Pesticide Uptake in Potatoes: Model and Field Experiments

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A dynamic model for uptake of pesticides in potatoes is presented and evaluated with measurements performed within a field trial in the region of Boyacá, Colombia. The model takes into account the time between pesticide applications and harvest, the time between harvest and consumption, the amount of spray deposition on soil surface, mobility and degradation of pesticide in soil, diffusive uptake and persistence due to crop growth and metabolism in plant material, and loss due to food processing. Food processing steps included were cleaning, washing, storing, and cooking. Pesticide concentrations were measured periodically in soil and potato samples from the beginning of tuber formation until harvest. The model was able to predict the magnitude and temporal profile of the experimentally derived pesticide concentrations well, with all measurements falling within the 90% confidence interval. The fraction of chlorpyrifos applied on the field during plant cultivation that eventually is ingested by the consumer is on average 10^{-4}—10^{-7}, depending on the time between pesticide application and ingestion and the processing step considered.

Introduction

With a global production of 330 million tons in 2009, potato is the fourth most important food crop after maize, wheat, and rice, making it the most important vegetable consumed worldwide (*1*). In some countries, potatoes represent a significant share of the annual diet (e.g., 42 kg per person (*2*) or 21% of the total fruit and vegetable diet in Colombia). At the same time, potato is known to be a crop with high pesticide use. This is especially so in emerging economies, where food quality-control programs have not been established, in particular, not for locally consumed food and where farmers are often not well trained in relation to good agricultural practices. Thus, the risk associated with pesticides may be of greater importance than in developed countries (*3*) and may lead to adverse health and environmental effects (*4*).

One method to evaluate the presence and magnitude of pesticides in agricultural products is pesticide fate and exposure modeling, including mathematical plant uptake models (*5*). Multimedia plant uptake and translocation models are widely used for predicting distribution pathways and residual concentrations of pesticides in plants and may serve as an alternative to expensive and time-consuming field trials and laboratory experiments. Several generic and crop-specific uptake models have already been developed for fate and exposure assessment of pesticides and other organic chemicals in plants (*5*−*15*). Two potato-specific plant uptake models were recently published (*16, 17*). Both models describe the diffusive flow of organic chemicals through potato tissues, enabling the estimation of pesticide bioconcentration factors in potato tubers by using a known pesticide concentration in soil as a starting point. Primary distribution of the pesticide directly after field application and the metabolism of the chemical in plant tissue were not taken into account in both models.

The aim of the present study is 3-fold:

(1) To develop a dynamic plant uptake model that takes all the steps from pesticide application, through primary field distribution (including dynamic plant growth), migration in soil (including tuber depth), and uptake and persistence in potatoes into account, enabling the prediction of time-dependent pesticide concentrations in soil and potatoes along the whole cultivation cycle.

(2) To measure uptake, translocation, and persistence behavior of chlorpyrifos in potatoes treated by a typical foliar spray application.

(3) To compare experimental results with model estimates in terms of human ingestion intake fractions of chlorpyrifos due to the consumption of potatoes in Colombia and evaluate the effects of typical food processing steps, like cleaning, washing, cooking, and storing.

Materials and Methods

Modeling Approach. Potato tubers are not connected to the root system and the transpiration stream; they are part of the stem that is loaded from the leaves via the phloem (*18*). For organic compounds such as pesticides, translocation downward in phloem is negligible, suggesting that the main uptake route for pesticides into potatoes is most likely to occur through the soil compartment (*19*). In order to model dynamic pesticide residues in potato tubers, we account for the following steps: distribution of pesticide directly after foliar spray application (primary distribution), dynamic penetration-depth-dependent pesticide concentrations in bulk soil, available fraction for plant uptake in soil−water, and pesticide uptake and persistence in potato tubers.

Primary Distribution of Pesticide after Spraying. The starting point for modeling dynamic pesticide concentrations in potatoes is the pesticide spray application. After a pesticide is applied, it can be (i) deposited on soil, (ii) deposited on plants, or (iii) removed from the field via wind drift (*20*). The soil deposition fraction needed for the calculation of pesticide concentrations in soil is given by the following equation (*5*):

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$$f_{soil} = e^{-k_p \times LAI} \quad (1)$$

where the pesticide capture coefficient k_p equals 0.35 in the case where the pesticide is applied without surfactants (*5*) and LAI is the one-sided leaf area index ($m^2_{leaves}\ m^{-2}_{soil}$). Time-dependent LAI values for complete cultivation cycles of potato plants were presented in ref *21* and used in this study. When the LAI is not available, an alternative approach using the percentage of ground cover can be used (*22*)

$$LAI = 0.0021C^{1.6133} \quad (2)$$

where C is the dynamic ground cover due to plant interception (%). Interception fractions of potato plants can be found in ref *23*.

Concentrations in Soil. The initial soil concentration in top soil, C_0, is calculated as (*20*)

$$C_0 = \frac{M_{app} f_{soil} \times 10^{-4}\ ha/m^2}{IPD_{soil} \times \rho_s \times 1000\ L/m^3} \quad (3)$$

where M_{app} is the mass of pesticide active ingredient applied per unit area (mg ha^{-1}), IPD_{soil} is the initial soil penetration depth (m), and ρ_s is the soil bulk density (kg L^{-1}).

Time- and Depth-Dependent Soil Concentrations. The principal processes affecting the transport of pesticides from the surface (top soil) to the depth of interest (tuber depth) and the concentrations at which they arrive are advection, dispersion, degradation, and sorption (*24*). Using the concept of convection time, which is based on chromatographic principles and thermodynamic hypothesis of partition among liquid, gaseous, and solid phases in soil, the time necessary for a pesticide to migrate from the surface to the depth of interest can be described by the pesticide travel time t_d (day) (*25*)

$$t_d = \frac{z\theta_{fc} \times RF}{v_e} \quad (4)$$

where z is the soil depth (m), θ_{fc} is the soil−water volumetric content, RF is the retardation factor, and v_e is the infiltration rate of water in soil media (m day^{-1}) (see Table 1). The retardation factor represents the delay of the pesticide leaching with regard to the water flow due to sorption in soil and gaseous and aqueous diffusion in soil. According to this partitioning assumption, a dissolved pesticide that undergoes linear equilibrium adsorption will be retarded with respect to the movement of water by the pesticide retardation factor which can be described as (*25*)

$$RF = 1 + \frac{\rho_s K_{D-pH}}{\theta_{fc}} + \frac{\delta H}{\theta_{fc}} \quad (5)$$

where ρ_s is the soil bulk density (kg L^{-1}), K_{D-pH} is the pH-dependent water−soil pesticide sorption coefficient (L kg^{-1}) calculated according to ref *26*, θ_{fc} is the soil−water volumetric content, δ is the soil−air volumetric fraction, and H is the water−air pesticide partition coefficient (dimensionless Henry's law constant). The time- and profile-depth-dependent soil concentration (mg kg^{-1}) at a certain tuber depth z (m) can finally be described as (*9*)

$$C_z(t) = \frac{C_0 e^{-k_r t} k_{ss-z}}{k_s}(1 - e^{-k_s t}) \quad (6)$$

where k_r is the removal rate in top soil (day^{-1}), which is the sum of the degradation rate in soil and the loss by volatilization; k_s is the degradation rate in soil media (day^{-1}); and $k_{ss\text{-}z}$ (day^{-1}) is the transfer rate constant between soil surface and the tuber depth z calculated as t_d^{-1}.

Concentration in Soil−Water. The mass transfer of organic contaminants through the potato peel was shown to occur predominantly from the soil solution (*17*). The time-dependent pesticide concentration in soil solution $C_w(t)$ can be estimated from the concentration in bulk soil and is given by (*16*)

$$C_w(t) = \frac{\rho_w C_z(t)}{(\rho_d f_{oc} K_{oc} + f_w + f_a H)} \quad (7)$$

where ρ_w (kg L^{-1}) and ρ_d (kg L^{-1}) are the wet and dry soil densities, respectively. The f_{oc}, f_w, and f_a coefficients are the volumetric fractions of organic carbon, water, and air of the soil, respectively. K_{oc} (L kg^{-1}) is the soil sorption partition coefficient of the pesticide, and H is the air/water partition coefficient of the pesticide.

Concentration in Potato Tubers. The uptake of pesticides into potatoes was shown to occur from the available portion of active ingredient in the water phase of the soil via diffusion through the peel and inner potato tissue (*17*). Plant uptake models for potato crops based on diffusive mass transfer of organic substances (*16, 17*) were used as a basis for the model presented here. The uptake of pesticides from the surrounding soil can generally be described by the following compartment system

$$\frac{dC_p}{dt} = k_u C_w - (k_e + k_g + k_d) C_p \quad (8)$$

where C_p (mg kg^{-1}) is the pesticide concentration in the potato (modeled as a homogeneous sphere), k_u (L kg^{-1} day^{-1}) is the pesticide uptake rate by potato, k_e (day^{-1}) is the pesticide depuration rate (which is calculated from the diffusion coefficient in potatoes describing a passive diffusion of pesticides by soil solution from tubers (*17*)), k_g (day^{-1}) is the potato growth rate, and k_d (day^{-1}) is the degradation rate in potato due to hydrolysis and oxidation. The rate constants k_u, k_e, and k_g were calculated according to ref *16*, while k_d was added as a new process which was determined experimentally in this study. The time-dependent pesticide concentration in potatoes, $C_p(t)$, is finally described by

$$C_p(t) = \frac{C_w(0) \times k_u (e^{-k_s t} - e^{-(k_e + k_g + k_d)t})}{(k_e + k_g + k_d - k_s)} \quad (9)$$

Ingestion Intake Fraction. The ingestion intake fraction is a common tool to express human fate and exposure and can be used as an indicator which describes the accumulation of pesticides in the human food chain (*27*). It is considered an effective metric for expressing the source-to-intake relationship and is commonly used in life cycle assessment or comparative risk assessment (*28, 29*). It is described here as the fraction of mass of pesticide released into the environment that is ultimately taken up into the human food chain and is expressed in kilograms of pesticide intake via potato consumption per kilogram of pesticide applied during the cultivation and can be calculated according to (*5*)

$$iF(t) = PF \times \frac{C_p(t) Y}{M_{app}} \quad (10)$$

where PF is the food processing factor, $C_p(t)$ is the concentration of pesticide at time t (kg kg^{-1}), Y is the yield (kg ha^{-1}), and M_{app} is the mass of active ingredient applied on the field (kg ha^{-1}).

Experimental Methods

Study Area. The study area, Vereda la Hoya, is located in the Department of Boyacá in Colombia. La Hoya ranges from

TABLE 1. Model Input Data

parameter	symbol	value	unit	ref
degradation half-life in potato	DT50p	17	days	[a]
degradation half-life in soil	DT50s	18	days	[a]
soil air fraction	δ	0.12	kg kg^{-1}	*17*
soil organic carbon content	f_{oc}	0.02	kg kg^{-1}	[b]
soil pore water fraction	θ_{fc}	0.25	L L^{-1}	[b]
Henry's law constant	H	2.8×10^{-4}		*30*
initial soil penetration depth	IPD_{soil}	0.01	m	*20*
organic carbon sorption constant	K_{oc}	8151	L kg^{-1}	*30*
octanol−water partition coefficient	log K_{ow}	4.7		*30*
pH	pH	6.8		[b]
potato radius	r	0.03	m	[b]
infiltration rate	v_e	8.5×10^{-3}	m day^{-1}	[b]
pesticide bulk density	ρ_{pest}	1.51	kg L^{-1}	*30*
potato density	ρ_{pot}	1.10	kg L^{-1}	*16*
soil bulk density	ρ_s	1.65	kg L^{-1}	[b]
soil dry density	ρ_d	1.10	kg L^{-1}	[b]
average tuber depth	z	0.12	m	[b]

[a] Obtained through inverse modeling (fitted to measured concentration decay, see Pesticide Concentrations in Soil). [b] Experimental data measured in this study; see below.

2700 to 3250 m above sea level, it has an area of 840 ha, and an average temperature of 12 °C (*31, 32*). It is a mountainous rural region in which the main source of income for the major part of the population is farming. The main agricultural product grown in la Hoya is potato, which is cultivated in two cycles per year, permitting two annual harvesting seasons with an average yield of 16 tonnes per hectare (*33*). The production of potato is carried out by smallholders, who make up more than 95% of the workforce, occupy about 56% of the potato-cultivated land, and provide 45% of the total production (*4*).

Design of Field Trial. The field trial was carried out on a 1324 m^2 agricultural plot located at 5°28′30.85″N/73°26′01.35″W and 2874 m above sea level. Potato plants were cultivated with a plant density of 2.33 plants m^{-2} between July 21 and December 29 of the year 2009, resulting in a total cultivation period of 162 days. Pesticides were applied by means of a lever-operated knapsack sprayer (20 L), which was filled from a larger tank (100 L) in which the pesticide solution was prepared. The detailed list of pesticides and amounts used during the cultivation cycle was documented in a journal (see Supporting Information). Meteorological conditions during the whole cultivation period were measured with a Vantage Pro-2 automatic meteorological station (Davis Instruments, Hayward, CA) located outside of the field at 2 m from the field border. Measured variables like precipitation, global radiation, temperature, relative humidity, vapor pressure deficit, wind speed, and wind direction were recorded every 15 min.

Pesticide Deposition on Soil Surface. The amount of pesticide deposited on soil depends on the following factors: application method, type of spray equipment, meteorological conditions, stage of growth of the crops, and the crop type (*34*). In order to measure the amount of pesticide reaching the soil surface after spray application, we conducted spray simulation experiments with the fluorescent tracer uranine (CAS# 518-47-8) serving as a surrogate compound for pesticide active ingredients. To measure tracer deposition on soil, water-sensitive papers were used as spray droplet collectors. A total of 32 high absorbent papers (HAPs) (5 × 5 cm) per trial were placed horizontally at 0.2 m from the soil surface prior to spraying (16 below the potato plant leaves and 16 on the furrow) as described in ref *35*. Uranine was mixed with water and then applied with an average dose of 0.364 mg L^{-1} by the same farmer, using the same preparation procedures and equipment usually used for the application of pesticides. After spraying, the HAPs were collected from the field, dried in an oven, placed in plastic bags, and stored in a dark environment until analysis. The amount of uranine on the papers after the spray experiments was detected with a LS 50B fluorescence spectrometer (Perkin-Elmer, Waltham, MA). The fluorescence intensity of the samples was converted to concentrations and then related to unit of paper area. Pesticide deposition fractions on soil were finally calculated as the average of the fractions measured below the plants and on the furrow. To measure the soil coverage by potato plants, a photograph of the studied plot section was taken before each trial at the same location from 2 m height perpendicular to the ground and then analyzed according to ref *35*.

Soil and Potato Sampling. In order to study the dynamics of pesticides along the cultivation cycle and especially during tuber growth, soil and potato samples were collected 100, 121, 130, 140, 148, 155, and 161 days after planting. A randomized sampling scheme was applied after dividing the test field into 16 subsectors of about 80 m^2 each (a detailed plan of the plot and location of soil and potato samples can be found in the Supporting Information). Soil and potatoes (1 kg each) were collected at three different randomly chosen subsectors inside the plot. Potatoes were collected at an average depth of 12 cm. Soil samples were taken as close as possible to the potatoes. Sampling dates were coordinated with the farmer in order to obtain samples which were treated close to the pesticide applications, not before potato tuber formation, and close to the harvest date. One additional composite soil sample (mixture of four subsamples from the top 20 cm of soil) was analyzed before planting in order to determine if pesticide residues in soil were present from past cultivation cycles.

Analytical Methods. *Preparation of Potato Samples.* Whole potatoes were homogenized in a Waring blender (Stephan Machinery UM12, Hameln, Germany). Thirty grams of homogenized sample were extracted with 60 mL of ethyl acetate, 35 g of anhydrous Na_2SO_4, and 5 g of $NaHCO_3$. Thirty milliliters of this extract were concentrated using a rotary evaporator and then cleaned up using a gel permeation chromatography (GPC) column. The final extract was concentrated and diluted to 2 mL with ethyl acetate. In order to evaluate the efficiency of the analytical procedures, a quality control was conducted. For each active ingredient, the linearity of the calibration curves was statistically assessed according to refs *36* and *37*, and the recovery of the methodology was evaluated using surrogate compounds (TPP and PCB 153). Each batch of samples was analyzed with a

blank and pesticide recovery samples and an internal standard [tris(2-chloro-1-(chloromethyl)ethyl) phosphate] added to each sample prior to injection. The quality-control procedures yielded good recoveries in the extraction process, resulting in a mean of 90% (67−118%) and a standard deviation of 11% (see Supporting Information). In order to determine the amount of pesticide removed from potatoes due to cleaning and washing, cooking, and storing, potatoes were cleaned with a paper towel, stored at ambient temperature (20 °C) for 17 days, and cooked in boiling water for 5 min, respectively.

Preparation of Soil Samples. Five grams of soil were extracted for 30 min with 30 mL of ethyl acetate using an ultrasonic bath sonicator (UBS). The samples were then centrifuged for 10 min at 6000 rpm, and 15 mL of the extract was kept for further analysis. The soil was dried with nitrogen and then extracted again for 30 min with 30 mL of methanol using the UBS. Samples were then centrifuged for 10 min at 6000 rpm, and 15 mL of the methanolic extract was kept for further analysis. Both the ethyl acetate and methanolic extract were mixed, and the final extract was concentrated and diluted to 2 mL with ethyl acetate ready for injection. As for the potato samples, the same quality-control procedures were conducted for soil samples, resulting in mean extraction recovery of 88% (80−94%) and a standard deviation of 6%.

Detection of Pesticide Residues. Pesticide residues were determined by means of gas chromatography (GC) and high-performance liquid chromatography (HPLC) according to refs *36*−*38*. Detailed information on apparatus, equipment setup, and chemicals used can be found in the Supporting Information.

Results and Discussion

Experimental Results: Pesticide Deposition on Soil Surface. Soil deposition fractions determined in the tracer experiment were on average 0.30, 0.33, and 0.75 after the first, second, and third application, respectively. Soil deposition fractions for the same application days calculated with eq 1 were 0.30, 0.26, and 0.91. Estimates calculated by the soil deposition model deviated between 1 and 21% from the experimental results. A mean error of 14% was observed between measurements and calculations. During the complete cultivation cycle, modeled soil deposition fractions can vary between 0.25 (full development of plant) and 1 (before leaf development), depending on the plant growth stage, stressing the importance of including dynamic plant growth in the calculation of pesticide deposition on soil and plants after foliar spray applications. Nevertheless, the model could be improved by including information on pesticide fractions washed or weathered off the plants after application.

Pesticide Concentrations in Soil. Active ingredients and metabolites detected in the experimental plot during the cultivation period can be found in Table S5 of the Supporting Information. Out of this list only the insecticide chlorpyrifos (CAS# 2921-88-2) was applied by the farmer. It was sprayed three times during the cultivation cycle (60, 83, and 123 days after planting) with an application dose of 0.435 kg a.i. ha^{-1} per application. Chlorpyrifos concentrations in soil samples collected between 100 and 161 days after planting ranged from 2.94 mg kg^{-1} after the third application and 1.41 mg kg^{-1} one day before harvest, with a coefficient of variation of 32% (see Figure 1). All measured concentrations were above the limit of detection (LOD) of the analytical method used (0.007 mg kg^{-1}). The degradation kinetics of chlorpyrifos were inversely fitted using a first-order decay equation [$C(t) = 3.18e^{-0.039}$; $n = 4$; $r^2 = 0.87$]. According to our experimental results, the half-life of chlorpyrifos in soil is 17.7 days. This is in accordance with experimental pesticide registration data used for regulatory purposes in the European Union, ranging from 2 to 65 days and an average of 21 days (*30*). The

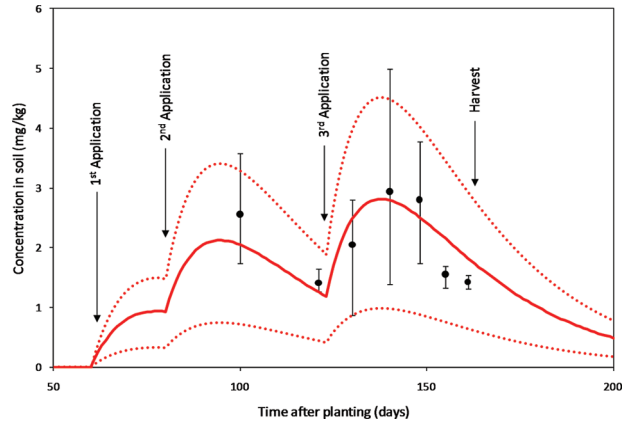

FIGURE 1. Chlorpyrifos concentrations in soil as a function of time. Measured mean concentrations ($n = 3$) are shown as black dots (the uncertainty bars denote the minimum and maximum values). The modeled concentration at an average tuber depth of 12 cm depth is indicated with the full line, while the dotted lines display the results for the 5th and 95th percentiles of variation in tuber depth (7 and 35 cm).

insecticide DDT (CAS# 50-29-3) and its metabolites, DDD (CAS# 72-54-8) and DDE (CAS# 72-55-9), were detected in all soil samples, including the sample taken before cultivation. We assume that these residues originate from a time period before DDT was banned from agricultural production in Colombia in 1986. The insecticides methyl-parathion (CAS# 298-00-0) and carbofuran (CAS# 1563-66-2) were both not used by the farmer but were detected in all soil samples collected after planting. Their presence in the test field is assumed to originate from cross-contamination such as wind drift from neighboring fields or contaminated sprayers. The following pesticides were applied by the farmer but were not detected in soil samples: chlorothalonil (LOD 0.001 mg kg^{-1}), cymoxanil (LOD 0.13 mg kg^{-1}), and metamidophos (LOD 0.049 mg kg^{-1}). The absence of these compounds was confirmed by model calculations (see below).

Pesticide Concentrations in Potatoes. Concentrations of chlorpyrifos in potato samples ($n = 7$) collected between 100 and 161 days after planting ranged from 0.006 mg kg^{-1} after the first application and 0.018 mg kg^{-1} after the third application with an average concentration of 0.013 mg kg^{-1} and a coefficient of variation of 66% (see Figure 2). All measured concentrations were above the limit of detection (0.006 mg kg^{-1}) of the analytical method used. The relatively high coefficient of variation can partly be explained by the fact that all concentrations were measured close to the detection limit, but also due to inhomogeneous spraying of pesticides and furthermore through variation in size of plants, depth of potatoes, and composition of soil. DDT, carbofuran, and methyl-parathion were not detected in potatoes although detected in all soil samples. This observation was confirmed by the plant uptake model (see below). Similar results have been obtained by other authors (*39*) for a variety of pesticides in potato fields, reporting that residues were found in soil but not in potato tubers.

Effects of Cleaning and Washing, Cooking, and Storing. Food processing studies provide basic information on the reduced level of residues in passing from the raw agricultural product to a processed commodity (*9*). The processing factor, ranging from 0 to 1, can be described as the ratio between the processed commodity and the raw product. Chlorpyrifos concentrations in cooked potatoes were reduced by 14%, resulting in a processing factor of 0.86. Similar processing factors (mean of 0.82) including data on

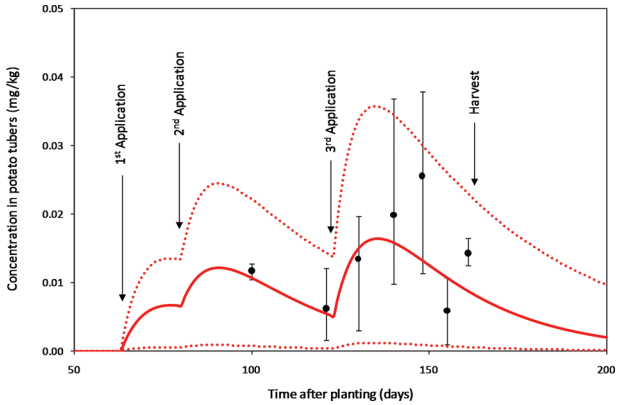

FIGURE 2. Chlorpyrifos concentrations in potatoes as a function of time. Measured mean concentrations ($n = 3$) are shown as black dots (the uncertainty bars denote the minimum and maximum values). The modeled concentration at an average tuber depth of 12 cm depth is indicated with the full line, while the dotted lines display the results for the 5th and 95th percentiles of variation in tuber depth (7 and 35 cm).

chlorpyrifos reduction in cooked potatoes were recently published (*40*). The stability of a pesticide due to boiling is mostly related to thermal breakdown, which is influenced by its degradation temperature (temperature at which the substance is no longer stable and begins to breakdown (*30*)). Chlorpyrifos has a degradation temperature of 170 °C (*30*), which can be considered as relatively high, explaining its stability during the boiling process. Concentrations in potatoes kept for 17 days at ambient temperature (20 °C) were reduced by 50%, resulting in a degradation half-life of 17 days due to storing. Chlorpyrifos half-lives on plants (only above ground grown crops) found in the literature ranged from 1 day up to 4 days (*41*−*43*). The value for potatoes presented in this study is on average 7 times higher, indicating that the degradation of chlorpyrifos in crops grown beneath the soil surface is slower. This could be explained by the fact that some of the most important sources for foliar pesticide breakdown like photodegradation and volatilization from plant surfaces (*44*) are not possible if the commodity is grown in soil. Chlorpyrifos concentrations in samples cleaned and washed before cooking were reduced by 56%, resulting in a processing factor of 0.44. Generally, it can be concluded that cleaning and washing potatoes with water is the food processing step which contributed most to the reduction of pesticide residues, probably due to the removal of attached soil particles, as shown by ref *45*.

Comparison of Model and Experimental Results. Pesticide residue concentrations of chlorpyrifos in soil obtained during the cultivation study and the corresponding model estimates are presented in Figure 1.

Model calculations show how the concentration of chlorpyrifos increases after each application, reaching a maximum level 15 days after the pesticide was applied. Maximum concentrations in soil increase with the number of applications, reaching 0.98, 2.21, and 2.91 mg kg^{-1}. Fifteen days after the last application the concentration decreases exponentially. The same trend can be observed in potatoes (see Figure 2) only that on average the maximum concentration is reached 11 days after the pesticide was applied. In general, concentrations in potatoes were shown to be lower, with maximum levels of 0.008, 0.015, and 0.021 mg kg^{-1} after the first, second, and third application, respectively. The average ratio between maximum concentrations in potatoes and soil is 0.0074, meaning that 0.74% of the mass found in soil is expected to be taken up into potato tissue. This is in accordance with a similar bioconcentration factor of 0.011 for chlorpyrifos in potatoes presented in ref *16*. The concentrations of chlorpyrifos in soil calculated by the model deviated between 7 and 43% from the mean of the experimental results. A mean error of 19% was observed between measurements and model estimates during the complete sampling period. Main factors for these deviations are variations in depth of soil profiles sampled and the fact that the model calculates with an average soil concentration from surface to the bottom of the tuber depth (7 and 35 cm depth representing the 5th and 95th percentile of variation in soil profile sampled). Concentrations of chloryrifos in whole potato tubers obtained in the cultivation study and the corresponding model estimates are presented in Figure 2.

The concentrations of chlorpyrifos in potato tubers calculated by the plant uptake model were in good accordance with the measured results. A mean error of 36% was observed between experimental results and model estimates during the sampling period. From Figures 1 and 2 it furthermore can be seen that experimentally derived chlorpyrifos concentrations in soil and potatoes are all within the range of the variability bands calculated with the 5th and 95th percentiles of the variation in tuber depth. Fifty-five days after the last application of chlorpyrifos, the model predicts concentrations that are under the detection limit of the pesticide. This is one advantage of the modeling approach, it can predict concentrations where the analytical methods would fail. Nevertheless, a clear limitation of the potato uptake model is the fact that tubers are considered to be homogeneous mixed spheres. This simplification (using a pesticide concentration in the potato that is integrated over the full volume of the tuber) could lead to an underestimation of removal processes, because it ignores the higher concentrations expected in the potato peel as described in ref *46*. Having used experimental soil concentrations of DDT, carbofuran, and methyl-parathion as a starting point for modeling residues in potatoes, modeled pesticide concentrations were all under the LODs of the analytical methods of the single pesticides. The same was shown for the pesticides that were applied by the farmer but were not detected in soil samples. The main reasons for this observation are low application rates (cymoxanil, glyphosate, and paraquat), resulting in possible maximum concentrations under the detection limit; fast degradation rates (mancozeb and metamidophos), resulting in advanced or complete degradation of the pesticide when soil samples were taken; and long time periods between application and sampling (chlorothalonil).

Ingestion Intake Fraction and Consumer Risk Assessment. We calculated the ingestion intake fraction using two scenarios. The first scenario is calculated assuming that the commodity is ingested on the day potatoes were harvested (conservative estimate) and the second scenario assuming a storing period of 3 months before consumption. Three months was estimated as the maximum storing time possible under Colombian conditions. Directly after harvest, cooked potatoes (without cleaning and/or washing) have an intake fraction of 10^{-4} ($kg_{ingested}\ kg_{applied}^{-1}$) but an intake fraction of 10^{-6} ($kg_{ingested}\ kg_{applied}^{-1}$) when stored for 3 months and then cooked. The intake fraction for washed and cooked potatoes varies between 10^{-5} and 10^{-7} ($kg_{ingested}\ kg_{applied}^{-1}$). Dynamic model calculations and experimentally derived intake fractions (using measured concentrations) via potato consumption corresponded well for chlorpyrifos, deviating less than a factor 2 from each other.

The maximum residue limit (MRL) is the maximum concentration of a pesticide residue that is legally permitted or recognized as acceptable in, or on, a food or agricultural commodity (*47*). The average chlorpyrifos concentration in

potatoes measured at harvest in this study (0.013 mg kg^{-1}) reaches 26% of the European MRL (0.05 mg kg^{-1} (*30*)) and 0.7% of the MRL set by the Codex Alimentarius (*48*) and therefore does not indicate any violation of international regulatory thresholds.

In order to evaluate potential chronic effects on human health, we use the acceptable daily intake (ADI), which is an estimate of the amount of a substance in food or drinking water, expressed on a body-mass basis, which can be ingested daily over a lifetime by humans without appreciable health risk (*47*). Using the average measured chlorpyrifos concentration of 0.011 mg kg^{-1} in cooked potatoes, the annual potato consumption rate of 42 kg $person^{-1}$, and the average body weight of 60 kg $person^{-1}$, we calculate a daily intake of 2.11×10^{-5} mg kg^{-1} bw day^{-1}, representing 0.2% of the ADI of chlorpyrifos (0.01 mg kg^{-1} bw day^{-1} (*30*)). The result of this analysis indicates that chlorpyrifos intake due to ingestion of potatoes studied in this work does not lead to significant chronic human health effects. Thus, it should be mentioned that during the studied cultivation period, average precipitation was relatively low and therefore the demand for pesticides (especially fungicides) in the study area was lower than in previous, more typical cultivation cycles.

As for future application, the model developed in this work could be combined with application data of local farmers in order to identify risks and, if necessary, measures to mitigate human exposure to pesticides. The model could furthermore serve as a pest management tool in advising farmers in regard to their pesticide application schemes and in the calculation of sufficient waiting times before harvest.

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Supporting Information Available

Detailed information on experimental design and model is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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