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Fractal-Based Scaling and Scale-Invariant Dispersion of Peak Concentrations of Crop Protection Chemicals in Rivers

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A new regulatory approach is needed to characterize peak pesticide concentrations in surface waters over a range of watershed scales. Methods now in common use rely upon idealized edge-of-field scenarios that ignore scaling effects. Although some watershed-scale regulatory models are available, their complexity generally prevents them from being used during the pesticide registration decision process, even though nearly all exposure to both humans and aquatic organisms can occur only at this scale. The theory of fractal geometry offers a simpler method for addressing this regulatory need. Mandelbrot described rivers as "space-filling curves" (Mandelbrot, B. B. *The Fractal Geometry of Natur*e; Freeman: New York, 1983), a class of fractal objects implying two useful properties we exploit in this work. The first is a simple power-law relationship in which log−log plots of maximum daily concentrations as a function of watershed area tend to be linear with a negative slope. We demonstrate that the extrapolation of such plots down to smaller watersheds agrees with edge-of-field concentrations predicted using the Pesticide Root Zone Model, but only when the modeling results are properly adjusted for use intensity within the watershed. We also define a second useful property, "scale-invariant dispersion", in which concentrations are well described by a single analytical solution to the convective−dispersion equation, regardless of scale. Both of these findings make it possible to incorporate the effect of watershed scale directly into regulatory assessments.

Introduction

As part of the pesticide registration decision process, the U.S. EPA and other regulatory agencies around the world currently assess potential concentrations of crop protection chemicals and their degradates in surface water using conservative scenarios evaluated with mechanistic models. For instance, the Pesticide Root Zone Model (PRZM) and the Exposure Analysis Modeling System (EXAMS) model are used to estimate concentrations in a standardized farm pond for ecological risk assessments and in an index reservoir for drinking water assessments (*1*). Neither of these assessment methods considers potential scaling affects associated with watershed area. The watershed-scale regulatory models that are available, such as HSPF and SWAT, are not routinely used for pesticide registration decisions (*1*). Instead, PRZM is used to generate runoff estimates from a uniform agricultural field, and these edge-of-field runoff loadings are fed directly into a standard surface water body, which is simulated using the EXAMS model.

In the case of the farm pond, the surface water body is assumed to be a completely mixed body of constant volume. Although residues are introduced into the surface water body via runoff, the pond is assumed to have no water discharge, so pond residues remain until they degrade, adsorb to sediment, or volatilize. It is also assumed that there is conservative transport of runoff to the reservoir, without any losses or attenuation due to degradation or sorption. Although one could conceive of the existence of the farm pond scenario, such situations are actually quite rare.

These limitations become even more important for larger-scale drinking water assessments. The simplified hydrology along with conservative assumptions regarding use in the watershed, spray drift, and pesticide parameters result in maximum daily concentrations 2 or more orders of magnitude higher than actually observed in targeted drinking water monitoring studies (*2*). The objective of the present study is to explore new ways to include these scaling effects via the relatively new science of fractal geometry (*3*).

Fractal geometry (i.e., fractal theory) has been used to describe the spatial scaling behavior of environmental variables from microscales within soil pores to large river basins. Burrough (*4*) and Green and Erskine (*5*), for example, showed that several soil and landscape variables displayed fractal behavior at the field scale. Rodriguez-Iturbe and Rinaldo (*6*) showed how fractals have been applied to landscape and river geometries up to basin scales in a manner consistent with geomorphological properties for minimizing the total energy expenditure. In addition to the morphology, transient hydrologic responses can follow fractal relationships according to the theory they defined as the "geomorphological instantaneous unit hydrograph" (*7*), describing the travel-time distribution of water particles in rivers. It logically should follow that chemical concentrations would display similar fractal behavior. To our knowledge, however, fractals have not been previously applied to estimating pesticide concentrations in rivers.

Previous work on the scaling of pesticides in surface water has focused mainly on the effects of scale on annual total loads, in which it was found that annual loads of a relatively persistent pesticide were independent of scale, when expressed as a percentage of the amount applied annually (*8*). Similar work with less persistent products, however, found that such load percentages decreased with scale, as would be anticipated due to losses during transport (*9*). Baker and Richards (*10*) discussed the effect of scale on the pattern of concentrations in surface water, and they reported that higher peak concentrations were observed in smaller watersheds; however, they did not relate this behavior to fractal theory.

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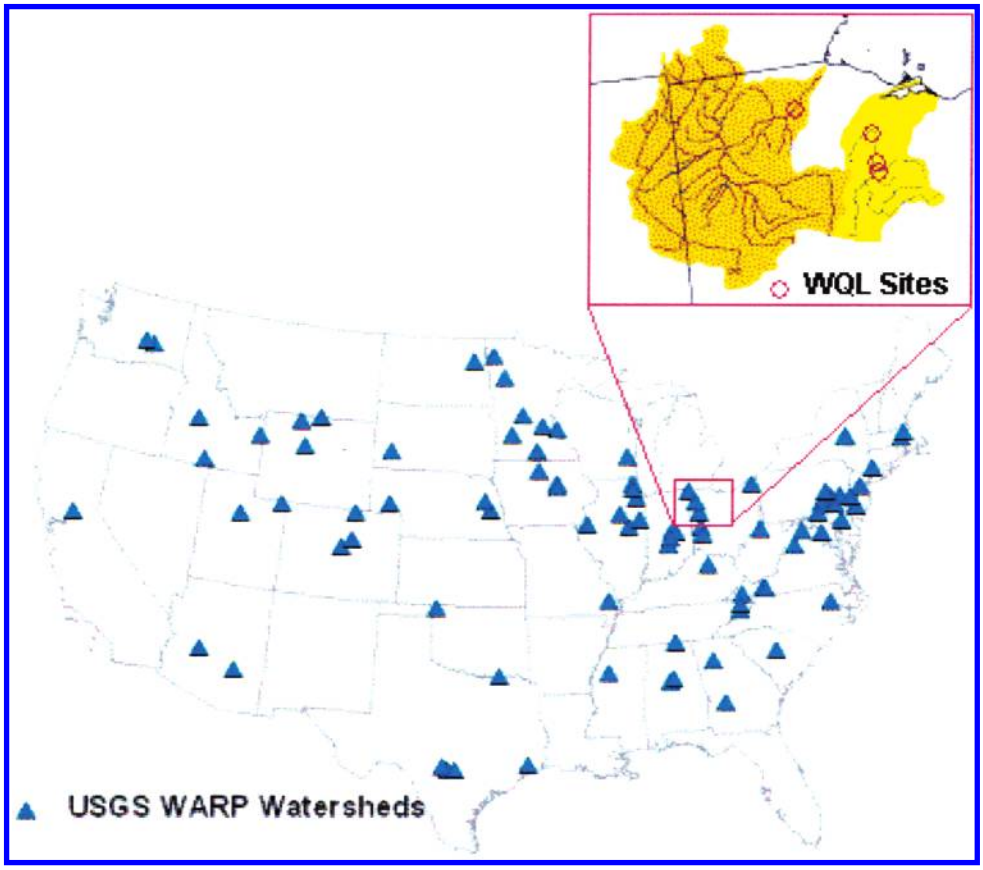

FIGURE 1. Blue triangles represent the centroids of 89 USGS watersheds included in this modeling. WARP is the name of a regression model being developed from these data by USGS. The inset map shows the four sites being monitored by the Heidelberg College Water Quality Laboratory (WQL) in Tiffin, OH.

Here, we will test the hypothesis that "peak" pesticide concentrations in rivers (defined as the maximum daily concentration within 1 year or the 99.7th percentile) scale with watershed area according to fractal theory, thus offering an improved method for estimating peak concentrations for regulatory purposes. We first present the data sources used in our study and then briefly describe the modeling theory and methodology. We conclude with a discussion of our observations and their regulatory consequence. A considerable amount of data and modeling methods investigated in this study cannot be included in the paper due to size constraints; however, they are available in the Supporting Information.

Data Sources

WQL Data Set. We studied two large monitoring data sets in the United States (Figure 1). The first (denoted the WQL data set) is from the Water Quality Laboratory of Heidelberg College in Tiffin, OH (*11*). The four rivers most intensively monitored by the WQL are shown in greater detail in Figure 2. For these four rivers, WQL has a temporally rich data set for a suite of more than a dozen pesticides from 1984 to present.

The WQL sampling program is stratified by season and flow, with sampling frequencies of several times daily during flow events in the spring and summer months, when pesticide concentrations are highest. Figure 3 contains an example of WQL data for the year 1996. This sampling regimen makes it possible to directly determine annual maximum daily concentrations (corresponding to a 99.7th percentile within 1 year) and lower quantiles, such as 95th and 90th. These three percentiles are given as a log−log plot versus watershed area for streamflow and a number of pesticides in Figure 4. The pesticide concentrations in Figure 4 are normalized to a use intensity of 1 kg/ha here and elsewhere in this paper based on estimation techniques explained more fully in the Supporting Information.

Some very important points emerge from the data in Figure 4. First, the 99.7th percentile (corresponding to maximum daily) concentrations and daily streamflows are 2−10 times higher than the 95th percentile concentrations and flows, depending on scale. Second, the 95th percentile concentrations and daily streamflows happen to be relatively independent of scale in these four watersheds. However, as described extensively by Baker and Richards (*10*), both peak concentrations and peak daily streamflows are strongly impacted by scale. In general, sharp peaks of short duration would be expected for small watersheds while broad peaks of longer duration would be expected for larger watersheds. This is also demonstrated by similar changes in the streamflows. These differences in hydrograph/chemograph shape help explain the changes in slope in the lines in Figure 4. As watershed area decreases, the maximum daily concentration (99.7th percentile) tends to increase, reflecting the higher peak concentrations. However, as watershed area decreases, the 90th percentile concentration decreases because of the sharper peak shape in the smaller watersheds.

Because of the large change in the use of the various chloroacetanilides during the 1990s, the graph of total chloroacetanilides (Figure 4h) may be more accurate than those for the individual products. In fact, the total value displays the expected scaling behavior while individual products may not, probably due to complementary errors in the use intensity estimates that were utilized in the normalization procedure.

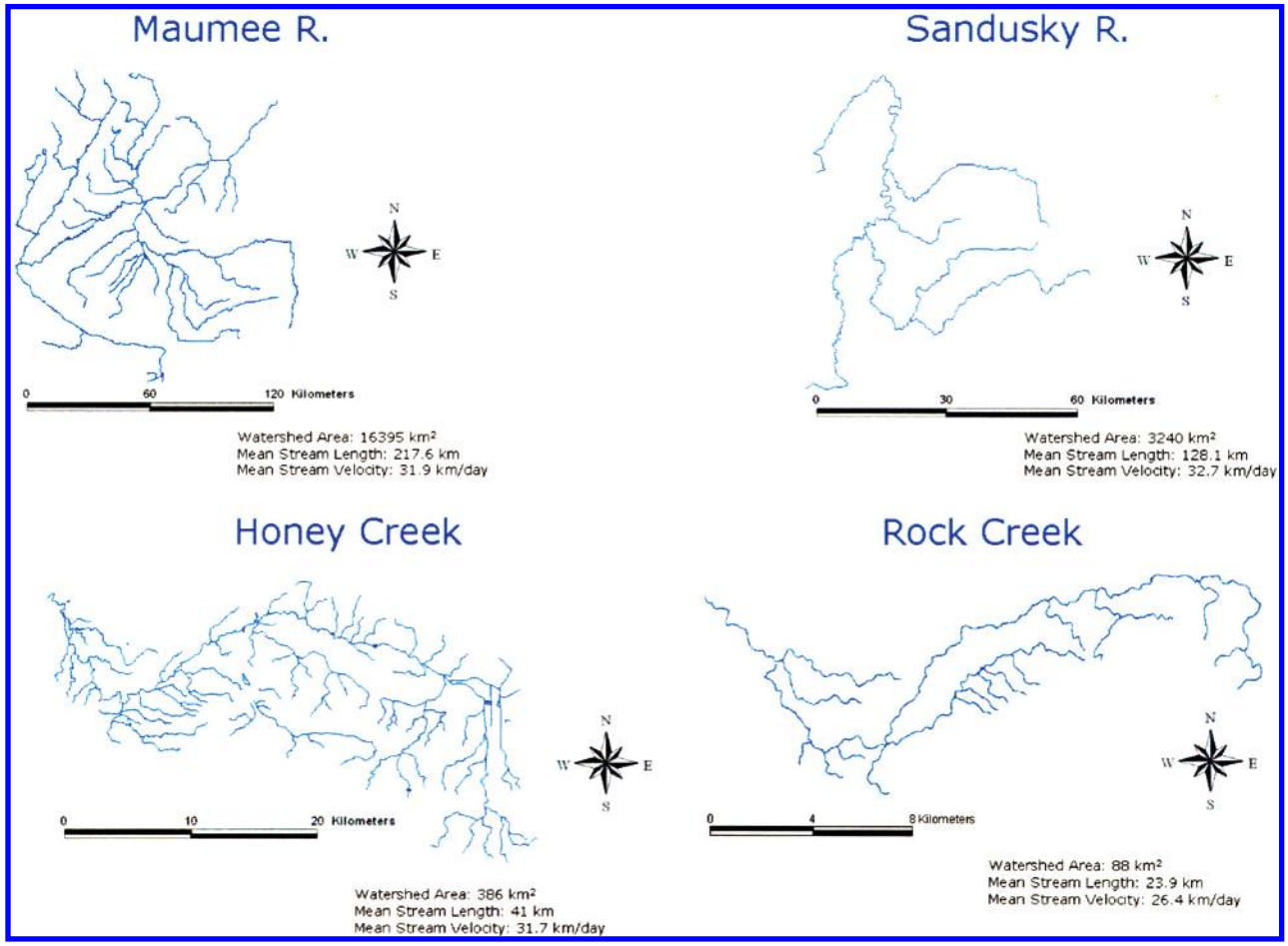

FIGURE 2. Maps show the stream networks upstream of four points being monitored by the Heidelberg College Water Quality Laboratory. The given mean stream length is the average of each branch shown here.

USGS Data Set. The other monitoring data set we studied is from an ongoing U.S. Geological Survey regression modeling study (*12*). It contains data from the USGS National Water Quality Assessment (NAWQA) Program and the National Stream Quality Accounting Network (NASQAN). The long-term goals of the NAWQA program are to describe the status and trends in the quality of a large, representative part of the nation's surface water and groundwater resources and to provide a sound, scientific understanding of the primary natural and human factors affecting the quality of these resources (*13*, *14*). NASQAN measures chemical concentrations in the nation's largest rivers.

Depth- and width-integrated samples were collected as part of the NAWQA program about every 1−3 weeks during the growing season and approximately monthly during the rest of the year. The NASQAN program collects samples approximately monthly with several additional samples collected during periods of high streamflow.

Modeling Methods

Estimating Maximum Daily Concentrations in the USGS Data Set. To estimate annual maximum daily concentrations (MDC) in the USGS data set, we sought to develop a regression equation relating MDC to lower observed quantiles of pesticide concentration (P95 and lower, if useful) and other available ancillary data. The regression method we developed is based on the reasonable assumption that the shape of the peaks in pesticide concentration should be similar to the shape of the peaks in the stream hydrograph. This is plainly suggested by the data in Figure 3. We call the sharpness of these peaks in daily streamflow hydrographs the "flashiness" and have defined a quantitative descriptor of this as the Richards path length (L_R). We define L_R as the total length of line segments connecting points on a hydrograph divided by the median flow ($\tilde{q}$) and time period monitored (t_N):

$$L_R = \frac{\sum_{t=1,N} \sqrt{(q_t - q_{t-1})^2 + (t_t - t_{t-1})^2}}{t_N * \tilde{q}} \qquad (1)$$

In this equation, the summation is carried out over all N times (t_t) for which streamflows (q_t) are measured. For the typical case in which we applied this equation (a year-long daily hydrograph), t_N is simply the number of days in the year and the second term within the radical is always unity. The appearance of median flow and time period monitored in the denominator provides normalization of this parameter with respect to the units used for streamflow and for the time period considered. We calculated Richards path length for all of the USGS watersheds and the four WQL watersheds (see Figure 5). It exhibits a power-law relationship with scale, but other variables (most likely soil runoff potential) introduce considerable scatter. Richards path length is correlated with the Hurst coefficient of temporal persistence (*15*), but the former offered improved explanatory power in the relationships tested here. Both provided far better fits than watershed area itself in the prediction of MDC. It should be noted that because the path length values shown in Figure 5 are based on daily average streamflow data, they understate the "true flashiness" of very small streams, which can exhibit sharp temporal variability on a time scale of less than 1 day. We merely point out this limitation and note that Richards path length is itself a fractal quantity in time whose value would

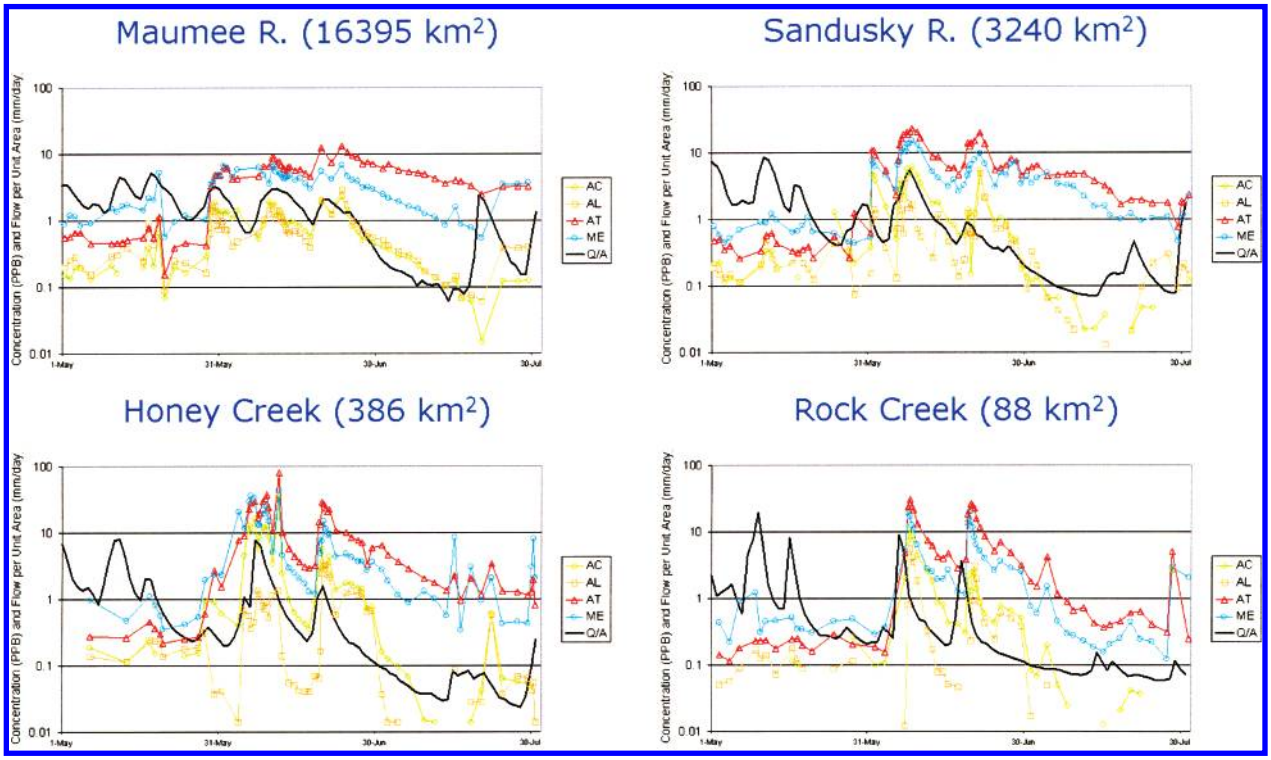

FIGURE 3. Surface water monitoring results from the Water Quality Laboratory. Each plot shows daily streamflow per unit area (Q/A) and concentrations of four herbicides: acetochlor (AC), alachlor (AL), atrazine (AT), and metolachlor (ME) during 1996, a high runoff year.

be found to increase as the time increment used in its determination is decreased.

We developed both pesticide-specific regression equations for MDC and regressions across multiple pesticides using combinations of the two common mobility and persistence parameters, K_{OC} (soil adsorption coefficient) and DT_{50} (50% dissipation time in soil). The atrazine-specific equation for MDC is

$$\log_{10}(\text{MDC} - \text{P95}) = 1.8 \times \log_{10}(\text{P95}) + 1.1 \times \log_{10}(L_R) - 0.75 \quad (2)$$

where P95 is the 95th percentile of atrazine concentration. R^2 for this regression was 0.68. Using this equation, we calculated atrazine MDC and plotted it as a function of watershed atrazine use intensity for the USGS data set (see Figure S2 in the Supporting Information). This figure suggests that atrazine MDC is directly proportional to use intensity except at very low atrazine use, where there appears to be a small level of background contamination, as evidenced by the non-zero *y*-intercept in the fitting equation. Similar models were obtained for other pesticides, and a pesticide-general model is given in the Supporting Information.

PRZM Modeling. The U.S. EPA computer model PRZM v 3.12 beta (*16*) was used to obtain estimated edge-of-field concentrations in runoff water and on eroded soil. Table S1 in the Supporting Information lists the compounds included in the simulations and the physical properties used for each. The simulations were conducted using 30 years (1961−1990) of daily meteorological data for Toledo, OH (*17*), assuming a single application per year at a rate of 1 kg/ha. This use rate was selected, rather than the maximum label rate, for simple convenience in order to avoid the need for subsequent normalization. The impact of this assumption is negligible due to the linear nature of the PRZM model (*16*).

To identify the appropriate soils for the PRZM simulations, the soils used for corn production in the 12 northeastern counties of Ohio (Defiance, Fulton, Hancock, Henry, Lucas, Ottawa, Paulding, Putnam, Sandusky, Seneca, Williams, and Wood) were examined. These counties include the watersheds in the WQL data set. The 1992 National Resources Inventory (*18*) was used to identify soils used for corn production in these counties. The NRI data listed 42 different soils as being associated with corn production. Of these, four soils (Hoytville, Blount, Toledo, and Mermill) accounted for 52% of the acreage. Soil property data for these soils were obtained from the SOILS-5 database (*19*). Selected properties are summarized in Table S2 of the Supporting Information.

For the PRZM simulations, the field was 1 ha in area, with a 2% slope and a 45-m hydraulic length. The Manning's roughness coefficient for overland flow as set at 0.014. The application date was assumed to be April 21 for all surface-applied compounds. Surface application without incorporation was simulated for all compounds except butylate, which was uniformly incorporated to 4 cm and had an earlier application date, April 18. All simulations assumed application to bare ground with no spray drift. Spray drift was not included due to the extremely small area occupied by river surfaces within these modeled watersheds, and the lack of evidence in the monitoring data for spray drift as a major contributor to surface water residues (Figure 3). We calculated daily edge-of-field concentrations by summing the total amount of pesticide in both dissolved and sorbed forms and assuming this completely dissolved in the amount of water associated with the runoff event. This neglects the effect of sedimentation that would typically reduce concentrations, and should therefore be viewed as providing an upper bound to the true dissolved concentration.

Fractal Modeling Theory. Any particular variable (v) that displays spatial scaling behavior may be said to "scale in distribution" such that the statistical moments (e.g., mean, variance and skewness) of the probability density function (pdf) of v can be represented at different scales by relatively simple equations and few parameters. In this case, we are addressing the temporal moments of concentration at each spatial scale. Rather than describing the entire pdf, however, our interest is focused on only the more extreme quantiles of the distribution that can be estimated from given detection

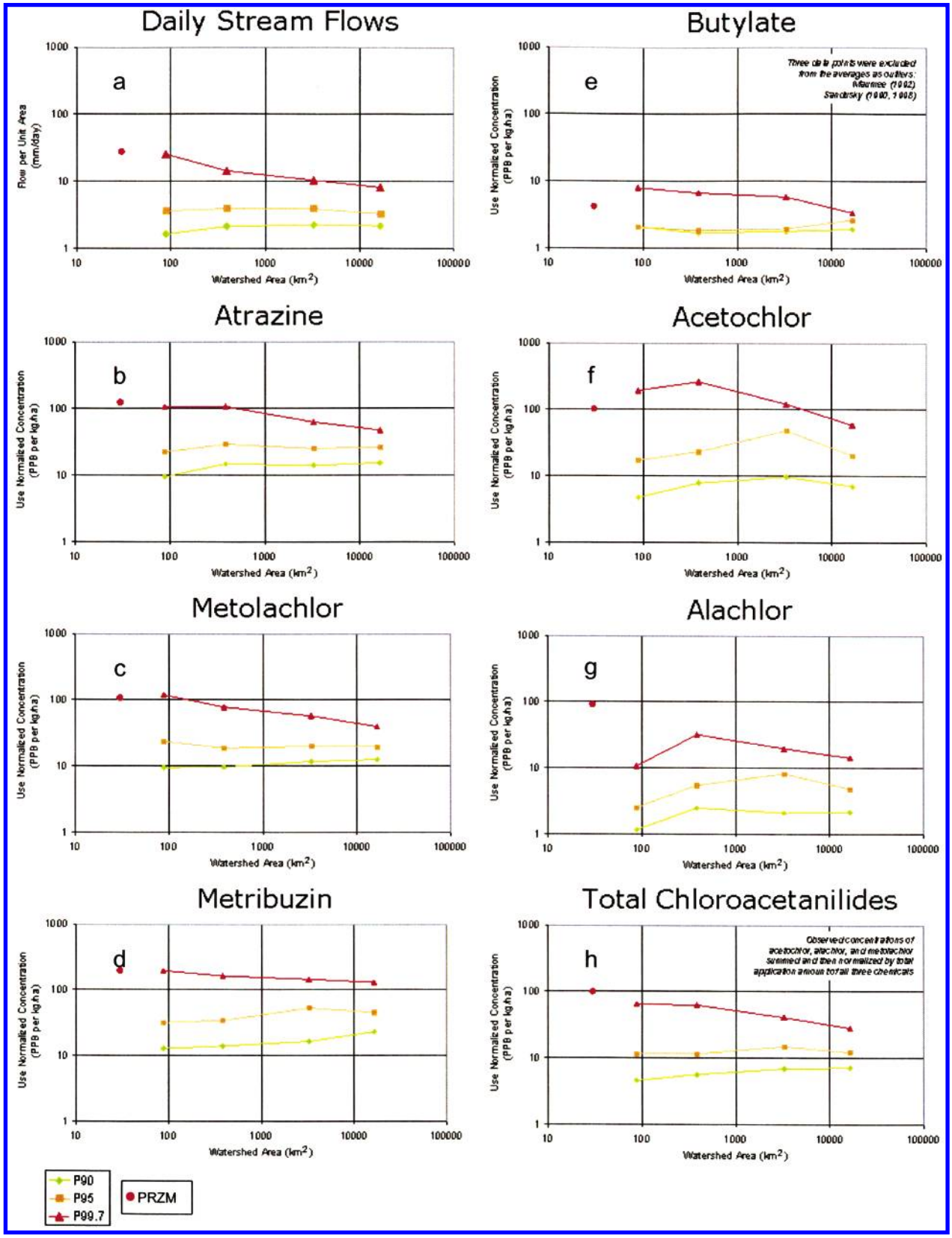

FIGURE 4. Each graph shows averages of several years of use-normalized upper quantile concentrations measured by WQL and daily streamflows measured at USGS gauging stations. The 99.7th percentile corresponds to the maximum daily value within 1 year. The solid circles are PRZM edge-of-field estimates of maximum daily concentrations, which are plotted at a watershed area of 30 km², corresponding to the appropriate watershed scale for such predictions (see text).

limits and frequencies of sample collection (90th, 95th, and 99.7th, in particular).

Self-similarity or *scale-invariance*, which states that certain properties of fractals are independent of scale, is seen in the plan geometry of rivers in Figure 2. Without having the scale present or some form of prior knowledge, one cannot discern the size of the river network from the map alone. Likewise, our subsequent results suggest that the characteristic branch-

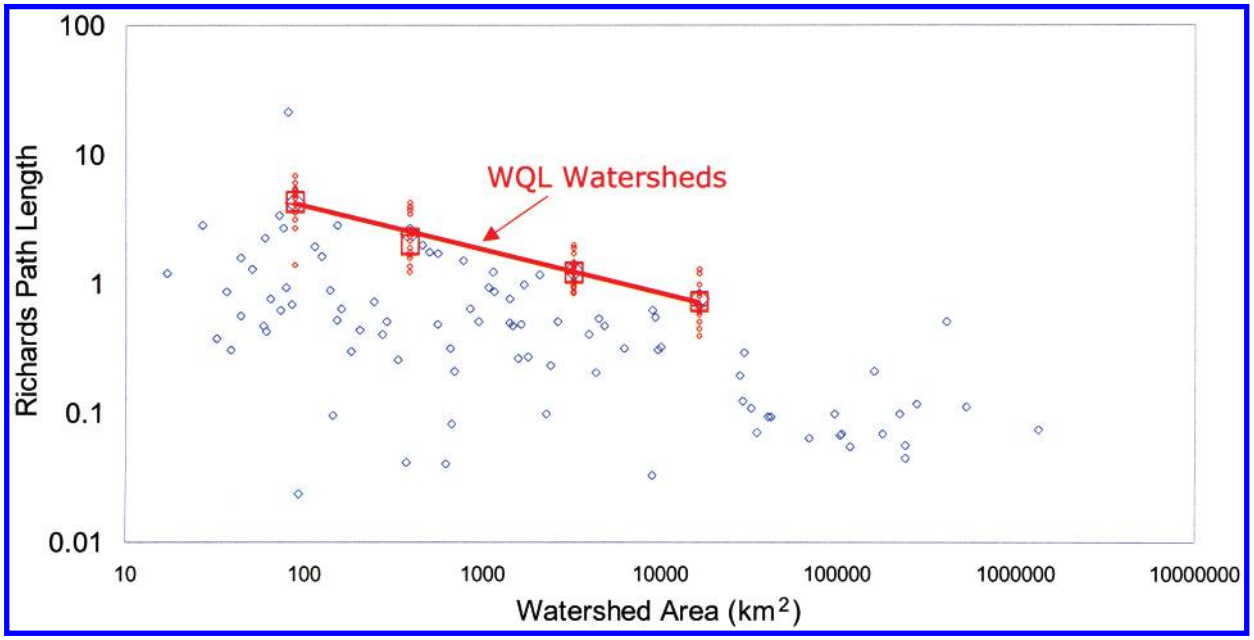

FIGURE 5. Richards path length (L_R) calculated for 1 year of streamflow data at the 89 USGS monitoring sites and during 1984−2000 at the four WQL watersheds. Quartile boxes, means, and individual annual values are plotted for the WQL data. The line connects the four mean values.

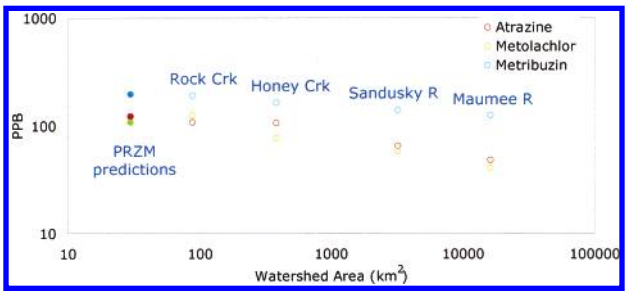

FIGURE 6. PRZM edge-of-field estimates represent the area-weighted averages for four modeled soils and are plotted at a watershed area of 30 km^2 as in Figure 4. Open circles are multi-year averages across years that had observed MDC values for all four WQL watersheds. Ten years met this criterion for all three of these pesticides: 1985, 1988−1991, and 1994−1998. Observed maximum daily concentrations are adjusted to a use rate of 1 kg/ha through the assumption that concentration is linearly proportional to use intensity within a site and year.

ing and twisting drainage pattern of water moving across a landscape has a profound level of self-similarity that is apparently present even within the tiny rivulets of water filtering downward through the soil pores. Because pesticides are carried along these same fractal paths, their concentration−time profiles exhibit a particular type of broadening with distance traveled defined here as *scale-invariant dispersion*. We model this scale-invariant dispersion through both power-law relationships and a particular analytical solution to the convection−dispersion equation (the PRZM-CDE model, see the Supporting Information), both of which appear to describe the manner by which peak pesticide concentrations in rivers are impacted by scale.

Results and Discussion

Comparison of PRZM Estimates with Observed Concentrations at Different Scales. As shown in Figure 6, we found that that the mean of the PRZM edge-of-field estimated concentrations for atrazine, metribuzin, and metolachlor are all very close to the average values seen in the smallest two WQL watersheds: Rock Creek and Honey Creek. As previously mentioned, the observed MDC values shown in Figure 6 have been normalized to a use rate of 1 kg/ha through the assumption that concentrations vary linearly with watershed use intensity.

The data in Figure 6 demonstrate the hypothesized fractal behavior for peak daily concentrations as a function of watershed scale. Results for additional compounds are summarized in Table 1. It is worth noting that the simple equivalence of PRZM edge-of-field estimated concentrations with observed monitoring data is likely due to the fact that the WQL watersheds are typified by high runoff soils with little base flow, such that most of the water in the streams at the times that peak pesticide concentrations occur is direct surface runoff water. In regions with different soils or higher base flow, significant dilution would be expected to occur, lowering the concentrations. This may be reflected in the somewhat lower average concentrations seen for the USGS data versus the WQL data.

Log−log plots were formed of the multi-year average maximum daily concentrations of all pesticides listed in Table 1 as a function of watershed area for the four WQL watersheds. Only atrazine, metolachlor, and metribuzin were found to have slopes significantly different from zero, and all of these were negative. These slopes are listed in Table 2, as are the slopes found for analogous graphs of observed maximum daily streamflows and the predictions of the PRZM-CDE model described in the Supporting Information. The slopes for observed maximum daily streamflow and observed maximum daily concentrations of both atrazine and metolachlor are all statistically indistinguishable from each other and fall in the narrow range of −0.17 to −0.21. We hypothesize—but leave for others to prove—that this slope is related to a fractal dimension of the larger Lake Erie drainage basin containing these four watersheds.

Use of CDE To Model Scaling Effects. In an attempt to develop a theoretical basis for these somewhat noisy trends in the data, we have pursued fits of the CDE model solution to the observed data (see the Supporting Information). We found that the CDE model fit the shape of the peaks quite well. Interestingly, the fitted k values for streamflow and atrazine are very close to the k values reported elsewhere (*20*) for the leaching of unretained and retained solutes, respectively. We interpret this to be direct experimental

TABLE 1. Multi-Year Average Predicted and Observed Maximum Daily Concentrations (PPB), with All Monitoring Data Normalized to Use Rate Assumed in Modeling (1 kg/ha)

	PRZM predictions (avg of all 30 yr) by soil						WQL monitoring data (1984−1999) by location			
pesticide	Blount	Hoytville	Mermill	Toledo	avg[a]	Rock Creek	Honey Creek	Sandusky River	Maumee River	USGS[b] monitoring
acetochlor	132.8	104.7	47.1	113.1	100.1	170.7	257.8	120.0	49.4	40.2
alachlor	122.3	93.2	46.2	100.9	90.7	11.1	31.9	19.5	14.1	37.9
atrazine	160.7	122.6	73.6	132.6	121.7	102.9	106.1	61.8	45.6	50.8
butylate	5.3	3.9	3.5	4.5	4.1	7.9	6.6	5.7[c]	3.3[c]	2.0
cyanazine	140.2	104.8	61.7	110.7	104.0	45.8	67.1	31.4	60.1	40.8
EPTC	141.1	102.9	63.0	112.0	103.6	279.0	129.3	1076.1	162.1	35.2
metolachlor	144.0	105.3	66.7	114.3	106.3	112.5	76.8	57.1	38.4	32.6
metribuzin	232.9	213.6	81.8	236.3	194.9	185.4	163.0	142.7	132.7	42.7
simazine	156.7	121.6	70.9	130.7	119.7	376.8	91.2	106.2	339.2	59.2

[a] Area-weighted average of four soils based on percent areas shown in Table S2. [b] Simple average of all data with five outlier values (predicted MDC > 1 ppm) removed. [c] Outlier values removed as in Figure 4: Maumee (1992) and Sandusky (1990, 1998).

TABLE 2. Statistical Comparison of Slopes of log−log Plots of Various Parameters vs Watershed Area[a]

parameter (all multi-year avg[b])	slope[c]
obsd max daily streamflow	−0.21 a
obsd max daily concn of atrazine	−0.17 a
predicted (PRZM-CDE model) max daily concn of atrazine[d]	−0.25 a
obsd max daily concn of metolachlor	−0.19 a
obsd max daily concn of metribuzin	−0.064 b

[a] No other pesticides had observed maximum daily concentration slopes significantly different from zero. [b] Multi-year averages include all years for which observed values are available, during the period 1984−1999. [c] Slope values followed by the same letter are not statistically different from each other at the 0.05 level of significance. [d] Average of all modeled years shown in Figure 7 (1961, 1963, 1970, 1985, 1988, 1989, 1990).

evidence for the scale-invariant dispersion that apparently governs solute transport across many orders of magnitude of spatial and temporal scale. As described in the Supporting Information, we have developed a simple hybrid model (PRZM-CDE) in which edge-of-field PRZM concentrations are transformed to a watershed scale.

We explore the ability of this PRZM-CDE model to simulate scale effects in Figure 7, which is analogous to the previous Figure 4, except that the solid symbols and lines are those determined by the PRZM-CDE model, and the scattered open symbols correspond to measured values. We show the results for 1985, 1988, 1989, and 1990, the four years for which we are able to directly compare estimated and measured values. We also show PRZM estimates for 1961, 1963, and 1970, which correspond to the maximum, minimum, and median runoff years from the 30-year PRZM simulation of atrazine behavior. In Figure 7h, we compare the multi-year averages for all years in which either modeling or observed values are available: these seven modeled years and the multi-year average observed atrazine concentrations during the period 1984−1999. We also include standard errors for the predicted and observed MDC values. These standard errors overlap for all four watersheds, suggesting that the model reliably predicts peak atrazine concentrations in these watersheds. Table 2 shows that the slopes of these predicted and observed maximum daily concentration plots are statistically indistinguishable (at the 0.05 significance level). In all cases studied, the PRZM-CDE model appears to mimic the observed scaling behavior of these three percentiles (P90, P95, and P99.7) extremely well.

One apparent anomaly in both Figures 4 and 7 deserves some additional discussion. In our analysis of these data, we have often found situations where the predicted and observed values of MDC in Rock Creek are lower than those in Honey Creek, the reverse of what is expected based on their relative areas. This may be due to the fact that the mean time for pesticide runoff to reach the monitoring location in Rock Creek is only about 36 h. This causes the main peak there to be so narrow in time that the 99.7th percentile concentration may be well down the shoulder of the primary chemograph peak, such that it is lower than that found in the larger Honey Creek watershed. A little reflection on this topic suggests that the *x*-axis in these plots of concentration versus watershed area may be equivalently considered to represent the time period over which field-scale runoff events are mixed. Watershed areas on the order of 30−100 km^2 correspond to a mixing time of about 1 day (depending on watershed geometry and streamflow velocity) and are therefore directly comparable to the daily runoff concentrations being reported by PRZM. This explains why it is appropriate to plot the unprocessed PRZM predictions at a watershed scale of 30 km^2 (as in Figure 4). Another implication of this observation is that extrapolation of the lines in Figure 6 to smaller watershed areas is inappropriate for daily concentrations.

Regulatory Consequences. This work was begun in an effort to fill a key regulatory need—the ability to predict peak crop chemical concentrations in rivers across a wide range of watershed scales. We have shown that the mathematical implications of fractal geometry offer two specific methods for incorporating the effect of scale into such regulatory assessments. The first approach is suitable for simple regression modeling. In this method, one uses the linear nature of log−log plots of maximum daily concentrations versus watershed area to model the effect of scale on peak concentrations. The second approach is suitable for more refined modeling in which the entire daily time series and/or frequency distribution is required. In this case, one uses the theory of scale-invariant dispersion to convert daily edge-of-field concentrations into realistic time series of concentrations for the watershed scale of interest. A simple computer program for carrying out these calculations is provided (see Supporting Information). In both cases, the techniques introduced here could be directly incorporated into any regulatory assessment where one wishes to account for the effect of scale.

An interesting theoretical finding is our observation that the same CDE solution accurately characterizes both leaching within the field (*20*) and long-range watershed transport. We interpret this to mean that scale-invariant dispersion governs these natural solute transport processes, whether vertically through the top few meters of a field over a period of several years or across hundreds of kilometers in a watershed over a period of several days. The apparent underlying cause is that water (by which the pesticides move) follows the same kind of fractal paths while moving either through or over

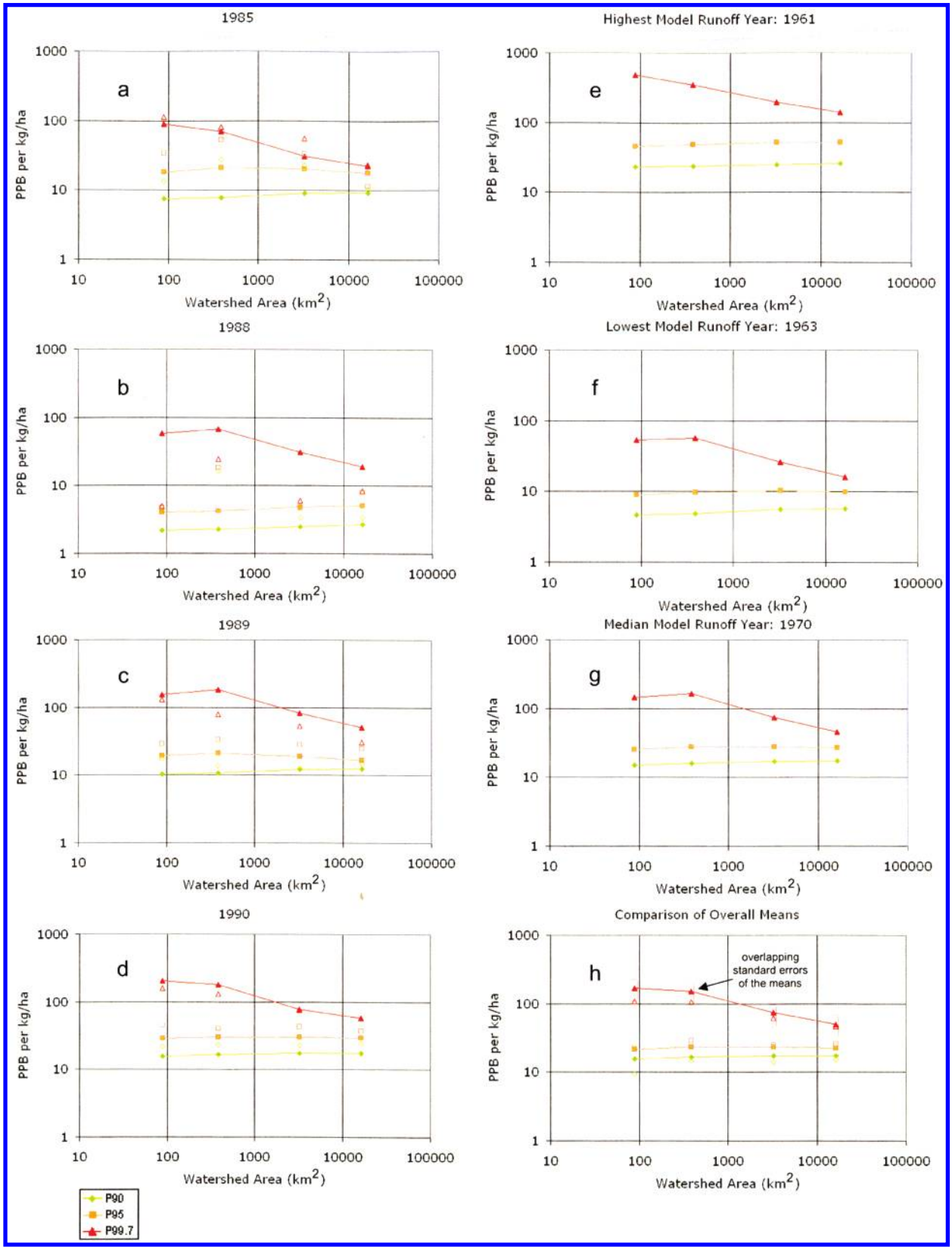

FIGURE 7. Solid symbols and lines in each graph are the upper-quantile atrazine concentrations (normalized to a 1 kg/ha use rate) as predicted by the coupled PRZM-CDE model for the four WQL watersheds. Observed values shown as open symbols are use-normalized observed values for the years shown (a–d) and multi-year averages (h). The multi-year average comparisons (h) include all years for which modeling and monitoring results are available as well as standard errors for observed and predicted 99.7th percentile concentrations.

soils, thus exhibiting self-similarity across many orders of magnitude.

An important practical finding of this work is the close correspondence of edge-of-field runoff concentrations calculated by PRZM with maximum daily values observed in smaller watersheds. However, it is essential to note that this encouraging result is based on the fact that all observed concentrations have been normalized based on use intensity.

Watersheds are usually selected for monitoring based on intensity of use with the highest use intensity favored. It may be possible to find small watersheds comprised essentially of all agricultural land, while there will be areas of nonagricultural land (and perhaps a wider variety of crops) in larger watersheds. Thus, the use intensity in monitored watersheds often decreases with increasing watershed area. Therefore, actual concentrations are likely to be higher in small watersheds than large watersheds selected for monitoring based only on use intensity. By normalizing the concentrations, the effect of use intensity is eliminated, while preserving the scale effects.

A limitation to the PRZM-CDE modeling approach presented here is that no in-stream loss mechanisms have been included. This is a conservative assumption for regulatory purposes, and it appears to be a reasonable simplification for the chemicals and watershed scales studied here. However, the reduction of in-stream loss rates with watershed scale in mass balance models such as SPARROW (*21*) suggests that great care would be required in order to maintain conservatism if such mechanisms were added to the PRZM-CDE model.

In regulatory applications of these new modeling approaches, it would become necessary to select the appropriate scale for the assessment of interest. In the case of drinking water, this should be relatively straightforward based on available information concerning the size of the watersheds actually used as drinking water sources. In the case of ecological assessments, it is likely that different scales would be appropriate based on the particular organism or ecosystem being evaluated. It is beyond the scope of this work to recommend any particular watershed scale, but we have endeavored to provide tools for conducting such scale-dependent regulatory assessments once the appropriate scale has been specified.

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Supporting Information Available

Some of the more detailed information. This material is available free of charge via the Internet at http://pubs.acs.org.

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