Impact Assessment of Pesticides Applied in Vegetable-Producing Areas in the Saharan Zone: the Case of Burkina Faso

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Acknowledgements

Abstract

The present thesis aimed at characterizing the extent of the pesticide contamination and resulting impacts on the environment and the human health in market gardening areas in Burkina Faso. Analytical procedures were developed and validated for multi-class pesticide analysis in water, soils, sediments, and human hair. Passive samplers were deployed and grab samples were collected during a three-year investigation period. Results indicated that pesticide levels in surface water exhibited seasonality patterns. During the dry season, pesticide levels were generally low (<0.03 µg L^{-1}). Isolated cases of higher concentrations were related to gardening activities. During the rainy season, pesticide contaminations were more frequent and exhibited higher concentrations. A larger variety of active substances was detected during this season, including banned organochlorine pesticides (chlordane, dieldrin, DDTs and endosulfan). These substances were also detected in soils and sediments in the study area. In total, twenty-three pesticides were detected in drinking water resources. Among them, atrazine, azadirachtin, carbofuran, chlorpyrifos, cypermethrin, dieldrin, imidacloprid, and profenofos presented levels exceeding the threshold limit for safe drinking water (> 0.1 µg L^{-1}). Hazards were also identified for fish, cladocerans, and benthic invertebrates all year round but mainly during gardening activities. The assessment of the dietary intake of pesticides via vegetables and water consumption also outlined hazardous situations. Exposure levels to chlorpyrifos, dieldrin, and lambda-cyhalothrin presented acute and chronic risks for children and adults. The present work also proposed a novel approach for the quantification of 37 multiclass pesticides in hair using a modified QuEChERS procedure. In addition to the simplification of sample treatment, this method offers a robust and sensitive tool for the biomonitoring of population exposure to pesticides. Hair samples collected from local populations were found positive to 17 active substances. For certain pesticides used in gardening such as acetamiprid, cypermethrin, and lambda-cyhalothrin, occupational exposure was found to be the main source of exposure. However, for other substances such as imidacloprid and deltamethrin, similar exposure between occupationally and non-occupationally exposed individuals suggested the prevalence of other sources of exposure (e.g. dietary intake, vector control activities, etc.). Levels detected in hairs are of concerns, as they were higher than reported in

some other areas of the globe and indicated exposure to endocrine disrupting chemicals and probable carcinogens. Finally, the potential risk reduction of various mitigation measures was assessed using three international risk exposure assessment models. Simulation results indicated that training the operators to comply with pesticide recommendations of use and using suitable protective equipment was not sufficient. Additional behavioral changes and regulation adaptations are needed to reduce the exposure of the individuals present in gardening areas (operators, workers, and bystanders). More incentive on regulation enforcement and compliance with the good agricultural practices are necessary to improve the sanitary conditions in rural areas.

Keywords: Pesticide exposure; Multiresidue analysis; Dietary intake; Human biomonitoring; Hair; QuEChERS; Risk assessment; Passive samplers; Water analysis; Soil analysis; Sediment analysis; Exposure model; GC-MS; UPLC-MS/MS; SPE; dSPE;

Résumé

La présente thèse visait à caractériser l'étendue de la contamination par les pesticides dans les zones maraichères au Burkina Faso afin d'évaluer l'impact qui en découle sur l'environnement et la santé humaine. Des méthodes d'analyse multi-résidus ont été développées et validées pour l'analyse de l'eau, des sols, des sédiments et des cheveux humains. Les données récoltées à l'aide de l'échantillonnage ponctuel et de capteurs passifs, sur une période de 3 ans, indiquent une variation saisonnière des concentrations de pesticides dans les eaux de surface. Au cours de la saison sèche, les concentrations étaient généralement faibles (<0,03 µg L^{-1}). Les rares pics de pollution observés provenaient de l'utilisation des pesticides dans le maraichage. En saison des pluies, la contamination des eaux était plus fréquente et les concentrations généralement plus élevées. Un plus grand nombre de substances ont été détectées durant cette saison, parmi lesquelles des pesticides organochlorés bannis (chlordane, dieldrine, endosulfan et DDTs). Ces substances persistantes dans l'environnement étaient également présentes dans les sols et les sédiments. Au total, vingt-trois pesticides ont été détectés dans les sources d'eau potable. L'atrazine, l'azadirachtin, le carbofuran, le chlorpyrifos, la cyperméthrine, la dieldrine, l'imidaclopride et le profenofos présentaient occasionnellement des concentrations impropres à la consommation (>0,1 µg L^{-1}). La contamination des eaux présentait également des risques pour les poissons, les cladocères et les invertébrés benthiques, principalement en saison sèche, pendant les activités de maraichage. L'évaluation de l'exposition aux pesticides via la consommation de légumes et d'eau a également mis en évidence des risques pour les consommateurs. Les niveaux d'exposition au chlorpyrifos, à la dieldrine et à la lambda-cyhalothrine présentaient des risques aigus et chroniques pour les populations. Une nouvelle approche permettant la quantification de 37 pesticides dans les cheveux humains à l'aide de la méthode QuEChERS a été développée dans le cadre du présent projet de recherche. Cette méthode offre un outil robuste et sensible pour le suivi de l'exposition des populations aux pesticides. Au total, 17 substances actives ont été détectées dans les cheveux provenant de populations rurales. Pour certaines substances telles que l'acétamipride, la cyperméthrine et la lambda-cyhalothrine, l'exposition professionnelle est apparue comme étant la prin-

cipale source d'exposition. En revanche pour d'autres pesticides, les similitudes observées entre les personnes exposées et non-exposées dans le cadre professionnel, suggèrent la prévalence d'autres sources d'exposition (ex. alimentation, lutte anti-vectorielle, etc.). Les concentrations détectées dans les cheveux sont préoccupantes, car plus élevées que dans d'autres régions du monde et indiquent une exposition à des substances classées perturbateurs endocriniens et cancérogènes. Enfin, l'efficacité des mesures d'atténuation proposées a été évaluée à l'aide de trois modèles internationaux d'évaluation des risques. Les simulations montrent que la formation des opérateurs pour se conformer aux normes d'utilisation des pesticides et l'utilisation d'équipements de protection appropriés ne sont pas suffisants. Davantage d'incitation à l'application de la réglementation et au respect des bonnes pratiques agricoles sont nécessaires afin d'améliorer les conditions sanitaires dans les zones rurales.

Mots-clés : Exposition aux pesticides; Analyse multi-résidus; Exposition alimentaire; Biosurveillance; Cheveux; Analyse de risque; Analyse de l'eau; Analyse du sol; Analyse de sédiment; Capteurs passifs; GC-MS; UPLC-MS/MS; SPE; dSPE;

Contents

List of Figures

List of Tables

Abbreviations list

24 HR	:	24-Hours Recall	**LOQ**	:	Limit Of Quantification
a.i.	:	active ingredient	**MRL**	:	Maximum Residue Limit
a.s.	:	active substance	**MS**	:	Mass spectrometer
ADI	:	Admissible Daily Intake	**MS/MS**	:	Tandem Mass spectrometer
AOEL	:	Acceptable Operator Exposure	**POCIS**	:	Polar Organic Chemical Integrative Samplers
ARfD	:	Acute Reference Dose	**POP**	:	Persistant Organic Polluant
CILSS	:	Committee for Drought Control in the Sahel	**PPE**	:	Personal Protective Equipment
CSP	:	Sahelian Comity of Pesticides	**PPP**	:	Plant Protection Product
DHI	:	Days-to-harvest interval	**REI**	:	Re-entry interval
dSPE	:	dispersive Solid Phase Extraction	**RSD**	:	Relative Standard Deviation
EC50	:	Half maximal Effective Concentration	**SPE**	:	Solid Phase Extraction
EU	:	European Union	**SPME**	:	Solid Phase Microextraction
GAP	:	Good Agricultural Practices	**SR**	:	Silicone Rubber
GC	:	Gas Chromatograph	**TWAC**	:	Time Weighted Average Concentration
GDP	:	Gross Domestic Product	**UPLC**	:	Ultra Performance Liquid Chromatography
LC50	:	Median Lethal Concentration	**WAPE**	:	Weighted Average Portion Estimates
LOD	:	Limit Of Detection	**WHO**	:	World Health Organization

Chapter 1   Introduction

Pesticides are widely used throughout the world in agriculture, veterinary medicine, and for vector control. Since the introduction in 1945 of the first manufactured organic pesticides, the production kept increasing to serve an escalating demand (Zhang et al., 2011). The worldwide consumption of pesticides is estimated around two million tons per year with the majority destined to agriculture (De et al., 2014). Since thirty years, herbicides alone represent nearly 50% of the global usage (EPA et al., 2017; Zhang et al., 2011). Europe and the United States account for respectively 45% and 25% of the global pesticide consumption (De et al., 2014). Agriculture plays a vital socio-economic role in Burkina Faso in terms of export, employment opportunities, and food self-sufficiency (Ouédraogo et al., 2011). This sector has known a large growth in the past decades but it is highly affected by drastic climatic conditions and important agricultural losses (~30% of the harvest) caused by insects and diseases (Toé, 2010a). Pesticides play therefore a pivotal role in a country where ~90% of the population draws its subsistence from agriculture and still struggle to ensure its food security (MAH et al., 2011a; Ouédraogo et al., 2011). However, with an average use per area of crop land of ~0.1 kg ha, the Burkina Faso ranks 141 over 165 countries (Figure 1:1, (FAO, 2017)).

Compared to the largest agricultural powers, if the general quantity of pesticide applied is not the primary concern, as many developing countries, pesticide misuse has considerable repercussions on human health and the environment. Unsafe use or misuse of pesticides constitutes a major source of contamination and poisonning in developing countries (Imran and Dilshad, 2011). Less than 12% of pesticide-users attended primary school in Burkina Faso. Poor educational level and high illiteracy rate (78%) drastically hamper compliance with the good agricultural practices (MAH et al., 2011b). Most of the users are not able to assimilate the safety precautions and directions of use, which result in irrational utilizations (MERSI et al., 2016). The main pesticide exposure pathways are dermal, oral, respiratory, and conjunctival routes. Protective equipment are rarely used because of their poor availability and low affordability for rural populations. Agriculture is not mechanized and spraying equipment is limited to hand carried lever-operated knapsack sprayer. Due to the low availability and high cost of these sprayers, many farmers use artisanal alternatives. The latter consists in throwing pesticides from a bucket containing the mixture using a broom or leaves (Wendé Alice Naré, 2015). Exposure to pesticides is considered to be one of the most important occupational risks in developing countries (Imran and Dilshad, 2011). In Burkina Faso, almost every farmer reported suffering from symptoms of acute illness during or after pesticide application (Toé, 2010b).

Pesticides are also a major source of anthropogenic stress on the ecosystem. It is estimated that less than 0.1% of pesticides applied reach their target pests. Hence, a large fraction is lost and will be likely to interfere with non-intended target. The volatilization from the treated surfaces and drift of the pesticides during application can increase concentration in the atmosphere (Pimentel, 1995). Pesticides might contaminate soils, as a large fraction is adsorbed at the surface of soil particles and can be persistent (Savadogo et al., 2006). They also enter the water system via multiple pathways: runoff, permeation through soil, atmospheric transfer, accidental release, etc. (McKnight et al., 2015). Misuse of pesticides can result in hazardous levels in environmental compartments. Environmental pollution ultimately affect terrestrial and aquatic biota (Leboulanger et al., 2009a; Ouattara et al., 2010) and human health.

Human exposure to environmental contamination occurs through direct contact (with spray drift or contaminated surfaces), through ingestion (e.g. water, fish, etc.), and through inhalation of vapors (volatilization from treated surfaces and atmospheric transport). In Burkina Faso, different crop types are cultivated depending on the seasons (e.g. cotton, cereals, vegetables, etc.). Farming activities are therefore characterized by long growing periods (6 - 8 months) with multiple pesticide applications. In addition to potential acute hazards, repeated occupational and environmental exposure to pesticides may trigger a variety of chronic health effects, such as cancers, neurologic effects, and reproductive effects (Ouédraogo et al., 2011; WHO/UNEP, 2012a).

Since 2013, the Swiss Agency for Development and Cooperation (SDS) has decided to fund a research program focusing on various environmental issues. The assessment of the impacts of pesticides in the Sahelian zone was included as a main research component in the framework of this 6 years program. This research project was entrusted to the partnership between Ecole Polytechnique Fédérale de Lausanne (EPFL) and Institut International d'Ingénierie de l'Eau et de l'Environnement (2iE). The present thesis was funded through this program. It aimed at characterizing the extent of the pesticide contamination and resulting impacts on the environment and the human health. The research plan was divided in five main components that structure the present report:

- the characterization of the current state of pesticide use in Burkina Faso and definition of the study objectives (Chapter 2, Chapter 3, and Chapter 4);

- the characterization of the contamination in environmental matrices, using innovative analytical methods adapted to the local context (Chapter 5);

- the risk assessment of dietary intake of pesticides (Chapter 6);

- the biomonitoring of pesticide exposure using a novel approach for the analysis of pesticides in human hair (Chapter 7 and Chapter 8);

- and the risk assessment of operator, worker and bystander exposure and mitigation measure proposals (Chapter 9).
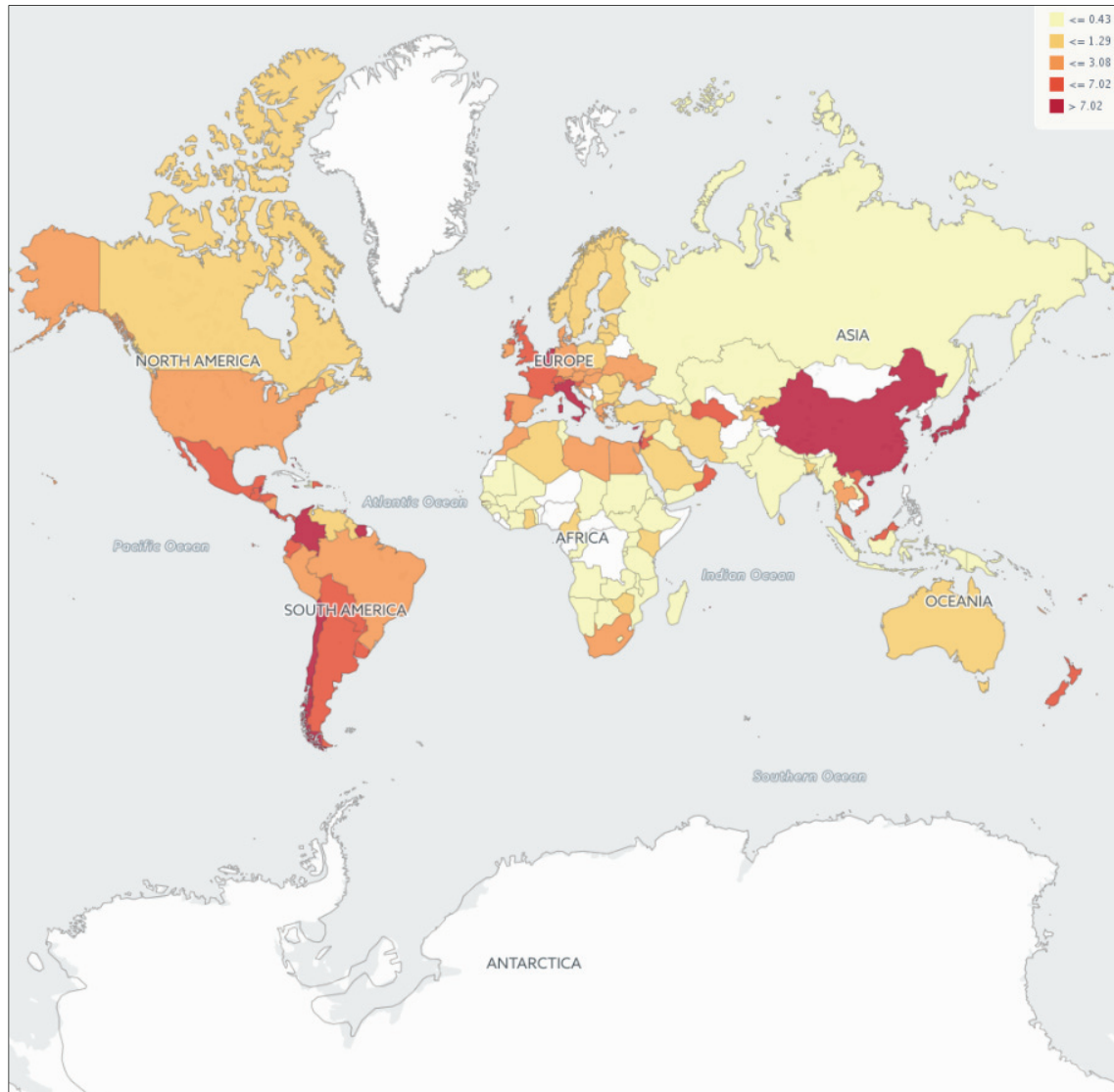
Figure 1:1 Average pesticide use per area of cropland 1990 - 2014 (FAO, 2017).

Chapter 2 Overview of pesticide burden in Burkina Faso

2.1 Agriculture in Burkina Faso

As a landlocked country, 85% - 95% of the population draws its subsistence from agriculture. The contribution of the agricultural sector to the gross domestic product (GDP) is ~33.3% (Ouédraogo et al., 2011). In 2012, the total area in cultivation was estimated to be 5.4 million hectares with cereals (sorghum, millet, corn, rice, and fonio) representing approximately 70% of the production.

The past decade is characterized by a large growth of agricultural production in Burkina Faso. Cereal production ranks first in this domain. Over the period 2000 - 2012, it has increased from 1'844'400 (2000) to 4'898'544 (2012) tons per years. Sorghum alone accounted for 43% of the cereals production followed by millet (30%) and corn (22%). Fonio and rice were produced to a lesser extent. Cash crops (cotton, groundnut, sesame, and soya) production arrives after with 1'148'100 tons produced in 2008 against 392'555 tons in 2000. Cotton accounted for approximately 60% of this production (followed by groundnuts (30%)). Subsistence crops production (yam, cowpea, potato, and voandzou) occupies the third position with 208'000 tons produced in 2000 and 783'300 tons in 2010. Cowpeas alone accounted for 80% of subsistence crops production (CountrySTAT Burkina Faso, 2017). Products grown in gardening are mainly: garlic, eggplant, carrots, cabbage, cucumbers, strawberries, okra, green beans, lettuce, onion, pepper, potato, and tomato. Gardening accounts for ~17% of the total country agricultural production with cabbage, onion, and tomatoes being the main products (World Bank, 2015). Figures available for 2008 show that fruit production (citrus, banana, mango, guava, papaya, and mahogany apple) accounts for only 5% of the total production with mango and guava being the main products (65%) (CountrySTAT Burkina Faso, 2017).

At the national scale, the majority of the incomes comes from breeding (51%), followed by cereals (13%), cotton (12%), oleaginous and protein crops (8.5%), fresh vegetables (5.4%), forest and gathering (3.4%), fruits (1.5%) and by-products of livestock (~1.5%, milk, eggs, etc.). The western regions including the "Hauts-Bassins", the "Cascades", and the "Boucle du Mouhoun" are the most productive regions of the country (Figure 2:1). These regions are also the main cotton and cereal-producing areas. Cotton represents respectively 32% and 27% of the farmer incomes in the "Boucle du Mouhoun" and the "Hauts-Bassins". Similarly, cereal production represents 20% and 24% of incomes in the "Boucle du Mouhoun" and the "Hauts-Bassins". Sugar cane production is limited to the Southwestern region of Burkina Faso (Banfora and Cascades region). Breeding constitutes the principal source of revenues in the Sahelian region ("Sahel", 92%), North region ("Nord", 67%), Center East ("Centre Est", 62%), Center North ("Centre Nord", 62%), and Central Plateau ("Plateau Central", 60%). Oleaginous and protein crop production participation in farmers' incomes is larger in the Eastern region ("Est", 14%), Center North ("Centre Nord", 11%) and in the North region ("Nord", 8%). Finally, vegetable and fruit production constitutes a significant source of revenues in the Center region ("Centre", 33%) (MAH et al., 2011a).
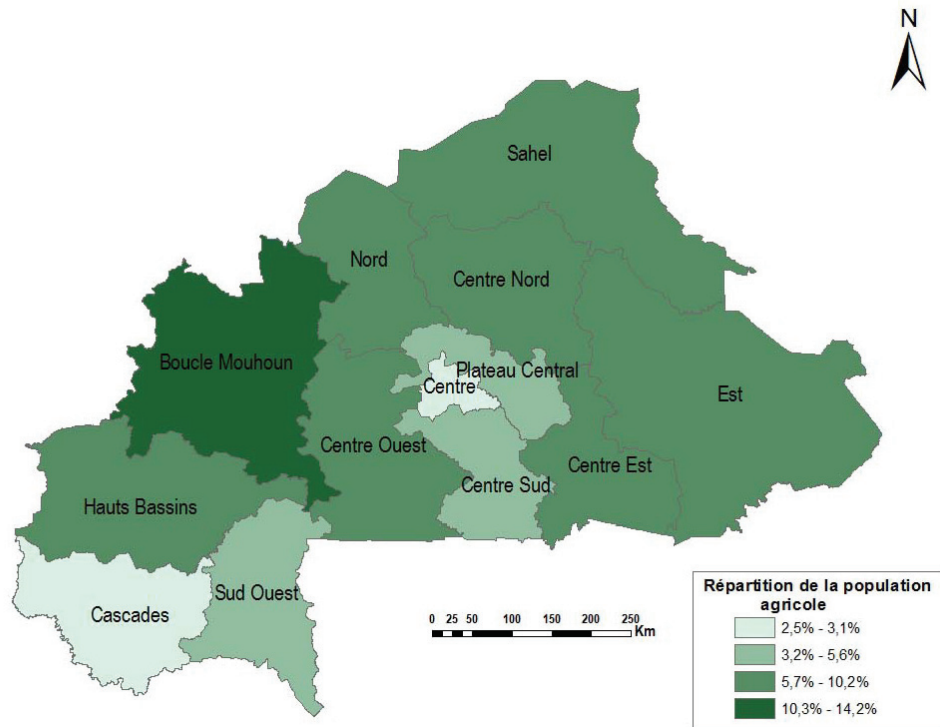
Figure 2:1 Regional distribution of the populations employed in agriculture (MAH et al., 2011a)

Burkina Faso is characterized by a dry tropical Sudano-Sahelian climate. According to Kagone (2006) citing Fontès (1983), the characteristics of the climates are:

- two marked seasons; a rainy season (hivernage) and a dry season;
- a unimodal rainfall curve;
- a dry season which is at least as long as the rainy one;
- a total absence of a cool season (the annual minimum monthly temperature is > 18 °C);
- and an increasing aridity from south to north.

The country is divided in four zones according to floristic and climatic characteristics (Figure 2:2).

Temperature and Rainfall
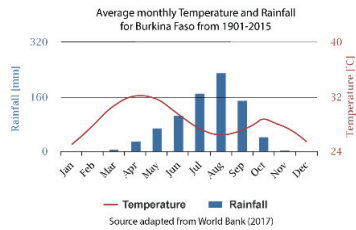
Climatic Zones
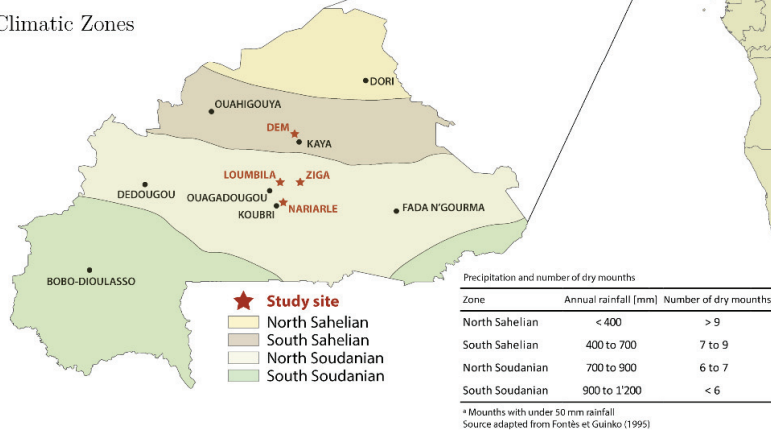
Figure 2:2 Climatic characteristics of the Burkina Faso
(map adapted from: (Fontès and Guinko, 1995), temperatures: (World Bank, 2017))

Agriculture is largely influenced by these particular climatic conditions. Cultivation of water demanding crops like cereals (rice, millet, maize, fonio, sorghum, etc.) and cotton is mainly limited to the rainy season (MAH et al., 2011c). On the other hand, irrigated cultures like vegetables and fruits are mainly cultivated during the dry season as an alternative to cash crops (MAH et al., 2011b).

Support provided by the government to farmers is low and most of them are not organized in working cooperatives (<40%). Farming is mainly of the traditional type performed with rudimentary equipment ("daba": traditional spade). Very little of the country's agriculture is mechanized. The agricultural population faces a precarious food security situation. Poor harvests due to crop losses (climatic conditions, pest attacks, etc.) affect ~70% of the households. The main consequences are the reduction of the number and quantity of meals consumed (MAH et al., 2011a). Crop losses due to pests and diseases can exceed 30% (Toé, 2010b). In a country where the majority of the population draws its subsistence from agriculture, maintaining sufficient yields and minimizing losses is a priority (Ouédraogo et al., 2011). In 2008, ~771'391'000 FCFA have been spent on solid (6'276 tons) and liquid (5'947 tons) pesticides to protect crops (MAH et al., 2011a).

2.2 Pesticide production and distribution

2.2.1 Production and importation

SAPHYTO is the lone official company producing pesticides in Burkina Faso and therefore ranking first in its domain. It imports active ingredients, fabricates products, and commercialized them. Created in 1989, this company located in the industrial area of Bobo-Dioulasso is active in agriculture, animal husbandry (veterinary practice), and public health (vector-borne diseases control) (MECV, 2005a). The principal formulations produced in Burkina Faso by SAPHYTO contain organophosphorus pesticides (Calthio C: chlorpyrifos and thiram) and pyrethroids (Cypercal 50 EC: cypermethrin, 3.5 million liters produced in 2011 (Ouédraogo et al., 2011)). However, the majority of pesticides used in Burkina Faso are imported from other countries. Points of origin include Senegal, Ivory Coast, Nigeria, Mali, South Africa, Tunisia, Japan, Indonesia, China, Thailand, Europe, and the United States. In 2010, the majority of the products found on the market originated from China (47%), France (33%), and Burkina Faso (20%) (MEF, 2015). From 1997 to 2001, more than thirteen million liters of liquid pesticides and 900 tons of solid pesticides were imported in Burkina Faso (Ouédraogo et al., 2011). With the growth of the agricultural production, these amounts must have increased over the past decades. Table 2:1 shows the volumes of imported pesticides controlled by the responsible national organization between 2010 and 2015. The difference with the total imported volumes presented above underlines the limitation of the existing control procedure.

Table 2:1 Imported pesticides controlled (kg)
by the Direction de la Protection des Végétaux et du Conditionnement (DPVC)
(source: data furnished by the DPVC)

Year	2010	2011	2012	2013	2014	2015
Insecticides	294'557	396'582	369'929	84'944	939'217	349'707
Herbicides	240'090	47'580	401'044	244'293	362'984	525'897
Total	534'647	444'162	770'673	429'237	1'302'201	875'604

2.2.2 Distribution

In 2008, 5'947 tons of liquid and 6'276 tons of solid pesticides were acquired by individual farmers (MAH et al., 2011a). Three channels of distribution can be distinguished in the country: specialized wholesalers, local mixed stores, and local marketplaces.

The large specialized stores are generally held by professional authorized resellers. They operate in the wholesale sector and supply pesticides at a regional to national level. They only make retail sales in their areas of settlement. As authorized resellers, they comply with the standard regulations and are equipped with safe storage facilities (dedicated ventilated room). The pesticides are presented and sold to customers in an exhibition hall and the personnel is well trained and equipped with personal protective equipment (MECV, 2005a). Wholesalers furnished principally large cotton and sugar companies (SOFITEX Société Chimique et Agricole du Burkina (SCAB),

Datong Enterprise, SN-SOSUCO, etc.) which subsequently provide their producers with suitable fertilizers and pesticides (Gomgnimbou et al., 2009; Toé, 2010b).

By opposition to specialized stores, **mixed stores** also sell other products alongside with pesticides. Some pharmaceutical depots store pesticides for households and agricultural applications. Local merchants sell pesticides in their boutiques alongside with other products (e.g. food, etc.). Contrary to specialized stores, these shops are generally not homologated and not equipped with suitable protective and safe storage equipment (i.e. personal protective equipment, aerated room, etc.). The absence of separation between products exposes the personnel and the consumers to potential hazards (leakage from damaged or non-suitable containers, volatilization of substances, and spilling on other stored items).

Finally, most of the individual producers buy their pesticides on **local marketplaces**. Storage on market stalls exposes the pesticides to high temperatures and neither protective equipment nor suitable storage precautions are taken (MERSI et al., 2016). Unlike cotton producers, gardeners generally purchased pesticides individually and with their own funds (MAH et al., 2011b).

Limited national and regional capacity and porous borders considerably limit pesticides control and regulation. The use of illegal sources of supply is established (MECV, 2005a; MERSI et al., 2016; Toé, 2010b). Reasons for illegal importation are the low availability and the higher cost of pesticides produced in Burkina Faso (Toé, 2010b). Some of the resellers also proceed to the repackaging of the products. Pesticides are commonly repackaged in locally available and non-labeled containers, inappropriate for pesticide conservation (Bassole and Ouédraogo, 2007). In some cases, this practice consists in mixing legal pesticides with illegal ones to improve profitability (Toé, 2010b). This operation is done by non-professionals thus leading to products with unknown specificities (content, concentration, toxicity, etc.).

2.2.3 Policy and institutional frame

The Permanent Interstate Committee for Drought Control in the Sahel (in French: "Comité Permanent Inter-Etats de lute contre la Sécheresse dans le Sahel" (CILSS)) was created in 1973, following the extreme droughts that occurred in the Sahelian region at the beginning of the 70s. It is composed of 13 member states located in the Sahelian zone (Benin, Ivory Coast, Burkina Faso, Cape Verde, Gambia, Guinea, Guinea Bissau, Mali, Mauritania, Niger, Senegal, Togo, and Chad). The general objective of the comity is to organize and support research for food security and the fight against the effects of drought and desertification to ensure resilience and ecological equilibrium. Since 1992, the CILSS is also responsible for the regulation of the pesticide homologation in the member states. The objective of this regional regulation was to bring together the expertise and resources in order to improve environmental and human health protection. The Sahelian Comity of Pesticides (in French: "Comité Sahélien des Pesticides (CSP)) commenced operations in 1994 as the executive body of this regional policy. The CSP provides two lists of pesticides. The first one lists the trade names of the authorized formulations in agriculture (general list) and the second one lists the formulations authorized for gardening. Since the creation of the

CSP, member states are not allowed to have an autonomous regulatory body in the field of pesticide homologation. Burkina Faso has created in 2000, the National Commission on Pesticides Control (in French: "Commission Nationale de Contrôle des Pesticides" (CNCP)) in charge of the application of the CSP directives in the country. This commission was placed under the authority of the Ministry of Agriculture and became operational in 2007. However, the CNCP struggles to take concrete actions as the decision process is shared between multiple regulation bodies (Ministry of Agriculture, Water resources, Sanitation and Food Security, Ministry of Environment and Fishery resources, Ministry of Health, Ministry of Economy and Finance, etc.).

Burkina Faso has also ratified 3 international conventions that influence pesticide regulation in the country. The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was ratified in 1999 and entered into force in 2000. However, to date the country has not ratified the Ban Amendment and no restriction has been implemented. The Rotterdam Convention was ratified in 2002 and entered into force in 2004. Through the Prior Informed Consent (PIC) procedure, this convention promotes shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment. No pesticide concerned by the PIC procedure is consented for importation in Burkina Faso. The Stockholm Convention on Persistent Organic Pollutants (POPs) was ratified by Burkina Faso in 2004 and entered into force in 2005. Among the 24 chemicals retained by the Convention for elimination of the production (Annex A), 14 are pesticides. The inventories conducted in 2001 and 2004 across the country confirmed that POPs were never produced in Burkina Faso. While they were still authorized, these chemicals were imported (e.g. DDT, etc.). Since the entry into force of the Convention, importation of POPs for agriculture or vector-borne diseases control is illegal (MECV, 2005a). However, importations and use of illegal formulations in the country is established. For example, investigators observed in 2004 a large decrease of the obsolete POPs stockpiles inventoried in 2001. In 2004, it was reported that Xylogil, a product widely used for wood protection, contained aldrin, dieldrin, and lindan and that mosquito repellent imported from China under the trade name "le Coq" contained DDT (MECV, 2007). Except for the Basel Convention, the signature of these international conventions had a positive impact on the regulation of hazardous substances in Burkina Faso. However, in practice the enforcement of these restrictions is still not effective. National strategies for pesticide and pest management are poorly applied due to the lack of human and financial resources (Mbengue Faye et al., 2010; Toé and Pare, 2011). The prevalence of illegal formulations on the market outlined in many inventories conducted across the country illustrates this lack of control (Bassole and Ouédraogo, 2007; Oyono Elle, 2008; Toé, 2010b; Wendé Alice Naré, 2015). In addition, even though it is recommended by the Stockholm Convention, the country has to date not implemented any monitoring plan for pesticides.

2.3 Domains of application

As the principal activity in the country, agriculture is the main user of pesticides. To a lesser extent, pesticides are also used for vector control and to protect cattle.

2.3.1 Public health

Pesticides are used for controlling vectors of public health importance. Indoor and outdoor space spraying, providing impregnated material for individual protection (e.g. mosquito net) and destruction of mosquito larvae are the principal activities conducted in the frame of the national malaria control program (in French: "Programme National de Lutte contre le Paludisme" (PNLP) (MS, 2011)). Resistance of the vectors to organochlorine and carbamate (MCHIP and USAID, 2013; Namountougou et al., 2012) has led to prefer the use of pyrethroids in this sector (Lu et al., 2015). However, recent detection of increased resistance level to pyrethroids (Toé et al., 2014) may question the pertinence of these substances in the future.

2.3.2 Cattle protection

In Burkina Faso, livestock production contributes to 12% of the gross domestic product and generates 19% of export earnings (Adakal et al., 2013). However, productivity in this domain is highly impacted by animal diseases. Little information exists on cattle treatment. A study conducted in 2013, documented tick-control (Adakal et al., 2013). If most of the stockbreeders sprayed conventional acaricides (73%), a significant proportion (15%) used pesticides intended for crop treatment. The main active ingredients contained in the formulations used were deltamethrin, cypermethrin, and amitraz.

2.3.3 Agriculture

As aforementioned, insects and diseases cause important agricultural losses in Burkina Faso. Pesticides are widely used for cash crops production (cotton and sugar cane) and in lesser proportions in market gardening and cereal production. Cotton alone accounts for 90% of pesticide use in Burkina Faso (Ouédraogo et al., 2011). Maize and rice are the only cereals that are treated to a significant extent (MA, 2001; MERSI et al., 2016).

In agriculture, pesticides are used at every stage of the production. Herbicides are applied before and during cultivation to eliminate plant species that compete with cash crops for space, nutrients and water (Hubbard, 2001). Due to associated costs, herbicides tend to be used only in cotton (Figure 2:4). Insecticides and fungicides are used during growth and after harvest in storage facilities to protect crops from rodents (rodenticides), insects (insecticides), and fungi (fungicides) (Bassole and Ouédraogo, 2007). In particular, locust control requires important use of pesticides in infested areas (Ilboudo et al., 2014a, 2014b).

Average use of pesticides per area of cropland in Burkina Faso (1998 - 2011) is estimated to 0.13 kg ha^{-1} (FAO, 2017). Variations between years might be explained by specific climatic conditions or market changes (Figure 2:3). For example, reduced use in 2004 might be a consequence of the drought (Toure et al., 2015) and first commercialization of the GMO (genetically modified organism) cotton in 2010 could justify a lower use that year.
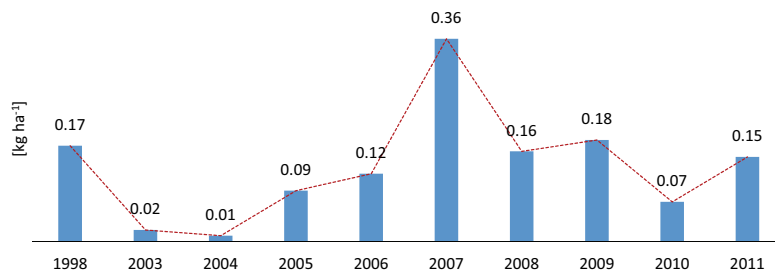
Figure 2:3 Average use of pesticides per area of cropland in Burkina Faso between 1998 and 2011 (FAO, 2017)

Globally, organophosphorus and pyrethroids (Figure 2:4) prevail in Burkina Faso (Oyono Elle, 2008; Son et al., 2016; Toé, 2010b; Wendé Alice Naré, 2015). However, variations can be observed at regional level. For example, in the eastern region (around Fada N'Gourma) the use of organochlorines, mainly endosulfan, was more common in cotton production (82% of the active ingredients, Ouédraogo et al. 2009). It is noteworthy that the use of endosulfan was reported by Ouédraogo et al. (2009) before its ban in the country in 2012 (Stockholm Convention on Persistent Organic Pollutants, 2017). The situation might have changed since the prohibition. However, illegal importations and lack of control makes it difficult to define the situation accurately in Burkina Faso. Formulations used rely highly on border proximity and availability. Cheaper formulations are often imported from bordering countries (Toé, 2010b). Due to their availability and large distribution, pesticides intended for cotton or commonly reused on other cultures. These facts underline the need for concrete monitoring across the country to draw precise conclusions on the real pesticide burden.
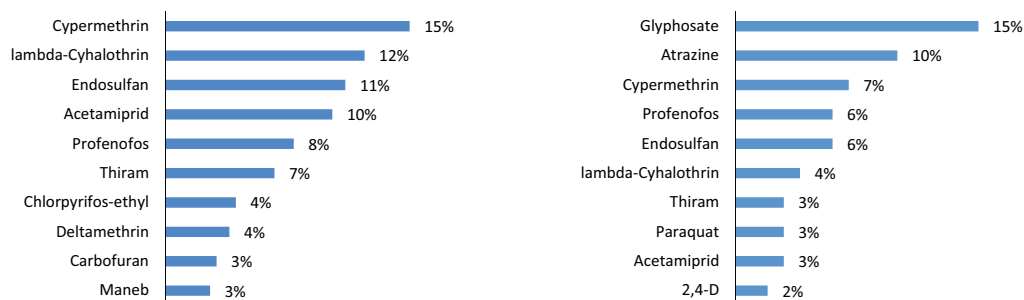
(a) Pesticides reported in gardening (n = 252)

(b) Pesticides reported in cotton production (n = 270)

Figure 2:4 Frequency of reporting of the 10 major active ingredients identified in the reviewed literature (appendix B)

2.4 Pesticide users knowledge and equipment

Pesticide users are generally young (under 40 years old) (Kêdowidé et al., 2010). Their professional experience is variable but the average is around 6 to 15 years. Main users appeared to be males but in some areas females are largely represented (up to ~50% (Congo, 2013; MAHRH and

DGPSA, 2007)). Most of the farmers are illiterate (~78%) and less than 12% attended primary school (MAH et al., 2011b).

As aforementioned, agriculture is mainly of the traditional type in Burkina Faso. Pesticide application is not mechanized and the most commonly used equipment (Figure 2:5, a) is hand carried lever-operated knapsack sprayer (Ouédraogo et al., 2011). However, a large fraction of the farmers is still using homemade alternatives (Wendé Alice Naré, 2015). Due to the cost and low availability of knapsack sprayers in rural areas, farmers often use a bucket to prepare pesticide mixture and dip leaves or a broom inside to throw the mixture on the crops (Figure 2:5, b and c).

(a) Knapsack sprayer and unlabeled mixture

(b) Buckets used for pesticide dilution

(c) Broom used for pesticide application

Figure 2:5 Equipment used for pesticide application

Little precautions are taken during the pesticide application. Personal protective equipment (PPE) is usually limited to normal clothing (i.e. not chemical-resistant) and a muffler made of synthetic fabric. Use of chemical-resistant protective suit and proper respirators are negligible (Bassole and Ouédraogo, 2007). Illiteracy also dramatically hampers the assimilation of label recommendations resulting in irrational use of pesticides (Son et al., 2017). Treatment of crops with unsuitable pesticides is common (e.g. application of pesticide intended for cotton on vegetables). Recommended doses are often exceeded; frequency of applications, re-entry intervals (REI), and days-to-harvest intervals (DHI) are not respected (section 4.3.5.2). Finally, operators often use several pesticides in combination. Mixtures are prepared by non-professionals that are not aware of the resulting toxicity. Reconditioning are usually made in unsuitable containers (e.g. beverage containers) that do not ensure safe storage and can be confused with beverages or foodstuffs in absence of proper labeling (Figure 2:5, a). This situation increases operator but also bystander and consumer exposure which might trigger health hazards. Many evidences of contamination and side effects of these practices were already observed in previous studies (section 2.5).

There is an important need for support in rural populations in order to achieve compliance with the good agricultural practices (GAP).

2.5 Evidences and effects of pollution due to pesticides in Burkina Faso

2.5.1 Obsolete stockpiles and contaminated sites

Management of obsolete pesticide stocks represents a large burden in developing countries. The lack of resources and infrastructure for collection and treatment, often leads to anarchic waste disposal. In the absence of national management, only large companies collect, store, and try to eliminate their waste. The national inventories conducted in 2001 and 2004 identified 9 contaminated sites resulting from unsafe storage of obsolete stockpiles. Pesticides accounted for a large fraction of these stocks in the form of solid and liquid formulations and empty containers (Table 2:2). The action plan for POPs and obsolete pesticides management proposed 3 disposal routes: landfilling, high temperature incineration (1500 °C) and reuse/reconversion (MECV, 2005b). However, in the absence of suitable infrastructure in the country, no action was undertaken and the stockpiles were illegally used. To date, the country is not equipped to perform other actions than reuse/reconversion. Some containers have been crushed and cast in concrete to form bricks (MECV, 2005b). SAPHYTO has also performed retitration of obsolete pesticides. Retitration consists in the addition of fresh active ingredients to the expired, so they are usable at least for one year (Ouédraogo et al., 2011). To date, the extent of the contamination of identified contaminated sites is unknown. Characterization was performed by simple organoleptic evaluations and no further analysis was conducted. Waste disposal is an important and unsolved issue in the country. The problematic of contaminated sites is therefore expected to increase with the increase use of pesticides in agriculture. In addition to the development of waste-treatment solutions, studies are needed to characterize the pollution (identification of contaminants and surface area and volume contaminated) and to propose remediation measures.

Table 2:2 Persistent and obsolete pesticide stockpiles inventoried in 2001-2004 (MECV, 2005b)

Type	Description	Quantities
Obsolete Pesticides Non POPs	Solid formulation	2'910.72 kg
	Liquid formulation	126'049.53 L
	Waste	119'415 empty containers
POPs (DDT)	Solid formulation	1'000 kg

2.5.2 Pesticide residues quantification in Burkina Faso

The present section focuses on the existing data regarding pesticide levels and impact assessment in previously studied matrices in Burkina Faso.

Only few studies quantified pesticides in environmental compartments in Burkina Faso. In the absence of national monitoring, the data tend to be scattered across multiple sources and actors. Finding and aggregating existing data is therefore a challenge. In the present work, 11 quantitative studies were retrieved (Congo, 2013; Ilboudo et al., 2014b; Mbaby, 2013; MECV, 2005b; MERSI et al., 2016; Ondo Zue Abaga et al., 2011; Ouattara et al., 2012; Oyono Elle, 2008; Savadogo et al., 2006; Soleri, 2013; Tapsoba et al., 2008). Studied environmental matrices included water, soils, and sediments. Endosulfan was the most detected pesticide in soils. Drinking water regulation in Burkina Faso refers to the WHO guidelines (MAHRH and MS, 2005). However, guideline values are not established for every substances detected in the environment. Measured levels were also compared to the European Union (EU) threshold limits for safe drinking water and European and Swiss environmental quality standards for inland waters. These limit values are generally more restrictive and therefore this approach is expected to be conservative. Concentrations of endosulfan in water exceeded both the EU limit value for drinking water (0.1 µg L^{-1}) and the environmental quality standards (EQS) proposed by the EU water framework directive for inland waters (Table 2:3). Endosulfan was detected mainly in cotton producing areas. However, as gardeners also used pesticides intended for cotton, it is likely to be present in soils and sediments from other agricultural areas. Endosulfan is classified as a POP listed in annex A of the Stockholm Convention (for elimination of the production) and is banned in the country since 2012 (Stockholm Convention on Persistent Organic Pollutants, 2017). Even though persistence might lead to further detection, prohibition is likely to have a positive impact on this situation. Follow-up is needed to assess the status of this pesticide across the country. Atrazine (and its metabolites), imidacloprid and linuron were the most commonly detected pesticides in water but concentrations were under the guideline values. On the other hand, levels of diazinon exceeded both the EU guidelines for drinking water and the Swiss EQS in areas where large amounts of pesticides are applied for locust control. Levels of aldrin, dieldrin, and heptachlor also largely exceeded the European limit value for drinking water and heptachlor exceeded the EU EQS. These high concentrations were the result of an accidental water pollution of the Houet River located in the city of Bobo-Dioulasso. These situations illustrate the absence of monitoring across the country. Only isolated scientific studies or single quantification after accidental releases are reported in the literature. The paucity of data makes it difficult to define the situation accurately.

Table 2:3 Levels of pesticides measured in water, soils, and sediments
((-): number of positive samples N.E.: Not Established)

	Water	Soil	Sediment	WHO guidelines for water [a]	EU guidelines for water[b]	EU MAC-EQS[c]	CH MAC-EQS[d]
	[ng L^{-1}]	[µg kg^{-1}]	[µg kg^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]	[ng L^{-1}]
Acetamiprid	-	-	15 - 30 (2)	N.E.	100	N.E.	N.E
Aldrin	56 - 220 (2)	0.2 - 20 (6)	-	30	30	Not applicable	N.E
Atrazine	0.3 - 19.8 (39)	-	-	100.10^3	100	2000	N.E
Desethylatrazine	0.2 - 14.6 (39)	-	-	100.10^3	100	N.E.	N.E
Deisopropylatrazine	0.1 - 11.8 (39)	-	-	100.10^3	100	N.E.	N.E
lambda-Cyhalothrin	-	-	7 - 10 (2)	N.E.	100	N.E.	N.E
Cypermethrin	-	-	16 (1)	N.E.	100	0.6	0.44
DDE	28 (1)	-	11 (1)	1000	100	N.E.	N.E
Diazinon	2020-2160 (10)	-	17 - 26 (3)	N.E.	100	N.E.	20
Dieldrin	81 - 110 (2)	-	-	30	30	Not applicable	N.E
Dimethoate	-	1.7 - 5 (5)	-	6000	100	N.E.	977
Diuron	0.2-12.9 (37)	-	-	N.E.	100	1800	250
Endosulfan	50 - 680 (5)	0.2 - 80 (57)	-	N.E.	100	10	N.E
beta-HCH	19 - 190 (2)	-	-	2000	100	N.E	N.E
Heptachlor	94 - 1280 (5)	-	-	N.E.	30	0.3	N.E
Imidacloprid	0.4 - 9 (37)	-	-	N.E.	100	N.E	100
Linuron	0.2 - 11.9 (37)	-	-	N.E.	100	N.E	1370
Omethoate	-	4 (3)	4 (3)	N.E.	100	N.E.	N.E
Parathion-ethyl	-	2 (1)	-	N.E.	100	N.E.	N.E
Paraquat	-	- (1)[e]	-	N.D,	100	N.E.	N.E
Profenofos	-	10 - 30 (8)	23 (1)	N.E.	100	N.E.	N.E
Quintozene	<10 (9)	-	-	N.E.	100	N.E.	N.E

[a] World Health Organization guidelines for drinking-water quality (WHO, 2011a)

[b] Limit values proposed by the European Directive 98/83/EC on the quality of water intended for human consumption (Directive 98/83/EC, 1998)

[c] Environmental Quality Standard (EQS) from the European Directive 2013/39/EU expressed as a maximum allowable concentration (MAC-EQS) in inland waters (DIRECTIVE 2013/39/EU, 2013)

[d] .Criteria proposed by the centre ecotox in Swtizerland

[e] Paraquat was detected in only one sample collected by MERSI et al. (2016), no concentration is presented due to inconsistency in given units ([µg L^{-1}])

To our knowledge, no scientific study was conducted on pesticide residues in food in Burkina Faso. Almost no control exists on the domestic market and importations. Studies conducted in western Africa outlined that pesticide residues in food exceeded the Maximum Residue Levels (MRLs) or the Admissible Daily Intake (ADI) proposed by the Codex Alimentarius (Bempah et al., 2011; Mawussi et al., 2009). The pesticides detected in these studies were similar to those quantified in the environmental matrices in Burkina Faso (aldrin, dieldrin, DDT, heptachlor, endosulfan, and HCH). Exceedance of MRL limits export potential and thus could have negative financial repercussions. Exports of horticultural products from developing nations have already been rejected by international markets because of residual levels of pesticides (Bempah et al., 2011). On the other hand, exceedance of the ADI presents a risk for the health of the consumers. Pesticide residues in food can be of particularly health significance in areas where the good agricultural practices are not enforced. According to Margni et al. (2002) the exposure resulting from direct transfer of the applied pesticides into food is about 10^3–10^5 larger than the diffuse intake induced by drinking water and inhalation. This reinforces the need for routine controls and enforcement of the good agricultural practices at the national level.

Similar to humans, pesticide exposure also affects the local biota. In 2001, contamination of the Houet River (Bobo-Dioulasso) was attributed to the release of lindan and thiram after washing pesticide containers of the CALTHIO formulation (produced by SAPHYTO). The contamination resulted in the death of hundreds of fishes. In November 2003, another contamination with heptachlor (MECV, 2005b) was detected in fish niches in the Houet River (0,26 – 1.28 µg L^{-1}). Fish has proved to be a suitable indicator of water contamination, aquatic biota exposure to chemicals, and bioaccumulation (Bouchaib et al., 2007; Pazou et al., 2006; Shayeghi et al., 2012). Human

exposure can also be derived via consumption of fishes. However, to our knowledge, no study on pesticide residues in fishes was conducted so far in Burkina Faso.

Finally, except the study conducted by Toé et al. (2000) on cholinesterase activity in the cotton-production region of Mouhoun in Burkina Faso (section 2.5.4), no pesticide residues analysis has been conducted on a human matrix.

2.5.3 Risk for the local biota

Non-target species are also affected by pesticide toxicity; the aforementioned accidental contamination of the Houet River (0) clearly illustrates the toxicity of pesticides on aquatic biota. Risk assessment studies performed in Burkina Faso used substance toxicity testing in laboratories, modelization tools and field observations.

Leboulanger et al (2009) isolated natural bacterial populations, phytoplankton cultures (one cyanobacterium, *Cylindrospermopsis raciborskii*, and one chlorophycea, *Monoraphidium sp.*), and two species of zooplankton (*Diaphanosoma excisum* and *Moina micrura*) from a reservoir lake in Burkina Faso (Loumbila Reservoir). Laboratory tests concluded that paraquat was moderately toxic to bacteria and phytoplankton, whereas deltamethrin was significantly toxic only to the zooplankton species. In addition, natural water extracts were also proved toxic to the same biological targets but no causal link was established with the aforementioned pesticides as they were not detected in these water extracts. This preliminary assessment suggested that further research is needed to explain the toxicity of the water of the reservoir. Risk characterization for aquatic species was also performed by Ilboudo et al (2014b) but using the risk quotient approach. Measured environmental concentrations (MEC) in areas treated for locust control were compared to toxicological reference values of standard test species (half-maximal effective concentration (EC_{50}) and Predicted No Effect Concentration (PNEC)). Risks were identified for aquatic invertebrates ($MEC/EC_{50}>1$) and in general for the aquatic ecosystem ($MEC/PNEC>1$). This study outlined the impact of pesticides in areas where large amounts are applied.

"Recent pesticides" are supposed to be less toxic to mammals. However, studies proved that honey bees are highly affected (disorientation, disrupted navigation, impaired memory, fluctuating asymmetry, diminished foraging and returning to hive, decreased hive activity, etc.) by neonicotinoids (e.g. imidacloprid) even at low doses (Pesticide Action Network Asia and Pacific, 2011). Ondo Zue Abaga et al. (2011) assessed the impact of pesticides on this sensitive specie (*Apis mellifera* Linnaeus) in Burkina Faso. Honeybees were sampled from two different sites. Hives were stationed in cotton plots treated with insecticides in Po area and others remained in an untreated orchard located nearby. The results underlined developmental instability in *A. mellifera* associated with insecticide treatments in the cotton-producing zones.

These findings underline pesticide burden in Burkina Faso for non-target local biota. Improved pesticide management and monitoring are necessary to reduce the impacts on the ecosystem.

2.5.4 Acute and chronic poisoning

Almost every farmer (70 – 80 %) interviewed during field studies affirmed experiencing sickness during or after pesticide applications. They generally mentioned itching eyes, headaches, gastro-intestinal upset, dermal reaction, respiratory disorders, and dizziness (Congo, 2013; Gomgnimbou et al., 2009; Toé, 2010b).

A study conducted in the cotton-producing area of the "Hauts-Bassins", the "Cascades", and the "Boucle du Mouhoun" showed that the first reason of acute poisoning was accidental intake (53%), followed by suicide (28%) and pesticide application (19%) (Toé, 2010b). The easy access to extremely toxic pesticides for rural populations has made them the preferred mean of suicide with an extremely high case fatality rate (Ouédraogo et al., 2011).

Another issue arising from pesticide use in rural areas is the lack of medical support in case of intoxication. The first problem is the diagnosis of intoxication. A large fraction of people suffering from intoxication refuses to admit it or do not go to a medical center when they feel the first symptoms of poisoning. Most of them prefer to use traditional medicine like drinking milk, oil, and tamarind juice (Bassole and Ouédraogo, 2007; Congo, 2013; Toé, 2010b). Drinking oil and/or milk might be a worsening factor because the majority of pesticides are soluble in fatty products (Ouédraogo et al., 2011). Therefore, drinking oil and/or milk could facilitate assimilation of pesticides, which are highly or moderately soluble in lipids (ex: organochlorines). Usually pesticide handlers only go to a medical center when their vital prognosis is engaged and even in these conditions, they hardly admit the link with pesticide handling. This behavior leads to the late detection of poisoning and put the patient in very dangerous situations (Toé, 2010b). The other problem is to establish a causal link with symptoms. Most of the first symptoms of pesticide acute poisoning are similar to other common diseases such as malaria (fever, headaches, etc.). In rural areas, the local medical staff has generally only little knowledge on pesticides and adapted cures in case of poisoning (Toé, 2010b). This lack of formation reduces the chances to identify the origin of the symptoms and provide a suitable cure in time. Again, the lack of education and proper training of the users but also of the medical staff leads to the underestimation of pesticides toxicity and put the population to great risks. In this context, information collected by questionnaire surveys presented above should also be interpreted with caution. These data rely on respondents' individual perception. Health is determined by numerous factors including personal health practices and behaviors (water and food quality, hygiene, etc.). In the absence of reliable medical diagnosis or pesticide exposure study, the causal link with pesticide is not straightforward.

The chronic exposure to pesticides may trigger a variety of chronic health effects, such as cancers, neurologic effects and reproductive effects (Ouédraogo et al., 2011; WHO/UNEP, 2012a). Chronic effects are inherently harder to detect due to the time lag between exposure and the onset of the disease. Therefore, the origin of symptoms is more difficult to trace. Although chronic poisoning due to pesticides is not well documented in Burkina Faso, the lack of precautions taken during pesticide handling might have negative effects on the long-term. The study conducted by Toé et al. (2000) in a cotton-producing region in Burkina Faso ("Boucle du Mouhoun") revealed that

more than 80% of pesticide users had lowered cholinesterase activity during at least two months after pesticide application. Even if, the cholinesterase inhibition is reversible, this study highlights the underlying effect of organophosphorus and pyrethroids pesticides (cholinesterase inhibitors) on the human body.

Recently, studies conducted in other parts of the world started to focus on the impacts of pesticides on the reproduction system. It appeared that pesticide application might adversely affect human and animal fertility. Pesticides can affect male and female fertility by several mechanisms. Repeated exposure led to induction of developmental abnormalities of the male reproductive tract, and directly or indirectly affected the function of normally developed gonads. Most of the conducted research are supportive that exposure to pesticides can result in a derangement of semen quality, quantity, and motility (Clementi et al., 2008; Kamijima et al., 2004). Interferences with the female reproductive system included altered hormonal balance and therefore menstrual cycle's perturbations (Clementi et al., 2008; Farr et al., 2006). Direct damage of the female gamete, interferences with fertilization and implantation, abnormal reproductive tract development/function were also observed for certain pesticides (Darko et al., 2008). A more than twofold increased risk of time-to-pregnancy prolonged and threefold increased risk for spontaneous abortion was noted among female greenhouse workers where large amounts of pesticides, like abamectine, imidacloprid, methiocarb, deltamethrin, and primicarb were used (Bretveld et al., 2008). These findings are of concerns considering that imidacloprid and deltamethrin ranged among the most used pesticides in Burkina Faso. Endocrine disruptions were not necessarily linked to high-level exposure. Studies outlined adverse impacts on fertility, even at levels lower than that which result in clinical manifestations of acute poisoning. Peiris-John and Wickremasinghe (2008) define low-level exposure as any form of occupational or environmental exposure that did not require any acute clinical intervention. For example, chlordane, chlorpyrifos, DDT, heptachlor and maneb are considered to be endocrine disrupting chemicals with low-dose effects (Vandenberg et al., 2012). Chlorpyrifos and maneb are still used in Burkina Faso. For others like DDT and heptachlor recent use was not reported but traces were found in soil and water (section 0).

Finally, combination of pesticides is also of concerns. Organophosphorous pesticides (OPs) are being increasingly used in combination with pyrethroids because they can synergistically increase the effects of pyrethroids. Studies conducted on pesticides used in Burkina Faso (Ilboudo et al., 2014a) and elsewhere (Perry et al., 2007), outlined the likelihood of higher hazards of pyrethroids arising from combination with organophosphorus. Synergistic toxic effects resulting from exposure during treatment or environmental exposure are difficult to predict and expose the ecosystem and the human populations to great risks.

Chapter 3 Case study definition: market gardening

3.1   Market gardening in Burkina Faso

Market gardening was introduced in Burkina Faso at the beginning of the 20th century (Kêdowidé et al., 2010). For many farmers it constitutes an alternative activity during the dry season since cash crop cultivation is restricted to the rainy season (e.g. cotton). Although certain sites are cultivated all year round, the majority is exploited during the dry season. In order to guaranty continuous access to water, gardening areas are mainly located around the lakes. Gardening accounts for ~16.5% of the total country agricultural production with onion (330'000 tons) and tomato (157'086 tons) being the main products (65% of cultivated surface areas). Other speculations: garlic, eggplant, carrots, cabbage, cucumbers, strawberries, okra, green beans, lettuce, peppers, potato, etc. are produced to a lesser extent. The production is generally intended for the domestic market except for green beans, which are mainly produced for export. Gardening speculations are generally grown on small plots (90%) covering 0.05 - 0.25 ha (World Bank, 2015). The rate of commercialization of the production is estimated at ~90% for a turnover of 82 billion FCFA (MAH et al., 2011b). Gardening is therefore more accurately defined as market gardening in Burkina Faso.

This sector presents important potentialities for the local economy and in the fight against poverty (MAHRH, 2007). The number of gardeners increased by ~53% between 2002 and 2005 and the sector generated ~400'000 employments out of a total of ~6 million workers. It represented about 6 billion FCFA of benefits and an average contribution of 4.5% to the gross domestic product in 2002. In 2005, gardening areas accounted for 8'879 ha with a total production estimated around 166'147 tons (Figure 3:1). In 2008, cultivated surface areas were tripled (25'967 ha) and the production was multiplied by four (Figure 3:1, CountrySTAT Burkina Faso (2017)). The regions « Boucle du Mouhoun ,» « Nord ,» « Plateau central ,» « Hauts Bassins ,» and « Centre Ouest » concentrate the largest surface areas cultivated for vegetable production (MAHRH and DGPSA, 2007).

Contrary to cotton and sugar producers, gardeners are individual producers. They possess their own production equipment. They decide which pesticides to use and purchase them with their own funds. However, this sector lacks of organization and infrastructure to ensure commercialization, conservation, and processing of the products. Less than 68% of the gardeners are organized in working cooperatives. Transformation is mainly of the traditional type and consists in drying the production surplus. The development of techniques and infrastructures for conservation and processing is insufficient and often restricted to individual initiative. The lack of organization of the distribution channels also limits the commercialization potential. As a result, losses of the production exceeds 40% (World Bank, 2015). Pesticides are used in gardening to improve yields and reduce losses during production and conservation. Active substances used are mainly neonicotinoids, pyrethroids, and organophosphates (Figure 2:4). Many studies have outlined the poor working conditions for the operators (ARFA, 2007; Bassole and Ouédraogo, 2007; Oyono Elle, 2008; Toé, 2010b). Issues are globally similar to the general consideration presented for the agricultural sector (section 2.4). Low level of education and lack of suitable spraying and protective

equipment lead to irrational and dangerous use of pesticides. The government had recognized the fruit and vegetable sector potential in the strategy for rural development. Nevertheless, although programs have been developed to encourage these activities and regulations have been implemented at national level, there is still little support and control of the production (Kêdowidé et al., 2010).
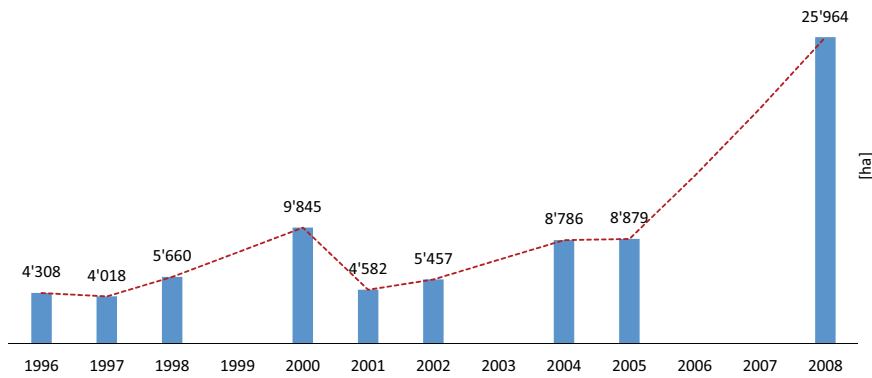
(a) Cultivated surface area [ha]
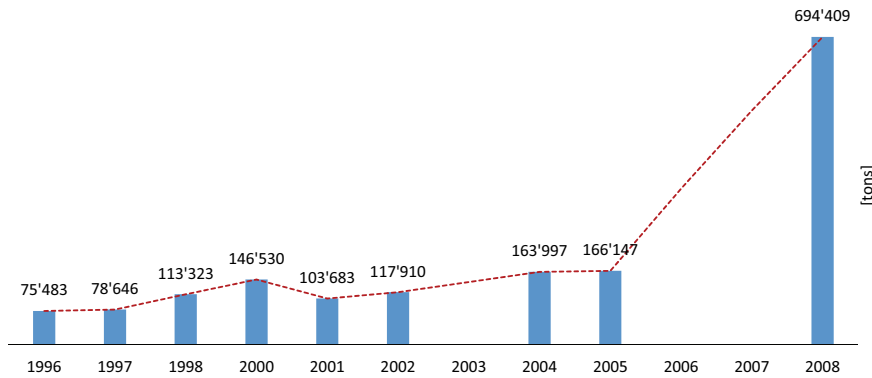
(b) Market gardening production [tons]

Figure 3:1 Cultivated surface areas and production of market gardening from 1996 to 2008
(The red lines are linear interpolations of the data and might not fully represent real trends)
(CountrySTAT Burkina Faso, 2017)

3.2 Reasons for choosing market gardening over cash crop productions

The aforementioned potential for the development of rural populations and the following observations have motivated the choice to focus on market gardening in the present thesis:

- gardening is a major source of revenues for farmers during the dry season;
- low compliance with the good agricultural practices is established and exposes the environment and the populations to great risks;
- contrary to cotton and sugar producers, gardeners do not benefit from any external support for the acquisition of production equipment and for pesticide selection;
- these activities are located around water reservoirs used for drinking water supply and fishing;
- gardening areas are generally located on flood plains. Following the recede of water during the dry season, crops are planted under the maximum annual water level. Therefore, some contaminants are likely to solubilize in water when cultivated lands are flooded during the rainy season;
- the specific social context in gardening areas: the low level of education and the poor knowledge on pesticides of the users hamper the enforcement of the good agricultural practices which may lead to hazardous exposure;
- the long growing season (~6 - 8 months) implies multiple pesticide treatments. Repeated exposure is likely to increase health risks of the exposed populations;
- low incomes generated by gardening may induce a preference for cheaper and illegal pesticide alternatives. Financial limitations also limit the access to suitable spraying and protective equipment;
- the lack of data concerning levels in the environment and occupational exposure in this sector;
- and the reinforcement of importation controls (residues of plant protection products) in developed countries can limit export potentials.

3.3 Objectives and motivations of the thesis

Various authors already outlined hazards from pesticide use on the environment and the populations in Burkina Faso. Field campaigns, chemical analysis, and biological studies underlined the impact of the poor compliance with the good agricultural practices (GPA). As a result, the link between pesticides and acute toxicity (human and environmental) is established. Almost every user affirmed experiencing illness after pesticide applications and hazardous environmental contamination were identified. In the same way, chronic poisoning is likely to occur from the continuous occupational and environmental exposures. However, no concrete measures have been undertaken to tackle these issues. Lack of financial and human resources and multiplicity of the stakeholders (users not organized in working cooperatives, regulation placed under the authority of multiple regulation bodies, etc.) have hampered the implementation of suitable solutions.

Based on the existing data, the following remarks can be made on the current situation in Burkina Faso:

- poor education level and training of the operators hamper the application the GPA;
- unsuitable use of pesticides does not allow meeting the objectives of crop protection and food security (~40% of the production is lost);
- there is a paucity of quantitative data regarding pesticide exposure and pollution;
- the country lacks of suitable infrastructures and resources to enforce existing management strategies, to implement suitable monitoring and tackle important issues such as waste treatment;
- due to insufficient analytical resources (equipment and technical staff) analyses are often outsourced to foreign laboratories. Analyzed substances were therefore not always relevant to the local context;
- existing data were collected during isolated research studies (one-off studies) or following accidental releases and are therefore more representative of local areas or isolated cases. There is an urgent need for routine controls of the domestic market and monitoring with standardized approaches;
- existing data are scattered between multiple sources, which makes retrieval and aggregation difficult;
- the lack of political support and the separation of regulatory functions hamper the enforcement of existing management strategies;
- there is a need for the development of integrated management strategies to reduce the impacts on the populations and the ecosystem. However, the support provided to the local research is insufficient, which hampers the development of solutions adapted to the local context. In addition, the lack of dissemination and communication of the scientific knowledge reduces the impact of this sector.

The current use of pesticides in Burkina Faso has consequent impacts on the population and the ecosystem and limits its potential for development. The literature review underlines the need for data collection using a harmonized approach and parameters adapted to the local context. New tools must be developed to reinforce the understanding of the problematic and help in the implementation of concrete solutions. These considerations have motivated the present thesis. The first objective was to develop analytical methods for pesticide analysis in foodstuffs and environmental and human matrices, suitable to the African context. Methods for multiresidue analysis were adapted to quantify substances used in the country. The protocols were developed to comply with technical resources available (frequent electricity supply failure, lack of analytical equipment, difficulty to import specific laboratory equipment and technical staff). In this domain, the present thesis also aimed to enhance 2iE (local partner in this project) analytical capacity in the field of pesticide analysis. This included the development of the laboratory of analytical chemistry in Ouagadougou (purchase of suitable equipment and glassware) and training of the technical staff. The third objective was to apply the developed methods for pesticide detection in pilot study areas, in order to identify the preferential accumulation compartments and substances linked to

potential human health or environmental hazards. Samples collected during field campaigns provided a three-year monitoring of pesticide occurrence in environmental matrices. Analysis of pesticides in foodstuffs and dietary studies allowed evaluating pesticide intake. Human exposure was also assessed by biomonitoring in a human matrix (hair). The fourth objective was to perform a comprehensive risk assessment of the current situation. Collected data was subsequently used to derive environmental and human exposure risks. The fifth objective was to capitalize collected data in a transferable database for further studies. Finally, the present thesis intended to provide recommendations for farmers and decision makers with on-field restitution of the results.

As aforementioned, it was decided to focus on the market gardening sector. Pesticide impacts have been extensively studied in developed countries but quantitative evaluations of pesticide burden is still lacking in developing countries and particularly in Burkina Faso. The present thesis proposes a refined quantification of environmental and human exposure to pesticides and provide a comprehensive assessment of the resulting hazards in market gardening areas. It constitutes a first diagnosis on the effective burden of pesticides use in market gardening in Burkina Faso.

3.4 Involvement of the stakeholders

This thesis is an applied research project. It involved large field campaigns for data collection. Field surveys were conducted with questionnaires and samples for chemical analysis were collected in rural areas. All these activities were conducted in direct contact and with the support of the local populations. Communication played a pivotal role in the success of this research project. In order to gain full support of the local populations and achieve a concrete impact, stakeholders must be identified and integrated since the beginning. **The dialog was established at four levels**. Each of them included different stakeholder categories and therefore different ways of communication. In order to respect the traditions and administrative procedures, consultation of stakeholders is recommended in the following order of priority.

As the present thesis included human participation and more particularly sampling of a human matrix (hair), the **first level** was to ensure that the research protocol was conformed to the national code of ethics. The research plan was submitted for approval to the national ethic comity of Burkina Faso. The protocol and collection of hair samples were approved by the national ethic comity in December 2015 ("Délibération n° 2015-12-010"). The **second level** consisted in gaining the approval and support of the local administrations. An audience was requested with the mayor of each municipality of the retained study areas to present the research plan and objectives. Even though, the mayor is now the official administrative chief of the villages, the traditional chiefs ("chief of the lands") have still a great influence on local populations in Burkina Faso. Each village has its own chief. It was therefore a prerequisite to get also the approval of every traditional chief of the villages concerned by the present study. Visits were organized directly on the field and a round table was organized in February 2016 (Figure 3:2, a) with the chiefs of the villages located around Loumbila Lake. The latter aimed at discussing the feasibility of hair sampling for biomonitoring exposure to pesticides. Indeed, although hairs are considered by scientists as a non-invasive matrix, they are given a certain importance in traditional beliefs. The belief that hairs might be

associated with black magic rituals is very strong in Burkina Faso and could have been an obstacle to the achievement of our objectives. The transparent presentation of the procedure and objectives led to the direct approval of the chiefs. The **third level** was the integration of the local populations. Workshops were organized in the city halls of the villages to present and discuss every phase of the project (Figure 3:2, b). Representatives of the village populations (gardeners, merchants, fishermen, etc.) and administrations (chiefs, mayors, local water comity, etc.) participated in the four organized events. In order to increase population participation, the 10 villages located around Loumbila Lake were also visited prior to interventions (Figure 3:2, c). Discussions were conducted in the center of the villages where every participant could intervene. This approach allowed integrating the expectations and specific requests from the studied populations. It was particularly helpful to tackle the sensitive issue of hair sampling. During these events, the participants presented their opinion and came with concrete solutions regarding sampling protocol (e.g. location for sample collection, etc.). T**he last level** of communication was the transfer of knowledge acquired during the present thesis. This phase includes all the aforementioned stakeholders (administrations, local populations, etc.) and was also extended to a larger audience. This included presentation and communication of the results to the scientific community via the organization of workshops (Figure 3:2, d), the publication of articles in scientific journals, and the participation in 5 international conferences (see. Curriculum Vitae). At the end of the project, participatory workshops will also be organized in the villages concerned by the present study in order to communicate the results to the local populations. Finally, workshops will be held at 2iE (in Ouagadougou) in order to transfer the acquired experience and knowledge to any interested organization (NGO, national laboratories, governmental institutions, etc.).

Although these interlocutors had different interests and expectations, they are inseparable and any project considering working in similar areas should include this communication scheme as a prerequisite. The retained approach greatly facilitated the successful adoption of the project by the local populations, which considerably saved time during field campaigns. We acknowledge that the present thesis in its design is more a scientific research project. However, the participation of the local populations in the definition of research orientations and the transfer of the results constitute a first step toward concrete impacts.

(a) Meetings with traditional chiefs

(b) Communication in local city halls

(c) Communication in the villages

(d) Scientific communications

Figure 3:2 Communication with the stakeholders

3.5 Database development

The above-mentioned research plan (section 3.3) led to the collection of considerable amounts of data from different types and origins. In the following chapters, multiple questionnaire surveys were conducted on the fields to provide a better understanding of the local context. Levels of pesticides were also quantified in samples from various matrices (water, soils, sediments, food, and hair). A database was developed in Excel to centralized and store this data for further use in the present thesis or future research projects. Input masks coded in Visual Basic guaranteed the homogenization of the recorded data. A unique identification number was assigned to each input in order to link the different tables together according to the 3 data structures presented in Figure 3:3. Excel worksheets were saved in the non-proprietary file format: comma-separated values format (csv) to facilitate further reuse. Every data file is accompanied by a metadata file describing its content and sources (questionnaire used, field description, reference, etc.). The "GPS" data table contains the geolocation of the collected information. The data stored (Table 3:1) in this database were used in the following chapters as raw data for statistical analysis and modelization or for the interpretation of the laboratory results. Data gaps are due to the aggregation of data from different sources, to the knowledge of the respondent regarding a given domain and the willingness to answer of the respondent. The database will be freely available online by the end of the present project (appendix A).

Table 3:1 Database content

Table name	Data content	Sources
Agricultural practices	501 gardeners	Questionnaire surveys (Chapter 4)
Pesticide use	426 users	Questionnaire surveys (Chapters 4 & 5)
Cultivated crops	385 gardener cultivation calendars	Questionnaire surveys (Chapter 4)
Dietary study	126 diets	Questionnaire surveys (Chapter 5)
Pesticide resellers [a]	31 pesticide resellers	Questionnaire surveys (Chapter 4)
Medical centers [a]	20 medical centers	Questionnaire surveys (Chapter 9)
Hair survey	110 persons	Questionnaire surveys (Chapters 7 & 8)
Analytical results	-	Laboratory analyses (Chapter 5 , 6, 7 & 8)

[a] The data collected during 2014 field surveys was not included in the databases but it can be found in Ohui (2014) and Zeba (2014)
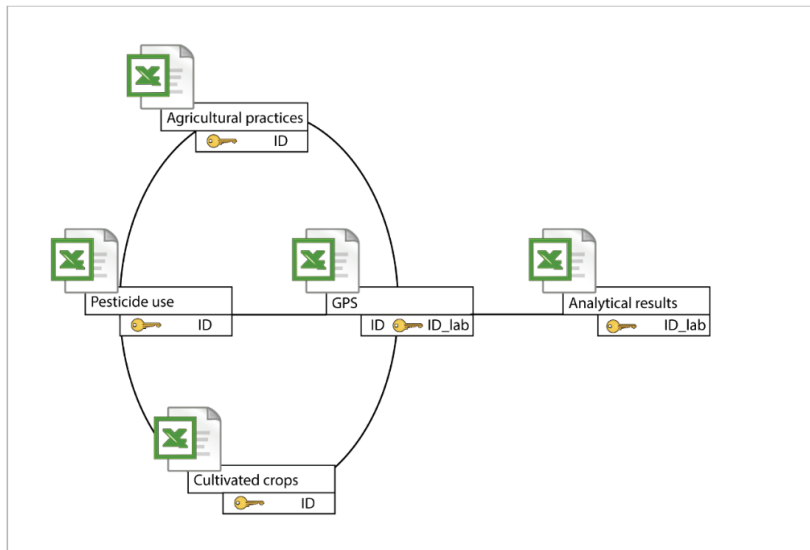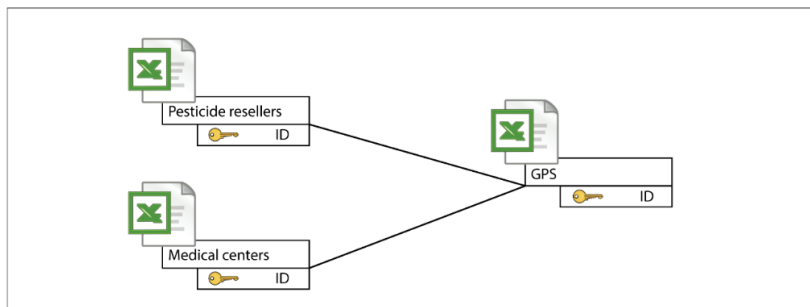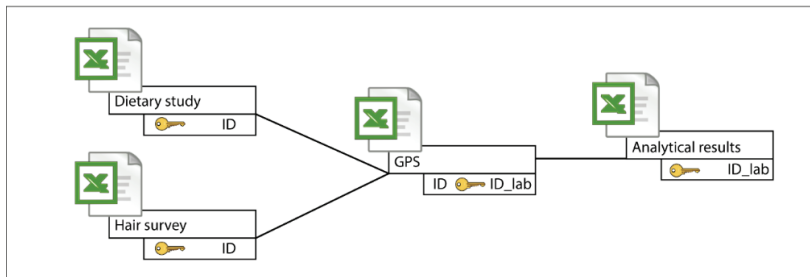
Figure 3:3 Structure of the developed databa

Chapter 4 Characterization of agricultural practices and target substance selection

4.1 Introduction

This chapter aims at characterizing local agricultural practices in the studied areas. Questionnaire surveys were conducted on the field between 2014 and 2015 in four gardening areas (Loumbila Lake, Dem Lake, Ziga Lake, and the Nariarlé Basin). When relevant, comparison between studied areas was made to determine whether behaviors were generic or site specific. Pesticide impacts have been extensively studied in developed countries but quantitative evaluations of pesticide burden is still lacking in developing countries and particularly in Burkina Faso. Previous studies focused mainly on the inventory of pesticide formulations used, related poisoning symptoms, and obsolete or illegal stockpiles. Only few studies performed a quantification of pesticide residues in environmental and human matrices. Defining a relevant list of target pesticides for further laboratory analysis was a prerequisite. A preliminary screening of pesticide levels in water, soils, and sediments was performed. It aimed at providing a first overview of the pesticide speciation and their effective presence in environmental compartments. Analytical results completed the inventories (field survey and literature compilation) and allowed deriving a list of target substances to be analyzed in further experiments conducted in the present thesis. Finally, as our resources and time were limited, the decision was made to concentrate our efforts on four gardening areas (Dem, Loumbila, Ziga, and the Nariarlé Basin) to provide a first global diagnosis and then to conduct a refined assessment in a pilot study area: Loumbila Lake. Therefore, this chapter also explored the possibility of generalizing conclusions of this thesis at the national level by comparing the results from field campaigns with other studies conducted across the country.

4.2 Methods for data collection

4.2.1 Selection of the study sites

The use of pesticide in market gardening is a common practice countrywide. The main objective was to collect up to date and harmonized data that allow further quantification and assessment of the environmental and health impact of pesticide use. The first step was to define a framework that ensures collection of representative and robust datasets. Narrowing the scope allows to increase sampling capacity (number of collected samples and sampling frequency) on given sites in order to provide a diagnosis with required confidence and precision for compliance checking. It was therefore decided to concentrate our efforts on four study areas. In a conservative approach (i.e. protective), selected sites must be representative of the global situation or the worst-case scenario.

Four study sites were selected based on the four criteria presented in Table 4:1. In order to guarantee continuous access to water during the dry season, gardening areas are located around water reservoirs. Most of these reservoirs are artificial. They were built to accumulate water during the rainy season and secure electricity and drinking water supply all year round. Anthropogenic activities conducted in the vicinity increase the pressure on this valuable resource. Contamination of water is likely to occur via multiple pathways (runoff, permeation through soil, atmospheric transfers, accidental release, etc.) when pesticides are applied in surrounding areas (McKnight et

al., 2015). **Priority was given to reservoirs supplying drinking water for the main cities.** Contamination of these water bodies could have an impact on large populations. **Intensity of gardening activities** was the second criteria for the selection of the study areas. Concentration of the activities in a given zone was expected to yield a larger impact on environmental compartments and human health. **Location and accessibility** of these sites were also considered for practical reasons. Remote rural areas might be difficult to access with transportation. Preserving the cold chain integrity in the absence of electricity and with high temperatures is a challenge. Sites were selected within a reasonable distance to the laboratory (Ouagadougou) and road access. Finally, **availability of data** was also a matter of concerns. Existing information were used to draft a preliminary diagnosis of the situation and assess the representativeness of the retained study areas. Possibility to compare our findings with previous studies also completed our analysis and provided a better understanding of the results and interpretation of observed trends. Loumbila, Ziga, and Dem reservoirs and the Nariarlé Basin (Figure 4:1) were retained for the assessment of the global context (Chapter 4 and Chapter 9). Based on the comparative evaluation of agricultural practices and individual behaviors presented in the present chapter, it was decided to concentrate our further efforts on a pilot study area: Loumbila Lake. This was made in an attempt to provide a refined diagnosis of the situation. The representativeness of. this study area allowed conclusions to be extended to the general context of gardening in the country. The following paragraphs provide a general description of the retained study areas. Descriptions vary in content due to the limited information available on these sites.

Table 4:1 Criteria retained for the selection of the study areas

Criteria	Justification for the selected sites
Water use	Dem reservoir supplies drinking water for Kaya;
	Loumbila (~30%) and Ziga (~70%) provide drinking water for the capital;
Intensity of the gardening activities	Loumbila Reservoir, Dem Reservoir, and the Nariarlé Basin are very dynamic sites (large populations and large cultivated surface areas).
	Gardening activities are conducted all year round around Ziga reservoir.
Location and access	Distance to the laboratory in Ouagadougou (sample conservation and transportation time and cost) and road access.
Existing data	Availability of data in the literature and from previous studies conducted at 2iE.
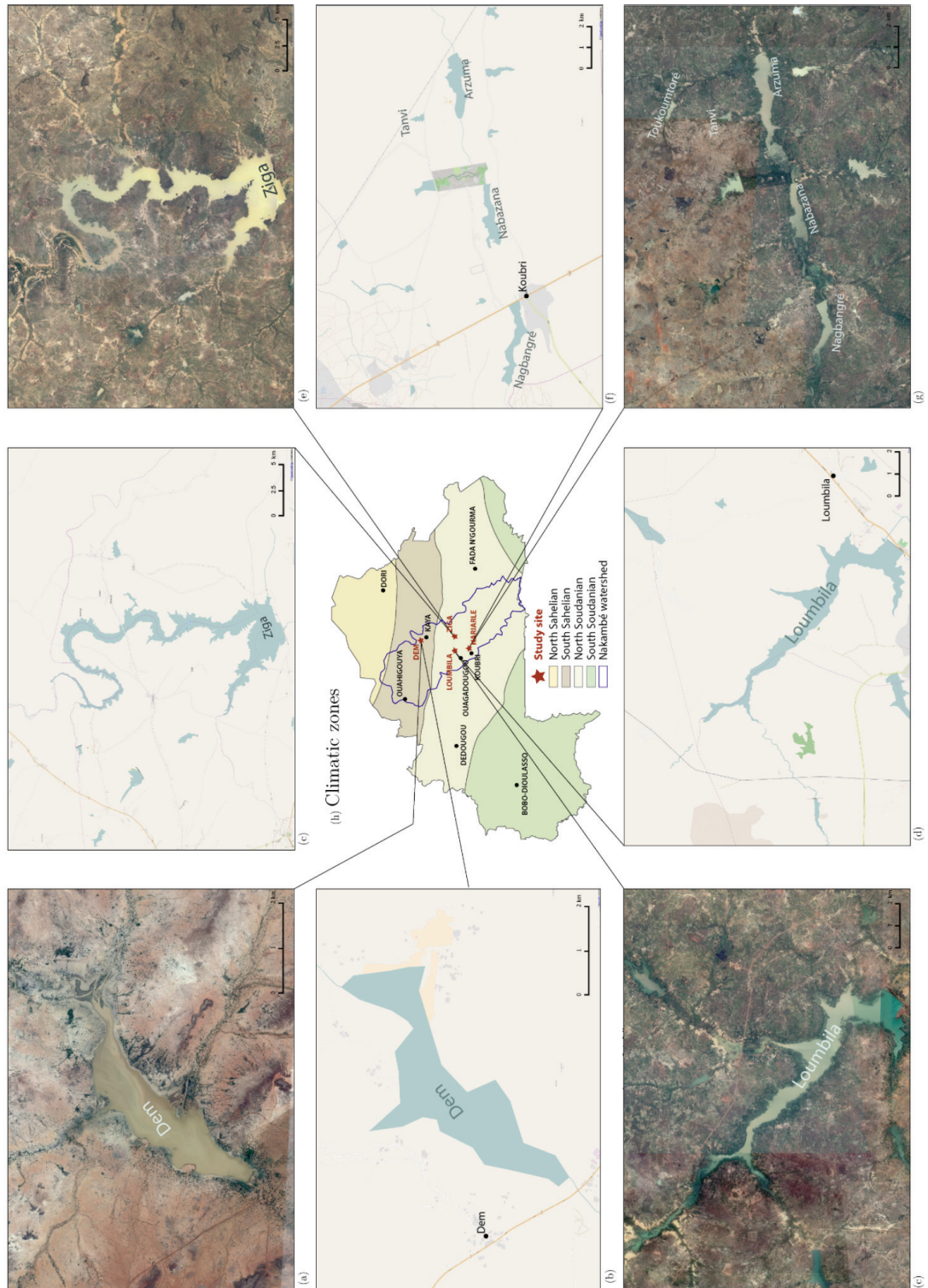
Figure 4:1 Locations of study areas

a,c,e,g: background map extracted from google earth imagery © 2017 CNES/ Airbus, DigitalGlobe

b,c,d,f: background map source: OpenStreetMap Contributors (2017)

h: map adapted from: Fontès and Guinko (1995)

The studied reservoirs are all included in the Volta Basin. The Volta Basin covers 400'000 km² located in 6 countries: Burkina Faso (43%), Ghana (42%), Togo (6%), Ivory Coast (3%), Mali (3%), and Benin (3%). The White Volta ("Volta Blanche" in French) takes its source in the north of Burkina Faso where it is called Nakambé and flows over 1'136.7 km to the north of Ghana (Mul et al., 2015). The studied areas are located in the center regions of the country. In these regions, gardening activities generate more than 30% of household revenues (country average ~5% (MAH et al., 2011a)).

4.2.1.1 Dem Reservoir

Dem reservoir is located in the Sanmatenga Province, at ~14 km from the capital of the province Kaya. The dam was built in 1950. The reservoir lake has a capacity of 15.17 million m³ and a surface area of 10 km². It is located in the Nakambé watershed (Figure 4:1). Water from the reservoir is used to supply Kaya (54'365 inhabitants in 2006 (MEF et al., 2009)) with drinking water and local agriculture production. With the reservoirs Bam and Sian, they cumulate ~45% of water resources of the Center-North region.

4.2.1.2 Ziga Reservoir

Ziga Reservoir is also located in the Sanmatenga Province at ~38 km from Ouagadougou. Built between 1998 and 2000, the dam presents a capacity of 200 Mm³ exploited since 2004. The reservoir lake covers 85 km² and is supplied by a 20'800 km² watershed (Garba et al., 1999). Ziga was initially built to ensure a sufficient water supply of Ouagadougou until 2025. The first construction phase (ZIGA I) achieved in 2007 included the construction of the dam, a pumping station, a water-treatment station (capacity of 3'000 m³ h⁻¹), and a canalization of 43 km. To date, Ziga Reservoir supplies 70% of the capital's drinking water. The second construction phase (ZIGA II) started in 2014. The new infrastructures planned include the doubling of the adduction capacity, construction of a new water-treatment station with a capacity of 4'500 m³ h⁻¹ and the densification of the distribution system (52'000 new connections and 160 public standpipes). Predictions indicated that ZIGA II will allow to cover the needs of the capital until 2030 (Reymond, 2016).

The increasing use of the reservoir for the water supply makes this resource extremely valuable for a large population. The construction of the dam secured large amounts of water accessible all year round. One specificity of this site is that water availability in the area allows the gardening activities to be conducted in every season. Since 2013, the ONEA (National Office for Water and Sanitation) with the support of the government has reallocated gardening areas downstream of the dam or in remote areas located upstream. The objective was to create a buffer zone between agricultural lands and the reservoir to protect the water resources from contamination. The irrigation system and motor pumps allow cultivation of vegetables at a sufficient distance from the lake. As lands are not flooded during the rainy season, gardeners can cultivate without discontinuity.

4.2.1.4 Nariarlé Basin

The Nariarlé Basin is located in the center region of the country in the Province Kadiogo. The capital of the province Koubri (43'928 inhabitants in 2006) is located at 25 km from Ouagadougou. The watershed extends up to 25 km in the north-south direction and 50 km in the east-west direction. This region constitutes an important source of food supply for the capital, Ouagadougou (Moiroux, 2006). With more than 50 reservoirs in about 1'000 km², the Nariarlé Basin presents the highest density of reservoirs in Western Africa (CECCHI P. et al., 2007). Almost half of the inventoried reservoirs (44%) are located in the municipality of Koubri (CM. Koubri, 2008). Water is used mainly for agricultural production. The area counts 6 dams, 40 natural water bodies, 8 cultivated plains, and 9 orchards. Surface areas occupied for market gardening has increased from 172 ha in 2004 to 536 ha in 2008. Vegetables productions are mainly sold on local marketplaces (Koubri, Péelé, Didri, Nakamtenga et Kiendpalogo) but also in Ouagadougou. Lettuce, cabbage, onion, and eggplant are the main speculations produced in this area (CountrySTAT Burkina Faso, 2017). Koubri is located on the national road RN5 that connects Ouagadougou to the Ghanaian border which facilitate transportation and trade of the products (CM. Koubri, 2008; Ohui, 2014).

4.2.1.5 Loumbila Reservoir

Loumbila reservoir is located in the Oubritenga Province in the region called "Plateau-Central". The municipality of Loumbila covers a surface area of 176.99 km² and hosted 27'932 inhabitants in 2006 (MEF et al., 2009). The city is located at ~15 km from the capital of the country. The dam was constructed in 1947 on the Massili River (influent of the Nakambé). The watershed covers a surface area of 2'120 km². The capacity of the reservoir was raised in 2004 from 35.98 to 42.2 Mm³ by a 40 cm increase of the spillway height. Water is exploited for its fisheries resources and for agriculture production but the primary function of the dam is to provide drinking water to Ouagadougou (Cecchi et al., 2004). Surveys conducted in 2013 identified ~2'686 gardeners working in the ~347 ha of cultivated areas surrounding the reservoir (Agence de l'eau du Nakambé, 2014).

4.2.2 Surveys on agricultural practices and literature review

In 2013, our partner 2iE performed two inventories on agricultural practices in the gardening areas located around Loumbila and Dem reservoirs. A first list of pesticides used in Burkina Faso was drafted based on these field surveys (Congo, 2013; Mbaby, 2013) and inventories proposed in the literature (15 studies, appendix B). The objective was to get a preliminary overview of the situation and prepare the field inventories planned in the frame of the present thesis (March - April 2014).

Data on agricultural practices was collected using two types of questionnaires directed toward two different groups of actors: pesticide final-users (gardeners) and resellers. Different questionnaires have been prepared in order to fully assess the subtleties of each actor. In order to get harmonized data, the content was inspired by the questionnaires used during the first fields campaigns conducted in 2013 (Congo, 2013; Mbaby, 2013). However, the latter were designed to provide a first

diagnosis of the situation. The questionnaires used aimed at gathering qualitative data (agricultural practices and sanitary risk, and inventoried pesticide formulations). In the present thesis, they were extended to fulfill our new objectives and acquire quantitative data. Additional questions on pesticide use (dose, frequency of application, treated surface area, mixing of pesticides, etc.), biopesticides use, and cultural calendar were added. The questionnaires mainly comprised open-ended questions; options were proposed only to help respondents who struggled to provide an answer. The following sections present the results of surveys conducted in 2014 and 2015. Statistical analyses were performed using the developed database (3.5) and the data of the 245 gardeners surveyed during this period.

4.2.3 Preliminary screening of pesticides in environmental matrices

A preliminary screening of water, soil, and sediment was conducted in 2014 in order to provide a first diagnosis on pesticide occurrence in environmental matrices.

4.2.3.1 Sampling plan

Samples were collected during the growing season in March-April 2014 in the four market gardening areas presented in section 4.2.1.

Knowing that the objective of this campaign was to get a first screening of the situation, a limited number of samples was collected on each site (Table 4:2). Apart from the site located near the outlet of the lakes (i.e. the inlet of the drinking water pumping facilities for Ziga Lake, Loumbila Lake, and Dem Lake), the choice of the sampling sites was based on the two following criteria: representativeness of the situation of the global area or of a particular activity in terms of agricultural practices or pesticide use. Samples were transferred on ice at the laboratory (~ 4°C).

Table 4:2 Sampling plan for the preliminary study

Sample description	Nb of samples	Location
Grab sample at the pumping inlet	3	Dem, Loumbila and Ziga
Grab sample in traditional well	2	Loumbila, Nariarlé
Grab sample near shore under cultivated area	7	Dem (3), Loumbila (3), Nariarlé[a] (3), Ziga (3)
Sediment samples	8	Dem (2), Loumbila (2), Nariarlé[a] (2), Ziga (2)
Soil samples	14	Dem (3), Loumbila (4), Nariarlé (3), Ziga (4)

[a] Samples were collected in Naba Zana Lake

4.2.3.2 Water analysis

Grab samples (1 L) were collected in borosilicate bottles. Pesticides were extracted by solid-phase extraction (SPE) using a procedure similar to the one presented in section 5.3.5. At this stage of the project, this method was used to conduct a preliminary screening of pesticides present in surface water. Therefore, isotopic dilution was performed with the addition of atrazine-d5 and PCB 30 as only surrogates (only atrazine-d5 was used for UPLC amenable substances) and GC amenable substances were separated using a 60 meters Phenomenex Zebron capillary column (ZB-5 MS, 60 m, 0.25 mm, 0.25 µm). Other analytical parameters were similar to section 5.3.5. The recoveries were optimized with the extraction of 1 L of mineral water (Evian water) fortified with 500 µL of the target analytes mix solution at ~250 ng mL^{-1}. Extraction recoveries of the target analytes presented in Table 4:6 were in the range of 30% - 120% (except Endosulfan sulfate: 150%).

4.2.3.3 Soil and sediment analysis

Sediments were sampled from randomly selected locations in the studied reservoir lakes. Samples were collected at 5 - 20 m from the shores (depth: ~30 - 40 cm) and placed in aluminum boxes. They were subsequently air-dried at room temperature (~28 °C) and stored in freezer (-20 °C) prior to analysis. Soils were sampled form randomly selected cultivated plots with an auger (sampling depth: ~10 - 20 cm) and stored in aluminum boxes in freezer (-20 °C) prior to analysis.

After removing coarse particles, samples were passed through a 2 mm sieve. Ten grams of homogenized sample were subsequently extracted by sonication (10 min) in acetone : hexane (1:4, v/v) followed by purification on chromatographic column packed with florisil. Cleanup on florisil was identified as the limiting step in the procedure. A large fraction of the target analytes was not recovered after elution. Sorbent type and activation can significantly affect purification efficiency (Zweig and Sherma, 1978). Therefore, different sorbent deactivation and florisil particle size were tested. The experimental setup was based on the study of Djurovic et al. (2012). Most of the target analytes had non-polar or intermediate polar character (Table 4:6). It was therefore suitable to use a polar sorbent for purification together with non-polar or moderately polar solvents (acetone (Ac), dichloromethane (DCM), ethyl acetate (EthAc), hexane (Hex)). Methanol (MeOH) and acetonitrile (ACN) fractions were further added to improve recovery of the polar analytes (e.g. acetamiprid, imidacloprid, etc.). Experimental conditions tested for the cleanup of soil and sediment extracts are presented in Table 4:3.

Optimization of the cleanup parameters was conducted with 0.5 mL of the target analytes mix solution at ~500 ng mL^{-1} introduced at the top of the purification column. Recovery assay was subsequently conducted on triplicate spiked soil samples at similar concentration for the validation of the final protocol. As for water, this method was used for a preliminary screening of pesticides present in soils and sediments. This procedure was not retained for the further analysis conducted in the present thesis, as the laboratory in Ouagadougou was not equipped to perform such procedure. Therefore, in depth validation was not performed and basic description of the development of the protocol and its efficiency are presented in following paragraphs in the event of development and use in a further research project.

Table 4:3 Experimental conditions tested for the cleanup of soil extracts

Cleanup	Setup 1	Setup 2	Setup 3	Setup 4
Sorbent	10 g Florisil (mesh 100 - 200)	5 g Florisil (mesh 60 - 100)	5 g Florisil (mesh 60 - 100)	5 g Florisil (mesh 100 - 200)
Deactivation	2% Water	2% Water	none	None
Elution	20 mL Hex 20 mL Hex : DCM 9 : 1 20 mL Hex : DCM 1 : 1 20 mL de DCM	30 mL Ac : Hex (1 : 4) 20 mL EthAc	30 mL Ac : Hex (1 :4) 20 mL EthAc	30 mL Ac : Hex (1 : 4) 20 mL EthAc

Cleanup	Setup 5	Setup 6	Setup 7	Setup 8
Sorbent	5 g Florisil (mesh 100 - 200)	5 g Florisil (mesh 100 - 200)	5 g Florisil (mesh 100 - 200)	5 g Florisil (mesh 100 - 200)
Deactivation	2% Water	none	2% Water	None
Elution	20 mL Hex 20 mL Hex : DCM 1 : 1 20 mL DCM 20 mL EthAc	30 mL Ac : Hex (1 : 4) 20 mL EthAc 20 mL MeOH	20 mL Hex 20 mL Hex : DCM 1 : 1 20 mL DCM 20 mL EthAc 20 mL MeOH	30 mL Ac : Hex (1 : 4) 20 mL EthAc 30 mL MeOH 40 mL ACN

Optimization of elution conditions helped to pass from 20 analytes with acceptable recovery (40% - 140%) in setup 1 to 45 in setup 6 (Table 4:3). Even though studies are supportive that elution with MeOH followed by ACN are suitable conditions for the elution of acetamiprid and imidacloprid, no analyte were detected in the ACN fraction (setup 8). On the other hand, MeOH addition helped to recover these two analytes in acceptable proportions but no significant change was observed with volume increase (20 mL in setup 6 or 30 mL in setup 8).

The best recoveries were achieved with setup 6. It also presents the advantage of providing a separation between GC and LC amendable analytes. Under these conditions, GC amendable analytes were recovered in significant amounts only in the Ac : Hex (1:4) fraction. EthAc fraction ensured solvent miscibility in the column but was discarded after elution as no analyte was recovered in this fraction.

After elution, Ac : Hex fraction was split for differential analysis of GC and UPLC amenable substances. Extracts were subsequently evaporated to dryness and reconstituted in the suitable solvent for further analysis on GC-MS (0.25 mL isooctane) and UPLC-MS/MS (0.25 mL of the mixture methanol : water (5:95, v/v) with 0.1% formic acid). MeOH fraction was evaporated to dryness and reconstituted 0.25 mL of the mixture methanol : water (5:95, v/v) with 0.1% formic acid prior to UPLC-MS/MS analysis. At this stage, isotopic dilution was performed with the addition of atrazine-d5 and PCB 30 as only surrogates (only atrazine-d5 was used for UPLC amenable substances) and GC amenable substances were separated using a 60 meters Phenomenex Zebron capillary column (ZB-5 MS, 60 m, 0.25 mm, 0.25 µm). Other instrument operating parameters were similar to appendix C. Extraction recoveries of the target analytes presented in Table 4:6 were in the range of 40% - 130%.

4.3 Results

4.3.1 Characteristics of the studied population

Gardeners surveyed were 33% women and 77% men. Respondents were between 17 and 79 years old, with the majority being under 45 years old. Most of them had between 6 and 20 years of experience in gardening (Figure 4:2). Among people who answered the question related to their education (n = 181), 77% had no education and only 23% attended primary school.

(a) Age of the respondents (n = 194) (b) Working experience in gardening (n = 238)
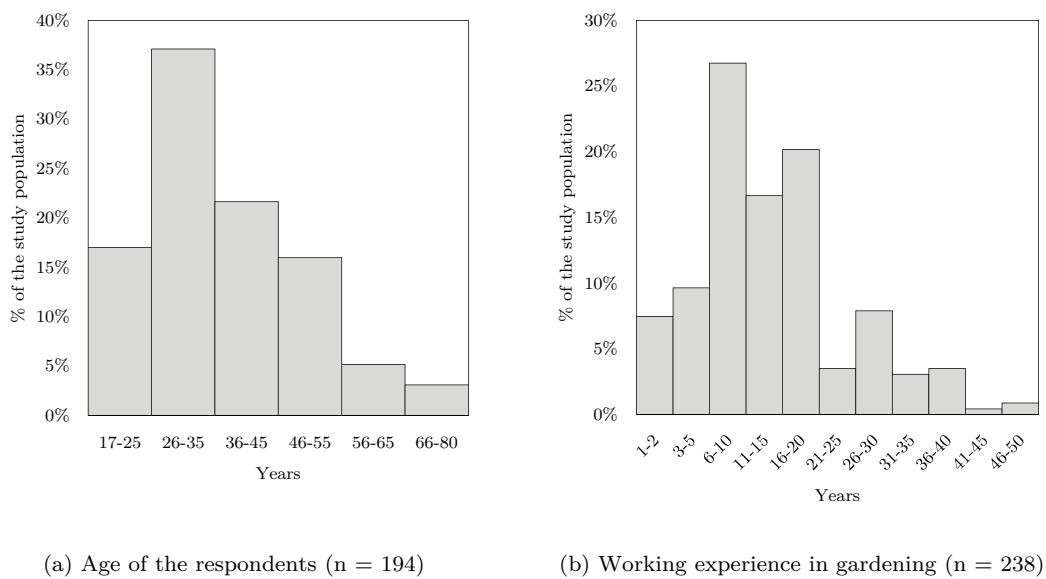
Figure 4:2 Age of the respondents and working experience in gardening

4.3.2 Pesticides used

During field surveys conducted in 2014 and 2015, 30 active ingredients were identified in 83 commercial formulations (Figure 4:3). Among these pesticides, a large number was intended for cotton treatment and only 13% were authorized by the CSP for gardening activities. Pesticide used were mainly avermectin, pyrethroids, neonicotinoid, and organophosphates with acetamiprid, cypermethrin, and lambda-cyhalothrin being the major reported active substances.

(a) Loumbila Lake (n = 360)

(b) Dem Lake (n = 49)

(d) Ziga Lake (n = 88)

(e) Nariarlé Basin (n = 285)
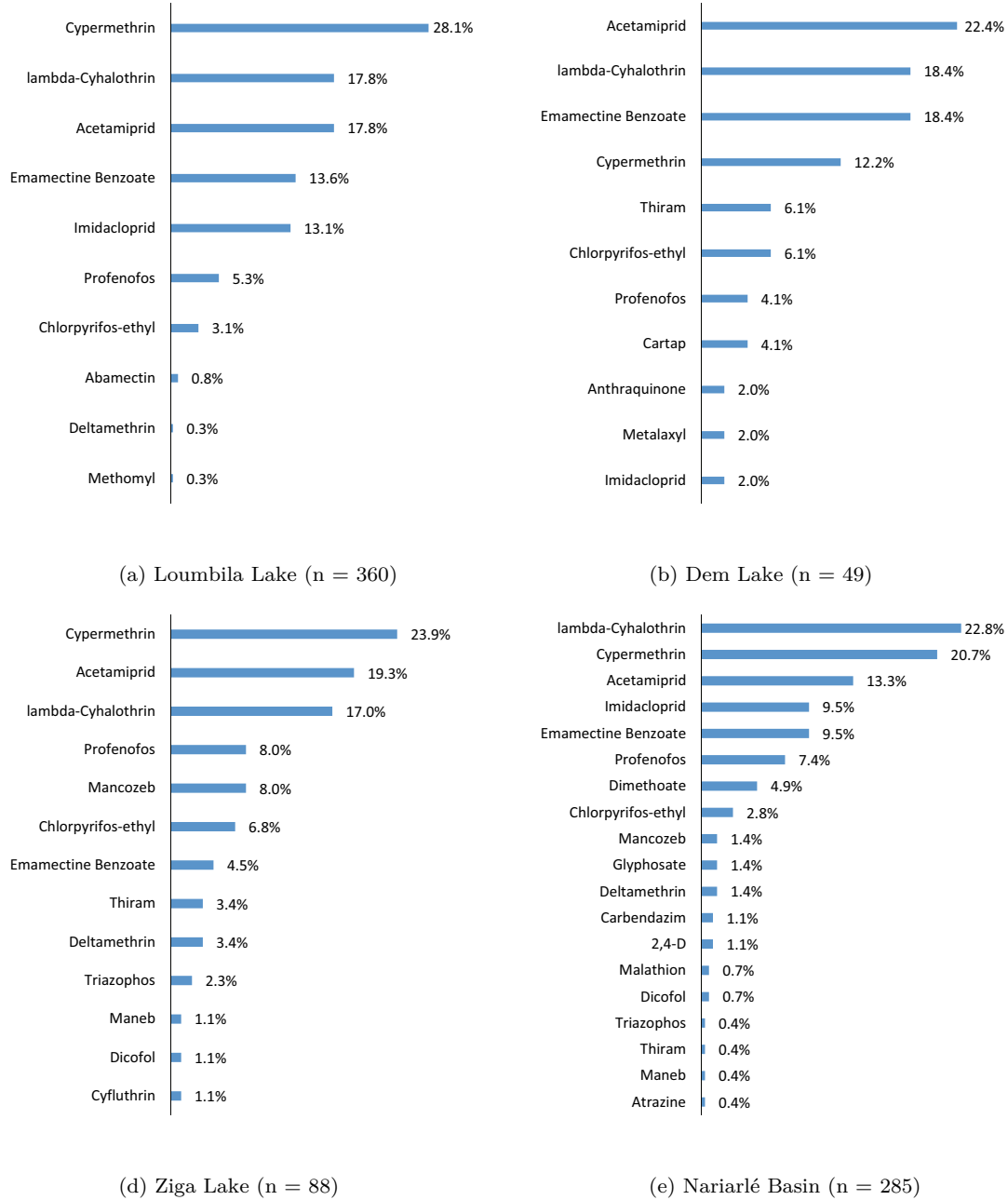
Figure 4:3 Frequency of reporting of identified active ingredients

In 2015, gardeners from Loumbila were asked to precise the reasons for the choice of the pesticide formulations. Pests, diseases, and cultivated crops were reported as the main factors influencing the choice of the pesticide formulation (Figure 4:4).
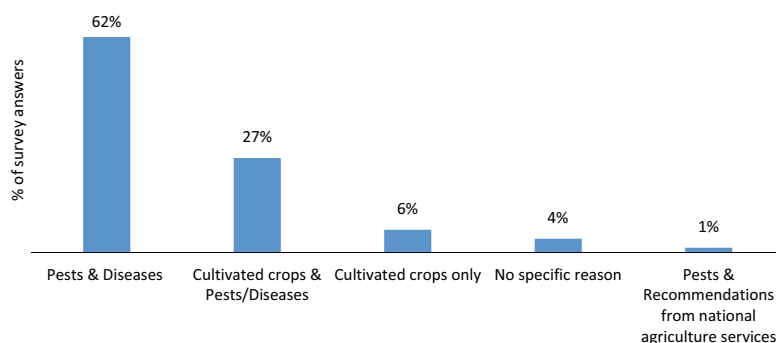
Figure 4:4 Factors influencing the choice of pesticide formulations (n = 184)

Compilation of the inventories of pesticides used in Burkina Faso found in the literature (Appendix B) yielded 265 commercial formulations and 88 different active ingredients (not presented). Together with the data collected during filed surveys, classification by intended use (cotton, sugarcane, gardening and storage), frequency of reporting and information on the most commonly used substances allowed to draft a preliminary list of target substances for the screening in environmental matrices.

The National Council on organic farming (CNAbio) in Burkina Faso recommends the use of biopesticides. Fungicides, insecticides, and bactericides can be prepared with local plants (CNAbio, 2017). Chili pepper and garlic decoctions were cited during surveys but not used. The only biopesticide used in the studied areas was prepared with neem seeds macerated in water. Among the respondents (n = 240), 37% knew the existence of these preparations but only 17% used them. Most of the users (78%) were from the Nariarlé Basin and were satisfied with the effectiveness. The main reason reported for not using these freely available products was the efforts required for the preparation and the treatment. Ingredients must be finely crushed, added to water and left few hours for maceration. Reduced efficiency is generally observed after few days so the mixture must be prepared before each application. These types of treatment might also require a higher frequency of application and thus more work. Even though it is encouraged by national institutions, only few people (n = 6) had received a training or information regarding the production of these "homemade pesticides".

4.3.4 Pesticide resellers

Over the 31 resellers that participated in the surveys, less than the half (39%) attended primary school and only 3 had received a formation regarding pesticides. Only 2 of them had accreditation and hence could be considered as officials. Pesticides were either sold in small shops in the cities or on market stalls (Figure 4:5). Most of the resellers did not sell only pesticides and plant protection products were exposed together with other items such as foodstuffs, vehicle parts, petroleum products, etc. None of the visited selling point was equipped for safe storage of pesticides (i.e. ventilated, equipped with protective materiel, etc.). Supplies were purchased from large official stores in the cities or illegally imported from surrounding countries (e.g. Ghana). No importance was accorded to the expiration date and homologation. Obsolete and banned pesticides (endosulfan, paraquat chloride, etc.) were found in local stores.

(a) Market stall   (b) Storage of pesticides with food

Figure 4:5 Local pesticide selling points

Most of the resellers sold knapsack sprayers. Personal protective equipment sold were very limited. The most commons were gloves and mufflers in synthetic fabric, which might protect from dust particles but not from vapor of organic chemicals. They explained that the demand for these equipment was low due to their cost. They also underlined their poor availability in rural areas and the difficulty for them to propose more specific equipment.

4.3.5 Organization of the work and work practices

4.3.5.1 Spraying equipment

Most of the pesticides used were diluted in water before treatment. Two different techniques were used to apply pesticides on the field: hand carried lever-operated knapsack sprayer or a bucket within which the operator dipped leaves or a broom (Figure 4:6). Knapsack sprayer was the most common application technique (80%) but artisanal methods were used as a cheap alternative in absence or malfunctioning of a sprayer. In the Nariarlé Basin, every gardener reported using a knapsack sprayer but this result might be biased by the desire of the respondents to hide unconventional techniques.

(a) Knapsack sprayer   (b) Broom and bucket

Figure 4:6 Pesticide application techniques

If most of the gardeners washed their spraying equipment on the field after each use (75%), a large fraction (20%) washed it in the dams (Figure 4:7).
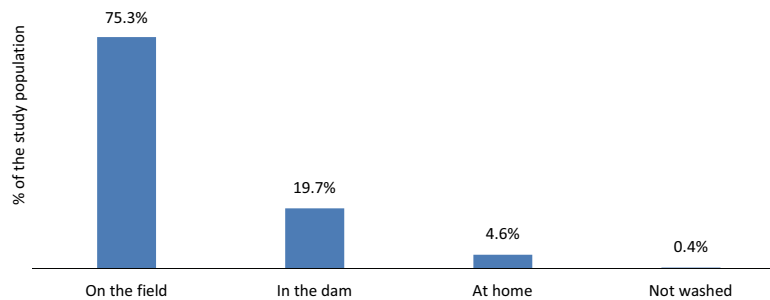
Figure 4:7 Cleaning of the spraying equipment (n = 239)

4.3.5.2 Dose, frequency of application, and delay before re-entring the field and before harvest

Application rate (quantity per surface area) and spray concentration exceeded manufacturer recommendations in respectively 72% and 56% of the cases. Most of the gardeners ignored that recommendations on the application rate were provided on formulations' labels, as they were not able to read them (high illiteracy rate). Moreover, 81% had received no formation on pesticide handling. In 2015, gardeners from Loumbila were asked to precise the factors influencing the dose of pesticide applied. Pests, diseases, and surface area treated were apparently the main factors influencing the quantity of pesticides applied (Figure 4:8). These answers are in accordance with the fact that ~40% of the gardeners affirmed that they increased the treatment frequency in case of pest attack or disease outbreak. However, comparison of doses applied and treated surface areas did not show any correlation (Figure 4:9). As aforementioned, gardeners were not able to read the labels. It was therefore not surprising to observe no rational use in terms of application rate and concentration.
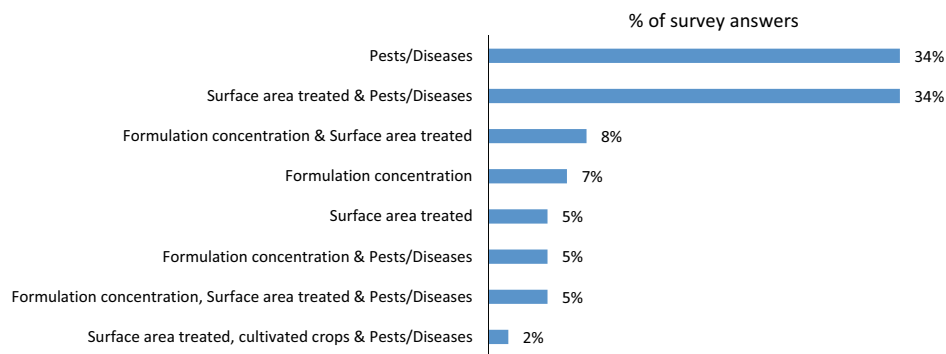
Figure 4:8 Factors influencing the dose of pesticide applied (n = 61)
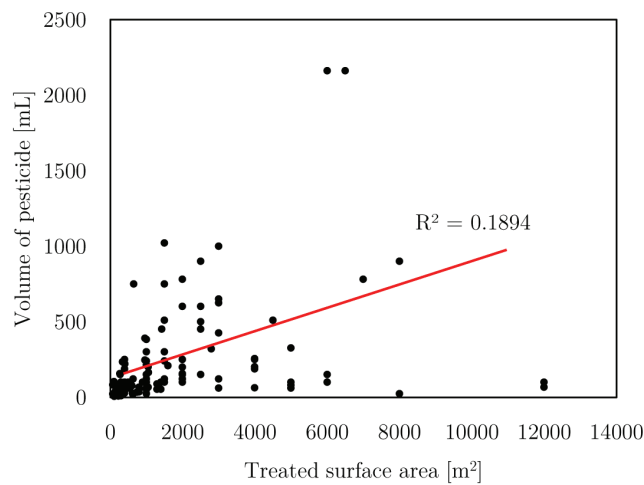
Figure 4:9 Relation between the quantity of pesticide formulation applied and treated surface area (n = 226)

Frequency of application normally depends on cultivated crops, commercial formulations, and field conditions (pest attacks, disease outbreak, etc.). Reported interval between treatments varied between 1 day and 90 days. Most of the gardener applied pesticides once a week (interval between applications of 7 days) or every two weeks (interval between applications 10 - 15 days). Treatment scheme was conditioned by random pest attacks and disease outbreaks in ~40% of the cases. Therefore, it was difficult to define accurately the treatment frequency. As for application rate, most of the gardeners ignored that recommended frequency of application was provided on formulations' labels, as they were not able to read them.

To prevent workers and consumers from excessive exposure, manufacturers are supposed to provide information on re-entry interval (REI) and days-to-harvest interval (DHI). REI and DHI are periods of time that must pass before re-entering the fields or harvesting vegetables. They should allow sufficient time for the dissipation of the pesticide residues and prevent hazardous exposure of the workers and the consumers. For most of the respondents, the REI was under 7 days (67%) and mainly around 3 days (26%). They affirmed that they learned it from their own experiences. The DHI was also not respected. Similarly to the dose and frequency of application, illiteracy hampered the comprehension of information provided on pesticide labels.

However, it is also noteworthy that information regarding the proper use of the pesticide (application rate, frequency of application, REI, and DHI) were missing on many commercial formulation labels. Some of the labels were also in foreign language (English), thus not comprehensible by local users. Many pesticide containers were also found without any label (Figure 4:10) as they were illegally imported or reformulated (mixture made by the gardener or the reseller).

Figure 4:10 Pesticide containers without label

Finally, most of the gardeners applied more than one pesticide formulation on their cultivated crops. In average, 3 pesticides were used with a maximum of 10 different formulations used by the same individual. 54% of the respondents indicated mixing pesticides together before application.

4.3.5.3 Time of the day of application and weather conditions

Most of the respondents applied pesticides between 10 am and 6 pm and respectively 25% and 12% before and after. They indicated that meteorological conditions were important and more precisely the wind and the insolation. 34% considered that both of these factors were important and 57% considered that only wind was relevant.

4.3.5.4 Personal protection

Gardeners wore only rudimentary personal protective equipment (PPE). The majority had no specific protection (68%), 31% wore a muffler made of synthetic fabric and only 11% wore gloves while handling pesticides (Figure 4:11, a). None of the survey participants had chemical-resistant workwear. They were all dressed with normal clothing covering partially their limbs (Figure 4:11, b). Most of them wore a tee-shirt (50%) and 18% a short during pesticide application. Clothes were changed and washed after each pesticide application in 64% of the cases (Figure 4:11, c).

(a) Specific protection (n = 186)

(b) Workwear (n = 113)

(c) Personal hygiene after application (n = 183)
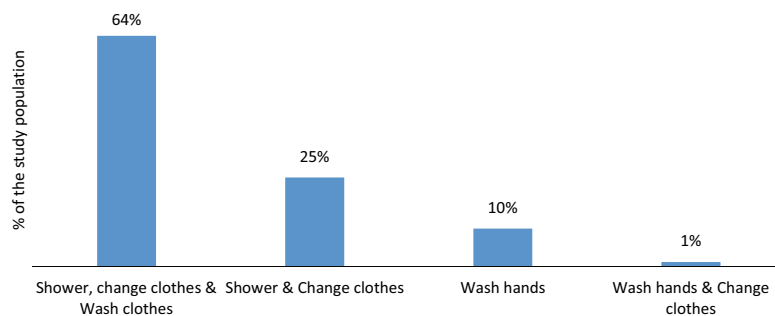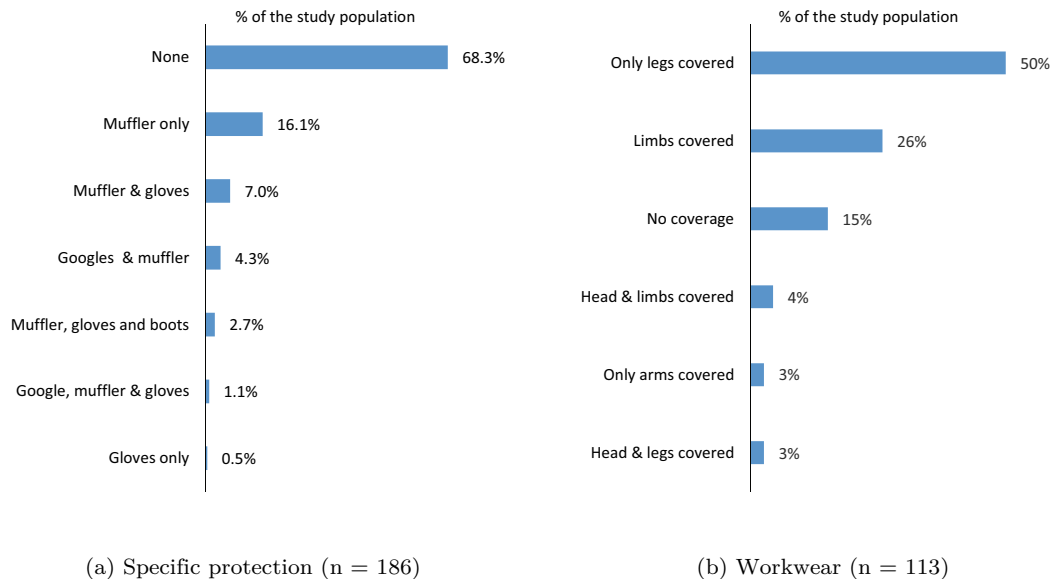
Figure 4:11 Personal protective equipment and personal hygiene

4.3.6 Storage and waste disposal

Users have to deal with three types of products after pesticide application: the leftovers (pesticides not applied on the fields), the empty containers, and the obsolete pesticides (Figure 4:12). Leftovers were stored on the fields and reused in most cases. Most of the time pesticides were stored on the field, either left between vegetable rows (69%) or buried (23%). Obsolete pesticides were used in 44% of the cases. Waste (Figure 4:12, d) were either buried (39%), thrown on the fields (35%) or burned (12%).

(a) Handling of leftovers (n = 184)   (b) Pesticide storage (n = 186)

(c) Handling of obsolete pesticides (n = 184)   (d) Disposal of empty containers (n = 187)
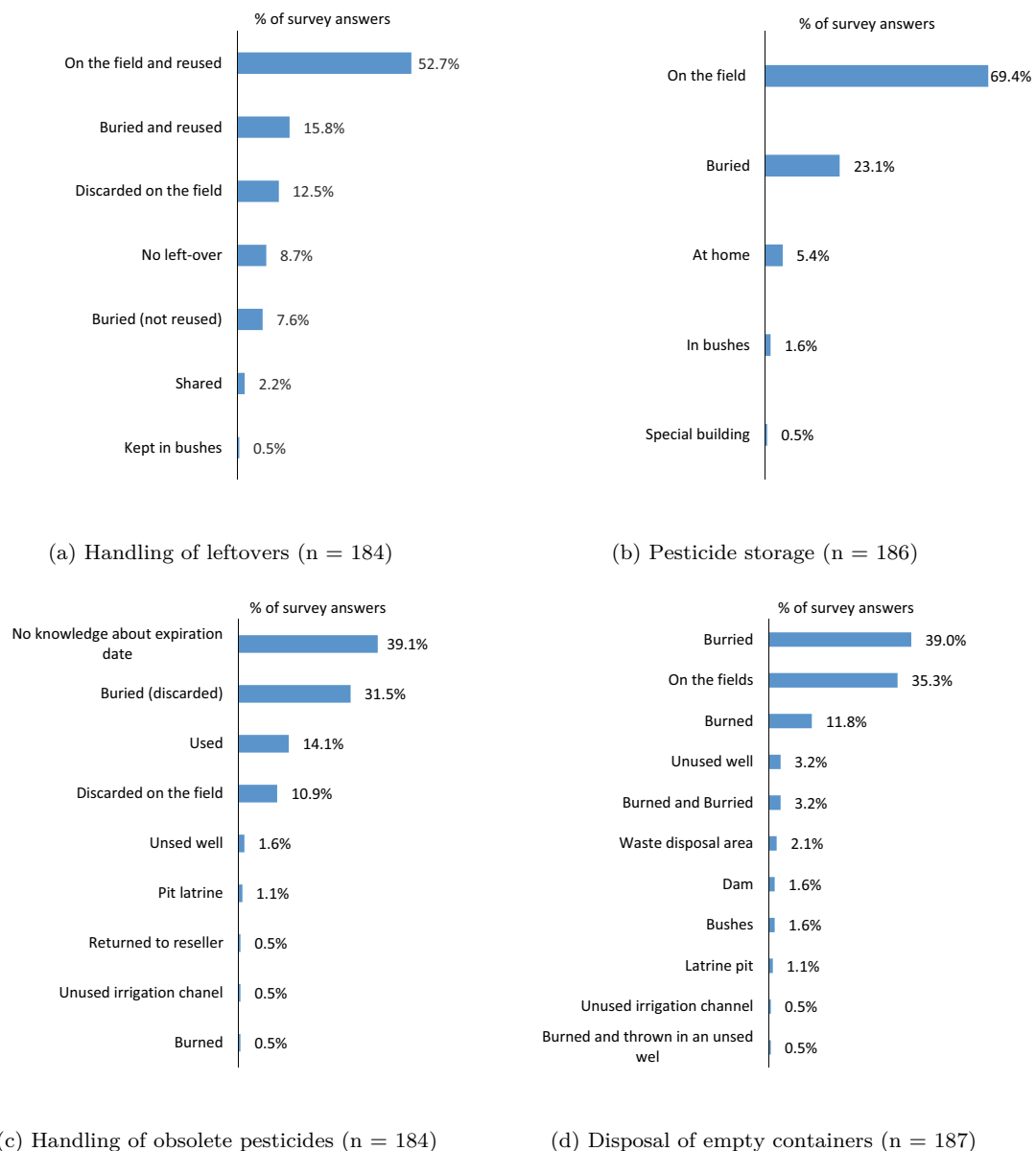
Figure 4:12 Handling of leftover, storage of pesticides, handling of obsolete pesticides and disposal of empty containers

4.3.7 Cultivated crops

In the studied areas, 19 different crops are cultivated during the dry season (Table 4:4). Maize is not produced in large quantities. It is planted between vegetable rows to protect the culture and the soil from the wind and the sun. The beginning of the growing season relies on the accessibility of the fields. Gardening areas are generally located in flood zone. Vegetables are planted as soon as the lands are dry enough. The topography, intensity of precipitation, and the distance from the lakes play a role in this process. In Ziga, Dem, and in the Nariarlé Basin, seeding may starts in September but in Loumbila the growing season starts in December/January.

Table 4:4 Cultivated crops in the studied areas

Cultivated crops	
Boulvaka (*Corchorus Tridens*)	Melon
Cabbage	Morenga
Carrot	Onion
Chili pepper	Okra (*Abelmoschus esculentus*)
Cucumber	Potato
Eggplant (*Solanum aethiopicum* & *Solanum melongena L*)	Sorrel (*Hibiscus sabdariffa*)
Green bean	Tomato
Green/Red pepper	Watermelon
Maize	Zucchini

In 2015, gardeners from Loumbila were asked to precise the reasons for the choice of the cultivated crops (Figure 4:13). Soil appeared to be the principal factor followed by water needs and costs/benefits (seeds, seedling, maintenance, etc.).
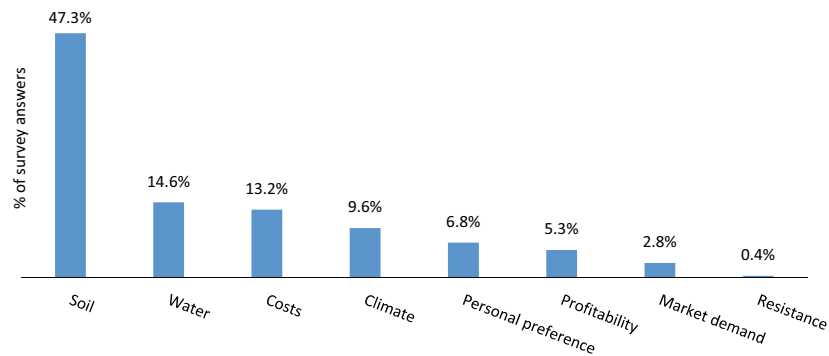
Figure 4:13 Factors influencing crop selection (n = 243)

4.4 Discussion on agricultural practices and identified risks

Field campaigns helped to characterize local agricultural practices and outlined the lack of training and knowledge regarding the good agricultural practices (GAP) in the studied areas. This situation might lead to excessive exposure of the operators, workers, and the consumers resulting in potential health hazards. Acetamiprid, cypermethrin, and lambda-cyhalothrin were the principal active ingredients found in formulations used in the studied areas. These findings are in accordance with recent studies conducted across the country (Son et al., 2017; Wendé Alice Naré, 2015).

4.4.1 Pesticide labeling

Three different problems associated with labeling were identified. First, information provided were not always sufficient to ensure a safe use of the products. Direction for use (application rate, frequency of application, dilution, intended use, etc.) were not always presented and most of the time were incomplete. Second, in many cases pesticide containers had no label. Illegal importations, pesticides mixing or repackaging usually led to label removal or loss. These practices leave the user with no proper information on how to handle the product. Medical centers visited during field campaigns also reported many cases of accidental poisoning due to the confusion of pesticide containers with beverages. Finally, communication through labels was most of the time ineffective. A large fraction of the users was illiterate and was therefore not able to read them. In addition, due to illegal importations from surrounding countries, some of the labels were in foreign languages (e.g. English), which completely hampers understanding.

Similar conditions were observed in other rural areas. Ouédraogo et al. (2011) already outlined the problems associated with containers labeling at national level. Bassole and Ouédraogo (2007) concluded that only 10 to 17% of the gardeners located in Bobo-Dioulasso, Ouahigouya, and Ouagadougou were able to read pesticide labels.

Measures must be undertaken to regulate pesticide labeling in the country. Containers with no or incomplete labels must be removed from the market. In order to ensure suitable and comprehensive labeling, it is recommended applying the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) proposed by the United Nations (United Nations, 2011).

4.4.2 Criteria for selection and suitability of treatment products

There is a multitude of commercial formulations for which application rate, frequency of application, day-to-harvest interval, etc. may vary. These formulations are intended to efficiently and safely eradicate certain pests and diseases, under particular conditions (concentration, climatic conditions, etc.) and on specific material (crops, protective nets, stored food, etc.). For this reason, the CSP defined a specific list of formulations authorized in gardening.

In the study areas, gardeners and resellers were not able to explain clearly why they were using or selling a given product. Gardeners affirmed that their choice was mainly driven by encountered pests and diseases. However, most of them were not able to name the pesticides that they were

using. Investigators had to ask for the containers to get the real names of the products. It is thus difficult to acknowledge that selection was made on purpose. Previous studies already outlined that most of the gardeners were incapable to describe, identify or recognize pests and link them to their potential effects on crops (ARFA, 2007; Oyono Elle, 2008). The lack of knowledge on pests, diseases, and related damaged hampers the selection of suitable treatment. Previous studies outlined that the criteria prevailing for the selection of plant protection products was their cost and their availability (Toé, 2010b).This explained why pesticides used were most of the time not intended for vegetables but for cotton treatment. This practice might result in undesirable residue levels even after processing (Kaushik et al., 2009; Keikotlhaile et al., 2010; Reiler et al., 2015).

4.4.3 Application methods

4.4.3.1 Equipment used for pesticide application

The most commonly used equipment in the studied areas was hand-carried lever-operated knap-sack sprayer (16 L). Similarly, 96% of the population interviewed in the Mouhoun region by Toé (2010a) was using knapsack sprayers. Nevertheless, not every gardener was able to maintain or afford such equipment and artisanal alternatives (broom and bucket) were used instead. These alternatives are also widespread in other areas. In Yitenga, less than 25% of the gardeners used sprayers (Oyono Elle, 2008) and less than 41% in Ouagadougou (Wendé Alice Naré, 2015). Watering can filled with pesticides was also used when no other equipment was available (Bassole and Ouédraogo, 2007).

Almost every farmer knows about sprayers but availability and high cost appeared to be the main reasons for finding alternatives. Well-designed sprayers present less risk of exposure to pesticide during application than rudimentary techniques presented above. Therefore, using the later exposes the user to greater poisoning risks.

4.4.3.2 Dilution preparation

Pesticides used in gardening were diluted in water prior application (emulsifiable concentrates (EC), wettable powder (WP), soluble powder (SP), etc.). The preparation of this dilution is critical regarding the risk of exposure. Indeed, this phase implies direct handling of pesticides and most of the time no safety precaution were taken:

- gardeners usually wore no PPE (risk of splashing, inhalation, etc.);
- mixing was done on the fields regardless of the sensitivity of the location (proximity of a water resources (lake, wells, and boreholes)).

The dilution together with the application technique condition the quantity of active ingredients applied on crops. It constitutes therefore a critical step regarding efficiency of the treatment and environmental and human exposure. Application rate (quantity per treated surface area) is defined by the manufacturer generally for each type of crop. Lower application rate may undermine the efficiency of the treatment. On the contrary, application of larger quantities can cause greater

damages to non-target species (most of the pesticides are nonspecific) and excessive exposure of the operators, re-entry workers, and consumers (potential increase of pesticide residues on crops).

Recommended application rate and mixture concentration were exceeded in many cases (72% and 56%). Lack of formation and difficulties to assimilate labels makes it difficult to ensure appropriate dosage accounting for target pests, suitability of the pesticide formulation, crop type, surface area to be treated, and recommended quantity. It is therefore not surprising that Son et al (2017) also observed a large variability of the applied doses between gardeners and exceedance of recommended doses.

Many authors also underlined the problematic of inappropriate mixture of pesticide formulations (Ouédraogo et al., 2011; Son et al., 2016; Toé, 2010c). This practice was widespread in the studied areas (54% of the operators) and might have consequent impacts. Commercial formulations are not intended to be mixed. Toxicity of mixture is difficult to predict. Combined toxic effect of a mixture of pesticides might be significantly higher than the toxicity of the compounds taken separately. These synergies were proved to cause potentially higher hazards for human health (Graillot et al., 2012) and the environment (Leboulanger et al., 2009b). Finally, mixtures also complicate the medical management of poisoned patients (Ouédraogo et al., 2011).

4.4.3.3 Pesticide application schedule

In cotton production, trading companies and agricultural services provide the producers with recommendations on the suitable pesticide formulations, doses, and number of applications based on the weather forecast and tests in experimental fields. Pesticides are generally applied ~6 times per growing period. The first treatment is performed ~30 days after seeding and after every 14 days (Ouédraogo et al., 2009).

Unfortunately, in gardening, operators did not benefit from similar support. Farmers generally decided to do the first application only after seeing damages caused by pests or diseases, rather than following the recommendations given by the pesticide manufacturer. Pesticides are supposed to protect crops and prevent these damages. In some cases, late application of pesticides can result in inefficiency of the treatment. Although accurate definition of pesticide application scheme was difficult to obtain, collected information were in accordance with previous studies. Frequency of application (every 6 to 9 days) reported by Oyono Elle (2008) was similar to the information collected in the studied areas and ARFA (2007) also observed increased treatment frequency (every 3 to 5 days) in case of high pest pressure. In the same way, REI and DHI were generally not respected in other gardening areas (ARFA, 2007; Son et al., 2016).

Treatments were generally conducted during the day, between 10 am and 6 pm. High temperatures (~30° C) and low relative humidity in the study areas might induce significant evaporation of spray droplets before they reach the target. Reducing droplets' size increases the influence of ambient air movements and thus increases spray drift. Moreover, higher temperatures increase dermal penetration and cutaneous blood flow, leading potentially to an amplified circulation of

pesticides within the body (Macfarlane et al., 2013). Evening and nighttime hours are characterized by stable atmospheric conditions. This absence of mixing limit the dispersion of pesticide droplets that may drift off the target but remain in the air as a concentrated cloud (Garreyn et al., 2007). Early morning application (with cooler temperatures) is therefore recommended.

4.4.4 Personal protective equipment

In the studied areas, personal protective equipment used did not offer a suitable protection. As a result, many farmers experienced symptoms of acute poisoning after pesticide application. Personal protective equipment constitutes the first user protection. It prevents from exposure during pesticides preparation, application, and other activities conducted in treated areas (irrigation, crop inspection, picking vegetables, etc.). The main routes of exposure are dermal, oral, respiratory and conjunctival routes (Imran and Dilshad, 2011). Therefore, suitable protective equipment should prevent exposure to pesticides through these routes (Figure 4:14).
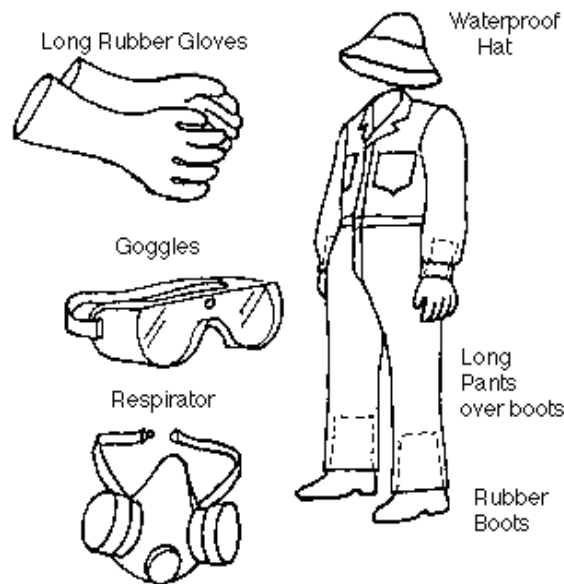
Figure 4:14 Personal protective equipment for pesticide application (Montana State University, 2007)

Field surveys conducted across the country also underlined a constant lack of protective equipment and the use of rudimentary material. Mufflers made of synthetic fabric were the most common protection, boots, hats, gloves goggles, etc. were used to a lesser extent (Bassole and Ouédraogo, 2007; Congo, 2013; Ouédraogo et al., 2009). In a study conducted in the western region, Toe (2010) found that only 1% of the farmers were equipped as presented in Figure 4:14. Behavioral change and equipment adaptation must be supported by providing information and training adapted to the education level of the users.

4.4.5 Storage of pesticides

The majority of the users was aware of the dangerousness of plant protection products and stored them in the fields far from home. However, storage techniques were rarely safe.

In the studied areas, 5.4% of the gardeners stored pesticides at home. This proportion was in the lower of range of previously reported estimations (18% in Tanghin, 12% in Boulmingou, 8% in Yitenga and 26 - 40 % in the eastern region (ARFA, 2007; Oyono Elle, 2008)). Pesticides were usually kept out of children reach (e.g. hidden in the house or placed in the granary), (Ouédraogo et al., 2011; Toé, 2010b). Direct contact with the substances but also inhalation from the volatilization of damaged or non-suitable containers might increase residential exposure.

Gardening areas were generally distant from residential areas. Storage of pesticide on the field was therefore the best alternative to prevent residential exposure. However, absence of dedicated storage facilities induced other problematic. Leftovers and new products were generally buried (15% - 23%) or hidden in the field (53% - 69%)). The volatilization and leaking might occur in presence of high temperature and damaged containers. The contamination could potentially affect soil, water, crops, and air in the surroundings and increase exposure of the individuals present on the fields. Contaminated sites inventoried during the national inventory of POPs and obsolete pesticides (MECV, 2005b) were the result of unsafe storage and unsafe wastes disposal (section 2.5.1).

In retail stores, in the presence of high temperature (evaporation) and unsuitable aeration, air contamination is likely to increase the exposure of the personnel. Finally, storage of the containers alongside with other sensitive items (e.g. food, beverage, etc.) presents a great risk of cross-contamination and a source of hazard for the consumer.

4.4.6 Equipment cleaning and waste handling

4.4.6.1 Equipment cleaning

Equipment used during pesticide application include workwear, PPE and spraying material.

Clothes wore during the treatments might be contaminated. Operators from the studied areas reported changing clothes and washing them in respectively 91% and 64% of the cases after each application. Cleaning clothes with water and soap is crucial to reduce dermal exposure (Garreyn et al., 2007). Ouédraogo et al. (2009) observed similar behaviors, 42 % of the clothes used for pesticides application were washed directly after application with soap, the rest of the farmers affirmed washing their clothes when they came back home. On the other hand, previous studies also outlined different trends. In studies conducted by ARFA (2007) and Oyono Elle (2008), 70% - 99% of the gardeners did not consider that changing or cleaning clothes was a priority and they only washed their hands after crop treatment. Differences are either the results of behavioral evolution with time or biased answers given by the respondents to hide certain practices.

In the same way, reuse of unwashed sprayers or other artisanal alternatives might enhance exposure to pesticides. Almost every gardener cleaned its equipment with water (99.6%). Although this

was an appropriate procedure, washing techniques might have an impact on water resources in the studied areas. Spraying equipment was often cleaned directly in the lakes, wells or in the close vicinity of them. Water contamination could affect aquatic life as well as the health of the consumers of these water resources. The safest procedure consisted in drawing water with a clean bucket and washing equipment on the field. It is also recommended wearing PPE while cleaning the spraying equipment. Ouédraogo et al. (2009) underlined that 86 % of the farmers never used gloves for washing equipment. Handling of contaminated material expose the operator to significant risk of poisoning.

It is recommended that, all the equipment is thoroughly washed with soap and water after each use (Garreyn et al., 2007). Water must be collected with a clean container and brought to the field where the cleaning will be performed. Contaminated water must be discarded on the field, between vegetable rows.

4.4.6.2 Waste handling

In most cases, there were little leftovers after application. Depending on the quantity, they were saved for further use or poured directly on the field. On the other hand, empty containers constitute a real problem, as the country has no infrastructure for collection and treatment of such contaminated material. Only large companies like SOFITEX, SAPHYTO, etc. collect, store, and try to eliminate their wastes. In the studied areas, empty containers were mainly buried (39%), abandoned in the nature (35%), burned (12%) or disposed in unused well (3%). These practices are likely to contaminate environmental compartments and ultimately cause harm to unintended targets (non-target species or individuals). As underlined by the national inventory of POPs (MECV, 2005b), the most adapted way to dispose of biological active substances is high temperature incineration (1500°C) and inert material can be recycled or buried in a landfill. However, these facilities are not available in the country. Solutions must be provided at regional/national level in order to ensure safe waste disposal.

Gardeners used pesticides with no consideration of the expiration date. Obsolete pesticides have generally unknown efficiency and toxicity. Only large companies like SAPHYTO tried to retitrate obsolete pesticides. Burkina Faso has a strong lack of organization and infrastructure for waste treatment and disposal. To date, no concrete action has been taken to manage wastes and obsolete formulations.

4.4.7 Target substances selection

With the experience from these field campaigns, we were able to issue the final list of target compounds for the project by crossing various sets of data according to the criteria presented in Table 4:5.

Table 4:5 Target pesticides selection criteria

Criteria	Description
Intended use	Used in gardening or for protection of harvests (food storage)
Frequency of which the substances have been inventoried	Reporting frequency in the studied areas and in the literature
Identification across different inventories	Simultaneous observation in 2, 3 or 4 of the studied sites and in gardening areas in Ouagadougou (Oyono Elle, 2008)
Presence over the time	Substances identified in 2015 and 2014 versus 2013 field surveys
Presence in the top 20 of the most inventoried substances	Cross-tabulation of the collected data (field surveys, literature, etc.)
Substances reported as the most commonly used	Based on the literature review and field surveys
Substances quantified in environmental matrices	Based on the literature review and section 4.4.8
Substances registered by the Stockholm Convention	Ex: substances like DDT and its metabolites were included
Metabolites of substances of particular interest	Ex: Atrazine metabolites: DIA, DEA ; DDT: DDD and DDE; etc.
Physicochemical properties and toxicity	Persistence and toxicity

The final list of target substances (Table 4:6) is composed of 45 substances from 11 pesticides groups: avermectin, carbamate, chloroacetamide, neonicotinoid, organochlorine, organophosphate, phenylurea, pyrethroid, tetranortriterpenoid, triazine, and urea. Some active ingredients were added together with their metabolites (e.g. atrazine, DTT, etc.). Except for emamectin benzoate, all these substances were screened in water, soil, and sediment collected in 2014 (section 4.4.8).

Characterization of agricultural practices and target substance selection

Table 4:6 Target substances retained in the thesis

	Active ingredient	Pesticide group	Pesticide type	Mode of action	log Kow	GC-MS	UPLC MS/MS
1	Acetamiprid	Neonicotinoid	Insecticide	Systemic with translaminar activity having both contact and stomach action. Acetylcholine receptor (nAChR) agonist.	0.8[a]		X
2	Acetochlor	Chloroacetamide	Herbicide	Selective, absorbed mainly by shoots and roots of germinating weeds. Lipid synthesis inhibitor.	4.14[a]	X	
3	Aldrin	Organochlorine	Insecticide	Central nervous system stimulant. GABA-gated chloride channel antagonist. Also stomach and contact toxin	6.5[a]	X	
4	Atrazine	Triazine	Herbicide	Selective, systemic action with residual and foliar activity. Inhibits photosynthesis (photosystem II).	2.7[a]		X
5	Desethylatrazine	Triazine	Herbicide	Selective, systemic action with residual and foliar activity. Inhibits photosynthesis (photosystem II).	1.51[b]		X
6	Deisopropylatrazine	Triazine	Herbicide	Selective, systemic action with residual and foliar activity. Inhibits photosynthesis (photosystem II).	1.15[b]		X
7	Azadirachtin	Tetranortriterpenoid	Insecticide	Interrupts the life cycle of flies by inhibiting the development of the eggs, larvae, or pupae and by blocking the molting of larvae or nymphs, and inhibiting mating and sex-	1.09[b]		X
8	Carbofuran	Carbamate	Insecticide, Nematicide, Acaricide, Metabolite	Systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	1.8[a]		X
9	alpha-cis-Chlordane	Organochlorine	Herbicide	Non systemic with contact, stomach and respiratory action. GABA-gated chloride channel antagonist.	6.10[h]	X	
10	gamma-trans-Chlordane	Organochlorine	Herbicide	Non systemic with contact, stomach and respiratory action. GABA-gated chloride channel antagonist.	6.22[h]	X	
11	Chlorpyrifos-ethyl	Organophosphate	Insecticide	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	4.7[a]	X	
12	Chlorpyrifos-methyl	Organophosphate	Insecticide, Acaricide	Non-systemic with contact, stomach and respiratory action. Acetylcholinesterase (AChE) inhibitor.	4[a]	X	
13	lambda-Cyhalothrin	Pyrethroid	Insecticide	Non-systemic, contact and stomach action. Some repellant properties. Sodium channel modulator.	5.5[a]	X	
14	alpha-Cypermethrin	Pyrethroid	Insecticide	Non-systemic with contact and stomach action. Sodium channel modulator.	5.5[a]	X	
15	beta-Cypermethrin	Pyrethroid	Insecticide	Non-systemic with contact and stomach action. Sodium channel modulator.	5.8[a]	X	
16	Deltamethrin	Pyrethroid	Insecticide, Metabolite,	Non-systemic with contact and stomach action. Sodium channel modulato	4.6[a]	X	
17	Diazinon	Organophosphate	Insecticide, Acaricide, Repellent,	Non-systemic with respiratory, contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	3.69[a]	X	X
18	Dieldrin	Organochlorine	Insecticide, Metabolite	Central nervous system stimulant. GABA-gated chloride channel antagonist.	3.7[a]	X	
19	Diuron	Phenylurea	Herbicide	Systemic, absorbed via roots, acts by strongly inhibiting photosynthesis	2.87[a]		X
20	Emamectin Benzoate	Avermectin	Insecticide	Stimulating the release of γ-aminobutyric acid, an inhibitory neurotransmitter	5[c]		X
21	alpha-Endosulfan	Organochlorine	Insecticide, Acaricide	Non-systemic with contact and stomach action, acts as a non-competitive GABA antagonist	3.83[d]	X	
22	beta-Endosulfan	Organochlorine	Insecticide, Acaricide	Non-systemic with contact and stomach action, acts as a non-competitive GABA antagonist	3.62[d]	X	
23	Endosulfan Sulfate	Organochlorine	Insecticide, Acaricide	Non-systemic with contact and stomach action, acts as a non-competitive GABA antagonist	3.66[d]	X	

Characterization of agricultural practices and target substance selection

#	Active ingredient	Pesticide group	Pesticide type	Mode of action	log Kow	GC-MS	UPLC MS/MS
24	Endrin	Organochlorine	Insecticide, Acaricide	Broad-spectrum, with contact and stomach action. Is a chloride channel-blocking agent.	3.2[a]	X	
25	Endrin aldehyde	Organochlorine	Insecticide, Acaricide	Broad-spectrum, with contact and stomach action. Is a chloride channel-blocking agent.	4.8[b]	X	
26	Endrin ketone	Organochlorine	Insecticide, Acaricide	Broad-spectrum, with contact and stomach action. Is a chloride channel-blocking agent.	4.99[b]	X	
27	alpha-HCH	Organochlorine	Insecticide, Acaricide	Acts as stimulant to the nervous system with contact and stomach action. GABA-gated chloride channel antagonist.	3.8[e]	X	
28	beta-HCH	Organochlorine	Insecticide, Acaricide	Acts as stimulant to the nervous system with contact and stomach action. GABA-gated chloride channel antagonist.	3.78[e]	X	
29	delta-HCH	Organochlorine	Insecticide, Acaricide	Acts as stimulant to the nervous system with contact and stomach action. GABA-gated chloride channel antagonist.	4[e]	X	
30	gamma-HCH	Organochlorine	Insecticide, Acaricide	Acts as stimulant to the nervous system with contact and stomach action. GABA-gated chloride channel antagonist.	3.72[e]	X	
31	Heptachlor	Organochlorine	Insecticide	Persistent, non-systemic contact and stomach poison with some fumigant action. Is a chloride channel-blocking agent.	5.44[a]	X	
32	Heptachlor epoxide a	Organochlorine	Insecticide	Persistent, non-systemic contact and stomach poison with some fumigant action. Is a chloride channel-blocking agent.	5.4[f]	X	
33	Heptachlor epoxide b	Organochlorine	Insecticide	Persistent, non-systemic contact and stomach poison with some fumigant action. Is a chloride channel-blocking agent.	5.4[f]	X	
34	Imidacloprid	Neonicotinoid	Insecticide, Veterinary treatment	Systemic with contact and stomach action. Acetylcholine receptor (nAChR) agonist.	0.57[a]		X
35	Linuron	Urea	Herbicide	Selective, systemic with contact and residual action. Inhibits photosynthesis (photosystem II)	3[a]		X
36	Methoxychlor	Organochlorine	Insecticide	Contact and stomach action. Central nervous stimulant, producing hyperactivity, convulsions and death.	5.83[a]	X	
37	trans-Nonachlor	Organochlorine	Herbicide	Non systemic with contact, stomach and respiratory action. GABA-gated chloride channel antagonist.	6.35[h]	X	
38	Omethoate	Organophosphate	Insecticide, Acaricide, Metabolite	Systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	-0.74[a]		X
39	o,p'-DDT	Organochlorine	Insecticide	Non-systemic stomach and contact action. Sodium channel modulator.	6.91[g]	X	
40	Oxychlordane	Organochlorine	Herbicide	Non systemic with contact, stomach and respiratory action. GABA-gated chloride channel antagonist.	5.48[b]	X	
41	p,p'-DDD	Organochlorine	Insecticide	Non-systemic stomach and contact action. Sodium channel modulator.	6.02[g]	X	
42	p,p'-DDE	Organochlorine	Insecticide	Non-systemic stomach and contact action. Sodium channel modulator.	6.51[g]	X	
43	p,p'-DDT	Organochlorine	Insecticide	Non-systemic stomach and contact action. Sodium channel modulator.	6.91[g]	X	
44	Profenofos	Organophosphate	Insecticide, Acaricide	Non-systemic with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	1.7[a]	X	X
45	Triazophos	Organophosphate	Insecticide, Acaricide, Nematicide	Non-systemic, broad spectrum with contact and stomach action. Acetylcholinesterase (AChE) inhibitor.	3.55[a]	X	X

a Lewis et al. (2016)
b EPI Suite v 4.1 (U.S. Environmental Protection Agency, 2012)
c U.S. Environmental Protection Agency (2009)
d ATSDR (2015)
e ATSDR (2005)
f ATSDR (2007)
g ATSDR (2002)
h Simpson et al., (1995)

4.4.8 First screening in environmental matrices

This preliminary work intended to provide a first screening of pesticides in environmental matrices and confirm the list of target substances for further analysis (section 4.4.7). Analytical methods were therefore not optimized and only qualitative information were derived from laboratory analyses (Table 4:7). In total, 10 pesticides from 5 pesticide groups: organophosphate (chlorpyrifos-ethyl, profenofos, and triazophos), organochlorine (endosulfan), neonicotinoid (acetamiprid and imidacloprid), pyrethroid (lambda-cyhalothrin), and triazine (atrazine, desethylatrazine (DEA), and deisopropylatrazine (DIA)) were detected in environmental matrices.

Acetamiprid, chlorpyrifos, imidacloprid, lambda-cyhalothrin, and profenofos are active ingredients of commonly used and authorized commercial formulations in market gardening in Burkina Faso. Their presence in environmental compartments was therefore not surprising. On the other hand, none of the authorized formulations contained atrazine, endosulfan or triazophos. The herbicide atrazine is not authorized in Burkina Faso and normally not used in vegetable production. Weed removal is generally performed manually due to financial limitations but also considering the reasonable size of cultivated plots. Atrazine and its metabolites (DEA and DIA) were already detected in 2013 in Loumbila Lake (Congo, 2013) and in other agricultural areas (Soleri, 2013). Use of atrazine in cotton production was reported in many inventories conducted across the country (Gomgnimbou et al., 2009; Ouédraogo et (MERSI et al., 2016)al., 2009; Savadogo et al., 2006; Toé, 2010b). Further research was therefore needed to characterize the extent of this contamination in the environment. Endosulfan is a POP prohibited by the Stockholm Convention (Annex A). Previous studies had already detected this substance in soils from cotton production and in water (Ouattara et al., 2012; Savadogo et al., 2006; Tapsoba et al., 2008). More research was needed to assess whether it was an isolated case of detection, an indication of recent use or the result of its remanence in the environment. Although triazophos is not authorized, its use was commonly reported by gardeners during field surveys.

Detection of these pesticides in environmental matrices confirmed the pertinence of their inclusion in the list of target substances for further analysis in this thesis. Chapter 5 intends to provide a better understanding of the detection of the aforementioned pesticides in environmental matrices.

Table 4:7 Pesticides detected in environmental matrices during the preliminary study

Water	Soil	Sediment
Acetamiprid	Acetamiprid	Profenofos
Atrazine	Atrazine	Triazophos
DIA	Endosulfan	
DEA	Imidacloprid	
Chlorpyrifos-ethyl	lambda-Cyhalothrin	
Imidacloprid	Profenofos	
Profenofos	Triazophos	
Triazophos		

4.5 Conclusion

This chapter presents a comprehensive description of agricultural practices in the four studied areas. Irrational use of pesticides was a result of the low education level and training of the operators and the resellers. Illiteracy and lack of knowledge regarding pests and diseases makes it difficult to select suitable formulation and follow the directions for use. Pesticide toxicity appeared to be underestimated by all the actors. Unsafe storage, waste disposal, and manipulation without protective equipment increase the risk of hazardous environmental and human exposure. Economical limitations also hampered the application of the good agricultural practices in these rural areas. The use of suitable spraying and personal protective equipment was limited by their cost. Finally, low availability of suitable equipment, services, and infrastructures also encouraged local populations to find alternatives. Knapsack sprayers and personal protection were not always found in remote rural areas. In the absence of national/regional waste management strategies, gardeners faced difficulties to get rid of the empty containers.

Operators and resellers require training to improve pesticide management. The association « Association des grossistes et détaillants d'intrants agricoles du Burkina Faso » (AGRODIA) and other structures have already started to create formation programs for pesticide resellers and others focused on the final users (farmers, etc.). The problematic concerning waste treatment sector must be handled at the regional/national scale. Solutions must be proposed by localities to improve waste disposal.

Comparison between studied sites and results from previous studies outlined that behaviors were similar across the country. These findings confirmed the representativeness of the studied areas and are supportive that discussed problematic are similar countrywide. This also comforted our approach to concentrate our further efforts on a pilot study area in order to provide a refined diagnosis. As aforementioned, Loumbila Lake was retained as the most suitable location to conduct the activities planned and fulfill the objectives of the present thesis.

Chapter 5 Pesticide levels in water, soils, and sediments

Published work:

The present chapter is an extended version of the work published in the following research paper:

Lehmann, E., Fargues, M., Nfon Dibié, J.-J., Konaté, Y., de Alencastro, L.F., 2017. Assessment of water resources contamination by pesticides in vegetable producing areas in Burkina Faso. Environmental Science and Pollution Research (In Press). DOI: 10.1007/s11356-017-0665-z.

Silicon rubber passive samplers, soil, and sediment analysis were included to complete the environmental diagnosis.

Web link:

-

Supplementary material:

Appendix C

Supplementary information are divided in four sections S1-S4 presenting the Figure S1 and the Table S1-S12.

Doctoral Candidate's contribution:

Main investigator and author

5.1 Introduction

Agricultural practices and resulting environmental impacts have been extensively studied in developed countries and under temperate climates but few studies focus on the conditions similar to the Sahelian zone. The preliminary study completed in April 2014 indicated the presence of pesticides in soil, sediment, and water (Chapter 4). In the absence of previous quantification of pesticides in the studied areas, this unique determination was not sufficient to provide a reliable diagnosis of the extent of the contamination. The ubiquity of pesticides in environmental matrices outlined the need for the implementation of a suitable monitoring with higher sampling frequency to account for seasonal variations. The present study was conducted around Loumbila Lake characterized by warm temperatures and the typical hydrological regime of the Sudano-Sahelian climate (Figure 2:2).

Research recently focused on developing simpler, cost-effective methods for monitoring pesticides in the environment, with a growing focus on passive sampler devices. Passive samplers accumulate chemicals by partition/absorption or adsorption processes and provide integrative (time-averaged) measurements (Harman et al., 2013). They offer an alternative to discontinuous water sampling with a low sampling frequency. This study used two types of passive samplers in order to cover the large range of physicochemical properties of the retained target analytes. The Polar Organic Chemical Integrative Samplers (POCIS) were originally designed to sample chemicals with octanol-water partition coefficient (K_{ow}) of less than ~ log K_{ow} 3 (Martínez Bueno et al., 2009). As many of the retained target analytes presented a log K_{ow} value higher than 3, a complementary screening of the hydrophobic substances was performed with silicone rubber (SR) strips. SR have been extensively used as passive samplers for the analysis of water contamination by substances presenting a log $K_{ow} > 3$ (Vrana et al., 2005). Although interpretation of the results is less straightforward, passive samplers offer a unique alternative to automatic sampling methods for continuous sampling in the study area. They eliminate the need for an energy/power supply and allow the entire sampling set-up to be miniaturized, which are prerequisites for investigation in remote rural areas (Vrana et al., 2005). The challenge with passive sampling methods is to derive water-concentration estimates from the amounts of chemicals accumulated by the sampler, using appropriate sampler-water exchange models. The uptake kinetics of these passive samplers have been extensively studied under temperate climatic conditions but there is little knowledge on their applicability under warm conditions (i.e. water temperature above 30°C). So far, in situ calibration was found to be the most suitable method for calculating time-weighted average concentration (TWAC) from passive samplers (Harman et al., 2012). In situ calibration was therefore performed for POCIS in order to assess their suitability in the local context and provide TWAC concentrations for the polar analytes detected during the preliminary study. Substances sampled by the SR were less likely to be found in water and were not frequently detected in previous studies conducted in Burkina Faso. For these reasons, calibration of SR was not included in the scope of the present study. They were only used to complement the POCIS, in an attempt to provide a preliminary screening of the hydrophobic target compounds. As it was the first deployment of passive samplers in the study area, grab water samples were collected in parallel for calibration and comparison

purposes. In addition, pesticide residue levels were also quantified in soil and sediments samples in order to complete the qualitative results from the preliminary study.

Pesticides may trigger multiple adverse health effects for human ranging from moderate toxicity to severe neurotoxicity, endocrine disruption, cancer, etc. (WHO/UNEP, 2012a). This work assessed consumers' risk by direct comparison of aquatic concentrations to standard threshold limits proposed by international regulations. Aquatic organisms are also affected by pollutants such as pesticides, which constitute a major anthropogenic stress on natural communities (Leboulanger et al., 2009b). Leboulanger et al. (2009) already outlined the toxicity of deltamethrin (a pesticide commonly used in gardening) and the water of Loumbila Lake to local species of zooplankton (*Diaphanosoma excisum* and *Moina micrura*). This study is the only one of its kind, studying the toxicity effects of pesticides on the local aquatic biota. Various alternative approaches have been proposed in order to link water concentrations of pesticides to effects on aquatic biota. Major challenges concern defining toxicity data (e.g. LC50s, EC50s, etc.) and addressing exposure to pesticide mixtures. In the this study, the ecological risk was assessed using the Pesticides Toxicity Index (PTI) (Nowell et al. 2014). The PTI is a toxic unit (TU) procedure that follows the concentration addition (CA) model. It has proved to be a robust screening tool for assessing complex environmental mixture of pesticides with similar, dissimilar, or unknown modes of action.

The main objective of this study was to develop and implement a suitable approach for investigating water, soil, and sediment contamination by pesticides in the study area. The kinetics of the POCIS were determined by in situ calibration to provide a first evaluation of the suitability of these passive samplers in field conditions. SR were used to provide a preliminary screening of the hydrophobic target analytes. Soil and sediments samples were analyzed in order to complete the diagnosis on pesticide accumulation in environmental compartments. Three years of monitoring data (2014 - 2016) were collected to account for seasonal variations. Measured concentrations were used to assess the potential impact of pesticides on human health and the ecological risk. The present project constitutes a pilot study. The methodology developed could be readily adapted to other sites to be monitored.

5.3 Experimental Section

5.3.1 Site description

Loumbila Reservoir (12°29'38'' N; 1°24'8'' W) is located on the Massili River in one of the most intensive gardening areas in Burkina Faso and supplies one-third of the capital's drinking water. In 2005, an estimated 700'000 urban dwellers relied on the Loumbila Reservoir (Michel, 2005). The rapid growth of the country's population over the past decade reinforces the importance of this resource. The Sudano-Sahelian climate is characterized by two seasons: a dry season, from October to June; and a rainy season from June to September. Vegetables are grown during the dry season (from January to June). Gardening areas are located on lake shorelines to guarantee continuous access to water (Figure 5:1, a and b). When the lake recedes during the dry season, crops are planted under the maximum annual water level (weir crest level). Therefore, contaminants are likely to solubilize in water when the water level rises (up to 4 meters) during the wet season (Michel, 2005). Traditional wells and boreholes are the two other sources of drinking water identified on the site (Figure 5:1, c and d). As the dry season progresses, the water surface of the lake shrinks enlarging the distance to access water. In response to this phenomenon, gardeners dig wells in the middle of the fields (Figure 5:1, d). These shallow wells (2 - 3 m) are hand-dug and present no structure (i.e. no casing). Their primary function is to minimize the distance to access water for watering but they are also used by the gardeners for drinking water. During the rainy season, the wells are submerged as the level of the lake rises.

There is little knowledge of the precise hydrogeological profile of the study area. The boreholes are generally dug at a depth of 45 m to 65 m to exploit deep groundwater aquifers. Shallow traditional wells (hand-dug wells) near the shore (~50 - 100 m) reach the accompanying aquifer of the lake (MOAD, 2013).

Borehole water is consumed at home while surface and well water is generally consumed during work at the field. Surface water and traditional wells are unsafe water sources because of the proximity to cultivated crops and the absence of protection measures (buffer zone, structure, cover, etc.).

(a) Cultivated plots on the shores of Loumbila Lake

(b) Cultivated plots on the shores of Loumbila Lake

(c) Borehole

(d) Traditional well
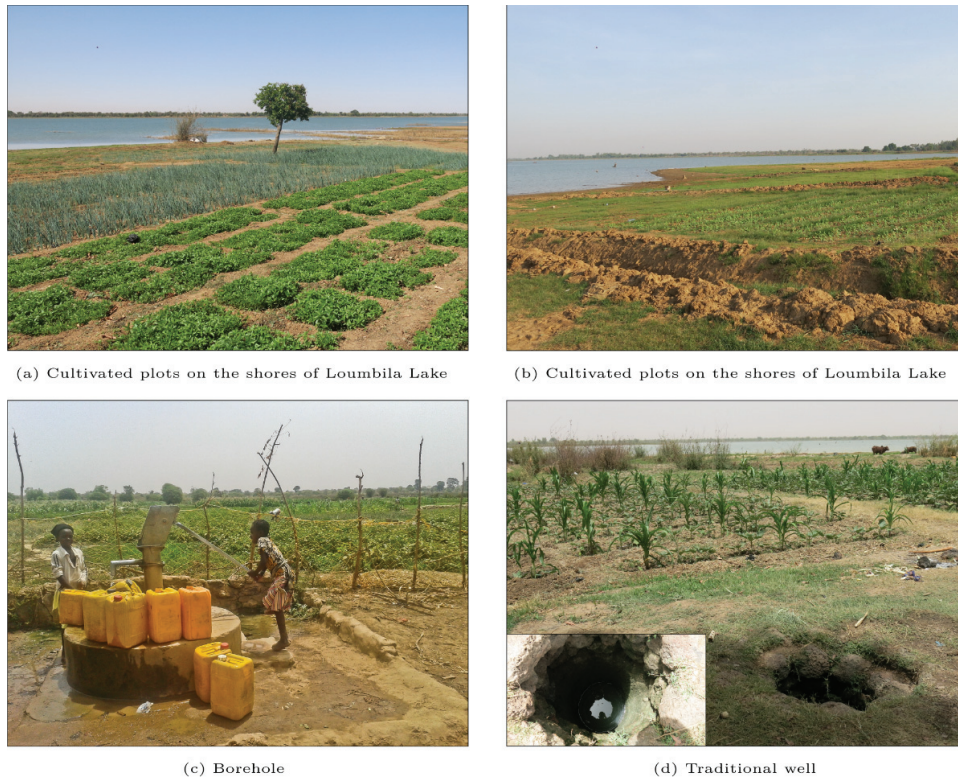
Figure 5:1 Water resources located near cultivated fields

5.3.2 Sampling plan for environmental impact assessment

Samples were collected between 2014 and 2016 in 10 villages located on the shore of Loumbila Lake: Loumbila (ONEA pumping station), Poedogo, Bendogo, Daguilma, Sag-nioniogo, Tabtenga, Noungou I, Noungou II, Nabdogo, and Pousghin (Figure 5:2).

Grab water samples (1L) were collected from randomly selected traditional wells (n = 27) and boreholes (n = 9) in March-April 2016 (Figure 5:2).

Seven sampling locations were selected for monitoring Loumbila Reservoir: 6 at the confluence of the streams feeding the lake during the rainy season, and one at the pumping station that supplies the capital Ouagadougou with drinking water (Figure 5:2). POCIS and SR were deployed in duplicates at the same locations. One grab water sample was collected at each sampling location during every sampling campaign (the day of retrieval when POCIS were deployed).

To account for seasonality, lake water was sampled during four different periods (Table 5:1): December; March - April; at the beginning of the rainy season (June - July); and in the middle of the rainy season (July - August). In total, 106 grab water samples, 18 soil samples, and 14 sediment samples were collected and 54 POCIS and 22 SR strips were deployed over a three-year period.

Table 5:1 Sampling plan for the monitoring of Loumbila Lake during three years

Period	March-April Gardening activities	June-July Beginning of the rainy season	July-August Mid-rainy season	December No culture
2014	-	-	-	Grab sampling only (5)
2015	Grab sampling (9) POCIS (4 [a]) Soil (6) Sediment (8)	Grab sampling (7) POCIS (6)	Grab sampling only (7)	-
2016	Grab sampling (28) POCIS (6 [a]) SR (6 [a]) Soil (7)	-	Grab sampling (14) POCIS (5 [a]) SR (5 [a]) Soil (6) Sediment (6)	-

[a] Number indicated correspond to the number of passive samplers, each sampler is composed of two units (i.e. 2 POCIS and 2 SR strips).
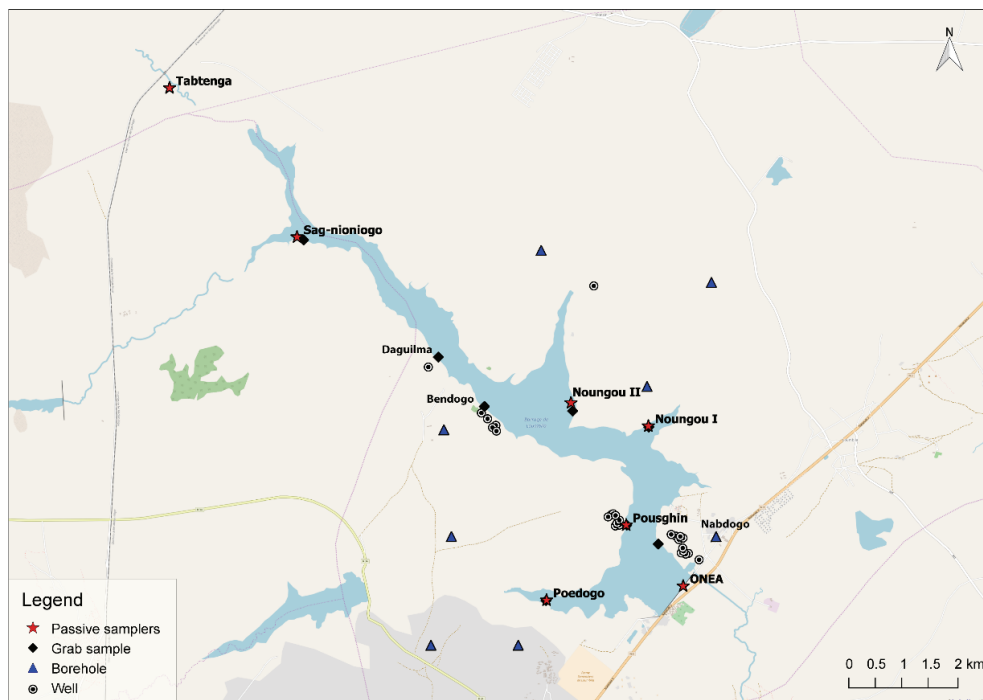
Figure 5:2 Sampling point locations (ONEA: pumping station)
(background map source: OpenStreetMap Contributors, 2017)

5.3.3 Preparation and deployment of the passive samplers

5.3.3.1 POCIS sorbent spiking

The POCIS contained 200 mg of Oasis® HLB (Hydrophilic-Lipophilic-Balanced) sorbent, enclosed between two polyethersulfone (PES) membranes held with stainless steel holder washers. Prior to assembling the POCIS device, the sorbent was spiked with the performance reference compound (PRC) DIA-d5 to about 1µg g^{-1} as proposed by Carpinteiro et al. (2016). The objective of using POCIS was to provide a more confident monitoring of polar pesticides that were identified in 2014 (section 4.4.8). Therefore, DIA-d5 was retained as a potentially suitable PRC based on previous studies conducted on triazines and imidacloprid (Belles, 2012; Mazzella et al., 2010).

5.3.3.2 SR preparation

SR was obtained from Altec Products Limited (UK) in the form of sheets of 0.30 × 0.30 m and 0.5 mm thickness. Cleaning method and setting-up of the samplers for deployment followed the procedure presented by Estoppey et al. (2014). SR sheets were cut in 0.20 × 0.90 m strips. Four mounting holes of 4-mm diameter were made at one end of the SR strips using a hole punch. These holes were situated at 8 mm from the end of the strip and were separated by 25 mm. For each campaign 18 strips were cleaned together by Soxhlet extraction (1 L extractor) using ethyl acetate (100 h) followed by methanol (48 h). SR strips were stored in the freezer (-20°C) in a 1 L amber glass bottle until deployment.

5.3.3.3 Passive samplers deployment

POCIS were deployed in duplicates for 21 days. All samplers were horizontality exposed with the PES membranes parallel to the water surface and protected in aluminum canisters (Figure 5:3, a). The aluminum canister was then fixed to ~1.5 m iron rod (diameter: 8 mm, Figure 5:3, b). SR were deployed the same day but for a 6-week duration. A stainless steel threaded rod (diameter: 5 mm, length: ~50 cm) was passed through the mounting holes of two strips and the strips were kept in place using nuts (Figure 5:3, c). The stainless steel rod was then fixed to the iron rod holding the POCIS (Figure 5:3, b).

Depending on the water depth, the iron rod was either directly planted in the lake (Figure 5:3, d) or attached to a floating buoy rope connected to a cement block located at the bottom of the lake (Figure 5:3, e).

(a) POCIS in aluminum canister   (b) Overview of passive samplers setup   (c) SR attached on iron rod

(d) Deployment in shallow water   (e) Deployment in deep water

Figure 5:3 Passive samplers setup

5.3.4 POCIS in situ calibration

During exposure, the enclosed receiving phase accumulates organic pollutants. The sampling rate (R_s) for each compound must be determined to estimate the TWAC of pollutants from accumulated amounts. The two-compartment model, with diffusion processes though the membrane, was first developed for semipermeable membrane devices (Huckins et al., 1993), and then widely applied to POCIS. If we assume first-order isotropic exchanges between sorbent and analytes, the two-compartment model can be estimated as follow:

$$C_{POCIS} = \overline{C_w} K_{sw}(1 - e^{-k_e t}) \hspace{3cm} 5:1$$

where C_{POCIS} is the concentration (µg g^{-1}) of the analyte in the sorbent at time t (days), $\overline{C_w}$ is the TWAC (µg L^{-1}) of the analyte in water, K_{sw} is the sorbent-water partition constant (L g^{-1}) and k_e (d^{-1}) is the elimination rate constant.

Accumulation of polar pesticides in POCIS exhibits two different regimes: kinetic and equilibrium regimes. The beginning of the uptake is generally characterized by a zero-order kinetic regime, in which the elimination rate k_e is negligible compared to the uptake rate k_u (L g^{-1} · d^{-1}). During this linear phase, the POCIS is integrative and the TWAC of each analyte in water can be estimated with:

$$C_{POCIS} = \overline{C_w} k_u t \hspace{3cm} 5:2$$

An equivalent relationship can be obtained from equation 5:2, introducing R_s (L d^{-1}) instead of k_u:

$$C_{POCIS} = \frac{\overline{C_w}\, R_s t}{M_{POCIS}} \hspace{3cm} 5:3$$

where M_{POCIS} (µg) is the mass of the receiving phase.

When the accumulation reaches the equilibrium regime, equation 5:1 can be reduced to:

$$K_{sw} = \frac{C_{POCIS}}{C_w} = \frac{k_u}{k_e} \hspace{3cm} 5:4$$

Calibration data can be acquired with laboratory (Ibrahim et al., 2013a) or in situ experiment (Mazzella et al., 2010). In situ calibration was retained in this study. Fourteen POCIS were directly exposed in the lake and duplicates were collected after days 4, 7, 10, 14, 18, 20, and 21 (from February 26th to March 18th 2016). Temperature, pH, conductivity, and suspended matter were measured at each retrieval period (SI Figure S3). In parallel, 1 L of water was sampled each day to derive water concentration.

PRC have been used to correct R_s from varying environmental conditions (Pesce et al., 2011). Under isotropic exchanges conditions, the PRC elimination rate constant is calculated as:

$$k_{e_{PRC}} = \frac{ln\big(C_{PRC0}/C_{PRC(t)}\big)}{t} \hspace{3cm} 5:5$$

in which C_{PRC0} and $C_{PRC(t)}$ respectively are the initially spiked concentration (µg g^{-1}) and the residual concentration of PRC in the receiving phase after an exposure time t (days).

To account for differences between exposure conditions during calibration and further deployment, the sampling rate is corrected as follow:

$$R_{s\ (corr)} = \frac{k_{e\ (PRC\ experiment)}}{k_{e\ (PRC\ cal)}} \times R_{s\ (cal)} \qquad\qquad 5{:}6$$

with $R_{s\ (corr)}$: the corrected sampling rate, $k_{e\ (PRC\ experiment)}$: the elimination constant of the PRC measured in the current experiment and $k_{e\ (PRC\ cal)}$ and $R_{s\ (cal)}$ the elimination constant of the PRC and the sampling rate measured during in situ calibration.

5.3.5 Water analysis

Pesticides were extracted from grab samples by solid-phase extraction (SPE). The method proposed by Lissalde et al., (2011) was adapted to cover the retained target analytes. Water was filtered through a 0.7µm glass fiber filter (Whatman GF/F), prior to spiking and extraction. An isotopic dilution was then performed, with the addition of 0.2 mL of labeled surrogates' solution (SI Table S2). A 1-L water sample was pumped through a 200 mg Water Oasis® HLB cartridge, preconditioned with 10 mL ethyl acetate, 10 mL methanol, and 5 mL water, using a VisiPrep 12-port manifold from Supelco. The cartridge was subsequently eluted using an automatic apparatus (GX-274 ASPEC®; Gilson) and the following fractions: 5 mL methanol, 5 mL methanol : ethyl acetate (1:1, v/v), and 5 mL ethyl acetate : hexane (1:4, v/v). After combination, the fractions were concentrated to 0.4 mL. An aliquot of 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of the mixture methanol : water (5:95, v/v) with 0.1% formic acid prior to UPLC-MS/MS analysis. The remaining 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of isooctane prior to GC-MS analysis. Material sources, purity and operating parameters for GC-MS and UPLC-MS/MS are provided in the Supporting Information (SI Section S1).

A total of 25 pesticides were included in the developed multiresidue analysis (Table 5:2). The recoveries were optimized with the extraction of 1 L of mineral water (Evian water) fortified with 200 µL of a 15-fold dilution of the target analytes stock solution (SI Table S1) and 200 µL of the appropriate surrogate solution (SI Table S2) in triplicate.

The limits of detection (LODs) and limits of quantification (LOQs) for the selected target analytes were defined as the analyte concentration that produced a peak with a signal-to-noise ratio of 3 and 10, respectively. They were experimentally determined by measuring the coincident instrumental response of standard pesticide solutions and procedural blanks, or negative samples.

Table 5:2 Multiresidue extraction recoveries, LOD and LOQ for target pesticides in water

Active ingredient	log Kow	% Recovery (%RSD)	% Recovery with Surrogate (%RSD)	LOD [ng L^{-1}]	LOQ [ng L^{-1}]
Avermectin					
Emamectin benzoate	5[a]	<10	<10	0.01	0.04
Carbamate					
Carbofuran	1.8[b]	66(2.5)	70(4.4)	0.25	0.85
Chloroacetamide					
Acetochlor	4.14[b]	93(14)	82(2.0)	1.00	3.30
Neonicotinoid					
Acetamiprid	0.8[b]	83(4.4)	106(3.5)	0.30	0.95
Imidacloprid	0.57[b]	85(3.9)	80(2.6)	0.20	0.70
Organochlorine					
Dieldrin	3.7[b]	74(6.5)	104(4.2)	1.14	3.80
alpha-Endosulfan	3.83[c]	50(7.1)	72(4.7)	0.85	2.90
beta-Endosulfan	3.62[c]	70(5.9)	99(3.9)	6.60	22.00
Endosulfan sulfate	3.66[c]	69(3.7)	96(16.4)	21.50	72.00
Organophosphate					
Chlorpyrifos	4.7[b]	65(1.6)	80(2.2)	17.00	57.00
Chlorpyrifos-methyl	4[b]	42(0.1)	52(2.1)	25.00	88.00
Diazinon	3.69[b]	68(13.3)	99(2.3)	0.07	0.25
Omethoate	-0.74[b]	11(1.6)	7(0.7)	0.25	0.85
Profenofos	1.7[b]	56(6.3)	82(9.6)	3.55	11.85
Triazophos	3.55[b]	66(1.2)	93(9.1)	0.07	0.25

Active ingredient	log Kow	% Recovery (%RSD)	% Recovery with Surrogate (%RSD)	LOD [ng L^{-1}]	LOQ [ng L^{-1}]
Pyrethroid					
lambda-Cyhalothrin	5.5[b]	18(8.1)	67(14.4)	2.00	6.75
alpha-Cypermethrin	5.5[b]	28(7.1)	99(6.3)	6.90	23.00
beta-Cypermethrin	5.8[b]	23(6.8)	75(6.5)	16.90	56.40
Deltamethrin	4.6[b]	49(17.5)	89(7.1)	12.25	41.90
Tetranortriterpenoid					
Azadirachtin	1.09[e]	87(5.3)	91(12.1)	16.45	54.80
Triazine					
Atrazine	2.7[b]	83(5.8)	93(1.4)	0.02	0.07
DEA	1.51[e]	85(3.9)	99(1.5)	0.05	0.18
DIA	1.15[e]	79(3.5)	92(1.3)	0.04	0.13
Urea					
Linuron	3[b]	68(1.9)	107(1.4)	3.00	10.00
Diuron	2.87[b]	81(13.9)	86(3.5)	10.00	33.40

[a] U.S. Environmental Protection Agency (2009)
[b] The Pesticide Properties DataBase (PPDB) from the University of Hertfordshire (Lewis et al., 2016)
[c] U.S. Department of Health and Human Services (2015)
[d] U.S. Department of Health and Human Services (2005)
[e] EPI Suite v 4.1 (U.S. Environmental Protection Agency, 2012)

The proposed multiresidue extraction procedure allowed successful quantification of 23 pesticides in water samples. Emamectin benzoate and omethoate recoveries were low (recoveries<10%) but had low variability (RSD<10%). Therefore, only qualitative (i.e. indicated as detected) information were derived from field samples for these two analytes in further experiments.

5.3.6 POCIS recovery and analysis

After exposure, the POCIS were transferred to the laboratory and dismantled. The receiving phase was packed into 6 mL empty SPE tubes with a polyethylene (PE) frit under vacuum by using a Visiprep SPE Manifold. The cartridges were left to dry for 30 min at room temperature before elution. As for SPE, an isotopic dilution was performed before elution by direct addition of 0.2 mL of the same labeled surrogate solution onto the upper frit of the cartridge. Elution, extract

separation, and reconditioning, prior GC-MS and UPLC-MS/MS analyses, were performed according to the SPE extraction procedure for water samples (section 5.3.5).

5.3.7 PDMS recovery and analysis

At retrieval, loosely attached particle matter (biofouling) was carefully removed from the surface of SR strips with lake water. Excess water was removed by patting the samplers dry with clean paper tissues. Samplers were wrapped in aluminum foils, placed in individual zipped plastic bags, and stored in the freezer (-20 °C) prior to analysis.

The strips of each sampler (including field controls) were weighed and cut into pieces (about 10 × 30 mm). Each couple of strips composing a sampler were placed into separate glass Soxhlet thimbles (100 mL) with sinters protected by sodium sulfate. Isotopic dilution was performed with the addition of 0.2 mL of labeled surrogate solution directly onto the strips (SI Table S2). The extraction was carried out for 12h with 150 mL of methanol : acetonitrile (1:2, v/v) at ~70 °C as proposed by Smedes and Booij (2012). The extracts were solvent exchanged to hexane and reduced to 1 mL in a rotary evaporator. Cleanup was performed on chromatographic columns packed with florisil (10 g previously deactivated with water (2% by wt.) and protected with 4 g of sodium sulfate) using a similar procedure than proposed by Adam et al. (2009). Extracts were eluted with the following fractions: 20 mL hexane, 40 mL hexane : ether (3:1, v/v), 40 mL hexane : ether (1:1, v/v) and 100 mL dichloromethane. Only the hexane : ether (3:1, v/v) and the dichloromethane fractions were kept for analysis and the rest was discarded. The retained fractions were then reduced separately to 1 mL in a rotary evaporator, evaporated to dryness, and reconstituted in 0.2 mL of isooctane prior to GC-MS analysis. Material sources, purity, and operating parameters for GC-MS are provided in the Supporting Information (SI Section S1).

Recovery assay was conducted to evaluate the efficiency of the analytical procedure for the retained target analytes. The recoveries were optimized with the extraction of cleaned SR strips in triplicates, fortified with 200 μL of a 30-fold dilution of the standards' stock solution (SI Table S1). Spiking solution (in methanol) was added directly onto the SR strips and the solvent was allowed to evaporate (~3 hours) prior to extraction. Isotopic dilution was performed with the addition of labeled internal standards' solution prior to injection (SI Table S2).

The SR are better suited for chemicals with log K_{ow} > 3 (Vrana et al., 2005), therefore they complete the POCIS that are more suitable for analytes with log K_{ow} < 4 (Morin et al., 2012). The extraction method presented here constitutes a preliminary attempt to recover target analytes in SR. Contrary to the POCIS, the SR were not calibrated for the sampling of the target analytes. They were only used to perform a complementary screening of the substances that were out of the range of application of the POCIS. Further developments are needed to optimize recovery rates and calibrate the samplers to derive TWAC. Therefore, results were only discussed in a semi-quantitative manner. Nevertheless at this stage of development, 14 substances were recovered in SR at a rate of 55% to 117%, with a relative standard deviation < 21% (Table 5:3)

Table 5:3 Extraction recoveries (Recovery) and relative standard deviation (RSD) for target pesticides in SR

Substance name	Recovery [%]	RSD [%]
cis-alpha-Chlordane	69%	17%
trans-gamma-Chlordane	74%	13%
Chlorpyrifos-ethyl	117%	7%
Dieldrin	56%	11%
alpha-Endosulfan	72%	17%
Endosulfan sulfate	56%	19%
Endrin Ketone	100%	11%
beta-HCH	54%	18%
Heptachlor epoxide b	75%	14%
Methoxychlor	84%	21%
trans-Nonachlor	82%	14%
∑(o,p'-DDT, p,p'-DDD)	77%	10%
p,p'-DDE	60%	18%
p,p'-DDT	81%	9%

5.3.8 Soil and sediment sample collection and analysis

Sediments were sampled at the same locations where passive samplers were deployed (Figure 5:2). Grab samples were collected by hand, directly under the passive sampler support (at 5 - 20 m from the shores and at a depth of ~30 - 40 cm) and placed in aluminum boxes. Collected samples were subsequently air-dried at room temperature (~28 °C) and stored in freezer (-20 °C) prior to analysis.

Soils were collected form randomly selected cultivated plots with an auger (sampling depth: ~10 - 20 cm). Each sample was representative of a chosen plot and was composed of several subsamples collected according to the sampling plan presented in the Figure 5:4. Homogenization and reduction of the composite samples were performed according to the method proposed by Mathieu and Pieltain, (1998). After reduction, the composite samples (200 – 300 g) were placed in aluminum boxes and stored in freezer (-20 °C) prior to analysis.
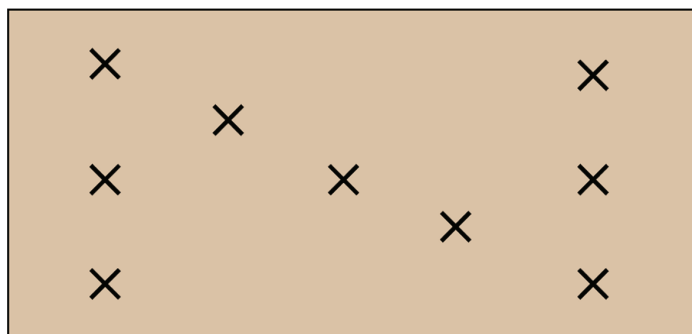
Figure 5:4 Sampling plan for the collection of soil subsamples (X) on a cultivated plot

Pesticide residues from soil and sediment samples were extracted using a modified AOAC 2007.01 QuEChERS (Quick Easy Cheap Rugged and Safe) extraction method (AOAC, 2007). After removing coarse particles, samples were passed through a 2 mm sieve. Ten grams of homogenized sample were added to a 50 mL centrifuge tube. An isotopic dilution was performed by adding 0.2 mL of labeled surrogate solution (SI Table S2). Solvent was allowed to evaporate prior to addition of 10 mL of 1% acetic acid (HOAc) in acetonitrile and extraction for 5 min in an ultrasonic bath. QuEChERS method was designed for matrix with at least 75 % water content (Correia-Sá et al., 2012). Adaptation of this methodology is therefore needed for dry samples. The addition of water to the sample prior to the QuEChERS extraction is used to weaken interactions of the analytes within the matrix and allows for the pores in the sample to be more accessible to the extraction solvent (Vera et al., 2013). Partitioning efficiency was tested with different sample-to-water ratios. The ratio 1:2 (sample/water) ensured the most adequate and reproducible partitioning in both soils and sediments. Therefore, 20 mL of Milli-Q water were added prior to addition of 4 g $MgSO_4$ and 1 g NaAc. The mixture was shaken vigorously for 1 min, vortexed for 1 min and centrifuged for 5 min at 3000 rpm. As the reaction with $MgSO_4$ is exothermic, the tubes were cooled in a water bath at room temperature. 6 mL of the supernatant were subsequently transferred for cleanup in a 12 mL dispersive SPE (dSPE) tube packed with 420 mg of Supel™QuE Z-Sep/C18 sorbent (Sigma-Aldrich, Switzerland) and vortexed for 1 min. After 5 min centrifugation at 4000 rpm, 4 mL of the supernatant were concentrated to 0.4 mL. An aliquot of 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of the mixture methanol : water (5:95, v/v) with 0.1% formic acid prior to UPLC-MS/MS analysis. The remaining 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of isooctane prior to GC-MS analysis. Material sources, purity, and operating parameters for GC-MS and UPLC-MS/MS are provided in the Supporting Information (SI Section S1).

This procedure was designed to ensure sufficient extraction time and homogenization, two critical factors influencing QuEChERS extraction. Vortex and sonication steps allowed preventing the formation of agglomerates and extending extraction times.

The recoveries were optimized with the extraction of 10 g of blank soil sample collected in the study area, fortified with 200 µL of a 15-fold dilution of the target analyte stock solution (SI Table S1) in triplicates. Spiking solution (in methanol) was added directly onto the samples and the solvent was allowed to evaporate (~3 hours) prior to extraction. Isotopic dilution was performed with addition of labeled internal standard solution prior to injection. 27 pesticides were recovered in soil at a rate of 37% to 138%, with a relative standard deviation < 19% (Table 5:4)

Table 5:4 Multiresidue extraction recoveries, LOD and LOQ for target pesticides in soil and sediment

Active ingredient	Recovery	RSD	LOD [µg kg⁻¹]	LOQ [µg kg⁻¹]
GC amenable substances				
alpha-cis-chlordane	57%	13%	0.22	0.72
gamma-trans-chlordane	59%	14%	0.22	0.72
Chlorpyrifos-ethyl	102%	1%	0.51	1.71
Chlorpyrifos-methyl	86%	2%	0.65	2.18
alpha-Cypermethrin	48%	4%	1.73	5.77
beta-Cypermethrin	37%	11%	1.95	6.49
Diazinon	51%	4%	0.33	1.11
Dieldrin	86%	6%	0.98	3.26
alpha-Endosulfan	64%	14%	0.22	0.72
beta-Endosulfan	138%	6%	2.19	7.29
Endrin	96%	9%	0.34	1.12
Endrin aldehyde	97%	2%	1.46	4.86
beta-HCH	84%	4%	0.28	0.92
delta-HCH	87%	4%	0.39	1.29
gamma-HCH	40%	3%	0.22	0.73
Heptachlor epoxide a	59%	18%	0.42	1.40
Heptachlor epoxide b	68%	13%	0.29	0.96
trans-Nonachlor	54%	14%	0.18	0.61
∑(o,p'-DDT,p,p'-DDD)	125%	13%	0.17	0.55
Oxychlordane	51%	17%	0.23	0.77
p,p'-DDE	73%	17%	0.22	0.73
p,p'-DDT	98%	2%	0.22	0.73
UPLC amenable substances				
Acetamiprid	98%	9%	0.33	1.09
Carbofuran	130%	9%	0.59	1.96
Diuron	123%	19%	0.37	1.25
Omethoate	75%	12%	0.52	1.73

5.3.9 Drinking water risk assessment

Risk assessment was performed by comparing the pesticide levels measured in drinking water sources of the study area to threshold limits of health significance. Drinking water regulation in Burkina Faso refers to the WHO guidelines (MAHRH and MS, 2005). However, among target substances, guideline values are established only for aldrin (0.03 µg L^{-1}), dieldrin (0.03 µg L^{-1}), atrazine (2 µg L^{-1}), carbofuran (5 µg L^{-1}), chlordane (0.2 µg L^{-1}), DDT (2 µg L^{-1}), lindan (9 µg L^{-1}), and methoxychlor (2 µg L^{-1}). In the present work, the limit values proposed by the European Directive 98/83/EC on the quality of water intended for human consumption (Directive 98/83/EC, 1998) were retained as the most restrictive in the domain and allowing to cover all the target substances. The parametric value of 0.1 µg L^{-1} applies to each individual pesticide. In the case of dieldrin, the parametric value is 0.030 µg L^{-1}. The threshold value for the sum of all individual pesticides detected and quantified in a monitoring procedure is fixed at 0.5 µg L^{-1}.

5.3.10   Ecological risk assessment

The risk resulting from exposure to measured environmental concentrations (MEC) of pesticides was assessed using the Pesticide Toxicity Index (PTI) proposed by Nowell et al. (2014). The PTI values were defined separately for fish, cladocerans, and benthic invertebrates, by using MEC and toxicity data (LC50s and EC50s) for appropriate test species in standardized tests. For a mixture of n pesticides, the PTI follows the CA model and was calculated as follow:

$$PTI_t = \sum_{i=1}^{n} \frac{MEC_i}{TC_{i,t}} \qquad 5:7$$

where MEC_i is the measured environmental concentration of the pesticide i, n is the number of detected pesticides in an environmental sample, and $TC_{i,t}$ is the toxicity concentration for the pesticide i for the taxonomic group t. Two types of PTI values have been defined for a given taxonomic group. The Median-PTI is calculated from equation 5:7 using the median of acute toxicity concentrations (MTC) available for each compound (LC50s and EC50s). The Sensitive-PTI is calculated using the sensitive toxicity concentration (STC), defined either as the 5th percentile or the minimum toxicity value for each compound toward a taxonomic group (if fewer than 12 toxicity values are available). The STC is a more sensitive indicator that was developed to better represent sensitive species or life stages that would be poorly described with the MTC. In its latest version, the PTI includes 492 pesticides and degredates. The toxicity concentration (TC) estimation for the target pesticides that were not included in this PTI (DEA, dieldrin and triazophos) was performed as presented by Nowell et al. (2014).

5.4 Results and Discussion

5.4.1 In situ calibration of the POCIS and kinetic elimination rate constants

Calibration took place during the dry season (March 2016). The maximum exposure duration of the samplers was 21 days. To ensure comparability between results, and in a screening perspective, the full 25 pesticide multiresidue analysis described above was applied to POCIS extracts. Nevertheless, although R_s values have been provided for a wider range, experiments are supportive that POCIS are better suited for chemicals with log $K_{ow} < 4$ (Morin et al., 2012). This should be kept in mind when interpreting results.

In situ calibration allows the samplers to be calibrated in similar environmental conditions to further deployments. However, target substances must be present in the environment and quantifiable in both water samples and POCIS throughout the in situ calibration experiment. Only atrazine and its metabolites (DEA and DIA) fulfilled this criteria with a quasi-steady concentration in water (Atrazine: 0.0151 ± 0.002 µg L^{-1}, DEA: 0.0053 ± 0.001 µg L^{-1}, DIA: 0.0023 ± 0.001 µg L^{-1}). Imidacloprid was also detected, but levels in the POCIS were under the LOQ, so did not allow for in situ calibration. No pesticide residues were found in POCIS blanks. The average relative standard deviations (RSDs) between POCIS replicates were respectively 11%, 17%, and 13% for atrazine, DEA, and DIA (and maximum RSD was respectively 23%, 27%, and 23% (t = 10 days not considered for DIA (Figure 5:6).

The concentration factor (Cf) was calculated for triazines as the ratio of the mass of accumulated analyte in the POCIS and the TWAC of the same analyte in water samples during the corresponding exposure time. For atrazine and DEA, linear regression with no intercept satisfactory fitted Cf values (Figure 5:5, $R^2 = 0.94$ and $R^2 = 0.81$ respectively). The corresponding $R_{s,in\ situ}$ (slope of the linear regression over 21 days of exposure) are 0.183 L d^{-1} and 0.231 L d^{-1} for atrazine and DEA.
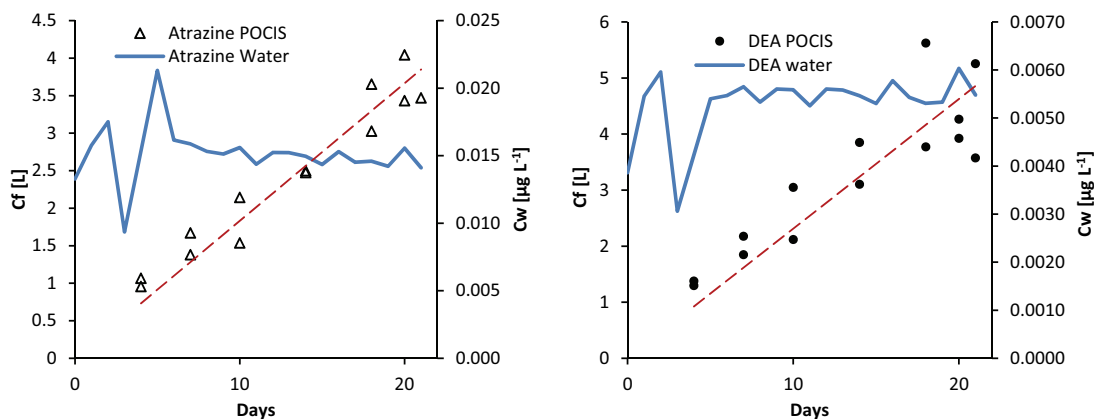
Figure 5:5 In situ variations of concentration factors in POCIS and water concentrations measured daily using grab samples during calibration experiment (Cf: Concentration factor, Cw: water concentration).

Over 21 days, the DIA uptake followed a curvilinear pattern (Figure 5:6). DIA uptake tended to be linear only during the first 7 days of exposure ($R^2 = 0.937$) as observed by Ibrahim et al. (2013b). The k_u and R_s for this period respectively were 1.64 Lg^{-1}·d^{-1} and 0.329 L d^{-1} (using equation 5:2 and 5:3). After the first seven days, the zero-order kinetic approximation based on the assumption that the elimination rate was negligible compared to the uptake rate was no longer valid and accumulation was better-modeled using equation 5:1.

The approach proposed by Mazzella et al. (2007) was used in a first attempt to define the kinetic parameters from equation 5:1. K_{sw} and k_e were respectively derived from the accumulation curve (K_{sw}=19.49 L g^{-1}) and equation 5:4 ($k_e = \frac{K_{sw}}{k_u}$=0.084 d^{-1}). Figure 5:6 shows the modeled accumulation of DIA using these parameters in equation 5:1. This estimation tended to underestimate the Cf, which would result in a conservative (protective) interpretation of the water concentration. It is noteworthy that when using equation 5:4, the accuracy of the k_e value strongly relies on K_{sw} and k_u determination. In this case, determining K_{sw} from the accumulation curve is not very robust, as the POCIS tend to reach the equilibrium only at 21 days. The calculation is therefore based on a point estimate. A "burst effect" is also likely to occur for substances with log k$_{ow}$ <3 in the first days of exposure (Thomatou et al., 2011). For these substances, calculating k_u based on short-term exposure data, can be biased and longer exposure period are recommended to reduce this effect.

It was outlined that equation 5:1 satisfactorily represented accumulation of DIA in POCIS over 21 days of exposure (Mazzella et al., 2010, 2007). Therefore, this study proposes to use a more robust statistical approach to define the kinetic parameters. A Nonlinear Least Squares (NLS) regression was subsequently applied to fit the full calibration dataset (i.e. Cf values over 21 days) with equation 5:1. Fitting of the data (Figure 5:6, $R^2 = 0.85$) resulted in $K_{sw_{fitted}}$ and $k_{e_{fitted}}$ values of: 19.47 L g^{-1}· and 0.1223 d^{-1}. Recalculating k_u with these parameters and equation 5:4 gave a $k_{u_{fitted}}$ value of 2.38 L g^{-1}·d^{-1} which corresponds to a seven-day $R_{s_{fitted}}$ of 0.476 L d^{-1}. These results confirm that the accumulation reached equilibrium after 21 days ($K_{sw} \approx K_{sw_{fitted}}$) and point out the underestimation of k_u in previous calculations. The two approaches yielded a difference of $\pm$0.031 µg L^{-1} on the final water concentration.
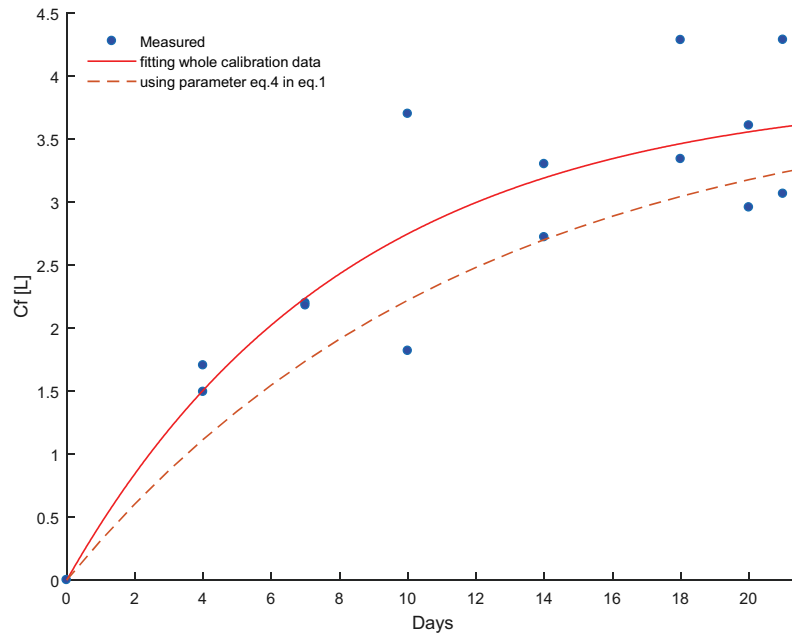
Figure 5:6 Evolution of concentration factor (Cf) measured with POCIS for DIA (points) and result of interpolations using equation 5:1 and fitting of the whole data set (plain line) or parameters from equation 5:4 (dashed line).

A comparison with Rs found in the literature showed that values for atrazine and DEA fell within the range of laboratory calibrations and in the upper range of data obtained in situ (Table 5:5). The Rs obtained for DIA in this work was higher than previously reported values. These high values obtained with quasi-stagnant water could be the consequence of the high temperatures observed in the study area (30.8 ± 1.3 °C during in situ calibration).

Table 5:5 Comparison of sampling rates between this study and values found in the literature

Molecules	Rs in situ (this work) [L d^{-1}]	Rs in laboratory [L d^{-1}]	Rs in situ [L d^{-1}]	Reference
Atrazine	0.183	0.042 - 0.240 0.009 - 0.430	0.059 0.11 0.333 0.26	Morin et al., 2012 Belles, 2012 Ibrahim et al., 2013b Carpinteiro et al., 2016
DEA	0.231	0.167 - 0.300 0.07 - 0.370	0.061 0.08 0.236	Morin et al., 2012 Belles, 2012 Ibrahim et al., 2013b
DIA	0.476	0.106 - 0.220 0.08 - 0.31	0.025 0.10	Morin et al., 2012 Belles, 2012

5.4.2 Applicability of PRC correction

DIA-*d5* desorption was also estimated from the in situ calibration experiment (Figure 5:7). The quasi-linear desorption of DIA-*d5* ($R^2 = 0.96$) during the first 7 days was in accordance with the quasi-linear accumulation observed for DIA. After this period, the kinetic tends to reach a second phase. Hence, the model of a first-order kinetic (equation 5:5) did not align with the data ($R^2 = 0.51$), rejecting the hypothesis of complete isotropic exchanges. As observed by Vermeirssen et al. (2013) the desorption was better described by a two-phase model ($R^2 = 0.87$):

$$\frac{C_{PRC(t)}}{C_{PRC0}} = \frac{C_{PRC,rapid\ (t=0)}}{C_{PRC0}} e^{-k_{rapid}\ t} + \frac{C_{PRC,slow\ (t=0)}}{C_{PRC0}} e^{-k_{slow}\ t}$$

in which C_{PRC0} and $C_{PRC(t)}$ respectively are the initially spiked concentration (µg g^{-1}) and the residual concentration of PRC in the receiving phase after an exposure time t (days). $C_{PRC,rapid\ (t=0)}$ and $C_{PRC,slow\ (t=0)}$ respectively are the concentrations of the initially sorbed compound (µg g^{-1}) that follow a rapid and slow desorption process and k_{rapid} and k_{slow} are the elimination rate constants for the rapid and slow desorption processes (d^{-1}).

This phenomenon might be explained by the bonding strength of the analyte with the sorbent and the environmental conditions. In the initial and rapid desorption phase, the POCIS was clean and released the more loosely bound analytes. The clogging of PES membrane pores might also be involved in desorption slowdown. Over time, biofilm grows on the surface and suspended matter settles on the membrane in the quasi-stagnant lake water. The environmental conditions in the study area: warm temperatures, slow current velocity and high suspended matter content particularly enhanced these phenomena. This obstruction may have constituted a barrier to DIA-*d5* desorption. Further research is needed to identify the exact origin of the observed two-phase desorption.

The model of a first-order kinetic and isotropic exchange conditions appeared to be valid assumptions only in the first phase. Fitting of this data with equation 5:5 ($R^2 = 0.93$) gave a value of $k_{e_{PRC}} = 0.142$ d^{-1}. $k_{e_{PRC}}$ compared favorably with $k_{e_{fitted}}$, but less with k_e values calculated with equation 5:4, respectively yielding a difference in the final concentration of $\pm$ 0.008 µg L^{-1} and $\pm$ 0.037 µg L^{-1} after 21 days of exposure (using equation 5:1). These results validate the value defined for $k_{e_{fitted}}$ and the quasi-linearity of DIA accumulation during the first 7 days of exposure. Therefore, $K_{sw_{fitted}}$ and $k_{e_{fitted}}$ were used for further calculations of the TWAC of DIA.
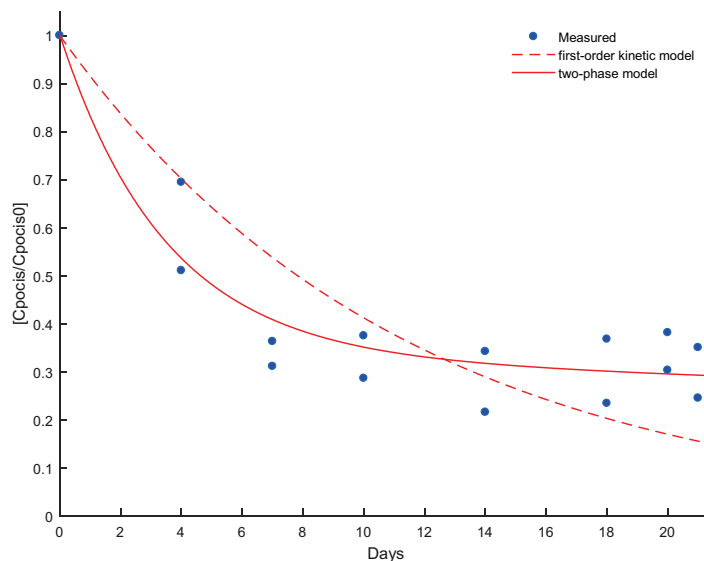
Figure 5:7. Measured and modelled desorption of the PRC DIA-*d5* over 21 days of exposure
(Cpocis: amount in the POCIS at a given time, Cpocis0: initial amount in the POCIS).

If deployment and calibration are performed in the same environmental conditions, water concentrations can be directly derived from POCIS concentrations using sampling rates with no further correction (Morin et al., 2012). In situ calibration and dry-season monitoring were respectively performed in March and April. Under the Sudano-Sahelian climate, climatic conditions are similar for these months. Pesticide residue concentrations measured in grab samples collected at each sampling point in April were comparable over the years (Figure 5:8) and with the calibration period (Figure 5:5). In this steady-state, applying equation 5:3 yielded no significant difference between TWAC measured with POCIS and concentrations measured with grab samples (difference $C_{w_{POCIS}} - C_w < 8$ ng L^{-1}). These results were consistent with stable concentrations observed in water during this period. They also validate the in situ calibration and the suitability of POCIS to measure water concentration of atrazine and its metabolites.

PRCs have been used to correct the R_s to account for differences between environmental conditions (temperature, flow, etc.) during calibration and exposure (Carpinteiro et al., 2016; Lissalde et al., 2014; Mazzella et al., 2010). In the present environmental conditions, isotropic exchange conditions were not achieved over a 21-day exposure period. The two-phase kinetics observed for desorption of the PRC DIA-*d5* did not comply with the sampling rate correction approach with PRC (equation 5:6). Therefore, caution must be taken when considering the TWAC measured with the POCIS during the rainy season (July - August), as the climatic conditions may differ from calibration conditions (lower temperatures and higher precipitation). Nevertheless, only two sampling points exhibited a significant difference (0.026 µg L^{-1} and 0.061 µg L^{-1}) between $C_{w_{POCIS}}$ and C_w in the middle of the rainy season (Figure 5:8). It is to be noted that during this period environmental conditions (mainly precipitation) induced a larger variability of pesticides concentrations, which could explain the larger discrepancies observed between water concentrations measured with grab sampling and TWAC.

5.4.3 Comparison of active sampling and POCIS for monitoring seasonal variations of pesticide concentrations in the lake

Of the 25 pesticides analyzed, 13 were detected (i.e. C_w > LOD) in grab samples (SI Table S7 and Table S8). Pesticide concentrations in the lake were quite stable from December to July and under 0.03 µg L^{-1}, except for cypermethrin and chlorpyrifos. These two pesticides exhibited short-term peaks of higher concentrations that were not detected in the following 3 to 4 days (cypermethrin (n = 3): 0.168 µg L^{-1}, 0.220 µg L^{-1}, and 0.840 µg L^{-1}; chlorpyrifos (n = 2): 0.045 µg L^{-1} and 0.086 µg L^{-1}). In mid-July and August, concentrations of triazine herbicides (atrazine, DEA and DIA) and imidacloprid increased (Figure 5:8). Imidacloprid and triazines were the only pesticides detected in every campaign and that followed a similar seasonal pattern across the years. Acetamiprid was also detected in July and June but concentration distribution exhibited no seasonal pattern (Figure 5:8). The other pesticides were not permanently detected during the monitoring period and appeared to be more representative of isolated cases of pesticide release in the environment.

The POCIS were deployed for 21 days and enabled detection of 10 pesticides (Figure 5:8 and SI Table S7 & 9). Similar to grab sampling, acetamiprid, atrazine, DEA, DIA and imidacloprid were the only pesticides detected throughout the year. No significant difference was observed between water concentrations measured by POCIS and grab samples for triazines. In situ calibration was not suitable for the other target substances and the singularity of the environmental conditions in the study area did not allow R_s to be estimated from the literature (SI Figure S3). Therefore, only qualitative interpretation of aquatic concentrations could be derived from the amounts accumulated in the POCIS. The presence of acetamiprid was detected more frequently with POCIS than with grab samples (Figure 5:8). The largest concentrations were observed in June 2015. In the case of imidacloprid, the mass of analyte accumulated during exposure exhibited the same seasonal patterns as described for grab samples (Figure 5:8). Pesticides detected by the POCIS included chlorpyrifos and dieldrin with a log K_{ow} > 4. For these two substances, the absence of correlation between the occurrence in passive and active sampling might originate from isolated contamination cases but also poor suitability of POCIS for these molecules as underlined by Morin et al., (2012). The same remark applies for cypermethrin, which was not detected with POCIS. Other substances with a log K_{ow} > 4 were never detected by either technique.

When the passive samplers are integrative, the TWAC can be seen as a more robust representation of the environmental conditions over the period of exposure compared to grab sampling. In the present study, correlation between active and passive sampling results helped confirm that trends observed with grab sampling were representative of seasonal variations and not only isolated peak concentrations. In 2015, POCIS confirmed that the runoff generated by the first rains (June - mid-July) did not induce a significant increase of pesticides concentrations in the lake except for acetamiprid and imidacloprid. In 2016, POCIS confirmed low levels of pesticides measured during gardening activities (March - April) in the previous year, and that there was a large increase for triazines and imidacloprid by the end of July (deployment in July - August). It is noteworthy that the use of atrazine in small-scale gardening is not common, due to associated costs. The increased

concentration of atrazine during the rainy season coupled with no use for gardening, suggests that there is lake contamination by other activities located upstream. Treatment of cultivated lands for cash-crop production (rice, cereals, etc.) during the rainy season might explain the increase of triazine levels.

On the other hand, acetamiprid and imidacloprid are widely used in gardening activities. Imidacloprid is considered to be persistent in soil, with a half-life of up to 191 days, while acetamiprid is generally not persistent in soil (Lewis et al., 2016). Nevertheless, experiments performed by Gupta and Gajbhiye (2007) suggest that acetamiprid persistence in soil could be highly influenced by moisture. Reduced microbial activity could result in substantive increase of acetamiprid half-life under the dry-soil conditions of the study area. Although pesticide application periods corresponded to low concentrations in the lake, imidacloprid and acetamiprid contamination might originate from gardening activities. These pesticides might have been mobilized from soil particles due to their persistence and moderate mobility in soil (Lewis et al., 2016), but also from contaminated wells and waste as water submerges the agricultural lands during the rainy season. Higher levels were detected in June 2015, which might indicate mobilization from the gardening areas dutring the first rains (first flush).

Finally, arbitrary detection of pesticides and low concentration levels did not allow for identifying spatial variations across the lake. No significant difference was observed between sampling points even when water flowed though tributaries during the rainy season (July - August).
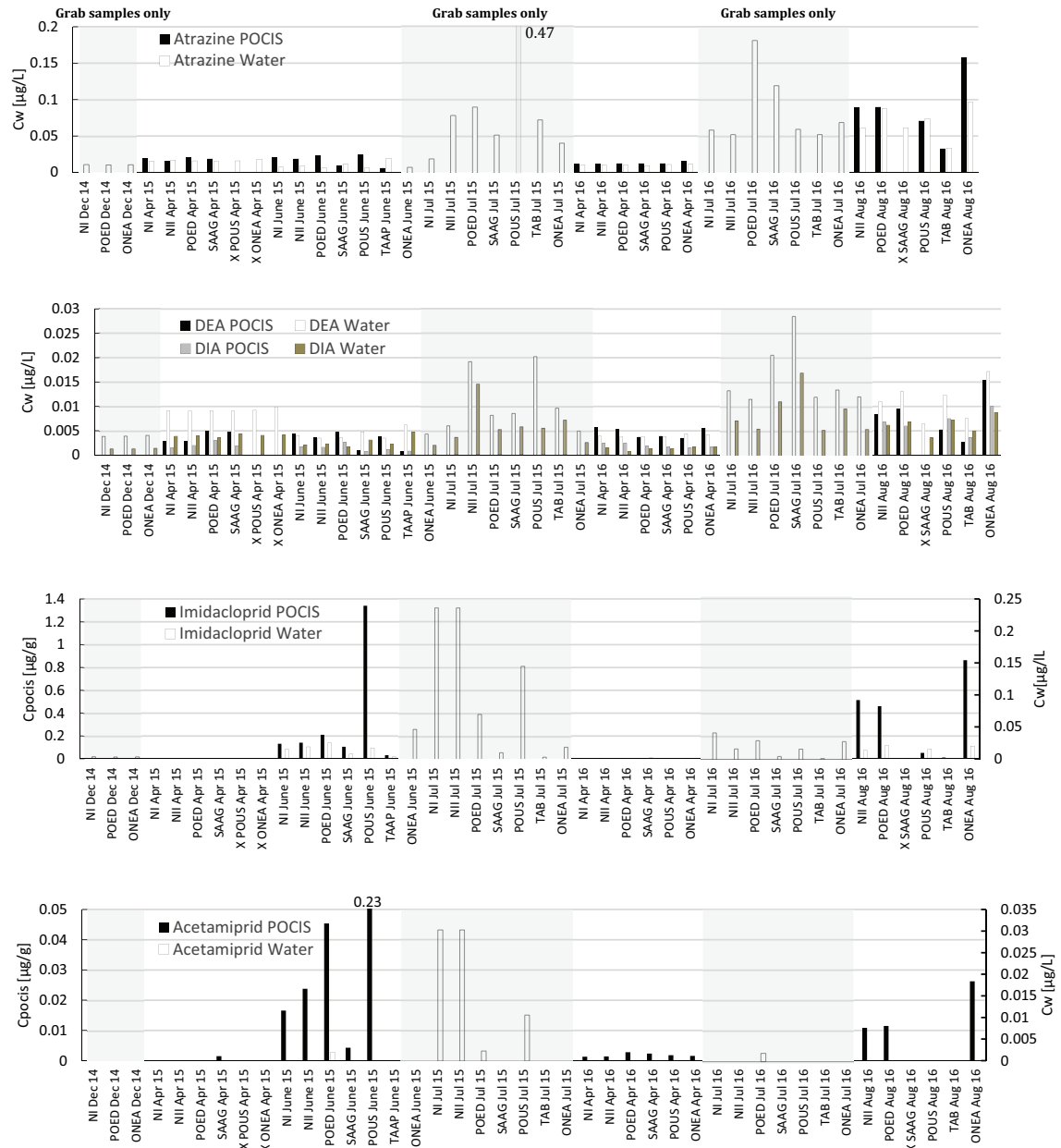
Figure 5:8 Pesticide concentrations in the lake (2014 - 2016) measured with grab samples and POCIS (X: not recovered after exposure) at 7 locations (ONEA (pumping station), Poedogo (POED), Sa-nigniogo (SAAG), Tabtenga (TAB), Noungou I (NI), Noungou II (NII), Pousghin (POUS)).

5.4.4 Complementary screening with SR

Except dieldrin, chlorpyrifos, alpha-endosulfan, and endosulfan sulfate, the substances analyzed in SR could not be recovered by SPE extraction and POCIS. SR was used to perform a complementary screening of the more hydrophobic target substances (log K_{ow} > 3). Twelve (12) target substances were detected in SR. The number of positive samples and the amounts accumulated in the samplers were always higher during the rainy season (Table 5:6). Chlorpyrifos was the most frequently detected pesticide (n = 12). Its detection in both seasons was not surprising as it commonly used in market gardening and in other types of agriculture (e.g. cotton, cereal-production, etc.). However, the other substances were not reported during surveys on agricultural practices conducted in market gardening areas. Their prevalence during the rainy season (in the absence of gardening activities) suggested the contamination of the water by other activities located upstream of the dam. Nevertheless, except methoxychlor, all the detected substances are banned as part of the Annex A (elimination of the production) of the Stockholm Convention. In the 70's methoxychlor has been tested as an alternative to DDT in many countries (U.S. EPA, 1975) but no official use in Burkina Faso was reported in the literature. To date, methoxychlor is not authorized by the CSP. Its presence in only one sample might be an isolated case of contamination. Further monitoring efforts would be needed to characterize the extent and origin of this pollution. In a similar way, we were not able to identify official uses of chlordane in the country. Chlordane is classified as a very persistent pesticide in soils but its half-life in soil (DT50 ~365 days, (Lewis et al., 2016)) does not suggest a very ancient use. On the other hand, dieldrin, DDT, and endosulfan were used in the country in agriculture and for vector control. DDT was used mainly in the 60's - 80's in agriculture and for malaria vector control (Dabiré et al., 2012) but 2001 and 2004 national inventories reported remaining stocks across the country (MECV, 2005b). The presence of the DDT isomers together with their degradation products DDE and DDD, may suggest a recent use. Endosulfan was only banned in 2012 (Stockholm Convention on Persistent Organic Pollutants, 2017) and was already detected in soils and water in previous studies (Ouattara et al., 2012; Tapsoba et al., 2008). As aforementioned (section 2.2.3), dieldrin was also found in 2004 in wood protection products used in Burkina Faso (MECV, 2005a). Except for endosulfan all these "official" uses dated from the past ~20 years and therefore illegal importation and application in activities conducted during the rainy season seem more likely.

Table 5:6 Pesticides detected with SR (*N.D.*: Not Detected)

	Number of positive samples	
Substance name	**Dry season (March - April 2016)**	**Rainy season (July - August 2016)**
cis-alpha-Chlordane	*N.D.*	3
trans-gamma-Chlordane	1	5
Chlorpyrifos-ethyl	5	6
Dieldrin	1	4
alpha-Endosulfan	*N.D.*	1
Endosulfan Sulfate	1	4
Methoxychlor	*N.D.*	1
trans-Nonachlor	*N.D.*	1
∑(o,p'-DDT, p,p'-DDD)	*N.D.*	5
p,p'-DDE	1	4
p,p'-DDT	*N.D.*	4

Although TWAC could not be derived from the SR in absence of suitable calibration, the screening of target substances provided valuable information. Similarly to POCIS and grab samples extracts, SR indicated seasonal variations of pesticide levels.

Compared to grab sampling, the detection of endosulfan with SR might be due to the integrative characteristic of the passive samplers (Booij et al., 2007). Exposed during 6 weeks, the SR might sample higher quantities of analytes and achieve lower detection limits. They are also more prone to capture isolated occurrence in water with regard to the longer sampling period compare to grab samples. This remark applies also to the higher frequency of detection of chlorpyrifos and dieldrin. Compared to POCIS, the higher frequency of detection of chlorpyrifos ($\log K_{ow} = 4.7$) and dieldrin ($\log K_{ow} = 3.2$) in SR is in accordance with the range of application of the POCIS ($\log K_{ow} < 3$-4). These results are supportive that SR could be a suitable tool to complete POCIS and standard water extraction technique (SPE) for the monitoring of pesticides in water. Further experimentations are need to fully assess the uptake kinetics in the local context (warm temperature, stagnant water, etc.) and provide calibrated sampling rates for the calculation of TWAC.

5.4.5 Pesticide levels in traditional wells

Twelve pesticides were detected in the traditional wells (Figure 5:9). In contrast to the lake, the sample concentrations were more variable and seemed influenced by surrounding pesticide applications (SI Table S10). Residues of pesticides used in gardening were present in every sampled well. Acetamiprid, imidacloprid, and profenofos were detected in more than 90% of the samples. Application of pesticides in the vicinity and washing clothes and equipment used for spraying were identified during field campaigns as possible contamination sources of pesticides from gardening. Although atrazine was not used on lands surrounding the wells, traces of the parent compound and its metabolites were found in every sample but at lower concentrations than in the lake. This contamination might originate when the lakeshore is submerged during the rainy season or from subsurface transportation of lake contaminants into the accompanying aquifer exploited by these shallow traditional wells. Finally, the proposed extraction procedure did not allow for quantifying emamectin benzoate, but this substance was detected in 74% of collected samples. Further investigations on emamectin benzoate levels in wells are needed to refine exposure and risk assessment.
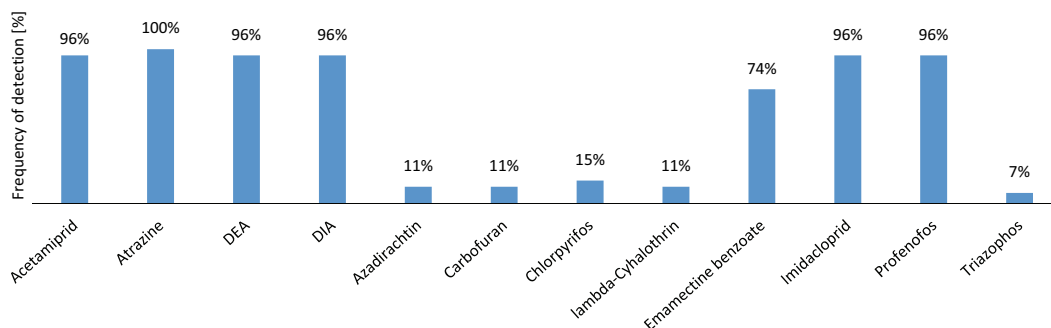
Figure 5:9 Frequency of detection of pesticides in traditional wells.

5.4.6 Borehole contamination

Only trace concentrations of acetamiprid (n = 2; 0.001 µg L^{-1} and < LOQ) were found in boreholes. This is consistent with the hypothesis that boreholes, which exploit deeper aquifers, are less affected by gardening activities in the study area than are the shallow traditional wells. Nevertheless, the proximity of treated fields and submersion of some of the infrastructure during the rainy season, makes them potentially vulnerable to pollution. Chlorpyrifos, cypermethrin and dieldrin are not expected to be mobile in soil but acetamiprid, carbofuran, imidacloprid, triazines, and triazophos are classified as moderately mobile, and profenofos as slightly mobile (Lewis et al., 2016). Traces of acetamiprid indicated that care should be taken. As a precautionary principle, it is recommended to implement a buffer zone between boreholes and cultivated lands. Groundwater monitoring should be used as a tool to control the quality and the origins of contamination of this important drinking water resource.

5.4.7 Pesticide levels in soils and sediments

Soil samples were collected in 2015 and 2016 during the dry season (6 samples collected in 2015 and 7 in 2016) and the rainy season (6 samples collected in 2016). As samples were not collected on similar plots and no clear difference was observed between levels from samples collected during the dry and the rainy season, results are presented as median, minimum and maximum concentrations with no differentiation between sampling periods (Table 5:7). Soils samples were found positive (level > LOD) to 10 pesticides. Except dieldrin, endosulfan, and DDT (and its metabolites), pesticides detected were used in gardening (field survey observations). The higher concentration was measured in the unique sample containing carbofuran (70.61 µg kg^{-1}). In the past decade, endosulfan was still used in cotton production and was the most commonly detected pesticide in soils (Ondo Zue Abaga et al., 2011; Ouattara et al., 2010; Savadogo et al., 2006; Tapsoba et al., 2008). Levels measured in Loumbila are in the lower range of previously reported concentrations (0.2 - 80 µg kg^{-1}, Table 2:3). These lower concentrations could be explained by the fact that endosulfan is banned since 2012 but also because the area was never cultivated for cotton production. However, due to their larger availability, gardeners often used pesticides intended for cotton treatment. It is therefore likely that endosulfan was also used in gardening when it was still authorized. Nevertheless, endosulfan is moderately persistent in soil and its half-life of 86 days (Lewis et al., 2016) suggests a relatively recent use. On the contrary, although it was rarely detected, the persistence of DDTs in soils (half-life: 6200 days (Lewis et al., 2016)) could suggest a past use. These findings support the assumption of the presence of other sources of contamination located upstream already discussed in section 5.4.3. Similarly to water (section 0), dieldrin was detected in soil without any use identified in the study area. As dieldrin is persistent in soil (half-life: 1400 days (Lewis et al., 2016)), it was not possible to identify the exact origin of this contamination. However, the lower detection frequency of these organochlorine pesticides compared to pesticides more common in gardening tends to suggest that use is not widespread.

Sediment samples were collected in 2015 during the dry season (n = 8) and in 2016 during the rainy season (n = 6). As for soil, no particular trend was observed between the samples collected

in different seasons. Results are therefore also presented as median, minimum and maximum concentrations with no differentiation between sampling periods (Table 5:7). Every pesticide detected in sediments (n = 6) was also detected in soil and water samples. Water pollution might occur through atmospheric deposition (spray drift), direct release (e.g. cleaning of spraying equipment in the lake) or contaminated runoff (leaching of pesticide from soil). As sediments are in direct contact with water, exchanges between these compartments are likely to occur depending on the physicochemical properties of the substances (Gobas and MacLean, 2003). In a similar way, the solid transport generated by intense precipitations during the rainy season could also explain the similarities between soils and sediments.

The detection of pesticides used in gardening in soil was expected. Low compliance with the good agricultural practices (e.g. non-respect of recommended pesticide dose and frequency of application) could explain the detection of residual quantities even after a certain time (detection during the rainy season). Little precautions taken during pesticide handling could also explain the water contamination (e.g. cleaning of contaminated spraying equipment in the dam) and thus the presence of pesticides in sediments. In addition, transfer of contaminated soil material in the lake is likely to occur through runoff due to the relatively short distance between treated fields and the lake and during the submersion of the cultivated lands in the rainy season.

Table 5:7 Pesticide levels in soils and sediments (n: number of samples)

Substance name	Soil [µg kg^{-1}]		Sediment [µg kg^{-1}]	
	Median (n)	Min - Max	Median (n)	Min - Max
Acetamiprid	2.33 (11)	1.19 - 3.66	N.D.	N.D.
Carbofuran	70.61 (1)	-	N.D.	N.D.
Chlorpyrifos-ethyl	6.72 (12)	3.08 - 204.31	5.55 (5)	1.84 - 12.67
alpha-Cypermethrin	9.16 (10)	5.82 - 21.09	12.95 (1)	-
beta-Cypermethrin	16.48 (6)	14.91 - 18.05	N.D.	N.D.
Dieldrin	4.13 (4)	-[a]	<LOQ (2)	-
aplha-Endosulfan	<LOQ (2)	-	1.07 (5)	0.74 - 1.49
beta-Endosulfan	11.32 (7)	0.94 - 20.7	2.23 (7)	1.16 - 13.24
∑(o,p'-DDT, p,p'-DDD)	<LOQ (2)	-	N.D.	N.D.
p,p'-DDE	6.51 (2)	3.16 - 9.87	2.07 (6)	-[a]

[a] Only one sample with concentration > LOQ

In addition to the previously discussed organochlorines (dieldrin, DDT, and endosulfan), chlorpyrifos is also considered "moderately persistent" to "persistent" in soils (Lewis et al., 2016). For the other detected substances, the soils are not particularly expected to act as a sink. The relatively short half-life reported for these pesticides suggested a low persistence (Table 5:8). The detected residues were therefore more likely to be the remaining of recent applications rather than the result of an accumulation after the growing season. In order to protect the water resources used for drinking water, the government recently imposed the implementation of a buffer zone between water reservoirs and cultivated lands in certain gardening areas. One year after its implementation, only chlorpyrifos, endosulfan, and DDT were detected in soils collected in the buffer zone around

Ziga Reservoir (in 2014). These findings were in accordance with the relatively short persistence of pesticides commonly used in gardening.

With intense precipitation, the slight increase of acetamiprid and imidacloprid observed at the beginning of the rainy season (section 5.4.3) probably originated from the leaching of flooded soils. Similarly, soils might also be the source of the larger releases of organochlorines during the rainy season (section 0). Model simulations performed by Shunthirasingham et al. (2010) are supportive that the increase of soil moisture during the rainy season in arid subtropical soils with low organic content, is the main driving factor of the release of organochlorine pesticides (chlordane, endosulfan and DDT). However, the absence of detection of chlordane (and its degradation product trans-nonachlor) in soils does not explain its detection in water during the rainy season (section 0). Chlordane was found to prevail in hairs collected from the populations located upstream of Loumbila Reservoir (Chapter 8). No soil sample was collected in this area. It is therefore possible that chlordane contamination was restricted to a certain geographical zone. Methoxychlor is also persistent in soils. Although it was detected in SR during the rainy season, it was not detected in soils of the study area. As for atrazine, detection in water and absence in other matrices could indicate a transport from other areas located upstream of the reservoir lake. It is recommended to pursue and extend the monitoring efforts to other cultivated areas located upstream in order to identify the origin and the trends (e.g. increase or decrease with time, etc.) of these pesticide contaminations.

Table 5:8 Half-life of pesticides in soils (source: Lewis et al. (2016))

Substance name	DT50 [days]	Interpretation
Chlorpyrifos	105	moderately persistent
Chlordane	365	very persistent
Acetamiprid	3	non-persistent
Carbofuran	14	non-persistent
alpha-Cypermethrin	35	moderately persistent
beta-Cypermethrin	27.1	non-persistent
Dieldrin	1400	very-persistent
alpha-Endosulfan	86	moderately persistent
beta-Endosulfan	86	moderately persistent
DDTs	6200	very persistent

5.4.8 Drinking water risk assessment

Traditional wells were also used as a source of drinking water by gardeners while working in the fields. Of the 27 wells investigated (SI Table S10), 7 samples exceeded the parametric value of 0.1 µg L^{-1} for four pesticides (azadirachtin (n = 2), chlorpyrifos (n = 1), imidacloprid (n = 3) and profenofos (n = 2)). In two of them, levels also exceeded 0.5 µg L^{-1} for the sum of pesticides. Hence, nearly 30% of the wells did not meet the quality standards for safe drinking water.

In the lake, the risk was mainly detected during the rainy season (SI Table S7 - S8). In that context, 7 samples exceeded the pesticide threshold limit for safe drinking water for 6 pesticides

(atrazine (n = 4), azadirachtin (n = 1), carbofuran (n = 1), chlorpyrifos (n = 1), dieldrin (n = 1), and imidacloprid (n = 2)). During the dry season (March 2016), 2 samples presented a risk in relation to peak release of cypermethrin, with one also exceeding 0.5 µg L^{-1} for the sum of pesticides. In total, only 2 samples exceeded 0.5 µg L^{-1} for the sum of pesticides. Except for azadirachtin and dieldrin, these active ingredients were present in locally available pesticide commercial formulations. Azadirachtin is generally found in artisanal biopesticides (neem seeds macerated in water) and dieldrin is not authorized in Burkina Faso.

It is noteworthy that, although the levels of atrazine and carbofuran presented a risk under the European Directive 98/83/EC, detected levels did not exceed the national threshold limits (2 µg L^{-1} and 5 µg L^{-1}). In the present work, the most restrictive threshold values were considered in order to ensure the most protective risk evaluation.

With only traces of acetamiprid, boreholes appeared to be the safest source of drinking water in the study area. While contamination of the traditional wells and boreholes will have an influence more restricted to the study area, contamination of the lake can have consequences at a larger scale. The pumping station located in Loumbila Lake supplies the capital with drinking water but no treatment ensures pesticide removal. Water quality and risk assessment at the consumer level in the city are out of the scope of the present work. Further monitoring of water quality at "the end of the pipe" would provide more insight into the persistence of the detected pesticides along the distribution system and the effective risk for consumers in Ouagadougou.

5.4.9 Ecological risk assessment

MTC and STC concentrations are shown in SI (Section S4). Median-PTI and Sensitive-PTI were calculated for each grab sample (n = 70, data not presented). Except for benthic invertebrates (n = 3), Median-PTI did not exceed the unity. STC-PTI results were compared to literature-reported levels of concern (i.e., PTI $\geq$ 1 high risk, 0.1 $\leq$ PTI < 1 medium risk, 0.01 $\leq$ PTI < 0.1 low risk) used for risk quotients in previous studies (Qu et al., 2011).

Benthic invertebrates are the most sensitive taxa (lowest STC and MTC in general) and thus the most affected by water quality. Risks were identified in every campaign except in December (Figure 5:10). Contrary to drinking water, samples presenting the highest ecological risk were collected during gardening activities in the dry season (i.e. March - April).
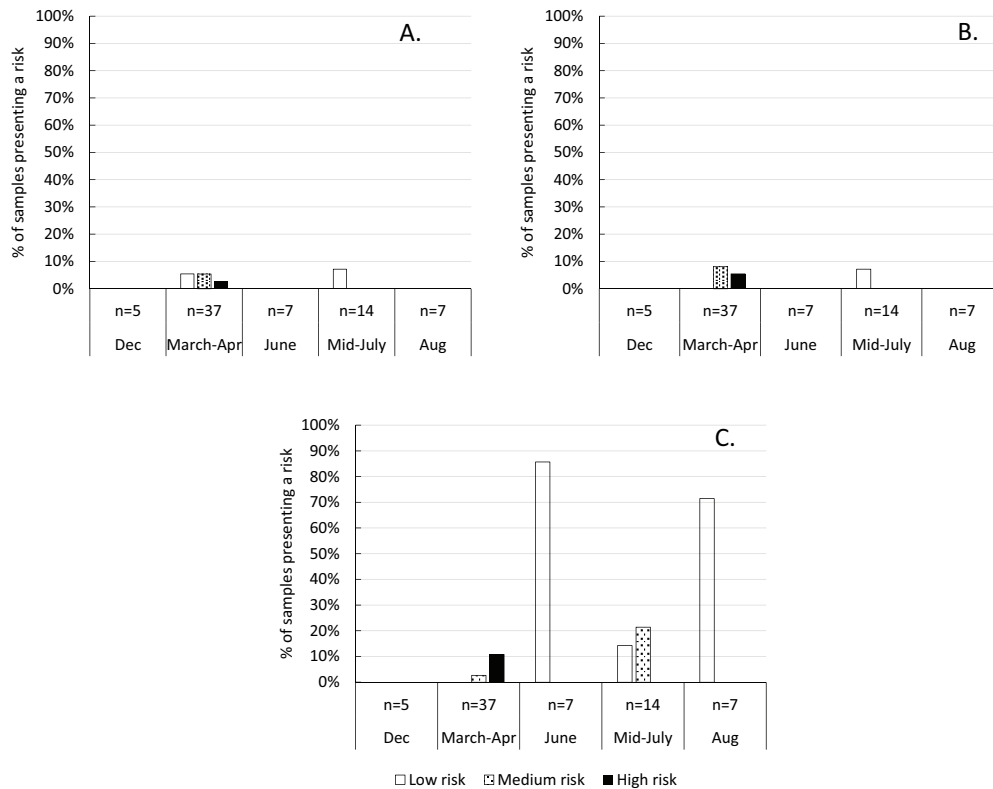
Figure 5:10 Percentage of samples presenting a risk for fish (A), cladocerans (B) and benthic invertebrates (C) using Sensitive-PTI (n: number of samples).

In samples presenting a risk (i.e. Sensitive-PTI > 0.01) the following pesticides alone: chlorpyrifos (n = 2), cypermethrin (n = 3), and dieldrin (n = 1) accounted for more than 99% of the PTI values for fish. Carbofuran (n = 1), chlorpyrifos (n = 2), and cypermethrin (n = 3) accounted for more than 99% of the PTI values for cladocerans. For benthic invertebrates, the average contribution to the risk of atrazine is 1% (n = 27), azadirachtin: 2% (n = 1), carbofuran: 73% (n = 1), chlorpyrifos: 99% (n = 2), cypermethrin: 99% (n = 3), dieldrin: 5% (n = 1), and imidacloprid: 77% (n = 27). Other pesticides contributed to a lesser extent. Cypermethrin and chlorpyrifos detection in water was systematically associated with a risk for the environment. These pesticides were detected during the in situ calibration experiment (March 2016). Their presence in water during gardening activities underlines the impact of pesticides use on the aquatic environment in the study area.

Previous studies underlined the ecological risks related to contamination of surface water by pesticides in Loumbila Lake and other reservoirs in Burkina Faso (Ilboudo et al., 2014b; Leboulanger et al., 2009b). Nevertheless, toxicity of pesticides on local species (i.e. from western African freshwater bodies) is still poorly known and standard test species are most of the time not indigenous. As Leboulanger et al. (2009) noted, use of ''local'' organisms (SI Section S6), rather than ''standardized'' laboratory cultured organisms would help refine ecological risk predictions.

5.5 Conclusions

Twenty-three pesticides were detected in drinking water resources: triazine, acetamiprid, and imidacloprid were the most commonly detected ones.

Flow velocity and temperature are normally the most critical parameters influencing chemical uptake in passive samplers, followed by biofouling (Harman et al., 2012). To our knowledge, no study exists on the uptake kinetics of POCIS in environmental conditions similar to the study area (high temperature, quasi-still water, and high suspended matter). To overcome this shortage, POCIS calibration was performed in situ rather than using R_s from the literature, not representative of the local situation. The present study constitutes a preliminary on-site assessment of the suitability of POCIS in such areas and results are promising. Even in the low-flow conditions of the study area, sampling rates for triazine herbicides were relatively high (probably linked to warm water temperatures). Further research is needed to identify the main driving factors of these chemical uptakes. Contrary to laboratory calibrations, target substances are not artificially introduced in the environment during the in situ calibration experiment. Therefore, only compounds present in the environment can be calibrated. For this reason, R_s could only be derived for triazine pesticides. Further calibration studies in similar environmental conditions are needed to extend the application to other pesticides. Sampling rate correction using DIA-*d5* as a PRC was not possible due to the absence of isotropic exchanges between uptake and desorption. Therefore, the suitability of the PRC DIA-*d5* to account for the impact of environmental conditions on the uptake under similar conditions to the study area is questioned. In situ/laboratory calibration is recommended for future investigation. The use of NLS regression on the calibration dataset proved to be a robust approach for estimating TWAC in case of nonlinear uptake. Although the SR were not calibrated, they were found to be a useful screening tool for hydrophobic compounds. Among the 12 pesticides detected in water with SR, 10 could not be detected with the other techniques. These results are supportive that SR could effectively complete POCIS or grab sampling for the monitoring of pesticides in Burkina Faso. Further studies including calibration experiments must be conducted to determine their suitability for the determination of TWAC of pesticides under the specific environmental conditions of the study area.

The combination of active and passive sampling provided a better understanding of fluctuations of concentrations over time. Concentrations in the lake exhibited seasonal variations related to pesticide applications in gardening. Leaching from soils can explain the increase observed for pesticide used in gardening at the beginning of the rainy season (e.g. acetamiprid and imidacloprid). On the other hand, traces of certain substances suggested other sources of contamination. Triazine and organochlorine pesticides were detected in water while no use was reported in the study area. Persistence and detection in soils and sediments could explain the release of certain pesticides used in the past. The combination of intense runoff and flooding of the cultivated lands during the rainy season could explain the larger concentrations observed during this period (e.g. for endosulfan and DDTs). However, pesticides such as triazine herbicides and chlordane were not detected in soils nor in sediment. The prevalence of chlordane in hairs from populations living in the area located upstream of the reservoir might indicate that the contamination was restricted to this

area. Although, as no sample was collected from this zone, transport from other areas located upstream can not be excluded. Even though, their origin is unclear, these contaminations are of concerns. Levels of atrazine potentially hazardous to human health were detected. Chlordane, dieldrin, DDT, and endosulfan are banned by the ratified Stockholm convention. Together with methoxychlor, these pesticides were proved to be endocrine disruptors (WHO/UNEP, 2012a) and chlordane (ATSDR, 2014), DDTs (U.S. EPA, 1988a), and dieldrin (U.S. EPA, 1988b) were classified as probable human carcinogens. Further research is needed to identify the sources and the extent of these pollution (i.e. spatial extent and concentrations).

Pesticides levels detected in the study area were globally low, suggesting a low impact of gardening activities on the drinking water resources. However, pesticides used in gardening, including one biopesticide, occasionally presented concentrations that are potentially hazardous to human health and the environment. Among the substances presenting a risk for water consumption, chlorpyrifos was classified as an endocrine disruptor with low-dose effects (WHO/UNEP, 2012a). Human health hazard appeared to prevail during the rainy season while environmental risks were mainly detected in the dry season during gardening activities. The present work suggested that seasonality was the main characteristic of the description of contamination trends in the study area. The findings of this study underlined that monitoring on a regular basis would help policy, health, and environmental impact assessment.

Chapter 6 Dietary intake of pesticides from vegetables and drinking water

Published work:

Lehmann, E., Turrero, N., Kolia, M., Konaté, Y., de Alencastro, L.F., 2017. Dietary risk assessment of pesticides from vegetables and drinking water in gardening areas in Burkina Faso. Sci. Total Environ. 601–602, 1208–1216. doi:10.1016/j.scitotenv.2017.05.285

Web link:

http://www.sciencedirect.com/science/article/pii/S0048969717314006?via%3Dihub

Supplementary material:

Appendix D

Supplementary information are divided in four sections S1-S4 presenting the Figure S1-S3 and the Table S1-S10.

Doctoral Candidate's contribution:

Main investigator and author

6.1 Introduction

Improper selection and use of pesticides on foodstuffs can result in undesirable levels of residues even after processing (Kaushik et al., 2009; Keikotlhaile et al., 2010; Reiler et al., 2015). Although, accidental intake, self-harm and occupational exposure are considered to be the major routes of exposure to pesticides in Burkina Faso (Toé, 2010b), dietary exposure is assumed to be five orders of magnitude higher than other routes, such as air and drinking water (Jolliet et al., 2003). Hence, pesticide residues in food might also constitute an important risk to human's health. To prevent health hazard and unnecessary exposure, Maximum Residue Limits (MRLs) and Admissible Daily Intake (ADI) have been defined at national levels and internationally for example in the Codex Alimentarius (WHO/FAO, 2017) or in the European Pesticides database (European Union, 2017). Although pesticide residue contamination in foodstuffs have been monitored for decades in most developed countries, vegetables in developing countries are not much investigated for pesticide contamination (Bempah et al., 2016). Studies conducted on food produced in West Africa have identified exceedance of MRLs and ADI suggesting a risk for consumers and the need for suitable monitoring and controls of food products (Bempah et al., 2011; Mawussi et al., 2009).

The present study assessed dietary exposure to pesticides from drinking water and consumption of vegetables produced in larger quantities in gardening areas in Burkina Faso (i.e.: tomatoes, cucumbers, sorrel (*Hibiscus sabdariffa*), okra (*Abelmoschus esculentus*), and two varieties of eggplant (*Solanum melongena L.* and *Solanum aethiopicum*)).The prerequisite for exposure assessment from food is the characterization of the population diet. Various methods exist which include diet history, diet recall, food frequency questionnaires, etc. (FAO/WHO, 2009). The majority of dietary studies use national consumption estimates, which might not be fully representative of local trends. In this study, questionnaire surveys were conducted on the field using the modified 24-hour recall method (24-HR) proposed by Gibson and Ferguson (1999). 24-HR method has the advantage to be faster, less invasive and easier for both the investigator, and the respondent than traditional food frequency or weighed food records. Collected data was aggregated to derive vegetables and water consumption. Multiresidue extraction procedure was developed and applied to determine pesticide levels in vegetables. Acute and chronic risk assessments were subsequently performed by comparison of single pesticide and cumulative exposure to Acute Reference Dose (ARfD) and ADI. This study proposes a comprehensive assessment of the dietary intake of pesticides from vegetables and water sources in a gardening area of a Sahelian country and the resulting risk for children and adults.

6.2 Material and method

6.2.1 Field investigations

The study was conducted in March-April 2015 and 2016 in 3 villages Pousghin, Nabdogo, and Noungou located on the shores of the lake Loumbila (Supplementary Information (SI) Figure S1).

6.2.1.1 Dietary survey and consumption data

In order to assess daily consumption of gardening commodities, a dietary survey was conducted on 126 persons using the modified 24-hour recall method (24-HR) proposed by Gibson and Ferguson (1999). Surveys were conducted during nine consecutive days in order to cover every weekday and any special events (i.e. market day, weekend, etc.). Local kitchen utensils were used to help respondents and investigators in quantity assessment. This approach was developed for application in rural areas in developing countries and was proved to reduce bias and memory lapses from the respondents. Attendants were randomly selected on the field or at household level (SI Figure S1). Priority was given to women as in rural areas they are usually in charge of cooking. Individual portions were directly derived from respondents' answers (i.e. individual diet). Single 24-HR can be also used to derive average intake of a group with the assumption that the subjects are representative of the study population (Gibson, 2005). The difference was made between products consumed raw and cooked (labeled as sauces) considering different recipes and their composition. It was noted that vegetable portions could vary between recipes and that some items were not consumed daily. As an example, when eaten raw, the full-vegetable unit (ex: tomato, *Solanum aethiopicum, etc.)* is generally consumed and a larger portion is ingested at once. Thus giving items a similar weight may lead to an overestimation of the average intake. This issue was handled by Carriquiry (2003) by introducing the propensity-to-consume items. Nevertheless, a single 24-HR does not provide sufficient data to apply the statistical approaches proposed. Therefore, the propensity-to-consume items was derived from their frequency of reporting in dietary surveys, assuming subjects' representativeness of the studied population. Data aggregation allowed to derive weighted average portion estimates (WAPE) for the whole studied population. Distinction was made between drinking water sources for average water consumption estimation. Boreholes and lake water data were aggregated while traditional wells were considered apart.

WAPE calculation included occurrence of the studied commodities in local recipes and occurrence of the final dishes in the diet of the study population. For a given food commodity/water source i, WAPE was calculated as follow:

$$WAPE_i = \sum_1^n \bar{F}_n Pu_n Pp_n \qquad 6:1$$

where, $\bar{F}_n$ is the average portion of a given food commodity in a recipe/volume of water from a source n (g pers^{-1}), Pu_n the probability that the food commodity is used in the given recipe ($Pu_n = 1$ for water consumption estimation) and Pp_n the probability of occurrence of the given recipe/use of the water source in the studied population diet.

A worthy issue is that data collected from field surveys always present gaps. They were attributed to the willingness to answer of the respondent and the understanding of the translator and the surveyor. Only data allowing estimation of individual portions were considered in WAPE's calculations and further risk assessment (n = 70). For other calculations, the full dataset was considered (n = 126).

6.2.1.2 Sampling procedure of gardening commodities and water

The gardening areas cultivated around Loumbila Lake reach up to 3.47 km². Studied vegetable species were selected based on their respective cultivated land area (Figure 6:2) and the likeliness of pesticide treatment before harvest. Gardeners reported that onion, carrot, and garlic were generally less subject to pesticide treatment as the edible part grows under the soil surface. Based on these criteria: tomato, cucumber, sorrel (*Hibiscus sabdariffa*), okra (*Abelmoschus esculentus*), and two varieties of eggplant (*Solanum melongena L.* and *Solanum aethiopicum*) were retained as target species for the present study (Figure 6:1).

(a) Tomato

(b) Sorrel

(c) Eggplant (*Solanum aethiopicum*)

(d) Eggplant (*Solanum melongena L*)

(e) Okra

(f) Cucumber
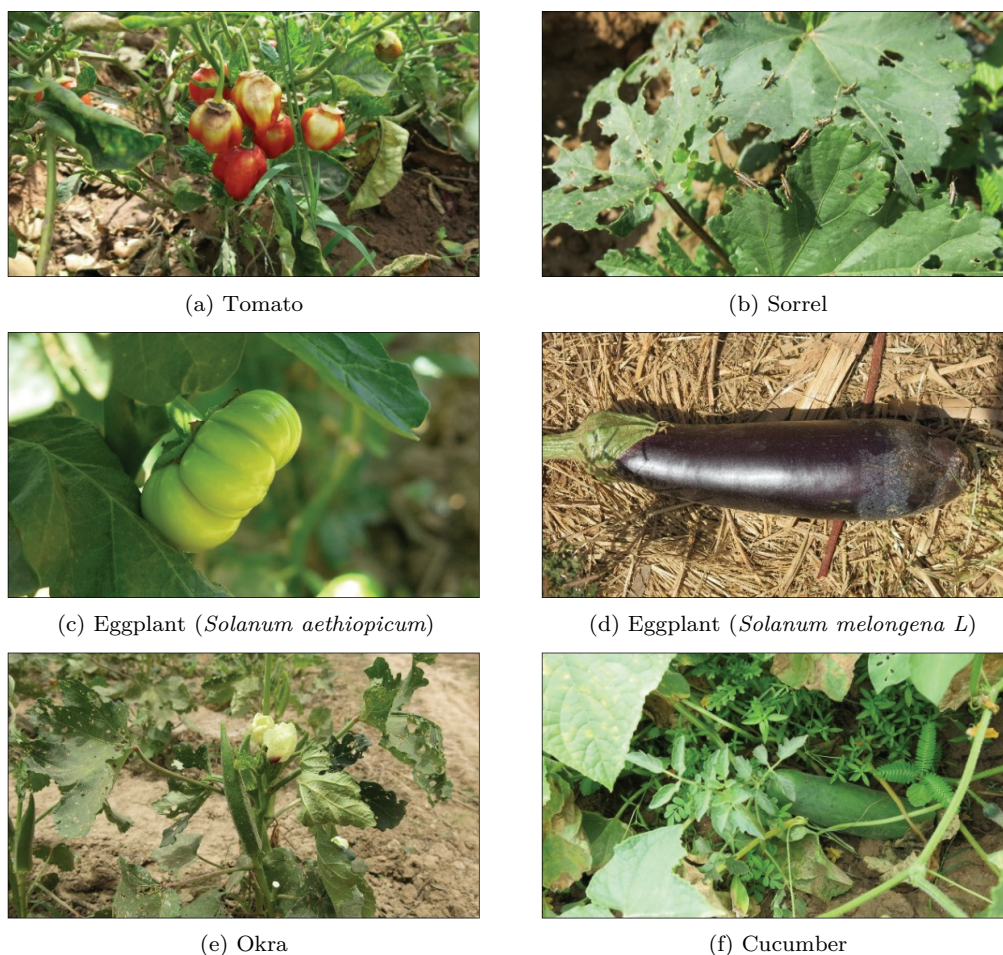
Figure 6:1 Studied crops
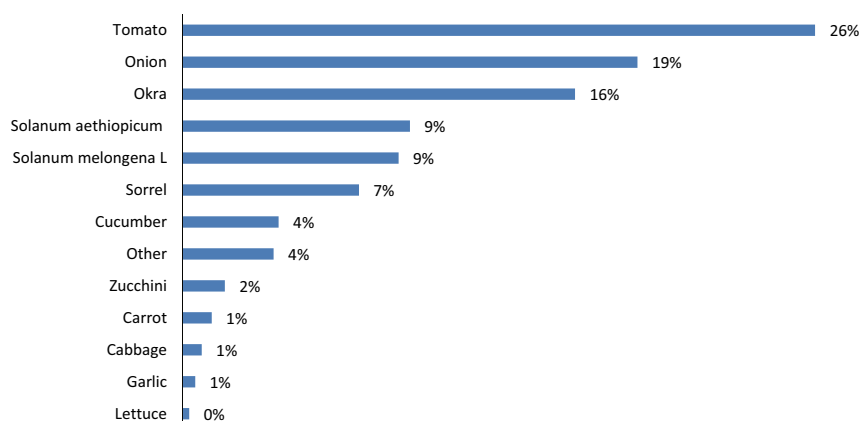
Figure 6:2 Repartition of cultivated surface areas between commodities (total surface area: 3.47 km^2)
(Source: Agence de l'eau du Nakambé (2014))

In rural areas in Burkina Faso, diet was found to be generally poor and monotonous (Savy et al., 2007). Nevertheless, seasonality and particularly food shortage periods might influence dietary diversity (Savy et al., 2006). Fresh vegetables are expected to present the higher levels of pesticide residues. As the objective of the present research was to study pesticides exposure from vegetable consumption, growing/harvesting period was retained as the more appropriate. Vegetable samples were collected by simple random sampling directly on the plot in the three villages located on the lakeshores and on local market stalls in March-April 2015 and 2016.

Laboratory sample size was defined according to the European Commision Directive 2002/63/EC (2002) in order to obtain representative samples to determine compliance with MRLs for pesticides. Samples collected on the field were wrapped in aluminum foil and placed in opaque plastic bags. They were stored at 4 °C for transportation and -20 °C at the laboratory for conservation. In total, 59 samples of vegetables were collected (i.e. tomato: n = 17, cucumber: n = 11, sorrel: n = 10, okra: n = 7, *Solanum melongena L.*: n = 8, and *Solanum aethiopicum*: n = 6). For each collected sample, the gardener responsible for the plot was asked to answer a questionnaire about his own agricultural practices (pesticides used, application rate, water used, etc.).

During the three-year monitoring study presented elsewhere (Lehmann et al., 2017a, Chapter 5), 70 surface water samples have been collected around the lake and more precisely near water inputs and areas with the highest gardening activity. In addition, 27 traditional wells and 9 boreholes were randomly sampled in the same areas where food samples have been collected.

Sampling points' location for food and water analysis is presented in supplementary information section S1.

6.2.2 Chemical Analysis

6.2.2.1 QuEChERS Extraction

Pesticide residues in food commodities were extracted using a modified AOAC 2007.01 QuEChERS (Quick Easy Cheap Rugged and Safe) extraction method. Composite samples were chopped into small pieces, and mixed. Ten grams of homogenized sample were added to a 50 mL centrifuge tube and isotopic dilution was performed with the addition of 0.2 mL of labeled surrogate solution (SI Table S2). Solvent was allowed to evaporate prior addition of 10 mL of 1% acetic acid (HOAc) in acetonitrile and extraction for 5 min in an ultrasonic bath. QuEChERS methods were designed for matrix with at least 75 % water content (Correia-Sá et al., 2012). Water addition was needed for okra (5 mL) and sorrel (10 mL). Then, 4 g $MgSO_4$ and 1 g NaOAc were added and the mixture was shaken vigorously for 1 min, vortexed for 1 min, and centrifuged for 5 min at 3000 rpm. As the reaction with $MgSO_4$ is exothermic, the tubes were cooled in a water bath at room temperature. 6 mL of the supernatant were subsequently transferred for cleanup in a 12 mL dispersive SPE (dSPE) tube packed with 420 mg of Supel™QuE Z-Sep/C18 sorbent (Sigma-Aldrich, Switzerland) and vortexed for 1 min. After 5 min centrifugation at 4000 rpm, 4 mL of the supernatant were concentrated to 0.4 mL. An aliquot of 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of the mixture methanol : water (5:95, v/v) with 0.1% formic acid prior to UPLC-MS/MS analysis. The remaining 0.2 mL was evaporated to dryness and reconstituted in 0.2 mL of isooctane prior to GC-MS analysis.

All samples were unprocessed vegetables directly collected on the plot or on market stalls. In traditional cuisine, cucumber and *Solanum melongena L* are peeled before being consumed. Therefore, these vegetables were peeled prior to homogenization. The skin and edible fraction were analyzed separately.

6.2.2.2 Water analysis

Details about the solid-phase extraction procedure of water samples have been presented elsewhere (Lehmann et al., 2017a, Chapter 5). Briefly, water was filtered through 0.7 µm glass fiber filters (GF/F Whatman; Florham Park, NJ) prior to spiking with appropriate labeled surrogates and extraction. A 1-L water sample was pumped through a 200 mg Waters Oasis HLB cartridge preconditioned with 10 mL ethyl acetate, 10 mL methanol, and 5 mL water. The cartridge was subsequently eluted with the following fractions 5 mL methanol, 5 mL methanol : ethyl acetate (1:1), and 5 mL ethyl acetate : hexane (1:4). After combination, the fractions were concentrated prior to separation and analysis on GC-MS and UPLC-MS/MS.

6.2.2.3 Apparatus and chemicals

Standards of analytes and deuterated compounds were purchased from Sigma-Aldrich (Switzerland), Dr. Ehrenstorfer (Germany), and Toronto Research Chemicals (Canada). Individual solutions of each analyte and deuterated compound and their dilution were prepared in appropriate solvent prior preparation of the stock solutions respectively in acetone and methanol (Table S1 and Table S2) and stored at −20 °C. Appropriate dilutions of these standards solutions were used to prepare calibration curves for further analysis on GC-MS and UPLC-MS/MS.

Ethyl acetate and methanol HPLC grade were acquired from Carlo Erba Reagents (France), formic acid from Sigma-Aldrich (Switzerland), acetone for residues analysis from Acros Organics (Belgium) and acetonitrile and n-hexane from Biosolve Chimie SARL (France). Anhydrous magnesium sulphate and sodium acetate (NaOAc) were purchased from Sigma-Aldrich, (Switzerland).

The gas chromatography analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph coupled with a Thermo Scientific ISQ Single Quadrupole MS (Waltham, MA, USA). The UPLC system consisted of a UPLC Waters Acquity coupled to a Waters Acquity Xevo TQ-S tandem quadrupole MS. Operating parameters are detailed in supplementary information (SI Section S2).

6.2.2.4 Quality control and quality assurance

In order to evaluate the efficiency of the analytical procedure, a recovery assay was conducted. Blank samples of tomato, cucumber, eggplant (Solanum melongena L.), and okra were spiked in triplicates at ~10 µg kg^{-1} and ~50 µg kg^{-1}. Over 31 pesticides analyzed, 25 presented recovery rates in the range of 47% - 155% for the four-vegetable species. The other substances (i.e. 6 pesticides) presented lower recovery rates for certain vegetable species. Nevertheless, they were kept in the multiresidue analysis due to low variability of the obtained results (i.e. low relative standard deviation between replicates). Detailed multiresidue extraction recoveries of studied commodities are presented in supplementary information (Table S7). The limit of detection (LOD) and limit of quantification (LOQ) for selected target analytes were defined as the analyte concentration that produced a peak with a signal-to-noise ratio of respectively 3 and 10 (Table 6:1). They were determined experimentally by measuring the coincident instrumental response of standard pesticide solutions and procedural blank or negative samples.

Table 6:1 LOD and LOQ for target pesticides in vegetables

Active ingredient	LOD [µg kg^{-1}]	LOQ [µg kg^{-1}]	Active ingredient	LOD [µg kg^{-1}]	LOQ [µg kg^{-1}]
Carbamate			*Organochlorine*		
Carbofuran	0.05	0.17	alpha-Chlordane	0.07	0.24
			gamma-Chlordane	0.06	0.2
Neonicotinoid			Dieldrin	5.89	19.64
Acetamiprid	0.03	0.09	alpha-Endosulfan	4.50	15
Imidacloprid	0.05	0.17	beta-Endosulfan	5.17	17.24
			Endosulfan sulfate	6.36	21.19
Pyrethroid			Endrin	5.87	19.57
Lambda-Cyhalothrin	2	6.68	alpha-HCH	15.00	50
alpha-Cypermethrin	6.74	22.45	gamma-HCH	15.00	50
beta-Cypermethrin	7	23.35	alpha-Heptachlor epoxide	3.00	10
Deltamethrin	3.26	10.86	beta-Heptachlor epoxide	3.00	10
			Hexachlorobenzene	3.00	10
Tetranortriterpenoid			trans-Nonachlor	0.07	0.24
Azadirachtin	4.11	13.7			
			Organophosphate		
Triazine			Chlorpyrifos	11.19	37.3
Atrazine	0.04	0.14	Chlorpyrifos-methyl	15.4	51.32
Desethylatrazine	0.01	0.04	Diazinon	2.43	8.11
Deisopropylatrazine	0.05	0.17	Omethoate	0.06	0.21
			Profenofos	2.1	7
Urea			Triazophos	0.02	0.06
Diuron	2.5	8.35			

6.2.3 MRL compliance and risk assessment

Compliance with MRLs was evaluated as the ratio of pesticide residues measured in or on food commodities and MRL values. As the entire foodstuff must be considered (Reg. EC No 396/2005, 2005), the sum of levels measured in the edible fraction and the skin was considered when they have been separately analyzed.

The ARfD and ADI were used as predicted no effect levels for acute and chronic consumers' exposures respectively (Reiler et al., 2015). The Estimated Daily Intake (EDI) of a given pesticide was derived from Renwick (2002) and is expressed here as:

$$EDI_{pest} = \frac{\sum(Cpest \times Fc \times Fp)}{bw} \qquad 6:2$$

where $Cpest$ is the concentration of a given pesticide residue on food, Fc is the food consumption, Fp the food processing factor, and bw the body weight. For each detected pesticide, hazard quotient (HQ) defined as the ratio of the pesticide intake to ARfD or ADI were used to derive the resulting risk. A HQ exceeding the unity (>100% of ARfD or ADI) indicates a risk.

$$HQ_{acute} = \frac{EDI}{ARfD} \qquad 6:3$$

$$HQ_{chronic} = \frac{EDI}{ADI} \qquad 6:4$$

A number of methods have been developed for cumulative risk assessment of pesticides in food. Cumulative effects of pesticides was subsequently evaluated using Hazard Index (HI) presented in previous studies (Boobis et al., 2008). When more than one residue is present, HQ of pesticides with common mode of action (MOA) were summed to account for cumulative toxicity.

$$HI = \sum_{i}^{n} HQ_i \qquad 6:5$$

MRL, ARfD, and ADI values have been extracted from the EU – Pesticides database (European Union, 2017). It is noteworthy that for some pesticides, not all the isomers or substances included in the definition of the residue (for compliance with MRL and for estimation of dietary intake) were analyzed. This concerns carbofuran, cypermethrin, dieldrin, and omethoate. For these substances, underestimation of the risk might be expected (SI Table S9).

HQ and HI were calculated for WAPE and individual diets considering median and maximal residue levels on commodities for acute risk assessment. As it supposed to represent a lifetime exposure, chronic hazard was calculated for WAPE and individual diets considering only median residue levels on commodities. The adult body weight is estimated to be 53 kg for women with at least one child under 5 years old (Savy et al., 2006). For children aged 11-16 years, WHO (2011)

proposed the parametric value of 32 kg for pesticide exposure assessment. Comparison with other studies suggested that these values complied respectively with average body weight of adults and children in rural areas of Burkina Faso (Wood, 2000). Considered scenarios for risk assessment are presented in Table 6:2.

Table 6:2 Scenarios considered for dietary risk assessment

Risk	Reference dose	Population	Body weight	Scenario name	Food consumption	Residue level
Acute Risk	ARfD	Children	32 kg	CH_AR_1	WAPE	Median
				CH_AR_2	WAPE	Maximum
				CH_AR_3	Individual diet	Median
				CH_AR_4	Individual diet	Maximum
		Adult	53 kg	A_AR_1	WAPE	Median
				A_AR_2	WAPE	Maximum
				A_AR_3	Individual diet	Median
				A_AR_4	Individual diet	Maximum
Chronic Risk	ADI	Children	32 kg	CH_CR_1	WAPE	Median
				CH_CR_2	Individual diet	Median
		Adult	53 kg	A_CR_1	WAPE	Median
				A_CR_2	Individual diet	Median

6.3 Results

6.3.1 Pesticide residues and MRL compliance

Over 31 pesticides analyzed in this study, 16 were detected in food or water samples (>LOD). Median and maximum concentrations in edible fractions (peeled vegetables) and drinking water used for risk evaluation are presented in Table 6:3.

13 target pesticides were detected in water. It is noteworthy that for some samples, threshold limits proposed by the European Directive 98/83/EC (1998) on the quality of water intended for human consumption (i.e. 0.1 µg L^{-1} for single pesticide and 0.5 µg L^{-1} for the sum of pesticides) were exceeded (Lehmann et al., 2017a, Chapter 5).

Residues from 14 different pesticides were quantified on food commodities. MRL compliance was verified for each sample and pesticide using the appropriate limit value. Over 59 vegetable samples 21 exceeded the MRLs for seven pesticides: acetamiprid (n = 1), carbofuran (n = 1), chlorpyrifos (n = 3), lambda-cyhalothrin (n = 5), dieldrin (n = 6), imidacloprid (n = 4), and profenofos (n = 11). Percentage of MRLs exceedance ranged from 100% to 2.99 10^4 % (see details in SI Section S4.). In this study, MRLs from the European Union (EU) were retained, as the EU is the most advanced in this domain and in the control of imported products. MRLs have been set for every

pesticides and commodities studied in this project. However, in the absence of a harmonized regulation, standards might vary depending on the country of interest. MRLs from the Codex Alimentarius are presented in SI (Table S9) for comparison purpose.

Table 6:3 Levels of pesticides in vegetable and water samples (*N.D.* : Not detected, <LOQ: LOD< residue level <LOQ)

Pesticides	Authorized by the CSP[c]		Tomatoes	Sorrel	*Solanum melongena L*	*Solanum aethiopicum*	Okra	Cucumber	Lake	Well
			[µg kg⁻¹]						[µg L⁻¹]	
Acetamiprid	Yes	Median	1.52	109.31	1.85	0.44	3.31	1.01	0.0018	0.0066
		Maximum	25.14	3055.39	1.85	1.67	145.08	2.73	0.0302	0.042
$\sum$ *Atrazine*[a]	No	Median	*<LOQ*	0.29	*<LOQ*	*N.D.*	*<LOQ*	*N.D.*	0.0237	0.0032
		Maximum		0.29					0.4942	0.0347
Azadirachtin	No	Median	*<LOQ*	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*	0.1126	0.2956
		Maximum							0.1126	0.4879
Carbofuran	No	Median	1.13	*N.D.*	0.47	2.16	*N.D.*	0.29	0.1097	0.0106
		Maximum	1.13		0.47	3.5		0.29	0.1097	0.0106
Chlorpyrifos	Yes	Median	90.6	100.82	*N.D.*	*N.D.*	*<LOQ*	*<LOQ*	0.0653	0.0448
		Maximum	667.45	590.48					0.0858	0.2022
λ-Cyhalothrin	Yes	Median	145.84	50.33	*<LOQ*	40.92	292.48	9.59	*N.D.*	0.0294
		Maximum	174.34	1661.77		41.63	330.71	10.38		0.0294
$\sum$ *Cypermethrin*[b]	Yes	Median	77.13	123.78	*<LOQ*	*N.D.*	184.31	*N.D.*	0.2197	*N.D.*
		Maximum	77.13	631.28			184.31		0.8392	
Dieldrin	No	Median	*<LOQ*	*<LOQ*	297.31	*N.D.*	*N.D.*	*<LOQ*	0.1069	*N.D.*
		Maximum			571.61				0.1069	
alpha-Endosulfan	No	Median	*N.D.*	26.2	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*
		Maximum		36.8						
Imidacloprid	Yes	Median	5.92	41.17	7.87	20.45	52.39	0.28	0.0039	0.0096
		Maximum	152.65	159.45	39.21	100.62	193.97	0.46	0.2355	0.384
Omethoate	No	Median	*N.D.*	3.74	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*
		Maximum		7.09						
Profenofos	Yes	Median	14.22	618.63	*N.D.*	5.04	132.96	*3.18*	*N.D.*	0.049
		Maximum	73.62	2999		5.04	208.76	*3.18*		0.1742
Triazophos	No	Median	0.49	0.52	*<LOQ*	*N.D.*	*N.D.*	*N.D.*	0.0007	0.0018
		Maximum	0.49	0.96					0.0225	0.0018

[a] Sum of atrazine and its metabolites desethylatrazine and deisopropylatrazine

[b] Sum of isomers: alpha-Cypermethrin and beta-Cypermethrin

[c] Active ingredient authorized in specified commercial formulations by the Sahelian Pesticides Committee (CSP) for application in gardening.

6.3.2 Consumption data

The majority of the respondents reported taking three meals per day (76%). Extreme values (1 or 4 meals) were always associated with a particular event (sickness, lack of money, celebration day, etc.). If most of the meals were home-made (~60%), a large fraction (~35%) was taken in local restaurants (named kiosk or maquis). Every respondent affirmed consuming at least one of the studied vegetables each day. Tomatoes, sorrel, and okra were the preponderant studied commodities in the local diet. Tô is a traditional porridge usually made with millet. Over 45 traditional dishes, Tô with vegetables sauce (okra or sorrel) was the most common dish (30%) followed by rice also served with vegetables sauce (16%). Raw vegetables such as cucumbers (3.6%), *Solanum aethiopicum* (~3%), and tomato (2%) were also reported as part of the diet (SI Figure S2.).

After harvest, food generally undergoes processing steps until it becomes the final commodities. Processing was proved to influence residual pesticide levels in food (Kaushik et al. 2009; Keikotlhaile et al. 2010; Liang et al. 2014). In the study area, vegetables undergone no particular process before being cooked at household level. Hence, local recipes were used to define the suitable processing factor in equation 6:2. Cucumber and eggplant (*S.melongena L*) were usually peeled. In certain cases sun dried okra was used for sauce preparation. Vegetables were usually washed with water before being consumed except when eaten raw directly on the field during the harvest. In the local diet, vegetables are boiled in 89% of the dishes and fried in 11%.

Effect of peeling on pesticide residues was assessed for cucumbers and eggplant (*S.melongena L*). Results are presented in Table 6:4. Average of the residual amounts are presented with no distinction between commodities due to the low number of samples. No processing factor was applied for peeling in risk assessment as only pesticide levels in the edible fraction were considered.

Table 6:4 Percentage of the total amount of pesticides (i.e. with skin) remaining in cucumber and eggplant (*S.melongena L*) after peeling (data not sufficient to derive impact of processing on profenofos).

	Mean	n	SD	Min	Max
Acetamiprid	35%	10	11%	21%	55%
Atrazine	0%	1	-	-	-
Carbofuran	53%	2	-	53%	100%
lambda-Cyhalothrin	16%	2	-	11%	20%
Dieldrin	57%	1	-	-	-
Imidacloprid	18%	8	12%	1%	40%

Impact of processing on pesticide residue levels was proved to be highly dependent on pesticide, crop, and process combination (Kaushik et al., 2009). Since data were only available for a limited number of these combinations of concern in the study area, pesticide-generic food processing factor of 0.6 was applied as proxy. This value was considered conservative (protective) as the sum of all processes undergone (i.e. drying, washing, boiling, and frying) are expected to reduce pesticide levels to a larger extent (Keikotlhaile et al., 2010; Liang et al., 2014).

24-HR surveys were subsequently used to derive consumed portions for each respondent (not presented) and WAPE using equation 1 (SI Section S5.). Meals were generally prepared by one person for many (ex: family, restaurant, etc.). When the meal was shared, equal repartition between participants was assumed with no distinction between adults and children. When water origin was not associated with wells or boreholes, it was considered that it originated from the lake. The average water consumption from the lake and traditional wells were respectively 1.74 L/pers/day and 2.29 L/pers/day.

6.3.3 Dietary risk assessment

6.3.3.1 Acute risk

For children and adults, WAPE exposure yielded no acute single pesticide nor cumulative exposure risk neither for median nor maximum residue levels (CH_AR_1&2 and A_AR_1&2). Same results were obtained when considering individual dietary exposures and median pesticide residue levels (CH_AR_3 and A_AR_3).

Acute risk was identified only in individual diets in worst case scenarios (CH_AR_4 and A_AR_4). In these scenarios, HQ_{acute} exceeded the unity for chlorpyrifos and lambda-cyhalothrin (Figure 6:3). Dietary exposure of children presented a risk related to chlorpyrifos concentrations in 7 diets and lambda-cyhalothrin in 4 diets (i.e. 16% of the studied population). Chlorpyrifos hazard (HQ>1) was found to be linked to the consumption of raw tomatoes directly on the field. For adults, dietary risk was identified in only one diet for chlorpyrifos as well as for lambda-cyhalothrin (i.e. 3% of the studied population).

The cumulative risk of organophosphates & carbamates and pyrethroids groups indicated a risk for children for respectively 9 (plus 1 value close to unity with 0.95) and 4 individual dietary exposures (Figure 6:3). For the same pesticides groups, the HI_{acute} indicated a risk in respectively 3 and 1 diets for adults. HI_{acute} was also close to the unity in 3 diets (0.97, 0.98 and 0.98) for the organophosphates & carbamate pesticides. Except for these 3 diets, all the population presented a $HI_{acute} < 0.85$. Chlorpyrifos alone accounted for at least 70% (up to 94%) of the cumulative risk of the organophosphates & carbamates group. Lambda-cyhalothrin accounted for ~99% of the HI_{acute} values of the pyrethroids group. Consumption of raw products was responsible of the observed risks for children and adults, in respectively 54% (n = 7) and 75% (n = 3) of the cases.
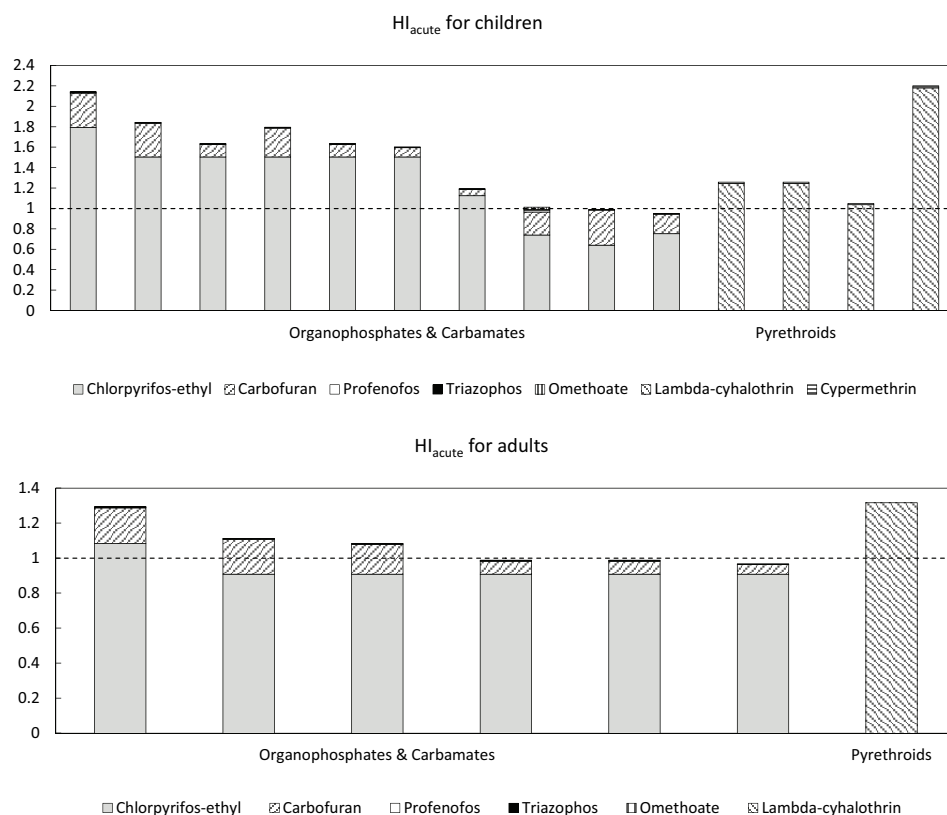
Figure 6:3 Acute hazard indexes exceeding/close to the unity calculated for children and adults based on individual diets and maximum pesticide residue levels (CH_AR_4 and A_AR_4)

6.3.3.2 Chronic risk

No chronic risk was observed when considering exposure from WAPE for children and adults (CH_CR_1 and A_CR_1). On the other hand, individual dietary intake exhibited a chronic risk for organophosphorus, organochlorine, and pyrethroids pesticides for children (CH_CR_2). Hazard quotients related to chlorpyrifos exposure exceeded the unity for 6 individual diets (i.e. 16% of the studied population). Lambda-cyhalothrin and dieldrin intake showed both a chronic risk in respectively 2 and 3 individual diets. Organophosphates and carbamates: (n = 6, plus one diet with $HI_{chronic}$=0.98), organochlorines (n = 3), and pyrethroids (n = 3) groups presented all chronic risks for cumulative exposure for children (Figure 6:4). Adults presented a chronic risk (A_CR_2) related only to dieldrin exposure in 3 diets (i.e. 4% of the studied population). Cumulative exposure did not show supplementary risk. The rest of the population presented a $HI_{chronic}$< 0.93.
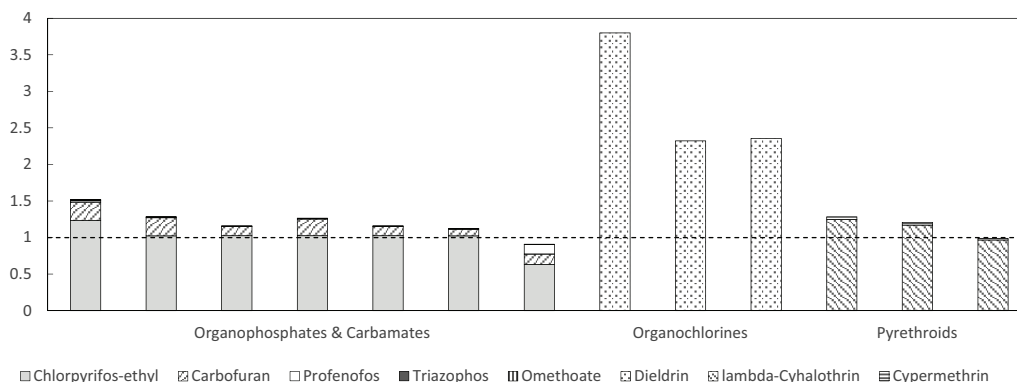
Figure 6:4 Chronic hazard indexes exceeding/close to the unity calculated for children based on individual diets and median pesticide residue levels (CH_CR_2).

6.4 Discussion

Carbamate, neonicotinoids, organochlorines, organophosphates, pyrethroids, triazines, and tetranortriterpenoid were detected. All the vegetable samples had at least one detectable pesticide residue. Every commodity presented an average of 3 pesticide residues except for sorrel which exhibited the higher contamination with an average of 6. Higher contamination of leafy vegetables was also observed in Ghanaian markets by Osei-Fosu et al. (2014).

In the present study, 36% of samples did not comply with MRLs. These findings underlined the lack of knowledge regarding Good Agricultural Practices (GAP) and pesticides use already observed in previous studies (Ouédraogo et al., 2011). Poor correlation between pesticides reported by gardeners during surveys and residues detected in samples illustrated this problematic highly linked with illiteracy and low level of education in rural areas. On the other hand, MRLs exceedance could result in prejudicial economic limitations. In Burkina Faso, the fruit and vegetable sector was retained as a leading sector in the government strategy for rural development. The growing demand of vegetables in the developed countries is associated with reinforced controls. Exports of horticultural products from developing nations have already been rejected by international markets because of residual levels of pesticides (Bempah et al., 2011). Moreover, as for some pesticides, isomers or other substances included in the definition of the residue for compliance with MRL were not analyzed; underestimation of MRLs exceedance might be expected.

24-HR surveys successfully provided consumption estimates of staple food items. Comparison with GEMS (Global Environment Monitoring System) Food Clusters proposed by WHO (2013) underlined the pertinence of local dietary surveys. As an example, the water consumption estimation of 0.4 g d^{-1} proposed for Burkina Faso (cluster G13) was surprisingly low. This value does not comply with field observations. Under the warm temperatures of the dry season, surveyed individuals consumed at least 3 times more than this prediction. GEMS vegetables/legumes consumption estimate (78.9 g d^{-1}) compares favorably with consumption estimation from this study, when only processed items are considered (average consumption: 80 g d^{-1}). However, GEMS estimate is less

relevant when raw products are included (average consumption: 220 g d^{-1}). Eating raw vegetables while working in the fields is a common practice in the study area (reported by ~38% of the respondents).

Food consumption estimations combined with pesticide residue levels allowed to derive dietary intake of target substances. Dietary risk was identified for organophosphates & carbamates, organochlorine, and pyrethroids groups. Risk for lambda-cyhalothrin was associated with higher consumption of sorrel. Exposure to dieldrin was induced by detection of this pesticide on eggplant (*Solanum melongena L*). Chlorpyrifos hazard was mainly linked to higher consumption of tomatoes.

Chlorpyrifos and lambda-cyhalothrin exposure exhibited an acute risk in single pesticide risk assessment (HQ>1) for both children and adults (CH_AR_4 & A_AR_4). Unsuitable use of pesticides can induce hazardous residue levels on food even after processing. Time before harvest, mixture concentration, and frequency of application recommendations were not respected and could vary greatly. Hazardous exposure of children to chlorpyrifos was linked to raw tomatoes consumption in 70% of the cases. Sorrel consumption was associated with hazardous exposure to lambda-cyhalothrin. Although hazards were associated with maximal concentrations, the fact that consumption of a single commodity exceeds the ARfD for a given pesticide suggests that acute intoxication is likely to occur. Thus, worst case scenario should not be underestimated.

Chronic risks were identified for dietary exposure to organophosphates, organochlorines, and pyrethroids. Long-term exposure covers average daily exposure over the entire lifetime. The detected risks are particularly of concerns as dieldrin and chlorpyrifos were recognized as endocrine disruptor chemicals (WHO/UNEP, 2012a) and dieldrin is also a probable human carcinogen (U.S. EPA, 1988b). To date, lambda-cyhalothrin was not classified as endocrine disruptor but endocrine-mediated mode of action could not be ruled out. It was also included in the list of candidates for substitution in Europe knowing that this substance was more toxic than those of the majority of the approved active substances within the group of insecticides (European Union, 2017). In the study area, the potential health burden also suggests that substitution must be undertaken.

Exposure to pesticide mixtures in cumulative risk assessment (HI) was associated with larger intake of pesticides with the same mode of action thus resulting in higher hazard for the consumer. Nevertheless, it is worth noting that only chlorpyrifos, lambda-cyhalothrin, and dieldrin presented a HQ close/exceeding the unity. Other pesticides were found in concentrations yielding smaller HQ values (lower pesticide concentrations detected or lower consumption of concerned commodities). Chlorpyrifos, lambda-cyhalothrin, and dieldrin do not share the same mode of action (MOA) thus, they are not considered in the same cumulative assessment group (CAG). Under these conditions, HIs which correspond to the sum of HQs from the same CAG will not yield a value significantly different from the HQs of these three pesticides. Nevertheless, for individual diets presenting HQs close to the unity, summing by similar MOA yielded HIs exceeding the threshold value of one. Joint use of several pesticide formulations alone or in combination for a single plot was reported by 50% of the gardeners in the study area. Multiresidue analysis was found to be a

robust tool in the present context as screening of a large list of target substances allowed to detect residues of pesticides not identified by investigators nor gardeners during field surveys. As afore-mentioned, lack of knowledge and illiteracy, but also poor labeling quality (i.e. written in foreign language, absence, etc.) and counterfeiting could have led to misinterpretations.

Acute risks were associated with maximum levels of pesticides and higher consumption of a given type of monitored food. In chronic risk assessment, only median pesticide residue levels were considered thus the difference also relied on the serving size. Every individual does not necessarily consume a given item each day and in similar proportions. For this reason, deterministic approach or average portions based on a single 24-HR might underestimate or overestimate individual dietary intake. To overcome this shortage, the assumption was made that between-person variation was representative of the propensity-to-consume a given item in the population. This assumption is supported by the fact that every respondent presented a similar socio-economic background, lived in the same area, and diet in rural areas is generally poor and monotonous (Savy et al., 2003). Calculated WAPE might be therefore closer to the usual dietary intake. In absence of extreme intake values, these average estimates yielded no acute nor chronic risk. Replicated 24-HR and food frequency questionnaire (FFQ) could be used in further studies to validate the estimation of propensity-to-consume items and refined the presented assessment. However, it is to be noted that relatively high standard variation of WAPE estimates, indicates a potentially large variation of the portion size (SI Table S10). These findings underline the pertinence of the deterministic approach that includes the extreme values.

The remark made for MRLs also applies to dietary risk assessment. As for some pesticides, isomers or other substances included in the definition of the residue for compliance with ADI/ARfD were not analyzed; underestimation of the risk might be expected. The list of target substances should be completed to improve the reliability of the risk assessment in further research.

The type of pesticide used was also of concerns. Over 16 pesticides detected, 7 were not authorized in gardening (Table 6:3) by the Sahelian Pesticide Committee (CSP) among which only one was authorized for cotton production (azadirachtin). Thus, 6 pesticides were not authorized in the CILSS (Permanent Interstates Committee for Drought Control in the Sahel) Member States with endosulfan and dieldrin being also banned at the international level. Burkina Faso has ratified the Stockholm convention, which ban the use and production of these persistent organic pollutants (entry into force March 2005). Production, selling and use of pesticides initially included in annex A of the Stockholm Convention (i.e. aldrin, chlordane, dieldrin, endrin, heptachlor, mirex, and toxaphene) are prohibited since 1996 in Burkina Faso. Though, national inventories on persistent organic pesticides conducted in 2001 and 2004 reported uses of wood protection products containing aldrin and dieldrin across the country (MECV, 2007). The prohibition of endosulfan is more recent as entered into force since October 2012 (Stockholm Convention on Persistent Organic Pollutants, 2017). Endosulfan was detected only in sorrel samples collected in 2016 which could suggest a recent use or its confinement in one area (Noungou Village sampled only in 2016). Pesticide formulations containing endosulfan such as *Rambo, Endocoton 500,* and Caïman *Rouge* have been identified during field surveys and must be removed from the market as soon as possible.

It is also noteworthy that contamination might also originate from other activities (ex: cotton or cereal production). For example, because of the associated costs, the use of atrazine in small-scale gardening is not common. None of the respondent reported using herbicides. The presence of atrazine on vegetables might be a consequence of the contamination of the lake water by other activities located upstream (Lehmann et al., 2017a, Chapter 5). Moreover, atrazine was detected on sorrel, which is a leafy vegetable. Application of herbicide directly on this culture would result in the death of the plant, which suggests that it was not intentionally applied. The findings of this study underline the lack of incentive to comply with the law and that monitoring on regular basis would help policy, health, and environmental impact assessment. Efforts must be continued and include larger number of samples, substances, and commodities analyzed to refine the risk evaluation.

Most of the risks came from the consumption of raw products (larger consumption of a product in a single portion). Processing factor of 1 was assigned to this practice as most of the vegetables were peaked on the plant and directly consumed. Risk assessment estimates are supportive that applying a processing factor of 0.6 would considerably reduce the risk for organophosphates and pyrethroids. Studies have shown that this reduction could be achieved by simply washing vegetables with water (Liang et al. 2014). A similar conclusion was made when changing processing factor of the other processed food items (i.e. fixed value of 0.6) to 1. The risks detected under these conditions suggested that cleaning vegetables with water before eating them considerably reduced health hazard. Further refinements could include the definition of specific processing factors based on local processes and pesticides used.

Except for atrazine and carbofuran, dietary exposure from vegetables was higher than water consumption. It is also noteworthy that the present study focused only on pesticide exposure resulting from consumption of the major vegetables cultivated in the study area. Local diets also include other cultivated commodities subject to pesticide applications (i.e. maize, red pepper, coffee, cowpeas, onion, carrots, etc.) that can increase the daily intake of chemicals (Mekonen et al., 2014). Veterinary treatment of cattle and exposure of fishes in contaminated environment have also been studied in West Africa and suggest possible dietary risks (Adakal et al., 2013; Lawrence et al., 2015). Finally, 91% of the respondents were gardeners, therefore occupational exposure will also add to the dietary intake yielding a larger health hazard.

6.5 Conclusion

The developed multiresidue analysis using QuEChERS extraction method allowed to successfully quantify 31 target substances in selected vegetables. Residues from 16 different active ingredients were found in food and water samples. MRLs and ADI exceedance are in accordance with previous studies conducted in West Africa (Mawussi et al., 2009). Nevertheless, comprehensive monitoring programs are still lacking and to our knowledge, this study constitutes a premiere in Burkina Faso. In rural areas of this country, diet was found to be generally poor and monotonous (Savy et al., 2003). Based on this assumption, the present study could be seen as a preliminary assessment of dietary exposure to pesticide trough vegetables in rural areas of Burkina Faso. In the studied

population, the worst-case scenarios of dietary cumulative exposure of children and adults presented an acute risk in respectively 19% (n = 13) and 6% (n = 4) of the cases (CH_AR_4 & A_AR_4). These estimates fell at 17% (n = 12) and 4% (n = 3) when considering chronic risk (CH_CR_2 & A_CR_2). Precautions must be taken, to reduce dietary exposure especially for children. These include regulations and recommendations enforcement at every scale, from the national policy application to the respect of the good agricultural practices on the field. More incentive on law application and training of the operators are prerequisites to improve consumer safety.

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Chapter 7 Development of a novel approach for pesticide analysis in human hair

Published work:

The present chapter is based on the following paper currently under revision for publication:

Lehmann, E., Oltramare, C., de Alencastro, L.F., 2017. Development of a modified QuEChERS method for multi-class pesticide analysis in human hair by GC-MS and UPLC-MS/MS. Anal. Chim. Acta. doi:10.1016/j.aca.2017.11.009.

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Supplementary material:

Appendix E

Supplementary information are divided in three sections S1-S3 presenting the Table S1-S4.

Doctoral Candidate's contribution:

Main investigator and author

7.1   Introduction

Human hair is extensively used in forensic and clinical sciences to detect drug exposure. Over the last decades, increasing interest is being observed in hair analysis for biomonitoring of human exposure to environmental contaminants. One of the principal shortages of currently used matrix is that blood, urine, saliva, breath, and sweat provide information only of recent exposure, maximum of several days (Tsatsakis et al., 2010). For this reason hair has become the most used "alternative matrix" for human biomonitoring (Esteban and Castaño, 2009). Chemicals tend to be stable in hair because no metabolism nor excretion occurs (Aleksa et al., 2012). Unlike other biological matrices, hair can account for long-term effects of environmental contaminants and provide an extended window of detection allowing retrospective analysis (Appenzeller and Tsatsakis, 2012). As a safe and non-invasive matrix, human hair presents numerous advantages, such as easy collection, low sampling cost, easy transport, and storage and require no medical staff (Salquèbre et al., 2012). The ongoing debate on the use of hair for biomonitoring chemical exposure concerns the differentiation between endogenous and external accumulation of substances. It is assumed that the internal dose in hair is representative of the systemic exposure and is mainly incorporated from blood. External contamination can occur through multiple pathways but is expected to remain on the surface of the hair scales (i.e. cuticle). Depending on chemical properties, sweat, and sebum could transfer chemical accumulated in skin compartments (Appenzeller and Tsatsakis, 2012). External contamination could also occur through particle deposition or direct exposure during pesticide application (spray drift and splashing). To date, no standardized procedure exists to fully differentiate between endogenous and external accumulation in hair (Appenzeller and Tsatsakis, 2012). Previously developed external decontamination procedures seemed to affect internally incorporated amount to some extent (Altshul et al., 2004; Hubbard, 2001). However, the necessity to fully differentiate between internal and external exposure depends on the research objectives and field of application. In forensic science, the differentiation between internal and external contamination is of interest in order to prevent false positives caused by environmental contamination not representative of the subject intake (Kintz, 2007). On the other hand, in environmental sciences some authors focused on the whole contamination (i.e. endogenous and external contamination). They considered that external deposition also represents chemicals to which the subjects have been exposed (Ostrea et al., 2009). Under these conditions, the decontamination procedure is performed in a homogenization perspective to remove the "easily removable chemicals" (ERC) that are likely to be affected by subjects' self-washing and induce significant variability in measured chemical concentrations (depending on the time elapsed between hair sampling and subjects' last washing) (Appenzeller and Tsatsakis, 2012).

Pesticides were proved to cause multiple adverse health effects ranging from moderate toxicity to severe neurotoxicity, endocrine disruption, cancers, etc. increasing the need to develop suitable approach for biomonitoring in human matrices. Diversity of target chemicals, small amounts of hair generally collected (limited to a few tens to a few hundred milligrams) and low levels of concentration of xenobiotics in hair require the development of highly sensitive analytical methods

covering a large range of analytes with different chemical properties (Salquèbre et al., 2012). Various extraction methods have been proposed in the literature including hydrolysis with chloric or sulfuric acid, soxhlet extraction, liquid-liquid extraction (LLE), extraction with organic solvent directly from the solid matrix, and more recently solid-phase microextraction (SPME) (Covaci et al., 2008; Duca et al., 2014b; Neuber et al., 1999; Salquèbre et al., 2012; Zhang et al., 2007). For multi-class analysis, some of the previously reported procedures included different protocols depending on the physicochemical properties of the target analytes (Dulaurent et al., 2008; Tsatsakis et al., 2008) or required substances derivatization (Tsatsakis et al., 2010). Hair is composed mainly of fibrous proteins (keratin), melanin, and lipids (relatively high percentage: 3.5% - 4%) (Balíková, 2005; Covaci et al., 2002). Purification might be needed to remove co-eluted matrix material and reduce analytical background noise. To date, purification techniques usually included elution of sample extracts with hexane and dichloromethane on chromatographic columns packed with acidified silica gel, deactivated alumina, or florisil (Covaci and Schepens, 2001; Gill et al., 2004; Wielgomas et al., 2012). Recently, an attempt was made to replace these labor-intensive cleanup steps by LLE or purification on solid-phase extraction (SPE) cartridges (Duca et al., 2014b).

The aim of this research was to assess the suitability of a modified Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method for the determination of multi-class pesticides in human hair. This method was originally developed for pesticide analysis in food matrices. Nevertheless, its versatility has led to the development of modified methods applicable outside of its traditional domain of applications. Lesueur et al. (Lesueur et al., 2008) were the first to analyze pesticides in soils with this method, Khan et al. (Khan et al., 2014) studied pesticide concentrations in tobacco, etc. It has proven to achieve good recovery and sensitivity in multiresidue analysis even when accounting for target analytes with a large range of different physicochemical properties (Nguyen et al., 2010). The original procedure can be adapted to the target analytes and matrix properties by varying buffer conditions (e.g. acid buffer), sample hydration, extraction solvent, dSPE adsorbent to remove matrix components and varying the sample/volume ratio in the different steps of the method (Vera et al., 2013). Further improvements can also be obtained by adaptation of extraction time and homogenization (e.g. shaking by hand, sonication, etc.).

This simple, cost effective, and versatile method appeared to be a suitable alternative to achieve multiresidue pesticide analysis in human hair. Contrary to some of the previously reported methods (Dulaurent et al., 2008; Tsatsakis et al., 2008), multi-class extraction is achieved in a single step by solvent extraction and salting out liquid–liquid partitioning from water with $MgSO_4$ (AOAC, 2007). The dispersive solid-phase extraction (dSPE) cleanup is easy to operate and faster compared to labor-intensive purification with chromatographic columns. The development of the protocol included the setting up of an adapted extraction method (sample incubation, sonication, and acidification) and optimization of the cleanup procedure (sorbent type, solvents used, and filtration). The list of analytes investigated comprised 37 pesticides from different chemical classes including avermectin, carbamate, chloroacetamide, neonicotinoid, organochlorine, organophosphate, pyrethroid, tetranortriterpenoid, triazine, and urea.

Finally, applicability of the method for biomonitoring of pesticide exposure was tested on field samples collected from volunteers living in a vegetable-producing area in Burkina Faso.

7.2 Material and method

7.2.1 Chemicals, reagents, and standard solutions

Standards of analytes, -C13 labeled and deuterated compounds were purchased from Sigma-Aldrich (Switzerland), Dr. Ehrenstorfer (Germany), and Toronto Research Chemicals (Canada). Individual dilution of each target analyte and deuterated compound were prepared in appropriate solvent prior the preparation of the stock solution containing the mixture of all the target analytes (Supplementary Information (SI) Table S1 and Table S2). Standard stock solutions were stored at −20 °C.

Methanol (MeOH) HPLC grade was acquired from Carlo Erba Reagents (France), isooctane from Acros Ogranics (Belgium), formic acid from Sigma-Aldrich (Switzerland), and acetonitrile (ACN) from Biosolve Chimie SARL (France). Sodium dodecyl sulfate (SDS), anhydrous magnesium sulfate ($MgSO_4$), and sodium acetate (NaOAc) were purchased from Sigma-Aldrich (Switzerland). For dispersive solid-phase extraction, 12 mL centrifuge tubes containing pre-determined amounts of SPE sorbents Supel™QuE Z-Sep+, Supel™QuE Z-Sep/C18, and Supel™QuE PSA were obtained from Sigma-Aldrich (Switzerland). Whatman Mini-UniPrep G2 syringeless 0.45 µm filter vials were purchased from GE Healthcare Life Science (Switzerland). Syringe 0.22 µm filters (BGB) were purchased from WWR (Switzerland).

7.2.2 Hair treatment and pesticide extraction

7.2.2.1 Hair collection

Large amounts of hair specimens used for method development were collected from clean waste containers provided by hairdressers from Switzerland and Burkina Faso (~500 g in total). Pooled samples differentiated only by country of origin were considered representative of specimens' diversity and suitable for method selectivity testing. Black color was the dominant pigmentation. As no information on origin was obtained and being waste material, no particular authorization was requested for the use of these pooled samples.

Field samples were collected from ten volunteers (6 females and 4 males) living in the village of Nabdogo located on the shore of Loumbila Lake, 20 kilometers from the capital of Burkina Faso, Ouagadougou. Market gardening constituted the major occupational activity in this area. Pesticides are applied to improve yield and protect vegetables from pests and diseases. Lack of knowledge regarding the good agricultural practices increases the risk of pesticide exposures in these rural areas (Ouédraogo et al., 2011). Among the volunteers, 5 were occupationally exposed to pesticides as producing vegetables in local market gardens. The rest of the study population was not occupationally exposed and composed of one teacher, one fisherman, and three merchants. Volunteers' age ranged from 25 to 54 years. Every participant was asked to answer a questionnaire

about is personal capillary hygiene practices (washing and cutting frequency, cosmetic products used, etc.) and use of pesticides (type, conditions of applications, personal protective equipment, etc.). About 300 mg of hairs (length ~1 cm) were collected preferentially from the posterior vertex region of the scalp, as close as possible to the skin, using an individual pair of scissors for each participant. Sample collection was performed by local medical staff. Dominant color of collected material was dark black. Samples were collected in aluminum foil, placed in paper envelopes, and conserved at room temperature in individual zipped plastic bags. The study was approved by the National Ethics Committee of Burkina Faso. All participants were fully informed about the procedure and objectives of the study (in their local language when needed) and provided written consent to take part in the study.

7.2.2.2 Hair decontamination

Similarly to Ostrea et al. (Ostrea et al., 2009), it was decided to focus on the whole hair exposure (i.e. endogenous and exogenous) considering that externally incorporated pesticides are also part of the individual exposure history. Therefore, decontamination was performed in a homogenization perspective to clear samples from externally deposited particle material (e.g. dust, etc.) and "easily removable chemicals" (ERC) present on hair surface. Soft external decontamination was achieved using an aqueous solution that mimicked shampoo to prevent variability induced by subjects' self-washing. Hair samples were washed for 4 min in Milli-Q water with 0.1% sodium dodecyl sulfate (SDS) under agitation (130 rpm). SDS solution was discarded after centrifugation at 3000 rpm for 1 min. Samples were subsequently rinsed twice with Milli-Q water using the same procedure to ensure complete SDS removal. For studies focusing more specifically on internal contamination of hair, hair decontamination could be further adapted using a more selective procedure (Duca et al., 2014a).

7.2.2.3 Pesticide extraction

Pesticide residues were extracted using a modified AOAC 2007.01 QuEChERS extraction method (AOAC, 2007). Decontaminated hairs were cut in 1 - 3 mm fragments. Two hundred milligrams of homogenized sample were added to a 10 mL polypropylene (PP) tube. Artificial contamination was performed by addition of 0.2 mL of the appropriate dilution of standard solutions of target analytes and labeled surrogates (isotopic dilution) directly onto the samples (SI Table S1-S2). Solvent was allowed to evaporate (~6 hours) prior to addition of 5 mL of ACN : water (1:1, v/v) and overnight incubation at 40 °C under agitation (130 rpm). Extraction was subsequently completed by 5 min sonication. Then 1 g $MgSO_4$ and 0.25 g NaAc were added and the mixture was shaken vigorously for 1 min, vortexed for 1 min, and centrifuged for 10 min at 4000 rpm. As the reaction with $MgSO_4$ is exothermic, the tubes were cooled in water at room temperature.

7.2.2.4 Cleanup and separation

Two milliliters of the supernatant were subsequently transferred for cleanup in a 12 mL dSPE tube packed with 500 mg of Supel™QuE Z-Sep+ sorbent, vortexed for 1 min, and centrifuged 5 min at 4000 rpm. The cleaned-up extract was then split for differential analysis of GC and UPLC amenable substances.

Composition of GC-MS fraction

0.7 mL of the cleanup extract was filtered through a 0.22 µm syringe filter. The 0.5 mL recovered was evaporated to dryness at 40 °C under a gentle stream of nitrogen before being reconstituted in 0.2 mL of isooctane for GC-MS analysis.

UPLC-MS/MS fraction

An aliquot of 0.5 mL of the purified ACN fraction was transferred in a 12 mL glass tube. dSPE sorbent was then rinsed twice with 1 mL MeOH (vortexed 1 min and centrifuged 5 min at 4000 rpm). After each rinse, 1 mL of the supernatant was transferred to the 12 mL glass tube. Combined fractions were subsequently evaporated to dryness, reconstituted in 0.4 mL of the mixture MeOH : water (5:95, v/v) with 0.1% formic acid and filtered with syringeless filter vial (0.45 µm) prior to UPLC-MS/MS analysis.

The developed protocol scheme is presented in box format in Figure 7:1.
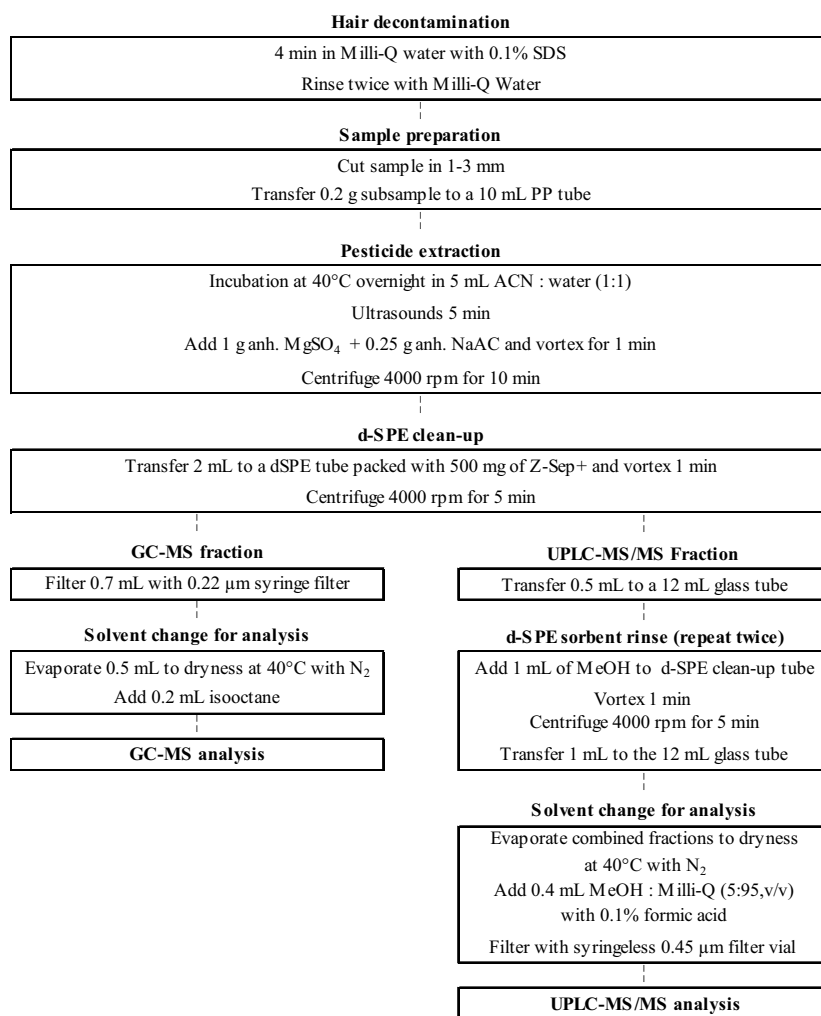
Figure 7:1 Final QuEChERS extraction procedure

7.2.3 Method development and optimization

7.2.3.1 Optimization of extraction parameters

Most of the existing pesticide extraction procedures in hair include an incubation step prior to extraction. The official QuECHERS AOAC 2007.01 (AOAC, 2007) method recommends acidification of acetonitrile with 1% acetic acid (HOAc). The effects of incubation and sample acidification on the detected levels of analytes were evaluated on triplicate blank hair samples spiked at ~2µg g^{-1} (i.e. 6-fold dilution of standard stock solution presented in SI Table S1). After artificial contamination, solvent was allowed to evaporate (~6 hours) prior to addition of 5 mL of ACN : water (1:1, v/v).

To assess the effect of incubation, 3 samples were extracted using the procedure presented in section 7.2.2.3 directly after ACN : water addition and 3 others were incubated overnight at 40°C under agitation (130 rpm) prior to extraction. Acidification effect was tested on triplicate spiked samples without incubation (n = 3), with addition in acetonitrile prior to incubation (n = 3), and with addition after incubation (n = 3).

7.2.3.2 Selection of dSPE cleanup sorbent

QuEChERS procedure considerably simplified and reduced sample treatment time. Nevertheless, aliquots made after extraction and cleanup imposed a preconcentration step prior to chromatographic analysis to achieve low limits of detection and quantification. Purification was therefore crucial to ensure sufficient reduction of the matrix co-eluted material. In its initial version, QuEChERS procedure included dSPE purification with primary secondary amine (PSA) sorbent (Anastassiades et al., 2003). Since then, PSA has probably been the most commonly used dSPE sorbent. To enlarge the scope of application of the method, researches have been directed toward the development of cleanup sorbents. The difference between commercial products lies principally between pigment, lipid, or fat removal. In the present work, 3 different cleanup sorbents were tested: Supel™ QuE PSA (magnesium sulfate: 1200 mg and Supelclean PSA: 400 mg), Supel™ QuE Z-Sep/C18 (Discovery® DSC-18: 300 mg and Z-Sep: 120 mg) and Supel™ QuE Z-Sep+ (Z-Sep+: 500 mg). Recovery assays were performed on triplicate blank hair samples spiked at ~2µg g^{-1} (i.e. 6-fold dilution of standard stock solution presented in SI Table S1).

7.2.3.3 Additional rinsing of the cleanup sorbent

Aliquots imposed a large reduction of the mass of analytes present in the extract prior to injection. Improvement of the mass of analytes recovered by additional rinsing of the cleanup sorbent was assessed for UPLC amenable substances. Spiked blank samples (n = 9) were extracted with the procedure presented in section 7.2.2.3. After separation of the organic phase by salting-out effect, 2 mL of the supernatant were transferred, vortexed, and centrifuged in a 12 mL PP tube packed with 500 mg of Supel™ QuE Z-Sep+. 1.2 mL of the ACN fraction were filtered through a 0.22 µm syringe filter and 0.5 mL was kept for analysis. Rinsing was performed by addition of 1 mL of ACN (n = 3) or MeOH (n = 3) in the dSPE tubes. After vortex and centrifugation, 1 mL of the supernatant was added to the previously collected 0.5 mL ACN fraction. Rinsing with

MeOH was performed twice. The combined fractions were finally evaporated to dryness and reconstituted in 0.4 mL of the mixture MeOH : water (5:95, v/v) with 0.1% formic acid and filtered with Whatman syringeless 0.45 µm filter vials prior to UPLC-MS/MS analysis. The effect of additional rinsing of the dSPE sorbent is presented as the percentage of increase of the mass of analytes in the injected fraction.

7.2.4 Instrumental conditions

7.2.4.1 GC-MS analysis

The gas chromatography analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph coupled with a Thermo Scientific ISQ Single Quadrupole MS (Waltham, MA, USA) operated in Single Ion Monitoring (SIM). The injection volume and composition were respectively 2 µL and isooctane. The injector was set to PTV splitless mode with an initial temperature of 75 °C and a maximal temperature of 300 °C at the end of the injection transfer phase (rate: 10 °C sec^{-1} in 2.5 min). Helium was used as the carrier gas (1.2 mL min^{-1}) and analytes were separated using a Phenomenex Zebron capillary column (ZB-5 MS plus, 20 m, 0.18 mm, 0.18 µm). The oven temperature program started at 80 °C for 0.5 min, followed by two successive linear increases of 50 °C min^{-1} to 150 °C and 5 °C min^{-1} to 300 °C; final temperature was held for 8.1 min. The ion source temperature was set to 250 °C and the ionization mode to electron ionization (EI). MS/SIM parameters of target pesticides analyzed in GC-MS are presented in Table 7:1.

Table 7:1 MS/SIM parameters for GC amenable molecule determination

Compound name	RT[a]	Target[b]	Q1[c]	Q2[d]
Pentachlorobenzene	4.25	248	248	252
Hexachlorobenzene	6.16	284	286	282
Diazinon	7.38	137	179	152
Acetochlor-d11	8.45	173.2	157.2	
Acetochlor	8.6	59	146	162
Chlorpyrifos-methyl	8.6	125	286	288
Chlorpyrifos-d10	9.94	324	200	
Chlorpyrifos-ethyl	10.11	197	314	316
Heptachlor epoxide b	11.28	353	355	351
Heptachlor epoxide a	11.41	353	355	351
Oxychlordane	11.82	387	391	389
gamma-trans-Chlordane	12.06	373	375	377
alpha-Endosulfan-d4	12.36	246	244	
alpha-cis-Chlordane	12.48	375	373	377
trans-Nonachlor	12.58	407	409	411
Profenofos	13.32	208	206	339
Dieldrin	13.34	263	261	265
p,p'-DDE	13.39	318	316	320
o,p'-DDT	14.8	235	237	165
p,p'-DDD	14.82	235	237	165
p,p'-DDT-C13	16.07	247.1	249.1	
p,p'-DDT	16.11	235	237	165
Methoxychlor	18.2	227	228	152
lambda-Cyhalothrin	20.11	181	197	208
trans-Cypermethrin-d6	23.33	169.1	171.1	
alpha-Cypermethrin	23.51	163	165	169
beta-Cypermethrin	23.61	163	165	169
Deltamethrin-d6	26.12	259	261	
Deltamethrin	26.28	181	253	255

[a] RT: retention time in minute; [b] Target: target ion; [c] Q1: Qualifier ion 1; [d] Q2: Qualifier ion 2

7.2.4.2 UPLC-MS/MS analysis

The UPLC system consisted of a UPLC Waters Acquity coupled to a Waters Acquity Xevo TQ-S tandem quadrupole MS. Separations were carried out on a Waters Acquity UPLC HSS T3 column (2.1×100 mm, 1.8 μ m) with oven temperature set at 30 °C. The injection volume was set to 30 µL. The mobile phase was composed of MeOH : water (5:95, v/v) with 0.1% formic acid (eluent A) and MeOH : water (95:5, v/v) with 0.1% formic acid (eluent B) at a flow rate of 0.4 mL min^{-1}. The chromatographic separation program started at 5% eluent B then increased linearly to 95% in 10 min; composition that was held for 6 min before returning to the initial conditions in 1 min and followed by an equilibration time of 3 min. The instrument was operated using an electrospray source in positive mode. Nitrogen, used as desolvation gas (600 °C, 1000 L h^{-1}), was provided by a nitrogen generator (Peak, MNOLA). The capillary voltage was 3 kV and the temperature of the ion source was fixed at 150 °C. Argon was used as collision gas at a pressure of 3.5×10^{-3} mbar. Compounds were detected in the multiple reaction monitoring (MRM) mode using two transitions per compound, except for deuterated compounds for which only one transition was used. The most intense daughter ion was used for the quantification of the response of each compound, and the other ones for confirmation purpose (Table 7:2).

Table 7:2 MS/MS parameters for UPLC amenable pesticide determination

Pesticides	RT[a] (min)	MRM Transitions 1 m/z	Ce 1 [b] (V)	MRM Transitions 2 m/z	Ce 2 [b] (V)
Omethoate	2.18	214.1 > 183.1	11	214.1 > 125.1	22
Deisopropylatrazine (DIA)	3.87	174 > 96	18	174 > 78.9	18
Imidacloprid-*d4*	4.16	259.9 > 213	18	259.9>179	18
Imidacloprid	4.29	256.1 > 209.1	16	256.1 > 175.1	19
Acetamiprid-*d3*	4.71	225.9 > 125.9	22	-	
Acetamiprid	4.74	223 > 126	25	223 > 56	15
DEA-*d6*	5.03	193.93 > 146.9	18	-	
Desethylatrazine (DEA)	5.12	188 > 146	16	188 > 78.9	26
Thiram	6.29	240.9 > 119.9	16	240.9 > 87.9	10
Carbofuran	6.49	222.11 > 165.1	16	222.11 > 123	21
Azadirachtin	7.34	743.3 > 725.4	28	743.3 > 625.3	38
Atrazine-*d5*	7.36	221.2 > 179.1	18	-	
Atrazine	7.43	216.1 > 174	18	216.1 > 96.1	23
Diuron-*d6*	7.64	239.2 > 78.04	20	-	
Diuron	7.87	233.1 > 160	21	233.1 > 188	32
Linuron-*d6*	8.18	256.86 > 161.95	20	-	
Linuron	8.21	249.1 > 182	16	249.1 > 160	18
Triazophos	8.76	314.1 > 161.9	18	314.1 > 118.9	35
Profenofos	10.23	372.9 > 302.6	20	372.9 > 127.9	40
Emamectin benzoate	10.34	886.6 > 158	35	886.6 > 126	38

[a] Retention time in minute; [b] Collision energy

7.3 Results

7.3.1 Incubation and acidification

Incubation of hair in aqueous solvents induces swelling. Although it is to a lesser extent compared to pure water, hair swells in contact with ACN : water (1:1, v/v) (Valko and Barnett, 1952). Swelling of hair fibers increases penetration of certain organic molecules into its structure and therefore influences contact of solvent with internally bound molecules (Velasco et al., 2009). This phenomenon is particularly of concerns for the extraction of biologically incorporated molecules lying in the whole hair structure. Only recovery of azadirachtin appeared to be negatively influenced by the incubation to a significant extent (-20%). Recovery rate was significantly increased with incubation for atrazine (+19%), chlorpyrifos-ethyl (+14%), chlorpyrifos-methyl (+17%), lambda-cyhalothrin (+26%), alpha-cypermethrin (+63%), beta-cypermethrin (+49%), deltamethrin (+89%), diazinon (+21%), hexachlorobenzene (+12%), methoxychlor (+24%), pentachlorobenzene (+12%), profenofos (+25%), and triazophos (+13%). For the other target analytes, incubation had no significant effect on recovered levels ($< \pm 10\%$).

Absence of acidification (results not presented) appeared to be the most suitable compromise and acidification step was not performed in further experiments.

7.3.2 Optimization of dSPE purification

Percentage of target analytes recovered were evaluated for the 3 different cleanup sorbents tested (Figure 7:2 and in SI Table S3.). None of these sorbent allowed recovering thiram from spiked samples. Cleanup using Supel$^{\text{TM}}$ QuE Z-Sep/C18 allowed to recover the largest number of target analytes, with 31 pesticides presenting recoveries in the range of 40% - 150%. Emamectin benzoate (8%), hexachlorobenzene (32%) and pentachlorobenzene (25%) presented the lowest recovery rates and matrix enhancement was observed for deltamethrin (>150%). Supel$^{\text{TM}}$ QuE Z-Sep+ also presented similar results for these analytes but in addition, omethoate (38%), profenofos (16%), and azadirachtin (39%) presented also low recovery rates. For the other analytes, overall recoveries were better using Supel$^{\text{TM}}$ QuE Z-Sep+ compared to Supel$^{\text{TM}}$ QuE Z-Sep/C18. With Supel$^{\text{TM}}$ QuE Z-Sep+, 22 analytes presented recoveries in the range 70% - 150% against 14 with Supel$^{\text{TM}}$ QuE Z-Sep/C18 (Figure 7:2).

Supel$^{\text{TM}}$ QuE PSA was the only sorbent allowing acceptable recovery of emamectin benzoate (49%). The lowest recovery was obtained for azadirachtin (34%) with this sorbent. The overall extraction recovery rates were found to be higher than the other sorbents for the 28 compounds presenting recoveries in the range of 40% - 150%. On the other hand, low recoveries and large deviation between replicates (>25%) were observed for pyrethroids. Lambda-cyhalothrin, alpha-cypermethrin, beta-cypermethrin, and deltamethrin did not meet validation criteria (recovery rate in the range of 40 - 150% and variability <25%). At the same time, matrix effects were also identified with enhanced instrumental responses observed for acetochlor and diazinon (>150%).
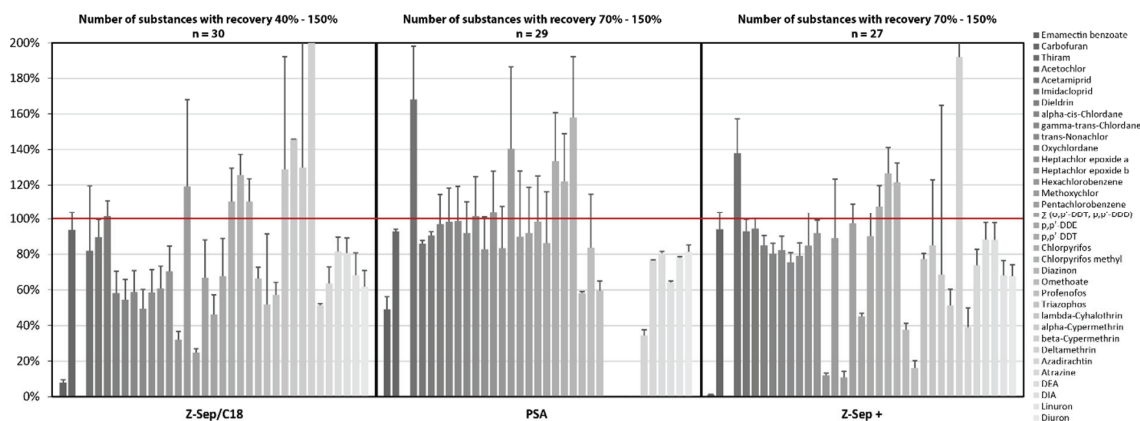
Figure 7:2 Evaluation of analyte recoveries for different dSPE sorbents (main bars correspond to the average recovery rates and error bars to the standard deviation)

The impact of the amount of cleanup phase on analyte recoveries was also assessed. Triplicate spiked samples were extracted and purified with only 200 mg of SupelTM QuE PSA (n = 3) or SupelTM QuE Z-Sep+ (n = 3) sorbents. With both sorbents, increase in overall recovery rates was also accompanied by increased matrix effects (SI Table S3). Azadirachtin was the only substance that was additionally recovered (recovery >40%), acetochlor, methoxychlor, lambda-cyhalothrin, alpha-cypermethrin, beta-cypermethrin, and deltamethrin were affected by the enhancement of instrumental response (recovery rate >150%).

It is noteworthy that purification was found to have a substantial impact on instrumental response sensitivity. In GC-MS, matrix co-eluted material led to the activation of the injector's liner resulting in rapid decrease of response sensitivity. After few sample injections (< 10), limit of detection increased considerably for certain analytes that could not even be detected in standard solutions of the calibration curves. DDT, lambda-cyhalothrin, cypermethrin, and deltamethrin were the most affected by this phenomenon. Identification of the reasons for injector's liner activation are not straightforward. Human hair is composed of water, lipids, proteins, trace elements, and pigments (Robbins, 2012). Even-though extracts were limpid, soluble co-eluted material such as fat could have influenced instrumental sensitivity. Therefore, Z-Sep+ was retained in the final procedure as being the most suitable sorbent to remove excess of lipids and pigments (manufacturer's specifications) and sample extract was additionally filtered after dSPE purification (0.22 µm syringe filter). This choice was made to the detriment of some UPLC amenable analytes (i.e. emamectin benzoate, omethoate, profenofos, and azadirachtin) that did not meet validation parameters with this sorbent (recovery in the range 40% - 150% and variability < 25%). However, it ensured a better quantification of pyrethroids (i.e. lambda-cyhalothrin, alpha-cypermethrin, beta-cypermethrin, and deltamethrin) commonly used in the study area (vegetable-producing area in Burkina Faso).

The effect of the additional rinsing of the dSPE sorbent (Z-Sep +) is presented as the percentage of increase of the mass of analytes in the injected fraction (Figure 7:3). Results were obtained by

comparison of the average mass of analytes recovered in the final extract (i.e. after dSPE cleanup) with no rinse and after one/two rinses with ACN/MeOH. Only traces of xenobiotics are generally found in hair increasing the need for low levels of detection. Mass of substances analyzed can be considerably reduced by the aliquots in the QuEChERS procedure. Rinsing of the dSPE sorbent was found to induce a significant increase in the mass of analytes recovered and therefore methanol rinse was implemented in the final cleanup procedure presented in section 7.2.2.4.
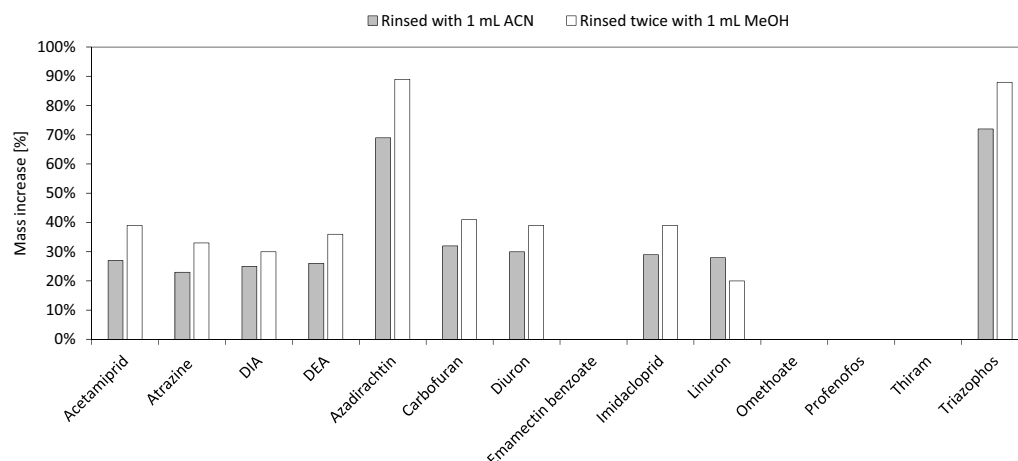
Figure 7:3 Percentage of increase of the mass of analytes in the injected fraction in UPLC-MS/MS after additional rinsing of Z-Sep+ sorbent with 1 mL ACN or 2 mL MeOH

7.3.3 Extraction recovery and limits of quantification and detection

Recovery assay was conducted to evaluate the efficiency of the analytical procedure. Decontaminated blank hair samples were spiked in triplicates at three different concentration levels ($\sim$ 50, 250, and 500 pg mg^{-1}). Isotopic dilution was performed with addition of labeled internal standard solution prior to injection. Only substances presenting recoveries in the range of 40% to 150% with variability (% relative standard deviation (RSD)) lower than 25% were finally retained.

As presented in section 7.3.2, cleanup with Z-Sep+ induced poor recovery (<40%) and/or high variability (>25%) of pentachlorobenzene, hexachlorobenzene, azadirachtin, emamectin benzoate, omethoate, profenofos (not detected), and thiram (not detected). In addition, at low concentration levels, diuron and triazophos presented poor recoveries in the final procedure. Validation criteria were therefore not met for these substances that were not retained in the final protocol. The rest of the analytes (i.e. 28) presented recovery rates in the range of 40 - 132% with relative standard deviation under 25% (Table 7:3).

The limit of detection (LOD) and limit of quantification (LOQ) for selected target analytes were respectively defined as the analyte concentration that produced a peak with a signal-to-noise ratio of 3 and 10. The LOD of the method for each analyte was evaluated from the chromatograms of samples spiked at 7 levels (~2, 5, 20, 40, 50, 250, and 500 pg mg^{-1}) and by measuring the coincident instrumental response of standard pesticide solutions and procedural blanks or negative samples.

LOQ definition also took into account results from recovery assays. Validated levels based on aforementioned criteria were used to confirm LOQ estimated from chromatograms.

The LOD values ranged from 0.18 to 86.6 pg mg^{-1} and the LOQ values from 0.6 to 288.5 pg mg^{-1} (Table 7:3). The differences observed in instrumental sensitivity were linked to the large varieties of the physicochemical proprieties of the target analytes. The use of a more sensitive mass-spectrometric system (i.e. MS/MS) resulted in globally lower LOD and LOQ for UPLC amenable substances. Pyrethroid pesticides cypermethrin and deltamethrin presented the highest LOD and LOQ values. With retained apparatus configurations, these substances presented the highest retention times and were particularly affected by instrumental conditions. Longer exposure to high temperatures might have played a role but it was mainly injector's liner activation (induced by matrix residues) that led to a drastic loss of instrumental sensitivity for these substances. For these reasons, higher detection and quantification limits were retained.

Due to the large diversity of chemical and physical properties of the target analytes, spiked concentration levels were adapted to molecules' sensitivity. Therefore, tested levels may differ from the abovementioned values for few molecules. Detailed levels of spiked concentrations for LOD, LOQ, and recovery assays are provided in SI Table S4.

Recovery rates and LOD of the proposed method were compared with values reported in the literature for pesticide residue analysis in human hair (Table 7:4). GC amenable molecules have been more studied than UPLC amenable compounds. LOD obtained for chlordane isomers, chlorpyrifos-ethyl, cypermethrin, diazinon, and DDT (with its metabolites) were lower or in the lower range of levels encountered in other studies. For other substances, higher LOD were retained in the present work. Recoveries of the GC amenable molecules were in the range of previously reported values ($\pm$ 10%) except for acetochlor, chlordane isomers, cypermethrin, deltamethrin, heptachlor epoxide isomers, and p,p'-DDE, which presented lower recoveries. Other methods already used acetonitrile to extract similar substances (Hardy et al., 2015; Salquèbre et al., 2012). Lower recoveries and higher LOD might be due to the use of a less sensitive apparatus (GC-MS) and to the inherent characteristics of the QuEChERS procedure (aliquots and retention in cleanup sorbent). Only few studies focused on polar pesticides analyzed in UPLC-MS/MS. With the developed procedure, LOD were in the range of 0.5 - 6.3 pg mg^{-1}, which is largely lower than previously reported levels (20 - 100 pg mg^{-1}) except for DEA (0.5 pg mg^{-1}). This is the first time that LOD lower than 1 pg mg^{-1} were reported for atrazine, DIA, and imidacloprid. Finally, no data was found for acetamiprid, chlorpyrifos-methyl, linuron, and methoxychlor and to our knowledge, their successful recovery in human hair is a premiere.

Development of a novel approach for pesticide analysis in human hair

Table 7:3 Analytical parameters of the target analytes in the developed method (N.D.: Not detected)

Compound name	Retained	% Recovery	%SD	#validated levels[a]	Surrogates	LOD [pg mg⁻¹]	LOQ [pg mg⁻¹]	r^2	Intra-day precision (%RSD)	Inter-day precision (%RSD)	% Accuracy	%RSD	Matrix effect [%]	% SD
GC amenable molecules														
Acetochlor	Yes	52.4%	21.0%	2	Acetochlor-d11	18.2	60.6	0.989	13.1%	15.6%	81.9%	16.7%	60.5%	25.5%
alpha-cis-Chlordane	Yes	64.4%	11.9%	3	alpha-Endosulfan-d4	0.6	2.0	0.995	6.9%	12.5%	99.2%	12.0%	37.5%	1.5%
gamma-trans-Chlordane	Yes	70.0%	13.2%	3	alpha-Endosulfan-d4	0.6	2.0	0.995	10.2%	18.8%	114.4%	17.5%	41.1%	15.8%
trans-Nonachlor	Yes	81.1%	6.3%	3	alpha-Endosulfan-d4	5.2	17.2	0.998	4.1%	8.3%	91.7%	6.0%	25.0%	12.3%
Oxychlordane	Yes	118.7%	0.5%	3	alpha-Endosulfan-d4	19.5	60.0	0.994	7.1%	11.1%	103.3%	10.6%	42.7%	23.6%
Chlorpyrifos-ethyl	Yes	90.2%	9.8%	3	Chlorpyrifos-d10	13.8	45.9	0.997	4.4%	10.4%	97.7%	22.4%	76.4%	15.0%
Chlorpyrifos-methyl	Yes	78.4%	5.2%	2	Chlorpyrifos-d10	10.5	35.0	0.992	5.0%	6.7%	72.0%	5.5%	49.0%	18.4%
λ-Cyhalothrin	Yes	76.5%	10.5%	3	p,p'-DDT-C13	20.6	68.5	0.993	15.8%	19.2%	125.8%	13.4%	241.3%	46.8%
∑ (α- & β-Cypermethrin)	Yes	54.8%	12.5%	2	trans-Cypermethrin-d6	86.6	288.5	0.996	2.0%	8.3%	70.2%	3.3%	194.2%	18.4%
Deltamethrin	Yes	47.1%	8.7%	3	Deltamethrin-d6	26.8	89.3	0.978	6.2%	14.8%	47.5%	9.7%	178.0%	27.9%
Diazinon	Yes	106.7%	18.4%	3	Acetochlor-d11	24.0	80.0	0.994	6.8%	8.5%	80.5%	8.0%	107.5%	7.2%
Dieldrin	Yes	72.3%	11.1%	2	alpha-Endosulfan-d4	6.1	20.5	0.984	7.5%	20.2%	75.6%	15.8%	72.8%	16.4%
alpha-Endosulfan	Yes	61.2%	13.2%	2	alpha-Endosulfan-d5	73.8	246.0	0.997	5.7%	10.2%	58.9%	11.7%	-6.2%	7.6%
Heptachlor epoxide a	Yes	99.6%	15.4%	3	alpha-Endosulfan-d4	8.3	69.1	0.994	5.9%	7.9%	102.9%	7.7%	15.9%	8.6%
Heptachlor epoxide b	Yes	73.9%	9.9%	2	alpha-Endosulfan-d4	2.0	6.8	0.997	8.4%	7.8%	98.9%	9.9%	37.3%	14.3%
Methoxychlor	Yes	132.3%	1.4%	3	p,p'-DDT-C13	6.2	20.5	0.985	6.5%	9.1%	166.4%	14.3%	200.5%	20.8%
p,p'-DDE	Yes	47.1%	9.3%	3	p,p'-DDT-C13	0.2	40	0.995	9.9%	16.4%	116.8%	11.5%	70.5%	18.6%
p,p'-DDT	Yes	78.4%	2.2%	3	p,p'-DDT-C13	1.2	4.1	0.998	7.4%	10.5%	106.5%	16.2%	151.8%	38.4%
∑ (o,p'-DDT , p,p'-DDD)[b]	Yes	68.5%	4.0%	3	p,p'-DDT-C13	0.6	2.0	0.993	9.8%	9.2%	85.1%	9.6%	90.0%	15.1%
Hexachlorobenzene	No	15.3%	5.5%	-	Acetochlor-d11	6.3	21.0	0.967	-	-	-	-	9.1%	3.7%
Pentachlorobenzene	No	11.1%	1.9%	-	Acetochlor-d11	6.5	21.7	0.987	-	-	-	-	12.6%	0.8%
Profenofos	No	*N.D*	-	3	alpha-Endosulfan-d4	-	-	0.973	-	-	-	-	229.6%	38.7%
UPLC amenable molecules														
Acetamiprid	Yes	75.5%	5.5%	3	Acetamiprid-d3	1.4	4.7	0.997	2.2%	3.0%	103.1%	3.3%	-4.0%	3.9%
Atrazine	Yes	71.0%	8.5%	3	Atrazine-d5	0.8	2.7	0.996	1.5%	4.2%	146.7%	9.9%	14.5%	8.3%
Deisopropylatrazine (DIA)	Yes	67.0%	3.7%	3	DEA-d6	0.5	1.6	0.997	2.1%	2.5%	112.5%	4.4%	-11.0%	6.3%
Desethylatrazine (DEA)	Yes	99.0%	0.0%	3	DEA-d6	0.7	2.3	0.995	1.1%	3.0%	143.4%	6.9%	23.1%	2.3%
Carbofuran	Yes	74.0%	5.1%	3	Acetamiprid-d3	2.5	8.2	0.997	4.7%	7.1%	109.3%	6.6%	5.3%	5.0%
Imidacloprid	Yes	97.0%	6.0%	3	Imidacloprid-d4	0.8	2.6	0.994	4.2%	3.9%	145.8%	5.5%	15.3%	2.8%
Linuron	Yes	40.3%	14.1%	3	Linuron-d6	6.3	21.0	0.993	5.6%	14.1%	177.0%	14.8%	10.2%	3.4%
Azadirachtin	No	23.0%	15.7%	3	Acetamiprid-d3	7.1	23.8	0.987	-	-	-	-	-50.4%	19.5%
Diuron	No	36.0%	22.0%	3	Diuron-d6	22.4	74.7	0.995	-	-	-	-	-10.2%	9.4%
Emamectin benzoate	No	10.0%	41.7%	3	Diuron-d6	1.16	3.86	0.979	-	-	-	-	-20.2%	26.9%
Omethoate	No	5.7%	19.0%	3	Acetamiprid-d3	-	-	0.991	-	-	-	-	-13.9%	5.2%
Profenofos	No	*N.D*	-	3	Diuron-d6	-	-	0.994	-	-	-	-	-	-
Thiram	No	*N.D*	-	3	Diuron-d6	-	-	-	-	-	-	-	-	-
Triazophos	No	22.7%	16.3%	3	Linuron-d6	0.8	2.7	0.998	-	-	-	-	-0.8%	5.2%

[a] Number of spiked levels (~ 50, 250 and 500 pg mg⁻¹) validated by recovery assays based on the following validation criteria: recovery rate in the range 40% - 150% and variability (%RSD) <25%

[b] Results for o,p'-DDT and p,p'-DDD are summed as they could not be separated with the present GC-MS configuration

Table 7:4 Comparison between recovery rates and LOD retained in this study and reported in the literature

Compound name	This study % Recovery	Literature % Recovery	This study LOD [pg mg^{-1}]	Literature LOD [pg mg^{-1}]	Reference
GC amenable molecules					
Acetochlor	52.4	96	18.2	1.5	(Raeppel et al., 2016)
alpha-cis-Chlordane	64.4	120	0.6	-[a]	(Hardy et al., 2015)
gamma-trans-Chlordane	70.0	85	0.6	0.1 - 0.2	(Covaci et al., 2008)
		118		-	(Hardy et al., 2015)
trans-Nonachlor	81.1	85	5.2	0.1 - 0.2	(Covaci et al., 2008)
Oxychlordane	118.7	85	19.5	0.1 - 0.2	(Covaci et al., 2008)
Chlorpyrifos-ethyl	90.2	87 - 112	13.8	30.5 – 488	(Ostrea et al., 2009)
Chlorpyrifos-methyl	78.4	-	10.5	-	Not found
λ-Cyhalothrin	76.5	101	20.6	-[a]	(Hardy et al., 2015)
		83 - 92		0.2	(Schummer et al., 2012)
		87 - 112		30.5 - 488	(Ostrea et al., 2009)
∑ (α- & β-Cypermethrin)	54.8	87 - 116	86.6	3.6 - 488	(Ostrea et al., 2014)
		100.8		390	(Ostrea et al., 2012)
Deltamethrin	47.1	114 - 142.3	26.8	-[a]	(Hardy et al., 2015)
Diazinon	106.7	87 - 112	24.0	30.5	(Ostrea et al., 2009)
Dieldrin	72.3	94	6.1	1	(Raeppel et al., 2016)
		72 -83		2	(Schummer et al., 2012)
alpha-Endosulfan	61.2	94	73.8	0.15	(Raeppel et al., 2016)
		73 - 120		1	(Schummer et al., 2012)
Heptachlor epoxide a	99.6	126	8.3	-[a]	(Hardy et al., 2015)
Heptachlor epoxide b	73.9	119	2.0	-[a]	(Hardy et al., 2015)
Methoxychlor	132.3	-	6.2	-[a]	Not found
		70 - 85		900	(Cuong et al., 2012)
		42 - 112		0.05	(Schummer et al., 2012)
		68.9		0.29	(Tzatzarakis et al., 2014)
p,p'-DDE	47.1	84	0.2	0.02	(Salquèbre et al., 2012)
		85		100 - 200	(Covaci et al., 2008)
		95		1.5	(Raeppel et al., 2016)
		78 -103		0.05	(Schummer et al., 2012)
		61.3		2.14	(Tzatzarakis et al., 2014)
p,p'-DDT	78.4	86	1.2	0.5	(Salquèbre et al., 2012)
		85		100 - 200	(Covaci et al., 2008)
		80 - 103		1	(Schummer et al., 2012)
∑ (o,p'-DDT , p,p'-DDD)	68.5	66.9	0.6	1.50	(Tzatzarakis et al., 2014)
UPLC amenable molecules					
Acetamiprid	75.5	-	1.4	-	Not found
Atrazine	71.0	102.3	0.8	100	(Hubbard, 2001)
Deisopropylatrazine (DIA)	67.0	102.5	0.5	100	(Hubbard, 2001)
Desethylatrazine (DEA)	99.0	-	0.7	0.5	(Dulaurent et al., 2008)
Carbofuran	74.0	-	2.5	50	(Dulaurent et al., 2008)
Imidacloprid	97.0	97.3	0.8	20	(Kavvalakis et al., 2013)n
Linuron	40.3	-	6.3	-	Not found

[a] No LOD provided

7.3.4 Linearity

Calibration curves were obtained by dilution in organic solvents of the standard stock solutions of target analytes with -C13 labeled and deuterated derivate used as internal standards. For GC-MS analysis, they were prepared in isooctane at 6 concentration levels: 8, 15, 65, 120, 315, and 580 ng mL^{-1}. For UPLC-MS/MS dilutions were prepared in the mixture MeOH : water (5:95, v/v) with 0.1% formic acid at 5 concentration levels: 6, 12, 60, 120, and 250 ng mL^{-1}. Calibration curves were computed using ratio of the area of each analyte to the area of labeled surrogates. Weighing factors of (1/x) were used in a simple linear regression model and linearity was assessed by the coefficient of determination (r^2). Instrument responses were linear for all the target substances retained in the investigated concentration range with $r^2 > 0.978$ (Table 7:3).

7.3.5 Precision and accuracy

Precision of the method was assessed by calculation of percent of relative standard deviation (% RSD) between measurements of spiked sample concentrations. Intra-day precision was evaluated by comparison of measured concentrations from blank samples spiked in triplicates at 50, 250, and 500 pg mg^{-1}. The same levels were considered to calculate inter-days precision over three consecutive days (n = 9). Concentrations were calculated using the corresponding standard solution curves. Intra-day precision ranged from 1.1% to 15.8% and inter-days precision from 2.5% to 20.2% for the retained target analytes (Table 7:3). Accuracy ranged from 40% to 177%. Lowest accuracy was observed for substances presenting the higher retention times (i.e. cypermethrin and deltamethrin).

7.3.6 Matrix effect

The matrix effect was evaluated by comparing a dilution of standard stock solution of target analytes (SI Table S1) to spiked blank hair sample extracts at concentration levels of ~17 pg mg^{-1} (n = 3) and ~50 pg mg^{-1} (n = 3) for UPLC and GC amenable substances respectively. Spiking and internal standards addition was performed before injection. Mean value of matrix effect expressed as percentages (%) is presented in Table 7:3. For target substances, matrix effect ranged from 50% to 241%. Pyrethroids were among the most affected substances, which is in accordance with remarks presented in previous sections. These findings underlined the limitation of dSPE cleanup in removing matrix components from final extract. However, application of surrogates' correction allowed to correct for these effects and achieve good accuracy (Table 7:3).

7.3.7 Level of pesticides in field samples

Surveys were used to identify participants' personal practices. Personal protective equipment were limited to normal clothing (i.e. not chemical-resistant) and occasionally a muffler made of synthetic fabric. Pesticide formulation trade names and composition used in vegetable production were inventoried during field surveys. Among target analytes, deltamethrin, imidacloprid, and cypermethrin were present as active ingredients in these formulations. Pesticide application was conducted with knapsack sprayers tacking wind direction and intensity into account. Except for one, all the

respondents had cut their hair within the last month. Men generally shaved their hair in the study area, so the collected hair strands were about ~1 cm long. Hair samples of the same length were also collected from women by selecting newly grown hair, cut as close as possible to the skin and preferentially from the back of the head. If we assume a growth rate of 1 cm month[-1] (Kavvalakis and Tsatsakis, 2012), samples were representative of the last month of pesticide exposure.

Pesticides were extracted from field samples using the developed analytical procedure. Results indicated the presence of 8 target pesticides (Table 7:5). The average number of residues in the studied population was 3 with a maximum of 6 for one individual. Every sample presented at least 2 residues. Neonicotinoid pesticides: acetamiprid and imidacloprid were detected (>LOD) in 90% of the samples.

Table 7:5 Concentrations of pesticides in hair samples from the study population [pg mg^{-1}]

Sample ID	Age	Gender	Occupation	Acetamiprid	gamma-trans-Chlordane	Chlorpyrifos	λ-Cyhalothrin	Deltamethrin	Dieldrin	Imidacloprid	p,p'-DDE
Occupationally exposed											
NAB_1	30	F	Gardener	150.5	3.2	<LOQ	-	-	30.7	369.4	<LOQ
NAB_2	47	F	Gardener	49.1	5.6	64.2	-	-	-	353.6	-
NAB_3	43	M	Gardener	32.9	-	-	-	189.8	-	-	<LOQ
NAB_4	25	F	Gardener	6.4	-	-	-	-	-	90.0	-
NAB_5	51	M	Gardener	<LOQ	-	-	-	-	-	13.0	-
			Mean	**59.8**	**4.4**	**64.2**	**-**	**189.8**	**30.7**	**206.5**	**-**
			±SD	**63.0**	**1.7**	**-**	**-**	**-**	**-**	**181.8**	**-**
			Median	**41.0**	**4.4**	**64.2**	**-**	**189.8**	**30.7**	**221.8**	**-**
Not occupationally exposed											
NAB_6	43	F	Merchant	69.0	-	137.5	-	-	-	43.1	-
NAB_7	31	F	Merchant	<LOQ	-	<LOQ	-	-	-	19.7	-
NAB_8	54	M	Merchant	<LOQ	-	-	-	-	-	28.5	<LOQ
NAB_9	27	F	Teacher	54.0	2.2	87.4	127.4	510.3	-	136.1	-
NAB_10	51	M	Fisherman	-	<LOQ	-	-	-	<LOQ	9.3	-
			Mean	**61.5**	**2.2**	**112.4**	**127.4**	**510.3**	**-**	**47.3**	**-**
			±SD	**10.6**	**-**	**35.5**	**-**	**-**	**-**	**51.2**	**-**
			Median	**61.5**	**2.2**	**112.4**	**127.4**	**510.3**	**-**	**28.5**	**-**

7.4 Discussion

The present study proposes a novel approach for the simultaneous detection and determination of multi-class pesticides in hair samples. In some of the previously reported multi-class methods, extraction was performed by differentiated procedures depending on the physicochemical properties of the target analytes (Dulaurent et al., 2008; Posecion et al., 2006; Tsatsakis et al., 2008). QuEChERS method achieved extraction of multi-class pesticides in a single procedure, which considerably simplifies sample treatment. At the same time, dSPE purification was easier to conduct compared to more labor-intensive techniques proposed in these studies (i.e. purification on chromatographic column). Recently, faster methods were presented for GC amenable pesticides. Extraction was also conducted with ACN : water but was followed by analysis using SPME (Hardy

et al., 2015; Salquèbre et al., 2012). However, some of the parent compounds could not be recovered with this technique (e.g. carbofuran, chlorpyrifos, and diazinon). To overcome this shortage, the extract was split and metabolites were analyzed or liquid injection was performed in parallel to quantify parent compounds. In the present study, QuEChERS extraction followed by liquid injection was preferred as being technically simpler to operate and easier to implement considering liquid injector a more accessible equipment. This protocol also presented the advantage to achieve the quantification of every GC amenable target analyte parent compounds with a single injection in GC-MS. Moreover, if we consider that only surrogates are added the first day and incubation is performed overnight, the global sample throughput of the proposed method is fairly high. It requires only one subsequent day and a single person to perform the extraction and the injection on analytical instruments of 12 samples. Nevertheless, multi-class analysis including analytes with opposite physicochemical properties always implies compromises. dSPE purification did not allow achieving similar sensitivity for certain target analytes (e.g. higher LOQ for pyrethroids).

To our knowledge, this is the first attempt for the simultaneous detection and determination of the retained target analytes in human hairs using QuEChERS procedure. dSPE cleanup sorbent had a crucial role in the recovery of the 37 tested pesticides. The final choice was a compromised between cleanup efficiency minimizing the matrix effects on analytical instrument response (GC-MS), and recovered analytes. Substances presenting low recovery rates (<40%) and high variability (>25%) were not retained. The final procedure was validated for 28 multi-class pesticides with recovery in the range of 40% to 132%.

LOD for GC amenable pesticides ranged from 0.2 to 86.6 pg mg^{-1}. Except for chlordane isomers, chlorpyrifos-ethyl, cypermethrin, diazinon, and DDT (with its metabolites), obtained LOD were higher than previously reported values. As aforementioned, recent studies using ACN : water extraction and SPME analysis achieved a higher sensitivity for similar GC amenable compounds (Hardy et al., 2015; Salquèbre et al., 2012). The use of a more sensitive mass-spectrometric system (i.e. tandem mass-spectrometric detector) might be an explanation but differences might also come from the inherent characteristics of the QuEChERS procedure (aliquots and retention in cleanup sorbent). Before splitting the extract for injection on analytical instruments, aliquots theoretically reduced (i.e. without considering extraction recovery rate) the initial mass of analytes by 60%. After splitting, only 20% were theoretically available for GC analysis. This reduction is significant in an attempt to reach sufficient sensitivity to detect trace levels in hair. For UPLC analysis, this reduction was slightly lower due to the additional rinsing of the dSPE sorbent with MeOH. At injection stage, ~36% of the initial mass of analytes was theoretically available. The more sensitive analytical apparatus used in combination with the UPLC (i.e. tandem mass-spectrometric detector) achieved lower detection limits. Globally, UPLC amenable substances have been less studied. The developed method achieved higher sensitivity for atrazine, carbofuran, and imidacloprid than previously reported in the literature (LOD< 1 pg mg^{-1}). Finally, to our knowledge, this study presents the first successful recovery of acetamiprid, chlorpyrifos-methyl, linuron, and methoxychlor residues from human hair.

Developed method successfully detected and quantified 8 pesticides from hairs collected in a vegetable-producing area in Burkina Faso. Limited number of samples did not allow identifying particular trend linked to occupational activities. Results exhibited an exposure of every individual to at least 2 target pesticides. Acetamiprid, chlorpyrifos, lambda-cyhalothrin, dieldrin, and DDT were not present in commercial formulations reported during surveys. Ouédraogo et al. (Ouédraogo et al., 2011) have underlined the poor educational level and knowledge regarding pesticide use in rural areas in Burkina Faso. Illiteracy but also poor labeling quality (i.e. written in foreign language, absence, etc.) and counterfeiting could have led to misinterpretations and induced a bias in given answers. Detection of pesticides that are not used in occupational activities might also be an indication of exposure via other routes. Indeed, pesticides detected in hair samples were also detected in water and vegetables consumed in the study area (Lehmann et al., 2017d, Chapter 6). Further studies, including a larger population were needed to assess whether occupational or passive exposure could be differentiated (Chapter 8).

7.5 Conclusion

To our knowledge, this study presents a premiere application of QuEChERS extraction procedure coupled with gas chromatography mass spectrometry and ultra-performance liquid chromatography tandem mass spectrometry for the simultaneous determination of multi-class pesticides in human hair. A sensitive, precise, and accurate procedure was developed for the detection and quantification of 28 pesticides. Particular improvement of the sensitivity was achieved for the UPLC amenable compounds. Validity was assessed for 37 pesticides. The transparent validation process, including presentation of the results for substances that did not meet validation criteria, provided useful insights on where efforts should be directed for further developments. Aside from analytical apparatus, the proposed protocol required low solvent quantities and cheap and conventional material accessible to any laboratory.

Application of the validated method to the analysis of field samples demonstrated its suitability for the detection of pesticide exposure. This easy to implement protocol could be a useful tool for biomonitoring population exposure and assessing application/efficiency of national/international policies.

Chapter 8 Biomonitoring of pesticide exposure using hair as an indicator

Published work:

The present chapter is based on the following paper currently under revision for publication:

Lehmann, E., Oltramare, C., Nfon Dibié, J.-J., Konaté, Y., de Alencastro, L.F., 2017. Assessment of human exposure to pesticides by hair analysis: the case of vegetable-producing areas in Burkina Faso. Submitt. to Environ. Int. doi:10.1016/j.envint.2017.10.025

Web link:

http://dx.doi.org/10.1016/j.envint.2017.10.025

Supplementary material:

Appendix F

Supplementary information are divided in four sections S1-S4 presenting Figure S1 and the Table S1-S6.

Doctoral Candidate's contribution:

Main investigator and author

8.1 Introduction

The worldwide application of pesticides in agriculture, veterinary medicine and for vector control has led to the multiplication of potential routes of exposures. Human exposure to pesticides can occur indirectly from environmental contamination (dietary intake or atmospheric contamination) or directly from occupational, agricultural and household use (Clementi et al., 2008). Pesticide operators are persons who mix, load, and apply pesticides (EFSA, 2014). Operators are likely both directly and indirectly exposed, which puts them at higher risk of both acute intoxication and long-term adverse health effects. Non-occupationally exposed population (workers, bystanders, inhabitants of treated area/household) is expected to only suffer from indirect exposure.

In practice, exposure is influenced by specific conditions, under which pesticides are handled (such as packaging, environmental conditions, personal protective equipment, etc.). Studies conducted in Burkina Faso have underlined the lack of knowledge regarding the good agricultural practices and the use of unsuitable and obsolete pesticides (Ouédraogo et al., 2011; Toé, 2010d). Improper packaging and high illiteracy rates in rural areas were among the main problematic hampering compliance with recommendations provided on pesticide labels. At a national level, various strategic plans have been proposed to ensure environment and health protection regarding pest control and pesticide handling (Mbengue Faye et al., 2010; MECV, 2005c; Toé and Pare, 2011). Nevertheless, most of these documents are poorly applied due to the lack of human and financial resources.

Although, hazardous conditions have been identified, there is a global paucity on data concerning human exposure to pesticides in rural areas as only one evaluation was conducted in this domain (Toé et al., 2000). In the absence of existing monitoring, the present study aimed to propose and implement a comprehensive indicator of population exposure to pesticides identified during field campaigns (Chapter 4).

The present work assesses the suitability of using hair as an indicator of human exposure to pesticides in rural areas of a Sahelian country. Hair samples were collected from 101 volunteers in 10 villages located in gardening areas around Loumbila Lake. Participants were selected from two distinct population groups: gardeners (operators) and non-occupationally exposed individuals (reference population) in order to assess both occupational and indirect exposures. In parallel, volunteers were asked to answer a questionnaire about their personal hygiene and agricultural practices. Multiresidue analysis was performed using the modified QuEChERS procedure proposed by Lehmann et al. (2017b,.Chapter 7). This method was initially validated for 28 multi-class pesticides. An attempt was made to validate 10 additional persistent organic pollutants (POPs) using similar validation parameters. Finally, analyses and survey results were used to derive populations' exposure, dominant influencing factors (sex, age, location, and personal protective equipment) and provide a comprehensive evaluation of advantages and limitations of using hair as a matrix for biomonitoring human exposure to pesticides. This work is part of a four-year study assessing pesticide use and the effects on the environment and human health in market-gardening areas in

Burkina Faso. Field surveys conducted in previous phases provided a comprehensive characterization of agricultural practices (Chapter 4) and assessment of environmental contamination (Chapter 5 and Chapter 6).

8.2 Material and method

8.2.1 Chemicals, reagents, and standard solutions

Standards of analytes, -C13 labeled and deuterated compounds were purchased from Sigma-Aldrich (Switzerland), Dr. Ehrenstorfer (Germany), and Toronto Research Chemicals (Canada). Individual solutions of each target analyte and deuterated compound were prepared in appropriate solvent prior to respective preparation of the stock solutions in acetone and methanol and storage at −20 °C (Supplementary information (SI) section S1).

Methanol (MeOH) HPLC grade was acquired from Carlo Erba Reagents (France), isooctane from Acros Organics (Belgium), formic acid from Sigma-Aldrich (Switzerland), and acetonitrile (ACN) from Biosolve Chimie SARL (France). Sodium dodecyl sulfate (SDS), anhydrous magnesium sulfate ($MgSO_4$) and sodium acetate (NaAc) were purchased from Sigma-Aldrich (Switzerland). For dispersive solid phase extraction (dSPE), 12 mL centrifuge tubes containing pre-determined amounts of SPE sorbent Supel™QuE Z-Sep+ (500 mg) were obtained from Sigma-Aldrich (Switzerland). Whatman Mini-UniPrep G2 syringeless 0.45 µm filter vials were purchased from GE Healthcare Life Science (Switzerland). Syringe filters (0.22 µm) were purchased from WWR (Switzerland).

8.2.2 Study populations

Field samples were collected in February 2016 from 101 volunteers living in 10 villages located on the shores of Loumbila Lake (Figure 8:1 and SI Fig. S1).
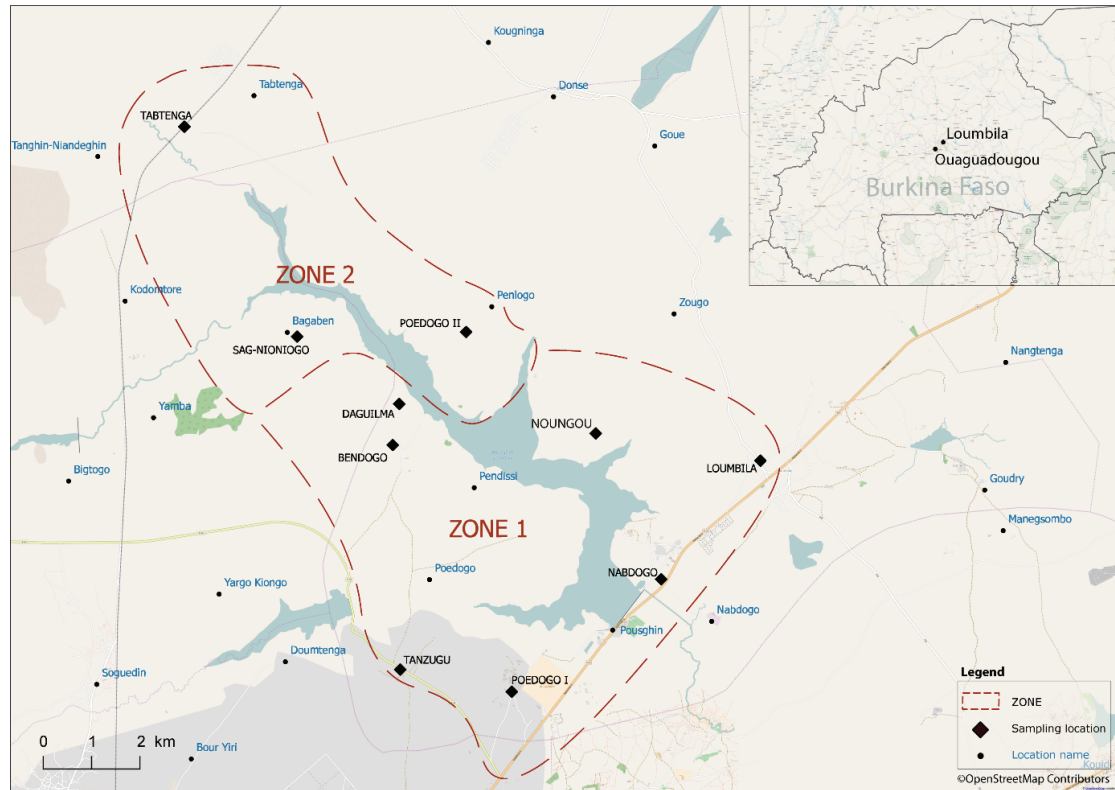
Figure 8:1 Location of the 10 villages concerned by the study and delimitations of Zones 1 and 2 (background map source: OpenStreetMap Contributors (2017))

Two populations were randomly selected in the study area to distinguish between occupational and environmental exposure: 56 gardeners (operators) and 45 non-occupationally exposed individuals (reference population). Operators were occupationally exposed by using pesticides for vegetable production in local market gardens. The reference population comprised individuals who were not occupationally exposed to pesticides but lived in the same area. This criterion is important, as the reference population would be therefore more representative of the environmental contamination of the study area. Member of this group covered various professions: merchants, homemakers, students, medical staff, restaurateurs, fishermen, builders, mechanics, butchers, stockbreeders, teachers, lumberjacks, and entrepreneurs. The studied population was 40% female, which was in accordance with the large proportion of female gardeners working in the study area (Agence de l'eau du Nakambé, 2014). Volunteers' ages ranged from 16 to 73 years (Figure 8:2). Each participant was asked to answer a questionnaire about their personal capillary hygiene practices (such as hair washing and cutting frequency, cosmetic products used, etc.) and use of pesticides (type, application conditions, personal protective equipment, etc.). The study was approved by the National Ethics Committee of Burkina Faso (deliberation n° 2015-12-010). All participants

were fully informed about the procedure and objectives of the study (in their local language when needed) and provided written consent to take part in the study.
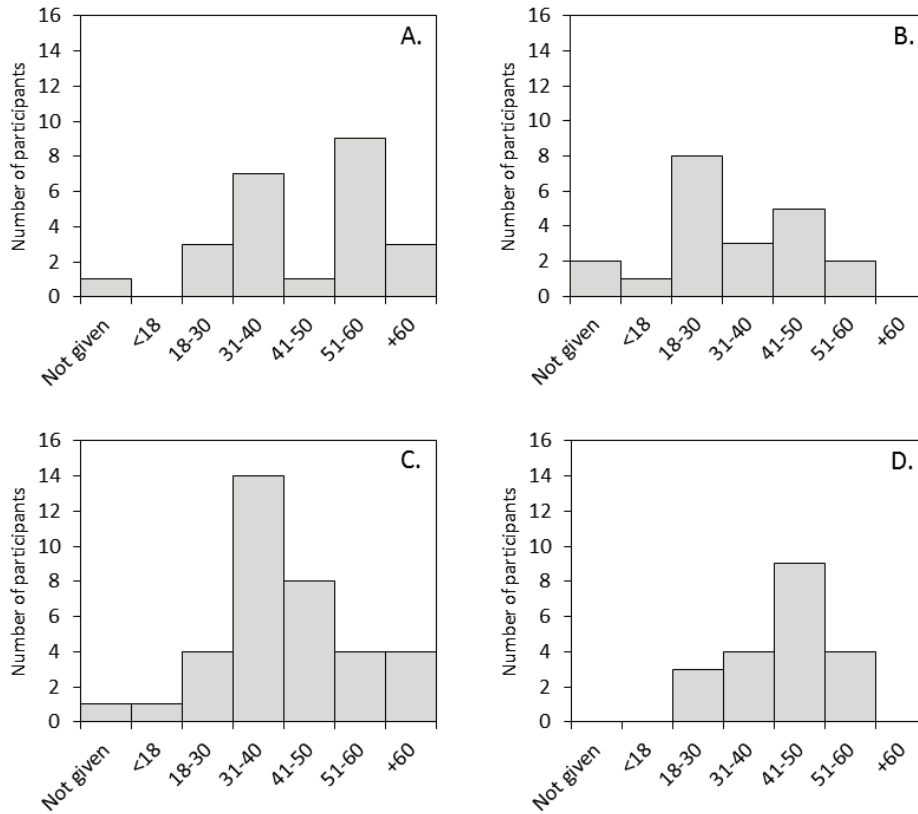
Figure 8:2 Population age distribution. (A. Males in reference population, n = 24, B. Females in reference population, n = 21, C. Males occupationally exposed, n = 36, D. Females occupationally exposed, n = 20)

8.2.3 Hair treatment and pesticide extraction

8.2.3.1 Hair collection

About 300 mg of hairs was collected from each volunteer, preferentially from the posterior vertex region of the scalp, as close as possible to the skin. A new pair of scissors was used for each participant. Sample collection was performed by local medical staff. Except for four respondents who refused to give an answer, each man had a haircut within the last month. Men generally shaved their hairs in the study area, so the collected strands were about ~1 cm long (Figure 8:3, a). Hair samples of the same length were also collected from women by selecting newly grown hair, cut as close as possible to the skin and preferentially from the back of the head (Figure 8:3, b). If we assume a growth rate of 1 cm month[-1] (Kavvalakis and Tsatsakis, 2012), samples were representative of the last month of pesticide exposure. The dominant color of collected material was

dark black. Samples were collected in aluminum foil, placed in paper envelopes, and stored in individual zipped plastic bags at room temperature.

(a) Hair sample collection on male

(b) Hair sample collection on female
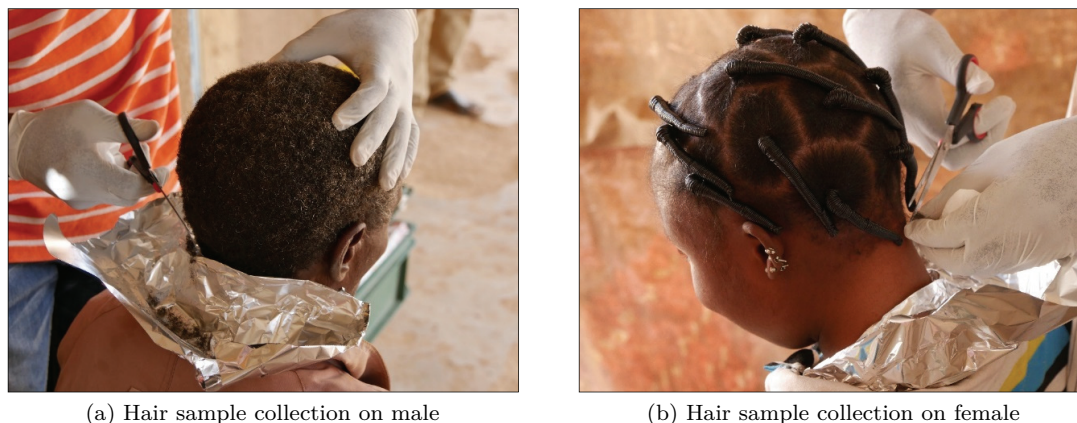
Figure 8:3 Hair sample collection

8.2.3.2 Hair decontamination

External decontamination was achieved using an aqueous solution that mimicked shampoo. Hair samples were washed for 4 min in Milli-Q water with 0.1% sodium dodecyl sulfate (SDS) under agitation (130 rpm). SDS solution was discarded after centrifugation at 3000 rpm for 1 min. Samples were subsequently rinsed twice with Milli-Q water using the same procedure to ensure complete SDS removal.

Hair grows on the body surface, so chemicals are incorporated by both endogenous and exogenous pathways. Internal dose that is representative of the systemic exposure is mainly incorporated from blood. External contamination can occur through multiple pathways but generally remains on the surface of the hair scales (i.e. cuticle). Depending on chemical properties, sweat and sebum could transfer chemical accumulated in skin compartments (Appenzeller and Tsatsakis, 2012). Contamination could also occur through particle deposition or direct exposure during pesticide application (spray drift and splashing). As underlined by Duca et al., (2014), no standardize procedure exists to fully differentiate between internal and external contamination of hair by pesticides. Previously developed external decontamination procedures affected internally incorporated amounts to some extent (Altshul et al., 2004; Hubbard, 2001). This work aimed to assess occupational exposure, using hair as a bioindicator. The assumption was made that differences between non-occupationally and occupationally exposed individuals were representative of occupational exposure. Similar to Ostrea et al. (2009), it was decided to focus on the whole hair exposure (i.e. endogenous and exogenous), considering that externally incorporated pesticides were also part of individual exposure history. Decontamination was performed from a homogenization perspective to clear samples from externally deposited particle material (e.g. dust, etc.) and "easily removable chemicals" (ERC) present on hair surface. This latter fraction is likely to be influenced by subjects' self-washing and induced significant variability in chemical analysis (Appenzeller and Tsatsakis,

2012). Soft decontamination that mimicked shampoo was retained (sodium dodecyl sulfate) assuming that every participant was likely to wash their hair, and the washing solution was discarded without analysis.

8.2.3.3 Pesticide extraction

Pesticide residues were extracted and analyzed using the analytical procedure presented elsewhere (Chapter 7 (Lehmann et al., 2017b)). Briefly, decontaminated hair was cut in 1 - 3 mm fragments. Isotopic dilution was performed by adding of 0.2 mL of the appropriate labeled surrogates directly onto the sample. A mix standard solution of the analytes was directly spiked onto the sample for artificial contamination, when needed. Two hundred milligrams of hair was extracted overnight in 5 mL of ACN : Water (1:1) at 40 °C under agitation, followed by 5 min of sonication. Separation was achieved by salting-out effect, using 1 g $MgSO_4$ and 0.25 g NaAc (CH3COONa). Two milliliters of the supernatant was subsequently cleaned-up by dSPE with 500 mg of Supel™QuE Z-Sep+ sorbent. The cleaned up extract was then split for differential analysis of GC-MS and UPLC-MS/MS amenable substances. After filtration (0.22 μm), 0.5 mL was evaporated to dryness, before being reconstituted in 0.2 mL of isooctane for GC-MS analysis. For UPLC-MS/MS analysis, dSPE sorbent was rinsed twice with 1 mL MeOH (to increase the mass of analyte recovered). The rinse solution (2 mL) was combined with 0.5 mL of the previous ACN cleaned-up fraction. Combined fractions were subsequently evaporated to dryness, reconstituted in 0.4 mL of the mixture MeOH : Water (5:95, v/v) with 0.1% formic acid, and filtered with syringeless 0.45 μm filter vials, prior to UPLC-MS/MS analysis.

8.2.3.4 GC-MS and UPLC-MS/MS analysis

The gas chromatography analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph, coupled with a Thermo Scientific ISQ Single Quadrupole MS (Waltham, MA, USA) operated in Single Ion Monitoring (SIM). Helium was used as the carrier gas (1.2 mL min^{-1}) and analytes were separated using a Phenomenex Zebron capillary column (ZB-5 MS plus, 20 m, 0.18 mm, 0.18 μm). The UPLC system comprised a UPLC Waters Acquity, coupled to a Waters Acquity Xevo TQ-S tandem quadrupole MS. Separations were carried out on a Waters Acquity UPLC HSS T3 column (2.1×100 mm, 1.8 μ m) with the oven temperature set at 30 °C. In addition to the 27 validated pesticides included in the method proposed by Lehmann et al. (2017b), an attempt was made to analyze the 10 pesticides presented in Table 8:2. Mass spectrometry detection method of the GC-MS was updated using the parameters presented in SI Table S3. Recovery rates of the target substances were in the range of 40% to 132% with a variability < 22% (% relative standard deviation (RSD)). The limits of quantification (LOQ) ranged from 1.6 to 288.5 pg mg^{-1}, and the limits of detection (LOD) from 0.2 to 86.6 pg mg^{-1} (SI Table S4 and Table 8:2). Table 8:1 presents the list of the 37 target analytes analyzed in the present study.

Table 8:1 Target substances analyzed in human hair

Active ingredient	GC-MS	UPLC-MS/MS	Active ingredient	GC-MS	UPLC-MS/MS
Carbamate			*Organochlorine (continued)*		
Carbofuran		×	Methoxychlor	×	
			trans-Nonachlor	×	
Chloroacetamide			Oxychlordane	×	
Acetochlor	×		∑ (o,p'-DDT , p,p'-DDD)ᵃ	×	
			pp' DDE	×	
Neonicotinoid			pp' DDT	×	
Acetamiprid		×			
Imidacloprid		×	*Organophosphate*		
			Chlorpyrifos-ethyl	×	
Organochlorine			Chlorpyrifos-methyl	×	
alpha-cis-Chlordane	×		Diazinon	×	
gamma-trans-Chlordane	×				
Dieldrin	×		*Pyrethroid*		
alpha-Endosulfan	×		lambda-Cyhalothrin	×	
beta-Endosulfan	×		alpha-Cypermethrin	×	
Endosulfan sulfate	×		beta-Cypermethrin	×	
Endrin	×		Deltamethrin	×	
Endrin aldehyde	×				
Endrin ketone	×				
alpha-HCH	×		*Triazine*		
beta-HCH	×		Atrazine		×
delta-HCH	×		DEA		×
gamma-HCH	×		DIA		×
Heptachlor	×				
Heptachlor epoxide a	×		*Urea*		
Heptachlor epoxide b	×		Linuron		×

ᵃ Results for: o,p'-DDT and p,p'-DDD are presented as the sum of the concentrations of these two target analytes as the analytical protocol did not achieved separation of the molecules.

8.2.3.5 Recovery assay and determination of limits of detection and quantification for 10 additional POPs

This study also attempted to evaluate the suitability of the method to determinate and quantify the 10 supplementary organochlorine pesticides presented in Table 8:2. These substances were retained in a monitoring perspective as part of the ratified Stockholm Convention, as well as because endosulfan and heptachlor were previously used and detected in environmental matrices (Lehmann et al., 2017d; MECV, 2005a). A recovery assay was conducted using decontaminated blank hair samples spiked in triplicates at three concentration levels ($\sim$ 50, 250 and 500 pg mg^{-1}). Isotopic dilution was performed with the addition of labeled internal standards' solution prior to injection. For the three tested concentration levels, validation criteria retained only recovery rates in the range of 40% to 150% with a variability of average validated levels (%RSD) lower than 25%.

The LOD and LOQ for the selected target analytes were defined as the analyte concentration that produced a peak with a respective signal-to-noise ratio of 3 and 10. The LOD of the method for each analyte was evaluated from the chromatogram of samples used in the recovery assay and by measuring the coincident instrumental response of standard pesticide solutions and procedural blank or negative samples. The LOQ definition also took into account results from recovery assays. Validated levels based on the aforementioned criteria were used to confirm the LOQ estimated from chromatograms.

8.2.4 Statistical analysis

Frequency of occurrence of positive samples (>LOD) was expressed as counts and percentages. The prevalence of positive samples was examined using Pearson's chi-square test. Levels of pesticides were expressed as median concentrations along with minimum and maximum values. The non-parametric Kurskal-Wallis test was used to examine differences between measured pesticide residue levels (>LOQ) from different subgroups in the studied populations. MATLAB 2017a (The MathWorks, Inc., Natick, Massachusetts, United States) was used for data analysis and a level of 0.055 was set as significant.

8.3   Results

8.3.1 Analytical parameters for the 10 additional POPs

Calibration curves were obtained by diluting standard stock solutions of target analytes with - C13-labeled and deuterated derivate used as internal standards in organic solvents. For GC-MS analysis, they were prepared in isooctane at 6 concentration levels: 8, 15, 65, 120, 315, and 580 ng mL^{-1}. Calibration curves were computed using ratio of the area of each analyte to the area of labeled surrogates. Weighting factors of (1/x) were used in a simple linear regression model and linearity was assessed by the coefficient of determination (r^2). Instrument responses were linear for all the target substances retained in the investigated concentration range with $r^2 > 0.954$ (Table 8:2).

According to retained validation criteria, only levels with recovery rates in the range of 40% to 150% and variability (% RSD) lower than 25% were validated. Considering these parameters, average recovery rates for validated levels ranged from 45% to 121% with variably under 19.5%.The LOD ranged from 15 to 250 pg mg^{-1} and the LOQ ranged from 36 to 500 pg mg^{-1} (Table 8:2).

Table 8:2 Analytical parameters for the 10 additional organochlorine pesticides tested

Compound name	%Recovery	%RSD	# validated levels[a]	Surrogates	LOD [pg mg^{-1}]	LOQ [pg mg^{-1}]	r^2
alpha-HCH	49.2%	7.6%	2	Acetochlor-d11	20	250	0.988
beta-HCH	47.3%	2.5%	1	Acetochlor-d11	250	500	0.976
gamma-HCH	91.1%	7.2%	1	Acetochlor-d11	150	500	0.982
delta-HCH	45.2%	13.9%	3	Acetochlor-d11	20	50	0.978
Heptachlor	77.3%	17.7%	1	Acetochlor-d11	150	500	0.989
Endrin	80.2%	7.3%	3	alpha-Endosulfan-d4	15	50	0.989
Endrin ketone	120.7%	9.7%	2	p,p'-DDT-C13	75	250	0.989
Endrin aldehyde	73.5%	6.9%	1	alpha-Endosulfan-d4	150	500	0.954
beta-Endosulfan	93.2%	19.5%	2	beta-Endosulfan-d4	75	250	0.979
Endosulfan sulfate	94.1%	17.1%	3	alpha-Endosulfan-d4	20	36	0.973

[a] Number of spiked levels validated by recovery assay based on the following validation criteria: recovery rate in the range 40%-150% and variability (%RSD) <25%

To the best of our knowledge no LOD/LOQ for the analysis of endrin aldehyde, endrin ketone, and endosulfan sulfate in hairs were presented in the literature. Lower LOD and LOQ values were recently reported for endrin (LOQ: 1 pg mg^{-1}), beta-endosulfan (LOD: 0.5 mg^{-1} and LOQ: 2 pg mg^{-1}), alpha-HCH (LOD: 0.01 pg mg^{-1} and LOQ: 0.05 pg mg^{-1}), beta-HCH (LOD: 0.02 pg mg^{-1} and LOQ: 0.1 pg mg^{-1}), delta-HCH (LOQ: 0.5 pg mg^{-1}), gamma-HCH (LOD: 0.02 pg mg^{-1} and LOQ: 0.1 pg mg^{-1}) compared to the present study (Duca et al., 2014b; Hardy et al., 2015; Salquèbre et al., 2012). In the present material configuration, low sensitivity of the analytical apparatus for these pesticides was detected. Lower concentration levels of standard analytes (8 and 15 ng mL^{-1}) were difficult to detect even in pure solvent from the calibration curves. The use of a more sensitive mass-spectrometric system in the aforementioned studies (tandem mass-spectrometric detector) might explain these differences, but it might also come from the inherent characteristics of the QuEChERS procedure. The QuEChERS method includes aliquots. Reduction of the initial mass of analyte combined with low instrumental sensitivity, ultimately led to retain higher LOD values. Low recovery rates obtained for alpha-HCH (49.2%), beta-HCH (47.3%), and delta-HCH (45.2%), but also the high limits of detection retained for the 10 POPs (15 - 250 pg mg^{-1}) might hamper the detection of trace levels in field samples. This should be remembered when interpreting the results.

8.3.2 Capillary hygiene, health, and pesticide application practices

Surveys were used to identify participants' personal practices. Hair was washed every day with ordinary soap or shampoo in 71% of the cases, and at least once per week in 10%. Nineteen women (i.e. 46%) reported using an after-shampoo product. Among the participants, 74% affirmed that hygiene was the main reason for cutting their hair. Except for four respondents who refused to give an answer, every man had a haircut within the last month. It is also noteworthy that 37% of the women in the study area commonly wore wigs, which could potentially reduce external contamination. Nevertheless, only one person always wore one, and others reported only occasional use. Therefore, wigs were not retained as an equipment reducing pesticide exposure.

Eighty percent of the population did not report either any specific disease or hair loss. Problems associated with health were reported in 7 cases, 2 subjects stated that their cosmetics induced dryness and hair loss, 3 people were not able to describe their symptoms, and 2 indicated having suffered from ringworm. Treatment received for ringworm could not be identified.

According to survey records, most of the gardeners used a knapsack sprayer (91%), and 86% considered wind direction and insolation to determine optimal application periods. Personal protective equipment (PPE) worn during pesticide handling was limited to ordinary clothing (i.e. not chemical-resistant) that did not always covered legs and arms (Figure 8:4). A rudimentary muffler made of ordinary fabric was used by 23% of the occupationally exposed population as the only respiratory protection. Additional protection included plastic boots, glasses, gloves, and hat. Among target substances, cypermethrin, deltamethrin, imidacloprid, and acetamiprid were respectively used by 57%, 45%, 36%, and 27% of the occupationally exposed population.
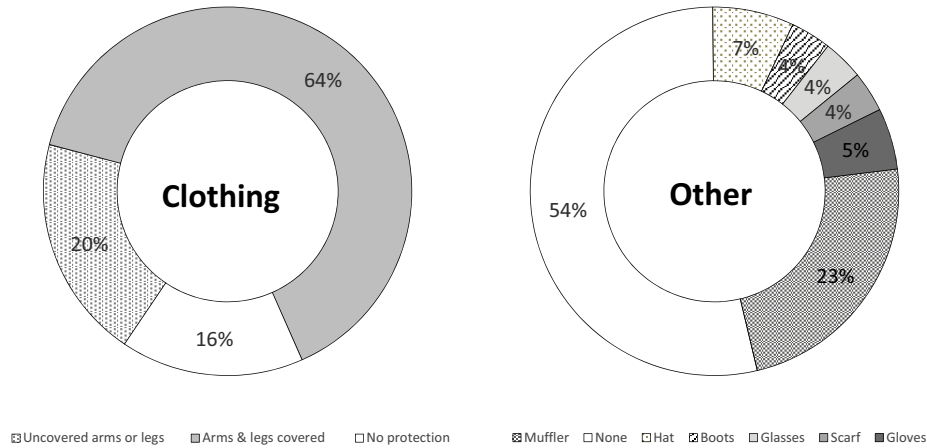
Figure 8:4 Reported personal protective equipment for pesticide application

8.3.3 Pesticides detected in studied populations

Positive samples (>LOD) indicated the presence of 17 target pesticides (Table 8:3). An average of four residues was found in the study population, with a maximum of nine per individual. Only one sample from the reference population had no residue of the target analytes. Neonicotinoid pesticides were the most frequently detected with at least one residue in 95% of the samples. Organochlorine, pyrethroid, and organophosphorus pesticides were respectively detected in 64%, 52%, and 18% of the population. Triazine and carbamate were found in less than 10% (Figure 8:5).

The Sahelian Pesticide Committee (CSP) is the authority responsible for pesticide homologations in the member states of the CILSS (Permanent Interstates Committee for Drought Control in the Sahel). The CSP proposes two lists of authorized pesticides classified by commercial formulation trade names (with mention of active ingredients) and intended uses (target pests and crops). The first list comprises 310 items and reports all authorized commercial formulations. The second, composed of 41 items, precise which pesticides are authorized in gardening (i.e. for vegetable production). Pesticides detected in hair samples were compared to active ingredients contained in authorized formulations (Figure 8:5). More than 60% of the detected molecules were present in authorized formulations. This concerned the detected neonicotinoid, pyrethroid, and organophosphorus pesticides, which are authorized for use in gardening. The rest was comprised substances that are not authorized by the CSP. Carbofuran and atrazine are not included in authorization lists and the detected organochlorine pesticides are part of the "dirty dozen" prohibited by the Stockholm Convention (ratified by Burkina Faso in 2004 and enforced in March 2005).
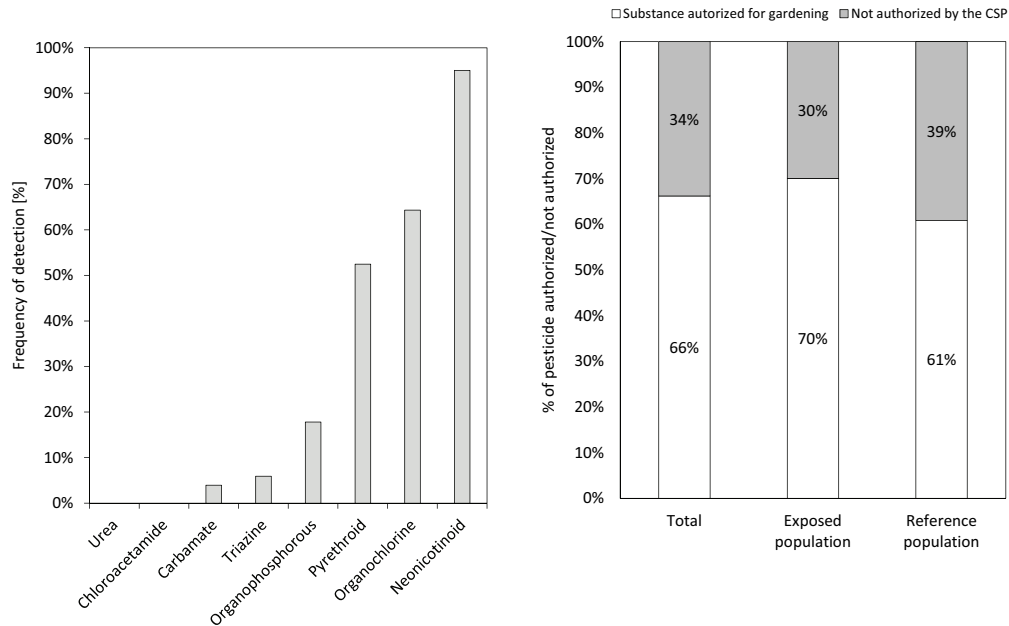
Figure 8:5 Frequency of detection of target substances classified by compound family name (left) and percentage of pesticide detected authorized by the CSP (right).

Table 8:3 shows the frequency of detection (i.e. level >LOD) of target substances. Studied populations were subsequently decomposed in specific subgroups to assess the impact of different factors such as occupational activity, sex, age, geographical location, and PPE. Group definitions ensured that each one contained sufficient individuals to allow for cross-comparison. Age classes were defined, based on repartition presented in Figure 8:2, and regrouped into individuals younger than 30, between ages 30 and 50, and older than 50 years. Assuming that pesticides used might rely on the availability of commercial formulations, the place of purchase could influence the study results. Geographical separation was based on access to the nearest potential selling point. Workers in Zone 1 were more likely to purchase their pesticides in Loumbila (Figure 8:1) while workers in Zone 2 were closer to villages located along the northern part of the lake (Pabré, Dapelogo, Donse, etc., see SI Figure S1). No certified coveralls or other chemical-resistant equipment was used. Therefore, the extent of body coverage was retained to assess the influence of PPE on pesticide exposure. A distinction was made between, arms or legs covered; arms and legs covered; and no protection. The latter category indicated that the operator did not care about wearing any particular protective equipment so random coverage was expected.

Imidacloprid was the most frequently detected pesticide (94.1%). Together with acetamiprid (67.3%) and gamma-trans-Chlordane (50.5 %), it was present in more than 50% of the samples. Cypermethrin and p,p'-DDE were detected in about 25% to 30% of the samples, and the frequency of detection of the other substances was less than 20%. Dieldrin (n = 4), alpha-cis-chlordane (n = 4), p,p'-DDT (n = 2), atrazine (n = 5), desethylatrazine (DEA, n = 3) and carbofuran (n = 4)

were detected in less than 5 samples in the overall population. Statistical analysis in subgroups was therefore not relevant for these substances. Except for p,p'-DDT, p values were only calculated for the overall population (Table 8:3).

The activity of gardening was found to induce significant prevalence of positive samples only for acetamiprid and lambda-cyhalothrin (p value = 0.024). The opposite tendency was observed for p,p'-DDE (p value = 0.024), for which positive samples were less frequently detected among vegetable producers. Sex had a significant influence on chlorpyrifos-ethyl, cypermethrin, and p,p'-DDE detection when considering the overall and reference populations. Chlorpyrifos-ethyl was detected more frequently in female samples, while cypermethrin and p,p'-DDE occurrence dominated in male samples. Age significantly affected the prevalence of sample positive for o,p'-DDT & p,p'-DDD in the reference population (in older age classes, of more than 50 years). Geographical location influenced the largest number of pesticides. A significantly higher prevalence of lambda-cyhalothrin and alpha-cis-chlordane was observed in Zone 2, but only when considering the overall population. Prevalence in Zone 2 was significant for cypermethrin in both overall and occupationally exposed populations. On the contrary, chlorpyrifos prevailed in samples from Zone 1 in overall and occupationally exposed populations. o,p'-DDT & p,p'-DDD were the only pesticides presenting a large prevalence in Zone 2 for every population. Finally, personal protective equipment only had a significant impact on acetamiprid exposure. It is noteworthy that the number of positives was surprisingly higher with workwear fully covering limbs.

Biomonitoring of pesticide exposure using hair as an indicator

Table 8:3 Frequency of detection of target pesticides and p values from Pearson chi-square tests (n = number of samples, N.D.: Not Detected)

Studied population (overall)

Group	Description	Acetamiprid % positive (n)	p Value	Imidacloprid % positive (n)	p Value	λ-Cyhalothrin % positive (n)	p Value	Σ (α- & β-Cypermethrin) % positive (n)	p Value	Deltamethrin % positive (n)	p Value	Dieldrin % positive (n)	p Value	α-cis-Chlordane % positive (n)	p Value	γ-trans-Chlordane % positive (n)	p Value
Total	n = 101	67.3 (68)	-	94.1 (95)	-	15.8 (16)	-	29.7 (30)	-	11.9 (12)	-	4.0 (4)	-	4.0 (4)	-	50.5 (51)	-
Activity	1: Gardening (n = 56)	76.8 (43)	**0.024**	96.5 (54)	0.261	23.3 (13)	**0.024**	30.4 (17)	0.509	10.8 (6)	0.686	1.8 (1)	0.211	3.6 (2)	0.823	50.0 (28)	0.912
	2: Other (n = 45)	55.6 (25)		91.2 (41)		6.7 (3)		24.5 (11)		13.4 (6)		6.7 (3)		4.5 (2)		48.9 (22)	
Sex	1: Female (n = 41)	63.5 (26)	0.488	92.7 (38)	0.629	17.1 (7)	0.779	17.1 (7)	**0.048**	17.1 (7)	0.183	2.5 (1)	0.517	7.4 (3)	0.153	48.8 (20)	0.904
	2: Male (n = 60)	70.0 (42)		95.0 (57)		15.0 (9)		35.0 (21)		8.4 (5)		5.0 (3)		1.7 (1)		50.0 (30)	
Age	1: <30 yrs. (n = 15)	60.0 (9)	0.796	86.7 (13)	0.174	6.7 (1)	0.513	6.7 (1)	0.183	20 (3)	0.608	0 (0)	0.592	0 (0)	0.142	33.4 (5)	0.335
	2: 30 - 50 yrs. (n = 52)	67.4 (35)		92.4 (48)		19.3 (10)		28.9 (15)		11.6 (6)		5.8 (3)		2 (1)		50.0 (26)	
	3: >50 yrs. (n = 30)	70.0 (21)		100.0 (30)		16.7 (5)		30.0 (9)		10.0 (3)		3.4 (1)		10.0 (3)		56.7 (17)	
Location	1: Zone 1 (n = 66)	65.2 (43)	0.522	92.5 (61)	0.340	10.7 (7)	**0.048**	19.7 (13)	**0.013**	7.6 (5)	0.066	6.1 (4)	0.137	0 (0)	**0.005**	47.0 (31)	0.484
	2: Zone 2 (n = 35)	71.5 (25)		97.2 (34)		25.8 (9)		42.9 (15)		20 (7)		0 (0)		11.5 (4)		54.3 (19)	

Occupationally exposed population (Operators)

Group	Description	Acetamiprid % positive (n)	p Value	Imidacloprid % positive (n)	p Value	λ-Cyhalothrin % positive (n)	p Value	Σ (α- & β-Cypermethrin) % positive (n)	p Value	Deltamethrin % positive (n)	p Value	Dieldrin % positive (n)	p Value	α-cis-Chlordane % positive (n)	p Value	γ-trans-Chlordane % positive (n)	p Value
Sex	1: Female (n = 20)	65.0 (13)	0.119	95.0 (19)	0.668	25.0 (5)	0.814	25.0 (5)	0.516	15.0 (3)	0.440	5.0 (1)	-	10.0 (2)	-	55.0 (11)	0.577
	2: Male (n = 36)	83.4 (30)		97.3 (35)		22.3 (8)		33.4 (12)		8.4 (3)		0 (0)		0 (0)		47.3 (17)	
Age	1: <30 yrs. (n = 5)	100.0 (5)	0.410	100.0 (5)	0.604	0 (0)	0.382	20.0 (1)	0.853	20.0 (1)	0.754	0 (0)	-	0 (0)	-	40.0 (2)	0.637
	2: 30 - 50 yrs. (n = 37)	73.0 (27)		94.6 (35)		24.4 (9)		32.5 (12)		10.9 (4)		2.8 (1)		2.8 (1)		48.7 (18)	
	3: >50 yrs. (n = 13)	77.0 (10)		100.0 (13)		30.8 (4)		30.8 (4)		7.7 (1)		0 (0)		7.7 (1)		61.6 (8)	
Location	1: Zone 1 (n = 34)	82.4 (28)	0.220	97.1 (33)	0.752	14.8 (5)	0.061	20.6 (7)	**0.048**	5.9 (2)	0.146	3.0 (1)	-	0 (0)	-	50.0 (17)	1.000
	2: Zone 2 (n = 22)	68.2 (15)		95.5 (21)		36.4 (8)		45.5 (10)		18.2 (4)		0 (0)		9.1 (2)		50.0 (11)	
PPE	1: Arms or legs covered (n = 13)	69.3 (9)	**0.035**	100.0 (13)	0.237	23.1 (3)	0.828	38.5 (5)	0.768	7.7 (1)	0.894	0 (0)	-	7.7 (1)	-	38.5 (5)	0.527
	2: Arms & legs covered (n = 36)	86.2 (31)		97.3 (35)		25.0 (9)		27.8 (10)		11.2 (4)		2.8 (1)		2.8 (1)		55.6 (20)	
	3: no PPE (n = 7)	42.9 (3)		85.8 (6)		14.3 (1)		28.6 (2)		14.3 (1)		0 (0)		0 (0)		42.9 (3)	

Reference population

Group	Description	Acetamiprid % positive (n)	p Value	Imidacloprid % positive (n)	p Value	λ-Cyhalothrin % positive (n)	p Value	Σ (α- & β-Cypermethrin) % positive (n)	p Value	Deltamethrin % positive (n)	p Value	Dieldrin % positive (n)	p Value	α-cis-Chlordane % positive (n)	p Value	γ-trans-Chlordane % positive (n)	p Value
Sex	1: Female (n = 21)	62.0 (13)	0.423	90.5 (19)	0.889	9.6 (2)	0.472	9.6 (2)	**0.029**	19.1 (4)	0.292	0 (0)	-	4.8 (1)	-	42.9 (9)	0.449
	2: Male (n = 24)	50.0 (12)		91.7 (22)		4.2 (1)		37.5 (9)		8.4 (2)		12.5 (3)		4.2 (1)		54.2 (13)	
Age	1: <30 yrs. (n = 10)	40.0 (4)	0.456	80.0 (8)	0.191	10.0 (1)	0.919	0.0 (0)	0.170	20.0 (2)	0.833	0 (0)	-	0 (0)	-	30.0 (3)	0.442
	2: 30 - 50 yrs. (n = 15)	53.4 (8)		86.7 (13)		6.7 (1)		20.0 (3)		13.4 (2)		13.4 (2)		0 (0)		53.4 (8)	
	3: >50 yrs. (n = 17)	64.8 (11)		100.0 (17)		5.9 (1)		29.5 (5)		11.8 (2)		5.9 (1)		11.8 (2)		53.0 (9)	
Location	1: Zone 1 (n = 32)	46.9 (15)	0.066	87.5 (28)	0.182	6.3 (2)	0.860	18.8 (6)	0.163	9.4 (3)	0.220	9.4 (3)	-	0 (0)	-	43.8 (14)	0.279
	2: Zone 2 (n = 13)	77.0 (10)		100.0 (13)		7.7 (1)		38.5 (5)		23.1 (3)		0 (0)		15.4 (2)		61.6 (8)	

Biomonitoring of pesticide exposure using hair as an indicator

Table 8:3 (continued) Frequency of detection of target pesticides and p values from Pearson chi-square tests (n = number of samples, N.D.: Not Detected)

Group	Description	Σ (o,p'-DDT, p,p'-DDD)[a] p Value	% positive (n)	p,p'-DDE p Value	% positive (n)	p,p'-DDT p Value	% positive (n)	Chlorpyrifos-ethyl p Value	% positive (n)	Atrazine p Value	% positive (n)	DEA p Value	% positive (n)	Carbofuran p Value	% positive (n)
Studied population (overall)															
Total	n = 101	-	12.9 (13)	-	24.8 (25)	-	2.0 (2)	-	15.8 (16)	-	5.0 (5)	-	3.0 (3)	-	4.0 (4)
Activity	1: Gardening (n = 56)	0.890	14.3 (8)	**0.024**	16.1 (9)	-	1.8 (1)	0.086	21.5 (12)	0.476	3.6 (2)	0.691	3.6 (2)	0.067	7.1 (4)
	2: Other (n = 45)		13.4 (6)		35.6 (16)		2.3 (1)		8.9 (4)		6.7 (3)		2.2 (1)		0 (0)
Sex	1: Female (n = 41)	0.689	12.2 (5)	**0.016**	12.2 (5)	-	2.5 (1)	**0.052**	24.4 (10)	0.365	7.4 (3)	0.795	2.4 (1)	0.696	4.9 (2)
	2: Male (n = 60)		15.0 (9)		33.4 (20)		1.7 (1)		10.0 (6)		3.4 (2)		3.3 (2)		3.3 (2)
Age	1: <30 yrs. (n = 15)	0.393	6.7 (1)	0.873	20.0 (3)	-	0 (0)	0.355	26.7 (4)	0.427	0 (0)	0.747	0 (0)	0.142	0 (0)
	2: 30 - 50 yrs. (n = 52)		11.6 (6)		23.1 (12)		2 (1)		17.4 (9)		7.7 (4)		3.8 (2)		1.9 (1)
	3: >50 yrs. (n = 30)		20.0 (6)		26.7 (8)		3.4 (1)		10.0 (3)		3.4 (1)		3.3 (1)		10.0 (3)
Location	1: Zone 1 (n = 66)	**<0.001**	3.1 (2)	0.870	24.3 (16)	-	0 (0)	**0.009**	22.8 (15)	0.222	3.1 (2)	0.961	3.0 (2)	0.679	4.5 (3)
	2: Zone 2 (n = 35)		34.3 (12)		25.8 (9)		5.8 (2)		2.9 (1)		8.6 (3)		2.9 (1)		2.9 (1)
Occupationally exposed population (Operators)															
Sex	1: Female (n = 20)	0.909	15 (3)	0.356	10.0 (2)	-	0 (0)	0.244	30.0 (6)	-	5.0 (1)	-	5.0 (1)	-	10.0 (2)
	2: Male (n = 36)		13.9 (5)		19.5 (7)		2.8 (1)		16.7 (6)		2.8 (1)		2.8 (1)		5.6 (2)
Age	1: <30 yrs. (n = 5)	0.707	20.0 (1)	0.495	0 (0)	-	0 (0)	0.559	40.0 (2)	-	0 (0)	-	0 (0)	-	0 (0)
	2: 30 - 50 yrs. (n = 37)		16.3 (6)		16.3 (6)		2.8 (1)		19.0 (7)		5.5 (2)		5.4 (2)		2.7 (1)
	3: >50 yrs. (n = 13)		7.7 (1)		23.1 (3)		0 (0)		23.1 (3)		0 (0)		0 (0)		23.1 (3)
Location	1: Zone 1 (n = 34)	**<0.001**	0 (0)	0.275	11.8 (4)	-	0 (0)	**0.013**	32.4 (11)	-	3 (1)	-	2.9 (1)	-	8.8 (3)
	2: Zone 2 (n = 22)		36.4 (8)		22.8 (5)		4.6 (1)		4.6 (1)		4.6 (1)		4.5 (1)		4.5 (1)
PPE	1: Arms or legs covered (n = 13)	0.478	15.4 (2)	0.439	15.4 (2)	-	0 (0)	0.379	7.7 (1)	-	7.7 (1)	-	7.7 (1)	-	15.4 (2)
	2: Arms & legs covered (n = 36)		11.2 (4)		19.5 (7)		2.8 (1)		25.0 (9)		2.8 (1)		2.8 (1)		5.6 (2)
	3: no PPE (n = 7)		28.6 (2)		0 (0)		0 (0)		28.6 (2)		0 (0)		0 (0)		0 (0)
Reference population															
Sex	1: Female (n = 21)	0.482	9.6 (2)	**0.005**	14.3 (3)	-	4.8 (1)	**0.025**	19.1 (4)	-	9.6 (2)	-	N.D.	-	N.D.
	2: Male (n = 24)		16.7 (4)		54.2 (13)		0 (0)		0 (0)		4.2 (1)		N.D.		N.D.
Age	1: <30 yrs. (n = 10)	**0.015**	0 (0)	0.792	30.0 (3)	-	0 (0)	0.191	20.0 (2)	-	0 (0)	-	N.D.	-	N.D.
	2: 30 - 50 yrs. (n = 15)		0 (0)		40.0 (6)		0 (0)		13.4 (2)		13.4 (2)		N.D.		N.D.
	3: >50 yrs. (n = 17)		29.5 (5)		29.5 (5)		5.9 (1)		0 (0)		5.9 (1)		N.D.		N.D.
Location	1: Zone 1 (n = 32)	**0.028**	6.3 (2)	0.669	37.5 (12)	-	0 (0)	0.182	12.5 (4)	-	3.2 (1)	-	N.D.	-	N.D.
	2: Zone 2 (n = 13)		30.8 (4)		30.8 (4)		7.7 (1)		0 (0)		15.4 (2)		N.D.		N.D.

[a] Results for: o,p'-DDT and p,p'-DDD are presented as the sum of the concentrations of these two target analytes as the analytical protocol did not achieved separation of these molecules.

8.3.4 Trends observed in pesticide concentrations

Pesticide concentration levels, measured in hair samples, were compared within the same sub-groups as in section 8.3.3. Values are only presented for concentration levels higher than the LOQ (Table 8:4). Since some of the samples had concentrations that were detectable but not quantifiable (i.e. LOD < sample concentration < LOQ), less data was available. Target substances with fewer than 8 samples with quantifiable levels were not considered suitable for statistical analysis, and were not included (SI Table S5).

In the overall studied population, the sum of alpha- & beta-cypermethrin had the highest median concentration (429.2 pg mg^{-1}) and the sum of o,p'-DDT & p,p'-DDD (6.3 pg mg^{-1}) showed the lowest median concentration.

The activity of gardening was found to induce significantly higher concentrations of acetamiprid and cypermethrins in hair samples. Sex (female) was a relevant factor when considering exposure to imidacloprid in overall and occupationally exposed populations. Females also presented higher concentration of lambda-cyhalothrin when considering the overall population. In the case of o,p'-DDT & p,p'-DDD, male samples presented higher concentrations (overall population). Age did not significantly affect pesticide concentration in hair. Geographical location had an influence on concentration of acetamiprid in overall and occupationally exposed populations and on concentration of gamma-trans-chlordane in overall and reference populations. The basic PPE used by gardeners did not significantly influence pesticide concentrations in hair.

Figure 8:6 compares levels measured in the present work to maximum levels detected in the literature (numerical data and sources are presented in SI Table S6). No previous detection in human samples was found for acetamiprid, atrazine, DEA, carbofuran, and deltamethrin. Except for DDT and its metabolites, levels measured in this study exceeded maximum concentrations reported in the literature.
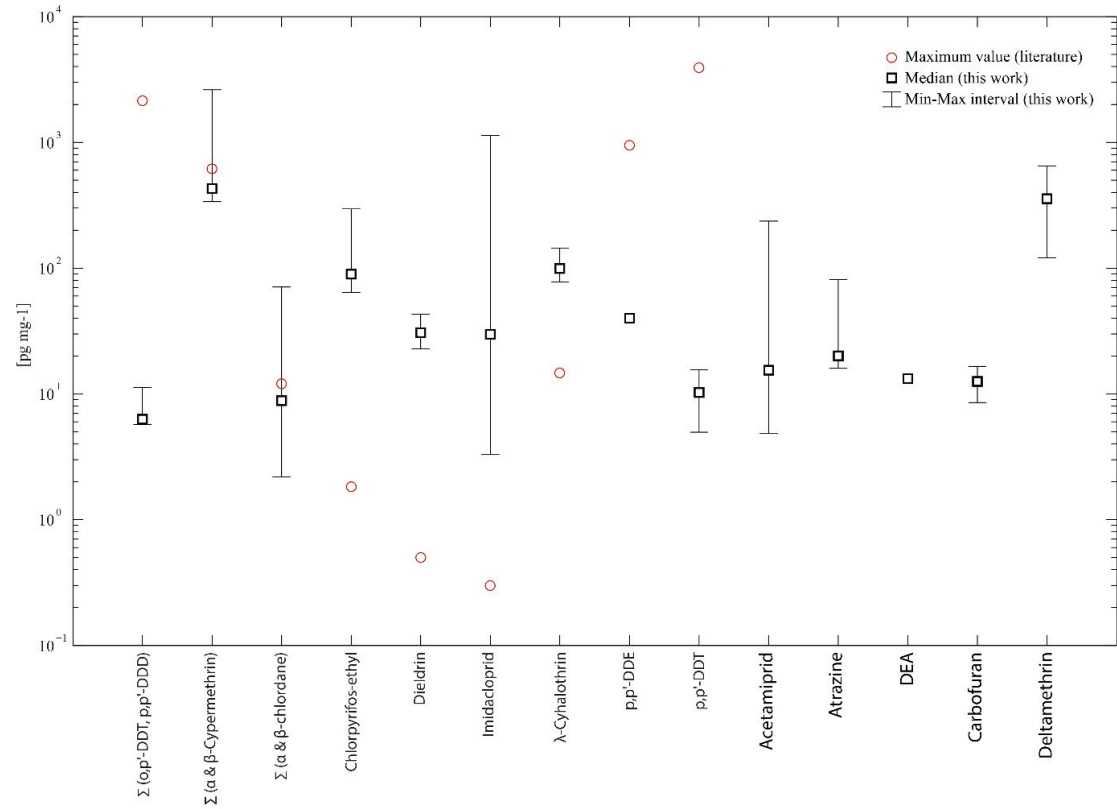
Figure 8:6 Comparison between concentrations found in this work and maximum concentrations reported in the literature for pesticide analysis in human hair
(median value (this work) for p,p'-DDE corresponds to the LOD, as no quantifiable level was found).

Biomonitoring of pesticide exposure using hair as an indicator

Table 8:4 Median, minimum, and maximum concentrations (pg mg^{-1}) of target analytes and results of Kruskal-Wallis tests (n = number of samples, *N.D.*: Not Detected)

Studied population (overall)

Group	Description	Acetamiprid p Value	Acetamiprid Median	Acetamiprid Min - Max	Imidacloprid p Value	Imidacloprid Median	Imidacloprid Min - Max	λ-Cyhalothrin p Value	λ-Cyhalothrin Median	λ-Cyhalothrin Min - Max	Σ (α- & β-Cypermethrin) p Value	Σ (α- & β-Cypermethrin) Median	Σ (α- & β-Cypermethrin) Min - Max
Total	n = 101		15.4 (51)	4.8 - 236.5		29.8 (90)	3.3 - 1133.6		99.2 (9)	77.8 - 143.4		429.2 (16)	337.9 - 2618.5
Activity	1: Gardening (n = 56)	0.053	25.2 (34)	4.8 - 236.5	0.114	36.5 (54)	4.5 - 637.6	0.796	99.2 (6)	78.6 - 143.4	0.023	634.3 (10)	355.0 - 2618.5
	2: Other (n = 45)		7.8 (17)	5.6 - 69.0		22.3 (36)	3.3 - 1133.6		124.3 (3)	77.8 - 127.4		374.9 (6)	337.9 - 451.4
Sex	1: Female (n = 41)	0.550	13.9 (20)	5.6 - 236.5	0.007	46.1 (36)	3.3 - 1133.6	0.027	127.4 (5)	99.2 - 143.4	0.083	705.7 (6)	374 - 2618.5
	2: Male (n = 60)		17.8 (31)	4.8 - 169.6		20.4 (54)	4.4 - 637.6		86.3 (4)	77.8 - 99.2		392.2 (10)	337.9 - 759.3
Age	1: <30 yrs. (n = 15)	0.355	26.7 (7)	6.4 - 114.6	0.317	46.5 (12)	10.9 - 637.6	0.449	127.4 (1)	127.4	0.329	759.3 (1)	759.3
	2: 30 - 50 yrs. (n = 52)		17.8 (27)	4.8 - 182.7		36.5 (46)	3.3 - 542.2		99.2 (5)	78.6 - 136.5		634.3 (8)	348.0 - 2618.5
	3: >50 yrs. (n = 30)		8.4 (14)	5.6 - 236.5		21.2 (28)	4.4 - 203.0		124.3 (3)	94.0 - 143.4		382.4 (4)	359.0 - 527.2
Location	1: Zone 1 (n = 66)	0.024	26.8 (31)	5.6 - 236.5	0.590	31.3 (58)	3.3 - 637.6	0.796	127.4 (3)	77.8 - 136.5	0.753	412.7 (8)	337.9 - 2618.5
	2: Zone 2 (n = 35)		9.8 (20)	4.8 - 71.8		29.3 (32)	4.4 - 1133.6		99.2 (6)	78.6 - 143.4		467.1 (8)	359.0 - 759.3

Occupationally exposed population (Operators)

Group	Description	Acetamiprid p Value	Acetamiprid Median	Acetamiprid Min - Max	Imidacloprid p Value	Imidacloprid Median	Imidacloprid Min - Max	λ-Cyhalothrin p Value	λ-Cyhalothrin Median	λ-Cyhalothrin Min - Max	Σ (α- & β-Cypermethrin) p Value	Σ (α- & β-Cypermethrin) Median	Σ (α- & β-Cypermethrin) Min - Max
Sex	1: Female (n = 20)	0.593	15.4 (11)	6.0 - 236.5	0.010	55.4 (19)	5.0 - 512.4	0.127	136.5 (3)	99.2 - 143.4	0.136	1305.4 (4)	374.0 - 2618.5
	2: Male (n = 36)		26.8 (23)	4.8 - 169.6		20.6 (35)	4.5 - 637.6		94.0 (3)	78.6 - 99.2		565.2 (6)	355.0 - 759.3
Age	1: <30 yrs. (n = 5)	0.600	18.7 (4)	6.4 - 114.6	0.323	51.1 (5)	17.3 - 637.6	0.643	*N.D.*	-	0.407	759.3 (1)	759.3
	2: 30 - 50 yrs. (n = 37)		27.7 (22)	4.8 - 182.7		38.6 (35)	5.0 - 542.2		99.2 (4)	78.6 - 136.5		665.2 (7)	355.0 - 2618.5
	3: >50 yrs. (n = 13)		9.0 (7)	5.8 - 236.5		20.6 (13)	4.5 - 163.9		118.7 (2)	94.0 - 143.4		450.6 (2)	374.0 - 527.2
Location	1: Zone 1 (n = 34)	0.044	32.3 (22)	5.9 - 236.5	0.950	40.0 (33)	4.5 - 637.6	0.380	136.5 (1)	136.5	0.602	959.9 (5)	355.0 - 2618.5
	2: Zone 2 (n = 22)		10.8 (12)	4.8 - 71.8		31.2 (21)	8.7 - 542.2		99.2 (5)	78.6 - 143.4		603.3 (5)	393.6 - 759.3
PPE	1: Arms or legs covered (n = 13)	0.582	11.7 (8)	5.9 - 182.7	0.245	55.4 (13)	5.0 - 512.4	0.770	99.2 (1)	99.2	0.580	1610.9 (2)	603.3 - 2618.5
	2: Arms & legs covered (n = 36)		26.8 (23)	4.8 - 150.5		23.2 (35)	4.5 - 637.6		99.2 (5)	78.6 - 143.4		596.2 (6)	355.0 - 1650.9
	3: no PPE (n = 7)		49.1 (3)	10.7 - 236.5		36.7 (6)	5.6 - 353.6		<LOQ	-		667 (2)	374.0 - 959.9

Reference population

Group	Description	Acetamiprid p Value	Acetamiprid Median	Acetamiprid Min - Max	Imidacloprid p Value	Imidacloprid Median	Imidacloprid Min - Max	λ-Cyhalothrin p Value	λ-Cyhalothrin Median	λ-Cyhalothrin Min - Max	Σ (α- & β-Cypermethrin) p Value	Σ (α- & β-Cypermethrin) Median	Σ (α- & β-Cypermethrin) Min - Max
Sex	1: Female (n = 21)	0.501	7.8 (9)	5.6 - 69.0	0.124	43.3 (17)	3.3 - 1133.6	0.221	125.8 (2)	124.3 - 127.4	0.064	429.2 (2)	407.1 - 451.4
	2: Male (n = 24)		8.0 (8)	5.6 - 46.1		15.7 (19)	4.4 - 112.7		77.8 (1)	77.8		353.5 (4)	337.9 - 390.8
Age	1: <30 yrs. (n = 10)	0.511	42.1 (3)	6.7 - 54.0	0.867	43.3 (7)	10.9 - 136.1	0.368	127.4 (1)	127.4	0.221	*N.D.*	-
	2: 30 - 50 yrs. (n = 15)		8.4 (5)	5.6 - 69.0		19.7 (11)	3.3 - 132.4		77.8 (1)	77.8		348 (1)	348.0
	3: >50 yrs. (n = 17)		7.8 (7)	5.6 - 46.1		24.0 (15)	4.4 - 203.0		124.3 (1)	124.3		374.9 (2)	359 - 390.8
Location	1: Zone 1 (n = 32)	0.248	8.4 (9)	5.8 - 69.0	0.571	20.6 (25)	3.3 - 203.0	1.000	102.6 (2)	77.8 - 127.4	0.513	348.0 (3)	337.9 - 451.4
	2: Zone 2 (n = 13)		7.0 (8)	5.6 - 42.1		24.8 (11)	4.4 - 1133.6		124.3 (1)	124.3		390.8 (3)	359 - 407.1

Biomonitoring of pesticide exposure using hair as an indicator

Table 8-4 (continued) Median, minimum, and maximum concentrations of target analytes (pg mg^{-1}) and results of Kruskal-Wallis tests (n = number of samples, N.D.: Not Detected)

Studied population (overall)

Group	Description	Deltamethrin			γ-trans-Chlordane			Σ (o,p'-DDT, p,p'-DDD)[a]		
		p Value	Median	Min - Max	p Value	Median	Min - Max	p Value	Median	Min - Max
Total	n = 101		356.7 (12)	120.7 - 648.3		7.6 (34)	2.2 - 42.8		6.3 (8)	5.7 - 11.2
Activity	1: Gardening (n = 56)	1.000	401.1 (6)	120.7 - 648.3	0.719	5.5 (22)	2.2 - 42.8	0.297	5.8 (3)	5.7 - 10.8
	2: Other (n = 45)		356.7 (6)	256.8 - 510.3		9.8 (12)	2.2 - 21.0		6.4 (5)	5.9 - 11.2
Sex	1: Female (n = 41)	0.570	381.2 (7)	133.2 - 634.3	0.427	5.1 (16)	2.2 - 42.8	**0.053**	5.8 (3)	5.7 - 6.1
	2: Male (n = 60)		282.5 (5)	120.7 - 648.3		10 (18)	2.3 - 32.9		10.4 (5)	5.9 - 11.2
Age	1: <30 yrs. (n = 15)	0.338	510.3 (3)	332.2 - 634.3	0.764	4.9 (5)	2.2 - 16.9	0.289	<LOQ	-
	2: 30 - 50 yrs. (n = 52)		393.5 (6)	120.7 - 648.3		5.2 (16)	2.3 - 42.8		5.8 (3)	5.7 - 10.8
	3: >50 yrs. (n = 30)		256.8 (3)	133.2 - 381.2		9.8 (11)	2.2 - 32.9		8.3 (4)	5.9 - 11.2
Location	1: Zone 1 (n = 66)	0.685	381.2 (5)	189.8 - 612.4	**0.016**	4.9 (22)	2.2 - 33.4	1.000	6.3 (2)	6.1 - 6.4
	2: Zone 2 (n = 35)		282.5 (7)	120.7 - 648.3		14.2 (12)	2.3 - 42.8		8.1 (6)	5.7 - 11.2

Occupationally exposed population (Operators)

Group	Description	Deltamethrin			γ-trans-Chlordane			Σ (o,p'-DDT, p,p'-DDD)[a]		
		p Value	Median	Min - Max	p Value	Median	Min - Max	p Value	Median	Min - Max
Sex	1: Female (n = 20)	0.827	612.4 (3)	133.2 - 634.3	1.000	4.5 (10)	2.2 - 42.8	0.221	5.7 (2)	5.7 - 5.8
	2: Male (n = 36)		189.8 (3)	120.7 - 648.3		5.9 (12)	2.3 - 32.9		10.8 (1)	10.8
Age	1: <30 yrs. (n = 5)	0.526	634.3 (1)	634.3	0.524	13.5 (2)	10.1 - 16.9	-	<LOQ	-
	2: 30 - 50 yrs. (n = 37)		401.1 (4)	120.7 - 648.3		5.4 (15)	2.3 - 42.8		5.8 (3)	5.7 - 10.8
	3: >50 yrs. (n = 13)		133.2 (1)	133.2		2.6 (5)	2.2 - 32.9		<LOQ	-
Location	1: Zone 1 (n = 34)	1.000	401.1 (2)	189.8 - 612.4	0.217	4.9 (15)	2.2 - 33.4	-	N.D.	-
	2: Zone 2 (n = 22)		383.7 (4)	120.7 - 648.3		16.9 (7)	2.3 - 42.8		5.8 (3)	5.7 - 10.8
PPE	1: Arms or legs covered (n = 13)	0.526	133.2 (1)	133.2	0.837	11.7 (4)	2.2 - 42.8	1.000	8.2 (2)	5.7 - 10.8
	2: Arms & legs covered (n = 36)		401.1 (4)	120.7 - 648.3		5.9 (16)	2.3 - 33.4		<LOQ	-
	3: no PPE (n = 7)		634.3 (1)	634.3		4.4 (2)	3.1 - 5.6		5.8 (1)	5.8

Reference population

Group	Description	Deltamethrin			γ-trans-Chlordane			Σ (o,p'-DDT, p,p'-DDD)[a]		
		p Value	Median	Min - Max	p Value	Median	Min - Max	p Value	Median	Min - Max
Sex	1: Female (n = 21)	1.000	356.7 (4)	256.8 - 510.3	0.078	6.7 (6)	2.2 - 13.5	0.480	6.1 (1)	6.1
	2: Male (n = 24)		393.5 (2)	282.5 - 504.5		10.7 (6)	4.9 - 21.0		8.4 (4)	5.9 - 11.2
Age	1: <30 yrs. (n = 10)	0.565	421.3 (2)	421.3	**0.037**	4.5 (3)	2.2 - 4.9	-	N.D.	-
	2: 30 - 50 yrs. (n = 15)		393.5 (2)	393.5		3.7 (1)	3.7		N.D.	-
	3: >50 yrs. (n = 17)		319.0 (2)	256.8 - 381.2		10.4 (6)	8.8 - 21.0		8.3 (4)	5.9 - 11.2
Location	1: Zone 1 (n = 32)	0.275	381.2 (3)	332.2 - 510.3	**0.028**	4.9 (7)	2.2 - 11.0	0.564	6.3 (2)	6.1 - 6.4
	2: Zone 2 (n = 13)		282.5 (3)	256.8 - 504.5		12.9 (5)	9.7 - 21		10.4 (3)	5.9 - 11.2

[a] Results for: o,p'-DDT and p,p'-DDD are presented as the sum of the concentrations of these two target analytes as the analytical protocol did not achieved separation of these molecules

8.4 Discussion

Results from hair analysis were expressed as percentage of positive samples (>LOD) and median concentrations for quantifiable samples (>LOQ). Differences between these two datasets for certain pesticides emphasized the need for low quantification limits and large study populations to conduct reliable statistical analysis. A sound example is p,p'-DDE which was largely detected (n = 25), but could not be quantified. Statistical analyses performed on both datasets (Table 8:3 and Table 8:4) did not show any opposite trends but instead revealed complementary information. The difference in exposure between operators and reference population were only significant for acetamiprid in both datasets. For the other substances, prevalence of positive samples and differences in median concentrations within subgroups were used indistinctively to describe the influence of retained parameters on pesticide exposures (occupational exposure, sex, age, location, and PPE).

Cash crops, such as cereals, cotton, rice, etc. are grown during the wet season from June to September, under the Sudano-Sahelian climate. Sampling took place during the dry season (February 2016), during which only vegetables are grown. This period was retained in an attempt to evaluate occupational exposure of vegetable growers. During this period, market gardening was the only occupational activity implying pesticide application in the study area. Therefore, it was not surprising that acetamiprid, lambda-cyhalothrin, and cypermethrin significantly prevailed in the occupationally exposed population. The gardeners reported using acetamiprid and cypermethrin which, along with lambda-cyhalothrin, were among the most commonly used pesticides in gardening in Burkina Faso (Son et al., 2017; Wendé Alice Naré, 2015). The survey conducted from 2013- to 2015 with 384 gardeners around Loumbila Lake (Chapter 4) reported that these three active ingredients were used in 86% of the cases. On the other hand, in the present work, 36% of the gardeners reported using imidacloprid, but no significant difference was identified between exposure of the operators and the reference population. Suitability of the analytical procedure is not at stake, as imidacloprid was detected and quantified in the overall population in more than 90% of the samples (never in procedural blanks). The absence of distinction between the exposed and reference populations was attributed to environmental contamination by imidacloprid, which is ubiquitous in the study area. A previous study underlined the presence of imidacloprid residues in vegetables produced and consumed around Loumbila Lake (Lehmann et al., 2017d, Chapter 6). Residues were also found in drinking water resources. A three-year investigation of the lake revealed the presence of imidacloprid throughout the year. Moreover, almost every sample from traditional wells (n = 26) in gardening areas were positive for this pesticide (Lehmann et al., 2017a, Chapter 5). It is noteworthy that these studies also reported acetamiprid, lambda-cyhalothrin, and cypermethrin in vegetables and water samples. Nevertheless, even if these pesticides were ubiquitous in food, they were more occasionally detected in water samples. Under these conditions, one could argue that water was the main environmental source of imidacloprid exposure. Additionally, as most of the food consumed in the area is boiled or fried, processing could have reduced dietary intake from vegetables (Lehmann et al., 2017d, Chapter 6).

Although previous studies underlined the contamination of drinking water resources in the study area by atrazine and its metabolites (Lehmann et al., 2017a, Chapter 5), they were not frequently detected ($<5\%$) in hair samples. These findings are in accordance with the low incorporation (even at high doses) of atrazine and deisopropylatrazine (DIA) into hair observed by Hubbard (2001). This also suggested that hair might not be a suitable matrix for biomotoring chronic exposure to these substances. More research is needed to understand the mechanisms of incorporation of triazines into hair.

Some commercial pesticide formulations containing chlorpyrifos ($n = 4$) and deltamethrin ($n = 3$) as active ingredients are authorized by the CSP. No significant difference was observed between operators and the reference population for these pesticides. Deltamethrin was detected in 12 samples, with a median concentration of 356.7 pg mg^{-1}, and 45% of the operators reported using it. This pesticide was also used in the country to treat mosquito nets for malaria prevention. A study showed that adults (manly women) in charge of handling (hanging, washing and re-impregnating) insecticide-treated mosquito nets exhibited side effects that could potentially be linked to deltamethrin intoxication (Lu et al., 2015). Although intoxication was not confirmed, exposure is inevitable. Therefore, deltamethrin exposure in the study area could have also occurred at household level, explaining the concentrations measured and the absence of significant difference between studied populations living in the same area. For this reason, we recommend collecting information regarding vector control methods used by the participants in questionnaire surveys in further research. For chlorpyrifos, lower use and low levels detected in hair (16 positive samples and 5 quantifiable ones) might explain failure to differentiate population exposures.

Organochlorine pesticides including chlordane (alpha and gamma isomers), dieldrin, o,p'-DDT, p,p'-DDT, p,p'-DDD, and p,p'-DDE were detected in hair samples mainly originating from Zone 2. Prevalence of p,p'-DDE in the reference population might indicate the use of DDT in other crop production, such as cotton, cereals, etc. during the rainy season. While, this could be a possible explanation, only one respondent reported working in such productions. As aforementioned, these pesticides are prohibited in the country as part of the ratified Stockholm convention. Even if age was significant only for o,p'-DDT & p,p'-DDD exposure (p value = 0.015), it is noteworthy that these persistent organochlorines were mainly found in older age-classes (>30 years old). As these pesticides have been banned since 2004, their detection in hair might be the consequence of past use (accumulation in the body) or remnants in the environment (traces of DDT and its metabolites, and chlordane isomers were detected in the water of the study area in 2016 (Chapter 5)). The quasi-absence of detection of the parent compound p,p'-DDT ($n = 2$), in comparison to its metabolite p,p'-DDE ($n = 25$) was also supportive that exposure occurred a certain time ago. Although p,p'-DDT is metabolized to p,p'-DDE into the body, it is worth noting that previous studies usually reported the detection of the parent compound together with its metabolites (Altshul et al., 2004; Wielgomas et al., 2012). Wielgomas et al. (2012) detected DDT and its metabolites in hair samples collected in Poland in 2009. The detection of these substances in hairs, almost 40 years after they were banned in Poland, suggests that detection in hair could be the consequence of the remanence in the body or the environment (i.e. passive exposure). In Burkina

Faso, national inventories of POP stockpiles conducted in 2001 and 2004 underlined the fraudulent disappearance of obsolete stocks and the presence of DDT in unauthorized mosquito repellents (MECV, 2005b). It is also to be noted that over the past 20 years, 13 African countries have been granted a specific exemption from the Stockholm Convention for the use of DDT in vector control (Stockholm Convention, 2017). Contamination from surrounding countries by atmospheric transport could also be suspected, as well as illegal importations due to the lack of controls. In the case of recent atmospheric contamination, the prevalence of p,p'-DDE is likely to originate from metabolization of the parent compound into the body. On the other hand, the detection of dieldrin more likely indicates a fraudulent application on cultures or at household level. Dieldrin was recently detected on vegetables (Lehmann et al., 2017d, Chapter 6) and in wood-protection products (MECV, 2007). These findings emphasized the lack of controls and monitoring of the enforcement of national and international policies.

Although the study area reported no use of the 10 organochlorine pesticides presented in section 3.1, they were added for screening purpose as part of the Annex A of the Stockholm Convention. To our knowledge, this study presents the first analysis of endrin aldehyde, endrin ketone, and endosulfan sulfate in hair. Nevertheless, none of the 10 organochlorines added to the protocol was detected in field samples. When values existed, the present analytical procedure did not allow for reaching the low LOD presented in previous studies. Applying a more sensitive method should be explored in further studies and might result in positive detection as endosulfan was already detected in the study area (Lehmann et al., 2017d, Chapter 6).

Imidacloprid, lambda-cyhalothrin, and chlorpyrifos-ethyl prevailed in female samples while, cypermethrin, o,p'-DDT & p,p'-DDD, and p,p'-DDE prevailed in male samples. A census conducted in the study area reported that women represented about 40% of the active population in gardening markets (Agence de l'eau du Nakambé, 2014). This proportion is in accordance with the results from the random sampling of the study population in this work. The quasi-equal implication in fieldwork did not explain differences observed in exposure between genders. However, women generally perform activities such as vector control and picking, sorting, and selling vegetables, which could explain the prevalence of pesticides used in the study area. Altshul et al. (2004) also observed significant differences between accumulated amounts of organochlorines in female and male hair (higher levels in female samples) but did not discuss their origins. Covaci et al., (2008) also reported higher DDTs content in women hair compared to men. This difference was attributed to the use of cosmetic products containing lanoline, prone to be contaminated with DDT. Lanoline was also present in cosmetic products used in the study area (trade name: Soft-Hair). The opposite gender repartition found for these substances in the present work might indicate that contamination is more likely to be the result of past use (men were previously more represented among farmers), rather than the use of cosmetics, which is mainly restricted to women in the study area. More research is needed to define if this phenomenon could be explained by physiological mechanisms, particular usages, or environmental exposures.

Survey results showed a lack of suitable protective equipment. Only ordinary clothes and rudimentary complementary equipment were used. According to EFSA (2014), light clothing should

reduce body exposure by 50%. In this study, covering the arms and legs with ordinary clothes had a negative or non-significant impact on preventing exposure. One explanation could be that observations made in the field indicated different behaviors. Operators did not always wear long sleeves and long pants. During intense heat waves, it was common to see gardeners applying pesticides barefooted, wearing only shorts and a tee shirt (Lehmann et al., 2016).

Application technique is also of concerns. Almost every participant reported using a knapsack sprayer. Nevertheless, previous studies (Wendé Alice Naré, 2015) and field surveys conducted in the study area between 2014 and 2015 (including 160 gardeners, Chapter 4) support the fact that more than 40% of the operators either permanently or occasionally use a broom or leaves to apply pesticides. Peer pressure and trying to hide unconventional practices might have biased the answers of the participants during questionnaire surveys.

These working practices are representative of the lack of knowledge/training regarding the good agricultural practices (GAP) already observed in rural areas in Burkina Faso (Ouédraogo et al., 2011; Son et al., 2017; Wendé Alice Naré, 2015). They could also explain the higher levels measured in the present work compared to previous studies. However, larger differences were expected between the operators and the reference population, regarding the poor application of the GAP and little care taken in handling pesticides (no PPE used for loading, mixing and application). Lambda-cyhalothrin is a sound example, as percent of positive samples (23%) indicated prevalence in the occupationally exposed population but no significant difference could be derived from measured concentrations in occupationally exposed and reference populations. As the studied populations originated from the same area, similarities might indicate an important contributions of environmental routes of exposure, such as dietary intake (water and food) and atmospheric exposure (inhalation and particulate deposition). The kinetics of pesticide incorporation into hair shaft are also poorly known. Wielgomas et al. (2012) demonstrated the stability of DDT and its metabolites incorporated into hair, but Altshul et al. (2004) observed a negative correlation between blood and hair levels for o,p'-DDE. Hubbard (2001) found that concentrations of atrazine and DIA increased in hair a few hours after exposure until it reached a maximum after approximatively 8 hours. This accumulation was followed by a decreasing phase, which reached a plateau in 3 days. Coupled with the possible impact of cosmetics and shampoo on internally incorporated substances, time since last exposure (TSLE) might influence concentrations in hair. It is worth noting that this study mainly focused on pesticide parent compounds. However pesticides undergo metabolization processes when entering the body (Kavvalakis et al., 2013; Kavvalakis and Tsatsakis, 2012). Therefore, part of the pesticide systemic dose might be metabolized before being accumulated into hair. Analyzing target pesticides metabolites could provide additional information on population exposure (e.g. better differentiation between occupationally exposed and reference populations) and should be explored in further studies. However, some metabolites are not specific (Kavvalakis and Tsatsakis, 2012). In this work, parent compounds were preferred as causal links are easier to establish with actual pesticide uses and routes of exposure. Previous studies support that pesticide parent compounds can be used as indicators for biomonitoring (Covaci et al., 2008; Kavvalakis et al., 2013; Tsatsakis et al., 2008; Wielgomas et al., 2012). As aforementioned, volunteers generally

had short hair. The collection of newly grown hair might explain the high frequency of detection of the parent compounds of pesticides used in the study area (i.e. acetamiprid, cypermethrin, imidacloprid, etc.). As exposure and accumulation likely occurred not long before sample collection, lower degradation of the incorporated amounts (internal and external) is expected (e.g. from metabolization, shampoo, cosmetic products, etc.). The sampling period could also influence pesticide accumulation. Samples were collected at the beginning of the growing period. Repeated exposure might also affect the amount of pesticide accumulated in hair (Kavvalakis et al., 2013). Assessment of pesticide concentrations in hairs at the end of the growing season (in June) might show different patterns. In this study, it was found that concomitant analysis of the prevalence of positive samples could complement information when concentrations failed to provide a clear tendency. Multiple sampling campaigns and taking into account the TSLE in further studies could give more information on incorporation dynamics in hair.

Finally, hairs was found to be a particularly convenient matrix for biomonitoring exposure in the study area. Safe collection that was, suitable for further analysis could be easily achieved by nontechnical staff. Storage at room temperature was also a major advantage of this matrix and more particularly in rural tropical areas with warm temperatures and no electricity. Multiresidue analysis allowed for screening a large number of pesticides (i.e. 38) in a single sample. This screening approach is particularly important in rural areas with low education levels and poor knowledge of the GAP. Indeed, illiteracy and lack of training regarding pesticides lead to irrational use in terms of doses, application frequency, and crop-pesticide associations (Ouédraogo et al., 2011; Son et al., 2017; Wendé Alice Naré, 2015). Although hair is considered by scientists as a non-invasive matrix, it is to be noted that it might not be in certain traditional cultures. Hair might have a certain importance in traditional beliefs, limiting accessibility even for scientific purposes. Therefore, it is essential to include the studied population in the early stages of the study design. Efforts must be directed toward a clear presentation of the objectives and the integration of the requests of the population regarding sample collection (location for sampling, sampling periods, etc.). In this study, local representatives of the population as well as traditional, religious, and administrative authorities were consulted before establishing a first contact with the study population. Each village was visited by the project team, prior to sample collection to define optimal sampling conditions. Thanks to clear communication and population integration in the early stages, no major difficulty was encountered. The same communication approach will be further used for onsite presentation of the results to stakeholders (i.e. local populations and authorities).

8.5 Conclusion

The selected approach achieved the screening of 38 pesticides in human hairs. Subdivision of studied populations into specific subgroups was found pertinent to assess relevant factors influencing exposure. Combining analyses of prevalence of positive samples and concentrations allowed for a better understanding of causal links. Trends observed in pesticides accumulation/detection in hairs were consistent with field observations and responses reported during surveys (except for application equipment and PPE). This study successfully detected 17 pesticides and quantified

residues from 16 pesticides. To our knowledge, it is the first detection of acetamiprid, atrazine, DEA, carbofuran, and deltamethrin in field samples. As expected, exposure to pesticides used in gardening was more significant for operators. Screening of other substances also indicated exposure to unauthorized pesticides. This exposure prevailed in a certain area (Zone 2), indicating the possibility for identifying geographical patterns and target intervention. Levels detected are concerning because they indicated larger exposure than previously reported in the literature, as well as exposure to endocrine disrupting chemicals (WHO/UNEP, 2012a) and probable carcinogens chlordane (ATSDR, 2014), DDTs (U.S. EPA, 1988a), and dieldrin (U.S. EPA, 1988b).

To the best of our knowledge, this is the first use of hair as a matrix for biomonitoring pesticide exposure in western Africa. Although many studies focused on inventories of pesticides used in Burkina Faso (Gomgnimbou et al., 2009; Son et al., 2017; Toé, 2010d; Wendé Alice Naré, 2015), assessments of human and environmental exposure are still lacking. Hair was found to be a suitable matrix for biomotoring human exposure to pesticides and assessing national/international policy enforcement. Nevertheless, interpretation of the results from hair analysis is not always straightforward. More research is needed, particularly on incorporating mechanisms and kinetics of pesticide accumulation in hair.

Finally, this work underlines the poor application of the GAP, lack of suitable equipment for protection and application, and the large environmental exposure of the overall population of the study area. In general, similar agricultural practices were found in other gardening areas across the country. This study could be considered a preliminary assessment of human exposure to pesticides and conclusions might be extended to other areas. This approach could be also applied to other sites to be monitored to obtain a refined assessment accounting for the local context. In the light of these findings, suitable preventive measures must be taken to improve operator protection and reduce the populations' exposure. These include regulation and recommendations enforcement at every level, from national policy application to the respect of the GAP in the field. More incentive on law application and operator training are prerequisites to improving population safety.

Chapter 9 Risk assessment of operator, worker, and bystander pesticide exposure and recommendation proposal

Supplementary material:

Appendix G

Supplementary information are divided in five sections S1-S4 presenting Tables S1-S7.

Related dataset available at: https://doi.org/10.5281/zenodo.1050294

9.1 Introduction

In the previous chapters, pesticide burden in Burkina Faso was characterized using chemical analytical methods in various matrices. Findings are of concerns as they outlined many hazardous situations for the environment and human health. The present chapter aims to propose mitigation measures in order to reduce human exposure to pesticide in the study area. The analytical approach was effective in providing a sound assessment of the current situation but is limited when it comes to foresee the impacts of mitigation measures. Predictive models offer a cost and time effective alternative to field experiments to predict human exposure to pesticide. Models are used worldwide to estimate the pesticide exposure of professional operators. In certain countries, they are also an integral part of the risk assessment during approval of plant protection products (PPP) and substances in PPP. To date, no harmonized procedure exists (Großkopf et al., 2013). Several models and exposure datasets have been developed for specific geographic areas and contexts, e.g. the German Model (Lundehn et al., 1992), the UK predictive operator exposure model (UK-HSE, 2017), the Occupational Pesticide Handler Unit Exposure Surrogate Reference Table (OPHED) used in the United States of America (U.S. EPA, 2016), etc. Unfortunately, no specific exposure model and dataset exist for the Sahelian region. To our knowledge, in Africa, only Ethiopia has developed a specific decision support system for assessing pesticide risk for operators and workers in greenhouses (Wilpfler et al., 2014).

In the absence of specific model, generic datasets developed by international bodies such as the United Nations are often used as an alternative. For this reason, an attempt was made to assess pesticide exposure in market gardening in Burkina Faso using the Generic Risk Assessment Model for Indoor and Outdoor Space Spraying of Insecticides (WHO, 2011b). However, this model was primarily designed for the risk assessment of operators and residents during space spraying activities to control vector-borne diseases. Space spraying differs from pesticide application techniques used in agriculture. It is based on the principle of dissemination of small particles that will remain airborne sufficiently long to make contact with flying target species. Because this type of treatment is not intended to leave a residual deposit, it involves a very low dosage of insecticide (WHO, 2011b). These characteristics are the main differences with spraying in agriculture where the substance is intended to reach its target crop as fast as possible and remain effective a certain time in order to avoid further pest attacks or disease outbreaks. However, the population exposure is expected to occur from similar sources and through similar routes. This modeled was therefore tested in an attempt to use generic exposure datasets. For simplification, it is referred as "WHO 2011" in the following sections.

As the representativeness of the aforementioned model to the local context is questionable, the two other models tested in the present work have been designed specifically for exposure assessment to pesticides in agriculture. They are European based and were retained as being the state of the art in this geographical area. The first one is called HArmonized environmental Indicators for pesticide Risk (HAIR) and is referred as "HAIR2014" in the present document (Kruijne et al., 2011). It is an update of the initial version issued in 2007 (Garreyn et al., 2007) in an attempt to

homogenize pesticide exposure estimation and risk assessment for operators, bystanders, residents, and workers in Europe. This model is principally based on the EUROPOEM (I&II) databases containing monitored exposure studies relevant to PPP in European agriculture (EUROPOEM, 1996; EUROPOEM II, 2002). In 2014, the EFSA (European Food Safety Authority) Panel on Plant Protection and their Residues issued a new guidance document that supports the use of a new predictive agricultural operator exposure model (EFSA, 2014). It was developed to pursue the harmonization effort and to provide an updated approach, more consistent with the current state of the technique. It is based on a statistical analysis of 34 exposure studies conducted between 1999 and 2009 (Großkopf et al., 2013). The guidance document proposes several models adapted to pesticide application techniques and exposure assessment of operators, bystanders, residents, and workers. For simplification, it is referred as "EFSA 2014" in the following sections.

Operators, bystanders, residents, and workers were included in the present risk assessment. Exposure estimation was conducted with the algorithms provided in models' documentation (EFSA, 2014; Kruijne et al., 2011; WHO, 2011b). Models use a tiered approach. In higher tiers, scenarios and parameters can be adapted to specific situations. In order to supply the models with local data, a survey was conducted on 284 gardeners, 31 resellers, and 27 health care centers located in the four gardening areas presented in section 4.2.1 (Loumbila, Dem, Ziga, and Nariarlé Basin). Models suitability and limitations were discussed regarding generic and local considerations. Finally, simulations were used to assess the impact reduction from the proposed mitigation measures under various scenarios. The outcomes allowed suggesting recommendations and prioritizing the actions that need to be taken to reduce health hazard in the studied areas.

9.2 Description of studied populations and exposure calculation

9.2.1 Studied population and data collection

Low education level was reported among rural populations in Burkina Faso. High illiteracy rate and lack of training drastically hamper compliance with the good agricultural practices. Recommendations provided on manufacturers' labels are rarely followed which result in irrational use in terms of doses, frequency of application, and crop-pesticide associations (Ouédraogo et al., 2011; Son et al., 2017; Wendé Alice Naré, 2015). Under these conditions, consideration of generic scenarios proposed in model documentation is not possible. Field surveys were conducted to collect data representative of local agricultural practices. Specific questionnaires directed toward three groups of actors: pesticide users (gardeners), distributors, and health care centers have been prepared to fully assess the subtleties of each actor. The two-year survey conducted during the growing season (February-May 2014-2015) allowed to collect data from 284 gardeners, 31 resellers, and 27 health care centers located around the lake of Loumbila, Ziga, Dem, and in the Nariarlé Basin. These four areas are characterized by intense market gardening activities (large surfaces and populations concerned).

Results from gardener surveys were used in risk assessment for exposure calculation (frequency of application, concentration/dilution of active substance (a.s.), personal protective equipment, etc.). Pesticide reseller surveys allowed gathering formulations information (recommended dose/frequency of application, a.s. concentration, etc.) from original manufacturer labels. Answers from medical staff were used to assess the actual health condition of the populations and were compared to estimated risk.

Data collected from field surveys always present gaps. They have been attributed to the willingness to answer and knowledge of the respondents, the understanding of the translator and the availability of the information. For the latter, it is worth noting that quality and availability of information concerning pesticide dosage was a recurrent issue. For example, recommended dose/dilution, frequency of application, etc. were not always available even on original manufacturer labels. To date, risk assessment models do not allow estimating the exposure from solid pesticides (i.e. powder, granules, etc.). However, gardeners in the studied areas used mainly liquid pesticide formulations (~83%). The present work focused therefore exclusively on these type of formulations. Only data allowing application rate calculation for liquid pesticides (i.e. without gaps) were considered in model calculations and further risk assessment (161 gardeners).

9.2.2 Application rate and dilution calculation

Application rate (AR) corresponds to the daily quantity of pesticide applied per treated surface area (mg a.s. ha^{-1} d^{-1}). It is calculated as follow:

$$AR = \frac{CF \times V_{formulation}}{Area} \qquad\qquad 9{:}1$$

where CF is the concentration of the a.s. in the formulation (mg mL^{-1}), $V_{formulation}$ is the volume of formulation (mL) used per application and *Area* the surface of the treated area (ha).

Liquid pesticide formulations are diluted in water prior application. Spray concentration (CS in mg a.s. L^{-1}) was calculated as follow:

$$CS = \frac{CF \times V_{formulation}}{N_{reservoir} \times V_{reservoir}} \qquad\qquad 9{:}2$$

where CF is the concentration of the a.s. in the formulation (mg mL^{-1}), $V_{formulation}$ (mL) is the volume of formulation added to water, $V_{reservoir}$ is the volume of water (L) in the reservoir used for the dilution, and $N_{reservoir}$ is the total number of reservoirs used to apply pesticide on the treated area.

In practice, only few gardeners were able to directly quantify $V_{formulation}$. When respondents failed to provide an estimation, they were ask to present their measuring equipment. $V_{formulation}$ was then estimated by multiplying the volume of the dosing utensil by the number of doses added to

the reservoir. Volumes of screw caps from various commercial formulations were measured and used when gardener provided only the formulation name.

Regarding terminology used in the present work, compliance with "recommended dose, quantities or amount" is achieved when both application rate and spray concentration recommended by manufacturers are respected. In the following sections, when the parameter (application rate or concentration) is not mentioned, inclusion of both is assumed.

9.2.3 Current body protection calculation

Field surveys reported that personal protective equipment (PPE) wore during pesticide handling was limited to ordinary clothing (i.e. not chemical-resistant) not always covering legs and arms. According to EFSA (2014), light clothing provide a 50% reduction of exposure. In order to account for the coverage extend of the currently used outfit, a corrected penetration factor for body exposure ($PPE_{body\ Corr}$) was calculated as follow:

$$PPE_{body\ Corr} = 1 - 0.5 \left(\frac{\sum Body\ part\ surface\ areas\ \times\ \%\ covered}{Total\ body\ surface\ area} \right) \qquad 9{:}3$$

For gloves and head protection, generic penetration factors of 0.1 and 0.5 were used (EFSA, 2014).

9.2.4 Modelization of pesticide exposure

This work aimed to assess the suitability and compare outcomes of three currently used pesticide exposure models. HAIR model is distributed in a software package proposing a user interface adapted to European countries. EFSA guidance (EFSA, 2014) provides an Excel calculation spreadsheet for exposure calculations. Unfortunately, this spreadsheet does not support assessment of multiple scenarios in terms of substances and agricultural practices and does not allow risk characterization. No calculator has been provided for users of WHO 2011 model documentation. In order to handle the large dataset of this project, exposure calculation model algorithms (EFSA, 2014; Kruijne et al., 2011; WHO, 2011b) have been implemented in MATLAB 2017a (The MathWorks, Inc., Natick, Massachusetts, United States). Developed algorithm allowed more flexibility in accounting for local data collected during field surveys and assessment of complex scenarios in a harmonized approach. Exposure was calculated for the three actors presented in section 9.2.4. Risk characterization was performed in a common module developed for single and cumulative pesticide exposure assessment (section 9.2.5).

Retained exposure models include a large number of parameters, thus making it impossible to discuss them all separately (EFSA 2014: 71 parameters, HAIR2014: 75 parameters and WHO 2011: 36 parameters). The following sections focus on the presentation of the main exposure pathways and comment differences in exposure calculation between models. Only simplified generic equations are presented. Details on parameter definitions, units, and exposure algorithms are presented in appendix G (section S4).

9.2.4.1 Operator exposure

Operators are persons involved in activities related to application of plant protection products. Such activities include mixing/loading the product into the application equipment, operation of the application equipment, repairing the application equipment whilst it contains the product, and emptying/cleaning the equipment used (definition adapted from EFSA (2014)).

In practice, exposure will be influenced by the task performed but also several important factors: type of equipment used, formulation, packaging, environmental conditions, protective clothing, personal protective equipment, hygienic behavior, dual activities, and duration of activity (Garreyn et al., 2007). Model algorithms include parameters (22 for EFSA 2014, 21 for HAIR2014, and 16 for WHO 2011) that allow taking into account some of these factors and the variation of their influence under different scenarios. Knapsack sprayer was the most common application equipment used in the studied areas. In the absence of other type of machinery (boom sprayer, aerial application etc.), hand-held downward application with knapsack sprayer was retained as the unique application technique.

Simplified internal (or systemic) exposure (IE) calculations algorithms are presented below (for detailed algorithms see. appendix G (section S4)).

$$IE(Operator)_{EFSA} = \begin{bmatrix} Expo_{head} \times PPE_{head} \\ Expo_{body} \\ Expo_{hand} \\ Expo_{respi} \times PPE_{respi} \end{bmatrix}_{Mix/load} \times \begin{bmatrix} DA \\ DA \\ DA \\ IA \end{bmatrix} + \begin{bmatrix} Expo_{head} \times PPE_{head} \\ Expo_{body} \\ Expo_{hand} \\ Expo_{respi} \times PPE_{respi} \end{bmatrix}_{application} \times \begin{bmatrix} DA \\ DA \\ DA \\ IA \end{bmatrix} \qquad 9:4$$

$$IE(Operator)_{HAIR} = \left(\begin{bmatrix} Expo_{hand} \\ Expo_{respi} \end{bmatrix}_{Mix/load} \times \begin{bmatrix} PPE_{hand} \\ PPE_{respi} \end{bmatrix} \times \begin{bmatrix} DA \\ IA \end{bmatrix} + \begin{bmatrix} Expo_{hand} \\ Expo_{body} \\ Expo_{respi} \end{bmatrix}_{application} \times \begin{bmatrix} PPE_{hand} \\ PPE_{body} \\ PPE_{respi} \end{bmatrix} \times \begin{bmatrix} DA \\ DA \\ IA \end{bmatrix} \right) \times AR \qquad 9:5$$
$$\times Area$$

$$IE(Operator)_{WHO} = [Expo_{hand}(N)]_{Mix/load} \times CF \times PPE_{hand} \times DA + \begin{bmatrix} Expo_{hand} \\ Expo_{respi} \end{bmatrix}_{application} \times CS \times \begin{bmatrix} PPE_{hand} \\ PPE_{respi} \end{bmatrix} \times DA \qquad 9:6$$

where $Expo_{body\ part}$ is the exposure estimation for a given body part (mg a.s. d^{-1}), $PPE_{body\ part}$ is the penetration factor of the personal protective equipment used for a given body part (%), $respi$ stands for respiratory tract, DA is the dermal absorption (%), IA is the inhalation absorption (%), AR is the application rate (mg a.s. ha^{-1} d^{-1}), $Area$ is the surface area treated (ha^{-1}), N is the number of daily application (-), CF is the concentration of the a.s. in the formulation (mg mL^{-1}), and CS is the spray concentration (mg mL^{-1}).

Tested models consider the same routes for the estimation of operator exposure. Dermal and inhalation exposure are accounted for during mixing/loading of the spraying equipment and application onto crops. However, they differ in the consideration of exposed body parts and exposure calculation.

EFSA 2014 includes head, hand, body, and respiratory tract exposure. Head exposure is not included in HAIR2014 and WHO 2011 considers only hands and respiratory tract exposure. EFSA

2014 and HAIR2014 share almost the same algorithm for modeling operator exposure. The principal difference lies in the fact that EFSA 2014 knapsack model uses surrogate exposure values for exposure estimation independent of the application rate and the surface area treated. In this model, fixed surrogate exposure values are proposed for head, hands, body, and respiratory tract depending on PPE used and are assumed valid for any surface area treated with less than 1.5 kg a.s ha^{-1}. HAIR2014 includes application rate and treated surface area in exposure calculation and PPE are accounted for using penetration factors. WHO 2011 model was developed for vector control at household level. Surface area treated is therefore not considered and application rate is replaced by concentration of the a.s. in the spray. Instead of using fixed surrogate values, exposure is derived from calculated volume of a.s. on hands and inhaled. PPE are accounted for using penetration factors. In model simulations, dermal, inhalation, and ingestion exposure were respectively multiplied by dermal absorption, absorption of the respiratory tract, and gastrointestinal absorption to derive the systemic exposure (IE). Respiratory and gastrointestinal absorption were set to 100% as recommended in every model guidance. Substance specific dermal absorption values were extracted from the EU-Pesticides database (European Union, 2017). Operators were assumed to be adults with a weight of 53 kg (Savy et al., 2006). It corresponds to the weight of women with a mean age < 29 years, which is considered a conservative (i.e. protective) value of adult body weight.

Four scenarios were evaluated. Scenario 1 aimed at giving a diagnosis of the current situation based on actual agricultural practices presented in section 9.3.1.1. Scenario 2 and 3 assessed the impacts of the training of the operators on pesticide dose application and the use of personal protective equipment respectively. Scenario 4 estimated the exposure and the risk when measures proposed in scenario 2 and 3 are implemented simultaneously. The ultimate goal of this approach was to assess whether providing equipment or formation separately could achieve sufficient risk reduction or if both were needed. Detailed parameters and scenario definitions are presented in appendix G (section S4).

In scenario 2, it was assumed that recommended application rates (mg a.s. ha^{-1}) and frequencies of application are respected for all the pesticide applied. Recommended dose/dilution of used commercial formulations was derived from original manufacturer labels. Recommended application frequency was not provided on every formulation label. 14 days was retained as the most common and conservative value.

If certified chemical-resistant coverall would provide the safer body protection, mitigation measure proposal must be put into perspectives and adapted to the local context. Indeed, under the warm temperatures of the Sudano-Sahelian climate (Figure 2:2), the discomfort of wearing such an equipment will hamper its acceptance by the users. Moreover, it is not likely that such equipment could be found and be affordable in remote rural areas. Similar remark could be made for protective mask. This material is costly, requires maintenance (filters need to be changed regularly), and is poorly available in Burkina Faso. Based on these considerations, lighter and locally available equipment was retained. Penetration factors presented in EFSA (2014) are supportive that a single

layer of work clothing covering arms, body, and legs, made of cotton (>300 g/m^2) or cotton/polyester (>200 g/m^2), would reduce exposure by 90%. Wearing a hood reduces head exposure by 50% and gloves hands exposure by 90%. Therefore, cotton workwear, any available head protection (i.e. cotton hood, bonnet, and hat), and disposable chemical-resistant gloves were the retained equipment proposed as mitigation measures in scenario 3 and 4. As aforementioned, EFSA is the only model that accounts for head, hands, and body exposure. Thus, it was the only model for which all these measures could be implemented. In HAIR2014, only gloves and workwear were taken into account. WHO 2011 accounts only for dermal exposure through hands, therefore only gloves were implemented as mitigation measure in the simulations.

9.2.4.2 Worker exposure

Workers are exposed to pesticides during their working activities, but are not involved in the application process (Kruijne et al., 2011). They are exposed during activities that involve entering an area or handling a crop that has been previously treated with a PPP (EFSA, 2014). Worker exposure depends therefore on precautions taken when entering fields and on operator agricultural practices. Considering that each operator had specific treatment practices, re-entry worker exposure was assessed for each treated plot (n = 161). Workers are not relevant for indoor/outdoor pesticide application for vector control. In this domain, re-entry exposure is considered only for residents and bystanders. Worker exposure was therefore not implemented in WHO 2011.

The main routes of exposure during post-application activities are dermal and inhalation. Contact with foliage inducing transfer of the dislodgeable foliar residue (DFR) is assumed to be the main source of exposure, followed by inhalation of vapor and/or airborne aerosols. Contact with soil particles and ingestion are expected to be negligible in comparison with skin and inhalation exposure.

In exposure calculation, the DFR is multiplied by a task dependent transfer coefficient (TC), the exposure duration, the penetration factor of the protective equipment, and the dermal absorption (equation 9:8 & 9:9). When chronic exposure is considered, a factor accounting for multiple application is introduced (multiple application factor: MAF). The difference between EFSA and HAIR2014 lies in the definition of the TC, the DFR, and the MAF in the first tier assessment.

EFSA 2014 model documentation provides various TC values depending on the type of PPE used while in HAIR2014 a fixed TC value is corrected by a penetration factor accounting for PPE exposure reduction potential (PPE$_{body}$).

Dissipation of the applied pesticide is expected to occur with relation to its physicochemical properties and the environmental conditions. In the absence of experimentally determined DFR value, EFSA guidance document (EFSA, 2014) recommends to consider an initial DFR (DFR0, potential dislodgeable amount available directly after application, i.e. in the absence of dissipation) of 3 µg a.s. cm^{-2} kg^{-1} a.s. ha. The same approach is proposed by Garreyn et al. (2007) in the initial HAIR documentation. However, by default, HAIR2014 calculator derives DFR (equation 9:9) from the ratio of the application rate and the leaf area index (LAI). Under these conditions, dissipation is

also neglected but DFR is crop depend due to the introduction of the LAI. In absence of local data, a LAI of 2 was retained based on the value proposed for "Outdoor: Market gardening: Fresh vegetables" in HAIR2014 model documentation (Kruijne et al., 2011).

In the same way, similar definition of the MAF are found in the EFSA guidance document (EFSA, 2014) and the initial HAIR documentation (Garreyn et al., 2007). This MAF definition aimed to account for the building-up of residue levels after multiple applications and considers potential dissipation between applications. It was introduced as a function of the number of applications, the application interval, and the dissipation of the residues expressed as a dissipation half-life (DT_{50}) assuming first order kinetic (equation 9:7). In a more conservative way, HAIR2014 calculator does not account for dissipation and the MAF refers to the number of application events (equation 9:9).

EFSA guidance concludes that outdoor application will result in rapid dissipation of vapor and aerosol. Under these conditions, inhalation exposure will have a lesser influence compared to dermal exposure and the model documentation advised to include this route only for indoor application exposure scenario (i.e. greenhouse). Inhalation was therefore implemented only in HAIR2014 model (equation 9:9).

Dermal and inhalation exposures were respectively multiplied by dermal absorption and absorption of the respiratory tract to derive the systemic exposure. Respiratory absorption was set to 100% as recommended in every model guidance. Substance specific dermal absorption values were extracted from the EU-Pesticides database (European Union, 2017). Algorithms for calculation of worker internal exposure (IE) can be summarized as follow (for detailed algorithms see. appendix G (section S4)):

$$MAF_{EFSA} = \frac{1 - e^{nki}}{1 - e^{ki}} \qquad \qquad 9{:}7$$

$$IE(Worker)_{EFSA} = \sum (Expo_{Dermal}(MAF \times AR \times DFR \times TC_{task} \times T_{task} \times DA)) \qquad 9{:}8$$

$$IE(Worker)_{HAIR} = \sum \left(Expo_{Dermal}\left(n \times \frac{AR}{LAI} \times TC_{task} \times T_{task} \times PPEbody \times DA\right) + Expo_{Inhal}(AR \times TSF_{task} \times T_{task} \times n) \right) \qquad 9{:}9$$

where MAF is the multiple application factor (MAF = 1 for acute exposure calculation), n is the number of application (n = 1 for acute exposure calculation), k is the first order degradation rate constant (d^{-1}), AR is the application rate (kg a.s. ha^{-1}), DFR is the dislogeable fraction (μg a.s. cm^{-2} kg^{-1} a.s. ha), TC_{task} is the transfer coefficient for a given task (cm^2 h^{-1}), T_{task} is the task duration (h), DA is the dermal absorption (%), LAI is the leaf area index (-), PPE_{body} is the penetration factor of body personal protective equipment (%) and TSF is the task specific factor (-).

Workers were assumed to be adults with a weight of 53 kg (Savy et al., 2006). During field surveys, three different worker profiles were identified. It was noted that vegetables are often harvested by

external resellers who sell them in surrounding markets or collect them for exportation. These workers (Worker 3) are involved only in activities concerning vegetable collection at maturity referred as "reaching/picking" vegetables in model documentations (Figure 9:1, a). The other worker profiles concerned people involved in vegetable cultivation and include additional tasks such as irrigation and inspection of the crops (Figure 9:1, b). Worker profile number 2 (Worker 2) cumulates all these tasks (i.e. reaching/picking, inspection and irrigation) and worker profile number 1 (Worker 1) considers that an external worker collects the vegetables (i.e. inspection and irrigation only). Duration was set to 2 hours for each task (i.e. recommended default value) but different frequencies were considered. Under the arid conditions of the study area, irrigation and inspection were considered to be conducted every day during the 6 months growing period (180 days). On the other hand, vegetables harvest will occur at maturity. Reaching/picking activities were given a lower frequency. It was set at once a week during 3 months in order to account for all crops and the fact that the same plot can be cultivated more than once with different commodities during the same season. Task exposures are summed for total exposure calculation (equation 9:8 & 9:9). EFSA 2014 documentation provides task-specific surrogate exposure values for TC accounting for PPE. TC definition provided in HAIR2014 documentations (Garreyn et al., 2007; Kruijne et al., 2011) did not achieve the same differentiation level. Therefore, a similar TC was applied to every tasks and PPE were accounted for using penetration factor corrections (PPE-body in equation 9:9).

Four exposure scenarios were evaluated. Workers do not participate in PPP application but will be exposed by contact or inhalation when they enter treated fields. Their exposure is therefore closely related to operator agricultural practices. Scenario 1 aimed at giving a diagnosis of the current situation; worker exposure was evaluated based on current operator agricultural practices (section 9.3.1.1). Scenario 2 assessed worker exposure considering that operators received a training on dose application (i.e. recommended application rate and frequency of application are respected). To date, workers wore no particular protective equipment. Scenario 3 evaluated the impact of providing workers with protective equipment. Similar protective equipment than for operators (section 9.2.4.1) were proposed and included workwear in cotton (i.e. arms and legs covered) and chemical-resistant disposable gloves. Finally, scenario 4 estimated risk reduction induced by simultaneous implementation of mitigation measures proposed in scenario 2 and 3. This approach aimed at assessing at which levels action was needed and more precisely, if modification of operator practices was sufficient or if workers should also wear PPE. Detailed parameters and model definitions are presented in appendix G (section S4).

(a) Harvest

(b) Watering

Figure 9:1 Activities perfomred by workers

9.2.4.3 Bystander exposure

"Bystanders are persons who could be located directly adjacent to the area where PPP application or treatment is in process or has recently been completed; whose presence is quite incidental and unrelated to work involving PPP, but whose position might lead them to be exposed; and who take no action to avoid or control exposure" (definition provided by EFSA (2014)).

In agricultural exposure models (i.e. EFSA 2014 and HAIR2014), four exposure pathways are usually considered for bystanders: spray drift, vapor, surface deposit, and entry into treated crops. Bystander internal exposure (IE) calculations can be summarized by the following generic equations (for detailed algorithms see. appendix G (section S4)):

$$IE(Bystander)_{EFSA} = DERMAL_{bystander}(Drift) + INHAL_{bystander}(Drift) + INHAL_{bystander}(Vapor) \\ + DERMAL_{bystander}(Surface\ deposits) + DERMAL_{bystander}(Re-entry) + INHAL_{bystander}(Re \\ -entry)$$

9:10

$$IE(Toddlers)_{EFSA} = Expo(Bystander)_{HAIR} + ORAL_{toddlers}(Hand\ to\ mouth) + ORAL_{toddlers}(Object\ to\ mouth)$$

9:11

$$IE(Bystander)_{HAIR} = DERMAL_{bystander}(Drift) + INHAL_{bystander}(Vapor) + DERMAL_{bystander}(Re-entry) \\ + INHAL_{bystander}(Re-entry)$$

9:12

$$IE(Toddlers)_{HAIR} = Expo(Bystander)_{HAIR} + DERMAL_{toddlers}(Lawn) + ORAL_{toddlers}(Hand\ to\ mouth) \\ + ORAL_{toddlers}(Object\ to\ mouth)$$

9:13

$$IE(Bystander)_{WHO} = INHAL_{bystander} + DERMAL_{bystander} + ORAL_{toddlers}(Hand\ to\ mouth)$$

9:14

where, $DERMAL$ is the dermal exposure, $Drift$ is the exposure from spray drift, $INHAL$ is the inhalation exposure, $Vapor$ is the exposure from vapor, $Surface\ deposits$ is the exposure from surface deposits, $Re\text{-}entry$ is the exposure from re-entry into treated fields, $ORAL$ is the oral exposure, $Hand\ to\ mouth$ is the exposure from turf via hand to mouth route, and $Object\ to\ mouth$ is the exposure from contaminated objects via object to mouth transfer.

WHO 2011 model does not account for spray drift and exposure sources are limited to vapor and contact with contaminated surfaces (equation 9:14). In EFSA 2014, exposure from spray drift includes dermal and inhalation exposure (equation 9:10). Surrogate values are proposed for various distances, as it is the main factor influencing this route. In HAIR2014, only dermal exposure from spray drift is included (equation 9:12).

Different datasets and parameters are used in every model but vapor exposure is calculated in a similar way (appendix G (section S4)). Same remark can be made for surface deposit exposure except for HAIR2014. Dermal exposure from surface deposit is not considered relevant for adults in this model.

Entry into treated crops is based on exposure from activities such as walking in treated fields. Re-entry exposure algorithm is the same as for workers (section 9.2.4.2) and therefore could not be implemented for WHO 2011. It is also worth noting that even if workers are included in HAIR2014 algorithm, re-entry of bystanders is not considered in model documentations. In the present work, re-entry of bystanders was implemented in HAIR2014 using its worker exposure algorithm (equation 9:9). Exposure duration for re-entry of bystanders was set to 15 min (i.e. recommended default value).

Contrary to operators and workers, not only adults have been identified as bystanders during field surveys. It was common that children and toddlers accompanied their parents on the fields (Figure 9:2). Exposure of bystanders was therefore assessed for the three following age classes: adults, children (11 - 16 years), and toddlers (2 - 3 years). Adults were assumed to weight 53 kg (Savy et al., 2006), children: 32 kg, and toddlers: 10 kg (WHO, 2011b). Additional exposure is expected for toddlers as a result of: crawling on contaminated lawn and ingestion of turf residues via hand-to-mouth and object-to-mouth transfers. EFSA 2014 algorithm integrates exposure via hand-to-mouth and object-to-mouth routes (equation 9:11). In addition, HAIR2014 includes dermal exposure from contact with contaminated lawn (equation 9:13). WHO 2011 accounts only for hand-to-mouth route of exposure (equation 9:14). Even if lawns or meadows are not present in the studied areas (due to arid climatic conditions), the related exposure pathways were maintained to account for crawling on contaminated soils and transfer of contaminated soil particles via hand-to-mouth.

(a) Children playing on the fields   (b) Harvest with toddlers

Figure 9:2 Chidren and toddlers on the fields

EFSA 2014 guidance document noted that it is unlikely that exposures from the different pathways occur contemporaneously and therefore proposes to keep them separated. On the other hand, HAIR2014 and WHO 2011 documentations did not recommend separation. In a protective and homogenization perspective, exposures were summed in all models. However, it is assumed that bystanders will not be present during every pesticide application and their exposure frequency was considered equal to the fourth of operator exposure frequency.

Four exposure scenarios have been evaluated to assess bystander exposure. Due to the cost and discomfort associated with warm temperatures, bystanders are not likely to wear any protective equipment. Only light clothing covering trunk, upper arms, and half legs were considered. Scenario 1, assessed bystander exposure under current agricultural practices. As for workers, bystander exposure is influenced by operator activities. For this reason, scenario 2 evaluated the impact of dose and treatment frequency adjustments proposed for operators, on bystander exposure. Spray drift exposure is highly dependent on distance between the sprayer and the individual. Bystanders were generally standing outside the cultivated plots but in the close vicinity to the treated areas. Increasing distance between bystanders and treated areas was proposed in scenario 3. Smaller distance supported by models (EFSA 2014: 2 m and HAIR2014: 8 m) were used for the modelization of current situation in scenario 1 and 10 meters was proposed as a mitigation measure in scenario 3. As spray drift is not supported by WHO 2011 model, only frequency of application and dose adjustment were retained as mitigation measures for bystanders. Finally, scenario 4 combines all the proposed mitigation measures (dose, frequency of application, and distance adjustments). Due to the large number of parameters included in bystander algorithms, details on parameters and scenario definition are provided in appendix G (section S4).

9.2.4.4 Dietary intake of pesticide

Dietary intake of pesticides accounts for exposure to pesticides through consumption of foodstuff and water. Application of pesticides in vegetable production was proved to result in detectable and hazardous levels of pesticides residues onto staple food and induced contamination of local water resources (Lehmann et al., 2017a, Chapter 5).

Every aforementioned actors is expected to be exposed through dietary intake. Dietary exposure depends on consumption habits and therefore may exhibit individual and regional variability. To our knowledge the dietary study presented in Chapter 6 is the only quantitative estimation of dietary intake of pesticides in Burkina Faso (Lehmann et al., 2017d, Chapter 6). However, this study included only vegetables and water consumption. Nevertheless, food is generally fried or boiled in rural populations' diet. These types of processing are expected to reduce residues to a large extend (section 0). Thus considering that fresh vegetables are potentially eaten raw, they are expected to yield the higher exposure. In the absence of supplementary local data and considering that diet was found to be generally poor and monotonous in rural areas (Savy et al., 2007), estimated daily intakes calculated for Loumbila population were used as surrogate values for dietary exposure in the present models. Median pesticide residue levels and weighted average portion estimates (WAPE) were used to account for usual consumption (Lehmann et al., 2017d, Chapter

6). Figure 9:3 present daily intake of a.s. from water and foodstuffs. Dietary intake was added to exposure of every individual presented in the above sections (section 9.2.5).
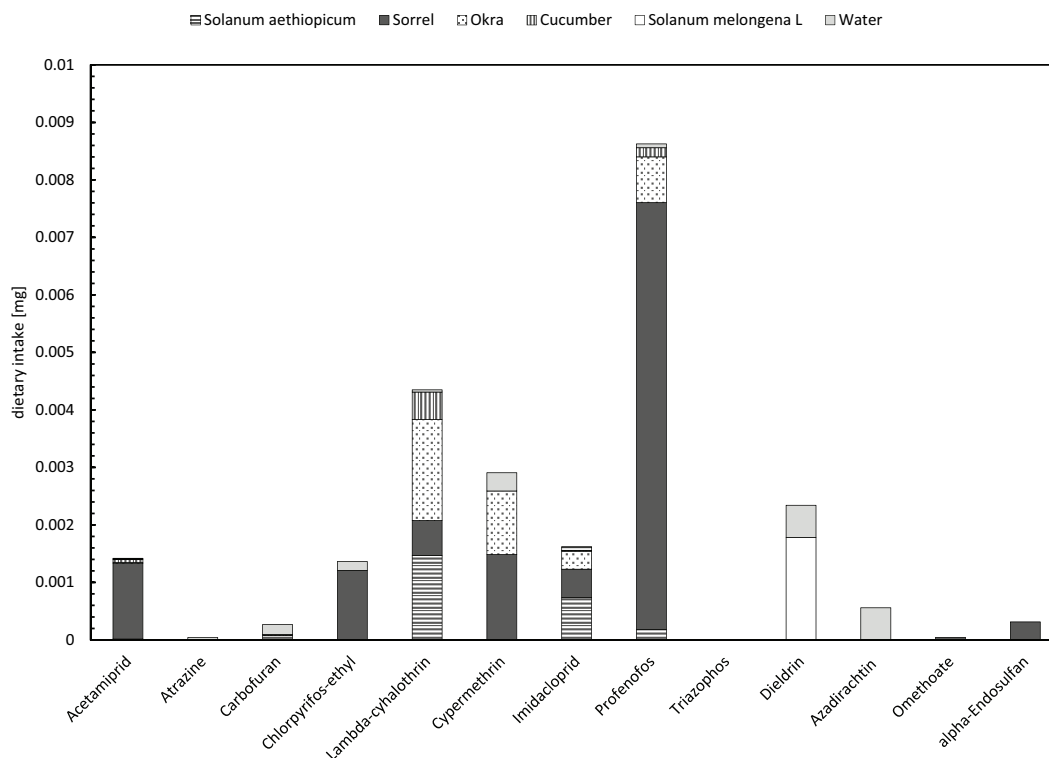
Figure 9:3 Contribution of vegetables and water to pesticide exposure considering median residue levels and WAPE

Enforcement of mitigation measures such as application of recommended pesticide dose (scenario 2 and 4) is expected to have an impact on pesticide residue levels into foodstuffs and water. However, estimation of these phenomena is not straightforward. It would require experimentation or modelization of the fate of chemicals after application, which is outside of the scope of the present study. As WAPES associated with median residue levels yielded exposures under the acute reference dose (ARfD) and admissible daily intake (ADI) (Chapter 6), the same dataset was considered for every scenario.

9.2.5 Risk assessment

Total internal exposure (IE) was calculated by summing the contributions via different routes presented in section 9.2.4. Risk characterization evaluates the probability of adverse effects occurring under the defined exposure conditions. Total internal exposure was therefore compared to tolerable systemic dose (TSD) using risk index (Kruijne et al., 2011), also called hazard quotient (HQ). This approach proposed in HAIR2014 and WHO 2011 documentations (Garreyn et al., 2007; Kruijne et al., 2011; WHO, 2011b), was modified to account for non-dietary and dietary exposures (EC - DG Health and Food Safety's, 2017). For short-term and single pesticide exposure, acute HQ was calculated for a given pesticide as follow:

$$HQ_{acute} = \frac{\sum IE_{non-dietary\ esposure}}{TSD_{acute\ non-dietary\ exposure}} + \frac{IE_{dietary\ exposure}}{TSD_{acute\ dietary\ exposure}}$$ 9:15

In case of multiple applications, time weighted average exposure is calculated by multiplying the acute internal exposure by the exposure frequency (EF) and dividing it by the averaging time (AT). HQ for chronic exposure for a given pesticide was calculated as follow:

$$HQ_{chronic} = \frac{\sum IE_{non-dietary\ esposure}}{TSD_{chronic\ non-dietary\ exposure}} \times \frac{EF_{non-dietary\ exposure}}{AT} + \frac{IE_{dietary\ exposure}}{TSD_{chronic\ dietary\ exposure}} \times \frac{EF_{dietary\ exposure}}{AT}$$ 9:16

The EF corresponds to the number of days of exposure during the growing period. The duration of the growing period was assumed to be 6 months (i.e. 6 × 30 = 180 days). AT was set to 365 days to obtain the annual exposure estimate. EF for non-dietary exposures depends on the pesticide application scheme. In scenario 1 (i.e. current practices), frequency of application reported by gardeners was used to determined EF (i.e. $EF_{non-dietary\ exposure} = \frac{180}{reported\ frequency\ of\ application}$). As aforementioned, in scenario 2 and 4 (i.e. including the training on pesticide doses), recommended frequency of application was set to 14 days, therefore $EF_{non-dietary\ exposure} = \frac{180}{14} = 12.86\ days$. Assuming that vegetables were available during the whole growing season, a daily dietary intake was considered during 6 months (EF$_{dietary\ exposure}$ = 6 × 30 = 180 days). It is noteworthy that, frequency of application is accounted for only in the assessment of chronic risk; acute risk is derived from a single application event.

Acute non-dietary acceptable exposure level (ANDAEL) and acceptable operator exposure level (AOEL) were respectively used as TSD in the assessment of acute and chronic risks from non-dietary exposures. ARfD and ADI were respectively used for acute and chronic risks assessment from dietary exposure. TSD values (SI Tables S2-S6) have been extracted from the EU – Pesticides database (European Union, 2017) and the Pesticides Properties DataBase from the University of Hertfordshire (Lewis et al., 2016). ANDAEL values were only available for a few number of substances. In the absence of ANDAEL, AOEL may be used in a first tier assessment. However, if the AOEL is exceeded by the exposure estimate, a comparison can be done against the ARfD of the active substance, corrected for the extent of oral absorption used in the derivation of the AOEL (EC - DG Health and Food Safety's, 2017). ARfD are set for dietary acute risk assessment. They can be therefore used only if parameters considered to base the guidance value for short-term exposure are relevant to non-dietary studies (EC - DG Health and Food Safety's, 2017; WHO, 2011b). In the present work, ARfD of a.s. used in market gardening in Burkina Faso have been checked to ensure that they were relevant for an acute non-dietary risk assessment. Routes of exposure and effects considered in studies used to derive ARfD were retained as validation criteria. When judged relevant, the corrected ARfD value was retained for the ANDAEL definition, otherwise the AOEL value was used (Table S4).

Most of the gardeners used more than one pesticide (section 9.3.1.1). Cumulative effects of pesticides was subsequently evaluated using Hazard Index (HI) based on the concentration addition

(CA) model (Bliss, 1939; Garreyn et al., 2007).When more than one pesticide was used by a given gardener, HQ of pesticides with common mode of action (MOA) were summed to account for cumulative toxicity:

$$HI = \sum_i^n HQ_i \qquad\qquad 9:17$$

When data was available, higher percentiles (90th-95th) of prediction levels were used to derive acute exposure and lower percentiles (75th and mean) were used for chronic exposure calculation.

Exposures yielding a HQ or HI higher than the unity were considered hazardous for the health of the assessed individual. For single pesticide exposure assessment, the individual was considered at risk when at least one pesticide he used yielded a HQ higher than the unity. In the same way, for cumulative pesticide exposure assessment, the individual was considered at risk when at least one group of pesticides with the same MOA yielded a HI higher than the unity.

9.2.6 Synthesis on scenarios definition

Similar dietary intake was assumed for every individual and in every scenario. The parameters varied in the simulation of non-dietary exposures are summarized in Table 8:1. Detailed parameters and model definitions are presented in Appendix G (section S4).

Table 9:1 Parameters varied in the simulation of non-dietary exposures

Operator

Model	Exposure description	Scenario 1 (SC1)	Scenario 2 (SC2)	Scenario 3 (SC3)	Scenario 4 (SC4)
EFSA 2014	Mixing, loading and application exposure	Current practices	Current PPE & Recommended frequency of application[a]	Proposed PPE & Current application frequency	Proposed PPE & Recommended frequency of application[a]
HAIR2014	Mixing, loading and application exposure	Current practices	Recommended dose, frequency of application	Proposed PPE & Current dose, frequency of application	Proposed PPE & Recommended dose, frequency of application
WHO 2011	Mixing, loading and application exposure	Current practices	Recommended dose, frequency of application	Proposed PPE & Current dose, frequency of application	Proposed PPE & Recommended dose, frequency of application

Worker

Model	Exposure description	Scenario 1 (SC1)	Scenario 2 (SC2)	Scenario 3 (SC3)	Scenario 4 (SC4)
EFSA	Re-entry dermal exposure	Current practices	Current PPE & Recommended dose, frequency of application	Proposed PPE & Current dose, frequency of application	Proposed PPE & Recommended dose, frequency of application
HAIR2014	Re-entry dermal exposure	Current practices	Current PPE & Recommended dose, frequency of application	Proposed PPE & Current dose, frequency of application	Proposed PPE & Recommended dose, frequency of application
	Re-entry inhalation exposure	Current practices	Current PPE & Recommended dose, frequency of application	Current practices (no PPE proposed for inhalation)	Current PPE & Recommended dose, frequency of application
WHO 2011	Re-entry exposure not supported	-	-	-	-

Bystander

Model	Exposure description	Scenario 1 (SC1)	Scenario 2 (SC2)	Scenario 3 (SC3)	Scenario 4 (SC4)
EFSA	Exposure from drift	Current practices	Current distance & Current dose, frequency of application	Proposed distance & Current dose, frequency of application	Proposed Distance & Recommended dose, frequency of application
	Inhalation exposure	Current practices	Recommended dose, frequency of application	Current practices (no PPE proposed for bystander)	Recommended dose, frequency of application
	Re-entry dermal exposure	Current practices	Recommended dose, frequency of application	Current practices (no PPE proposed for bystander)	Recommended dose, frequency of application
HAIR2014	Exposure from drift	Current practices	Current distance & Recommended dose, frequency of application	Proposed distance & Current dose, frequency of application	Proposed Distance & Recommended dose, frequency of application
	Inhalation exposure	Current practices	Recommended dose, frequency of application	Current practices (no PPE proposed for bystander)	Recommended dose, frequency of application
	Re-entry dermal exposure	Current practices	Recommended dose, frequency of application	Current practices (no PPE proposed for bystander)	Recommended dose, frequency of application
	Re-entry inhalation exposure	Current practices	Recommended dose, frequency of application	Current practices (no PPE proposed for bystander)	Recommended dose, frequency of application
WHO 2011	Bystander exposure	Current practices	Current frequency & Recommended dose	Recommended frequency & Current dose	Recommended frequency & Recommended dose[b]

[a] EFSA 2014 algorithm did not allow to adjust the application rate, therefore only chronic risk is affected by frequency adaptation in SC2 and SC4

[b] Only the pesticide dose and the frequency of application were adjusted in bystander exposure assessment in WHO 2011. As acute exposure is impacted only by the dose adjustment, acute risk was calculated only for SC1 and SC2.

9.3 Results from pesticide exposure assessment

9.3.1 Operator practices and risk assessment

9.3.1.1 Operator agricultural practices

In total, 161 gardeners provided sufficient data for exposure and risk assessment. Half of them reported using more than one commercial formulation on a given crop (average: 2 and maximum: 7). The present dataset recorded 339 different uses of the 52 reported formulations (Table S7). A large number of these commercial formulations were a mix of two active substances (47%). Operators were therefore found to be exposed to more than one active ingredient in 76% of the cases (3 pesticides per person in average) and 524 different uses of the 17 identified active ingredients (Table 9:2) were recorded. According to their description in the Pesticides Properties DataBase from the University of Hertfordshire (Lewis et al., 2016), the MOA of these a.s. matched with their affiliation to a given substance group (i.e. a.s. presented 10 different MOA (Table 9:2)). Among reported pesticide formulations, only 8 (15%) were authorized in Burkina Faso for use in gardening and 10 (19%) for cotton and cereal production. Except atrazine and paraquat chloride, active ingredients used were present in authorized formulations.

Table 9:2 Active substances identified in commercial pesticide formulations used by gardeners

Pesticide name	Substance group	Pesticide name	Substance group
2,4 D (amine salt)	Alkylchlorophenoxy	Dimethoate	Organophosphate
Emamectine Benzoate	Avermectin	Triazophos	Organophosphate
Paraquat chloride	Bipyridylium	Glyphosate	Phosphonoglycine
Mancozeb	Carbamate	Lambda-cyhalothrin	Pyrethroid
Acetamiprid	Neonicotinoid	Cypermethrin	Pyrethroid
Imidacloprid	Neonicotinoid	Deltamethrin	Pyrethroid
Chlorpyrifos-ethyl	Organophosphate	Cyfluthrin	Pyrethroid
Profenofos	Organophosphate	Atrazine	Triazine
Malathion	Organophosphate		

Due to the low level of education and high illiteracy rate, operators were not able to calculate a.s. dilution and read recommendations provided on pesticide labels. It was therefore not surprising that application rate (mg a.s. ha^{-1}) and spray dilution (mg a.s. mL^{-1}) exceeded manufacturer recommendations in respectively 76% (n = 432) and 43% (n = 330) of the evaluated cases. It is also worth noting that every reported dose (n = 524) could not be evaluated because application rate and/or concentration dilution were not always provided on the original product label. Absence of data had an influence on the assessment of the impact of mitigation measures (i.e. application of recommended dose). Developed algorithm ignores missing data and performs evaluation only on full dataset, which explain that different numbers of cases were evaluated depending on the considered parameters. This also means that in scenario 2 and 4, pesticides presenting incomplete data were ignored. In practice, this would suggests that we considered that commercial products, which were not provided with sufficient information for safe use (respecting the GAP), were removed from the market.

Another example of the difficulties encountered by the gardeners in the application of dose recommendations, is the absence of correlation between the surface treated and the quantity of a.s. applied (data not presented). Interval between applications varied between 1.5 and 30 days. Half of the operators reported that application frequency depended on pest attacks or disease occurrence (51%) and 47% indicated that pesticides were applied periodically. The rest did not answer or explained that pesticide application relied upon products availability. Frequency of application was rarely indicated on labels. Comparison between available information indicated that 14 days was the most conservative (i.e. protective) value. It was therefore retained as the proposed frequency for mitigation measures.

For respondents who answered questions related to PPE (n = 85), only 23% and 7% wore respectively gloves and head protection (hat) while handling PPPs. Penetration factor was set to 10% for hands covered with gloves and 50% for protected head (EFSA, 2014). The only reported respiratory protection was mufflers made of ordinary fabric, unlikely to protect from organic chemical vapors. In the absence of suitable protective equipment, penetration factor was set to 100% for inhalation. None of the operator wore certified coverall neither recommended cotton workwear (section 9.2.4.1). Due to warm temperatures, most of the operators did not wear long sleeves and trousers. During field surveys, it was common to observe clothes not fully covering arms and legs (Figure 9:4).

(a) Normal clothing not covering arms and legs   (b) Normal clothing covering arms and legs

Figure 9:4 Clothes worn by gardeners while working on the field

Trunk was generally covered with ordinary light clothing (penetration factor: 50%, see section 9.2.3). Adjusted penetration factor was calculated for body exposure (PPE_{body}) using equation 9:3 to account for varying limb coverage extend. In the absence of reported data, light clothing covering half legs and upper arms was assumed in scenario 1 depicting current practices (Figure 9:5).
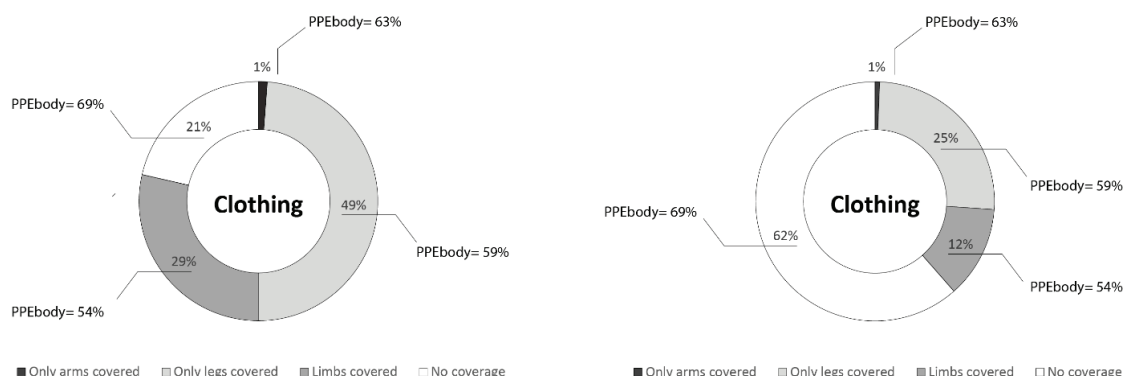
Figure 9:5 Extend of body protection and adjusted penetration factor (PPEbody). The percentages are given for respondent answers (left, n = 85) and for the whole population (right, n = 161) with missing data replaced by no coverage (i.e. only half-legs and half-upper arms covered).

9.3.1.2 Risk characterization for operators

Operator risk assessment was performed in four scenarios using algorithms presented in appendix G (section S4). It is noteworthy that EFSA 2014 knapsack model uses fixed surrogate values for operator exposure assessment independent of applied dose and treated surface area. Only frequency of application could be adjusted in scenario 2 and scenario 4, thus only chronic risk simulations are affected.

Training on pesticide dose application considered that recommended application rate (kg a.s. ha^{-1}), spray dilution (mg L^{-1}), and frequency of application were respected. As aforementioned, recommended PPE included: cotton coverall (or jacket with long sleeve and trousers), chemical-resistant disposable gloves and head protection (hood, hat, etc.).

Total systemic exposure was calculated as the sum of exposures occurring during mix/loading of the pesticide in knapsack sprayer and application onto crops. Risk characterization was performed for single (HQ) and cumulative pesticide exposure (HI). Results are presented as percentage of users at risk in Figure 9:6. For every scenario, the following notation is used: "Model Name (% HQ>1, % HI>1)".

9.3.1.2.1 Acute risk

Figure 9:6 underlines differences between model outputs in SC1. According to EFSA 2014 simulations, 100% of the studied individuals presented a potential acute health risk in the current situation. With 47% to 70% of the studied population at risk, HAIR2014 (47%, 51%) and WHO 2011 (62%, 68%) gave a less pessimistic diagnosis.

EFSA 2014 algorithm was not suitable to assess acute risk reduction from training on dose application in SC2 (application rate not supported). HAIR2014 (39%, 44%) predicted a ~7% risk reduction in SC2 with recommended application rate. On the contrary, WHO 2011 (66%, 70%) outputs indicated a slight increase of the risk when the recommended dose is applied. This can be explained by the fact that in 53% of the cases, applied dose was lower than recommended. Economic limitations might be the cause of this parsimonious use of purchased formulations.

When considering risk reduction induced by proposed PPE in SC3, no risk reduction is expected according to EFSA 2014 estimations. HAIR2014 (17%, 17%) predicted a ~30% risk reduction and WHO 2011 (56%, 56%) only ~6%. In this scenario, no significant difference was observed between single (HQ) and cumulative risk assessment (HI).

As dose adjustment is not supported in EFSA 2014, effect of this measure on acute risk can not be evaluated with this model in SC4. On the other hand, it is straightforward that combination of the proposed mitigation measures in SC4 yielded the larger risk reduction in HAIR2014 simulations. Nevertheless, a small but significant portion of the population (8%) still presented an acute risk. Remaining risks were attributed to profenofos and acetamiprid acute toxicity. For profenofos, 25% of the users of this a.s. presented a risk and 6% for acetamiprid. For WHO 2011 (61%, 62%), risk estimates were lower than in SC2 but higher than in SC3 due to the impact of pesticide dilution observed in SC2. A large number of a.s. were still yielding a risk in this model. With respectively 97% and 40% of the individuals at risk, lambda-cyhalothrin and profenofos users were the most affected. Users presenting a risk related to acetamiprid, emamectin benzoate, imidacloprid, and cypermethrin use were in the range of 15% to 30 %.

None of the proposed mitigation measures alone nor in combination allowed to achieve a totally safe situation for all users.

9.3.1.2.2 Chronic risk

Similar to acute risk assessment, outputs of chronic risk assessment differed between models.

In SC1, HQ and HI yielded similar risk estimations. EFSA 2014 indicated a chronic risk for ~64% of the users. HAIR2014 estimated that 11% of the operators presented a potential chronic risk while WHO 2011 29%.

EFSA 2014 (25%, 32%) model predicted a 42% and 32% risk reduction for single and cumulative pesticide exposure with recommended doses and application frequency in SC2. According to HAIR2014 predictions, no risk is expected if recommended doses are applied at the proposed frequency (SC2). Under similar hypothesis, WHO 2011 indicated a ~24% reduction of operator chronic risk (SC2), with 5% of the users that would still be at risk.

In SC3, the use of the proposed PPE reduced chronic risks by 47% in EFSA 2014 (16%, 17%). HAIR2014 (2%, 3%) estimations predicted a ~7% risk reduction. On the other hand, only a ~5% risk reduction was predicted by WHO 2011 (24%, 24%). WHO 2011 algorithm accounts for dermal exposure by contact of the pesticides with hands during mixing/loading and for dermal and inhalation during pesticide application. In this model, inhalation was found to be the predominant route of exposure of the operator. Under these conditions, it is not surprising that mitigation measures proposing gloves (SC3) will not induce a large risk reduction.

HAIR2014 was the only model indicating no risk for both single and cumulative pesticide exposure in SC4. EFSA 2014 detected health hazard for 3% of the operators but only for cumulative exposure (HI). In this scenario, only emamectin users presented a risk (13%). In WHO 2011, 5% of the

studied population was still presenting a potential risk (HQ & HI) in SC4. Only users of lambda-cyhalothrin (1%) and emamectin benzoate (17%) presented a risk in WHO 2011 predictions for this scenario.
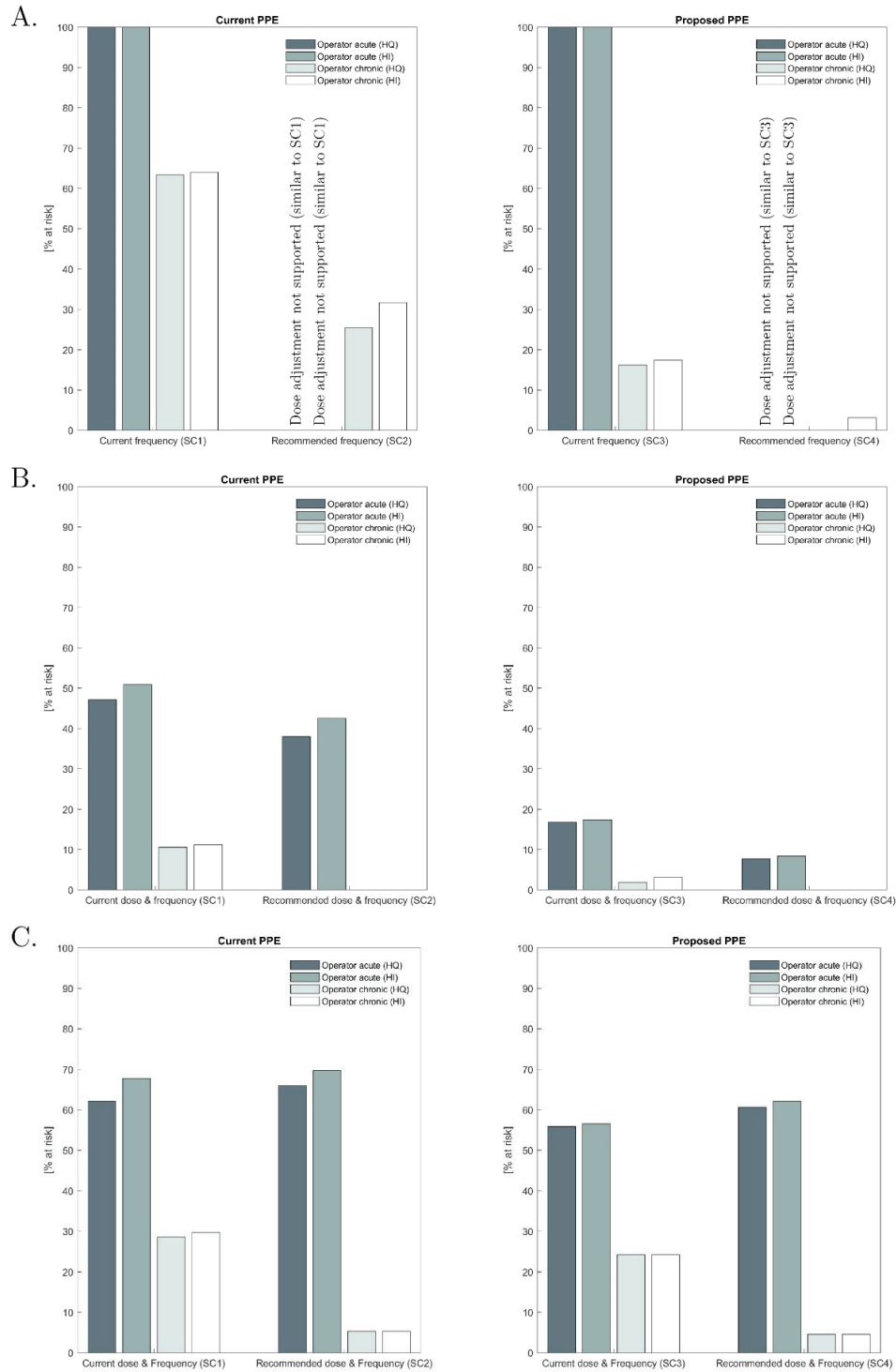
Figure 9:6 Risk characterization for operator single pesticide exposure (HQ) and cumulative pesticide exposure (HI) calculated with EFSA 2014 (A), HAIR2014 (B), and WHO 2011 (C)

9.3.2 Risk characterization for workers

As aforementioned, WHO 2011 algorithm did not support worker exposure modelization. Therefore, only EFSA 2014 and HAIR2014 worker exposure estimations are evaluated in Figure 9:7. Algorithms presented in appendix G (section S4) were used to derived worker exposure and resulting risk according to 4 scenarios.

Risk characterization was performed for single (HQ) and cumulative pesticide exposure (HI) for the 3 worker profiles (section 9.2.4.2). Results are presented as percentage of workers at risk in Figure 9:7. For every worker profile (Table 9:3), the following notation is used: "Worker profile number (% HQ>1, % HI>1)".

Table 9:3 Description of worker profiles

Worker profile	Tasks performed
Worker 1	Inspection and irrigation
Worker 2	Reaching/picking, inspection and irrigation
Worker 3	Reaching/picking

9.3.2.1.1 Acute risk

The working group that produced EFSA guidance document (EFSA, 2014) judged that available data was not reliable enough to proceed with acute exposure assessment. Acute risk was therefore implemented only for HAIR2014.

Under current agricultural practices (SC1), health hazard was identified in every exposure scenario (Worker 1 (21%, 25%), Worker 2 (34%, 39%), and Worker 3 (9%, 11%)).

With recommended dose (SC2), risk was identified for single and cumulative pesticide exposure for Worker 2 (8%, 10%) and only in cumulative pesticide exposure assessment for Worker 1 (-, 2%). The reduction induced by operator training was therefore estimated to be ~21 - 23% for Worker 1, ~26 - 29% for Worker 2, and ~9 - 11% for Worker 3. In this scenario vegetable collection did not induce an acute risk for Worker 3.

When considering only proposed PPE as mitigation measure (SC3), similar results were obtained for Worker 2 (6%, 7%) and a slightly higher percentage of the population was at risk in Worker 1 (2%, 4%) and Worker 3 (-, >1%) profiles.

Finally, with mitigation measures proposed in SC2 and SC3 together, no acute risk for any worker profile was detected in SC4.

9.3.2.1.2 Chronic risk

Worker chronic risk was evaluated with both EFSA 2014 and HAIR2014 models. In the current situation (SC1), a higher fraction of the population presented a chronic risk compared to acute risk. Estimations differed between models. HAIR2014 estimations (Worker 1 (91%, 91%), Worker 2 (91%, 91%), and Worker 3 (32%, 45%)) indicated that a larger portion of the studied population was at risk compared to EFSA 2014 (Worker 1 (48%, 53%), Worker 2 (49%, 53%) and Worker 3 (3%, 5%)).

Large discrepancies between model outputs were also found in SC2. EFSA 2014 indicated a risk only when considering HI for Worker 1 (-, 5%) and Worker 2 (-, 5%) profiles, which suggested a risk reduction up to 48%. On the other hand, HAIRS2014 indicated a large exceedance of threshold value for HQ and HI in Worker 1 (60%, 69%) and Worker 2 (73%, 77%) profiles. According to this model, the risk reduction was about ~22 - 31% for profile 1, ~14 - 18% for profile 2, and up to 35% for profile 3.

Estimated results also differed between EFSA 2014 and HAIR2014 in SC3. EFSA 2014 indicated that 11% of the workers presented a risk in profiles 1 and 2 (HQ & HI), while HAIR2014 identified a larger risk in every profiles (Worker 1 (58%, 61%), Worker 2 (60%, 63%), Worker 3 (9%, 9%)). In this scenario, EFSA 2014 estimations expected a lower risk reduction than for SC2 (~5% lower). On the contrary, HAIR2014 predicted a slightly larger risk reduction with proposed PPE compared to the application of recommended practices for worker profiles 1 and 2 (~30% risk reduction) but not for 3 (~23 - 26% risk reduction).

Application of all the proposed mitigation measures (SC4), indicated safe conditions in EFSA 2014 simulations, while HAIR2014 indicated that 5% of workers were still be at risk when considering HI in worker profiles 1 and 2. Emamectin benzoate was again producing the higher percentage of chronic risk for its users. Neonicotinoids and organophosphates were the two other groups of pesticides presenting a risk for their users (1% and 11% respectively).
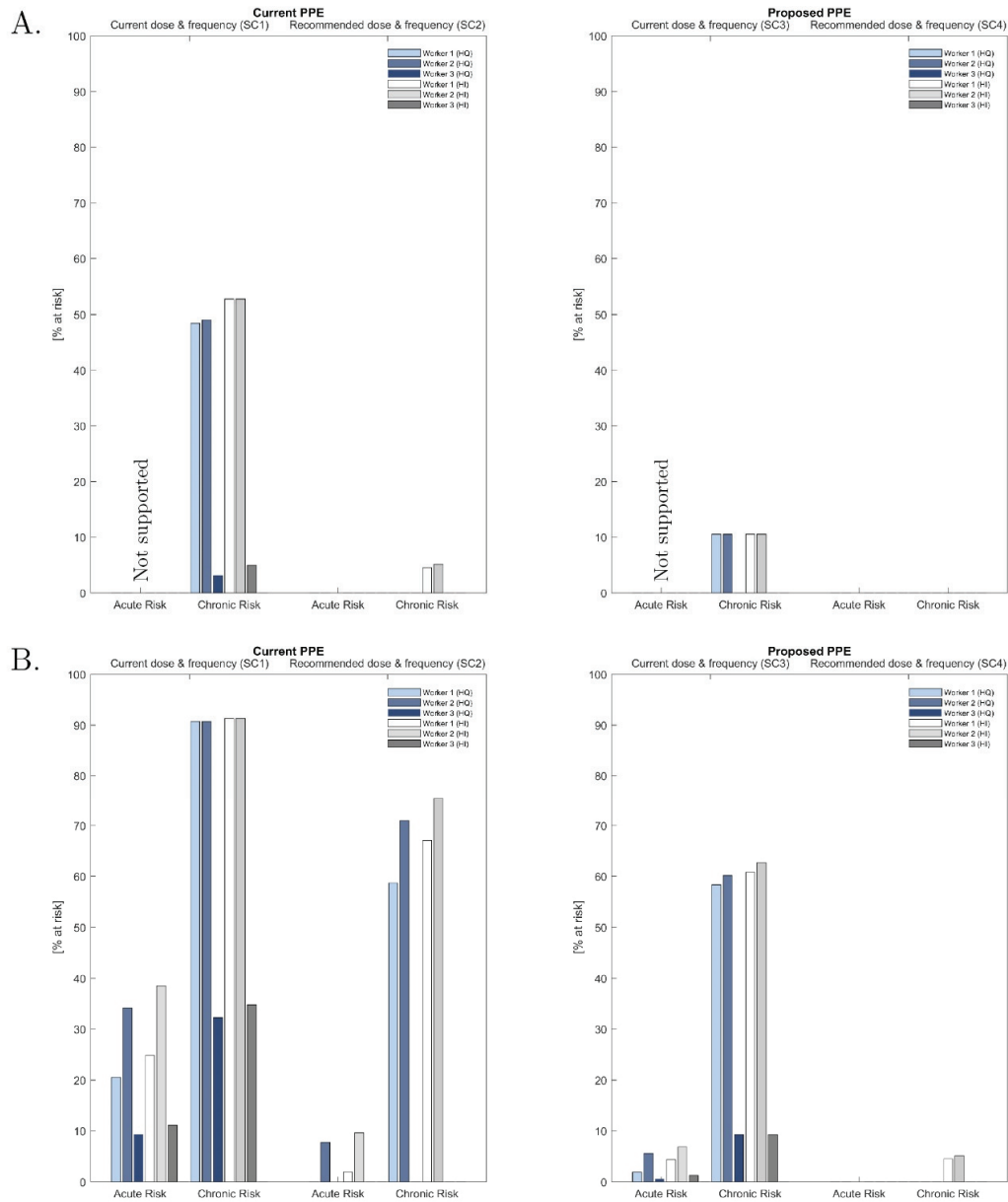
Figure 9:7 Risk characterization for worker single pesticide exposure (HQ) and cumulative pesticide exposure (HI) calculated with EFSA 2014 (A) and HAIR2014 (B).

9.3.3 Risk characterization for bystanders

Bystanders are persons who are not implied in any agricultural activities but are present on the fields, in the vicinity of treated areas. Bystanders were generally family members (adults, children, and toddlers) accompanying operators or workers during their gardening activities.

Cultivated plots are contiguous in the studied areas. Bystanders had to cross treated crops to access a given plot. In EFSA 2014 and HAIR2014, contact with treated crops was implemented in a similar way than workers. Risk assessment results for bystanders are presented in Figure 9:8. In the following paragraphs, for every age classes the following notation is adopted: "age class (% HQ>1, % HI>1)".

9.3.3.1.1 Acute risk

Model outputs differed in the characterization of the current situation (SC1). EFSA 2014 and WHO 2011 presented the larger fractions of populations at risk. EFSA 2014 simulations yielded the worst situation with risks present in every groups (adults (6%, 9%), children (60%, 60%), and toddlers (65%, 65%)), followed by WHO 2011 (adults (11%, 12%), children (19%, 23%), and toddlers (56%, 57%)). According to HAIR2014, only toddlers (1%, 2%) presented an acute risk in SC1.

With recommended dose (SC2), risk was identified by EFSA 2014 for children (58%, 58%) and toddlers (58%, 58%) with a risk reduction of ~2 - 5% compared to SC1. WHO 2011 simulations indicated also a risk for children (-, 2%) and toddlers (58%, 61%). The slight increase of the risk for toddlers might be linked to the fact that 53% of the operators applied a dilution lower than recommended. HAIR2014 detected no risk in SC2.

EFSA 2014 indicated a potential risk for bystanders even at 10 m from the sprayer in scenario 3 (adults (3%, 5%), children (60%, 60%), and toddlers (61%, 63%)). HAIR2014 predictions indicated no difference with SC1, only toddlers (1, 2%) presented a risk. As only the pesticide dose could be adjusted in WHO 2011, acute risk was not calculated for SC3 and SC4 (similar to SC1 and SC2).

When considering mitigations measures proposed in SC2 and SC3 together (SC4), EFSA 2014 indicated a large remaining risk for children (58%, 58%) and toddlers (58%, 58%). The risk reduction of only 7% for these groups was attributed to the acute toxicity of lambda-cyhalothrin. On the opposite, HAIR2014 indicated no risk for the studied populations in SC4.

9.3.3.1.2 Chronic risk

HAIR2014 was the only model where health hazard was present in every age groups (adults (4%, 6%), children (2%, 2%), and toddlers (9%, 9%)) in SC1. In EFSA 2014, only adults and toddlers were subject to hazards (adults (1%, 1%) and toddlers (2%, 4%)) and only children and toddlers were at risk in WHO 2011 (children (1%, 1%) and toddlers (2%, 4%)).

SC2 yielded no chronic risk in EFSA 2014 and HAIR2014. Hazard was detected only for toddlers (1%, 1%) in WHO 2011 model.

With distance from sprayer set to 10 meters in SC3, only toddlers (2%, 2%) presented a chronic risk in EFSA 2014 predictions. On the other hand, HAIR2014 predictions indicated hazard for every age groups (adults (4%, 6%), children (2%, 2%), and toddlers (9%, 9%)). Modifying frequency of application in WHO 2011 induced a chronic risk reduction up to 3%. Only toddlers (1%, 1%) were still presenting a risk in SC3.

None of the model predicted a chronic risk in scenario 4 (SC4).

It as to be noted that under chronic risk assessment, EFSA 2014 and HAIR2014 yielded higher risks for adults than children.
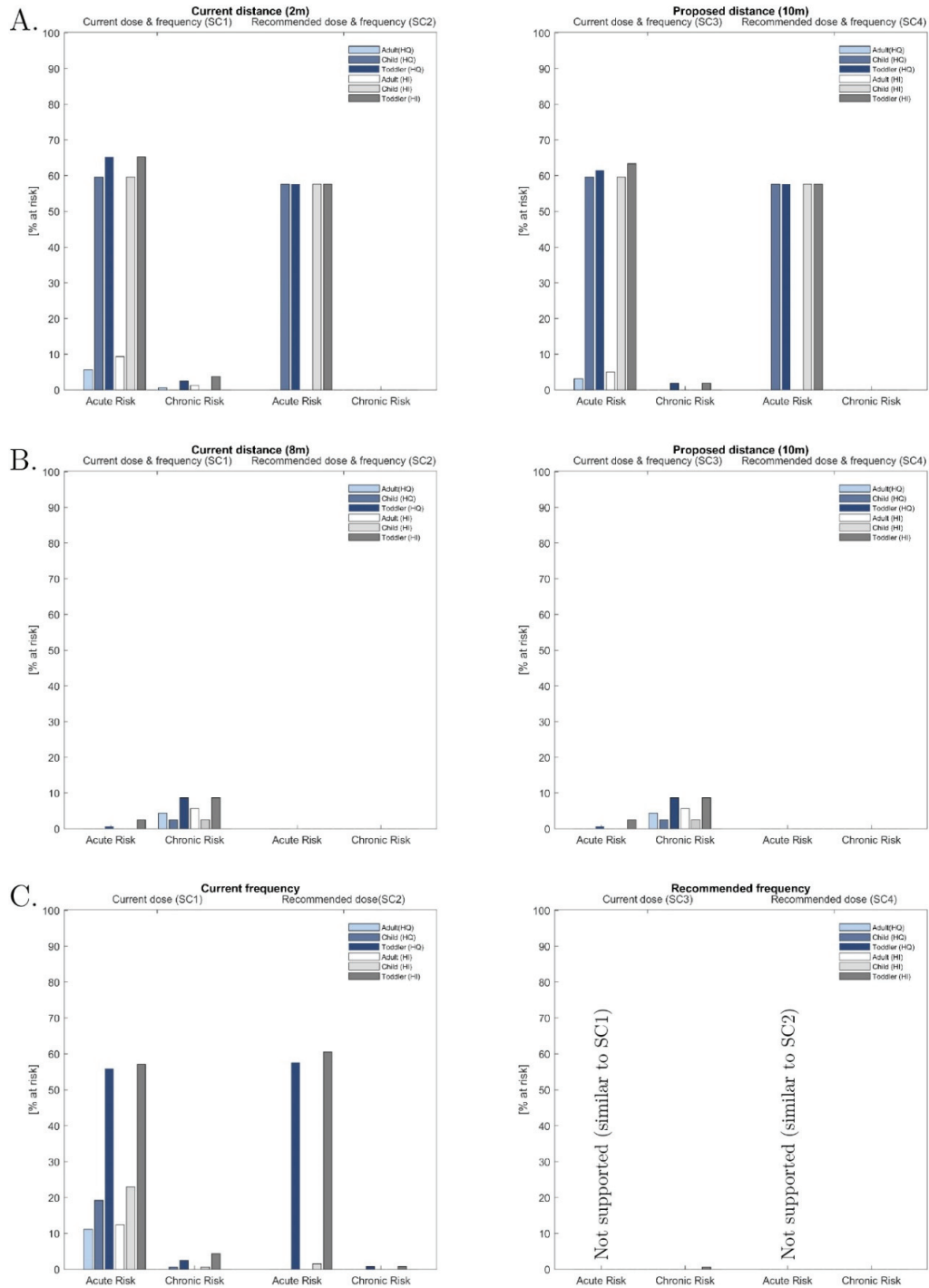
Figure 9:8 Risk characterization for bystander single pesticide exposure (HQ) and cumulative pesticide exposure (HI) calculated with EFSA 2014 (A), HAIR2014 (B) and WHO 2011 (C)

9.3.4 Illness associated with pesticide exposure

Acute illnesses associated with pesticide use was reported by 30% of the operators (n = 47). Symptoms presented in Figure 9:9 generally appeared soon after spraying or during the following night. Headache and stomachache were the most frequently reported symptoms. Similar symptoms were also reported in previous studies (Lu et al., 2015; Toé, 2010b). However, as aforementioned, these information rely only on respondents' perception. Health is determined by numerous factors including personal health practices and behaviors (water and food quality, hygiene, etc.). In the absence of reliable medical diagnosis, the causal link with pesticide is not straightforward and should be interpreted with caution.

None of the staff from rural medical centers received a specific training regarding pesticide poisoning and was aware of the type of products used in their working area. Medical centers surveyed had registered 17 poisoning cases related to pesticides in the past year, with 4 having led to the patient's death. Among these 17 poisoning cases, 3 were self-induced intoxications, 6 occurred after consumption of gardening products, the rest occurred after accidental exposure to pesticides. Children under 3 years old were involved in 5 cases of accidental poisoning. They had accidentally found pesticide containers while playing on the fields and put them to mouth. Most of the rural medical centers were not equipped to face these kind of issues. Only one reported having atropine, other treated patients with activated charcoal, hydrocortisone, aluminum hydroxide, and antibiotics.

It is worth noting that, acute adverse health effects resulting from exposure to pesticide and symptoms from commonly contracted illnesses such as malaria and bacterial poisoning are very similar (headache, stomachache, fever, vomiting, etc.). Many patients could not explain the cause of their intoxication neither could the nurse. It is therefore likely that some of the other recorded poisoning cases were also side effects of pesticides.
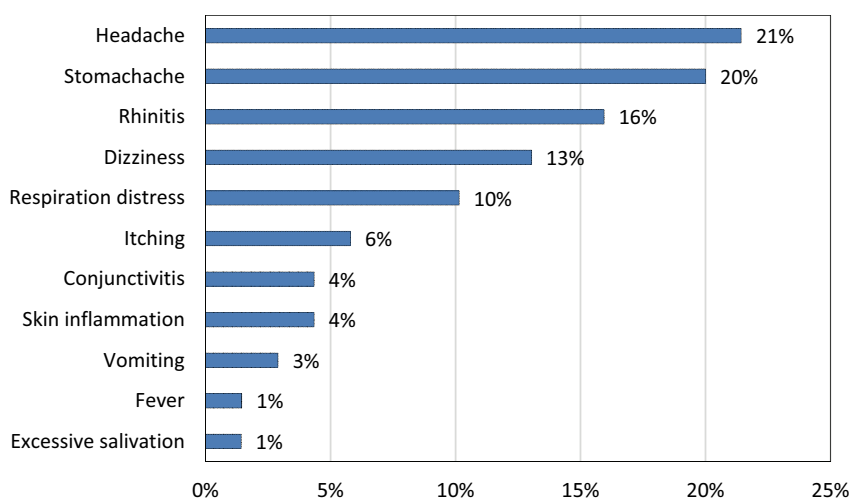
Figure 9:9 Symptoms reported to have occurred after pesticide application (n = 70)

As explained in section 2.5.4, chronic poisoning is not well document in Burkina Faso. Chronic effects are inherently harder to detect due to the time lag between exposure and the onset of diseases. Compared to acute poisoning, establishing causal link with pesticide is more difficult. However, the results from the model simulations outlined potentially hazardous chronic exposure for every studied populations due to little precautions taken during pesticide handling (inadequate PPE, pesticides doses, frequency of application, etc.). Among the pesticides tested in the present model, chlorpyrifos classified as potential endocrine disruptor was ubiquitous in matrices analyzed in the study area. This situation is of concerns as studies have shown that even low dose exposure may trigger cancers, neurologic effects, and reproductive effects (section 2.5.4).

9.4 Discussion on pesticide exposure assessment outputs

9.4.1 Handling of divergent behaviors in risk assessment

Every gardener had his own treatment scheme paying little attention to formulation used and manufacturer recommendations. The absence of correlation between treated surface area and applied pesticide dose is a sound example. This approach is of concerns as this irrational use makes it more difficult to characterize current situation and propose suitable solutions. Gardening activities in Sahelian countries are difficult to control due to the number of actors implied. General diagnosis poorly applies and variability reduces the possibility to foresee outcomes. Models allowed integrating individual specificities and providing a diagnosis based on a large population sample assumed representative of the local context. Due to the large variability between cases, the deterministic approach is the most recommended.

9.4.2 Model limitations and suitability

Outputs from the three models differed in the extent of the estimated population at risk. A first explanation lies in the differences between considered routes and sources of exposure for a similar actor. This is problematic and further model developments must reach a consensus on which pathways and routes of exposure to include. This remark particularly applies to EFSA 2014 and HAIR2014, which were designed for a similar use. Indeed, it was expected that WHO 2011 differs from other as it was not intended for pesticide application on crops. The second reason for the observed differences is that models rely on different sets of data, which ultimately influences algorithm design and outputs.

The working group that designed EFSA 2014 dataset and algorithm proposed this model in a harmonization perspective to tackle these issues. It is supposed to provide a more up-to-date version of European models such as HAIR2014. Starting from this consideration, results from EFSA 2014 should be seen as more reliable in the current state of practices. Unfortunately, this applies to European like context. To date, available exposure data did not allow to provide a dose dependent model for operators using knapsack sprayer (Großkopf et al., 2013). Instead, exposure surrogate values are provided for a treated surface equivalent to 1 ha. If it is common in Europe to apply a homogenous treatment on a comparative surface, this was not the case in the studied

areas. Most of the cultivated plots had a size smaller than 1000 m^2 (60%). As no relation was found between applied quantities and surfaces treated, this approach might be suitable to assess current situation but will be less representative when considering modelization of mitigation measures such as application of the recommended pesticide dose for a given surface area. For the other stakeholders (workers and bystanders), EFSA 2014 integrates all the relevant features from the other models. It is to be noted, that EFSA 2014 documentation did not provide any recommendation on how to perform risk assessment from modelized exposure. In the present work, risk ratios proposed in HAIR2014 and WHO 2011 documentations were applied (Garreyn et al., 2007; Kruijne et al., 2011; WHO, 2011b). EFSA guidance must also propose a harmonized approach for the risk assessment in further release.

As being a previous version of European exposure models, HAIR2014 features similar approach to EFSA 2014 except that HAIR2014 operator exposure algorithm integrates application rate and treated surface area. Similar algorithms are used for worker exposure calculations but in addition, HAIR2014 documentation considers that inhalation route is relevant and recommends considering no dissipation of dislogeable fraction between applications, which constitutes a more conservative (i.e. protective) approach. Bystander algorithm does not allow assessing exposure at a lower distance than 8 meters from the sprayer. This limitation did not really influence the representativeness of the modelized current situation. It is likely that bystanders already stay at a similar distance from the sprayer. Dermal exposure for adults and children only comes from spray drift in this model. Contrary to EFSA 2014, contact with contaminated surfaces is only integrated for toddlers crawling on lawns.

It is also noteworthy that under similar conditions, EFSA 2014 and HAIR2014 bystander algorithms predicted lower chronic risks for children compared to adults. These results are questionable as children are expected to be more vulnerable due to their physiological and behavioral characteristics. Larger surface area, higher oxygen, food, water requirement per unit of body weight, higher breathing and consumption rate, higher skin permeability, less efficient metabolism processes, are factors that determine the unique vulnerability of toddlers, infants, and children (Garreyn et al., 2007). Concerning behavioral specificities, in this work, it was decided to include exposure from lawn crawling and hand to mouth and object to mouth transfer only for toddlers as proposed in current model documentations (EFSA, 2014; Kruijne et al., 2011). Garreyn et al. (2007) proposed to consider them also for infants and children. Exposure routes definition must be revised in further model documentations in order to provide results more consistent with body development and actor behaviors.

As aforementioned, international guidance are often followed in the absence of specific governmental position for a given domain. This was the main reason for retaining WHO 2011 model despite its intended use for vector control rather than agricultural exposure assessment. Some features such as consideration of treated surface area, exposure assessment for gardening activities other than pesticide application (i.e. inspection, irrigation, harvesting, etc.), and distance from treatment equipment for bystanders are therefore not supported. WHO 2011 exposure algorithm is not based

on application rate (kg a.s. ha^{-1}) but relies on formulation and spray concentrations (g L^{-1}). Application of the proper dose of pesticide should refer to the spraying of the recommended amount of a.s. per treated surface area (application rate in kg a.s. ha^{-1}) at the recommended concentration (g L^{-1}). Differences observed between the compliance with recommended application rate and dilution suggested that these parameters were not considered together. However, applying the right amount of a.s. at a high or low concentration might have a different impact on individual exposure. Same comment applies to the application of the recommended concentration at a high or low application rate. In mitigation measures assessment scenarios, PPP could be considered as applied in conformed proportions, which is not necessarily the case when modelizing current practices. Dilution is therefore particularly relevant when assessing current situation. Finally, WHO 2011 algorithm does not integrate head and body exposure. Not only hands are expected to be exposed during pesticide handling. Omitting exposure pathways might induce underestimation of exposure and resulting risk. It also provides less flexibility in the assessment of mitigation measures using PPE. Even though it is expected to be more generic, the intended use of this model questions its representativeness in the context of agriculture and will not be recommended for further applications in market gardening.

Algorithms and datasets comparison suggested that EFSA 2014 integrated all the features needed to perform a comprehensive pesticide exposure assessment. It is also expected to correspond to the current state of the art and therefore should be preferred. Nevertheless, the knapsack model results are most likely unrealistic. Using surrogates values independent of application practices is very conservative and lack flexibility. When assessing mitigation measures, it was not possible to assess the impact of dose reduction. Considering this factor irrelevant is probably unrealistic and over-protective. Exposure studies on pesticide mixing, knapsack loading, and hand-held pesticide applications are needed to provide a more suitable algorithm (Großkopf et al., 2013). In the meantime, it is recommended to use HAIR2014 algorithm in parallel to model operator exposure.

In further model developments, it is recommended to express pesticide exposure as a function of spray concentration, volume applied, and treated surface area. Model documentations should also provide comprehensive explanations of how to perform risk characterization under defined exposure conditions. Integration of cumulative pesticide exposure is also important. Most of the current models do not account for cumulative exposure, while it is common that a person use more than one PPP on a given plot/crop. In the present work, developed risk assessment algorithm integrated cumulative exposure assessment using HI based on the CA model. This approach was found relevant in the studied context. In many cases, risks were identified for cumulative exposure while considering only single exposure was not sufficient to detect a risk.

Exposure models do not cover every specific local practices. Aside from knapsack sprayer, operators also diluted pesticides in a bucket and used brooms or leaves to apply pesticides. In order to provide consistent exposure estimates for the studied areas, studies should be conducted in the Sahelian region to provide reliable exposure data corresponding to the current state of the technique. Database of monitored operator exposures must be constituted. In addition, a total dietary study should be conducted to account for the total pesticide dietary intake.

Finally, regulatory agencies must review the definition of ANDAEL and provide assessors with suitable guidance values for non-dietary exposure acute risk assessment.

9.4.3 Model outputs: discussion on risk assessment

Knowing limitations presented in the above section and bearing in mind that models are only a simplification of the reality, it is expected that modelled exposure diverge from the effective internal exposure. Rather than exact estimates, the most important information given by these algorithms is the presence or absence of potential health risks and the extend of impact reduction resulting from mitigation measures.

As expected, every model agreed that current situation yields significant acute and chronic risks for every studied populations. These findings are in accordance with operators and other individuals (medical center reports) reporting symptoms after pesticides applications or vegetable consumption. Occupationally exposed individuals (i.e. operators and workers) presented higher risks than bystanders not involved in gardening activities.

None of the proposed mitigation measures was sufficient to prevent completely operators from hazardous exposures. Nevertheless, significant risk reduction is expected in scenario 4 according to HAIR2014 (~40%) and all the models agreed that less than 5% of the operators are likely to present a chronic risk.

Providing workers with PPE was not sufficient to prevent risk completely. On the other hand, adjustment of pesticide dose and frequency of application had a large impact on this population. All the models agreed that single pesticide exposure would yield neither acute nor chronic risk if recommended pesticide dose and application frequency are respected. Only a small residual risk is still predicted by HAIR2014 for cumulative pesticide exposure (4 - 5%) in scenario 4 (probably linked to the very protective approach retained for the DFR calculation in this model).

Increasing the distance between bystanders and spraying activities was not sufficient. In combination with adjustment of quantities of pesticide applied, only adults would be safe. Indeed even with these measures, model predictions indicated a significant remaining risk for children and toddlers.

Based on these results it is advised that gardeners use the proposed PPE and that efforts should be directed toward enforcement of pesticide manufacturers' recommendations. These actions are expected to have a significant impact on gardeners, workers, and adult present on the fields during pesticide application (bystander). Risks detected for children and toddlers suggest that they must be kept away from the gardening areas.

9.4.4 Prioritization of actions for pesticide impact mitigation

In a first attempt, proposed mitigation measures have been limited to potentially available and affordable protective equipment and to actions that could be easily implemented (cost effective and easily acceptable for the local population). Unfortunately, simulation results indicated that

proposed mitigation measures will not completely prevent operators from hazardous exposures and that additional actions are needed.

Reducing risk, either hazard or the exposure, needs a strategical or systemic approach. Garreyn et al. (2007) (referring to Brouwer et al. (1994)), proposed four levels of action organized in descending preference in the following subsections.

9.4.4.1 Reduction or elimination of the source of exposure

Substitution of pesticides or replacement by formulations with lower application rates is expected to have a large and easily measurable impact on the users. Products use can be restricted by administrative controls. The CSP is in charge of delivering pesticide authorizations for the member states of the CILSS (section 2.2.3). Changing authorization has therefore a regional impact. However, survey results underlined the lack of policy enforcement in the studied areas. Most of the pesticides used by gardeners and available on the market (survey on resellers) were not authorized. This situation is not restricted to the studied areas. Poor application of national legislations and lack of controls on importations of pesticides are common country wide (Ouédraogo et al., 2011). Human, financial, and technical resources must be allocated to the establishment of suitable routine control procedures. Implementation of these procedures at national scale need a strong political support and takes time. Therefore, local impact can only be expected in the long-term with this approach.

Change in pesticides used can be also achieved by changing users' habits. The product's choice can be oriented toward the less harmful and persistent alternatives. The success of this approach relies on the efficiency of the recommended replacement product at two levels. First, proposed alternative must ensure reduction or elimination of the targeted risk. This supposes that the proposed pesticide is either less hazardous or the formulation requires lower application rates (or both). Second, in order to ensure a lasting situation, proposed alternative must suit the user needs. Gardener must be informed on how to choose the most suitable products or be properly advised by the resellers. If alternative does not fulfil the attempts of the user, they will turn back to their current practices. This approach could achieve a significant risk reduction on a relatively short-term. In practice, this can be done by training the pesticide resellers on how to choose suitable formulations and advise customers on the way to use them (crop-pesticide association, dilution, application rate, and frequency). In a longer-term, user demand might influence formulations available on the market. This bottom-up approach seems more suitable to the local context.

Among the pesticides authorized by the CSP for gardening, emamectin benzoate, lambda-cyhalothrin, and profenofos were the main responsible for the remaining risks after application of the proposed mitigation measures. Emamectin benzoate presented the lowest AOEL of all the a.s. used. This explains its large implication in chronic risks detected by the model simulations. In Europe, lambda-cyhalothrin was included in the list of candidates for substitution, given that the AOEL is significantly lower than those of the majority of the approved active substances within the group of insecticides and that lambda-cyhalothrin meets the criteria to be considered a bioaccumulative and toxic substance (EC - DG Health and Food Safety's, 2015). In addition, lambda-

cyhalothrin presented the lowest ANDAEL of all the a.s. used. It is also to be noted that dietary intake of lambda-cyhalothrin in the study area was already outlined as potentially inducing acute and chronic risks (Chapter 6). The problematic of lambda-cyhalothrin is not restricted to the study area. Studies conducted in other regions of Burkina Faso already outlined that this substance was among the principal a.s. responsible for the recorded poisoning cases (MERSI et al., 2016; Toé, 2010b). Profenofos is already banned in Europe and it has been proved to potentially cause neuronal and endocrine perturbations (Lu et al., 2017; Memon et al., 2015; WHO/UNEP, 2012b). It is therefore advised to withdraw authorization for the formulations containing these a.s. and in the meantime advise users on suitable alternatives.

When considering alternatives wettable powder (WP) formulations should also be proscribed. Handling of WP formulations generates higher exposure via inhalation and hand contact than liquid (emulsifiable concentrate (EC)) or wettable granule (WG) formulations (Garreyn et al., 2007). When possible, the latter formulations must be preferred (less risk of splashing during mixture preparation). Alternatives must also take into account environmental considerations. The less persistent and hazardous alternatives for both human health and the environment must be preferred.

Labels are often the only media to communicate direction for use to the final user. Measures must be undertaken to regulate pesticide labeling in the CILSS member states. Label quality must be retained as a criterion for the selection of commercial pesticide formulations authorized by the CSP. In order to ensure suitable and comprehensive labeling, it is recommended applying the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) proposed by the United Nations (United Nations, 2011).

Finally, more support should be provided to research for the development of innovative solutions adapted to the local context. Priority should be given to the development of reduction strategies, biological control methods, and biopesticides. Diffusion of scientific knowledge should also be reinforced to achieve the effective implementation of alternatives.

9.4.4.2 Replacement or modification of processes or equipment

As aforementioned, each individual cultivates vegetables on small surface areas. Regarding the size of the cultivated plots and the generated incomes, it is not likely that spraying become mechanized. On the contrary, it was observed that people struggle to acquire or maintain knapsack sprayers and instead used (~30%) broom or leaves to apply pesticides (Figure 2:5). The priority is therefore to proscribe these artisanal alternatives and encourage the use of knapsack sprayers. Gardeners should organized themselves in small groups in order to be able to afford this equipment. By using it in turn, they will reduce their dermal exposure.

9.4.4.3 Organization of work and re-entry on treated field

9.4.4.3.1 Operators

Plots are contiguous in the study areas. Operators should therefore advice persons conducting activities on surrounding plots when planning a spraying session.

Meteorological conditions must be taken into account for the selection of the optimal conditions for pesticide application. Gardeners integrated already wind direction and intensity as an important factor. Temperature is also important. Higher temperatures increase dermal penetration and cutaneous blood flow, leading potentially to an amplified circulation of pesticides within the body (Macfarlane et al., 2013). High temperatures and low relative humidity might also induce significant evaporation of spray droplets before they reach the target. Reduction of the size of the droplet increases the influence of ambient air movements and thus increases spray drift. Evening and nighttime hours are characterized by stable atmospheric conditions. Application must be conducted in the morning when temperatures are lower and sufficient mixing occurs in atmospheric layers (Garreyn et al., 2007).

For activities conducted near sensitive water resources (e.g. catchment area, borehole, etc.), a buffer zone must be implemented to prevent from contamination. Definition of sensitive resources and restricted area surrounding them must be defined by the national regulation bodies.

Frequency of application recommended by manufacturers has been discussed in previous sections and must be respected. In addition, re-entry interval (REI) and days-to-harvest interval (DHI) (also called: preharvest interval (PHI)) must be also respected. The REI and the DHI are periods of time that must pass before respectively reentering a treated area or vegetables can be harvested after the application of a PPP. These information are normally provided on formulation labels but very few gardeners were aware of these restrictions. It is imperative to respect the DHI in order to prevent the aforementioned poisoning cases linked to vegetable consumption. Improvement on these practices can be achieved by training the operators or the resellers that would further advise customers. Training of the operators and pesticides resellers should also raise awareness regarding the risk associated with inappropriate mixture of pesticide formulations. Toxicity of mixture is difficult to predict and to integrate in existing risk assessment procedures.

Efforts must also be directed toward the promotion of methods of substitution or for the reduction of pesticide use. Technical itineraries must be defined at regional levels in order to provide farmers with crop calendars and recommendations on crop rotations and suitable associations (inter cropping, etc.). Finally, in order to facilitate information transfer, coordination of activities, discussion between stakeholders, and large-scale implementation of recommendations, it is advised that gardeners organized themselves in worker cooperatives.

9.4.4.3.2 Workers

Before entering crops, workers must informed themselves when the last treatment occurred in order to respect the REI and the DHI.

9.4.4.3.3 Bystanders

As for workers, bystanders are advised to informed themselves when the last treatment occurred in order to respect the REI. However, current fields' organization is not suitable for bystanders. All the areas surrounding the lakes are cultivated leaving no space between fields. Safe areas protected by a buffer zone are therefore not possible to implement. Physical barriers are also not

an option due to hydrological conditions. Even though efficiency of natural (vegetation barrier) or artificial barriers were proved (Garreyn et al., 2007), annual flooding of the sites would flush away any permanent installations. Medical reports have proved the unsuitability of gardening sites for children. It is therefore advised that bystanders especially children and persons with toddlers stay outside the cultivated perimeters.

9.4.4.4 Personal protection

9.4.4.4.1 Operators

For operators, the willingness to use a personal protective equipment will lie in its affordability and comfort during use. In the current state of the technology, waterproof, and chemical-resistant coverall offers the best protection (<5% penetration). Nevertheless, as other PPE, using it alone will not be sufficient to prevent from hazard completely. HAIR2014 simulations indicated a similar risk reduction with this equipment (penetration factor of 5%) than with cotton PPE (penetration factor of 10%) under current practices. Moreover as aforementioned, discomfort induced when working in warm conditions makes this solution unsuitable for the studied areas where the average temperature reaches up to 32 °C during the growing season (average temperature from 1901 - 2015, (World Bank, 2017)). Cotton workwear are therefore recommended. They also present the advantage of being less expensive and locally available. Simple washable hat or bonnet could be used to protect head. Disposable chemical-resistant gloves can be acquired in local stores.

Personal hygiene is also important. After each use, protective equipment must be cleaned with water and soap (Garreyn et al., 2007). It is advised to perform this task on the field and discard water directly in the vicinity of the crops. This would reduce the risk of contamination of other areas or resources (e.g. water, soil, etc.). Hands, hairs, and body must be thoroughly washed with water and soap after each application. If hygiene measures are respected, PPE could be also shared between operators to reduce individual costs.

9.4.4.4.2 Workers

For workers who are also operators, it is advised that they use their aforementioned protective equipment whenever they performed activities on the fields. For external workers, imposing PPE is a difficult task. As they never handle pesticide directly, they are less aware of the risk and will be less willing to invest in specific equipment. Improvement of operators' practices should be the preferred way to reduce worker exposure. Nevertheless, it is recommended that workers wear at least clothes covering legs entirely and long sleeves. They can always ask for the help of an operator in the case that they are not properly equipped.

9.5 Action plan for the management and the reduction of pesticide use

A strategical and systemic approach must be developed to improve pesticide management and reduce usage in the Saharan zone. Sufficient financial and human resources must be allocated to the development and the enforcement of a pesticide management and reduction plan. Actions are needed at multiple scales. At the international level, decisions taken by the CSP will have an impact on the situation in the CILSS member states. In Burkina Faso, a close coordination between national regulation bodies must be established to implement measures at national and regional scale. Based on the outcomes of the present thesis, the following actions constitute a preliminary basis for the development of a national/international pesticide management and reduction plan.

International Level (IL): CILSS member states

Action IL 1	Revise pesticide authorizations
Description	- Revision of the existing authorizations taking into account the current state of the technique and the local context - Substitution of pesticides or replacement by formulations with lower application rates - Selection of the less persistent and less hazardous alternatives for the environment and human health - Withdraw current authorizations for: emamectin benzoate, lambda-cyhalothrin, and profenofos
Participant(s)	Comité Sahélien des Pesticides (CSP)
Target	CILSS member states
Indicator	Updated authorization lists

Action IL 2	Improve pesticide label quality
Description	- Define guidelines for minimum label requirement based on the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) proposed by the United Nations (United Nations, 2011). - Include label quality in the criteria for the selection of commercial pesticide formulations authorized by the CSP - Propose solutions adapted to illiterate persons
Participant(s)	Comité Sahélien des Pesticides (CSP)
Target	CILSS member states
Indicator	Compliance of the labels with the defined guidelines

National Level (NL): Burkina Faso

GENERAL

Action NL 1	Provide a definition of the good agricultural practices adapted to the local context
Description	- Provide a definition of the good agricultural practices accounting for the current state of the technique and the local context
Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques, Ministère de l'environnement, de l'Economie Verte et des Changements Climatiques, Ministère de la Santé
Target	Users and vendors of phytopharmaceutical products
Indicator	Guidelines report

Action NL 2	Support research in the field of plant protection products and for the development of alternative solutions

Description	- Allocate resources to the research sector (human and financial)
	- Invest in equipment and infrastructures
	- Develop a national research fund to promote research and innovation in the domain
	- Share scientific knowledge on the website of the pesticide reduction and management plan
	- Example of research topics:
	  - Test and selection of resistant and productive local varieties and seeds
	  - Development of methods of substitution and for reduction of the use of phytopharmaceutical products
	  - Assessment of pesticide toxicity
	  - Development of analytical methods for quantification in various matrices
	  - Etc.

Participant(s)	Ministère de l'Enseignement Supérieur, de la Recherche Scientifique et de l'Innovation, Conseil National de l'Agriculture Biologique au Burkina Faso
Target	Scientists and technicians
Indicator	Scientific projects in the field of plant protection New equipment and infrastructures Research fund Scientific communications on the website of the pesticide reduction and management plan

Action NL3	Develop a communication plan on pesticide prevention

Description	- Specify objectives, target publics, messages, media, and planning
	- Improve transparency in the domain:
	    - Publication of annual activity report
	    - Publication of data on sales and importations of pesticides
	- Develop a website to present the activities of the pesticide reduction and management plan and facilitate communication

Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques
Target	General public
Indicator	Validated communication strategy Website online

Protection of the aquatic environment

Action NL4	Define guidelines for drinking water quality
Description	- Review existing guidelines - Define guideline values of health significance for relevant pesticides not included in the current regulation - Update the current legislation on drinking water quality standards
Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques, Ministère de l'environnement, de l'Economie Verte et des Changements Climatiques
Target	General public
Indicator	Guideline values for relevant pesticides Updated national drinking water quality standards

Action NL5	Define Environmental Quality Standards
Description	- Define guideline values for the protection of the aquatic environment and to provide indication on the ecosystem quality - Integrate the Environmental Quality Standards in the national legislation
Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques, Ministère de l'environnement, de l'Economie Verte et des Changements Climatiques
Target	General public
Indicator	Environmental Quality Standards Integration of the Environmental Quality Standards in the national legislation

Action NL6	Define restrictive guidelines for activities conducted in high-risk sensitive areas
Description	Guidelines directed toward owners and occupants of property located in catchment areas, protected areas, and other high-risk sensitive areas. - Provide harmonized definitions of high-sensitive areas including extend of the restricted zone for each type of sensitive resource. - Precise the activities authorized in restricted zones - Set the restrictions for authorized activities located in restricted zones - Integrate the guidelines for the activities conducted in high-risk sensitive areas in the national policy
Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques, Ministère de l'environnement, de l'Economie Verte et des Changements Climatiques
Target	Owners and occupants of property located in catchment areas, protected areas, and other high-risk sensitive areas.
Indicator	Guidelines for activities conducted in high-risk sensitive areas Integration of the guidelines for the activities conducted in high-risk sensitive areas in the national policy

Action NL7	Implement a compulsory buffer zone to protect water resources
Description	- For each type of sensitive water resource (surface water, wells, boreholes, etc.), define the characteristics of the compulsory buffer zone (size, surface characteristics, required amenities, restrictions in the buffer zone, etc.) - Integrate the standardized definitions of the buffer zone in the national policy to protect water resources
Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques, Ministère de l'environnement, de l'Economie Verte et des Changements Climatiques
Target	Activities conducted near water resources
Indicator	Guidelines for the implementation of buffer zones to protect water resources Implementation of a buffer zone around sensitive water resources is compulsory and integrated in the national policy

Action NL8	Informing and raising awareness of occupants of property located in high-risk sensitive areas

Description	- Provide targeted information to occupants of property located in high-risk sensitive areas.
	- Conduct trainings on the field on:
	  - The implementation of the guidelines for activities conducted in high-risk sensitive areas
	  - The implementation of the guidelines for the implementation of compulsory buffer zones to protect water resources

Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques
Target	Owners and occupants of property located in catchment areas, protected areas, and in the vicinity of sensitive water resources
Indicator	Number of occupants of property located in high-risk sensitive areas trained

Action NL9	Monitoring of water contamination by pesticides in catchment areas and protected areas

Description	- Define a national monitoring plan:
	   - Identify the strategic locations for the monitoring of the major catchment areas and protected areas
	   - Identify the relevant monitoring techniques
	   - Define monitoring periods and sampling frequency
	- Gather existing and acquired data in a database

Participant(s)	Ministère de l'Agriculture et des Aménagements Hydrauliques
Target	Scientists and Regulation bodies
Indicator	Pesticide levels and variations within catchment areas and protected areas Storage of existing and acquired data in a database

Monitoring of intoxication

Action NL 10	Monitoring of intoxication and assessment of the sanitary situation
Description	- Collect data from intoxication cases - Analyze trends and evolution of the sanitary situation - Centralized medical data in a database
Participant(s)	Ministère de la Santé
Target	Scientists and Regulation bodies
Indicator	Description of the sanitary situation Database to centralized medical data

Food quality control

Action NL 11	Reinforce food quality control
Description	- Increase control of Maximum Residue Limits (MRL) in imported food commodities - Increase control of Maximum Residue Limits (MRL) in food commodities traded on the domestic market
Participant(s)	Direction de la Protection des Végétaux et du Conditionnement, Laboratoire National de Santé Publique
Target	Imported commodities and commodities traded on the domestic market
Indicator	Pesticide concentrations in food commodities and compliance with the MRL

Action NL 12	Assessment of dietary intake of pesticides
Description	- Dietary surveys at national level - Risk assessment of dietary intake of pesticides
Participant(s)	Institut National de la Statistique, Ministère de la Santé, Direction de la Protection des Végétaux et du Conditionnement, Laboratoire National de Santé Publique
Target	Scientists and Regulation bodies
Indicator	Dietary survey results Risk assessment of dietary intake of pesticides

Implementation of the pesticide reduction and management plan

Action NL 13	Implementation of the actions planned by the pesticide reduction and management plan
Description	- Direction and control of the implementation of the actions planned by the pesticide reduction and management plan
Participant(s)	Commission National de Contrôle des Pesticides
Target	Stakeholders involved in the implementation of the pesticide reduction and management plan
Indicator	Annual report on the advancement of the implementation of the pesticide reduction and management plan

Regional level (Burkina Faso)

Action RL 1	Training of the pesticide users and vendors on the good agricultural practices
Description	- Diffusion of the good agricultural practices on the field - Particular focus on: - pesticide selection, - application rate - REI and DHI - personal protection - management of obsolete and leftover pesticides and pesticide packaging - crop selection and rotation - Provide online open access to the training material on the website of the pesticide reduction and management plan
Participant(s)	Direction de la Vulgarisation et de la Recherche et Développement, Direction régionale de l'Agriculture et des Ressources Halieutiques, Conseil National de l'Agriculture Biologique au Burkina Faso
Target	Users and vendors of phytopharmaceutical products
Indicator	Number of pesticide users and vendors trained Online open access to training material

Action RL 2	Promotion of methods of substitution and rational use of phytopharmaceutical products
Description	- Organization of workshops to present the methods of substitution and rational use of phytopharmaceutical products - Prepare a brochure presenting the proposed methods of substitution and approaches for rational use of PPP - Provide online open access to the training material on the website of the pesticide reduction and management plan
Participant(s)	Direction de la Vulgarisation et de la Recherche et Développement, Direction régionale de l'Agriculture et des Ressources Halieutiques, Conseil National de l'Agriculture Biologique au Burkina Faso
Target	Users and vendors of phytopharmaceutical products
Indicator	Number of pesticide users and vendors trained Brochure developed Number of brochures distributed Online open access to training material

Action RL 3	Advice farmers for the selection of resistant seeds and local varieties and definition of crop calendar
Description	- Propose a selection of resistant varieties and seeds adapted to the local context - Definition of crop calendar and technical itineraries
Participant(s)	Direction de la Vulgarisation et de la Recherche et Développement, Direction régionale de l'Agriculture et des Ressources Halieutiques, Conseil National de l'Agriculture Biologique au Burkina Faso
Target	Farmers
Indicator	Selection of resistant varieties and seeds adapted to the local context Crop calendar and technical itineraries

Action RL 4	Improve medical care and support in rural areas
Description	- Training of the medical staff on issues related to pesticide intoxication and suitable procedure to handle intoxication cases - Provide rural medical centers with suitable equipment and cures to handle intoxication cases
Participant(s)	Ministère de la Santé
Target	Rural populations
Indicator	Number of trained medical staff Distributed equipment and cure

9.6 Conclusion

This study provides a comprehensive assessment of the exposure of the population to pesticide in the studied areas. Three currently used models were tested. Integration of the local situation was done by using results from field surveys as inputs. Risk assessment was performed using hazard quotient (HQ) for single pesticide exposure and hazard index (HI) for cumulative pesticide exposure. Algorithms and datasets comparison outlined suitability and limitations of these models. The main limitations being a consistent integration of pesticide dilution, application rate, and volume applied as parameters in the calculation of operator exposure and the absence of consensus on relevant routes of exposure.

A diagnosis of the situation was provided based on simulation results. In the current situation, poor application of the good agricultural practices, ultimately led to hazardous exposure of the gardeners. The lack of precautions taken during pesticide application had repercussions on workers and bystanders present on the fields. Even if exposure was higher in occupationally exposed populations, acute and chronic hazards were detected in every groups. These results must be taken seriously as retained models are also used by international regulatory bodies for risk assessment and approval of PPP (Großkopf et al., 2013).

Mitigation measures have been proposed and assessed in 3 scenarios. The evaluation concludes that keeping bystander at a reasonable distance from the sprayer and providing operators and workers only with PPE is not sufficient. Additional measures must be undertaken to improve working practices. This includes training of the operators and pesticide resellers on pesticide selection and on the application of the GAP. Alternatives to formulations containing emamectin benzoate, lambda-cyhalothrin, and profenofos must be preferred. In the long-term, it is also advised that changes occur at a national/regional scale by implementing routine controls on imported and locally produced products and by revising the list of authorized substances. Formulation authorization should take into the particular context of the CILSS member states and particularly the lack of technical and financial means and the poor level of education of the rural populations by selecting the less hazardous alternatives.

Finally, behavior changes must be accepted by people entering treated areas. The spatial configuration of cultivated areas does not leave space for implementation of safe areas for bystanders. They must be kept away from the treated fields especially the most sensitive populations (i.e. toddlers, infant, and children).

Even if worst-case scenario was always retained as a precautionary principle, model simulations are always a simplification of the reality. Accidental exposures cannot be predicted. Frequency of application is not always a fixed parameter. Treatment scheme might be modified in case of disease outbreaks or pest attacks. More complex mechanisms can occur when considering exposure to multiple pesticides (e.g. synergistic effects of pesticide mixtures are not accounted for in the CA model). Other routes of exposure might be also relevant if different working scenarios are considered. Persons who cumulate different activities will also cumulate exposures resulting from each

task performed (e.g. a worker could also apply pesticide). In Burkina Faso, seasonality will also have an impact on exposure. Gardening activities are generally conducted around permanent lakes during the dry season. As the lake surface shrinks crops are planted under the maximal annual water level on surfaces that will be flooded during the next rainy season. Cultivated surfaces are therefore unsuitable for implementation of permanent buildings. In the present study, cultivated areas were considered far enough from residential areas to rule out residential exposure. This situation would be different if exposure was evaluated during the rainy season. Water availability in June-September does not restrict cultivated areas to lake surroundings and crops are planted near the habitations. Single individual could therefore cumulate operator, worker, bystander, and residential exposure. Different activities are also expected to be associated with different type of pesticides resulting in different acute and chronic hazards. In the long-term, persons cumulating various activities might also suffer from different chronic effects.

The present work outlined the actual health burden associated with pesticide use in gardening areas. Risk assessment results are of concerns. Actions must be taken in order to reduce pesticide exposure and health hazard in rural areas in Burkina Faso. Sustainable changes will be achieved only with the commitment of all the stakeholders in the domain. Reinforcement of administrative controls and behavioral changes require both short and long-term actions. Regional/national strategies must be adapted in order to propose actions suitable to the local context. Existing national strategic plans must be revised and sufficient technical, human, and financial resources must be allocated in order to reach their objectives. Raising local awareness is a priority. Efforts must be directed toward a better enforcement of the good agricultural practices. All stakeholders in the domain must acquire the minimum knowledge required for safe use and how to handle related issues. This will not be achieved without reinforced training/educations of users, workers, medical staff, and bystanders. In the end, improving management and selection of pesticide will also reduce environmental burden. Application of the recommended mitigation measures is therefore expected to have positive impacts on human health and indirectly on the environment.

Chapter 10 General conclusion

The present study proposes a comprehensive assessment of the pesticide burden in market gardening in Burkina Faso. The framework of the 3E program funded by the Swiss Agency for Development and Cooperation (SDC) allowed establishing a study design adapted to the local context. A preliminary study was conducted in 2014 (February-March) to characterized the situation and fully understand the local factors contributing to this problematic. This preliminary work allowed to define the orientations of the following three-year research work and to draft the list of target substances representative of the pesticides used in the study area. If pesticides play a pivotal role in meeting the agricultural products demand, the use of toxic chemicals is not without risk. The poor educational level and high illiteracy rate among users drastically hamper compliance with the good agricultural practices. Unsafe use or misuse of pesticides constitutes a major source of poisoning and anthropogenic stress on the ecosystem. Human and environmental health hazards are also the consequences of a weak legislative framework and the lack of political oversight in this domain. This lack of guidance precludes the development of the agricultural domain toward integrated and sustainable pesticide management. Sufficient financial and human resources must be allocated to the development and implementation of a strategic management plan improving and reducing pesticide use. The lack of support for the research also contributes to the poor development of solutions adapted to the local context. Moreover, the insufficient diffusion of the scientific knowledge hampers the implementation of innovative alternatives.

Although previous studies outlined the potential risks, there is still little knowledge of the effective impacts of pesticide use in Burkina Faso. In the absence of national monitoring and routine controls, existing data mainly come from point-off research projects. Effects of regulation enforcement and environmental impacts of pesticide use are generally only observed in the long-term, increasing the need for routine controls and monitoring. One of the main forces of the present study is that the proposed diagnosis is based on three years of on-site investigations and monitoring. Market gardening is the main activity for many farmers during the dry season. This domain knows an important growth due to the increasing demand for fresh vegetable products. Market gardening occupies a central position in the problematic of pesticide use across the country. Pesticides are generally applied throughout the growing season (~6 - 8 months). Repeated exposures induce therefore an important pressure on the local populations and the ecosystem in gardening areas. However, the impact could potentially extend to larger populations. Gardening areas are located around water reservoirs and many of them are used to supply drinking water in the cities. Vegetables produced are intended to be sold on the domestic market or elsewhere. Water and food contamination could therefore have large-scale consequences. These reasons, together with the lack

of reliable knowledge of the pesticide burden in this sector have motivated the choice of studying market gardening in the present thesis. This diagnosis of the situation comes nearly one century after gardening was introduced in the country.

10.1.1   Achieved results

The main achievement of the present work is the acquisition of quantitative data from a large variety of mediums affected by pesticide exposure. This required the adaptation and the development of innovative analytical protocols suitable to the matrices of interest and the large variety of physicochemical properties of the retained target analytes. Achieved results are the outcomes of five research components that structured the present thesis and allowed fulfilling the six objectives presented in section 3.3.

<u>The first research component focused on the characterization of the agricultural practices</u>. Understanding the local situation was a prerequisite to establish a relevant research plan and for the interpretation of the analytical results. Questionnaire surveys included a large number of individuals representing the local situation (n = 501). Results confirmed the low compliance with the good agricultural practices. The central problematic was the low level of education and knowledge of the operators on pesticides. Misuse had large consequences on the health of the rural populations. A large portion of the respondents affirmed experiencing sickness after pesticide application. Poisoning cases reported by the staff of the medical centers outlined that little precautions taken during pesticide handling triggered worrisome health issues. Many cases of intoxication during pesticide application were recorded over the past year and accidental intake presented a high fatality rate. Similar to operators, pesticide resellers presented a poor education level and knowledge about sold products. Most of them were not homologated resellers and were not aware of pesticide regulations. A large fraction of the pesticides sold was illegally imported because they were cheaper and easily available. Under these conditions, users were not provided with suitable guidance, which explains the irrational use observed on the field.

<u>The second research component focused on the characterization of the contamination in environmental matrices</u>. Misuse of pesticides can result in hazardous contamination of the environment. Pesticide levels were quantified in water, soils, and sediments. Different methods were developed in order to account for matrix specificities and the large variety of physicochemical characteristics of the analyzed compounds. Surface water, boreholes, and traditional wells were the three sources of drinking water identified during field surveys. A method for multiresidue analysis using SPE extraction was validated for 25 multi-class pesticides in water. Nearly 30% of the traditional well water did not meet quality standards for safe drinking water (levels > 0.1 µg L^{-1}). No quantifiable levels of pesticides were found in the boreholes, which suggested that pesticide contamination did not reach the groundwater. However, detection of traces of acetamiprid in one sample might be the indicator of a potential future degradation of this resource. For surface water, an innovative monitoring approach was proposed to complement the application of the conventional grab sampling technique. Recently developed passive samplers were deployed during the three-year monitoring of Loumbila Reservoir. This technique was found very suitable for the local context as

passive samplers eliminate the need for an energy/power supply and allow the entire sampling set-up to be miniaturized. The complementarity between Passive Organic Chemical Integrative Samplers (POCIS) and Silicon Rubber (SR), allowed the screening of 37 pesticides in surface water. Their deployment over the three-year monitoring of Loumbila Reservoir allowed the characterization of seasonal variations. Their high-sampling frequency and integrative capacity achieved the identification of trends and substances that could not be detected with conventional low frequency sampling. At this stage of development, the lack of calibrated sampling rates does not allow them to fully substitute grab sampling. However, these preliminary results are promising. With further calibration experiments, they could offer a robust alternative to conventional sampling techniques. The monitoring of Loumbila Lake indicated that pesticide levels exhibited seasonal patterns. During the dry season, pesticide levels were generally low (<0.03 µg L^{-1}). Isolated cases of higher concentrations were related to gardening activities. During the rainy season, pesticide contamination were more frequent and exhibited higher concentrations. A larger variety of active substances was detected during this season, including banned organochlorine pesticides (chlordane, dieldrin, DDTs, methoxychlor, and endosulfan). In total, twenty-three pesticides were detected in drinking water resources. Among them, atrazine, azadirachtin, carbofuran, chlorpyrifos, cypermethrin, dieldrin, imidacloprid, and profenofos presented levels exceeding the threshold limit for safe drinking water (> 0.1 µg L^{-1}). Hazards were also identified for fish, cladocerans, and benthic invertebrates all year round but mainly during gardening activities. It is to be noted that detected triazine herbicides and organochlorines are not used in the study area. Their detection suggested a transport by water during the rainy season from other agricultural activities located upstream of the reservoir (e.g. cotton or rice production). A multiresidue analytical method for the quantification of pesticides in soils and sediments was also validated for 27 multi-class pesticides. Pesticides detected in sediments (n = 6) likely originated from soils and water contamination as they were also detected in these matrices. The majority of the pesticides detected in soil samples (n = 10) were commonly used in gardening activities. They probably originated from the last growing season, as most of them were not likely to be persistent in this matrix. On the other hand, the organochlorines observed in water were also present in soils. Their persistence characteristic could indicate a past use, and their release by leaching during the rainy season could be another explanation of their presence in water. More research is needed to identify the sources of these contaminations. In general, pesticide levels measured in environmental compartments were low and the short persistence of observed hazardous concentrations did not support a large potential for acute intoxication. On the other hand, chlordane, chlorpyrifos, dieldrin, DDT, endosulfan, and methoxychlor were classified as endocrine disruptors (WHO/UNEP, 2012a) and chlordane (ATSDR, 2014), DDTs (U.S. EPA, 1988a), and dieldrin (U.S. EPA, 1988b) were recognized as probable human carcinogens. Chronic effects induced by repeated exposure to these substances, even at low doses, cannot be excluded.

The third research component focused on the risk assessment of dietary intake of pesticides in the study area. Pesticide levels were assessed in 6 of the most produced vegetable commodities (tomato, cucumber, okra, *Solanum aethiopicum, Solanum melongena L,* and sorrel), using a modified QuEChERS method validated for 31 active substances. Vegetables were found positive to 16 multi-

class pesticides (carbamate, neonicotinoids, organochlorines, organophosphates, pyrethroids, triazines, and tetranortriterpenoid). The lack of compliance with the good agricultural practices was outlined by the exceedance of the maximum residue limits (MRLs) in 36% of the samples. Although the production is mostly destined to the domestic market, these levels could limit the potential of export and the development of this sector. The dietary survey allowed evaluating the intake of pesticides via water and vegetable consumption. Hazards were mainly associated with the consumption of raw vegetables. Exposure levels to chlorpyrifos, lambda-cyhalothrin, and dieldrin were potentially hazardous for both adults and children (acute and chronic risks). This study focused only on vegetable consumption but additional exposure may also be expected from other agricultural products (e.g. cereals). However, the present findings are supportive that the consumption of raw products constitutes the main source of pesticide intake. As most of the other foodstuffs are consumed fried or boiled and less subject to pesticide treatment, lower exposure is expected. Dietary exposure also depends on individual habits and is therefore subject to inter-individual and regional variability. Nevertheless, the diet of rural populations is generally poorly diversified due to the low availability of food (quantity and diversity) and economical limitations (Savy et al., 2007). As agricultural practices are likely to be comparable across the country, the present study could be seen as a preliminary evaluation of the major component of dietary exposure to pesticides in the rural populations of Burkina Faso.

The fourth research component focused on the biomonitoring of pesticide exposure in a human matrix. The present study proposed an innovative analytical approach for the determination and the quantification of pesticides in human hair. A novel QuEChERS protocol was developed and validated for the analysis of 37 pesticides. This method achieved multi-class pesticide extraction and sample purification for analysis on GC-MS and UPLC-MS/MS in a single procedure, which considerably simplified sample treatment. In addition, dSPE purification eliminated the need for labor-intensive cleanup techniques. Compared to previous analytical procedures, particular improvement of the sensitivity was achieved for the UPLC amenable compounds (atrazine, carbofuran, and imidacloprid). To the best of our knowledge, this method also allowed the first successful recovery of acetamiprid, chlorpyrifos-methyl, linuron, and methoxychlor residues from human hair. Hair presented numerous advantages such as simple and safe collection and easy transport and storage. Due to the stability of the substances accumulated in hair, samples can be stored at room temperature, which is a considerable advantage in warm regions with low access to electricity. Applicability of the method was tested on samples collected from volunteers living in a gardening area. Hair was found to be a robust and sensitive indicator for the biomonitoring of population exposure to pesticides. Analysis revealed that exposure was influenced by multiple factors such as age, gender, and geographical location. As expected, the poor personal protective equipment used in the study area was found inefficient in reducing individual exposure. Hairs of the volunteers were positive to 17 pesticides. For certain active substances such as acetamiprid, cypermethrin, and lambda-cyhalothrin, occupational exposure was identified as the main source of exposure. However, for other substances such as imidacloprid and deltamethrin, similarities between occupationally and non-occupationally exposed individuals suggested the prevalence of other sources of exposure (e.g. dietary intake, vector control activities, etc.). Levels detected in hairs are of

concerns, as they were higher than reported in other areas of the globe and indicated exposure to endocrine disrupting chemicals and probable carcinogens detected in environmental matrices (DDTs, chlordane, and dieldrin). This easy to implement protocol was found very adapted to the local context (easy collection and sample storage). It could be of great use for the monitoring of population exposure and for the assessment of the efficiency/enforcement of national/international policies. To the best of our knowledge, the detection of acetamiprid, atrazine, DEA, carbofuran, and deltamethrin in field samples is a premiere. This study was also the first use of hair as a matrix for biomonitoring pesticide exposure in Western Africa.

The fifth research component focused on the risk assessment of operator, worker, and bystander exposure and recommendation proposal. The analytical approaches used in the aforementioned research components allowed characterizing the current situation. This diagnosis constitutes the prerequisite for the proposition of mitigation measures. Risk assessment models were used to complement this approach and evaluate the potential impact reduction achieved by mitigation measures under various exposure scenarios. In the absence of an African alternative, 3 international exposure assessment models were tested. Two European-based models used for pesticide homologation and one model developed by the World Health Organization were retained. These models relied on different algorithms and exposure datasets, which explain the discrepancies observed between simulation outputs. The WHO model was retained in an attempt to use a generic international model rather than the two regional-based others (European). However, it was primarily designed for indoor/outdoor space spraying for vector control. Its intended purpose and spraying technique poorly represent the state of the art in agriculture. It is therefore not recommended to use this model in further risk exposure assessment in agricultural domains. In the absence of local alternative, the two European models already provided valuable outputs. Simulation results indicated that training the operators to comply with pesticide recommendations of use and using suitable protective equipment was not sufficient. Additional behavioral changes and regulation adaptations are needed to reduce the exposure of the individuals present in gardening areas (operators, workers, and bystanders). Emamectin benzoate, lambda-cyhalothrin, and profenofos were the main responsible for the risks in evaluated scenarios. Removing these pesticides from the market could largely reduce the risks. National and international regulation bodies must revise the homologated substances and select pesticide formulations more suitable to the local context. In addition, more incentive on regulation enforcement and compliance with the good agricultural practices are necessary to improve the sanitary conditions in rural areas. Strategic management plan for the reduction and improvement of pesticide use must be developed and implemented at national level.

In parallel to these research activities, the present project also aimed at enhancing the analytical capacity of our partner 2iE, in Ouagadougou. The objectives were to develop the infrastructure necessary to support the activities conducted during this thesis and to enhance the knowledge of our partner in a new field of expertise for further research projects. The chemistry laboratory was equipped with the basic material necessary for organic analytical chemistry (basic glassware, SPE manifold, rotary evaporator pump, soxhlet extractor, distillation equipment, etc.). The technical

staff was trained for active sampling (water, soil, sediment, food, and hair) and passive samplers' deployment. The methods developed in the present thesis already provided a large panel of analytical procedures for pesticide multiresidue extraction in various matrices, which can now be conducted on-site. It is also to be noted that most of the protocols for pesticide analysis (multiresidue analysis in soil, sediment, food, and hair samples) were obtained by the adaptation of the original QuEChERS extraction method (AOAC, 2007). QuEChERS extraction is simple to operate even by non-technical staff. The only essential equipment is a centrifuge, which is accessible for most of the laboratories. Using a unique technique for different types of analysis also facilitated the training of the laboratory staff. Unfortunately, the expensive analytical instruments used during this thesis (GC-MS and UPLC-MS/MS) could not be acquired due to economic limitations. This sophisticated equipment also requires a high maintenance and supply of consumables that are difficult to obtain in a country where these activities are not well developed. To date acquisition of this equipment is not planned. Although, it could be of great use as only few other structures in the country are equipped with similar instruments.

In order to facilitate knowledge transfer, all the data collected during these 4 years of investigations were stored in a database. This database will be freely available (online) for any further research project. Finally, in order that the outcomes of the present work also benefit the local populations, on-site restitution of the results will be conducted by the end of the project. Workshops will be organized with all the identified stakeholders (gardeners, authorities, scientists, NGOs, etc.). Presentations of the results will also be held directly in the studied villages in order to reach as many people as possible.

10.1.2 Future development

Only few studies performed a quantification of pesticide residues in environmental and human matrices in Burkina Faso. Therefore, many topics are still to be addressed, among them:

- The assessment of environmental and human exposure to pesticides in sugar and cotton producing regions.
- The analysis of the pesticide residues present in the effluents of water treatment stations that supply the cities with drinking water originating from reservoirs surrounded by agricultural activities.
- The assessment of the total dietary intake of pesticides; i.e. including all the major food items consumed across the country (i.e. cereals, fruits, etc.).
- The assessment of the hazard induced by pesticide application for vector control at household level.
- The assessment of the effects of pesticide treatment on the cattle and the resulting hazards for the consumers.
- The exposure risk assessment to pesticides for aquatic, soil, and sediment biota.
- The evaluation of the toxicity of pesticide associations/mixtures and more specifically the identification of potential synergistic toxic effects between pesticides used in Burkina Faso.

- The implementation of a large-scale monitoring plan to characterized the national pesticide burden in water resources.
- The test and selection of seeds and local varieties resistant and productive in the local environment (pests, diseases, climatic conditions, etc.).

The present thesis constitutes a preliminary evaluation of pesticide burden in areas that were not previously studied. Therefore, further work is need to complete the development of the proposed approach.

The use of passive samplers for the monitoring of water quality in Sahelian regions is a novel approach. Two different types of passive samplers were necessary to cover the large variety of physicochemical properties of the pesticides applied in agriculture. POCIS and SR were found to be suitable for screening purpose and to assess seasonal variations of water contaminants. SR also allowed the detection of pesticides that could not be detected with conventional grab sampling technique. However, the uptake kinetics of these samplers is still poorly known under the specific environmental conditions of the study area (warm temperatures, stagnant water, etc.). Further calibration studies are needed to derive time-weighted average concentrations. In addition to monitoring applications, we also recommend the use of passive samplers for the further identification of pollution sources. Samplers can be rapidly deployed at several strategic locations along river streams. They could be therefore used to identify the origin of organochlorine contamination during the rainy season.

Hair was found to be a robust and sensitive indicator for the biomonitoring of pesticide exposure. However, influence of gender and similarities observed between occupationally exposed and non-occupationally exposed populations suggested that different physiological processes might influence pesticide accumulation. More research should be conducted to get a better understanding of the mechanisms of pesticide accumulation into the hair shaft. Pesticides can be metabolized when they enter the body. Further project should consider analyzing parent compounds together with their metabolites. It could provide valuable information on the fate of pesticides into the body and provide additional information regarding individual exposure when parent compound cannot be detected. Understanding pesticide accumulation in hair is critical for the definition of levels of health significance and for risk assessment. Simultaneous sampling of other biological matrices such as blood or urine could help understanding the transfer dynamic of the pesticide systemic dose into hair. Finally, pesticide analysis in hair was conducted during the dry season. A similar sampling during the rainy season should be performed in order to assess the suitability of hair for the monitoring of seasonal variations. It might also exhibit other exposure patterns (e.g. effect of repeated exposure, etc.) and type of contamination.

As mentioned, exposure risk assessment models offer a time and cost-effective alternative to laboratory and field experiments. They can be used for research purposes but also by regulators to complete the evaluation of active substances during the homologation process. To date, no African-based model exists. In the Sahelian region, existing exposure data must be compiled to create a

harmonized database. Studies must be conducted to complete this data and develop a model suitable to the current state of the technique.

Finally, emamectin benzoate was widely used in market gardening in Burkina Faso. Exposure to this substance was frequently associated with hazards in the model simulations due to its low AOEL. The relatively high toxicity of emamectin benzoate and its ubiquity in water samples indicated a potential risk for the population. However, the developed analytical protocols did not allow quantifying this substance in water, nor in other matrices. Development of analytical methods for the quantification of this pesticide would allow a better characterization of the effective risks. The same remarks apply also to thiram. Although field surveys reported a lower use compared to emamectin benzoate, this active ingredient was present in pesticide formulations produced in Burkina Faso. At this stage of development, analytical procedures could not be validated for this substance and further developments are needed.

To conclude, the present work outlined the actual health burden associated with pesticide use in gardening areas. Although there are still questions to be addressed, the situation is likely to be similar in other agricultural areas across the country. Therefore, the outcomes of the present research project can be seen as a preliminary evaluation of pesticide impacts in market gardening areas of Burkina Faso. The present thesis also proposed various analytical methods that could serve as a basis for further research projects or monitoring activities. Actions must be undertaken to reduce the exposure of the populations. More incentive on regulation enforcement and compliance with the good agricultural practices are necessary to improve the sanitary conditions in rural areas. These conditions cannot be achieved without the commitment of all the stakeholders and a strong political support. Human and financial resources must be allocated to the reinforcement of administrative controls, revision of regional/national management strategies, and for the education of rural populations. Pesticides can have consequent impacts on populations' development (impaired health, environmental degradation, expensive remediation measures, etc.). Contamination of surface water resources was surprisingly low considering the proximity of treated fields and little precautions taken during pesticide+

 handling. Market gardening was not identified as the only and major source of environmental contamination. Absence of precipitation (limited pesticide transportation), high temperature (pesticide degradation), and economical restrictions (low affordability of pesticides) might have played a significant role. However, environmental exposure is not the only route of exposure for the local populations. Occupational activities, vector control, dietary intake, etc. also contribute. If to date, the risks are still limited, a long-term vision is necessary in order to ensure a safe development of the rural populations.

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Award

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Publication in peer-reviewed journals

2017   **Lehmann, E.**, Turrero, N., Kolia, M., Konaté, Y., de Alencastro, L.F., 2017. Dietary risk assessment of pesticides from vegetables and drinking water in gardening areas in Burkina Faso. Sci. Total Environ. 601–602, 1208–1216. doi:10.1016/j.scitotenv.2017.05.285

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2017   **Lehmann, E.**, Oltramare, C., Nfon Dibié, J.-J., Konaté, Y., de Alencastro, L.F., 2017. Assessment of human exposure to pesticides by hair analysis: the case of vegetable-producing areas in Burkina Faso. Submitt. to Environ. Int. doi:10.1016/j.envint.2017.10.025

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- Risk assessment related to water in urban and rural area;
- Industrial water quality and treatment processes;
- Environmental monitoring to assess the impact of new constructions.

2010   **Intern BG Consulting engineers (3 months), Lausanne (Switzerland).** Definition of the water management plan for Swiss municipalities. Calculation and analysis of the replacement values of water supply networks in Swiss municipalities and prioritization of the interventions.

2010   **Internship in Burkina Faso in collaboration with EPFL and CREPA (3 months)**. Assessment of the management of an irrigation system used by 600 people in a market gardening area. Evaluation of the system hydraulic design and current irrigation practices. Design of measures to improve water management.

2009   **Consultant in environment for the company: SARL des carrières Chavaz père & fils, France** (1 month). Definition of the environmental strategy of the company. Prioritization and implementation of actions. Sensitization of the staff to environmental problematics. Preparation of the application and the audit to obtain the label (level 4) of the charter of the quarry's industries. The company was granted the desired certification the year following our collaboration.

Projects

2013-2016   **Development of an analytical chemistry laboratory for pesticide analysis at Institut International d'Ingénierie de l'Eau et de l'Environnement (Ouagadougou, Burkina Faso).**

Since 2011   **Environmental monitoring of various construction sites in Switzerland**

2012-2014   **Environmental diagnosis of 4 valleys concerned by hydroelectric exploitation in the context of the opening of the French hydroelectric market to competition (France).**

2012-2013   **Development of a new treatment process for wastewater generated by underground gas storage: evaporation in a vegetated basin (Storengy, France).** Design of the basin and phytoremediation processes.

2012   **Management of construction sites for the construction of wetlands and green spaces in gas storage sites (Storengy, France).**

2012   **Environmental impact assessment of the realization of a motorway bypass in Geneva (OFROU, Switzerland).**

2011-2013   **Environmental impact assessment of the development of a 4th railway line between Lausanne and Renens (SBB, Switzerland).**

2011   **Master thesis in collaboration with UNICEF: Assessment of water quality in 10 villages of the Province of Ganzourgou (Burkina Faso).** Management of field surveys and subsequent laboratory analysis (teams composed of engineers and technicians). Diagnosis on the current situation and assessment of the efficiency of UNICEF activities.

Conferences

2016   **Society For Hair Testing - The International Association of Forensic Toxicologists (SOFT-TIAFT) joint annual meeting** (30th August 2016) in Brisbane (Australia), oral presentation untitled: "Assessment of occupational exposure to pesticides with multi-class pesticide residues analysis in human hairs using a modified QuEChERS extraction method, case study of gardening areas in Burkina Faso.

2016   **9th European Conference on Pesticides and Related Organic Micropollutants in the Environment and 15th Symposium on Chemistry and Fate of Modern Pesticides** (6th October 2016) in Santiago de Compostela (Spain), oral presentation untitled: "Pesticide application in gardening: assessment of resulting impacts on water resource quality using grab samples and POCIS, case study of Loumbila Lake, Burkina Faso." This presentation was granted the award of the best young scientist presentation.

2016   **European Pesticide Residues Workshop** (24th - 27th Mai 2016) in Limassol, Cyprus.

Poster 1: "Levels of 48 pesticides in vegetables and water and evaluation of health risk resulting from dietary intake in gardening areas in Burkina Faso."

Poster 2: "Assessment of operator and worker exposure in gardening areas in Burkina Faso using the new AOEM proposed by EFSA guidelines."

2016   **68th symposium on crop protection** (17th May 2016) in Ghent (Belgium), oral presentation untitled: "Pesticide use in gardening areas in Burkina Faso and evaluation of the resulting risk for the operators using the new AOEM proposed by EFSA guidelines".

2014   **Forum Africa Water 2014** (13th March 2014) in Ouagadougou (Burkina Faso), poster presentation.

Appendix A

Online access to the database of the project

Online access to the database will be available by the end of the project. In the meantime, please send your access request to lehmann.edouard@gmail.com.

Appendix B

List of studies included in the preliminary assessment of pesticides used in Burkina Faso

ARFA. 2007. Utilisation Des Pesticides Chimiques En Cultures Maraîchères et Cotonnières Dans La Région Est Du Burkina Faso.

Bam-Dem-Siam/Mbaby, Augustin. 2013. "Risques Associés à L'usage Des Esticides Autour de Petites Retenues D'eau: Cas Du Continuum Bam-Dem-Siam." 2iE.

Bassole, D., & Ouédraogo, L. (2007). Problématique de l ' utilisation des produits phytosanitaires en conservation des denrées alimentaires et en maraîchage urbain et péri urbain au Burkina Faso : cas de Bobo Dioulasso , Ouahigouy

Congo, A. K. (2013). Risques sanitaires associés à l'utilisation de pesticides autour de petites retenues: cas du barrage de Loumbila (p. 68). Loumbila.

Gomgnimbou, A. P. K., Savadogo, P. W., Nianogo, A. J., & Millogo-rasolodimby, J. (2009). Usage des intrants chimiques dans un agrosystème tropical : diagnostic du risque de pollution environnementale dans la région cotonnière de l ' est du Burkina Faso, 13(4), 499–507.

Hyrkäs, W., & Pernholm, S. (2007). Impact of market gardening on surface water reservoirs in Burkina Faso. Lund university.

Mbaby, Augustin. 2013. "Risques Associés à L'usage Des Esticides Autour de Petites Retenues D'eau: Cas Du Continuum Bam-Dem-Siam." 2iE.

Ouédraogo, M., Tankoano, A., Ouédraogo, T. Z., & Guissou, I. P. (2009). Étude des facteurs de risques d'intoxication chez les utilisateurs de pesticides dans les exploitations cotonnières de Fada N'Gourma. Environnement, Risque & Santé, 8(n°4), 1–5.

Ouedraogo, R., Pare, S., Toé, A.M., Guissou, I.P., 2012. Pesticides risk assessment by PIRI for surface water in sugar cane cultivation in Burkina Faso. J. Environ. Hydrol. 20, 1–10.

Oyono Elle, André Eric Martial. 2008. "Risques Environnementaux et Sanitaires Liés À L ' Utilisation Des Pesticides Dans Le Maraîchage Au Burkina : Cas Des Sites de Tanghin , Boulmiougou et Yitenga." 2iE.

Savadogo, P. W., Traoré, O., Mariam, T., Tapsoba, K. H., Sedogo, P. M., & Bonzi-Coulibaly, L. Y. (2006). Variations de la teneur en résidus de pesticides dans les sols de la zone cotonnière du Burkina Faso. *Journal Africain des Sciences de l'Environnement, Vol.1*, 29–39. Retrieved from http://www.docstoc.com/docs/45971065/Variation-de-la-teneur-en-résidus-de-pesticides-dans

SAWADOGO, L. M. (2012). Utilisation des pesticides dans les cultures Maraîchères en zone urbaine et périurbaine de Ouagadougou : Etude des risques toxicologiques. Université de Ouagadougou.

Sou, Y. M. (2009). Recyclage des eaux usées en irrigation: potentiel fertilisant, risques sanitaires et impacts sur la qualité des sol (p. 178). Lausanne.

Toe, A. M. (2010). Étude pilote des intoxications dues aux pesticides agricoles au Burkina Faso.

Toé, A.M., Pare, S., 2011. Plan de lutte anti-parasitaire et de gestion des pesticides. Ministère de l'économie et des finances.

Appendix C

Supplementary material of Chapter 5

Section S1. Material details

Standards of analytes and deuterated compounds were purchased from Sigma-Aldrich (Switzerland), Dr. Ehrenstorfer (Germany), and Toronto Research Chemicals (Canada). Individual solutions of each analyte and deuterated compound and their dilutions were prepared in appropriate solvent prior preparation of the stock solutions (Table S1 and Table S2) and stored at −20 °C. Appropriate dilutions of these standard solutions were used to prepare calibration curves for further analysis on GC-MS and UPLC-MS/MS.

Ethyl acetate and methanol HPLC grade were acquired from Carlo Erba Reagents (France), dichloromethane HPLC grade and formic acid from Sigma-Aldrich (Switzerland), acetone and isooctane for residue analysis from Acros Organics (Belgium), ether from Fluka (Belgium), and acetonitrile and n-Hexane from Biosolve Chimie SARL (France). Solid-phase extraction (SPE) cartridges, containing 200 mg of the Oasis HLB (Hydrophilic-Lipophilic-Balanced) sorbent, were obtained from Waters (USA). Empty polypropylene SPE cartridges (6 mL volume) and frits (1/2 in. 20 μm) were bought from Agilent Technologies (USA). POCIS stainless steel rings (i.d. 5.4 cm, available sampling area ~ 46 cm^2) were provided by ExposMeter AB (Sweden) and polyethersulfone (PES) membranes (90 mm, pore 0.1 μm) by PALL Science (USA). GF/F glass fiber filters (0.7 μm pore size) were supplied by Whatman (UK). SR was obtained from Altec Products Limited (UK) in the form of sheets of 0.30 × 0.30 m and 0.5 mm thickness. Anhydrous magnesium sulfate (MgSO$_4$), sodium acetate (NaOAc), and 12 mL centrifuge tubes containing pre-determined amounts of SPE sorbents Supel™QuE Z-Sep/C18 were obtained from Sigma-Aldrich (Switzerland).

Table S1 Concentration of standard stock solution in acetone

Pesticide name	µg mL⁻¹	Pesticide name	µg mL⁻¹
Acetamiprid	19.1	Diazinon	15.7
Acetochlor	11.7	Dieldrin	10.2
Atrazine	11.2	Diuron	11.5
Desethylatrazine	9.6	Emamectin benzoate	15.7
Deisopropylatrazine	6.5	alpha-Endosulfan	10.1
Azadirachtin	11.4	beta-Endosulfan	10.1
Carbofuran	34.5	Endosulfan sulfate	10.2
Chlorpyrifos	24.2	Imidacloprid	10.4
Chlorpyrifos-methyl	9.9	Linuron	10.8
lambda-Cyhalothrin	19.3	Omethoate	30.4
alpha-Cypermethrin	81.6	Profenofos	62.1
beta-Cypermethrin	91.8	Triazophos	12.7
Deltamethrin	87.5		

Table S2 Concentration of internal standard stock solution and dilution for samples fortification

Surrogates	Cstock[a]	CSPE&POCIS[b]	C SR[c]	C soil&sediment[d]
Acetamiprid-d3	2.1	0.2	0.105	0.525
Acetochlor-d11	2.1	0.2	0.105	0.525
Atrazine-d5	2.5	0.2	0.125	0.625
Chlorpyrifos-d10	2.3	0.2	0.115	0.575
trans-Cypermethrin-d6	6.8	0.7	0.34	1.7
DEA-d6	2.2	0.2	0.11	0.55
trans-Deltamethrin-d6	9.3	0.9	0.465	2.325
Diuron-d6	2.2	0.2	0.11	0.55
alpha-Endosulfan-d4	3.2	0.3	0.16	0.8
beta-Endosulfan-d4	3.3	0.3	0.165	0.825
Imidacloprid-d4	4.2	0.4	0.21	1.05
Linuron d6	3.3	0.3	0.165	0.825

[a] Concentration of surrogate stock solution of target analytes in acetone (µg mL⁻¹)

[b] Concentration of diluted surrogate solution in methanol for water and POCIS fortification (µg mL⁻¹)

[c] Concentration of diluted surrogate solution in methanol for SR fortification (µg mL⁻¹)

[d] Concentration of diluted surrogate solution in methanol for soil and sediment fortification (µg mL⁻¹)

The gas chromatography analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph coupled with a Thermo Scientific ISQ Single Quadrupole MS (Waltham, MA, USA). The injection volume and composition were respectively 2 µL and isooctane. The injector was set to PTV splitless mode with an initial temperature of 75 °C and a maximal temperature of 300 °C at the end of the injection's transfer phase (rate: 10 °C sec⁻¹ in 2.5 min). Helium was used as the carrier gas (1.2 mL min⁻¹) and analytes were separated using a Phenomenex Zebron capillary column (ZB-5 MS plus, 20 m, 0.18 mm, 0.18 µm). The GC/MS oven program is given in Table S3. The ion source temperature was set to 250 °C and the ionization mode to Electron Ionization (EI). Target pesticides analyzed in GC-MS are presented in Table S4.

Table S3 GC/MS oven program

	Rate [°C min⁻¹]	Temperature [°C]	Hold Time [min]	Total Time [min]
Initial		80	0.5	0.5
Ramp 1	50	150		1.5
Ramp 2	5	300	8.1	38.1

Table S4 Target substances analyzed in GC-MS and corresponding surrogates

Pesticide name	Surrogate	Pesticide name	Surrogate
Acetochlor	Acetochlor-*d11*	Deltamethrin	trans-Deltamethrin-d6
Chlorpyrifos	Chlorpyrifos-*d10*	Dieldrin	alpha-Endosulfan-d4
Chlorpyrifos-methyl	Chlorpyrifos-*d10*	alpha-Endosulfan	alpha-Endosulfan-d4
lambda-Cyhalothrin	alpha-Endosulfan-d4	beta-Endosulfan	beta-Endosulfan-d4
alpha-Cypermethrin	trans-Cypermethrin-d6	Endosulfan sulfate	alpha-Endosulfan-d4
beta-Cypermethrin	trans-Cypermethrin-d6		

The UPLC system consisted of a UPLC Waters Acquity coupled to a Waters Acquity Xevo TQ-S tandem quadrupole MS. The injection volume and composition were respectively 30 µL and methanol : water (5:95, v/v) with 0.1% formic acid. Separations were carried out on a Waters Acquity UPLC HSS T3 column (2.1×100 mm, 1.8 µm) with oven temperature set at 30 °C. The mobile phase flow was set at 0.4 mL min⁻¹ and the corresponding gradient composition is given in Table S5.

Table S5. UPLC linear gradient composition

Time [min]	% A[a]	% B[b]	Flow rate [mL min⁻¹]
Initial	95	5	0.4
10	5	95	0.4
17	95	5	0.4

[a] A: methanol : water (5:95, v/v) with 0.1% formic acid

[b] B: methanol : water (95:5, v/v) with 0.1% formic acid

Nitrogen, used as desolvation gas (600 °C, 1000 L h⁻¹), was provided by a nitrogen generator (Peak, MNOLA). The capillary voltage was 3 kV and the temperature of the ion source was fixed at 150 °C. Argon was employed as collision gas at a pressure of 3.5×10^{-3} mbar. Compounds were detected in the multiple reaction monitoring (MRM) mode using two transitions per compound, except for some deuterated compounds for which only one transition was used. The most intense daughter ion was used for the quantification of the responses of each compound, and the other one was used for confirmation purpose (Table S6).

Table S6 ESM

Pesticides	MRM Transitions 1	MRM Transitions 2	RT[a] [min]	Surrogates
Acetamiprid	223 > 126	223 > 56	4.74	Acetamiprid-*d3*
Atrazine	216.1 > 174	216.1 > 96.1	7.43	Atrazine-*d5*
Deisopropylatrazine	174 > 96	174 > 78.9	3.87	DEA-*d6*
Desethylatrazine	188 > 146	188 > 78.9	5.12	DEA-*d6*
Azadirachtin	743.3 > 725.4	743.3 > 625.3	7.34	Imidacloprid-*d4*
Carbofuran	222.11 > 165.1	222.11 > 123	6.49	Acetamiprid-*d3*
Diazinon	305.1 > 169	305.1 > 96.9	9.7	Linuron-*d6*
Diuron	233.1 > 160	233.1 > 188	7.87	Diuron-*d6*
Emamectin benzoate	886.6 > 158	886.6 > 126	10.34	Linuron-*d6*
Imidacloprid	256.1 > 209.1	256.1 > 175.1	4.29	Imidacloprid-*d4*
Linuron	249.1 > 182	249.1 > 160	8.21	Linuron-*d6*
Omethoate	214.1 > 183.1	214.1 > 125.1	2.18	Acetamiprid-*d3*
Profenofos	372.9 > 302.6	372.9 > 127.9	10.23	Linuron-*d6*
Triazophos	314.1 > 161.9	314.1 > 118.9	8.76	Linuron-*d6*
Acetamiprid-*d3*	225.9 > 125.9	-	4.71	-
Atrazine-*d5*	221.2 > 179.1	-	7.36	-
DEA-*d6*	193.93 > 146.9	-	5.03	-
DIA-*d5*	178.9 > 136.97	178.9 > 101	3.8	DEA-*d6*
Diuron-*d6*	239.2 > 78.04	-	7.64	-
Imidacloprid-*d4*	259.9 > 213	-	4.16	-
Linuron-*d6*	256.86 > 161.95	-	8.18	-
Chlorpyrifos-*d10*	361.8 > 98.74	-	10.8	-

[a] Retention time in minute

Section S2. Environmental conditions during in situ calibration
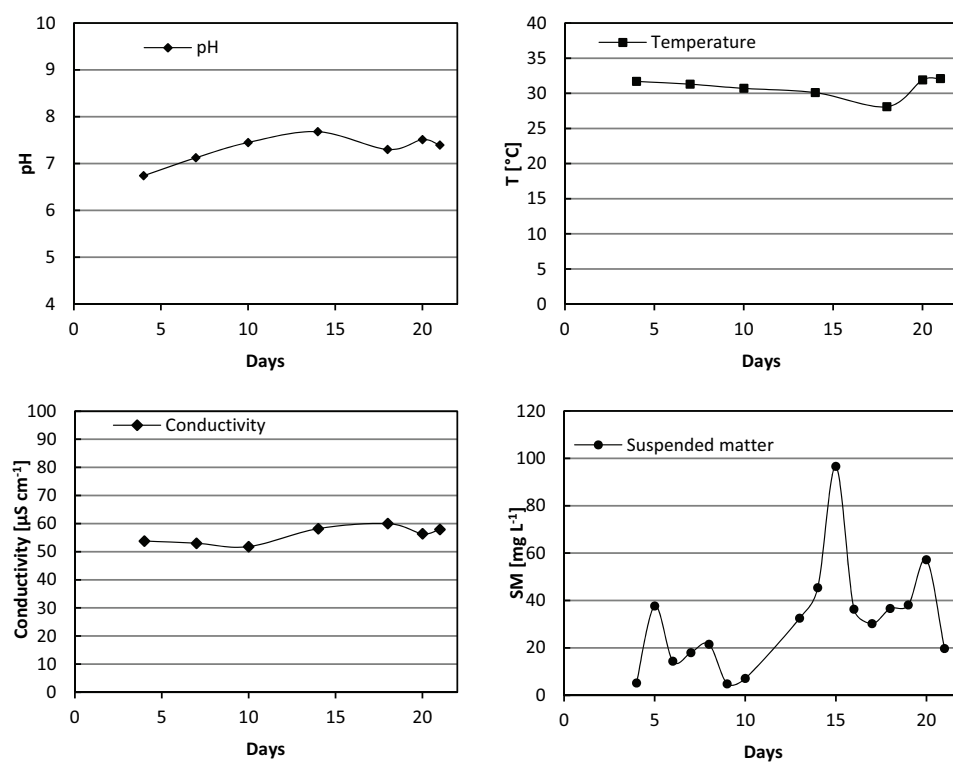
Figure S1 Environmental conditions during in situ calibration experiment

Section S3. Pesticide levels measured in water resources

The following tables present the levels of pesticide measured in samples from 9 villages located on the coast of Loumbila lake: ONEA (pumping station), Poedogo (POED), Bendogo (BEN), Daguilma (DAG), Sag-nioniogo (SAAG), Tabtenga (TAB), Noungou I (NI), Noungou II (NII), Nabdogo (NAB), Pousghin (POUS) in December (Dec), March (Mar), April (Apr), June (June), July (Jul) and August (Aug).

Table S7 Time weighted average concentration (TWAC) of triazines from POCIS duplicate (mean) and water concentration measured with grab samples (Cw) from the lake in µg L^{-1}. *N.M*: Not Measured.

Sample name	TWAC Atrazine	Cw Atrazine	TWAC DEA	Cw DEA	TWAC DIA	Cw DIA
NI Dec 14	*N.M*	0.0117	*N.M*	0.0040	*N.M*	0.0014
POED Dec 14	*N.M*	0.0113	*N.M*	0.0040	*N.M*	0.0014
ONEA Dec 14	*N.M*	0.0115	*N.M*	0.0041	*N.M*	0.0015
NI Apr 15	0.0194	0.0156	0.0028	0.0091	0.0015	0.0039
NII Apr 15	0.0152	0.0169	0.0029	0.0091	0.0020	0.0040
POED Apr 15	0.0208	0.0160	0.0049	0.0091	0.0030	0.0036
SAAG Apr 15	0.0188	0.0152	0.0048	0.0091	0.0019	0.0044
POUS Apr 15	*N.M*	0.0159	*N.M*	0.0092	*N.M*	0.0041
ONEA Apr 15	*N.M*	0.0181	*N.M*	0.0099	*N.M*	0.0041
NI June 15	0.0208	0.0071	0.0043	0.0040	0.0018	0.0021
NII June 15	0.0189	0.0086	0.0037	0.0035	0.0016	0.0024
POED June 15	0.0230	0.0065	0.0048	0.0036	0.0027	0.0018
SAAG June 15	0.0095	0.0117	0.0010	0.0048	0.0008	0.0031
POUS June 15	0.0242	0.0065	0.0038	0.0035	0.0012	0.0022
TAB June 15	0.0058	0.0194	0.0008	0.0062	0.0008	0.0048
ONEA June 15	*N.M*	0.0078	*N.M*	0.0044	*N.M*	0.0021
NI Jul 15	*N.M*	0.0193	*N.M*	0.0061	*N.M*	0.0038
NII Jul 15	*N.M*	0.0784	*N.M*	0.0192	*N.M*	0.0146
POED Jul 15	*N.M*	0.0897	*N.M*	0.0082	*N.M*	0.0054
SAAG Jul 15	*N.M*	0.0518	*N.M*	0.0086	*N.M*	0.0059
POUS Jul 15	*N.M*	0.4683	*N.M*	0.0202	*N.M*	0.0056
TAB Jul 15	*N.M*	0.0723	*N.M*	0.0097	*N.M*	0.0073
ONEA Jul 15	*N.M*	0.0408	*N.M*	0.0050	*N.M*	0.0027
NAB Mar16[a]	0.0129	0.0141	0.0048	0.0054	0.0024	0.0022
NI Apr 16	0.0120	0.0101	0.0057	0.0039	0.0024	0.0015
NII Apr 16	0.0119	0.0102	0.0054	0.0037	0.0024	0.0008
POED Apr 16	0.0125	0.0098	0.0037	0.0038	0.0019	0.0014
SAAG Apr 16	0.0125	0.0090	0.0039	0.0038	0.0017	0.0013
POUS Apr 16	0.0126	0.0109	0.0035	0.0044	0.0015	0.0017
ONEA Apr 16	0.0154	0.0112	0.0055	0.0042	0.0017	0.0017
NI Jul 16	*N.M*	0.0588	*N.M*	0.0133	*N.M*	0.0072
NII Jul 16	*N.M*	0.0523	*N.M*	0.0116	*N.M*	0.0055
POED Jul 16	*N.M*	0.1808	*N.M*	0.0205	*N.M*	0.0111
SAAG Jul 16	*N.M*	0.1192	*N.M*	0.0285	*N.M*	0.0169
POUS Jul 16	*N.M*	0.0596	*N.M*	0.0120	*N.M*	0.0052
TAB Jul 16	*N.M*	0.0523	*N.M*	0.0135	*N.M*	0.0096
ONEA Jul 16	*N.M*	0.0689	*N.M*	0.0121	*N.M*	0.0054
NII Aug 16	0.0892	0.0613	0.0083	0.0110	0.0068	0.0062
POED Aug 16	0.0899	0.0873	0.0095	0.0131	0.0060	0.0068
SAAG Aug 16	*N.M*	0.0613	*N.M*	0.0064	*N.M*	0.0036
POUS Aug 16	0.0709	0.0738	0.0052	0.0123	0.0075	0.0072
TAB Aug 16	0.0326	0.0335	0.0027	0.0075	0.0037	0.0050
ONEA Aug 16	0.1578	0.0966	0.0153	0.0172	0.0100	0.0087

[a] POCIS from Nabdogo (NAB) in March 2016 was collected during the calibration experiment after 21 days of exposure.

Table S8 Levels of pesticide detected with grab samples from the lake in µg L^{-1}. N.D: Not Detected, <LOQ: trace level (i.e. LOD< concentration of pesticide <LOQ). Lambda-cyhalothrin was detected in only one sample (NI Dec 14) at trace level (<LOQ) and therefore is not displayed in this table.

Sample name	Acetamiprid	Azadirachtin	Carbofuran	Chlorpyrifos	alpha-Cypermethrin	beta-Cypermethrin	Dieldrin	Imidacloprid	Profenofos	Triazophos
NAB Dec 14	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0037	N.D	N.D
LOU Dec 14	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0039	N.D	N.D
NI Dec 14	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0040	N.D	N.D
ONEA Dec 14	N.D	N.D	N.D	<LOQ	N.D	N.D	N.D	0.0038	N.D	N.D
POED Dec 14	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0037	N.D	N.D
BEN Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0010	N.D	N.D
DAG Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0011	N.D	N.D
NAB Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
SAAG Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
POUS Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
POED Apr 15	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	<LOQ	N.D	N.D
NI Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
NII Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
ONEA Apr 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
NI June 15	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0149	N.D	N.D
NII June 15	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0187	N.D	N.D
TAB June 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0033	N.D	N.D
ONEA June 15	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0154	N.D	N.D
POUS June 15	<LOQ	<LOQ	N.D	<LOQ	N.D	N.D	N.D	0.0166	N.D	N.D
POED June 15	0.0019	N.D	N.D	N.D	N.D	N.D	N.D	0.0249	N.D	N.D
SAAG June 15	N.D	<LOQ	N.D	N.D	N.D	N.D	N.D	0.0077	N.D	N.D
NI Jul 15	<LOQ	N.D	N.D	N.D	N.D	N.D	0.1069	0.0471	N.D	N.D
NII Jul 15	0.0302	0.1126	N.D	N.D	N.D	N.D	N.D	0.2355	N.D	0.0225
TAB Jul 15	N.D	<LOQ	N.D	N.D	N.D	N.D	N.D	0.0040	N.D	N.D
ONEA Jul 15	<LOQ	N.D	<LOQ	N.D	N.D	N.D	N.D	0.0194	N.D	N.D
POUS Jul 15	0.0106	N.D	0.1097	<LOQ	N.D	N.D	N.D	0.1449	N.D	N.D
POED Jul 15	0.0023	N.D	N.D	<LOQ	N.D	N.D	N.D	0.0702	N.D	N.D
SAAG Jul 15	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0107	N.D	N.D
NAB Mar 16[a]	<LOQ	N.D	N.D	<LOQ	<LOQ	N.D	N.D	N.D	N.D	N.D
NAB Mar 16[a]	0.0020	N.D	N.D	N.D	N.D	N.D	N.D	0.0009	N.D	N.D
NAB Mar 16[a]	0.0087	N.D	N.D	N.D	0.1036	0.1161	N.D	0.0009	N.D	N.D
NAB Mar 16[a]	0.0015	N.D	N.D	N.D	N.D	N.D	N.D	0.0009	N.D	0.0008
NAB Mar 16[a]	0.0020	N.D	N.D	N.D	N.D	N.D	N.D	0.0061	N.D	N.D
NAB Mar 16[a]	0.0026	N.D	N.D	0.0447	N.D	N.D	N.D	0.0014	N.D	N.D
NAB Mar 16[a]	0.0013	N.D	N.D	N.D	N.D	N.D	N.D	0.0008	N.D	N.D
NAB Mar 16[a]	0.0012	N.D	N.D	N.D	N.D	N.D	N.D	0.0009	N.D	N.D
NAB Mar 16[a]	0.0022	N.D	N.D	N.D	N.D	N.D	N.D	0.0010	N.D	N.D
NAB Mar 16[a]	0.0019	N.D	N.D	N.D	N.D	N.D	N.D	0.0010	N.D	N.D
NAB Mar 16[a]	0.0014	N.D	N.D	N.D	N.D	N.D	N.D	0.0017	N.D	0.0007

Sample name	Acetamiprid	Azadirachtin	Carbofuran	Chlorpyrifos	alpha-Cypermethrin	beta-Cypermethrin	Dieldrin	Imidacloprid	Profenofos	Triazophos
NAB Mar 16[a]	0.0016	N.D	N.D	N.D	N.D	N.D	N.D	0.0033	N.D	N.D
NAB Mar 16[a]	0.0014	N.D	N.D	N.D	0.0721	0.0960	N.D	0.0014	N.D	0.0007
NAB Mar 16[a]	0.0017	N.D	N.D	N.D	N.D	N.D	N.D	0.0012	N.D	0.0009
NAB Mar 16[a]	0.0017	N.D	N.D	N.D	N.D	N.D	N.D	0.0027	N.D	N.D
NAB Mar 16[a]	0.0013	N.D	N.D	N.D	N.D	N.D	N.D	0.0013	N.D	N.D
NAB Mar 16[a]	0.0035	N.D	N.D	0.0858	N.D	N.D	N.D	0.0040	N.D	0.0007
NAB Mar 16[a]	0.0018	N.D	N.D	N.D	N.D	N.D	N.D	0.0015	N.D	N.D
NAB Mar 16[a]	0.0016	N.D	N.D	N.D	0.5051	0.3341	N.D	0.0012	N.D	0.0009
NAB Mar 16[a]	0.0020	N.D	N.D	N.D	N.D	N.D	N.D	0.0026	N.D	N.D
NAB Mar 16[a]	0.0018	N.D	N.D	N.D	N.D	N.D	N.D	0.0057	N.D	0.0008
NAB Mar 16[a]	0.0013	N.D	N.D	N.D	N.D	N.D	N.D	0.0013	N.D	N.D
NI Apr 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
NII Apr 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
ONEA Apr 16	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	<LOQ	N.D	N.D
POUS Apr 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
SAAG Apr 16	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0015	N.D	N.D
POED Apr 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
POED Jul 16	0.0019	N.D	N.D	N.D	N.D	N.D	N.D	0.0292	<LOQ	N.D
POUS Jul 16	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0162	N.D	N.D
SAAG Jul 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0046	N.D	N.D
ONEA Jul 16	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0278	N.D	N.D
TAB Jul 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0015	N.D	N.D
NI Jul 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0413	<LOQ	0.0005
NII Jul 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0165	N.D	0.0013
ONEA Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0201	N.D	<LOQ
TAB Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D	N.D
NI Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0136	N.D	0.0006
POED Aug 16	<LOQ	N.D	N.D	N.D	N.D	N.D	N.D	0.0206	N.D	<LOQ
SAAG Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0012	N.D	N.D
POUS Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0154	N.D	0.0004
NII Aug 16	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0132	N.D	0.0005

[a] Samples collected in Nabdogo (NAB) in March 2016 correspond to the water samples collected during the calibration experiment

Table S9 Amount of analytes accumulated in the POCIS over 21 days of exposure in µg g^{-1}. N.D: not detected, <LOQ: trace level (i.e. LOD< concentration of pesticide <LOQ)

Sample name	Acetamiprid	Azadirachtin	Chlorpyrifos	Dieldrin	Imidacloprid	Profenofos	Triazophos	DIA-*d5*
NI Apr 15_1	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.2188
NI Apr 15_2	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0961
NII Apr 15_1	N.D	N.D	N.D	N.D	<LOQ	N.D	N.D	0.2435
POED Apr 15_1	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.6209
POED Apr 15_2	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.6654
SAAG Apr 15_1	N.D	N.D	N.D	N.D	N.D	N.D	N.D	0.0634
SAAG Apr 15_2	0.0015	N.D	N.D	N.D	0.0047	N.D	N.D	0.2152
SAAG June 15_1	N.D	N.D	N.D	N.D	0.0374	N.D	N.D	0.2132
SAAG June 15_2	0.0043	N.D	N.D	N.D	0.1743	N.D	N.D	0.1826
NII June 15_1	0.0238	N.D	N.D	N.D	0.2689	N.D	N.D	0.1399
NII June 15_2	N.D	N.D	N.D	N.D	0.0143	N.D	N.D	0.1179
TAB June 15_1	N.D	0.1110	0.5197	0.2612	0.0319	N.D	N.D	0.3143
NI June 15_1	0.0148	N.D	N.D	0.1384	0.1070	N.D	N.D	0.0800
NI June 15_2	0.0183	N.D	N.D	N.D	0.1578	N.D	N.D	0.0793
POED June 15_1	0.0452	N.D	N.D	N.D	0.2100	N.D	N.D	N.D
POED June 15_2	0.0456	N.D	N.D	N.D	0.2124	N.D	N.D	0.0308
POUS June 15_1	0.2261	0.5367	N.D	N.D	1.3405	0.0959	0.0010	N.D
NAB Mar 16_1[a]	0.0048	N.D	N.D	N.D	0.0103	N.D	N.D	0.1425
NAB Mar 16_2[a]	0.0036	N.D	N.D	N.D	0.0073	N.D	N.D	0.2037
NI Apr 16_1	0.0013	N.D	N.D	N.D	0.0019	N.D	N.D	0.0960
NI Apr 16_2	0.0014	N.D	N.D	N.D	0.0021	N.D	N.D	0.0872
NII Apr 16_1	0.0013	N.D	N.D	N.D	0.0020	N.D	N.D	0.1221
NII Apr 16_2	0.0014	N.D	N.D	N.D	0.0023	N.D	N.D	0.0448
ONEA Apr 16_1	0.0013	N.D	N.D	N.D	0.0018	N.D	N.D	0.0946
ONEA Apr 16_2	0.0018	N.D	N.D	N.D	0.0018	N.D	N.D	0.0108
POUS Apr 16_1	0.0019	N.D	N.D	N.D	0.0024	N.D	N.D	0.0403
POUS Apr 16_2	0.0017	N.D	N.D	N.D	0.0023	N.D	N.D	0.0562
SAAG Apr 16_1	0.0025	N.D	N.D	N.D	0.0039	N.D	N.D	0.0933
SAAG Apr 16_2	0.0021	N.D	N.D	N.D	0.0043	N.D	N.D	0.0738
POED Apr 16_1	0.0026	N.D	N.D	N.D	0.0039	N.D	N.D	0.0531
POED Apr 16_2	0.0030	N.D	N.D	N.D	0.0042	N.D	N.D	0.1334
POUS Aug 16_1	N.D	N.D	N.D	N.D	0.0628	N.D	N.D	0.8958
POUS Aug 16_2	N.D	N.D	N.D	N.D	0.0411	N.D	N.D	0.6270
ONEA Aug 16_1	0.0204	N.D	N.D	N.D	0.6185	N.D	N.D	0.2069
ONEA Aug 16_2	0.0321	N.D	N.D	N.D	1.1089	N.D	N.D	0.2098
NII Aug 16_1	0.0096	N.D	N.D	N.D	0.4811	N.D	0.0081	0.5244
NII Aug 16_2	0.0121	N.D	N.D	N.D	0.5487	N.D	0.0129	0.2707
TAB Aug 16_1	N.D	N.D	N.D	N.D	0.0118	N.D	N.D	1.0981
TAB Aug 16_2	N.D	N.D	N.D	N.D	0.0117	N.D	N.D	0.9846
POED Aug 16_1	0.0111	N.D	N.D	N.D	0.4689	N.D	N.D	0.2035
POED Aug 16_2	0.0119	N.D	N.D	N.D	0.4521	N.D	N.D	0.7027

[a] POCIS from Nabdogo (NAB) in March 2016 were collected during the calibration experiment after 21 days of exposure.

Table S10 Levels of pesticide measured in traditional wells (March-April 2016) in µg L^{-1}.

Sample name	Acetamiprid	Atrazine	DEA	DIA	Azadirachtin	Carbofuran	Chlorpyrifos	lambda-Cyhalothrin	Emamectin benzoate[a]	Imidacloprid	Profenofos	Triazophos
NCP Z4	0.0274	0.0003	0.0007	0.0004	N.D	N.D	0.2022	N.D	N.D	0.0361	0.1742	N.D
NCP Z1	0.0022	0.0031	0.0025	0.0009	N.D	0.0106	0.0502	N.D	N.D	0.3840	0.0521	<LOQ
NCP Z2	N.D	0.0014	0.0021	0.0008	N.D	N.D	N.D	N.D	N.D	0.1201	0.0531	N.D
NCP Z5	0.0037	0.0010	0.0009	0.0004	N.D	N.D	N.D	N.D	N.D	0.0130	0.1165	N.D
NCP Z3	0.0014	0.0021	0.0094	0.0076	N.D	N.D	N.D	N.D	N.D	0.0031	0.0288	N.D
EAU_LOU_P_01 27_02_16	<LOQ	0.0019	0.0014	0.0008	N.D	N.D	0.0394	N.D	(0.0015)	0.0008	<LOQ	N.D
EAU_LOU_P_01 04_04_16	0.0188	0.0014	0.0012	0.0007	N.D	N.D	N.D	N.D	(0.0017)	0.0023	<LOQ	N.D
EAU_LOU_P_02	0.0014	0.0011	0.0012	0.0006	N.D	N.D	N.D	N.D	(0.0018)	0.0033	<LOQ	N.D
EAU_LOU_P_03	0.0012	0.0006	0.0009	0.0005	N.D	N.D	N.D	N.D	(0.0015)	0.0035	N.D	N.D
EAU_LOU_P_04	0.0224	0.0005	0.0010	0.0005	N.D	N.D	N.D	0.0294	(0.0019)	0.0430	0.0142	N.D
EAU_LOU_P_05	<LOQ	0.0007	0.0009	0.0004	N.D	N.D	N.D	N.D	N.D	0.0055	<LOQ	N.D
EAU_LOU_P_06	0.0129	0.0007	0.0009	0.0005	N.D	N.D	N.D	N.D	(0.0014)	0.0295	0.0252	N.D
EAU_LOU_P_07	0.0020	0.0012	0.0017	0.0009	N.D	N.D	N.D	N.D	(0.0031)	0.0009	<LOQ	N.D
EAU_LOU_P_08	0.0010	0.0004	0.0015	0.0009	N.D	N.D	N.D	<LOQ	(0.0028)	N.D	<LOQ	N.D
EAU_LOU_P_09	0.0018	0.0006	0.0020	0.0012	N.D	N.D	N.D	N.D	(0.0032)	0.0016	0.0127	N.D
EAU_LOU_P_10	0.0233	0.0008	0.0010	0.0005	N.D	<LOQ	0.0332	N.D	N.D	0.0572	0.0490	N.D
EAU_POU_P_01	0.0011	0.0004	0.0020	0.0016	<LOQ	N.D	N.D	N.D	(0.0018)	0.0053	<LOQ	N.D
EAU_POU_P_02	0.0032	0.0009	0.0027	0.0021	N.D	N.D	N.D	N.D	(0.0017)	0.0034	<LOQ	N.D
EAU_POU_P_03	0.0383	0.0022	0.0019	0.0010	N.D	N.D	N.D	N.D	(0.0016)	0.0294	0.0347	0.0018
EAU_POU_P_04	0.0091	0.0010	0.0045	0.0035	0.4879	N.D	N.D	N.D	(0.0016)	0.0470	<LOQ	N.D
EAU_POU_P_05	0.0073	0.0008	0.0034	0.0027	0.1033	N.D	N.D	N.D	(0.0016)	0.0394	<LOQ	N.D
EAU_POU_P_06	0.0347	0.0204	0.0110	0.0034	N.D	N.D	N.D	<LOQ	(0.0018)	0.3697	<LOQ	N.D
EAU_DAG_P_01	0.0058	0.0010	0.0015	0.0007	N.D	N.D	N.D	N.D	(0.00169	0.0091	<LOQ	N.D
EAU_DAG_P_02	0.0420	0.0005	0.0013	0.0008	N.D	N.D	N.D	N.D	(0.0030)	0.0306	0.0119	N.D
EAU_DAG_P_03	0.0094	0.0003	0.0014	0.0009	N.D	N.D	N.D	N.D	(0.0015)	0.0050	0.0648	N.D
EAU_DAG_P_04	0.0054	0.0002	0.0006	0.0003	N.D	N.D	N.D	N.D	(0.0016)	0.0100	0.0569	N.D
EAU_PEN P_01	0.0251	0.0002	N.D	N.D	N.D	N.D	N.D	N.D	(0.0001)	0.0039	<LOQ	N.D
Frequency of detection (n = 29)	96%	100%	96%	96%	11%	11%	15%	11%	74%	96%	96%	7%
Min	0.001	0.0002	0.0006	0.0003	0.1033	0.0106	0.0332	0.0294	-	0.0008	0.0119	0.0018
Max	0.042	0.0204	0.011	0.0076	0.4879	0.0106	0.2022	0.0294	-	0.384	0.1742	0.0018
Standard deviation	0.0131	0.0038	0.0025	0.0016	0.2720	-	0.0809	-	0.0007	0.1002	0.0460	-

[a] Quantitive data of emamectin benzoate was not considered in calculation due to poor recovery rate of the extraction procedure (~6%). The concentrations in brackets should be considered as qualitative data and were displayed to underline the presence of emamectin benzoate in traditional wells.

Section S4. Ecological risk assessment

Table S11 Toxicity values for detected pesticides

Pesticide name	Fish			Cladocerans			Benthic invertebrates		
	No. species	STC [µg L⁻¹]	MTC [µg L⁻¹]	No. species	STC [µg L⁻¹]	MTC [µg L⁻¹]	No. species	STC [µg L⁻¹]	MTC [µg L⁻¹]
Acetamiprid	1	100000	100000	1	49800	49800	2	3.73	26.865
Atrazine	19	4500	20500	5	6900	18550	6	125	10100
DEA[a]	1	100	100	5[b]	6900[b]	18550[b]	3	2000	3000
DIA	1	17000	17000	1	126000	126000	1	7200	7200
Azadirachtin	3	4000	33000	2	626.1	93500	3	14	20970
Carbofuran	28	123.762	530	3	2.036	38.6	14	0.17448	220
Chlorpyrifos	24	2.446	108	8	0.05306	0.25	33	0.07	0.8125
lambda-Cyhalothrin	7	0.2223	3.42	4	0.04	0.39	13	0.01364	0.0473
Cypermethrin	14	0.416	4.7	1	0.36	1	10	0.002	0.069
Dieldrin[a]	23	2.41	4.89	1	79.5	200	3	30	40
Imidacloprid	1	229100	229100	2	832	13900	5	0.65	5.75
Profenofos	11	13.5	42	1	0.5	1.06	3	0.8	1.61
Triazophos[a]	2	5200	5920	1	12.92	12.92	1	36	1940

[a] Toxicity values estimated in the current study (i.e. not available in Nowell et al. (2014) PTI database) using ECOTOX database (U.S. Environmental Protection Agency, 2016). The 5th percentile was used as STC only for dieldrin and fish. For the other pesticides, STC was set as the minimum of available toxicity values (fewer than 12 values available).

[b] In absence of reliable toxicity data of DEA on cladocerans, values for Atrazine were used.

No specific inventory exists of the fish populations in Loumbila Lake, but the most common species identified in similar reservoirs across the country are: *Barbus macrops, Brycinus nurse, Barbus ablabes, Oreochromis niloticus, Sarotherodon galillaeus et Coptodon zillii* (Mano, 2016). During its experiments, Ouéda et al. (2007) identified 26 species of cladocera and benthic invertebrates in Loumbila Lake (Table S12).

Table S12. List of cladocerans and benthic invertebrates identified by Ouéda et al., (2007) in Loumbila Lake

Classification	Species identified
Cladoceran	*Alona rectangular* Sars, 1962; *Ceriodaphnia affinis* Lilljeborg, 1990; *Ceriodaphnia cornuta* Sars, 1885; *Daphina barbarta* Weltner, 18898; *Diaphanosoma excisum* Sars, 1885; *Macrothrix spinose* King, 1852, and *Moina micrura* Kurz, 1874.
Copepoda	*Mesocyclop leuckarti Claus*, 1857 ; and *Tropodiaptomus incognitus* Dussart and Gras, 1966
Rotifera	*Brachionus caudatus* Barrois, 1894 ; *Brachionus falcatus* Zacharias, 1898 ; *Brachionus quadridentatus* Hermann, 1783 ; *Filina longiseta* Ehrb, 1834 ; *Filinia opoliensis* syn. ; *Tetramastix opoliensis* Zacharias, 1898 ; *Keratella tropica Apstein*, 1907 ; *Lecan luna* Müller, 1776 ; *Platyas quadricornis* Ehrb., 1832 ; *Pompholyx complanata* Gosse, 1851 ; *Asplanchna* sp., *Collotheca* sp., Epiphane sp., *Gastrophus* sp., *Hexarthra* sp., *Polyartha* sp., *Trichocerca* sp. and *Trichotria* sp.

Appendix D

Supplementary material of Chapter 6

Section S1. Surveys and sampling point locations

The present study was conducted in March-April 2015 and 2016 in 3 villages: Pousghin (2015), Nabdogo (2015) and Noungou (2016) located on the shores of Loumbila Lake (12°29'38'' N; 1°24'8'' W), 20 km far from the capital Ouagadougou.
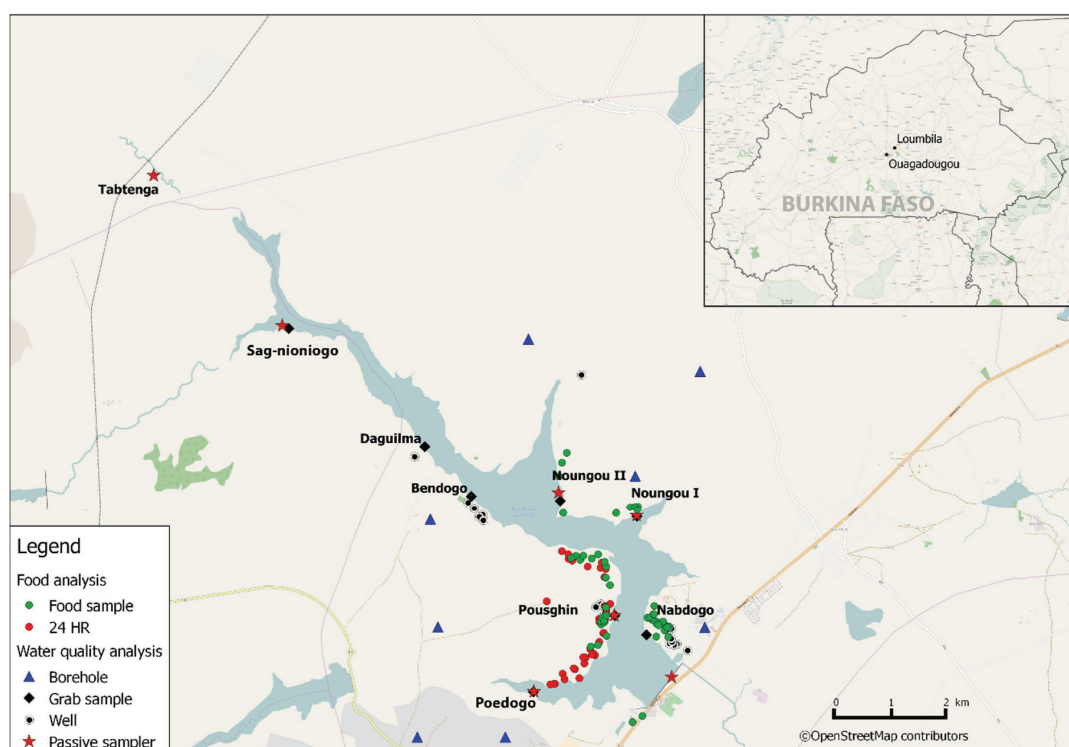
Figure S1 Surveys and sampling points location in the study area Loumbila Lake, one borehole (12°31'32.8"N 1°19'57.5"W) is out of the map (source background map : OpenStreetMap Contributors, 2017)

Section S2. Material details

Table S1 Concentration of standard stock solution in acetone

Pesticide name	µg mL⁻¹	Pesticide name	µg mL⁻¹
Acetamiprid	19.1	Diuron	11.5
Atrazine	11.2	alpha-Endosulfan	10.1
Desethylatrazine	9.6	beta-Endosulfan	10.1
Deisopropylatrazine	6.5	Endosulfan sulfate	10.1
Azadirachtin	11.4	Endrin	10.2
Carbofuran	34.5	alpha-HCH	10.3
alpha-Chlordane	10.1	gamma-HCH	10.2
gamma-Chlordane	10.2	alpha-Heptachlor epoxide	13.5
Chlorpyrifos	24.2	beta-Heptachlor epoxide	10.2
Chlorpyrifos-methyl	9.9	Hexachlorobenzene	10.6
lambda-Cyhalothrin	19.3	Imidacloprid	10.4
alpha-Cypermethrin	81.6	Omethoate	30.4
beta-Cypermethrin	91.8	Profenofos	62.1
Deltamethrin	87.5	trans-Nonachlor	8.6
Diazinon	15.7	Triazophos	12.7
Dieldrin	10.2		

Table S2. Concentration of surrogate stock solution and dilution for sample fortification

Surrogates	Cstock[a]	Csample[b]
Acetamiprid-d3	2.1	0.53
Acetochlor-d11	2.1	0.53
Atrazine-d5	2.5	0.63
Chlorpyrifos-d10	2.3	0.58
trans-Cypermethrin-d6	6.8	1.7
Desethylatrazine-d6	2.2	0.55
trans-Deltamethrin-d6	9.3	2.33
Diuron-d6	2.2	0.55
alpha-Endosulfan-d4	3.2	0.8
beta-Endosulfan-d4	3.3	0.83
Imidacloprid-d4	4.2	1.05

[a] Concentration of surrogate stock solution of target analytes in acetone (µg mL⁻¹)

[b] Concentration of diluted surrogate solution in methanol for vegetable sample fortification (µg mL⁻¹)

The gas chromatography analyses were performed on a Thermo Scientific Trace 1310 gas chromatograph coupled with a Thermo Scientific ISQ Single Quadrupole MS (Waltham, MA, USA). The injection volume and composition were respectively 2 µL and isooctane. The injector was set to PTV splitless mode with an initial temperature of 75 °C and a maximal temperature of 300 °C at the end of the injection's transfer phase (rate: 10 °C sec^{-1} in 2.5 min). Helium was used as the carrier gas (1.2 mL min^{-1}) and analytes were separated using a Phenomenex Zebron capillary column (ZB-5 MS plus, 20 m, 0.18 mm, 0.18 µm). The GC/MS oven program is given in Table S3. The ion source temperature was set to 250° C and the ionization mode to EI. Target pesticides analyzed in GC-MS are presented in Table S4.

Table S3 GC/MS oven program

	Rate [°C min^{-1}]	Temperature [°C]	Hold Time [min]	Total Time [min]
Initial		80	0.5	0.5
Ramp 1	50	150		1.5
Ramp 2	5	300	8.1	38.1

Table S4 Target substances analyzed in GC-MS and corresponding surrogates

Pesticide name	Surrogate	Pesticide name	Surrogate
cis-alpha-Chlordane	alpha-Endosulfan-*d4*	beta-Endosulfan	alpha-Endosulfan-*d4*
trans-gamma-Chlordane	alpha-Endosulfan-*d4*	Endosulfan sulfate	alpha-Endosulfan-*d4*
Chlorpyrifos	Chlorpyrifos-*d10*	Endrin	alpha-Endosulfan-*d4*
Chlorpyrifos-methyl	Chlorpyrifos-*d10*	alpha-HCH	Acetochlor-*d11*
lambda-Cyhalothrin	Chlorpyrifos-*d10*	gamma-HCH	Acetochlor-*d11*
alpha-Cypermethrin	trans-Cypermethrin-*d6*	Heptachlor epoxide a	Acetochlor-*d11*
beta-Cypermethrin	trans-Cypermethrin-*d6*	Heptachlor epoxide b	Acetochlor-*d11*
Deltamethrin	trans-Deltamethrin-*d6*	Hexachlorobenzene	Acetochlor-*d11*
Diazinon	Acetochlor-*d11*	trans-Nonachlor	alpha-Endosulfan-*d4*
Dieldrin	alpha-Endosulfan-*d4*	Profenofos	alpha-Endosulfan-*d4*
alpha-Endosulfan	alpha-Endosulfan-*d4*		

The UPLC system consisted of a UPLC Waters Acquity coupled to a Waters Acquity Xevo TQ-S tandem quadrupole MS. The injection volume and composition were respectively 30 µL and methanol:water (5:95, v/v) with 0.1% formic acid. Separations were carried out on a Waters Acquity UPLC HSS T3 column (2.1×100 mm, 1.8 µm) with oven temperature set at 30 °C. The mobile phase flow was set at 0.4 mL min^{-1} and the corresponding gradient composition is given in Table S5.

Table S5 UPLC linear gradient composition

Time [min]	% Aª	% Bᵇ	Flow rate [mL min⁻¹]
Initial	95	5	0.4
10	5	95	0.4
17	95	5	0.4

ª A: methanol/water (5:95, v/v) with 0.1% formic acid
ᵇ B: methanol/water (95:5, v/v) with 0.1% formic acid

Nitrogen, used as desolvation gas (600 °C, 1000 L h⁻¹), was provided by a nitrogen generator (Peak, MNOLA). The capillary voltage was 3 kV and the temperature of the ion source was fixed at 150 °C. Argon was employed as collision gas at a pressure of 3.5×10^{-3} mbar. Compounds were detected in the multiple reaction monitoring (MRM) mode using two transitions per compound, except for deuterated compounds for which only one transition was used. The most intense daughter ion was used for the quantification of the response of each compound, and the other one was used for confirmation purpose (Table S6).

Table S6 ESM

Pesticides	MRM Transitions 1	MRM Transitions 2	RTª [min]	Surrogates
Acetamiprid	223 > 126	223 > 56	4.74	Acetamiprid-*d3*
Atrazine	216.1 > 174	216.1 > 96.1	7.43	Atrazine-*d5*
Deisopropylatrazine	174 > 96	174 > 78.9	3.87	DEA-*d6*
Desethylatrazine	188 > 146	188 > 78.9	5.12	DEA-*d6*
Azadirachtin	743.3 > 725.4	743.3 > 625.3	7.34	Acetamiprid-*d3*
Carbofuran	222.11 > 165.1	222.11 > 123	6.49	Acetamiprid-*d3*
Diuron	233.1 > 160	233.1 > 188	7.87	Diuron-*d6*
Imidacloprid	256.1 > 209.1	256.1 > 175.1	4.29	Imidacloprid-*d4*
Omethoate	214.1 > 183.1	214.1 > 125.1	2.18	Acetamiprid-*d3*
Triazophos	314.1 > 161.9	314.1 > 118.9	8.76	Diuron-*d6*
Acetamiprid-*d3*	225.9 > 125.9	-	4.71	-
Atrazine-*d5*	221.2 > 179.1	-	7.36	-
DEA-*d6*	193.93 > 146.9	-	5.03	-
Diuron-*d6*	239.2 > 78.04	-	7.64	-
Imidacloprid-*d4*	259.9 > 213	-	4.16	-

ª Retention time in minute

Section S3. Quality control and quality assurance

In order to evaluate the efficiency of the analytical procedure a recovery assay was conducted. Blank samples of tomato, cucumber, eggplant (*Solanum melongena L.)* and okra were spiked in triplicates with 0.2 mL of a 20 folds (~10 µg kg^{-1}) and 4 folds (~50 µg kg^{-1}) dilution of the stock solution presented in Table S. Substances with low recovery rate (<20%) have been kept in the multiresidue analysis due to low variability of the obtained results (i.e. low relative standard deviation between replicates).

Table S7 Multiresidue extraction recoveries for target pesticides in vegetables (% Recovery with surrogates, %SD: %Standard Deviation)

Pesticides	Tomato		Eggplant		Cucumber		Okra	
	% Recovery	%SD	% Recovery	%SD	% Recovery	%SD	% Recovery	%SD
Acetamiprid	60%	2%	65%	3%	59%	2%	58%	2%
Atrazine	122%	4%	127%	3%	108%	5%	107%	4%
Desethylatrazine	155%	4%	147%	2%	126%	5%	145%	7%
Deisopropylatrazine	107%	3%	118%	11%	110%	11%	109%	4%
Azadirachtin	83%	6%	110%	5%	108%	19%	90%	11%
Carbofuran	71%	4%	73%	4%	61%	4%	72%	4%
cis-alpha-Chlordane	138%	9%	137%	20%	127%	16%	75%	5%
trans-gamma-Chlordane	125%	5%	97%	6%	105%	6%	66%	10%
Chlorpyrifos	71%	9%	63%	1%	72%	9%	61%	8%
Chlorpyrifos-methyl	90%	1%	70%	7%	68%	1%	73%	4%
lambda-Cyhalothrin	98%	13%	84%	7%	73%	5%	54%	7%
alpha-Cypermethrin	103%	1%	101%	4%	87%	12%	82%	3%
beta-Cypermethrin	82%	2%	74%	1%	62%	7%	67%	3%
Deltamethrin	47%	4%	33%	2%	34%	6%	40%	4%
Diazinon	87%	4%	90%	3%	114%	2%	84%	2%
Dieldrin	90%	12%	90%	17%	76%	5%	144%	17%
Diuron	67%	8%	67%	9%	78%	5%	70%	6%
alpha-Endosulfan	73%	3%	56%	7%	91%	21%	86%	7%
beta-Endosulfan	85%	13%	82%	5%	89%	13%	124%	37%
Endosulfan sulfate	107%	19%	102%	2%	60%	10%	115%	26%
Endrin	67%	5%	118%	19%	87%	18%	72%	1%
alpha-HCH	45%	12%	59%	5%	17%	2%	32%	5%
gamma-HCH	54%	7%	63%	20%	84%	10%	60%	32%
Heptachlor epoxide a	67%	2%	69%	3%	67%	5%	63%	5%
Heptachlor epoxide b	15%	2%	16%	2%	15%	2%	13%	2%
Hexachlorobenzene	37%	8%	50%	4%	40%	6%	21%	2%
Imidacloprid	59%	2%	88%	6%	47%	2%	54%	5%
trans-Nonachlor	97%	3%	79%	4%	86%	4%	57%	10%
Omethoate	74%	7%	60%	2%	60%	6%	78%	8%
Profenofos	129%	21%	51%	8%	37%	5%	43%	5%
Triazophos	49%	5%	41%	9%	37%	20%	17%	2%

Section S4. Pesticides residues and MRL compliance

Table S8 Percentage of exceedance of the MRL values in vegetables (corresponding number of samples)

	Tomatoes	Sorrel	*Solanum melongena L*	*Solanum aethiopicum*	Okra	Cucumbers
Acetamiprid	-	102%(1)	--	-	-	-
Carbofuran	-	-	-	175% (1)	-	-
Chlorpyrifos	133% (1)	2016 - 1180% (2)	-	-	-	-
lambda-Cyhalothrin	117-174% (2)	332%(1)	140% (1)	-	110% (1)	
Dieldrin	-	-	-	230-5700% (2)	-	165-412%(4)
Imidacloprid	-	148-319% (4)	-		-	-
Profenofos	-	1006%-2.99 10^4% (7)	-	-	1920% (1)	438-1930% (3)

高

Appendix D

Table S9 MRL values in vegetables from the European Union Pesticide database (EU) and from the Codex Alimentarius (CA) (*N.E: Not Established*) (source: European Pesticides database (European Union, 2017) and Codex Alimentarius (WHO/FAO, 2017))

Pesticides		Tomatoes	Sorrel	*Solanum melongena* L	*Solanum aethiopicum*	Okra	Cucumber	Residue definition
		[mg kg⁻¹]						
Acetamiprid	EU	0.5	3	0.2	0.2	0.2	0.3	
	CA	0.2	N.E	0.2	0.2	0.2	0.3	
∑(Atrazine)[a]	EU	0.05*	0.05*	0.05*	0.05*	0.05*	0.05*	
	CA	N.E	N.E	N.E	N.E	N.E	N.E	
Azadirachtin	EU	1	1	1	1	1	1	
	CA	N.E	N.E	N.E	N.E	N.E	N.E	
Carbofuran*	EU	0.002*	0.005*	0.002*	0.002*	0.002*	0.002*	Sum of carbofuran (including any carbofuran generated from carbosulfan, benfuracarb or furathiocarb) and 3-OH carbofuran expressed as carbofuran)
	CA	N.E	N.E	N.E	N.E	N.E	N.E	carbofuran and 3-hydroxy carbofuran expressed as carbofuran
Chlorpyrifos	EU	0.01*	0.05*	0.4	0.4	0.5	0.05*	
	CA	N.E	N.E	N.E	N.E	N.E	N.E	
λ-Cyhalothrin	EU	0.1	0.5	0.5	0.5	0.3	0.1	Cyhalothrin (sum of all isomers)
	CA	0.3	N.E	0.3	0.3	0.3	0.05	
∑(Cypermethrin)[b],*	EU	0.5	0.7	0.5	0.5	0.5	0.2	Cypermethrin (cypermethrin including other mixtures of constituent isomers (sum of isomers))
	CA	0.2	N.E	0.03	0.03	N.E	0.07	cypermethrin (sum of isomers)
Dieldrin*	EU	0.01*	0.01*	0.01*	0.01*	0.01*	0.02	Aldrin and Dieldrin (Aldrin and dieldrin combined expressed as dieldrin)
	CA	-	0.05	N.E	N.E	N.E	0.1	Aldrin and Dieldrin
alpha-Endosulfan	EU	0.05*	0.05*	0.05*	0.05*	0.05*	0.05*	Sum of alpha- and beta-isomers and endosulfan-sulphate expresses as endosulfan)
	CA	0.5	N.E	0.1	0.1	N.E	1	Sum of alpha endosulfan, beta endosulfan and endosulfan sulfate
Imidacloprid	EU	0.5	0.05*	0.5	0.5	0.5	1	
	CA	0.5	N.E	0.2	0.2	N.E	1	
Omethoate*	EU	0.02*	0.02*	0.02*	0.02*	0.02*	0.02*	Dimethoate (sum of dimethoate and omethoate expressed as dimethoate)
	CA	N.E	N.E	N.E	N.E	N.E	N.E	The MRLs apply to residues that may have resulted from the use of formothion, dimethoate or omethoate.
Profenofos	EU	10	0.01*	0.01*	0.01*	0.01*	0.01*	
	CA	10	N.E	N.E	N.E	N.E	N.E	
Triazophos	EU	0.01*	0.01*	0.01*	0.01*	0.01*	0.01*	
	CA	N.E	N.E	N.E	N.E	N.E	N.E	

[a] ∑(Atrazine): atrazine, desethylatrazine, and deisopropylatrazine

[b] ∑(Cypermethrin): alpha- and beta-cypermethrin

* Substances described in residue definition not fully covered in this study

259

Section S5. Consumption data
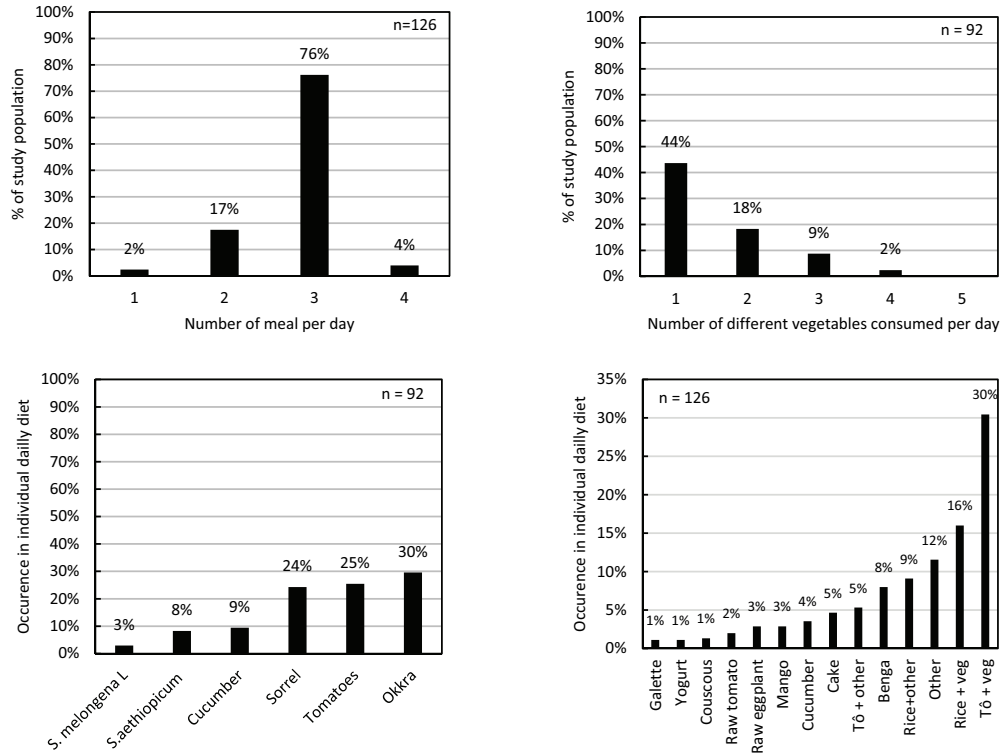
Figure S2 Description of local consumption habits

Table S10 Weighted average portion estimates for the study population

	Tomatoes	Sorrel	*Solanum melongena L*	*Solanum aethiopicum*
	[kg]	[kg]	[kg]	[kg]
Sauces	0.03 ± 0.013	0.02 ± 0.013	0.01 ± 0.013	0.01 ± 0.003
Raw	0.04 ± 0.010	-	-	0.05 ± 0.024
Total	0.07 ± 0.023	0.02 ± 0.013	0.01 ± 0.013	0.06 ± 0.027

	Okra	Cucumber	Tap & Borehole	Well
	[kg]	[kg]	[L]	[L]
Sauces	0.01 ± 0.006	-	-	-
Raw	-	0.05 ± 0.024	0.56 ± 0.31	0.92 ± 0.26
Total	0.01 ± 0.006	0.05 ± 0.024	0.56 ± 0.31	0.92 ± 0.26

Figure S3 presents the contribution of vegetables and water to pesticide exposure based on average consumption and median residue levels.
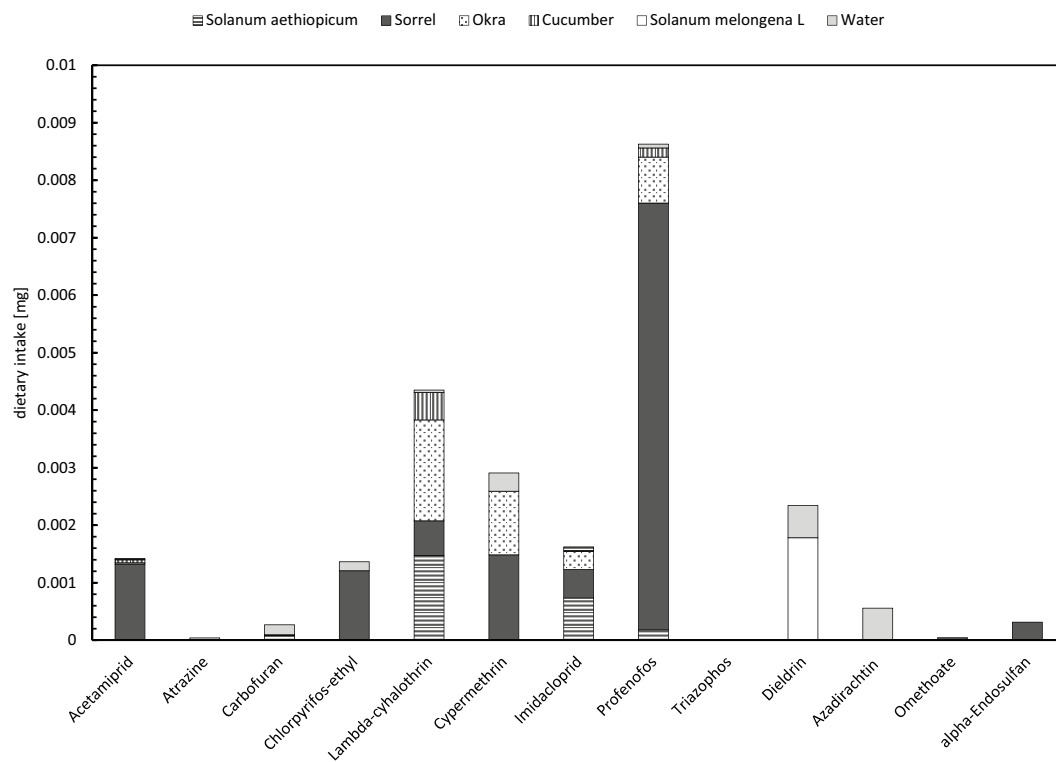
Figure S3 Contribution of vegetables to pesticide exposure considering WAPE and median residue levels.

Appendix E

Supplementary material of Chapter 7

Section S1. Stock solutions

The following mix standard solutions of the analytes and labeled compounds were used to prepare calibration curves and solutions for sample fortification.

Table S1 Concentration of standard stock solution in acetone

Pesticide name	µg mL^{-1}	Pesticide name	µg mL^{-1}
Acetamiprid	19.1	Diuron	11.5
Acetochlor	11.7	Emamectin-benzoate	15.7
Atrazine	11.2	Heptachlor epoxide a	13.5
Desethylatrazine	9.6	Heptachlor epoxide b	10.2
Deisopropylatrazine	6.5	Hexachlorobenzene	10.6
Azadirachtin	11.4	Imidacloprid	10.4
Carbofuran	34.5	Linuron	10.8
alpha-cis-Chlordane	10.1	Methoxychlor	10.4
gamma-trans-Chlordane	10.2	Omethoate	30.4
Oxychlordane	2.4	o,p'-DDT	7.8
Chlorpyrifos-ethyl	24.2	p,p'-DDD	10.5
Chlorpyrifos-methyl	9.9	p,p'-DDE	10.3
lambda-Cyhalothrin	19.3	p,p'-DDT	10.3
alpha-Cypermethrin	81.6	Pentachlorobenzene	10.9
beta-Cypermethrin	91.8	Profenofos	62.1
Deltamethrin	87.5	Thiram	46.3
Diazinon	15.7	trans-Nonachlor	8.6
Dieldrin	10.2	Triazophos	12.7
alpha-Endosulfan	10.1		

Table S2 Concentration of internal standard stock solution and dilution for sample fortification

Surrogates	C_{stock}[a]	C_{hair}[b]
Acetamiprid-d3	2.2	0.6
Acetochlor-d11	3.1	0.8
Atrazine-d5	3.1	0.8
Chlorpyrifos-d10	2.4	0.6
trans-Cypermethrin-d6	10.6	2.6
DEA-d6	2.3	0.6
trans-Deltamethrin-d6	10.7	2.7
Diuron-d6	2.5	0.6
alpha-Endosulfan-d4	3.6	0.9
Imidacloprid-d4	4.8	1.2
Linuron d6	5.4	1.3
pp'-DDT C13	1.8	0.4

[a] Concentration of surrogate stock solution of target analytes in acetone (µg mL^{-1})
[b] Concentration of diluted surrogate solution in methanol for hair sample fortification (µg mL^{-1})

Section S2. Optimization of dSPE purification

dSPE sorbents suitability was assessed by performing recovery assays on triplicate blank hair samples spiked at ~2µg g^{-1} (i.e. 6 fold dilution of standard stock solution presented in Table S1). Results are presented as percent of target analyte recovered Table S3.

Table S3 Recovery rates obtained for target analytes with the 3 dSPE sorbents (*N.D.*: Not detected)

Substance name	dSPE sorbent				
	Z-Sep/C18	PSA	PSA 200 mg	Z-Sep +	Z-Sep + 200 mg
Avermectin					
Emamectin benzoate	8%	49%	54%	1%	16%
Carbamate					
Carbofuran	94%	93%	102%	94%	109%
Thiram	*N.D.*	*N.D.*	*N.D.*	*N.D.*	*N.D.*
Chloroacetamide					
Acetochlor	82%	>150%	>150%	138%	>150%
Neonicotinoid					
Acetamiprid	90%	86%	109%	93%	100%
Imidacloprid	101%	90%	118%	94%	125%
Organochlorine					
Dieldrin	58%	97%	105%	85%	103%
alpha-Endosulfan	57%	95%	94%	83%	89%
alpha-cis-Chlordane	54%	98%	112%	80%	105%
gamma-trans-Chlordane	59%	99%	115%	82%	108%
trans-Nonachlor	49%	92%	101%	76%	101%
Oxychlordane	59%	102%	112%	79%	115%
Heptachlor epoxide a	61%	83%	125%	85%	122%
Heptachlor epoxide b	70%	105%	119%	92%	122%
Hexachlorobenzene	32%	83%	40%	12%	24%
Methoxychlor	119%	140%	147%	89%	>150%
Pentachlorobenzene	25%	90%	42%	11%	31%
∑ (o,p'-DDT, p,p'-DDD)	67%	92%	115%	97%	133%
p,p'-DDE	46%	98%	105%	45%	73%
p,p'-DDT	68%	86%	63%	90%	118%
Organophosphate					
Chlorpyrifos-ethyl	111%	134%	142%	108%	142%
Chlorpyrifos methyl	126%	122%	135%	127%	142%
Diazinon	111%	>150%	148%	122%	122%
Omethoate	66%	58%	116%	38%	135%
Profenofos	52%	84%	116%	16%	77%
Triazophos	57%	60%	71%	77%	30%
Pyrethroid					
lambda-Cyhalothrin	129%	-	16%	85%	>150%
alpha-Cypermethrin	146%	-	-	69%	>150%
beta-Cypermethrin	130%	-	-	51%	>150%
Deltamethrin	>150%	-	8%	>150%	>150%
Tetranortriterpenoid					
Azadirachtin	51%	34%	41%	39%	61%
Triazine					
Atrazine	64%	77%	92%	74%	64%
Desethylatrazine	82%	81%	93%	88%	86%
Deisopropylatrazine	81%	64%	102%	88%	102%
Urea					
Linuron	68%	78%	100%	68%	69%
Diuron	62%	81%	110%	68%	86%

Section S3. Quality control and quality assurance

Validation procedure included spiking of blank hair samples with levels of 2, 5, 20, 40, 50, 250 and 500 pg mg^{-1}. Due to the large diversity of chemical and physical properties of the target analytes, spiked concentration levels were adapted to molecules' sensitivity. Detailed tested levels are presented in Table S4.

Table S4 Spiking levels used for method validation

Substance name	Level 1[a] [pg mg^{-1}]	Level 2[b] [pg mg^{-1}]	Level 3[v] [pg mg^{-1}]	Level 4[d] [pg mg^{-1}]	Level 5[e] [pg mg^{-1}]	Level 6[f] [pg mg^{-1}]	Level 7[g] [pg mg^{-1}]
Acetamiprid	4.7	9.6	38.7	81.0	100.0	498.6	1025.1
Acetochlor	2.8	5.8	23.2	48.6	60.6	302.0	620.8
Atrazine	2.7	5.5	21.9	45.9	57.2	285.0	585.8
Desethylatrazine (DEA)	2.3	4.8	19.1	40.0	48.2	240.2	493.8
Desisopropylatrazine (DIA)	1.6	3.2	12.9	27.1	33.1	165.0	339.2
Azadirachtin	2.2	4.5	18.1	38.0	56.0	279.0	573.5
Carbofuran	8.2	16.7	66.9	140.0	180.9	901.6	1853.6
alpha-cis-Chlordane	2.3	4.6	18.5	38.6	2.1	10.3	21.2
gamma-trans-Chlordane	2.3	4.6	18.6	38.9	2.0	10.2	20.9
Chlorpyrifos	5.6	11.4	45.9	96.1	120.1	598.4	1230.3
Chlorpyrifos-methyl	2.2	4.4	17.8	37.3	49.8	248.4	510.6
lambda-Cyhalothrin	4.8	9.8	39.5	82.7	100.6	501.2	1030.5
alpha-Cypermethrin	20.0	40.8	163.6	342.6	408.9	2038.3	4190.5
beta-Cypermethrin	22.4	45.6	182.9	383.1	461.3	2299.4	4727.2
Deltamethrin	16.7	33.9	136.2	285.3	440.4	2195.2	4513.0
Diazinon	4.2	8.5	34.3	71.8	77.2	384.6	790.6
Dieldrin	2.3	4.6	18.5	38.8	4.1	20.5	42.1
Diuron	2.7	5.6	22.4	46.9	61.9	308.8	634.8
Emamectin benzoate	3.9	7.9	31.5	66.0	82.5	411.1	845.1
Heptachlor epoxide a	3.3	6.8	27.1	56.8	69.1	344.7	708.6
Heptachlor epoxide b	2.3	4.6	18.6	39.0	2.0	10.2	20.9
Hexachlorobenzene	2.6	5.2	21.0	44.0	60.5	301.3	619.5
Imidacloprid	2.6	5.2	20.9	43.8	53.2	265.1	545.0
Linuron	2.6	5.2	21.0	44.0	56.0	279.1	573.9
Methoxychlor	2.3	4.7	19.0	39.7	20.5	102.2	210.1
trans-Nonachlor	2.1	4.3	17.2	36.1	43.3	215.8	443.7
Omethoate	6.0	12.3	49.2	102.9	153.6	765.6	1573.9
o,p'-DDT	2.0	4.0	16.2	33.9	38.7	193.1	397.0
Oxychlordane	2.4	4.9	19.5	40.9	12.4	61.7	126.8
Pentachlorobenzene	2.7	5.4	21.7	45.5	55.6	276.9	569.3
p,p'-DDD	2.3	4.8	19.1	39.9	4.1	20.3	41.8
p,p'-DDE	2.3	4.7	18.7	39.3	4.1	20.5	42.1
p,p'-DDT	2.3	4.7	18.7	39.1	4.1	20.3	41.8
Profenofos	15.4	31.4	126.1	264.1	308.3	1536.7	3159.2
Thiram	10.9	22.2	89.0	186.4	254.0	1266.1	2602.9
Triazophos	2.7	5.5	22.2	46.4	66.1	329.7	677.8

[a] Referred as spiking level of 2 pg mg^{-1} in the manuscript
[b] Referred as spiking level of 5 pg mg^{-1} in the manuscript
[c] Referred as spiking level of 20 pg mg^{-1} in the manuscript
[d] Referred as spiking level of 40 pg mg^{-1} in the manuscript
[e] Referred as spiking level of 50 pg mg^{-1} in the manuscript
[f] Referred as spiking level of 250 pg mg^{-1} in the manuscript
[g] Referred as spiking level of 500 pg mg^{-1} in the manuscript

Appendix F

Supplementary material of Chapter 8

Section S1. Stock solutions

The following mix standard solutions of the analytes and labeled compounds were used to prepare calibration curves and solutions for sample fortification.

Table S1 Concentration of standard stock solution in acetone

Pesticide name	µg mL^{-1}	Pesticide name	µg mL^{-1}
Acetamiprid	19.1	Endrin aldehyde	10.2
Acetochlor	11.7	Endrin ketone	10.2
Atrazine	11.2	alpha-HCH	10.3
Desethylatrazine	9.6	beta-HCH	10.7
Deisopropylatrazine	6.5	delta-HCH	10.3
Azadirachtin	11.4	gamma-HCH	10.2
Carbofuran	34.5	Heptachlor	10.2
alpha-cis-Chlordane	10.1	Heptachlor epoxide a	13.5
gamma-trans-Chlordane	10.2	Heptachlor epoxide b	10.2
Oxychlordane	2.4	Hexachlorobenzene	10.6
Chlorpyrifos-ethyl	24.2	Imidacloprid	10.4
Chlorpyrifos-methyl	9.9	Linuron	10.8
lambda-Cyhalothrin	19.3	Methoxychlor	10.4
alpha-Cypermethrin	81.6	Omethoate	30.4
beta-Cypermethrin	91.8	o,p'-DDT	7.8
Deltamethrin	87.5	p,p'-DDD	10.5
Diazinon	15.7	p,p'-DDE	10.3
Dieldrin	10.2	p,p'-DDT	10.3
Diuron	11.5	Pentachlorobenzene	10.9
Emamectin-benzoate	15.7	Profenofos	62.1
alpha-Endosulfan	10.1	Thiram	46.3
beta-Endosulfan	10.1	trans-Nonachlor	8.6
Endosulfan sulfate	10.2	Triazophos	12.7
Endrin	10.3		

Table S2 Concentration of internal standard stock solution and dilution for sample fortification

Surrogates	C$_{stock}$[a]	C$_{hair}$[b]
Acetamiprid-d3	2.2	0.6
Acetochlor-d11	3.1	0.8
Atrazine-d5	3.1	0.8
Chlorpyrifos-d10	2.4	0.6
trans-Cypermethrin-d6	10.6	2.6
DEA-d6	2.3	0.6
trans-Deltamethrin-d6	10.7	2.7
Diuron-d6	2.5	0.6
alpha-Endosulfan-d4	3.6	0.9
alpha-Endosulfan-d4	3.2	0.3
Imidacloprid-d4	4.8	1.2
Linuron d6	5.4	1.3
pp'-DDT C13	1.8	0.4

[a] Concentration of surrogate stock solution of target analytes in acetone (µg mL^{-1})

[b] Concentration of diluted surrogate solution in methanol for hair sample fortification (µg mL^{-1})

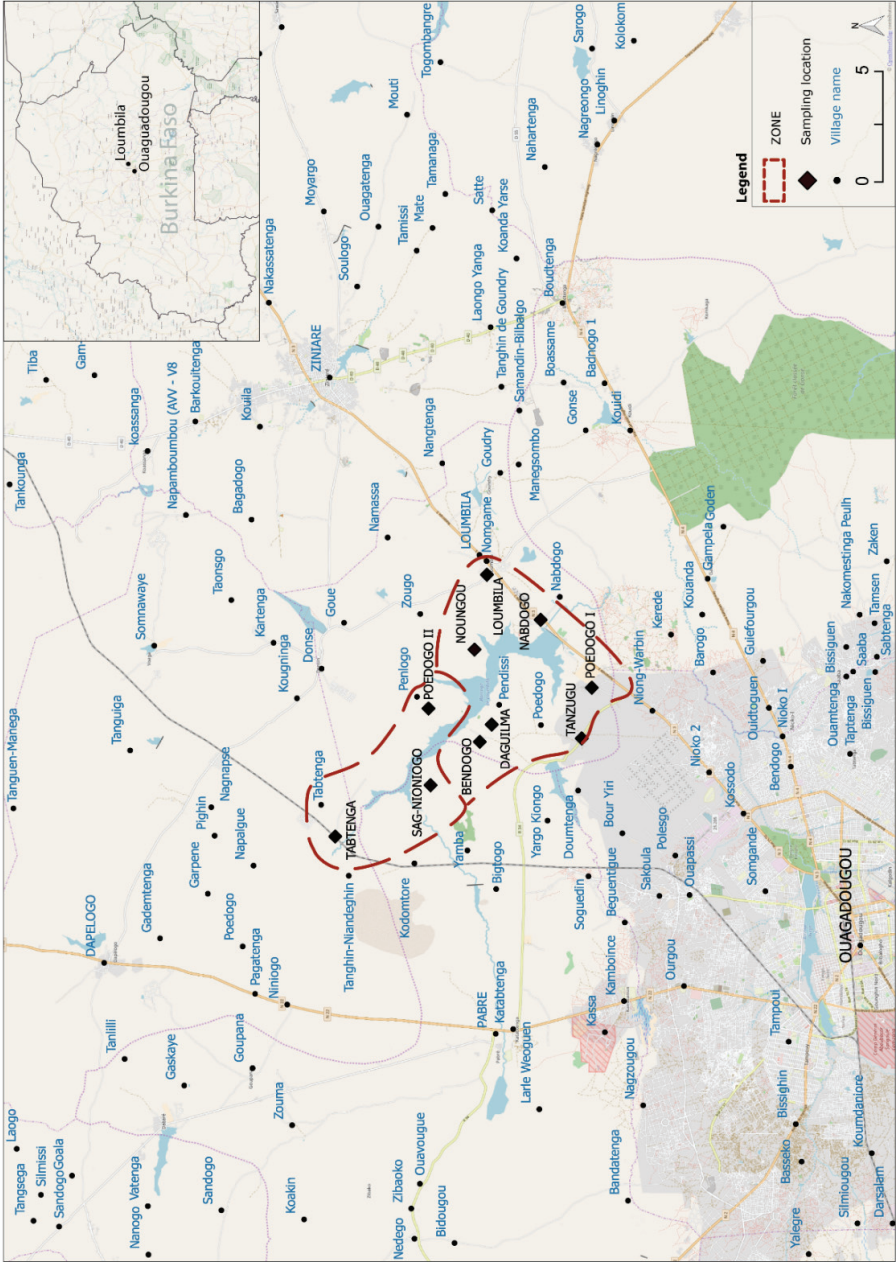# Section S2. Overview of the study area

Figure S1 Overview of the study area (background map source: OpenStreetMap Contributors (2017))

Section S3. Target substance parameters

Table S3 MS/SIM parameters for GC amenable molecule determination (10 additional organochlorines)

Compound name	RT[a] [min]	Target[b] m/z	Q1[c] m/z	Q2[d] m/z
alpha-HCH	6.11	181	219	217
beta-HCH	6.73	181	217	219
gamma-HCH	6.94	181	219	217
delta-HCH	7.7	181	217	219
Heptachlor	8.95	100	272	274
Endrin	14.01	263	281	265
beta-Endosulfan-d4	14.35	246	244	
beta-Endosulfan	14.45	195	237	241
Endrin aldehyde	14.96	67	345	250
Endosulfan sulfate	15.79	272	274	239
Endrin ketone	17.33	67	317	281

[a] RT: retention time in minute; [b] Target: target ion; [c] Q1: Qualifier ion 1; [d] Q2: Qualifier ion 2

Table S4 Analytical parameters for QuEChERS extraction of 28 pesticides, data from Lehmann et al. (2017)

Compound name	% Recovery	%SD	Surrogates	LOD [pg mg⁻¹]	LOQ [pg mg⁻¹]	% Accuracy	%RSD
GC amenable molecules							
Acetochlor	52.4%	21.0%	Acetochlor-d11	18.2	60.6	81.9%	16.7%
alpha-cis-Chlordane	64.4%	11.9%	alpha-Endosulfan-d4	0.6	2.0	99.2%	12.0%
gamma-trans-Chlordane	70.0%	13.2%	alpha-Endosulfan-d4	0.6	2.0	114.4%	17.5%
trans-Nonachlor	81.1%	6.3%	alpha-Endosulfan-d4	5.2	17.2	91.7%	6.0%
Oxychlordane	118.7%	0.5%	alpha-Endosulfan-d4	19.5	60.0	103.3%	10.6%
Chlorpyrifos-ethyl	90.2%	9.8%	Chlorpyrifos-d10	13.8	45.9	97.7%	22.4%
Chlorpyrifos-methyl	78.4%	5.2%	Chlorpyrifos-d10	10.5	35.0	72.0%	5.5%
λ-Cyhalothrin	76.5%	10.5%	p,p'-DDT-C13	20.6	68.5	125.8%	13.4%
∑ (α- & β-Cypermethrin)	54.8%	12.5%	trans-Cypermethrin-d6	86.6	288.5	70.2%	3.3%
Deltamethrin	47.1%	8.7%	Deltamethrin-d6	26.8	89.3	47.5%	9.7%
Diazinon	106.7%	18.4%	Acetochlor-d11	24.0	80.0	80.5%	8.0%
Dieldrin	72.3%	11.1%	alpha-Endosulfan-d4	6.1	20.5	75.6%	15.8%
alpha-Endosulfan	61.2%	13.2%	alpha-Endosulfan-d5	73.8	246.0	58.9%	11.7%
Heptachlor epoxide a	99.6%	15.4%	alpha-Endosulfan-d4	8.3	69.1	102.9%	7.7%
Heptachlor epoxide b	73.9%	9.9%	alpha-Endosulfan-d4	2.0	6.8	98.9%	9.9%
Methoxychlor	132.3%	1.4%	p,p'-DDT-C13	6.2	20.5	166.4%	14.3%
p,p'-DDE	47.1%	9.3%	p,p'-DDT-C13	0.2	40	116.8%	11.5%
p,p'-DDT	78.4%	2.2%	p,p'-DDT-C13	1.2	4.1	106.5%	16.2%
∑ (o,p'-DDT , p,p'-DDD)[b]	68.5%	4.0%	p,p'-DDT-C13	0.6	2.0	85.1%	9.6%
UPLC amenable molecules							
Acetamiprid	75.5%	5.5%	Acetamiprid-d3	1.4	4.7	103.1%	3.3%
Atrazine	71.0%	8.5%	Atrazine-d5	0.8	2.7	146.7%	9.9%
Deisopropylatrazine (DIA)	67.0%	3.7%	DEA-d6	0.5	1.6	112.5%	4.4%
Desethylatrazine (DEA)	99.0%	0.0%	DEA-d6	0.7	2.3	143.4%	6.9%
Carbofuran	74.0%	5.1%	Acetamiprid-d3	2.5	8.2	109.3%	6.6%
Imidacloprid	97.0%	6.0%	Imidacloprid-d4	0.8	2.6	145.8%	5.5%
Linuron	40.3%	14.1%	Linuron-d6	6.3	21.0	177.0%	14.8%

Section S4. Pesticide concentrations in hair samples

Table S**5** Median, minimum and maximum concentrations for pesticides measured in less than 8 samples
(pg mg^{-1})

Pesticide	Exposed population (operators)			Reference population		
	Nb. >LOQ	Median	Min-Max	Nb. >LOQ	Median	Min-Max
Carbamate						
Carbofuran	2	12.5	8.6 - 16.6	0	N.D.	-
Organochlorine						
alpha-cis-Chlordane	2	20.3	12.8 - 28	2	20.9	9.7 - 32.1
Dieldrin	1	30.7	-	2	32.9	22.8 - 43.1
p,p'-DDE	0	<LOQ	-	0	<LOQ	-
p,p'-DDT	1	5.0	-	1	15.6	-
Organophosphate						
Chlorpyrifos-ethyl	2	179.8	64.2 - 295.4	3	89.7	87.4 - 137.6
Triazine						
Atrazine	1	21.7	-	3	18.4	16.1 - 80.8
Desethylatrazine (DEA)	1	13.2	-	0	-	-

Table S6 Comparison between concentrations found in this work and maximal concentrations found in the literature
(pg mg^{-1})

Pesticides	This work			Literature	
	Median	Min	Max	Max	Reference
∑ (o,p'-DDT, p,p'-DDD)	6.3	5.7	11.2	2135	Tsatsakis et al. (2008)
∑ (α- & β-Cypermethrin)	429.2	337.9	2618.5	614.7	Ostrea et al. (2014)
∑ (α- & β-Chlordane)	20.3	9.6	32.1	12	Zhang et al. (2007)
Chlorpyrifos-ethyl	89.7	64.2	295.3	1.83	Ostrea et al. (2009)
Dieldrin	30.7	22.8	43.0	0.5	Covaci et al. (2008)
Imidacloprid	29.8	3.3	1133.6	0.3	Kavvalakis et al. (2013)
lambda-Cyhalothrin	99.2	77.8	143.4	14.7	Schummer et al. (2012)
p,p'-DDE	40.0			946	Covaci et al. (2008)
p,p'-DDT	10.3	5.0	15.6	3920	Covaci et al. (2008)
Acetamiprid	15.4	4.8	236.5	*No data found*	-
Atrazine	20.1	16.0	80.7	*No data found*	-
Carbofuran	12.5	8.5	16.6	*No data found*	-
Deltamethrin	356.7	120.7	648.3	*No data found*	-

Appendix G

Supplementary material of Chapter 9

Section S1. Target substances DT 50

Table S1 DT50 (days required for 50% dissipation of the initial concentration)

Active substance	DT50[a] [days]	Plant name	Compartment	Reference
2,4 D (amine salt)	9			EFSA (2014)
Acetamiprid	2.54	zucchini	leaf	Fantke and Juraske (2013)
Atrazine	5			EFSA (2014)
Chlorpyrifos-ethyl	3			EFSA (2014)
Cyfluthrin	5			EFSA (2014)
alpha-Cypermethrin	5	tomato	leaf	Fantke and Juraske (2013)
Cypermethrin	7.3	tomato	leaf	Fantke and Juraske (2013)
Deltamethrin	3	african eggplant	leaf	Fantke and Juraske (2013)
Dimethoate	6	tomato	leaf	Fantke and Juraske (2013)
Emamectine Benzoate	4.9	celery	leaf	Fantke and Juraske (2013)
Glyphosate	3			EFSA (2014)
Imidacloprid	3			EFSA (2014)
lambda-Cyhalothrin	5			EFSA (2014)
Malathion	3			EFSA (2014)
Mancozeb	13.87	tomato	leaf	Fantke and Juraske (2013)
Paraquat chloride	30			EFSA (2014)
Profenofos	5.4	tomato	fruit	Fantke and Juraske (2013)
Triazophos	11.9	tomato	fruit	Fantke and Juraske (2013)

[a] When no value were available in EFSA (2014), the most conservative value from Fantke and Juraske (2013) was retained

Section S2. Tolerable systemic doses

Table S2 Dermal absorption of target active substance in risk assessment

Active substance	Dermal Absorption [%]	Reference
2,4 D (amine salt)	10.00%	European Union (2017)
Acetamiprid	33.70%	European Union (2017)
Atrazine	5.60%	European Union (2017)
Chlorpyrifos-ethyl	1.00%	European Union (2017)
Cyfluthrin	10.00%	European Union (2017)
alpha-Cypermethrin	10.00%	European Union (2017)
Cypermethrin	10.00%	European Union (2017)
Deltamethrin	10.00%	European Union (2017)
Dimethoate	2.00%	European Union (2017)
Emamectin benzoate	2.00%	European Union (2017)
Glyphosate	3.00%	European Union (2017)
Imidacloprid	2.00%	European Union (2017)
lambda-Cyhalothrin	0.30%	European Union (2017)
Malathion	15.00%	European Union (2017)
Mancozeb	0.24%	European Union (2017)
Paraquat chloride	0.50%	European Union (2017)
Profenofos	90.00%	European Union (2017)
Triazophos	10.00%	European Union (2017)

Table S3 Acutre reference dose for target substances in risk assessment

Active substance	ARfD [mg kg bw^{-1} d^{-1}]	Reference
2,4 D (amine salt)	0.15	European Union (2017)
Acetamiprid	0.1	European Union (2017)
Atrazine	0.1	European Union (2017)
Chlorpyrifos-ethyl	0.005	European Union (2017)
Cyfluthrin	0.02	European Union (2017)
alpha-Cypermethrin	0.04	European Union (2017)
Cypermethrin	0.2	European Union (2017)
Deltamethrin	0.01	European Union (2017)
Dimethoate	0.01	European Union (2017)
Emamectine Benzoate	0.01	European Union (2017)
Glyphosate	0.5	European Union (2017)
Imidacloprid	0.08	European Union (2017)
lambda-Cyhalothrin	0.005	European Union (2017)
Malathion	0.3	European Union (2017)
Mancozeb	0.6	European Union (2017)
Paraquat chloride	0.0005	European Union (2017)
Profenofos	1	European Union (2017)
Triazophos	0.001	European Union (2017)

Table S4 Acute non-dietary acceptable exposure level for target substances in risk assessment

Active substance	ANDAEL [mg kg bw^{-1} d^{-1}]	Effects considered ARfD definition; ANDAEL definition	Reference
2,4 D (amine salt)	0.15	ANDAEL = AOEL	European Union (2017)
Acetamiprid	0.025	Systemic ANDAEL available	EFSA (2012a)
Atrazine	0.01	ANDAEL = AOEL	European Union (2017)
Chlorpyrifos-ethyl	0.005	ARfD: neurotoxicity rat study; ANDAEL = ARfD (no correction)	European Union (2017)
Cyfluthrin	0.02	ARfD: neurotoxicity rat study; ANDAEL = ARfD (no correction)	European Union (2017)
alpha-Cypermethrin	0.018	ARfD: neurotoxicity rat study; ANDAEL = ARfD corrected for oral absorption (45%)	European Union (2017)
Cypermethrin	0.1	ARfD: neurotoxicity rat study; ANDAEL = ARfD corrected for oral absorption (55%)	European Union (2017)
Deltamethrin	0.0075	ANDAEL = AOEL	European Union (2017)
Dimethoate	0.01	ARfD: neurotoxicity rat study; ANDAEL = ARfD (no correction)	EFSA (2006)
Emamectine Benzoate	0.006	ANDAEL = ARfD corrected for oral absorption (55%)	EFSA (2012)
Glyphosate	0.1	ARfD: Developmental toxicity; ANDAEL = ARfD corrected for oral absorption (20%)	European Union (2017)
Imidacloprid	0.08	ANDAEL = AOEL	European Union (2017)
lambda-Cyhalothrin	0.001	ARfD: neurotoxicity dog; ANDAEL = ARfD corrected for oral absorption (25%)	European Food Safety Authority (2015)
Malathion	0.03	ANDAEL = AOEL	European Union (2017)
Mancozeb	0.3	ARfD: teratogenicity in rats ; ANDAEL = ARfD corrected for oral absorption (50%)	European Union (2017)
Paraquat chloride	0.0005	Systemic ANDAEL available	European Union (2017)
Profenofos	1	Only ARfD available	European Union (2017)
Triazophos	0.05	ANDAEL = AOEL	European Union (2017)

Table S5 Acceptable exposure level for target substances in risk assessment

Active substance	AOEL [mg kg bw^{-1} d^{-1}]	Reference
2,4 D (amine salt)	0.15	European Union (2017)
Acetamiprid	0.025	European Union (2017)
Atrazine	0.01	Lewis et al. (2016)
Chlorpyrifos-ethyl	0.001	European Union (2017)
Cyfluthrin	0.02	European Union (2017)
alpha-Cypermethrin	0.01	European Union (2017)
Cypermethrin	0.06	European Union (2017)
Deltamethrin	0.0075	European Union (2017)
Dimethoate	0.001	European Union (2017)
Emamectine Benzoate	0.0003	European Union (2017)
Glyphosate	0.1	European Union (2017)
Imidacloprid	0.08	European Union (2017)
lambda-Cyhalothrin	0.00063	European Union (2017)
Malathion	0.03	European Union (2017)
Mancozeb	0.035	European Union (2017)
Paraquat chloride	0.0004	European Union (2017)
Profenofos	1 (Only ARfD available)	European Union (2017)
Triazophos	0.05	Lewis et al. (2016)

Table S6 Adimissible dailly intake for target substances in risk assessment

Active substance	ADI [mg kg bw^{-1} d^{-1}]	Reference
2,4 D (amine salt)	0.05	European Union (2017)
Acetamiprid	0.7	European Union (2017)
Atrazine	0.02	European Union (2017)
Chlorpyrifos-ethyl	0.001	European Union (2017)
Cyfluthrin	0.003	European Union (2017)
alpha-Cypermethrin	0.015	European Union (2017)
Cypermethrin	0.05	European Union (2017)
Deltamethrin	0.01	European Union (2017)
Dimethoate	0.001	European Union (2017)
Emamectine Benzoate	0.0005	European Union (2017)
Glyphosate	0.3	European Union (2017)
Imidacloprid	0.06	European Union (2017)
lambda-Cyhalothrin	0.0025	European Union (2017)
Malathion	0.3	European Union (2017)
Mancozeb	0.05	European Union (2017)
Paraquat chloride	0.004	European Union (2017)
Profenofos	0.03	European Union (2017)
Triazophos	0.05	European Union (2017)

Section S3. Commercial formulations identified during field surveys

Table S7 Commercial formulations identified during field surveys

Trade name	Active substance 1	Qty a.s. 1 [g L⁻¹]	Active substance 2	Qty a.s. 2 [g L⁻¹]	Authorized in gardening
ADWUMA WURA	Glyphosate	480	-	-	No
AGRAZINE 500	Atrazine	500	-	-	No
AKAPE	Imidacloprid	200	-	-	No
ATTAKAN C 344 SE	Imidacloprid	200	Cypermethrin	144	No
CAIMAN B19	Emamectine Benzoate	19.5	-	-	No
CALLIFOL 480 EC	Dicofol	480	-	-	No
CAPT 88 EC	Acetamiprid	16	Cypermethrin	72	Yes
CAPT 96 EC	Acetamiprid	24	Cypermethrin	72	Yes
CONQUEST C 88 EC	Acetamiprid	16	Cypermethrin	72	No
CONTI-ZEB	Mancozeb	2.5	-	-	No
COTALM P 318 EC	lambda-Cyhalothrin	18	Profenofos	300	No
CRICRON	lambda-Cyhalothrin	18	Profenofos	300	No
CURACRON	lambda-Cyhalothrin	18	Profenofos	300	No
CURACRON 500 EC	Profenofos	500	-	-	No
CURACRON 720 EC	Profenofos	720	-	-	No
CYMETOX SUPER	Cypermethrin	30	Dimethoate	250	No
CYPALM T 186 EC	Cypermethrin	36	Triazophos	150	No
CYPERCAL 50 EC	Cypermethrin	50	-	-	Yes
D-BAN SUPER	Chlorpyrifos	0.48	-	-	No
DECIS 12.5 EC	Deltamethrin	12.5	-	-	No
DELTACAL 12.5 EC	Deltamethrin	12.5	-	-	Yes
DI-GROW	Deltamethrin	12.5	-	-	No
DIMEX 400 EC	Dimethoate	400	-	-	No
DJIGIKAN 800 EC	Malathion	800	-	-	No
DUEL 336 EC	Profenofos	300	Cypermethrin	36	No
DURSBAN B 318 EC	Cyfluthrin	18	Chlorpyrifos	300	No
DURSBAN C 186 EC	Chlorpyrifos	150	Cypermethrin	36	No
EMA 19.2 EC	Demectine Benzoate	19.2	-	-	No
EMACOT 019 EC	Emamectine Benzoate	19	-	-	No
ERA FTE+ 324 EC	Profenofos	300	Deltamethrin	24	No
GRAMOSHARP SUPER	Paraquat chloride	276	-	-	No
HERBEXTRA 720 SL	2,4 D (amine salt)	720	-	-	No
HERCULES 50 SC	2,4 D (amine salt)	720	-	-	No
HITCEL 440 EC	Profenofos	400	Cypermethrin	40	No
IBIS A 52 EC	Cypermethrin	36	Acetamiprid	16	No
K-OPTIMAL	lambda-Cyhalothrin	15	Acetamiprid	20	Yes
LAMANET	lambda-Cyhalothrin	15	Acetamiprid	20	No
LAMBDA BEST 2.5 EC	lambda-Cyhalothrin	25	-	-	No
LAMBDA MASTER 2.5 EC	lambda-Cyhalothrin	25	-	-	No
LAMBDA SUPER 2.5 EC	lambda-Cyhalothrin	25	-	-	No
LAMBDACAL P 212 EC	Profenofos	200	lambda-Cyhalothrin	12	No
LAMBDEX S.E.C	lambda-Cyhalothrin	18	Profenofos	300	No
PACHA 25 EC	lambda-Cyhalothrin	15	Acetamiprid	10	Yes
PERFECTO 175 SC	lambda-Cyhalothrin	125	Imidacloprid	50	No
POLYTRINE C 186 EC	Cypermethrin	36	Profenofos	150	No
POLYTRINE C 336 EC	Profenofos	300	Cypermethrin	36	No
PROTECT 1.9 EC	Emamectine Benzoate	19.2	Abamectine	-	No
ROCKY SUPER	lambda-Cyhalothrin	0.025	-	-	No
SUMITEX 40 EC	Dimethoate	400	-	-	No
SUNPYRIFOS 48% EC	Chlorpyrifos	480	-	-	Yes
TANGO 500 EC	Profenofos	500	-	-	No
TITAN 25 EC	Acetamiprid	25	-	-	Yes

Section S4. Model parameters and scenarios definition

Model parameters and scenarios definition for operator, worker, and bystander exposure (Excel spreadsheet) are available at:

https://doi.org/10.5281/zenodo.1050294