Simazine transport in undisturbed soils from a vineyard at the Casablanca valley, Chile

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ABSTRACT

Simazine is a soil-active herbicide that has been applied worldwide in agricultural soils, being the second most commonly detected herbicide in groundwater and surface waters. Although its use has been restricted in many countries of Europe, it is still applied in many locations around the world in orchards, vineyards and forestry. Therefore, it is important to study its fate and transport in the environment. This paper investigates simazine transport in undisturbed bare soils from a vineyard at the Casablanca valley, Chile. In the study site, shallow groundwater tables (<1.0 m depth) and high simazine levels (>15 μg L^{-1}) in the groundwater were observed and thus, there is potential for simazine to be transported further away through the saturated zone. The soils from the study site were characterized and the hydrodynamic transport parameters were determined. Column leaching experiments showed that the two-site chemical non-equilibrium model correctly represented simazine transport. It was found that 36.3% of the adsorption sites achieve instantaneous equilibrium and that the first-order kinetic rate of the non-equilibrium sites was 6.2×10^{-3} h^{-1}. Hydrus 2D was used to predict the transport of simazine in the study site under natural field conditions. Simulation results showed that simazine concentrations at depths shallower than 2.1 m are above the maximum contaminant level of 4 μg L^{-1} (defined by the U.S. Environmental Protection Agency). The timing of herbicide application was found to be important on simazine leaching and the main processes involved in simazine transport were degradation and adsorption, which accounted for 95.78 and 4.19% of the simulated mass of pesticide, respectively. A qualitative agreement in the timing and magnitude of simazine concentration was obtained between the simulations and the field data. Therefore, the model utilized in this investigation can be used to predict simazine transport and is a valuable tool to assess agricultural practices to minimize environmental impacts of simazine.

1. Introduction

The use of pesticides has been a common practice to improve agricultural productivity. However, their inappropriate use can have detrimental effects on human health and on the environment (Márquez et al., 2005; Chang et al., 2008). Soil and groundwater contamination by pesticides has been extensively documented around the world (Kolpin et al., 1998; Close et al., 1999; Lapworth et al., 2006). Simazine is the second most commonly detected pesticide in groundwater and surface waters in the United States, Europe, and Australia (Barbash et al., 2001; Wilson et al., 2011), as it has been widely used to control broadleaf weeds in agricultural and non-crop fields (Gunasekara et al., 2007). Even though its use has been restricted in many countries of Europe, simazine is still applied in many locations around the world, principally in orchards, vineyards and forestry production (Chang et al., 2008; Flores et al., 2009; Morgante et al., 2012). Therefore, it is important to study its fate and transport in the environment.

Pesticide transport in soils has been widely studied under field and laboratory conditions (Gamerdinger et al., 1991; Pang et al., 2000; Pot et al., 2011). These studies have shown that non-

equilibrium processes must be included when studying pesticide transport. Chemical non-equilibrium models have given particularly good results for representing the transport of many organic and inorganic chemicals; in which sorption occurs mainly on organic carbon and have both rate limited and instantaneous sorption (Pot et al., 2011). However, there are few laboratory or field studies on triazine herbicides, other than atrazine, that investigated their degree of non-equilibrium. Gamerdinger et al. (1991) studied non-equilibrium sorption and degradation of atrazine, simazine and cyanazine in two soils (silty clay and silt loam) from New York. They found evidence that atrazine transport can be represented using non-equilibrium kinetic models. The non-equilibrium sorption of simazine and cyanazine was found to be similar than that of atrazine. Close et al. (1999) and Pang et al. (2000) studied pesticide transport of picloram, atrazine and simazine through two New Zealand soils. At depths shallower than 1.1 m, they monitored simazine levels that were higher than 4 μg L^{-1}, which is the simazine maximum contaminant level (MCL) defined by the U.S. Environmental Protection Agency (EPA). Mao and Ren (2004) also reported a chemical non-equilibrium behavior for atrazine in sandy soils. Chang et al. (2008) performed a comparative study of three different pesticide transport simulation models to determine the simazine's groundwater vulnerability in a citrus orchard located in the Rio Grande Valley.

Although simazine has been widely used in Chilean agricultural soils, mostly because of the pressure to produce high-quality food for consumers around the globe, only few studies have addressed groundwater contamination by pesticides in these soils. Its fate in this environment only has been studied in one vineyard located in the Casablanca Valley (Alister et al., 2005; Suárez et al., 2007; Kogan et al., 2007) and in one avocado plantation located in the Aconcagua Valley (Flores et al., 2009; Morgante et al., 2012). Most of these studies have used experimental data to determine the physicochemical properties of the pesticide and to evaluate leaching indexes to investigate the mobility of the pesticides through the soil. Since monitoring chemical concentrations in soils is typically very expensive, the use of mathematical models appears as a cost- and time-effective approach to assists decision makers in the prediction of groundwater contamination (Pang et al., 2000), and to design management strategies to minimize adverse impacts of chemicals on the environment (Chang et al., 2008). In Chile, only one study has addressed the challenge of developing mathematical tools to assist Chilean decision makers to predict groundwater contamination by pesticides (Suárez et al., 2007). In that study, simazine transport was investigated in unsaturated sandy soil columns collected in a vineyard from the Casablanca Valley, Chile. They determined that chemical non-equilibrium processes govern

pesticide transport, and evaluated the transport of simazine under hypothetical field conditions. However, that investigation used disturbed soils to assess the "most risky" conditions for pesticide application, i.e., coarse soils and shallow groundwater tables. Therefore, even though it enabled to determine the main processes governing simazine transport, the soils used were not directly representative of the entire soil profile of the vineyard.

The aim of this work is to study the transport of simazine under natural conditions using undisturbed bare soils from the vineyard located in the Casablanca valley, Chile. It is important to note that although plant growth modifies soil moisture dynamics, e.g., due to root water uptake (Doussan et al., 2006) or due to soil compaction (Berli et al., 2008; Aravena et al., 2011), the investigation of these complex processes is out of the scope of this work. The specific objectives of this investigation are: (1) to explore how much simazine can reach the groundwater under natural field conditions; (2) to generate the required information to study simazine transport using mathematical models. In particular, to determine the representative soil hydraulic properties and the hydrodynamic parameters of the study site; (3) to investigate the main mechanism of simazine transport; and (4) to improve the previous model developed by Suárez et al. (2007), by studying groundwater flow and simazine transport in a two-dimensional representative transect of the soil profile from the vineyard subject to natural meteorological conditions. To achieve these objectives, groundwater levels and simazine concentration were monitored throughout a 2-year period in the study site. The spatial variability of the soil properties was investigated in undisturbed soil cores, and the hydrodynamic properties and the main mechanisms of simazine transport were determined in soil column leaching experiments. Finally, a numerical simulation of two-dimensional groundwater flow and simazine transport was performed in a representative transect within the study site. This simulation was utilized to investigate simazine transport under natural field conditions for a time-period of six years, and showed how valuable are these tools to assist decision makers in the prediction of groundwater contamination.

2. Materials and methods

2.1. Study site and field methods

The study site corresponded to a vineyard in the Casablanca Valley, Chile (33°16′ S; 71°23′ W). The field site is shown in Fig. 1 and in the Google Maps file that is available in the online version of this article. A field plot of approximately 75 × 200 m inside the study site was used in this investigation. Thirty two piezometers
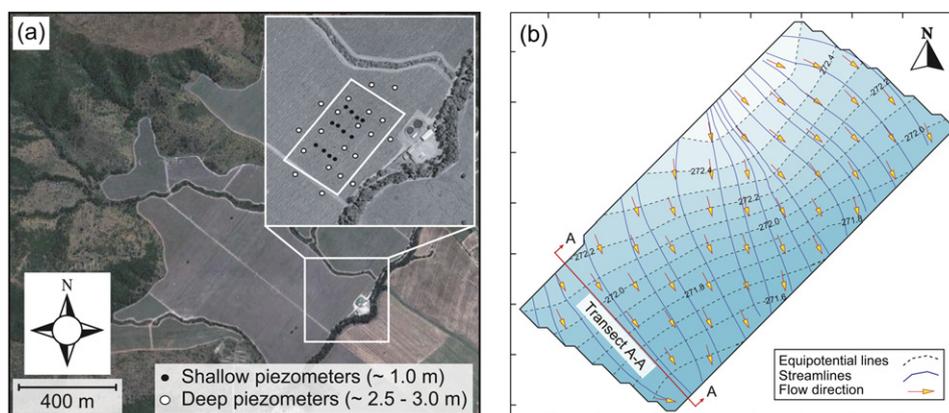

Fig. 1. (a) Location of the piezometers sand of the field plot in the vineyard. (b) Groundwater streamlines in the field plot (September, 2003).

were installed in the field site to characterize the soil from the vineyard (as described in the next section), to monitor phreatic levels and to monitor simazine concentrations in the groundwater. Twenty of the piezometers were drilled until a depth of approximately 2.5–3.0 m and the remainders were drilled until a depth of approximately 1.0 m. The groundwater table was monitored on a monthly basis between the years 2003 and 2005 using an electrical contact meter (KLL, SEBA Hydrometrie, Germany). The groundwater flow field inside the field plot was determined by monitoring the groundwater table levels. The main flow paths during the year 2003 were identified and transect A–A (Fig. 1b) was selected as a representative flow path transect. To monitor simazine concentrations in the field, groundwater samples were collected from the piezometers by lowering plastic flasks into them. The water samples were frozen to stop simazine degradation and taken to the laboratory. Simazine concentrations in the water samples were analyzed by an ELISA simazine test kit with a detection limit of 0.03 μg L^{-1} (Strategic Diagnostics Inc., 1997) and confirmed by gas chromatography with mass detection (Quintana et al., 2001).

2.2. Soil characterization

The installation of the piezometers allowed the collection of a total of 80 undisturbed soil core samples (with a grid sampling pattern at a density of 15 samples ha^{-1}). These soil samples were used to determine soil texture and to identify homogeneous zones in the field. The soil samples were obtained at four different stratums: 0–15, 15–30, 30–60, and 60–90 cm depth (Alister et al., 2005). In each stratum, five homogeneous zones were identified using cluster analysis (Fig. 2). The soil physicochemical properties of each of these zones were statistically equal ($p > 0.1$) and they were treated as blocks. The methods to estimate physicochemical properties as well as linear adsorption coefficients of each homogeneous zone are presented by Alister et al. (2005). A linear sorption model was assumed because triazines showed this behavior at the doses used in the field (Mao and Ren, 2004; Suárez et al., 2007).

To estimate the soil hydraulic properties, which are required to solve the Richards' (1931) equation for water flow under unsaturated conditions, 75 additional undisturbed soil samples were collected at the four different stratums using a 5.7-cm diameter soil core sampler (Soilmoisture Equipment Corp., Santa Barbara, CA). The saturated hydraulic conductivity was determined in triplicate by using a constant head permeameter (Soil Measurement System, Tucson, AZ), and the water retention curve was estimated using a 1600 5-bar pressure plate extractor (Soilmoisture Equipment Corp., Santa Barbara, CA) under drying conditions (from 0 to 3 bar of suction). The experimental water retention curve was then used in the RETC code (van Genuchten et al., 1991) to estimate the water retention parameters of the van Genuchten model (1980). The unsaturated hydraulic conductivity was determined using Mualem's (1976) model.

2.3. Determination of hydrodynamic and transport parameters

Tracer experiments were performed in two undisturbed soil columns to determine the hydrodynamic properties of the soil and the transport parameters of simazine in the study site. These columns were taken near transect A–A, as shown in Fig. 2, and brought to the laboratory for further analyses.

The first column (8.4-cm inner diameter, 12-cm long) was taken from the 60–90 cm depth stratum. It was collected using a sharp-edge PVC pipe that was driven vertically into the ground. The column was then removed from the ground and brought to the laboratory. Conservative and reactive tracer experiments were carried out in the experimental setup described by Suárez et al. (2007). Unsaturated conditions were maintained by applying 0.6 bar of suction at the bottom of the soil column. An average water flux density of 3.16 cm^3 h^{-1} was injected at the soil surface. Chloride (Cl$^-$), at a concentration of 524 mg L^{-1}, was used as the conservative tracer by applying a solute pulse of KCl for 20 h. Effluent volumes were collected every 4 h using a fraction collector (Retriever II, Teledyne Isco, Inc., Lincoln, NE) and the effluent concentration of Cl$^-$ was measured with a 96-17 ionplus® Orion chloride-selective electrode (Thermo Electron Corporation, Beverly, MA). The duration of the conservative tracer experiment was approximately 200 h (8 days). The inverse solution algorithm of Hydrus 2D (Simunek et al., 1999) was used to estimate the longitudinal and transversal dispersivities (α_L and α_T, respectively), assuming $\alpha_T = 0.1\alpha_L$ (Domenico and Schwartz, 1998) and using a representative value of 1.9×10^{-9} m^2 s^{-1} for the molecular diffusion of chloride in water (Lobo et al., 1998). In the inversion process, the flow within the soil column was modeled as a two-dimensional axisymmetrical flow.

In the reactive tracer experiment, a 20-h pulse of simazine was applied at the soil surface. A solution with a concentration of 17.54 mg L^{-1} was used to achieve 2 kg a.i. ha^{-1}, which is the typical maximum field dose (Alister et al., 2005). Since the soil column was taken from the field before the herbicide application, the residual simazine concentration measured in the field by Alister et al. (2005) was assumed to be the initial simazine concentration in the soil column. Effluent volumes were collected every 4 h using a fraction collector (Retriever II, Teledyne Isco, Inc., Lincoln, NE) and were immediately frozen to halt herbicide degradation. Simazine concentrations in water samples were analyzed with the methods previously described. The duration of the reactive tracer experiment was approximately 1400 h (50 days). The inverse solution algorithm of Hydrus 2D was used to fit the transport parameters for simazine. The present work utilized the two-site chemical non-equilibrium model (Simunek and van Genuchten, 2008) for simazine transport (described below). This model was selected because a previous study, performed in disturbed sandy soil columns taken from the study site, did not show physical non-equilibrium behavior and correctly represented simazine transport assuming two-site chemical non-equilibrium processes (Suárez et al., 2007). This was confirmed in the current experiments, which were performed in undisturbed soil columns. The half life (TD$_{50}$) of simazine was estimated by numerical inversion with Hydrus 2D. The TD$_{50}$ value was allowed to vary between the range observed in previous investigations performed in the study site (Alister et al., 2005; Kogan et al., 2007; Suárez et al., 2007).

To validate the transport parameters, a simazine leaching experiment was carried out in the second soil column (90-cm long). This soil column was collected using a PVC pipe of 100-cm height and 20-cm internal diameter. The PVC pipe was introduced into a sharp-edge steel tube and was driven vertically into the ground. The soil column was carefully removed from the ground and the steel tube was detached from the PVC pipe. Therefore, a 90-cm long undisturbed soil column was obtained. The soil column was carefully brought to the laboratory, and equipped with three TDR probes (TRIME-GR, MESA systems Co., Medfield, MA) to monitor water contents at 15, 30, and 60 cm depth. A steel base-cap was installed at the bottom of the soil column. The middle of the steel base was threaded and coupled to a 1-m long 20-mm diameter PVC pipe. The PVC pipe was filled with glass wool to create suction in the bottom of the soil column, which is more representative of field conditions (Boll et al., 1992; Alister et al., 2005). The additional transit time produced by the inclusion of the PVC pipe filled with glass wool was found to be negligible compared to the transit time of water through the soil column (Knutson and Selker, 1996). For
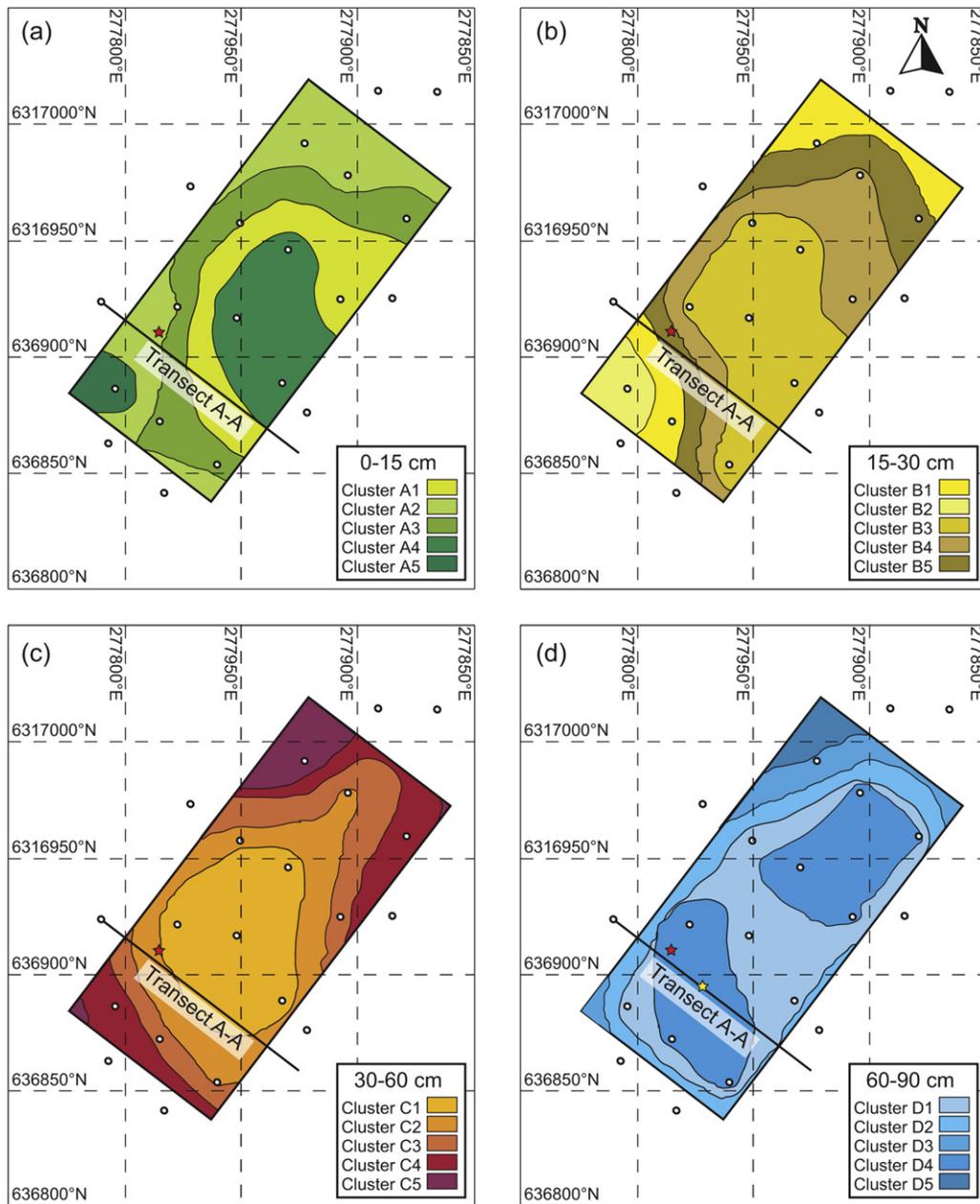
Fig. 2. Homogeneous zones (or clusters) in the experimental field plot (a) 0—15 cm depth. (b) 15—30 cm depth. (c) 30—60 cm depth. (d) 60—90 cm depth. The yellow star on the 60—90 cm stratum represents the approximate location of the first undisturbed soil column (12-cm long), while the red star on each stratum represents the approximate location of the second undisturbed soil column (90-cm long). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the conditions tested in the leaching experiment, the average suction at the bottom of the soil column was 68 cm (Boll et al., 1992). It was assumed that the soil within the column consisted of the four different stratums observed in the field. To determine the soil hydraulic properties of this column, the inverse solution of Hydrus 2D was used to fit the temporal evolution of the water contents at different depths within the column. In the inversion process, the soil hydraulic properties of each stratum were restricted by assuming a maximum variability of ±15% in the soil hydraulic properties (that were estimated using the undisturbed soil samples collected in the field), while the transport parameters were assumed to be equal to those obtained in the 12-cm soil column. Prior to the herbicide application, the column was flushed with water to have near zero initial concentration in the soil. Simazine was applied at a concentration of 128 mg L^{-1} in 50 mL

(equivalent to the field dose). After the application of simazine, the soil column received 258 mm of water throughout the experiment, which simulated natural rainfall observed in the field plus 30 mm of additional rain every 15 days until the 75th day. The duration of the leaching experiment was 100 days. Effluent volumes were collected on a daily basis in plastic flasks and were immediately frozen to halt simazine degradation. Simazine concentrations in water samples were measured using the analytical methods described earlier.

2.4. Simulation of simazine leaching under field conditions

In this work, the Richards' (1931) and the advective-dispersive equations (Domenico and Schwartz, 1998) were used to model the transient coupled isothermal water flow and solute transport in

the subsurface. Many models, which incorporate the processes of interest in pesticide leaching, have been proposed to simulate solute transport. Commonly utilized models include: LEACHM (Huston and Wagenet, 1992), PRZM-3 (Carsel et al., 2003), and Hydrus 1D/2D (Simunek et al., 1999, 2008). In general, these models solve the previous equations using analytical or numerical solutions. In this work, the Hydrus 2D code was employed to numerically solve the governing equations. The one- and two-dimensional versions of the Hydrus package efficiently solve the governing equations and have been successfully utilized to simulate pesticide transport in partially saturated soils (Pang et al., 2000; Kohne et al., 2009; Pot et al., 2011). Detailed descriptions of solute transport theory, including local equilibrium and non-equilibrium assumptions for representing adsorption exchange processes in soils are available elsewhere (Valocchi, 1985; van Genuchten and Wagenet, 1989). As described before, the two-site chemical non-equilibrium model for simazine transport was used in this investigation. This model assumes that the adsorption potential can be represented by two types of adsorption sites: Type-1 sites that achieve instantaneous equilibrium, and Type-2 sites that are time dependent and are represented by a first-order kinetic term. Adsorption on Type 1 and 2 sites is described by (Jellali et al., 2010):

$$S_1 = FK_dC \tag{1}$$

$$\frac{\partial S_2}{\partial t} = \alpha_2[(1 - F)K_dC - S_2] \tag{2}$$

where S_1 and S_2 [M M^{-1}] are the solute concentrations in the sorbed phase for the Type 1 and 2 sites, respectively; F [−] is the fraction of all the sites that are at equilibrium, i.e., Type-1; K_d [L^2 M^{-1}] is the linear adsorption coefficient; C [M L^{-3}] is the solute concentration in the liquid phase; t [T] is time; and α_2 [T^{-1}] is the first-order kinetic coefficient.

To investigate simazine leaching under field conditions, two-dimensional simulations were performed using Hydrus 2D. Transect A−A (5 m depth and 75 m long) was chosen to be the domain for the simulations (Fig. 3). This transect was selected because it is oriented in the same direction than the groundwater streamlines (Fig. 1b). Thus, three-dimensional effects on water flow and simazine transport are minimized. In addition, the estimation of the transport parameters was performed in columns extracted near this transect. The soil properties (e.g., hydraulic conductivity, water retention curve, linear adsorption coefficients) were interpolated from the previously identified five homogeneous zones.
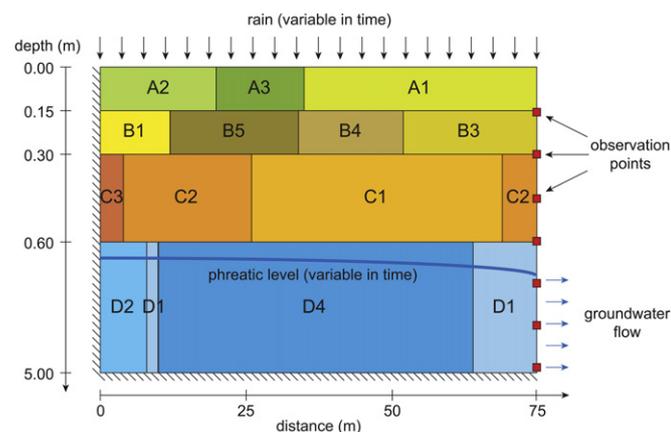

Fig. 3. Domain for the numerical simulations and soil classification in Transect A−A, according to the results of the cluster analysis. The properties of each homogeneous zone (A1−3, B1−5, C1−3, and D1−4) are presented in Table 1.

Four different stratums were considered: 0−15, 15−30, 30−60, and 60−500 cm depth. The soil properties between 60 and 90 cm depth were used for depths deeper than 90 cm. Although the soil properties at deeper depths (>90 cm) were not measured, a visual inspection of the soil cores obtained from the 2.5−3.0 m depth piezometers showed a very uniform soil profile below 60 cm depth. Hydrodynamic and transport parameters were determined from the leaching experiments as described above. The soil surface (the upper boundary) was represented using an atmospheric boundary condition. Meteorological data (e.g., precipitation, potential evaporation) were obtained near the vineyard in the Casablanca station (33°20′ S; 71°25′ W). For simazine, the upper boundary was considered as a concentration flux boundary condition, where the input concentration was fixed to obtain the field dose of simazine applied each year (i.e., 2 kg a.i. ha^{-1}). The application of simazine was considered to take place once a year at the end of the third week of August, as performed in the field. To represent the groundwater table, the bottom of the domain was set as a no-flux boundary, and the initial pressure head was set to 0 m. In the field, groundwater levels were strongly influenced by precipitations. Thus, to simulate mounding of the groundwater table, which is calculated within Hydrus 2D, a no-flux boundary was located at the lower left-hand side of the domain and a seepage face was located at the lower right-hand side of the domain. These lower boundary conditions also represent an aquifer with no-mixing through its depth. The initial conditions used for water flow were equilibrium from the lowest point in the domain. The initial concentration of simazine in the soil profile was assumed to be uniform and equal to the residual simazine concentration measured in the field before herbicide application (Alister et al., 2005). The aim of these simulations was to improve the predictions performed by Suárez et al. (2007), which studied the most risky conditions for simazine leaching under hypothetical field conditions, and to qualitatively compare the simazine concentrations observed in the field.

3. Results and discussion

3.1. Simazine transport under natural conditions

Fig. 4a shows the evolution of the mean depth to groundwater measured in the field. During 2003 the groundwater table was very shallow, with highly variable depths that ranged between 0.7 and 2.6 m. The year 2004 was drier and the groundwater levels were always deeper than 3.0 m (all the piezometers were dry). During 2005, the groundwater table rose to similar levels than those observed during 2003. The shallow groundwater tables observed in the study site clearly shows that there is potential for the pesticide to be transported further away through the saturated zone (Barbash et al., 2001; Lapworth et al., 2006). Fig. 4b shows the simazine concentration measured in the field. These concentrations were obtained from different piezometers, and represent their mean concentration. During 2004, because it was not possible to collect water samples from the piezometers, simazine concentrations were obtained from leachates of 100-cm long undisturbed laboratory soil columns subject to the natural conditions observed in the field (Alister et al., 2005). Although these data are not representative of the simazine levels at more than 3.0 m depth, it does provide an upper boundary for the simazine concentration expected in the groundwater. From Fig. 4b it can be observed that higher concentrations of simazine occur in or after August of each year. In the field, simazine was applied during the third week of August. Therefore, higher simazine concentrations were expected after the herbicide application. However, according to the manufacturer specifications, it was not expected to observe concentrations as high as those
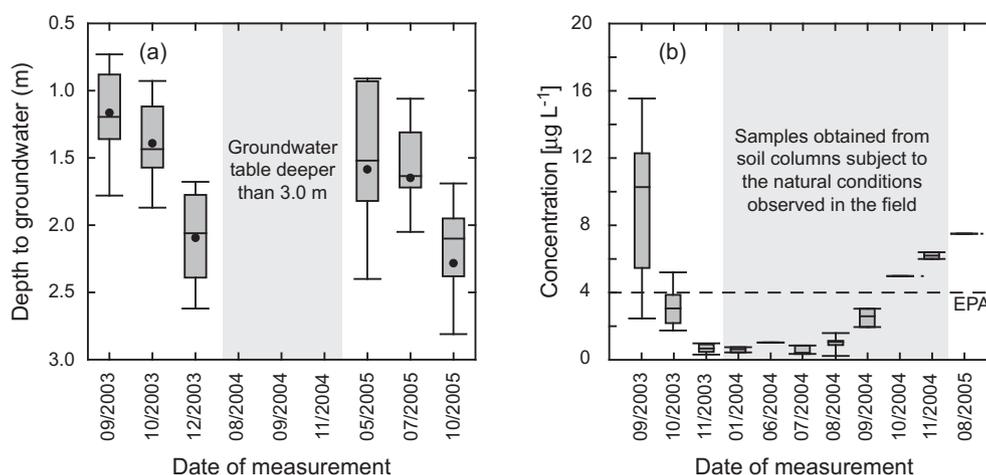
Fig. 4. Field results indicating maximum, minimum, mean, and upper and lower quartiles of the observed variables. (a) Depth to the groundwater table measured in all the piezometers of the study site. The black circles represent the mean depth in the piezometers near transect A–A. (b) Simazine concentration from samples collected in all the piezometers of the study site. When the groundwater table was deeper than 3.0 m, these concentrations were obtained from the leachates of 1.0-m long undisturbed laboratory soil columns subject to the natural conditions observed in the field. The dashed line represents the U.S. EPA maximum contaminant level for simazine.

measured in the field during the year 2003, which were higher than 15 μg L^{-1} and generally above the MCL. Moreover, these high concentrations were observed during the time-period where groundwater levels were very shallow (Fig. 4a). Thus, simazine will reach the saturated zone and will be transported faster and with a smaller capacity of being degraded by the environment (Kolpin et al., 1998; Pang et al., 2000; Gunasekara et al., 2007). Also, periods of lower simazine concentrations were observed when the groundwater table was deeper. For instance, during 2004 the concentration levels measured in the 100-cm long soil columns were lower than the MCL. Note however that, after the application of simazine, these columns also showed an increased concentration that surpassed the MCL. The results presented in Fig. 4 emphasize the importance of analyzing together solute transport and the characteristics of the study site such as groundwater levels, which is typically neglected in experimental investigations that study physicochemical properties or dissipation of the pesticides (Flores et al., 2009; Kogan et al., 2007; Morgante et al., 2012).

3.2. Soil properties

A soil textural analysis revealed that the soil from the study site was comprised of 50% loam, 30% sandy clay loam, 12.5% sandy

loam, and 7.5% clay loam, with an average bulk density of 1.39 ± 0.08 g cm^{-3} (average ± standard deviation). The textural classification of the soil is presented in Supplementary Fig. 1 of the Electronic Annex (in the online version of this article). The five homogeneous zones identified in each stratum are presented in Figs. 2 and 3. The hydraulic properties of each homogeneous zone in transect A–A are presented in Table 1. The goodness of fit of the van Genuchten model (1980) to the water retention data was very good, with coefficients of determination (r^2) higher than 0.98 for all the clusters. Both the residual and saturated water contents increased slightly with depth and were relatively uniform within each stratum, with values of 0.039 ± 0.002 cm^3 cm^{-3} and 0.389 ± 0.001 cm^3 cm^{-3}, respectively. The saturated water content was smaller than that obtained in the disturbed columns (with coarser sandy soils) tested by Suárez et al. (2007). However, for suctions higher than 0.1 m, the hydraulic properties of the undisturbed soils showed more retention of water than the disturbed and coarser soils of the study site. Also, it is important to note that both water retention curves (undisturbed and disturbed soils) showed a rapid desaturation with capillary pressure, which is a characteristic of medium sand (Klute, 1994). The average saturated hydraulic conductivity was 13.9 ± 3.8 cm d^{-1}, which is consistent with the textural classification of the soil (Domenico and

Table 1
Hydraulic properties of the soil and transport parameters in transect A–A for different stratums and clusters. The spatial distribution of the clusters is shown in Fig. 2. ρ: soil bulk density; θ_r: residual water content; θ_s: saturated water content; α: inverse of the air entry pressure; n, m: empirical parameters; K_s: saturated hydraulic conductivity; K_d: linear adsorption coefficient.

Stratum	Cluster	ρ (g cm^{-3})	θ_r (cm^3 cm^{-3})	θ_s (cm^3 cm^{-3})	α (cm^{-1})	n (–)	m (–)	K_s (cm d^{-1})	K_d (cm^3 g^{-1})
0–15 cm	A1	1.42	0.0373	0.3883	0.1539	1.3187	0.2405	11.73	1.045
	A2	1.45	0.0371	0.3878	0.1486	1.3303	0.2473	12.46	1.104
	A3	1.45	0.0371	0.3880	0.1514	1.3242	0.2437	12.08	1.104
15–30 cm	B1	1.41	0.0381	0.3893	0.1585	1.3170	0.2374	11.27	1.244
	B3	1.35	0.0381	0.3895	0.1635	1.3119	0.2335	11.03	0.746
	B4	1.35	0.0381	0.3895	0.1620	1.3114	0.2338	10.98	0.554
	B5	1.35	0.0381	0.3894	0.1603	1.3135	0.2352	11.08	0.554
30–60 cm	C1	1.37	0.0389	0.3895	0.1473	1.3221	0.2418	11.96	0.542
	C2	1.30	0.0389	0.3892	0.1408	1.3394	0.2509	13.12	0.548
	C3	1.23	0.0389	0.3890	0.1378	1.3496	0.2559	13.85	0.554
60–90 cm	D1	1.48	0.0427	0.3904	0.1100	1.4097	0.2848	19.83	0.502
	D2	1.47	0.0428	0.3904	0.1094	1.4198	0.2886	21.59	0.980
	D4	1.47	0.0427	0.3904	0.1100	1.4084	0.2844	19.41	0.805

Schwartz, 1998). This hydraulic conductivity is one order of magnitude smaller than that obtained by Suárez et al. (2007). This was expected since the soils used by Suárez et al. (2007) corresponded to coarse sandy soils that were employed to evaluate the most risky conditions for groundwater contamination.

The linear adsorption coefficients varied between 0.502 and 1.244 $cm^3 g^{-1}$, with an average value of 0.791 ± 0.270 $cm^3 g^{-1}$. These values are in agreement with those reported in the literature (Wauchope et al., 1992; Alister et al., 2005), which varies between 0.65 (sand with 0.9% organic matter and pH of 6.5) and 4.31 $cm^3 g^{-1}$ (clay with 4.8% organic matter and pH of 5.9).

3.3. Hydrodynamic and transport parameters

The results from the conservative (chloride) tracer experiment performed in the 12-cm long column are presented in Fig. 5a. The chloride recovery was greater than 90%, which supports the hypothesis that chloride serves as a non-reactive tracer. The chloride breakthrough curve (BTC) did not show evidence of non-equilibrium processes, and was represented correctly ($r^2 = 0.982$) using the local equilibrium assumption (Valocchi, 1985) with
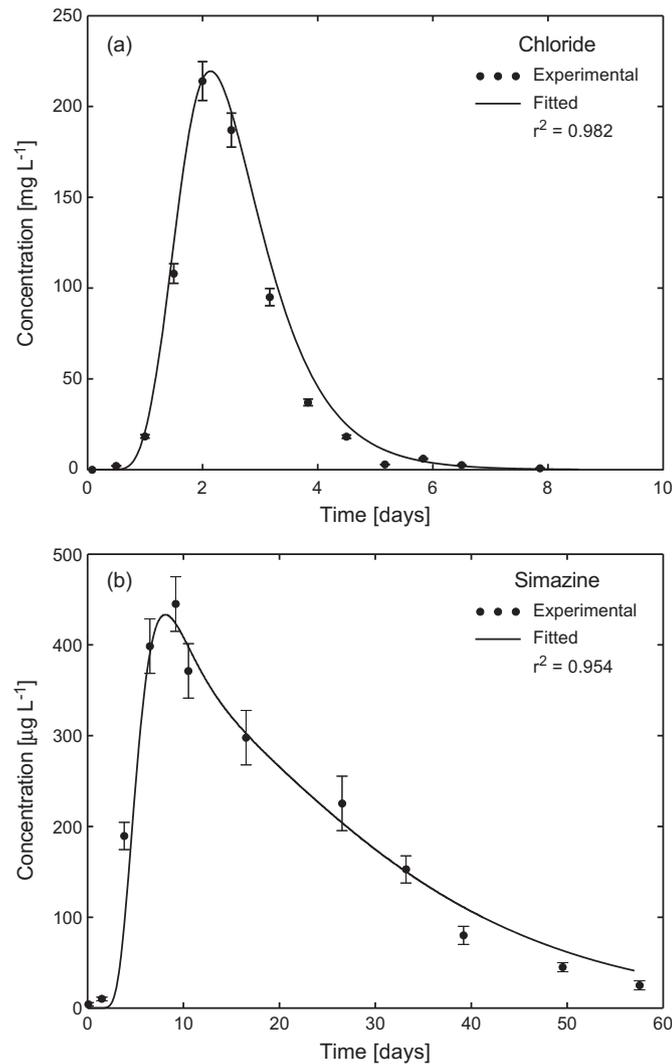

Fig. 5. Measured and fitted breakthrough curves in the 12-cm long soil column. (a) Conservative tracer experiment (chloride). (b) Reactive tracer experiment (simazine). Error bars represent the standard error of the mean (4 samples). This column was exposed to a uniform water flux density of 3.16 $cm^3 h^{-1}$ (13.7 $mm d^{-1}$).

a longitudinal dispersivity of 1.938 ± 0.164 cm (95% confidence interval estimated using the inverse solution of Hydrus 2D). This value is one order of magnitude greater than the mean value obtained by Suárez et al. (2007) and by the relationship between length scale and longitudinal dispersivity found by Schulze-Makuch (2005). However, it should be pointed out that dispersivity values commonly vary in one order of magnitude or more (Schulze-Makuch, 2005). For instance, Silliman and Simpson (1987) reported longitudinal dispersivity values on the same order of magnitude than those presented in this work (for the same length scale).

Fig. 5b shows the results from the reactive (simazine) tracer experiment carried out in the 12-cm long column. The simazine BTC was asymmetric and exhibited long tailing. It was not possible to correctly describe this behavior using the local equilibrium assumption (Valocchi, 1985). Thus, non-equilibrium sorption processes become important for simazine transport. Since the chloride BTC showed no evidence of physical non-equilibrium, the two-site non-equilibrium model was utilized to represent the experimental values. This selection was supported by a previous investigation in the study site (Suárez et al., 2007). The fraction of the sites that are at equilibrium (F) was found to be 36.3%, and was very similar to that obtained by Suárez et al. (2007) in the disturbed soils from the study site (with $F = 39.5\%$). The F values were also very similar to those obtained by Gamerdinger et al. (1991), which varied between 22.0 and 41.0%. On the other hand, the undisturbed soils presented much smaller kinetic rates ($\alpha_2 = 6.2 \times 10^{-3} \pm 2.9 \times 10^{-4}$ h^{-1}) for the adsorption of Type-2 sites compared to those obtained by Suárez et al. (2007), which reported that $\alpha_2 = 1.0 \times 10^{-1}$ h^{-1}. Nonetheless, the kinetic rates obtained in the undisturbed soils are closer to those obtained by Gamerdinger et al. (1991), which reported values of α_2 between 1.9 and 7.0×10^{-2} h^{-1} when studying simazine transport in disturbed silty soils (30.1% sand, 55.2% silt, and 14.7% clay). If one compares the experiments between the undisturbed and disturbed soil from the study site, the solute exchange between the Type-2 sites and the liquid phase in the undisturbed soil should be slower than that occurring in the disturbed soil, resulting in more solute mobilized in the liquid zone. Following this discussion, one might think that the undisturbed soil could be potentially more dangerous, in terms of simazine leaching, than the disturbed soils tested by Suárez et al. (2007). This would be true when the saturated hydraulic conductivity of the undisturbed soil is larger than that of the disturbed soil, which is not the case. However, it is important to note that having a smaller value of α_2 should result in an earlier arrival time of the solute. The TD_{50} of simazine was estimated in 12 days. This value is on the lower range of the values reported in the literature (Wauchope et al., 1992; Pang et al., 2000; Gunasekara et al., 2007), which are in the range between 11 and 149 days. The estimated TD_{50} is also very similar to the TD_{50} of simazine determined in the field site, which varied between 13 and 31 days (Alister et al., 2005; Kogan et al., 2007).

As explained before, the validation of the transport parameters was performed in a 90-cm long undisturbed soil column, assuming that the soil within the column consisted of the four different stratums observed in transect A–A. The soil hydraulic properties of this column were estimated using the inverse solution of Hydrus 2D. In the fitting process, the modeled water contents were fitted to the experimental data by varying the hydraulic properties of the four different stratums that are present in transect A–A (Table 1), and assuming a maximum variability of ±15% in the hydraulic properties. Fig. 6 presents the experimental and fitted water content evolutions in the soil column. The observed trends were represented reasonably well with the numerical model, with r^2 values always larger than 0.81. The modeled water contents at 15-cm depth reproduced reasonably well the observed data; however, it

did not match all the peaks that were observed in the experiments (e.g., at days 1 and 20), and slightly underestimated the observed values. At 30-cm depth, the modeled and observed data agrees fairly well, with an r^2 of 0.97. The main differences occur at the peaks, where the model slightly overestimates the observed data. On the other hand, at 60-cm depth, albeit the general trend of the observed data was reproduced reasonably well by the model and the r^2 value of the fitting was 0.90, the observed data have more variability that was not captured by the model. In the first 20 days of simulation, the model significantly underestimates the observed water contents observed at a depth of 60 cm. This is likely due to the lack of information regarding the initial moisture conditions inside the column (in particular for depths between 30 and 60 cm). In the numerical inversion, the initial moisture conditions were interpolated from the TDR measurements at 15, 30, and 60 cm
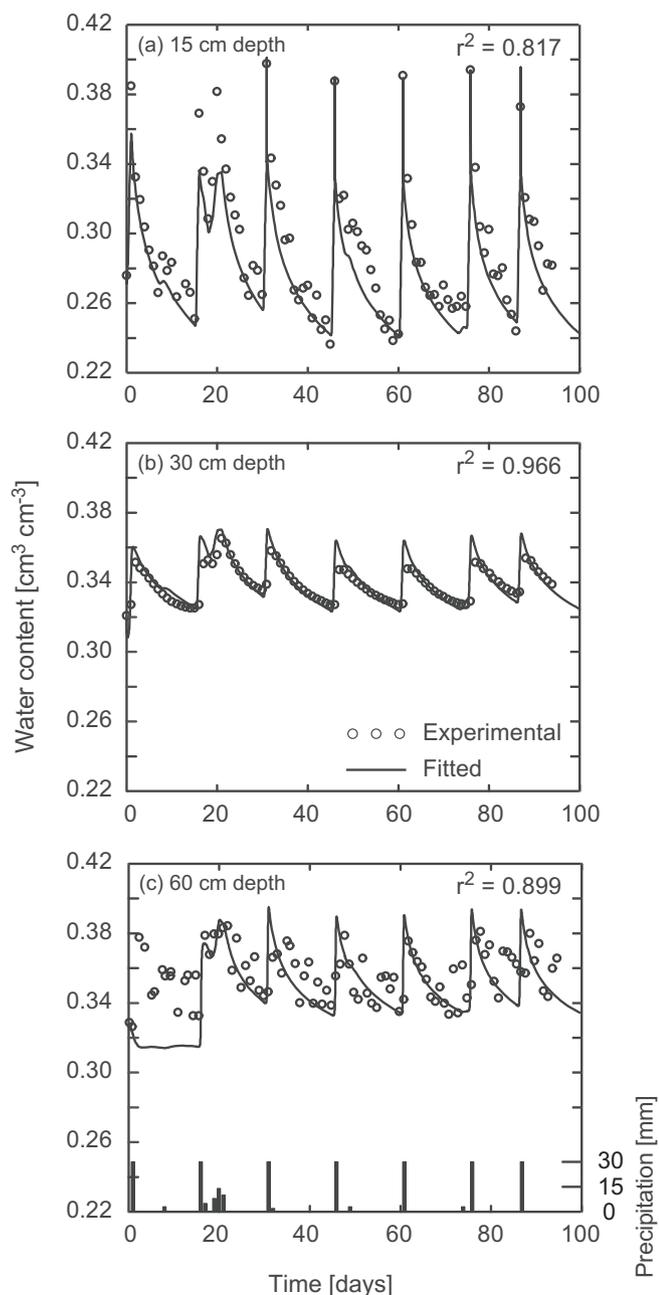
depth. However, since this column was flushed with water before these experiments (to have near zero initial concentration of simazine), it is possible that the moisture distribution between 30 and 60 cm was higher than that assumed in the modeling. In addition, the experimental water budget in this column showed differences of approximately 5%, while the model only had 0.6% of error in the water balance.

After water transport within the column was reproduced with the numerical model, the values of F, α_2, and TD_{50} obtained in the 12-cm long column were utilized to validate simazine transport in the 90-cm long column. Fig. 7 shows the comparison between the observed and modeled BTC of simazine in the column of 90 cm long. The results are very good with an r^2 value of 0.93. The first experimental measurement was higher than the modeled values probably due to a difference between the assumed initial conditions used in the model. It is possible that the flushing was not long enough to remove all the residual simazine contained in the soil column, producing the difference between the experimental and modeled data point. Then, approximately between 25 and 70 days, the observed data were reproduced reasonably well by the model; and after 80 days, the model slightly underestimated the measured values.

3.4. Simulation of simazine leaching under field conditions

To investigate simazine leaching under field conditions, two-dimensional simulations were performed in transect A–A (Fig. 3) using Hydrus 2D. Since this transect is oriented in the same direction than the groundwater streamlines, three-dimensional effects on water flow and simazine transport are minimized. Meteorological data (on a daily basis) between the years 2000 and 2005 were used to drive the simulations. Fig. 8 shows the BTCs at different depths over the 6-years simulation. These BTCs were observed at the exit of the numerical domain, i.e., at the observation points located at the right-hand side of Fig. 3. For depths shallower than 2.1 m the concentrations of simazine are above the MCL of $4\ \mu g\ L^{-1}$. The results from this simulation also show that the timing of herbicide application has significant impacts on its mobilization. Simazine application just before a precipitation event results in high herbicide concentrations deeper in the ground. On the other hand, when simazine is applied in a drier period, lower
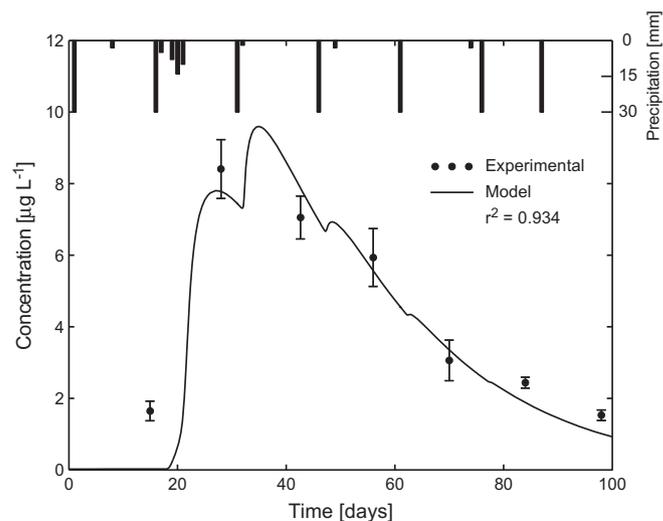

Fig. 6. Water content evolution at different depths in the 90-cm long soil column.

Fig. 7. Measured and modeled simazine breakthrough curves in the 90-cm long soil column. Error bars represent the standard error of the mean (4 samples).
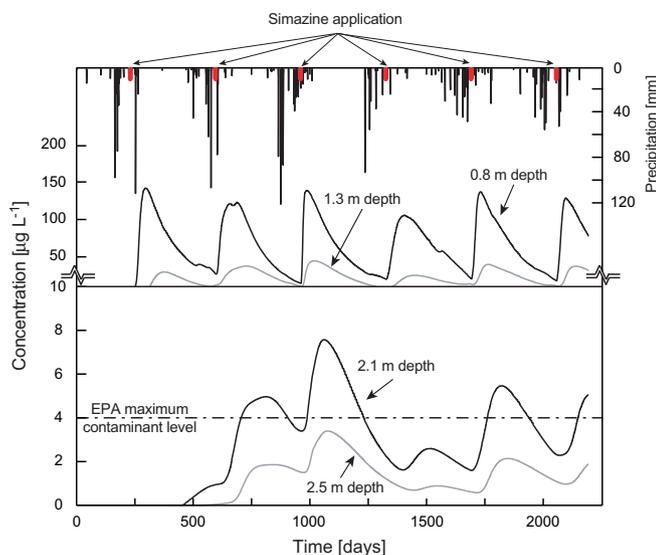
Fig. 8. Results from the 6-year simulation in which the application of simazine was considered to take place once a year at the end of the third week of August (as performed in the field). The simulation begins in January 1st, 2000 and finishes in December 31st, 2005.

concentrations of simazine are observed throughout the soil profile (e.g., see Fig. 8 at approximately 1300 days). These findings are in agreement with previously published data (Liu and Prather, 2000; Pang et al., 2000; Alister et al., 2005).

The main processes involved in simazine transport were degradation (95.78% of the simulated solute mass) and adsorption (4.19% of solute mass), and the remainder simazine (0.02%) was transported with the groundwater outside the domain. Although the simazine transported with the groundwater was a small fraction of the applied simazine, it is important to note that it could become important depending on the environmental conditions. For instance, Barriuso et al. (1997) reported that simazine can persist in the environment for more than 8 months depending on the pH and the available organic matter.

The results of this simulation are also in agreement with the results presented by Suárez et al. (2007). They studied simazine transport, under hypothetical field conditions, for different recharge rates in a coarser and disturbed soil from the study site, with the aim of evaluating the most unfavorable (or "most risky") conditions. They found that simazine levels can be as high as 45 μg L^{-1} at depths of 1 m when recharge rates are on the order of 180 mm year^{-1} (which corresponds to 50% of the annual rainfall). Here, using the conditions observed from the field, the simazine concentration levels are similar to those presented by Suárez et al. (2007). At first glance this was surprising since they studied simazine transport under most unfavorable conditions and thus, it was expected to obtain much lower simazine levels than those presented by Suárez et al. (2007). The most likely reason why these two simulations were similar, in terms of simazine concentration levels, is due to the mean precipitation considered in the simulations. Between the years 2000 and 2005, a mean precipitation of 554 mm year^{-1} was monitored near the study site. This precipitation is 50% higher than the historical precipitation observed in the field (360 mm year^{-1}), which was the value used by Suárez et al. (2007). Note also that the simazine breakthrough (or arrival time) occurred earlier in the current simulations than in those reported by Suárez et al. (2007), which is also explained primarily by the precipitation rates and in a lesser degree by the lower values of α_2. Having high concentrations of this herbicide is an important

concern because groundwater is the main potable water supply in the rural zones located near the study site. Fortunately, the information collected from this and previous studies (Alister et al., 2005; Kogan et al., 2007; Suárez et al., 2007) was used to manage herbicide application in the study site; moreover, after a few years simazine application was halted because it clearly mobilized deeper into the ground than the depths specified by the manufacturer.

Even though the simulations may not exactly represent what is happening in the field, e.g., due to heterogeneities or due to other processes not included in the modeling, it is important to point out that the results of the numerical simulation (Fig. 8), which used a classical chemical non-equilibrium model, are in a qualitative agreement with the prediction of timing and magnitude of the simazine concentrations observed in the field (Fig. 4). Therefore, even when there may be occurring other physical processes that affect the fate and transport of solutes within the soil, such as preferential flow (e.g., Simunek and van Genuchten, 2008) or alterations in the soil structure due to root growth (Aravena et al., 2011), the numerical model used in this investigation has the potential to predict simazine transport under natural conditions, and hence, is a valuable tool to improve the management of herbicides in agricultural fields.

4. Conclusions

Simazine transport was investigated in undisturbed bare soils from a vineyard located in the Casablanca valley, Chile. In the study site, the groundwater table was found to be very shallow, with depths to groundwater ranging from 0.7 m to more than 3.0 m. It was found that simazine concentrations in the groundwater were higher when the groundwater table was shallower, achieving concentrations higher than 15 μg L^{-1} and generally above the MCL (4 μg L^{-1}) defined by the EPA. Thus, there is potential for simazine to be transported further away through the saturated zone.

To further investigate simazine transport, the soil hydraulic characteristics of the study site were explored. The hydrodynamic transport parameters were estimated and validated in soil columns experiments, in which chemical non-equilibrium processes were found to correctly represent simazine transport. It was found that approximately 36% of the adsorption sites achieved instantaneous equilibrium, while 64% of the adsorption sites showed slower adsorption processes with an average first-order kinetic rate of 2.9 × 10^{-4} h^{-1}.

Hydrus 2D was utilized to predict simazine transport in a two-dimensional transect of the field site. Six-year simulations were driven by the meteorological conditions observed in the field. Based on the simulation results, when the depth to groundwater was shallower than 2.1 m, simazine concentrations were above the MCL. In addition, when simazine was applied just before a precipitation event, higher concentrations of the herbicide were found deeper in the soil profile. The main processes involved in simazine transport were degradation and adsorption, which accounted for 95.78 and 4.19% of the simulated mass of pesticide, respectively. The numerical simulations showed a qualitative agreement with the field data in both timing and magnitude of simazine concentrations. Thus, the numerical model used in this investigation has the potential to predict simazine transport under natural conditions and is a valuable tool to assess agricultural practices.

Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jenvman.2012.12.026.

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