



Behaviour of metalaxyl as copper oxychloride–metalaxyl commercial formulation vs. technical grade–metalaxyl in vineyards–devoted soils

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ABSTRACT

The objective of this work is to assess the sorption of metalaxyl applied as a copper oxychloride (CO)–metalaxyl formulation, for a set of selected soils devoted to vineyards. The method involved batch incubation of soils suspended with a commercial copper oxychloride–metalaxyl-based fungicide in 0.01 M CaCl₂. Afterwards, the metalaxyl concentration remaining in solution was determined by high-performance liquid chromatography (HPLC). The amount of dissolved metalaxyl in the fungicide suspension depends mainly on the soil pH, its potential acidity, and the cation exchange capacity. Of the approx. 20% metalaxyl retained by the solid colloids, the effect of organic matter colloids in soils (15–20 mg kg⁻¹) had a poor contribution (six times lower) than the copper oxychloride colloids (40%, w/w) in the commercial fungicide formulation (100–130 mg kg⁻¹). When comparing these retention data with the behaviour of metalaxyl used as a technical grade fungicide of about 100% purity (10–15 mg kg⁻¹ in solids), it is clear that the commercial formulation increases a 30% retention of metalaxyl by soil (15–20 mg kg⁻¹ in solids). The overall effect of the metalaxyl formulation plus soil show values of 10 times higher retention than technical grade–metalaxyl plus soil. Commercial formulation can decrease the mobility of soluble metalaxyl in agricultural soils with regard to the expected values obtained from batch studies using analytical grade–metalaxyl. Therefore, the effect of surfactants should be considered in the assessment of water contamination by the pesticides used in agriculture.

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1. Introduction

Copper oxychloride–metalaxyl mixtures are commonly sprayed on crop foliage to control fungal diseases in a number of crops. Fungicide enters the soil by off-target deposition and wash-off from treated foliage [1]. Farmers apply fungicides in response to the losses induced by rainfall; therefore, they often repeat the application up to 15 times in rainy weather. Intensive application of fungicides is associated to their occurrence in water wells [2], surface waters [3], and soils and sediments [4]. Use of complex mixtures based on copper oxychloride and organic based active compounds is widespread. Partition between soil–liquid phases plays an important role in the fate of pesticides in agricultural lands, and it is a valuable tool for modelling purposes [5]. Partition data are usually made from batch experiments using aqueous solutions of pure active pesticides, which mean [5] technical grade standards. However, current commercial fungicide formulations are mixtures containing the active substances plus adjuvants that improve their effectiveness and make more suitable to the spray application.

These substances, such as surfactants [6,7], may have influence on the soil–liquid phase partition of pesticides in field conditions. Also, presence of organic co-solvents in the soil solution influences the partition and kinetics in laboratory [8]. However, influence of solid adjuvants on the soil–water partition experiments of metalaxyl is not published yet.

The main objective of this work is to assess the sorption of metalaxyl applied as a commercial copper oxychloride–metalaxyl formulation for a set of selected soils devoted to vineyards. Influence of the commercial formulation on the metalaxyl sorption process is also evaluated and results are compared to those obtained from batch experiments with technical grade standards. In view of the environmental implications of the problem of the off-target deposition into soil, the approach used here is to analyze the soil–water partition of metalaxyl.

2. Experimental

2.1. Soil samples and kaolinite

Four composite soil samples, each made up of five points of the top 0–20 cm, were obtained from each of four Rías Baixas vineyards in the Galician province of Pontevedra (North-Western

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Table 1
Characteristics of the commercial product.

Ridomil Gold Plus	
Commercial brand	Syngenta Agro, S.A.
Composition	2.5% (w/w) of mefenoxam (equivalent to 24 g kg ⁻¹ of metalaxyl-M) 40% (w/w) of copper as copper oxychloride Amorphous silica
No. CAS	Mefenoxam: 70630-17-0 Copper as copper oxychloride: 1332-65-6 Amorphous silica: 7631-86-9/112926-00-8
Formulation	Wettable powder (WP)
Physical characteristics	Solid, light blue to green
Density of the formula	0.36 g/cm ³
Solubility of the formula	Miscible in water

Spain). Once in the laboratory, the samples were thoroughly mixed and dried at room temperature, passed through a 2 mm mesh sieve and homogenized before analysis [9]. Also, tests were made with kaolinite in order to compare the results with soils. Kaolinite was obtained from kaolin (Sigma–Aldrich, Steinheim, Germany). X-ray diffraction analysis shows that the mineral phase is kaolinite, with traces of microcline and quartz. Kaolinite contains less than 0.1% of organic carbon (C). Prior to use, kaolinite was clean-washed and equilibrated with 0.01 M CaCl₂ (pH 5.7) by five repeated cycles of stirring during 15 min, centrifugation for 30 min at 300 × g, phase separation, and re-suspension in a new fresh 0.01 M CaCl₂ with a solid to solution ratio of 2:10 (w/v).

2.2. Fungicides

Commercial fungicide was Ridomil Gold Plus (RGP) from Syngenta Agro (O Porriño, Spain), which is a wettable powder containing copper oxychloride (40%, w/w in copper) and metalaxyl (2.5%, w/w of M-mefenoxam, the 100% active metalaxyl isomer), plus any other components not shown by the manufacturer [10]. The main characteristics of the commercial product are summarized in Table 1. Copper oxychloride is an assemblage of cupric hydroxy minerals. The most decompose in acid environments and are stable at pH >6 [11], while others (i.e., paratacamite) are stable in oxidizing, acid environments [12]. Mineral composition of the fungicide samples used here was analyzed by X-ray diffraction (Siemens D-5000, Siemens, Karlsruhe, Germany), resulting in a mixture of atacamite and paratacamite, being former the most abundant. The particle size of the fungicide powders equilibrated in 0.01 M CaCl₂ (pH 5.7) was measured over the range of 0.6 nm to 6 μm of the equivalent particle diameter by dynamic light scattering on Zetasizer Nano (Malvern Instruments, Ltd., UK), resulting in a mean hydrodynamic diameter of 1046 μm and a distribution with of 396 μm. Technical grade-metalaxyl was obtained from Riedel-de Haën (Seelze-Hannover, Germany), with purity higher than 99%. All organic solvents used for sample preparation were residue analysis grade. HPLC grade solvents were employed for the HPLC work.

2.3. Analytical methods

Current and potential soil acidities were determined by measuring the pH of 1:2.5 (w/v) soil/liquid suspensions in water and in 0.1 M KCl, respectively, using a combined glass electrode. In addition pH of 1:10 (w/v) soil/liquid suspensions in CaCl₂ 0.01 M was also determined. Organic carbon content (C) was determined by elemental analysis on a ThermoFinnigan 1112 series NC instrument (Austin, USA). The proportions of sand (the 0.05–2.00 mm fraction), silt (0.002–0.05 mm), and clay (<0.002 mm) were determined by the wet sieving and pipette methods [13]. Exchangeable cations (Na, K, Ca and Mg) were extracted with 0.2 M NH₄Cl [14],

and exchangeable Al was extracted with 1 M KCl. Effective cation exchange capacity (ECEC) was calculated as the sum of exchangeable Na, K, Ca, Mg and Al. Soluble Cu is referred to its concentration in the aqueous phases after 24 h incubation with 0.01 M CaCl₂ (pH 5.7) with a solid to solution ratio of 2:10 (w/v). Total Cu content (Cu_T) was measured by the aqua-regia method until total digestion [15]. All inorganic cations were measured in the extracts by atomic absorption spectrometry (AAS) using a Thermo Solar M series spectrometer (Austin, USA).

High-performance liquid chromatography (HPLC) analyses were carried out on a Thermo HPLC system (TermoQuest, Rodano, Italy) equipped with a SCM1000 vacuum membrane degasser, a P4000 binary pump, an AS1000 autosampler, a column heater from Jones chromatography (Model 7981) and a microUVIS20 detector linked to a PC computer running the 2.51 version ChromCard software program (TermoQuest, Rodano, Italy).

Separations were performed with a Luna C18 (150 mm × 4.6 mm i.d., 5.0 μm particle size) analytical column obtained from Phenomenex (Madrid, Spain) and a guard column (4.0 mm × 3.0 mm i.d., 5.0 μm particle size) containing the same packing material. The temperature of the HPLC column was kept constant at 30 °C. The mobile phases were methanol (A) and water (B). The gradient was 40% B for 7.0 min, changed to 5% B in 3 min, hold for 5 min and finally changed to 40% B in 0.1 min giving an analysis time of 25 min, taking into account the column equilibration time. The injection volume was set to 50 μL at a flow rate of 0.70 mL/min. Metalaxyl detection was carried out at 220 nm.

2.4. RGP–water partition

To assess the partition of metalaxyl between solid and liquid phases of the RGP formulation a set of batch experiments were done. In each assay, an amount of RGP (0.1, 0.2, 0.4, 0.6, 0.8 and 1.2 g L⁻¹) was suspended in 10 mL of CaCl₂ 0.01 M solution, and these suspensions were shaken at 200 rpm for 24 h at 25 ± 1 °C, after which they were centrifuged for 15 min at 300 × g. Metalaxyl concentrations and pH of the supernatant were measured following centrifugation. These experiments were done by quintuplicate. The concentrations thus obtained were used as control measures in calculations of the batch sorption equilibrium with soil or kaolinite.

2.5. Kinetic experiments

Preliminary kinetic tests were performed in a stirred suspension of RGP in 100 mL CaCl₂ 0.01 M (containing 20 mg L⁻¹ of metalaxyl) with 10 g of soil at 25 ± 1 °C. In addition, control samples were prepared without soil. Suspensions were sampled at 1, 4, 8, and 30 min, and at 2, 8 and 24 h, and immediately centrifuged for 15 min at 300 × g to measure the concentration of metalaxyl in the liquid phase. These experiments were done by duplicate (*n* = 2).

2.6. Fungicide soil batch experiments

To measure the soil–water partition of metalaxyl in a range of concentrations, two sets of batch experiments were performed with soil or kaolinite: one using technical grade-metalaxyl and the second using the RGP formulation containing both metalaxyl and copper oxychloride. In each assay, 1 g of soil sample or 2 g of kaolinite was suspended in 10 mL of the fungicide/CaCl₂ 0.01 M solution, and these suspensions were shaken at 200 rpm for 24 h at 25 ± 1 °C, after which they were centrifuged for 15 min at 300 × g. Metalaxyl concentration and pH of the supernatant were measured following centrifugation. These experiments were done by triplicate (*n* = 3).

For the first set of experiments solid–liquid partition, aqueous solutions of technical-grade metalaxyl (2.5, 5, 10, 15, 20, and 30 mg L⁻¹) were made up by adding the appropriate volume of

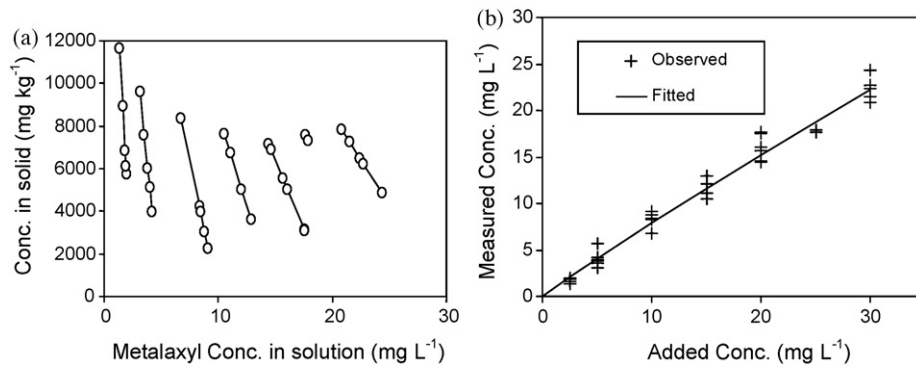


Fig. 1. (a) Solid–liquid partition of the fungicide metalaxyl in a set of RGP suspensions (0.1, 0.2, 0.4, 0.6, 0.8 and 1.2 g L⁻¹) in 10 mL of 0.01 M CaCl₂ after 24 h of incubation. (b) Relationship between the observed and calculated concentrations in solution points, and the best fitting line.

metalaxyl stock solution (1 g L⁻¹ in methanol) to 0.01 M CaCl₂ (pH 5.7).

For the second set of experiments, aqueous suspensions of RGP (0.1, 0.2, 0.4, 0.6, 0.8, and 1.2 g L⁻¹), corresponding to metalaxyl concentrations ranged from 2.5 to 30 mg L⁻¹ were made up by adding the appropriate volume of RGP stock suspension (8 g L⁻¹ in distilled water) to 0.01 M CaCl₂ (pH 5.7). Stock suspension of RGP was kept homogeneous by vigorous vortex stirring. It may also be worth pointing out that the fungicide concentration in the off-target spray and canopy drip are very high; the concentration of metalaxyl in the spray at the recommended dosage is 100 mg L⁻¹.

3. Results and discussion

3.1. Metalaxyl in RGP–water suspensions

Due to the variety of constituents of the commercial formulations, interaction of metalaxyl with the non-soluble adjuvants of RGP should be considered before studies with soil. Metalaxyl release from RGP was reported for the same RGP sample in a previous work [16,17], indicating that from successive batch desorption steps the 76% is released into the liquid phase by solubilisation, the 5% is desorbed, and the 19% is retained by the solid phase of the fungicide formulation. The maximum metalaxyl concentration in the sorption experiments was 0.03 g L⁻¹ (corresponding to 1.2 g L⁻¹ of RGP), less than its solubility limit in water (8.4 g/L at 25 °C [12,18]).

Partition of metalaxyl between solid and liquid phases in a set of control samples (Fig. 1a), confirms that the system does not behave as a sorption isotherm, as shown previously [16]. Note that the distribution data roughly describes a curve with a minimum of sorption in a range of dissolved concentrations from 5 to 10 mg L⁻¹.

The relationship between estimated concentration of metalaxyl after RGP addition and the measured concentration in solution, shown in Fig. 1b, was fitted by an exponential function:

$$c = Kc_e^n \quad (1)$$

where c is the measured solution concentration, K a ratio coefficient, c_e the estimated concentration from the complete dissolution of metalaxyl from RGP, and n is an empirical exponent. The best fitting values of $K=0.91 \pm 0.1$ and $n=0.94 \pm 0.04$ give a model efficiency [19] of 0.976. These figures show that the measured concentrations are lower than those expected from dilution, the exponent value also show that with higher fungicide addition the observed concentration deviates more than from the expected. This behaviour indicates an increasing matrix effect as a result of the influence of the other ingredients of the RGP formulation (adjuvants), which decrease solubilisation.

Table 2
Soil characteristics^a.

Soil	pH _W	pH _{KCl}	pH _{CaCl2}	C (%)	ECEC	Sand (%)	Silt (%)	Clay (%)	Cu _T
A	7.4	6.6	6.21	3.6	33.2	46	35	19	60
B	7.0	5.4	5.48	3.1	12.8	67	15	18	107
C	5.3	4.6	4.86	3.1	8.6	53	30	17	96
D	5.5	5.0	5.36	4.1	24.7	65	19	16	274

^a C, total organic carbon; ECEC, effective cation exchange capacity (cmol_(C) kg⁻¹); Cu_T, total Cu content measured in the aqua-regia plus hydrofluoric acid extracts (mg kg⁻¹).

3.2. Soils

The soils had the same sandy loam texture class, organic carbon (C) contents ranged from 3.1 to 4.1% (w/w), clay contents ranged from 16 to 19% (w/w), pH_W from 5.3 to 7.4, and pH_{KCl} from 4.6 to 6.6, as it can be seen in Table 2. The neutral pH values of soils A and B are attributable to lime addition. The effective cation exchange capacity (ECEC) ranged from 8.6 to 33.2 (cmol_(C) kg⁻¹). Total copper (Cu_T) contents ranged from 60 to 274 mg kg⁻¹ due to application of Cu-based fungicides (Table 2).

3.3. Kinetics

Kinetic experiments are displayed in Fig. 2. It shows a decay of the dissolved metalaxyl concentration with regard to the control in which decay was negligible. Decay rate decreased with time in all soils and it was negligible from 8 to 24 h of incubation. Kinetic was

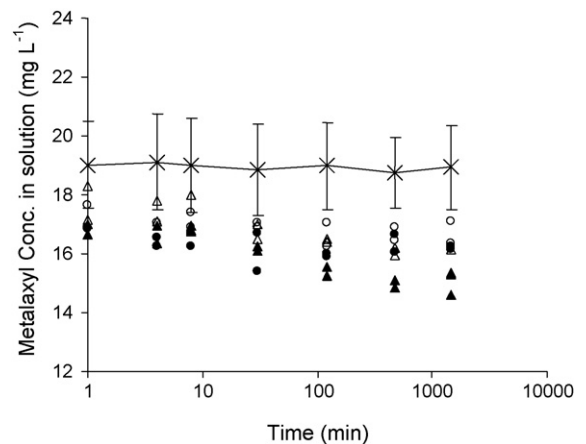


Fig. 2. Time course of the metalaxyl concentration in solution, applied as RGP. Line denotes the control sample and symbols denote incubation with soil A (○), soil B (△), soil C (●), and soil D (▲).

quite similar for all soils, but soil B sorbed more metalaxyl than the others (at about a 10%). Metalaxyl is stable in moderate acid environments [20], and it is likely that depletion in the aqueous phase may be caused by slow sorption kinetics, commonly related with transport control [21]. We will then assume that depletion of dissolved metalaxyl in the suspensions results from the partition between sorbed and in solution phases.

3.4. Fungicide soil batch experiments

The first effect to be considered of the RGP addition to soil suspension is the change in pH. As it can be seen in Fig. 3, addition of RGP to the control suspensions increased the pH due to dissolution of Cu oxychloride [22]. In addition, changes in the pH were observed when RGP was added to the soils: a pH increment was observed for soils, independently of the concentration of RGP added. With additions of RGP, pH increases by the buffer effect of copper oxychloride. These results suggest that the effect of additions of fungicide leads to the copper oxychloride minerals to contribute to the control of pH and therefore to induce changes in the sorption of metalaxyl by soil. For instance, adsorption of technical grade-metalaxyl by soil was 2–3 times higher when it was adsorbed from a solution of pH 2.5 than when the solution pH was at 5.5 [9].

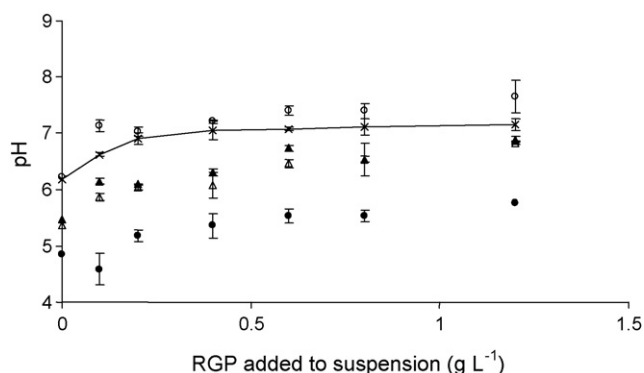


Fig. 3. Effect of the addition of RGP in the pH of the fungicide suspensions with 0.01 M CaCl₂ after 24 h of incubation. Line shows the control sample. Symbols denote incubation with kaolinite (□), soil A (○), soil B (▲), soil C (●), and soil D (△).

To evaluate the metalaxyl partition between the soil and the aqueous phase, metalaxyl concentration in the solid phase was calculated as

$$C_{\text{solid}} = \frac{(C_{\text{total}} - C_{\text{liquid}})V}{m} \quad (2)$$

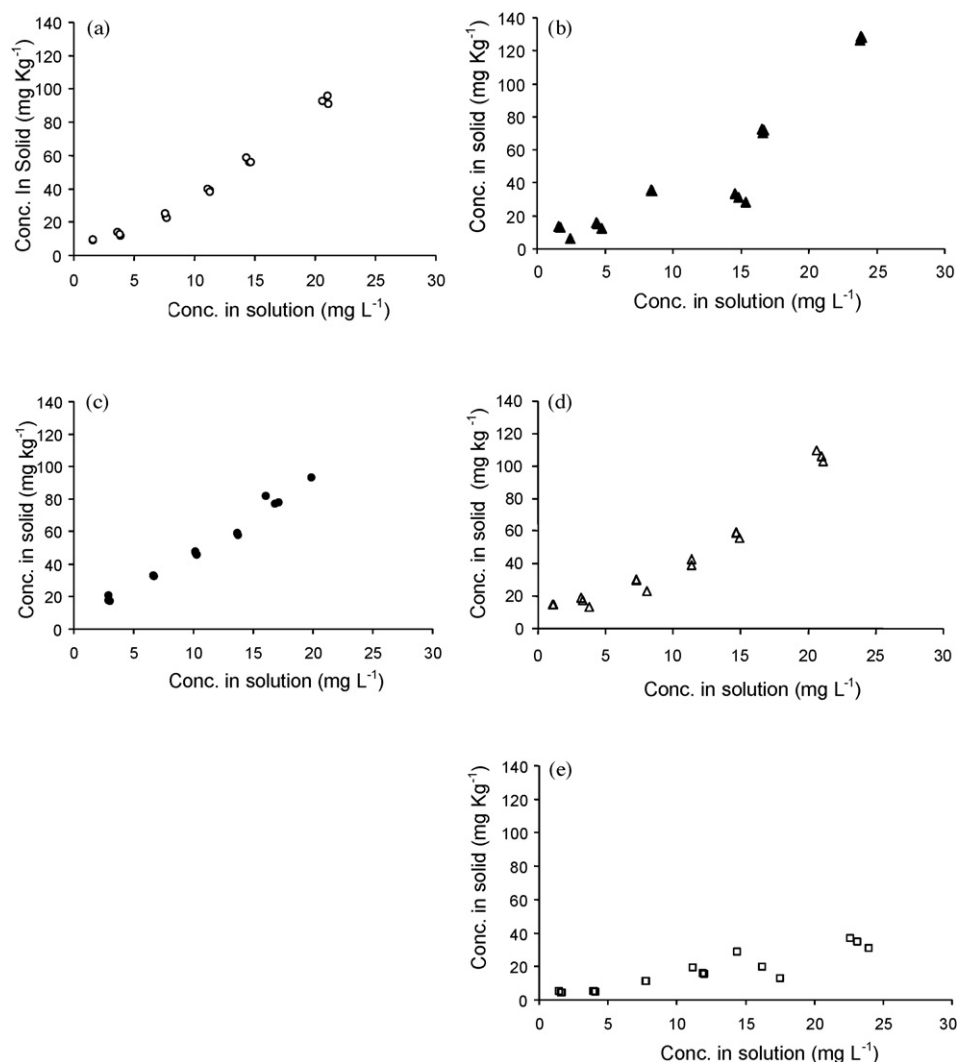


Fig. 4. Partition of metalaxyl, applied as RGP, between the solid and liquid phase. Where solid concentration (C_{solid}) is the difference between the metalaxyl concentration added to the soil (C_{total}) and the metalaxyl concentration measured in the solution at the equilibrium (C_{liquid}). Symbols denote incubation with kaolinite (□), soil A (○), soil B (▲), soil C (●), and soil D (△).

being C_{solid} (mg kg^{-1}) the metalaxyl concentration in the solid phase; C_{total} (mg L^{-1}) the estimated metalaxyl concentration added to the suspension; C_{liquid} (mg L^{-1}) the measured concentration in the liquid phase after incubation (24 h); V the volume of the liquid phase (L); m the mass of solid (soil or kaolinite) in the suspension (kg). As it can be seen in Fig. 4, partition data of metalaxyl between solid and the aqueous phase describe roughly straight lines. A detailed review of the curves shows that increasing the total concentration in the suspension favour the concentration in solid. This behaviour is consistent with the decrease of the measured concentration in solution observed in control experiments as described above (Fig. 1b), suggesting that the solid adjuvants present in the commercial formulation contribute together with soil to increase the total metalaxyl concentration in solid.

Soil B (Fig. 4b) shows more sorption than the other soils. It also shows a drop in the solid concentration at point of the dissolved metalaxyl concentration 16 mg L^{-1} . The different behaviour of soil B (with a 10% more sorption) may be related with its maximum difference between pH_w and pH_{KCl} (1.6 units) and its low ECEC ($12.8 \text{ cmol}_{(c)} \text{ kg}^{-1}$). This combination of factors contributes to decrease the ionic character of the surface in soil B and therefore to increase the non-ionic interactions that could favour the sorption of non-ionic solutes [23].

In addition, kaolinite-RGP/CaCl₂ 0.01 M suspensions (Fig. 4e) sorbed about three times less metalaxyl than soils, supporting that the soil organic matter is the most likely candidate to explain the metalaxyl sorption.

As stated above, a fraction of the metalaxyl added to the suspension is sorbed to the adjuvants of the pesticide formulation and not to the soil. Therefore, a way to estimate the real sorbed concentration in soil is using the concentrations measured in the control tests samples.

$$C_{\text{sorbed}} = \frac{(C_{\text{control}} - C_{\text{liquid}})V}{m} \quad (3)$$

being C_{control} the metalaxyl concentration in solution measured in RGP/CaCl₂ 0.01 M suspensions without soil or kaolinite. Sorption isotherms calculated using this equation are shown in Fig. 5 and the best fitted obtained are shown in Table 3.

Of the approx. 20% metalaxyl retained by the solid phase (Section 3.1), the effect of organic matter in soils has a contribution six times lower (maxima retentions of $15\text{--}20 \text{ mg kg}^{-1}$; Fig. 5) than the colloids in the commercial fungicide formulation ($100\text{--}130 \text{ mg kg}^{-1}$; Fig. 4). When comparing the retention behaviour of metalaxyl both used as commercial formulation (this work) and as a technical grade fungicide of about 100% purity [9]

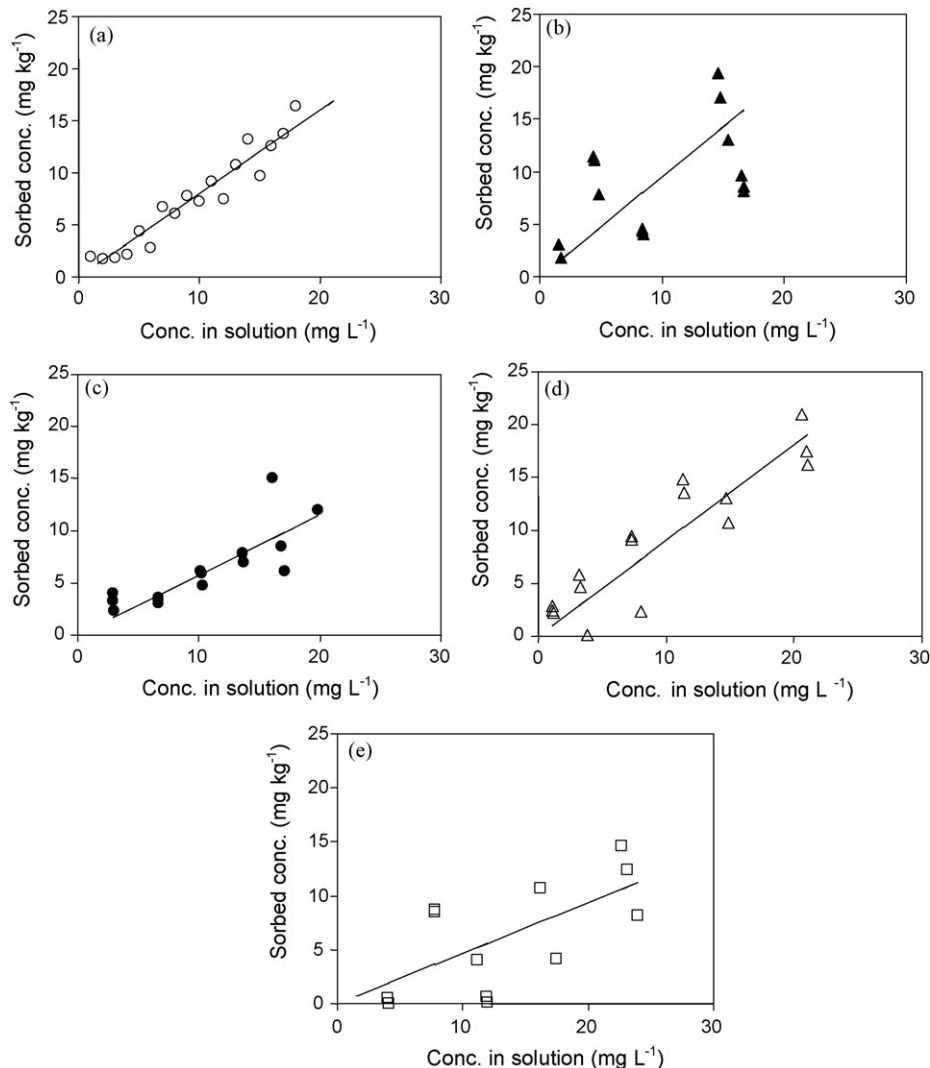


Fig. 5. Partition of metalaxyl, applied as RGP, between the solid and liquid phase. Sorbed concentration is the difference between the metalaxyl concentration measured in the control test samples (C_{control}) and the metalaxyl concentration measured in the solution at the equilibrium (C_{liquid}). Symbols denote incubation with kaolinite (\square), soil A (\circ), soil B (\blacktriangle), soil C (\bullet), and soil D (\triangle). Line represented the best fitted equations.

Table 3

Fitting parameters (average \pm standard deviation) obtained after adjustment to the Freundlich equation, that can be used to estimate the real sorbed concentration in target soil and kaolinite.

Soil	Freundlich		
	K	n	E
A	1.18 \pm 0.26	0.822 \pm 0.08	0.923
B	3.67 \pm 2.39	0.314 \pm 0.24	0.144
C	0.72 \pm 0.41	0.917 \pm 0.21	0.662
D	1.55 \pm 0.6	0.807 \pm 0.13	0.824
Kaolinite	0.65 \pm 0.72	0.927 \pm 0.34	0.454

in solids (10–15 mg kg⁻¹), a slight increment in the retention of metalaxyl by soil (30%) was observed when the commercial formulation was applied. In addition the overall effect of the formulation plus soil in this latter case show values 10 times higher in favour of the commercial formulation (10–15 mg kg⁻¹ vs. 100–130 mg kg⁻¹). These results indicate an interaction of adjuvants and soil, contributing to an overall increase in retention in the solid phase. Since the presence of methyl-ester based surfactants in the RGP formulation was proved before by us [10], the mechanisms of metalaxyl retention could be related with the presence of surfactants in commercial formulations [24,25]. When pesticides and surfactants coexist in soils the pesticides could be adsorbed by surfactants previously adsorbed into the soil, which will increase their retention [24]. For example, Andrades et al. demonstrated an increase in the adsorption of metalaxyl (19%) by soils saturated with surfactant with respect to the natural soils [25]. However, when pesticides applied to soil contain surfactant additives, as occurs in a commercial formulation, the surfactant concentration that accompanies the pesticides is fairly high; consequently pesticide retention may increase or decrease drastically depending on the particular pesticide and surfactant [24].

4. Conclusions

The behaviour of metalaxyl as copper oxychloride–metalaxyl commercial formulation vs. technical grade–metalaxyl was studied in vineyards–devoted soils. A pH increment was observed after the addition of RGP to the soils or to the control suspensions, independently of the concentration of RGP added. This effect can be related with the buffer effect of copper oxychloride (40% (w/w) in the commercial formulation). Variations in the pH can induce changes in the sorption of metalaxyl to the soil. Studies made with kaolinite–RGP/CaCl₂ 0.01 M suspensions showed that soil organic matter is the most likely candidate to explain the sorption of metalaxyl by soil. Nevertheless, of the approx. 20% metalaxyl retained by the solid colloids, the effect of organic matter colloids in soils (15–20 mg kg⁻¹) had a poor contribution (six times lower) than the copper oxychloride colloids (40%, w/w) in the commercial fungicide formulation (100–130 mg kg⁻¹). When comparing this retention data with the behaviour of metalaxyl used as a technical grade fungicide of about 100% purity (10–15 mg kg⁻¹ in solids), it is clear that, the commercial formulation increase a 30% retention of metalaxyl by soil (15–20 mg kg⁻¹ in solids). The overall effect of the commercial formulation plus soil show values of 10 times higher retention than technical grade–metalaxyl plus soil.

The amount of dissolved metalaxyl depends mainly on the interaction of three factors: soil pH, its potential acidity, and the cation exchange capacity. The surfactants and soil have a synergic effect on the overall retention of metalaxyl. This should be considered in the estimation of metalaxyl mobility in agricultural soils.

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References

- [1] R. Rial Otero, B. Cancho Grande, M. Arias Estevez, E. Lopez-Periago, J. Simal Gándara, Procedure for the measurement of soil inputs of plant-protection agents washed off through vineyard canopy by rainfall, *J. Agric. Food Chem.* 51 (2003) 5041–5046.
- [2] P.N.M. Schipper, M.J.M. Vissers, A.M.A. van der Linden, Pesticides in ground-water and drinking water wells: overview of the situation in the Netherlands, *Water Sci. Technol.* 57 (2008) 1277–1286.
- [3] Z. Vryzas, G. Vassiliou, C. Alexoudis, E. Papadopoulou-Mourkidou, Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece, *Water Res.* 43 (2009) 1–10.
- [4] A. Bermúdez-Couso, M. Arias-Estévez, J.C. Nóvoa-Muñoz, E. López-Periago, B. Soto-González, J. Simal-Gándara, Seasonal distributions of fungicides in soils and sediments of a small river basin partially devoted to vineyards, *Water Res.* 41 (2007) 4515–4525.
- [5] M. Arias-Estévez, E. López-Periago, E. Martínez-Carballo, J. Simal-Gándara, J.C. Mejuto, L. García-Río, The mobility and degradation of pesticides in soils and the pollution of groundwater resources, *Agric. Ecosyst. Environ.* 123 (2008) 247–260.
- [6] M.C. Hernández-Soriano, M.D. Mingorance, A. Peña, Dissipation of insecticides in a mediterranean soil in the presence of wastewater and surfactant solutions. A kinetic model approach, *Water Res.* 43 (2009) 2481–2492.
- [7] S. Paria, Surfactant-enhanced remediation of organic contaminated soil and water, *Adv. Colloid Interface Sci.* 138 (2008) 24–58.
- [8] J.E. López-Periago, M. Arias-Estévez, B. Soto-González, S. Trelles-Reinoso, J. Simal-Gándara, Influence of methanol on the dynamics of the retention and release of cyprodinil by an agricultural soil, *J. Agric. Food Chem.* 54 (2006) 4751–4757.
- [9] M. Arias, M. Paradelo, E. López, J. Simal-Gándara, Influence of pH and soil copper on adsorption of metalaxyl and penconazole by the surface layer of vineyard soils, *J. Agric. Food Chem.* 54 (2006) 8155–8162.
- [10] E. Pose-Juan, R. Rial-Otero, E. Martínez-Carballo, E. Lopez-Periago, J. Simal-Gándara, Determination of metalaxyl and identification of adjuvants in wettable powder pesticide technical formulas, *Anal. Bioanal. Chem.* 394 (2009) 1535–1544.
- [11] T.L. Woods, R.M. Garrels, Phase relations of some cupric hydroxy minerals, *Econ. Geol.* 81 (1986) 1989–2007.
- [12] W. Janusz, A. Galgan, M. Reszka, Electrical double layer at the CuO₂ aqueous solution of alkali metal chlorides interface, *Physicochem. Probl. Miner. Process.* 40 (2006) 161–174.
- [13] G.W. Gee, J.W. Bauder, Particle-size analysis, in: A. Klute (Ed.), *Methods of Soil Analysis. Part 1-Physical and Mineralogical Methods*, 2nd ed., American Society of Agronomy Inc., Soil Science Society of America, Madison, Wisconsin, 1986, pp. 383–411.
- [14] M.E. Sumner, W.P. Miller, Cation exchange capacity and exchange coefficients, in: D.L. Sparks (Ed.), *Methods of Soil Analysis. Part 3-Chemical Methods*, 3rd ed., American Society Agronomy, Soil Science Society of America, Madison, Wisconsin, 1996, pp. 1201–1230.
- [15] L.R. Hossner, Dissolution for total element analysis, in: D.L. Sparks (Ed.), *Methods of Soil Analysis. Part 1-Chemical Methods*, 3rd ed., American Society of Agronomy, Soil Science Society of America, Madison, Wisconsin, 1996, pp. 49–64.
- [16] M. Paradelo, M. Arias-Estévez, J.C. Nóvoa-Muñoz, P. Pérez-Rodríguez, A. Torrado-Agrasar, J.E. López-Periago, Simulating washoff of Cu-based fungicide sprays by using a rotating shear device, *J. Agric. Food Chem.* 56 (2008) 5795–5800.
- [17] E. Pose-Juan, M. Paradelo-Pérez, R. Rial-Otero, J. Simal-Gándara, E. Lopez-Periago, Detachment of sprayed colloidal copper oxychloride–metalaxyl fungicides by a shallow water flow, *Pest. Manage. Sci.* 65 (2009) 615–623.
- [18] C.D.S. Tomlin (Ed.), *The Pesticide Manual*, 12th ed., British Crop Protection Council Publication, Surrey, U.K., 2000.
- [19] J.E. Nash, J.V. Sutcliffe, River flow forecasting through conceptual models. Part 1—a discussion of principles, *J. Hydrol.* 10 (1970) 282–290.
- [20] P. Sukul, M. Spittler, Metalaxyl: persistence, degradation, metabolism, and analytical methods, *Rev. Environ. Contam. Toxicol.* 164 (2000) 1–26.
- [21] G. Sposito, *Chemical Equilibria and Kinetics in Soils*, 1st ed., Oxford University Press, Oxford, UK, 1994.
- [22] E. Pose, R. Rial-Otero, M. Paradelo, J.E. López-Periago, Influence of soil characteristics on copper sorption from a copper oxychloride fungicide, *J. Agric. Food Chem.* 57 (2009) 2843–2848.
- [23] T.A.T. Aboul-Kassim, B.R.T. Simoneit, Interaction mechanisms between organic pollutants and solid phase systems, in: T.A.T. Aboul-Kassim, B.R.T. Simoneit (Eds.), *Pollutant-Solid Phase Interactions. Mechanisms, Chemistry and Modeling*, 1st ed., Springer-Verlag, Berlin Heidelberg, 2001, pp. 107–167.

- [24] M. Sánchez-Camazano, M. Arienzo, M.J. Sánchez-Martín, T. Crisanto, Effect of different surfactants on the mobility of selected non-ionic pesticides in soil, *Chemosphere* 31 (1995) 3793–3801.
- [25] M.S. Andrades, M.S. Rodríguez Cruz, M.A. Bernal, M.J. Sánchez-Martín, M. Sánchez-Camazano, Influencia de la modificación de suelos con un surfactante catiónico en el incremento de adsorción de pesticidas por suelos, in: J. Álvarez-Benedí, P. Marinero (Eds.), *Estudios de la Zona No Saturada del Suelo*, vol. VI, Instituto Tecnológico Agrario de Castilla y León, Junta de Castilla y León, España, 2003, pp. 343–348.