

ASSESSING THE POTENTIAL FOR PESTICIDE LEACHING FOR THE PINE FOREST AREAS OF TENERIFE

RICARDO DIAZ-DIAZ† and KEITH LOAGUE*‡

†Applied Biology Research Center (CIBA-ITC), Technological Institute of the Canary Islands, Cebrían 3,
35203 Las Palmas, Gran Canaria, Spain

‡Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA

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Abstract—Currently, no guidelines cover use of pesticides in the forested areas of the Canary island of Tenerife. An index-based model (*Li*) was used to rank the leaching potential of 50 pesticides that are, or could be, used for management purposes in the pine forest areas of Tenerife. Once the pesticides with the greatest leaching potential were identified, regional-scale groundwater vulnerability assessments, with consideration for data uncertainties, were generated using soil, climatic, and chemical information in a geographic information system framework for all pine forest areas of the island. Process-based simulations with the pesticide root zone model for the areas and pesticides of highest vulnerability were conducted to quantitatively characterize the leaching potentials. Carbofuran, hexazinone, picloram, tebuthiuron, and triclopyr were each identified as being potential leachers.

Keywords—Forestry Pesticides Leaching Index model Process-based simulation

INTRODUCTION

The use of pesticides in modern agriculture can result in groundwater contamination [1]. The impact of pesticide use in forestry, as related to groundwater contamination, has received considerably less attention. Pesticide use in forest management falls into two main categories. The first consists of applying herbicides, soil insecticides, and fumigants for site preparation before reforestation; using herbicides to control undesired vegetation during initial tree growth; and applying insecticides and fungicides to prevent and control sporadic outbreaks of pests. The second is the application of herbicides to clear firebreaks and road edges. Pesticide applications in forest management began during the late 1950s and early 1960s, with chlorinated insecticides such as DDT. During the 1970s and 1980s, new insecticides and fungicides replaced the organochlorines (e.g., DDT) in nurseries and seed orchards [1]. In many cases, organochlorines are still manufactured today for use in less-developed countries.

The use of pesticides in forest management increased at approximately the same time as the public recognized the risks associated with regional-scale applications of agrochemicals [2]. Until the early 1980s, very little information was available regarding the direct and/or indirect impacts of pesticides on groundwater quality in forest ecosystems. Much of the information that was available 20 years ago came from studies performed in coastal areas of the northwestern United States [3]. During the last decade, some research has been conducted regarding the fate of pesticides within forest ecosystems in coastal areas of the southwestern United States [2]. Direct impacts of pesticide use in forest ecosystems on nontarget organisms have also been reported. Terrestrial invertebrate populations were impacted by applications of hexazinone (3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-(1H,3H)-dione) [4], and fish populations were impacted by

applications of carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl-*n*-methylcarbamate) [5]. To our knowledge, the assessment of potential groundwater contamination resulting from pesticide applications in forested areas has not been previously reported.

The focus of this study was to estimate the potential for groundwater contamination on the Canary island of Tenerife resulting from the use of pesticides in forest management. In Tenerife, no guidelines currently cover the use of pesticides in forested areas, despite the ongoing use of some chemicals. The herbicide glyphosate (isopropylamine salt of *N*-(phosphonomethyl)glycine) has recently been employed to maintain roads across Tenerife pine forests. An index-based model was used to rank the leaching potential of 50 pesticides that are, or could be, used for forest management in the Tenerife forests. Once the pesticides having the greatest leaching potential were identified, regional-scale groundwater vulnerability assessments, with consideration for uncertainty, were generated using soil, climatic, and chemical information in a geographic information system (GIS) framework for all pine forest areas. Following the regional-scale leaching assessments, process-based simulations for an area with high leaching potential were conducted to quantitatively characterize the potential groundwater contamination.

MATERIALS AND METHODS

Study area

The largest (2,038 km²) of the seven islands in the Canary archipelago (Fig. 1), Tenerife is located in the Atlantic Ocean near the coast of the western Sahara, between 27°59' and 28°35'N and 16°04' and 17°00'W. Tenerife has a roughly tetrahedral shape, with steep relief (except in coastal areas) and a truncated apex at 2,000 m, on which the 3,718-m Mount Teide rises. The geographic location of the archipelago as well as the local wind regime give rise to a warm and relatively dry climate, with a sharp and striking contrast between the

* To whom correspondence may be addressed
(keith@pangea.stanford.edu).

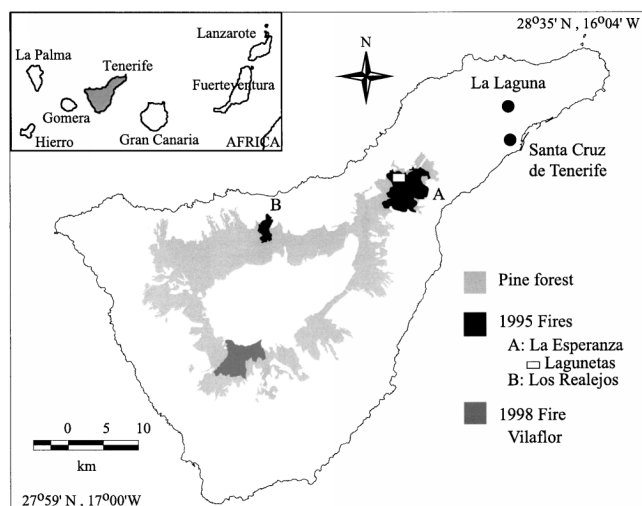


Fig. 1. Distribution of the pine forests across Tenerife, Canary Islands, Spain. The areas of Tenerife impacted by fires in 1995 (La Esperanza [A] and Los Realejos [B]) and in 1998 (Vilaflor) are identified. The area known as Lagunetas is located in the area of the 1995 fires.

humid, northern windward slope and the arid, southeastern-to-southwestern leeward slope [6,7]. Winds blowing along the northern coast rise with the slope up to 800 m, where the endemic *Pinus canariensis* is the dominant species (i.e., 95% of the 43,000 ha of Tenerife forest). The Tenerife pine forest extends on a ring-shaped band (Fig. 1), the lower and upper limits of which are from 500 to 1,000 m and 2,000 to 2,200 m, respectively, along the northern slope and from 800 to 1,000 m up to 1,800 to 2,000 m, respectively, along the southern slope [8]. The pine forests in Tenerife are essential to the water balance of the island. As in most insular systems, groundwater in Tenerife occurs as a freshwater lens floating on a saline water body. Virtually all potable water in Tenerife comes from groundwater. Protecting the groundwater resources in Tenerife is absolutely essential.

During the dry season (May through September), the risk of fire in the Tenerife forests is significant. This risk becomes extreme during the hottest months of the year (July and August). In a given year, generally no more than 200 ha of forest are impacted by fires across Tenerife. Occasionally, however, fires spread out of control and devastate much larger areas. In 1983, more than 6,000 ha of the northwestern forest were impacted by fire [9,10]. In 1995, two forest fires (Fig. 1) impacted 500 and 2,700 ha, respectively [11]. In 1998, the most recent large forest fire (Fig. 1) in Tenerife impacted 2,000 ha.

Assessment of leaching potential

Two different approaches were used in a two-phase effort to assess the leaching potential of selected pesticides for the pine forest areas of Tenerife. The first was a relatively simple, index-based model for ranking the leaching potential of a selected suite of pesticides. The second was a process-based model for simulating the concentrations of leaching pesticides, changing with time, throughout the soil profile. The use of an index-based model to target areas of concern for process-based simulations greatly reduces the computational effort [12,13] required for regional-scale vulnerability assessments.

Ranking pesticide leaching potential. If one assumes that the relative behavior of a group of pesticides will be similar under the same environmental conditions, then a ranking of their leaching potential can be made. Assessments of pesticide

leaching potential are based on the intrinsic properties of the chemicals and standardized environmental properties. Several indices (or screening models) for pesticide leaching have been reported in the literature [14–20]. The attenuation factor [21], for example, has seen considerable use during the last decade for assessing non-point source, regional-scale groundwater vulnerability, as related to pesticide use in cropped areas, in both Hawaii [22] and Tenerife [23,24].

One of the newest indices, and a more rigorous representation of pesticide leaching than past indices, is the leaching index (Li) [25]. The leaching index was recently coupled to a soil-based GIS for regional-scale, non-point source pesticide leaching assessments for the cropped areas of Tenerife [26]. The leaching index can be defined as

$$Li = \frac{LM_t}{M_0} = \frac{J_{L(0)}}{M_0 k_{dis}} [1 - \exp(-k_{dis}t)] \quad (1)$$

where LM_t is the total amount of leaching from a soil layer during the time interval t , $J_{L(0)}$ is the initial leaching flux from the soil surface, M_0 is the initial mass of pesticide applied, and k_{dis} is the disappearance rate constant. The LM_t term in Equation 1 is defined as

$$LM_t = \int_{t_1}^{t_2} J_{L(t)} dt = \frac{J_{L(0)}}{M_0 k_{dis}} [\exp(-k_{dis}t_1) - \exp(-k_{dis}t_2)] \quad (2)$$

where $J_{L(t)}$ is the leaching flux at time t and $(t_2 - t_1)$ is the time interval. The two variables in Li ($J_{L(0)}$ and k_{dis}) are defined as

$$J_{L(0)} = \frac{M_0}{V_T Z_T} q \frac{S}{P} \quad (3)$$

$$k_{dis} = \frac{\ln 2}{t_{1/2}} + \frac{qS/P}{V_T Z_T} + \frac{D_V}{V_T Z_T} \quad (4)$$

where q is the net groundwater recharge, S is the water solubility, P is the vapor pressure, V_T is the total volume of soil, Z_T is the total fugacity capacity, and D_V is the volatilization reaction parameter. The spatial variable downward flux of soil water (i.e., recharge) was estimated with the following water-balance approach:

$$q = P - ET - R \quad (5)$$

where P is the precipitation, ET is the evapotranspiration, and R is the runoff. The three terms in Equation 4 are related, respectively, to the reaction, leaching, and volatilization processes. Sorption is accounted for in Equation 4 in both the second and third terms. The terms V_T and Z_T in Equations 3 and 4 are defined as

$$V_T = [(Adn_a) + (Ad\theta_{FC}) + (Adf_{oc}) + (Ad(1 - n - f_{oc}))] \quad (6)$$

$$Z_T = \left[\frac{1}{RT} + \frac{S}{P} + \left(\frac{S}{P} K_{oc} \rho_b \right) + \left(\frac{S}{P} K_{mn} \rho_b \right) \right] \quad (7)$$

where A is the soil surface area, d is the compliance depth (taken as 0.25 m), n_a is the air-filled soil porosity or volumetric air content of the soil (i.e., $n_a = n - \theta_{FC}$), n is the total porosity of the soil (i.e., $n = 1 - \rho_b/\rho_p$, where ρ_b is the soil bulk density and ρ_p is the particle density), and K_{mn} is the soil mineral matter/water partition coefficient. The four terms in Equations 6 and 7 are related, respectively, to the air, water, organic matter, and mineral matter compartments of the soil. The complete development of the term D_V in Equation 4 is reported elsewhere [26].

As used in this study, Li is based on a constant time interval

of one year. This duration was assumed to be sufficient to eliminate more than 90% of residues of most pesticides from the surface soil layer. The Li represents the fraction of the total pesticide applied that will leach from the surface soil to a compliance depth during an elapsed time interval. Leaching estimates with Li range between zero and one; the larger the value, the more likely that the pesticide will leach. The simplifying assumptions and major limitations of Li are reported elsewhere [26].

First-order uncertainty analysis was used to estimate the impact of data uncertainties, via error propagation, associated with the assessments of pesticide leaching potential (with Li) due to the uncertainty in the parameters for conditions in Tenerife. For the special case in which the variables X_i (i.e., f_{oc} , θ_{FC} , θ_{WP} , ρ_b , ρ_p , q , K_{oc} , and $t_{1/2}$) in Li are uncorrelated, first-order analysis reduces to the familiar first-order error propagation equation, which is given by

$$\sigma_{Li}^2 = \sum_i \left(\frac{dg}{dX_i} \right) \sigma_{X_i}^2 \quad (8)$$

The component first-order uncertainty analysis equations used to estimate the standard deviations (i.e., S_{Li}) for the Li estimates are provided elsewhere [26]. Only the conservative (i.e., $Li + S_{Li}$) uncertainty case, relative to the data uncertainties, for the Li estimates was considered.

Process-based simulation. The process-based model used to simulate the near-surface fate and transport of Li targeted pesticides was the pesticide root zone model (PRZM-2) [27]. The PRZM-2 is a dynamic, compartmental, one-dimensional (i.e., vertical), deterministic-conceptual, numerical model that simulates solute transport in unsaturated soil systems within and below the root zone. Two PRZM-2 components were employed: the water-balance algorithm, and the solute-transport algorithm.

The free drainage approach used in this study routes (as plug flow) soil water in excess of the field capacity to the next-lower zone. The entire soil profile was assumed to drain of excess water with every time step. The wilting point was used as the lower limit to which plants can extract water from the soil matrix. The water balance-determined soil-water velocities were passed to a finite-difference approximation of an equation for vertical solute transport. The spatial increments used in the transport equation were the same as those used in the water-balance calculations. The PRZM-2 water-balance calculations were performed on a daily step.

The vertical, unsaturated profile soil-water velocities were estimated with the following simple relationship:

$$\theta^{t+1} = \theta^t + (v_i - v_{i-1})\Delta t \quad (9)$$

where θ is the soil-water content; t and $(t + 1)$ denote the beginning and the end of the time step, respectively; v is the velocity of the soil water; i is the soil layer index; and Δt is the time step.

The one-dimensional advection equation for the vertical, transient transport of a decaying, sorbing, and volatilizing pesticide (in heterogeneous soil profiles) is given by

$$\begin{aligned} D_g \frac{\partial^2 (n_a C_g K_H)}{\partial z^2} - \frac{\partial (C_w \theta v)}{\partial z} - C_w [K_s (\theta + K_d \rho_b)] + \frac{M_0}{A \Delta z} \\ = \frac{\partial [C_w [K_s (\theta + K_d \rho_b) + n_a K_H]]}{\partial t} \end{aligned} \quad (10)$$

where D_g is the molecular diffusivity of the pesticide in the

air-filled pore space, n_a is the volumetric air content of the soil, C_g is the gaseous concentration of the pesticide, K_H is the Henry's constant, z is the vertical space dimension, C_w is the dissolved concentration of the pesticide, K_s is the chemical first-order decay constant for the solid and dissolved phases, K_d is the partition coefficient between the dissolved and solid phases, M_0 is the mass gain from pesticide application at the surface, A is the cross-sectional area of the soil column, and Δz is the space increment. Dissolved-phase dispersion was not considered in the PRZM-2 simulations.

The assumptions made for the PRZM-2 simulations, each of which is reasonable, are that one-dimensional fluid flow and solute transport is representative; that drainage is free; that hydrodynamic dispersion is not appreciable; that volatilization is only important for bare soil surfaces; that preferential flow is not appreciable; that sorption is linear, reversible, and instantaneous; that decay is first order, with constant rate coefficients; and that a daily time step is sufficient.

Data

Distribution of pine forests and soils. The areas covered by pine forest on Tenerife are identified in Figure 1. The map shown was created based on information from an island-wide land-cover distribution summary [28] and on supplemental data regarding the distribution of pine forests across Tenerife [8]. The soils map shown in Figure 2a shows the distribution of the two soil orders (Entisols and Inceptisols) for the pine forest areas of Tenerife. Figure 2a was abstracted from the soil-order map for the entire island [23]. Comparing the pine forest distribution map (Fig. 1) with the soil-order map (Fig. 2a) reveals that approximately 75% of the soils in the pine forest areas are Inceptisols. The soils data for the two soil orders in the pine forest areas are given in Table 1. Table 2 summarizes the soils data for the horizons in the profile at the Lagunetas (Fig. 1) location.

Evapotranspiration and recharge. An annual water-balance was employed for the pine forest areas of Tenerife. The water-balance estimates were based on an average of 40 years of monthly rainfall and temperature data from climatic stations located across Tenerife. Evapotranspiration for the study area was estimated as a fraction of the potential evaporation and is dependent on the relative soil-water content in the root zone. Potential evapotranspiration was estimated according to the method described by Thornthwaite and Matter [29]. The average annual temperature estimates for the pine forest areas of Tenerife, as required for the method described by Thornthwaite and Matter, were previously reported [26]. Recharge was estimated to occur whenever the soil-water content in the root zone exceeded the field capacity (θ_{FC}). The average soil-water content was estimated as $(\theta_{FC} - \theta_{WP})$, where θ_{WP} is the wilting point. If the potential evapotranspiration was greater than $(\theta_{FC} - \theta_{WP})$, then evapotranspiration was taken as $(\theta_{FC} - \theta_{WP})$. Experimental evapotranspiration data [30] were used to estimate the depth of the soil layer participating in evaporative exchange as 0.1 m. The annual distribution of precipitation for the study area has been previously reported [26]. Island-wide average runoff for Tenerife has been estimated as 2% of precipitation [30]. Runoff losses were assumed to be 2% of total precipitation at each location. The recharge map, as developed for this study, for the pine forest areas of Tenerife is shown in Figure 2b. The average recharge rates for the two soil orders in the pine forest areas are given in Table 1.

Pesticides. A total of 50 pesticides were selected for this

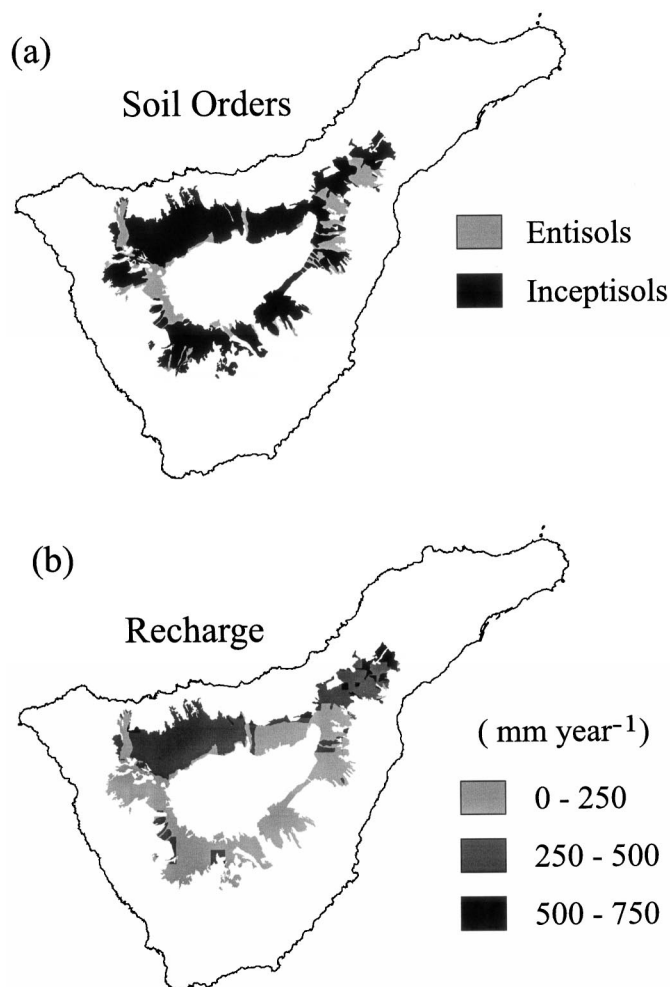


Fig. 2. **a.** Distribution of the soil orders Entisols and Inceptisols for the pine forest areas of Tenerife, Canary Islands, Spain. **b.** Distribution of average recharge rates for the pine forest areas of Tenerife.

study. Of these 50 pesticides, 49 have been reported as being used in forest management in the United States [1,2], and one (i.e., aminotriazole) is a pesticide widely used in other forested areas of Spain [31]. The pesticides included in this study are listed in the Appendix. The properties for the pesticides are given in Table 3. The standard deviations listed in Table 3 for K_{oc} and $t_{1/2}$ were estimated, assuming uniform distributions, using previously reported data [32]. The soil adsorption coefficient (K_d), in Equation 10, is estimated as

$$K_d = K_{oc} \cdot f_{oc} \quad (11)$$

where the values of f_{oc} and K_{oc} are given, respectively, in Tables 2 and 3. The relationship between $t_{1/2}$ (Table 3) and the decay rate (K_s), as shown in Equation (10), is given by

$$K_s = \frac{\ln 2}{t_{1/2}} \quad (12)$$

The Henry's constant (K_H), as shown in Equation 10, is estimated as

$$K_H = \frac{MW P}{R \cdot T S} \quad (13)$$

where R is the universal constant for an ideal gas (i.e., 0.0624 mm Hg m³ mol⁻¹ K⁻¹); T is the temperature (taken here as 273 K); and MW , S , and P are given in Table 3.

Table 1. Soil data (f_{oc} , θ_{FC} , θ_{WP} , ρ_b , ρ_p) and recharge rates (q) for the two soil orders in the pine forest areas of Tenerife, Canary Islands, Spain [23,24,26]^a

| Parameter | Taxonomic category (order level) | |
|---|----------------------------------|-------------|
| | Entisols | Inceptisols |
| f_{oc} (dimensionless) | | |
| n | 39 | 47 |
| \bar{X} | 0.02 | 0.04 |
| SD | 0.02 | 0.03 |
| CV | 1.1 | 0.8 |
| θ_{FC} (m ³ m ⁻³) | | |
| n | 39 | 60 |
| \bar{X} | 0.22 | 0.39 |
| SD | 0.09 | 0.19 |
| CV | 0.4 | 0.5 |
| θ_{WP} (m ³ m ⁻³) | | |
| n | 39 | 60 |
| \bar{X} | 0.11 | 0.22 |
| SD | 0.08 | 0.12 |
| CV | 0.7 | 0.5 |
| ρ_b (kg m ⁻³) | | |
| n | 6 | 17 |
| \bar{X} | 1,140 | 644 |
| SD | 378 | 107 |
| CV | 0.3 | 0.2 |
| ρ_p (kg m ⁻³) | | |
| n | 6 | 17 |
| \bar{X} | 2,643 | 2,775 |
| SD | 5 | 38 |
| CV | 0.002 | 0.01 |
| q (mm year ⁻¹) | | |
| n | 478 | 893 |
| \bar{X} | 95 | 278 |
| SD | 120 | 162 |
| CV | 1.3 | 0.6 |

^a f_{oc} = soil organic carbon, θ_{FC} = soil-water content at field capacity, θ_{WP} = soil-water content at the wilting point, ρ_b = bulk density, ρ_p = particle density, q = recharge (based on water-balance calculations), n = sample size, \bar{X} = mean, SD = standard deviation, CV = coefficient of variation.

RESULTS AND DISCUSSION

Index-based pesticide leaching assessments

Ranking leaching potential. An index-based model (Li) was employed to rank the leaching potential of the 50 pesticides listed in the Appendix for the pine forest areas of Tenerife. The pesticide properties are given in Table 3. The soil properties and recharge rates are given in Table 1. A decreasing-

Table 2. Characteristic data for the soil profile at the Lagunetas site (see Fig. 1)^a

| Soil horizon | L (m) | Δz (m) | f_{oc} (%) | θ_{FC} (m ³ m ⁻³) | θ_{WP} (m ³ m ⁻³) | ρ_b (kg m ⁻³) |
|--------------|-------|----------------|--------------|---|---|--------------------------------|
| 1 | 0.2 | 0.005 | 3.3 | 0.48 | 0.18 | 600 |
| 2 | 0.7 | 0.005 | 1.1 | 0.47 | 0.25 | 700 |
| 3 | 0.8 | 0.005 | 0.2 | 0.35 | 0.23 | 1,200 |
| 4 | 1.3 | 0.025 | 0.01 | 0.35 | 0.22 | 1,200 |
| 5 | 7.0 | 0.1 | 0.0 | 0.35 | 0.22 | 1,200 |

^a L = thickness of soil layer, Δz = space increment (i.e., for PRZM-2), f_{oc} = soil organic carbon, θ_{FC} = soil-water content at field capacity, θ_{WP} = soil-water content at the wilting point, ρ_b = bulk density.

Table 3. Properties of the pesticides listed in the Appendix [32]^a

| Pesticide | <i>P</i> (mm Hg) | <i>S</i> (mg/L) | <i>K</i> _{oc} (ml/g) | <i>S</i> _{<i>K</i>_{oc}} (ml/g) | <i>t</i> _{1/2} (d) | <i>S</i> _{<i>t</i>_{1/2}} (d) | <i>MW</i> (g/mol) |
|---------------------|-------------------------|--------------------|----------------------------------|---|--------------------------------|---|----------------------|
| 2,4-DB | 8.0 × 10 ⁻⁶ | 890 | 20 | 12.1 | 10 | 4.0 | 221.0 |
| 2,4-DB | 0.0 | 46 | 440 | 0.0 | 5 | 1.2 | 294.2 |
| Acephate | 1.7 × 10 ⁻⁶ | 818,000 | 2 | 0.3 | 3 | 2.3 | 183.2 |
| Aldicarb | 3.0 × 10 ⁻⁵ | 6,000 | 30 | 21.1 | 30 | 22.2 | 190.3 |
| Aminotriazole | 4.4 × 10 ⁻⁷ | 360,000 | 100 | 53.2 | 14 | 5.8 | 84.1 |
| Atrazine | 2.9 × 10 ⁻⁷ | 33 | 100 | 39.3 | 60 | 29.4 | 215.7 |
| Azinphos-methyl | 2.0 × 10 ⁻⁷ | 29 | 1,000 | 894.9 | 10 | 8.7 | 317.3 |
| Benomyl | 1.1 × 10 ⁻¹⁰ | 2 | 1,900 | 548.5 | 67 | 101.4 | 290.3 |
| Bifenoxy | 2.4 × 10 ⁻⁶ | 0.4 | 10,000 | 6,925.9 | 7 | 3.5 | 342.1 |
| Captan | 8.0 × 10 ⁻⁸ | 5.1 | 200 | 172.3 | 2.5 | 2.2 | 300.6 |
| Carbaryl | 1.2 × 10 ⁻⁶ | 120 | 300 | 296.8 | 10 | 5.2 | 201.2 |
| Carbofuran | 6.0 × 10 ⁻⁷ | 351 | 22 | 27.7 | 50 | 22.8 | 221.3 |
| Chloropicrin | 18.0 | 2,270 | 62 | 23.0 | 1 | 0.0 | 164.4 |
| Chlorothalonil | 1.0 × 10 ⁻³ | 0.6 | 1,380 | 1,275.9 | 30 | 24.8 | 265.9 |
| Chlorpyrifos | 1.7 × 10 ⁻⁵ | 0.4 | 6,070 | 6,045.4 | 30 | 38.4 | 350.6 |
| Dazomet | 3.0 × 10 ⁻⁶ | 3,000 | 10 | 1.4 | 7 | 0.0 | 162.3 |
| DCPA | 2.5 × 10 ⁻⁶ | 0.5 | 5,000 | 692.8 | 100 | 24.8 | 332.0 |
| Diazinon | 6.0 × 10 ⁻⁵ | 60 | 1,000 | 507.2 | 40 | 7.8 | 304.3 |
| Dicamba | 0.0 | 400,000 | 2 | 7.8 | 14 | 2.3 | 221.0 |
| Dichlorprop | 3.0 × 10 ⁻⁶ | 50 | 1,000 | 239.6 | 10 | 1.2 | 335.3 |
| Dicloran | 1.3 × 10 ⁻⁶ | 7 | 1,000 | 1,324.4 | 60 | 11.3 | 207.7 |
| Diflubenzuron | 9.0 × 10 ⁻¹⁰ | 0.08 | 10,000 | 1,099.9 | 10 | 16.7 | 310.7 |
| Dimethoate | 2.5 × 10 ⁻⁵ | 39,800 | 20 | 4.9 | 7 | 1.4 | 229.3 |
| Diphenamid | 3.0 × 10 ⁻⁸ | 260 | 210 | 42.4 | 30 | 8.7 | 239.3 |
| Diuron | 6.9 × 10 ⁻⁸ | 42 | 480 | 252 | 90 | 86.0 | 233.1 |
| Fenvalerate | 1.1 × 10 ⁻⁸ | 0.002 | 5,300 | 8,573.7 | 35 | 65.2 | 419.9 |
| Fosamine | 4.0 × 10 ⁻⁶ | 1,790,000 | 150 | 0.0 | 8 | 0.9 | 170.1 |
| Glyphosate | 0.0 | 900,000 | 24,000 | 19,045.3 | 47 | 49.7 | 169.1 |
| Hexazinone | 2.0 × 10 ⁻⁷ | 33,000 | 54 | 9.5 | 90 | 43.3 | 252.3 |
| Imazapyr | 0.0 | 11,000 | 100 | 0.0 | 90 | 179.6 | 261.3 |
| Lindane | 3.3 × 10 ⁻⁵ | 7 | 1,100 | 3,381.5 | 400 | 400.1 | 290.9 |
| Malathion | 8.0 × 10 ⁻⁶ | 130 | 1,800 | 492.8 | 1 | 0.4 | 330.3 |
| Maneb | 0.0 | 6 | 2,000 | 508.7 | 70 | 16.7 | 265.3 |
| Metalaxyl | 5.6 × 10 ⁻⁶ | 8,400 | 50 | 74.5 | 70 | 44.2 | 279.3 |
| Methylbromide | 1,800 | 13,400 | 22 | 3.8 | 55 | 6.9 | 94.9 |
| Metsulfuron-methyl | 2.5 × 10 ⁻¹² | 9,500 | 35 | 7.5 | 30 | 47.9 | 381.4 |
| Naled | 2.0 × 10 ⁻⁴ | 2,000 | 180 | 13.6 | 1 | 0.0 | 381.0 |
| Napropamide | 1.7 × 10 ⁻⁷ | 74 | 700 | 139.1 | 70 | 22.2 | 271.4 |
| Oxyfluorfen | 2.0 × 10 ⁻⁷ | 0.1 | 100,000 | 0.0 | 35 | 2.9 | 361.7 |
| Permethrin | 1.3 × 10 ⁻⁸ | 0.006 | 100,000 | 38,672.9 | 30 | 28.6 | 391.3 |
| Phosmet | 4.9 × 10 ⁻⁷ | 20 | 820 | 92.4 | 19 | 4.6 | 317.3 |
| Picloram | 0.0 | 200,000 | 16 | 44.2 | 90 | 74.2 | 241.5 |
| Sethoxydim | 1.6 × 10 ⁻⁷ | 4,390 | 100 | 0.0 | 5 | 2.6 | 327.5 |
| Simazine | 2.2 × 10 ⁻⁸ | 6.2 | 130 | 34.1 | 60 | 39.8 | 201.7 |
| Sulfometuron-methyl | 6.0 × 10 ⁻¹⁶ | 70 | 78 | 0.0 | 20 | 2.3 | 364.4 |
| Tebuthiuron | 2.0 × 10 ⁻⁶ | 2,500 | 80 | 177.8 | 360 | 282.3 | 228.3 |
| Thiram | 1.0 × 10 ⁻⁵ | 30 | 670 | 0.0 | 15 | 0.0 | 240.4 |
| Triadimefon | 1.5 × 10 ⁻⁸ | 71.5 | 300 | 98.7 | 26 | 15.6 | 293.8 |
| Trichlorfon | 2.0 × 10 ⁻⁶ | 120,000 | 10 | 10.5 | 10 | 7.8 | 257.4 |
| Triclopyr | 0.0 | 2,100,000 | 20 | 67.4 | 46 | 17.3 | 357.5 |

^a *P* = vapor pressure, *S* = water solubility, *K*_{oc} = soil organic carbon/water partition coefficient, *S*_{*K*_{oc}} = standard deviation for *K*_{oc}, *t*_{1/2} = half-life in soil, *S*_{*t*_{1/2}} = *t*_{1/2} standard deviation, *MW* = molar mass.

order list of *Li*, *S*_{*Li*}, and (*Li* + *S*_{*Li*}) estimates for the 50 pesticides, for both the Entisols and Inceptisols, is presented in Table 4. Perusal of these results leads to four generalized comments. First, *Li* and *S*_{*Li*} estimates vary tremendously. Second, the *S*_{*Li*} estimates are slightly larger than the *Li* estimates. Third, the pesticide ranking is, with the exception of 2,4-D and dazomet, the same for both soil orders. Fourth, the pesticide rankings are slightly modified for several chemicals when the uncertainty in the *Li* estimates (i.e., *Li* + *S*_{*Li*}) is taken into account. For example, triclopyr precedes carbofuran, and metalaxyl precedes hexazinone, in (*Li* + *S*_{*Li*}) rankings. These changes were the same for both soil orders.

Based on the *Li* classification scheme proposed for agri-

cultural soils [33], the results in Table 4 suggest that, for the pine forest areas of Tenerife, the potential leachers (i.e., *Li* > 0.2) are picloram, tebuthiuron, carbofuran, triclopyr, and hexazinone for the Inceptisols and picloram and tebuthiuron for the Entisols. The *Li* values for pesticides commonly applied in forested lands in the United States (e.g., 2,4-D and glyphosate) were orders of magnitude smaller than the five pesticides targeted here as leachers. Picloram has been reported to occur in both shallow and deep groundwater in the United States [34–36]. Tebuthiuron has been recently detected at very low concentrations in groundwater in the United States [37]. Carbofuran, which is currently applied in Tenerife to control nematode populations [23,24,26], has also been detected in

Table 4. Li , S_{Li} , and $(Li + S_{Li})$ estimates for the pesticides listed in the Appendix for the pine forest areas of Tenerife, Canary Islands, Spain^a

| | Inceptisols | | | Entisols | | |
|---------------------|-------------|----------|---------------|----------|----------|---------------|
| | Li | S_{Li} | $Li + S_{Li}$ | Li | S_{Li} | $Li + S_{Li}$ |
| Picloram | 0.364 | 0.672 | 1.000 | 0.246 | 0.553 | 0.799 |
| Tebuthiuron | 0.298 | 0.643 | 0.941 | 0.183 | 0.464 | 0.647 |
| Carbofuran | 0.211 | 0.250 | 0.462 | 0.133 | 0.231 | 0.364 |
| Triclopyr | 0.207 | 0.461 | 0.669 | 0.130 | 0.339 | 0.469 |
| Hexazinone | 0.197 | 0.187 | 0.384 | 0.120 | 0.195 | 0.315 |
| Metalaxyl | 0.171 | 0.266 | 0.438 | 0.104 | 0.213 | 0.317 |
| Dicamba | 0.147 | 0.134 | 0.281 | 0.094 | 0.137 | 0.231 |
| Imazapyr | 0.126 | 0.222 | 0.348 | 0.074 | 0.167 | 0.241 |
| Aldicarb | 0.116 | 0.134 | 0.250 | 0.070 | 0.121 | 0.190 |
| Metsulfuron-methyl | 0.106 | 0.175 | 0.280 | 0.063 | 0.134 | 0.197 |
| Atrazine | 0.091 | 0.096 | 0.187 | 0.053 | 0.090 | 0.143 |
| Trichlorfon | 0.075 | 0.084 | 0.159 | 0.045 | 0.075 | 0.120 |
| Simazine | 0.073 | 0.082 | 0.155 | 0.042 | 0.074 | 0.116 |
| 2,4-D | 0.054 | 0.050 | 0.104 | 0.032 | 0.049 | 0.081 |
| Dazomet | 0.054 | 0.039 | 0.093 | 0.032 | 0.045 | 0.077 |
| Sulfometuron methyl | 0.040 | 0.036 | 0.076 | 0.023 | 0.037 | 0.059 |
| Dimethoate | 0.038 | 0.031 | 0.069 | 0.022 | 0.033 | 0.056 |
| Acephate | 0.036 | 0.037 | 0.073 | 0.022 | 0.033 | 0.055 |
| Diuron | 0.031 | 0.042 | 0.074 | 0.018 | 0.034 | 0.052 |
| Lindane | 0.031 | 0.101 | 0.132 | 0.018 | 0.061 | 0.079 |
| Diphenamid | 0.025 | 0.025 | 0.050 | 0.014 | 0.024 | 0.038 |
| Aminotriazole | 0.023 | 0.025 | 0.048 | 0.013 | 0.023 | 0.035 |
| Napropamide | 0.018 | 0.018 | 0.036 | 0.010 | 0.017 | 0.027 |
| Triadimefon | 0.016 | 0.018 | 0.034 | 0.009 | 0.016 | 0.024 |
| Dicloran | 0.011 | 0.018 | 0.029 | 0.006 | 0.013 | 0.019 |
| Fosamine | 0.009 | 0.009 | 0.018 | 0.005 | 0.009 | 0.014 |
| Sethoxydim | 0.008 | 0.009 | 0.017 | 0.005 | 0.008 | 0.013 |
| Diazinon | 0.007 | 0.008 | 0.016 | 0.004 | 0.007 | 0.011 |
| Benomyl | 0.007 | 0.011 | 0.018 | 0.004 | 0.008 | 0.012 |
| Maneb | 0.006 | 0.007 | 0.013 | 0.004 | 0.006 | 0.010 |
| Carbaryl | 0.006 | 0.009 | 0.015 | 0.003 | 0.007 | 0.010 |
| Phosmet | 0.004 | 0.004 | 0.009 | 0.002 | 0.004 | 0.007 |
| Thiram | 0.004 | 0.004 | 0.008 | 0.002 | 0.004 | 0.006 |
| Chlorothalonil | 0.004 | 0.006 | 0.010 | 0.002 | 0.004 | 0.006 |
| Methylbromide | 0.004 | 0.007 | 0.011 | 0.001 | 0.002 | 0.003 |
| DCPA | 0.004 | 0.004 | 0.007 | 0.002 | 0.003 | 0.005 |
| Chloropicrin | 0.002 | 0.002 | 0.005 | 0.001 | 0.002 | 0.003 |
| Captan | 0.002 | 0.003 | 0.006 | 0.001 | 0.003 | 0.004 |
| 2,4-DB | 0.002 | 0.002 | 0.004 | 0.001 | 0.002 | 0.003 |
| Azinphos-methyl | 0.002 | 0.003 | 0.005 | 0.001 | 0.002 | 0.003 |
| Dichlorprop | 0.002 | 0.002 | 0.004 | 0.001 | 0.002 | 0.003 |
| Fenvalerate | 0.001 | 0.003 | 0.005 | 0.001 | 0.002 | 0.003 |
| Naled | 0.001 | 0.001 | 0.002 | 0.001 | 0.001 | 0.002 |
| Chlorpyrifos | 0.001 | 0.002 | 0.003 | 0.001 | 0.001 | 0.002 |
| Glyphosate | 0.000 | 0.001 | 0.001 | 0.000 | 0.000 | 0.001 |
| Diflubenzuron | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 |
| Bifenox | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Malathion | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Oxyfluorfen | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Permethrin | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |

^a Li = leaching index (values range between 0.0 and 1.0), S_{Li} = standard deviation for Li .

groundwater in the United States [37], with impacts on non-target organisms being reported [5]. Hexazinone and triclopyr residues have and have not, respectively, been reported in shallow groundwater [34,38]. The five-targeted leachers in this study were selected for regional-scale leaching assessments for the pine forest areas of Tenerife.

Regional-scale assessments. As discussed above, the five pesticides selected for the regional-scale study (i.e., picloram, tebutiuron, carbofuran, triclopyr, and hexazinone) are all potential leachers. The following Li classification scheme was adopted for this study to identify the areas of highest vulnerability: $Li > 0.5$, very likely leacher; $0.2 < Li < 0.5$, likely leacher; and $Li < 0.2$, moderately likely leacher. In all, 1,433

polygons were used to represent the pine forest areas of Tenerife, the overlying soil, and the recharge information for regional-scale pesticide leaching estimates (with Li) in a GIS format.

Figure 3 presents the Li and $(Li + S_{Li})$ estimates for the five targeted pesticides for the pine forest areas of Tenerife. Inspection of Figure 3 shows that the most vulnerable areas were on the northern slope, with two hot spots of potential vulnerability (one in the northeast and one in the northwest). In general, the leaching potentials were greatest for the Inceptisols and areas of higher recharge. The impact of the high pesticide leaching potentials for the northeastern part of the Tenerife pine forest (Fig. 3) are of particular significance due

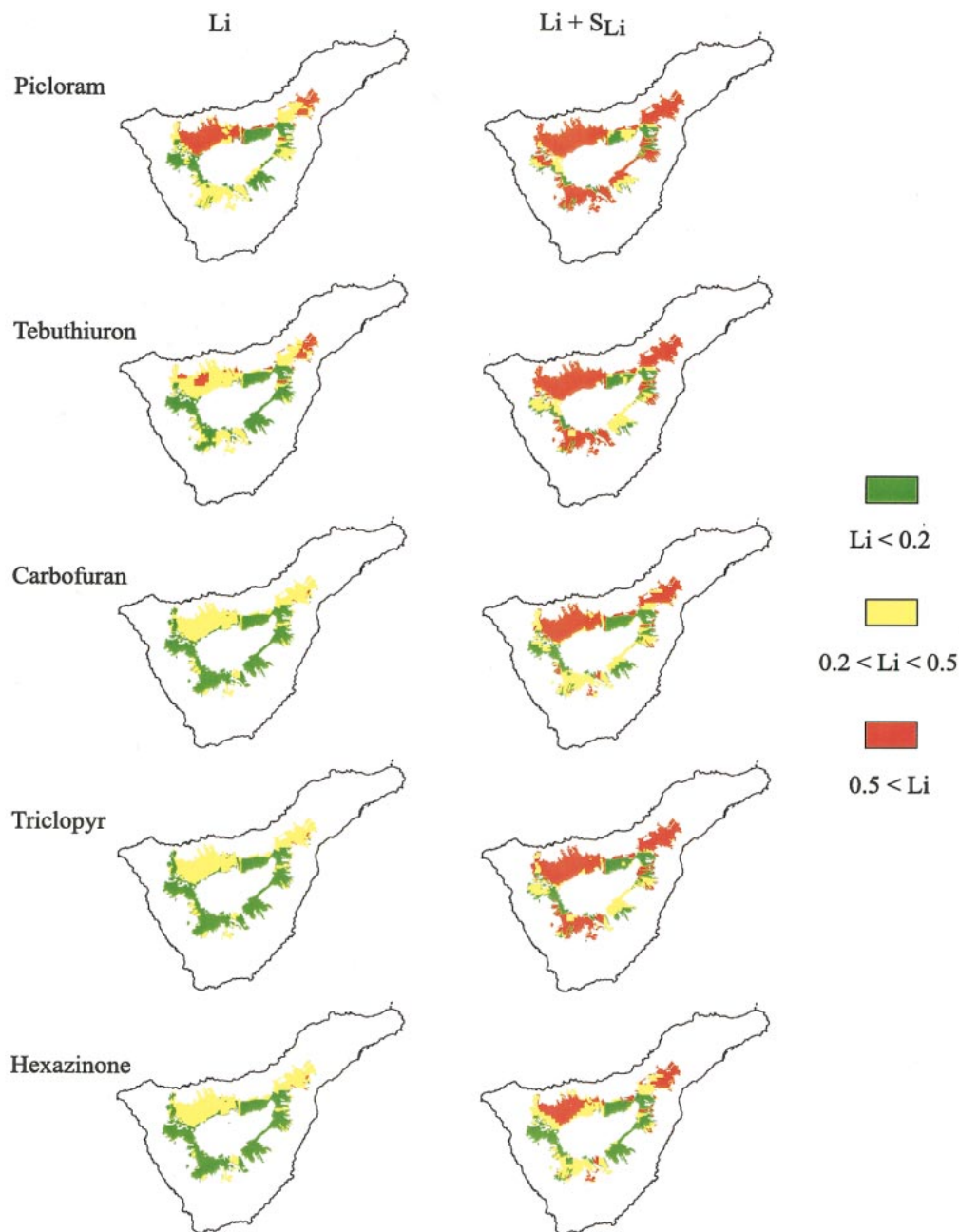


Fig. 3. Groundwater vulnerability estimates (Li and $Li + S_{Li}$) for the pine forest areas of Tenerife, Canary Islands, Spain, for five selected pesticides.

to the relatively close proximity of this area to the most important urban centers (Fig. 1) and the highest groundwater extraction rates on the island.

Process-based simulation of pesticide leaching

The pine forest area selected for the process-based simulations (with PRZM-2) is known as Lagunetas (Fig. 1). The Lagunetas area is recreational land that was impacted by the 1995 fire. The depth to the water table in the Lagunetas area is between 120 and 140 m [39]. The information required for the five-year, near-surface PRZM-2 simulations includes soil, meteorological, vegetation, and pesticide parameters. The soil data that represent the five horizons in the soil profile (classified as Inceptisols) for the Lagunetas area are given in Table

2. The rainfall and temperature data were based on the time series averages. The rainfall was uniformly disaggregated from the monthly averages to daily values. Potential evapotranspiration was estimated within the PRZM-2 water balance from temperature data. For the PRZM-2 simulations, the maximum interception storage, root depth, coverage, and canopy height for *Pinus canariensis* were assumed to be 0.0025 m, 1.2 m, 90%, and 9 m, respectively. The characteristics of the five target pesticides are given in Table 3. The $t_{1/2}$ values shown in Table 3 were only used for the surface soil with a degradation rate one order of magnitude smaller for each subsequent soil horizon. The molecular diffusivity in air (D_g), as shown in Equation 10, for each of the five pesticides was assumed to be $0.43 \text{ m}^2 \text{ d}^{-1}$. The single 1996 surface application rate for

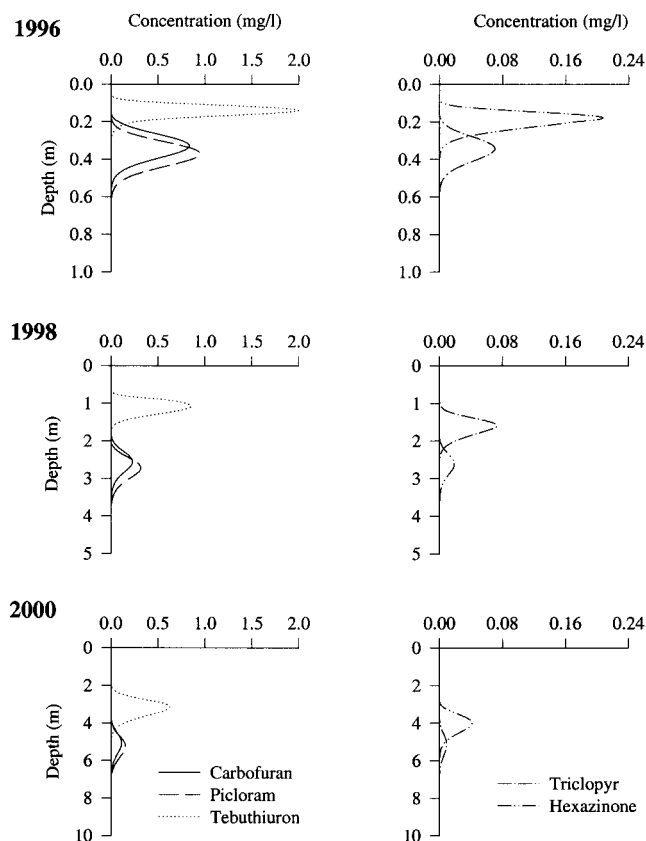


Fig. 4. Stimulated dissolved-phase concentration profiles for five selected pesticides for one, three, and five years after application. The concentration profiles correspond to the last day of the year. Different scales are used for carbofuran, picloram, and tebuthiuron (left side) and for triclopyr and hexazinone (right side).

each of the five pesticides was 19.0 (carbofuran), 1.7 (hexazinone), 5.0 (picloram), 4.5 (tebuthiuron), and 2.0 (triclopyr) kg ha^{-1} [2].

The simulated concentration profiles for the five targeted pesticides for 1996, 1998, and 2000 (i.e., the last day of each year) are shown in Figure 4. Inspection of Figure 4 leads to three observations. First, the maximum simulated concentration each year was for tebuthiuron, followed in decreasing order by picloram, carbofuran, hexazinone, and triclopyr. Second, the predicted concentration for tebuthiuron five years after application (i.e., year 2000) was greater than 0.5 mg/L, whereas the other four pesticides showed peak concentrations that exceed 0.1 $\mu\text{g/L}$ five years after application. (The European limit for a single chemical in drinking water is 0.1 $\mu\text{g/L}$ [40].) Third, five years after application, none of the chemicals showed a maximum concentration peak deeper than 6 m.

The results in Figure 4 illustrate the potential vulnerability of groundwater in the study area to contamination from the targeted pesticides. However, several sources of uncertainty for the PRZM-2 simulations relate to the assumptions necessary for this study. For example, the disaggregation of rainfall and temperature data from monthly averages to daily values was very simplistic. Four comments, related to the PRZM-2 simulations, are worth consideration. First, overestimates of pesticide leaching concentrations could have resulted from the disaggregation of average monthly rainfall values (i.e., simulating recharge as a continuous input vs pulse inputs). Second, overestimates or underestimates of pesticide leaching concentrations could have resulted from reduced or increased $t_{1/2}$ val-

ues, respectively, in the lower soil horizons. Third, underestimates of pesticide leaching concentrations could have resulted from the inability of the PRZM-2 to simulate transport via preferential flow paths. Fourth, overestimates of pesticide leaching concentrations could have resulted from lateral dispersion not being considered (i.e., PRZM-2 is a one-dimensional, vertical model).

CONCLUSIONS

An index-based model (*Li*) was used to rank the leaching potential of 50 pesticides for conditions specific to the pine forest areas of Tenerife. Based on the *Li* estimates, carbofuran, hexazinone, picloram, tebuthiuron, and triclopyr were each targeted as potential leachers. Regional-scale groundwater vulnerability assessments were prepared using *Li*, in a GIS-driven format, for the pine forest areas of Tenerife for the five targeted pesticides. Two hot spots on the northern side of the study area were identified on the vulnerability maps, with their locations corresponding to soils classified as Inceptisols and having high recharge rates. The uncertainties in the leaching assessments, as related to the uncertainties in the soil, recharge, and pesticide data, were significant. Process-based leaching simulations of five years each with PRZM-2 for a site in the Tenerife pine forest that was shown to be vulnerable (with *Li*) were conducted for the five targeted pesticides. The PRZM-2 simulations indicated that each of the five targeted pesticides can be expected to leach out of the near-surface at undesirable concentrations, eventually impacting groundwater resources. Pesticides such as 2,4-D and glyphosate appear (based on their *Li* rankings) to be possible alternatives to the five pesticides focused on in this study for use in forest management in Tenerife.

The process-based simulation approach is much more data-demanding, especially for regional scales, than the index-based ranking approach, but it provides the estimates of pesticide concentrations that are needed in the decision-management arena for regulatory and remediation purposes. The two-phase approach for assessing the leaching potential of alternative pesticides, as demonstrated here for Tenerife, can be useful for other regional-scale forested areas.

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APPENDIX

Pesticides included in this study [1,2]

| Common name | Chemical name | Formula | Use |
|---------------------|---|--|-------------|
| 2,4-D | Dimethylamine salt of 2,4-dichlorophenoxy acetic acid | C ₈ H ₆ Cl ₂ O ₃ | Herbicide |
| 2,4-DB | Dimethylamine salt of 4-(2,4-dichlorophenoxy)butyric acid | C ₁₀ H ₁₀ Cl ₂ O ₃ | Herbicide |
| Aminotriazole | 1H-1,2,4-triazol-3-amine; 2-amino- <i>s</i> -triazole | C ₂ H ₄ N ₄ | Herbicide |
| Atrazine | 2-Chloro-4-ethylamino-6-isopropylamino- <i>S</i> -triazine | C ₈ N ₁₄ ClN ₅ | Herbicide |
| Acephate | <i>O,S</i> -dimethyl acetylphosphoramidithioate | C ₄ H ₁₀ NO ₃ PS | Insecticide |
| Aldicarb | 2-Methyl-2-(methylthio)-propionaldehyde <i>O</i> -(methylcarbamoyl)oxime | C ₈ H ₁₄ N ₂ O ₂ S | Insecticide |
| Azinphos-methyl | <i>O,O</i> -dimethyl <i>S</i> -[4- <i>oxo</i> -1,2,3-benzotriazin-3(4H)-yl)methyl]phosphorodithioate | C ₁₀ H ₁₂ N ₃ O ₃ PS ₂ | Insecticide |
| Benomyl | Methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate | C ₁₄ H ₁₈ N ₄ O ₃ | Fungicide |
| Bifenoxy | Methyl-5-(2,4-dichlorophenoxy)-2-nitrobenzoate | C ₁₄ H ₉ Cl ₂ NO ₅ | Herbicide |
| Captan | <i>cis-N</i> -(trichloromethyl)thio-4-cyclohexene-1,2-dicarboximide | C ₁₀ H ₂ Cl ₄ NO ₂ S | Fungicide |
| Carbaryl | 1-Naphthyl- <i>N</i> -methylcarbamate | C ₁₂ H ₁₁ NO ₂ | Insecticide |
| Carbofuran | 2,3-Dihydro-2,2-dimethyl-7-benzofuranyl- <i>n</i> -methylcarbamate | C ₁₂ H ₁₅ N ₃ O ₃ | Insecticide |
| Chloropicrin | Trichloronitromethane | CCl ₃ NO ₂ | Nematicide |
| Chlorothalonil | Tetrachloroisophthalonitrile | C ₆ Cl ₄ N ₂ | Fungicide |
| Chlorpyrifos | <i>O,O</i> -diethyl <i>O</i> -(3,5,6-trichloro-2-pyridyl)-phosphorothioate | C ₉ H ₁₁ Cl ₃ NO ₃ PS | Insecticide |
| Dazomet | 3,5-Dimethyl-1,3,5-thiadiazine-2-thione; tetrahydro-3,5-dimethyl-1,3,5-t | C ₈ H ₁₀ N ₂ S ₂ | Fumigant |
| DCPA | Dimethyl 2,3,5,6-tetrachloro-1,4-benzenedicarboxylate | C ₁₀ H ₆ Cl ₄ O ₄ | Herbicide |
| Diazinon | <i>O,O</i> -diethyl- <i>O</i> -(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate | C ₁₂ H ₂₁ N ₂ O ₃ PS | Insecticide |
| Dicamba | Amine salt of 2-methoxy-3,6-dichlorobenzoic acid | C ₈ Cl ₂ O ₃ H ₆ | Herbicide |
| Dichlorprop | Butoxyethyl ester of (±) 2-(2,4-dichlorophenoxy)propanoic acid | C ₈ H ₈ Cl ₂ O ₃ | Herbicide |
| Dicloran | 2,6-Dichloro-4-nitrobenzeneamine | C ₆ H ₄ Cl ₂ N ₂ O ₂ | Fungicide |
| Diflubenuron | <i>N</i> -[[[(4-chlorophenyl)amino]carbonyl]-2,6-difluorobenzamide | C ₁₄ H ₈ ClF ₂ N ₂ O ₂ | Insecticide |
| Dimethoate | <i>O,O</i> -dimethyl <i>S</i> -(<i>N</i> -methylcarbamoylmethyl) phosphorodithioate | C ₅ H ₁₂ NO ₃ PS ₂ | Insecticide |
| Diphenamid | <i>N,N</i> -dimethyl- <i>α</i> -phenylbenzeneacetamide | C ₁₆ H ₁₇ NO | Herbicide |
| Diuron | 3-(3,4-Dichlorophenyl)-1,1-dimethylurea | C ₉ H ₁₀ Cl ₂ N ₂ O | Herbicide |
| Fenvalerate | Cyano(3-phenoxyphenyl)methyl 4-chloro- α -(1-methylethyl)benzeneacetate | C ₂₆ H ₂₂ ClNO ₃ | Insecticide |
| Fosamine | Ammonium salt of ethyl(aminocarbonyl)phosphanate | C ₃ H ₁₁ N ₂ O ₄ P | Herbicide |
| Glyphosate | Isopropylamine salt of <i>N</i> -(phosphonomethyl)glycine | C ₃ H ₈ NO ₃ P | Herbicide |
| Hexazinone | 3-Cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4-(1H,3H)-dione | C ₁₂ H ₂₀ N ₄ O ₂ | Herbicide |
| Imazapyr | Isopropylamine salt of 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5- <i>oxo</i> -1H-imidazol-2-yl] 3-pyridinecarboxylic acid | C ₁₃ H ₁₅ N ₃ O ₃ | Herbicide |
| Lindane | 1,2,3,4,5,6-Hexachlorocyclohexane (γ -BHC) | C ₆ H ₆ Cl ₆ | Insecticide |
| Malathion | Diethyl (dimethoxyphosphinothioyl)thiobutanoate | C ₁₀ H ₁₉ O ₆ PS ₂ | Insecticide |
| Maneb | [[1,2-Ethanediybis(carbamodithioato)](2-)manganese | (C ₄ H ₂ MnH ₂ S ₄) _x | Fungicide |
| Metalaxyl | <i>N</i> -(2,6-dimethylphenyl)- <i>N</i> -(methoxyacetyl)-alanine methyl ester | C ₁₅ H ₂₁ NO ₄ | Fungicide |
| Methylbromide | Bromomethane | CH ₃ Br | Fumigant |
| Metsulfuron-methyl | Methyl ester of metsulfuron: 2-[[[(4-Methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl]amino]sulfonyl]benzoic acid | C ₁₄ H ₁₅ N ₅ O ₆ S | Herbicide |
| Naled | 1,2-Dibromo-2,2-dichloroethyl dimethyl phosphate | C ₄ H ₇ Br ₂ Cl ₂ O ₄ P | Insecticide |
| Napropamide | <i>N,N</i> -diethyl-2-(1-naphthalenyloxy)propanamide | C ₁₇ H ₂₁ NO ₂ | Herbicide |
| Oxyfluorfen | 2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene | C ₁₅ H ₁₁ ClF ₃ NO ₄ | Herbicide |
| Permethrin | 3-Phenoxyphenylmethyl(1RS)- <i>cis, trans</i> -3-(2,2-dichloroethenyl)-2,2-dimethyl cyclopropane carboxylate (~60% <i>trans</i> , 40% <i>cis</i> isomers) | C ₁₂ H ₂₀ Cl ₂ O ₃ | Insecticide |
| Phosmet | <i>S</i> -[(1,3-dioxo-2H-isindol-2-yl)methyl] <i>O,O</i> -dimethyl phosphorodithioate | C ₁₁ H ₁₂ NO ₄ PS ₂ | Insecticide |
| Picloram | Potassium salt of 4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid | C ₆ H ₃ Cl ₃ N ₂ O ₂ | Herbicide |
| Sethoxydim | (±)2[1-(Ethoxyimino)butyl]-5-[2-(ethylthio)propyl-3-hydroxy-2-cyclohexen-1-one | C ₁₇ H ₂₉ NO ₃ S | Herbicide |
| Simazine | 2-Chloro-4,6- <i>bis</i> (ethylamino)- <i>s</i> -triazine | C ₇ H ₁₂ ClN ₅ | Herbicide |
| Sulfometuron-methyl | Methyl ester of sulfometuron: 2-[[[(4,6-dimethyl-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl]benzoic acid | C ₁₅ H ₁₆ N ₄ O ₅ S | Herbicide |
| Tebuthiuron | <i>N</i> -[5-(1,1-dimethyl)-1,3,4-thiadiazol-2-yl]- <i>N,N'</i> -dimethylurea | C ₉ H ₁₆ N ₄ OS | Herbicide |
| Thiram | Tetramethylthioperoxydicarbonic diamide | C ₆ H ₁₂ N ₂ S ₄ | Fungicide |
| Triadimefon | 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone | C ₁₄ H ₁₆ ClN ₃ O ₂ | Fungicide |
| Trichlorfon | Dimethyl (2,2,2-trichloro-1-hydroxyethyl)phosphonate | C ₄ H ₈ Cl ₃ O ₄ P | Insecticide |
| Triclopyr | Triethylamine salt of 3,5,6-trichloro-2-pyridinyloxyacetic acid | C ₇ H ₄ Cl ₃ NO ₃ | Herbicide |