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Assessment of field re-entry exposure to pesticides: A dislodgeable foliar residue study

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HIGHLIGHTS

- Spray applications were conducted in pepper and tomato greenhouses.
- An SC insecticide and an EC fungicide were applied.
- Dislodgeable foliar residue and worker dermal exposure studies were carried out.
- Transfer coefficient (TC) values were determined.
- TC values were in agreement with current EFSA guideline values in most of the cases.

GRAPHICAL ABSTRACT

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ABSTRACT

A dislodgeable foliar residue study was conducted in greenhouse pepper and tomato on the island of Crete, Greece, following the spray application of an SC insecticide (with active substance (a.s.) tebufenozide) and an EC fungicide (a.s. bupirimate). Furthermore, for the assessment of worker exposure to pesticides – as a result of re-entering the treated crops – a worker dermal exposure study was carried out during the tasks of tying or pruning, which allowed the transfer coefficient values for the specific tasks to be determined. Pesticide residues were analysed with an in house developed and fully validated HPLC-ESI/MS analytical method. The results from the study resulted in transfer coefficient values which were in agreement with current EFSA guideline values in most of the cases with the exception of bupirimate in a tomato greenhouse. In that case, high potential dermal exposure and low dislodgeable foliar residue values were observed, which is thought to be due to the moist leaves collected during sampling and monitoring, which led to greater than expected transfer coefficient values.

1. Introduction

Worker exposure to a pesticide is defined as the exposure that takes place when entering the treated field (Dong and Beauvais, 2013) or when handling treated produce (Krol et al., 2005) or coming into contact with pesticide residues on work surfaces in the workplace (Geno

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et al., 1996; Hubal et al., 2008). Although field re-entry exposure concerns also persons that could be located within or directly adjacent to the area where pesticide application or treatment has carried out, this specific case of exposure is part of the bystander/resident exposure assessment to pesticides since it is considered to be incidental and unrelated to work activities and tasks involving pesticides. Thus, re-entry exposure assessment concerns principally workers in agricultural fields. Workers are persons who, as part of their employment, enter an area that has been treated previously with a pesticide or who handle a crop that has been treated with a pesticide (EFSA Guidance, 2014). Worker exposure depends on the specific tasks performed (*e.g.* harvesting, pruning/thinning, maintenance) (indicatively see Coronado et al., 2004). The main route of exposure is considered to be the dermal one (Worgan and Rosario, 1995). However, in specific cases such as for volatile pesticides, other routes of exposure and specifically inhalation for re-entry especially in protected crops have to be considered.

Dermal exposure is the outcome of direct contact with pesticide residues on surfaces such as foliage, while determining factors are, apart from the amount of residue on foliage, the intensity of contact with foliage, the overall duration of contact, and the penetration of residues through clothing. In order to reduce the potential exposure, as a general good agricultural practice, in the first instance the re-entry of workers in the treated field is prohibited until enough time has passed, to ensure that airborne pesticide residues have deposited, or liquid spray has dried.

There are several complex scientific as well as regulatory issues associated with the assessment of worker exposure to pesticides during re-entry to the treated field. These issues originate mainly from the uncertainties related to the limited data available and the lack of the appropriate exposure estimation tool, such as an algorithm that could be used by regulators and risk assessors to estimate the re-entry exposure (Dong and Beauvais, 2013) considering representative, realistic and science based input values. Data from actual measurements during different tasks carried out by workers in crops following application of plant protection products (PPPs) could provide valuable information for the pragmatic worker exposure estimation. Consequently, generation of such data can be encompassed in exposure models assisting their validation.

The dislodgeable foliar residue (DFR) is defined as the quantity of pesticide residue that can be transferred from the two-sided foliar surface of a plant. In this context, DFR denotes the potentially available pesticide residue that the worker can be exposed to during the different tasks carried out. Dermal exposure from contact with residues on foliage is currently estimated as the product of the DFR, the transfer coefficient (TC) and the task duration (EFSA Guidance, 2014; Korpalski et al., 2005). The TC, expressed in cm^2/h, is a parameter related to the transfer of residues from the plant surface to the clothes or skin of the worker that should be taken into account. The TC is not dependent on the pesticide applied, but it depends on the intensity of contact with the foliage, *i.e.* the task performed, the crop type and it is expressed per time unit. The first studies to determine TC values based on the DFR and the dermal exposure were conducted in 1982 when Popendorf and Leffingwell found a linear relationship between the DFR level and the dermal exposure to organophosphorus pesticides. In this regard, the authors stated that the ratio of DFR to exposure can vary depending on crop type and working activity (Popendorf and Leffingwell, 1982). van Hemmen et al. (1995) grouped TCs by activity type and contact type, using the studies presented by Krieger et al. (1992).

In the scientific open literature, various studies have come to light regarding the assessment of dermal exposure to pesticides during re-entry of workers, including DFR studies (Belsey et al., 2011; Suganthi et al., 2008). In this context, it is apparent that studies that will address and include critical parameters that affect DFR, such as crop type, pesticide formulation type, and particular activities conducted by workers in field are of fundamental importance.

In the present work, both worker exposure levels and DFR in the two different crops, using different pesticides formulations and tasks carried out, were measured. Consequently, TC for the tasks performed was calculated as the quotient of worker potential dermal exposure (PDE) and the respective DFR. With regard to the active substances dealt within this study, for bupirimate (structure in Fig. 1) the only published work regarding re-entry dermal exposure and DFR measurement concerned greenhouse (in ornamentals) application of bupirimate (Jongen et al., 1992), while no such relative study has been found for tebufenozide (structure in Fig. 1).

For each individual pesticide, several analytical studies have been published. Indicatively, Soler et al. reported the analysis of bupirimate residues in oranges comparing triple quadrupole and quadrupole ion trap mass analyzers (Soler et al., 2005a). The same group also reported the analysis of bupirimate in citrus fruits using single quadrupole LC-MS (Soler et al., 2005b). Bupirimate has been included in a routine analytical approach referring to a multiresidue method for fruit and vegetables (Kmellar et al., 2010), where analysis was conducted by LC-MS/MS. As regards tebufenozide has been integrated into a multi-residue method for the determination of several pesticides in matrices with high water capacity by LC–MS/MS without clean-up (Madureira et al., 2012). Additionally, tebufenozide was analysed in processed fruits and vegetables by LC-ESI-MS/MS (Sannino et al., 2004). However, to the best of our knowledge, there are limited references to the simultaneous identification of these analytes in a single analytical method (Thermo-Scientific).

With regard to extraction of pesticides from crops, plants and their parts, several procedures have been applied in different studies. Solid-liquid extraction, liquid-liquid extraction (LLE), solid-phase extraction (SPE), as well as their variations are typical procedures followed by many research groups in case of several matrices including leaves of food and vegetable commodities (indicatively see Barriada-Pereira et al., 2004; Hassan et al., 2013; Leiva et al., 2016). Cutting edge approaches such as pressurized liquid extraction in conjunction with SPE (Rodrigues et al., 2016) or the QuEChERs method (Machado et al., 2017) have been applied successively for the same purpose. Organic

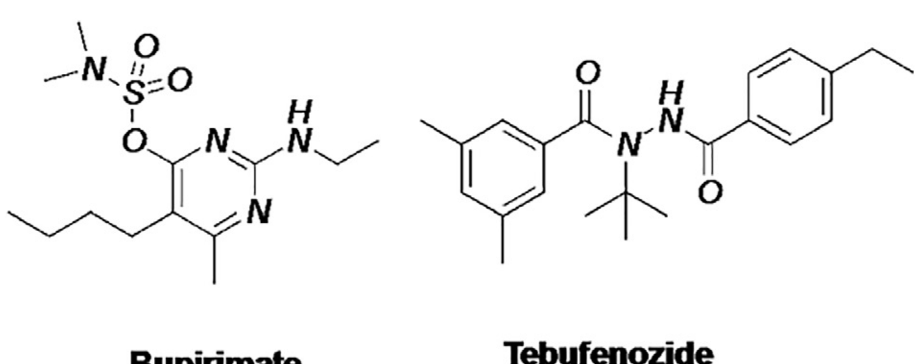

Fig. 1. Chemical structures of bupirimate and tebufenozide.