Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Chemosphere 67 (2007) 1102–1107
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Human intake fractions of pesticides via greenhouse tomato consumption: Comparing model estimates with measurements for Captan

R. Juraske [a,*], A. Antón [b], F. Castells [a], M.A.J. Huijbregts [c]

[a] *Department of Chemical Engineering, ETSEQ, Universitat Rovira i Virgili, Av. Països Catalans 26, 43007 Tarragona, Spain*
[b] *Departament de Technologia Horticola, Institut de Recerca i Tecnologia Agroalimentària (IRTA), Centre de Cabrils, 08348 Cabrils, Barcelona, Spain*
[c] *Department of Environmental Science, Faculty of Science, Radboud University Nijmegen, 6500 GL Nijmegen, The Netherlands*

Received 28 February 2006; received in revised form 26 October 2006; accepted 24 November 2006
Available online 16 January 2007

Abstract

Human intake due to pesticide residues in food commodities can be much higher than those related to water consumption and air inhalation, stressing the importance to correctly estimate pesticide uptake into plants and predict subsequent intake by humans. We calculated the human intake fraction of captan via tomato consumption taking into account the time between pesticide application and harvest, the time between harvest and consumption, the absorption of spray deposit on plant surfaces, transfer properties through the cuticle, degradation inside the plant and loss due to food processing. Human population intake fractions due to ingestion were calculated for complete, washed and peeled tomatoes. The calculated intake fractions were compared with measurements derived from an experimental setup in a Mediterranean greenhouse. The fraction of captan applied in the greenhouse as plant treatment that eventually is ingested by the human population is on average 10^{-2}–10^{-5}, depending on the time between pesticide application and ingestion of tomatoes and the processing step considered. Model and experimentally derived intake fractions deviated less than a factor of 2 for complete and washed tomatoes and a factor of 3 for peeled tomatoes. Intake fractions due to air inhalation and consumption of drinking water are expected to be significantly lower (5–9 orders of magnitude) than those induced by the intake of tomatoes in this case study.

Keywords: Captan; Human intake fraction; Life Cycle Impact Assessment (LCIA); Pesticide fate and exposure model

1. Introduction

A variety of pesticides is used in greenhouses to maintain high crop yields. An important side effect of the use of pesticides is the potential harm they can cause to humans and the environment. In recent years there has been an increasing concern that pesticides constitute a risk to the general human population through residues in the food supply (Gold et al., 2001; Bolognesi, 2003). Since plants form the basis of food webs, potentially harmful organic contaminants could find their way into human populations via this route. At present, the level of uncertainty associated with predicted organic contaminant doses via this exposure pathway exceeds the level of uncertainty associated with other potential pathways like inhalation and contamination due to drinking water (Collins and Fryer, 2003).

Pesticide residue evaluation in agricultural products can be measured by analytical methods. These experimental approaches are often limited by high costs, the time involved, and analytical detection limits. An alternative approach to the classical laboratory analysis is pesticide fate and exposure modelling. A greenhouse tomato model developed by Antón et al. (2004), describes human exposure pathways for pesticides applied in greenhouses in Spain. For all pesticides, exposure via tomato intake represented the most important exposure pathway for humans.

* Corresponding author. Tel.: +349778553; fax: +34977559621.
E-mail address: ronnie.juraske@urv.cat (R. Juraske).

0045-6535/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2006.11.047

However, the uncertainty in the estimates of this pesticide pathway was large. Therefore, further development and increasing understanding of how plants accumulate and eliminate pesticides will have substantial benefits for risk assessment purposes.

This study updates the tomato exposure part of the greenhouse model of Antón et al. (2004) and now includes model estimations of human exposure via complete, washed, and peeled tomatoes, respectively. It also validates the model estimations with experimental data for captan (CAS 133-06-2), a fungicide that is commonly used in greenhouses.

2. Materials and methods

2.1. Fate and exposure model

2.1.1. Deposition on fruits after spraying

Since (i) pesticide deposition on soil, (ii) deposition on plants and (iii) wind drift from the greenhouse must sum up to one, the plant deposition fraction (f_{plant}) of a pesticide after application is given by:

$$f_{\text{plant}} = 1 - (f_{\text{drift}} + f_{\text{soil}}) \tag{1}$$

The drift fraction (f_{drift}) used in the model is fixed to a value of 0.05 derived from the work of Egea González (1999) and Leistra et al. (2001). They presented drift fractions between 0.01 and 0.09 for the application in greenhouses depending on the vapour pressure of the active ingredient. With a simple exponential model, based on plant growth stage and capture efficacy, the soil deposition is described by the following equation:

$$f_{\text{soil}} = \mathrm{e}^{-k_{\text{p}} \times \text{LAI}} \tag{2}$$

where k_{p} is the pesticide capture coefficient (–) and LAI is the leaf area index ($\text{m}^2_{\text{leaves}}\text{m}^{-2}_{\text{soil}}$). According to Gyldenkaerne et al. (1999), pesticide capture coefficients (k_{p}) of 0.35 and 0.55 are suggested for the pesticide spray solutions prepared with and without surfactants or adjuvants, respectively.

The fraction that reaches the fruit (f_{fruit}) is derived from the plant deposition fraction (f_{plant}) by correction for the difference between the leaf area index (LAI) and the fruit area index (FAI):

$$f_{\text{fruit}} = \frac{\text{FAI}}{\text{LAI}} \times f_{\text{plant}} \tag{3}$$

The fruit area index is calculated by:

$$\text{FAI} = N \times A \times \delta \tag{4}$$

where N is the number of fruits per plant (–), A is the surface area of a tomato calculated as a sphere surface (m^2) and δ is the plant density per unit area (m^{-2}).

2.1.2. Concentration in fruit

The decline of pesticide concentration with time is often described according to first-order kinetics (Beulke and Brown, 2001) and can be written as:

$$C_{\text{tomato}}(t) = C_0 \times \mathrm{e}^{-k_{\text{r}} \times t} \tag{5}$$

where $C_{\text{tomato}}(t)$ is the concentration at time t (mg kg^{-1}), C_0 is the concentration at time zero (mg kg^{-1}) and k_{r} is the removal rate (days^{-1}). The concentration at time zero (C_0) can be written as:

$$C_0 = \frac{f_{\text{fruit}} \times M_{\text{applied}}}{M_{\text{fruit}}} \tag{6}$$

where f_{fruit} is the fruit fraction (–), M_{applied} is the mass of active ingredient applied in the greenhouse (kg m^{-2}) and M_{fruit} is the mass of fruits at the time of application (kg m^{-2}). The removal rate k_{r} is the sum of the degradation rate (k_{d}), the growth rate (k_{g}) and the loss by volatilization (k_{v}) and is given by:

$$k_{\text{r}} = k_{\text{d}} + k_{\text{g}} + k_{\text{v}} \tag{7}$$

Pesticide concentration in the peeled tomato can be described as a cascade of two compartments with transport from the spray deposition on the cuticle to the inner part of the plant. The reverse transfer (translocation of pesticide out of the plant) can be neglected due to the rapidity of the transfer. The concentration of a pesticide as a function of time in a peeled tomato can be described as:

$$C_{\text{peeled tomato}}(t) = \frac{C_0 \times k_{\text{d-c}}}{k_{\text{r,in}} - k_{\text{r,out}}} \times (\mathrm{e}^{-k_{\text{r,out}} \times t} - \mathrm{e}^{-k_{\text{r,in}} \times t}) \tag{8}$$

In the case that the removal rates inside ($k_{\text{r,in}}$) and outside ($k_{\text{r,out}}$) of the plant are equal, the concentration in peeled fruits as a function of time can be approximated by:

$$C_{\text{peeled tomato}}(t) \approx C_0 \times k_{\text{d-c}} \times t \times \mathrm{e}^{-k_{\text{r}} \times t} \tag{9}$$

In order to calculate the pesticide concentration in a peeled tomato, the transfer and permeability properties of agrochemicals through plant cuticles are required. The plant cuticle is an extracellular lipophilic biopolymer covering leaf and fruit surfaces. Its main function is the protection from uncontrolled water loss (Schreiber, 2005). In agriculture, plant cuticles often represent the major barrier for pesticides sprayed on the leaf surface. The permeation through the cuticle depends on the solute mobility in the limiting skin, the path length of the limiting skin and the partition coefficient between the cuticle and the deposited surface residue (Baur et al., 1997, 1999; Schönherr et al., 1999). The transfer rate between pesticide spray deposit and the cuticle ($k_{\text{d-c}}$) can be described as:

$$k_{\text{d-c}} = k^* \times K_{\text{cw}} \tag{10}$$

where k^* is the solute mobility in plant cuticles (day^{-1}) and K_{cw} the cuticle-water partition coefficient. Schreiber (2005) describes a linear relationship between the molecular weight (MW) of a solute and its solute mobility in plant cuticles (k^*) which can be written as:

$$\log k^* = -0.011 \times \text{MW} - 2.46 \tag{11}$$

The partition coefficient between cuticle and surface residue (K_{cw}) can be calculated from the octanol-water partition