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Variability of pesticide residues in geological profiles (0–120 cm) – preliminary study on experimental fields at Winna Góra (Poland)

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Abstract: Technological progress and the growing demand for food have led to increasing pesticide use, resulting in their frequent detection in soils, surface waters, and groundwater. However, studies on their migration into deeper soil profile layers remain limited, particularly for a broad range of pesticides. Therefore, in this study, conducted under controlled conditions at the Field Experimental Station in Winna Góra (central Poland), the vertical and spatial distribution of a broad range of pesticide residues in soils was examined. Soil samples were collected every 20 cm down to a depth of 120 cm from two boreholes at each of three fields: EF17, EF49, and EF83. A total of nearly 400 pesticides were analyzed using ultra-performance liquid chromatography coupled to triple quadrupole mass spectrometry (UPLC-MS/MS). Twenty-three substances were identified. Among the detected compounds, fungicides (64%) and herbicides (32%) dominated. The total concentrations of substances in the analyzed soils from individual boreholes ranged from 110.63 to 980.01 μg/kg. Most compounds were detected within the upper 40 cm of the soil profile, while below this depth residues such as dimethomorph, chloridazon, fenpropimorph, fluopicolide, fluxapyroxad, metribuzin, and the metabolite 2,6-dichlorobenzamide were found. No substances were detected in the 100–120 cm interval. The obtained results highlight the importance of topography and lithology for the spatial and vertical migration of pesticides. No significant effect of pH_{KCl} on pesticide migration within the soil profile was observed. The conducted study represents one of the first such broad investigations addressing pesticide migration into deeper parts of soil profiles and emphasizes that, even in the case of glacial tills, the potential risk to shallow groundwater may still be significant.

Keywords: pesticides in soils, vertical distribution of pesticides, migration of pesticides, topography

INTRODUCTION

Technological advances and the steadily rising demand for food over recent decades have led to a substantial increase in the amount of pesticides used (Tudi et al. 2021). According to the Food and Agriculture Organization of the United Nations (2024), in 2022 the global quantity of pesticides applied in agriculture totaled 3.70 million tons of active ingredients, indicating a twofold increase since 1990. While the intensification of pesticide use has increased yields, it has simultaneously raised the risk of residue accumulation in soils and of migration to groundwater and surface waters (Tang et al. 2021, Maggi et al. 2023). Maggi et al. (2023) reported that, globally, about 10% of applied pesticides remain in soils as persistent residues, and a further about 7% migrate below the root zone.

Additionally, Tang et al. (2021) estimated that as much as 64% of the world's agricultural land lies within a pesticide-contamination risk zone for more than one active ingredient, and 31% is at high risk, which underscores the global scale of the problem. Among the high-risk areas, approx. 34% are regions of high biodiversity, 5% are regions threatened by water scarcity, and 19% are in low- and middle-income countries, thus representing areas where environmental quality is a crucial aspect. Furthermore, pesticide residues can accumulate in agricultural products and enter the food chain, posing potential acute and chronic health risks to humans (EFSA et al. 2025). These factors underscore the need to develop research into both the toxic impacts of pesticide residues on organisms (e.g., Wan et al. 2025, Zhou et al. 2025) and their behavior in the environment. In response to the latter need, numerous studies have investigated pesticide migration, degradation, and persistence in both soil (e.g., Baczyński et al. 2018, Pérez-Rodríguez et al. 2021, Medić Pap et al. 2023) and aquatic (e.g., Dragon et al. 2018, 2019, Pietrzak et al. 2022) environments. To date, most publications have focused on pesticide migration in the upper soil profile (0–20 cm, and in some cases up to 0–40 cm) (e.g., Maliszewska-Kordybach et al. 2014, Silva et al. 2019, Vrščaj et al. 2022, Froger et al. 2023, Li et al. 2023, Riedo et al. 2023, Knuth et al. 2024), whereas only a few have described their occurrence below 40 cm from the surface (e.g., Zhang et al. 2009, Weaver et al. 2012, Artikov et al. 2018, Collin et al. 2022, Yao et al. 2022, Mosquera-Vivas et al. 2024, Šunjka et al. 2024, Loose et al. 2025). However, studies on pesticides below a depth of 40 cm in the soil profile have so far focused mainly on organochlorine pesticides (e.g., Zhang et al. 2009, Weaver et al. 2012, Artikov et al. 2018, Collin et al. 2022, Yao et al. 2022), while broader analyses conducted under controlled conditions remain relatively scarce (e.g., Loose et al. 2025). Moreover, only a limited number of studies demonstrating pesticide migration into deeper soil-profile layers have so far been conducted in Poland, and these have primarily focused on individual pesticides (e.g., Paszko & Muszyński 2017, Siek & Paszko 2021).

In addition to accidental or intentional releases, there are two principal pathways by which pesticides enter the soil environment: (1) deposition and runoff to the soil during foliar spraying (Rial-Otero et al. 2003), with approx. 50% of the product reaching the soil (Pérez-Lucas et al. 2019), and (2) the release of granules applied directly to the soil environment (López-Pérez et al. 2006), which naturally leads to higher concentrations. Pesticide leaching, driven by water percolation through the soil profile, especially during intense precipitation, may result in the contamination of shallow aquifers and deeper soil horizons (Arias-Estévez et al. 2008). The persistence of pesticides in soils has been shown to depend on adsorption rates onto soil particles, which are influenced by the organic-matter content, soil texture, soil pH, and temperature (Kodešová et al. 2011, Pérez-Lucas et al. 2019, Bondareva & Fedorova 2021). Their mobilization is mainly controlled by physical transport processes, including leaching, diffusion, erosion, and surface runoff, while microbial assimilation, biodegradation, transformation, and plant uptake may further affect their persistence and distribution in the soil profile (Pérez-Lucas et al. 2019).

In particular, the role of soil microorganisms is well documented, as they play an important role in pesticide degradation, especially in the surface soil layer (Dechesne et al. 2014, Walder et al. 2022). However, it should be emphasized that the potential for pesticide biodegradation decreases markedly with increasing soil depth (e.g., Rodríguez-Cruz et al. 2006, Badawi et al. 2013a). This is related to a decrease in the abundance and heterogeneity of soil microbial communities, which reach their highest densities

in the near-surface layer characterized by a continuous supply of organic substrates (Rosenbom et al. 2014). It should also be noted that degradation efficiency strongly depends on the type of pesticide, the microbial communities present, and the spatial variability of both factors (Dechesne et al. 2014).

Additionally, many studies have focused on the relationship between pesticide migration and soil composition (e.g., Kodešová et al. 2011, Copaja & Sepúlveda 2022, McGinley et al. 2022). Studies have shown that soils with high clay content (>20%) and high organic-matter content can retard water movement and favor pesticide binding, while also supporting greater diversity and abundance of soil organisms that may influence pesticide degradation, transformation, persistence, and distribution in the soil profile (Pérez-Lucas et al. 2019, McGinley et al. 2022). A high risk of intensified pesticide migration has also been demonstrated for soils with high sand content (>45%) (McGinley et al. 2022). Such soil conditions occur in many parts of the world, including Poland (Ballabio et al. 2016). It should be emphasized, however, that Ukalska-Jaruga et al. (2020) found that only 6.5% of agricultural soils in Poland exceeded the permissible concentrations for organochlorine pesticides, and no exceedances were observed for non-chlorinated pesticides. Accordingly, the present study was conducted on experimental fields and focused on the occurrence and migration of pesticide residues in vertical soil profiles down to a depth of 120 cm.

The specific objectives of this study are: (1) to determine the presence of pesticide residues in soils at depths of 0–120 cm; (2) to assess the vertical and spatial distribution of pesticides as a function of their application on experimental fields, depth, and pH_{KCl}; and (3) to relate terrain morphology and lithology to pesticide migration.

MATERIALS AND METHODS

Research area

The study was conducted at the Field Experimental Station in Winna Góra of the Institute of Plant Protection – National Research Institute (PSD) in Poznań, Poland, which has been operating in its current form since 2005. The PSD manages fields with a total area of 97.51 ha, where preregistration, post-registration, and commercial studies of plant protection products are carried out. The station is equipped with technical facilities that enable the implementation of experimental research across the full scope of plant-protection studies and the acquisition of precise information on crops and the applied pesticides. In this study, three experimental fields were selected for investigation: EF17, EF49, and EF83 (Fig. 1).

From a physico-geographical perspective, Winna Góra is located within the Central European Lowland, in the Września Plain mesoregion (Solon et al. 2018). The morphology of this area was shaped by the activity of the Leszno Phase of the Vistulian glaciation (Gawroński 2001). The surface deposits within the PSD are dominated by glacial till. The groundwater level in this area ranges from 0.5 to 3.7 m (Nowak 2011).

The study area belongs to the temperate climate zone, within the agro-climatic district with the lowest precipitation in Poland (Tomczyk & Bednorz 2022). Precipitation during the study period, from May 2021 to May 2022, is shown in Figure 2. Before sampling, at the turn of February 2022, no precipitation was recorded, while in early May 2022, directly prior to sampling, the precipitation was low. The mean annual air temperature was 8°C, with July and August being the warmest months.

Soil sampling

The sampling was carried out twice: on 5 March 2022 and 8 May 2022. Sampling sites were selected to represent different crop types and, consequently, different pesticides applied, and also to be distributed across various parts of the experimental field, thereby reflecting topographic and lithological variability. To ensure representativeness, soil samples were collected from two boreholes (Drill 1 and Drill 2) at each of the three selected experimental fields. Sampling was conducted in March and May at EF17 and EF49, and in March only at EF83. At the time of sampling, the fields were designated for potato cultivation (EF17), spring barley (EF49), and rape (EF83), respectively. Samples were collected every 20 cm down to a depth of 120 cm within the soil profile and placed in tightly sealed zip-lock bags. For this purpose, an Edelman hand auger with a diameter of 20 cm (Edelman, Royal Eijkelkamp) was used. Each soil sample was also classified *in situ* using the roll test and macroscopic description to determine the approximate content of individual particle-size fractions.

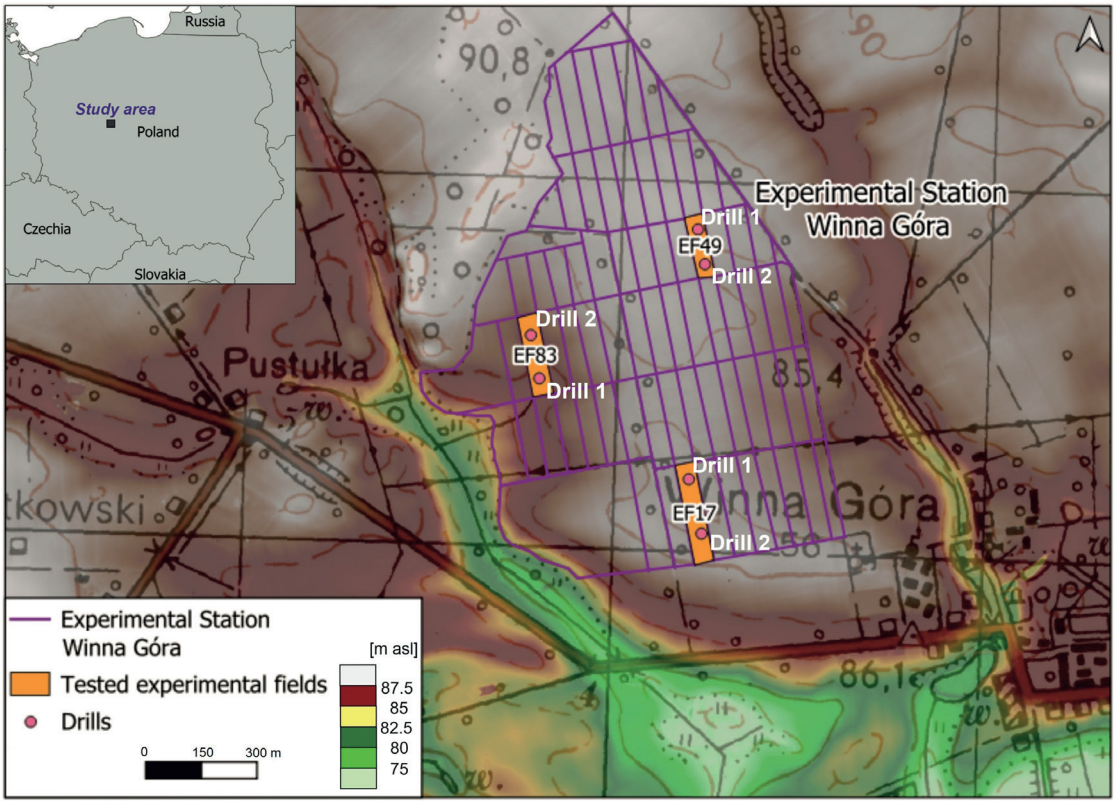

Fig. 1. *Location map of the experimental fields (EF17, EF49, and EF83) and drilling sites at the Field Experimental Station in Winna Góra of the Institute of Plant Protection – National Research Institute in Poznań*

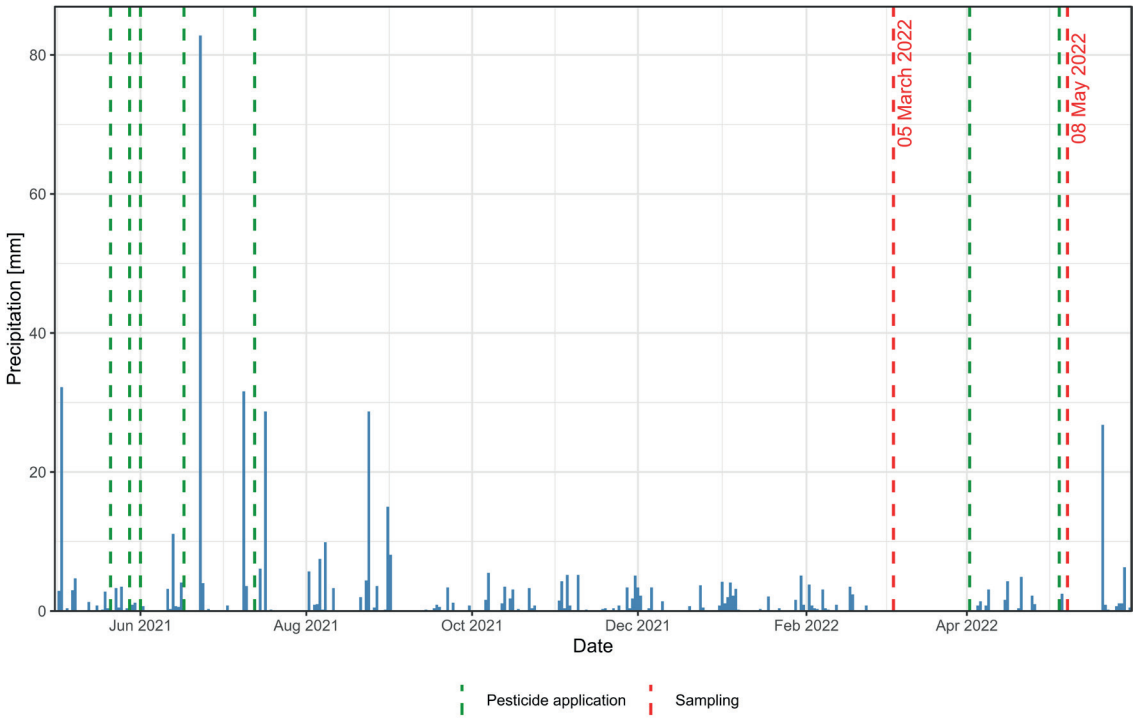

Fig. 2. *Daily precipitation totals in the experimental fields at Winna Góra during the study period (based on data from the Institute of Meteorology and Water Management, Nowa Wieś Podgórna station)*

Chemicals and reagents

Acetonitrile, methanol, and formic acid of high purity (for LC-MS) were obtained from Merck (Darmstadt, Germany). Acetone with LC-MS grade was purchased from Sigma Aldrich (Steinheim, Germany). Citrate extraction tubes containing 4 g magnesium sulfate, 1 g sodium chloride, 0.5 g dibasic sodium citrate sesquihydrate, and 1 g tribasic sodium citrate dihydrate were purchased from Merck (Darmstadt, Germany). Water for the samples was prepared from an Elix-3/Milli Q Academic 10 (Billerica, MA, USA) water purification system. EnviroClean extraction tubes containing 0.9 g magnesium sulfate, 0.3 g PSA, and 0.15 g ChloroFiltr were purchased from UCT (Bristol, PA, USA). Deionized water of resistivity 18.2 MΩ·cm was prepared with a Milli-Q Plus system from Merck Millipore (Burlington, Massachusetts, USA). Certified Reference Materials (CRM) of pesticides and internal standard (ISTD) isoproturon-D6 were obtained from Dr. Ehrenstorfer (Steinheim, Germany) and all CRMs were characterized by purity greater than 99%.

Analytical standards were prepared at concentrations of about 1,000 µg/mL in acetone, and then an intermediate stock standard mixture at the level of 10 µg/mL in acetone was prepared from the stock solutions. The combined working standards were prepared by serial dilution of the stock solutions with acetone. All stock and working standard solutions and ISTDs were stored in a freezer at approximately –20°C until the analyses.

Sample preparation procedure

The method of preparing dry soil for the analysis of pesticide residues using an ultra-performance liquid chromatograph coupled with a mass spectrometer is defined in the PN-EN 15662:2018-06 norm (Polski Komitet Normalizacyjny 2018). A 10 g homogenized and dried soil sample was weighed into a polypropylene centrifuge tube (50 mL), an internal standard at a concentration of 0.25 ng/mL, 10 mL of acetonitrile, and 5 mL of deionized water was added and the mixture was shaken for 5 min (490 rpm, horizontal shaker, IKA, Staufen, Germany). The buffer mixture (citrate extraction tube, Supel™ QuE, Merck, Darmstadt, Germany) was then added and shaken for another 5 min on an orbital shaker (Multi Reax, Heidolph, Schwabach, Germany). The sample was centrifuged (4,500 rpm, T = 15°C, Rotina 420R, Hettich, Kirchlengern, Germany) for 3.5 min. A 6 mL aliquot of the acetonitrile supernatant was transferred to a 15 mL polypropylene centrifuge tube (PSA tube, Supel™ QuE, Merck, Darmstadt, Germany) containing 0.9 g anhydrous magnesium sulfate and 0.15 g PSA. The contents were vortexed for 2 min and centrifuged for 3.5 min at 4,500 rpm. For the UPLC-MS/MS instrumental analysis, 2 mL of the supernatant were evaporated to dryness under nitrogen, reconstituted in 0.25 mL of acetonitrile and 0.25 mL of LC phase (0.5% formic acid and 0.1% 1M ammonium formate in water and 0.5% formic acid and 0.1% 1M ammonium formate in methanol, 95:5, v/v; all solvents LC-MS grade, Merck, Darmstadt, Germany). Finally, the extract was transferred through a 0.22 µm syringe filter membrane (Millex®, Merck, Darmstadt, Germany) into autosampler bottles.

UPLC-MS/MS conditions

The LC-MS/MS system consisting of an Eksigent expert ultraLC 100-XL (Eksigent Technologies, Dublin, CA, USA) coupled to a QTRAP 6500 triple quadrupole mass spectrometer (AB Sciex Instruments, Foster City, CA, USA) was used for the analysis of the pesticides. A 10 µL aliquot (cooled to 8°C ±1°C) was injected into a Kinetex core-shell C_{18} 100 Å (100 mm × 2.1 mm, 2.6 µm) column (Phenomenex, Torrance, CA, USA) at a 40°C column temperature. The gradient was composed of solvents A (0.1% formic acid and 5 mM ammonium formate in water) and B (0.1% formic acid and 5 mM ammonium formate in methanol) at a flow rate of 0.5 mL/min. The gradient elution was started with 95% A and 5% B and held for 1.0 min, then rose linearly to 10% A and 90% B in 35 min and held for 5.0 min. The composition of the mobile phase was returned to the starting condition over 0.1 min (flow rate was increased to 1.0 mL/min), followed by a column re-equilibration phase of 1.9 min. The total time of data acquisition was 45 min. The MS/MS 6500 QTRAP was operated in electrospray ionization positive (ESI+)

mode, at a capillary voltage of 4,500 V, desolvation temperature of 400°C, entrance potential (EP) of 10 V, with nitrogen as the curtain (CUR), nebulizer (GS1) and auxiliary (GS2) gas, at a pressure of 30, 60 and 50 psi, respectively. Nitrogen was also used as the collision gas. The ionization and MS/MS collision energy settings were optimized while continuously infusing the pesticide solution at a flow-rate of 100 µL/min via a syringe pump. For all pesticides, the parent and one or two daughter ions were selected, and the first one was used for quantification and the others for confirmation. Data acquisition was performed in the multiple reaction monitoring mode (MRM). The Analyst software version 1.6.2 and MultiQuant software version 3.0.2 (AB Sciex) were used for data acquisition and processing. In total, 23 substances were detected among the nearly 400 analyzed active substances; the list of detected substances is presented in the supplementary files in Table S1, while the quality parameters of the determinations are provided in Table S2 (both Tables S1 and S2 are available online as supplementary material to the article).

Determination of soil pH

For the samples in which pesticides were detected, as well as for the samples immediately underlying them, the pH was determined in 1 M KCl at a 1:5 soil-to-solution ratio (pH_{KCl}; Al-Busaidi et al. 2005, International Organization for Standardization 2021). Measurements were performed using a WTW Multi 350i multiparameter meter (Weilheim, Germany).

RESULTS

Vertical changes in pesticide residue concentrations

Pesticides were detected in all examined experimental fields in both sampling series. EF83 and EF17 were characterized by higher pesticide concentrations, whereas EF49 showed much lower concentrations. The highest total pesticide concentration was observed in EF17 Drill 1 in May 2022 (980.01 µg/kg) and in EF83 Drill 1 in March 2022 (962.36 µg/kg). The lowest pesticide concentrations were detected in EF49 Drill 1 (110.63 µg/kg) and Drill 2 (129.54 µg/kg) in May 2022.

Generally, the total pesticide concentrations were higher in March 2022 than in May 2022, except for EF17 Drill 1, where higher concentrations were recorded in May. In the case of EF49, the total pesticide concentration in May was approximately half that recorded in March. In EF17, the differences between the results were large and depended on the drilling location. In Drill 1, a lower total pesticide concentration was detected in March (504.78 µg/kg) than in May (980.01 µg/kg). In Drill 2, almost three times more pesticides were detected in March (702.01 µg/kg) than in May (249.64 µg/kg). In EF83, high concentrations were recorded in both Drill 1 and Drill 2 (962.36 µg/kg and 685.83 µg/kg, respectively).

In most of the examined sampling points, pesticides were detected in the first 40 cm of the profile (Fig. 3). At greater depths, pesticide residues appeared much less frequently. No pesticide residues were observed below a depth of 100 cm in any of the studied experimental fields. In EF49 (Fig. 3), both in March and May, pesticides were detected only in the 0–20 cm and 20–40 cm intervals. The total pesticide concentrations obtained in these samples were similar to each other. The highest value (193.86 µg/kg) was recorded in Drill 2 at a depth of 20–40 cm in March, while the lowest (11.23 µg/kg) was recorded in Drill 1 at a depth of 20–40 cm in May. The obtained total pesticide concentrations in this experimental field were lower compared to EF17 and EF83.

In EF17, pesticide residues were detected at depths ranging from 0 to 80 cm, depending on the time and location of drilling (Fig. 3). In March, in Drill 1, pesticide residues were detected at depths 0–20 cm and 20–40 cm at similar concentrations: 268.76 µg/kg and 236.02 µg/kg, respectively. In Drill 2, the concentrations at depths 0–20 cm and 20–40 cm were higher than in Drill 1, and amounted to 330.95 and 359.8 µg/kg, respectively. In Drill 2, pesticides were also detected at a concentration of 11.26 µg/kg at a depth of 60–80 cm. At the same depth, pesticides were found in this location at a concentration of 249.64 µg/kg in May. This was the only depth at which pesticides were detected at Drill 2 in May. At this time, in Drill 1, pesticides were observed at depths of 20–40 cm (789.95 µg/kg) and 40–60 cm (190.06 µg/kg). No tested substances were detected in the 0–20 cm layer.

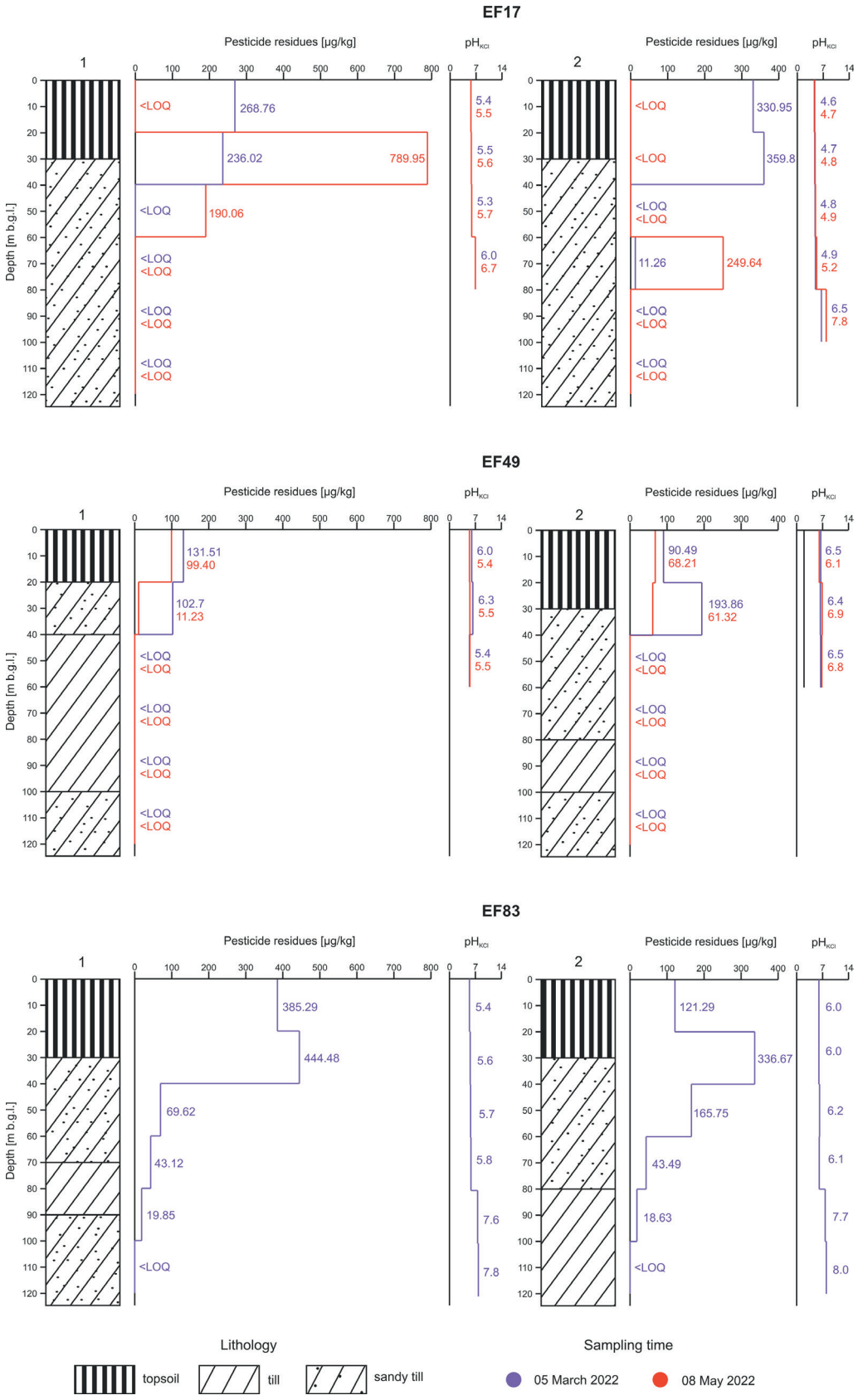

Fig. 3. *Drilling profiles, total pesticide residue concentrations and pH_{KCl} at individual depths on EF17 (potatoes), EF49 (spring barley) and EF83 (rape)*

The deepest pesticide residues were detected in EF83 (Fig. 3). In both drills, pesticides were detected at depths from 0 to 100 cm. In samples taken from a depth of 0–20 cm, the pesticide concentrations were 385.29 µg/kg (Drill 1) and 121.29 µg/kg (Drill 2). The total pesticide concentrations were highest at depths of 20–40 cm (444.48 µg/kg in Drill 1, and 336.67 µg/kg in Drill 2), and then decreased with depth, reaching concentrations close to 20 µg/kg at a depth of 80–100 cm.

pH_{KCl} did not show clear trends in relation to the total pesticide concentrations in the individual fields or on different sampling dates; however, it exhibited considerable variation between the experimental fields. Only in the lower parts of the profiles were marked increases in pH_{KCl} observed, where pesticides were absent or occurred at very low concentrations. At EF17 in Drill 1, pH_{KCl} ranged from 5.3 to 5.7 at depths of 0–60 cm, while at 60–80 cm it increased to 6.0 in March and 6.7 in May. In Drill 2, pH_{KCl} values ranged from 4.6 to 5.2 down to 80 cm, and below this depth the pH increased to 6.5 and 7.8 in March and May, respectively. At EF49, pH_{KCl} in Drill 1 ranged from 5.4 to 6.3, while in Drill 2 it ranged from 6.1 to 6.9. At EF83, relatively stable pH values were observed down to 80 cm, ranging from 5.4 to 5.8 in Drill 1 and from 6.0 to 6.2 in Drill 2. At depths of 80–100 cm and 100–120 cm, pH_{KCl} ranged between 7.6 and 8.0 in both drills.

Vertical distribution of individual pesticide residues

Among the 23 substances detected in the analyzed samples, fungicides dominated in terms of total concentration, accounting for 64%, followed by herbicides (32%), insecticides (2%), and metabolites (2%) (Fig. 4). The highest number of substances was detected in EF17 (13 substances), and the lowest in EF49 (8 substances) (Fig. 5, Table S1). The most frequently detected pesticides were boscalid (12 times), fluxapyroxad (detected 11 times), and fluopicolide (10 times). Six pesticides were observed only once (diflufenican, fenpropidin, metrafenone, nicosulfuron, phenmedipham and bixafen). A detailed list of the detected pesticides is presented in Table S1.

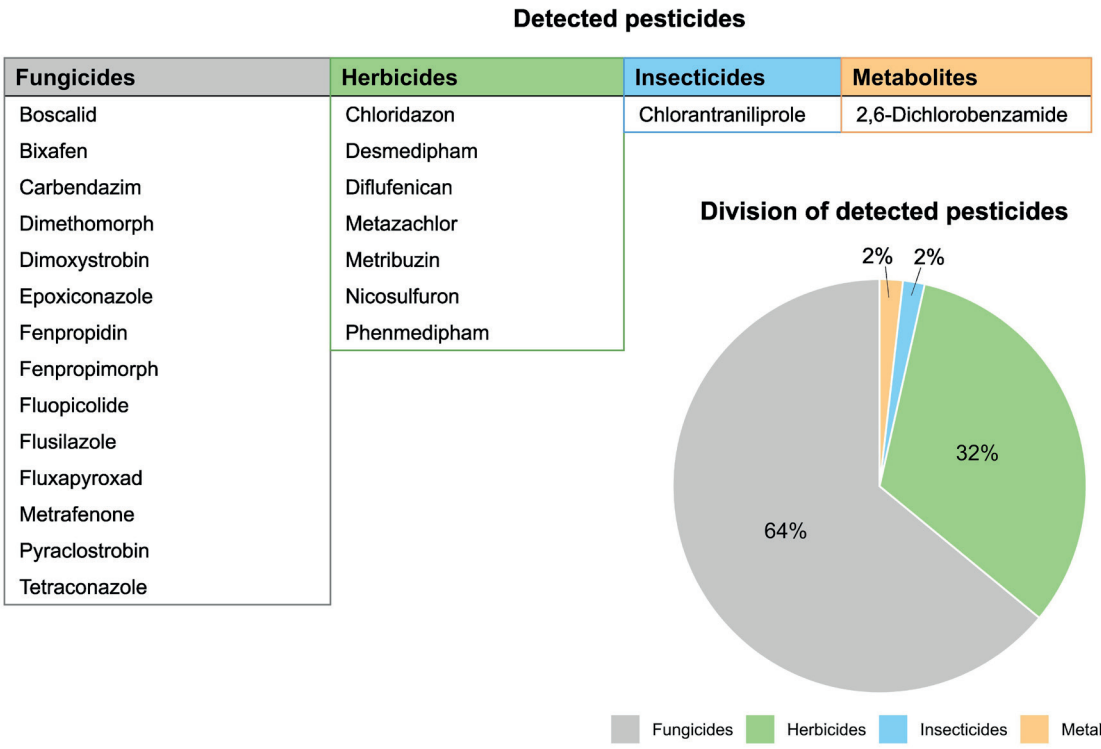

Fig. 4. Classification of detected pesticide residues according to biological function and their percentage share in total concentration

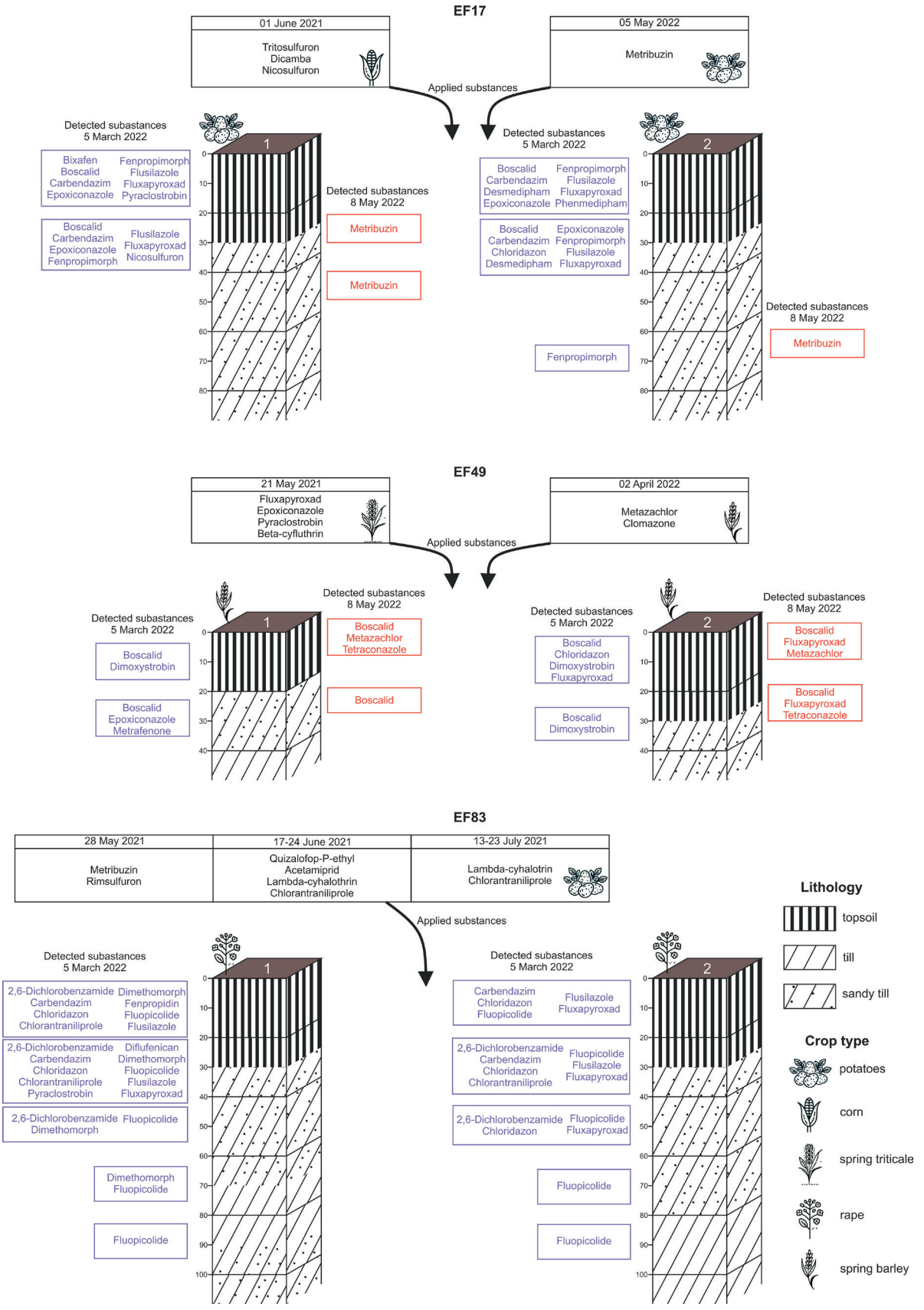

Fig. 5. *Summary of applied and detected pesticide residues in two sampling campaigns (March and May 2022) on the experimental fields in Winna Góra*

Most of the substances were present only in samples taken from shallow depths. The pesticides detected at greater depths, below 60 cm, included dimethomorph, fenpropimorph, fluopicolide and metribuzin. The highest concentration at this depth interval (60–80 cm) was recorded for metribuzin (249.64 μg/kg).

At EF17, in both drills in March, all samples from the depths of 0–20 cm and 20–40 cm contained boscalid, carbendazim, epoxiconazole, fenpropimorph, flusilazole, and fluxapyroxad. In addition, in Drill 1, pyraclostrobin and bixafen were detected at 0–20 cm, and nicosulfuron at 20–40 cm. In Drill 2, desmedipham was found at 0–20 cm and 20–40 cm, phenmedipham at 0–20 cm, and chloridazon at 20–40 cm (Fig. 5). At depths greater than 40 cm in March, only fenpropimorph was detected (60–80 cm in Drill 2), which was also present in the upper soil layers. Among the substances detected in March, only nicosulfuron had been applied during the treatment in June 2021 (Fig. 5). In May at EF17, only metribuzin was detected, which had been applied a few days before sampling (Fig. 5). Metribuzin was found at depths of 20–40 cm and 40–60 cm in Drill 1, and at 60–80 cm in Drill 2.

In EF49, boscalid was present in all samples in which any substances above the limit of quantification were detected. This pesticide occurred in both drills at depths of 0–40 cm; however, it was not applied to the field in the period from May 2021 to May 2022. Another pesticide that was detected in three samples in EF49 despite it not being applied was dimoxystrobin. In May 2021, EF49 was treated with epoxiconazole, among others, which was detected in one sample in March 2022 at a depth of 20–40 cm, and fluxapyroxad, which was detected in samples at a depth of 0–20 cm in March 2022, and 0–20 cm and 20–40 cm in May 2022. Metazachlor was applied to EF49 in April 2022 and was detected at a depth of 0–20 cm in Drill 1 and Drill 2 in May 2022. Pyraclostrobin and clomazone, even though they were applied to the field and were among the tested substances, were not detected in the tested samples.

At EF83 in March, Drill 1 contained 2,6-dichlorobenzamide, dimethomorph, and fluopicolide in all samples from 0 to 60 cm. However, no migration into the 40–60 cm layer was observed for carbendazim, chloridazon, chlorantraniliprole or flusilazole, which were detected at 0–20 cm and 20–40 cm. In addition, at 0–20 cm in Drill 1, fenpropidin was found, while at 20–40 cm, diflufenican, pyraclostrobin, and fluxapyroxad were detected (Fig. 5). In Drill 2, chloridazon, fluopicolide, and fluxapyroxad were present from 0 to 60 cm. Moreover, in Drill 2, carbendazim and flusilazole were detected at 0–20 cm and 20–40 cm, while 2,6-dichlorobenzamide was detected at 20–40 cm and 40–60 cm. Chlorantraniliprole occurred only at 20–40 cm in Drill 2. At depths greater than 60 cm (60–80 cm and 80–100 cm), fluopicolide was detected in both drills, which was also present in all upper samples. Additionally, at 60–80 cm in Drill 1, dimethomorph was found, which was also present in the shallower layers (Fig. 5). Among all pesticides detected at EF83, only chlorantraniliprole had been applied earlier, in June and July 2021.

DISCUSSION

Studies conducted by Zhang et al. (2009), Weaver et al. (2012), Artikov et al. (2018), Collin et al. (2022), Yao et al. (2022), Mosquera-Vivas et al. (2024), Šunjka et al. (2024), and Loose et al. (2025) demonstrated that the migration of pesticides below 40 cm is a globally observed phenomenon, although relatively rarely investigated due to the predominant focus on the topsoil. Research has traditionally concentrated on the topsoil because most pesticides undergo strong sorption to soil organic matter and mineral colloids and are intensively degraded in the microorganism-rich surface layer (Fenner et al. 2013, Bondareva & Fedorova 2021). The present study, conducted in the PSD, confirmed under controlled conditions the migration of pesticides to depths exceeding the topsoil horizon. This was primarily observed at EF17 and EF83. However, it should be emphasized that the concentrations detected below 40 cm were considerably lower than those in the upper soil layers (0–40 cm) (Fig. 3). The only exception was observed during the May sampling at EF17, where metribuzin was applied (Fig. 5). Relatively high concentrations of this herbicide were found

at depths of 20–60 cm in Drill 1 and 60–80 cm in Drill 2 (Table S1). This is consistent with the relatively high capacity of metribuzin to migrate downward through the soil profile (Kolupaeva et al. 2020). As a herbicide, it is characterized by high water solubility and generally low soil sorption, which together provide it with a strong potential for leaching through the soil profile (Singh 2006, López-Piñeiro et al. 2013). It should also be noted that despite its relatively rapid degradation in the soil environment, small residues of metribuzin may persist in soil for more than one year, potentially leading to its migration into groundwater (Conn et al. 1996, Kjær et al. 2005). Nevertheless, at EF83 no residues of metribuzin were detected in March 2022, despite its application in May 2021.

At depths greater than 40 cm in March, fenpropimorph was also detected in Drill 2 at EF17, as well as substances such as 2,6-dichlorobenzamide, fluopicolide, dimethomorph, chloridazon, and fluxapyroxad at EF83. In the case of EF83, these compounds were also detected in the upper part of the analyzed profile (Fig. 5). Among these substances, only 2,6-dichlorobenzamide is not used as a pesticide but rather represents a degradation product of fluopicolide (EFSA et al. 2019), and its presence in this case is likely directly linked to that. It should also be emphasized that none of the listed pesticides had been applied during the year preceding the study (Fig. 5). Among the compounds identified, only fluxapyroxad should reasonably be considered as a residue from applications prior to May 2021, due to its high persistence in soils (Wu et al. 2015). In the case of EF17, the occurrence of fenpropimorph at a depth of 60–80 cm appears to be incidental, as it was not detected in the second drill or during the May sampling, and was present only in low amounts, making it difficult to unequivocally determine its source.

In the case of EF83, the topography of the area appears to be an important factor responsible for the accumulation of numerous substances (Fig. 1). Previous studies have shown that pesticides can be transported by surface runoff and the associated soil erosion, either in dissolved form or adsorbed onto soil particles, leading to their redistribution between fields (Ulrich et al. 2013, Commelin et al. 2022). Consequently, the location of EF83 in the lowland part of the study area, along the natural path of surface flow toward the watercourse (Fig. 1), may facilitate the migration of pesticides from surrounding fields. The associated water supply may further enhance their downward movement within the soil profile, even for pesticides such as chloridazon, which is strongly sorbed onto soil particles (Cuevas et al. 2008), and dimethomorph, which is generally only sparingly soluble in water (Liang et al. 2011). The results obtained highlight that topography can be one of the key factors determining pesticide migration within the soil profile and, consequently, their potential to reach groundwater. It should be noted that pesticides for which no application was reported in the previous year were detected across all the investigated fields.

The greatest consistency between the applied and detected pesticides was observed at EF49, which was characterized by a relatively small number of detected compounds and limited migration within the soil profile, up to a maximum depth of 40 cm. This may be related to the relatively flat topography of the site and its comparatively elevated location (Fig. 1), which likely restricted the inflow and migration of pesticides from adjacent fields. Nevertheless, boscalid was detected in all samples, despite not having been applied in the preceding year. Due to its considerable persistence (Karlsson et al. 2016), it may have been applied before the study period. In addition, pesticides such as epoxiconazole, metazachlor, and fluxapyroxad, which were applied during the study period, were also detected in the samples (Fig. 5).

The results of the present study also indicate that, alongside terrain topography, an important factor determining the downward migration of pesticides in the soil profile is the lithology of the area. This is particularly noticeable in EF49, where generally lower sand fraction contents were found in the till compared to the other two fields. In general, as shown by McGinley et al. (2022), it is assumed that a higher sand fraction content and lower clay fraction content promote increased pesticide migration. However, it should be emphasized that the significance of granulometric

composition for the migration of a specific pesticide varies depending on its properties (Kodešová et al. 2011). Among the studied pesticides, the sand fraction content may significantly influence the migration of, for example, metribuzin and phenmedipham (McGinley et al. 2022). It should also be emphasized that a key factor responsible for pesticide migration deep into the soil profile is the occurrence of preferential water flow (Blackwell 2000, Zhang et al. 2018). This mechanism involves the rapid transport of water and dissolved substances through preferential pathways, such as cracks, root channels, or earthworm burrows (so-called biopores), bypassing the surrounding soil matrix (Zhang et al. 2018, Holbak et al. 2022). As a result, this process can cause infiltration to considerable depths, even of strongly sorbing pesticides that would normally be retained in the upper soil layers (Traub-Eberhard et al. 1994, Zhang et al. 2018). However, it should be emphasized that studies have shown enhanced activity of soil microorganisms along preferential water-flow pathways, which may substantially reduce the amount of pesticides ultimately reaching groundwater (e.g., Mallawatantri et al. 1996, Badawi et al. 2013b). At the same time, pesticide biodegradation in deeper soil layers is often characterized by a lag phase, which may allow pesticides to migrate to greater depths before degradation becomes effective (Dechesne et al. 2014). This is probably related to the time required for soil microbial populations capable of degrading pesticides to reach sufficient abundance (Rosenbom et al. 2014).

The soil pH_{KCl} analyses did not allow for a clear association between acidic/alkaline pH and the detected pesticide concentrations, despite the fact that pH, along with clay fraction content and organic matter, is one of the most important soil parameters influencing pesticide mobility (Silva et al. 2019, Bondareva & Fedorova 2021). It should be emphasized, however, that specific relationships vary among different groups of pesticides depending on their ionization capacity (acidic pesticides, basic pesticides, non-ionic pesticides) (Rasool et al. 2022). Noteworthy among the analyzed soils are the acidic to slightly acidic pH_{KCl} conditions in Drill 2 at EF17, where the presence of metribuzin was confirmed. As early as Ladlie et al. (1976), it was observed that metribuzin under acidic conditions is characterized by greater persistence but reduced mobility, which, however, did not outweigh its generally high capacity for migration in the studied conditions (Kolupaeva et al. 2020). The migration potential of most pesticides detected below 40 cm at EF83, such as dimethomorph (EFSA 2006), fluopicolide (Lewis et al. 2016), and fluxapyroxad (Lewis et al. 2016), is not significantly influenced by pH.

The examined proportions of pesticide groups (Fig. 4), which, according to their total concentrations, can be arranged in descending order as fungicides > herbicides > insecticides, may be determined by local conditions and the characteristics of the applied substances (e.g., Hvězdová et al. 2018, Silva et al. 2019, Kruć-Fijałkowska et al. 2022, Knuth et al. 2024). Nevertheless, the detection of only one insecticide, chlorantraniliprole, in March at EF83, which had been applied in June and July 2021, is noteworthy. However, cross-sectional studies conducted across Europe indicate that insecticides and their metabolites are commonly detected in agriculturally used soils (Silva et al. 2019, Knuth et al. 2024).

Overall, the present study is among the relatively few investigations that combine a broad pesticide-residue screening with vertical profiling down to 100 cm. This depth range is directly relevant to assessing the potential risk of shallow groundwater contamination, as pesticide residues may migrate from agricultural soils toward groundwater through the soil–groundwater system (Guzzella et al. 1996, Li et al. 2025). Nevertheless, one aspect that requires further detailed investigation is the relationship between pesticide migration into deeper parts of sediment profiles and precipitation intensity. A significant relationship between pesticide migration, rainfall events, and soil moisture was indicated by Loose et al. (2025). However, that study focused on 25 selected pesticides; therefore, broader future research is needed to examine precipitation-driven deep pesticide migration toward groundwater under controlled conditions, such as those provided by the PSD. Future studies should also consider the role of soil microorganisms, which may be of key importance when pesticide transport toward

groundwater occurs via preferential water-flow pathways (Mallawatantri et al. 1996, Badawi et al. 2013b, Dechesne et al. 2014).

CONCLUSION

The conducted study indicates that pesticide migration into deeper parts of soil profiles may occur even in deposits such as till and sandy till. Pesticide residues were detected down to a depth of 100 cm, whereas no analyzed substances were found in the 100–120 cm interval. These results highlight the possibility of pesticide migration into deeper soil-profile layers and, consequently, their potential contribution to shallow groundwater contamination. Among the analyzed pesticides, fungicides and herbicides accounted for the highest proportions, representing 64% and 32% of the total concentrations, respectively. The only detected metabolite was 2,6-dichlorobenzamide, whose presence was linked to fluopicolide. The substances detected below 40 cm included dimethomorph, chloridazon, fenpropimorph, fluopicolide, fluxapyroxad, metribuzin, and 2,6-dichlorobenzamide, indicating that these compounds should be given particular attention in future studies on pesticide migration in soil profiles.

Moreover, the study highlights the importance of topography and lithology as factors controlling the spatial distribution and downward migration of pesticides. Pesticide residues that had not been applied in the year preceding the study were detected in all the examined fields, which may indicate the mobility of these substances between individual fields or their origin from earlier applications. No direct relationship was observed between pH_{KCl} and pesticide migration within the soil profile. The obtained results indicate the need for further development of monitoring studies on pesticide residue migration into deeper zones of the geological environment (>40 cm), particularly in the context of groundwater and soil protection.

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Table S1. *Pesticide residues concentrations [µg/kg] in soils on experimental fields in Winna Góra*

Table S2. *List of tested active substances along with quality parameters*