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Simulating Washoff of Cu-Based Fungicide Sprays by Using a Rotating Shear Device

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Foliar washoff causes a loss of copper-based pesticides sprayed on crops, leading to an increase in the number of applications and contamination of the soil with Cu. In field studies, the variables that determine the amount of Cu loss are difficult to control. An experimental setup based on a rotating shear device (RSD) was used to estimate the influence of physical factors in the loss of Cu due to washoff of three copper-based fungicides: copper oxychlorhide (CO), Bordeaux mixture (BM), and a mixture of copper oxychlorhide and propylene glycol (CO-PG). Full factorial designs were used to model the loss of Cu from fungicides sprayed on the polypropylene surface of the RSD. Variables in the experiments were rotation speed, wash water volume, and fungicide dose. Good reproducibility was obtained for Cu loss, with a coefficient of variation less than 8%. Mean Cu losses were 27.0, 33.0, and 13.5% of the copper applied in fungicide for the BM, CO, and CO-PG, respectively. Empirical equations were obtained to calculate Cu losses from the rotation speed, wash water volume, and dose, as well as their interactions. CO losses were consistent with a model of particle detachment in which such losses depended on a threshold boundary shear stress required to initiate particle motion. Also, percent CO losses were found to be significantly correlated with the linear momentum at the surface boundary. The momentum values obtained in the RSD tests were similar to those estimated for a rainfall event of 20 mm h^{-1} lasting 10 min. The most important mechanism in the loss of CO was the erosion of Cu-bearing particles.

KEYWORDS: Fungicide loss; washoff; copper; shear stress

INTRODUCTION

For the past several decades, copper-based fungicides have been widely applied to crops to control fungal diseases. The effectiveness of these treatments can be diminished by the loss of fungicide due to washoff. Consequently, growers need to perform repeat applications. Moreover, the Cu-enriched canopy drip may contribute to raising Cu concentrations in soil above phytotoxic levels. Although no previous studies on washoff of copper-based fungicides have been previously reported, we found evidence that canopy drip carries Cu-based fungicides in suspension during rain episodes. Moreover, studies have found significant levels of Cu in runoff from citrus croplands (*1*) and accumulation of Cu in soil at vineyards (*2–8*). Cu concentrations in vineyard soil can even exceed the limits set by the European Union. Foliar washoff under natural conditions is complex due to the natural variability in the controlling factors. These include the dynamics of rainfall on the pesticide-coated plant, the characteristics of the leaf surface, the properties of the pesticide, and the nature of the bond between the pesticide and the leaf surface.

Improved understanding of these factors is important for evaluating the risk of pesticide loss and the environmental effects of pesticide drift into sensitive areas (*9*). The study of foliar washoff can also help to optimize fungicide use in agriculture through such measures as better application schedules or spray techniques. Researchers are also interested in assessing formulations of copper-based fungicides that are designed to improve the effectiveness and safety of traditional application methods.

Rainfall simulation tests provide a means to reproduce washoff by rain and examine its effects in terms of rainfall intensity and duration and also the kinetic energy of drops (*10*). However, the hydrodynamics of drop impact on dry and wet surfaces is complex and poses the typical problems of nonintegrable singularity in surface shear stress at the three-phase contact line, vertical compression, and air entrapment under raindrops or lateral jets, among others (see references cited in refs *11* and *12*). Because of its complexity, rainfall washoff is normally modeled in terms of correlations and empirical equations as in RZWQM (*13*). We believe simplified experimental systems can facilitate the analysis of some specific mechanisms involved in rainfall washoff dynamics. The effect of hydrodynamic shear on particle detachment has been

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Table 1. Specifications of the Commercial Fungicides Used in This Work

name	provider	description[a]	dosage (kg L^{-1})	CAS no.	chemical formula
Covicampo bordelés (BM)	Agrides S.A., Tarragona, Spain	Bourdeaux mixture, wetting powder 20% Cu	0.20	8011-63-0	$CuSO_4 \cdot 3Cu(OH)_2 \cdot 3CaSO_4$
Oxicol-50 (CO)	Insecticidas MAFA, S.L. Castellón, Spain	copper oxychlorhide 50%, wetting powder	0.40	1332-40-7	$CuCl_2 \cdot 3Cu(OH)_2$
ZZ-Cuprocol (CO-PG)	Syngenta Agro S.A., Pontevedra, Spain	copper oxychlorhide 65.4%, 1, 2- Propanediol 2.01% in aqueous suspension (density 1.94 g/cm^3)	0.29	1332-40-7, 57-55-6	$CuCl_2 \cdot 3Cu(OH)_2$, $C_3H_8O_2$

[a] All active ingredients are technical grade. The Cu content is expressed in percentage by the manufacturer.

examined in a number of studies (*14, 15*). In this work, we assumed boundary surface shear stress at the solid−liquid interface to be a firm candidate for causing detachment of particulate fungicides. The objective of this study was to analyze the washoff induced by boundary surface shear stress with a simplified laboratory setup based on a rotating shear flow device (RSD). This device allows the user to control a water film flowing over the fungicide on the surface and to obtain water samples to determine the amount of fungicide lost.

The RSD was used to analyze the effects of time, rotation speed, wash water volume, and fungicide dose on the percentage of Cu lost. A comparison was made among three copper-based fungicides for commercial use: Bordeaux mixture (BM) based on calcium−copper sulfate, copper oxychloride without additives (CO), and ZZ-Cuprocol, a commercial mixture containing copper oxychloride and propylene glycol (CO-PG).

MATERIAL AND METHODS

Specifications of the commercial fungicides used in the experiments are shown in **Table 1**. The copper content in each fungicide was determined in quintuplicate by acid digestion with aqua-regia and hydrofluoric acid until the sample was completely dissolved (*16*).

Suspensions were prepared by mixing the fungicides with 500 mL of distilled water in the proportions indicated by the manufacturer (**Table 1**). They were thoroughly mixed in an end-over-end shaker for 1 h, and the pH was measured. To determine the ratio of particulate Cu to total Cu in the suspensions, an aliquot of each suspension was filtered through a membrane of 0.45 μm pore size and used to determine dissolved Cu. Another aliquot was acidified with 13.5 M HNO_3 to dissolve any particulate Cu in the suspension to determine total Cu.

The average particle size diameter of the fungicide powders in the aqueous suspensions was measured over the range 0.6 nm to 6 μm by dynamic light scattering on Zetasizer Nano equipment from Malvern Instruments, Ltd. (Malvern, United Kingdom).

The shearing experiments were performed in a thermostatized RSD (**Figure 1**). The device used a rotating chamber made from a cylindrical polypropylene vessel in which the fungicide was sprayed on the inner wall. We chose polypropylene because the most important properties of surfaces determining water flow dynamics were the contact angle between the water drop and the solid surface and surface roughness (*12*). Because roughness depended on the particular length scale, it varied markedly between plant species and was difficult to reproduce, so we chose to use a smooth surface. Also, polypropylene has a contact angle with water of 84° (*17*), which falls in the range for many common leaf surfaces (*18*). When the chamber was partially filled with water and closed at the top, the rotating axis could be oriented horizontally so that the rotation formed a circulating water film. The shear exerted by the water at the solid−liquid interface can be simplified as:

$$\tau = 2\mu \mathbf{u}/z \quad (1)$$

where τ is the boundary surface shear stress (Pa), μ is the water viscosity (8.9×10^{-4} Pa s at 25 °C), $\mathbf{u}$ is the velocity of the water film at its surface (m s^{-1}), and z is the water film thickness (m).

The average thickness of the water film was calculated by dividing the volume of water into the wet surface area. The wet area was measured with an error less than 5 cm^2 from digital photographs of colored water samples flowing at 12, 24, or 36 rpm (rpm) in the RSD.

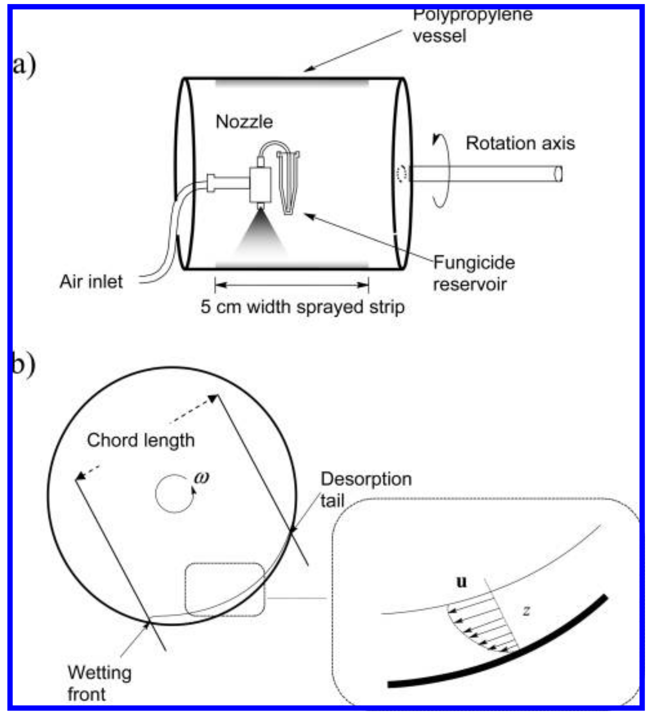

Figure 1. Schematic of the RSD. (**a**) Application of fungicide spray (side view). (**b**) Front view while shearing. The circle represents the cross-section of the rotating chamber, with fungicide sprayed on the inner wall. ω is the rotation speed, **u** is the flow velocity, and z is the water film thickness. The inset shows the shear flow field (arrows) in a section of the water film.

A volume of 1 mL of suspension containing the fungicide in the form of a wettable powder was sprayed at a distance of 2 cm on a 5 cm wide strip on the inner wall of the chamber with rotation at 36 rpm, using an atomization nozzle taken from a model PFP7 flame photometer from Jenway Ltd. (Jenway, United Kingdom); no pesticide was applied to the two 1.5 cm wide strips bordering the mouth and the bottom of the chamber to avoid the border effects of water film at the borders. The mean diameter of the strip where the fungicide was sprayed was 7.4 cm, and its surface area was 215 cm^2. The application volume and dosage fell in the ranges commonly used to prevent mildew infection in vineyards. The size of the droplets depositing on the surface and their distribution patterns were similar to those for natural leaves. The sprayed fungicide was then evaporated, and its dry residue was incubated for 24 h at 25 °C.

The proportion of Cu lost by spray drift in the air during application of the fungicide was determined from the known amount of Cu sprayed into the open chamber. Sprayed fungicide was immediately added with 50 mL of a 1 M HNO_3 rinse solution; then, the chamber was closed and shaken vigorously to dissolve and measure all Cu sticking to its walls. This determination was made in quintuplicate.

The amount of Cu removed from the walls of the rotating chamber in the washoff tests involving the RSD was determined by measuring

Table 2. Domain and Codification of Independent Variables Analyzed by Means of a First-Order Orthogonal Factorial Design[a]

codified values	natural values (V_n)		
X	ω	v	t
−1	12	10	10
0	24	30	17.5
+1	36	50	25

Influence of ω, v, and Dose (d) in the of Loss of Cu from OC, BM, and CO-PG

codified values	natural values (V_n)		
X	ω	v	d
−1	12	10	1
0	24	30	2
+1	36	50	3

[a] Codification: $X = (V_n - V_o)/\Delta V_n$. Decodification: $V_n = V_o + (\Delta V_n X)$. V_n, natural value; X, coded value; V_o, natural value in center of domain; ΔV_n, increment of V_n corresponding to one unit of X. Influence of rotation speed (ω), water volume (v), and rotation time (t) in the of loss of Cu from CO and BM.

the total Cu in the wash water; drift losses were provided for in the mass balance calculations. The concentration of Cu in the water samples and the fungicide digestions were measured by air−acetylene flame atomic absorption using a Solaar M5 spectrophotometer (Themo Fisher Scientific Inc., United States).

The kinetics of Cu loss was evaluated by measuring the concentration of Cu in wash water at different times. After the fungicide was sprayed and dried in the RSD, 50 mL of distilled water was carefully poured into the chamber, and rotation was started (36 rpm). From 1 min after the start of the experiment until the end of the experiment at 72 h, 1 mL of wash water was sampled at discrete times. The total Cu concentration in the samples was measured by flame photometry.

The influence of physical variables on fungicide loss was studied by experimental factorial designs. To design the experiments, it was assumed that the loss of Cu by washing was determined by (i) the solubilization of the Cu in the fungicide and (ii) the erosion of fungicide particles. Given that shear strength depended on both the rotation speed and the volume of water, these two factors were separated in the factorial designs to differentiate their respective influences on Cu loss.

The first factorial design examined the effects of rotation speed (ω, rpm), volume of water introduced into the RSD (v, mL), and rotation time (t, min). Time was included to model its interaction with the other two variables. The second factorial design was intended to determine the interaction between the applied dose of fungicide (d) and ω and v.

The two-level full factorial orthogonal designs involved three variables and four replicates in the center of the experimental domain. Levels of t, d, v, and ω, together with their respective codifications, are shown in **Table 2**.

Copper loss in the circulating water as a percentage of the amount sprayed was used as the dependent variable. The significance of the model coefficients was evaluated using Student's t test ($\alpha < 0.05$). Model consistency was verified by Fisher's F test ($\alpha < 0.05$). The effects of the individual factors and their interactions on copper loss were studied according to the methods of refs *19* and *20*.

RESULTS AND DISCUSSION

Flow Characteristics of the RSD. The water flow characteristics in the RSD are compared with those of natural raindrops in **Table 3**. Surface boundary shear stress in the RSD was estimated from ω and v values imposed by the factor designs of **Table 2**. Reported values of peak surface boundary shear stress induced by raindrop impact were roughly estimated to fall in the range 10−200 Pa on the basis of indirect measurements and computer simulations (*21*). These values are several times greater than in the RSD. The water film thickness of the desorption tail in the RSD (see **Figure 1**) was thinner; as a result, the surface boundary shear stress can increase about 20 times with respect to the estimates based on the average thickness. While the boundary shear stress induced by raindrops has a very limited effect in time and space (*21*), shearing in the RSD is sustained in time and encompasses a substantial fraction of the surface. RSD and rainfall raindrop impact may be compared in terms of their respective linear momenta parallel to the surface, which are given by

$$\mathbf{p} = \tau A t \qquad (2)$$

where, A and t are the area of the water solid interface and rotation time in the RSD and the area and duration of the impact, respectively, in the raindrops. **p** values in the RSD were estimated to be of the same order of magnitude as in a rainfall episode of 20 mm h^{-1} lasting 10 min (viz. 5×10^3 impacts of a drop 3 mm in equivalent diameter for the same time (**Table 3**).

Washoff Kinetics. The fungicide Cu content, particle size, pH, and amount of Cu in the doses sprayed on the RSD for each of the three commercial formulations are shown in **Table 4**. The soluble Cu concentration in the CO and BM suspensions was 1.8 and 0.92 mg L^{-1}, respectively, while the total Cu concentration was 43 (CO) and 8.9 mg L^{-1} (BM), respectively. Therefore, only 4.2% of Cu in CO and 10% of Cu in BM dissolved in the spraying suspensions. This suggests that Cu losses probably occurred mainly through erosion of particulate fungicide.

The time course of the loss of Cu in the wash water is shown in **Figure 2**; at the end of the experiment (72 h), the losses were 43, 21, and 14% of the sprayed Cu for CO, BM, and CO-PG, respectively. In the first minute, 35, 21, and 8.7% for CO, BM, and CO-PG were lost. Most of the loss occurred at 10 min in all cases, which indicates rapid kinetics. The time scale for the Cu loss rate is consistent with the erosion rates from agglomerates of silica particles (*15*). The kinetics in the RSD differed from that of rainfall-induced washoff by effect of the typical flow velocities resulting from a raindrop impact exceeding those in the RSD; also, raindrops impact gradually, making detachment more time-dependent than in the RSD.

The amount of copper lost from CO-PG was lower than for the other fungicides. A probable explanation is its smaller particle size, which increases the number of interparticle and particle−surface bonds per unit area; however, propylene glycol may also facilitate adhesion of active ingredients to the target surface.

Factorial Experiments. Tables S1 and S2 in the Supporting Information summarize the experimental copper losses, along with the responses predicted by the model and the statistics for the factorial design. The model equations fitted by regression analysis are

$$\mathrm{Cu\%\ (CO)} = 25.9 + 15.7\omega_c - 3.8v_c - 4.4\omega_c v_c \qquad (3)$$

$$\mathrm{Cu\%\ (BM)} = 25.5 + 4.9\omega_c + 5.6v_c + 3.5t_c \qquad (4)$$

where subscript c denotes coded variables. In eq 3, the model terms ω, v, and the interaction ω and v were found to be significant according to Student's t test ($\alpha < 0.05$). In eq 4, ω, v, and t were significant but not the interactions. An analysis of variance (ANOVA) applied to the four mean square ratios with an F test ($\alpha < 0.05$) confirmed the consistency of the two models. The statistical tests show that the model provides good estimations of the Cu lost. The residuals produced by the models were randomly distributed.

Table 3. Water Flow Characteristics in the Tests Involving the RSD and Estimations for a Rainfall Episode of 20 mm h^{-1} Lasting 10 min

	cm	raindrop[a]	tests in the RSD				
ω	rpm		12	12	24	36	36
v	mL		50	10	30	50	10
z	cm	0.3	0.9	0.3	0.6	0.7	0.2
u	cm s^{-1}	700	0.086	0.086	0.17	0.26	0.26
τ	Pa	10−200[b]	1.68×10^{-4}	4.73×10^{-4}	4.81×10^{-4}	6.43×10^{-4}	2.52×10^{-4}
p	kg m s^{-1}	3.5×10^{-3}−7.1×10^{-2}[c]	3.9×10^{-4}	6.1×10^{-4}	9.5×10^{-4}	1.9×10^{-3}	3.5×10^{-3}

[a] Terminal velocity of a 3 mm equivalent diameter falling water drop reported by Epema and Riezebos (*22*). [b] Data reported by Hartley and Julien (*21*). The shear stress τ in the RSD was calculated from eq 1, using the specific gravity of water, $\rho = 977$ kg m^{-3}, and the absolute viscosity, $\mu = 8.9 \times 10^{-4}$ Pa s, at 25 °C. [c] Linear momentum as calculated for 5×10^3 drop impacts on a surface of 215 cm^2 lasting 10 ms each under the assumption that the impact area was identical with the circular cross-section of the drop and using τ values over the range 10−200 Pa.

Table 4. Fungicide Properties and Dosages in the Washoff Experiments[a]

	units	CO	BM	CO-PG
mean particle size	μm	0.979	0.902	0.315
particle size distribution width	μm	0.272	0.385	0.122
Cu concentration in fungicide	mg g^{-1}	535 (2.8)	222 (1.1)	462 (1.8)
concentration of fungicide in the suspension for spraying	g L^{-1}	4.4	2.1	2.9
[Cu] in suspension	g L^{-1}	2.14 (0.011)	0.44 (0.002)	1.34 (0.001)
percentage of sprayed Cu that adhered to RSD wall	%	79 (1.3)	81 (5.9)	74 (1.2)
pH of the suspensión		6.6	5.8	6.4

[a] Standard deviations are in parentheses.

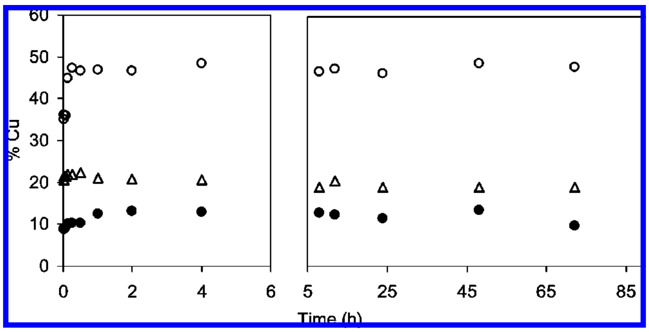

Figure 2. Time course of the cumulative percentage of Cu lost in the wash water during kinetic experiments done with the RSD. Experimental conditions were as follows: rotation speed, 36 rpm; water volume, 50 mL. Sprayed doses contained 1.7 mg of copper oxychlorhyde (empty circles), 0.36 mg of BM (triangles), and 0.99 mg of CO-PG (filled circles).

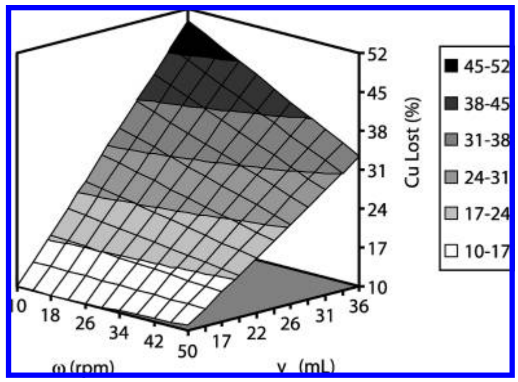

Figure 3. Surface response of the model for the proportion of Cu lost from CO as a function of the rotation speed (ω, revolutions per min), water volume (v, mL), and their interaction ($v\omega$).

The rotation speed and the volume of water had a significant effect on Cu loss from CO. Time was not a significant factor in the experimental range (10 and 25 min). Increased rotation speed caused a significant increase in Cu loss, while a greater water volume produced the opposite effect.

The response surface (**Figure 3**) illustrates the behavior of the model with respect to ω, v, and their interaction. In the case of BM, all three variables influenced the response, but the interactions were not significant. This indicates that Cu loss is time-dependent in the range of the experiments. In contrast to CO, the water volume for BM is a positive factor in the Cu loss. This suggests that erosion of the fungicide particles is not the only significant process; the dissolution of BM may also play a role. The absence of interaction between v and ω verifies that the shear strength has less influence on the loss of Cu from BM. The absence of interaction between t and ω or v indicates that the latter variables had no effect on the loss kinetics.

The variables and levels used to study the influence of fungicide dose in the second factorial design are shown in **Table 2**. Tables S3−S5 summarize the observed Cu losses along with the predicted values and the factorial design statistics. The experimental error at the center of the domain produced a coefficient of variation less than 8%. The models for estimating the percentage of Cu lost for the CO, BM, and CO-PG are given by eqs 5, 6, and 7, respectively

$$\text{Cu\% (CO)} = 27.7 + 10.0\omega_c - 8.8d_c - 7.9\omega_c d_c \quad (5)$$

$$\text{Cu\% (BM)} = 33.3 + 5.5\omega_c + 6.6v_c - 3.3d_c \quad (6)$$

$$\text{Cu\% (CO-PG)} = 13.5 + 3.5\omega_c + 3.8v_c - 6.1d_c - 3.7v_c d_c \quad (7)$$

The calculated losses agreed reasonably well with the experimental data (**Figures 4–6**). The most notable feature of these equations is the negative influence of dose on the loss rate for all three fungicides, indicating that the fungicide adheres more strongly to the chamber walls at higher doses. One interpretation is that a higher dose increases the contact surface between the fungicide and the wall of the RSD. For CO, volume alone did not have a significant influence on Cu loss, but its interaction with the other two variables was significant. The negative interaction between ω and d indicated that dose had a greater effect than ω. For BM (eq 6), the effects of the variables were independent; both v and ω contributed positively to Cu loss, but higher doses decreased the relative loss. The relation-

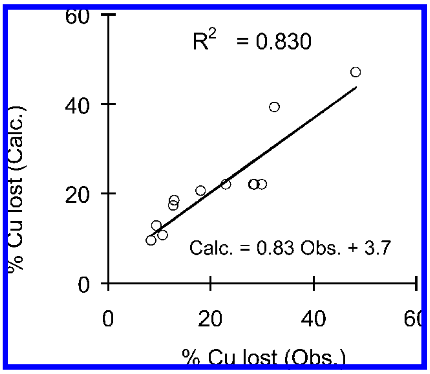

Figure 4. Percentage of Cu lost in the washoff of copper oxychlorhide using the RSD. Observed data vs percentages calculated by the model (eq 4).

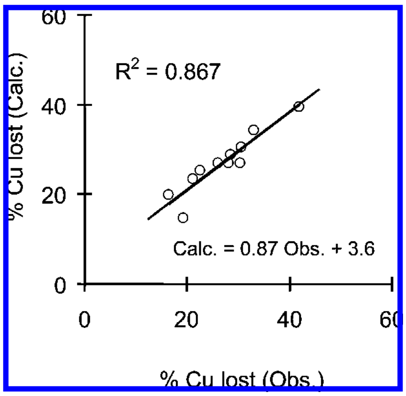

Figure 5. Percentage of Cu lost in the washoff of BM using the RSD. Observed data vs percentages calculated by the model (eq 5).

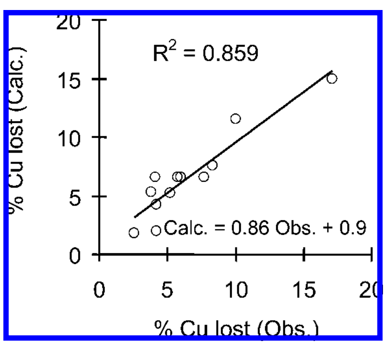

Figure 6. Percentage of Cu lost in the washoff of CO-PG mixture using the RSD. Observed data vs percentages calculated by the model (eq 6).

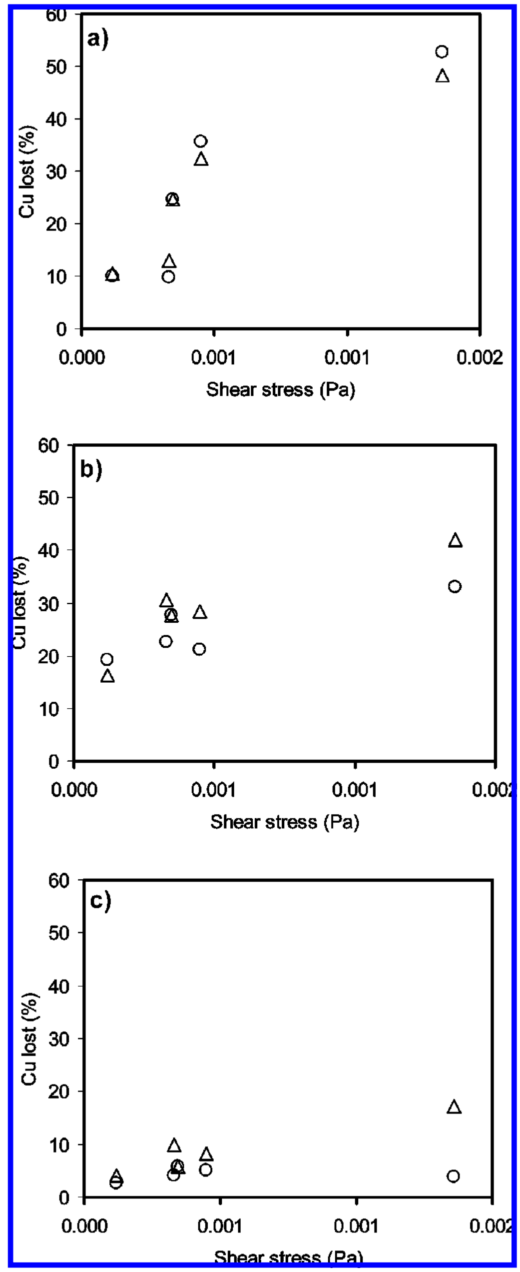

Figure 7. Relationship between flow shear stress and the proportion of Cu lost in the RSD corresponding to (**a**) CO, (**b**) BM, and (**c**) CO-PG. Data for a single dose (circles) and a triple dose (triangles).

ship between Cu loss and dose was the same for BM as for CO. As in the earlier experimental design, the lack of interaction between ω and v indicates that shear strength is not the main mechanism for Cu loss. The model for CO-PG (eq 7) indicates that the percentage loss was smaller than for CO and BM. The absolute values of the coefficients for ω and v were smaller than for CO and BM (eqs 5 and 6), but the coefficient for d was twice the coefficients for the other two models. The percentage loss was also influenced positively by ω and v and negatively by the dose, with d the most influential factor. The negative interaction between v and d and the lack of interaction between ω and d suggest that erosion had less influence than solubilization on Cu loss for CO-PG. The smaller percentage of loss for CO-PG may be due to its smaller particle size; smaller particles have a greater number of binding sites per unit area.

On the basis of a mechanistic interpretation, the interaction between v and ω is consistent with the fact that shearing depends on the average speed and the thickness of the water film, as indicated by eq 1. The relationship between the proportions of copper lost in relation to the magnitude of the boundary shear stress for the three fungicides is illustrated in **Figure 7**. An increase in boundary shear stress was associated with an increased proportion of copper lost. The plot was roughly linear for BM and CO-PG but S-shaped for CO. About 10% of Cu was washed at $\tau < 1$ mPa, above which the fungicide loss rate increased rapidly with the boundary shear stress, the increase being attenuated as τ approached 2 mPa. This behavior is consistent with a model of particle detachment in which CO losses depend on the threshold flow shear stress required to initiate particle motion. **Figure 8** shows the variation of the proportion of CO lost with the linear momentum. The results suggest that only part of the linear momentum at the surface boundary can be transmitted as a mechanical impulse to fungicide particles—most of it, however, is transmitted to water.

On the basis of the results, Cu loss in the RSD depends on the type of fungicide. Cu loss from the copper oxychlorhide depends

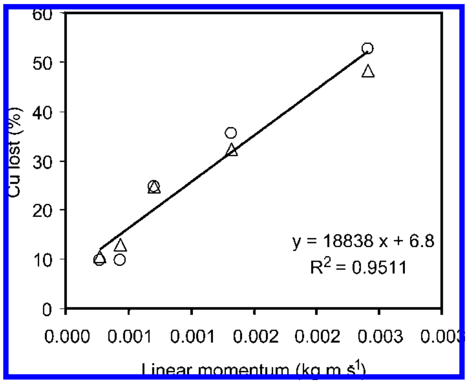

Figure 8. Relationship between the linear momentum for the shear flow parallel to the surface and the proportion of CO lost as measured in the RSD. Data for a single dose (circles) and a triple dose (triangles).

on erosion of fungicide particles. For the BM, Cu loss depends on dissolution and erosion. Loss from CO-PG was about half that of the copper oxychlorhide and five times less than for the BM at the center of the experimental domain of the factorial design. In the light of these results, using CO-PG can be effective with a view to reducing Cu losses through washoff of Cu-based fungicides sprayed onto a polypropylene surface. The percentages of Cu loss presented in this paper were obtained on a polypropylene surface. Although the results cannot be extrapolated to field conditions, they were used to analyze the loss of fungicides via surface shear stress-related processes and also to develop experimental designs more closely reproducing actual scenarios (e.g., by tuning the experimental factor levels with simulated rain on natural leaves and analyzing fungicide losses as a function of estimated boundary shear stress and linear momenta).

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Supporting Information Available: Information regarding the statistics of factor analysis (Tables S1−S5). Experimental results and statistical analyses for the washoff model for CO, BM, and CO-PG mixture, describing the effects of rotation speed (ω), wash water volume (v), rotation time (t), and dose (d). Table that shows experimental % of Cu lost in wash water from chamber wall and the calculated model; coefficients for the terms of the model and their significance by Student's t test ($\alpha < 0.05$); and consistency of the models verified by Fisher's F test ($\alpha < 0.05$) and regression coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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