



# Pesticide residues in European agricultural soils – A hidden reality unfolded

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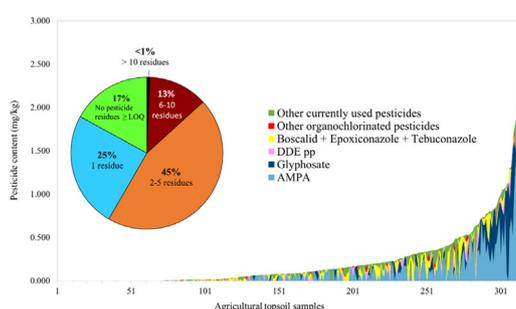
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## HIGHLIGHTS

- 76 residues of pesticides were analyzed in 317 EU agricultural topsoils.
- 83% of the soils contained 1 or more residues, 58% contained mixtures.
- 166 different mixtures were identified.
- Predicted concentrations of individual residues were occasionally exceeded.
- The combined effects of residue mixtures need to be assessed.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Pesticide use is a major foundation of the agricultural intensification observed over the last few decades. As a result, soil contamination by pesticide residues has become an issue of increasing concern due to some pesticides' high soil persistence and toxicity to non-target species. In this study, the distribution of 76 pesticide residues was evaluated in 317 agricultural topsoil samples from across the European Union. The soils were collected in 2015 and originated from 11 EU Member States and 6 main cropping systems. Over 80% of the tested soils contained pesticide residues (25% of samples had 1 residue, 58% of samples had mixtures of two or more residues), in a total of 166 different pesticide combinations. Glyphosate and its metabolite AMPA, DDTs (DDT and its metabolites) and the broad-spectrum fungicides boscalid, epoxiconazole and tebuconazole were the compounds most frequently found in soil samples and the compounds found at the highest concentrations. These compounds occasionally exceeded their predicted environmental concentrations in soil but were below the respective toxic endpoints for standard in-soil organisms. Maximum individual pesticide content assessed in a soil sample was  $2.05 \text{ mg kg}^{-1}$  while maximum total pesticide content was  $2.87 \text{ mg kg}^{-1}$ . This study reveals that the presence of mixtures of pesticide residues in soils are the rule rather than the exception, indicating that environmental risk assessment procedures should be adapted accordingly to minimize related risks to soil life and beyond. This information can be used to implement monitoring programs for pesticide residues in soil and to trigger toxicity assessments of mixtures of pesticide residues on a wider range of soil species in order to perform more comprehensive and accurate risk assessments.

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## 1. Introduction

Pesticides have strongly contributed to the increased food production observed over the last few decades. Since 1960, world average

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yields of rice, wheat and maize more than doubled as pesticide use increased by 15 to 20 fold, and as fertilizer use, irrigated land and cultivated land increased by 7, 2 and 1 fold, respectively (Oerke, 2006). Globally, around 3 million tons of pesticides are applied annually, corresponding to a market value of USD 40 billion (Pimentel, 2009). In the European Union (EU), there are almost 500 active substances approved for use in pesticides (EC, 2018), with annual sales of 374,000 tons of pesticides [average data 2011–2016 for the EU-28; (EUROSTAT, 2018)].

Despite the benefits of pesticides on crop yields and of their relevance for the economy, intensive and widespread pesticide use raises serious environmental and health concerns. Diffuse pollution by agrochemicals has become a major soil threat (Stolte et al., 2016), and as such, it may affect several of the United Nations Sustainable Development Goals linked with the soil environment (Keesstra et al., 2016; Pérez and Eugenio, 2018). Soil contamination raises concerns on soil functions, soil biodiversity and food safety but also on the off-site transport of contaminants via wind and water driven erosion. Such off-site transport may impair sink ecosystems functioning and represent additional exposure routes to soil contaminants for humans and other non-target organisms (FAO and ITPS, 2017; Pérez and Eugenio, 2018).

Despite the several implications of soil contamination, the monitoring of pesticide residues in soil is not required at the EU level, in contrast to the water monitoring regulated by the EU Water Framework Directive. Moreover, large scale international studies on soil contamination by pesticide residues are scarce and often limited to one single pesticide, or to only a few compounds (Covaci et al., 2002; Ruzicková et al., 2008; Silva et al., 2018). Several studies have already characterized the distribution of currently used and of no-longer approved pesticides in soil at the national or regional level (e.g., Orton et al., 2013; Masia et al., 2015; Pose-Juan et al., 2015; Qu et al., 2016; Chiaia-Hernandez et al., 2017; Hvezdova et al., 2018), but the different sampling periods, different sampling strategies, different analytical methods and different analyte lists among these studies prevent a comprehensive overview of the distribution of pesticides residues in EU soils.

Reference or maximum levels in soils for no-longer approved and highly persistent and obsolete pesticides, such as DDTs, HCHs, atrazine and dieldrin, are included into the legislation of some European countries (Carlon, 2007). However, although a couple of these countries' regulations include admissible levels for unspecified "other pesticides" (Carlon, 2007), thresholds for approved, currently used pesticides do not exist. Concentrations/content of approved pesticides in soil are often interpreted based on their predicted environmental concentrations (PEC). Such PEC values are calculated based on worst case conditions and are used in the review process of individual active substances. PECs are calculated for the main crops to which the substance is applied, considering recommended application rates (highest dose per application, highest number of applications and the lowest applications interval), a default soil bulk density ( $1.5 \text{ g cm}^{-3}$ ) and tillage depth (5 cm for permanent crops and 20 cm for annual crops), typical interception fractions by plants, and the longest degradation rates of the substance in soil from laboratory or field studies (Ockleford et al., 2017). In the conclusion report of each approved active substance, different PECs are presented: the initial PECs of the active substance and of its major metabolites (immediately after pesticide application), the short and long term PECs (1–4 and 7–100 days after application, respectively), and, if the substance or metabolite has a 90% degradation time above 365 days, the background or plateau concentrations (after multi-year applications) and the PEC accumulated (sum of PEC initial and plateau concentrations)

Current pesticide risk assessment relies on the comparison of toxicity exposure ratios (TERs) and trigger values. TERs are calculated for single residues by dividing ecotoxicologically relevant concentrations for indicator organisms by the residue's highest PEC (PEC initial or PEC accumulated). The ecotoxicologically relevant concentration is the  $LC_{50}$  (concentration resulting in the mortality of 50% of the exposed individuals) or the NOEC (highest No Observed Effect Concentration), in the

case of acute/short-term toxicity or chronic/reproductive toxicity assessments, respectively. The in-soil indicator organisms are the earthworms *Eisenia fetida* and *E. andrei*, the springtails *Folsomia candida* and *F. fimetaria*, the mite *Hypoaspis aculeifer* and nitrogen transformation microorganisms (Ockleford et al., 2017). TERs lower than 10 or 5, the trigger values for, respectively, acute and chronic exposures of earthworms and other soil macroorganisms (EC, 2011), indicate an unacceptable risk for such organisms. The risk for soil microorganisms is not based on TERs but on the percentage of effect compared to a control; an effect above 25% after 100 days of exposure represents an unacceptable risk (Ockleford et al., 2017). Despite the clear importance of PEC values on the risk assessment procedure, the validation of PECs in soil with field data from pesticide monitoring programs is still missing.

As a first approach to address these data gaps, we analyzed 76 prioritized pesticide residues (of current use and of no-longer approved pesticides) in 317 agricultural topsoils, originated from 11 EU countries and 6 cropping systems. Different geographical regions were expected to represent different pesticide application patterns (from different incidence of pests, non-chemical pest management costs and pesticide products applied) as well as different environmental and edaphic conditions (factors with great impact on pesticide persistence in soils). Different crops were expected to represent different susceptibilities to pests and, therefore, different pesticide application patterns too. Data on frequency of occurrence and concentrations of pesticide residues in soil could provide valuable information on the geographical areas or crops of higher concern as well as on the usefulness of existing PECs. The adequacy of current pesticide risk assessment for in-soil organisms is also discussed.

## 2. Materials and methods

### 2.1. Soil samples

The presence and the concentration of multiple pesticide residues were analyzed in 317 topsoil samples; 300 agricultural topsoil samples were selected from the pool of topsoils collected during the Land Use/Cover Area Frame Survey (LUCAS) 2015 survey [see Toth et al., 2013 and Orgiazzi et al., 2018 for more information on LUCAS surveys] and 17 topsoil samples from Portuguese vineyards, where we were studying the transport of pesticide residues by surface runoff (Silva et al. in prep).

The LUCAS topsoil samples originated from 10 European Union (EU) Member States and 6 main crop classes. The selected Member States/countries have the highest agricultural area and pesticide use in arable land and permanent croplands of the Northern (United Kingdom and Denmark), Southern (Italy, Greece, Spain), Eastern (Hungary and Poland) and Western EU regions [The Netherlands, France and Germany; (FAO, 2013, 2014)]. In each of these countries, the crops with the highest pesticide use per hectare or the highest cultivated area were selected (Muthmann, 2007). The selected soil samples included soils used in the production of (i) cereals, (ii) permanent crops, (iii) root crops, (iv) non-permanent industrial crops, (v) dry pulses, flowers and fodder crops and (vi) vegetables. Some extra samples from bare soils previously used as croplands (EUROSTAT, 2009, 2012) were selected and categorized as class (vii) others. The main crop classes (i–vi) were defined according the classification adopted in the LUCAS 2015 survey (E4 LUCAS (ESTAT), 2015a). The land cover types included in each crop class is presented in Table S1. We then selected soil samples from different NUTS 2 regions [EU territorial units of regional level; see EUROSTAT, 2015 for information on the Nomenclature of Territorial Units for Statistics (NUTS) classification system] and with different soil properties [data retrieved for each sampling point from the LUCAS survey 2009 topsoil dataset; (ESDAC, 2009; Panagos et al., 2012)].

The number of topsoil samples used in this study are listed by EU region, country, NUTS 2 region and main crop class in Table S2. The number of topsoil samples collected in Portugal was lower than it was in the

other countries (17 versus 30 samples per country) and all samples belonged to the same crop class (permanent crops) and NUTS 2 region (PT16). Portuguese data were integrated into the Southern EU results.

Each LUCAS topsoil sample was a mixture of five subsamples (0–15/20 cm): four subsamples collected at 2 m north, south, east and west of a central LUCAS subsampling point. For crops planted in rows, the subsamples were collected along a linear transept in a inter row strip (between two crop rows), with a 2 m distance between each of two subsamples (E4 LUCAS (ESTAT), 2015b). The Portuguese samples were collected following these LUCAS sampling procedures. The 317 topsoil samples were collected between April and October of 2015, air dried at ambient temperature for at least one week until the final soil moisture content was below 6% (w/w). The dried samples were sieved with 2-mm sieve and frozen at  $-20^{\circ}\text{C}$  until chemical determinations could be carried out.

## 2.2. Selection of the pesticide residues

An initial list of the pesticide residues of interest was obtained based on the active substances most often applied to the selected crops (Muthmann, 2007) and on the findings of previous studies concerning the distribution of pesticide residues in EU agricultural soils (Covaci et al., 2002; Ružicková et al., 2008; Orton et al., 2013; Masia et al., 2015; Pose-Juan et al., 2015; Qu et al., 2016). Additionally, considering their high soil persistence, the pesticides banned by the Stockholm Convention were also included in the list. Finally, the major metabolites of the selected active substances (of both currently used pesticides and of banned pesticides) were added to the list too.

Due to logistical and financial limitations, some compounds on this initial list were not analyzed. To start, inorganic compounds, plant growth regulators and botanical agents were excluded from this study. Then, priority was given to compounds that could be analyzed by a multi-residue method, excluding compounds such as mancozeb, fosetyl, metiram or thiram. Nevertheless, considering the high use and relevance of glyphosate-based herbicides, we used a single residue method for the determination of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA). Finally, some compounds were excluded due to analytical limitations, namely by poor recoveries (<70%).

The final list consisted of 76 pesticide residues (34 insecticides, 27 fungicides and 15 herbicide residues; Table S3), from now on called analytes, which were analyzed in each of the 317 topsoil samples. A subset of the analysis, namely the glyphosate and AMPA results, has been recently published in Silva et al. (2018). Nevertheless, as glyphosate and AMPA significantly contribute to the total pesticide load in soils, we considered these compounds in the current study as well.

## 2.3. Chemicals and reagents

The reference standards of glyphosate (98%) and AMPA (98%) and the isotope labeled internal standards of glyphosate (1, 2- $^{13}\text{C}$   $^{15}\text{N}$ ;  $100\ \mu\text{g mL}^{-1}$ , 1.1 mL) and AMPA ( $^{13}\text{C}$ ,  $^{15}\text{N}$ ;  $100\ \mu\text{g mL}^{-1}$ , 1.1 mL) were obtained from Dr. Ehrenstorfer (Germany). The reference standards of the other analytes were purchased from Dr. Ehrenstorfer (Germany) or Riedel-de Haen (Germany).  $^{13}\text{C}_3$ -labeled caffeine and PCB-198 were purchased from Sigma-Aldrich (USA) and from Dr. Ehrenstorfer (Germany), respectively. C18 (40  $\mu\text{m}$ , Prep LC) was purchased from J.T. Baker (The Netherlands). Sodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ; 99.5% ACS reagent) and ammonium acetate ( $\text{NH}_4\text{Ac}$ ; ~98%) were obtained from Sigma-Aldrich (USA), and potassium hydroxide (KOH; 85%) and magnesium sulfate ( $\text{MgSO}_4$ ;  $\geq 99.8\%$ ) were purchased from Sigma-Aldrich (France) and Sigma-Aldrich (Japan), respectively. Ammonium formate ( $\text{HCO}_2\text{NH}_4$ ; 99%) and 9-fluorenylmethoxycarbonyl chloride (FMOC-Cl;  $\geq 99.0\%$ ) were purchased from Sigma-Aldrich (Switzerland). Hydrochloric acid (HCl; 37%), formic acid ( $\text{CH}_2\text{O}_2$ ; 98–100%) and ammonia solution ( $\text{NH}_3$ ; 25%) were purchased from Merck (Germany). Acetic acid

( $\text{CH}_3\text{COOH}$ ;  $\geq 99.8\%$ ) was obtained from Biosolve BV (The Netherlands) and sodium acetate ( $\text{CH}_3\text{COONa}$ ; 99%) from Alfa Aesar GmbH & Co KG (Germany). Acetonitrile ( $\text{C}_2\text{H}_3\text{N}$ ; 99.95% LC grade) and methanol (MeOH; 99.98%) were purchased from Actu-All Chemicals (The Netherlands). Primary secondary amine sorbent (PSA) was purchased from Agilent Technologies Netherlands B.V. (The Netherlands).

## 2.4. Chemical determinations

The topsoil samples were thawed the day before the extraction of pesticide residues was carried out. The samples were then stirred with a spoon until visually homogenous samples were obtained. Four aliquots were taken from each sample: two aliquots of 5 g (air-dry weight) for the multi-residue method and two aliquots of 2 g (air-dry weight) for the determination of glyphosate and AMPA.

For the determination of multi-residues, the QuEChERS approach was adapted for soil samples, using a methodology similar to the one described by Anastassiades et al. (2003) and Mol et al. (2008). Briefly, each 5 g soil aliquot was spiked with  $50\ \mu\text{L}$  of  $^{13}\text{C}_3$ -caffeine  $10\ \mu\text{g mL}^{-1}$  [used as surrogate standard to check the overall procedure in the liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis, not used for quantification] and mixed with 5 mL Millipore water and 10 mL of acetonitrile containing 1% acetic acid (ACN 1% HAc; extraction solvent) within a 50 mL greiner tube. The tube with this mixture was agitated (end-over-end) for 60 min, after which, 1 g of sodium acetate and 4 g of magnesium sulfate were added to the tube. The tube was then vortexed and centrifuged (5 min, 3500 rpm) and the supernatant was collected: part to be analyzed using LC-MS/MS, with electrospray ionization (ESI) in positive mode, and part to be analyzed using gas chromatography-high-resolution mass spectrometry (GC-HRMS). For the LC-MS/MS analysis,  $125\ \mu\text{L}$  of the supernatant,  $125\ \mu\text{L}$  of ACN 1% HAc and  $250\ \mu\text{L}$  of Millipore water were added directly into a LC filter vial to be analyzed. For the GC-HRMS analysis, there was an extra clean-up step:  $1500\ \mu\text{L}$  of the supernatant were transferred into an Eppendorf tube containing 38 mg of primary secondary amine (PSA), 38 mg of C18 and 250 mg of magnesium sulfate. Then,  $38\ \mu\text{L}$  of PCB-198  $1\ \mu\text{g mL}^{-1}$  (used as injection standard in the GC-HRMS analysis) was added to the Eppendorf. The Eppendorf was then centrifuged (15 min, 13,000 rpm) and  $200\ \mu\text{L}$  of the cleaned supernatant was transferred into an amber glass vial to be analyzed.

Glyphosate and AMPA analysis were conducted following the procedure described by Bento et al. (2016) and Yang et al. (2015). In short, each 2 g dry weight aliquot was mixed with 10 mL of potassium hydroxide 0.6 M (extraction solvent) within a 50 mL greiner tube. The tube was agitated (end-over-end) for 60 min and centrifuged (30 min, 3500 rpm). Then, 1 mL of the supernatant was transferred into a 10 mL centrifuge tube to which was also added  $80\ \mu\text{L}$  of hydrochloric acid 6 M (obtaining a pH of approximately 9),  $40\ \mu\text{L}$  of a mix solution of glyphosate and AMPA isotopically labelled internal standards  $5\ \mu\text{g mL}^{-1}$ , 0.5 mL of borate buffer 5% and 0.5 mL of 9-fluorenylmethoxycarbonyl chloride 6.5 mM (FMOC-Cl; derivatisation agent). The tube was briefly vortexed (10–15 s) and then allowed to react for 30 min. After this time, the reaction was stopped by adding  $50\ \mu\text{L}$  of formic acid 98–100% to the tube. The tube was briefly vortexed again and 0.5 mL of the derivatized extract was transferred into a LC filter vial to be analyzed through LC-MS/MS with ESI in negative mode.

## 2.5. Quality control

The chemical determinations and the quality control of the analytical results were performed according to the guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed (EC, 2015). Briefly, 3 sets of multi-pesticide calibration standards were prepared for LC-MS/MS-based multi-method, GC-HRMS-based multi-method and glyphosate/AMPA analysis, respectively. Each set of calibration standards was prepared from a mix solution that combined the reference standards of all

compounds that were going to be analyzed by the respective analytical method. The calibration standards for LC-MS/MS analysis were prepared in solvent (multi-method: ACN 1% HAc + Millipore water; glyphosate/AMPA: Millipore water) while the calibration standards for GC-HRMS analysis were matrix-matched. In the LC-MS/MS analysis, a calibration curve of calibration standards (multi-method: 1.25, 3.125, 6.25, 12.5 and 50 ng mL<sup>-1</sup>; glyphosate/AMPA: 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 µg mL<sup>-1</sup>) was injected at the start, middle and end of each sample sequence. For GC-HRMS analysis, as the sample sequences were shorter, a calibration curve (2.5, 10, 25, 50 and 100 ng mL<sup>-1</sup>) was injected only at the start and at the end of each sequence. The calibration curves presented satisfactory linearity of response versus concentration, with correlation coefficients above 0.99 and residuals of response lower than ±20%.

Each sample sequence included also 3 to 6 fortified blank soils (i.e., agricultural soils from a previous study that were tested during the method development and that did not contain any of the tested residues) and 3 to 6 fortified soil samples (a 5th aliquot was randomly taken from 3 to 6 EU agricultural topsoil samples). These soils were spiked with the mix solutions of the reference standards and analyzed as the EU agricultural topsoil samples. For the LC-MS/MS-based multi-method the spiking levels were 0.01 and 0.05 mg kg<sup>-1</sup>, for the GC-HRMS-based multi-method, 0.005 and 0.05 mg kg<sup>-1</sup>, and for glyphosate and AMPA determinations, 0.05 and 0.25 mg kg<sup>-1</sup>. The recoveries obtained in the fortified soils were between 70 and 120%.

The lowest calibration level included in analyses was used as the reporting limit, i.e. the threshold for reporting results. Such reporting limits were equal to the limits of quantification (LOQ) of the compounds. To facilitate further comparisons on the occurrence of pesticide residues in soil, there was a single LOQ for all the compounds analyzed by the same method. A LOQ of 0.01 mg kg<sup>-1</sup> was achieved for the pesticide residues measured by the LC-MS/MS-based multi-method while for the compounds measured by GC-HRMS this LOQ was of 0.005 mg kg<sup>-1</sup>, and for glyphosate and AMPA this was 0.05 mg kg<sup>-1</sup>. The list of compounds analyzed by LC-MS/MS-based multi-method and by GC-HRMS is presented in Table S4 and Table S5, respectively. The LC-MS/MS and GC-HRMS apparatus and conditions are described in Tables S6 and S7, respectively.

Each of the 76 analytes were identified according to (i) the retention time and peak shape of the respective reference standard (or of the isotopically labelled internal standard, in the case of glyphosate and AMPA) and (ii) the ion ratio, with ratios between the quantification and confirmation transitions within ±30% of the average ion ratio of the calibration standards. The response of the GC-HRMS analytes was normalized according to the response of PCB-198, and the glyphosate and AMPA response was normalized according to the response of the isotopically labeled analogues. The concentration of the analytes was calculated based on bracketing calibration, with a matrix-matched calibration standard (LC-MS/MS-based multi-method 3.125 ng mL<sup>-1</sup>; GC-HRMS-based multi-method 10 ng mL<sup>-1</sup>) or with a solvent standard containing the labels for glyphosate and AMPA (0.1 µg mL<sup>-1</sup>) analyzed every 10–15 injections/samples.

As each compound was analyzed in duplicate (two soil aliquots for the multi-residue method and two aliquots for glyphosate and AMPA determinations), the mean content of both aliquots was considered to be the content in the sample. The content in each of the two aliquots was within ±35% the mean content of both aliquots. In the few cases (<2% all positive results) where the compound content was equal or above the LOQ in just one of the aliquots, this ≥LOQ value was assumed as the content of the sample (conservative approach). This was only because both the values < LOQ and the values ≥ LOQ were very close to the LOQ value.

## 2.6. Data analysis

Only pesticide residue content equal to or above the respective LOQs was considered in data analysis (data entries where the analyte content was below the LOQ were left empty). Due to the analytical method chosen, and as the results for phthalimide may not originate only from

folpet (Lach and Bruns, 2016), only qualitative results are provided for this compound and no concentrations in soil are given. As a result, phthalimide was considered in the number of residues present in soil but it was not considered in the total pesticide content.

Due to privacy issues, the number of pesticide residues in soil and the total pesticide content in soil (i.e. sum of the content of the individual pesticide residues ≥ LOQ per soil sample) could not be given for the individual sampling points, instead this information is presented at the EU region, country, NUTS 2 region and cropping system level. Normal distribution and homogeneity of variances of the number of residues and of the total pesticide content in soil were tested using the Shapiro-Wilk and Levine's tests, respectively. As parametric assumptions were not satisfied, even after log<sub>10</sub>, log<sub>10</sub>(x + 1), ln, square root or exponential data transformation, non-parametric Kruskal-Wallis tests were used to compare the number of residues in soil and the total pesticide content in soil among different EU regions, countries and cropping systems. In the presence of significant effects (p < 0.05), Bonferroni-corrected Mann-Whitney tests were performed to test differences between each two EU regions, countries or crop systems. Statistical analyses were not performed at the NUTS 2 level due to the very reduced number of samples in some NUTS 2 regions (Table S2).

Principal Component Analysis (PCA) and Spearman's rank correlations were used to explore possible relationships between the content of pesticides in soil and the pesticide and soil properties. The pesticide properties, obtained from the Pesticide Properties Database (PPDB, 2017) or from the PAN Pesticide Database (PAN Pesticide Database, 2017), included: half-life time in soil (DT<sub>50</sub>, days; indicator of soil persistency), solubility in water at 20 °C (Sw, mg L<sup>-1</sup>), octanol-water partition coefficient (Log P, at pH 7 and 20 °C; indicator of bioaccumulation potential), vapor pressure at 25 °C (Vp, mPa; indicator of volatility), GUS index (indicator of leaching potential), and organic carbon-water partition coefficient (Koc, mL g<sup>-1</sup>; indicator of soil adsorption and mobility). The basic soil properties (pH, organic carbon content, % silt and % clay) were extracted from the 317 individual sampling points, from the LUCAS survey 2009 topsoil dataset (ESDAC, 2009). The statistical analyses, the PCAs and the Spearman's correlations analysis were performed using SPSS 22.0.

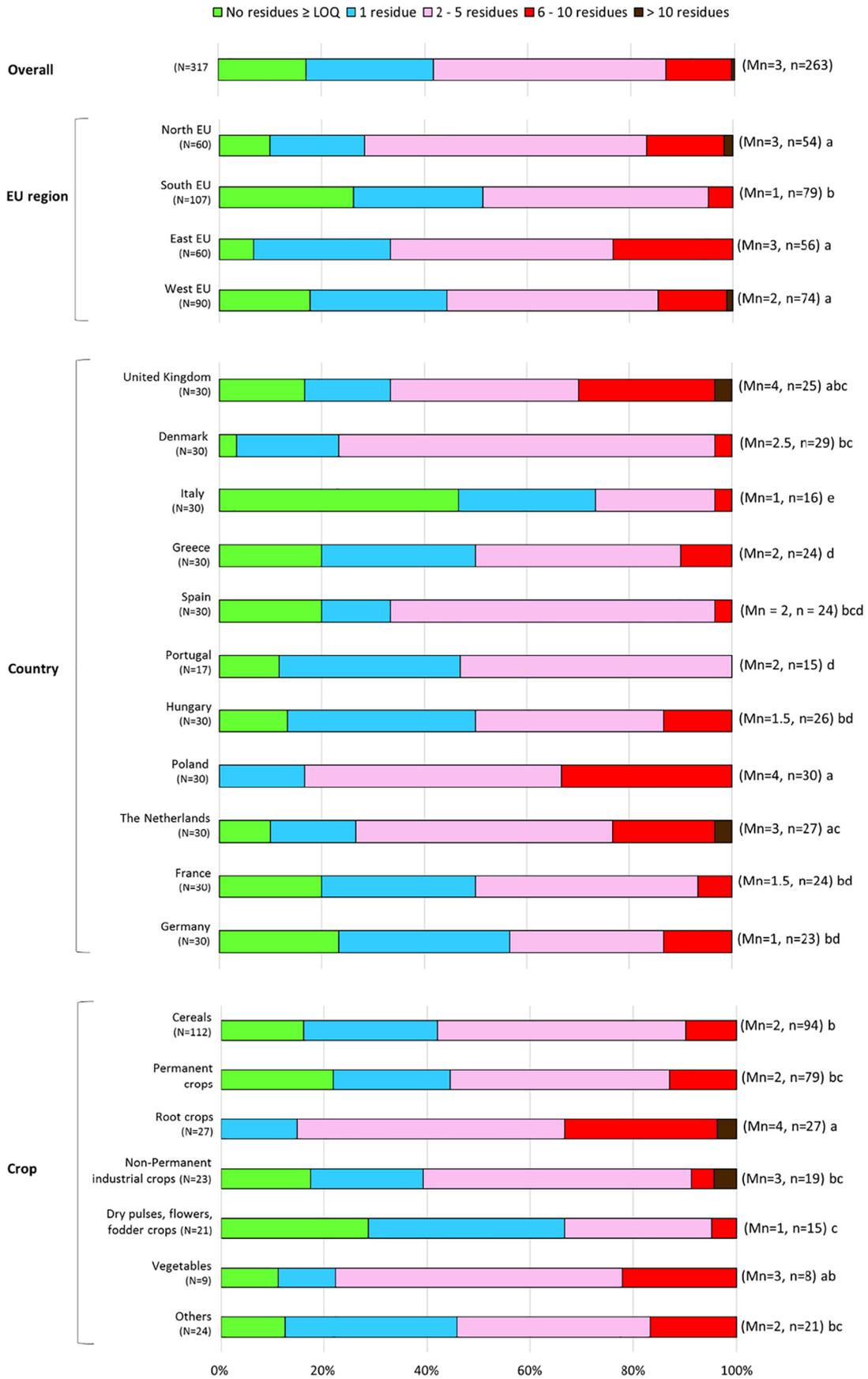
In the figures, to simplify comparisons, the number of pesticide residues in soil and the total pesticide content in soil were aggregated by classes: "0, 1, 2–5, 6–10, >10 residues" and "No residues ≥ LOQ, ≥LOQ–0.05, ≥0.05–0.15, ≥0.15–0.5, ≥0.5–1, ≥1 mg kg<sup>-1</sup>", respectively. The class thresholds of 0.05, 0.15, 0.5 and 1 mg kg<sup>-1</sup> correspond, respectively, to the 22<sup>nd</sup>, 50<sup>th</sup>, 81<sup>st</sup> and 93<sup>rd</sup> content percentile of the samples containing quantifiable pesticide residues (nq; nq is the number of samples containing pesticide residues minus the number of samples with just phthalimide). The NUTS 2 maps using these classes were produced in ArcGIS 10.4.

The measured content of the most common pesticide residues in soil (i.e. present in >10% tested soils) was compared with their predicted environmental concentrations in soil (PECs from the EFSA conclusion reports of these substances), or in the case of the banned DDTs, with national soil screening values. Additionally, the maximum measured content of each of these residues were used to calculate a second set of TER values for in-soil organisms, where TER = (LC<sub>50</sub> or NOEC)/maximum measured content. The NOECs and LC<sub>50</sub> values for in-soil organisms were also obtained from the EFSA conclusion reports. As the content of DDE pp. and DDTs (sum of DDT and its metabolites) in soil were very similar, and considering the higher availability of DDTs screening values than of DDE pp screening values, only DDTs levels were explored. The screening values of DDTs in European countries are compiled in Carlon (2007).

## 3. Results

### 3.1. Number of pesticide residues in soil

Overall, only in 17% of the tested agricultural topsoils no pesticide residues were detected [i.e. glyphosate and AMPA content < 0.05 mg kg<sup>-1</sup>, the content of the 46 compounds measured by the LC-



**Fig. 1.** Distribution of the frequency of topsoil (0–15/20 cm) samples with no quantified pesticide residues, 1 pesticide residue and multiple pesticide residues by EU region, country and cropping system. N-number of tested samples; Mn-median number of residues in the soils containing pesticide residues; n-number of soils containing pesticide residues. The lowercase letters in the right panel denote significant differences in the number of pesticide residues in soil among EU regions, countries and crops (Bonferroni-corrected Mann-Whitney tests; a > b > c > d > e).

MS/MS-based multi-method (Table S4)  $<0.01 \text{ mg kg}^{-1}$  and the content of the 28 compounds analyzed by GC-HRMS (Table S5)  $<0.005 \text{ mg kg}^{-1}$ . In 25% of the topsoils, a single pesticide residue was quantified while 58% of the topsoils had multiple residues present. Results indicate a predominance of mixtures of a few residues in soil (2–5) relative to mixtures of moderate (6–10) or large numbers of residues ( $>10$ ; Fig. 1).

The number of pesticide residues varied significantly within the EU region ( $p < 0.01$ ), country ( $p < 0.01$ ), and cropping system ( $p < 0.01$ ; Fig. 1). The Southern regions of the EU had the highest frequency of soils with no pesticides (26%), and significantly less residues in soil than the Northern, Eastern and Western EU regions. Eastern parts of the EU had the highest frequency of soils with pesticide residues (93%) and the highest frequency of samples with  $\geq 6$  residues in soil (23%).

The number of different pesticide residues in soil was significantly lower in Italy than in the other EU Member States (but note that the number of samples by crop varied among countries, Table S2), with 53% of the soils containing pesticide residues. In the remaining countries, at least 75% of the soils had pesticide residues, with a maximum of 100% in Poland. Portuguese soil samples contained the least complex mixtures, being the only country where all of the samples had  $<6$  compounds (Fig. 1).

None of the soil samples collected from the NUTS 2 regions UKC2, UKH1, DE12, DE13, DE26, ITF1, ITH2, ITI4, EL63 and HU23 contained pesticide residues (Fig. 2; note that, except for UKH1, these NUTS 2 regions are represented by a single soil sample only). Conversely, the tested soils from the UKF1, UKJ1, UKM5, DE91, DEB1, ITH1, PL21, PL52

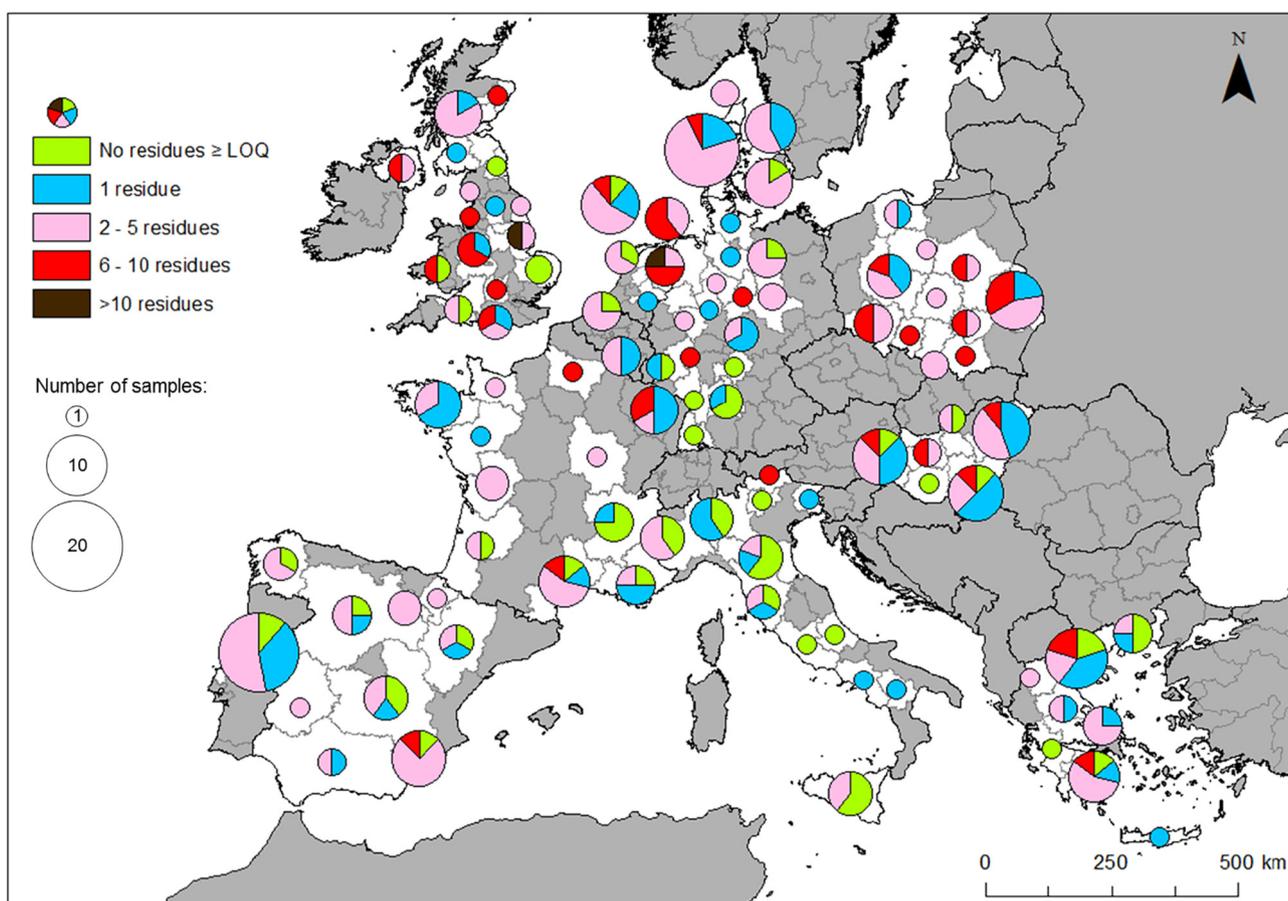
and FR22 regions contained mixtures of at least 6 residues (Fig. 2; just one soil sample was analyzed from each of these NUTS 2 regions).

Soils from root crops had significantly more pesticide residues than the soils from other crops: 100% of the tested soils from root crops contained pesticide residues and 85% of the samples had multiple residues. On the other hand, soils from dry pulses, flowers and fodder crops, with the highest frequency of soils with none (29%) and with a single pesticide residue (38%), had significantly fewer residues than the soils from the other crops (Fig. 1).

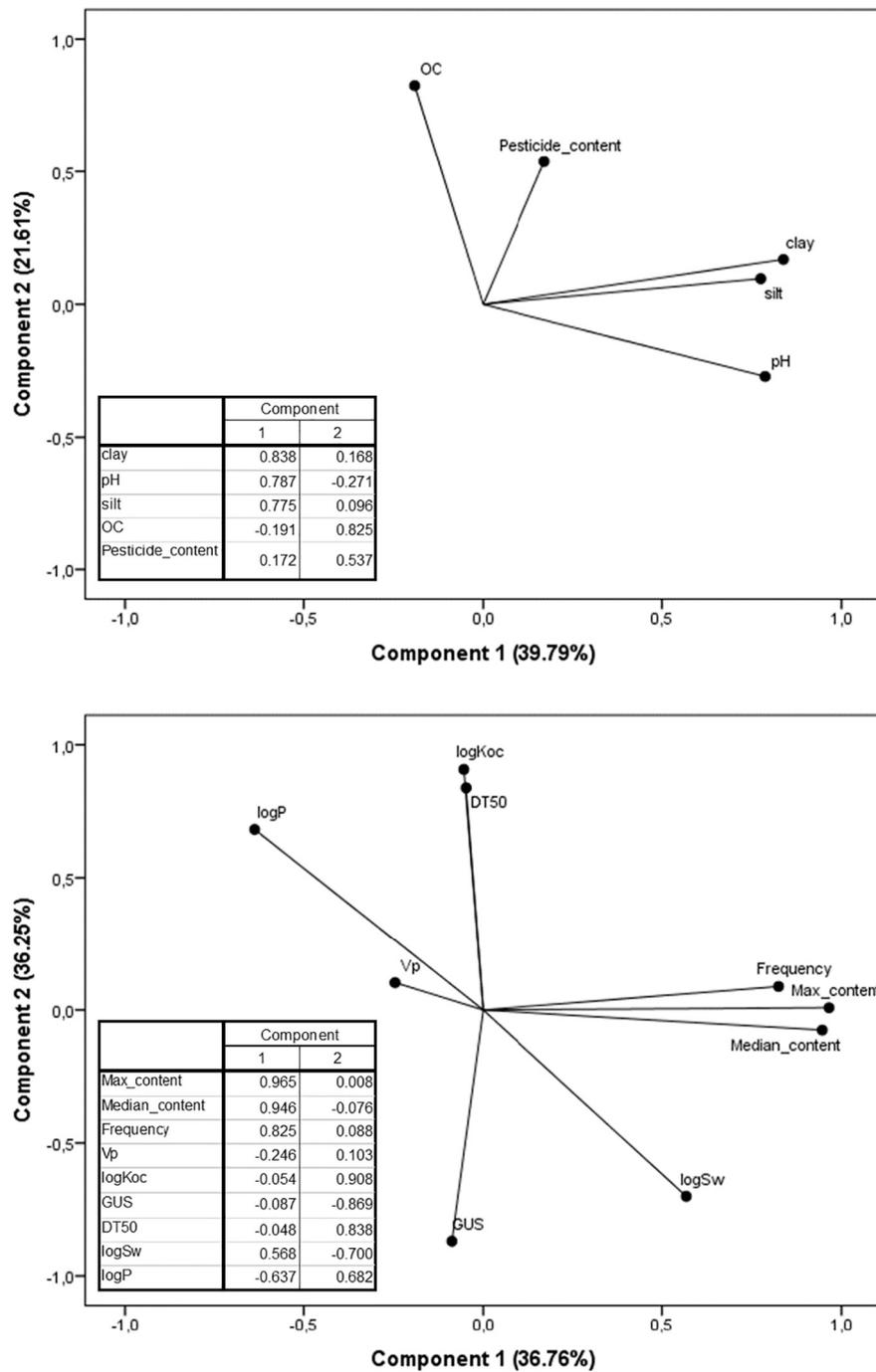
### 3.2. Type of pesticide residues in soil

Overall, 43 different residues (approximately 57% of the tested analytes) were present in the tested soils (Table S8). European soils revealed a high diversity of pesticide combinations; a total of 166 pesticide combinations were observed in soils; 150 corresponded to mixtures of  $\geq 2$  residues (Table S9). The most common mixtures in soil were glyphosate (GLY) + AMPA and GLY + AMPA + phthalimide (PTI), both present in 2% of the samples (Table S9). GLY and AMPA were often combined with other pesticide residues; such mixtures corresponded to 25% of pesticide combinations in soil and to 18% of the samples. Mixtures of GLY + AMPA + PTI and other residues were way less common, corresponding to 6% of pesticide combinations and to 3% of the samples (Table S9).

Pesticide composition in soil varied among EU region, country and cropping system. In North and East EU, the most common mixtures in soil included an organochlorinated compound (mostly DDE pp) and AMPA or PTI while in South and West EU, they included combinations



**Fig. 2.** Number of pesticide residues in EU agricultural topsoils (0–15/20 cm) at the NUTS 2 level. The pie-charts represents the proportion of soil samples with 0, 1 and multiple pesticide residues (2–5, 6–10,  $>10$ ) in each NUTS 2 region. The size of the pie-charts represents the sampling effort by NUTS 2 regions, with bigger circles corresponding to a higher number of soil samples. The exact number of topsoil samples tested in each NUTS 2 region is provided in Table S2. NUTS 2 designations were not included in the map to improve readability, but they are provided in Fig. S1. The white and grey areas in the map represent sampled and not-sampled NUTS2 regions, respectively. Note that some white areas are completely covered by the respective pie-charts, but they can be easily identified in Fig. S1.



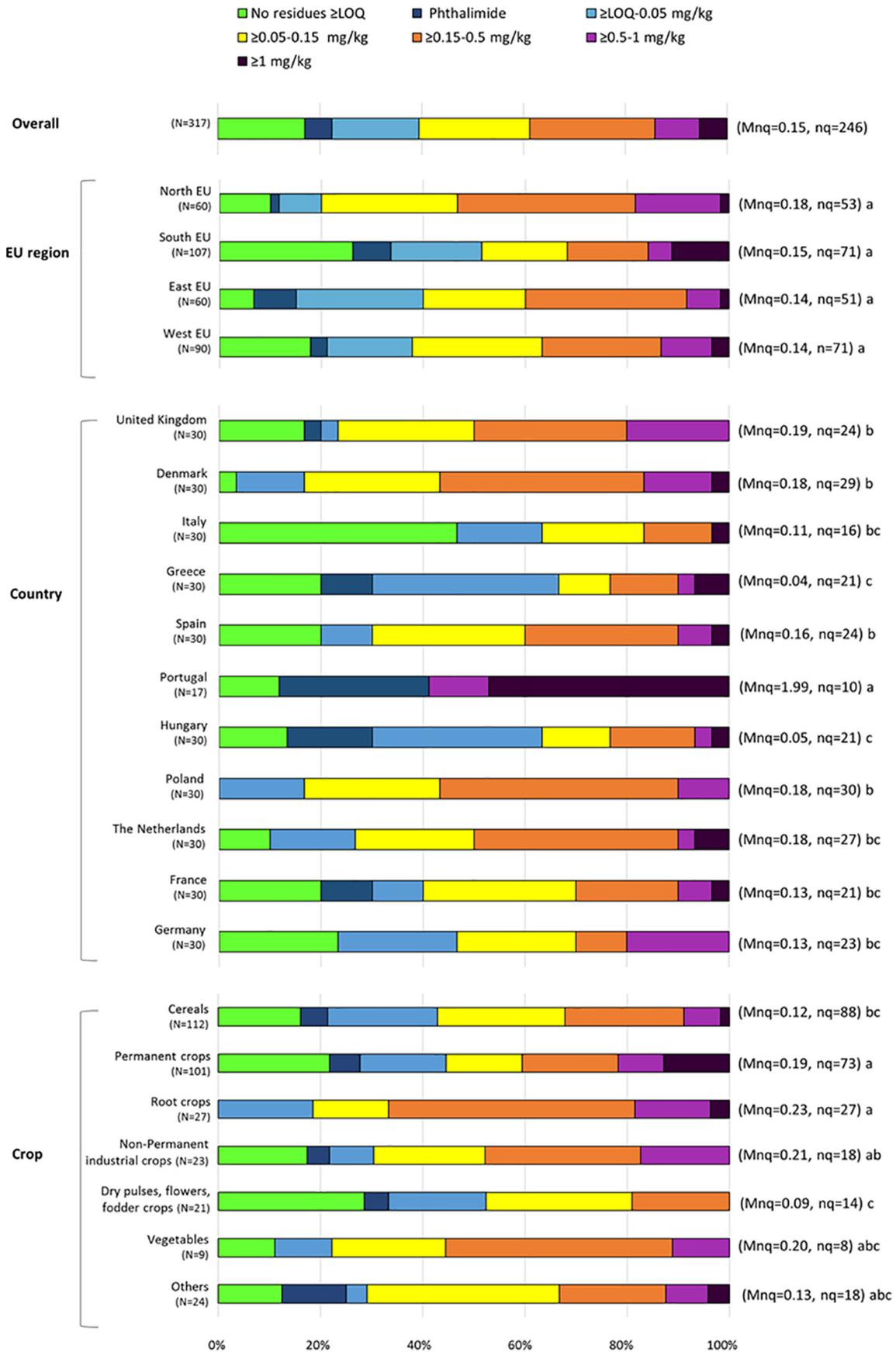
**Fig. 3.** Principal component analysis (PCA) of the frequency of detection and of the pesticide content in soil, and soil and pesticide properties. In (A), the total pesticide content is represented along basic soil properties (number of soils containing quantifiable pesticide residues,  $N_q = 246$ ). In (B), the frequency and the median and maximum contents of the different pesticide residues quantified in soil are related to their pesticide properties (number of pesticides = 42). OC-organic carbon content ( $\text{g kg}^{-1}$ ); DT<sub>50</sub>-soil half-life time; Koc-organic carbon-water partition coefficient ( $\text{mL g}^{-1}$ ); LogP-octanol-water partition coefficient at pH 7 and 20 °C; Sw-solubility in water at 20 °C ( $\text{mg L}^{-1}$ ); Vp-vapor pressure at 25 °C (mPa); GUS leaching potential index.

of AMPA, GLY, PTI and folpet (FOL; Table S10). Country results were in line with respective EU region results (Table S11). In cereals, the most common mixture was DDE pp + PTI, in permanent crops AMPA + GLY and AMPA + GLY + PTI, and in the remaining classes, each pesticide mixture appeared just once (Table S12).

The majority (60%) of the pesticide residues present in the EU soils were non-persistent ( $\text{DT}_{50} < 30$  days) or moderately persistent compounds ( $\text{DT}_{50}$ : 30–100 days). Persistent ( $\text{DT}_{50}$ : 100–365 days) and very persistent compounds ( $\text{DT}_{50} > 365$  days) represented 16 and 23%

of the residues found, respectively. Fourteen of the compounds present in soils were active substances, or metabolites of active substances, no longer approved in the EU markets at the time of sampling (e.g. DDTs, dieldrin or procymidone).

Only 7 compounds were quantified in >10% of the soil samples (Table S8): glyphosate, AMPA, DDE pp. (metabolite of the long since banned DDT), boscalid, epoxiconazole, tebuconazole (all broad-spectrum fungicides) and phthalimide [PTI; metabolite of the broad-spectrum fungicide folpet and a potential artefact; (Lach and Bruns,



**Fig. 4.** Distribution of total pesticide content in the topsoil samples from different EU regions, countries and cropping systems, by content classes. The pesticide content classes thresholds of 0.05, 0.15, 0.5 and 1 mg kg<sup>-1</sup> correspond, respectively, to the 22<sup>nd</sup>, 50<sup>th</sup>, 81<sup>st</sup> and 93<sup>rd</sup> content percentile of the samples containing quantifiable pesticide residues (nq = 246). N-number of tested samples; Mnq-median pesticide content in the soils containing quantifiable pesticide residues; nq-number of soils containing quantifiable pesticide residues. The lowercase letters in the right panel denote significant differences in pesticide content among EU regions, countries and crops (Bonferroni-corrected Mann-Whitney tests; a > b > c).

2016]). AMPA was the most frequent compound in soils, present in 42% of the samples (Table S8).

### 3.3. Content of total pesticide residues in soil

The soils containing quantifiable pesticide residues (246 out of 317) had a median and a maximum total pesticide content of 0.15 and 2.87 mg kg<sup>-1</sup>, respectively (Table S8). Fig. 3A indicates that soil properties influence pesticide content in soil, with organic carbon content showing a strong positive correlation with total pesticide content.

No significant differences were found in the total pesticide content among EU regions ( $p = 0.51$ ), but pesticide content varied significantly among EU countries ( $p < 0.01$ ) and cropping systems ( $p = 0.04$ ; Fig. 4). Despite having the highest frequency of pesticide-free soils, and significantly less pesticide residues in soil than the other EU regions, the Southern EU region had the highest frequency of soils with pesticide contents  $\geq 1$  mg kg<sup>-1</sup> (11% versus the 3% of West EU, and the 2% of North and East EU; Fig. 4). The Portuguese soil samples presented the highest pesticide content by far, mostly attributed to glyphosate and AMPA content, with a median and a maximum total pesticide content of 1.99 and 2.87 mg kg<sup>-1</sup>, respectively. Soils from Greece and Hungary had the lowest pesticide content, with median values of 0.04 and 0.05 mg kg<sup>-1</sup> and with maximum values of 1.06 and 1.32 mg kg<sup>-1</sup>, respectively. Pesticide content was  $\geq 0.05$  mg kg<sup>-1</sup> in all the topsoil samples collected from the following NUTS 2 regions: UKF1, UKM5, DE91, DE92, DEA5, DEB1, FR22, FR26 and ITH1 (Fig. 5; but note that just one soil sample was analyzed in each of these regions). Soils from permanent crops had the highest frequency of soils with pesticides content  $\geq 1$  mg kg<sup>-1</sup> (13%) and the highest pesticide content (2.87 mg kg<sup>-1</sup>). Nevertheless, the highest median pesticide content was observed in soils with root crops (0.23 mg kg<sup>-1</sup>; permanent crops had a median content of 0.19 mg kg<sup>-1</sup>). Soil samples from dry pulses, flowers and fodder crops had the lowest median and the lowest maximum pesticide content, 0.09 and 0.36 mg kg<sup>-1</sup>, respectively (Fig. 4).

### 3.4. Contribution of individual pesticide residues

The most common compounds in soils (present in >10% of soil samples), AMPA, boscalid, epoxiconazole, DDE pp., glyphosate and tebuconazole, also had the highest content in soil (Table S8). The levels of these pesticides in soil were weakly correlated with both soil and pesticide properties (Table S13 and Fig. 3B, respectively).

Glyphosate and AMPA contributed the most to the total pesticide content in soils (Fig. 6), with a maximum content of 2.05 and 1.92 mg kg<sup>-1</sup>, respectively (Table S8). Boscalid levels in soil were 3 to 5 times lower than those of glyphosate and AMPA, with a median and a maximum content of 0.04 and 0.41 mg kg<sup>-1</sup>, respectively. DDE pp., epoxiconazole and tebuconazole had a median content of 0.02 mg kg<sup>-1</sup>, with maximum values ranging from 0.16 to 0.31 mg kg<sup>-1</sup>. The content of some less common compounds such as prothioconazole, azoxystrobin, linuron, difenoconazole, cymoxanil, chlorpyrifos and penconazole were comparable to those of DDE pp., epoxiconazole and tebuconazole (Table S8).

The measured content of the most common compounds in soil was often within or below their respective PEC range (i.e. initial PEC, long term PEC and the accumulated PEC). Nevertheless, occasionally the measured content of glyphosate, epoxiconazole and of tebuconazole exceeded the respective PECs accumulated (Fig. S2, Table S12). Measured levels of glyphosate and epoxiconazole exceeded predicted levels for cereals (GLY: 0.34 and 0.60 > 0.03 mg kg<sup>-1</sup>; EPI: 0.16 > 0.13 mg kg<sup>-1</sup>), while for tebuconazole it occurred in samples from vineyards (0.19 > 0.12 mg kg<sup>-1</sup>) and from oilseed rape (0.18 > 0.14 mg kg<sup>-1</sup>). For both epoxiconazole and tebuconazole, our maximum measured values exceeded the PEC values used in the TERs calculations for in-soil organisms. Nevertheless, as the maximum measured content of these residues were very close to their highest PEC, the

TERs from the approval reports and the TERs calculated based on maximum measured levels are very similar (Table S15).

In line with PEC results, measured DDTs' contents occasionally exceeded the respective country-screening values (Fig. S3), namely the Italian limit for residential/public use (0.015 and 0.016 > 0.01 mg kg<sup>-1</sup>), the Dutch target value (0.07, 0.05 and 0.04 > 0.01 mg kg<sup>-1</sup>) and the permissible concentration for Polish agricultural topsoils (0.12, 0.06, 0.06, 0.05, 0.04, 0.04 and 0.03 > 0.025 mg kg<sup>-1</sup>).

## 4. Discussion

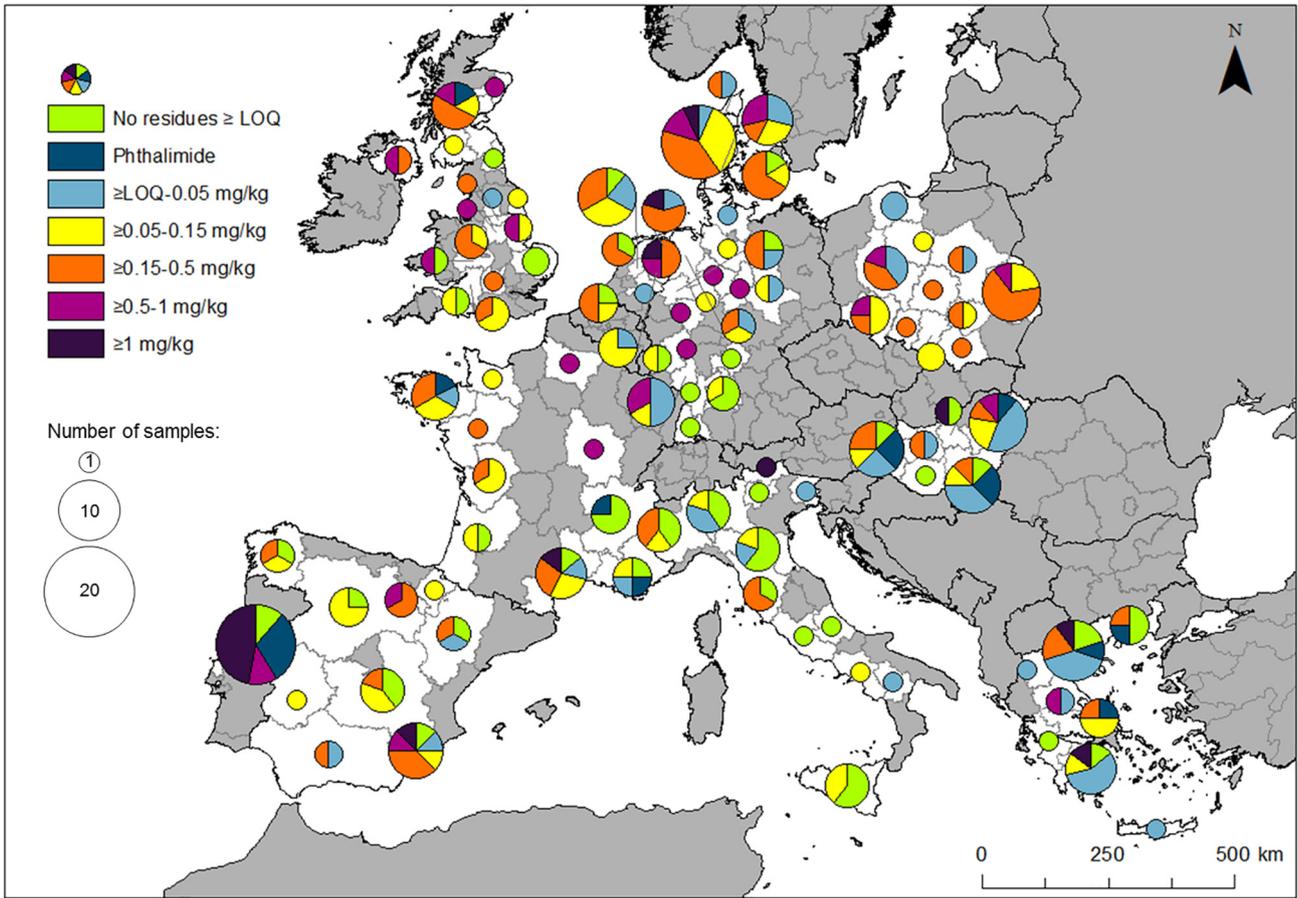
### 4.1. Pesticide residues in EU agricultural soils

The soils from the Southern EU regions presented the lowest number of pesticide residues and the highest pesticide content. The available data on pesticide use in arable land and on permanent crops in EU countries indicate that southern countries apply more pesticides than countries from other EU regions (FAO, 2014). Nevertheless, these data correspond to pesticide use from 2005 to 2009, and use patterns may have altered since then. Pesticide sales data from 2014 to 2015 [the year of the soils sampling and the year before that; (EUROSTAT, 2018)] indicate that Spain, Italy and France had some of the highest pesticide use in Europe, but that might be a result of their larger agricultural area (FAO, 2014) and not of higher application rates in agricultural sites per se. As information of pesticide application is not available for the soil sampling points, and as other factors might have affected the pesticide results by country/region (e.g. different number of soil samples selected per crop system, different climate and soil conditions), no clear conclusions can be drawn between the diversity of products and pesticide use in the different EU regions and the occurrence and measured content of pesticide residues in soil.

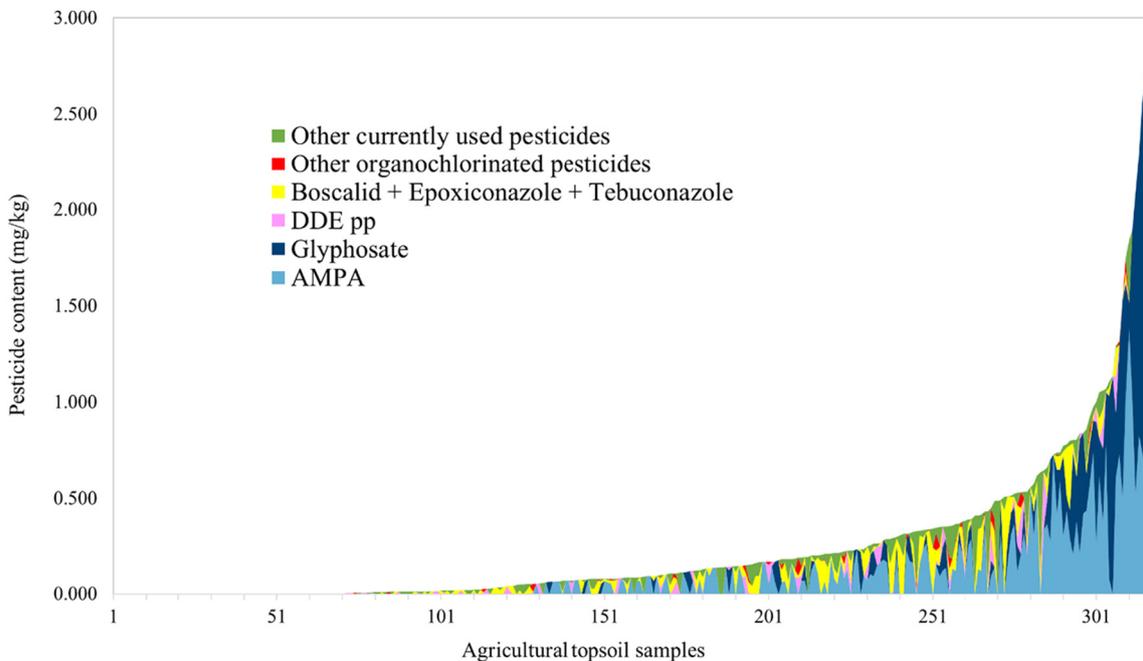
The tested soils from root crops and permanent crops presented the highest pesticide contents, which is in line with the reported intensive pesticide use in these crops (Muthmann, 2007). However, more recent detailed data on pesticide use are required for robust interpretations of pesticide content in the soils of different crop systems. The production of food on soils containing pesticide residues is a concern with respect to possible uptake of residues by the (following) crop. Although this is an aspect covered in pesticide registration requirements (rotational crop studies need to be carried out in certain cases), it may increase residue burden and is an issue in organic farming. According to the EFSA report (EFSA, 2018), 6.5% of the organic food samples analyzed during 2013–2015 from EU Member States, Iceland and Norway contained pesticide residues. For conventionally produced food samples, this value was 44.5%. In total, 184 different pesticide residues were detected in the food samples (out of the 213 tested residues), including long since banned pesticides such as DDT, dieldrin, chlordane, heptachlor and hexachlorobenzene; residues which are also present in EU agricultural soils (this study).

As total pesticide content in soils is highly dependent of the number and type of residues analyzed, only the content of the individual pesticide residues was compared with other studies. Glyphosate and AMPA had the highest content in soil by far, with maximum values of 2.05 and 1.92 mg kg<sup>-1</sup>, respectively. Our glyphosate measurements were in agreement with the range of concentrations observed in other European soils while our AMPA measurements were higher than those noted in literature (see the range of other studies in Table S14). The predominance of glyphosate and AMPA in the tested soils is probably the result of the popularity of glyphosate-based herbicides and the higher application rate of these herbicides compared to other pesticides (Table S14).

Fungicide residues were also common in agricultural soils of the EU, namely boscalid, epoxiconazole, tebuconazole and phthalimide (>10% of soils). The presence of boscalid, epoxiconazole and tebuconazole in soils is not unexpected since they are approved, broad spectrum and moderately-persistent or persistent fungicides. The content of these 3



**Fig. 5.** Distribution of total pesticide contents in EU agricultural topsoils (0–15/20 cm) at the NUTS 2 level. The pie-charts represents the proportion of soil samples from each NUTS 2 region with pesticide content in each content class. The pesticide content class thresholds of 0.05, 0.15, 0.5 and 1 mg kg<sup>-1</sup> correspond, respectively, to the 22<sup>nd</sup>, 50<sup>th</sup>, 81<sup>st</sup> and 93<sup>rd</sup> of the overall pesticide content in contaminated samples ( $n_q = 246$ ). The size of the pie-charts represents the sampling effort by NUTS 2 regions, with bigger circles corresponding to a higher number of soil samples. The exact number of topsoil samples tested in each NUTS 2 region is provided in Table S2. NUTS 2 designations were not included in the map to improve readability, but they are provided in Fig. S1. The white and grey areas in the map represent sampled and not-sampled NUTS2 regions, respectively. Note that some white areas are completely covered by the respective pie-charts, but they can be easily identified in Fig. S1.



**Fig. 6.** Pesticide distribution across the 317 EU agricultural topsoil samples. Topsoil samples (numbered from 1 to 317) were organized by increasing total pesticide content.

compounds was below  $0.5 \text{ mg kg}^{-1}$ , corroborating the range of concentrations found in previous studies (see ranges in Table S14). As mentioned above, phthalimide is not only a metabolite of the approved broad-spectrum fungicide folpet but may also originate from other sources, e.g. a reaction product of phthalic anhydride with primary amines (Lach and Bruns, 2016). Therefore, interpretations of its presence in soil should be performed carefully.

The main insecticides detected in soils were DDTs. Soil contamination by DDTs has been widely studied in Europe (Table S14), with a maximum reported content of  $5.83 \text{ mg kg}^{-1}$  in topsoils from Romania (Ene et al., 2012), a much higher value than the maximum content of  $0.31 \text{ mg kg}^{-1}$  measured in this study. DDTs are some of the few pesticide residues for which screening values are available for almost all European countries. Nevertheless, the type of screening values and the admissible DDTs content in soil is country-specific (Carlon, 2007), hindering comparisons and generalizations on the extent of soil contamination. Neonicotinoid insecticides are highly discussed due to their negative effect on bees, and their use has recently been banned in the EU. Imidacloprid, the only neonicotinoid analyzed in this study, was present in 7% of the EU topsoil samples at a maximum content of  $0.06 \text{ mg kg}^{-1}$ .

#### 4.2. Main limitations of the current risk assessment procedure

Pesticide risk assessment, performed according to EFSA regulations, is based on the comparison of toxicity exposure ratios (TERs) and trigger values. The adequacy of current TERs is discussed here by closely examining the two components of this ratio: the ecotoxicologically relevant concentrations for indicator species and the PEC values.

The potential toxic effects of single active substances and metabolites on in-soil organisms are evaluated in a limited number of standard tests, for the maximum exposures of 56 days. The indicator organisms [*Eisenia fetida*, *E. andrei*, *Folsomia candida*, *F. fimetaria*, *Hypoaspis aculeifer* and N transformation microorganisms; (Ockleford et al., 2017)] represent <0.005% of the >1 million species living in soil (FAO and ITPS, 2017). Ockleford et al. (2017) compared the sensitivity of current standard species to several pesticides with the sensitivity of other species from the same taxonomic group and concluded that standard species might not always be the most sensitive, resulting in an underestimating of pesticide toxicity in the EFSA procedures. This uncertainty should be accounted in the risk assessment procedure, and an increase of the current trigger values for soil organisms should be considered.

Furthermore, community shifts are not addressed by EFSA, although changes in community structure are known to be the most significant effects of some pesticides (FAO and ITPS, 2017). The equilibrium between the organisms beneficial for plant growth and soil pathogens can be easily disturbed in cases where the two groups of organisms have different sensitivities to pesticide residues. For example, the abundance of *Pseudomonas fluorescens* diminishes after the application of glyphosate-based herbicides, which results in a dominance of the root pathogen *Fusarium* spp. (Kremer and Means, 2009; Zobiole et al., 2011). Such community imbalances might adversely affect crop health and soil ecosystem services (Zobiole et al., 2011).

As shown by this study, the presence of multiple residues in soil is the rule rather than the exception. However, no ecotoxicological endpoints are presented for mixtures in EFSA conclusion reports. Urgent attention is required to address the toxicity of the mixtures of residues present in soil, especially considering the possibility of combined effects of different residues on different taxa, resulting in indirect effects on the structure and functioning of the community (SCHER et al., 2012).

Regarding the exposure assessment, PECs are calculated based on recommended application rates, which may not necessarily be the actual application rates. Actual application rates are often not available, especially for individual substances, and a validation of the PECs by field data is lacking. Some of our measurements exceed the highest PECs, which could be a result of over application of pesticides or of the

deposition of contaminated soil particles eroded from surrounding areas, a factor not considered in the PEC calculation. Such underestimations on levels of pesticide in soil translates into TER overestimations, and potentially into risk underestimations. In this study, as the measured concentrations of the most common pesticide residues in soil were almost always below or within the respective PECs range, the TER values from EFSA were the most conservative approach. In the few situations where the PEC used in TER calculations were exceeded by our pesticide measurements (namely for epoxiconazole and tebuconazole), and as the highest measured concentrations of these pesticides in soil were very close to their highest PEC, no major impact would be expected on risk assessment of these substances. Nevertheless, since the application data in the sampling points were not available, the measured values in this study may or may not correspond to the highest field levels, immediately after pesticide application.

#### 4.3. Limitations of this study and recommendations for future research

Using topsoil samples from an existing monitoring program, initially not focused on pesticides, brought some limitations to this study. For instance, information on farming systems is not available for the LUCAS soil sampling points, and was not a criterion in the sample selection. Such information could have provided interesting insights on the extent of soil contamination by pesticide residues for different farming systems.

The measured pesticide concentrations are average concentrations of the topsoil layer (0–15/20 cm). However, pesticide residues often accumulate on the soil surface. For example, the levels of AMPA and glyphosate can be up to 2 to 3 times higher in the top 1–2 cm of the soil surface layer than deeper in the profile (Laitinen et al., 2006; Yang et al., 2015). Underestimations of soil surface pesticide content will lead to underestimations of the potential export of pesticide residues to the surrounding environment by water and wind erosion processes and of the risk to soil quality (Silva et al., 2018). This limitation of average content for the top 15/20 cm soil layer is also common to EFSA predictions. PEC initial values refer to the average content of the substance in the upper 5 cm of soil, while for background values it relates to a soil depth of 5 (permanent crops) or 20 cm (annual crops). Future assessments (field monitoring programs and PEC calculations) should consider residue distribution at different topsoil depths and should focus on the uppermost 1 cm of the soil surface layer, in particular.

As our soil sampling period (April–October) coincides with the recommended application period of several pesticides, the measured contents of currently applied pesticides may correspond to background levels (in case the pesticide was applied just after sampling), to the contents after a single or multiple pesticide applications (which could explain the big proportion of non-persistent compounds found in soils) or even to the accumulated content (in case of very persistent compounds). For this reason, the measured contents were compared against all the PEC values included in the respective active substances reports: PEC initial, long term PEC and accumulated PEC. In future works, sampling in early spring, right before the first pesticide applications, should provide a better indication of background values of currently used pesticides (Hvezdova et al., 2018), an information that might be highly relevant for soil management.

Since measured pesticide data results of a single sampling time in 2015, the representativeness of data should be addressed. First, considering the large spatial scale covered in this study (and all the variability associated with it), it is unlikely that pesticide results are occasional or accidental. Then, as pesticide patterns are usually very similar among consecutive years our assessment of 2015 is most probably typical for the years immediately before and after the sampling. The plateau level of persistent and very persistent substances might oscillate slightly though: it is expected to increase with time for currently applied compounds, and to reduce for banned compounds. Another reason to believe that our results could be extrapolated for the current soil

situation is the fact that none of the most relevant pesticides of this study (in terms of frequency and concentration in soil) was banned from EU markets since the sampling time. And the ones that had their approval extended in the meantime (glyphosate) kept the same recommended applications rates. Of course, some very recently approved substances might have replaced some of older approved ones but, as the use of individual active substances is not available in EU databases, it would be too speculative to assume significant changes in the pesticide products used by EU farmers in such a short period of time.

Despite the criteria used in sample selection intended to represent a realistic worst case scenario, the selected samples represent most probably a mixture of field conditions. Although the samples originated from countries and crops with a reported high pesticide use in the past, there is no certainty on how intensive pesticide application in the sampling points really was. Furthermore, as information on farming systems is not available, it is possible that some samples have been collected in organic fields, with no or very regulated pesticide applications. Therefore, it is likely that some of the samples might have been originated from agricultural fields with more intensive pesticide use and others from fields with less intensive use. Application data would be necessary to evaluate whether the lower pesticide concentrations (at least of currently applied compounds) and the less complex mixtures correspond to field with less intensive pesticide use.

The 76 prioritized pesticides residues analyzed in the EU agricultural topsoils correspond to <20% of the active substances available on the EU market, indicating that the total amount of pesticide residues in EU soils might even be higher than presented in this study and the actual residue mixtures even more extensive and complex, also with regard to possible effects on soil life.

Finally, harmonized EU soil protection policies are required to achieve sustainable food production. Such policies should not only address the introduction of a pesticide to the market (EC, 2009) and the reduction of pesticide inputs (EU, 2009), but also the monitoring of actual pesticide residue content and pesticide composition in soils as well as the establishment of well-founded soil quality standards. For this purpose, effects of mixtures of pesticide residues on soil biota require more attention, and preferably should become one of the important indicators for approval of new products to the market. Additionally, more sustainable agronomic practices should be adopted to reduce pesticide applications and prevent further soil contamination. Erosion related transport of contaminated soil particles to other areas, water bodies and to the atmosphere requires particular attention. Pesticide residues should be also monitored in dust since contaminated small particle soil fractions, once emitted into the atmosphere, can be inhaled by humans and animals (Bento et al., 2017).

#### 4.4. Main findings and implications

- A total of 76 pesticide residues (active substances and metabolites) were analyzed in 317 European agricultural topsoil samples; of those, 43 residues were detected (57%). Considering that we tested <20% of the active substances currently approved in the EU markets, pesticide residue occurrence in soils might actually be higher.
- Pesticide residues were present in 83% of the tested agricultural soils and 58% of the soils contained multiple residues. The presence of multiple pesticide residues in the soil environment is apparently the rule rather than the exception.
- Pesticide composition varied greatly among individual soil samples, with a total of 166 different pesticide combinations. The most common pesticides mixtures in soils were GLY + AMPA and GLY + AMPA + PTI. The toxic effects of actual pesticide mixtures on soil life are virtually unknown.
- Maximum total pesticide content in soil was 2.87 mg kg<sup>-1</sup>. Glyphosate and its main metabolite AMPA contributed the most to total pesticide content in soil. The measured content of individual pesticide residues in soil occasionally exceeded the related predicted

environmental levels (PECs) from EFSA, raising concerns whether PECs are realistic or conservative enough.

- Soil contamination by pesticide residues should be an integral aspect in the characterization of overall soil quality. So far, there is no EU legislation for thresholds or quality standards for total or individual pesticide residues in soil, accounting for potential effects on soil biota in the widest possible sense. Unfortunately, no adequate soil protection policies are yet in place to combat and reverse this hidden threat.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.10.441>.

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