Contents lists available at SciVerse ScienceDirect



Ecotoxicology and Environmental Safety



journal homepage: www.elsevier.com/locate/ecoenv

PURE: A web-based decision support system to evaluate pesticide environmental risk for sustainable pest management practices in California

Yu Zhan, Minghua Zhang*

Department of Land, Air, and Water Resources, University of California, Davis, CA 95616, USA

ARTICLE INFO

ABSTRACT

Article history: Received 16 February 2012 Received in revised form 22 May 2012 Accepted 24 May 2012 Available online 15 June 2012

Keywords: Pesticide Environmental risk Exposure Toxicity Emission potential mitigating pesticide impacts on ecosystem and human health. This paper presents the Pesticide Use Risk Evaluation (PURE) decision support system (DSS) for evaluating site-specific pesticide risks to surface water, groundwater, soil, and air across pesticide active ingredient (AI), pesticide product, and field levels. The risk score is determined by the ratio of the predicted environmental concentrations (PEC) to the toxicity value for selected endpoint organism(s); except that the risk score for the air is calculated using the emission potential (EP), which is a pesticide product property for estimating potential volatile organic compound (VOC) emissions by California Environmental Protection Agency (CEPA). The risk scores range from 0 to 100, where 0 represents negligible risk while 100 means the highest risk. The procedure for calculating PEC in surface water was evaluated against monitoring data for 41 pesticide Als, with a statistically significant correlation coefficient of r=0.82 (p<0.001). In addition, two almond fields in the Central Valley, California were evaluated for pesticide risks as a case study, where the commonly acknowledged high-risk pesticides gained high risk scores. Simazine, one of the most frequently detected pesticides in groundwater, was scored as 74 (the moderate high risk class) to groundwater; and chlorpyrifos, one of the frequently detected pollutants in surface water, was scored as 100 (the high risk class) to surface water. In support of pesticide risk quantitative assessment and use of reduced-risk pesticide selection, the PURE-DSS can be useful to assist growers, pesticide control advisors, and environmental protection organizations in mitigating pesticide use impacts on the environment.

Farmers, policy makers, and other stakeholders seek tools to quantitatively assess pesticide risks for

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

Modern agriculture heavily relies upon pesticides for controlling pests, weeds, and crop diseases to assure food production (Juraske et al., 2007). However, their use has been recognized to pose negative impacts on ecosystem and human health since the 1960s (Carson, 1962). Residues of insecticides and herbicides are often detected in surface water and groundwater in intensive agricultural areas (Domagalski, 1997a, 1997b; Zhang et al., 2005). A national groundwater survey reported that pesticides were detected in 48.4% of 2485 groundwater sampled sites throughout the United States (Kolpin et al., 2000). Furthermore, the declines of amphibian populations in California has been found to highly correlate with pesticide use in upwind croplands (Davidson, 2004). Exposure to pesticides has been associated with gastric cancer among farm workers (Mills and Yang, 2007) and neurodevelopment anomalies among children (Bouchard et al., 2010).

E-mail address: mhzhang@ucdavis.edu (M. Zhang).

To mitigate the negative impacts of pesticides, growers, policy makers, and environmental protection organizations seek tools to quantitatively measure potential pesticide impacts or risks.

While pounds of pesticide have been used as a proxy for risk evaluation in the past, robust pesticide risk models/indicators provide more accurate risk estimation by incorporating physiochemical and toxicological properties of pesticides, as well as site-specific environmental conditions (Bockstaller et al., 2008; Levitan, 2000; Stenrod et al., 2008). In the last two decades, more than a hundred pesticide risk indicators (with or without supporting software) were developed around the world (Bockstaller et al., 2009; Trevisan et al., 2009; van Bol et al., 2002), varying considerably in purpose, the environmental recipient(s) of the risk (henceforth to be called environmental compartments or non-targeted organisms), implementation scale, and methodologies such as risk ratio, scoring, and fuzzy system (Labite et al., 2011). As a result, they often incorporate default values and/or assumptions into their variables and algorithms that reflect their specific purpose, and can therefore be less effective when transferred to new scenarios and questions for which they were not designed.

^{*} Corresponding author. Fax: +1 530 752 1552.

^{0147-6513/\$ -} see front matter @ 2012 Elsevier Inc. All rights reserved. http://dx.doi.org/10.1016/j.ecoenv.2012.05.019

Rτ

California's Central Valley is one of the most agriculturally productive regions in the world, which supplies 8% of the nation's agricultural output on less than 1% of the nation's farmland (Reilly et al., 2008). The state produces more than 350 commodities, resulting in an annual revenue of \$36.6 billion dollar industry (CDFA, 2011). California also has some of the most thorough agricultural pesticide use data—the Pesticide Use Reporting (PUR) database in the nation, collected by the agricultural commissioners and managed by the California Department of Pesticide Regulation (CDPR). Since 1990, all agricultural pesticide applications have been legally required to be reported, creating a wealth of data available to policy makers, researchers, and the public to assist in monitoring and modeling pesticide use trends. The goal of the paper was to describe the development of the Pesticide Use Risk Evaluation (PURE) decision support system (DSS) and to demonstrate the usefulness of the DSS to assist California growers in maintaining the high productivity while reducing risks to the environments, and hence achieving sustainable pest management practices.

2. Material and methods

2.1. DSS description

2.1.1. Main procedures

An agricultural field typically receives multiple pesticide applications, and a single pesticide product may contain multiple active ingredients (AIs). Therefore, the PURE-DSS uses a hierarchical structure to aggregate pesticide risks across AI, pesticide product, and field levels. The risk values (*RV*) are aggregated additively within each environmental compartment (Eq. (1)), a method adapted from the concentration addition concept (Finizio et al., 2005; Vaj et al., 2011; Verro et al., 2009) which has been demonstrated as a valuable means for assessing mixture toxicities (Backhaus et al., 2003; Vighi et al., 2003).

$$RV_i = \sum_i RV_{ij} \tag{1}$$

where RV_i is the accumulated product (or field) level risk value for the *i* environmental compartment, RV_{ij} is the AI (or product) level risk value for the *i* environmental compartment of AI (or product) *j*, and *i* represents an environmental compartment which can be A—air, G—groundwater, S—soil, or W—surface water. It should be noted that the risk values for air are unavailable at AI level, which are calculated at the product-level by using the product property—emission potential (*EP*).

The Al level risks for groundwater, soil, and surface water are assessed by the risk ratio approach, in which the ratios of the predicted environmental concentration (*PEC*) to the toxicity value (*Tox*) are calculated as follows (Reus et al., 2002):

$$RV = \frac{PEC}{Tox}$$
(2)

where *Tox* is the toxicity value of the indicator organism(s) potentially exposed to the pesticides existing in that environmental compartment. The details are listed in Eqs. (6), (14), (16), (19), and (21).

Other studies have calculated the pesticide concentration in soil or water using dynamic and sophisticated models such as GLEAMS (Knisel, 1993), PRZM (Carsel et al., 1998), or SWAT (Nietsch et al., 2005). However, the aim of PURE-DSS is not to simulate dynamic concentration but to determine relative risks. Thus, deterministic and empirical models are adapted for calculating *PEC* under a worst case scenario, in which maximum exposure is assumed both in time and space. For air risk, the potential VOC emissions are assumed to be all emitted to the air under any environmental conditions. For surface water risk, a runoff event will occur via rainfall or irrigation three days after a pesticide application. In addition, a few other assumptions are made due to data availability: (1) linear dose-response relationships in toxicity, (2) indicator organism(s) in one environmental compartment is/are representative for the communities in that environment, i.e., no species sensitivity distributions, and (3) no mitigation practices after pesticide applications.

As the risk values vary across multiple magnitudes and are generally lognormal distributed, the risk values are then transformed to risk scores (R) as follows:

$$R_i = 25(\log RV_i + 2) \tag{3}$$

where 2 and 25 are scaling factors in order to make the majority of the risk scores fall between 0 and 100. To provide more intuitive results, negative risk scores reflecting negligible risks are assigned a value of 0; while risk scores over 100 representing extremely high risks are assigned a value of 100. Since most of the

risk scores are between 0 and 100, condensing the risk scores at the two extreme ends have little effect on the integrity of the risk scores.

As a conservative measure, the integrated risk score (R_T) is calculated as the maximum of all the separate risk scores (R_i) , one for each environmental compartment, as a way to protect the most vulnerable environmental compartment:

$$= \max\{R_i\} \tag{4}$$

where *i* represents an environmental compartment which can be *A*—air, *G*—groundwater, *S*—soil, or *W*—surface water. Finally, the risk scores are divided into four classes, i.e., low (I; $0 \le R \le 25$; $RV \le 0.01$), moderate low (II; $25 < R \le 50$; $0.01 < RV \le 0.1$), moderate high (III; $50 < R \le 75$; $0.1 < RV \le 1$), and high (IV; $75 < R \le 100$; RV > 1).

2.1.2. Air risk value calculation

The calculation of the air risk value (*RV_A*) is derived from the methodology for determining volatile organic compound (VOC) potential emission (CEPA, 2007a). At present VOC emission is the main issue of pesticide impact on the air quality in California (CEPA, 2012), so PURE-DSS currently only relies on emission potential (EP) to evaluate the air risk. VOCs contribute to the formation of ground-level ozone which degrades air quality and threatens human and ecosystem health. In addition to vehicle exhaust, the primary VOC source, many active or inert ingredients of pesticides are VOCs. CDPR maintains an *EP* inventory database for estimating VOC potential emission, which contains the *EP* values of all the pesticides registered in California (CEPA, 2005b), or set with a median TGA EP of the same formulation type (e.g., dust, emulsifiable concentrate, or pressurized liquid) if analysis results are unavailable (CEPA, 2002).

In addition, the application method adjustment factor (*AMAF*) is used to refine the VOC emission calculation for a set of commonly used fumigants (i.e., 1,3-D, chloropicrin, methyl bromide, metam-sodium, metam-potassium, dazomet, and sodium tetrathiocarbonate) during the peak ozone season (May–October) in California (CEPA, 2007a). *RV_A* is calculated as follows:

$$RV_A = RATE \cdot EP \cdot AMAF$$
 (5)

where *RATE* is the pesticide product application rate (g m⁻²), *EP* is the emission potential (–), and *AMAF* is the application method adjustment factor (–) which is fumigant- as well as application method-specific. *AMAF* was derived based on 15-year field monitoring data, including direct emission flux measurements and soil column measurements (CEPA, 2007a). For example, the *AMAF* is 0.65 when applying 1,3-D via shallow injection with high permeability tarp or no tarp-broadcast and is 0.26 when applying the same fumigant via deep injection with high permeability tarp or no tarp-broadcast. See Table 22 of CEPA (2007a) for a complete set of *AMAF*. Due to a lack of data, the AMAF of non-fumigant pesticides currently are set as 1.

2.1.3. Groundwater risk value calculation

The groundwater risk value (RV_G) is calculated using the risk ratio approach described by Padovani et al. (2004), modified via the inclusion of aerobic degradation process (e_S^{-3K} in Eq. (7)), adjustment coefficients (a and b in Eq. (10)), and temperature correction coefficient (f_t in Eq. (11)). RV_G is determined as the ratio of the predicted environmental concentration in groundwater (PEC_G ; mg l⁻¹) to the acceptable daily intake (ADI; mg kg⁻¹) (Eq. (6)).

$$RV_G = \frac{10 \cdot PEC_G}{ADI} \tag{6}$$

where 10 is a safety factor for compensating modeling uncertainties and scales RV_G to similar ranges of RV_A , RV_S , and RV_{W} , and PEC_G is estimated by the modified Leach Quantity index (Khan and Liang, 1989) as follows:

$$PEC_G = \frac{RATE \cdot C_{AI} \cdot (1 - f_{int}) \cdot e^{-3 \cdot K_{SO}} \cdot AF}{P}$$
(7)

where C_{Al} is the percent concentration of the active ingredient in the pesticide formulation, f_{int} is the fraction of the pesticide formulation intercepted by crops, K_{SO} is the aerobic degradation rate constant in soil (day⁻¹) (Eq. (11)), *P* is the soil porosity, and *AF* is the attenuation factor (Rao et al., 1985), which has been employed to assess pesticide leaching risk to groundwater in different regions (Bernard et al., 2005; de Paz and Rubio, 2006; Stenemo et al., 2007).

$$P = 1 - \frac{BD}{PD}$$
(8)

where *BD* is the soil bulk density (kg m⁻³), and *PD* is the soil particle density (kg m⁻³; default: 2650 kg m⁻³).

$$AF = e^{-365 \cdot K_{SA} \cdot L \cdot FC \cdot RF/Q}$$
(9)

where 365 is a unit conversion factor, K_{SA} is the anaerobic degradation rate constant in soil (day⁻¹) (Eq. (11)), *L* is the groundwater level (m), *FC* is the field capacity, *RF* is the retardation factor, and *Q* is the annual groundwater recharge (m).

$$RF = \frac{FC + BD \cdot OC \cdot K_{OC} + a \cdot (P - FC) \cdot K_H}{b \cdot FC}$$
(10)

where OC is the organic carbon content (0.580M; OM: organic matter content), K_{OC} is the organic carbon sorption constant $(m^3 kg^{-1}), (P-FC)$ is the soil air content, K_H is the Henry's law constant, and a and b are adjustment coefficients (default: 500 and 100 respectively for calibrating the Leach Quantity index to groundwater monitoring data in California).

The degradation rate constants (dav^{-1}) are derived from half lives by considering the decay of pesticides obey first order kinetics:

$$K_i = \frac{\ln 2 \cdot f_t}{DT_i} \tag{11}$$

where *i* is SO (soil aerobic), SA (soil anaerobic), or W (water), K_i is the aerobic (K_{SO}) or anaerobic (K_{SA}) degradation rate constant in soil, or a degradation rate constant in water (K_W), DT_i is the measured half-life in soil or water (day), and f_t is the temperature correction coefficient (Boesten and Vanderlinden, 1991):

$$f_t = e^{\gamma(t-t_0)} \tag{12}$$

where γ is a constant (default: 0.08), *t* is the on-site annual or monthly average daily temperature (°C), and t_0 is the temperature at which the half-life was measured (°C; default: 20 °C).

2.1.4. Soil risk value calculation

Both short-term and long-term risks are accounted in the calculation of the soil risk values. A few highly toxic pesticides may have short half-lives, while a few moderately toxic pesticides may have long half-lives. Comparing the risks of the above two categories of pesticides requires evaluation of the combined effects of short-term and long-term exposures. Thus, the risk value for soil (RV_S) is calculated as the maximum of the short-term (RVSS) and long-term (RVSL) risk values for soil:

$$RV_S = \max RV_{SS}, RV_{SL} \tag{13}$$

Similar to the methodology used for groundwater, RV_{SS} is determined as the ratio of the short-term predicted environmental concentration in soil (PEC_{SS} ; mg kg⁻¹) to the acute 50%-lethal concentration to earthworms (LC_W ; mg kg⁻¹):

$$RV_{SS} = \frac{1000 \cdot PEC_{SS}}{LC_W} \tag{14}$$

where 1000 is a safety factor accounting for the possibility that other soil organisms can be more sensitive than earthworms and scales RV_G to similar ranges of RV_A, RV_S, and RV_W, and PEC_{SS} is estimated as follows:

$$PEC_{SS} = \frac{1000 \cdot RATE \cdot C_{AI} \cdot (1 - f_{int})}{DEPTH \cdot BD}$$
(15)

where 1000 is a unit conversion factor, and DEPTH is the thickness of top soil (m; default: 0.05 m).

RV_{SL} is calculated as the ratio of the long-term predicted environmental concentration in soil (PEC_{SL} ; mg kg⁻¹) to the chronic no-observed-effect concentration to earthworms (*NOEC_W*; mg kg⁻¹):

$$RV_{SL} = \frac{1000 \cdot PEC_{SL}}{NOEC_W} \tag{16}$$

where 1000 is a safety factor (same as 1000 in Eq. (14)), the calculation of PEC_{SL} is adapted from the European Pesticide Hazard Information and Decision Support System (EUPHIDS) (Beinat and van den Berg, 1996):

$$PEC_{SL} = \frac{PEC_{SS} \cdot (1 - e^{-K_{SO} \cdot t_{ex}})}{4 \cdot K_{SO} \cdot t_{ex}}$$
(17)

where 4 is a factor to account for the different soil depths used in calculating PEC_{SS} and PEC_{SL} (0.05 m and 0.2 m for PEC_{SS} and PEC_{SL} respectively), K_{SO} is the degradation rate constant in soil (Eq. (11)), and t_{ex} is the exposure-time interval (day; default: 21 day, the typical time interval used to measure NOEC).

2.1.5. Surface water risk value calculation

As seen in the calculation of RV_{S} , the risk value for surface water (RV_W) is determined as the maximum of the short-term (RV_{WS}) and long-term (RV_{WI}) risk values for surface water:

$$RV_W = \max\{RV_{WS}, RV_{WL}\}\tag{18}$$

RV_{WS} is the ratio of the short-term predicted environmental concentration in surface water (PEC_{WS} ; mg L⁻¹) to the acute toxicity to aquatic organisms (LEC_A ; mg L^{-1}):

$$RV_{WS} = \frac{PEC_{WS}}{LEC_A} \tag{19}$$

where LECA is the minimum of the acute 50%-lethal/effective concentration to aquatic organisms (i.e., fish, algae, and Daphnia):

 $LEC_A = \min\{LC_F, EC_A, EC_D\}$ (20)

where LC_F is the acute 50%-lethal concentration to fish (mg l⁻¹), EC_A is the acute 50%-effective concentration to algae (mg 1^{-1}), and EC_D is the acute 50%-effective concentration to Daphnia (mg l^{-1}).

RV_{WL} is the ratio of the long-term predicted environmental concentration in surface water (PEC_{WL} ; mg l⁻¹) to the chronic toxicity to aquatic organisms ($NOEC_A$; $mg l^{-1}$):

$$RV_{WL} = \frac{PEC_{WL}}{NOEC_A} \tag{21}$$

where NOECA is the minimum of the chronic no-observed-effect concentration to aquatic organisms:

$$NOEC_A = \min NOEC_F, NOEC_A, NOEC_D$$
 (22)

where $NOEC_{F/A/D}$ is the chronic no-observed-effect concentration to fish, algae, or Daphnia (mg l^{-1}) respectively.

PEC_{WS} and PEC_{WL} are calculated using Eqs. (23) and (34) respectively, which are modified from EUPHIDS (Beinat and van den Berg, 1996). It considers that pesticides are transported to surface water primarily through spray drift and water runoff. Thus, the pesticide concentration in surface water may change dramatically at two event points: 0-the pesticide application day, and 1-the day when runoff water reaches the surface water.

$$PEC_{WS} = \max\{PEC_{W0}, PEC_{W1}\}$$
(23)

where PEC_{W0} (mg l⁻¹) is the predicted environmental concentration of the pesticide in surface water on the day of the pesticide application; and PEC_{W1} is the predicted environmental concentration of the pesticide in surface water when runoff water reaches the surface water.

$$PEC_{W0} = RATE \cdot C_{AI} \cdot f_{dri} \tag{24}$$

where f_{dri} is the drift coefficient calculated by the integrated form of the Drift Calculator (FOCUS, 2001), which was based on the BBA drift data (BBA, 2000) for ground applications and the Tier 1 regressions from the AgDrift model (SDTF, 1999) for aerial applications.

$$\begin{aligned} f_{dri} &= \frac{1}{z_2 - z_1} \Big[\frac{A}{B^+} (H^{B^+1} - z_1^{B^+1}) + \frac{C}{D^+1} (z_2^{D^+1} - H^{D^+1}) \Big] & \text{for } z_1 \leq H \leq z_2; \\ f_{dri} &= \frac{A}{(z_2 - z_1)(B^+1)} \Big[z_2^{B^+1} - z_1^{B^+1} \Big] & \text{for } z_2 < H; \text{ and } \\ f_{dri} &= \frac{C}{(z_2 - z_1)(D^+1)} \Big[z_2^{D^+1} - z_1^{D^+1} \Big] & \text{for } z_1 > H \end{aligned}$$

г.

. .

where A, B, C, D and H are crop type specific constants (Table 1), and z_1 and z_2 are the distances from the edge of treated field to the closet and farthest edges of surface water body respectively (m; default: $z_2 - z_1 = 1$ m).

$$PEC_{W1} = PEC_{D1} + PEC_{R1} \tag{26}$$

where PEC_{D1} is the remaining concentration of PEC_{W0} when runoff water from the field reaches the surface water (mg l^{-1}); and PEC_{RI} is the predicted environmental concentration in surface water of the pesticide transported by water runoff $(mg l^{-1}).$

$$PEC_{D1} = PEC_{D0} \cdot e^{-(3+t_{ch})\cdot K_W}$$

$$\tag{27}$$

where t_{ch} is the channel flow duration (day), which is adapted from Nietsch et al. (2005)

$$t_{ch} = \frac{0.62 \cdot D \cdot n^{0.75}}{SL^{0.375}}$$
(28)

where D is the distance from the field to surface water (km), n is Manning's roughness coefficient, and SL is the slope.

 PEC_{RI} , the predicted environmental concentration in surface water of the pesticide transported by water runoff, is calculated as follows:

$$PEC_{R1} = \frac{RATE \cdot (1 - f_{int}) \cdot e^{-3 \cdot K_S} \cdot R_{OFF} \cdot e^{-t_{ch} \cdot K_W}}{(1 + K_{OC} \cdot OC) \cdot R_M}$$
(29)

where R_M is the monthly maximum daily water input (the sum of rainfall and irrigation; mm), and R_{OFF} is the quantity of water lost by runoff (mm) calculated using the SCS Curve Number Method (SCS, 1972):

$$R_{OFF} = \frac{(0.039 \cdot R_{\rm M} - 0.2 \cdot M)^2}{0.039 \cdot (0.039 \cdot R_{\rm M} + 0.8 \cdot M)}$$
(30)

where 0.039 is a unit conversion factor, and M is the potential maximum retention after runoff begins (inches).

$$M = \frac{1000}{CN_{\rm s}} - 10 \tag{31}$$

where CN_s is the slope-adjusted curve number (Nietsch et al., 2005).

$$CN_{\rm s} = \frac{CN_3 - CN_2}{3} \cdot (1 - 2 \cdot e^{-13.86 \cdot SL}) + CN_2 \tag{32}$$

$$CN_3 = CN_2 \cdot e^{0.00673 \cdot (100 - CN_2)} \tag{33}$$

where CN_2 and CN_3 are the moisture condition II and III curve numbers respectively. CN_2 can be looked up from an empirical table with the soil hydrology group and land use type (Nietsch et al., 2005).

Table 1

Constants for estimating drift coefficients (FOCUS, 2001).

Crop type	Α	В	С	D	Н
Arable crops and vegetables < 50 cm	2.759	-0.9778	2.759	-0.9778	1 ^a
Hops	58.247	-1.0042	8654.9	-2.8354	15.3
Vines (late application) and vegetables > 50 cm	44.769	-1.5643	44.769	-1.5643	1 ^a
Vines (early application)	15.793	-1.6080	15.793	-1.6080	1 ^a
Pome/stone fruit (late application)	60.396	-1.2249	210.7	-1.7599	10.3
Pome/stone fruit (early application)	66.702	-0.7520	3867.9	-2.4183	11.4
Aerial application	50.470	-0.3819	281.1	-0.9989	16.2

^a The drift coefficient is irrelative to H since A=C and B=D; and H=1 is to generalize the calculations by using the same set of equations for all crop types.



Fig. 1. Map of the Orestimba Creek watershed. USGS gage #11274538 is the watershed outlet.

 PEC_{WL} is determined as the average concentration in surface water from the pesticide application to a time interval of exposure (t_{ex}).

$$PEC_{WL} = \frac{(3 + t_{ch}) \cdot PEC_{W01} + t_{ex} \cdot PEC_{W12}}{3 + t_{ch} + t_{ex}}$$
(34)

where PEC_{W01} is the average predicted environmental concentration in surface water before runoff water from the field reaches the surface water (mg l⁻¹); and PEC_{W12} is the average predicted environmental concentration in surface water during the exposure days after runoff water from the field reaches the surface water (mg l⁻¹).

$$PEC_{W01} = \frac{PEC_{W0} \cdot (1 - e^{-(3 + t_{ch}) \cdot K_W})}{(3 + t_{ch}) \cdot K_W}$$
(35)

$$PEC_{W12} = \frac{PEC_{W1} \cdot (1 - e^{-t_{ex} \cdot K_W})}{t_{ex} \cdot K_W}$$
(36)

2.2. Input data sources and preparation

The input data to the DSS include environmental conditions, pesticide properties, and pesticide application records (Table A.2). Fig. A1 shows the database scheme of the PURE-DSS. These data were compiled from various data sources detailed in the following sections.

2.2.1. Environmental conditions

The relevant environmental conditions include soil properties, meteorological conditions, groundwater depth (*L*), ground slope (*SL*), and distance to surface water (*D*). Soil properties including bulk density (*BD*), sand content (*SC*), clay content (*CC*), organic matter content (*OM*), and hydrological group (*HG*) were obtained from the SSURGO and STATSGO database (NRCS, 2008). Meteorological conditions including precipitation (*P*), temperature (*T*), and reference evaportanspiration (*ET_o*) were acquired from the California Irrigation Management Information System (CIMIS) (CDWR, 2010). Groundwater depth was downloaded from the USGS groundwater data service (USGS, 2010). Ground slope was derived from the Digital Elevation Model (DEM) dataset downloaded from the Geospatial Data Gateway (NRCS, 2008). Distance to surface water was derived from a digital stream map of California (Cal-Altas, 2011). It should be noted that *SC*, *CC*, and *ET_o* are not directly input to the PURE-DSS, but are used for estimating field capacity

by the equations proposed by Saxton and Rawls (2006) and irrigation amount (I) by the Basic Irrigation Scheduling program (Snyder et al., 2007) respectively. The annual total groundwater recharge (Q) was estimated by the water balance model: Q=P+I-ET-R, where R is water runoff.

2.2.2. Pesticide properties

Pesticide product properties, including the *EP* and percentage of active ingredients content, were extracted from the product/label database maintained by California EPA (CEPA, 2010a). The properties of active ingredients, including sorption coefficient (K_{OC}), Henry's law constant (K_H), aerobic (DT_{SO}) and anaerobic (DT_{SA}) half-life in soil, half-life in water (DT_W), acute (LEC_A) and chronic ($NOEC_A$) toxicity to aquatic organisms, acute (LC_W) and chronic ($NOEC_W$) toxicity to earthworms, and the Acceptable Daily Intake (ADI), were obtained from the Pesticide Properties Database (PPDB, 2009) and the PestChem database from California EPA (CEPA, 2009).

2.2.3. Pesticide application records

The pesticide application records were queried from the Pesticide Use Reporting (PUR) database maintained by CDPR (CEPA, 2010c), which contains pesticide application information such as pounds of active ingredient and product used, locations of township, range and section, and crops received the applications, date of the pesticide use, and grower and fields identifications. The data from 1992 to 2009 were used for the study.

2.3. DSS evaluation

In evaluating the DSS's procedure for calculating *PEC* in surface water, the Pearson's correlation method was applied to test the correlation between the predicted annual average load (*Load_P*) and the observed annual average load (*Load_P*). Due to the scarcity of field-edge pesticide monitoring data, the evaluation was carried out at watershed level. The predicted annual load of a pesticide was calculated by summing the field-edge yields of this pesticide in the entire watershed in one calendar year. The field-edge yield of one application was the product of the total field-edge yield per area (i.e., $PEC_{W0} + PEC_{W1}$ calculated with PURE-DSS) and the field area. *Load_Q* was estimated by multiplying the observed concentration with measured stream flow rate. Pesticide monitoring data were usually available for one or two days on a monthly basis, and the pesticide loads in

the rest days were interpolated from available days (Luo et al., 2008). In the Central Valley, California, the Orestimba Creek Watershed (Fig. 1) where agricultural pesticide application accounted for almost all pesticide uses was chosen as the study area to evaluate the DSS. The watershed boundary was defined by the California Central Valley Region Water Quality Control Board (CEPA, 2007b) based on natural streams and man-made irrigation canals. A United States Geological Survey (USGS) site (#11274538) is located at the watershed outlet, which has been monitoring the stream flow and other parameters from 02/25/1991 to present (USGS, 2011). The in-stream pesticide concentration monitoring records

 Table 2

 Parameters of environmental conditions, excluding monthly meteorological conditions.

Parameter	Unit	Value
Bulk density	g cm ⁻³	1670
Sand content	%	41
Clay content	%	22
Organic matter content	%	0.74
Hydrological group	-	В
Ground slope	%	8
Groundwater depth	m	6.5
Annual total groundwater recharge	mm	400
Annual mean of daily average temperature	deg.	15
Distance to surface water	m	50

Table 3

Monthly meteorological conditions.

Month	Mean of daily average temperature (deg.)	Maximum daily water input (mm)
1	7	35
2	10	23
3	12	21
4	14	17
5	18	18
6	21	17
7	22	17
8	22	17
9	19	17
10	15	17
11	10	18
12	7	22

Table 4

Pesticide product properties.

sampled near this USGS site during the last two decades were compiled into a database by CDPR (CEPA, 2011). The pesticide properties and application records were summarized in Table A.1 in the Appendices.

2.4. Case study: almonds in the Central Valley, California

The PURE-DSS was applied to evaluate the environmental risk of past pesticide use on two almond fields of similar size (27 and 28 ha respectively) in the Central Valley, California. The two fields were within the same section ($\approx 1.6 \times 1.6 \text{ km}^2$) as defined by the Public Land Survey System (USDI, 2009). The pesticide risk scores were calculated in the order of pesticide AI, pesticide product, and field levels. Tables 2–6 list the input data of environmental conditions, pesticide properties, and pesticide application records. Due to data limitation, four pesticide (Table 6).

3. Results and discussion

3.1. DSS evaluation

Fig. 2 shows that the observed average annual load ($Load_{o}$) is well correlated with the predicted load (*Load*_{*n*}), with a correlation coefficient of r(41) = 0.82 (p < 0.001). While the annual loads are generally over-predicted because of the worst-case scenario configured in the PURE-DSS (i.e., a water input event will occur three days after a pesticide application) and the loss during the transportation from the field edges to the watershed outlet, the systematic over-prediction maintains relative scoring among pesticide applications. The relatively-low correlation coefficient was due to the uncertainties existing in the modeling process and the monitoring data. First, considering the data availability and the purpose (i.e., determining pesticide relative risk), PURE-DSS used an empirical rather than a sophisticated model in predicting pesticide concentrations. Second, the monitoring data were scarce, which were available for one or two days on a monthly basis. When calculating the "observed annual loads", the unavailable days were interpolated from the available days. Finally, input parameters (e.g., K_{OC} , DT_{SO} , and DT_W) usually measured under standard conditions in laboratories can vary widely under different environmental conditions. This evaluation work is the first step of the long term DSS evaluation process, which requires more validation evidence with monitoring or experimental data

Pesticide product	Use type	EP (%) ^a	Active ingredient (AI) ^b	AI (%) ^b
ABBA 0.15 EC	Insecticide	39.15	Abamectin	1.9
Abound flowable Fungicide	Fungicide	11.10	Azoxystrobin	22.9
Agri-Mek 0.15 EC Miticide/Insecticide	Miticide/insecticide	55.10	Abamectin	2.0
Chateau herbicide SW	Herbicide	3.70	Flumioxazin	51.0
Dimilin 2L	Insecticide	6.56	Diflubenzuron	22.0
Extinguish Professional Fire Ant Bait	Insecticide	3.70	s-Methoprene	0.5
First Choice Gavicide Super 90	Miticide/insecticide	1.64	Mineral oil	99.0
Gramoxone Inteon	Herbicide	5.71	Paraquat dichloride	30.1
Kocide 101	Fungicide	6.11	Copper hydroxide	77.0
Lorsban-4E	Insecticide	51.32	Chlorpyrifos	44.9
Omite-6E	Acaricide	16.51	Propargite	69.2
Pristine Fungicide	Fungicide	1.02	Boscalid	25.2
			Pyraclostrobin	12.8
Prowl H ₂ O Herbicide	Herbicide	5.71	Pendimethalin	38.7
Rely Herbicide	Herbicide	15.14	Glufosinate-ammonium	11.3
Roundup Weathermax Herbicide	Herbicide	4.80	Glyphosate, potassium salt	48.8
Rovral Brand 4 Flowable Fungicide	Fungicide	8.30	Iprodione	41.6
Shark EW	Herbicide	5.85	Carfentrazone-ethyl	21.3
Sim-Trol 4L	Herbicide	0.94	Simazine	42.8
Valent Volck Supreme Spray	Miticide/Insecticide	0.42	Petroleum oil, unclassified	97.4
Warrior Insecticide With Zeon Technology	Insecticide	29.06	Lambda-cyhalothrin	11.4

^a Pesticide emission potential database (CEPA, 2010b).

^b Pesticide product/label database (CEPA, 2010a).

Table 5		
Pesticide active ingredient properties	(PPDB,	2009).

Active ingredient	K_{OC} (ml g ⁻¹)	K _H	DT _{SO} (day)	DT _{SA} (day)	DT _W (day)	LEC_A (mg L ⁻¹)	$NOEC_A$ (mg L ⁻¹)	LC_W (mg kg ⁻¹)	$NOEC_W$ (mg kg ⁻¹)	ADI (mg kg ⁻¹)
Abamectin	5638	2.70E-03	31	143	395	0.00012	0.00006 ^a	33	1	0.0025
Azoxystrobin	528	7.40E-09	59	95	31	0.23	0.04	283	20	0.2
Boscalid	809	5.18E-08	200	-	30	2.7	0.1	1000	110	0.04
Carfentrazone-ethyl	18	2.97E-04	1	1	9	0.012	0.001 ^b	820	73	0.03
Chlorpyrifos	9373	6.69E-01	79	136	72	0.0001	0.00005 ^a	129	13	0.01
Copper hydroxide	12,000	1.96E-07	2600	-	S	0.009	0.00045 ^b	677	15	0.15
Diflubenzuron	7585	4.76E-04	13	34	222	0.0026	0.00004	500	36	0.01
Flumioxazin	245	6.36E-02	14	1	1	0.000852	0.0001 ^a	982	142	0.009
Glufosinate-ammonium	785	4.48E-09	20	37 ^c	30	46.5	18	1000	250	0.021
Glyphosate, potassium salt ^d	6920 ^c	1.46E-07	66	22	35	4.4	2	480	29	0.3
Iprodione	373	3.61E-04	28	32	2	0.66	0.17	1000	102	0.06
Lambda-cyhalothrin	21,0000	1.84E-02	39	128	233	0.00021	0.0001 ^a	1000	50	0.005
Mineral oil	9090000	1.64E-03	65	-	-	1.28	0.005	750	183	-
Paraquat dichloride	10,0000	4.00E-09	1720	644	30	0.32	0.08 ^b	1000	250	0.004
Pendimethalin	15,000	1.29E-03	42	41	28	0.006	0.003	1000	33	0.125
Propargite	7283	1.03E-03	81	290	63	0.014	0.006	378	29	0.007
Pyraclostrobin	8444	9.40E-06	71	3	30	0.006	0.003 ^a	567	0.4	0.03
Simazine	97	5.47E-05	106	77	28	0.04	0.02 ^a	1000	223	0.005
s-Methoprene	2535	8.86E-01	10	-	1	0.36	0.04 ^b	-	25	0.05

Italic, obtained from the PestChem database (CEPA, 2009).

-, unavailable.

^a *NOEC* was replaced with 0.5 *LC* as *NOEC* > 0.5 *LC*.

^b The Quantitative Structure-Activity Relationships (Swanson et al., 1997) were used to estimated the missing data.

^c Obtained from the Pesticide Action Network (PAN) pesticide database (Kegley et al., 2011).

^d The properties of glyphosate were used to fill the missing data.

in other watersheds and sensitivity/uncertainty analysis (Saltelli et al., 2010) showing the effect of the uncertainties in input parameters on risk scores.

3.2. Case study

3.2.1. AI-level risk scores

Fig. 3 shows the risk scores of surface water, groundwater, and soil for applied active ingredients in the order of the AI-level integrated risk scores from the highest to the lowest for the two almond fields. The integrated risk scores of chlorpyrifos (100), diflubenzuron (94), copper hydroxide (83), pyraclostrobin (79), and pendimethalin (75) were classified as high risk, which suggests minimizing the use of these AIs or implementing mitigation practices after application. In addition, the following Als require use with caution: (1) to surface water, chlorpyrifos (100; IV), diflubenzuron (94; IV), and the other ten AIs classified as moderate high or high risk; (2) to groundwater, simazine (74; III); and (3) to soil, pyraclostrobin (79; IV) and chlorpyrifos (76; IV). The results show that the PURE-DSS was able to identify chlorpyrifos and simazine as high risk compared to the remaining 17 AIs, a conclusion validated by reports such as the national groundwater survey which reported that simazine detected in 14.8% samples, the third most frequently detected pesticide in groundwater (Kolpin et al., 2000). Similarly, surface water monitoring data show that chlorpyrifos has been frequently detected in the main San Joaquin River and its tributaries (CEPA, 2005a). Other low risk score chemicals were also in line with the known risk patterns. It should be noted that AI-level risk scores are intermediate and hidden results in the PURE-DSS, but productlevel risk scores are the final results presented to the DSS users.

3.2.2. Product-level risk scores

Table 6 shows the integrated and separate risk scores for all the pesticide products applied on the two fields. The integrated risk scores of "Lorsban-4E" (100; IV) containing chlorpyrifos and "Pristine Fungicide" (79; IV) containing boscalid and pyraclostrobin were classified as high risk. Investigating the separate risk scores of these pesticides, "Lorsban-4E" had high risks to surface water (100; IV), soil (75; IV), and air (85; IV); and "Pristine Fungicide" had high risk to soil (79; IV). The product-level risk scores except the air risk scores were determined by their Als. For example, the risk scores of "Pristine Fungicide" were aggregated over its two active ingredients—boscalid and pyraclostrobin. Other low score products also showed reasonable matching with the common knowledge.

Most of the existing pesticide risk assessment tools/models only provide AI-level risk evaluations (e.g., Trevisan et al., 2009; Verro et al., 2009). If growers or pest control advisors use those tools/models, they have to look up the AIs contained in a pesticide product and aggregate AI-level risks if that pesticide product contains multiple AIs. On contrast, the PURE-DSS has precompiled the pesticide product-AI information and has programmed AIlevel risk aggregations for multiple-AI products. Since growers and pest control advisors (the main targeted users of the PURE-DSS) are more familiar with pesticide products than pesticide AI, product-level risk scores are more convenient for them in practical pest management.

3.2.3. Field-level risk scores

Fig. 4 shows the monthly field-level integrated and separate risk scores for the two fields. The risk scores of surface water, soil, air, and integrated for field 2 had similar monthly trends; the risk scores in May and July were close to each other and much higher than those in March. However, field 1 had relatively varying trends for different types of risk scores. For instance, the risk score of surface water for field 1 in August was the lowest (R_W =3), while its risk score of soil was lowest in July (R_W =9). In addition, groundwater risk scores were highest in December and July for field 1 and 2 respectively, which were caused by preemergent and

Table	6			
-------	---	--	--	--

Pesticide application rates and product-level risk scores.

Month	Product name	RATE (kg ha ^{-1})	R_T	R _W	R_G	R _S	R_A
(a) Field 1							
2	Gramoxone Inteon	1.41	48	29	0	36	48
2	Shark EW	0.04	31	31	0	0	10
2	Prowl H ₂ O Herbicide	2.50	73	73	0	66	54
2	First Choice Herbicide Activator	0.14	-	-	-	-	-
2	First Choice Ultra Pro	0.52	-	-	-	-	-
3	Pristine Fungicide	0.77	79	45	-	79	22
5	Rely Herbicide	2.71	65	0	1	23	65
5	Chateau Herbicide SW	0.26	63	63	0	15	24
5	First Choice Herbicide Activator	0.14	-	-	-	-	-
5	ABBA 0.15 EC	0.72	67	67	0	50	61
5	Abound Flowable Fungicide	1.02	51	24	8	46	51
5	First Choice Gavicide Super 90	8.14	61	-	-	61	53
7	Warrior Insecticide With Zeon Technology	0.18	65	65	0	9	43
7	First Choice No Foam B	0.34	-	-	-	-	-
7	Extinguish Professional Fire Ant Bait	0.92	38	0	-	-	38
8	Roundup Weathermax Herbicide	3.18	62	3	0	62	55
12	Prowl H ₂ O Herbicide	3.00	75	75	0	68	56
12	Sim-Trol 4L	0.95	74	44	74	37	24
(b) Field 2							
3	Rovral Brand 4 Flowable Fungicide	0.67	44	0	9	30	44
3	Dimilin 2L	0.52	94	94	0	30	38
3	Kocide 101	0.56	83	83	-	57	38
3	Valent Volck Supreme Spray	4.07	31	-	-	-	31
5	Lorsban-4E	5.01	100	100	0	75	85
5	Abound Flowable Fungicide	1.02	51	24	8	46	51
5	Agri-Mek 0.15 EC Miticide/Insecticide	0.89	70	70	0	53	67
5	Valent Volck Supreme Spray	8.14	38	-	-	-	38
7	Lorsban-4E	5.01	100	100	0	75	85
7	Omite-6E	2.48	68	68	26	64	65
7	Miller Nu-Film-17	0.20	-	-	-	-	-

-, risk scores were not evaluated due to data unavailability.

Bold, moderate high (III) or high (IV) risk.



Fig. 2. Relationship between observed and predicted average annual pesticide loads of 41 pesticides used in the Orestimba Creek watershed during 1992–2009. The correlation coefficient is r(41)=0.82 (p < 0.001). The line represents theoretical perfect fit.

dormant herbicide applications. Moreover, Fig. 5 shows the yearly field-level risk for the two fields. It shows that field 2 had much higher risk to surface water and air than field 1, and field 1 had much higher risk to groundwater than field 2. The differences between the two fields in the order from the largest to

the smallest are surface water, groundwater, air, and soil. The differences between these separate risk scores show that the PURE-DSS is capable of discriminating the risks to different environmental compartments. The integrated risk score of field 1 (R_T =88) is lower than that of field 2 (R_T =100).

In the PURE-DSS the field-level risk scores of one field represent the overall environmental risks posed by the pest management practices on that field. A field is the elementary management unit for pest control and other farm activities. Different fields (even owned by the same grower) usually have different pest management practices, such as choosing different combinations of pesticides or applying pesticides on different dates. Comparing field-level risk scores of various pest management practices would facilitate users in adopting more environmentally friendly ones. In addition, the growers having field-level risk scores higher than county/state averages may gain more incentives to improve their pest management practices for better environmental protection.

4. Conclusions

The PURE-DSS can quantitatively and accurately evaluate pesticide risks for guiding California growers to select reducedrisk pesticides to use in their crops. This DSS can be used as a valuable tool for farmers, and can also be useful for policy analysis and eco-label development among agricultural communities. A website with a user friendly interface based on the PURE-DSS was developed for California growers, freely accessible at http:// pure.ucdavis.edu. A California grower ID assigned in the PUR database (CEPA, 2010c) is required to perform the risk evaluation. In the future, the website will integrate the research results of



Fig. 3. Al-level risk scores sorted by integrated risk score, which is the maximum risk for a single environmental compartment (Eq. (4)). Average risk scores were used for the Als that were applied twice: abamectin, azoxystrobin, chlorpyrifos, and pendimethalin. All the risk scores for s-methoprene were 0 or unavailable. The risk scores of surface water and groundwater for mineral oil were unavailable due to lack of input data.





Fig. 5. Yearly field-level risk scores in 2008 (the integrated risk scores for field 1 and 2 are 88 and 100 respectively).

Integrated Pest Management (IPM) and Best Management Practice (BMP) (Reichenberger et al., 2007; Zhang et al., 2010) to provide growers with more options for lowering the pesticide risks. Furthermore, a few other important organisms will be incorporated in the future version of PURE-DSS, such as birds, bees, beneficial insects, and small mammals. Finally, linking this online risk evaluation tool with information on pest control efficacy and economics of different pest management practices would establish a comprehensive decision support platform for farmers to arrive at sustainable pest management practices.

Acknowledgment

Authors wish to acknowledge USEPA for funding the study (#X8-96982801-0 and #PE96958301), and the Packard Foundation for providing the fellowship. Authors would also like to thank Mike Grieneisen and Kimberly Steinman for their comments for the initial manuscript and thank the anonymous reviewers for providing very helpful comments and suggestions to improve this manuscript.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ecoenv.2012.05.019.

References

- Backhaus, T., Altenburger, R., Arrhenius, A., Blanck, H., Faust, M., Finizio, A., Gramatica, P., Grote, M., Junghans, M., Meyer, W., Pavan, M., Porsbring, T., Scholze, M., Todeschini, R., Vighi, M., Walter, H., Grimme, L.H., 2003. The BEAM-project: prediction and assessment of mixture toxicities in the aquatic environment. Cont. Shelf Res. 23, 1757–1769.
- BBA, 2000. Bekanntmachung des Verzeichnisses risikomindernder Anwendungsbedingungen für Nichtzielorganismen. Bundesanzeiger Nr. 100, 9879-9880, Germany, May 26, 2000.
- Beinat, E., van den Berg, R., 1996EUPHIDS, a decision support system for the admission of pesticides. Report no. 712405002. National Institute of Public Health and the Environment, Bilthoven, the Netherlands.
- Bernard, H., Chabalier, P.F., Chopart, J.L., Legube, B., Vauclin, M., 2005. Assessment of herbicide leaching risk in two tropical soils of Reunion Island (France). J. Environ. Qual. 34, 534–543.
- Bockstaller, C., Guichard, L., Keichinger, O., Girardin, P., Galan, M.B., Gaillard, G., 2009. Comparison of methods to assess the sustainability of agricultural systems. A review. Agron. Sustain. Dev. 29, 223–235.

- Bockstaller, C., Guichard, L., Makowski, D., Aveline, A., Girardin, P., Plantureux, S., 2008. Agri-environmental indicators to assess cropping and farming systems. A review. Agron. Sustain. Dev. 28, 139–149.
- Boesten, J.J.T.I., Vanderlinden, A.M.A., 1991. Modeling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ. Qual. 20, 425–435.
- Bouchard, M.F., Bellinger, D.C., Wright, R.O., Weisskopf, M.G., 2010. Attentiondeficit/hyperactivity disorder and urinary metabolites of organophosphate pesticides. Pediatrics. Peds., 2009–3058.
- Cal-Altas, 2011. The California Spatial Information Library (CaSIL)—Hydrologic Features. http://atlas.ca.gov/download.html#/casil/inlandWaters (verified 05/2012).
- Carsel, R., Imhoff, J., Hummel, P., Cheplick, J., Donigian Jr, A., 1998. PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.0. US EPA.
- Carson, R. L., 1962. Silent Spring. Riverside Press, Cambridge, MA, USA.
- CDFA, 2011. California Department of Food and Agriculture: 92 Years Protecting and Promoting Agriculture in the Golden State. http://www.cdfa.ca.gov/ CDFA-History.html (verified 05/2012).
- CDWR, 2010. California Irrigation Management Information System. California Department of Water Resources, the Office of Water Use Efficiency, Sacramento, CA < http://www.cimis.water.ca.gov/ > (verified 05/2012).
- CEPA, 2002. Methodology for Determining VOC Emission Potentials of Pesticide Products. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/intro.pdf (verified 05/2012).
- CEPA, 2005a. Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Diazinon and Chlorpyrifos Runoff into the Lower San Joaquin River (Final Staff Report). California Environmental Protection Agency, Central Valley Regional Water Quality Control Board, Sacramento, CA. http://www.swrcb.ca.gov/rwqcb5/water_isgot/sulphur_creek_staff_final.pdf) (verified 05/2012).
- CEPA, 2005b. Estimation of Volatile Emssion Potential of Pesticide by Thermogravimetry. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/tga_method.pdf (verified 05/2012)..
- CEPA, 2007a. Pesticide Volatile Organic Compound Emission Adjustments for Field Conditions and Estimated Volatile Organic Compound Reduction-Revised Estimates. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA < http://www.cdpr.ca.gov/docs/emon/pubs/ ehapreps/analysis_memos/1955_sanders.pdf> (verified 05/2012).
- CEPA, 2007b. San Joaquin River Watershed Surface Water Ambient Monitoring Program (SWAMP). California Environmental Protection Agency, Sacramento, CA <http://www.waterboards.ca.gov/water_issues/programs/swamp/> (verified 05/2012).
- CEPA, 2009. The PestChem Database. California Environmental Protection Agency, Sacramento, CA.
- CEPA, 2010a. California Product/Label Database. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA http://www.cdpr.ca.gov/docs/label/labelque.htm (verified 05/2012).
- CEPA, 2010b. DPR's Pesticide Product Emission Potential Data. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA <http://www.cdpr.ca.gov/docs/emon/vocs/vocproj/ep_data/2008_ep.zip> (verified 05/2012).
- CEPÀ, 2010c. Pesticide Use Reporting (PUR) Database. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA <http://www.cdpr.ca.gov/docs/pur/purmain.htm> (verified 05/2012).
- CEPA, 2011. Surface Water Database—Complete Chemical Analysis Results. California Environmental Protection Agency, Sacramento, CA <http://www.cdpr.ca.gov/docs/emon/surfwtr/surfcont.htm > (verified 05/2012).
- CEPA, 2012. Annual Report on Volatile Organic Compound Emissions from Pesticides: Emissions for 1992–2010. California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA.
- Davidson, C., 2004. Declining downwind: amphibian population declines in california and historical pesticide use. Ecol. Appl. 14, 1892–1902.
- de Paz, J.M., Rubio, J.L., 2006. Application of a GIS-AF/RF model to assess the risk of herbicide leaching in a citrus-growing area of the Valencia Community, Spain. Sci. Total Environ. 371, 44–54.
- Domagalski, J., 1997a. Pesticides in Surface and Ground Water of the San Joaquin-Tulare basins, California: Analysis of Available Data, 1966 through 1992. US Geological Survey Water-Supply. (paper. 1–74).
- Domagalski, J., 1997b. Results of a prototype surface water network design for pesticides developed for the San Joaquin River Basin, California. J. Hydrol. 192, 33–50.
- Finizio, A., Villa, S., Vighi, M., 2005. Predicting pesticide mixtures load in surface waters from a given crop. Agric. Ecosyst. Environ. 111, 111–118.
- FOCUSS, 2001. "FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC". Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2., 245pp.
- Juraske, R., Anton, A., Castells, F., Huijbregts, M.A.J., 2007. PestScreen: a screening approach for scoring and ranking pesticides by their environmental and toxicological concern. Environ. Int. 33, 886–893.
- Kegley, S. E., Hill, B. R., Orme, S., Choi, A. H., 2011. PAN Pesticide Database, Pesticide Action Network. North America (San Francisco, CA). http://www.pesticideinfo.org> (verified 05/2012).

- Khan, M.A., Liang, T., 1989. Mapping pesticide contamination potential. Environ. Manage. 13, 233–242.
- Knisel, W., 1993. GLEAMS Groundwater Loading Effects of Agricultural Management Systems—Version 2.10. Department Publication. 5.
- Kolpin, D.W., Barbash, J.E., Gilliom, R.J., 2000. Pesticides in ground water of the United States, 1992–1996. Ground Water 38, 858–863.
- Labite, H., Butler, F., Cummins, E., 2011. A review and evaluation of plant protection product ranking tools used in agriculture. Human Ecol. Risk Assess. 17, 300–327.
- Levitan, L., 2000. "How to" and "why": assessing the enviro-social impacts of pesticides. Crop Prot. 19, 629–636.
- Luo, Y.Z., Zhang, X.Y., Liu, X.M., Ficklin, D., Zhanga, M.H., 2008. Dynamic modeling of organophosphate pesticide load in surface water in the northern San Joaquin Valley watershed of California. Environ. Pollut. 156, 1171–1181.
- Mills, P.K., Yang, R.C., 2007. Agricultural exposures and gastric cancer risk in Hispanic farm workers in California. Environ. Res. 104, 282–289.
- Nietsch, S.L., Arnold, J.G., Kiniry, J.R., Williams, J.R., 2005. Soil and Water Assessment Tool Theoretical Documentation. Version 2005. Texas Water Resource Institute, College Station, TX.
- NRCSS, 2008. USDA-NRCS Geospatial Data Gateway. <http://datagateway.nrcs. usda.gov/> (verified 05/2012).
- Padovani, L., Trevisan, M., Capri, E., 2004. A calculation procedure to assess potential environmental risk of pesticides at the farm level. Ecol. Indic. 4, 111–123.
- PPDBB, 2009. The Pesticide Properties Database (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, funded by UK national sources and the EU-funded FOOTPRINT project (FP6-SSP-022704). < http://sitem.herts.ac.uk/aeru/footprint/en/index.htm > (verified 05/2012).
- Rao, P.S.C., Hornsby, A.G., Jessup, R.E., 1985. Indexes for ranking the potential for pesticide contamination of groundwater. Soil Crop Sci. Soc Fl. Proc. 44, 1–8.
- Reichenberger, S., Bach, M., Skitschak, A., Frede, H.G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; a review. Sci. Total Environ. 384, 1–35.
- Reilly, T.E., Dennehy, K.F., Alley, W.M., Cunningham, W.L., 2008. Ground-Water Availability in the United States, vol. 1323. U.S. Geological Survey Circular 70p. Also availabe online at http://pubs.usgs.gov/circ/1323/ (verified 05/2012).
- Reus, J., Leendertse, P., Bockstaller, C., Fomsgaard, L., Gutsche, V., Lewis, K., Nilsson, C., Pussemier, L., Trevisan, M., van der Werf, H., Alfarroba, F., Blumel, S., Isart, J., McGrath, D., Seppala, T., 2002. Comparison and evaluation of eight pesticide environmental risk indicators developed in Europe and recommendations for future use. Agric. Ecosyst. Environ. 90, 177–187.
- Saltelli, A., Annoni, P., Azzini, I., Campolongo, F., Ratto, M., Tarantola, S., 2010. Variance based sensitivity analysis of model output. Design and estimator for the total sensitivity index. Comput. Phys. Commun. 181, 259–270.
- Saxton, K.E., Rawls, W.J., 2006. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Sci. Soc. Am. J. 70, 1569–1578.

- SCS, 1972. National Engineering Handbook, Section 4, Hydrology. US Department of Agriculture, Soil Conservation Service, Washington, D.C.
- SDTFF, 1999. AgDrift, Spray Drift Task Force Spray Model. Version 1.11.
- Snyder, R. L., Orang, M., Bali, K., Eching, S., 2007. The Basic Irrigation Scheduling Manual. http://biomet.ucdavis.edu/irrigation_scheduling/bis/BIS.htm> (verified 05/2012).
- Stenemo, F., Ray, C., Yost, R., Matsuda, S., 2007. A screening tool for vulnerability assessment of pesticide leaching to groundwater for the islands of Hawaii, USA. Pest. Manage. Sci. 63, 404–411.
- Stenrod, M., Heggen, H.E., Bolli, R.I., Eklo, O.M., 2008. Testing and comparison of three pesticide risk indicator models under Norwegian conditions—a case study in the Skuterud and Heiabekken catchments. Agric. Ecosyst. Environ. 123, 15–29.
- Swanson, M.B., Davis, G.A., Kincaid, L.E., Schultz, T.W., Bartmess, J.E., Jones, S.L., George, E.L., 1997. A screening method for ranking and scoring chemicals by potential human health and environmental impacts. Environ. Toxicol. Chem. 16, 372–383.
- Trevisan, M., Di Guardo, A., Balderacchi, M., 2009. An environmental indicator to drive sustainable pest management practices. Environ. Modell. Softw. 24, 994–1002.
- USDI, 2009. The Public Land Survey System (PLSS). U.S. Department of the Interior, Bureau of Land Management, Washington, DC <http://nationalatlas.gov/arti cles/boundaries/a_plss.html > (verified 05/2012).
- USGSS, 2010. USGS Groundwater Data for the Nation. United States Geographical Survey. < http://waterdata.usgs.gov/nwis/gw> (verified 05/2012).
- USCSS, 2011. National water information system: Web interface. U.S. Geographical Survey. Washington, D.C. http://waterdata.usgs.gov/nwis> (verified 05/2012).
- Vaj, C., Barmaz, S., Sorensen, P.B., Spurgeon, D., Vighi, M., 2011. Assessing, mapping and validating site-specific ecotoxicological risk for pesticide mixtures: A case study for small scale hot spots in aquatic and terrestrial environments. Ecotoxicol. Environ. Safe. 74, 2156–2166.
- van Bol, V., Debongnie, P., Pussemier, L., Maraite, H., Steurbaut, W., 2002. Study and Analysis of Existing Pesticide Risk Indicators. Veterinary and Agrochemical Research Center, Teruren, Belgium.
- Verro, R., Finizio, A., Otto, S., Vighi, M., 2009. Predicting pesticide environmental risk in intensive agricultural areas. I: screening level risk assessment of individual chemicals in surface waters. Environ. Sci. Technol. 43, 522–529.
- Vighi, M., Altenburger, R., Arrhenius, A., Backhaus, T., Bodeker, W., Blanck, H., Consolaro, F., Faust, M., Finizio, A., Froehner, K., Gramatica, P., Grimme, L.H., Gronvall, F., Hamer, V., Scholze, M., Walter, H., 2003. Water quality objectives for mixtures of toxic chemicals: problems and perspectives. Ecotoxicol. Environ. Safe. 54, 139–150.
- Zhang, M., Wilhoit, L., Geiger, C., 2005. Assessing dormant season organophosphate use in California almonds. Agric, Ecosyst. Environ. 105, 41–58.
- Zhang, X.Y., Liu, X.M., Zhang, M.H., Dahlgren, R.A., Eitzel, M., 2010. A review of vegetated buffers and a meta-analysis of their mitigation efficacy in reducing nonpoint source pollution. J. Environ. Qual. 39, 76–84.