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Occurrence of Chlorotriazine herbicides and their transformation products in arable soils[☆]

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ABSTRACT

Chlorotriazine herbicides (CTs) are widely used pest control chemicals. In contrast to groundwater contamination, little attention has been given to the circumstances of residue formation of parent compounds and transformation products in soils.

Seventy-five cultivated floodplain topsoils in the Czech Republic were sampled in early spring of 2015, corresponding to a minimum of six months (current-use terbuthylazine, TBA) and a up to a decade (banned atrazine, AT and simazine, SIM) after the last herbicide application. Soil residues of parent compounds and nine transformation products were quantified *via* multiple residue analysis using liquid chromatography – tandem mass spectrometry of acetonitrile partitioning extracts (QuEChERS). Using principal component analysis (PCA), their relation to soil chemistry, crops and environmental parameters was determined.

Of the parent compounds, only TBA was present in more than one sample. In contrast, at least one CT transformation product, particularly hydroxylated CTs, was detected in 89% of the sites, or 54% for banned triazines. Deethylated and bi-dealkylated SIM or AT residues were not detectable. PCA suggests the formation and/or retention of CT hydroxy-metabolite residues to be related to low soil pH, and a direct relation between TBA and soil organic carbon, and between deethyl-TBA and clay or Ca contents, respectively, the latter pointing towards distinct sorption mechanisms. The low historic application of simazine contrasted by the high abundance of its residues, and the co-occurrence with AT residues suggests the post-ban application of AT and SIM banned triazines as a permitted impurity of TBA formulations as a recent, secondary source.

The present data indicate that topsoils do not contain abundant extractable residues of banned parent chlorotriazines, and are thus likely not the current source for related ground- and surface water contamination. In contrast, topsoils might pose a long-term source of TBA and CT transformation products for ground and surface water contamination.

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1. Introduction

The plant protection products (PPPs) atrazine (AT, 1-Chloro-3-

ethylamino-5-isopropylamino-2,4,6-triazine), simazine (SIM, 6-Chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine) and terbuthylazine (TBA, *N-tert*-butyl-6-chloro-*N'*-ethyl-1,3,5-triazine-2,4-diamine; see graphical abstract for structures) and their hydroxylated, deethylated and/or deisopropylated (-OH, -DE, -DI) metabolites – SIMs, ATs and TBAs, respectively – are members of the chlorotriazine (CT) family of compounds. The parent compounds are used as systemic herbicides against pre- and post-emergence broadleaf weeds predominantly in maize and sorghum cultures.

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While AT, along with SIM, was banned in the European Union in 2004, it is still one of the most widely used herbicides in the United States and Australia (Allinson et al., 2015), despite its abundance in ground and surface waters (Kodeš et al., 2013; Sánchez-González et al., 2013; Sassine et al., 2016; Tappe et al., 2002; White et al., 2016). SIM and AT are endocrine disruptors, highly toxic to aquatic life, and SIM is classified as a suspected carcinogen (EC, 2008, 2016; Farruggia et al., 2016).

Despite their ban, the continued presence of SIM and AT in ground- and surface water has been reported in many European countries (Kodeš, 2015; Kodeš et al., 2013; Sánchez-González et al., 2013; Vonberg et al., 2014a, 2014b). Slow leaching from topsoils, where concentrations are highest within the soil profile (Vonberg et al., 2014a), poor degradation in the saturated zone, and continued illegal application (Sassine et al., 2016; Tappe et al., 2002; Vonberg et al., 2014b) are referred to as the most likely reasons for their prevalence in groundwater. TBA was introduced as a hydrophobic, less mobile replacement for AT and SIM, and authorized for use in 20 countries of the EU, including the Czech Republic (CR). However, a similar potential for terbuthylazine as groundwater contaminant has been identified (Dousset et al., 1997; Gerstl et al., 1997).

In the CR, following an annual application of 130 tons active ingredient until 2004 (CISTA, 2016), AT was still present in 9% of groundwater samples in 2012, exceeding the groundwater reference value of 0.1 µg/L in 1.7% of all samples (Kodeš et al., 2013). Annual application of simazine was limited to 0.1 tons preceding its ban (CISTA, 2016). Groundwater concentrations of simazine and hydroxysimazine were detectable, however below the reference value. Dealkylated products from AT or SIM transformation were exceeding thresholds in a few cases (Kodeš, 2015; Kodeš et al., 2013). TBA is, despite its annual application of approximately 110 tons since the ban of AT (CISTA, 2016), less abundant, with TBA, TBA-OH and TBA-DE exceeding reference values in 0.2% of the investigated samples (Kodeš et al., 2013). Groundwater data represent a generic reflection of sorption and degradation processes occurring in the vadose zone, but little is known about the formation and retention of CT transformation products in soils.

Mineralisation and partial transformation of SIM, AT and TBA is mediated by common soil microbes (Kontchou and Gschwind, 1995; Mandelbaum et al., 1995; Satsuma, 2010; Wang et al., 2014). Two pathways produce a limited number of abiotic and microbial transformation products. Chlorohydrolysis yields 2-hydroxylated products, i.e. SIM-OH, AT-OH and TBA-OH (Barra Caracciolo et al., 2010; Karanasios et al., 2013; Mandelbaum et al., 2008). Abiotic hydroxylation is quantitatively relevant and influenced by soil pH and clay content (Bailey et al., 1968; Horrobin, 1963), and catalysed by humic and fulvic acids in the case of AT (Laird and Koskinen, 2008). Secondly, microbial *N*-dealkylation yields deisopropylated (-DI), deethylated (-DE), and bi-dealkylated products (CT-DA) (Jurina et al., 2014; Nagy et al., 1995).

All three investigated triazine herbicide parent compounds are weakly basic, and under circumneutral soil pH conditions present as neutral, moderately hydrophobic (log K_{ow} 2.7, 2.3 and 3.4 for AT, SIM, and TBA, respectively (PPDB, 2016)) species capable of hydrophobic interactions with soil. They are relatively persistent in soils, with soil half-lives of up to 433, 167 and 150 days for AT, TBA and SIM, respectively (Charnay et al., 2005; Grenni et al., 2012; Kruger et al., 1993; Stipičević et al., 2015; Wauchope et al., 1992), although reported numbers vary widely (PPDB, 2016).

Little is known on the environmental factors shaping the formation and retention of chlorotriazine transformation products that may persist over several vegetation periods. Pesticide residues in soil may cause injury on microbial communities and non-target plants e.g. during crop rotation and pose, depending on the

strength of sorbent-sorbate interaction, a potential long-term risk for ground and surface water pollution, soil quality deterioration and human health (Hildebrandt et al., 2008; Kodeš et al., 2013; Sassine et al., 2016; White et al., 2016). Even strongly bound residues may become available over time due to changes in sorption site biochemistry effected by microbial activity or agricultural practice including the addition of chemicals (Gevao et al., 2000).

The present study is based on a comprehensive survey of pesticide (fungicides, herbicides and insecticides) residues in 75 agricultural topsoil floodplain locations in the Czech Republic acquired in early 2015, encompassing 91 currently used and legacy pesticides and selected metabolites (overview presented in Hofman et al., 2016). The occurrence of pesticide residues has been studied on comparably large soil and substance data sets particularly in Korea (Noh et al., 2012; Park et al., 2013) and Spain (Gamon et al., 2003; Padilla-Sanchez et al., 2015; Plaza-Bolanos et al., 2012), and we hypothesize that such data collections enable for the identification of priming soil and environmental factors, such as pH, soil textural and compositional features, climate, agricultural management and others, determining the formation of herbicide residues. Particularly, we aim to identify key factors determining the formation and retention of the chlorotriazine herbicides atrazine, simazine and terbuthylazine, and the role of topsoils as a source for banned triazines leaching into groundwater.

2. Material and methods

2.1. Sampling of arable soils

Seventy-five different intensively used agricultural fields were selected as monitoring locations because of their history in monitoring projects for other pollutants (Vácha et al., 2014). These soils represent typical fluvisols of Central Europe and are located at river alluvial terraces and alluvial floodplains at altitudes between 130 and 400 m above sea level over the whole Czech Republic. Soils were sampled in late February and early March 2015, and therefore, a minimum of six months and eight to ten years (considering the post-ban consumption of existing stocks of pesticides banned in 2004) are expected to have passed since the last permitted application of the current-use TBA and the banned herbicides AT and SIM, respectively.

Soil was collected from the 0 to 25–30 cm layer using a stainless steel spade (see graphical abstract). Nine subsamples of the same weight (about 1.5 kg) were taken in a distance of 50 m in a 3 × 3 grid of a 100 × 100 m area and mixed together. Soil samples were dried slowly for three weeks in March 2015 at ambient conditions (10–15 °C) in a roof-protected area to limit changes in pesticide concentrations. The dried soil was crushed mechanically, then homogenized, sieved to a 2 mm fraction and stored in glass bottles in the dark at 4 °C. On this sample, all analyses were performed. All analytical results are expressed on a dry weight basis. The crop types for three years prior to sampling (2012, 2013 and 2014) were identified using Earth Observation technology (Foerster et al., 2012).

2.2. Soil characterization

The physico-chemical properties of the samples were determined using standardized methods. The total organic carbon content (TOC) was analysed on a LECO RC612 multi-element analyser as CO₂ evolving between 100 and 540 °C measured via an infrared detector. The total nitrogen content (N) was measured by the Kjeldahl method according to ISO 11261 (ISO, 1995a). Soil pH in H₂O suspensions was measured according to ISO 10390 (ISO, 2005). Ca²⁺, Mg²⁺ and K⁺ were determined in BaCl₂ at pH 8.1 according to

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