supelpak-2, Supelco, USA) and another PUF layer, separated by cotton wool, as this configuration has been shown to be the most efficient to collect gaseous pesticides (Dobson et al., 2006; López et al., 2017a, 2018). Prior sampling, PUFs and XAD-resins were pre-cleaned via Soxhlet-extraction with acetone and methanol for eight hours each.

At each site, soil samples were collected near (<50 m) the air sampler on the agricultural field (i.e. table grapes in Hex River Valley and pome fruits in Grabouw) at Day 1 and Day 7. For each sample, an area of about 10 m^2 was selected and nine individual soil sub-samples (uppermost 5 cm, horizon A) distanced about 1 m from each other were collected using a stainless steel spade. These sub-samples were mixed in a plastic container and reduced in volume (repeated three times in total). Triplicate samples of about 100 g of soil were collected and placed in a plastic storage container. In Hex River Valley, the soil was brownish-yellow, with fine sand, loose, single grain structure, and minimal vegetation. In Grabouw, the soil was brownish and consisted of a mixture of sand, clay and silt, full of nutrients from decomposed organic matter. Due to precipitation events that occurred prior the soil sampling in Grabouw, the collected soil samples were left overnight drying at ambient temperature.

All the samples taken were transported in a cooling box at 5 °C to the School of Public Health and Family Medicine at the University of Cape Town, where they were kept in a freezer at -18 °C until shipment to the RECETOX Centre.

2.2. Sample preparation

All air samples were extracted with methanol using an automated warm Soxhlet extractor (Büchi Extraction System B-811, Switzerland) 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 0.45 μm, Chromservis, Czech Republic) and were again concentrated.

Prior extraction, soil samples were dried at room temperature and sieved using a 2 mm mesh in order to remove impurities. The soil moisture was determined in each sample and the soil mass used to estimate the CUPs concentrations in soils in ng g^{-1} (dry weight) was corrected for the soil moisture. The extraction of the soil samples was done following a quick, easy, cheap, effective, rugged, and safe (QuEChERS) method (Anastassiades et al., 2003; Bruzzoniti et al., 2014; Lesueur et al., 2008; Y. Yu et al., 2016). About 5 g of soil was taken and placed into 50 mL centrifuge plastic tube. Then, 5 mL of distilled water and 10 mL of acetonitrile were added. The tubes were closed and shaken intensively for about one minute and placed under a ultrasonic bath for about 15 min. The Quechers extract pouch (i.e. consisting of 4 g of magnesium sulfate, 1 g of sodium chloride, 1 g of sodium citrate dehydrated and 0.5 g of sodium hydrogencitrate sesquihydrate) was added, and the tubes were quickly shaken and placed into ice to cool down for 5-10 min. The tubes were again manually shaken for about one minute and centrifuged for five minutes at 3000 rpm. Then, 5 mL of the supernatant acetonitrile was placed into a 20 mL vial and evaporated to almost dryness under a gentle stream of nitrogen and 1 mL of methanol was added.

2.3. Chemical analysis

CUPs were analyzed using an Agilent 1290 High-Performance Liquid Chromatograph (HPLC, Agilent, USA) consisting of a vacuum degasser, a binary pump, a thermostated autosampler (10 °C) and a thermostated column compartment kept at 30 °C. The column was a Phenomenex Luna C-18 endcapped (3 μm) 100 × 2.0 mm i.d., equipped with a Phenomenex SecureGuard C18 guard column (Phenomenex, Torrance, CA, USA). The mobile phase consisted of 0.1% formic acid in water (A) and 0.1% formic acid in methanol (B). The binary pump gradient was non-linear (increase from 50% B at 0 min (after 3.5 min column equilibration) to 80% B at 3 min, then increased to 95% B at 6.5 min, and then 100% B for 1.5 min), with a flow rate of 0.25 mL min^{-1}. For the analysis, 5 μL of the individual sample was injected. CUPs were quantified using a mass spectrometer (AB Sciex Qtrap 5500, AB Sciex, Concord, ON, Canada) with electrospray ionization (ESI+) in which ions were detected in the positive mode. The ionization parameters were as follows: capillary voltage, 5.5 kV; desolvation temperature, 400 °C; Curtain gas 15 psi, Gas1 40 psi, Gas2 30 psi. Identification of individual CUPs was based on a comparison of ion ratios and retention times (Table S1) with corresponding isotopically labelled standards and quantification was using internal standards: acetochlor-D11, alachlor-D13, atrazine-D5, carbendazim-D4, chlorotoluron-D6, chlorpyrifos-D10, dimethoate-D6, diuron-D6, fenitrothion-D6, isoproturon-D6, metamitron-D5, metazachlor-D6, metribuzin-D3, pendimethalin-D5, prochloraz-D7, propiconazole-D5, pyrazon-D5, simazine-D10, S-metolachlor-D6, tebuconazole-D6 and terbuthylazine-D5 (Toronto Research Chemicals, Canada; Dr. Ehrenstorfer LGC Standards, UK; Chiron AS, Norway; and Neochema, Germany). Analytes were quantified using isotope dilution method. Instrumental limits of detection and quantification (iLODs and iLOQs) were estimated as the quantity of analyte with a signal to noise ratio of 3:1 and 10:1, respectively, and are presented in Table S1, along the retention times.

In total, 28 samples of air (i.e. 14 QFFs and 14 sandwiches) and 12 samples of soil (i.e. four samples in triplicates) were analyzed for 30

CUPs including nine insecticides (i.e. azinphos methyl, carbaryl, chlorpyrifos, diazinon, dimethoate, fenitrothion, malathion, parathion methyl and pirimicarb), 17 herbicides (i.e. acetochlor, alachlor, atrazine, chlorotoluron, chlorsulfuron, dimethachlor, diuron, fluroxypyr, isoproturon, metamitron, metazachlor, metribuzin, pendimethalin, pyrazon, simazine, S-metolachlor and terbuthylazine) and four fungicides (i.e. carbendazim, prochloraz, propiconazole and tebuconazole) (Table S2). Among the 30 CUPs quantified (based on the analytical methods available), 27 have been registered for agricultural use in South Africa (AVCASA, 2017), 15 are among the most used pesticides globally (Maggi et al., 2019), 12 are characterized as priority active ingredients that need to be monitored in France (Hulin et al., 2021), five as highly hazardous pesticides and nine as high-risk pesticides (Jepson et al., 2020) (Table S2).

2.4. Quality assurance and quality control

In total, six field blanks (only for air, consisting of three QFFs and three sandwiches) and six solvent blanks (three for air and three for soil, consisting of the solvent used for extraction) were analyzed as per samples. In general, blank levels of most individual analytes were below detection or otherwise low (Table S3). However, for few CUPs, the levels found in the blanks were similar to or higher than those found in some of the environmental samples. This was the case in soils for atrazine, diazinon and isoproturon which had usually low levels in the environmental samples (see Section 3.1) and for chlorpyrifos, dimethachlor, pendimethalin and S-metolachlor in PUF/XAD/PUF and acetochlor and pendimethalin in QFF, for which the levels in field blanks were higher than those in solvent blanks (Table S3), suggesting some possible contamination during sampling and transport. The CUP concentrations reported here have been blank corrected by subtracting the average of the field blanks (solvent blanks for soil). Limits of quantification (LOQs) were determined as the maximum between the iLOQs and the average of the field blanks (solvent blanks for soil) plus three times their standard deviations (LOQb).

The recoveries were assessed from spike recovery tests of QFFs, PUF/XAD/PUFs and standard LUFA 2.2 soil. The CUP recoveries ranged from 72.9% ± 9.3% (azinphos methyl) to 112% ± 10.1% (terbuthylazine) for QFFs, from 40.1% ± 7.2% (diazinon) to 118% ± 5.7% (carbaryl) for PUF/XAD/PUF and from 74.5% ± 8.9% (chlorsulfuron) to 123.6% ± 11.5% (chlortoluron) in soil (Table S4). Besides few exceptions (i.e. chlorotoluron, dimethachlor and fenitrothion in soils and diazinon in PUF/XAD/PUF), all the procedural recoveries were in the range of 70-120% and had a standard deviation lower than 20%, demonstrating acceptable results in regard to accuracy and precision.

2.5. Human intakes via inhalation and soil ingestion

The daily intake of pesticides via inhalation ($DI_{inhalation}$, in pg day^{-1} kg^{-1}) was estimated based on the exposure assessment models developed within the US Exposure Factors Handbook (U.S. Environmental Protection Agency (EPA), 2011) as:

$$DI_{inhalation} = \frac{C_{air}, t \times IR \times ED}{AT \times BW}$$

where $C_{air,t}$ is the total (gas and particles) concentration (in pg m^{-3}) of a given pesticide, IR is the inhalation rate (in m^3 day^{-1}), ED is the exposure duration (unitless), AT is the averaging time (unitless) and BW is the body weight (in kg). All the input parameters used (U.S. Environmental Protection Agency (EPA), 2011) are provided in Table S5. In addition to inhalation, the daily intake via ingestion of soil ($DI_{ingestion\_soil}$, in pg day^{-1} kg^{-1}) was estimated as (U.S. Environmental Protection Agency (EPA), 2011):

$$Dingestion\_soil = \frac{Csoil \times IngRsoil \times ED}{AT \times BW}$$

where C_{soil} is the soil concentration (in pg g^{-1}) and $IngR_{soil}$ is the soil ingestion rate (in g day^{-1}, Table S5). We have assumed that the absorption factors related to the inhalation of particle-phase, gas-phase and to the soil ingestion were 1.00 for all CUPs investigated following the existing recommendations (EFSA, 2014; WHO, 2018). The estimation of these daily intakes was conducted for three subgroups: infants (i.e. 6 to 12 months), children (6 to 11 years) and adults (>21 years). For each of these subgroups, the daily uptakes were estimated using both the median and the maximum concentrations observed for each site in both air and soil.

In order to evaluate the possible health hazards related to the inhalation and soil ingestion of pesticides, the hazard quotients (HQs, unitless) of individual pesticides were estimated as:

$$HQ = \frac{Dinhalation + Dingestion\_soil}{RfD}$$

where RfD is the reference dose (in pg kg^{-1} day^{-1}). The RfDs used in this study, which represent chronic exposure, were the acceptable daily intake (ADIs, in pg kg^{-1} day^{-1}) from all routes of exposure rather than the acceptable operator exposure levels (AOELs) which considers only exposure via inhalation, and were obtained from European databases (Lewis et al., 2016) and are provided in Table S6. A HQ higher than 1 indicated that a potential risk exists.

The cumulative pesticide exposure for specific pesticide classes was estimated using Hazard Index (HI, unitless) or relative potency factors (RPFs, unitless) (Coscollà et al., 2017; Yusà et al., 2014). HI was used for those chloroacetamides and triazines, separately, as they have a same effect on target organs. For these two pesticide classes, HIs were estimated as:

$$HI = \sum HQn$$

where HQ_n is HQ of the nth pesticide belonging to the group of chloroacetamides or triazines. On the other hand, the RPF approach, which has been largely applied for dioxins and furans (Degrendele et al., 2014; Van den Berg et al., 2006) or polycyclic aromatic compounds (Degrendele et al., 2021; Tomaz et al., 2016) but also for neonicotinoids (Zhang et al., 2019; Zhou et al., 2020), was used for those pesticides which have the same mode of action, i.e. the carbamates, the organophosphates and the triazoles (Blaznik et al., 2016; Boon et al., 2008; van Klaveren et al., 2009; Li, 2018; Quijano et al., 2016). RPFs were estimated by normalizing the potencies (PEs) of all pesticides in a mixture to that of an index chemical (IC), which is well studied with an extensive toxicological database (Zhang et al., 2018), and is defined as (OECD, 2018):

$$RPFn = \frac{PEIC}{PEn}$$

where chemical n is a pesticide member of a cumulative assessment group (i.e. organophosphates, carbamates and triazoles). The pesticides carbaryl, chlorpyrifos and tebuconazole were selected as the ICs for the organophosphates, carbamates and triazoles, respectively. For organophosphates and carbamates, the potencies used were the benchmark doses at which acetylcholinesterase activity in brain of female rats was reduced by 10% compared to background activity (BMD_{10}, in pg kg^{-1} day^{-1}) (Boon et al., 2008; US EPA, 2005; Epa, 2002) while for triazoles, it was the no observed adverse effect level (NOAEL, in pg kg^{-1} day^{-1}) doses of liver toxicity (Cui et al., 2021; EFSA, 2009). The PEs and RPFs used in this study are shown in Table S6. The cumulative exposure (CE, in in pg day^{-1} kg^{-1}) for each of these three pesticide classes were determined as:

$$CE = \sum DIE \times RPF$$

Therefore, the CEs reported here for each selected pesticide chemical class are reported as pg equivalent to that index compound.

2.6. Data analysis

For statistical analysis and estimations of the human uptakes, when a compound was found in at least one sample, its concentrations which were lower than LOD, iLOQ or LOQb were assigned LOD/2, iLOQ/2 and LOQb/2, respectively. For acetochlor, the LOQb from the particulate phase was one order of magnitude higher than the one from gaseous phase, leading to higher uncertainties in the reported concentrations and particulate mass fractions.

Mann-Whitney tests were used to compare the differences between the two studied areas and the three population groups in terms of pesticide levels and daily pesticide intake. We considered a p-value <0.05 to be statistically significant.

3. Results

3.1. Levels of pesticides in soils

In this study, out of the 30 CUPs targeted, nine were quantified (i.e. >LOQ) in at least one of the soil samples collected in the two areas (Table S7). These were atrazine, carbaryl, chlorpyrifos, diazinon, isoproturon, pirimicarb, simazine, tebuconazole and terbuthylazine. In Hex River Valley, eight pesticides were quantified at least once in soils, while it was only six for Grabouw. Chlorpyrifos was found in all samples and had the highest concentrations (up to 63.6 ng g^{-1}, dry weight), followed by carbaryl (up to 1.10 ng g^{-1}), tebuconazole (up to 0.212 ng g^{-1}), simazine and terbuthylazine (up to 0.089 ng g^{-1}) while the other pesticides had lower concentrations (<0.100 ng g^{-1}) (Table S7, Fig. 1).

For most of the CUPs quantified, the soil concentrations were similar among the two study areas and the sampling days (Fig. 1, Table S7). However, chlorpyrifos levels were significantly higher in Grabouw compared to Hex River Valley, while the opposite was found for tebuconazole (Fig. 1). Although diazinon, isoproturon and pirimicarb were only found in Hex River Valley and carbaryl was only found in Grabouw, the differences between the two sites were not obvious due to the low levels and/or to the large variability within the triplicates (Table S7). The levels of atrazine and pirimicarb were higher on Day 1 compared to Day 7 in Hex River Valley, similar to simazine in Grabouw. The soil levels of chlorpyrifos in Grabouw increased about 45% from Day 1 to Day 7.

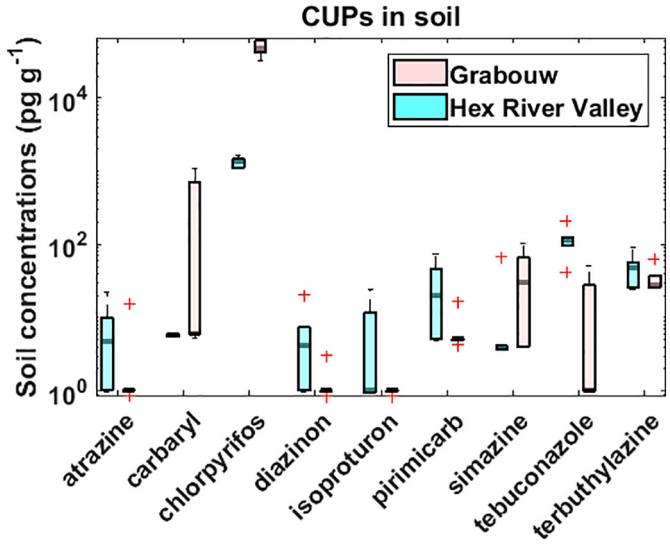

Fig. 1. Soil concentrations (pg g^{-1}) of individual CUPs in the two study areas in Western Cape, South Africa (N = 12). Boxplots represent the 25–75th percentile, whiskers represent the minimum and maximum values and the line within the box represents the median value.

3.2. Levels of pesticides in air

Among the 30 CUPs investigated, 14 pesticides consisting of nine herbicides (i.e. chlorotoluron, chlorsulfuron, diuron, fluroxypyr, isoproturon, metamitron, metribuzin, pendimethalin and pyrazon), four insecticides (i.e. dimethoate, fenitrothion, parathion methyl and pirimicarb) and one fungicide (i.e. prochloraz) were never quantified in the samples while seven CUPs (i.e. acetochlor, alachlor, atrazine, azinphos methyl, diazinon, dimathachlor and metazachlor) were found in 7–43% of the samples. On the other hand, carbaryl, chlorpyrifos, malathion, simazine, tebuconazole and terbuthylazine were quantified in every sample, while carbendazim, propiconazole and S-metolachlor were found in 50–79% of the samples (Tables S8-S9). The total (gas and particles) concentrations of individual CUPs measured at both sites spanned over five orders of magnitude and ranged from 0.181 pg m^{-3} (atrazine) to 25.0 ng m^{-3} (carbaryl) (Table S10, Figs. 2 and S2). Carbaryl, tebuconazole and terbuthylazine were the pesticides showing the highest concentrations (i.e. up to 25.0, 22.2 and 1.94 ng m^{-3}, respectively), followed by chlorpyrifos and malathion (0.1–1 ng m^{-3}), while the remaining pesticides usually had lower concentrations (<0.1 ng m^{-3}) (Fig. 2). Spatial differences in CUPs atmospheric levels across the two agricultural areas were found for seven CUPs. Indeed, the levels of malathion, propiconazole, simazine, tebuconazole and terbuthylazine were significantly higher in Hex River Valley, while carbaryl and azinphos methyl exhibited higher levels in Grabouw (Figs. 2 and S2).

A large dominance towards the particulate phase (i.e. the average measured particulate mass fraction $\theta > 0.800$) was found for all CUPs regardless of the sampling site investigated, except for acetochlor, alachlor (only in Grabouw) and dimethachlor which had an average θ of 0.299–0.647 (Tables 1 and S11).

3.3. Daily uptakes of pesticides (via inhalation and soil ingestion) and hazard risks

The daily uptakes via inhalation and soil ingestion of individual pesticides for infants, children and adults are presented in Tables S12–S13 while the total (i.e. inhalation and soil ingestion) daily uptakes are presented in Table S14 and, for children, in Fig. 3 (using median concentrations) and Fig. S3 (using maximum concentrations). The total daily intake of individual pesticides for infants, children and adults ranged

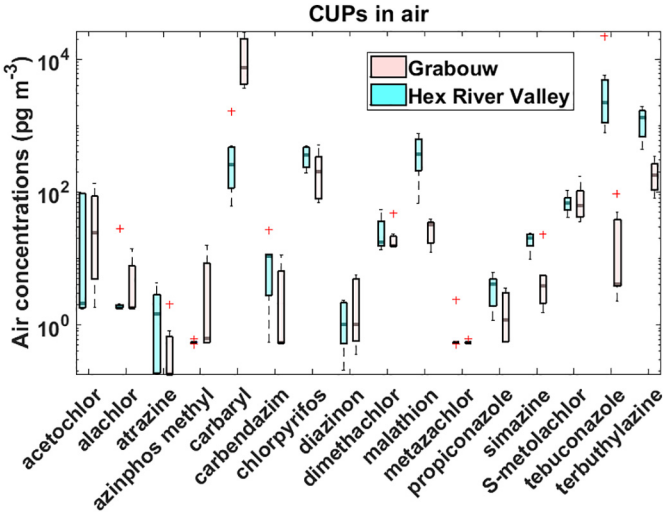

Fig. 2. Total (gas and particles) concentrations (in pg m^{-3}) of individual CUPs in air in the two study areas in Western Cape, South Africa (N = 14). Boxplots represent the 25-75th percentile, whiskers represent the minimum and maximum values (excluding outliers which are shown as the red crosses) and the line within the box represents the median value.

Table 1
Particulate mass fractions of individual CUPs measured in the two study areas in Western Cape, South Africa. Only the samples for which CUPs were >LOQ in at least one of the sampled phases were considered.

	N	Min	Max	Mean	Median	SD
Acetochlor	5	0.0368	0.897	0.349	0.0641	0.420
Alachlor	3	0.0658	0.969	0.647	0.906	0.504
Atrazine	6	0.890	0.979	0.947	0.952	0.0320
Azinphos methyl	3	0.961	0.983	0.971	0.969	0.0110
Carbaryl	14	0.985	1.00	1.00	1.00	4.70E-03
Carbendazim	7	0.967	0.990	0.976	0.976	0.0706
Chlorpyrifos	14	0.806	0.973	0.924	0.954	0.0589
Diazinon	6	0.958	0.984	0.969	0.967	0.0122
Dimethachlor	5	0.0517	0.674	0.299	0.292	0.256
Malathion	14	0.925	1.00	0.978	0.982	0.0239
Metazachlor	1	0.870		0.870	0.870	
Propiconazole	8	0.900	0.955	0.930	0.932	0.0186
Simazine	14	0.941	1.00	0.983	0.992	0.0192
S-metolachlor	11	0.686	0.916	0.800	0.791	0.0694
Tebuconazole	14	0.857	1.00	0.975	1.00	0.0432
Terbuthylazine	14	0.999	1.00	1.00	1.00	3.69E-04

Note: CUPs = current use pesticides, N = number of samples, Min = minimum, Max = maximum and SD = standard deviation.

from 0.126 fg kg^{-1} day^{-1} (isoproturon) to 14.7 ng kg^{-1} day^{-1} (chlorpyrifos) (Table S14). The pesticide uptake of infants was significantly higher (3.13 times) than those of adults, while no significant differences were observed between children and adults. The contribution of inhalation to the total daily intake is presented in Table S15. Besides those CUPs which were found only in one environmental matrice (i.e. pirimicarb and isoproturon in soils and acetochlor, alachlor, azinphos methyl, carbendazim, dimethachlor, malathion, metazachlor, propiconazole and S-metolachlor in air), soil ingestion generally represented a minor exposure pathway (i.e. <5%) compared to inhalation, although this was slightly higher for infants and children than for adults (Table S15) due to the higher soil ingestion rate for this age category (Table S5). However, in Grabouw, where high concentrations of chlorpyrifos were found in soils (Fig. 1), soil ingestion was as important as or even higher than uptake via inhalation (i.e. contributing for 7.70–56.3% to the total daily intake, Table S15).

Across the three population groups, the daily intakes of malathion, propiconazole, tebuconazole and terbuthylazine were significantly higher in Hex River Valley compared to Grabouwwhile those of carbaryl were significantly higher in Grabouw than in Hex River Valley (Fig. 3). In terms of chemical groups, triazoles and triazones were significantly higher in Hex River Vally, while those of carbamates were higher in Grabouw. Regarding pesticide types, the daily uptakes of herbicides and fungicides were significantly higher in Hex River Valley, while for insecticides, it was in Grabouw.

The composition profiles of daily uptakes of pesticides varied between Hex River Valley and Grabouw, both in terms of individual pesticides, chemical groups or pesticide types (Figs. 3 and S3). In terms of individual pesticides, daily intakes (determined using the median concentrations) for the three population groups were dominated by tebuconazole and terbuthylazine in Hex River Valley (contributing for 47.5% and 28.3%, respectively) and by carbaryl in Grabouw (91.7%). In terms of chemical groups, triazoles, triazines and organophosphates contributed to 47.6%, 28.8% and 15.8%, respectively, in Hex River Valley, while in Grabouw, carbamates dominated the daily intake (91.7%). Finally, in terms of pesticide types, in Grabouw, insecticides represented the largest share of pesticide uptakes (i.e. 96.3%), while in Hex River Valley, it was fungicides and herbicides (47.8% and 30.8%, respectively). No differences were found in Grabouw whether the median or the maximum concentrations were used. However, in Hex River Valley, the contribution of tebuconazole to the daily uptake from all pesticides shifted from 47.5% when using the median concentrations to 81.1% when the maximum concentrations were used (Figs. 3 and S3).

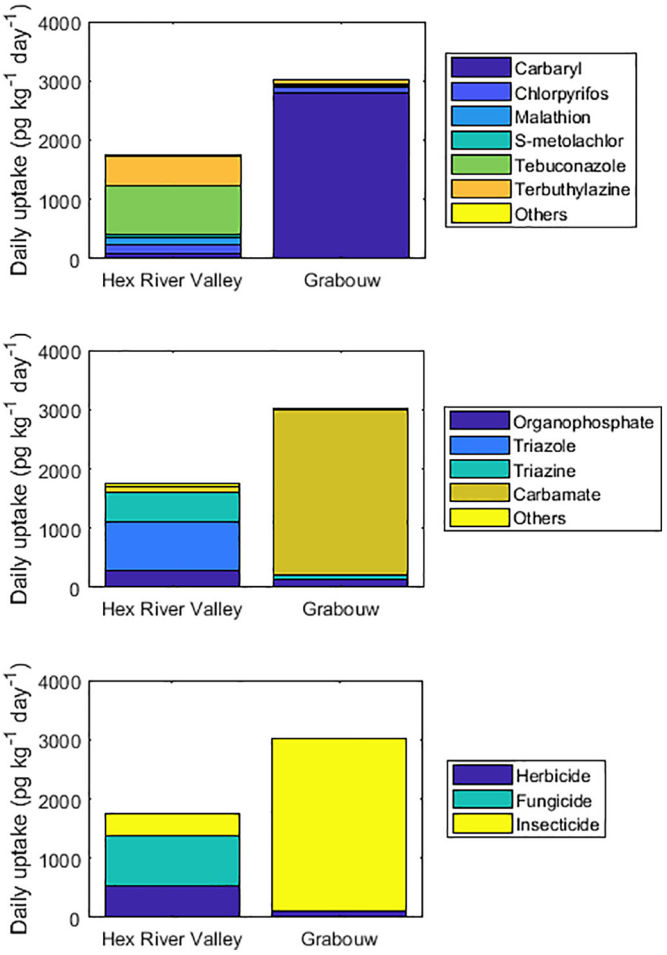

Fig. 3. Total (via soil ingestion and inhalation) daily intakes of pesticides categorized per active ingredient, chemical class and pesticide type for children using the median soil and air concentrations in the two study areas in Western Cape, South Africa.

All the hazard quotients estimated in this study were three to 12 orders of magnitude lower than one, with carbaryl, chlorpyrifos and terbuthylazine having the highest hazard quotients (up to 2.00E-03) (Table S16). Regarding cumulative exposure, the hazard indexes were ranging from 3.05E-07 to 2.39E-05 and from 8.65E-06 to 2.87E-04 for chloroacetamides and triazines, respectively (Table S17), suggesting negligible risks. The cumulative exposures estimated for organophosphates, carbamates and triazoles were 4.41E-08-5.23E-07, 4.87E-08-1.47E-05 and 1.74E-09-1.31E-05, respectively (Table S17). These were significantly lower (i.e. from three to eight orders of magnitude) than the acceptable daily intakes (Table S6) of the index chemicals (i.e. chlorpyrifos, carbaryl and tebuconazole, respectively), suggesting also minor risks.

4. Discussion

4.1. Presence of CUPs in soil and air

In the two study areas, out of the 30 targeted CUPs, 16 and nine were found in air and soil, respectively. While the presence of CUPs in agricultural soils is related to their past application, their presence in air could result from primary or secondary emissions but also from atmospheric transport at the regional or global scales. It is generally thought that CUPs are shortlived compounds in air and, therefore, not persistent. As such, their estimated half-lives are considerably lower than the one in soils (Table S2). However, one should keep in mind that there are large uncertainties with the reported half-lives of CUPs both in soils

and in air. Indeed, half-lives in soils are generally determined from laboratory experiments with aged pesticides that had bound more tightly to soils over time and might not represent the half-lives in actual field conditions (Boivin and Poulsen, 2017; Das et al., 2020; Fenner et al., 2013; Lewis et al., 2016). For example, half-lives of chlorpyrifos in soils reviewed by Mackay et al. (2014) were in the range of 7 to 30 days, while those determined from field experiments following fresh pesticide application were in the order of only few hours (Das et al., 2020; Ngan et al., 2005). In the air, the reported half-lives consider only the gas-phase reactions towards hydroxyl radicals (OH) as a major degradation pathway of pesticides in the atmosphere (Atkinson et al., 1999), while those occurring on the particulate phase with OH, ozone or nitrate, which are much slower (Mattei et al., 2019; Socorro et al., 2015), are neglected. For the less volatile pesticides which are mainly bound to particles, their real atmospheric half-lives might be considerably longer (Socorro et al., 2016). A recent field study supports the idea that pesticides might be more persistent in air than in soils as the authors determined half-lives of chlorpyrifos of 2 h and 13 h in soils and in the gas phase, respectively, although lower half-lives were reported in the particulate phase (i.e. 0.3 h), probably related to the settling of particles upon pesticide application (Das et al., 2020).

4.2. CUPs in soils

Besides the importance of agricultural soils, the knowledge on the presence of CUPs in African soils is rather limited (Mawussi et al., 2014). The results from this study highlight the simultaneous presence of pesticide mixtures in South African agricultural soils, which is consistent with previous studies based on field measurements in Europe (Hvezdova et al., 2018; Silva et al., 2019), or modeling at the global scale (Tang and Maggi, 2021). The presence of a pesticide in soils is related to its degradation half-life, water solubility and vapor pressure. Pesticides with a long half-life, low water solubility and low vapor pressure are more likely to persist in the soil after their initial application (Fu et al., 2020). Chlorpyrifos, which is among the five pesticides expected to be most frequently found in agricultural soils at the global scale (Tang and Maggi, 2021), was the only pesticide quantified in every soil sample (Table S7). Tebuconazole and terbuthylazine also had high quantification frequencies, similar to previous studies on European agricultural soils (Hvezdova et al., 2018; Silva et al., 2019). According to Lewis et al. (2016), the degradation half-lives in soil of chlorpyrifos, tebuconazole and terbuthylazine are 386, 63 and 72 days, respectively, suggesting some moderate to high persistence. Except for chlorpyrifos, the levels of CUPs quantified in South African soils were much lower (i.e. several orders of magnitude) than those found in 12 European countries (Hvezdova et al., 2018; Silva et al., 2019) (Table S18). Levels of chlorpyrifos were similar to those found in Europe (Hvezdova et al., 2018; Silva et al., 2019), New Zealand (Das et al., 2020) or China (Fu et al., 2020). In Grabouw, chlorpyrifos levels exceeded the generic soil limit value for non-chlorinated pesticides in the Czech Republic of 10 ng g^{-1} (MoE CR, 1994), but were 3-181 times lower than the median lethal dose for soil macroorganisms other than earth worms (i.e. 200 ng g^{-1}) (Lewis et al., 2016). The concentrations of the sum of co-occurring pesticides found in Hex River Valley (1.21-1.98 ng g^{-1}) were lower than the Dutch limit (i.e. 70 ng g^{-1}) (VROM, 2006), while those in Grabouw (i.e. 32.9-64.4 ng g^{-1}) were only slightly lower or close to it. Given the limited amount of pesticides targetted in this study, further assessment of the soil contamination by pesticides should be performed, particularly for Grabouw.

4.3. CUPs in air

The presence of pesticide mixtures was also found in air. In particular, six CUPs (i.e. carbaryl, chlorpyrifos, malathion, simazine, tebuconazole and terbuthylazine) were found in every air sample. These CUPs are known to be used for agricultural use in South Africa (AVCASA, 2017; Dabrowski et al., 2014), and except for terbuthylazine, they are also among the most used active ingredients applied to the six dominant crops (i.e. corn, soybean, wheat, cotton, rice and alfalfa) worldwide (Maggi et al., 2019). In addition, carbaryl, chlorpyrifos and simazine were identified among the pesticides requiring risk mitigation due to their possible harmful effects (Jepson et al., 2020) and tebuconazole among the priority pesticides to be monitored in France (Hulin et al., 2021). Carbaryl, chlorpyrifos and terbuthylazine were already frequently found in air at 20 sampling sites from 12 countries in Africa (Fuhrimann et al., 2020), chlorpyrifos and tebuconazole at six sites in Southern France (Désert et al., 2018) and terbuthylazine at six sites in the Valencia region in Spain (Coscollà et al., 2013). This highlights their widespread occurrence in air not only at the African scale but also worldwide, requiring further measures to reduce their potential negative environmental effects and the related human exposure.

Significant differences in the atmospheric concentrations of seven CUPs were observed between the two sites, with carbaryl and azinphos methyl being higher in Grabouw where pome fruits are cultivated and malathion, propiconazole, simazine, tebuconazole and terbuthylazine in Hex River Valley where agriculture is largely (98%) dominated by grape fruits. Out of these seven CUPs, only terbuthylazine exhibited similar spatial variations in air and in soil samples, while the soil levels of the remaining CUPs were similar between the two sites. In addition, levels of chlorpyrifos showed spatial differences in soils that were not seen in air. Soil levels of CUPs are only representative of specific agricultural fields where pesticides were applied, while air is generally representative of larger areas, affected by both primary emissions and by atmospheric transport from other source regions.

The atmospheric concentrations of CUPs were compared with those previously published worldwide (Table S19). The atmospheric levels of carbaryl, tebuconazole, terbuthylazine and malathion found in this study were generally much higher than those previously reported in France (Coscollà et al., 2010; Désert et al., 2018; Sanusi et al., 2000; Sauret et al., 2008; Schummer et al., 2010; Villiot et al., 2018), Spain (Coscollà et al., 2009, 2013, 2014; López et al., 2017b), Czech Republic (Degrendele et al., 2016b), Brazil (Nascimento et al., 2017), or in the North Sea (Mai et al., 2013). Besides the evidence of carcinogenicity of carbaryl (Kim et al., 2017), the few studies investigating its levels in ambient air reported lower levels (Table S19). Surprisingly, higher levels of simazine were recently reported in the Arctic Sea (Gao et al., 2019), suggesting ongoing transport to the Arctic. In general, chlorpyrifos levels found in this study were much higher than those found at remote sites such as in the Arctic (Balmer et al., 2019), in the Great Lakes (Wang et al., 2018) or in the Bohai Sea (Liu et al., 2018), at rural or urban sites in Canada (Hayward et al., 2010), Spain (López et al., 2017b), Czech Republic (Degrendele et al., 2016b), Brazil (Nascimento et al., 2017) or France (Désert et al., 2018), but considerably lower than those found in the USA (Bradman et al., 2007; Gibbs et al., 2017; Gordon et al., 1999) or, surprisingly, in indoor air in Australia (Wang et al., 2019) and South Korea (Kim et al., 2013). Worth to mention, atrazine levels found in this study were lower than those recently reported in Chicago and Cleveland in US where it is also allowed to be used (Wang et al., 2018). These comparisons highlight the spatial characteristics of pesticide use and their related atmospheric fate, with South Africa being a large pesticide user and pesticide emitter reflected by the relatively high concentrations of several pesticides found in the air.

4.4. Gas-particle partitioning of CUPs

The gas-particle partitioning observed in this study, with a large dominance towards the particulate phase of almost all CUPs is surprising. For the less volatile CUPs (e.g. carbendazim, diuron), this is consistent with previous studies (Degrendele et al., 2016b; Mai et al., 2013). However, atrazine, alachlor, metazachlor, S-metolachlor, tebuconazole and terbuthylazine were previously found to be distributed between the gaseous and the particulate phases (Degrendele et al., 2016b;

Sauret et al., 2008; Scheyer et al., 2008; Schummer et al., 2010). Similarly, chlorpyrifos, which has been one of the compound the most investigated in both atmospheric phases, was mainly found (i.e. $\theta < 0.3$) in the gas phase (Degrendele et al., 2016b; Sadiki and Poissant, 2008; Van Dijk and Guicherit, 1999) with some seasonal variations observed (i.e. $\theta = 0.27$-0.51 and 0.01-0.02 in winter and summer, respectively) (Li et al., 2014; Liu et al., 2018).

The large dominance of CUPs onto the particulate phase found in this study could arise from several factors. Firstly, one cannot exclude some possible contamination of the gas phase samples during sampling, transport and analysis, characterized by high limits of quantifications determined from the field blanks for several CUPs (see Section 2.f. and Tables S4 and S9). However, similar gas-particle partitioning results were found when using the raw results (i.e. without blank subtraction, Tables S11 and S20), which tends to limit this hypothesis.

Secondly, the gas-particle partitioning of CUPs, as for other organics, is influenced by several factors such as their physico-chemical properties (e.g. vapor pressure, octanol-air partition coefficient), the meteorological conditions (i.e. temperature, relative humidity and precipitation) but also the characteristics of ambient particles (Degrendele et al., 2016b; Sauret et al., 2008; Scheyer et al., 2008; Schummer et al., 2010). Because of their polarity, the gas-particle partitioning of CUPs is not only governed by absorption into organic matter, but also by adsorption onto the mineral or the soot constituents of the particles (Degrendele et al., 2016b; Götz et al., 2007). The aerosol composition was not determined in this study, and therefore its influence on the gas-particle partitioning of CUPs, if any, cannot be verified.

Thirdly, as this study occurred during the main season of pesticide application, we hypothesize that the pesticide formulation and/or application technique affected the gas-particle partitioning of CUPs through mass transport kinetics limitations (non-equilibrium), as previously suggested (Sadiki and Poissant, 2008; Scheyer et al., 2008). Two studies tend to support this hypothesis. Indeed, at a rural site in the Czech Republic, we have previously found that the particulate fraction of chlorpyrifos was about 10-times higher for two samples collected during the main pesticide application season (i.e. $\theta = 0.19$ and 0.33) compared to the remaining samples collected over two years (average $\theta = 0.04$) (Degrendele et al., 2016b). Moreover, in a recent study done in New Zealand investigating the fate of chlorpyrifos in air, soil and leaves following application to a field of purple tansy, Das et al. (2020) reported a particulate fraction of 0.36 in the 24 h following pesticide application, but only 0.09 in the 24–48 h and null (i.e. only in the gas-phase) 48–120 h after application. Several studies have shown that the formulation adjuvants, i.e. the other chemicals which are applied along the active ingredients during spraying activities, could largely affect the volatilization of pesticides from surfaces (Houbraken et al., 2015, 2018) or soils (Das and Hageman, 2020) and, therefore, affect their environmental fate (Grillo et al., 2021). In addition, the nozzle types used during spraying can also largely influence the droplet size (Perine et al., 2021) and therefore the pesticide capacity to evaporate from sprayed droplets. Considering the similarities of CUPs partitioning at the air-soil interface and at the gas-particle interface previously demonstrated (Degrendele et al., 2016b), one might suggest that the presence of adjuvants and/or the type of spraying technique used could greatly affect the gas-particle partitioning of pesticides, particularly during spraying activities, although more research in this area is certainly needed.

Fourth, given that OH concentrations in South Africa are up to 20 times higher than those in Europe (Spivakovsky et al., 2000), the gaseous degradation of CUPs, which is faster than the one on the particulate phase (Mattei et al., 2019; Socorro et al., 2015, 2016) might have been enhanced, leading to high particulate fractions. In addition, higher is the amount of pesticides coated on the surface of the particles, lower will be the degradation kinetics (El Masri et al., 2016; Mattei et al., 2019; Socorro et al., 2017). Therefore, one might suggest that upon pesticide application, the high density of pesticide molecules within the sprayed particles might favor their persistence in the particulate phase.

4.5. Human intake via inhalation and soil ingestion

To our knowledge, this is the first study performed in South Africa or even in Africa assessing the human exposure via inhalation and soil ingestion of a wide range of CUPs. The pesticide daily intakes of infants were significantly higher than those of adults, due to their lower body weights and inhalation rates and higher soil ingestion rates (Table S5), which is consistent with previous studies (Doan et al., 2021; Li et al., 2014; Zhou et al., 2020) and highlights that infants are a vulnerable group for pesticide exposure. Compared to inhalation, soil ingestion represented a minor pathway (i.e. <5% of the total daily intake) for most of the CUPs investigated, in agreement with previous studies (Morgan et al., 2014; Simcox et al., 1995). However, in the case of chlorpyrifos in Grabouw, in some cases, the uptake via soil ingestion was higher than from inhalation (Table S15). This highlights that this exposure pathway could be important and should be considered in future health impact assessment of pesticides, particularly for agricultural residents who are generally exposed to higher levels of pesticides than those in urban areas (López et al., 2017b; Zhou et al., 2020).

The daily intakes of pesticides via inhalation reported here were in the same range than those found in New Zealand (Wang et al., 2019), Vietnam (Doan et al., 2021), and USA (Morgan et al., 2014) but were considerably higher than those found in China (Li et al., 2014; Zhou et al., 2020) and Brazil (Nascimento et al., 2017) and much lower compared to those reported from Spain (López et al., 2017b) (Table S21). However, these comparisons should be taken with caution as every study analyzed a different amount and set of pesticides (Table S21), and therefore differences might not reflect differences in pesticide use and exposure. In addition, uncertainties exist with the absorption factors used in this study for inhalation and ingestion (i.e. 1.00 for all CUPs). Although these are the recommended values (EFSA, 2014; WHO, 2018), they only represent worst-case scenarios as, in reality, not all the CUPs inhaled or ingested would reach the target organs. Indeed, a recent and interesting modeling study estimated that the absorption factors related to the inhalation of 22 pesticides ranged from 0.62 to 1.00 and from 0.47 to 1.00 for the particle- and gas-phase, respectively (Wei et al., 2020). Unfortunately, absorption factors determined from this model or from experimental studies were not available for all CUPs investigated here, and therefore the reported daily intakes are likely to be overestimated by a factor up to two.

The levels and composition of pesticide environmental exposure was influenced by the type of crop cultivated as they differed largely between the residents of the two distinct agricultural sites (consisting for 98% of table grapes in Hex River Valley and for 81% of pome fruits in Grabouw). This highlights the significant role of crop-specific pesticide use on human exposure to pesticides, even within small spatial scales. For example, habitants living in Grabouw are exposed via inhalation and soil ingestion to carbaryl levels about 30 times higher than those in Hex River Valley. Similarly, habitants living in Hex River Valley are exposed to about 500 times higher levels of tebuconazole than those in Grabouw. Although these differences could be reflected in terms of pesticide class or pesticide type (Fig. 3), such comparisons should be taken with caution for several reasons. Firstly, not all the pesticides belonging to a specific class or type have been analyzed in this study (e.g. the organophosphates dichlorvos, tetrachlorvinphos or azamethiphos). Secondly, the toxicity of individual pesticides can vary greatly among a same pesticide class and/or type (Eddleston et al., 2005) and the effect of pesticide mixtures is still not well understood (Belden et al., 2007; Siviter et al., 2021). Last, the spatial variations observed for a specific pesticide class or type might not reflect the spatial variations of individual pesticides. For example, while carbamates levels were significantly higher in Grabouw compared to Hex River Valley, in reality, the two carbamates quantified exhibited different seasonal variations, with carbaryl being significantly higher in Grabouw and pirimicarb in Hex River Valley (although not significant) (Table S14). Similarly, while the daily intakes of organophosphates or chloroacetamides were not statistically

different between the two sites, clear spatial variations were observed for malathion. The same reflection could also hold considering the pesticide type. Therefore, future studies assessing human exposure to pesticides should focus on the basis of individual pesticide rather than by pesticide classes or types which may not be representative.

Even in the worst-case scenario, the health risks, estimated via hazard quotients for individual pesticides or via hazard index or relative potency factors for selected pesticide chemical groups were several orders of magnitude lower than the reference dose, which suggest a low health risk from inhalation and soil ingestion of pesticides in the studied areas. Low health risks were also found by many other studies (Doan et al., 2021; Li et al., 2014; López et al., 2017b; Nascimento et al., 2017; Wang et al., 2019; Yera et al., 2020). However, the health risks presented here might be underestimated for several reasons. First, additional routes of exposures such as dietary ingestion or dust ingestion were not considered. Pesticide intake via inhalation is usually higher than from dust ingestion (Kim et al., 2013; Schleier et al., 2009), but lower than from food ingestion (Clayton et al., 2003; Lu et al., 2006; Wilson et al., 2003). For example, daily uptakes of chlorpyrifos of preschool children in North Carolina via dietary ingestion, inhalation, and both soil and dust ingestion were estimated to be 2.5, 1.42 and 0.156 mg kg^{-1} day^{-1}, respectively (Morgan et al., 2014). Secondly, although the amount of CUPs investigated in this study is rather high compared to many other studies, it only represents a minor fraction of all pesticides available in the South African market (AVCASA, 2017; Dabrowski et al., 2014) and applied in the two study areas (Curchod et al., 2020). Indeed, neither glyphosate, mancozeb and pesticides in the group of pyrethroids and neonicotinoids, which are all used in high amounts in the study areas (Curchod et al., 2020), nor transformation products were investigated although some of them could have significant adverse health effects (Fenner et al., 2013). Last, the possible synergistic adverse effects of individual pesticides (Zhou et al., 2020) were not considered for all the pesticides investigated, although it has been shown to be important for non-target organisms for different pesticides (Siviter et al., 2021) such as triazines, organophosphates or neonicotinoids (Maloney et al., 2018; Pape-Lindstrom and Lydy, 1997; R. X. Yu et al., 2016). As carbaryl, chlorpyrifos and terbuthylazine had the highest hazard quotients, further studies should assess the human uptakes via other exposure pathways in order to deepen our understanding of the human exposure to these pesticides in these two agricultural areas.

5. Conclusions

This study assessed the occurrence of 30 CUPs in soils and air of two agricultural sites in South Africa and evaluated the related human exposure via soil ingestion and inhalation. Large differences between the residents of the two agricultural sites were found in terms of levels and composition of pesticide environmental exposure highlighting the significant role of crop-specific pesticide use on human exposure to pesticides. Pesticide mixtures were found in both soil and air samples, in which up to nine and 16 individual pesticides were found, respectively. Spatial variations in pesticide concentrations between the two sites were found more frequently in air than in soils. In the air, a large dominance towards the particulate phase was observed for most of the CUPs, which could be related to mass transport kinetics limitation (non-equilibrium) following pesticide application. Given the importance of gas-particle partitioning for the environmental fate of CUPs, future studies should assess the impact of pesticide formulation and spraying parameters on the gas-particle partitioning of CUPs. This is the first study to assess the human exposure to a wide range of pesticides via inhalation and soil ingestion of African residents. Exposure levels were substantially below reference doses. Future studies should focus on other environmental matrices at the household level (e.g. dust) to determine the impact of agricultural activities on the residential exposure of agricultural residents.

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CRediT authorship contribution statement

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Declaration of competing interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Analytical parameters, physico-chemical properties of CUPs, concentrations in individual CUPs in soil and air, particulate mass fractions of individual CUPs, daily uptakes of CUPs and hazard quotients are provided. Supplementary data to this article can be found online at doi: https://doi.org/10.1016/j.scitotenv.2021.150455.

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