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COMPARISON OF TWO PARAMETRIC METHODS TO ESTIMATE PESTICIDE MASS LOADS IN CALIFORNIA'S CENTRAL VALLEY[1]

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ABSTRACT: Mass loadings were calculated for four pesticides in two watersheds with different land uses in the Central Valley, California, by using two parametric models: (1) the Seasonal Wave model (SeaWave), in which a pulse signal is used to describe the annual cycle of pesticide occurrence in a stream, and (2) the Sine Wave model, in which first-order Fourier series sine and cosine terms are used to simulate seasonal mass loading patterns. The models were applied to data collected during water years 1997 through 2005. The pesticides modeled were carbaryl, diazinon, metolachlor, and molinate. Results from the two models show that the ability to capture seasonal variations in pesticide concentrations was affected by pesticide use patterns and the methods by which pesticides are transported to streams. Estimated seasonal loads compared well with results from previous studies for both models. Loads estimated by the two models did not differ significantly from each other, with the exceptions of carbaryl and molinate during the precipitation season, where loads were affected by application patterns and rainfall. However, in watersheds with variable and intermittent pesticide applications, the SeaWave model is more suitable for use on the basis of its robust capability of describing seasonal variation of pesticide concentrations.

(KEY TERMS: pesticides; loading; SeaWave; SineWave; modeling; Central Valley.)

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INTRODUCTION

Pesticides are applied in California on a variety of land use settings including agricultural, urban, and mixed uses. The movement of pesticides into the environment is affected by many factors. Among the more important are rainfall relative to time of application, the type of irrigation used, land slope, amount and type of vegetation cover, soil properties (e.g., permeability, organic matter content), and physical properties of the pesticide. Off-site movement of these chemicals is a recognized environmental problem. Organophosphate (OP) insecticides are the most actively managed group of pesticides in the western United States (Zhang *et al.*, 2004). This is due to their toxicity to aquatic invertebrates (Kuivila and Foe, 1995; de Vlaming *et al.*, 2000), which are important prey organisms for fish, and their effect on salmon behavior (Scholz *et al.*, 2000; Sandahl

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et al., 2005). On a state level, a variety of management efforts, including those related to total maximum daily load (TMDL) plans by the California Environmental Protection Agency (CalEPA, 2009), were developed to prevent the movement of OP insecticides to streams. In 2004, all urban uses of the OP insecticide diazinon were eliminated (USEPA, 2006). In addition, significant restrictions have been placed on agricultural uses of diazinon, including cancellation of its use on many crops, a reduction in application rates, a reduction in the number of allowable annual applications, and restrictions on the methods of application.

To adequately assess mass loads, an appropriate model must be utilized. A previous study by the U.S. Geological Survey (USGS) National Water Quality Assessment Program (NAWQA) (Domagalski *et al.*, 2008) describes application of the software program LOADEST2, a parametric multivariate regression model that uses a rating-curve method to quantify loads of pesticide or nutrient in streams. Seasonal differences in concentrations of agricultural chemicals in the streams were described using LOADEST2 with first-order sine and cosine functions in decimal time [and hereinafter referred to as the Sine Wave model (SineWave)]. Load estimates can be made on an annual, seasonal, or monthly basis (Cohn *et al.*, 1989; Crawford, 1991). Although this model has been used in a variety of studies and has been successful in predicting mass loads for nutrients, suspended sediment, and dissolved organic carbon (Saleh *et al.*, 2003; Langland *et al.*, 2004; Sprague *et al.*, 2008), there has been limited use of the SineWave model for pesticides because of the abrupt seasonal changes in pesticide concentrations due to application patterns and difficulty in establishing a relationship between concentrations and stream discharge (Runkel *et al.*, 2004).

More recent studies by Vecchia *et al.* (2008) and Sullivan *et al.* (2009), describe using the Seasonal Wave (SeaWave) model to describe seasonal variations in pesticide concentrations. The SeaWave model is designed to handle complexities often found in pesticide data, such as seasonal variability in concentration caused by pesticide application patterns, the relationship between concentration and streamflow, and the often large number of detections below laboratory reporting levels (RLs).

The purpose of this study is to use the SeaWave and the SineWave models to estimate mass loads of four pesticides (carbaryl, diazinon metolachlor, and molinate), two of each that were measured in two watersheds, Arcade Creek and Sacramento River. Results from both models are compared to identify the more suitable statistical tool to be used when calculating loadings of pesticide in watersheds with a variety of land use settings and pesticide use patterns. The pesticides selected for this study, were used to illustrate different scenarios of pesticide applications in the state of California. For this same reason, the two watersheds used in this study were selected because they vary in size and land use; Arcade Creek, a relatively small watershed covering an area of about 82 km^2, with predominant urban land use, and the Sacramento River, a much larger watershed covering an area of about 61,700 km^2, with a mixture of land uses.

METHODS

Data Used for Model

Pesticide concentration data processed by Martin (2009) for the two stream-sampling sites were used in this study to maintain a consistent dataset across multiple applications. Censoring is common in pesticide data and refers to a pesticide concentration reported as less than some value. Censoring occurs because the analyzing laboratory is unable to detect the pesticide or quantify its concentration in the sample. The censoring level is set by the laboratory and is based upon analyses of samples into which known quantities of pesticides have been added. In this article and for the purpose of comparing pesticide concentrations in different regions across the nation, the USGS adopted a uniform method of censoring pesticide data. For the data collection period, a consistent minimum RL was determined for each pesticide and set to the *maximum long-term method detection level* (Martin, 2009). Samples with atypically high RLs due to sample matrix interference or subpar lab quality assurance were left as is. The consistent censoring level eliminates the possibility of an induced temporal structure from changes in the censoring level, thus producing a "better" coefficient for time. That better time coefficient for the trend model also means a better time coefficient for the load model (Martin, 2009).

Concentration data were corrected for analytical recovery errors. The NAWQA Program, as part of its quality control (QC)/quality assurance plan, requires the spiking of pesticide mixtures into environmental water samples at a frequency of 5% of all samples collected. The recoveries of each analyte, as measured by these field spikes, were smoothed using a 1.5-year moving average (Martin *et al.*, 2009). Concentrations for corresponding time periods were adjusted using the smoothed recovery value. Additional details of the recovery correction methods are given by Martin (2009) and Martin *et al.* (2009). In addition to the analysis of pesticide

TABLE 1. Pesticide Data From Two Watersheds Used for the Model Evaluation in This Study.

Watershed Name	Begin Date	End Date	Pesticide	Number of Samples
Arcade Creek	11/26/1996	09/28/2005	Carbaryl RL = 0.03	88 (29)
Arcade Creek	11/26/1996	09/28/2005	Diazinon RL = 0.003	88 (0)
Sacramento River	11/15/1996	09/28/2005	Metolachlor RL = 0.006	104 (68)
Sacramento River	11/15/1996	09/29/2005	Molinate RL = 0.002	93 (25)

Notes: RL, reporting limit, in micrograms per liter. Values in parentheses are number of censored samples (with concentrations below the reporting limit).

recoveries, the dataset was checked for any occurrences of pesticides in QC blank samples. An examination of the QC data revealed no problems with false positive detections.

The period of record, number of detections and nondetections for each site, and reporting limits for each pesticide are shown in Table 1. Estimates of the amount of pesticides applied in each of these watersheds were obtained from the California Department of Pesticide Regulation (CaDPR, 2009) for the duration of the study (1997-2005). Streamflow data for both sites were obtained from the USGS National Water Information System (NWIS) (http://ca.water.usgs.gov/nwisweb.html).

Mass Load Calculations

Mass loads of pesticides for the period of this study (1997-2005) were calculated by the rating-curve method using the two models SineWave and SeaWave. Both models were implemented within the S-PLUS statistical software package (TIBCO, 2008). The rating-curve method is a multiple regression model of constituent concentration or load as a function of flow, decimal time, and seasonal variables (Cohn, 2005). Temporal differences of pesticide concentrations in the streams can be described on seasonal bases by aggregating daily load estimates from the model over different seasons. In this analysis, two seasons were defined for the time period of the study; a precipitation season (October through March), and an irrigation season (April through September). Output of both models includes a statistical summary, the average daily flux, the variance of the average daily flux, and the 95% confidence interval for the average daily flux. The uncertainty associated with each estimate of mean load is expressed in terms of the standard error prediction (SEP), which represents the variability that may be attributed to the model calibration (parameter uncertainty) (Cohn *et al.*, 1992).

In general terms, a load is an integrated mass flux over some time interval $\{t_a, t_b\}$:

$$L = \int l(t)\,\mathrm{d}t = \int kc(t)Q(t)\,\mathrm{d}t, \tag{1}$$

where L is the total load; l is the instantaneous load, for time t; k is a unit conversion factor, for time t; c is the instantaneous measured concentration, for time t; Q is the instantaneous flow, for time t.

To better compare results obtained from the models, it is important to have an understanding of the specific form of each model, identifying the different variables used in each model to calculate loads.

Sine Wave Model

The general form of the regression equation for the SineWave model is:

$$\ln(C_i) = \beta_0 + \beta_1 \ln(Q_i) + \beta_2[\ln(Q_i)]^2 + \beta_3(T_i) + \beta_4(T_i)^2 + \beta_5 \sin(2\pi T_i) + \beta_6 \cos(2\pi T_i) + \varepsilon_i, \tag{2}$$

where ln is the natural logarithm function; C_i is the daily concentration, in micrograms per liter, for day i; Q_i is the measured daily mean flow, in cubic meters per second, for day i; T_i is the time of observation, in decimal years, for day i; $\beta_0, \ldots, \beta_6$ is the fitted model coefficients; and ε_i is the error for day i.

In practice, the times of observation and the mean daily flows are centered (by subtracting their sample means) to reduce colinearity and are described in the explanatory variables. Loads were derived from the coefficients obtained from Equation (2). The quadratic terms shown in Equation (2) were dropped when they were not at a level of significance of 0.05. This model assumes that concentrations are subject to a seasonal pattern driven by external factors that can be described by a first-order Fourier series (sine and cosine terms) (Runkel *et al.*, 2004). It is important to mention that the SineWave model fits the pesticide concentrations to a standardized annual sine-cosine signal and unlike the SeaWave model, it does not take into account the half-life of the pesticide nor does it account for multiple applications of the pesticide in the watershed.

Seasonal Wave Model

The general form of the regression equation for this model is:

$$\ln(C_i) = \beta_0 + \beta_1 \ln(Q_i) + \beta_2[\ln(Q_i)]^2 + \beta_3(T_i) + \beta_4(T_i)^2 + \beta_5 W(T_i) + \varepsilon_i, \quad (3)$$

where W is the seasonal wave.

As with the SineWave model, the times of observation and the mean daily flows are centered to reduce colinearity in the explanatory variables. Loads were derived from the coefficients obtained from Equation (3) and the quadratic terms shown in Equation (3) were dropped when they were not significant at a level of significance of 0.05. The seasonal wave (W) was implemented as described by Vecchia *et al.* (2008), where W describes the annual cycle of pesticide occurrence in a stream. In general, W is the unique, periodic solution to the following differential equation:

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}T} W(T) &= \lambda(T) - \varphi W(T), \qquad [0 \le T \le 1] \\ \lambda(T) &= \sum_{k=1}^{12} \omega_k I\left(\frac{k-1}{12} \le T \le \frac{k}{12}\right), \\ W(T+j) &= W(T), \qquad j = 0, \pm 1, \pm 2, \ldots \end{aligned} \quad (4)$$

where $W(T)$ is the total amount (kilograms) of a particular pesticide in the basin at time T that is available for transport to the stream; $\lambda(T)$ is the instantaneous input function (kilograms per year); ω_k is the instantaneous input rate for the approximately one-month interval beginning at monthly time $(k - 1)/12$; by convention, the rates are relative rates scaled from 0 to 1; φ is the decay rate that controls the rate at which pesticides are removed from the stream system; and I is the indicator function with $I\ (a \le t < b) = 1$, if t lies in the given interval, and $\mathrm{I}\ (a \le t < b) = 0$ otherwise.

The function W depends on two parameters, $\omega = \{\omega 1, \ldots, \omega 12\}$ and φ as included in Equation (4). Parameter φ condenses various important transport processes such as sorption, microbial degradation and mineralization, photodegradation, plant uptake, volatilization, and soil slope and permeability into a single value useful in describing the retention and mobility of the pesticide in the watershed being modeled. The value of $(12/\varphi = h)$ approximates the half-life (in months) of the pesticide in the watershed and is the value that is typically used to specify φ (Vecchia *et al.*, 2008). The values considered for φ and ω for this study are shown in Table 2.

Equation (4) was applied to the two streams for each of the four selected pesticides. Unlike the standardized fitted sine-cosine signal of the SineWave model, the SeaWave model output of this function provides a list of multiple forms of W with the ω and h values corresponding to each model accompanied with an Akaike Information Criterion (AIC) value for each model (Akaike, 1981). The best choice for W for each site was determined using the highest AIC value. Figure 1 shows a composite seasonal wave W superimposed upon the pesticide concentration data and streamflow in the different watersheds. The magnitude, shape, and peak location of W varies for these four pesticides (Figure 1). It is affected by the amount and time period in which pesticides are applied and removed in the different watersheds. In some cases, W has one peak (Figure 1C). This indicates that in the Sacramento

TABLE 2. Model Choices for Describing Seasonal Variation of Pesticides Application Rates (equation 3).

Model Number	$h = 12/\varphi$	$\omega 1$	$\omega 2$	$\omega 3$	$\omega 4$	$\omega 5$	$\omega 6$	$\omega 7$	$\omega 8$	$\omega 9$	$\omega 10$	$\omega 11$	$\omega 12$
1	1, 2, 3, 4	0	0	0	0	0	1	0	0	0	0	0	0
2	1, 2, 3, 4	0	0	0	0	0	1	1	0	0	0	0	0
3	1, 2, 3, 4	0	0	0	0	0	1	1	1	0	0	0	0
4	1, 2, 3, 4	0	0	0	0	0	1	1	1	1	0	0	0
5	1, 2, 3, 4	0	0	0	0	1	1	1	1	1	0	0	0
6	1, 2, 3, 4	1	1	1	1	1	1	1	1	1	0	0	0
7[1]	1, 2, 3, 4	0	0	1	1	1	0	0	0	1	0	0	0
8	1, 2, 3, 4	0	0	1	1	1	0	0	0	0	1	0	0
9	1, 2, 3, 4	0	0	1	1	1	0	0	0	0	0	1	0
10	1, 2, 3, 4	0	0	1	1	1	0	0	0	0	0	0	1
11	1, 2, 3, 4	0	0	1	1	1	0	0	0.75[2]	0.75	0	0	0
12	1, 2, 3, 4	0	0	1	1	1	0	0	0	0.75	0.75	0	0
13	1, 2, 3, 4	0	0	1	1	1	0	0	0	0	0.75	0.75	0
14	1, 2, 3, 4	0	0	1	1	1	0	0	0	0	0	0.75	0.75

[1]In the two peak Wave model, the primary peak application rate is always three months.
[2]The secondary peak application rate is lower (0.75) but lasts for a longer time period (two months).

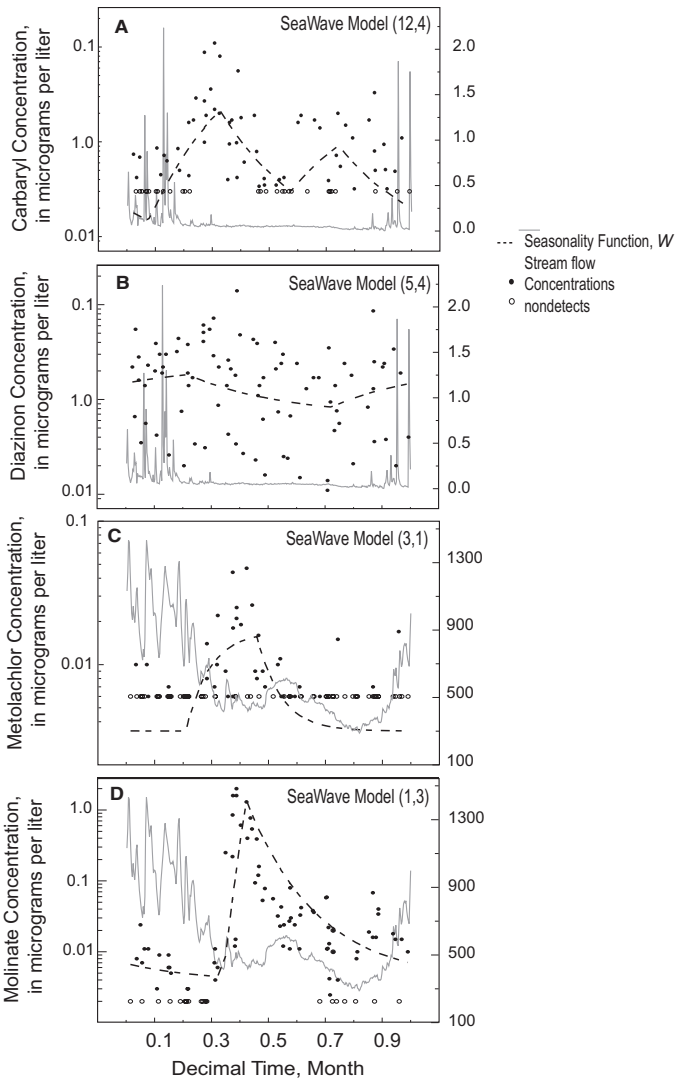

FIGURE 1. The Composite Seasonal Wave Form (W) for the Entire Time Period of Study, 1997 to 2005. Values in parentheses are ω and φ, respectively, used for the model simulation. (A) Best-fit model for seasonal wave pulse for carbaryl in Arcade Creek. (B) Best-fit model for seasonal wave pulse for diazinon in Arcade Creek. (C) Best-fit model for seasonal wave pulse for metolachlor in the Sacramento River. (D) Best-fit model for seasonal wave pulse for molinate in the Sacramento River.

River watershed, metolachlor was being applied, or transported to the stream, once during the year with the main application and transport occurring during the late spring (Figure 2C). The rate of decrease of W is related to the half-life of the pesticides in the watershed. In this case, metolachlor has a small half-life ($h = 1$) and is removed from the watershed within a few months (Figure 1C). In a different scenario, molinate in the Sacramento River watershed is applied on rice fields once a year in late spring. Water in rice fields is managed according to state regulations, where the water must be held for at least 28 days before it can be released (Newhart, 2002). The fields are flooded in late April and early May, when molinate is applied (Figure 2D). Some of the initially applied water, containing pesticide residues is released in late May which accounts for the peak in molinate concentrations shown in Figure 1D. Released water is then replaced with new water allowing diluted concentrations of molinate to remain in the rice fields for a longer time period ($h = 3$). This is illustrated in a wide single peak seasonal wave W form shown in Figure 1D.

It is possible for W to have a double peak (Figure 1A), which indicates that in this watershed there are multiple applications or processes that transport pesticides to the stream. For example, carbaryl in the Arcade Creek watershed is applied twice in the year – once in the spring (March and April) with the presence of precipitation as a main transport mechanism of pesticides to the stream and a second application of less magnitude during the summer (June through August) when irrigation is the main transport mechanism (Figure 2A). Figure 1A reflects this multiple pesticide application and transport. The seasonal W shown in Figure 1A has a $\omega = 12$ and an $h = 4$ that represents a two peak wave with a long half-life (Table 2). The pattern of pesticide occurrence does not always correspond to the seasonality function W. For example, Figure 2B shows that diazinon is applied throughout the year, which is reflected in the relatively small seasonal variation with no distinct peaks in concentration shown in Figure 1B.

It is important to note that for multiple years of data, and potentially different application times, or transport to the river because of different hydrologic conditions, the timing of the major peak of the final defined sine and cosine wave, as well as the composite W for the entire time period (1997 to 2005), might be slightly shifted from the true location for any given year (Vecchia *et al.*, 2008).

The Empirical Correlogram

One of the assumptions of linear regression is that residuals are independent. Serial correlation may be exhibited for data collected over time, such as constituents in water, which violates the assumption of independence (Helsel and Hirsch, 2002). Time-series methods easily address data that are spaced uniformly, but are not easily applied to data collected at varying time intervals. The empirical correlogram described in this section is a method to portray and diagnose potential serial correlation in data collected at varying time intervals. The correlogram will effectively show a distinct periodic signal rather than

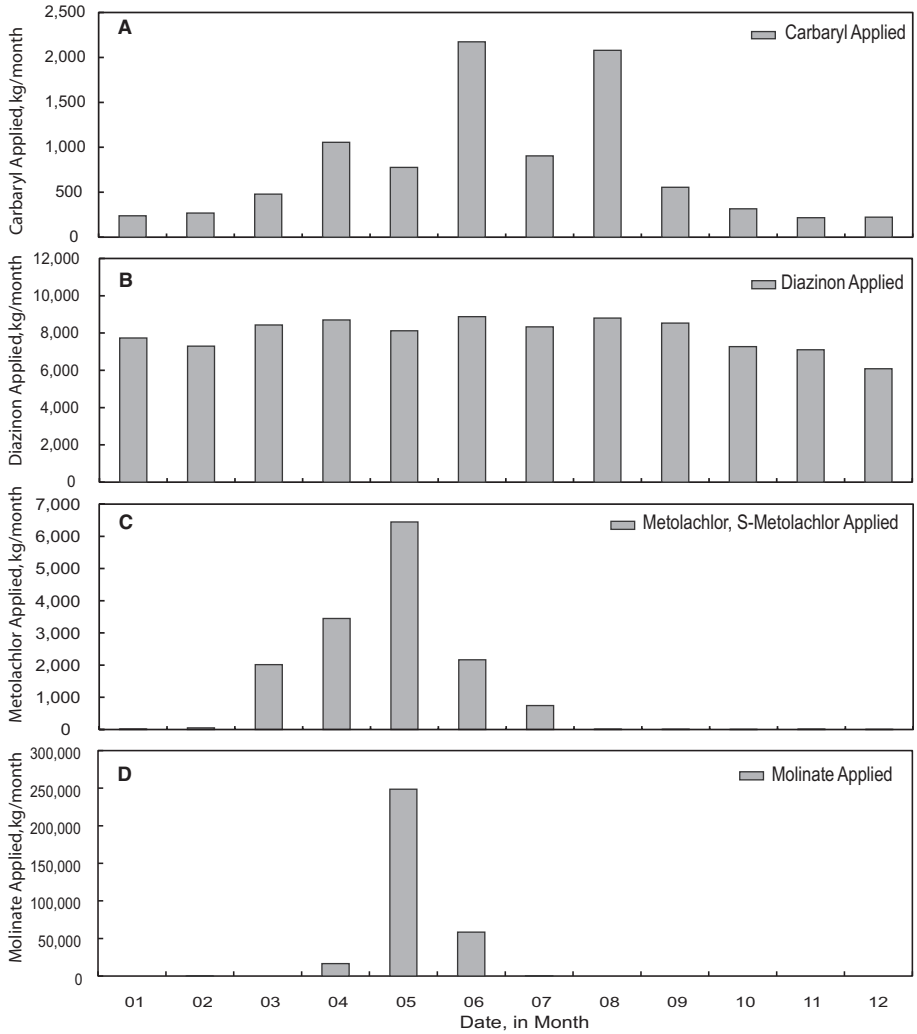

FIGURE 2. Pesticide Use Data Obtained From the California Department of Pesticide Regulation, in Average Kilograms of Pesticides Applied Per-Month, 1997 to 2005. (A) Carbaryl applied in the Arcade Creek watershed. (B) Diazinon applied in the Arcade Creek watershed. (C) Metolachlor applied in the Sacramento River watershed. (D) Molinate applied in the Sacramento River watershed.

a time-varying signal that can be evident in the time-series plot. In traditional time-series analysis, for a discrete set of equally spaced observations $\{x_1, x_2, \ldots, x_N\}$, the correlation between observations for any discrete difference in time, r_k, can be computed as,

$$r_k = \frac{\sum_{j=1}^{N-k} \left(x_j - \bar{x}\right)\left(x_{j+k} - \bar{x}\right)}{\sum_{j=1}^{N} \left(x_j - \bar{x}\right)^2}, \tag{5}$$

where N is the number of observations, x_j is the observation at a discrete time j, and $\bar{x}$ is the mean of all observations (Chattfield, 1980). To define the residual empirical correlogram, let

$$x_j = e_{t(j)}, \quad j = 1, 2, \ldots, N$$

denote the residual from regression model (1) or (2), where $t(j)$ is the time (in Julian day) of the jth observation. Also let

$$d_{jk} = t(k) - t(j)$$

be the difference between the jth and the kth sampling time and define the standardized residual cross-product for each pair of observations,

$$c_{jk} = \frac{(x_j - \bar{x})(x_k - \bar{x})}{\frac{1}{N}\sum_{e=1}^{N}(x_e - \bar{x})}, j = 1, \ldots, N; k = j = 1, \ldots, N. \tag{6}$$

The residual empirical correlogram for a given time lag, Δt, is obtained by applying a kernel smoothing

function to the standardized cross-products, where the cross-products with d_{jk} close to Δt receive more weight than those with d_{jk} far from Δt,

$$r_{\Delta t} = \frac{\sum_{j=1}^{N} \sum_{k=j+1}^{N} K(d_{jk} - \Delta t)\ c_{jk}}{\sum_{j=1}^{N} \sum_{k=j+1}^{N} K(d_{jk} - \Delta t)}, \tag{7}$$

where

$$K(u) = \begin{cases} 1 & \frac{|u|}{c}, |u| \leq c \\ 0, & |u| > c \end{cases}$$

and u is the difference between the two lag times (j, k).

The function K, used to calculate weights for the correlogram, is called a triangle kernel function because the weighting scheme is shaped like a triangle, and is scaled by c so that half the area of the triangle is between −0.25 and 0.25 (TIBCO, 2008). The scaling factor is about 0.854. For censored data, the deviance residual is used as an approximation for the actual value. The standardized residual cross-product is plotted against the difference in time for all points where Δt is >0. This approach assumes that the very short-term random fluctuations in sampled values are large enough that there is an almost immediate change in the correlation from 0.0 to the computed value at some small increment in time. If the residuals contain a seasonal fluctuation due to lack of fit, then the correlogram will exhibit an oscillation at the same frequency (Chattfield, 1980).

RESULTS

Statistical Analyses

There are two main factors affecting the presence and concentration of pesticides in the streams; the amount of pesticides applied in the watershed (data available from CaDPR, 2009), and the manner in which these pesticides are transported throughout the system (runoff following precipitation or irrigation, and groundwater transport). In this study, carbaryl has two main application periods in the urbanized Arcade Creek watershed, the first in spring (March through April) and the second in summer (June through August) (Figure 2A). During the first application period, spring rainstorms still occur, but during the second application period there is little rainfall but extensive landscape irrigation. It appears that the transport of carbaryl is more likely to occur as a result of rain rather than irrigation, as the largest modeled peak occurs during the first application period corresponding with high flows in Arcade Creek (Figure 1A). These multiple applications allow carbaryl to remain in the watershed for a long time period (Figure 1A). Figures 3A and 3B show the residual empirical correlogram plotted over a lag time of one and a half years, using both SeaWave and SineWave, respectively. Figure 3B shows that there are two well-defined periods when SineWave overestimated values, and two periods when SineWave underestimated values. This is reflected in a well-defined cyclical kernel smooth-line pattern, with two peaks per year shown in Figure 3B. On the other hand, the SeaWave model provides a better estimate of values throughout the year and this is reflected in a flat kernel smooth-line pattern shown in Figure 3A. Residual variance values obtained from both models also indicate that SeaWave was more successful in capturing the seasonal occurrence for carbaryl in the Arcade Creek watershed (Table 3).

Diazinon, an insecticide, was applied at various times throughout the year in the Arcade Creek watershed throughout the duration of the study (Figure 2B). In 2004, all urban uses of diazinon were eliminated nationwide because of the effect of diazinon on human health (USEPA, 2006). In addition, watershed management TMDL plans were instituted in agricultural areas to reduce diazinon toxicity to aquatic invertebrates. Figures 3C and 3D show the residual empirical correlogram plots for diazinon in Arcade Creek using both SeaWave and SineWave, respectively. The empirical correlograms show no seasonal variation because both models predicted the seasonality (or in this case, lack of seasonality) well, leaving no seasonal structure in the residuals (Figures 3C and 3D).

In the Sacramento River watershed, the herbicide metolachlor is applied during late spring and early summer while spring rainstorms still occur. Given the high flows in the Sacramento River, and single application on crops, metolachlor is removed from the watershed in a relatively short time period (Figure 1C). The residual empirical correlogram plots from the SeaWave and SineWave models for metolachlor at the Sacramento River site shown in Figures 3E and 3F respectively indicate that both models were equally successful in capturing the seasonal occurrence pattern for metolachlor in the watershed. This is reflected in a flat kernel smooth line shown in Figures 3E and 3F.

It was expected that maximum concentrations of molinate would occur in the May to June time frame with decreasing concentrations after that. The initially applied irrigation water cannot be held on the field for the entire growing season because it causes

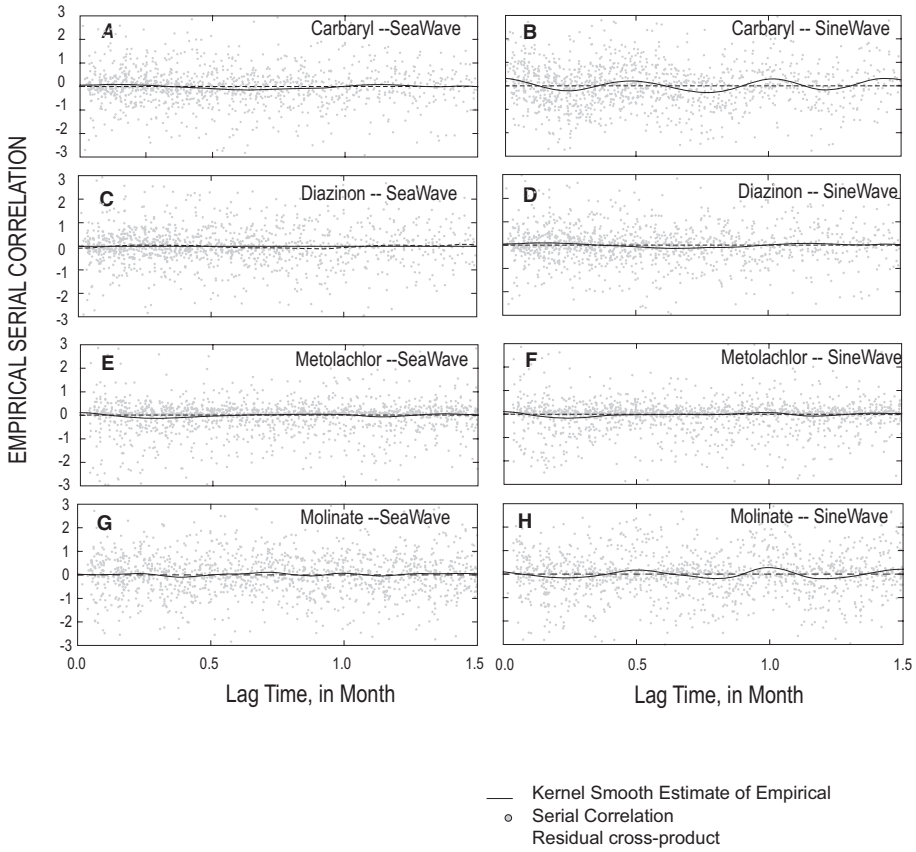

FIGURE 3. Examples of Empirical Correlogram Plots Using the SeaWave and SineWave Models. Lag time represents one and a half calendar years; (A) carbaryl-SeaWave in Arcade Creek; (B) carbaryl-SineWave in Arcade Creek; (C) diazinon-SeaWave in Arcade Creek; (D) diazinon-SineWave in Arcade Creek; (E) metolachlor-SeaWave in Sacramento River; (F) metolachlor-SineWave in Sacramento River; (G) molinate-SeaWave in Sacramento River; and (H) molinate-SineWave in Sacramento River.

TABLE 3. Statistical Model Output for the SeaWave and SineWave Models.

Site Name	Land Use	Pesticide	Number of Observations	Number of Censored Observations	SeaWave Model Residual Variance	SeaWave R^2	SineWave Model Residual Variance	SineWave R^2
Arcade Creek	Urban	Carbaryl	88	29	0.77	0.84	1.28	0.74
Arcade Creek	Urban	Diazinon	88	0	0.34	0.92	0.31	0.93
Sacramento River	Mixed	Metolachlor	104	68	0.49	0.41	0.58	0.38
Sacramento River	Mixed	Molinate	93	25	2.23	0.51	3.69	0.27

problems with the crop and therefore, the farmers release some water periodically and flood with new irrigation water, thus gradually diluting the molinate concentrations till it is completely removed from the watershed in the late summer. Figures 3G and 3H show residual empirical correlogram plots for molinate. Figure 3H shows that the SineWave model was unsuccessful in capturing the seasonal variability of molinate concentrations in the watershed. This is reflected in a well-defined cyclical kernel smooth-line pattern shown in Figure 3H. On the other hand, the SeaWave model better captured the seasonal variability as indicated by a flat kernel smooth line shown in Figure 3.

Pesticide Mass Loads

Seasonal mass loads of pesticides for the Arcade Creek and Sacramento River watersheds were calculated using the SeaWave and the SineWave models. Loads were calculated for two different seasons, a precipitation season (October through March) and an irrigation season (April through September). Figure 4

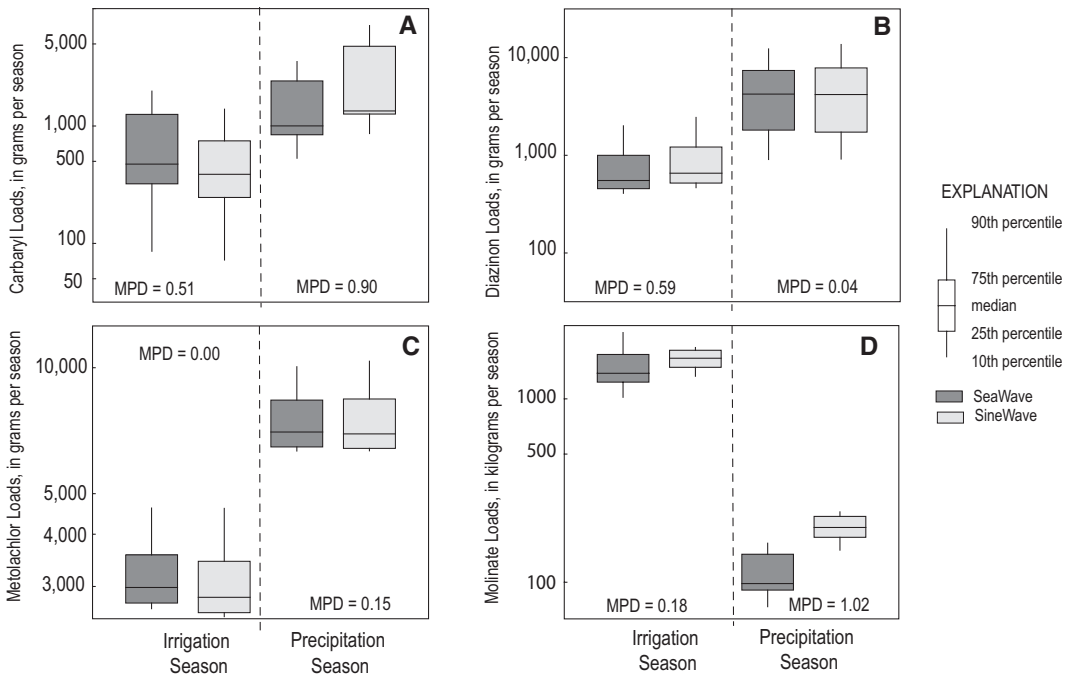

FIGURE 4. Box Plots Showing Seasonal Loads Computed Using the SeaWave and the SineWave Models for an Irrigation Season (April-September) and a Precipitation Season (October-March). Model Percent Difference (MPD) is indicated and a value >0.7 indicates that the two models are significantly different. (A) Carbaryl at Arcade Creek; (B) diazinon at Arcade Creek; (C) metolachlor at Sacramento River; and (D) molinate at Sacramento River.

is a graphical representation of model output displaying the differences between the results of the two models. Traditional methods used to compare paired observations, either the paired t-test or the Wilcoxon signed-rank test, are not appropriate for these data because the seasonal loads are not independent – they are computed from regression models based on the same calibration data and estimated from the same daily flow data. Also, the t-test is very sensitive to constant small differences in model output, therefore an approximation statistic method, the Model Percent Difference (MPD), was used to evaluate differences in model output. This method is not as sensitive as the t-test to constant small differences in model output.

The MPD value is defined as:

$$\mathrm{MPD} = 200 \times \left[\frac{(L_{\mathrm{SeaWave}} - L_{\mathrm{SineWave}})/(L_{\mathrm{SeaWave}} + L_{\mathrm{SineWave}})}{\%\mathrm{SEP}}\right] \quad (8)$$

L_{SeaWave} is the load calculated using the SeaWave model; L_{SineWave} is the load calculated using the SineWave model; %SEP is the mean percent standard error of prediction for both SeaWave and SineWave.

For a single observation, the statistic would be expected to be within −2.0 to 2.0 about 95% of the time. For eight observations (representing eight years of simulation), the same approximate 95% confidence limits are $-2.0/8^{1/2}$ to $2.0/8^{1/2}$ or about −0.7 to 0.7. For this study, the comparison between the seasonal loads for the SeaWave and the SineWave models were classified as substantially different if MPD were >0.7 and not substantially different if MPD were <0.7. Figure 4 shows that during the precipitation season, the SeaWave and SineWave models are statistically different only for calculated loads for carbaryl in the Arcade Creek and molinate in the Sacramento River watersheds, where the MPD associated with the loads are significant >0.7. On the other hand, during the irrigation season the models are statistically comparable for all pesticides in the two watersheds where MPD is <0.7. These results are related to the shape of the seasonal wave for W used to simulate the occurrence of these different pesticides in the two watersheds. In general, when the width of W is greater than the width of one-half of the wavelength of the fitted sine-cosine signals, then the estimated loading value obtained from the SineWave and SeaWave models are significantly different and MPD is >0.7. This is illustrated in Figures 1A and 1D, where W for carbaryl and molinate has a large half-life (h = 4 and 3 respectively). On the contrary, when the width of W is less than the width of one-half of the wavelength of the sine-cosine signal

then the estimated loading value obtained from the SineWave and SeaWave models are similar and MPD is <0.7 (Figure 1C, h = 1 for metolachlor).

SUMMARY AND CONCLUSIONS

The occurrence of pesticides in streams is greatly affected by the amount of pesticide use, the application pattern in the watershed, and the way pesticides are transported to streams. In this study, mass loads for four pesticides (carbaryl, diazinon, metolachlor, and molinate) in two watersheds with different size and land uses (Arcade Creek; small with urban land use, and Sacramento River; large with mixed land uses) were calculated using the SeaWave and the SineWave models. Results of the two models were compared in an attempt to identify the most useful tool for analyzing pesticide concentration data under different application conditions.

Results for this study are affected by the ability of the SineWave and SeaWave models to capture the seasonal variation of pesticides concentrations in the watersheds. Unlike the SineWave model, where a standardized sine-cosine signal is applied to simulate pesticides concentrations, the SeaWave model output provides a list of multiple forms of a seasonal wave (W) to account for the variability in pesticide concentrations in the watersheds. In this study, the four pesticides represent four different application and transport patterns.

The first example was carbaryl in the Arcade Creek watershed. This insecticide is applied twice a year, in spring and summer. The transport of carbaryl is mostly affected by precipitation. Results show that the SeaWave model was more successful than the SineWave in capturing the seasonal variability in carbaryl occurrence in the Arcade Creek watershed caused by the multiple application of carbaryl in the watershed. As a result and during the precipitation season (October through March) when the flows in Arcade Creek are high, the calculated loads from the SeaWave and SineWave models were substantially different with a MPD >0.7.

The second example was that of diazinon in the urbanized Arcade Creek watershed. Diazinon was applied repeatedly throughout the year, which means that there was no seasonal variability in diazinon concentrations in the Arcade Creek. This was reflected in the inability of the SeaWave model to define a strong application peak wave form W for this pesticide. As a result, both models predicted the seasonality (or in this case, lack of seasonality) well, leaving no seasonal structure in the residuals.

The third example was that of metolachlor in the Sacramento River watershed. Metolachlor is applied in the late spring/early summer. It has a short half-life and is removed from the system by the end of the summer. Results show that both models simulated the peak in metolachlor concentration well – the width of the SeaWave form W is smaller than the width of one-half the wavelength of the sine-cosine signal fitted by the SineWave model. Calculated loads from both models when compared statistically show that results are not substantially different with a MPD <0.7.

The final example was molinate in the Sacramento River watershed. This herbicide is applied in late spring on rice fields, which are highly controlled flow systems. The rice fields are flooded in late April to early May and molinate is applied. Some of this initial water is then removed in late May and replaced with new water allowing the molinate to remain on the fields but in diluted concentrations till the water is fully drained from the fields in the late summer. By fitting the sine-cosine signal to the data, the SineWave model was unsuccessful in capturing seasonal variability of molinate concentrations. This is reflected in a well-defined cyclical kernel smooth-line pattern fitted to the SineWave model residuals. On the other hand, the SeaWave was successful in simulating seasonal variability in molinate concentrations caused by the variability in pesticides transport by fitting a suitable seasonal W form to the data.

On the basis of these results, in watersheds with variable and intermittent pesticide applications, the SeaWave model would be more suitable to use, due to its robust capability of describing seasonal variation of pesticides concentrations in the watershed.

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