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Uptake and persistence of pesticides in plants: Measurements and model estimates for imidacloprid after foliar and soil application

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ABSTRACT

The uptake and persistence behaviour of the insecticide imidacloprid in tomato plants treated by (i) foliar spray application and (ii) soil irrigation was studied using two plant uptake models. In addition to a pesticide deposition model, a dynamic root uptake and translocation model was developed, and both models predict residual concentrations of pesticides in or on fruits. The model results were experimentally validated. The fraction of imidacloprid ingested by the human population is on average 10^{-2} to 10^{-6}, depending on the time between pesticide application and ingestion, the processing step, and the application method. Model and experimentally derived intake fractions deviated by less than a factor of 2 for both application techniques. Total imidacloprid residues were up to five times higher in plants treated by foliar spray application than by soil irrigation. However, peeling tomatoes treated by spray application reduces the human intake fraction by up to three orders of magnitude. Model calculations suggest that drip-irrigation in a closed hydroponic system minimizes worker and consumer exposure to pesticides and prevents runoff of pesticide by spray drift and leaching into the environment.

1. Introduction

Uptake, translocation and persistence of pesticides in plants may lead to high toxic substance levels that are a hazard to human health and ecosystems, and there is considerable research interest in the prediction of these residues amounts [1]. The transfer of organic chemicals into plants occurs via two major pathways: (i) desorption from soil followed by root uptake from soil solution and (ii) transfer from air through dry and wet deposition of particles on plant surfaces, followed by desorption into the inner parts of the plant [2]. Studies describing the transfer of pesticides into plants are important for the development and validation of plant uptake models allowing the prediction of contaminant accumulation, translocation and transformation in edible parts of plants, which represent the main entry of pesticides into the food chain.

Experiments designed to measure plant uptake and translocation under controlled environmental conditions provide insight and information enabling the development of mathematical plant uptake models. The prediction of pesticide uptake was first reported by Shone and Wood [3] who described a relationship between the concentration of pesticides in roots and external solution (soil water), the RCF (root concentration factor). They furthermore established a relationship between the translocation (concentration in xylem sap) and the external solution of pesticides, the TSCF (transpiration stream concentration factor). Briggs et al. [4] followed by correlating the RCF and TSCF to the lipophilicity of pesticides.

Based on these studies, several uptake models have already been developed for fate and exposure assessment of pesticides and other organic chemicals in plants [5–15]. Although these models have successfully demonstrated the most probable distribution pathways of pesticides in plants, none of the listed models was directly applicable for the simulation of dynamic root uptake and translocation of imidacloprid into tomato fruits treated by soil application (local drip-irrigation). Imidacloprid (CAS# 138261-41-3) is a broad-spectrum neonicotinoid systemic insecticide recommended for different crops for the control of various sucking pests [16]. It can be applied by both foliar spray application and in soil application [17], and was used in this case study for the comparison of both application techniques and for the validation of the developed root uptake model for tomato fruits.

For the development and improvement of modern pest management and fate and exposure assessment of pesticides in edible crops, a new approach is needed in order to have a better understanding of the overall impact of pesticides on human health when the same active ingredient is applied to crops by different application techniques. The present paper addresses these needs, aiming

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at the following specific goals:

- To measure the uptake, translocation and persistence behaviour of imidacloprid in tomato fruits treated by (i) standard foliar spray application and (ii) soil application using direct localised drip-irrigation into root zone.
- To develop a dynamic root uptake model for pesticides aiming at the estimation of time dependent contaminant concentrations in fruits (edible part of tomato crops).
- To compare the experimental results with model estimates in terms of human population intake fractions of imidacloprid due to the consumption of tomatoes and to compare those with indirect exposure pathways like air inhalation and consumption of drinking water.

2. Materials and methods

2.1. Root uptake and translocation model

The processes involved in the uptake and distribution of pesticides from soil into roots, stem and fruits are described in the following sections. Specific model input parameters are presented in Table 1.

2.1.1. Concentration in soil solution

The time dependent concentration of pesticide in the soil solution is given by the initial concentration of active ingredient in the irrigation solution which is prepared before irrigation and the removal rate of the pesticide in soil media [18], and can be described as a first order equation:

$$C_{\text{soil solution}}(t) = C_0 e^{-k_{\text{r,soil}} t} \quad (1)$$

where $C_{\text{soil solution}}(t)$ is the pesticide concentration at time t (mg kg^{-1}), C_0 the initial concentration at time zero (mg kg^{-1}) and $k_{\text{r,soil}}$ is the removal rate of the pesticide in the soil media (day^{-1}).

2.1.2. Concentration in roots

The uptake of pesticides from soil solution into roots depends on the properties of the chemicals and of the plant [9]. The main processes considered are advective uptake with transpiration and diffusion. The concentration in plant roots can be described as a cascade of two compartments with transport from the soil solution to the inner part of the plant. The time dependent concentration of pesticide in roots can be described as:

$$C_{\text{roots}}(t) = \frac{C_{\text{soil}}(t) k_{\text{soil-root}}}{\sum k_{\text{r,roots}}} (1 - e^{-\sum k_{\text{r,roots}} t}) \quad (2)$$

where $C_{\text{roots}}(t)$ is the root pesticide concentration at time t (mg kg^{-1}), $C_{\text{soil}}(t)$ the time dependent concentration (mg kg^{-1}) in the soil solution, $k_{\text{r,roots}}$ the removal rate of the pesticide in the roots (day^{-1}), and $k_{\text{soil-root}}$ is the transfer rate between soil solution and roots (day^{-1}). Methodological developments for the transport of pesticides from soil to roots were described by Trapp and Matthies [6] and Charles [13]. The concentration ratio between xylem sap and soil solution, the transpiration stream concentration factor, corresponds to the fraction of substance that enters the xylem. Consequently, the fraction of pesticide that enters the plant with the transpiration stream but is reflected back by the endodermis is considered to remain in the roots. According to this assumption, the transfer rate from soil solution to the roots ($k_{\text{soil-root}}$) can be written as:

$$k_{\text{soil-root}} = \frac{Q_{\text{w}}(1 - \text{TSCF})}{V_{\text{s}} K_{\text{sw}}} \quad (3)$$

where Q_{w} is the plant transpiration stream (m^3 day^{-1}), V_{s} the volume of soil (m^{-3}), TSCF the transpiration stream concentration factor and K_{sw} is the partition coefficient between bulk soil and soil water. The TSCF accounts for the reduction in concentration of active ingredient in the pore water as it crosses the root membrane and moves through the xylem to the stem. Burken and Schnoor [19] proposed the following TSCF correlation based on the octanol/water partition coefficient (K_{ow}):

$$\text{TSCF} = 0.756 \ \exp\left[-\frac{(\log K_{\text{ow}} - 2.50)^2}{2.58}\right] \quad (4)$$

The availability of a pesticide in soil water solution is given by the partition coefficient between bulk soil and soil water (K_{sw}) [13]. It considers the different fractions composing the bulk soil, the matrix, the solution, the gas fractions and the equilibrium between the different phases [6] and can be written as:

$$K_{\text{sw}} = P_{\text{w}} + K_{\text{aw}}(P_{\text{a}} - P_{\text{w}}) + (OC\, K_{\text{oc}}) \frac{\rho_{\text{bs}}}{\rho_{\text{w}}} \quad (5)$$

where P_{w} and P_{a} are the volume fractions of water and air in soil (l l^{-1}), K_{aw} is the partition coefficient between air and water (dimensionless Henry's Law constant), OC the fraction of organic carbon (kg kg^{-1}), ρ_{bs} and ρ_{w} are the densities of dry soil and water (kg m^{-3}) and K_{oc} is the partition coefficient between organic carbon and water which was described by Sabljic et al. [20] and can be written as:

$$\log K_{\text{oc}} = 0.81 \log K_{\text{ow}} + 0.1 \quad (6)$$

2.1.3. Concentration in stem

Water and solutes are transported upward from the roots into other plant parts through the xylem [2]. This flux is driven by the water potential gradient, created throughout the plant during transpiration. It is a combination of the solubility of the pesticide in water and within the cell membrane that determines the translocation of the contaminant to the upper parts of the plant [9]. The concentration of pesticide residue in the stem as a function of time can be described as:

$$C_{\text{stem}}(t) = \frac{C_{\text{roots}}(t)\ k_{\text{roots-stem}}}{\sum k_{\text{r,stem}}} (1 - e^{-\sum k_{\text{r,stem}} t}) \quad (7)$$

where $C_{\text{stem}}(t)$ is the pesticide concentration in the stem at time t (mg kg^{-1}), $C_{\text{roots}}(t)$ the time dependent concentration (mg kg^{-1}) in the roots, $k_{\text{r,stem}}$ the removal rate of the pesticide in the stem

Table 1
Model input parameters.

Input parameter			Unit
Correction plant lipids/octanol	b	0.9	–
Density of dry soil	ρ_{bs}	1.5	kg l^{-1}
Density of plant	ρ_{r}	0.9	kg l^{-1}
Density of water	ρ_{w}	1	kg l^{-1}
Dimensionless Henry's law constant	K_{aw}	3.84E−08	–
Fraction of air in soil	P_{a}	0.1	–
Fraction of organic carbon	OC	0.02	kg kg^{-1}
Fraction of water in soil	P_{w}	0.3	–
Lipid weight fraction in plant	$P_{\text{r,l}}$	0.025	kg kg^{-1}
Mass of fruits	M_{f}	0.96	kg/plant
Mass of roots	M_{r}	0.2	kg/plant
Mass of soil	M_{s}	0.22	kg/plant
Mass of stem	M_{st}	0.56	kg/plant
Octanol/water partition coefficient	K_{ow}	3.71	–
Plant transpiration stream	Q_{w}	2.4	l/day plant
Water weight fraction in fruits	$P_{\text{r,w}}$	0.87	kg kg^{-1}
Water weight fraction in root	$P_{\text{r,w}}$	0.16	kg kg^{-1}
Water weight fraction in stem	$P_{\text{r,w}}$	0.13	kg kg^{-1}

(day^{-1}) and $k_{root-stem}$ is the transfer rate between the roots and the stem (day^{-1}), which can be written as:

$$k_{root\text{-}stem} = \frac{Q_w}{V_r K_{rw}} \quad (8)$$

where Q_w is the plant transpiration stream ($m^3\ day^{-1}$), V_r the root volume (m^{-3}) and K_{rw} is the partition coefficient between roots and water. Partitioning of water with roots is characterized by the lipophilic behaviour of the substance and by the composition of the plant tissue [9,13] and can be described as:

$$K_{rw} = (P_{r,w} + P_{r,l}\ K_{ow}^{b})\frac{\rho_r}{\rho_w} \quad (9)$$

where $P_{r,w}$ and $P_{r,l}$ are the water and lipid weight fraction of the root ($kg\,kg^{-1}$), K_{ow} the octanol/water partition coefficient, b an empirical constant to correct differences between plant lipids and octanol and ρ_r and ρ_w are the densities of roots and water ($kg\,m^{-3}$).

2.1.4. Concentration in fruits

The main routes for water and nutrition transport into sink organs such as fruits are xylem and phloem. Phloem translocation from leaves to sink organs is driven by the pressure flow of sap which is regulated by long distance transport in the plant and post-phloem transport in sink organs [21]. Respiration of fruits closely relates to the phloem sap flux which is responsible for the growth of the fruit [22]. The concentration of pesticide in fruits can be written as:

$$C_{fruit}(t) = \frac{C_{stem}(t)\ k_{stem-fruit}}{\sum k_{r,fruit}}(1 - e^{-\sum k_{r,fruit}\cdot t}) \quad (10)$$

where $C_{fruit}(t)$ is the pesticide concentration in the fruits at time t ($mg\,kg^{-1}$), $C_{stem}(t)$ the time dependent pesticide concentration ($mg\,kg^{-1}$) in the stem, $k_{r,fruit}$ the removal rate of the pesticide in the fruits (day^{-1}) and $k_{stem-fruit}$ is the transfer rate between the stem and the fruits (day^{-1}) which can be written as:

$$k_{stem-fruit} = \frac{Q_w}{V_{st} K_{stw}} \quad (11)$$

where Q_w is the plant transpiration stream ($m^3\ day^{-1}$), V_{st} the volume of the stem (m^{-3}) and K_{stw} is the partition coefficient between the stem and water. Similar to the partitioning of water with root tissue, the partitioning between stem and fruit is characterized by the lipophilic behaviour of the substance and by the composition of the plant specific tissue and can be approximated by:

$$K_{stw} = (P_{st,w} + P_{st,l} K_{ow}^{b})\frac{\rho_{st}}{\rho_w} \quad (12)$$

where $P_{st,w}$ and $P_{st,l}$ are the water and lipid weight fraction of the stem ($kg\,kg^{-1}$), K_{ow} is the octanol/water partition coefficient, b an empirical constant to correct differences between plant lipids and octanol and ρ_{st} and ρ_w are the densities of stem tissue and water ($kg\,m^{-3}$).

2.2. Spray deposition model

Pesticide concentrations on and within plants treated by foliar spray application were estimated using the pesticide fate and exposure model described by Juraske et al. [14], which allows one to calculate the concentration of a pesticide as a function of time between application and harvest. The model takes the time between harvest and consumption, absorption of pesticide spray deposit on plant surfaces, transfer properties through the cuticle, degradation of active ingredient on and inside the plant and loss of pesticide due to food processing like washing and peeling into account. Degradation rates of pesticides in/on plants were used according to the extrapolation routines described by Juraske et al. [23] in which degradation rates in/on vegetation can be calculated from more abundant ready degradation rate data for soil.

2.3. Human intake fraction

The intake fraction (iF) is described as the fraction of mass of chemical released into the environment that is ultimately taken in by the human population [24,25]. In this case study, the intake fraction is expressed in kg intake due to tomato consumption per kg of pesticide applied in the greenhouse ($kg_{ingested}\ kg_{applied}^{-1}$). The estimation of dynamic human intake fractions of imidacloprid was conducted using the pesticide fate and exposure model described by Juraske et al. [14].

2.4. Experimental procedures

2.4.1. Design of the field trials

In order to compare measured and estimated pesticide residue levels, and to compare the uptake and persistence of imidacloprid in tomato fruits treated by (i) foliar spray application of tomato plants cultivated in soil and (ii) soil chemigation using drip-irrigation of hydroponically grown tomatoes, two field trials were carried out in two similar greenhouses located in the Institut de Recerca i Tecnologia Agroalimentària, Cabrils (Barcelona).

2.4.2. Spray application on tomato plants cultivated in soil

Tomato plants, cultivar *Caramba*, were cultivated in a spring–summer cycle with a density of 2.2 plants m^{-2} and a total yield of 16 $kg\,m^{-2}$ of tomato fruits. The treatment was carried out using a portable motor sprayer equipped with a gun nozzle using the following commercial formulation: (Confidor®20 LS; 20% of imidacloprid p/v (200 $g\,l^{-1}$); soluble concentrate; Bayer CropScience) on June 6, 2006. Spraying was carried out at the recommended concentration of 0.15 g a.i. l^{-1} and a total consumption of 0.3 l m^{-2}. The leaf area index was measured as 2.46. The weight of fruits at the day of application was 2.4 $kg\,m^{-2}$. Fruits ($n = 15$) were sampled before and 1 h after the treatment and again after 1, 3, 7, 14, 21 and 28 days.

2.4.3. Soil chemigation of hydroponically grown tomato plants

The cultivation of hydroponic tomato plants, cultivar *Caramba*, was carried out in bags of perlite with localised watering and a total yield of 26 $kg\,m^{-2}$ of tomato fruits. Water was delivered to each plant by a drip-irrigation stake that delivered water at a rate of 4 l h^{-1} directly into the root zone. Imidacloprid (Confidor®20 LS; 20% of imidacloprid p/v (200 $g\,l^{-1}$); soluble concentrate; Bayer CropScience) was applied by chemigation, utilizing a drip-irrigation system on June 6, 2006. Chemigation was carried out at the recommended dose of 600 g a.i. ha^{-1} by adding the active ingredient directly into the watering system. A total consumption of 0.8 l of irrigation solution was applied to each plant. Fruits ($n = 15$) were sampled before and directly after the treatment and again after 1, 3, 7, 14, 21 and 28 days.

2.4.4. Analytical method

The analysis of imidacloprid residues was carried out by adapting analytical methods described by Fernandez-Alba et al. [26] and Obana et al. [27], both used in the determination of imidacloprid in tomato plants.

Whole tomatoes ($n = 5$) were homogenized in a waring blender. Twenty grams of homogenized tomatoes were extracted with acetonitrile (100 ml) for 2 min with an Ultra-Turrax® T18-basic disperser (IKA®, Staufen, Germany). The extract, with a paper filtration, was transferred to a 200-mL separatory funnel. Sodium

chloride (5 g) was added, and the solution was shaken for 1 min to salt out the water layer. An aliquot of the extract (50 ml) was collected. Ten millilitres of the organic extract layer was evaporated to dryness using a gentle nitrogen stream, and the residue was dissolved in acetonitrile (5 ml). This final solution was filtered through a polytetrafluorethylene (PTFE) membrane filter disc (0.45 μm) attached to the end of a syringe (10 ml) ready for HPLC (triplicate) analysis. The same procedures described above were used for the sample preparation of tap water washed and peeled tomato fruits. In order to avoid contamination from the deposition residue on the outer side of the cuticle, all tomato samples were washed before peeling.

In order to evaluate the efficiency of the analytical procedures, a recovery assay was conducted. Samples of untreated tomato fruits were spiked with 2, 1, 0.5 and 0.1 mg l^{-1} of imidacloprid standard solution and processed according to the extraction procedure four times. The recovery assay yielded good recoveries in the extraction process, from 84 to 96% with a maximum standard deviation of 9%. These levels can be considered as satisfactory for residue determinations of imidacloprid and are comparable to results reported by Obana et al. [27] and Blasco et al. [28]. Coefficient of determination (r^2) in the range of 0.1–2 mg l^{-1} was 0.997 ($n = 5$). In order to determine the amount of pesticide removed from the fruit due to home processing, tomato fruits were washed with cold (21 °C) tap water. The water used for washing in all processing steps was tap water without detergents.

2.4.5. Apparatus and chemicals

High-performance liquid chromatography (HPLC) analysis was carried out using an Agilent Technologies 1100 Series (Santa Clara, CA, USA) analytical system, equipped with a photodiode-array detector. HPLC separation was conducted using a Hypersil ODS-C18 (5 μm particle size) column (4.6 × 250 mm ID) (Agilent Technologies, Santa Clara, CA, USA) and the temperature was maintained at ambient (23 °C). The isocratic mobile phase was acetonitrile/water (30:70 v/v) at a flow rate of 1 ml min^{-1}. The sample size was 20 μl and the detector was set at 270 nm. Acetonitrile was a HPLC grade solvent (Riedel de Haën, Seelze, Germany). Imidacloprid standard solution (100 mg l^{-1}) was purchased from LGC Promochem, Barcelona, Spain.

3. Results and discussion

3.1. Foliar spray application

Pesticide residue concentrations in whole tomato fruits obtained in the dissipation study of imidacloprid after spray application and the corresponding first-order decay fit are presented in Fig. 1.

Average residue concentrations of imidacloprid on tomato fruits ranged from 1.60 mg kg^{-1} at day 0 to 0.18 mg kg^{-1} 28 days after the spray application with a coefficient of variation of 6%. The degradation kinetics of imidacloprid deposits were well described by a first-order decay equation ($C(t) = 1.5e^{-0.085t}$; $r^2 = 0.97$). According to our experimental results, the half-life of imidacloprid is 8.2 days if applied on tomato fruits. Imidacloprid half-lives on plant surfaces found in the literature ranged from 3 days [29] up to 32 days [30]. The value reported in this study lies within the range of experimental values found in the literature. However, experimental half-life values of imidacloprid on plants show large variation. This could be explained by the fact that half-lives were measured on different kinds of crops with different plant surface properties and that the experiments were conducted under different environmental conditions (temperature, relative humidity and UV irradiation). The

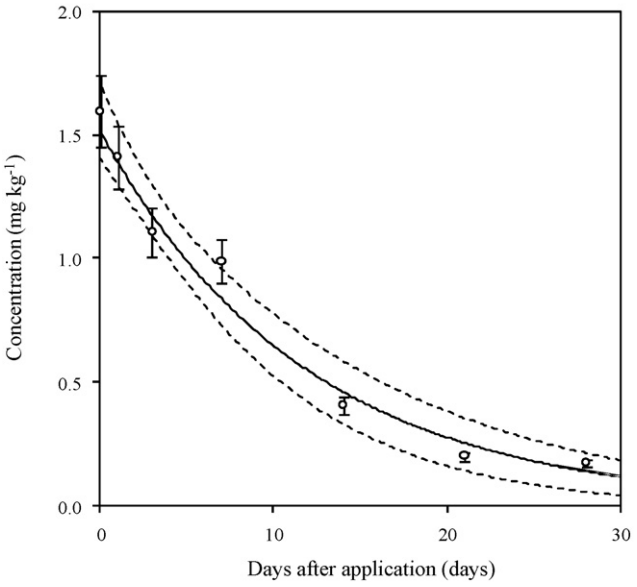

Fig. 1. Dissipation of measured mean imidacloprid residues (○, ±S.E.) from tomato fruits treated by foliar spray application, first-order decay fit (—) and 95% confidence intervals (- -).

concentrations of imidacloprid on tomato fruits calculated by the spray deposition model deviated between 2 and 27% from the field experiment results. A mean error of 12% was observed between experimental results and model estimates during the complete dissipation study (28 days).

Imidacloprid residues were not detectable in peeled tomatoes collected throughout the whole field experiment. The maximum concentration of imidacloprid in peeled tomato fruits estimated by the model was 0.001 mg kg^{-1} (day 6 after the spray application), a concentration which lies approximately 100 times under the detection limit of the experimental setup. However, measurements and model estimates indicate that imidacloprid from spray deposition on the plant surface does not tend to cross through the cuticle of tomato fruits and suggest a low potential for bioaccumulation. This can be clarified by the fact that each agrochemical has specific transfer and permeability properties to cross through plant cuticles. The permeation through plant cuticles depends on the solute mobility in the limiting skin, the path length of the limiting skin and the partition coefficient between cuticle and deposited surface residue [1,31]. The latter is directly related to the octanol/water partition coefficient (K_{ow}), which is a key parameter in the studies of the environmental fate of chemical substances. It is a useful parameter in the prediction of adsorption behaviour of pesticides. Nemeth-Konda et al. [32] reported log K_{ow} values between 0.56 and 0.92, relatively low values suggesting a low hydrophobicity of imidaloprid. The low octanol/water partition coefficient furthermore indicates low adsorption behaviour of the active ingredient into organic matter. Nauen et al. [17] and Buchholz and Nauen [33] reported that imidacloprid can be penetrated through plant cuticles via diffusion, but in contrary to our experiments, the active ingredient was applied using surfactants or emulsifiers (leaf wetting agents) favouring penetration. However, the main portion of imidacloprid applied to the plants resided on the surface or in the epicuticular waxes of the cuticle.

Food processing studies provide basic information on the reduced levels of residues in passing from the raw agricultural commodity to a processed commodity. The processing factor can be described as the residue level in the processed product divided

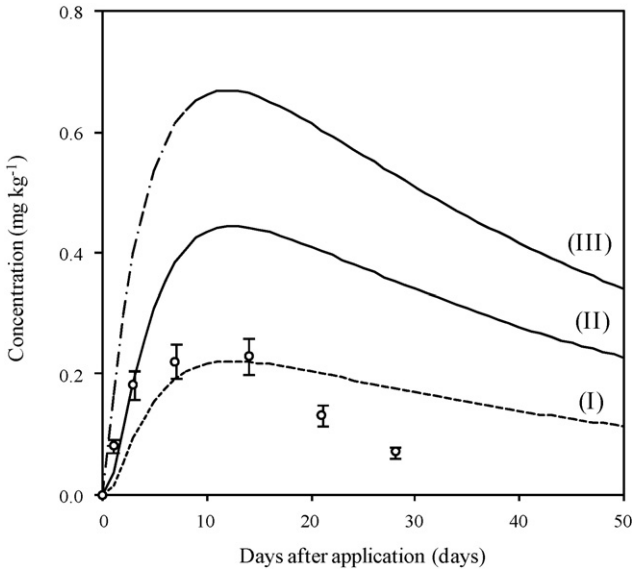

Fig. 2. Measured (◯, ±S.E.) and modelled imidacloprid concentrations in tomato fruits (I), stem (II) and roots (III) treated by soil chemigation.

by the residue level in the raw agricultural commodity. Imidacloprid concentrations on tomatoes were reduced by 22% when washed in cold tap water (21 °C). From these results an experimental tap water washing processing factor of 0.78 can be estimated for imidacloprid. Processing factors for imidacloprid reported in the literature vary between 1 (0% of imidacloprid removed from cherries) reported by Spiegel and Neigl [34] and 0.25 (75% of imidacloprid removed from grapes) reported by Spiegel [35]. The value reported in this study lies within the experimental values found in the literature. However, the experimental processing factors for imidacloprid show large variation when applied to different types of crops. Generally it can be concluded that washing tomato fruits with tap water can substantially reduce pesticide residues and that including food processing factors is of importance for human intake fraction estimates of pesticides.

3.2. Root uptake and translocation after chemigation

Pesticide residue concentrations in whole tomato fruits obtained in the dissipation study of imidacloprid after direct soil chemigation and the corresponding estimates calculated using the root uptake and translocation model are presented in Fig. 2.

Imidacloprid was not detectable in tomato fruits collected directly after chemigation (Fig. 2). The same result was obtained using the root uptake model. According to model estimates, no imidacloprid residues are to be found in roots and stem directly after chemigation. For chemicals taken into roots to reach the xylem, they must penetrate a number of layers: the epidermis, cortex, endodermis, and pericycle [1,2]. At the endodermis all materials must pass through at least one cell membrane. An immediate uptake of active ingredient directly after irrigation is therefore not expected.

The maximum residue in tomato fruits (0.23 mg kg^{-1}) was detected 14 days after chemigation. Maximum imidacloprid concentration in tomato fruits predicted by the root uptake model was 0.22 mg kg^{-1} for day 13 after the pesticide was applied. Measurements and model estimates for imidacloprid concentrations in tomato fruits correspond well from the day of application until day 14 after chemigation. For the rest of the experiment, model calculations overestimated the measured values by a factor of two. A mean error of 22% was observed between experimental results and model estimates during the complete uptake and translocation study (28 days). An underestimation of the metabolism rate of imidacloprid in fruits used in the model compared to field conditions may be one explanation for this result.

Estimated imidacloprid concentrations in roots were the highest throughout the whole experiment compared with concentrations in stem and fruits. Slower degradation of imidacloprid in soil compared to metabolism in plant tissue [17,18] and the fact that a fraction of active ingredient is reflected back by the endodermis and remains in the roots [9] are the main factors leading to higher concentrations in roots.

Imidacloprid concentrations in whole tomato fruits measured after foliar spray application were higher than those detected in whole fruits treated by soil application throughout the entire dissipation study. Assuming that the typical time of tomato consumption is between day 7 and 21 after the pesticide application, imidacloprid concentrations in fruits after spray application exceeded those in fruit after soil application by up to a factor of five indicating that the use of drip-irrigation systems for the application of systemic pesticides would have advantages over spray applications. It would minimize worker and consumer exposure to the pesticide, result in a uniform application, and prevent runoff of pesticide by spray drift into the environment. A comparative field study of the systemic efficacy of imidacloprid against whiteflies conducted by Buchholz and Nauen [33] revealed that the active ingredient was more effective after soil application as compared with foliar application. van Iersel et al. [36] reported that the control of whiteflies was better after subirrigation than on hand-watered plants that received a drench application of imidacloprid. These results demonstrate that soil application of imidacloprid is a viable alternative to the standard spray application not only in terms of human and ecosystem health but also in terms of pest control quality. However, peeled tomatoes treated by spray application show lower concentrations of active ingredient compared to tomatoes treated by drip-irrigation. From these results a possible advantage for spray application can be drawn as peeling tomatoes treated by drip-irrigation would not minimize residual concentrations of pesticides.

3.3. Comparison of measured and estimated human intake fractions

Measured and modelled time dependent intake fractions of imidacloprid for (i) unwashed, (ii) washed and (iii) washed and peeled tomatoes, representing the fraction of pesticide applied in the greenhouse that eventually passes into the human population through direct ingestion of fruits, are presented in Table 2. The intake fraction for unwashed tomatoes varies between 10^{-2} and 10^{-3} ($kg_{ingested}\ kg^{-1}_{applied}$) for both application techniques, depending on the time of consumption. The intake fraction for washed tomatoes treated by spray application ranges between 10^{-2} and 10^{-3} ($kg_{ingested}\ kg^{-1}_{applied}$), while the intake fraction for washed and peeled tomatoes varies between 10^{-5} and 10^{-6} ($kg_{ingested}\ kg^{-1}_{applied}$).

In order to compare intake fractions from direct ingestion of tomato fruits to those deriving from air inhalation and the consumption of drinking water, the commonly used multi-media fate, exposure and effect model USES-LCA 2.0 [25] was applied. Intake fraction for imidacloprid due to air inhalation and drinking water consumption varies between 10^{-5} and 10^{-9} ($kg_{ingested}\ kg^{-1}_{applied}$). Intake fractions due to air inhalation and consumption of drinking water are expected to be significantly lower (up to six orders of magnitude) than those for the intake of tomatoes in this case study. These results are consistent with those presented by Margni et al.

Table 2
Time dependent human population intake fractions ($kg_{ingested}\ kg^{-1}_{applied}$).

	Days after application						
	0	1	3	7	14	21	28
Foliar spray application							
iF (unwashed)							
Measured	8×10^{-2}	7×10^{-2}	6×10^{-2}	5×10^{-2}	2×10^{-2}	1×10^{-2}	9×10^{-3}
Modelled	8×10^{-2}	7×10^{-2}	6×10^{-2}	4×10^{-2}	2×10^{-2}	1×10^{-2}	7×10^{-3}
iF (washed)							
Measured	6×10^{-2}	6×10^{-2}	4×10^{-2}	4×10^{-2}	2×10^{-2}	8×10^{-3}	7×10^{-3}
Modelled	6×10^{-2}	5×10^{-2}	5×10^{-2}	3×10^{-2}	2×10^{-2}	1×10^{-2}	6×10^{-3}
iF (peeled)							
Measured	nd	nd	nd	nd	nd	nd	nd
Modelled	0	3×10^{-5}	7×10^{-5}	7×10^{-5}	4×10^{-5}	$2 \times \times 10^{-5}$	4×10^{-6}
Soil application							
iF (unwashed)							
Measured	nd	4×10^{-3}	9×10^{-3}	1×10^{-2}	1×10^{-2}	7×10^{-3}	4×10^{-3}
Modelled	0	4×10^{-3}	9×10^{-3}	1×10^{-2}	1×10^{-2}	9×10^{-3}	8×10^{-3}

nd: not detectable.

[37] and Juraske et al. [14] and confirm the potential importance of intake of pesticides by ingestion of food as a direct route into the human population.

4. Conclusions

From this study it can be concluded that the human population intake fraction of imidacloprid is typically 10^{-2} to 10^{-6} ($kg_{ingested}\ kg^{-1}_{applied}$). Ingestion of food (e.g. tomatoes) was shown to be the dominant intake pathway of imidacloprid compared with consumption of drinking water and air inhalation. Model calculations and measurements corresponded well. Deviation in less than a factor of two for both pesticide application methods (foliar spray and soil irrigation) was observed. Furthermore, it has been demonstrated that a selection of the most appropriate pesticide application method and most effective post harvest food processing technique can minimize the human intake fraction of imidacloprid due to tomato consumption by up to three orders of magnitude. Washing eatable parts of crops with water can contribute significantly to the reduction of pesticide residues and thus substantially reduce the human intake fraction. Washing the final agricultural product directly after harvest could furthermore reduce intake fractions as residues on plant surfaces which potentially tend to move into the plant would be removed at the earliest possible date.

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References

[1] S. Trapp, Plant uptake and transport models for neutral and ionic chemicals, Environ. Sci. Pollut. Res. 11 (2004) 33–39.
[2] C. Collins, M. Fryer, A. Grosso, Plant uptake of non-ionic organic chemicals, Environ. Sci. Technol. 40 (2006) 45–52.
[3] M.G.T. Shone, A.V. Wood, Comparison of uptake and translocation of some organic herbicides and a systemic fungicide by barley.1. Absorption in relation to physicochemical properties, J. Exp. Bot. 25 (1974) 390–400.
[4] G.G. Briggs, R.H. Bromilow, A.A. Evans, Relationships between lipophilicity and root uptake and translocation of non-ionized chemicals by barley, Pestic. Sci. 13 (1982) 495–504.
[5] S. Trapp, L. Pussemier, Model calculations and measurements of uptake and translocation of carbamates by bean plants, Chemosphere 22 (1991) 327–339.
[6] S. Trapp, M. Matthies, Generic one-compartment model for uptake of organic chemicals by foliar vegetation, Environ. Sci. Technol. (1995) 2333–2338.
[7] H. Hung, D. Mackay, A novel and simple model of the uptake of organic chemicals by vegetation from air and soil, Chemosphere 35 (1997) 959–977.
[8] M. Severinsen, T. Jager, Modelling the influence of terrestrial vegetation on the environmental fate of xenobiotics, Chemosphere 37 (1998) 41–62.
[9] S. Trapp, Modelling uptake into roots and subsequent translocation of neutral and ionisable organic compounds, Pest Manag. Sci. 56 (2000) 767–778.
[10] T. Fujisawa, K. Ichise, M. Fukushima, T. Katagi, Y. Takimoto, Improved uptake models of nonionized pesticides to foliage and seed of crops, J. Agric. Food Chem. 50 (2002) 532–537.
[11] S. Trapp, D. Rasmussen, L. Samsoe-Petersen, Fruit tree model for uptake of organic compounds from soil, SAR QSAR Environ. Res. 14 (2003) 17–26.
[12] A. Antón, F. Castells, J.I. Montero, M. Huijbregts, Comparison of toxicological impacts of integrated and chemical pest management in Mediterranean greenhouses, Chemosphere 54 (2004) 1225–1235.
[13] R. Charles, Modelling Pesticides Residues, Doctoral Thesis, Swiss Federal Institute of Technology (EPFL), 2004.
[14] R. Juraske, A. Anton, F. Castells, M.A.J. Huijbregts, Human intake fractions of pesticides via greenhouse tomato consumption: comparing model estimates with measurements for Captan, Chemosphere 67 (2007) 1102–1107.
[15] T.E. McKone, R.L. Maddalena, Plant uptake of organic pollutants from soil: bioconcentration estimates based on models and experiments, Environ. Toxicol. Chem. 26 (2007) 2494–2504.
[16] F.J. Byrne, N.C. Toscano, Uptake and persistence of imidacloprid in grapevines treated by chemigation, Crop Prot. 25 (2006) 831–834.
[17] R. Nauen, U. Reckmann, S. Armborst, H.P. Stupp, A. Elbert, Whitefly-active metabolites of imidacloprid: biological efficacy and translocation in cotton plants, Pestic. Sci. 55 (1999) 265–271.
[18] M.A. Sarkar, S. Roy, R.K. Kole, A. Chowdhury, Persistence and metabolism of imidacloprid in different soils of West Bengal, Pest Manag. Sci. 57 (2001) 598–602.
[19] J.G. Burken, J.L. Schnoor, Predictive relationships for uptake of organic contaminants by hybrid poplar trees, Environ. Sci. Technol. 32 (1998) 3379–3385.
[20] A. Sabljic, H. Gusten, H. Verhaar, J. Hermens, QSAR modelling of soil sorption. Improvements and systematics of log KOC vs. log KOW correlations, Chemosphere 31 (1995) 4489–4514.
[21] M. Malone, J. Andrews, The distribution of xylem hydraulic resistance in the fruiting truss of tomato, Plant Cell Environ. 24 (2001) 565–570.
[22] S. Kawabata, H. Sasaki, R. Sakiyama, Role of transpiration from fruits in phloem transport and fruit growth in tomato fruits, Physiol. Plant. 124 (2005) 371–380.
[23] R. Juraske, A. Antón, F. Castells, Estimating half-lives of pesticides in/on vegetation for use in multimedia fate and exposure models, Chemosphere 70 (2008) 1748–1755.
[24] D.H. Bennett, M.D. Margni, T.E. McKone, O. Jolliet, Intake fraction for multimedia pollutants: a tool for life cycle analysis and comparative risk assessment, Risk Anal. 22 (2002) 905–918.
[25] M.A.J. Huijbregts, J. Struijs, M. Goedkoop, R. Heijungs, A. Jan Hendriks, D. Van De Meent, Human population intake fractions and environmental fate factors of toxic pollutants in life cycle impact assessment, Chemosphere 61 (2005) 1495–1504.

[26] A.R. Fernandez-Alba, A. Valverde, A. Aguera, M. Contreras, S. Chiron, Determination of imidacloprid in vegetables by high-performance liquid chromatography with diode-array detection, J. Chromatogr. A 721 (1996) 97–105.
[27] H. Obana, M. Okihashi, K. Akutsu, Y. Kitagawa, S. Hori, Determination of acetamiprid, imidacloprid, and nitenpyram residues in vegetables and fruits by high-performance liquid chromatography with diode-array detection, J. Agric. Food Chem. 50 (2002) 4464–4467.
[28] C. Blasco, M. Fernandez, Y. Pico, G. Font, J. Manes, Simultaneous determination of imidacloprid, carbendazim, methiocarb and hexythiazox in peaches and nectarines by liquid chromatography-mass spectrometry, Anal. Chim. Acta 461 (2002) 109–116.
[29] I. Mukherjee, M. Gopal, Environmental behaviour and translocation of imidacloprid in eggplant, cabbage and mustard, Pest Manag. Sci. 56 (2000) 932–936.
[30] K. Vogeler, T. Clark, A. Brauner, Metabolism of [methylene-14C]-imidacloprid (NTN 33893) in apples, Report No. PF3676 (internal report) Bayer AG, Leverkusen, 1992.
[31] L. Schreiber, Polar paths of diffusion across plant cuticles: new evidence for an old hypothesis, Ann. Bot. 95 (2005) 1069–1073.
[32] L. Nemeth-Konda, G. Fuleky, G. Morovjan, P. Csokan, Sorption behaviour of acetochlor, atrazine, carbendazim, diazinon, imidacloprid and isoproturon on Hungarian agricultural soil, Chemosphere 48 (2002) 545–552.
[33] A. Buchholz, R. Nauen, Translocation and translaminar bioavailability of two neonicotinoid insecticides after foliar application to cabbage and cotton, Pest Manag. Sci. 58 (2002) 10–16.
[34] K. Spiegel, A. Neigl, Determination of residues of imidacloprid on sweet cherry after spray application of Confidor 200 SL in the field in Italy and Spain (fruit, washed fruit, preserve, stoned fruit, washings)-processing study, Report No. RA-3047/99 (internal report), Report No. RA-3047/99, Bayer AG, Leverkusen, 2000.
[35] K. Spiegel, Determination of residues of imidacloprid on grape (bunch of grape, berry, washed berry, juice, washing water, pomace and retentate) after spray application of Confidor 200 SL in the field in Portugal and Italy, Report No. RA-3030/99 (internal report), Bayer AG, Leverkusen, 2001.
[36] M.W. van Iersel, R.D. Oetting, D.B. Hall, Imidacloprid applications by subirrigation for control of silverleaf whitefly (Homoptera: Aleyrodidae) on poinsettia, J. Econ. Entomol. 93 (2000) 813–819.
[37] M. Margni, D. Rossier, P. Crettaz, O. Jolliet, Life cycle impact assessment of pesticides on human health and ecosystems, Agric. Ecosyst. Environ. 93 (2002) 379–392.