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First surveillance of pesticides in soils of the perimeter of Tadla, a Moroccan sugar beet intensive area

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Abstract With the long-term application of pesticides on sugar beet farms in the irrigated perimeter of Tadla in Morocco for over 50 years, pesticide monitoring is necessary to assess soil health. The objective of our study was to monitor multiple pesticide residues in topsoil samples collected from post-harvest sugar beet fields and verify their migration to deep soil layers. Topsoil and deep soil samples were collected from arbitrarily selected sugar beet fields in the IPT. In this study, a target-screening method was applied. All target pesticides were detected in soil samples, with tefluthrin being the most frequently detected pesticide. The residue with the highest concentration in soil samples was DDE. All the soil samples contained a mixture of pesticide residues, with a maximum of 13 residues per sample. The total pesticide content decreased toward more profound layers of soil, except in one field where it reached a concentration of 348 µg/kg at the deeper soil layer. For pesticides detected at the three soil depths, only tefluthrin concentration increased in the deep soil layer. The results provide comprehensive and precise information on the pesticide residue status in sugar beet soils warning against the multiple risks that this contamination can cause. This study indicates the need of regular monitoring of pesticides over a large area of the perimeter to enable decision-makers to pronounce the impacts of the extension and intensification of sugar beet cultivation at the irrigated perimeter of Tadla.

Introduction

Soils produce many ecosystem goods and services (Arrouays et al., 2012; de Groot et al., 2012) and their quality is directly linked to food security, human health, and the sustainability of environmental resources (Cheng, 2003; Liu et al., 2013). The assessment of the sanitary quality of soils to ensure food security, to prevent risks to biodiversity, and avoid contamination of groundwater has been considered a priority for many countries (Panico et al., 2022; Schleiffer & Speiser, 2022). Pesticides are a major source of degradation of soil health (Qu et al., 2016). Their widespread and indiscriminate use in intensive agriculture has significantly improved yields but

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has also resulted in their persistent presence in soils (Kopittke et al., 2019; Patel, 2009). In the irrigated perimeter of Tadla, agriculture is a vital component of the economy, primarily centered on the cultivation of citrus fruits and sugar beets using intensive agricultural practices. The sugar beet crop covers an area of 12,500 hectares in the irrigated region of Tadla, ensuring the production of 880,000 tons. This enables the production of over 110,000 tons of white sugar, contributing 22% to the national production. However, sugar beet crop heavily depends on pesticides to maintain such a high production level in this area (ORMVAT, 2019). Given the challenging climatic conditions of the region, characterized by the increasing scarcity of water, and considering the health and environmental effects of pesticides, an urgent pesticide residue monitoring system is needed for fields of sugar beet crop, which has a long-established presence in this region. This is essential for better managing and controlling pesticide residues in the soil while safeguarding the local environment and human health against potential adverse effects.

Early detection of changes in soil quality is key to maintaining healthy soil (García et al., 2022; Masiá et al., 2015; Souza et al., 2023). Many countries around the world have conducted monitoring programs for pesticide residue in soils: in Europe (Silva et al., 2018, 2019), in Asia (Liu et al., 2016; Murugan et al., 2013; Pan et al., 2019; Picó et al., 2020; Rafique et al., 2016), in America (Primost et al., 2017), and in Africa (Dankyi et al., 2014; Osesua et al., 2017). And this is due to a couple of causes, including (i) their use in proliferation with ignorance of their good handling practices (Bernhardt et al., 2017); (ii) their toxicity, mobility, and bioaccumulation capacities; and (iii) their occurrence in other matrices such as water (Schulze et al., 2019), crops (Medina-Pastor and Triacchini, 2020), and human beings (Bevan et al., 2017). From those soil-monitoring programs and studies with the theme of pesticides monitoring soil, it has been consistently revealed the presence of organochlorines pesticides (OCPs) and their transformation products (TPs) in soil samples. Despite the worldwide ban on their production and trade, these highly persistent contaminants have been found in soil samples across various regions, including Italy (Qu et al., 2019a), China (Pan et al., 2019; Wang et al., 2023; Yao et al., 2023), Argentina (Lupi et al., 2019), Nigeria (Osesua et al., 2017), and

India (Kumar et al., 2014). Among the commonly detected OCPs, p,p′-dichlorodiphenyltrichloroethane (DDT) and its metabolite 1-dichloro-2,2-bis (p-chlorophenyl) ethylene (DDE) were frequently observed (Kosubová et al., 2020), and many studies also report the presence of dieldrin, chlordane, and heptachlor (Lupi et al., 2019; Pan et al., 2019; Qu et al., 2019a). The persistence of OCPs residues in the soil can be attributed to their historical use (Yadav et al., 2016). Heptachlor, especially in its oxidized form, continues to linger in the soil long after its discontinuation (Aigner et al., 1998). Dieldrin, an epoxide of aldrin, degrades very slowly in soil, water, and sediment, potentially affecting concentrations in these environmental compartments over time (Shegunova et al., 2007). As a result, even after decades of prohibition, the stability, resistance to degradation, and lipophilic nature of OCPs have led to their significant accumulation in various ecosystem components (Qu et al., 2019a, 2019b). In a complementary context, research focused on monitoring currently used pesticides in agricultural soils consistently identifies several frequently employed pesticides, including boscalid, metalaxyl, glyphosate, and its main derivative aminomethyl-phosphonic acid (AMPA) (Sabzevari & Hofman, 2022). Organophosphates (OPPs) and pyrethroids (PYs), often used in combination to reduce pesticide resistance, have been identified in a soil monitoring study conducted in China (Yao et al., 2023). Triazole compounds have also been frequently detected in European arable soils (epoxiconazole, tebuconazole, tetraconazole, penconazole, difenoconazole), with some reaching high concentrations in soil (epoxiconazole: 160 ng.g^{-1} and tebuconazole: 190 ng.g^{-1}) (Froger et al., 2023; Silva et al., 2018, 2019). Individual pesticide concentrations have reached recorded levels of 1000 ng.g-1 in European agricultural soils, associated with azoxystrobin (Froger et al., 2023). For both banned and currently used pesticides, soil contamination is a major concern, emphasizing the essential need for monitoring pesticide contamination in agriculture. Moreover, in Africa, especially Morocco, there are limited published monitoring results compared to other regions (Matthews et al., 2011). Conducting monitoring in unexplored Moroccan regions like the irrigated perimeter of Tadla will provide valuable insights into pesticide contamination and its environmental impact.

Studies conducted in agricultural regions worldwide have consistently revealed that agricultural soils are the most pesticide-contaminated (Froger et al., 2023; Geissen et al., 2021; Hvězdová et al., 2018; Riedo et al., 2021). Frequently, multiple residues were detected in agricultural soil samples, resulting in cumulative total measured pesticide concentrations ranging from 300 to 2870 (Froger et al., 2023; Kosubová et al., 2020; Silva et al., 2019). For instance, twenty-five pesticides were still detectable in European soils even after their anticipated degradation, and 45% of applied pesticides remained detectable in Swiss agricultural soils, despite their relatively short dissipation half-life (less than 1 year) (Chiaia-Hernandez et al., 2017; Froger et al., 2023). This persistence is often attributed to the fact that agricultural soils are frequently used for crop cultivation and experience secondary concentration from neighboring areas (Liu et al., 2016). Additionally, the presence of a high number of pesticide residues in cultivated soils (10–20 pesticide residues) amplifies the risks to the agricultural ecosystem particularly given that the effects of pesticide mixtures remain largely unknown (Cáceres et al., 2010; Coronado et al., 2011; Geissen et al., 2021; Villanneau et al., 2011). The presence of these contaminated soils increases the risk of potentially hazardous compounds entering the food chain. Furthermore, extensive research has highlighted the significant consequences of prolonged pesticide use in agriculture on human health (Alavanja & Bonner, 2012; Kumar et al., 2016), biodiversity (Aktar et al., 2009), and aquatic and terrestrial ecosystems (Kapsi et al., 2019; King & Aaron, 2015; Masiá et al., 2015; Qu et al., 2016; Serra et al., 2020; Sidhu et al., 2019). The high levels of pesticide residues in soil, and the contamination risks these pose to surface water and groundwater quality, emphasize the need to understand pesticide dissipation in soil which is influenced by various factors (Kumar et al., 2022). Consequently, monitoring soil pesticide residues remains essential for evaluating the presence of pesticides, notably their persistent mixtures, which can endure, accumulate over time, and impact various ecosystem components.

Sugar beet occupies a strategic position within the irrigated perimeter of Tadla, and its management relies on the application of significant quantities of pesticides (MAPMDREF, 2022). The persistence of pesticide residues in the soil of sugar beet farms has not yet been investigated in this region and constitutes a first step in trying to enforce a sustainable use of pesticides for environmental conservation at the level of the irrigated perimeter of Tadla. The aim of this research was the following: (i) to assess the distribution of residue levels for 20 pesticides across 10 sugar beet fields, (ii) to establish meaningful connections between monitoring results, soil characteristics, and pesticide properties to identify the critical factors influencing pesticide distribution in soils, and (iii) to investigate pesticide migration patterns at three specific sites with depth soils and balanced textures.

Materials and methods

The area selected for the sampling was located in the irrigated perimeter of Tadla, a region in central Morocco where sugar beet is one of the most important crops, accounting for 12,500 hectares of the cultivated area for the agricultural campaign of 2019–2020 (ORMVAT, 2019). The irrigated perimeter is divided into three region areas (Fig. 1): sub-area of the perimeter in the province of Azilal, sub-area of the perimeter in the province of Beni Mellal, and sub-area of the perimeter in the province of Fkih Ben Saleh, with arid to semi-arid climates prevailing, recording an average rainfall annually of approximately 373.8 mm and average minimum and maximum temperatures respectively of 3.32 °C and 24.86 °C. The perimeter is characterized with a dry season from April to October and a wet season from November to March. Temperatures are low in winter, causing morning frosts, and high in summer, characterized by frequent waves of chergui (ORMVAT, 2019). The pursuit of agriculture (sugar beet crops) in this area necessitates irrigation, especially in light of the past two consecutive years of drought. The sampling sites were located to include sugar beet fields with different characteristics across the three sub-areas of the irrigated perimeter particularly with different surface area, different agricultural production of sugar beet crops, and the availability of water resources for irrigation. Three municipalities were designated across two sub-areas of the perimeter: the municipality of Sidi Jaber (sub-area included in the province of Beni Mellal), the municipality of Ouled Gnaou (sub-area included in the province of Beni Mellal), and the municipality of Afourar (sub-area included in the province of Azilal), and the third sub-area was excluded because
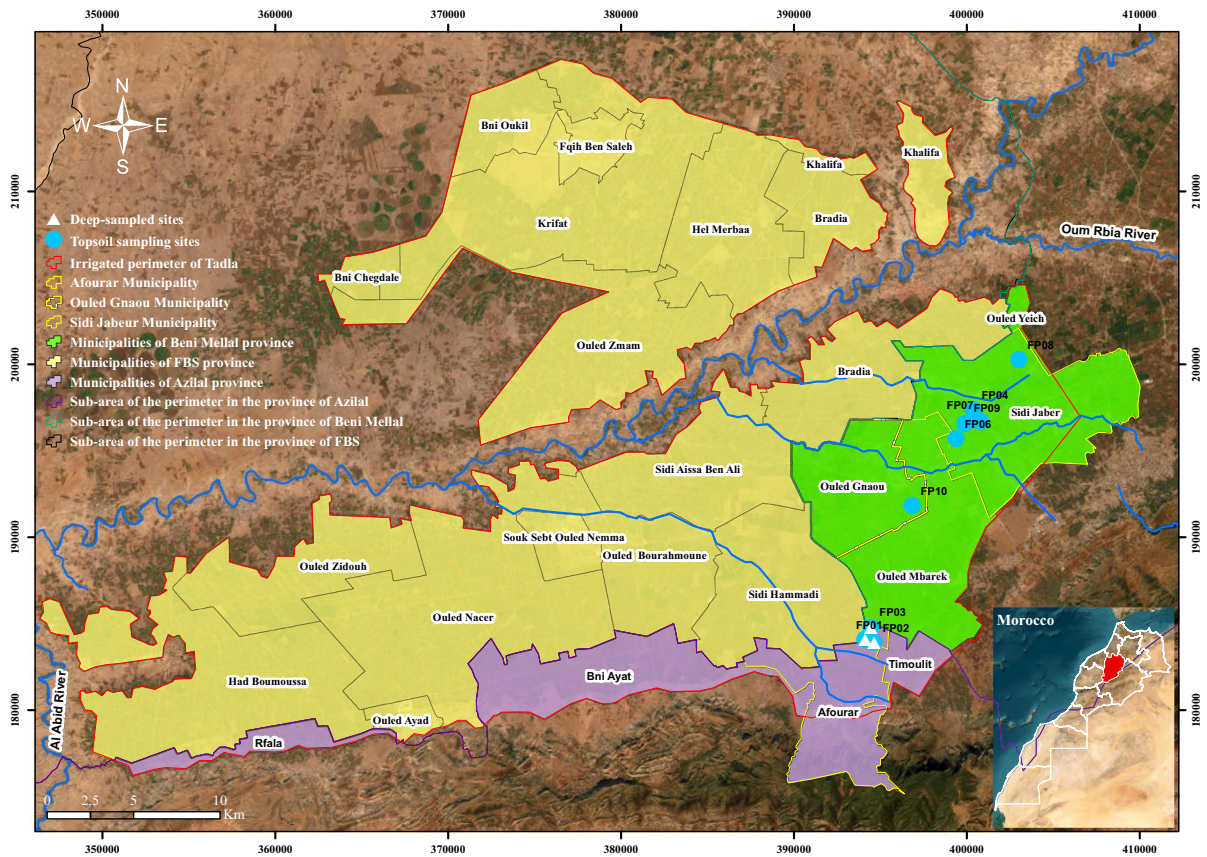
Fig. 1 Map of the location of soil samples taken from fields previously cultivated with sugar beet

of scarcity of water which influenced the expansion of sugar beet in this region (Fig. 1). With an irrigated surface of respectively 7209.5 ha, 1989.81 ha, and, 4187.67 ha, the municipalities of Sidi Jabeur, Afourar, and Ouled Gnaou were favorable for the agricultural production of sugar beet. The municipality of Afourar was characterized by an average yield per hectare of approximately 52.9 tons of sugar beet over an area of 400 ha in the five previous normal crop years, with the rural municipality of Sidi Jaber having an agricultural vocation and a large area of sugar beet covering 360 ha, while sugar beet occupied an area of 435.45 ha in the municipality of Ouled Gnaou (ORMVAT, 2019). The predominant soils at the level of these municipalities are subtropical brown isohumic soils in Afourar municipality; favorable to irrigated agriculture because of their depth and balanced texture, with moderately deep red fertialitic soils that are found in the municipalities of Sidi Jaber and Ouled Gnaou and also found in the municipality

of Afourar (ORMVAT, 2019). Ten sampling sites were arbitrarily designated across the three municipalities of the two sub-areas of the irrigated perimeter to address the following objectives: (i) determine the distribution of the residues levels of 20 pesticides in soil of sugar beet fields; (ii) relate the monitoring results with soil properties and pesticides properties to identify keys properties affecting the concentration and the distribution for these compounds in the soil; and (iii) determine the residues levels of pesticides in depth layers of soil for three specific sites with a depth soil and balanced texture.

Sampling sites: sugar beet fields

The soil sampling sites were agricultural sites that had previously been cultivated with sugar beet crop. Sugar beet crop need tillage, fertilization, irrigation, and pest and disease control. Table 1 outlines these commonly adopted farming practices with scenarios

Table 1 Farming practices commonly adopted in sugar beet fields in the irrigated perimeter of Tadla

Farming practices	Indications
Tillage and seed-bed preparation	*Deep plowing*: during the period from June to August *Seedbed preparation*: between September and November
Sowing	The sowing period is from early September to mid-November ● *Early sowing:* the last half of September and the first decade of October ● *Mid-season sowing:* the last two decades of October and the first decade of November ● *Late sowing:* after the first decade of November
Fertilization	● *Mineral fertilizers:* The application of the formula 13–23-13S-6SO3 is done at a rate of 4 quintals/ha after sowing ● *Nitrogen fertilizers:* Two applications of ammonium nitrate 33.5% formula are required, with a rate of 4.5 quintals/ha. The first application should be done in December, and the second one in February, with a 2/3 portion in December and the remaining 1/3 in February
Irrigation	The irrigation frequency, which can be as high as 40 times during the crop cycle, at intervals of every 3 to 5 days, is adjusted according to the plant's needs until the final 15 days of the cultivation period
Control of weed	Example of weeds found in sugar beet fields at the irrigated perimeter of Tadla (Baye et al., 2012): *Juncus bufonius L., Ranunculus trilobus Desf, Ranunculus muricatus L., Anagallis arvensis, Phalaris minor, Ammi majus, Picris echioides, Ammi visnaga L., Cichorium intybus* Three treatments are administered per crop cycle: ● *Treatment 1:* Formula 1: Venzar (400 g/ha) + Safari (60 g/ha) + Mito (1 kg/ha) + Goltix (1 kg/ha) or Betasana trio (1L/ha) Active ingredients: Lenacil, Triflusulfuron-methyl, Metamitron, or Lenacil, Triflusulfuron-methyl, Metamitron, Phenmedipham, Desmedipham, Ethofumesate Formula 2: Mito (1 kg/ha) + Betasana trio (1L/ha) or Goltix (1 kg/ha) + Betasana trio (1L/ha) Active ingredients: Metamitron, Phenmedipham, Desmedipham, Ethofumesate ● *Treatment 2:* Formula 1: Safari (60 g/ha) + Betanal expert (1L/ha) + Bison (0.5L/ha) + Twister (1L/ha) Active ingredients: Triflusulfuron-methyl, Phenmedipham, Desmedipham, Ethofumesate, Clethodim Formula 2: Oblix (1L/ha) + Mito (1 kg/ha) or Oblix (1L/ha) + Goltix (1 kg/ha) Active ingredients: Ethofumesate, Metamitron ● *Treatment 3:* Formula: Bison (0.5L/ha) or Betanal expert (1L/ha) Active ingredients: Phenmedipham, Desmedipham, Ethofumesate
Control of disease	Example of disease agents in sugar beet crop at the irrigated perimeter of Tadla (Elhousni et al., 2023): *Cercospora beticola, Uromyces betae, Erysiphe betae* One fungicidal treatment is applied per cycle: ● *Treatment 1:* Bachlor or Rex duo Active ingredients: tetraconazole or epoxiconazole and thiophanate-methyl
Control of pest	Example of pathogens in sugar beet crop at the irrigated perimeter of Tadla (ORMVAT, 2022): *Cassida vittata, Spodoptera littoralis, Pegomye betae, Agriotes spp., Conorhynchus mendicus, Agrotis segetum* Three to four insecticidal treatments are applied per cycle: ● *Treatment 1:* Force 0.5G (20 kg/ha) or CRATER (15 kg/ha) Active ingredients: tefluthrin or chlorpyrifos-ethyl ● *Treatment 2:* CASALPHA (1/10 L) or KARATE (0.25L/ha) Active ingredients: Alpha-cypermthrin or Lambda cyhalothrin ● *Treatment 3:* BRIGADA GEO (10 kg/ha) Active ingredients: bifenthrin ● *Treatment 4:* AVAUNT (1/4 L) Active ingredients: indoxacarb

of pesticide application (date, dose, active ingredient) by beet growers in the irrigated perimeter of Tadla. A total of ten sugar beet fields were arbitrarily designated for the monitoring network and were assigned codes ranging from FP01 to FP10. The area selected for the sampling at each site represents the

area where sugar beet crop have been previously cultivated. All the field sites use irrigation, either by utilizing groundwater from wells, surface water, or both. Characteristics related to the farm size, its sugar beet production, the rural municipality of affiliation, and the agricultural campaign are reported for each sampled site in Table 2.

Soil sample collection

Soil physicochemical characterization and soil fertility

Soil samples were taken from the sugar beet fields, and the particle size, organic fertility, and pH were analyzed to characterize these fields. The soil samples were collected after the harvest of sugar beet crop before the beginning of the next agricultural season (in September). Samples were collected using an auger at a depth of 20 cm. To cover the variability and heterogeneity of each of the 10 fields, sampling was carried out according to the Hay method (Sabbe & Marx, 1987), and 13 samples of 100 g were taken from each field. All 13 samples were mixed to obtain a composite sample representative of each field, with a mass of 1 kg. The composite samples were transported in paper bags to the laboratory for physicochemical characterization of the soils.

Characterization of pesticide residues in soils

To analyze pesticide residues in the soil of sugar beet fields, soil samples were taken from the topsoil from 0 to 20 cm. This layer is most concerned with the accumulation of pesticides (Hvězdová et al., 2018). The soil samples were taken from fields in September before the start of the agricultural season. Soil samples were collected after the harvest of sugar beet crop before the beginning of the next agricultural season. A composite sample of 13 samples was collected to ensure the representativeness of each field. Samples were collected using an auger and stored in glass boxes. Soil samples were air-dried, and sieved through a 2 mm sieve and stored at 4 °C. Approximately 1 kg of soil from each field was collected.

Characterization of pesticide migration to deep soil layers

To verify the migration of pesticides, only the fields from the Afourar municipality (FP01, FP02, and FP03), characterized by their depth soils and balanced textures, were sampled. In the rural municipalities of Sidi Jaber and Ouled Gnaou, the selected fields are characterized by soils that are slightly developed rendzines, which limited their sampling to the 0–20 cm surface without extending the sampling to deeper layers. Samples were collected at three soil depths: 0–20 cm, 20–40 cm, and 40–60 cm using an auger and stored in glass boxes. Soil samples were air-dried, and sieved through a 2-mm sieve and stored at 4 °C. The soil samples were collected before the start of the agricultural season.

Physicochemical analysis of soil properties

The pH of the soils (pH-water) was measured in water: soil (1:2.5) ratio, using a pH meter with a glass

Table 2 Characteristics of sampled sugar beet fields

Sampling site	Municipality	Field size (ha)	Root yield (tons)	Sugar content (%)
FP01	Afourar	1.8	120	13
FP02	Afourar	1.8	110	12.85
FP03	Afourar	1.8	100	13.77
FP04	Sidi Jabeur	4.79	45	17.5
FP05	Sidi Jabeur	5	50	18
FP06	Sidi Jabeur	14	25	20
FP07	Sidi Jabeur	4.79	56	17.72
FP08	Sidi Jabeur	4.79	40	15
FP09	Sidi Jabeur	4.79	30	12
FP10	Ouled Gnaou	16	45	18

electrode (Rhoades, 1982). The organic matter content was determined using the method of Walkley and Black by multiplying the % organic carbon by 1.724. The particle size analysis was performed using the Robinson pipette method. The clay and silt contents were determined by sedimentation according to Stocks' law. The physicochemical characteristics of the selected soils were determined and are shown in Table 3. The soil texture was generally sandy clay loam or sandy loam; the soil pH was in the 8.41 to 8.74 range, and the OM content was between 1.539 and 3.53%.

Analysis of pesticide residues in soil

Target pesticides

The physicochemical properties such as soil sorption coefficient (K_{oc}), half-life soil degradation (DT_{50}), solubility in water (S_w), vapor pressure (Vp), GUS leaching potential index (Gus index), and octanol–water partition coefficient (Log P) for the target pesticides are presented in Table 4. Nineteen pesticides and one transformation product were targeted in soils from the studied area. Azoxystrobin, deltamethrin, tebuconazole, tetraconazole, epoxiconazole, tefluthrin, bifenthrin, difenoconazole, ethofumesate, pyriproxyfen, and cypermethrin are pesticides commonly used in sugar beet crop. For those that are prohibited for use such as isopropalin, heptachlor, propiconazole, chlordane, dieldrin, and primiphos-methyl, DDT, and its derivative DDE (IUPAC PPDB Search, n.d.), it is necessary to define their status in the soil of sugar beet fields in the irrigated perimeter of Tadla.

Pesticide extraction technique

Solution preparation for the calibration curve

Twenty standards were prepared individually from 20 formulations with purities of 97–99%. Acetonitrile (90% purity) was used as the solvent to prepare the solutions. From the stock solution prepared at a concentration of 1000 mg/kg, four solutions (1, 2, 3, and 4) were prepared with concentrations respectively of 5, 1, 0.5, and 0.1 mg/kg for each target pesticide. Five concentrations, namely: 10, 20, 50, 100, and 200 µg/kg, were chosen as points for the calibration curve. These concentrations were prepared from solutions 4, 4, 3, 3, and 2 respectively. A blank sample was prepared with acetonitrile, and the fortified control sample was prepared by mixing 0.5 ml of the daughter solution 1 of all target pesticides. Using organic solvents (see sample extraction and analysis), a calibration curve was obtained after injection of the seven solutions (5 concentration points, blank and fortified solutions).

Sample extraction and analysis

Soil samples (25 g wet weight) were transferred to a 500-ml bottle and extracted with 50 ml of acetone and 100 ml petroleum ether. The mix was mixed with 300 ml of ultrapure water and filtrate. The organic phase was transferred to a 250-ml bottle and mixed with anhydrous sodium sulfate. The extract was concentrated and 5 ml of acetonitrile was added prior to vialing. For solvent evaporation, the extract was transferred through a nitrogen flux, and 0.25 ml of acetonitrile was added to the drop. A volume of 2 µL was injected into the gas

Table 3 Soil properties of selected fields in the irrigated perimeter of Tadla, OM%: organic matter content, clay %: clay content, Silt %: silt content, and Sand %: sand content

Soil samples	Texture	pH	MO%	Clay %	Silt %	Sand %
FP01	Sandy Loam	8.54	1.8	22	34	44
FP02	Sandy Clay	8.6	1.774	28	18	54
FP03	Silty Clay	8.67	1.539	40	42	18
FP04	Silty Sandy	8.48	3.249	26	40	34
FP05	Silty Sandy	8.45	2.505	30	36	34
FP06	Silty Sandy	8.41	3.53	26	40	34
FP07	Silty Clay	8.63	3.061	36	44	20
FP08	Clayey Silty	8.68	2.836	40	36	24
FP09	Silty Clay	8.74	2.66	28	48	24
FP10	Clayey Silty	8.6	1.797	38	38	24

Table 4 Physicochemical properties of the molecules monitored during the study. K_{oc}, soil sorption coefficient; DT_{50}, half-life soil degradation; S_w, solubility in water at 20 °C (mg l⁻¹); Vp, vapor pressure at 20 °C (mPa); *Gus index*, GUS leaching potential index; *Log P*, octanol–water partition coefficient at pH 7, 20 °C. All data from IUPAC PPDB Search (n.d.), except for (a): from EU Commission (2023)

Target pesticides	Koc Lkg⁻¹	DT$_{50}$ days	S$_w$ at 20 °C mg l⁻¹	Vp at 20 °C mPa	GUS index	Log P
Isopropalin	10,000 Non-mobile	100 Persistent	0.11 Low	1.17 Low volatility	0.00 Low leachability	5.29 High
Heptachlor	24,000 Non-mobile	285 Persistent	0.056 Low	53 Highly volatile	−0.91 Low leachability	5.44 High
Azoxystrobin	589 Slightly mobile	78 Moderately persistent	6.7 Low	1.10×10^{-07} Low volatility	3.10 High leachability	2.5 Low
Pyriproxyfen	21,157 Non-mobile	10 Non-persistent	0.37 Low	1.33×10^{-02} Low volatility	−0.20 Low leachability	5.37 High
Deltamethrin	10,240,000 Non-mobile	58.2 Moderately persistent	0.0002 Low	0.0000124 Low volatility	−3.98 Low leachability	4.6 High
Tebuconazole	1000[a] Slightly mobile	63 Moderately persistent	36 Low	1.30×10^{-03} Low volatility	1.86 Transition state	3.7 High
Tetraconazole	3.56 Highly mobile	61 Moderately persistent	156.6 Moderate	0.18 Low volatility	2.47 Transition state	3.63×10^{03} High
Propiconazole	1086 Slightly mobile	71.8 Moderate	150 Moderate	0.056 Low volatility	1.58 Low leachability	3.72 High
DDT	151,000 Non-mobile	6200 very persistent	0.006 Low	0.025 Low volatility	−3.89 Low leachability	6.91 High
DDE	50000[a]	5000 very persistent	0.12 Low	-	-	6.51 High
Tefluthrin	112,900 Non-mobile	37 Moderately persistent	0.016 Low	8.4 Moderately volatile	−2.52 Low leachability	6.4 High
Bifenthrin	236,610 Non-mobile	26 Non-persistent	0.001 Low	0.0178 Low volatility	−2.66 Low leachability	6.6 High
Epoxiconazole	1073[a] Slightly mobile	353.5 Persistent	7.1 Low	3.5×10^{-04} Low volatility	2.09 Transition state	3.3 High
Difénoconazole	6.12[a] Highly mobile	130 Persistent	15.0 Low	3.33×10^{-05} Low volatility	0.83 Low leachability	4.36 High
Ethofumesate	150[a] Moderately mobile	21.6 Non-persistent	50 Moderate	0.36 Low volatility	3.04 High leachability	2.7 Moderate
Cypermethrin	288,735 Non-mobile	23.0 Non-persistent	0.004 Low	0.00038 Low volatility	−2.38 Low leachability	5.8 High
Lenacil	165 Moderately mobile	49.7 Moderately persistent	2.9 Low	1.7×10^{-06} Low volatility	3.02 High leachability	1.69 Low
Chlordane	20,000 Non-mobile	365 Very persistent	0.1 Low	1.3 Low volatility	−0.77 Low leachability	2.78 Moderate
Dieldrin	12,000 Non-mobile	1400 Very persistent	0.14 Low	0.024 Low volatility	−0.26 Low leachability	3.7 High
Pirimiphos-methyl	1100 Slightly mobile	39 Non-persistent	11 Low	2.00×10^{-03} Low volatility	1.53 Low leachability	4.2 High

chromatography-tandem mass spectrometry (GC–MS/MS) system.

The pesticides were analyzed by a CG- MS/MS with an HP–5MS UI column with a migration capacity of 1,1 ml/min under the following instrumental conditions: an initial temperature of 60 °C remains for 1 min, and increases by 10 °C/min up to 250 °C and remains for 5 min; ramp 1 has a temperature of 40 °C/min, up to 170 °C, and stays for 0 min, and ramp 2 increases by 10 °C up to 310 °C and stays 3 min. The injection port was operated at 70 °C, and detectors MS 1 at 150 °C and MS 2 at 150 °C, with the source temperature set at 280 °C. The 2μL injection was carried out with an Agilent autosampler. Helium was used as the carrier gas at 1.2 mL min^{-1}. The MASSHUNPER software was used for sample processing. The limit of quantification of this technique is 1 PPB, and the limit of detection is 0.1%

Statistical analysis

In addition to principal component analysis, Pearson correlations were conducted firstly, to investigate the relationship between the frequency (Freq) and the maximum residual concentration detected for each pesticide (Max), and their physicochemical properties such as K_{oc}, DT_{50}, S_w, Vp, Gus index, and Log P, and secondly, to explore the connection between the total residual quantity for each sugar beet field in the sampling network and the soil properties of selected fields. Pearson correlations were also used to relate the residual concentration of individual pesticides and the soil characteristics. Data of the residual concentration of pesticides in sites FP01, FP02, and FP03 determined at three different sampling depths (0–20 cm, 20–40 cm, and 40–60 cm, respectively) were subjected to a one-way analysis of variance (ANOVA) to assess how sampling depth affects the residual concentration of pesticides. The least significant difference (LSD) test at a confidence level of 95% was used to separate means. IBM SPSS (version 22; USA) statistical software was used.

Results

Pesticide detection in topsoil from sugar beet fields

Up to 2021, over 28 active ingredients from multiple chemical functional categories were commonly used for sugar beet crops, and more than 20 pesticide product formulations were available for this crop in the irrigated perimeter of Tadla (MAPMDREF, 2022). To detect and quantify pesticides, soil analysis was conducted according to a targeted screening of nineteen pesticides and one transformation product. The results of the analysis of the residues demonstrate the presence of pesticides in topsoil samples from the ten selected fields before the start of the agricultural campaign (Table 5). Tefluthrin is the most frequently detected pesticide (DF = 90%). Epoxiconazole is also one of the most frequently detected pesticides, followed by the transformation product DDE. DDE, in addition to being frequent in soil samples (DF = 70%), was present at concentrations greater than 10 μg/kg. Cypermethrin, difenoconazole, and DDT were detected at high frequencies in the tested soils (DF = 50%). Cypermethrin and difenoconazole can reach concentrations greater than 10 μg/kg. Pesticides banned from use, such as isopropalin, heptachlor, chlordane, dieldrin, and pirimiphos-methyl, were detected at frequencies of 10%, 30%, 10%, 20%, and 30%, respectively. Other pesticides most commonly used in sugar beet crop, such as azoxystrobin, deltamethrin, tebuconazole, bifenthrin, ethofumesate, and lenacil, also had low detection frequencies. The Concentrations and detection frequencies of the pesticides varied from one pesticide to another. However, despite the low frequency of detection in the soil, some pesticides can reach concentrations above 10 μg/kg (deltamethrin and pirimiphos-methyl).

The residual concentration of pesticides can provide useful information about their use and their pollution status in topsoil of sugar beet fields. In the topsoil of sugar beet fields, tefluthrin was detected with a mean concentration of 2.910 μg/kg. Five pesticides, namely, epoxiconazole, difenoconazole, tetraconazole, propiconazole, and tebuconazole, belonging to the triazole family, were detected with the mean concentration of 1.40, 4.60, 1.944, 0.40, and 0.30 μg/kg, respectively. Three pyrethroid pesticides (Alpha-cypermethrin, deltamethrin, and bifenthrin) were detected with the mean concentration respectively of 2.20, 2.40, and 0.20 μg/kg. A uniform low concentration was found between other commonly used pesticides in sugar beet crops such as ethofumesate, lenacil, and azoxystrobine, with mean concentration of 0.50, 0.90, and 0.10 μg/kg respectively. DDT is still detected in sampled topsoils and the concentration of

Table 5 List of pesticides detected in soil samples taken from the surface 0–20 cm of sugar beet fields with detection frequencies according to the three concentration ranges ([C] = concentration)

Detected pesticides	Detection frequency	Frequency [C] < 1 µg/kg	Frequency [C] > = 1 µg/kg	Frequency [C] > 10 µg/kg
Isopropalin	10%		10%	
Heptachlor	30%		30%	
Azoxystrobin	10%		10%	
Pyriproxyfen	10%		10%	
Deltamethrin	20%		10%	10%
Tebuconazole	20%	10%	10%	
Tetraconazole	30%	10%	20%	
Propiconazole	10%		10%	
DDT	50%		50%	
DDE	70%		10%	60%
Tefluthrin	90%	10%	80%	
Bifenthrin	20%	10%	10%	
Epoxiconazole	80%	10%	70%	
Ethofumesate	10%		10%	
Alpha-cypermethrin	50%		40%	10%
Lenacil	10%		10%	
Chlordane	10%		10%	
Difenoconazole	50%	10%	10%	30%
Dieldrin	20%		20%	
Pirimiphos-methyl	30%	10%	10%	10%

DDE observed (37 µg/kg) was higher compared to parent compound. In addition, dieldrin, chlordane, iso-propaline, pyriproxyfen, heptachlore, and pirimiphos-methyl can still detected in topsoil of sugar beet fields with related low mean concentrations of 1.20, 0.10, 0.80, 0.10, 0.50, and 2.30 µg/kg respectively. The results of concentrations of pesticides residues showed variations between residual concentrations of pesticides suggesting variable distribution of pesticides in topsoil of sugar beet fields.

All soil samples from the selected sugar beet fields contained pesticides, and the total residual quantity of pesticides are ranging from 5 to 137 µg/kg. The distribution of the total residual quantity of pesticides in the sugar beet fields selected from the three municipalities is shown in Fig. 2. The soil sample with the highest total concentration was that at site FP03, collected from a sugar beet field in Afourar municipality, with a total residual quantity of pesticides of 137 µg/kg (Fig. 3). Samples taken from FP01 and FP02 in the same municipality showed total residual quantity of pesticides of 128 and 94 µg/kg. The soil sample collected from the municipality of Ouled Gnaou (FP10) had a total residual quantity of 65 µg/kg. In the municipality of Sidi Jaber, the total residual quantity of pesticides ranges from 3 to 100 µg/kg. Four fields in the same municipality (FP07, FP09, FP05, and FP06) had the lowest total residual quantity of pesticides (3, 5, 8, and 17 µg/kg). Thus, large variations were observed among the three municipalities selected in this study. Similarly, this variation in total residual quantities of pesticides even resides between sugar beet fields belonging to the same rural municipality, indicating the variation in the application of pesticides in the different sugar beet fields.

Detected concentration: maximum, median, minimum

The minimum, maximum, mean, and median pesticide residual concentrations are listed in Table 6. DDE had the highest concentration which is 114 µg/kg. The pesticides deltamethrin, difenoconazole, and pirimiphos-methyl also showed significant concentrations of 22, 18, and 18 µg/kg, respectively. Pesticides banned from use are still detected at significant concentrations in the soils; the same is true for pesticides of recent use.

Fig. 2 Distributions of total residual quantity of pesticides in topsoil samples from sugar beet fields of different municipalities
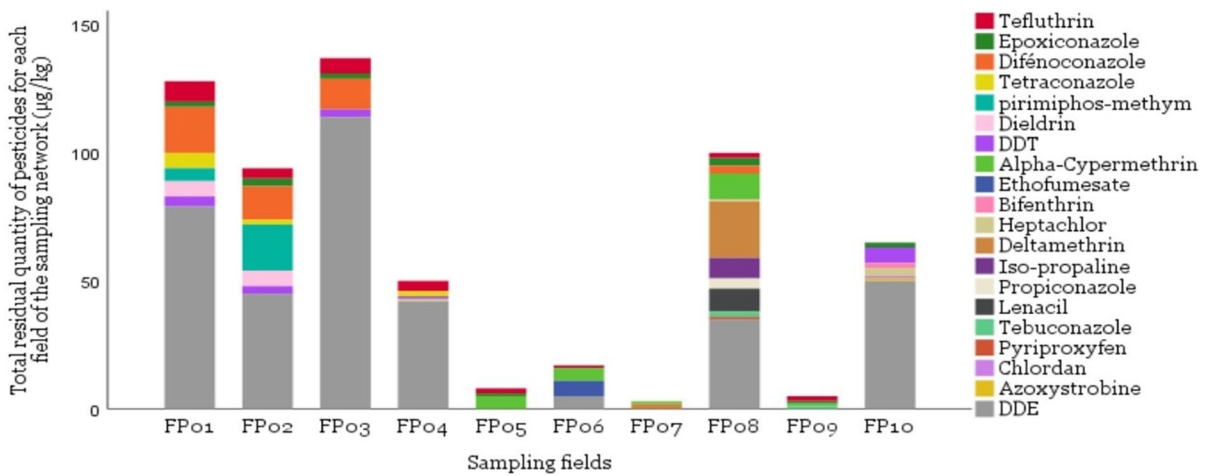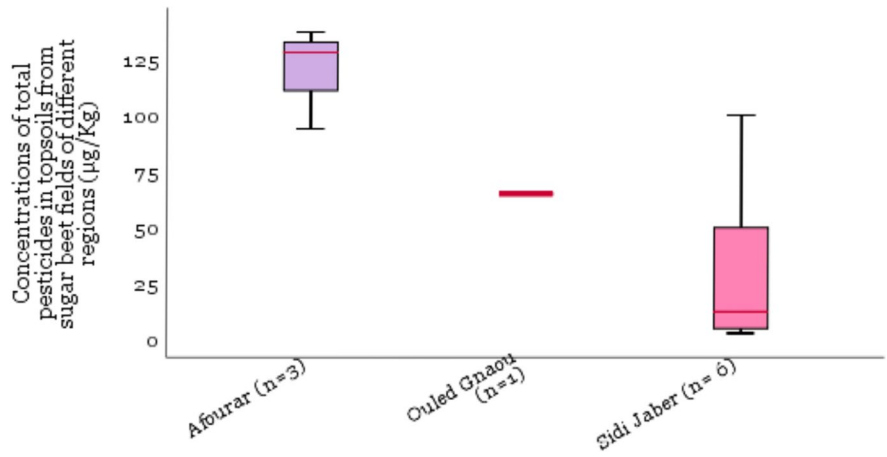

Fig. 3 Total residual quantity of pesticides for each field from the sampling network

Detected multiple residues of pesticides

The presence of multiple pesticide residues is the result of the application of different pesticide treatments and formulations with several ingredients (Coronado et al., 2011; Li et al., 2023; Lozowicka, 2015). All the soil samples contained multiple pesticide residues, with a maximum of 13 residues per sample. Soil samples with five pesticide residues represented 40%, whereas those with a residue number above five represent 60% of all samples. The profile of multiple pesticide residues varies from one municipality to another and even within selected fields in the same municipality. In the municipality of Afourar, the number of residues in the three selected fields oscillates between 6 and 8, with a mixture of six residues

present in the three sites, namely, tefluthrin, epoxiconazole, difenoconazole, DDT, pirimiphos-methyl, and DDE. The number of pesticide residues fluctuated between 3 and 13 for the six fields selected from the municipality of Sidi Jaber. In the municipality of Ouled Gnaou, only one site was selected for soil sampling and contained nine pesticide residues in total. Considering the presence of these large numbers of multiple pesticide residues in the tested soils, the quality of the soils is questioned after the cultivation of sugar beet.

Several types of pesticides are used in sugar beet crop in the irrigated perimeter of Tadla (Table 1). The multiple residues detected in the tested soils were differentiated according to the three classes of pesticides: insecticides, fungicides, and herbicides.

Table 6 Maximum, minimum, mean, and median residual concentrations of pesticides detected in surface soils of sugar beet fields. ([C] = concentration)

Pesticides	Max [C] μg/kg	Min [C] μg/kg	Mean [C] μg/kg	Median [C] μg/kg
Tefluthrin	8	Trace	2.910	2
DDE	114	5	37	45
Epoxiconazole	3	Trace	1.40	2
Alpha-cypermethrin	10	1	2.20	5
Ethofumesate	5		0.50	
Difénoconazole	18	Trace	4.60	12
Tetraconazole	6	2	1.944	2
Deltamethrin	22	2	2.40	2
Iso-propaline	8		0.80	
Lenacil	9		0.90	
Som. Heptachlore	3	1	0.50	1
DDT	6	1	1.70	3
Bifenthrine	2		0.20	Trace
Propiconazole	4		0.40	
Tebuconazole	2	1	0.30	1
Azoxystrobine	1		0.10	
Pyriproxyfen	1		0.10	
Chlordan	1		0.10	
Dieldrin	6		1.20	6
Pirimiphos-methyl	18	Trace	2.30	5

Ten insecticides—organochlorines (four insecticides), organophosphates (one insecticide), pyrethroids (four insecticides), and cyclodienes (one insecticide)—were detected in the tested soils. All the sites contained insecticides. Three fields selected for the collection of soil samples have a single pesticide (tefluthrin), 4 fields have two insecticides (tefluthrin and cypermethrin or cypermethrin and deltamethrin), one field has 3 insecticides (tefluthrin, heptachlor, and bifenthrin), and finally 2 fields have 5 insecticides which are respectively tefluthrin, heptachlor, pyriproxyfen, cypermethrin and deltamethrin or tefluthrin, heptachlor, chlordan, DDT and bifenthrin. Of the ten selected fields, only two herbicides were detected (FP06 and FP08). Fungicides were detected in eight sugar beet fields, with FP08 containing five fungicides at a time (teraconazole, propiconazole, tebuconazole, epoxiconazole, and difenoconazole). To improve yield, beet growers tend to apply more insecticides and fungicides, which are more common in the tested soils than herbicides.

Relationship between detected pesticides and their properties

The presence of pesticides in soil depends on the application history, soil properties, pesticide properties, and climatic conditions (Hvězdová et al., 2018). In this study, the relationships between the maximum residual concentration of pesticides (Max), their frequency in soils (Freq), and their properties (K_{oc}, DT_{50}, S_w, Vp, Gus index, and Log P) were explored using PCA (Fig. 4). The first four components in PCA explained 77.973% of the data variability 31.012% in PC1, 18.910% in PC2, 15.279% in PC3, and 12.754% in PC4, reflecting the largest amount of original information. The DT_{50}, detection frequency, and the maximum residual concentration of different pesticides were positively related and constituted the first principal component. The octanol–water partition coefficient, Log P, water solubility, and the Gus index are also positively correlated and constitute the second component, while the vapor pressure of pesticides
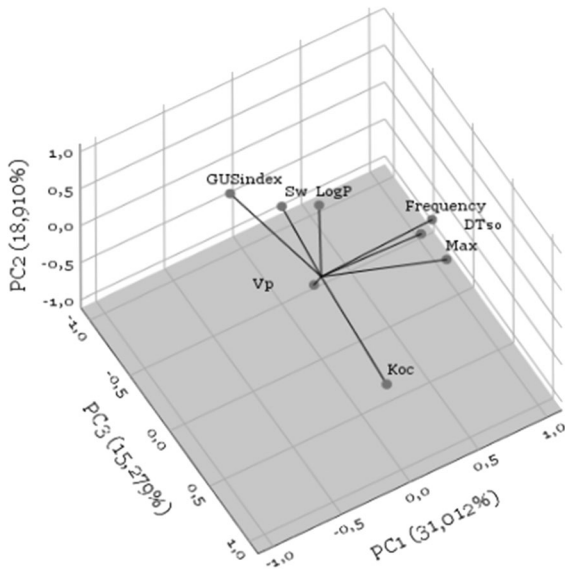
Fig. 4 Relationship between the physicochemical properties of pesticides and their detection in the sampled soils of sugar beet fields. Max: the maximum residual concentration of pesticides detected in sampled soils

constitutes the principal component 3, and the organic carbon–water partition coefficient is related to the principal component 4. A positive correlation was found between the maximum residual concentration of pesticides and their frequency in soils (0.532), and between the maximum residual concentration of pesticides and their DT_{50} (0.434). Similarly, a strong positive correlation exists between the water solubility of pesticides (S_w) and their Log P (0.676), and between the S_w and the Gus index (0.416). The properties of pesticides influence their fate in soil (Aryal et al., 2020), and these results demonstrate the influence of the DT_{50} property on the frequency of detection of pesticides, as much as the maximum residual concentration of pesticides.

The correlation coefficients between the maximum residual concentration of pesticides in soils and their GUS index were positive and significant (0.798, $p < 0.005$), indicating that this factor influence the maximum residual concentration of pesticides in soils. The correlation coefficients between the maximal residual concentration of pesticides and their DT_{50} were positive but not significant (0.434, $p > 0.05$), indicating that this factor do not influence the maximum residual concentration of pesticides in soils. Insignificant negative correlations were found

between the maximum residual concentration of pesticides in soils and their S_w (-0.231, $p > 0.05$).

Relationship between detected pesticides and soil properties

Soil properties influence the pesticide residue content of soil (Aryal et al., 2020). The relationships between the total residual quantity of pesticides of the sampled fields and their soil properties were explored using principal component analysis (Fig. 5). The properties of the tested soils are presented in Table 3. The clay content, sand content, and pH were correlated with the total residual quantity of pesticides (Total pesticide content) of the sampled soils. The principal component analysis, by its two main components, explained 79.117% of the variability of the data 42.372% for PC1 and 36.745% for PC2, which reflects the basis of the original information. The pH, clay content, and silt content affect the composition of the first component. The total residual quantity of pesticides of the sampled soils (Total pesticide content) was involved in the composition of component 2. The total pesticide residue content was negatively correlated with the organic matter content (-0.690), in contrast to clays (0.198).

The correlation coefficients between the total residual quantity of pesticides of the sampling network and the clay content, sand content, and pH were not significant (0.189, 0.189, 0.264 respectively, with $p > 0.05$), indicating that these factors were not influencing the total residual quantity of pesticides in soils of the sampled fields. Significant negative correlations were found between the total residual quantity of pesticides in soils and their organic matter contents (-0.690, $p < 0.05$).

Influence of pesticides and soil properties on pesticides residues in soils

Bivariate correlations were obtained between the soil characteristics and the residual concentrations for each individual compound in all sampled fields in order to verify whether there is a possible relationship between the soil properties responsible for pesticide retention by soils and the residual concentration detected of pesticide. The most significant correlations were obtained between the residual concentration of tetraconazole and the
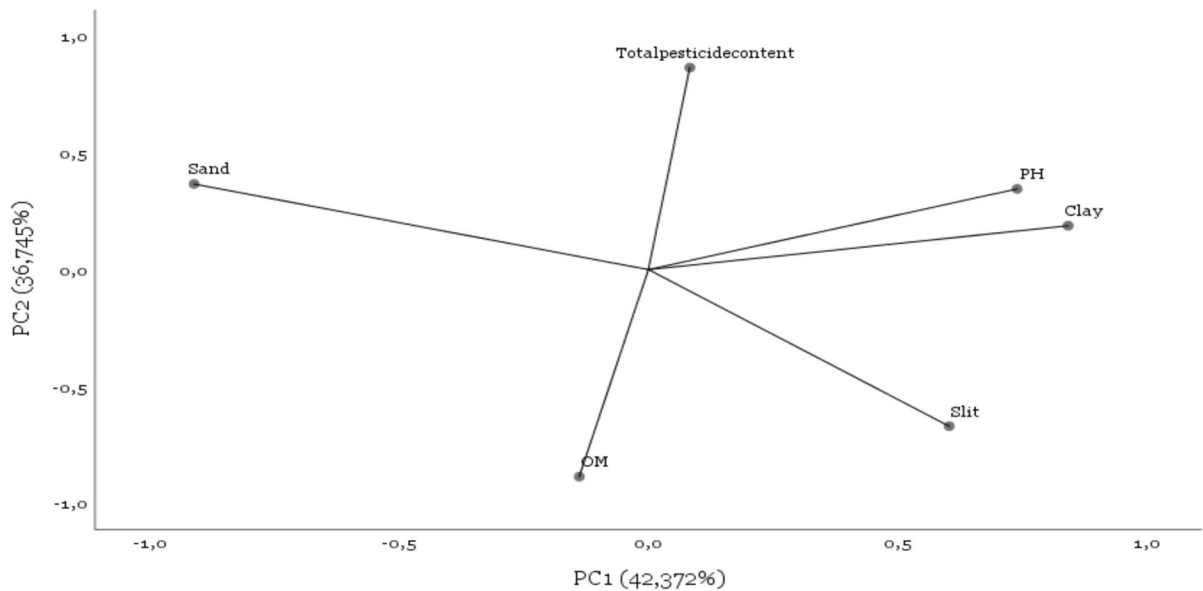
Fig. 5 Relationships between the soil properties of the soils tested and their total content of pesticide residues. (Total pesticide content): the total residual quantity of the sampling fields

inorganic fraction (sand ($r = 0.652$, $p < 0.04$), texture ($r = 0.654$, $p < 0.04$)). Other positive significant correlations were obtained between the inorganic fraction and the residual concentration of dieldrin (sand ($r = 0.835$, $p < 0.003$)) and the residual concentration of primiphos-methyl (sand ($r = 0.817$, $p < 0.004$)). Significant negative correlations were obtained between the inorganic fraction and the residual concentration of difenoconazole (texture ($r = -0.815$, $p < 0.004$)), the residual concentration of tetraconazole (texture ($r = -0.640$, $p < 0.046$)), and the residual amount of pirimiphos methyl (silt ($r = -0.893$, $p < 0.001$)). Negative correlations were obtained between the inorganic fraction and the residual amount of dieldrin (texture ($r = -0.79$, $p < 0.006$), silt ($r = -0.76$, $p < 0.011$)).

The most significant correlations were obtained between the organic fraction and the residual concentration of difenoconazole (soil OM ($r = 0.710$, $p < 0.004$)). Significant negative correlations were obtained between the organic fraction and the residual concentration of epoxiconazole (soil OM ($r = 0.721$, $p < 0.019$)) and the residual concentration of DDT (soil OM ($r = -0.792$, $p < 0.006$)). The residual concentration of the pesticides bifenthrin, alpha-cypermethrin, azoxystrobin, chlordane, deltamethrin, isopropalin, propiconazole, lenacil, pyriproxyfen, DDE,

ethofumesate, and heptachlore was not related to any soil characteristic.

Distribution of pesticides located on a 60 cm deep soil profile from sugar beet fields

Considering the migration capacity of pesticides in the soil, monitoring pesticide residues in deep soil layers is relevant for evaluating the mobility of pesticides and their risks to adjacent superficial groundwater. To verify the migration of pesticides, three selected fields (FP01, FP02, and FP03) from the Afourar municipality were sampled at three soil depths: 0–20 cm, 20–40 cm, and 40–60 cm. In FP01, the total residual quantity of pesticides was 128 µg/kg in the topsoil, 23 µg/kg in the middle soil layer, and 31 µg/kg in the deep soil (Table 7). Five identical molecules were detected in the three soil layers, tefluthrin, tetraconazole, DDE, epoxiconazole, and difenoconazole, indicating their migration through these soil layers. The residual concentration of tefluthrin decreases from the surface to the depth, passes from 8 µg/kg to 6 µg/kg and finally to 1 µg/kg. The pesticide tetraconazole is detected at residual concentrations of 6 µg/kg, traces, and 2 µg/kg in the deep soil. Epoxiconazole was detected in approximately similar residual concentrations in the three

Table 7 Maximum, minimum, and median residual concentrations of pesticides detected in different layers of soils of the three sugar beet fields from Afourar municipality

Pesticides	Soil depth = 0–20 cm			Total residual quantity of pesticides(µg/kg)		
	Min (µg/kg)	Max (µg/kg)	Med (µg/kg)	FP01	FP02	FP03
Tefluthrine	4	8	6	113	65	132
Difenoconazole	12	18	13			
DDE	45	114	79			
Epoxiconazole	2	3	2.5			
Tetraconazole	6		6			
Pesticides	Soil depth = 20–40 cm			Total residual quantity of pesticides (µg/kg)		
	Min (µg/kg)	Max (µg/kg)	Med (µg/kg)	FP01	FP02	FP03
Tefluthrine	2	27	6	23	37	47
Difenoconazole	0.1	8	2			
DDE	13	26	18			
Epoxiconazole	4	1	2.5			
Tetraconazole	0.1		0.1			
Pesticides	Soil depth = 40–60 cm			Total residual quantity of pesticides(µg/kg)		
	Min (µg/kg)	Max (µg/kg)	Med (µg/kg)	FP01	FP02	FP03
Tefluthrine	1	304	51	27	339	55
Difenoconazole	0.1	9				
DDE	4	25	22			
Epoxiconazole	1		1			
Tetraconazole	2		2			

soil depths, which are from surface to depth: 2 µg/kg, trace, and 1 µg/kg. The residual concentration of difenoconazole decreased from the surface to the depth of the soil; thus, it goes from 18 µg/kg in the topsoil to 4 µg/kg in the middle soil layer and 1 µg/kg in the deep soil layer. For DDE, its residual concentration decreases from 79 µg/kg in the topsoil, to 13 µg/kg in the middle soil layer, and 22 µg/kg in the deep soil. In this field, the pesticide residue content decreased toward deeper soil.

In FP02, the total residual quantity of pesticides for the three layers was approximately 92 µg/kg in the surface soil, 39 µg/kg in the middle soil layer, and 348 µg/kg in the deep soil (Table 7). Four molecules were found in the three soil layers: tefluthrin, DDE, epoxiconazole, and difenoconazole. The residual concentration of tefluthrin increases from the surface toward the deep soil and increases from topsoil concentrations of 4 µg/kg and 2 µg/kg to 304 µg/kg in deep soil. Epoxiconazole was detected

at approximately similar residual concentrations in the three soil layers, which were from surface to the deep soil at 3 µg/kg, 1 µg/kg, and 1 µg/kg. The residual concentration of difenoconazole decreases from the surface to the deep soil; thus, it goes from 13 µg/kg in the topsoil to 8 µg/kg in the middle soil layer and 9 µg/kg in the deep soil. For DDE, its residual concentration decreases from 45 µg/kg in the topsoil, to 26 µg/kg in the middle soil layer, and 25 µg/kg in the deep soil. At this site, the total residual quantity of pesticides varied from one layer of soil to another; however, it was very high in deep soil. Similarly, the pesticides detected at the level of the three layers showed a variable behavior: the pesticides epoxiconazole, difenoconazole, and DDE; their residual concentration decreases toward the depth of the soil, unlike teluthrin, which is more concentrated toward the deep soil layer.

At FP03, the total residual quantity of pesticides decreased from 137 µg/kg in the topsoil, 47 µg/kg in

the middle soil layer, and 55 µg/kg in the deep soil (Table 7). Three pesticides were detected in three soil layers tefluthrin: DDE, and difenoconazole. The residual concentration of tefluthrin increased from the surface at 6 µg/kg to deep soil at 51 µg/kg. Unlike tefluthrin, the residual concentration of DDE decreased toward deep soil after being detected at very high concentrations in the topsoil 114 µg/kg. The same trend was observed for difenoconazole, which goes from a residual concentration of 12 µg/kg in topsoil to 2 µg/kg in the middle soil layer, to be detected in trace amounts in deep soil. At this site, it is clear that the total residual quantity of pesticides decreases toward deeper soil and pesticide migration does not take place in the same way; tefluthrin, for example, accumulates and difenoconazole decreases in deep soil.

To statistically compare the distribution of residual concentration of pesticides detected in the different layers of soils, an analysis of variance was carried out. The recorded residual concentrations of pesticides in the different layers of monitored soils were not significantly different for a confidence level of 95% ($p > 0.1$).

Discussion

Monitoring pesticides in sugar beet fields is essential to understand the current pesticide pollution in this specific crop, which is crucial for raising public awareness and developing strategies to combat soil pollution in the irrigated perimeter of Tadla in Morocco. To detect and quantify these contaminants in the soil, 10 sugar beet fields belonging to three municipalities in the irrigated perimeter of Tadla, in central Morocco, were selected. Analysis of the tested soils highlighted the presence of pesticides on the topsoil and for those monitored in depth; analysis revealed the presence of pesticides residues even in the deep soil layers of these sugar beet fields. In the topsoil samples, pesticide residues were detected at varying concentrations and different detection frequencies from one field to another. Currently used pesticides are detected as frequently as those historically used. The total residual quantity of pesticides per sugar beet field showed variation among fields, municipalities, and even within fields of the same municipality. In fields where soil samples

were collected at three different depths, a pattern of diminishing total residual quantity of pesticides in deeper soil layers in most fields was apparent. However, this trend varies depending on the pesticides, with some showing migration to deeper soil layers (40–60 cm). The majority of compounds detected at these three sites were similar, with almost all compounds detected at the three depths. For tefluthrin, its residual concentration decreased toward the depth of the soil in field FP01, while it increased toward deep soil in fields FP02 and FP03, unlike difenoconazole and DDE, whose residual concentrations decreased from topsoil to deep soil in all fields. The analysis of variance was carried out on the individually residual concentration of pesticides analyzed in the different soil layers to compare the distribution of pesticides residues detected in the three layers of soils. The recorded concentrations for pesticides residues in the different layers of monitored soils were not significantly different. Indeed, the homogeneity in the distribution of pesticides, regardless of soil depth, could be explained by the nature of the deep-sampled soils, which are isohumic soils characterized by the homogeneity of organic matter throughout the soil profile. It is highly likely that this homogenous distribution of pesticides is influenced by the homogeneity of organic matter, which acts as a determining factor in the distribution of pesticides in the soil.

In soil samples taken from the topsoil of sugar beet fields, DDE and tefluthrin are the most frequently detected pesticides indicating the frequent use of tefluthrin among sugar beet growers. Difenoconazole, deltamethrin, and pirimiphos-methyl had the highest maximum concentrations after DDE. Pesticides that are now banned from use, such as isopropalin, heptachlor, chlordane, dieldrin, pirimiphos-methyl, and DDT are still detected in sampled topsoil. Previous studies have reported the presence of higher level of DDT in soils compared to the observed mean concentration found in this study (Qu et al., 2019a). Dieldrin was still detected in high concentration (with mean concentration of 1.20 µg/kg) due to highly persistence in soil (long half-life of 1400 days) (IUPAC PPDB Search, n.d.). Significant concentrations of tefluthrin were detected. With the exclusion of usage as a factor, tefluthrin were primarily influenced by its affinity for soil organic matter which might explain the elevated concentrations of this compound in the sampled topsoils ($K_{oc} = 112,900$ Lkg^{-1}) (IUPAC PPDB

Search, n.d.). The three pyrethroids (cypermethrin, delthametrin, and bifenthrin) found in the sampled topsoils were also detected in soil from other regions, frequently at higher concentrations (Bragança et al., 2019; Han et al., 2017; Liu et al., 2016). Except for propiconazole, triazole pesticides (epoxiconazole, tebuconazole, tetraconazole, and difenoconazole) exhibited a common characteristic of significant concentrations and frequent detection, indicating their widespread use in treating sugar beet crops. The pesticides currently in use are detected as frequently as those historically employed. This persistence of residues, whether it encompasses a single growing season for commonly used pesticides or extends over years for historically banned pesticides, can have adverse consequences. This emphasizes the importance of continuous long-term monitoring of these chemicals to minimize their impact on the environment, wildlife, water quality, and human health.

The total residual quantity of pesticides per sugar beet field varied from one field to another, from one municipality to another, and between fields from the same municipality. Sixty percent of the selected sugar beet fields contained multiple residues of more than 5 pesticides. The number of pesticide residues reached 13 in the tested soils. Through PCA, we have shown that the total residual quantity of pesticides is negatively correlated with the organic matter content and positively correlated with clay content. The PCA revealed the relationships between total residual quantity of pesticides and the inorganic properties of the tested soils, while the correlation analysis demonstrated the lack of significant correlation between these inorganic properties, namely, pH, clay content, and sand content, and the total residual quantity of pesticides. However, a significant negative correlation was found between the total residual quantity of pesticides and the organic matter content. The inverse relationship observed between the total residual quantity of pesticides and the organic matter content highlights the significant role of soil organic matter, as demonstrated by numerous studies (Liu et al., 2018; Vangronsveld et al., 2009; Yavari et al., 2015), in the retention, and in degradation of pesticides. Similarly, through PCA, we revealed a relationship between the maximum residual concentration of pesticides and their detection frequency with their DT_{50}, yet the correlation suggests the absence of a significant correlation between these variables. However, note should

be taken of the positive but not significant relationship between the maximum residual concentration of pesticides and their DT_{50} (0.434, $p > 0.05$). Nevertheless, a significant positive correlation was identified between the maximal detected concentration for pesticides and their Gus index. These findings suggest that factors other than half-life duration may influence the frequency of detected pesticides, and that the Gus index could be a better indicator to assess the maximum residual concentration of pesticides in sampled soils.

To assess the behavior and presence of pesticide compounds in soil samples, a correlation was conducted between the residual concentration of these compounds and the soil characteristics, with the aim of establishing meaningful connections with these soil characteristics. Significant positive correlations have been observed between the mineral fraction of sand in the sampled soils and the residual concentration of the compounds dieldrin, pirimiphos-methyl, and tebuconazole, indicating a specific preference for this mineral fraction over others. This finding implies that the distribution and behavior of these compounds in the soil may be influenced by the presence of the sand fraction. Regarding the organic fraction of the tested soils, a positive correlation has been established with the residual concentration of the pesticide difenoconazole, suggesting a preference for soils rich in organic matter. However, negative correlations have been observed concerning the pesticides DDT and Epoxiconazole. This suggests that these pesticides have a lower affinity for soil organic matter. This result may imply that these compounds are less sensitive to soil organic matter, which, in turn, can influence their mobility and persistence in organic-rich soils compared to other pesticides. The residual concentrations of the pesticides tefluthrin, bifenthrin, alpha-cypermethrin, azoxystrobin, chlordane, deltamethrin, isopropalin, propiconazole, lenacil, pyriproxyfen, DDE, ethofumesate, and heptachlore were not related to any soil characteristic. This highlights the presence of other factors and mechanisms responsible for the distribution, mobility, and persistence of these pesticides in the soil. All these results highlight the variability and complexity of interactions between pesticides and the characteristics of the sampled soils.

Monitoring pesticide residues in agricultural soils provides information on their fate in ecosystems

(Sabzevari & Hofman, 2022). This study highlights the presence of pesticide residues in agricultural soils previously cultivated with sugar beet and sampled at the beginning of the next agricultural campaign. The total pesticide residue content varies from one sugar beet field to another, from one municipality to another, and even between fields in the same municipality. The highest total concentrations of pesticides were recorded in soils FP01 (128 μg/kg for eight pesticides), FP02 (94 μg/kg for eight pesticides), and FP03 (137 μg/kg for five pesticides) of the rural municipality of Afourar and FP08 (100 μg/kg for thirteen pesticides) of the rural municipality of Sidi Jaber. This variability in the concentrations detected in soil reflects, on one hand the types and quantities of pesticides used and all the pathway of dispersion that these pesticides are subjected to after application. According to the results obtained in these agricultural soils, the organochlorines isopropalin, heptachlor, chlordane, dieldrin, and DDT were still detected in the soil, at significant concentrations (8, 1, 3, 6, and 6 μg/kg respectively). They all share a Gus index classifying them as non-mobile and DT_{50} values qualifying them as persistent or very persistent (Table 3). These factors strongly contribute to their continued presence in the agricultural sampled soils. The application of difenoconazole, detected at a maximum concentration of 18 μg/kg in the soil, aims to combat fungal diseases that affect sugar beet crops around the middle of their growth cycle. This high concentration is likely due to recent repeated applications toward the end of the growth cycle. As for deltamethrin, its high level (18 μg/kg) could result from recent and frequent applications to combat pests affecting sugar beet. Highly persistent DDE is largely responsible for its concentration in the sampled fields (114 μg/kg). It should be noted that the high level of DDE in soils could come from the degradation of the DDT. The pesticide tefluthrin, which recorded the highest concentration at depths of 40–60 cm (304 μg/kg), is classified with a DT_{50} rating as moderately persistent and a Gus index indicating low mobility. Its high concentration could be attributed to other factors such as repeated use over the years or the impact of certain agricultural practices like irrigation. The quantities of pesticides present in the soil after the end of the sugar beet agricultural season raise questions about the quantities taken up by the roots and leaves of sugar beet. Several studies have revealed the presence

of contaminants at the beginning of the next agricultural campaign (Dankyi et al., 2014; Hvězdová et al., 2018; Primost et al., 2017; Scherr et al., 2017). These can persist after several vegetative periods and pose a threat to non-target plants, such as rotational crops. Similarly, the migration of certain pesticides to deep soil layers (tefluthrin) increases the potential risk of groundwater contamination. Prado-Lu and Leilanie (2015) conducted deep soil sampling and detected the following five pesticides profenofos, triazophos, chlorpyrifos, cypermethrin, and malathion at 100 cm soil deep. The literature is rich in studies confirming the contamination of groundwater resources by pesticides. In Africa, research studies, such as Khreit et al. (2020), Olisah et al. (2020), Rimayi et al. (2018), and Sorensen et al. (2015), reported the presence of the pesticides chlorpyrifos, dieldrin, imidacloprid, acetamiprid, atrazine, azadirachtin, profenofos, carbofuran, cypermethrin (Rimayi et al., 2018), and 2,4-D (Khreit et al., 2020) in groundwater. Thus, this work provides the first report on pesticide contamination in sugar beet fields and underlines the risk of contamination of superficial groundwater by highlighting the migration of some of the detected pesticides. Groundwater is a crucial component for the survival and maintenance of the entire ecosystem and the production of drinking water. Taking into account all these considerations and the importance of groundwater in the climatic, agricultural, and social contexts of the irrigated perimeter of Tadla, groundwater need to be protected through pesticide residue monitoring programs.

Agricultural intensification has already caused a significant loss of biodiversity due to the unsustainable use of pesticides (Shackelford et al., 2015; Topping & Lagisz, 2012). The literature is rich in terms of studies and reports that confirm that the injudicious use of pesticides in agriculture can cause damage to non-target organisms, which has led to a significant decline in biodiversity (Hallmann et al., 2017; Pereira et al., 2009). This study revealed the presence of multiple pesticide residues, with a minimum of 3 and a maximum of 13 residues per sample. Mixtures of 5 pesticides were the most common, found in 50% of the samples. The validation procedure for pesticides for their marketing is based on the evaluation of their effect on a limited number of microorganisms, and the new procedure put in place by EFSA for the evaluation of the effects of mixtures (Committee et al., 2019) is no longer applicable because data and procedures

relating to the long-term effects of multiple pesticide residues on non-target and native species and communities are not yet available (Geissen et al., 2021). Pesticides can negatively affect various soil microorganisms (Uwizeyimana et al., 2017; Van Bruggen et al., 2018), while others thrive, sometimes resulting in an imbalance between beneficial and pathogenic microorganisms (Van Bruggen et al., 2018). Earthworms and microorganisms play a key role in soil fertility; however, the consequences of multiple pesticide-contaminated soils remain unclear (Geissen et al., 2021). Since pesticide pollution of soils raises concerns about soil biodiversity, soil functions, and food security, this study represents the first investigation of pesticides in the soils of sugar beet fields that provides comprehensive and accurate information on the status of 20 pesticides for risk assessment in the context of the expansion and intensification of sugar beet cultivation at the irrigated perimeter of Tadla.

Conclusion

This study provides the first report on pesticide contamination in sugar beet fields in irrigated perimeter of Tadla and highlights the migration of some detected pesticides and their risk of groundwater contamination. The quantities of pesticides that remain in the soil before the start of the next agricultural season raise questions regarding their effects on rotational crops. The effects of the multiple pesticide residues highlighted in this study are unknown and need to be studied for native non-target species of irrigated perimeter of Tadla, particularly for soil organisms. Finally, to provide comprehensive information on the extent of pesticide contamination in irrigated perimeter of Tadla, this study needs to be replicated to include more sugar beet fields. Soil monitoring can be performed simultaneously with sugar beet and groundwater monitoring. This study provides comprehensive and precise information on pesticides in the soils and can be used for designing soil monitoring programs for sugar beet crop in irrigated perimeter of Tadla.

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