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A mathematical environmental transport model of roadside applied herbicides at the site scale (~100 m) was stochastically applied using a Monte-Carlo technique to simulate the concentrations of 33 herbicides in stormwater runoff. Field surveys, laboratory sorption data, and literature data were used to generate probability distribution functions for model input parameters to allow extrapolation of the model to the regional scale. Predicted concentrations were compared to EPA acute toxicity end points for aquatic organisms to determine the frequency of potentially toxic outcomes. Results are presented for three geographical regions in California and two highway geometries. For a given herbicide, frequencies of potential toxicity (FPTs) varied by as much as 36% between region and highway type. Of 33 herbicides modeled, 16 exhibit average FPTs greater than 50% at the maximum herbicide application rate, while 20 exhibit average FPTs less than 50% at the minimum herbicide application rate. Based on these FPTs and current usage statistics, selected herbicides were determined to be more environmentally acceptable than others in terms of acute toxicity and other documented environmental effects. This analysis creates a decision support system that can be used to evaluate the relative water quality impacts of varied herbicide application practices.

Introduction

Since the passage of the Clean Water Act in the 1970s, point source pollution has become increasingly regulated and controlled in the United States. To further control sources of water pollution, nonpoint sources have become a topic of growing significance. Pesticides, a prime example of nonpoint source pollution, have been studied extensively because of their intentional release into the environment over wide areas and potential for disastrous side effects. Two important questions raised in the application of pesticides are what is the environmental risk, and what decisions can be made to minimize this risk? Environmental risk assessments are typically based on models that predict environmental concentrations of constituents of concern such as pesticides. These models generally predict an estimated environmental concentration for an application site based on its geographic and climatic features or a general site based on conservative characteristics. A common way to assess environmental risk is to compare predicted concentrations to known ecological end points, as Peterson (*1*) does. This provides a decision support system to evaluate chemical selection and/or application practices.

An improvement to this process is to apply these models stochastically. By using probability distribution functions (PDFs) to represent geographic and climatic characteristics, probabilities of obtaining varying estimated environmental concentrations can be generated. Typically this is done to account for spatial variations of these parameters either at the site (*2*) or catchment (*3*) scale. However, stochastic simulations can also be used to extrapolate site scale modeling to the regional scale by conducting regional site-surveys or using available data that represent the general distribution of sites over the entire region, as Soutter and Musy show (*4*). Huber et al. (*5*) extend this approach to the realm of chemical selection by evaluating multiple specific herbicides, but do not compare the results to an environmental end point, and so do not actually characterize their environmental risk. Probst (*6*), on the other hand, uses this method and includes a combination of the estimated environmental concentrations with biological end points to evaluate environmental risk for various agricultural management practices and various pesticides.

As seen in the cases of Probst and others (*7, 8*), most pesticide runoff research has been focused on agricultural applications. Herbicides are also commonly applied along roadsides to improve driver visibility, reduce the risk of fire, and prevent damage to the road surface, and this has not been the subject of much research. At the discharge points of the runoff that transports these herbicides, acute aquatic toxicity to algae has been observed experimentally (*9*). A physically based, one-dimensional, mathematical model was developed previously to model the transport of these roadside applied herbicides to adjacent receiving waters (*10*). The model predicts event mean concentration (EMC) for a storm event, which is defined as

$$\mathrm{EMC} = \frac{\text{Total herbicide loss}}{\text{Total runoff volume}} \tag{1}$$

In this paper, the model is applied stochastically using a Monte-Carlo method for the range of scenarios in California to extrapolate the site scale (~100 m) model to the regional (statewide) scale. First, appropriate PDFs of various input parameters needed to predict EMC are extracted from the statewide data collected by site survey or literature review. Using these PDFs, a set of random values for the parameters representative of various possible conditions was generated for each model run. The model explained in (*10*) was used to predict the EMC associated with all sets of randomly generated parameters for a number of commonly used herbicides in California highways. By comparing the results to environmental end points of these herbicides, the frequency of potential toxic outcomes, referred to as frequency of potential toxicity (FPT), is found for different roadside herbicide applications. Finally, acknowledging that using acute toxicity to aquatic organisms as the sole indicator of environmental risk is very limiting, the literature on the most promising herbicides is surveyed to establish other environmental effects, such as carcinogenicity, teratogenic effects, mutagenicity, etc., and the resulting most favorable herbicides are selected. The results can be used to guide decisions about which herbicides to apply, the effect of the application rate,

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TABLE 1. Site Characteristics from Statewide Survey Used As Basis for Establishing Frequency Distributions of Model Site Geometry Parameters

site I.D.[a]	county	site profile	width of road surface (m)	slope across the road surface (degrees)[b]	width of slope (m)	range of grassed slopes (degrees)
1–34/299E	Humboldt County	T1	11.98	0.99	40.69	5.10–6.66
1–35/36E	Humboldt County	T2	4.03	0.26	4.17	9.99–12.77
1–36/101N	Mendocino County	T2	18.09	1.41	69.06	0.5–13.03
1–38/253W	Mendocino County	T1	14.61	0.92	38.04	17.00–27.00
2–1/36N	Tehama County	T1	8.53	3.17	1.53	9.71–36.00
3–05/99N	Sacramento County	T1	9.00	0.83	6.76	8.7
3–06/80W	Placer County	T2	17.07	N/A	7.99	0.20–11.12
3–07/50W	El Dorado County	T1	20.73	N/A	5.67	9.58–23.71
4–35/680S	Solano County	T1	10.36	N/A	16.24	2.89–17.69
4–38/680N	Contra Costa County	T1	24.38	N/A	7.54	3.75–7.90
4–39/580W	Alameda County	T2	21.95	0.83	4.29	46.5
5–03/25S	San Benito County	T1	11.58	0.84	11.91	7.32–14.32
5–05/227N	San Luis Obispo County	T1	10.95	N/A	11.39	6.53–46.49
6–05/198E	Kings County	T1	9.75	0.90	12.27	4.42–19.03
6–06/99S	Tulare County	T1	11.89	N/A	8.26	6.00–6.21
6–209/41N	Fresno County	T1	17.68	N/A	12.54	23.74
8–07/10E	Riverside County	T2	10.36	N/A	22.67	4.67–11.21
8–08/10W	Riverside County	T1	14.02	N/A	28.30	3.45–4.21
8–10/91E	Riverside County	T2	21.34	N/A	9.11	1.04–2.66
10–02/120E	Tuolumne County	T2	11.27	1.59	7.62	21.8
10–03/5N	San Joaquin County	T1	14.02	N/A	14.05	8.18–21.20
10–4/132E	Mariposa County	T2	8.23	2.69	9.14	5.97–47.68
11–97/15S	San Diego County	T2	28.04	N/A	0.34	45.5
11–98/805S	San Diego County	T2	21.34	N/A	20.18	7.77
11–104/15N	San Diego County	T2	20.73	N/A	2.45	34.54–48.60

[a] First number refers to Caltrans district, second number refers to the site number in that district, third number and letter represent highway number and direction of traffic on that side of the road. [b] N/A - data not available.

and in understanding the relative impacts of regional precipitation patterns and highway geometries.

The objectives of this study are to (i) stochastically apply the model for the range of scenarios found in California, (ii) compare resulting concentrations to EPA acute toxicity thresholds to determine the frequency of potentially toxic outcomes, and (iii) select the most environmentally acceptable herbicides with respect to acute toxicity. In meeting these objectives, a decision support system will be established that can be used to answer the following questions: what is the environmental risk of applying these herbicides, and which herbicides should be applied to minimize this risk? This can lead to policy change or management decisions that promote more environmentally benign practices.

Experimental Section

Estimation of Input Frequency Distributions. Geometric, storm, and soil parameters were used to characterize sites. Additional parameters used for modeling were application area and application rate.

Site geometry was determined via surveying for 25 locations across California during site visits (Table 1). The 25 sites were part of a previous statewide effort to characterize stormwater runoff quality by the California Department of Transportation (Caltrans) and were selected to be representative of varied geography, topography, traffic load, and surrounding land usage (*11*). The site profile represents one of two basic highway geometries (Figure 1). A type 1 (T1) geometry (also known as *fill* or *convex*) exists when the road surface is at a higher elevation than the immediate surrounding area. Runoff from the road surface thus washes over the adjacent spray zone and is attenuated along the grassed area before reaching a ditch, drain, or adjacent receiving water. A type 2 (T2) geometry (also known as *cut* or *concave*) exists when the road surface is at a lower elevation than the surrounding area. Runoff from the surrounding area runs over the spray zone with no slope to attenuate the herbicides, while runoff from the road surface runs directly into the storm drain or receiving water and serves to dilute the herbicide concentrations. PDFs were derived to approximate this input data. Figures S1−S4 in the Supporting Information show histograms of the site survey data and the PDFs used to approximate grassed area slope, road slope, road width, and grassed area width.

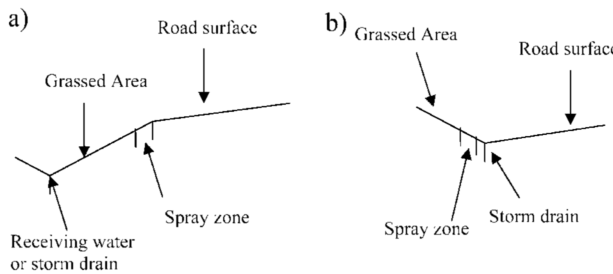

FIGURE 1. Highway geometry cross-sections showing (a) type 1 (T1) and (b) type 2 (T2).

Data from weather stations for particular sites located in northern, central, and southern California were used to construct PDFs for storm intensity and duration for each region. Details on the derivation of these distributions and the accompanying Figure S5 can be found in the Supporting Information.

The general shape of each parameter's histogram data is indicative of the most appropriate type of PDF, so the most-likely best-fit PDFs chosen from normal, log-normal, uniform, exponential, and gamma distributions were fit to the data. The PDF whose fit exhibited the smallest Kolmogorov–Smirnov "D" value was selected. Table 2 summarizes the function chosen to approximate each input variable as well as the fitted parameters for each function.

Fifty-seven roadside soil samples were taken from the above 25 sites and analyzed (*11*). These data were used to estimate the frequency distributions for all soil parameters. Hydraulic conductivity, residual water content, and other

TABLE 2. Model Input Parameters and Their Associated Probability Distribution Functions

parameter	frequency distribution function	parameters
grassed area slope (°)	log-normal[a]	$\sigma = -0.2443$, $\mu = -1.4563$
road slope (degrees)	log-normal[a]	$\sigma = 0.5981$, $\mu = 0.08627$
road surface width (m)	gamma[b]	$\lambda = 6.09$, $\theta = 2.44$
grassed area width (m)	log-normal[a]	$\sigma = 1.098\,54$, $\mu = 2.314\,52$
application zone width(m)	discrete	
soil organic content (%)	log-normal[a]	$\sigma = 0.796\,43$, $\mu = 0.291\,694$
precipitation duration index (DI)	log-normal[a]	Table S1
precipitation intensity index (II)	log-normal[a]	Table S1
clay (%)	clay/(non sand fraction) = log-normal	$\sigma = -1.13$, $\mu = 0.24$
sand (%)	100-%sand = log-normal	$\sigma = 3.42$, $\mu = 0.44$
saturated water content	normal[c]	$\sigma = 0.4125$, $\mu = 0.0093$

[a] Log-normal distribution: $f(x;\mu,\sigma) = e^{-(\ln x-\mu)^2/2\sigma^2}/x\sigma\sqrt{2\pi}$.
[b] Gamma distribution: $f(x;\lambda,\theta) = x^{\lambda-1}e^{-x/\theta}/\theta^k\Gamma(k)$.
[c] Normal distribution: $f(x;\mu,\sigma) = e^{-(x-\mu)^2/2\sigma^2}/\sigma\sqrt{2\pi}$.

parameters related to moisture retention in soil were estimated based on soil textural properties (sand percentage and/or clay percentage) using literature relationships as described in the Supporting Information. Details on the derivation of these distributions and accompanying figures (Figures S6−S12) can be found in the Supporting Information.

Application area width in most cases is 1.36 m (4.46 ft) and in some cases 2.04 m (6.69 ft). In some rare cases it can also be 2.72 m (8.92 ft). No data were found to provide the specific percentage of each case statewide. It is estimated that in 70% of the cases the width is 1.36 m, in 25% of the cases the width is 2.04 m, and in 5% of the cases it is 2.72 m.

Herbicide manufacturers suggest a range for the application rate of each herbicide. Since the runoff model is linear in application rate, a constant application rate of 1 mg/m^2 was assumed for initial modeling. Individual herbicide results are subsequently scaled by their suggested minimum and maximum application rates. Herbicide degradation by biotic or abiotic processes during runoff was neglected due to the short time-scales associated with the short distance from spray-zone to model runoff prediction point. Only the first storm event following application was modeled, so degradation between application and runoff was also neglected.

Monte-Carlo Simulation. Huang et al. found that sorption processes were the controlling factor in herbicide mobility and thus, in conjunction with application rate, are expected to exert primary control on receiving water concentrations following storm events (*12*). Because of this, and to limit the total number of simulations required, 33 herbicides were divided into 8 categories based on their approximate organic carbon normalized distribution coefficient, K_{OC}, defined as

$$K_{OC} = \frac{C_S}{C_W \times f_{OC}} \quad (2)$$

where C_S is the herbicide concentration in soil (mg/kg), C_W is the herbicide concentration in water (mg/L), and f_{OC} is the mass fraction of organic carbon in soil (g/g). Table 3 shows the herbicides modeled and their associated physical, chemical, and toxicological properties.

The model was used to estimate the EMC in the water leaving the highway right-of-way (e.g., in the ditch or storm drain) following the first storm event after application. The model contains a flow component that uses the kinematic wave model for surface runoff coupled with Richard's equation for infiltration and a transport module that takes into account herbicides' advection, dispersion, and exchange with soil in the surface runoff as well as transport and retardation in the shallow subsurface. Extensive explanation of the model can be found in ref (*9*).

The model was run for 10 000 sets of input data generated according to the PDFs mentioned above for each combination of the 8 herbicide categories, 3 meteorological regions, and 2 basic highway types. For many of the cases, the specific combination of variables in the experiment resulted in very little surface runoff. In these cases, the EMC was very small because retardation and small flow velocities in the subsurface prevented the herbicides from reaching the receiving water during the first event. Concentrations could not be realistically calculated for these events, so these cases were simply ignored in the final results. This was equivalent to ignoring any storm event which did not produce runoff above a threshold value (0.1 L per meter of highway). The remaining experimental data sets contained between 355 and 4825 simulation runs for each combination scenario. The specific number of runs for each case can be found in Table S2 of the Supporting Information.

The EMC results obtained for each of the herbicide groups for a unit application rate were scaled by the minimum or maximum application rates for each herbicide in the group to obtain individual herbicide EMCs. These EMCs were then compared to the minimum toxicity threshold for each herbicide, and the percentage of the EMCs greater than this limit was designated the frequency of potential toxicity (FPT), or

$$\mathrm{FPT} = \frac{\text{Number of events with EMC > endpoint}}{\text{Number of events}} \times 100 \quad (3)$$

The end point for each herbicide was the lowest of the EPA acute toxicity (*18*) values for three organism types (algae, water flea, and fish; see Table 3). Table S3 in the Supporting Information shows a detailed breakdown of toxicity thresholds for different species.

Results and Discussion

Figure 2 shows a sample frequency distribution of EMC values for the herbicide Sulfometuron Methyl applied to a T1 site in the Northern California region. Histograms for each category and region/highway type for the original application rate of 1 mg/m^2 are shown in Figures S13−S26 in the Supporting Information.

The histograms illustrate that the frequency associated with EMC bins decays rapidly. This decay becomes steeper as K_{oc} increases (i.e., increasing category number), signifying the ability of high K_{oc} herbicides to readily adsorb to organic matter in the soil. The reason for this sharp decay is likely due to many variables each of which can alone result in almost complete attenuation of the herbicide. For example, low precipitation intensity (low II), long storms (high DI), high soil organic content, high hydraulic conductivity, and wide grassed areas can each limit EMC in many cases. T1 highway geometries generally result in lower EMCs than T2 geometries (i.e., the histograms decay more quickly), indi-

TABLE 3. Herbicide Properties

category	herbicide	K_{oc} (L/kg)[a]	log K_{oc}	ref[b]	app. rate (mg/m^2)[c]	end point (ppb)[d]	species[d]
1	Dicamba	2	0.30	13	7.0–224.2	10	blue-green algae
1	Clopyralid	30.2	1.48	13	10.5–55.9	5900	green algae
1	Chlorsulfuron	33.5	1.53	13	1.3–15.8	10	water flea
1	Bromacil	34	1.53	13	168–2692	5.9	green algae
1	Triclopyr	59	1.77	13	112.1–896.6	260	rainbow trout
2	Sulfometuron Methyl	85	1.93	13	5.3–42.1	2.6	green algae
2	Simazine	100	2.00	13	112–448	4.1	green algae
2	Sethoxydim	100	2.00	13	10.5–52.5	250	diatom
2	Halosulfuron-Methyl	115	2.06	13	3.5–7.1	3.6	green algae
3	Mefluidide	200	2.30	14	14.0–112.1	100 000[e]	fish (nonspecific)[e]
3	Tebuthiuron	340	2.53	13	112.1–672.5	49	green algae
3	Dichlobenil	400	2.60	14	440.1–2200.9	2700	green algae
3	Paclobutrazol	400	2.60	15	200 000–800 000	16 200	grass carp, white amur
3	Isoxaben	567	2.75	13	55.5–111.8	870	sheepshead minnow
3	Glufosinate	620	2.79	15	56–168	1023	green algae
4	Norflurazon	673	2.83	15	110–882	9.6	green algae
4	Propyzamide	800	2.90	13	57.2–228.6	500	green algae
4	Diuron	804	2.91	13	67–1345	0.37	algal mat
4	Napropamide	835	2.92	13	219.7–405.7	2600	green algae
4	Clethodim	900	2.95	13	2.6–28.0	11 400	green algae
5	Pelargonic Acid	1000	3.00	15	1060–9424	64 000	water flea
5	Dithiopyr	1043	3.02	16	57–172	17	green algae
5	Oryzalin	1390	3.14	13	224.2–672.5	24	blue-green algae
5	Oxyfluorfen	1500	3.18	13	14.0–224.2	0.676	green algae
5	Oxadiazon	2300	3.36	15	224.2–448.3	3.4	diatom
5	Cacodylic Acid	2660	3.42	16	286–858	14 000	diatom
6	Fluazifop-P-Butyl	5800	3.76	15	10.6–126.0	230[f]	green algae[f]
6	Methylarsonic acid	7000	3.85	17	84.1–504.3	1800	green algae
7	Trifluralin	9900	4.00	13	42.0–224.1	7.2	rainbow trout
7	Pendimethalin	11 100	4.05	13	165.0–447.2	2.4	green algae
7	Prodiamine	12 470	4.10	13	55–167.6	83	water flea
8	Glyphosate	31 690	4.50	13	28–1120.8	10	water flea
8	Diquat	100 000	5.00	13	52.3–837	19	diatom

[a] Average value of cited range. [b] Reference for K_{oc} values. [c] All application rates were taken from herbicide labels. [d] Unless otherwise noted, all toxicity data were taken from ref (*18*); ppb = μg/L. More detailed toxicity information can be found in Table S3 in the Supporting Information. [e] Source ref (*19*). [f] Source ref (*20*).

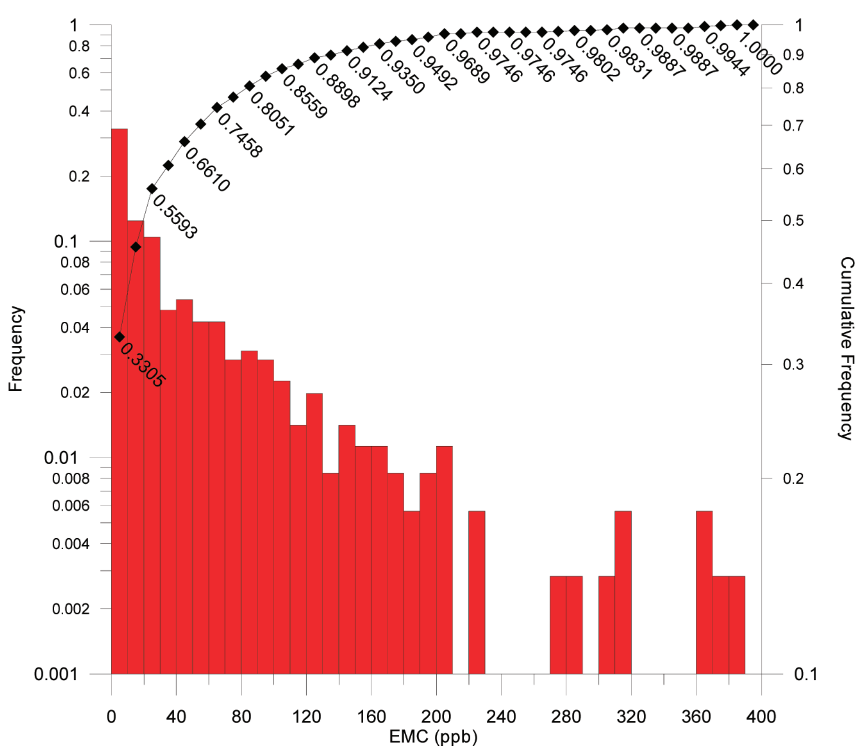

FIGURE 2. Histogram showing simulation results for Sulfometuron Methyl (Category 2) applied at its maximum application rate for the north region, T1.

TABLE 4. Application Rates, Minimum Toxicity Thresholds, and Average Frequencies of Potential Toxicity (FPT) at Minimum and Maximum Application Rates

herbicide[a]	min.−max. application rate (mg/m^2)	min. app. rate avg. FPT (%)[b]	min. app. rate range of FPTs (%)	max. app. rate avg. FPT (%)[b]	max. app. rate range of FPTs (%)
Bromacil*	168.0–2692.0	55	42–70	71	55–85
Cacodylic Acid*	286.0–858.0	0	0–0	0	0–0
Chlorosulfuron**	1.3–15.8	1	0–2	22	13–35
Clethodim	2.6–28.0	0	0–0	0	0–0
Clopyralid**	10.5–55.9	0	0–0	0	0–0
Dicamba	7.0–224.0	13	6–23	52	41–68
Dichlobenil	440.0–2201.0	2	0–5	31	25–38
Diquat**	52.3–837.0	1	0–3	42	31–59
Dithiopyr	57.0–172.0	61	47–76	88	77–97
Diuron**	67.0–1345.0	99	97–100	100	98–100
Fluazifop-p-butyl**	10.6–126.0	0	0–0	4	1–7
Glufosinate	56.0–168.0	0	0–0	2	0–5
Glyphosate**	28.0–1121.0	1	0–3	70	56–86
Halosulfuron-Methyl*	3.5–7.1	37	23–59	54	39–75
Isoxaben**	55.0–112.0	0	0–0	1	0–2
Mefluidide*	14.0–112.0	0	0–0	0	0–0
Methylarsonic Acid	84.0–504.0	0	0–0	1	0–2
Napropamide*	220.0–406.0	0	0–0	1	0–3
Norflurazon*	110.0–882.0	93	84–99	98	95–100
Oryzalin**	224.0–673.0	87	75–97	95	89–100
Oxadiazon**	224.0–448.0	98	94–100	99	96–100
Oxyfluorfen**	14.0–224.0	94	86–100	99	97–100
Paclobutrazol	200 000.0–800 000.0	94	87–98	97	94–100
Pelargonic Acid*	1060.0–9424.0	0	0–0	1	0–1
Pendimethalin**	165.0–447.0	90	80–99	96	91–100
Prodiamine**	55.0–168.0	1	0–3	9	3–17
Propyzamide	57.2–229.0	0	0–1	4	6–19
Sethoxydim**	10.5–52.5	0	0–0	6	3–15
Simazine*	112.0–448.0	89	82–93	94	89–96
Sulfometuron Methyl**	5.3–42.1	55	40–76	87	79–93
Tebuthiuron	112.0–673.0	65	58–73	94	88–98
Triclopyr**	112.0–897.0	8	3–14	31	22–47
Trifluralin	42.0–224.0	30	20–47	78	64–92

[a] No stars denotes herbicide was never used by Caltrans on highway rights-of-way from July 2003 to June 2004; one star (*) indicates the herbicide was moderately used (the total number of incidences of one-star herbicides made up 10% of the total number of incidences of herbicide use, and each of these herbicides was used less than any of the two star herbicides); two stars (**) indicates the herbicide was heavily used (the total number of incidences of two-star herbicides made up 90% of the total number of incidences of herbicide use, and each of these herbicides was used more than any of the one-star herbicides). [b] The average is of the results of the 6 region−highway type combinations.

cating that attenuation along the slope in T1 results in greater benefits than lower velocity runoff over the spray zone and highway runoff dilution in T2. In general the north region tends to result in the highest EMCs, while the central region tends to result in the lowest EMCs, being only slightly lower than the south region. The reason for the high EMCs in the north region can be seen in the II and DI PDFs shown in Supporting Information Figure S5. II is on average greater in the north than the other two regions, leading to greater herbicide mobilization and loading. However, duration is on average lower than that in the central region and similar to that in the south, meaning low total volumes of runoff during storm events and therefore less significant dilution effects. The difference between south and central regions is not very significant; the reason for it is not as evident by inspection, but is likely due to similar II but slightly higher DI in the central region.

Table 4 shows the application rates, average and range of FPTs for minimum and maximum application rates. The averages and ranges are for the six possible combinations of region and highway type. Individual region−highway type frequencies are shown in Tables S4 and S5 in the Supporting Information.

The results show wide variation in the frequency of potentially toxic EMCs. There are multiple causes for high toxicities. High application rates, high mobility (low K_{oc}), and low toxicity thresholds each contribute to higher FPTs. Among region−highway type combinations, those herbicides for which the frequencies are bounded by 0% or 100% values (very low or very high frequencies) exhibit narrow ranges of FPTs, while others show ranges of 6% to as great as 36%. This result is important in showing that for some herbicides, toxicity risk can greatly vary between regions and site geometries, and decision makers should take this fact into account when establishing management practices. Of the 33 herbicides, 16 showed average FPTs above 50% at the maximum application rate. At the minimum application rate, 20 showed average FPTs less than 50%, and 19 of these were 13% or lower. These results highlight the extreme variability in environmental risk between herbicides and between minimum and maximum application rates.

It should be noted that these frequencies are based on EMCs in the roadside drainage ditch or storm drain, but waters containing these herbicides will typically be diluted upon mixing with a larger water body such as a river or lake. Therefore, the concentration that the target organism sees will most likely be far less than the computed EMC. Furthermore, acute toxicity levels are the results of tests of duration of 24 (algae), 48 (water flea), or 96 (fish) hours, which is likely longer than the exposure that will be seen by organisms exposed to the highway runoff. Nevertheless, the results provide a conservative concentration in light of the difficulty of characterizing dilution and duration of exposure effects on a regional scale. Furthermore, since storms not generating significant runoff were neglected in the analysis, the FPTs are only representative of those storms that do generate significant runoff (greater than 0.1 L per meter of highway).

The results also show that estimating relative risk of different herbicides can be complex, necessitating analysis of several variables and employing a calibrated physical model. For example, Halosulfuron Methyl, Sulfometuron Methyl, and Simazine possess very similar log K_{oc}s (2.06, 1.93, and 2.00, respectively) and toxicity end points (3.6, 2.6, and 4.1 ppb, respectively), while Halosulfuron Methyl and Sulfometuron Methyl also possess similar application rates (3.5–7.1, 5.3–42.1 mg/m^2; Simazine = 112.0–448.0 mg/m^2). Despite this, their average minimum−maximum application rate FPTs are 37–54%, 55–87%, and 89–94%, respectively. The rankings of these herbicides in terms of relative risk would have been difficult by inspection of only these three variables without applying a physical model.

Of the 14 roadside-applied herbicides used most frequently by Caltrans, which represent 90% of the application incidences from July 2003 to June 2004 (*21*), 6 herbicides—Oryzalin, Diuron, Sulfometuron Methyl, Oxyfluorfen, Oxadiazon, and Pendimethalin—have average FPTs over 50% even at the minimum application rate. Of the remaining 8, 4 have documented environmental effects other than acute toxicity that are cause for concern. Triclopyr is somewhat mobile and persistent, and there is some evidence that it can cause chronic toxicity or teratogenic effects (*22, 23*). Diquat is also persistent, and causes severe eye and dermal irritation (*24–26*). Isoxaben and Prodiamine are both possible carcinogens. Therefore, the most environmentally acceptable high-use herbicides appear to be Glyphosate, Clopyralid, Chlorosulfuron, and Fluazifop-P-Butyl. This is not to suggest that these should be used above all others, as different chemicals target different types of plants and are designed for different types of use (e.g., pre-emergent vs post-emergent).

Each of these has potential concerns as well, however. Glyphosate, along with the other 3 herbicides (as well as many others), is often formulated with other inactive ingredients that themselves may cause acute toxicity or other negative environmental effects. The EPA does not regulate these inactive ingredients to the same degree as the active ingredients and also does not require manufacturers to label their products with these ingredients. Clopyralid and Chlorsulfuron are both very mobile, and Clopyralid can be very persistent in the environment. In some tests, Fluazifop-P-Butyl caused pre/post natal toxicity in rats (*27*), and there are some concerns about inhalation effects (*26*). More research on these herbicides needs to be conducted to determine if they are indeed more favorable than those with higher FPTs.

There are several notable sources of uncertainty in the results. Regional effects are only broadly considered, as only one weather station from each region was included in the analysis. Along these lines, sites included in the 25-site survey may not be totally representative of highway sites statewide, but this assumption is nevertheless made. Herbicides whose K_{oc} exhibited large ranges (up to 1.43 log units) were lumped into a single category; this effect is particularly significant for categories 1 and 8. It is difficult to characterize how long after application of the herbicide that runoff occurs. Therefore, the assumption made in this analysis is that runoff occurs immediately after application. This is seldom the case in practice, and this time may sometimes be long enough to allow degradation of the herbicide to become an important factor.

This analysis forms a tool that decision-makers can use to make management decisions that result in more environmentally benign practices. It can also be modified and used in a predictive manner to ascertain effects of changing application practices. For example, if best management practices that lengthened the distance to the receiving water and reduced the roadside slope were instituted, what impact would these changes of the input PDFs have on FPTs? Or, for example, if climate change altered typical storm intensity or duration, how would risk be altered? An extension of this decision support system could be incorporating systematic weighting of all the various environmental side effects along with acute toxicity and possibly other biological end points to numerically determine the "best" herbicide for a given region and geometry.

Despite the multitude of variables that control EMC in the environment, decision-makers can control relatively few. Assuming that spraying must be done, when, what, and how much to spray are the main management variables. This analysis gives managers insight into what herbicides to use and briefly how much should be sprayed, but looks beyond the chemicals themselves by referencing them to their geographic and meteorological setting.

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Supporting Information Available

Parameter probability distribution function estimation and figures, reference tables, and additional tables and figures showing selected results. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Peterson, R. K. D.; Hulting, A. N. G. A comparative ecological risk assessment for herbicides used on spring wheat: the effect of glyphosate when used within a glyphosate-tolerant wheat system. *Weed Sci.* **2004**, *52*, 834–844.

(2) Loll, P.; Moldrup, P. Stochastic analyses of field-scale pesticide leaching risk as influenced by spatial variability in physical and biochemical parameters. *Water Resour. Res.* **2000**, *36*, 959–970.

(3) Lindahl, A. M. L.; Kreuger, J.; Stenstrom, J.; Gardenas, A. I.; Alavi, G.; Roulier, S.; Jarvis, N. J. Stochastic modeling of diffuse pesticide losses from a small agricultural catchment. *J. Environ. Qual.* **2005**, *34*, 1174–1185.

(4) Soutter, M.; Musy, A. Coupling 1D Monte-Carlo simulations and geostatistics to assess groundwater vulnerability to pesticide contamination on a regional scale. *J. Contam. Hydrol.* **1998**, *32*, 25–39.

(5) Huber, A.; Bach, M.; Frede, H. G. Modeling pesticide losses with surface runoff in Germany. *Sci. Total Environ.* **1998**, *223*, 177–191.

(6) Probst, M.; Berenzen, N.; Lentzen-Godding, A.; Schulz, R. Scenario-based simulation of runoff-related pesticide entries into small streams on a landscape level. *Ecotoxicol. Environ. Safety* **2005**, *62*, 145–159.

(7) Nystrom, B.; Bjornsater, B.; Blanck, H. Effects of sulfonylurea herbicides on non-target aquatic micro-organisms - Growth inhibition of micro-algae and short-term inhibition of adenine and thymidine incorporation in periphyton communities. *Aquat. Toxicol.* **1999**, *47*, 9–22.

(8) Okamura, H.; Piao, M.; Aoyama, I.; Sudo, M.; Okubo, T.; Nakamura, M. Algal growth inhibition by river water pollutants in the agricultural area around Lake Biwa, Japan. *Environ. Pollut.* **2002**, *117*, 411–419.

(9) Huang, X.; Fong, S.; Deanovic, L.; Young, T. M. Toxicity of herbicides in highway runoff. *Environ. Toxicol. Chem.* **2005**, *24*, 2336–2340.

(10) Massoudieh, A.; Huang, X.; Young, T. M.; Marino, M. A. Modeling fate and transport of roadside-applied herbicides. *J. Environ. Eng.* **2005**, *131*, 1057–1067.

(11) Huang, X.; Young, T. M. *Evaluation of Factors Controlling Herbicide Runoff To Surface Water*; University of CA: Davis, CA, 2005.

(12) Huang, X.; Pedersen, T.; Fischer, M.; White, R.; Young, T. M. Herbicide runoff along highways. 1. Field observations. *Environ. Sci. Technol.* **2004**, *38*, 3263–3271.

(13) Tomlin, C.; *The Pesticide Manual: a World Compendium*; 11th ed.; British Crop Protection Council Publications: Farnham, U.K., 1997.

(14) Vogue, P. A.; Kerle, E. A.; Jenkins, J. J. OSU Extension Pesticide Properties Database, 1994; http://ace.orst.edu/info/npic/pp-dmove.htm; Accessed 2/2006.

(15) Roberts, T. R.; Hutson, D. H. *Metabolic Pathways of Agrochemicals*; Royal Society of Chemistry: Cambridge, U.K., 1998.

(16) Pesticide Action Network North America. PAN Pesticides Database, 2006. http://www.pesticideinfo.org/; Accessed 9/2005.

(17) United States Department of Agriculture, Agricultural Research Service. ARS Pesticide Properties Database, 1995; http://www.ars.usda.gov/SP2UserFiles/ad_hoc/12755100DatabaseFiles/PesticidePropertiesDatabase/IndividualPesticideFiles/MSMA.TXT; Accessed 9/2007.

(18) U.S. Environmental Protection Agency. ECOTOXicology Database System, Version 4.0, 2006; http:/www.epa.gov/ecotox/; Accessed 3/2006.

(19) Information Ventures Inc. Mefluidide pesticide fact sheet. U.S. Department of Agriculture, 1995; http://www.pesticideinfo.org/references/83601-83–6usda%20.doc.

(20) Syngenta Crop Protection UK Ltd. Fusilade MAX Product Label, 2002; http://www.fluorideaction.org/pesticides/msds/fluazifop-p-butyl.product.use.fusilade.max.pdf.

(21) Caltrans Storm Water Program Annual Report: Fiscal Year 2003–2004; California Department of Transportation: Sacramento, CA, 2005.

(22) Hanley, T. R.; Thompson, D. J.; Palmer, A. K.; Beliles, R. P.; Schwetz, B. A. Teratology and reproduction studies with Triclopyr in the rat and rabbit. *Fundam. Appl. Toxicol.* **1984**, *4*, 872–882.

(23) U.S. Environmental Protection Agency Office of Pesticide Programs. Reregistration eligibility decision document: Triclopyr; U.S. Government Printing Office: Washington, DC, 1998.

(24) Stevens, J. T.; Sumner, D. D. Herbicides. In *Handbook of Pesticide Toxicology*; Hayes, W. J., Laws, E. R., Eds.; Academic Press: New York, 1991; pp 10–88.

(25) Chevron Chemical Company. Diquat herbicide h/a for aquatic plant treatment; Agricultural Chemicals Division, 1986.

(26) Weed Science Society of America *Herbicide Handbook*, 7th ed. Champaign, IL, 1994.

(27) U.S. Environmental Protection Agency Report of the food quality protection act FQPA) tolerance reassessment progress and risk management decision (TRED) for Fluazifop-P-butyl; USEPA: Washington, DC, 2005.

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