

Residue Findings of Triazole Derivative Metabolites in Food

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Introduction

One of the largest and most important pesticide groups are the triazole-fungicides. They are employed for the control of a wide range of fungal diseases on fruit, vegetables, nuts, pulses and grain and act systemically. Triazole-fungicides and a few other pesticides containing the 1,2,4-triazole moiety metabolize to various common metabolites containing this group, the so-called triazole-derivative metabolites (TDMs). The most important among them are 1,2,4-triazole (TRZ), 1,2,4-triazole alanine (TA), 1,2,4-triazole acetic acid (TAA), and 1,2,4-triazole lactic acid (TLA).

Analytical method

TDMs are extremely polar making their analysis very challenging. Using isotopically labeled internal standards (IL-ISs) helps eliminate quantitation errors related to matrix-effects and has opened the way for a straightforward sample preparation using the QuPPE method, without any cleanup or enrichment step. Analysis is conducted by LC-MS/MS involving Differential Mobility Spectrometry (DMS) [1].

Residue findings

4,689 samples (thereof 642 organic) from the local market were analyzed for TDMs.

Table 1: Overview of findings in conventional and organic crops

Analyte	No. of samples analyzed	No. of samples with levels \geq LOQ	% of samples \geq LOQ	Min. [mg/kg]	Max. [mg/kg]	Mean of positives [mg/kg]
Conventional samples						
TRZ	4041	55	1.4%	0.01	0.074	0.018
TA	4047	1969	49%	0.01	1.4	0.082
TAA	4043	440	11%	0.01	0.79	0.053
TLA	2972	699	24%	0.01	2.4	0.059
Organic samples						
TRZ	641	6	1.0%	0.01	0.042	0.021
TA	642	194	30%	0.01	1.1	0.056
TAA	641	63	10%	0.01	1.0	0.066
TLA	441	52	12%	0.01	0.18	0.027

TA was overall the predominant TDM.

Table 2: TA findings in selected products (conv. and organic)

Groups	Conventional			Organic			Ratio conv. vs org. % positives (mean of pos.)
	No. of samples \geq LOQ	% of samples \geq LOQ	Mean of pos. [mg/kg]	No. of samples \geq LOQ	% of samples \geq LOQ	Mean of pos. [mg/kg]	
Cereals	61	86%	0.238	29	94%	0.112	0.9 (2.1)
Stone fruit	232	87%	0.144	19	76%	0.079	1.1 (1.8)
Sprout vegetables	147	74%	0.093	12	41%	0.033	1.8 (2.8)
Leafy vegetables	315	40%	0.089	17	18%	0.031	2.2 (2.9)
Fruiting vegetables	319	45%	0.063	40	38%	0.029	1.2 (2.2)
Baby food	17	89%	0.034	18	58%	0.060	1.5 (0.6)

TLA was found in exotic fruit (0.153 mg/kg on average in conventional products, with the highest values being detected in mango, pineapples and papayas), berries including grapes (0.048 mg/kg on average in conventional products, with the highest values being detected in currants) as well as in wine.

TAA was predominant in cultivated mushrooms (0.074 mg/kg on average in conventional products). This correlates well with the information compiled by EFSA [2] indicating high TAA levels in cereal straw, which is widely used as substrate to cultivate mushrooms. In contrast, none of the wild mushrooms analyzed contained any TDM residue.

Discussion

Overall, TDM residues in conventional products were found more frequent and, on average, in significantly higher amounts than in products labelled organic. Still, the percentage and average concentration of TDMs in organic products is surprisingly high and needs to be studied thoroughly. Potential reasons include the following:

- Drift from neighboring fields
- Current illegal use of triazole fungicides
- Current illegal use of TRZ-containing nitrification inhibitors (NI)
- Use of triazoles prior to conversion to organic farming
- Use of NIs prior to conversion to organic farming

Drift and/or illegal usage to this extent is highly unlikely, and non-TRZ-based NIs are by far more common. Therefore the most likely explanation of the rather high number of TDMs-containing organic products is, that at least one of the TDMs shows a very high persistence and a limited leaching potential despite its high polarity. Active uptake by succeeding plants and accumulation/ persistence in perennial crops seems likely.

Summary

TA was the TDM compound most frequently detected. Roughly half of the conventional and one-third of the organically labelled products contained it at levels \geq LOQ. TLA and TAA were also frequently found whereas TRZ exceeded only rarely the LOQ. Overall, TDM residues were more frequently detected in conventional than in organically labelled products. The frequency of various annual and perennial organic products containing significant TDMs levels suggest a persistence of the TDM-moiety over many years both in plants and the environment.

References

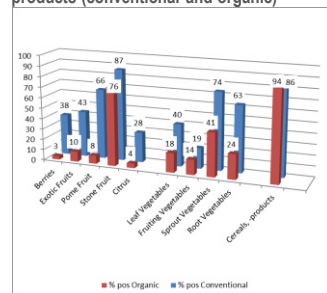
1. E-Journal CVUA Stuttgart May, 2016
2. EFSA, personal communication, Oct. 2015

Acknowledgement

Standards were kindly donated by Bayer CropScience (Monheim, Germany)

Trivial Names / Codes	Chemical Structures
1,2,4-Triazole (TRZ) CGA-71019	
Triazole acetic acid (TAA) CGA-142856	
Triazole alanine (TA) CGA-131013	
Triazole lactic acid (TLA) CGA 205369	

Figure: Frequency of TA findings in selected products (conventional and organic)



EPRW 2016



Baden-Württemberg