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Comparing ecological risks of pesticides: the utility of a Risk Quotient ranking approach across refinements of exposure

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Abstract: Environmental risk assessment of pesticides and other chemicals often uses the Risk Quotient (RQ) method to characterize risk quantitatively. An RQ is calculated by dividing an environmental exposure value by a toxicity end-point value. Tier 1 RQs, which are characterized by highly conservative toxicity and exposure assumptions, are used primarily for screening out negligible risks in regulatory decision making. It has been argued that the tier 1 RQ approach is valuable for making direct comparisons of quantitative risk between pesticides. However, an outstanding question is whether relative risks among pesticides would change if refinements of exposure are incorporated into the RQ calculations. This study tested that hypothesis. Aquatic ecological risk assessments were conducted for 12 herbicide and 12 insecticide active ingredients used on agricultural crops in the USA. The pesticides were chosen because surface-water monitoring data for them were available as part of the United States Geological Survey's National Water-Quality Assessment Program (NAWQA). Ecological receptors and effects evaluated were aquatic non-vascular plants (acute risk), aquatic vertebrates (acute risk) and aquatic invertebrates (acute risk) for the herbicides and aquatic vertebrates (acute and chronic risk) and aquatic invertebrates (acute and chronic risk) for the insecticides. The data indicate that there were significant statistical correlations between numerical rankings of tier 1 RQs and RQs using refined environmental exposures. The results support the hypothesis that numerical ranking of RQs for the purpose of comparing potential ecological risks is a valid approach because the rankings are significantly correlated regardless of the degree of exposure refinement.

Keywords: pesticide exposure; pesticide toxicity; comparative risk assessment; risk ranking

1 INTRODUCTION

Environmental risk assessment of pesticides and other chemicals often uses the Risk Quotient (RQ) method to express risk quantitatively. An RQ typically is calculated by dividing an environmental exposure value by a toxicity end-point value. Therefore, the RQ is a ratio of exposure to effect. The RQ then can be used by risk analysts and other decision makers to assess whether the value exceeds any predetermined threshold levels of concern.

Several methods have been presented for the purpose of making comparisons of environmental risk among pesticides. Most approaches have focused primarily on toxicity comparisons.[1–3] Maud *et al.*[4] observed poor correlations between five ranking methods of 133 pesticides when those rankings were based on toxicological data only. Finizio *et al.*[5] incorporated physico-chemical properties and environmental fate considerations into a pesticide rating system. Peterson and Hulting[6] argued that approaches based on toxicity comparisons alone are more limited and less accurate than incorporating environmental exposures and integrating them with toxicity. Therefore, they evaluated ecological risks of spring wheat herbicides by comparing tier 1 RQs for several ecological end-points. Tier 1 RQs, which are characterized by highly conservative toxicity and exposure assumptions, are used primarily for screening out negligible risks in regulatory decision making. The methodology employed by Peterson and Hulting[6] is similar to approaches used by the United States Environmental Protection Agency (USEPA) to evaluate petitions for reduced risk represented by the registration of new pesticide active ingredients.[7]

Because of its standardized effects (toxicity) and exposure assumptions, Peterson and Hulting[6] argued that the tier 1 RQ approach was valuable for making direct comparisons of quantitative risks between pesticides. However, an outstanding question as a result of their study was whether relative risks

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among pesticides would change if refinements of exposure were incorporated into the RQ calculations. Therefore, Peterson and Hulting[6] hypothesized that relative risks or rankings between pesticides would be proportionally similar regardless of tier. Consequently, the primary objective of this study was to test that hypothesis.

2 METHODOLOGY

Aquatic ecological risk assessments were conducted for 12 herbicide and 12 insecticide active ingredients used on agricultural crops in the USA. The herbicide active ingredients were 2,4-dichlorophenoxy acetic acid (2,4-D), alachlor, atrazine, bromoxynil, dicamba, diuron, ethalfluralin, MCPA, metribuzin, thiobencarb, triallate and trifluralin and the insecticide active ingredients were azinphos-methyl, carbaryl, carbofuran, chlorpyrifos, diazinon, disulfoton, ethoprop, malathion, methomyl, parathion-methyl, oxamyl and permethrin. These active ingredients were chosen because surface-water monitoring data for them were available as part of the United States Geological Survey's National Water-Quality Assessment Program (NAWQA).[8] Further, the pesticides represent a variety of toxicological mode-of-action classes (especially for the herbicides).

Aquatic ecological effects, exposures and risks were evaluated in this study. Ecological receptors and effects evaluated were aquatic non-vascular plants (acute risk), aquatic vertebrates (acute risk) and aquatic invertebrates (acute risk) for the herbicide active ingredients and aquatic vertebrates (acute and chronic risk) and aquatic invertebrates (acute and chronic risk) for the insecticide active ingredients.

For all ecological receptors, the most sensitive toxicity end-points which were publicly available were used for this assessment. Data sources for toxicity for each ecological receptor are referenced in each table.

2.1 Toxicity

2.1.1 Non-target aquatic plants

Toxicological effects for the green alga *Selenastrum capricornutum* Printz (a non-vascular plant surrogate species) were used in this assessment for the herbicides. For non-endangered aquatic plant species, the EC_{50} (50% growth inhibition) was used as the toxicological end-point.[9]

2.1.2 Aquatic invertebrates

Acute toxicities of pesticides to waterflea (*Daphnia magna* Straus) were used in this assessment. This species traditionally has been the preferred test organism to assess freshwater invertebrate toxicity and risk from pesticides. The 48- or 96-h EC_{50} (immobilization of 50% of the individuals) typically is used as the acute toxicity end-point.[10] The 21-day lowest-observed-effect-concentration (LOEC) typically is used as the chronic toxicity end-point.[11]

2.1.3 Aquatic vertebrates

Acute toxicities of pesticides to the rainbow trout, *Oncorhynchus mykiss* (Walbaum) (a cold-water surrogate species), and the bluegill sunfish, *Lepomis macrochirus* Rafinesque (a warm-water surrogate species), were used. These two species historically have been used to establish the toxicity of a pesticide active ingredient to aquatic fish. The 96-h LC_{50} was used as the acute toxicity end-point.[12] The lowest LC_{50} for each pesticide from either fish species was used as the toxicological end-point in the risk characterization. The LOEC from the fish early-stage toxicity study was used as the toxicity end-point.[13]

2.2 Exposure

The model, the Generic Expected Environmental Concentration Program (GENEEC v. 2.0), was used in this assessment to provide conservative estimates of surface-water concentrations (tier 1) of the pesticides.[14] The model was developed by the USEPA and primarily uses the chemical application rate, soil adsorption partition coefficient and degradation half-life values to estimate runoff from a 10-ha field into a 1 ha by 2 m deep static pond. The model calculates conservative or high-end exposure values following pesticide application to a highly erosive and steep upland slope, with heavy rainfall occurring within 2 days. GENEEC calculates both acute and chronic generic expected environmental concentration values. It considers reduction in dissolved pesticide concentration due to adsorption of pesticide to soil or sediment, incorporation, degradation in soil before wash-off to a water body, direct deposition of spray drift into the water body and degradation of the pesticide within the water body.

For this assessment, maximum agricultural crop single-use application rates for each pesticide, soil adsorption coefficient (K_{oc}), aerobic soil degradation half-life, water solubility, hydrolysis, photolysis and aerobic aquatic metabolic half-life values were used as inputs in the model. The physico-chemical properties were obtained from the United States Department of Agriculture Pesticide Properties Database[15] or from each pesticide's Material Safety Data Sheet (MSDS). All applications of pesticides were assumed to occur via standard ground application equipment. Peak, 21-day and 60-day expected environmental concentration values were used in this study.

Refined estimates of pesticide concentrations in surface water were obtained from the NAWQA online data warehouse.[16] As part of the NAWQA program, numerous pesticides and pesticide degradation products are analyzed in surface-water samples collected at 162 sites in 42 river basins (NAWQA study units) located throughout the USA. (See Martin *et al.*[17] for details of analytical and sampling methodology.) All data on the database are provisional and subject to change.

Pesticide concentration data used in this study were from samples obtained from 1991 through 30

September 2003. Data were collected at discrete time intervals each year only from streams near agricultural sites. Only data greater than reporting limits (limits of quantitation) for each pesticide and site were used to determine the mean and maximum concentrations. Insecticide concentrations greater than the reporting limit were obtained from the following 24 States: Arizona, California, Colorado, Connecticut, Delaware, Florida, Georgia, Idaho, Maryland, Minnesota, Montana, North Carolina, Nebraska, New Mexico, New York, Ohio, Oregon, Pennsylvania, Tennessee, Texas, Virginia, Washington, Wisconsin and West Virginia. Herbicide concentrations greater than the reporting limit were obtained from the same 24 States in addition to the following eight States: Massachusetts, North Dakota, New Hampshire, New Jersey, Nevada, South Carolina, Utah and Vermont.

2.3 Risk characterization

Ecological risks in this study were assessed by integrating toxicity and exposure. To accomplish this, the Risk Quotient (RQ) method was used. For each ecological receptor, an RQ was calculated by dividing the estimated or actual environmental concentration by the appropriate toxicity end-point. The toxicity end-points for each ecological receptor and pesticide environmental concentration estimates are discussed above.

For each pesticide type (herbicide or insecticide) and aquatic risk type, toxicities and the three RQs based on refinements of estimated and actual environmental exposures were ranked numerically from highest toxicity or RQ to lowest. The numerical rankings were then subjected to Spearman's rank correlation analysis[18] (PROC CORR, SAS v. 9.0) to determine if rankings were statistically different between the types of rankings.

3 RESULTS

Numerical rankings of RQs using tier 1, NAWQA maximum and NAWQA mean environmental concentrations for most types of aquatic organism risks were significantly correlated (Tables 1 and 2). This indicates that there was strong agreement between tier 1 RQs and RQs using actual pesticide environmental monitoring data. Also, numerical rankings of toxicity were significantly correlated with the RQ rankings (Table 1). This was not surprising given that the toxicity value is the denominator for all RQs evaluated in this study.

Only one acute risk ranking comparison (toxicity and tier 1 rank for herbicides and waterflea) was not significantly correlated (Table 1). However, several chronic risk ranking comparisons for insecticides were not significantly correlated (Table 2).

As expected, RQs based on tier 1 exposure assumptions were greater than RQs based on maximum or mean exposure values from NAWQA surface-water monitoring data (Tables 3–5). Reductions in RQs based on surface-water monitoring values compared with tier 1 values were substantial. However, the reductions were highly variable depending on the specific pesticide. Indeed, reductions ranged from 1.8- to 618-fold for NAWQA maximum values and from 45.6- to 2,802-fold for NAWQA mean values (Tables 6 and 7). Clearly, reductions in exposure and RQs are not proportionately similar among active ingredients as exposure estimates are refined. This is not unexpected because of differences among

Table 1. Spearman's rank correlation values between pesticide risk ranking approaches for aquatic organism acute risks[a]

	Tier 1	NAWQA maximum	NAWQA mean
Herbicides-green algae			
Toxicity	0.937***	0.902***	0.888***
Tier 1		0.916***	0.944***
NAWQA maximum			0.979***
Herbicides — fish			
Toxicity	0.916***	0.741**	0.832***
Tier 1		0.755**	0.853***
NAWQA maximum			0.867***
Insecticides — fish			
Toxicity	0.888***	0.664*	0.902***
Tier 1		0.720**	0.825***
NAWQA maximum			0.664*
Herbicides — waterflea			
Toxicity	0.552	0.587*	0.657*
Tier 1		0.937***	0.972***
NAWQA maximum			0.965***
Insecticides — waterflea			
Toxicity	0.811**	0.580*	0.881***
Tier 1		0.804**	0.888***
NAWQA maximum			0.657*

[a] * $P \leq 0.05$;
** $P \leq 0.01$;
*** $P \leq 0.001$.

Table 2. Spearman's rank correlation values between insecticide risk ranking approaches for chronic aquatic organism risks[a]

	Tier 1	NAWQA maximum	NAWQA mean
Insecticides — waterflea			
Toxicity	0.462[a]	0.410	0.725**
Tier 1		0.573*	0.482
NAWQA maximum			0.504
Insecticides — fish			
Toxicity	0.350	0.480	0.799**
Tier 1		0.706**	0.406**
NAWQA maximum			0.545

[a]* $P \le 0.05$;
** $P \le 0.01$.

pesticides in application rates and use patterns. In this assessment, maximum application rates for agricultural crops were used as input assumptions for the GENEEC model. The NAWQA surface-water monitoring data reflect values based on numerous application rates and use patterns throughout the USA.

3.1 Location analysis

Analyses also were conducted to determine if toxicity rankings and RQ rankings were affected by specific location. Maximum and mean NAWQA pesticide data were used for locations in which surface-water concentrations were greater than recording limits for 10 or more insecticides or herbicides. For herbicides, those locations were Orestimba Creek at River Road, Crows Landing, Stanislaus County, California and Granger Drain, Granger, Yakima County, Washington. For insecticides, only the Orestimba Creek location could be used. Ecological effects end-points evaluated were green algae for herbicides and waterflea for insecticides. The results reveal that rankings of RQs using tier 1, NAWQA maximum and NAWQA mean environmental concentrations for herbicides and green algae and insecticides and waterflea were significantly correlated (Table 8).

3.2 Toxicity rankings and low use-rate insecticides

With the exception of permethrin, the 24 herbicide and insecticide active ingredients evaluated have relatively high application rates ($\mathrm{g\,AI\,ha^{-1}}$). These high application rates may contribute to surface-water loading of pesticides and therefore may be responsible for the statistically significant correlation between rankings based on toxicity and RQ. Consequently, the correlation of numerical rankings between toxicity and RQs may not be statistically significant when also considering pesticides with low application rates. Unfortunately, this hypothesis is difficult to test. Many pesticides with low application rates have been registered only relatively recently. Therefore, publicly available information on ecotoxicity is limited. Further, concentrations of these pesticides in surface water either have not been detected above recording limits or they are not currently being detected at quantifiable levels. To evaluate whether application rates have an effect on the rankings, we analyzed toxicity and tier 1 rankings for the following 12 insecticides: azinphos-methyl, bifenthrin, carbaryl, chlorpyrifos, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, malathion, methomyl, permethrin and spinosad. Seven of the insecticides (bifenthrin, cyfluthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, permethrin and spinosad) have low maximum application rates compared with the other five insecticides. Of the low-rate insecticides, only permethrin had surface-water concentrations above recording limits. Therefore, only toxicity and tier 1 rankings were compared.

The results indicate that numerical rankings were not statistically correlated (Spearman correlation coefficient $= 0.343$; $P = 0.276$). This suggests that, for low-rate pesticides, rankings based solely on toxicity may not be useful to predict relative risks among pesticides. Further, these results support the importance of incorporating environmental exposure into comparisons of pesticide risk.

3.3 Probabilistic analysis

An analysis also was conducted to determine if RQ rankings based on Monte Carlo simulations of toxicity and exposure probabilities were correlated with other toxicity and RQ rankings. Monte Carlo simulations were conducted for both the 12 herbicides and 12 insecticides. For each pesticide, probability density functions were determined for both toxicity and environmental exposure. Toxicity values were obtained from the USEPA One-Liner Database.[19] All non-target aquatic vertebrate acute toxicity data (LC_{50}) were used to produce probability density functions. This included data for freshwater, marine and estuarine fish species. Acute toxicity to fish was chosen as the effects end-point because testing on several species allowed for the development of probability density functions. Environmental exposure values were obtained from the NAWQA online data warehouse.[16] For each pesticide, all values greater than the reporting limit over all locations were used to produce probability density functions. We used Monte Carlo analysis (Crystal Ball 2000™ v. 5.2; Decisioneering, Denver, CO, USA) to perform 5000 iterations for distributional analysis using the input probability density functions described above for each pesticide. The software model calculated 5000 RQs by randomly selecting a value from the distributions of each variable based on its probability of occurrence. The RQs at the 90th percentile of occurrence for each pesticide (simulation model output) were then ranked

Table 3. Non-target aquatic organism environmental concentrations, Risk Quotients and rankings for herbicides (acute exposure and risk)

Active ingredient	Application rate (g AI ha^{-1})	Peak EEC (ppb)[a]	Sign[b]	EC_{50} (ppb)[c]	RQ[d]	NAWQA maximum (ppb)	RQ	NAWQA mean (ppb)	RQ	Toxicity rank	Tier 1 rank	NAWQA maximum rank	NAWQA mean rank	Toxicity Data Source
Green algae														
2,4-D	367	86.38		33,200	0.0026	15	0.0005	0.407	0.00001	11	11	10	11	19
Alachlor	642	109.42		1.64	66.7195	38.2	23.2927	0.232	0.1415	1	2	1	2	20
Atrazine	734	189.8		49	3.8735	76	1.551	0.709	0.0145	7	5	3	3	21
Bromoxynil	92	5.74		51	0.1126	0.93	0.0182	0.126	0.0025	8	8	7	7	22
Dicamba	367	107.91	>	3,700	0.0292	0.68	0.0002	0.136	0.00004	10	10	11	10	19
Diuron	1101	206.04		2.4	85.85	14	5.8333	0.465	0.1938	2	1	2	1	23
Ethalfluralin	312	14.7		25.3	0.581	0.36	0.0142	0.037	0.0015	6	7	8	8	19
MCPA	239	62.01		122,000	0.0005	0.68	0.00001	0.16	0.000001	12	12	12	12	19
Metribuzin	367	108.47		20.8	5.2149	3.88	0.1865	0.092	0.0044	5	4	5	4	19
Thiobencarb	734	99.54		17	5.8553	0.93	0.0547	0.061	0.0036	4	3	6	6	24
Triallate	826	11.02		140	0.0787	0.65	0.0046	0.031	0.0002	9	9	9	9	19
Trifluralin	367	15.37		7.52	2.0439	1.74	0.2314	0.029	0.0039	3	6	4	5	25
Waterflea														
2,4-D	367	86.38		54	1.5997	15	0.2778	0.407	0.0075	3	1	1	1	19
Alachlor	642	109.42		7,700	0.0142	38.2	0.005	0.232	0.00003	9	8	6	7	19
Atrazine	734	189.8		49,000	0.0039	76	0.0016	0.709	0.00001	10	9	8	9	19
Bromoxynil	92	5.74		32	0.1794	0.93	0.0291	0.126	0.0039	2	3	2	2	22
Dicamba	367	107.91	>	110,000	0.001	0.678	0.00001	0.136	0.000001	11	10	11	11	19
Diuron	1101	206.04		1,400	0.1472	14	0.01	0.465	0.0003	7	4	3	5	23
Ethalfluralin	312	14.7		18,100	0.0008	0.36	0.00002	0.037	0.000002	1	11	10	10	19

MCPA	239	62.01	>	180,000	0.0003	0.68	0.000003	0.16	0.000001	12	12	12	12	19
Metribuzin	367	108.47		4,180	0.026	3.88	0.0009	0.092	0.00002	8	7	9	8	19
Thiobencarb	734	99.54		101	0.9855	0.93	0.0092	0.061	0.0006	5	2	4	3	24
Triallate	826	11.02		91	0.1211	0.65	0.0071	0.031	0.0003	4	5	5	4	26
Trifluralin	367	15.37		560	0.0275	1.74	0.0031	0.029	0.00005	6	6	7	6	19
Fish														
2,4-D	367	86.38		110,000	0.0008	15	0.0001	0.407	0.000004	11	11	9	9	19
Alachlor	642	109.42		1,800	0.0608	38.2	0.0212	0.232	0.0001	6	6	2	6	20
Atrazine	734	189.8		4,500	0.0422	76	0.0169	0.709	0.0001	8	7	4	5	19
Bromoxynil	92	5.74		53	0.1083	0.93	0.0176	0.126	0.0024	3	4	3	1	22
Dicamba	367	107.91	>	130,000	0.0008	0.678	0.00001	0.136	0.000001	12	10	12	12	19
Diuron	1101	206.04		1,950	0.1057	14	0.0072	0.465	0.0002	7	5	6	4	19
Ethalfluralin	312	14.7		32	0.4594	0.36	0.0113	0.037	0.0012	1	1	5	2	19
MCPA	239	62.01		91,000	0.0007	0.68	0.00001	0.16	0.000002	10	12	11	11	19
Metribuzin	367	108.47		42,000	0.0026	3.88	0.00009	0.092	0.000002	9	9	10	10	27
Thiobencarb	734	99.54		560	0.1778	0.93	0.0017	0.061	0.0001	4	3	7	7	24
Triallate	826	11.02		1,200	0.0092	0.65	0.0005	0.031	0.00003	5	8	8	8	26
Trifluralin	367	15.37		41	0.3749	1.74	0.0424	0.029	0.0007	2	2	1	3	19

[a] EEC, estimated environmental concentration.
[b] Toxicity sign '>' signifies that the EC_{50} or LC_{50} is greater than the highest dose tested.
[c] Toxicity end-point; EC_{50} for green algae and waterflea, LC_{50} for fish.
[d] RQ (Risk Quotient) = EEC or actual concentration ÷ toxicity end-point.

Table 4. Non-target aquatic organism environmental concentrations, Risk Quotients and rankings for insecticides (acute exposure and risk)

Active ingredient	Application rate (g AI ha^{-1})	Peak EEC (ppb)[a]	EC_{50} (ppb)[b]	RQ[c]	NAWQA maximum (ppb)	RQ	NAWQA mean (ppb)	RQ	Toxicity rank	Tier 1 rank	NAWQA maximum rank	NAWQA mean rank	Toxicity data source
Waterflea													
Azinphos-methyl	367	49.25	1.13	43.5841	3.37	2.9823	0.09	0.0751	6	5	5	4	28
Carbaryl	1377	283.02	2.77	102.1733	33.5	12.0939	0.1	0.0365	7	4	1	7	19
Carbofuran	257	68.4	29	2.3587	32.2	1.1103	0.03	0.0011	10	11	7	11	19
Chlorpyrifos	642	22.99	0.1	229.9	0.4	4.01	0.02	0.2	1	2	3	2	19
Diazinon	734	68.07	0.5	136.14	3.81	7.62	0.06	0.114	4	3	2	3	19
Disulfoton	551	32.92	13	2.5323	3.34	0.2569	0.33	0.0252	9	10	9	9	29
Ethoprop	2203	575.86	44	13.0877	5.75	0.1307	0.1	0.0023	11	8	11	10	30
Malathion	1147	34.2	1	34.2	1.14	1.14	0.03	0.032	5	6	6	8	31
Methomyl	165	44.14	7.6	5.8079	3	0.3947	0.37	0.0488	8	9	8	6	32
Parathion-methyl	551	113.52	0.14	810.8571	0.52	3.7429	0.09	0.6429	3	1	4	1	33
Oxamyl	367	53.49	420	0.1274	0.16	0.0004	0.1	0.0002	12	12	12	12	19
Permethrin	73	1.86	0.11	16.9091	0.019	0.1727	0.008	0.0727	2	7	10	5	19
Fish													
Azinphos-methyl	367	49.25	4.1	12.0122	3.37	0.822	0.09	0.0207	4	2	1	1	28
Carbaryl	1377	283.02	760	0.3724	33.5	0.0441	0.1	0.0001	10	9	6	10	19
Carbofuran	257	68.4	88	0.7773	32.2	0.366	0.03	0.0003	6	7	2	8	19
Chlorpyrifos	642	22.99	1.8	12.7722	0.401	0.2228	0.02	0.0111	2	1	4	2	19
Diazinon	734	68.07	90	0.7563	3.81	0.0423	0.06	0.0006	7	8	7	6	19
Disulfoton	551	32.92	39	0.8441	3.34	0.0856	0.33	0.0084	5	6	5	4	29
Ethoprop	2203	575.86	300	1.9195	5.75	0.0192	0.1	0.0003	8	5	9	9	30
Malathion	1147	34.2	4	8.55	1.14	0.285	0.03	0.008	3	3	3	5	19
Methomyl	165	44.14	670	0.0659	3	0.0045	0.37	0.0005	9	11	10	7	32
Parathion-methyl	551	113.52	1,000	0.1135	0.524	0.0005	0.09	0.00009	11	10	11	11	33
Oxamyl	367	53.49	3,700	0.0145	0.16	0.00004	0.1	0.00003	12	12	12	12	19
Permethrin	73	1.86	0.79	2.3544	0.019	0.0241	0.008	0.0101	1	4	8	3	19

[a] EEC, estimated environmental concentration.

[b] Toxicity end-point; EC_{50} for waterflea, LC_{50} for fish.

[c] RQ (Risk Quotient) = EEC or actual concentration ÷ toxicity end-point.

Table 5. Non-target aquatic organism environmental concentrations, Risk Quotients and rankings for insecticides (chronic exposure and risk)

Active ingredient	Application rate (g AI ha^{-1})	Peak EEC (ppb)[a]	EC_{50} (ppb)[b]	RQ[c]	NAWQA maximum (ppb)	RQ	NAWQA mean (ppb)	RQ	Toxicity rank	Tier 1 rank	NAWQA maximum rank	NAWQA mean rank	Toxicity data source
Waterflea													
Azinphos-methyl	367	38.85	0.4	97.125	3.37	8.425	0.09	0.2123	7	7	5	6	28
Carbaryl	1377	251.21	1.5	167.4733	33.5	22.3333	0.1	0.0673	9	6	2	9	19
Carbofuran	257	57.39	27	2.1256	32.2	1.1926	0.03	0.0011	11	11	10	11	19
Chlorpyrifos	642	15.93	0.08	199.125	0.4	5.0125	0.02	0.25	3	4	6	5	19
Diazinon	734	61.98	0.32	193.6875	3.81	11.9063	0.06	0.1781	6	5	3	7	19
Disulfoton	551	15.61	0.07	223	3.34	47.7143	0.33	4.6857	1	1	1	1	29
Ethoprop	2203	530.46	2.4	221.025	5.75	2.3958	0.1	0.0421	10	2	8	10	30
Malathion	1147	5.4	0.1	54	1.14	11.4	0.03	0.32	4	8	4	4	31
Methomyl	165	22.76	0.8	28.45	3	3.75	0.37	0.4638	8	9	7	2	32
Parathion-methyl	551	51.72	0.25	206.88	0.52	2.096	0.09	0.36	5	3	9	3	33
Oxamyl	367	46.58	5,700	0.0082	0.16	0.00003	0.1	0.00002	12	12	12	12	19
Permethrin	73	0.9	0.08	11.25	0.02	0.2375	0.008	0.1	3	10	11	8	19
Fish													
Azinphos-methyl	367	26.19	420	0.0624	3.37	0.008	0.09	0.0002	8	8	6	9	28
Carbaryl	1377	190.95	680	0.2808	33.5	0.0493	0.1	0.0001	11	6	4	11	19
Carbofuran	257	59.43	6	9.905	32.2	5.3667	0.03	0.0052	2	1	1	2	19
Chlorpyrifos	642	9.21	2.1	4.3857	0.4	0.191	0.02	0.0095	1	2	2	1	19
Diazinon	734	10.82	550	0.0197	3.81	0.0069	0.06	0.0001	10	11	8	12	19
Disulfoton	551	17.37	420	0.0414	3.34	0.008	0.33	0.0008	8	9	7	5	29
Ethoprop	2203	120.47	54	2.2309	5.75	0.1065	0.1	0.0019	5	3	3	3	30
Malathion	1147	17.44	44	0.3964	1.14	0.026	0.03	0.0007	4	5	5	6	19
Methomyl	165	36.61	1,500	0.0244	3	0.002	0.37	0.0002	12	10	10	8	32
Parathion-methyl	551	81.2	80	1.015	0.52	0.0066	0.09	0.0011	6	4	9	4	33
Oxamyl	367	98.96	500	0.1979	0.16	0.0003	0.1	0.0002	9	7	12	10	19
Permethrin	73	0.516	28	0.0184	0.02	0.0007	0.008	0.0003	3	12	11	7	19

[a] EEC, estimated environmental concentration.
[b] Toxicity end-point; EC_{50} for waterflea, LC_{50} for fish.
[c] RQ (Risk Quotient) = EEC or actual concentration ÷ toxicity end-point.

Table 6. Reductions in RQ (aquatic organism acute risks)

Active ingredient	Tier 1 ÷ NAWQA maximum	RQ reduction (T1/maximum) (%)	Tier 1 ÷ NAWQA mean	RQ reduction (T1/mean) (%)
Herbicides				
2,4-D	5.8	82.63	212.2	99.53
Alachlor	2.9	65.09	471.6	99.79
Atrazine	2.5	59.96	267.7	99.63
Bromoxynil	6.2	83.80	45.6	97.80
Dicamba	159.2	99.37	793.5	99.87
Diuron	14.7	93.21	443.1	99.77
Ethalfluralin	40.8	97.55	397.3	99.75
MCPA	91.2	98.90	387.6	99.74
Metribuzin	28.0	96.42	1179.0	99.92
Thiobencarb	107.0	99.07	1631.8	99.94
Triallate	17.0	94.10	355.5	99.72
Trifluralin	8.8	88.68	530.0	99.81
Insecticides				
Azinphos-methyl	14.6	93.16	580.1	99.83
Carbaryl	8.4	88.16	2802.2	99.96
Carbofuran	2.1	52.92	2206.5	99.95
Chlorpyrifos	57.3	98.26	1149.5	99.91
Diazinon	17.9	94.40	1194.2	99.92
Disulfoton	9.9	89.85	100.4	99.00
Ethoprop	100.1	99.00	5701.6	99.98
Malathion	30.0	96.67	1068.8	99.91
Methomyl	14.7	93.20	119.0	99.16
Parathion-methyl	216.6	99.54	1261.3	99.92
Oxamyl	334.3	99.70	551.4	99.82
Permethrin	97.9	98.98	232.5	99.57

Table 7. Reductions in RQ (aquatic organism chronic risks)

Active ingredient	Tier 1 ÷ NAWQA maximum	RQ reduction (T1/maximum) (%)	Tier 1 ÷ NAWQA mean	RQ reduction (T1/mean) (%)
Waterflea				
Azinphos-methyl	11.5	91.33	457.6	99.78
Carbaryl	7.5	86.66	2487.2	99.96
Carbofuran	1.8	43.89	1851.3	99.95
Chlorpyrifos	39.7	97.48	796.5	99.87
Diazinon	16.3	93.85	1087.4	99.91
Disulfoton	4.7	78.60	47.6	97.90
Ethoprop	92.3	98.92	5252.1	99.98
Malathion	4.7	78.89	168.8	99.41
Methomyl	7.6	86.82	61.3	98.37
Parathion-methyl	98.7	98.99	574.7	99.83
Oxamyl	291.1	99.66	480.2	99.79
Permethrin	47.4	97.89	112.5	99.11
Fish				
Azinphos-methyl	7.8	87.13	308.5	99.68
Carbaryl	5.7	82.46	1890.6	99.95
Carbofuran	1.8	45.82	1917.1	99.95
Chlorpyrifos	23.0	95.65	460.5	99.78
Diazinon	2.8	64.79	189.8	99.47
Disulfoton	5.2	80.77	53.0	98.11
Ethoprop	21.0	95.23	1192.8	99.92
Malathion	15.3	93.46	545.0	99.82
Methomyl	12.2	91.81	98.7	98.99
Parathion-methyl	155.0	99.35	902.2	99.89
Oxamyl	618.5	99.84	1020.2	99.90
Permethrin	27.2	96.32	64.5	98.45

from highest RQ to lowest and compared with the other ranking types.

For both herbicides and insecticides, RQs based on Monte Carlo simulations were correlated to all other ranking types (Table 9). This suggests that even when probabilistic refinements in both toxicity and exposure are incorporated into the RQ calculation, the rankings are still significantly correlated to tier 1 RQs.

4 DISCUSSION

The results reported here support the hypothesis that numerical ranking of RQs for the purpose of comparing potential ecological risks is a valid approach because the rankings are significantly correlated regardless of the degree of exposure refinement. For the comparisons between tier 1, NAWQA maximum and NAWQA mean RQs,

Table 8. Spearman's rank correlation values between pesticide risk ranking approaches for specific locations[a]

	Tier 1	NAWQA maximum	NAWQA mean
Herbicides — green algae California			
Toxicity	0.981***	0.872***	0.836**
Tier 1		0.872***	0.818**
NAWQA maximum			0.918***
Herbicides — green algae Washington			
Toxicity	0.927***	0.927***	0.952***
Tier 1		0.939***	0.952***
NAWQA maximum			0.988***
Insecticides — waterflea California			
Toxicity	0.782**	0.782**	0.909***
Tier 1		0.936***	0.909***
NAWQA maximum			0.936***

[a] * $P \leq 0.05$;
** $P \leq 0.01$;
*** $P \leq 0.001$.

Table 9. Spearman's rank correlation values between pesticide risk ranking approaches for acute toxicity to fish[a]

	Tier 1	NAWQA maximum	NAWQA mean	MC 90th percentile[b]
Herbicides				
Toxicity	0.916***	0.741**	0.832***	0.874***
Tier 1		0.755**	0.853***	0.867***
NAWQA max.			0.867***	0.804**
NAWQA mean				0.923***
Insecticides				
Toxicity	0.888***	0.664*	0.902***	0.874***
Tier 1		0.720**	0.825***	0.818***
NAWQA max.			0.664*	0.713**
NAWQA mean				0.895***

[a]* $P \leq 0.05$;
** $P \leq 0.01$;
*** $P \leq 0.001$
[b] MC 90th percentile = Monte Carlo simulation at the 90th percentile.

the toxicity end-point was the same. Therefore, the correlations among RQ rankings also were correlations among exposure rankings. Although tier 1 exposure estimates based on GENEEC modeling are highly conservative, analysis of rankings with more refined exposure estimates revealed significant correlation.

Rankings based only on toxicity also were statistically correlated to the three RQ estimates. However, rankings based only on toxicity most likely are not as robust as rankings based on RQs, as the analysis based on low use-rate insecticides seems to indicate. Therefore, rankings based solely on toxicity should not be used or should be used with caution.

Even though the data indicate that tier 1 RQs can be used to rank numerically and compare ecological risks from pesticides, they cannot be used to estimate accurately the quantitative risk for an individual pesticide within a specific use and location scenario. This is because both hazard and exposure assumptions are highly conservative and therefore overestimate risk. This is evident by comparing RQs from this study based on tier 1 environmental exposure assumptions to RQs based on actual environmental exposures.

The assessment presented here potentially is limited because only refinements in RQs for non-target aquatic organisms were evaluated. A more robust analysis ideally should also include exposure and toxicity refinements associated with terrestrial systems. Unfortunately, actual pesticide residue data in terrestrial systems are largely lacking for most pesticides, making comparisons extremely difficult.

Despite the potential limitations of this analysis, the data support the initial hypothesis. Therefore, rankings among pesticides based on tier 1 RQs, especially for acute risks, should largely reflect RQs based on refined environmental exposure estimates and actual values. Consequently, in decisions involving comparisons among pesticides lower cost risk assessment approaches (such as tier 1 RQs) have utility and can be used with acceptable confidence.

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