Dynamics of Pesticides in Potato Crops

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This study investigated the behavior of pesticides commonly used on potato in a part of northwestern Spain with a large area devoted to this crop. Experimental potato plots were treated with commercial formulations of two insecticides, a nematicide, a herbicide, and a combination of two fungicides, and the concentrations of the active ingredients were monitored throughout the growing season in the 0−1 and 1−15 cm soil layers, in water dripping off the potato plants, and in the potatoes themselves. The technique used for pesticide determination was gas chromatography with mass selective detection. For potato analyses, pesticide extraction was optimized. The only pesticide ever detected in potato tubers was metalaxyl, the concentration of which never exceeded half the maximum residual limit even when it was applied several times more often than is officially recommended for potato crops. Metalaxyl was also the only pesticide detected in wash-off, apparently due to its being more soluble in water than the other pesticides applied to the growing plants. A mathematical model of pesticide transport in soil was fitted to the experimental data using the program HYDRUS-1D.

KEYWORDS: Pesticides; potatoes; transport in soil; gas chromatography; mass selective detection

INTRODUCTION

Despite there having been considerable research on biological and other "nonchemical" methods of preventing or fighting crop disease (*1, 2*), pesticides are currently the farmer's main means of crop protection. However, in the interests of public and environmental health, they must be used in such a way that dangerous levels of pesticides or toxic pesticide degradation products neither remain in crops when they reach the public nor accumulate in surface and subterranean water bodies (*3*).

Potato crops are liable to attack by potato beetles, aphid-spread viruses, and blight. In Galicia (northwestern Spain), the risk of infection and disease is favored by high humidity and generally abundant spring rains, and the consequent heavy use of pesticide chemicals is of particular environmental concern in the neighborhood of Xinzo de Limia, where for many years extensive areas have been devoted exclusively to potato production. Nevertheless, relatively little information is available concerning the environmental mobility of pesticides applied to potato crops.

In this study we addressed the issue posed above. To this end we treated experimental potato plots with commercial formulations of two insecticides, a nematicide, a herbicide, and a combination of two fungicides, in each case in accordance with the manufacturers' instructions (except for dosage levels,

which constituted one of the experimental variables); throughout the growing season we monitored the concentrations of the active chemicals in the 0−1 and 1−15 cm soil layers, in water dripping off the potato plants, and in the potatoes themselves. For potato analyses, pesticide extraction was optimized. In addition, we fitted a mathematical model of pesticide transport in soil to the experimental data.

EXPERIMENTAL PROCEDURES

Pesticides. **Table 1** lists the pesticides employed in the field experiments. Samples of the active ingredients with purities >99.5% were purchased from Riedel-de-Haën (Seelze, Germany). Lindane (97% pure), employed as internal standard in the analytical determinations, was purchased from Aldrich (Steinheim, Germany).

Experimental Plots and Sampling. Field experiments were conducted between April and September 2004 at a site owned by the Instituto Ourensán de Desenvolvemento Económico (INORDE) in Xinzo de Limia (Ourense, Spain) at which the soil had a pH in water of 5.5 and organic matter, available P, and available K contents of 2.9%, 130 ppm, and 96 ppm, respectively (available P was determined by extraction at pH 8.2 with sodium bicarbonate and available K by extraction at pH 7 with ammonium acetate). Twelve 9 m² plots, each with four rows of 10 potato plants (*Solanum tuberosum* var. Kennebec), were divided into four groups of three randomly located replicate plots (A, B, C, and D), which were treated and sampled in accordance with the calendar shown in **Table 2**. Group A plots (not shown in **Table 2**) were untreated controls, group B plots were given the number of treatments and treatment dosages recommended by the manufacturers, and plots of groups C and D were given higher dosages (for products applied

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Table 1. Pesticides Applied

commercial product	physical form	active ingredient(s) (concentration)	biological activity	manufacturer (location)
Curasol	granulate	carbofuran (5%)	insecticide nematicide	Fitolux S.A. (Madrid, Spain)
Nemacur	granulate	fenamiphos (10%)	insecticide nematicide	Bayer CropScience AG (Monheim, Germany)
Eclipse 70 WG	water-dispersible granulate	metribuzin (70%)	herbicide	Comercial Química Massó (Barcelona, Spain)
Keshet 2.5 EC	solution	deltametrin (2.5% w/v)	insecticide	Makhteshim Agan España S.A. (Valencia, Spain)
Sponsor Combi	wettable powder	metalaxyl (10%) folpet (40%)	fungicide	Comercial Química Massó (Barcelona, Spain)

Table 2. Pesticide Treatment and Sampling Calendar [Treatment Levels in Kilograms per Hectare (Curasol, Nemacur, Eclipse, and Sponsor Combi) or Liters per Hectare (Keshet 2.5 EC)]

		plot group		
date	application/sampling	B	C	D
April 22	Curasol	20	30	40
	Nemacur	20	30	40
April 28	soil sampling			
May 12	Eclipse 70 WG	0.5	1.0	1.5
May 14	soil sampling			
May 31	Keshet 2.5 EC		0.5	
	Sponsor Combi		2.5	
June 2	soil sampling			
June 21	Keshet 2.5 EC	0.5		
	Sponsor Combi	2.5		
	soil sampling			
June 24	water sampling			
July 5	Keshet 2.5 EC	0.5		
	Sponsor Combi	2.5		
	soil sampling			
July 12	water sampling			
July 16	Keshet 2.5 EC		0.5	
	Sponsor Combi		2.5	
	soil sampling			
July 17	water sampling			
July 22	potato sampling			
July 28	Keshet 2.5 EC			0.5
	Sponsor Combi			2.5
Aug 9	Keshet 2.5 EC			0.5
	Sponsor Combi			2.5
Aug 19	potato sampling			
Sept 7	soil sampling			
Sept 20	potato sampling			

just once during the growth cycle) or a greater number of treatments (for products applied repeatedly). Liquid formulations were applied with a hand-held sprayer, and solid formulations were scattered by hand and mixed into the top 15 cm of soil with a rotary cultivator.

On each soil sampling date, 10 samples were taken at random locations from both the 0–1 cm and 1–15 cm layers of each plot (6 from ridge tops and 4 from ridge sides), and the 10 samples of each layer were pooled to make an aggregate sample for that layer weighing ~500 g. The fraction smaller than 2 mm was separated from this aggregate sample by sifting and stored at 4 °C pending analysis for pesticides. Whenever soil was sampled on the same day as pesticides were applied, application preceded sampling.

The plots were watered by sprinklers on four occasions: June 24, July 1, July 12, and July 17. On June 24, July 12, and July 17, water dripping off the potato plants was collected, measured, and stored at 4 °C in amber glass bottles pending analysis.

On each potato sampling date, seven potato tubers were randomly selected from each plot and cleaned, and each seven-tuber sample was weighed and stored at 4 °C in a polyethylene bag pending analysis.

Pesticide Extraction. *Soil.* In light of previous work on fungicides in soil (*4*), pesticides were extracted from 10 g (moist weight) soil samples as follows. The sample was placed in a 40 mL EPA glass vial (from Wheaton, Millville, NJ) containing 15 mL of a buffer solution of pH 8 consisting of anhydrous sodium carbonate (3.6% w/v) and sodium polyphosphate (0.8% w/v) in distilled water. The vial was stoppered with a seal with a Teflon-faced silicone septum and was sonicated for 10 min at room temperature. Ethyl acetate was added (10 mL), and the mixture was shaken mechanically at 200 rpm for 45 min. The organic phase was drawn off with a Pasteur pipet, dried over anhydrous Na_2SO_4 (0.15 g), and filtered, and 8 mL of this solution was transferred to a 25 mL round-bottom flask and concentrated to dryness at 40 °C in a rotary evaporator. The resulting residue was redissolved in 0.5 mL of a 4 mg/L solution of lindane (the internal standard) in ethyl acetate, and this solution was vortexed, after which it was transferred to an autosampler vial for gas chromatography. The recovery efficiency of the whole extraction procedure ranged from 85 to 100% (depending on the pesticide), with relative standard deviations of 10–15%.

Wash-off. As in previous work (*4*), pesticides were extracted from 25 mL water samples contained in the same vials as above, as follows. Ethyl acetate (10 mL) was added, the mixture was sonicated for 5 min at room temperature and then shaken mechanically at 200 rpm for 15 min, and the organic phase was drawn off with a Pasteur pipet. The aqueous phase was re-extracted in the same way with another 10 mL of ethyl acetate, and the pooled organic extracts were treated in the same way as for soil samples. The recovery efficiency of the whole extraction procedure was in all cases >95% and the relative standard deviation <10%, in good agreement with the findings of a previous study of similar pesticides (*13*).

Potato Tubers. The potatoes of each seven-potato sample were separated into three regions: peel, outer region, and core. Each region was homogenized in a food mixer, and 50 g of homogenate was transferred to a 250 mL polypropylene carbonate flask (from Nalgene, Rochester, NY) and treated with 150 mL of 1:1 acetone/dichloromethane (see below) and 20 g of anhydrous sodium sulfate (to remove water). This mixture was sonicated for 10 min at room temperature, shaken in a reciprocating shaker for a further 10 min, and centrifuged at 4000 rpm for 10 min at 10 °C. The organic phase was concentrated to dryness at 40 °C in a 300 mL rotary evaporator, and the residue was dissolved in 1.5 mL of a 1 mg/L solution of lindane in acetone. After vortexing, the resulting solution was transferred to an autosampler vial for gas chromatography.

The extraction solvent, 1:1 acetone/dichloromethane, was chosen on the basis of pesticide recovery (see Results and Discussion) in experiments in which triplicate samples of potato homogenate were spiked with 100 μg/kg of each pesticide active ingredient (dissolved in acetone), left for 1 h for the acetone to evaporate (in preliminary experiments there was found to be no advantage in prolonging this time for up to 11 h), and extracted with 1:3, 1:1, or 3:1 acetone/dichloromethane, 1:3, 1:1, or 3:1 (ethyl acetate)/hexane, 1:1 (ethyl acetate)/dichloromethane, or 1:1 acetone/hexane as described above, after which the extracts were analyzed as described below (GC-MS). The generality of the extraction method was verified in experiments in which no significant difference was observed between the recoveries of pesticides from samples prepared from potatoes grown on four different soils.

GC-MS. Gas chromatography was performed on a Fisons GC 8000 apparatus equipped with a J&W Scientific 30 m × 0.25 mm DB-17 fused silica capillary column with a 0.50 μm film of 50% phenyldimethylpolysiloxane and an MSD 800 electron impact mass-selective

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detector. The chromatograph was operated at 70 eV and linked to a desktop computer running ThermoQuest Masslab 1.4. Samples (1 μL) were injected with the injector running in splitless mode for 5 min and with a 10:1 split ratio thereafter, at a temperature of 240 °C. The column head pressure of the carrier gas, helium, was maintained at 100 kPa. The oven temperature was initially held at 50 °C for 1 min and then increased to 180 °C at 35 °C/min, held at 180 °C for 1 min, increased to 280 °C at 5 °C/min, and held at 280 °C for 25 min. The transfer line temperature was 275 °C. During optimization of MS detection parameters, MS was performed in full scan mode (40−400 amu) after a solvent delay of 15 min. *m/z* values chosen for single ion monitoring (SIM) on the basis of high *m/z*, high peak intensity, and specificity for the corresponding pesticide were as follows (the intensities of multiple SIM peaks were added for quantitation): for the internal standard lindane (eluting at 15.8 min), 111, 183, and 219; for carbofuran (16.6 min), 149 and 164; for metalaxyl (18.6 min), 132 and 206; for metribuzin (19.1 min), 144 and 198; for fenamiphos (23.6 min), 154, 217, and 303; for folpet (24.3 min), 104 and 262; and for deltametrin (47.5 min), 181 and 252.

Statistical Analysis. The statistical significance of differences among mean pesticide levels in samples from different plot groups, dates, or potato regions was estimated by analyses of variance followed by multiple-range tests. All statistical calculations were performed using SPSS 12.0 for Microsoft Windows.

Modeling Transport in Soil. The vertical transport of the pesticides in the 0−1 and 1−15 cm soil layers was modeled using HYDRUS-1D v. 3.0 (*5*) to solve convection−dispersion equations together with a modified form of Richards's equation that includes a sink term due to van Genuchten and Wierenga (*6*) to account for water uptake by plant roots. These equations were parametrized partly by a priori determination of experimental quantities and partly by fitting the equations to the experimental data for pesticide concentrations in soil. The parameters determined a priori, using soil cores with a volume of 100 cm^3 taken from the 0−20 cm soil layer, were the saturated hydraulic conductivity K_s [according to Klute and Dirksen's method (*7*)] and the saturated and residual water contents, θ_s and θ_r, respectively. The parameters α and n of van Genuchten's equations were estimated by fitting [according to the method described by Vandam et al. (*8*)] and used to calculate water retention and the unsaturated hydraulic conductivity as per van Genuchten (*9*). The dispersivity (*D*), the fraction of immobile water (*f*), and the rate constant for transfer of pesticides between mobile and immobile water (ω) were estimated by fitting [according to van Genuchten and Wierenga's method (*6*)] using Br$^-$ as tracer. The equilibrium constants for desorption of pesticides from the solid phase (K_d), the rate constants for first-order pesticide degradation (*S*), and realistic minimum and maximum search limits were necessary for the parameter search procedure; these were taken from the literature (*10*, *11*) in preliminary computations.

To obtain the time-dependent water balance required to fit the model, rainfall data were obtained from the Xinzo de Limia meteorological station. Daily reference evapotranspiration ET$_0$ was calculated according to the Penman−Monteith method (*12*) and was divided between reference evaporation from soil, ET$_e$, and potential crop transpiration, ET$_c$, using the method and potato crop coefficients of the FAO guidelines (*12*).

As discussed under Results and Discussion, we concentrated on the behavior of metalaxyl, metribuzin, and fenamiphos. Modeling the behavior of metalaxyl required estimation of the time course of the input of metalaxyl to the soil, which comprised both metalaxyl reaching the soil directly during application and wash-off during watering and rainfall episodes. In view of the experimental finding that metalaxyl remained almost exclusively in the 0−1 cm layer (see Results and Discussion), direct input during each application was estimated from the concentration determined in this layer immediately following the first application of Sponsor Combi. Wash-off was calculated from application, watering, and rainfall data using the differential equation (*13*)

$$dm/dR = -0.17m^{1/2} \qquad (1)$$

where *R* is accumulated rainfall (cm), *m* is the mass of metalaxyl on
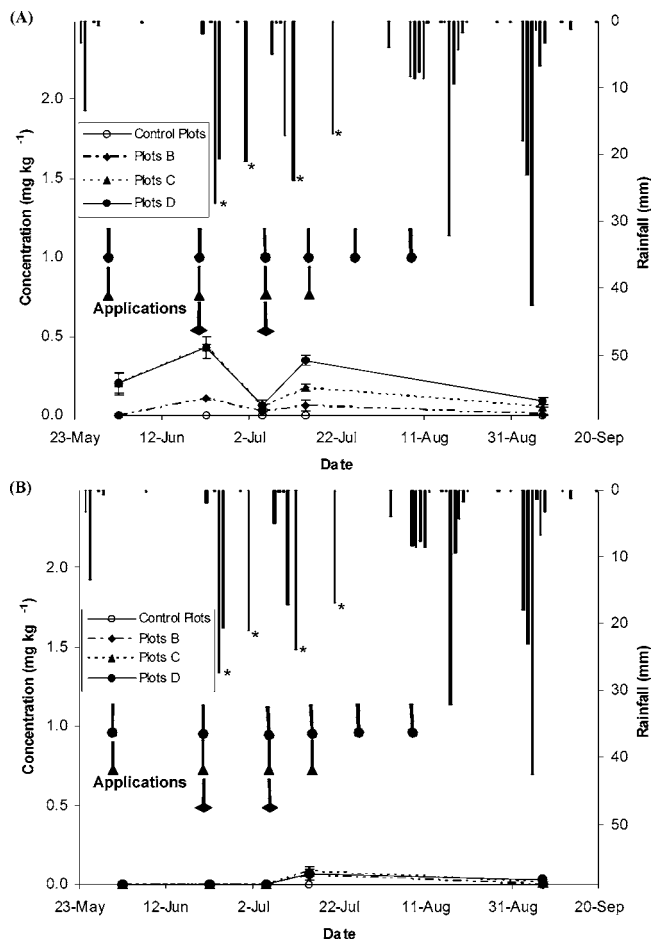
Figure 1. Dynamics of metalaxyl in soil (**A**, 0–1 cm layer; **B**, 1–15 cm layer) and watering (∗) and rainfall episodes during the study period. Each application in plots B–D was of 2.4 mg/kg.

plants that is susceptible to being washed off (mg), and the contribution to *m* made by each dose was estimated as a percentage of the dose by fitting eq 1 to the measured wash-off data.

Modeling of the behavior of metribuzin and fenamiphos in soil required conversion of the known input data (kilograms per hectare) into milligrams per kilogram of soil. For metribuzin it was assumed, for the same reasons as in the case of metalaxyl, that all input was taken up uniformly by the top 1 cm of soil. Fenamiphos was applied in a solid formulation that was incorporated into the soil with a rotary cultivator in a single application before plant emergence, and it was assumed that this resulted in uniform mixing into the top 15 cm of soil.

RESULTS AND DISCUSSION

None of the pesticides used were on any occasion detected in the soil, wash-off, or potatoes of control plots. In what follows, we concentrate on the behavior, in the other plots, of metalaxyl, representative of an active ingredient of a formulation repeatedly applied in liquid form during the growing season; metribuzin, representative of an active ingredient of a formulation applied just once, before plant emergence, in liquid form; and fenamiphos, representative of an active ingredient of a formulation applied just once, before plant emergence, as a solid microgranulate.
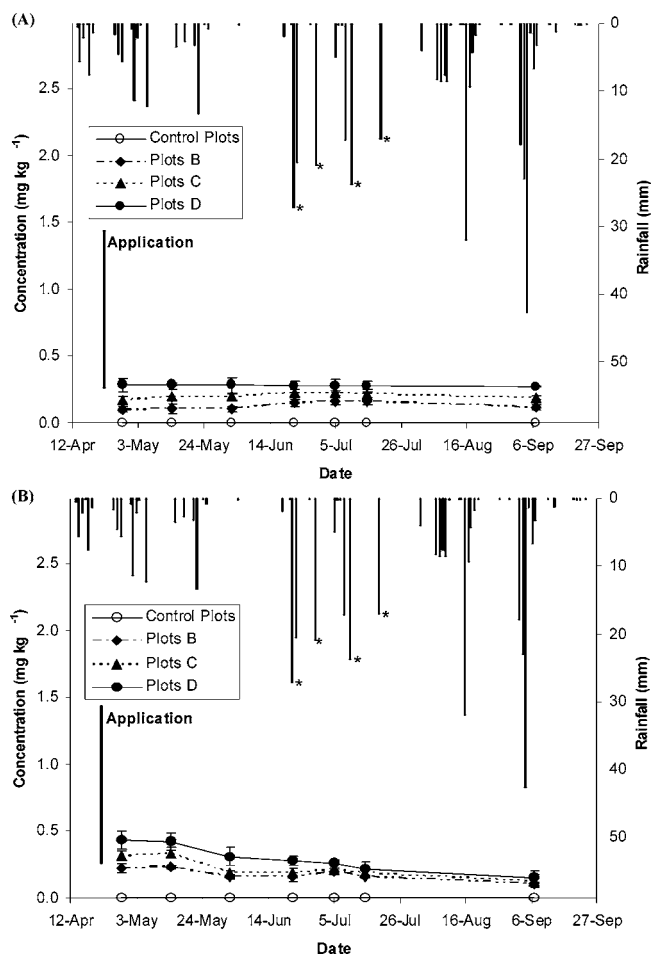
Behavior of the Pesticides in Soil. Panels **A** and **B** of **Figure 1** show the concentrations of metalaxyl (milligrams per kilogram of dry soil) that were detected in the 0−1 and 1−15 cm soil layers, respectively, together with application, rainfall, and
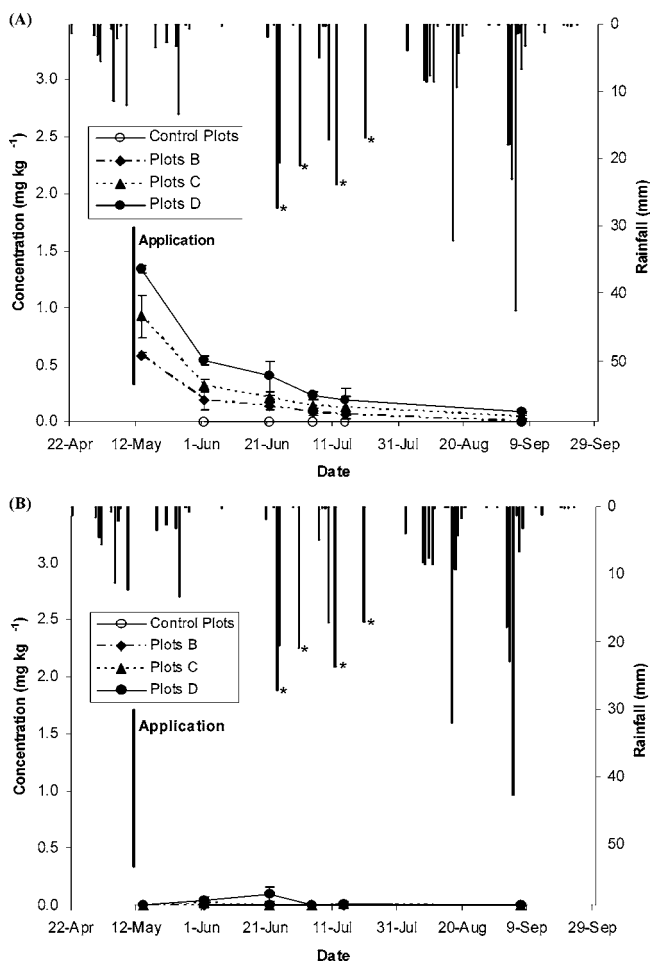
Figure 2. Dynamics of metribuzin in soil (**A**, 0–1 cm layer; **B**, 1–15 cm layer) and watering (∗) and rainfall episodes during the study period.

Figure 3. Dynamics of fenamiphos in soil (**A**, 0–1 cm layer; **B**, 1–15 cm layer) and watering (∗) and rainfall episodes during the study period.

watering events during the experimental period. With variations depending on the application program for each plot group, in the 0−1 cm layer metalaxyl concentration rose during the early dry period, fell almost to zero following watering in late June, rose again to ∼0.5 mg/kg as the result of further application-(s), and fell to <0.1 mg/kg following rainfall in mid and late August. In the 1−15 cm layer, the fungicide was detected only after watering, presumably as the result of being transported by the applied water—metalaxyl has high solubility in water [8.4 g/L (*14*)] and low K_{oc} [30 L/kg (*15*)]. Although the correlation between metalaxyl levels and water input seems to be clear, microbial degradation will also have contributed to its disappearance, its half-life in sandy soils under aerobic conditions being just 10−17 days (*16*). When applied following the manufacturer's instructions (group B plots), soil metalaxyl content never exceeded 0.1 mg/kg.

In the 0−1 cm layer, metribuzin concentration fell steadily to 0.2 mg/kg or less between application on May 12 and the final sampling on September 7 (**Figure 2A**), probably as the result of transport to lower layers and off plot by water input— the solubility of metribuzin in water is quite high [1.0 g/L (*14*)] and its K_{oc} low [60 L/kg (*17*)]. The small concentration still detected in group D plots in September suggests that a proportion of this pesticide may have become protected from volatilization, photodegradation, and biodegradation processes. In the 1−15 cm layer (**Figure 2B**), it was detected only in group D plots, where it began to be quantifiable in June, following rainfall in late May, and peaked (at 0.1 mg/kg) prior to the late June watering events; by mid-July it was undetectable.

As noted above, both metalaxyl and metribuzin were practically undetectable in soil by the end of the growing season, and their accumulation from year to year is not a matter of concern, although there may be a risk of their reaching bodies of water because of their solubility. By contrast, the concentration of fenamiphos in the 0−1 cm layer remained practically constant following its application in late April (**Figure 3A**), despite its considerable solubility in water [329 mg/L (*18*)] and medium-high K_{oc} [219 L/kg for soils with an organic matter content of 3.5%, similar to that of our experimental plots (*19*)]. The fenamiphos content of the 1−15 cm layer did fall slightly, from 0.2 to 0.4 mg/kg, upon application of <0.15 mg/kg in early September (**Figure 3B**). The persistence of fenamiphos is probably attributable not only to its solubility being less than those of metalaxyl and metribuzin but also to a slow degradation rate. However, further sampling at the beginning of the following growing season suggested that there is little risk of its accumulation in soil from year to year.

Behavior of Pesticides in Wash-off Water. The absence of any pesticides in the control plots confirms that none were present in the water used for watering the plots, which was taken from irrigation canals at the experimental site. The only pesticide ever detected in wash-off water in the treated plots was metalaxyl, which was found in concentrations of 22−33 μg/L with no significant differences between the plot groups. Folpet, which was applied together with metalaxyl, was never detected, probably owing to its chemical instability [$t_{1/2(30\ °C)}$ = 1 day (*13*)].

Performance of the Analytical Method for Determination of Pesticides in Potatoes. Table 3 lists the recoveries of the

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Table 3. Average Recovery with Various Combinations of Extraction Solvent

| pesticide | acetone/ dichloromethane | | | ethyl acetate/ hexane | | | ethyl acetate/ dichloromethane | acetone/ hexane |
	1:3	1:1	3:1	1:3	1:1	3:1	1:1	1:1
carbofuran	86	90	95	104	107	93	70	63
metalaxyl	104	92	90	113	103	103	67	59
metribuzin	77	89	68	79	87	70	46	37
fenamiphos	52	87	87	81	69	86	41	53
folpet	68	85	99	90	83	99	54	67
deltametrin	102	86	62	47	50	62	65	114

Table 4. Recoveries, Precisions, Linear Dynamic Ranges, Determination Coefficients (r^2), and Limits of Detection (LOD) and Quantitation (LOQ) for the Determination of the Selected Pesticides in Potatoes

pesticide	recovery (%)	precision (%)	linear range (μg/kg)	r^2	LOD (μg/kg)	LOQ (μg/kg)
carbofuran	94	10	5–1000	0.998	2	5
metalaxyl	98	11	10–1000	0.999	3	10
metribuzin	93	9	5–1000	0.999	2	5
fenamiphos	85	13	2–1000	0.992	1	2
folpet	80	14	10–1000	0.997	3	10
deltametrin	86	7	4–1000	0.983	1	4

Table 5. Average Concentration ± Standard Deviation (Micrograms per Kilogram) of Metalaxyl in Samples of Potatoes Given Various Pesticide Treatments[a]

plot group	tuber region	July 22, 2004	Aug 19, 2004	Sept 20, 2004
B	peel	16.8 ± 0.9 a (C)	16.2 ± 0.2 ab (C)	15.4 ± 0.2 b (BC)
	outer	17.8 ± 0.5 a (C)	18.3 ± 0.8 a (B)	16.2 ± 0.8 b (B)
	core	17.8 ± 0.5 a (C)	18.7 ± 0.7 a (B)	15.6 ± 0.5 b (BC)
C	peel	18.4 ± 0.5 a (BC)	17.2 ± 0.7 ab (BC)	16.8 ± 0.2 b (AB)
	outer	19.5 ± 0.7 a (AB)	18.9 ± 0.5 a (B)	16.5 ± 0.1 b (AB)
	core	19.5 ± 0.7 a (AB)	20.9 ± 0.5 a (AB)	16.6 ± 0.5 b (AB)
D	peel	20.8 ± 0.3 a (A)	22.0 ± 0.8 a (A)	17.3 ± 0.6 b (A)
	outer	21.6 ± 0.5 a (A)	17.9 ± 0.8 ab (B)	16.2 ± 0.7 b (B)
	core	21.6 ± 0.5 a (A)	20.1 ± 0.9 a (AB)	17.3 ± 0.6 b (A)

[a] Multiple-range tests for pairwise differences between group averages were performed at the 95% confidence level. Groups detected as significantly different are marked with different letters (a–c for rows; A–C for columns).

active ingredients in the experiments carried out to orient selection of the solvent to be used for their extraction from potatoes. The 1:1 mixture of acetone and dichloromethane was chosen because it was the only solvent with which all of the active ingredients had recoveries of ≥85%. With this choice of extractant, the overall performance characteristics of the analytical method are as listed in **Table 4**.

Behavior of Pesticides in Potato. The only pesticide detected in potato at any time during the study was metalaxyl, which is sprayed on the aerial parts of the plant and reaches the tubers via the vascular system. The concentrations measured, which were never greater than half the maximum residual limit [50 μg/kg (20)], varied little (except for a gradual fall following the final application), differed little between different regions of the tuber, and were affected only slightly by the number of doses received (**Table 5**). This last finding suggests that the number of applications of metalaxyl is not critical for safety.

Similar results have been obtained by other authors for a variety of pesticides. For example, Pang et al. (21) found no pesticide in potatoes following application in the field; Andersen
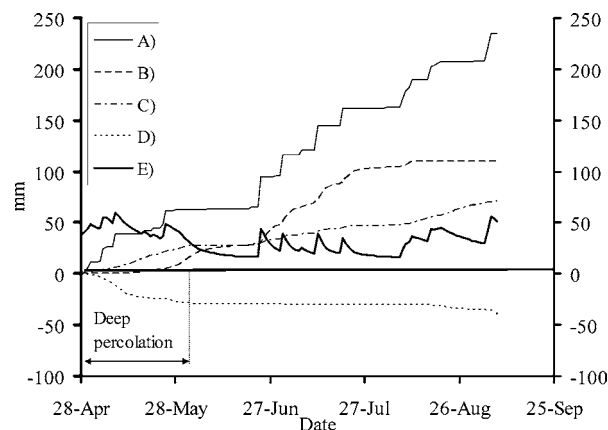
Figure 4. Soil water balance during the study period, as calculated by HYDRUS-1D: (**A**) cumulative rainfall + watering (final value = 235 mm); (**B**) cumulative crop transpiration (109 mm); (**C**) cumulative evaporation from bare soil (71 mm); (**D**) cumulative deep percolation below the root zone (39 mm); (**E**) gain of water stored in the soil (15 mm). Arrows mark the main period of potential loss of pesticide to groundwater.

Table 6. Soil Physical Parameters Used in HYDRUS-1D for Pesticide Transport Modeling (Mean Values Determined in Preliminary Experiments, with Standard Deviations in Parentheses)

bulk density	1.26 (0.21)	g cm^{-3}
saturated water content	0.42 (0.026)	cm^3 cm^{-3}
residual water content (air-dried)	0.03 (0.02)	cm^3 cm^{-3}
saturated water permeability (K_s)	102 (72)	cm/day
van Genuchten–Mualem soil water retention function parameter α	0.034 (0.017)	cm
van Genuchten–Mualem soil water retention function parameter n	2.58 (0.27)	
vertical solute dispersivity (D)	0.526 (0.24)	cm
fraction of immobile water (f)	0.16 (0.14)	
first-order solute transfer coefficient between mobile and immobile water (ω)	14 (0.43)	day^{-1}

et al. (22) reported that dieldrin, chlorprophan, endosulfan, and tolclofos-methyl never exceeded their maximum detection limits.

Modeling Results. The soil data used for modeling are listed in **Table 6**, and the evolution of the water balance during the experimental period is shown in **Figure 4**. Most infiltration below the root zone occurred in May.

The direct input of metalaxyl to the soil during each application was estimated as 0.24 mg/(kg of soil), which on the assumption of exclusive initial uptake by the top 1 cm of soil amounts to 10% of the applied dose. The fraction of each dose of metalaxyl that was retained by plants in a form susceptible to being washed off, estimated as described under Experimental Procedures, was 4%, and the course of wash-off input to the soil that was calculated on this basis using eq 1 is shown in **Figure 5** for group D plots. The total wash-off input of metalaxyl to the soil in group D plots (the sum of all the inputs shown in **Figure 5**) amounted to 3.8% of the total dose applied to these plots. The course of metalaxyl concentration in the 0–1 and 1–15 cm soil layers, as estimated by the HYDRUS-1D model ($r^2 = 0.9602$), is shown in **Figure 6A**. The optimized value of K_d was 5.4 ± 0.3 L/kg [a value similar to that obtained by Sukop and Cogger (23)], and the optimized value of S was 0.37 ± 0.02 day^{-1} (half-life of 2 days).

Under the assumptions noted in Experimental Procedures, the dosages of metribuzin in plots of groups B, C, and D amounted to initial concentrations of 3.35, 6.70, and 10.00 mg/kg, respectively, in the top 1 cm of soil. The time course of the
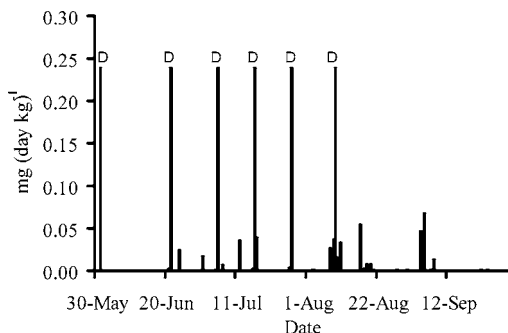
Figure 5. Time course of input of metalaxyl to soil by direct deposition of spray (marked by a "D" on the top of the bars) and wash-off (unmarked bars).
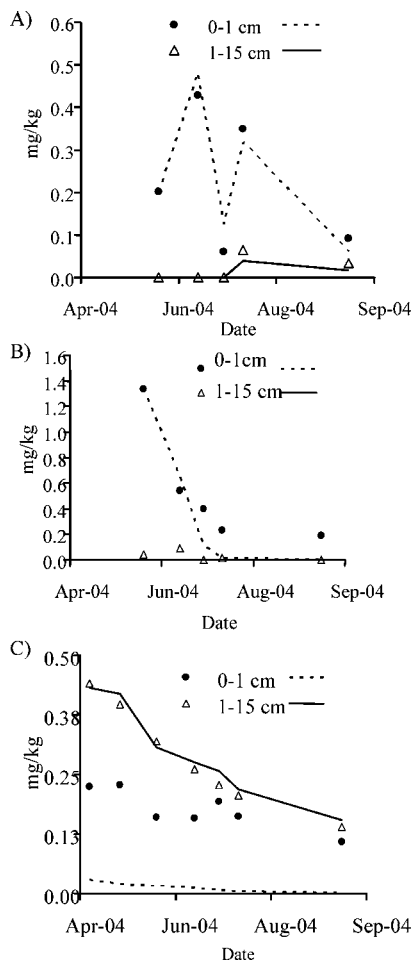
Figure 6. Time course of the concentrations of metalaxyl (**A**), metribuzin (**B**), and fenamiphos (**C**) in the 0–1 cm (●) and 1–15 cm (△) layers of group D plots, together with the HYDRUS-1D models fitted using the optimized values of K_d and S stated in the text (- - -, 0–1 cm; —, 1–15 cm).

concentration in the 0−1 and 1−15 cm layers of group D plots according to the HYDRUS-1D model fitted using optimized values of 2.3 ± 0.8 L/kg for K_d and 0.090 ± 0.001 day^{-1} for S (half-life of 8 days) is shown in **Figure 6B** ($r^2 = 0.9356$).

The dosages of fenamiphos in plots of groups B, C, and D amounted to initial concentrations of 1.28, 1.90, and 2.55 mg/kg, respectively, in the top 15 cm of soil. The values afforded for group D plots by HYDRUS-1D using optimized values of 5.20 ± 0.11 L/kg for K_d [a value similar to that obtained by other authors (*10*)] and 0.0097 ± 0.0002 day^{-1} for S [half-life of 70 days, ∼7 times longer than was reported by Guo (*11*)]

are shown in **Figure 6C** ($r^2 = 0.9662$) and imply that only ∼10% of the group D fenamiphos dose was taken up by the plants. However, the results of the model for the 0−1 cm layer are gross underestimates, suggesting that release of fenamiphos from its solid formulation occurred throughout the study period in a slow, sustained manner that was not captured by the model and which may be attributable to the soil having remained for 105 days with a matrix potential lower than −1.60 mPa.

To sum up, the dissipation half-lives in the field were 2 and 8 days, respectively, for metalaxyl and metribuzin, active ingredients of formulations applied in liquid form. Metribuzin was applied just once before plant emergence, but metalaxyl was repeatedly applied to the potato plants and was the only pesticide found in potato tubers. The direct input of metalaxyl to the soil during each application was estimated as 10% of the applied dose, whereas the total wash-off input of metalaxyl to the soil amounted to 3.8% of the total dose applied. Fenamiphos was, on the other hand, applied in a solid formulation that was incorporated into the 15 cm soil layer with a rotary cultivator in a single application before plant emergence and showed the largest dissipation half-life (70 days). For all of the studied pesticides, the courses of concentrations in the 15 cm soil layers were well fitted by the HYDRUS-1D model ($r^2 > 0.9355$). Optimized values of K_d in the field were lower for metribuzin (2.3 L/kg) than for metalaxyl and fenamiphos, with more ready adsorption (5.2−5.4 L/kg). The HYDRUS-1D model can then satisfactorily be used to estimate the thermodynamic and kinetic parameters governing the dissipation of the studied pesticides in the 15 cm soil layer of field experiments, the zone in which roots or tubers are located.

LITERATURE CITED

(1) Libman, G. N.; MacIntosh, S. C. Registration of biopesticides. In *Entomopathogenic Bacteria: from Laboratory to Field Application*; Charles, J., Delecluse, A., Nielsen-Le Roux, C., Eds.; Kluwer Academic Publications: Dordrecht, Holland, 2000; pp 333−336.

(2) Escriche, B.; González-Cabrera, J.; Herrero, S.; Ferré, J. Insecticidal effects of *Bacillus thurigiensis* crystal proteins. Potency differences depending on the tested strain. *Phytoma* **2001**, *129*, 40−45.

(3) Coscollá, R.; Gamón, M. Pesticide residues on Spanish food commodities. *Phytoma* **2001**, *129*, 46−51.

(4) Rial-Otero, R.; González-Rodríguez, R.; Cancho-Grande, B.; Simal-Gándara, J. Parameters affecting extraction of selected fungicides from vineyard soils. *J. Agric. Food Chem.* **2004**, *52*, 7227−7234.

(5) Šimůnek, J.; Šejna, M.; van Genuchten, M. Th. *The HYDRUS-1D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated media*, version 2.0; IGWMC-TPS-70; International Ground Water Modeling Center, Colorado School of Mines: Golden, CO, 1998.

(6) van Genuchten, M. Th.; Wierenga, P. J. Solute dispersion coefficients and retardation factors. In *Methods of Soil Analysis, Part 1*; Klute, A., Ed.; ASA, CSSA, and SSSA: Madison WI, 1986; pp 1025−1054.

(7) Klute, A.; Dirksen, C. Hydraulic conductivity and diffusivity: laboratory methods. In *Methods of Soil Analysis, Part 1*; Klute, A., Ed.; ASA, CSSA, and SSSA: Madison WI, 1986; pp 687−734

(8) Vandam, J. C.; Stricker, J. N. M.; Droogers, P. Inverse method to determine soil hydraulic functions from multistep outflow experiments. *Soil Sci. Soc. Am. J.* **1994**, *58*, 647−652.

(9) van Genuchten, M. T. A closed form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 892−898.

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(10) Green, R. E.; Schneider, R. C.; Gavenda, R. T.; Miles, C. J. Utility of sorption and degradation parameters from the literature for site-specific pesticide impact assessments. In *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*; SSSA Special Publication 32; SSSA and ASA: Madison, WI, 1993.

(11) Guo, M. *Transport and Fractionation of Dissolved Organic Matter in Soil Columns*; Lippincott Williams & Wilkins: Baltimore, MD, 2003; pp 108−118.

(12) Allen, R. G.; Pereira, L. S.; Raes, D.; Smith, M. *Crop Evapotranspiration−Guidelines for Computing Crop Water Requirements*; FAO: Rome, Italy, 1998.

(13) Rial Otero, R.; Cancho Grande, B.; Arias Estévez, M.; López Periago, E.; Simal Gándara, J. Procedure for the measurement of soil inputs of plant-protection agents washed off through vineyard canopy by rainfall. *J. Agric. Food Chem.* **2003**, *51*, 5041−5046.

(14) Tomlin, C., Ed. *The Pesticides Manual*, 12th ed.; British Crop Protection Council Publication: Surrey, U.K., 2000.

(15) Arias, M.; Paradelo, M.; López, E.; Soto, B.; Simal-Gándara, J. Significance of pH and copper level in the adsorption of the fungicides metalaxyl and penconazole in the surface layer of vineyard soils. *J. Agric. Food Chem.* **2006**, submitted for publication.

(16) Diaz Diaz, R.; Gaggi, C.; Sanchez-Hernandez, J. C.; Bacci, E. The role of soil and active ingredient properties in degradation of pesticides: a preliminary assessment. *Chemosphere* **1995**, *30*, 2375−2386.

(17) Ahrens, W. H., Ed. *Herbicide Handbook*, 7th ed.; Weed Science Society of America: Champaign, IL, 1994.

(18) Yalkowsky, S. H., He, Y., Eds. *Handbook of Aqueous Solubility Data*; CRC Press: Boca Raton, FL, 2003; p 934.

(19) Gawlik, B. M.; Feicht, E. A.; Karcher, W.; Kettrup, A.; Muntau, H. Application of the European reference soil set (EUROSOILS) to a HPLC-screening method for the estimation of soil adsorption coefficients of organic compounds. *Chemosphere* **1998**, *36*, 2903−2919.

(20) *Off. J. Eur. Communities* **1998**, *290/L* (Oct 29).

(21) Pang, G.; Chao, Y.; Fan, C.; Zhang, C.; Li, X.; Liu, Y. Modification of AOAC multiresidue method for determination of synthetic pyrethroid residues in fruits, vegetables and grains. Part II: acetone extraction system. *J. AOAC Int.* **1995**, *78*, 1489−1496.

(22) Andersen, J. H.; Poulsen, M. E. Results from monitoring of pesticide residues in fruits and vegetables on the Danish market, 1998−99. *Food Addit. Contam.* **2001**, *18*, 906−931.

(23) Sukop, M.; Cogger, C. G. Adsorption of carbofuran, metalaxyl, and simazine: K_{OC} evaluation and relation to soil transport. *J. Environ. Sci. Health* **1992**, *B27*, 565−590.