



Short communication

Identification and characterization of tebuconazole transformation products in soil by combining suspect screening and molecular typology



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ABSTRACT

Pesticides generate transformation products (TPs) when they are released into the environment. These TPs may be of ecotoxicological importance. Past studies have demonstrated how difficult it is to predict the occurrence of pesticide TPs and their environmental risk. The monitoring approaches mostly used in current regulatory frameworks target only known ecotoxicologically relevant TPs. Here, we present a novel combined approach which identifies and categorizes known and unknown pesticide TPs in soil by combining suspect screening time-of-flight mass spectrometry with *in silico* molecular typology. We used an empirical and theoretical pesticide TP library for compound identification by both non-target and target time-of-flight (tandem) mass spectrometry, followed by structural proposition through a molecular structure correlation program. *In silico* molecular typology was then used to group TPs according to common molecular descriptors and to indirectly elucidate their environmental parameters by analogy to known pesticide compounds with similar molecular descriptors. This approach was evaluated via the identification of TPs of the triazole fungicide tebuconazole occurring in soil during a field dissipation study. Overall, 22 empirical and 12 yet unknown TPs were detected, and categorized into three groups with defined environmental properties. This approach combining suspect screening time-of-flight mass spectrometry with molecular typology could be extended to other organic pollutants and used to rationalize the choice of TPs to be investigated towards a more comprehensive environmental risk assessment scheme.

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1. Introduction

Pesticides are used in agriculture to ensure high crop yields and quality. This large group of xenobiotic compounds and their transformation products (TPs) have globally been identified as

major contaminants of natural water resources (Hutzinger, 2013; Lewis and Maslin, 2015). The United States Environmental Protection Agency (U.S. EPA) estimates that 2.4 billion kilograms of pesticides are released per year. They support important economic sectors of agriculture, but also significantly contribute to environmental pollution (U.S. EPA, 2011). Another aspect that makes pesticides a chemical group of particular interest is their rapidly evolving market which is continuously enriched with new molecules. In order to reach the market, new pesticide molecules have to undergo an environmental risk assessment (ERA) procedure based on a large set of data submitted by the pesticide companies and

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evaluated by the official authorities (e.g. the Plant Protection Products and their Residues panel (Regulation EC 1107/2009, 2009) of the European Food Safety Authority (EFSA) for Europe). This procedure is periodically repeated to re-evaluate the currently registered pesticide molecules. Once released into the agro-ecosystem, pesticides and their TPs can diffuse away from their target point and contaminate surrounding water resources (U.S. EPA, 2015), with reciprocal impact on non-target organisms supporting key ecosystemic services (Bozdogan, 2014). The properties of TPs such as bioavailability, mobility and ecotoxicity can substantially differ from the parent compound (Sinclair et al., 2010; Tixier et al., 2000), and although their biological efficacy is usually lower (Boxall et al., 2004), they could be highly ecotoxicologically relevant (Fenner et al., 2013). In Europe, *a posteriori* monitoring of the contamination of water and air resources by pesticides is imposed by the corresponding directives (EU Air Quality Directive, 2008/50/EC, 2008; EU Water Framework Directive, 2000/60/EC, 2000). By contrast, no monitoring of soil contamination by pesticides is required at the EU level. This ensues from the lack of a corresponding directive, although the need for some kind of regulation was proposed to the European Commission (Van-Camp et al., 2004). Thus, if an unacceptable risk for the environment becomes evident several years after the introduction of a pesticide to the market, its use becomes restricted, and if monitoring studies reveal that no alleviation of the risk is achieved, the pesticide is removed from the market. Past experience has shown that the knowledge of the existence of ecotoxicologically relevant TPs typically emerges only 20–30 years after a given pesticide has first been marketed (Fenner et al., 2013). Currently used monitoring approaches for pinpointing ecotoxicologically relevant pesticide TPs are often restricted to water samples. They do not prevent the contamination of natural resources, and impose mitigation actions only after contamination has been reported. Novel approaches able to identify potential TPs and *in silico* assessment of their ecotoxicity and environmental contamination could offer a solution to this issue.

The knowledge gap about the existence or properties of pesticide TPs derived from abiotic and biotic processes in the environment may be the reason why relevant TPs have been overlooked for so long. Conventional analytical methods focus on the monitoring of the so-defined 'ecotoxicologically relevant' pesticide TPs or TPs 'relevant for groundwater contamination' (OECD Guideline ENV/JM/MONO (2007)17, 2007; Regulation EC 1107/2009, 2009). Consequently, most studies focus on a limited number of molecules identified as targets through monitoring approaches and calibrated against reference standards. Therefore, they often provide only a partial view of the complex transformation patterns of pesticides in the environment. Thus, there is a need to develop an innovative approach by combining powerful analytical methods also detecting unknown TPs, with categorization methods based on the chemical features of TPs.

The analytical techniques suitable to detect unknown and suspected molecules in the absence of reference standards are high resolution mass spectrometry (MS), namely quadrupole time-of-flight MS (QTOF-MS) and Fourier transform MS (FT-MS), as well as nuclear magnetic resonance (NMR) spectroscopy (Ibanez et al., 2005). These techniques are often combined in forensics (Reitzel et al., 2012) or medicine (Zeng et al., 2013), where QTOF-MS is used for screening for new unknown molecules and then supplemented by NMR spectra for the structural elucidation of a compound. NMR spectroscopy is an effective method for confirming molecular structures, but it is less appropriate for analyzing TPs from environmental samples because of its rather poor sensitivity, generally three orders of magnitude lower than MS (Ibanez et al., 2005).

Categorization of unknown and suspected molecules can be achieved by *in silico* molecular typology that clusters potential TPs according to their properties (Servien et al., 2014).

In this study, we present a new approach for the analysis of agricultural soil samples treated with a pesticide by combining high-resolution QTOF-MS with *in silico* molecular typology. Our approach provides the profiles and the molecular structures of unknown and suspected pesticide TPs in soil, using a compound library containing empirical (already known) and theoretical (yet unknown) TPs. It consists of three main steps: (i) construction of an in-house pesticide-specific TP library based on a literature survey and listing of suspect TPs, (ii) QTOF-MS analyses of soil extracts by non-target MS to screen TPs against this library, followed by target tandem MS using an ion inclusion list to propose their structure via accurate mass daughter ions and a molecular structure correlation (MSC) program, and (iii) categorization of detected TPs based on *in silico* analysis using molecular typology.

To demonstrate the potential of this novel approach, the transformation of the triazole fungicide tebuconazole (TCZ) was investigated in a field dissipation study. TCZ was chosen as a model compound because, although it has been on the market for quite some time (27 years) (Börner et al., 2009), there are still significant knowledge gaps regarding its environmental fate, its transformation in soil and the ecotoxicological impact of potential TPs (EFSA, 2014). The potential formation of various triazole TPs is particularly relevant, because they are recalcitrant to biodegradation, and they possibly interact with the hormone regulation network of non-target organisms by inhibiting the cytochrome P450-dependent conversion of lanosterol to ergosterol (Rieke et al., 2014; Shalini et al., 2011). The applied approach is of interest for improving future environmental fate studies to become more comprehensive, thus strengthening ERA.

2. Material and methods

2.1. Library setup of TCZ TPs

An in-house TCZ TP library was constructed based on a thorough literature review including research papers (cited in the results section entitled 'Empirical TCZ TPs') and data sets from the pesticide company on the transformation pattern of TCZ within various matrices. Literature search was performed via 'Web of Science' and 'Google' using search terms such as 'tebuconazole AND metabolite', 'tebuconazole AND transformation product', 'tebuconazole AND degradation'. The resulting library was composed of 47 empirical (already detected in at least one study) and 29 theoretical TPs. Theoretical TPs were created based on expert knowledge taking into account common reaction processes in organic chemistry and biochemistry likely leading to probable molecules. The TCZ TP library contains the name, molecular formula, molecular structure and mass of each molecule (Supplementary data, Table S1). Initial pretests of chemical analysis were carried out on a subset of soil samples randomly chosen from the field study to search for TCZ TPs. Retention times of TPs proposed via MSC were then added to the library as an additional parameter for identification purposes in MS screening.

2.2. TCZ field dissipation study

The field dissipation study was conducted on an agricultural field in North Italy (45°05'22.1"N 9°45'58.6"E) in fall/winter 2013/14. The soil was characterized as loamy sand (4.2% clay, 13.5% silt, 82.3% sand) with a pH of 7.3 and an organic matter content of 4.5%. The field had not been treated with pesticides for more than five years, and was cropped with winter wheat. A commercial

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