Degradation and thermodynamic adsorption process of carbofuran and oxadicyl in a Colombian agricultural soil profile

Degradación y termodinámica del proceso de adsorción del carbofurano y oxadicil en un perfil de suelo agrícola de Colombia

Carmen S. Mosquera-Vivas[1], Nelson Obregon-Neira[2], Raúl E. Celis-Ossa[2],
Jairo A. Guerrero-Dallos[1], and Carlos A. González-Murillo[2]

ABSTRACT

Carbofuran and oxadixyl pesticides are used in Colombia to control pests and fungi, but their mobility through the soil profile is poorly understood. This study showed degradation and adsorption processes of these compounds in a Melanudands soil (0-100 cm) from Colombia using laboratory incubation and the batch equilibrium methods. First-order kinetic models indicated that the degradation rates of carbofuran (0.013-0.006 day^{-1}) and oxadixyl (0.013-0.008 day^{-1}) decreased at deeper soil layers, suggesting that the pesticides were more persistent in the sub-surface (60-100 cm) than in the surface layers (0-40 cm). The thermodynamic approach showed that the adsorption of both pesticides was similar, an exothermic and spontaneous process. The carbofuran and oxadixyl coefficient of distribution (5.8-0.3 L kg^{-1}) and the percentage of adsorption (71.2-11.3%) were very similar in the surface layers (0-40 cm) and decreased with the soil depth. The organic carbon (OC) and clay content showed a positive correlation with the pesticide adsorption throughout the soil profile; therefore, mathematical equations were developed from multiple linear regression models for these soil properties and initial concentration. The equations were important to the estimation of the mobility of the compounds using leaching models under laboratory and field conditions.

Key words: pesticide persistence, soil pollution, sorption, chemical degradation, forecasting.

RESUMEN

El carbofurano y oxadicil se aplican en diferentes cultivos en Colombia, pero su transporte a través del perfil del suelo se ha estudiado muy poco. Se evaluó la degradación y la adsorción de ambos plaguicidas en un suelo Melanudands (0-100 cm) mediante el método indirecto e incubaciones bajo condiciones de laboratorio. Las tasas de degradación del carbofurano (0,013-0,006 día^{-1}) y oxadicil (0,013-0,008 día^{-1}) disminuyeron en las capas más profundas del perfil; lo cual indica que los plaguicidas fueron más persistentes en las capas sub-superficiales (60-100 cm) que en las capas superficiales (0-40 cm). La adsorción fue un proceso exotérmico y espontáneo. Los coeficientes de distribución (5,8-0,3 L kg^{-1}) y los porcentajes de adsorción (71,2-11,3%) de ambos plaguicidas fueron muy similares en los primeros 40 cm y disminuyeron con la profundidad. Con modelos de regresión lineal múltiple entre la adsorción de los plaguicidas y el contenido de carbón orgánico (CO), las arcillas y la concentración inicial, se obtuvieron ecuaciones matemáticas, las cuales muestran como el CO y las arcillas controlan el transporte de ambos pesticidas a través del perfil. Estas ecuaciones son útiles para estimar el transporte del carbofurano y oxadicil en el suelo.

Palabras clave: persistencia de los plaguicidas, contaminación del suelo, sorción, degradación química, técnicas de predicción.

Introduction

Pesticides are chemicals used to control insects, weeds and/or endemic diseases in order to enhance food production and to protect forests, plantations and fibers (Ecobichon, 2001; Mamy and Barriuso, 2007; Sattler *et al.,* 2007). Carbofuran is an insecticide banned in Europe and the USA (PAN, 2015; EPA, 2015); in spite of this fact, Latin American and Asian farmers have been using it regularly to control pests in vegetable and fruit crops (Farahani *et al.,* 2007;

Valencia *et al.,* 2008; Pimmata *et al.,* 2013). On the other hand, oxadixyl is a fungicide applied to potato, tomato, onion, cut roses and fruit crops (ICA, 2016). The fate of pesticides in the atmosphere-plant-soil system depends on their behavior in the soil. Once the foliar application was carried out, the pesticides moved to the air by volatilization, to the surface water by runoff, to the groundwater by leaching or remained in the soil (adsorption) and were perhaps degraded (Tiryaki and Temur, 2010). The degradation and adsorption processes are critically important

to understanding the off-site impact of pesticides applied to field crops in order to protect the environment (Gebremariam *et al.,* 2012).

Pesticide degradation rates in soils were dependent upon: the soil type, microorganisms, pesticide type, soil temperature, soil water content, and light irradiation (Shelton and Parkin, 1991; Tariq *et al.,* 2006; Bermúdez-Couso *et al.,* 2013; Pimmata *et al.,* 2013; Dhanasekara *et al.,* 2015). For instance, the natural pyrite degraded nearly 40% of the carbofuran within 100 h (Dhanasekara *et al.,* 2015) and the degradation of the insecticide in the soils with indigenous microorganisms was more rapid that in the sterile soils (Pimmata *et al.,* 2013); although, Tariq *et al.* (2006) found similar behaviors for sterile and non-sterile soils.

Soil adsorption was the main factor that was responsible for the carbofuran dissipation under darkness (Bermúdez-Couso *et al.,* 2013). Adsorption is the net accumulation of a substance at the interface between a solid phase and an aqueous solution phase (Sposito, 1989; Delle, 2001). The physical and chemical soil properties affect the amount of the chemical adsorbed on the soil solid surface. The OC content, the clay content, the cation exchange capacity (CEC) and the pH seemed to control the adsorption of carbofuran in both the tropical and temperate soils (Delle, 2001; Gupta *et al.,* 2006; Krishna and Philip, 2008; Valencia *et al.,* 2008; Singh and Srivastava, 2009; Bermúdez-Couso *et al.,* 2012). In regards to oxadixyl degradation and adsorption, the only available data are those provided by the "pesticide properties database" (PPDB, 2015) for temperate soils. Aldana *et al.* (2011) showed that oxadixyl was a mobile fungicide in soil columns at a 0-30 cm depth and it might be leached through the soil profile. In the understanding of the adsorption equilibrium between the solid (adsorbent) and liquid phases of soils, thermodynamics play a fundamental role. To have significant adsorption of a chemical in soils, the free energy of adsorption (ΔG_{ads}) must be negative and since ($\Delta Gads$) = ($\Delta Hads$)-T($\Delta Sads$), this requires an enthalpy of adsorption ($\Delta Hads$) negative that adsorption entropy ($\Delta Sads$). The entropy of adsorption (ΔS_{ads}) must be negative due a rotational freedom of the adsorbed substance that is less than the liquid phase substance (Ruthven, 1984).

Most degradation and adsorption studies of carbofuran and oxadixyl have focused on the topsoil layer (Shelton and Parkin, 1991; Tariq *et al.,* 2006; Farahani *et al.,* 2007; Valencia *et al.,* 2008; Aldana *et al.,* 2011; Bermúdez-Couso *et al.,* 2012; Pimmata *et al.,* 2013; Martínez-Cordón *et al.,* 2015). How these pesticides behave throughout the soil profile is poorly understood. Therefore, the aim of this study was to assess the degradation and adsorption of the pesticides carbofuran and oxadixyl (commonly used in Colombia) in one Melanudand soil as a function of soil depth (0-100 cm).

Materials and methods

Soils

Five soil layers (Melanudands), S1 to S5, acquired at different vertical depths in the soil profile (S1: 0-20 cm, S2: 20-40cm, S3: 40-60 cm, S4: 60-80 cm and S5: 80-100 cm), were used in this study. The soil layers were taken in an agricultural landscape in the region of Tenjo-Cundinamarca (Colombia), located at 2,595 m a.s.l. These layers were air-dried and sieved through a US standard sieve with 2.38 mm mesh openings (number 8) for adsorption experiments; whereas, the soil layers for degradation study were kept at field water content. The physical and chemical properties of the soil are summarized in Tab. 1.

Pesticides

Carbofuran [(2,2-dimethyl-3H-1-benzofuran-7-yl) N-methylcarbamate] and oxadixyl [N-(2,6-dimethylphenyl)-2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)acetamide] pesticides (≥ 98% purity) were provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Degradation process

The pesticide degradation was studied with laboratory incubation experiments (Mamy and Barriuso, 2007; Mosquera-Vivas *et al.,* 2010). Ten g (10.00) of dry soil (S1-S5) were placed in a 50 mL centrifuge tube and spiked with 0.250 mL of the pesticide mixture. Carbofuran and oxadixyl were added at reported field doses of a.i. 0.31 and 1.0 kg ha^{-1}, respectively. These samples were then inserted in 500 mL jars containing 20 mL of 2 M NaOH (on top) and a sealed vial with 10 mL of distilled water. The samples were incubated under unsaturated field moisture conditions (Tab. 1) at 18ºC in the dark for 102 d. After incubation times of 0, 1, 3, 7, 14, 31, 45, 60, 76 and 102 d, two soil samples from each depth were dried on foil containers at room temperature (18ºC) for 3 d. The samples were then placed in centrifuge tubes, spiked with PCB 103 (surrogate compound) and extracted with 20 mL of ethyl acetate and shaken for 15 min. Na_2SO_4 (5.0 g) and $NaHCO_3$ (1.7 g) were then added and the samples were shaken for 15 min again. The samples were centrifuged at 7,500 rpm for 15 min and the organic supernatants (10 mL) concentrated to 2 mL. An aliquot of PCB 52 (internal standard) was then added before injecting the samples into a CG-MS system. The limit of

TABLE 1. Physical and chemical properties of the soil in the region of Tenjo-Cundinamarca (Colombia).

| Soil layer | OC (%) | pH | CEC (cmol(+) kg^{-1}) | Texture | | | ρ_r (g mL^{-1}) | N (%) | P (mg kg^{-1}) |
				Clay (%)	Silt (%)	Sand (%)			
S1 (0-20 cm)	10.3±0.3	6.3±0.2	57.8	16.0	32.0	52.0	2.0	0.87	>116
S2 (20-40 cm)	10.7±0.8	5.8±0.1	58.0	16.0	32.0	52.0	2.0	0.87	64.4
S3 (40-60 cm)	9.6±0.4	5.2±0.3	46.5	14.0	20.0	66.0	2.1	0.81	27.9
S4 (60-80 cm)	4.8±0.7	5.3±0.2	38.2	10.0	12.0	78.0	2.2	0.37	10.0
S5 (80-100 cm)	2.7±0.8	5.4±0.1	32.6	6.0	18.0	76.0	2.4	0.18	8.6

| Soil layer | EA (cmol(+) kg^{-1}) | Ion exchange (cmol(+) kg^{-1}) | | | | ECEC (cmol(+) kg^{-1}) |
		Ca	K	Mg	Na	
S1 (0-20 cm)	0	36.9	2.4	9.2	0.7	49.1
S2 (20-40 cm)	0	24.7	1.9	6.9	0.6	34.0
S3 (40-60 cm)	0.3	12.0	1.3	3.7	0.4	17.6
S4 (60-80 cm)	0.2	5.3	0.9	2.1	0.4	9.0
S5 (80-100 cm)	0.2	3.8	0.8	1.9	0.5	7.2

OC (organic carbon) Walkley-Black method; pH, 1:1 water-soil ratio; CEC (cationic exchange capacity) is obtained by ammonium exchange with NaCl with units of meq/100 g of dry soil; texture, Bouyoucos method; ρ_r (particle density) pycnometer method; N (nitrogen) calculated from OC (factor = 0.0862); P, Bray II method; EA (exchange acidity) extraction with KCl 1 M; ECEC (effective cationic exchange capacity) is sum of the ions extracted with ammonium at pH = 7.0 with units of meq/100 g of dry soil.

detection (LOD) was 0.008 µg g^{-1} for carbofuran and 0.028 µg g^{-1} for oxadixyl. The limits of quantification (LOQ) were 0.020 µg g^{-1} and 0.118 µg g^{-1} for carbofuran and oxadixyl, respectively. The recovery of the pesticides was 103.3±7.8% for carbofuran and 79.1±5.9% for oxadixyl. For instance, the recovery of PCB 103 was 91.9% with a RSD of 1.4%.

The first-order kinetic model was fitted to obtain the degradation rate (k) and the half-life ($t_{1/2}$) of the two pesticides (Eq. 1 and 2):

$$C_t = C_0 e^{-kt} \tag{1}$$

$$t1/2 = \ln(1/2)/-k \tag{2}$$

where C_t is the pesticide concentration at time t and C_0 is the initial concentration of the pesticide.

Adsorption process

The adsorption process was obtained by using the batch equilibrium method (Mamy and Barriuso, 2007; Langeron *et al.*, 2014). All of the pesticides were studied together in a mixture solution according to the field data. Five test substances were prepared in 0.01 M CaCl$_2$. The concentration ranges were 0.13 - 0.40 mg L^{-1} for carbofuran and 0.49 - 2.16 mg L^{-1} for oxadixyl. All of the experiments were executed with samples of pesticides in 0.01 M CaCl$_2$ and blanks with soil in 0.01 M CaCl$_2$.

Ten g (10.00) of dry soil (S1-S5) were placed in 50-mL centrifuge tubes and a 20.0 mL aliquot of the mixture

was added to each tube. The soil-water slurry was shaken for 24 h at 20ºC and centrifuged at 7,000 rpm for 30 min. The supernatant was removed, weighed and extracted by liquid-liquid extraction. The supernatant was spiked with PCB 103 and the extraction was carried out with 20.0 mL of ethyl acetate and shaken for 15 min. NaCl was added and the sample was shaken again for an additional 15 min before sonication for 15 min. The organic phase was concentrated to 1 mL. An aliquot of PCB 52 was added to the samples before injection into a CG-MS system. The pesticide and PCB 103 recoveries by liquid-liquid extraction were 89.5±8.5% for carbofuran, 81.9±5.8% for oxadixyl and 84.9±7.1% for PCB 103.

The coefficient of distribution (k_d) was calculated as the average of the subsamples for each layer (Eq. 3):

$$k_d = \frac{\Sigma \frac{\left(\frac{x}{m}\right)_i}{(C_{eq})_i}}{n} \tag{3}$$

Ceq is the equilibrium concentration of the pesticide (mg L^{-1}) in the soil solution and n is the number of the data.

Finally, the soil organic carbon-water partitioning coefficient, k_{OC}, was obtained by normalizing the k_d coefficients to the OC content (Eq. 4):

$$k_{oc} = \frac{k_d}{\%OC} * 100 \tag{4}$$

Pedotransfer functions (PTF) were used to estimate the k_d values of the pesticides from the OC content, clay content and pH (Weber *et al.*, 2004; Singh *et al.*, 2014). Weber *et al.*

(2004) used 13 data points to get a linear model between linear model between the k_d of carbofuran as the carbofuran as a dependent variable, and the OC and the clay content as independent variables. In order to obtain multiple linear regression models for both pesticides, we performed a multicollinearity test using Pearson correlation coefficients and the variance inflation factor (VIF) with all of the data ($n = 22$) throughout the soil profile. Linear parameters were obtained for the combination of the OC content, the clay content and the initial concentration of the substances, where VIF was used to select the best linear equations.

Pesticide quantification

The quantification of the pesticides in the soil and aqueous phases was performed using an Agilent (Santa Clara, CA) model 7890A gas chromatography coupled to a 5975C mass spectrometer detector. The chromatography system was equipped with a multimode inlet, autosampler and HP5-MS (30 m x 250 μm x 0.25 μm) column. The carrier gas used was helium and the injection volume was 4 μL with the solvent vent mode. The MS transfer line was kept at 280°C and the quantification was performed using selected ion monitoring (SIM).

Thermodynamic approach

Adsorption enthalpy (ΔH_{ads}) is given by (Goss and Schwarzenbach, 1999):

$$\Delta H_{ads} = -4.17 \ln \left(\frac{K_d^{T_r}}{1.0 \times 10^3 \overline{SS}} \right) - 88.1 \tag{5}$$

where, K_d^T is the coefficient of distribution at T_r (reference temperature = 293 K) and $\overline{SS}$ is the average specific surface of the soil, which can be estimated as (Vighi and Di Guardo, 1995)

$$\overline{SS} = 100.0 \left(100.0 f_{o6} + 2.0 f_{cl} + 0.4 f_{st} + 0.005 f_{sd} \right) \tag{6}$$

where f_{oc} is the soil carbon fraction, f_{cl} is the soil clay fraction, f_{st} is the soil silt fraction and f_{sd} is the soil sand fraction.

Adsorption free energy at T_r is calculated as:

$$\Delta G_{ads} = -RT \ln k_d \tag{7}$$

where R is the gas constant and k_d is:

$$P_{sln} \leftrightarrow P_{ads} \tag{8}$$

$$k_d = \frac{[P_{ads}]}{[P_{sln}]} \tag{9}$$

$$k_d = \frac{x/m \rho_p}{C_{eq}} \tag{10}$$

where $[P_{ads}]$ is the equilibrium concentration of the pesticide in the soil solid (mole L^{-1}), $[P_{sln}]$ is the equilibrium concentration of the pesticide in the soil solution (mole L^{-1}) and ρ_p is the density of the particles (kg L^{-1}).

Adsorption entropy can be calculated according to (Ruthven, 1984)

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T_r} \tag{11}$$

ΔS_{ads} can be used to understand the adsorption process described in the reaction below:

$$S_{(s)} + 2 P_{(sln)} \leftrightarrow S - P_{(ads)} + P_{(sln)} \tag{12}$$
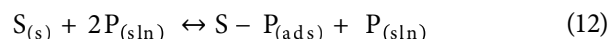
where $S_{(s)}$ is the soil solid, $P_{(sln)}$ is the pesticide in the soil solution and $S - P_{(ads)}$ is the pesticide adsorbed in the soil solids.

Results and discussion

Degradation process

The first-order kinetic models for carbofuran and oxadixyl in the soil profile are shown in Fig. 1. The degradation rate (k) and the half-life time ($t_{1/2}$) calculated from this model are given in Tab. 2. Carbofuran was completely degraded in S1 after 7 d of incubation. In S2-S4, the model fitted accurately to data with coefficients of determination (R^2) >0.75 and the null hypothesis (H$_0$: k = 0 and C$_0$ = 0) were rejected at a 95% confidence level. The k values of the insecticide (0.006-0.013 d^{-1}) decreased from S2 to S3 and remained constant in S4, which may be explained by the change of microbial activity throughout the soil profile. Soil microorganisms play an important role in the pesticide degradation process (Mosquera-Vivas *et al.,* 2010; Pimmata *et al.,* 2013) and, in our soil, the amount of CO_2 evolved during the microbial respiration was found to decrease in S1-S3, after which it was constant (Fig. 2); accordingly, the decreasing of microbial activity allowed the k values to decrease. It is seemed with k value of carbofuran in S5 where the concentration remained unchanged; hence, the first-order kinetic showed a poor fit, as was expected. The degradation rates of 2,4-D and atrazine decreased with the increasing soil depth, which was due to the microbiota decrease through the soil profile (Kruger *et al.*, 1993; Veeh *et al.,* 1996). Microbial degradation is an important degradation pathway of carbofuran in neutral and acid soils (Evert, 1991; Pimmata *et al.,* 2013). $t_{1/2}$ values of the insecticide increased at deeper soil depths. $t_{1/2}$ for soil layers S1 and S2 (10.5-53.3 d^{-1}) is within the range reported by Pimmata *et al.* (2013) and Tariq *et al.* (2006) for Pakistan and Thailand

soils (1.6-69.3 d^{-1}); although, $t_{1/2}$ in soil layers at a depth of 40-100 cm is higher than the former ones, suggesting the insecticide was more persistent at the deeper layers in the studied soil profile.

The first-order kinetic fit well to oxadixyl degradation data with R^2 values between 0.83 and 0.95, and the null hypothesis (H_0: k = 0 and C_0 = 0) was rejected at a 95% confidence level, except in S5 (Fig. 1 and Tab. 2). k values of the oxadixyl were similar in S1-S3 (0.012-0.013 d^{-1}) and slightly decreased to 0.008 d^{-1} in S4. This behavior might be explained by the fact that the biotic process occurs mainly in S1 and S2, where the amount of CO_2 evolved during the microbial respiration was higher than in S3 and S4 (Fig. 2). In layers S3 and S4, the abiotic process probably degraded the fungicide. It seems that hydrolysis controlled the degradation process in layers at a depth of 40-80 cm because the oxadixyl showed a heterocyclic ring system, which is liable to hydrolysis (Roberts and Hutson, 1998). In contrast to the carbofuran, the oxadixyl was degraded to nearly 10.0% of its maximum concentration during 102 d of incubation in S5, confirming the hydrolysis reaction as well. The $t_{1/2}$ of the oxadixyl also increased at the deeper soil layers (Tab. 2). The $t_{1/2}$ of the fungicide in S1-S3 was smaller than the values published in the pesticide properties database in topsoils from temperate regions (PAN, 2015; PPDB, 2015), showing that the oxadixyl degraded faster under tropical conditions and it was more persistent at deeper soils layers, i.e. in S4 and S5.

Adsorption process

The k_d and k_{oc} values and the adsorption percentage for the carbofuran and oxadixyl in soil layers S1-S5 are shown in Fig.3. k_d values and the adsorption percentage for both

pesticides were higher in S1-S2 than in S3-S5. Although the carbofuran and oxadixyl showed an aromatic ring, a heterocyclic ring and oxygen atoms, which are liable to adsorb the pesticides in our soil with the same physical interactions. The adsorption behavior for the carbofuran and oxadixyl through the soil profile can be explained by the decrease in the OC content, clay content, CEC and ECEC. The k_d values revealed a positive correlation with the OC content (r = 0,97 and 0.92), clay (r = 0.97 an d 0.93), CEC (r = 0.99 and 0.99) and ECEC (r = 0.88 and 0.95). Similar trends have been published by Delle (2001), Valencia *et al.* (2008), Singh and Srivastava (2009), Bermúdez-Couso *et al.* (2012), and Pimmata *et al.* (2013). Positive correlation between k_d, ECEC and OC showed the role of the oxygen atoms in the retention capacity of both pesticides in the soils. The oxygen atoms attracted electron density (electronegativity) and the negative net of the soil repelled the pesticides; as a consequence, the k_d values were very small (0.3-5.8 L kg^{-1}). The decreasing values of carbofuran and oxadixyl adsorption with soil depth might be explained by the decreased concentration of the divalent cations, Ca^{2+} and Mg^{2+} (Tab. 1). These cations form soil-divalent cation-pesticides linkages.

The k_{oc} values of the insecticide and the fungicide in S1-S5 varied from 40.3 to 13.7 L kg^{-1} and from 55.6 to 11.1 L kg^{-1}, respectively. The carbofuran range of the k_{oc} at a depth of 0-60 cm (Fig. 3) was within the one reported for Colombian soils (Valencia *et al.*, 2008); however, all of the k_{oc} values were lower than that found for tropical soils from India and Malaysia. (Farahani *et al.,* 2007; Krishna and Philip, 2008; Singh and Srivastava, 2009), it might suggest the adsorption of the insecticide was affected by the soil genesis. In contrast, the oxadixyl range of the k_{oc} at a depth of 0-40 cm

TABLE 2. Degradation of carbofuran and oxadixyl in a Colombian agricultural soil profile obtained by a first-order kinetic model fit.

| Pesticide | Soil layers | Degradation rate | | $t_{1/2}$ (d) | R^2 | ANOVA | |
		-K (1 d^{-1})	$t_{student}$ Probability			F_{Cal}	Probability
Carbofuran	S1	--	--	10.5[a]	--	--	--
	S2	0.013±0.002	0.001	53.3	0.79	30.14	0.001
	S3	0.008±0.001	0.001	86.6	0.83	34.63	0.001
	S4	0.006±0.001	0.003	115.5	0.75	20.58	0.003
	S5	0.0008	0.258	866.4	0.18	1.53	0.258
Oxadixyl	S1	0.012±0.002	0.004	57.8	0.89	34.06	0.004
	S2	0.012±0.002	0.001	57.8	0.89	40.18	0.001
	S3	0.013±0.001	0.0001	53.3	0.95	89.19	0.0001
	S4	0.008±0.002	0.004	86.6	0.83	23.99	0.004
	S5	0.0007	0.116	990.2	0.50	4.00	0.116

F_{cal}, is Fisher distribution from ANOVA test; [a] estimated from experimental data. Soil layers (cm): S1, 0-20; S2, 20-40; S3, 40-60; S4, 60-80; S5, 80-100.
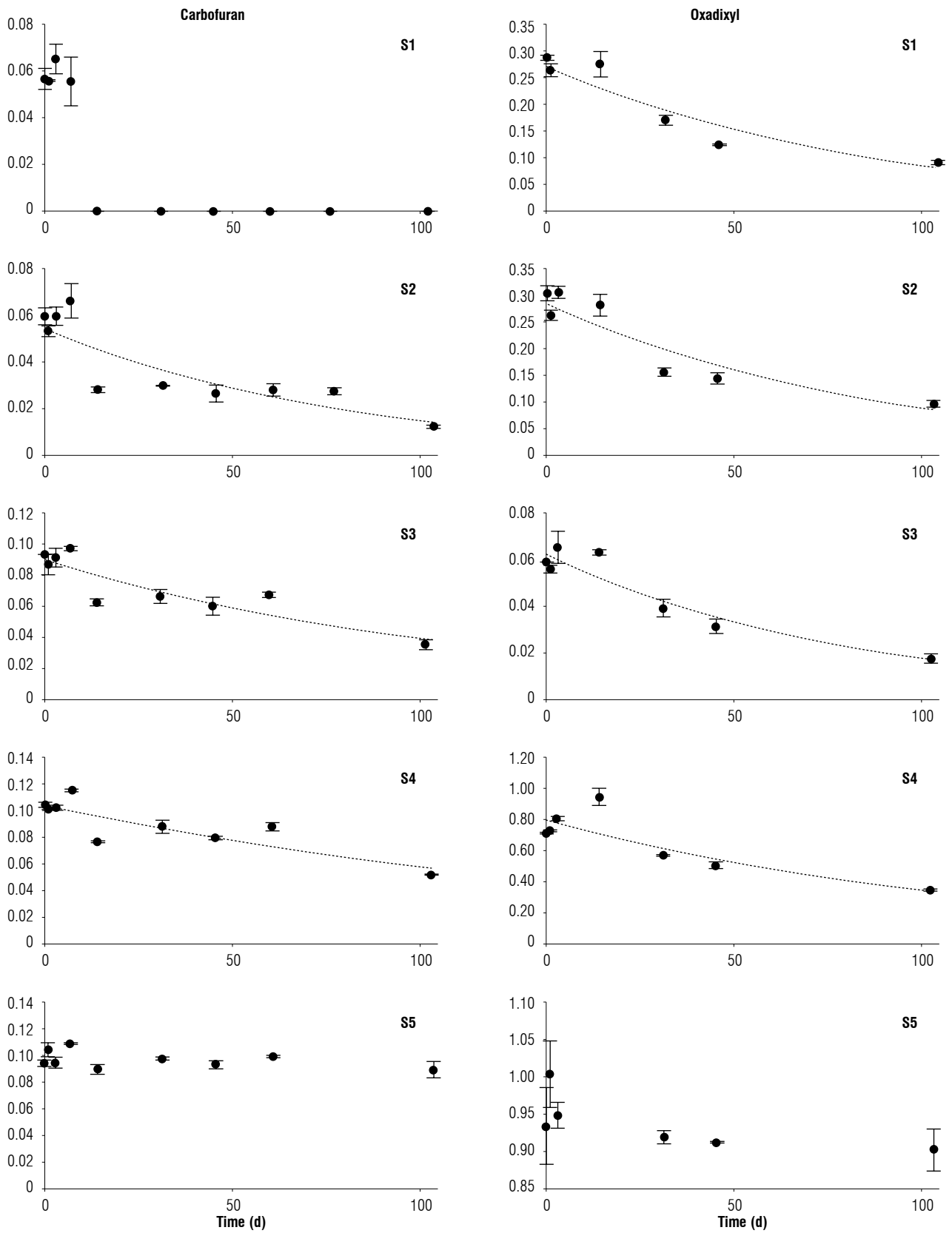
FIGURE 1. Degradation (mg kg^{-1}) of the carbofuran (left) and oxadixyl (right) in a Colombian agricultural soil profile. Soil layers (cm): S1, 0-20; S2, 20-40; S3, 40-60; S4, 60-80; S5, 80-100. Error bars indicate standard deviation.
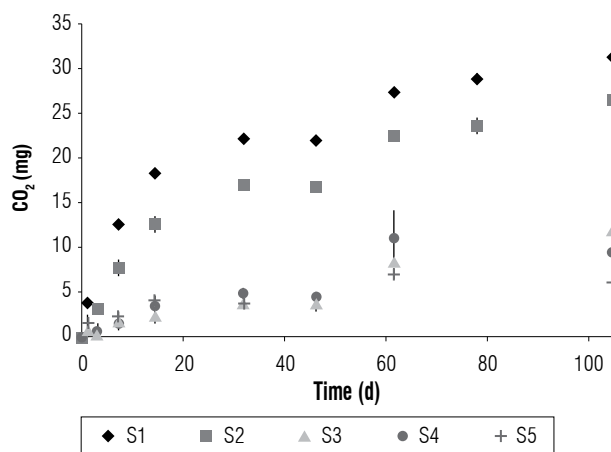
FIGURE 2. Microbial respiration in a Colombian agricultural soil profile contaminated with carbofuran and oxadixyl profile. Soil layers (cm): S1, 0-20; S2, 20-40; S3, 40-60; S4, 60-80; S5, 80-100.

was higher than that reported for temperate and tropical soils; although, the range of the Koc at a depth of 40-100 cm was within the range published in the literature (PAN, 2015; EPA, 2015; Martínez-Cordón *et al.*, 2015), indicating that the adsorption of the fungicide in our topsoil (0-40 cm) was higher than those found in other topsoils. This behavior could result from the composition of the soil organic matter throughout the profile.

The multiple linear regression models for the carbofuran and oxadixyl throughout the soil profile are summarized in Eqs 13-18:

Carbofuran:

$$k_d = -1.373 + 0.677\%\,OC + 0.672\,C_i, R^2 = 0.89 \tag{13}$$
$$C_i = \text{initial concentration}$$

$$\%\,Ads = -6.889 + 6.266\%\,OC + 15.303\,C_i, R^2 = 0.96 \tag{14}$$
$$\%\,Ads = \text{Percentage of adsorption}$$

$$k_d = -2.780 + 0.404\%\,Clay + 0.797\,C_i, R^2 = 0.89 \tag{15}$$

$$\%\,Ads = -25.252 + 5.304\%\,Clay + 16.970\,C_i, R^2 = 0.95 \tag{16}$$

Oxadixyl:

$$\log\%\,Ads = 0.531 + 1.276\log\%\,OC + 0.071\log C_i, R^2 = 0.94 \tag{17}$$

$$\log\%\,Ads = -0.435 + 1.896\log\%\,Clay + 0.074\log C_i, R^2 = 0.96 \tag{18}$$

These models can be used to calculate the coefficient of distribution and/or the adsorption percentage using the OC and clay content. To calculate k_d and the percentage of adsorption from PTF may reduce the cost and time in chemical analysis to predict the mobility of carbofuran and oxadixyl in Colombia soils. Furthermore, the models confirmed the relationship between the adsorption of pesticides and the OC and clay content.

The enthalpy, entropy and free energy values of the adsorption of the pesticides in layers S1-S5 are summarized in Tab. 3. The Fig. 4 shows the adsorption free energy of the carbofuran and oxadixyl throughout the soil profile. All of the thermodynamic approaches were negative, except the free energy for both pesticide in soil layer S5, suggesting that the adsorption of the pesticides in our soils was exothermic and spontaneous and the rotational freedom of the adsorbed chemicals was less than the liquid phase chemicals (Ruthven, 1984). Furthermore, ΔG_{ads} was similar for the carbofuran and oxadixyl throughout the soil profile (Tab. 3 and Fig. 4). Negative free energy (ΔG_{ads}) has also been published for the adsorption of carbofuran in India soils at a depth of 0-30 cm (Singh and Srivastava, 2009). Low values of free energy indicate that the adsorption of the pesticides in soil solids is often promoted by weak

TABLE 3. Enthalpy, entropy and free energy of the carbofuran and oxadixyl in a Colombian agriculture soil.

Pesticide	Soil layers	ΔH_{ads} (kJ mole^{-1})	ΔS_{ads} (kJ mole^{-1} K^{-1})	ΔG_{ads} (kJ mole^{-1})
	S1	-7.03±0.35	-0.01	-4.97±0.21
	S2	-7.30±0.52	-0.01	-5.25±0.30
Carbofuran	S3	-5.89±0.63	-0.01	-4.25±0.37
	S4	-4.00±1.47	-0.01	-1.65±0.86
	S5	-2.59±1.22	-0.01	0.39±0.71
	S1	-8.57±1.04	-0.01	-5.87±0.61
	S2	-8.41±1.16	-0.01	-5.90±0.68
Oxadixyl	S3	-5.87±0.98	-0.01	-4.23±0.57
	S4	-4.56±1.28	-0.01	-1.98±0.75
	S5	-1.69±1.14	-0.01	0.92±0.67

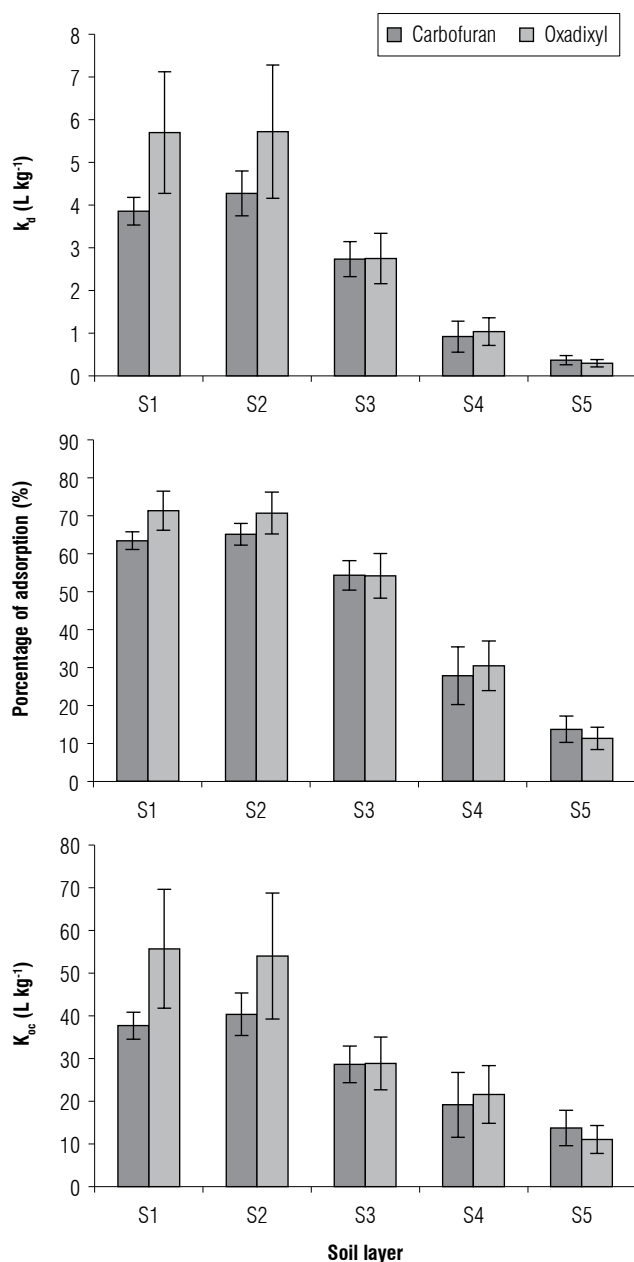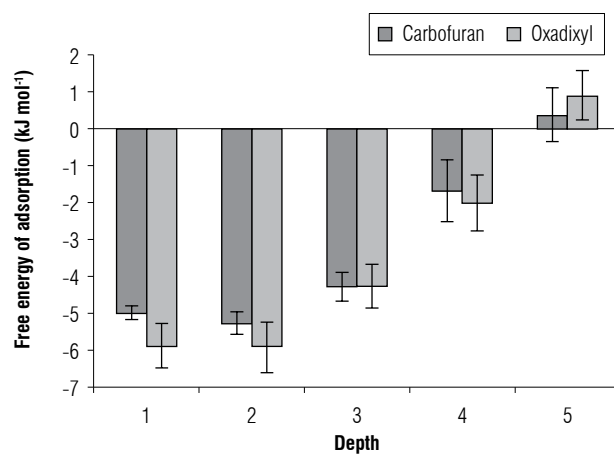Soil layers (cm): S1, 0-20; S2, 20-40; S3, 40-60; S4, 60-80; S5, 80-100.

FIGURE 4. Free energy of carbofuran and oxadixyl in a Colombian agricultural soil. Error bars indicate standard deviation.

Positive free energy for the insecticide and fungicide in S5 showed that the adsorption of both pesticides was not a spontaneous process, i.e. carbofuran and oxadixyl prefer the soil aqueous solution.

Conclusion

The high microbial activity played a key role reducing the transport of both pesticides at a depth of 0-40 cm. If carbofuran and oxadixyl reach deeper soil layers (60-100 cm), they might constitute a risk for groundwater pollution due to their persistence and mobility, as shown above.

Acknowledgements

Literature cited

Aldana, M., R. de Prado, and M.J. Martínez. 2011. Leaching of oxadixil and tebuconazole in Colombian soil. Commun. Agric. Appl. Biol. Sci. 76, 909-914.

Bermúdez-Couso, A., D. Fernández-Calviño, I. Rodríguez-Salgado, J.C. Nóvoa-Muñoz, and M. Arias-Estévez. 2012. Comparison of batch, stirred flow chamber, and column experiments to study adsorption, desorption and transport of carbofuran within two acidic soils. Chemosphere 88, 106-112. Doi: 10.1016/j.chemosphere.2012.02.078

Bermúdez-Couso, A., J.C. Nóvoa-Muñoz, M. Arias-Estévez, and D. Fernández-Calviño. 2013. Influence of different abiotic and biotic factors on the metalaxyl and carbofuran dissipation. Chemosphere 90, 2526-2533. Doi: 10.1016/j.chemosphere.2012.10.090

FIGURE 3. Distribution coefficient (k_d), adsorption percentage and distribution coefficient normalized for the organic carbon content (k_{oc}) of the pesticides in Colombian agriculture soil. Error bars indicate standard deviation.

physical forces (Weber, 1993; Singh and Srivastava, 2009). For instance, the carbofuran and oxadixyl were adsorbed less than the dimethomorph (data not shown) and this is in accord with their chemical structure. Dimethomorph shows two aromatic ring system and chlorine atom, while carbofuran and oxadixyl exhibit one aromatic ring system without a chlorine atom. The aromatic rings increase π-π stacking interactions and the chlorine atom promotes hydrophobic interactions between pesticide and aromatic components of soil organic matter.

Delle S., A. 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. J. Phys. Chem. Ref. Data 30, 187. Doi: 10.1063/1.1347984

Dhanasekara, S.A.K.M., A.N.B. Attanayake, A.C. Herath, N. Nanayakkara, A. Senaratne, S.P. Indrarathne, and R. Weerasooriya. 2015. Partial degradation of carbofuran by natural pyrite. Environ. Nanotech. Monit. Manage. 4, 51-57. Doi: 10.1016/j.enmm.2015.07.002

Ecobichon, D.J. 2001. Pesticide used in developing countries. Toxicology 160, 27-33. Doi: 10.1016/S0300-483X(00)00452-2

EPA, Environmental Protection Agency. 2015. Carbofuran cancellation process. In: www.epa.gov/oppsrrd1/reregistration/carbofuran/carbofuran_noic.htm; consulted: August, 2015.

Evert, S. 1991. Environmental fate of carbofuran. In: Department of Pesticide Regulation, http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/carbofuran.pdf; consulted: April, 2016.

Farahani, G.H.N., Z. Zakaria, A. Kuntom, D. Omar, and B.S. Ismail. 2007. Adsorption and desorption of carbofuran in Malaysian soils. Adv. Environ. Biol. 1, 20-26.

Gebremariam, S.Y., M.W. Beutel, D.R. Yonge, M. Flury, and J.B. Harsh. 2012. Adsorption and desorption of chlorpyrifos to soils and sediments. Rev. Environ. Contam. Toxicol. 215, 123-175. Doi: 10.1007/978-1-4614-1463-6_3

Goss, K.U. and R.P. Schwarzenbach. 1999. Empirical prediction of heats of vaporization and heats of adsorption of organic compounds. Environ. Sci. Technol. 33, 3390-3393. Doi: 10.1021/es980812j

Gupta, V.K., I. Ali, Suhas, and V.K. Saini. 2006. Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes. J. Colloid Interf. Sci. 299, 556-563. Doi: 10.1016/j.jcis.2006.02.017

ICA, Instituto Colombiano de Agricultura. 2016. Registro nacionales-marzo de 2016. In: www.ica.gov.co/getdoc/d3612ebf-a5a6-4702-8d4b-8427c1cdaeb1/REGISTROS-NACIONALES-PQUA-15-04-09.aspx; consulted: April, 2016.

Krishna, K.R. and L. Philip. 2008. Adsorption and desorption characteristics of lindane, carbofuran and methyl parathion on various Indian soils. J. Hazard. Mater. 160, 559-567. Doi: 10.1016/j.jhazmat.2008.03.107

Kruger, E.L., L. Somasundaram, J.R. Coast and R.S. Kanwar. 1993. Persistence and degradation of [14C]atrazine and [14C] deisopropylatrazine as affected by soil depth and moisture conditions. Environ. Toxicology Chem. 12, 1959-1967. Doi: 10.1002/etc.5620121102

Langeron, J., A. Blondel, S. Sayen, E. Hénon, M. Couderchet, and E. Guillon. 2014. Molecular properties affecting the adsorption coefficient of pesticides from various chemical families. Environ. Sci. Pollut. Res. 21, 9727-9741. Doi: 10.1007/s11356-014-2916-6

Mamy, L. and E. Barriuso. 2007. Desorption and time-dependent sorption of herbicides in soils. Eur. J. Soil Sci. 58, 174-187. Doi: 10.1111/j.1365-2389.2006.00822.x

Martínez-Cordón, M.J., M.I. Aldana-Castañeda, and J.A. Guerrero-Dallos. 2015. Modelación matemática del transporte de oxadixyl en suelos de cultivo de cebolla. Rev. Ambient. Água 10, 327-337. Doi: 10.4136/ambi-agua.1565

Mosquera-Vivas, C.S., M.J. Martínez-Cordón, and J.A. Guerreo-Dallos. 2010. 14C tebuconazole degradation in Colombian soils. Commun. Agric. Appl. Biol. Sci. 75, 173-181.

PAN. 2015. Which pesticides are banned in Europe? In: PAN UK Food & Fairness, www.pan-europe.info/Resources/Links/Banned_in_the_EU.pdf; consulted: April, 2016.

Pimmata, P., A. Reungsang, and P. Plangklang. 2013. Comparative bioremediation of carbofuran contaminated soil by natural attenuation, bioaugmentation and biostimulation. Int. Biodeter. Biodegr. 85, 196-204. Doi: 10.1016/j.ibiod.2013.07.009

PPDB. 2015. The PPDB pesticide properties Database. In: http://sitem.herts.ac.uk/aeru/ppdb/en/; consulted: April, 2016.

Ruthven, D.M. 1984. Physical adsorption and the characterization of porous adsorbents. pp. 29-85. In: Ruthven, D.M. (ed.). Principles of adsorption and adsorption process. John Wiley & Sons. New York, NY.

Roberts, T. and D.H. Hutson. 1998. Metabolic pathway of agrochemicals: insecticide and Fungicide, Part 2. The Royal Society of Chemistry, Cambridge, UK.

Sattler, C., H. Kächele, and G. Verch. 2007. Assessing the intensity of pesticide use in agriculture. Agric. Ecos. Environ. 119, 299-304. Doi: 10.1016/j.agee.2006.07.017

Shelton, D.R. and T.B. Parkin. 1991. Effect of moisture on sorption and biodegradation of carbofuran in soil. J. Agric. Food Chem. 39, 2063-2068. Doi: 10.1021/jf00011a036

Singh, R.P. and G. Srivastava. 2009. Adsorption and movement of carbofuran in four different soils varying in physical and chemical properties. Adsorpt. Sci. Technol. 27, 193-203. Doi: 10.1260/026361709789625270

Singh, B., A. Farenhorst, J. Gaultier, D. Pennock, D. Degenhardt, and R. McQueen. 2014. Soil characteristics and herbicide sorption coefficients in 140 soil profiles of two irregular undulating to hummocky terrains of western Canada. Geoderma 232-234, 107-116. Doi: 10.1016/j.geoderma.2014.05.003

Sposito, G. 1989. The chemistry of soils. Oxford University Press, Oxford, UK.

Tariq, M.I., S. Shahzad Afzal, and I. Hussain. 2006. Degradation and persistence of cotton pesticides in sandy loam soils from Punjab, Pakistan. Environ. Res. 100, 184-196. Doi: 10.1016/j.envres.2005.05.002

Tiryaki, O. and C. Temur. 2010. The fate of pesticide in the environment. J. Biol. Environ. Sci. 4, 29-38.

Valencia, E.M., J.A. Guerrero, A. de Yunda, and M.J. Martínez. 2008. Evaluación de la adsorción-desorción de 14C-carbofuran y Furadan 3SC® en tres suelos de Cundinamarca (Colombia). Rev. Colomb. Quim. 37, 79-91.

Veeh, R.H., W.P. Inskeep, and A.K. Camper. 1996. Soil depth and temperature effects on microbial degradation of 2,4-D. J. Environ. Qual. 25, 5-12. Doi: 10.2134/jeq1996.00472425002500010002x

Vighi, M. and A. Di Guardo. 1995. Predictive approaches for the evaluation of pesticide exposure. pp. 73-100. In: Vighi, M. and E. Funari (eds.). Pesticide risk in groundwater. CRC Press, Boca Raton, FL.

Weber, J.B. 1993. Ionization and sorption of fomesafen and atrazine by soils and soil constituents. Pest Manag. Sci. 39, 31-38. Doi: 10.1002/ps.2780390105

Weber, J.B., G.G. Wilkerson, and C.F. Reinhardt. 2004. Calculating pesticide sorption coefficients (k_d) using selected soil properties. Chemosphere 55, 157-166. Doi: 10.1016/j.chemosphere.2003.10.049