Procedure for the Measurement of Soil Inputs of Plant-Protection Agents Washed off through Vineyard Canopy by Rainfall

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Soil inputs produced by rainfall waters washed off through a Ribeiro vineyard (Galicia, northwestern Spain) confirmed that levels recovered are <5% of the added fungicides. Laboratory studies showed that some fungicides were degraded in the ODS cartridge used for the collection of fungicides washed off by rainfall. Procymidone wash-off data obtained in the vineyard can be explained by a first-order rate mass transfer model. A procedure for the collection of wash-off waters based on octadecylsilane solid phase extraction, followed by an analytical method of reverse-phase liquid chromatography with diode array detection is presented for the evaluation of fungicide inputs into soils after being washed off vineyards by rainfalls. Quality parameters of the analytical method yielded good precision (RSD < 10%) and low detection limits (ranging between 1 and 21 μg/L).

INTRODUCTION

Fungicides are used to control molds and mildews on crops and in the soil, as well as on golf courses, turf farms, and ornamentals (*1*). Many fungicides, including copper salts, ziram, maneb, chlorothalonil, captan, and mancozeb, are highly toxic to aquatic life. Some of these compounds cause chronic toxicity as well. Ziram, maneb, mancozeb, and benomyl are endocrine disruptors. Captan, chlorothalonil, iprodione, maneb, and mancozeb are classified as probable or possible human carcinogens by the U.S. Environmental Protection Agency (*2*). Very few studies to date have tested for fungicides washed off by rainfall.

Fungicides make their way into waterways, lakes, oceans, nature preserves, wildlife refuges, forests, and urban areas by many routes. In agricultural areas (*3*), massive amounts of fungicides are introduced into the environment through aerial and ground spraying of crops. Soil and storage fumigations, as well as chemigation (application of fungicides with irrigation water), use large quantities of fungicides also. Environmental contamination occurs when fungicides drift away from the application site through the air and rainwater, infiltrate groundwater by leaching through the soil, run off treated land with stormwater or irrigation water, or otherwise migrate away from the application site (*4*, *5*).

In rainy months, storms wash fungicides off fields and orchards and into nearby surface waters. The amount of fungicide that washes into the receiving water depends on a number of factors, including the amount and identity of fungicide applied, water solubility of the fungicide, and type of soil and vegetation present in the application area. Whereas some fungicides bind irreversibly to soil organic matter and mineral particles and are transported only via sediments, others dissolve readily in water and infiltrate the soil or travel with the overland flow into streams, agricultural drains, and rivers (*6*, *7*).

In the environment, fungicides degrade into a variety of other substances as a result of interactions with soil, water, sunlight, and oxygen (*8*). The presence and potential environmental effects of fungicide breakdown products are only now being included in environmental fate studies by the agencies responsible for monitoring concentrations of these compounds in the environment. When these breakdown products are monitored, they are commonly found in measurable quantities in water, sediments, and plant and animal tissues (*9*). Fungicides are also degraded by living organisms. Soil microbes are responsible for catalyzing the breakdown of many fungicides, and in mammals, most fungicides are broken down in the liver to more soluble compounds, which are then excreted. Generally, fungicide breakdown products are less toxic than the fungicide itself. The rate of breakdown of a particular fungicide in the environment is a function of the fungicide, its location (whether it is adsorbed to soil or sediment particles, on an exposed leaf

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surface, in water, etc.), temperature, soil or water pH, and moisture content of the surrounding medium.

Because fungicides are known to have adverse effects on public health and the environment, a variety of policies have been adopted in an effort to minimize these impacts (*10*). However, despite extensive regulation, new pesticides are introduced into the market without their impact and fate being tested in all ecosystems. The main aim of this work was to develop a procedure for the collection of fungicides washed off by rainfall from canopy to soil. The collection procedure was followed by an analytical multiresidue method to estimate the fungicide inputs into soils. A pilot experimental setup was conducted in a vineyard of Ribeiro (Galicia, northwestern Spain) to obtain contaminated rainfall samples and assess the performance of the whole procedure screening for the residues of the fungicides. The analytical method used is based on solid phase extraction (SPE) and liquid chromatography followed by diode array detection (HPLC-DAD) (*11*). It is not possible to determine tebuconazole with this method; for those interested in such a determination, we propose a method based on gas chromatography followed by mass spectrometry detection (GC-MSD) (*12*).

EXPERIMENTAL PROCEDURES

Chemicals, Solvents, Disposables, and Small Apparatus. Pestanal grade standards of carbendazim [CAS Registry No. 10605-21-7], cymoxanil [CAS Registry No. 57966-95-7], cyprodinil [CAS Registry No. 121552-61], dichlofluanid [CAS Registry No. 1085-98-9], fenhexamid [CAS Registry No. 126833-17-8], folpet [CAS Registry No. 133-07-3], fludioxonil [CAS Registry No. 131341-86-1], metalaxyl [CAS Registry No. 057837-19-1], thiophanate-methyl [CAS Registry No. 23564-05-8], penconazole [CAS Registry No. 66246-88-6], pyrimethanil [CAS Registry No. 53122-28-0], procymidone [CAS Registry No. 32809-16-8], and vinclozolin [CAS Registry No. 050471-44-8] (purity > 99%, for all) were purchased from Riedel-de-Haën (Seelze, Germany). Carbofuran (99.5%), used as an internal standard, was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Methanol and water for liquid chromatography were purchased from Merck (Darmstadt, Germany), and acetonitrile for liquid chromatography was from Panreac (Barcelona, Spain).

Waters 360 mg Sep-Pak C_{18} Plus cartridges (Mildford, MA) were used as solid phase extraction (SPE) minicolumns for purification and concentration. The ends of the cartridges were capped in the fungicide stability experiments with plastic caps ($^3/_{16}$ and $^1/_4$ in. i.d.; Supelco, Bellefonte, PA). A Visiprep solid phase extraction vacuum manifold (Supelco) was used to simultaneously process up to 24 SPE tubes. The Visidry drying attachment (Supelco) was used to dry up to 24 SPE tubes at one time and can be used with any inert gas supply. It is also useful for evaporating and concentrating recovered samples. Nitrogen C-50 of analytical quality was supplied by Carburos Metálicos (Vigo, Spain). Homogenization of SPE extracts was achieved by vortex agitation (Heidolph Reax Top).

Stock Standard Solutions. A stock standard solution (∼1000 mg/L) of each fungicide was prepared in methanol by weighing ∼0.025 g of the analyte into a 25 mL volumetric flask and diluting to volume. An intermediary mixed standard solution was prepared by dilution in acetonitrile of the stock standard solutions to give a concentration of ∼100 mg/L for each fungicide. Stock and intermediary standard solutions of the internal standard, carbofuran, were prepared in the same way. All solutions were stored in the dark at 4 °C and were stable for at least 6 months.

Fortified aqueous solutions were prepared by diluting intermediary mixed standard solutions with the appropriate volumes of water to yield desired concentrations, keeping internal standard concentration at 1 or 5 mg/L.

Liquid Chromatographic System. High-performance liquid chromatography (HPLC) analyses were carried out on a Thermo HPLC system equipped with an SCM1000 vacuum membrane degasser, a
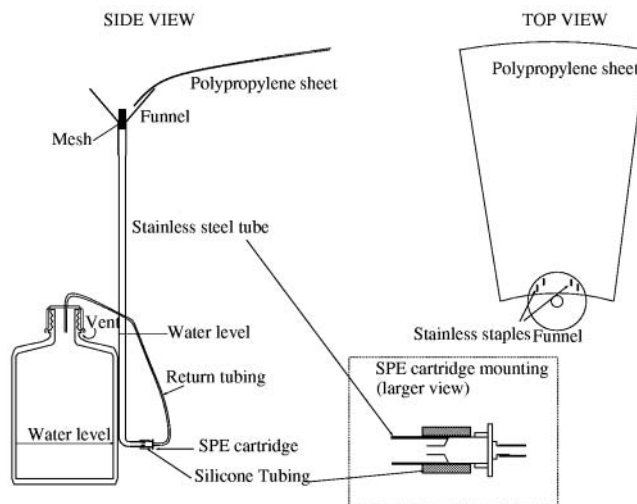

Figure 1. Sampling device for plant-protection agents washed off by rainfalls.

P2000 binary pump, an AS 1000 autosampler, a column heater from Jones chromatography (model 7981), and a UV6000LP diode array detector linked to a PC computer running the ChromQuest version 2.51 software program (TermoQuest).

Procedure for Collection and Determination of Plant-Protection Agents in Rainfall. Previously, laboratory studies were developed to estimate fungicide stability in the SPE cartridge during 2 weeks. For this purpose a total of 33 ODS cartridges were loaded with 50 mL of ultrapure water spiked at a levels of 1 mg/L of each fungicide. Three of the cartridges were eluted, and the eluates were analyzed the same day the experiment started. The others 30 cartridges were processed as follows: their ends were capped, and the whole cartridges were wrapped in aluminum foil; 15 cartridges were stored at low temperature (5 °C) and 15 at high temperature (30 °C); at five time intervals (1, 4, 7, 11, and 14 days), 3 of the cartridges exposed at low and high temperature were taken and processed.

Samples of vineyard wash-off rainwater were collected using a device developed by us. The device is based on a polypropylene sheet that drains the rain onto a funnel with a mesh followed by a vertical stainless steel tube, which provides the necessary pressure drop to force the water to pass through the SPE cartridge; water is finally recovered in an amber bottle by means of a polypropylene tube (**Figure 1**). The fungicides carried away by rainwater were adsorbed into the SPE cartridge (C_{18}, 360 mg), which was previously conditioned with 5 mL of methanol followed by 10 mL of water without allowing the cartridge to dry out before its installation. To avoid the degradation of fungicides, the SPE cartridge was preserved from the sunlight by using aluminum foil. The cartridge was sampled and replaced every 2−3 weeks during August and September and every 6−7 weeks thereafter until the end of the year. Sampling was always after a peak of rainfall. Rainwater passing through the cartridge was collected in an amber bottle, which allows rainfall volume to be measured, and this volume is correlated with the rainfall recorded by the metereological station located in the experimental area. Cartridges loaded after heavy rains were sampled as soon as possible and always within a week to prevent fungicide degradation. All cartridges were dried and stored at 4 °C until elution and analysis. The 360 mg C_{18} Sep-Pak cartridges collected from the experimental vineyard field were dried by blowing nitrogen for 20 min. Adsorbed pesticides were eluted by 2 mL of acetonitrile/water (90:10, v/v); this organic mix contained carbofuran (5 mg/L), which was used as internal standard. Homogenization of the eluate was achieved with vortex agitation prior to the chromatographic analysis. Dilutions were made before analysis when necessary.

For determination of fungicides by HPLC-DAD, an aliquot (50 μL) was injected into the Ultracarb 5 μm ODS 30% C (250 × 4.6 mm i.d.) analytical column (Phenomenex, Torrence, CA). The guard column (50 × 4.6 mm i.d.) was packed with dry 40 μm Pelliguard LC-18 (Supelco). The fungicides were eluted at 40 °C, with a constant flow rate of

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Table 1. Recoveries, Repeatabilities, Reproducibilities, Linear Dynamic Ranges, Determination Coefficients (r^2), Limits of Detection (LOD), and Limits of Quantitation (LOQ) of the Method for the Determination of Fungicides in Rainfall Waters

fungicide	recovery ± repeatability[a] (%) ± RSD (%)	reproducibility[b] ± RSD (%)	linear range[c] (μg/L)	determination coefficient (r^2)	LOD[a] (μg/L)	LOQ[a] (μg/L)
carbendazim	102 ± 2.4	7.3	50–1000	0.9995	5	14
cymoxanil	112 ± 1.5	2.5	25–1000	0.9990	1	3
thiophanate-methyl	108 ± 4.4	7.3	50–1000	0.9965	21	45
metalaxyl	112 ± 1.4	2.4	25–1000	0.9990	7	17
pyrimethanil	110 ± 1.7	3.2	25–1000	0.9990	1	2
fludioxonil	111 ± 1.2	2.2	25–925	0.9987	3	6
fenhexamid	107 ± 1.2	4.9	25–800	0.9964	5	11
folpet	101 ± 4.1	4.2	25–925	0.9986	1	3
procymidone	108 ± 1.5	4.8	25–800	0.9974	2	5
penconazole	102 ± 1.6	5.5	25–750	0.9963	3	7
cyprodinil	101 ± 1.9	5.5	25–1000	0.9997	4	12
vinclozolin	111 ± 1.9	4.9	25–925	0.9965	3	8
dichlofluanid	95 ± 8.1	9.7	50–1000	0.9994	10	21

[a] $n = 7$. [b] $n = 6$. [c] $n = 10$.

1.5 mL/min at the following gradient conditions for the mobile phase acetonitrile (A)/ultrapure water (B): 15 min isocratic elution at A:B = 25:75, followed by 5 min linear gradient to 30:70 and isocratic elution for 20 min, followed by 20 min linear gradient to 50:50 and isocratic elution for 18 min, followed by a 1 min linear gradient to 90:10, followed by a 11 min linear gradient to recover initial conditions and keep them for 15 min. Detection was carried out at wavelengths between 200 and 300 nm, and quantification was done at 200 nm for practically all target compounds, at 204 nm for fenhexamid and fludioxonil, at 224 nm for folpet, at 240 nm for cymoxanil, and at 270 nm for cyprodinil and pyrimethanil. The HPLC-DAD method used is a multiresidue method and allows the determination of a few more fungicides than those selected in the field study design. Other authors might be interested in field studies with a different selection; this is the reason we will provide data on the quality parameters of other fungicides that are possible to determine with the method together with data on the stability of those fungicides in the SPE cartridges used for sampling.

Evaluation of the Performance Characteristics of the Analytical Determination. Method performance was assessed by evaluating quality parameters such as recovery values, repeatability, reproducibility, linearity, and limits of detection and quantitation. All values obtained are summarized in **Table 1**. For this purpose, ultrapure water samples were previously fortified with the fungicides and treated following the experimental conditions described. The repeatability and reproducibility of the method were assessed by analyzing seven spiked ultrapure water samples ($\sim$250 μg/L of each fungicide) on the same day and a total of nine spiked ultrapure water samples ($\sim$250 μg/L) during 3 days in 2 different weeks, respectively. The relative standard deviation (RSD %) for repeatability was <5%, except for dichlofluanid, and for reproducibility was <10% for all. These values show the good precision of the multiresidue method proposed. On the other hand, recoveries are >95% for all target compounds. Calibration curves for the fungicides were prepared by plotting area relative to that of the internal standard (carbofuran) versus the analyte concentration using a total of 10 spiked ultrapure water samples (25–1000 μg/L). Linear ranges and determination coefficients (r^2) corresponding to each fungicide are better than 0.996. Limits of detection and quantitation were evaluated following the recommendations of the American Chemical Society (*13*). As tested experimentally detection and quantitation limits were, respectively, in the 1–21 and 2–45 μg/L range (**Table 1**).

Ultrapure and rainfall water samples were examined to study the matrix effect. It was initially confirmed that all samples were not contaminated with the studied fungicides. Water samples were then spiked at a level of 250 μg/L and treated following the experimental procedure described under Procedure for Collection and Determination of Plant-Protection Agents in Rainfall. Triplicate analyses were performed for each sample. Quantitation was performed using the calibration line for each fungicide with carbofuran as internal standard. The results were statistically evaluated by applying a two-tailed *F* test (at 95% confidence level) to the variances and a one-tailed *t* test (at

90% confidence level) to the means of the different test samples. Statistical evaluation of the results showed that the recoveries for all fungicides were constant in ultrapure and rainfall waters within the statistical allowances.

Experiments Conducted at Ribeiro Vineyard Experimental Treatment Plots. The field research was conducted during June 2002– January 2003 at A Quinza, an experimental vineyard field located in Ribadavia, Galicia (northwestern Spain). This experiment was carried over to determine the levels of fungicides in vineyard wash-off rainwater. The aim was to estimate the inputs of soil pollution by fungicides.

This study was performed in four 150 m² plots of A Quinza experimental field. Each experimental plot presented six vineyard rows of 12.1 m each and with 10 plants, as can be seen in **Figure 2**. The average plant height was 0.8 m and average width 0.6 m. Two sampling devices were placed in the center of the two middle vineyard rows of each experimental plot. These vineyards produced Treixadura white grapes, a common variety of grape in the area of Ribeiro, one of the so-called certain quality wines produced in specified regions. Each experimental plot was treated with a different antifungal treatment against gray mold (*Botrytis cinerea*), powdery mildew (*Uncinula necator*), and downy mildew (*Plasmopara viticola*) using the pesticide formulations described in **Table 2**.

Fungicides were applied in accordance with the manufacturer's label instructions before grape ripening and harvest in five time intervals (June 14 at grape formation, July 3 at bunch formation, and August 2 and 20 and September 10 during grape coloring). All applications were performed for treating gray mold, powdery mildew, and downy mildew except the first and fourth applications (June 14 and August 20, respectively), in which gray mold fungicides were not used. All applications were made using a hand-held sprayer. Vineyard-protection formulations of interest were mixed and diluted with water as required during vineyard growth to give the concentrations reported in **Table 2**; 4, 7, 10, 10, and 10 L were used, respectively, in the applications over time.

During the field experiments, air temperature (maximum and minimum) and rainfall were daily recorded by the metereological station located in the experimental area. The five sampling events were on August 20, September 10 and 27, November 20, and January 16.

RESULTS AND DISCUSSION

The total sprayed volume with the solution of fungicides was 34.8 m³. The surface of the polypropylene sheet collecting the wash-off waters is 0.05 m², which makes a collection volume of 0.04 m³ taking into account the average plant height. With these data, the level of fungicide added during the different treatments, and the accumulated level measured in the waters, it was possible to calculate the fungicide percentage recovered in the waters. From the highest to the lowest fungicide inputs
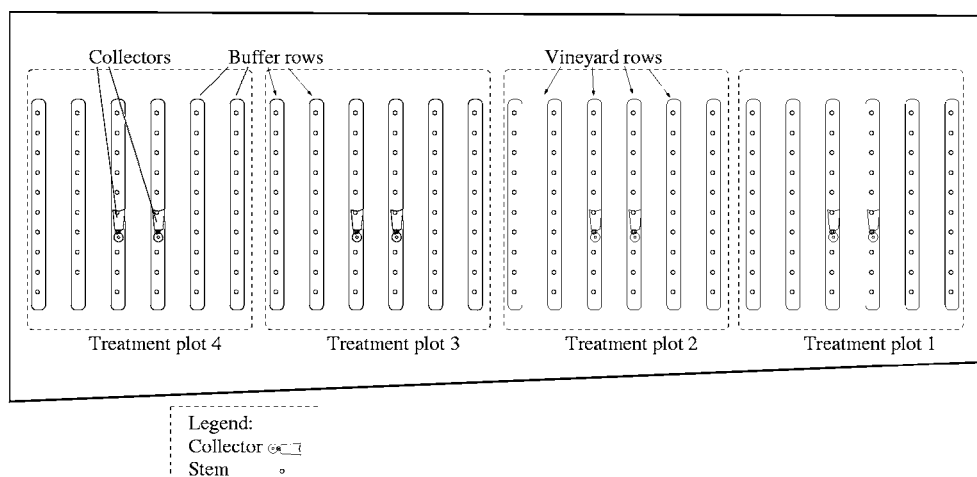
Figure 2. Ribeiro vineyard experimental treatment plots.

Table 2. Commercial Vineyard-Protection Formulations Used in the Case Study

	fungicide formulation (%)	recommended dosage	commercial name	manufacturer
first exptl plot				
powdery mildew	Cu (20%)	500 g/hL	Caldo Bordalés Quimur	Sarabia
downy mildew	tebuconazole (25%)	40 g/hL	Folicur 25 WG	Bayer
gray mold	procymidone (50%)	100 g/hL	Sumisclex 50 WP	Massó
second exptl plot				
powdery mildew	metalaxyl (10%) + folpet (40%)	200 g/hL	Ridomil Combi	Ciba-Geigy
downy mildew	tebuconazole (25%)	40 g/hL	Folicur 25 WG	Bayer
gray mold	pyrimethanil (40%)	200 mL/hL	Scala	Aventis
third exptl plot				
powdery mildew	Cu (20%)	500 g/hL	Caldo Bordalés Quimur	Sarabia
downy mildew	penconazole (10%)	40 mL/hL	Topas 10 EC	Ciba-Geigy
gray mold	cyprodinil (37.4%) + fludioxonil (25%)	133 g/hL	Switch	Syngenta Agro
fourth exptl plot				
powdery mildew	Cu (20%) + folpet (10%)	500 g/hL	Camposan	Agroindustrial
downy mildew	penconazole (10%)	40 mL/hL	Topas 10 EC	Ciba-Geigy
gray mold	fenhexamid (50%)	321 g/hL	Teldor	Bayer

Table 3. Summary of Balance of Fungicides Applied and Released by Wash-off

fungicide	line	applied (μg/m^3)	released (μg/m^3)	released fraction (%)
procymidone	1	15529	458	2.95
metalaxyl	2	9413	116	1.23
folpet	2	37650	11	0.03
folpet	4	23530	38	0.16
pyrimethanil	2	33977	253	0.74
penconazole	4	1873	8	0.42
cyprodinil	3	15417	46	0.30
fludioxonil	3	10306	84	0.82
fenhexamid	4	49742	133	0.27

onto soil the following gradient was found: procymidone (1−5%) > metalaxyl (0−3%) > pyrimethanil and fludioxonil (0−2%) > fenhexamid and cyprodinil (0−1%) > folpet and penconazole (0−0.5%). As an average, release of fungicides by wash-off was in the range of 0.03−2.95% for folpet and procimydone, respectively (**Table 3**). These recovery values can be mainly explained in terms of fungicide stability and transport. Laboratory studies of the fungicides' stability in the SPE cartridge at differents temperatures (5 and 30 °C) allowed us to obtain the information in **Table 4**. Carbendazim, cyprodinil, fludioxonil, metalaxyl, penconazole, procymidone, and pyrimethanil were stable. Degradation rate and half-life parameters of the applied fungicides, calculated using the degradation percentages at 30 °C, are shown in **Table 5**. Release fractions (percent) of procymidone, metalaxyl, fludioxonil, and folpet are

Table 4. Fungicide Stability Experiments in SPE Cartridges at Different Temperatures [Average Percentages Remaining of Those Unstable ($n = 3$)]

| fungicide	temp (°C)	day 1	4	7	11	14
cymoxanil	5	100	100	100	100	100
	30	100	80	74	62	50
thiophanate-methyl	5	60	24	20	11	10
	30	15	0	0	0	0
fenhexamid	5	95	90	85	82	80
	30	90	87	83	81	80
folpet	5	100	97	95	90	85
	30	50	5	0	0	0
vinclozolin	5	100	100	100	100	100
	30	100	90	83	67	50
dichlofluanid	5	70	44	34	20	10
	30	30	5	0	0	0

positively correlated with the thermal stability in SPE cartridges (**Table 5**; **Figure 3**). In the case of pyrimethanil, cyprodinil, and penconazole, there is no such relationship due to the influence of solubility, vapor pressure, or affinity to leaf surface among other factors.

The transport controlling mechanism is difficult to identify. In the present study, the fraction of fungicide released was very small and wash-off was very fast after a small amount of rain. The cumulative mass ratio of sprayed/released fungicide along the experiment versus cumulative rainfall is plotted in **Figure 4**. As it can be seen in this figure, the highest recovery

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Table 5. First-Order Degradation Rate, Half Life, Water Solubility, and Vapor Pressure of the Fungicides Applied in the Experimental Plots

fungicide	degradation rate[a] (h^{-1})	half-life[a] (days)	water solubility[b] (mg L^{-1}, pH 7, 25 °C)	vapor pressure[b] (Pa)
cyprodinil	0.03	480	13	5.1×10^{-4} (25 °C)
fludioxonil	0.09	189	1.8	7.1×10^{-7} (20 °C)
folpet	18	1	1.0	1.3×10^{-3} (20 °C)
metalaxyl	0.07	238	7100	2.9×10^{-4} (20 °C)
penconazole	0.02	966	73	3.7×10^{-4} (25 °C)
procymidone	0.03	490	4.5	1.8×10^{-2} (25 °C)
pyrimethanil	0.03	480	121	2.2×10^{-3} (25 °C)

[a] Experimental values obtained at 30 °C ($n = 3$). [b] From ref *18*.
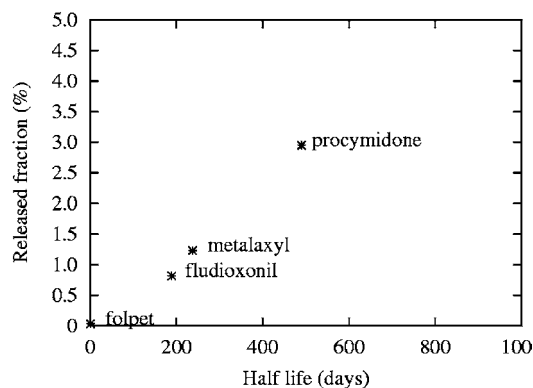
Figure 3. Fraction of released fungicide versus the half-life calculated in SPE cartridge incubated at 30 °C.
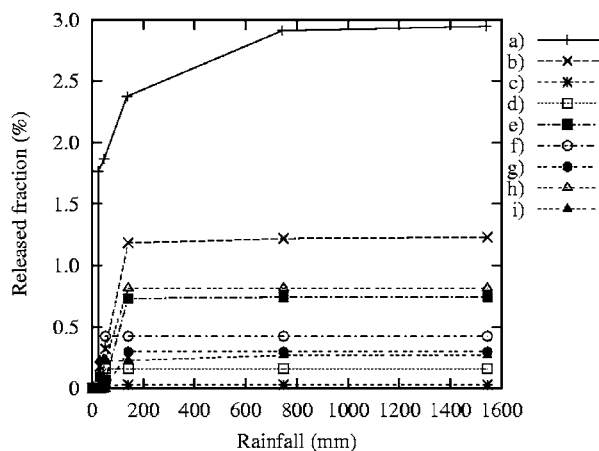
Figure 4. Cumulative released fraction of fungicides versus cumulative rainfall: (a) procymidone, (b) metalaxyl, (c) folpet (line 2), (d) folpet (line 4), (e) pyrimethanil, (f) penconazole, (g) cyprodinil, (h) fludioxonil, and (i) fenhexamid. The five sampling events were on Aug 20, Sept 10 and 27, Nov 20, and Jan 16.

of fungicides by wash-off was after a cumulative rainfall of 140 mm, corresponding to 106 days after the first application. Release did not increase during the following 1431 mm of cumulative rainfall; only procymidone was washed off during that period (0.57%). Metalaxyl and procymidone are two examples of, respectively, soluble and insoluble fungicides (**Table 5**). Their different solubilities explain their behaviors; release of metalaxyl appears to be linear with the first 140 mm of rainfall until exhaustion, but procymidone releases exponentially with rainfall. Considering that procymidone is sprayed as a wettable powder and taking into account its low solubility in water, the mechanism that controls its release and transport from canopy to soil is the detachment of the powder that has procymidone attached to it, whereas the mechanism that controls
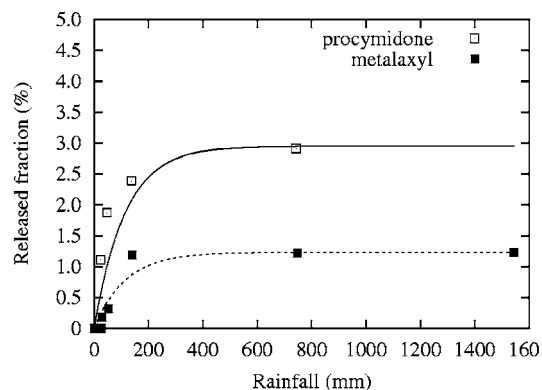
Figure 5. Observed data (symbols) and first-order fitting model of release (lines) corresponding to metalaxyl and procymidone; cumulative released fraction of fungicides versus cumulative rainfall.

the release and transport of metalaxyl is its solubility. The shape of the release curves was very steep for all fungicides tested, which agrees with a model of sharp depletion of soluble or detachable solid fractions.

Some equations describing cumulative fractional losses of fungicides as a function of cumulative fractional wash-off volume were provided by some authors. McDowell et al. (*14*) reported that the fraction of parathion-methyl washed from cotton plants decreased exponentially with time after application and linearly with load on the plants. Pick et al. (*15*), using overhead irrigation, concluded that endosulfan, cypermethrin, and carbaryl (wettable powder) become more resistant to wash-off with time after application. On the basis of the measured data from fenvalerate on cotton in the southern United States, McDowell (*16*) proposed a set of equations estimating concentration in rainfall water as a function of wash-off volume, independent of rain intensity. The behavior of fungicide wash-off can be modeled by a surface diffusion type model (*17*). In the case of high wash flow, the detachment is fully controlled by the mass transfer process

$$-\mathrm{d}C/\mathrm{d}R = -K_R C^n$$

where $\mathrm{d}C/\mathrm{d}R$ is the depletion rate of fungicide with the rainfall, K_R is the single mass transfer coefficient, and n is the order of the process. This model, initially valid to describe the release of soluble compounds, may be useful to describe both diffusion-controlled and detachment-controlled processs and compare the predictions of this model for wash load transport of metalaxyl and procymidone. In **Figure 5** the mass transfer model is shown. For procymidone, best fit for mass transfer K_R coefficient was 0.025 mm^{-1} and the order of the process was 1. For metalaxyl, the process simulates an order of reaction of 0.5, with a release constant of 0.017 mm^{-1}. Decreasing the order of the release process suggests that it is less dependent from the mass of fungicide stored on the leaves and is affected by the variability of the wash-off on the leaf surfaces.

In summary, soil inputs produced by rainfall waters washed off through a Ribeiro vineyard (Galicia, northwestern Spain) confirmed that the levels recovered are <5% of the added fungicides. This is related to the stability of the fungicides in the SPE cartridge used for water collection and their release from canopy to soil. Laboratory studies showed that some fungicides were degraded in the ODS cartridge used for the collection of fungicides washed off by rainfall; this is why cartridges once loaded with rainfall waters must be sampled and replaced within a week. Procymidone wash-off data

obtained in the vineyard can be explained by a first-order rate mass transfer model, whereas in the case of metalaxyl its release process is less dependent on the mass of fungicide stored on the leaves and is more affected by the variability of the wash-off on the leaf surfaces.

The wash-off water collection device and procedure developed by us together with the analytical multiresidue method proposed were suitable to determine the input of fungicides into soil by rainfall. The HPLC-DAD method had good linearity, precision, and accuracy and was highly sensitive. The quantitation process required the use of an internal standard to correct for errors in solid phase extraction and chromatographic performance.

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