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Currently and recently used pesticides in Central European arable soils

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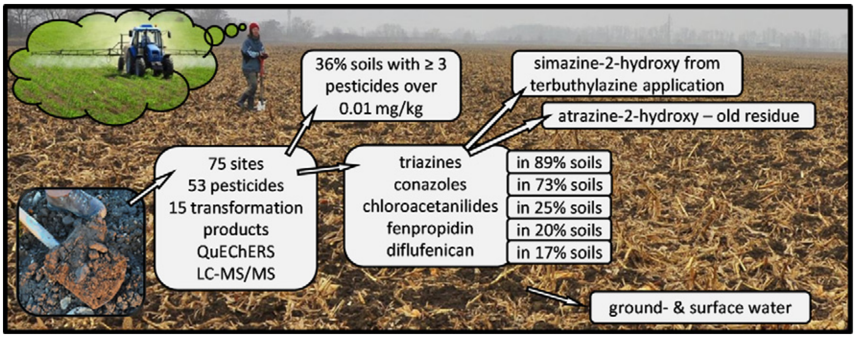
HIGHLIGHTS

- 53 pesticides and 15 transformation products analysed in 75 arable soils
- Multiple pesticide residues with noticeable levels were found in a high number of soils.
- Triazines and conazoles are most frequent and present at high concentrations.
- Significant simazine entry to soils as terbuthylazine impurity indicated
- Links found to the results of CR water monitoring

GRAPHICAL ABSTRACT



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ABSTRACT

Although large amounts of pesticides are used annually and a majority enters the soil to form short- or long-term residues, extensive soil surveys for currently used pesticides (CUPs) are scarce. To determine the status of CUPs' occurrence in arable land in Central Europe, 51 CUPs and 9 transformation products (TPs) were analysed in 75 arable soils in the Czech Republic (CR) several months after the last pesticide application. Moreover, two banned triazines (simazine and atrazine) and their TPs were analysed because of their frequent detection in CR waters. Multi-residue pesticide analysis on LC-MS/MS after soil QuEChERS extraction was used. The soils contained multiple pesticide residues frequently (e.g. 51% soils with ≥5 pesticides). The levels were also noticeable (e.g. 36% soils with ≥3 pesticides exceeding the threshold of 0.01 mg/kg). After triazine herbicides (89% soils), conazole fungicides showed the second most frequent occurrence (73% soils) and also high levels (53% soils with total conazoles above 0.01 mg/kg). Frequent occurrence was found also for chloroacetanilide TPs (25% of soils), fenpropidin (20%) and diflufenican (17%). With the exception of triazines' negative correlation to soil pH, no clear relationships were found between pesticide occurrence and soil properties. Association of simazine TPs with terbuthylazine and its target crops proved the frequent residues of this banned compound originate from terbuthylazine impurities. In contrast, frequent atrazine-2-hydroxy residue is probably a legacy of high atrazine usage in the past. The occurrence and levels of compounds were closely associated with their solubility, hydrophobicity and half-life. The results showed links to CR water-monitoring findings. This study represents the

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first extensive survey of multiple pesticide residues in Central European arable soils, including an insight into their relationships to site and pesticide properties.

1. Introduction

Current systems of agricultural management and crop production indispensably rely on the use of herbicides, fungicides and insecticides, amounting to about 3.3×10^6 t/y worldwide, of which 0.42×10^6 t/y in Europe (2010–2014 data from FAOSTAT (FAO, 2016)). Pesticide use is justifiable by the need to assure sufficient food and feed quantity and quality, while at the same time it presents one of the largest intentional inputs of potentially hazardous compounds into soil, water, air and crops. Even if pesticides are applied according to regulations, only a minor amount reaches its targets while the rest represents potential short- or long-term environmental and yield contaminants, with a wide range of possible negative impacts.

Currently used pesticides (CUPs) are intended to be more environmentally friendly than banned organochlorine pesticides (UNEP, 2016) due to their higher effectiveness towards pests (enabling lower doses), lower persistence and lower non-target toxicity. Nevertheless, numerous pesticides currently used in the world are fairly persistent and toxic (Chambers et al., 2014; Hayes, 2009; Hester et al., 2012; Hrouzková and Matisová, 2012). For example, some 150 compounds among the EU-approved pesticides pose acute aquatic toxicity (level 1), nine compounds are toxic for reproduction (levels 1A/1B) or endocrine disruptors, six are suspected carcinogens, and about 50 compounds fulfil two PBT criteria (EU, 2016; European Commission, 2015). Several CUPs are listed as priority substances for EU water policy (European Commission, 2011). Although CUP half-lives are generally shorter than those of organochlorinated pesticides, repeated use of them can lead to their gradual accumulation in the environment ("pseudo-persistence") as their degradation is slower than their input to the environment. It seems that several CUPs follow the scheme of legacy organochlorinated pesticides, e.g. presence in remote areas or persistence over more than a decade (Jablonowski et al., 2011; Kurt-Karakus et al., 2011). This issue is aggravated by the biotic or abiotic generation of pesticide transformation products (TPs) with distinctly different properties than their parent molecules. TPs may exert higher toxicity, persistence or mobility and contaminate non-target environments such as surface and ground water (Belfroid et al., 1998).

Agricultural soil is the first recipient of pesticides after their application. If the compounds bind strongly to soil, mostly the case of hydrophobic and cationic compounds, their persistence in the soil is increased, their availability to (bio)degradation and mobility is decreased, and they may form long-term bound residues. For many pesticides or their TPs, soils become the prevalent non-point source of pesticide pollution of groundwater (leaching of soluble compounds and compounds bound to colloids) and/or surface water (runoff of soluble compounds, compounds bound to colloids and soil particles, transport from groundwater). This is the main mechanism, along with spray drift, direct applications, spills etc., responsible for the repeated findings of CUPs in water-monitoring programs (Antic et al., 2015; Kodes et al., 2013; Loos et al., 2009; Loos et al., 2010; Mortl et al., 2010; Sanchez-Gonzalez et al., 2013; Sehonova et al., 2012; Szekacs et al., 2014). Due to slow continuous release from soils, even compounds banned for many years (e.g. atrazine and simazine) are still found in water at high frequency and levels (Barchanska et al., 2017; Mortl et al., 2010; Vonberg et al., 2014a; Vonberg et al., 2014b).

Although agricultural soil is a primary sink and key reservoir of pesticides, large soil surveys (e.g. with a number of sites and compounds exceeding 10) of agricultural soils for CUPs are surprisingly rare. The largest published studies cover Korea (Park et al., 2013), Spain (Fernandez-Alvarez et al., 2010; Gamon et al., 2003; Martinez Vidal et al., 2010), Hungary (Mortl et al., 2010; Szekacs et al., 2014) and the USA (Carey et al., 1979). Monitoring of CUPs in soils should be considered an indispensable national or international action, because it is: i) a necessary post-registration control and warning tool; ii) a valuable feedback to phytosanitary authorities and verification of the regulation process (e.g. validation of environmental fate models); iii) a logical complementary action to water monitoring; iv) a source of realistic data on the environmental impact of agricultural activities; v) an important soil quality indicator (EEA, 2006); vi) a valuable data support for sustainable environment policy, decision-making in land use management, environmental protection and agricultural practices; and vii) a means to measure effectiveness after the banning of individual compounds.

The objective of the present study was to characterize pesticide residues in arable soils of the Czech Republic as a representative of Central European countries. Using a multi-residue approach, 53 individual CUPs and 15 selected TPs were analysed in 75 soils from agriculturally used floodplains. We hypothesized that, despite regulatory efforts, multiple co-occurring residues are detectable at a considerable portion of the investigated sites and that residual concentrations frequently exceed threshold values. The subsequent goals were: a) to identify pesticides (groups and individuals) occurring most frequently and/or at the highest levels, b) to identify site and pesticide properties most closely related to CUP occurrence and concentrations, c) to provide a comparison to related water quality monitoring data. In contrast to our recently published article, where we focused solely on the development of residues of triazine herbicides (Scherr et al., 2017), this paper presents the overall results of the survey and discusses the other groups of pesticides.

2. Materials and methods

2.1. Soils

For this study, 75 fields with arable soil were selected from the largest available set of monitored agricultural soils in the Czech Republic (CR). It contains over 100 fields located mainly on intensively cultivated floodplains and which have already been monitored for other pollutants and soil properties (Skala et al., 2017). The selected 75 arable soils represent well Czech (and therefore Central European) arable land, as by means of their properties (Table S1, Supplementary material) they fit the typical ranges known for arable soils in CR (Polakova et al., 2017).

Soil sampling and processing were performed as described in our previous paper (Scherr et al., 2017). Briefly, soil samples were collected from the plough layer (0–25 cm), the most relevant layer for the occurrence of pesticides (Feng et al., 2015; Kucharski et al., 2014; Pose-Juan et al., 2015). The samples were taken in late February and early March 2015 to detect the possible oldest (3–4 months) residues of pesticides, similarly as in other studies (Gamon et al., 2003; Sanchez-Gonzalez et al., 2013), as the usual agricultural practice in CR is application of pesticides in November at the latest and in March at the earliest. The slowly dried, homogenized and sieved (2 mm) samples were stored in glass bottles in the dark at 4 °C before the analyses. The dry matter content of the samples was measured and all analytical results were expressed using dry weight basis.

The soils were analysed for their physico-chemical properties as described previously (Scherr et al., 2017). An overview of their main features is provided in Table S1 (Supplementary material). The crop types for three years prior to the sampling (2012, 2013 and 2014)