A Markov-Renewal Extension of a Deterministic State-Variable Model of the Transport and Fate of a Toxic Chemical in the Environment

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ABSTRACT

Specifications for stochastic Markov-renewal (MR) models are compared with those for deterministic, dynamic, state-variable (SV) models. Numerical predictions provided by MR models are qualified by probabilities. A case study is demonstrated in which the fate of the herbicide atrazine upon application in the watershed of an Iowa lake is tracked. Comparisons of numerical results on an MR model with those obtained in an earlier study employing an SV model show that explicit allowance for statistical variability in measured concentrations of a target chemical species assist substantially in interpreting differences between predicted and measured concentrations of the species. It is concluded that MR models provide a feasible alternative to SV models for predicting the fate of chemical species in aquatic environments in cases involving zero- or first-order kinetics of transfer and transformation of those species.

COMPARISONS BETWEEN MARKOV-RENEWAL AND STATE-VARIABLE MODELS

A linear, deterministic, continuous-time state-variable model has the *Markov* property, i.e., projections of future values of dependent variables depend upon present values only. Its specification includes (i) continuous-variable definitions of states or compartments within which elements of a target population reside at given times, (ii) coupled linear, first-order differential equations of balance for the population, one equation for each compartment, (iii) external input functions, and (iv) initial conditions and parameters. Solutions give time-dependent net balances of the population in each compartment, the population being treated as continuous.

A discrete-state, continuous-time Markov-renewal (MR) model of the same

population treats individuals separately, each being tracked through compartments in time. Effects of randomness are accounted for in (i) arrival patterns of individuals from sources external to the collection of compartments, referred to hereafter as the system, (ii) lengths of residence times in compartments for individuals, and (iii) routing of individuals among compartments. A solution to the MR model provides more information about the transport and fate of the target population than its deterministic counterpart, including: (i) distributions of magnitudes of net balances of the population in compartments at fixed times, (ii) distributions of lengths of times required for individuals to move between any two compartments, (iii) distributions of numbers of times individuals recycle among compartments, and (iv) distributions of lengths of times required for an individual to be transported from one given compartment to another given compartment. Unless otherwise specified, individuals are assumed to move among compartments independently in a statistical sense, each following the same given probabilistic routing protocol.

If the Markov-renewal model happens to be purely Markovian, i.e., distributions of residence times in all nonabsorbing compartments are of the negative-exponential type, then the correspondence between the first-order differential equations defining the dynamics of the state-variable model and the Chapman-Kolmogoroff equations specifying the interval transition probability functions for each compartment of the MR model are easily seen. Indeed, they are mathematically equivalent. It is expected, therefore, that in such cases there is a correspondence between the solutions to the two models. The correspondence is noted by comparing the solution to the state-variable model with the expected-value functions of the time-indexed random variables denoting the numbers of individuals in each compartment. Most linear, time-invariant, first-order state-variable systems have MR counterparts, but the converse is not true.

CASE EXAMPLE—TRANSPORT AND FATE OF A HERBICIDE IN AN IOWA ECOSYSTEM

The transport and fate of the biodegradable, soluble herbicide atrazine, widely used for broadleaf-weed control, was modeled by Schnoor et al. [1] employing a single-compartment, deterministic, linear state-variable model. The dependent variable predicted the concentration of total (dissolved plus particulate) atrazine in the water column of (well-mixed) Lake Rathbun (351,000 acft) surrounded by a 535-square-mile watershed onto which applications of a commercial preparation of atrazine are made annually during April and May at levels of 0.5–0.8 kg/ha.

Conceptual Model

A preparation of atrazine is applied to soil and plant surfaces of the watershed, whereupon it immediately begins to undergo transport, transfer, and transformation. Fractions of the chemical enter (i) the atmosphere by volatilization and photolysis, (ii) the biota by biouptake, and (iii) the soil column by gravity and adsorption. Decay occurs by hydrolysis and biolysis. Particulate and soluble fractions enter the water table, whereupon they are transported into the water column of Lake Rathbun. Particulate atrazine enters interstitial sediments by gravity; part of it reenters the water column by scour. Exchanges occur between dissolved and particulate fractions in the water column by adsorption and desorption. Dissolved atrazine enters biota present in lake waters by biouptake. Dissolved and particulate atrazine are also removed from the water column by photolysis, hydrolysis, biolysis, and volatilization. A total of eight compartments are therefore defined, subsets of which may be considered for inclusion in a numerical model, depending upon availability of estimates of stoichiometric coefficients and rate constants. Zero- and first-order rate constants have more often been found to fit laboratory measurements than second-order ones. A crucial step in modeling the transport and fate of toxic chemicals in the environment is a determination of which rate constants dominate.

Four additional compartments that act as sinks, accumulating atrazine over time, are (i) atmosphere, (ii) deep soil, (iii) deep-water sediments, and (iv) lake discharge. Knowledge of decay rates of the chemical indicate which, if any, of the sinks should be included in a numerical model. Of the twelve possible compartments identified above for possible inclusion in a numerical model, Schnoor et al. selected dissolved and particulate atrazine in the lake water column and combined them into a single compartment labeled "total" atrazine.

Deterministic State-Variable Numerical Model

A time-varying model of the total atrazine concentration in the (assumed) well-mixed water column of Lake Rathbun was specified by two equations of material balance:

$$\frac{dV}{dt} = q_{in} - q_{out}, \tag{1}$$

$$\frac{dc}{dt} = \left(q_{in}c_{in} - q_{out}c - KV\frac{c}{1 + k_p M} \right.$$
$$\left. - k_s V\frac{k_p Mc}{1 + k_p M} - c\frac{dV}{dt} \right)\frac{1}{V}, \tag{2}$$

where

$$18 \text{ May } 1978 < t < 18 \text{ May } 1978 + 72 \text{ days},$$

$V = $ lake volume (liters),
$q_{in} = $ flow rate into reservoir (liters/day),
$q_{out} = $ flow rate out of reservoir (liters/day),
$c = $ concentration of total atrazine (μg/liter),
$c_{in} = $ inflow concentration of total atrazine (μg/liter),
$c_{out} = $ concentration of total atrazine in reservoir discharge (μg/liter),
$K = $ sum of pseudo-first-order reaction rate constants in dissolved phase (hydrolysis, oxidation, photolysis, volatilization and biotransformation) (liters/day),
$k_s = $ sedimentation rate constant (liters/day),
$k_p = $ solids-water partition coefficient [(μg/kg)/(μg/liter)],
$M = $ suspended-solids concentration (kg/liter).

Losses of atrazine from the water column due to sorption and biotransformation were determined to occur rapidly ($0.01 < K < 0.05$). Sedimentation losses were negligible ($k_s \approx 0$; $k_p M \approx 0.01$), as herbicides were approximately 99 percent in the dissolved phase. The mean hydraulic detention time of the reservoir was approximately 162 days during the study period of high runoff [$q/V = 1/(162 \text{ days})$; $q = $ mean daily inflow or outflow when reservoir volume is constant]. The initial concentration of total atrazine in the reservoir on 18 May 1978 was approximately $c(0) = 0.15$. Inflow hydrographs showed a stable low-level runoff from the watershed into the reservoir for about 35 days subsequent to 18 May 1978, followed by a period of relatively high runoff. Outflow data were not available. It is assumed for MR-model development that the outflow hydrograph displays a pattern similar to that of inflow. Mean daily ratios q_{in}/V and q_{out}/V averaged over the period of the study are both assumed to be equal to 1/162. Concentrations of total atrazine in inflow, discharge, and the reservoir water column are graphically interpolated (Table 1) from Schnoor et al. [1]. Published computed concentrations from the Schnoor model assumed an input concentration of atrazine double the measured concentration. A value of K equal to 0.01, the lowest rate estimate available from literature sources, was assumed. The effect of assuming high input rate coupled with low fractional daily loss from the reservoir water column is to inflate the computed concentration in the water column as well as the concentration in the lake discharge. Computed concentrations did not match measured concentrations in the water column, either in trend or in monthly averages, in marked contrast to results obtained in a companion study of the herbicide alachlor in the same watershed. Because the alachlor

TABLE 1

COMPUTED AND MEASURED CONCENTRATIONS OF TOTAL ATRAZINE[a]

Date 1978	Measured Inputs (μg/liter)		Reservoir (μg/liter)		Measured discharge (μg/liter)
	Sta. 1	Sta. 2	Computed	Measured	
18 May	0.1	0.1	0.15	0.15	0.13
25 May	0.2	0.2	—	—	—
31 May	0.5	0.5	0.14	—	0.67
7 June	0.8	0.8	—	—	—
14 June	—	—	0.13	1.20	0.82
23 June	1.0	0.8	0.12	—	—
29 June	9.9	13.9	0.40	0.65	1.10
6 July	9.8	3.5	0.78	—	—
14 July	5.3	5.3	0.91	0.95	0.67
21 July	12.5	4.3	1.20	—	—
28 July	2.8	2.5	1.10	0.65	0.50

[a]Source: Schnoor et al. [1].

model yielded computed concentrations consistent with measured concentrations, it was speculated that the lack of fit of the atrazine model was not due to channeling or other form of incomplete mixing in the reservoir. Possible reasons suggested were (i) unmeasured sources of atrazine, and (ii) analytical-chemistry problems of measuring concentrations near the detection limit of 0.2 μg/liter.

Markov-Renewal Model of Total Atrazine

The concentration of total atrazine in a typical one-liter cell in the well-mixed (instantaneously and completely mixed) water column of the reservoir is modeled discretely (counts of micrograms per liter). Complete and instantaneous mixing implies that the statistical distribution function of particle residence time in a cell is of the negative-exponential form. Available data do not justify an assumption of incomplete mixing in any form. It is assumed that the ratios q_{in}/V and q_{out}/V are equal when averaged over the study period 18 May 1978 to 28 July 1978.

Inputs of total atrazine to a typical cell of the reservoir are assumed to be distributed completely at random in time with intensity function $(q_{in}/V)c_{in}(t)$. This assumption implies a Poisson probability distribution of the concentration of total atrazine input to a typical one-liter cell of the reservoir at any predetermined time t during the study period. Stated equivalently, at any time t in the study period the percentages of one-liter

cells predicted to contain $0, 1, 2, \ldots$ μg of total atrazine are computed as percentage points of a Poisson probability distribution with mean given by Equation (4.1). The assumption of a Poisson distribution of atrazine input is plausible in view of measured data on inflow concentrations. The MR model makes explicit allowances, computed in terms of probabilities, for differences between computed and measured concentrations in (i) input, (ii) the water column of the reservoir, and (iii) discharge at any given time during the study period. A complete model solution is derived: (i) concentration of total atrazine in the input flow [Equations (3), (3.1)]; (ii) concentration of total atrazine in a typical one-liter cell of the reservoir [Equations (4), (4.1)]; (iii) concentration of total atrazine in the discharge from the reservoir [Equations (5), (5.1)]. Recycling of atrazine between particulate and dissolved phases in the reservoir may occur, but separate accounting of balances in the two fractions is not maintained. It is assumed that particles, once removed by the discharge from the reservoir water column, do not return via the input during the study period.

An analytical solution to the model is obtained:

$$\text{Prob}\left(C_{\text{in}}(t) = C_{\text{in}}\right) = \frac{\left[m_1(t)\right]^{C_{\text{in}}}}{C_{\text{in}}!}e^{-m_1(t)} \qquad C_{\text{in}} = 0, 1, 2, \ldots, \quad 0 < t < 72,$$

$$(3)$$

where:

(i) $C_{\text{in}}(t)$ is a Poisson-distributed random variable describing the cumulative input of total atrazine (micrograms per liter) prorated into a typical one-liter cell of the reservoir by the day 18 May 1978 + t;

(ii) $m_1(t)$ is the mean of $C_{\text{in}}(t)$:

$$m_1(t) = \frac{q_{\text{in}}}{V}\int_0^t c_{\text{in}}(x)\,dx;\qquad (3.1)$$

and

$$\text{Prob}\left(C(t) = c\right) = \frac{\left[m_2(t)\right]^c}{c!}e^{-m_2(t)} \qquad (c = 0, 1, 2, \ldots, \quad 0 < t < 72), \quad (4)$$

where:

(i) $C(t)$ is a Poisson-distributed random variable describing the net concentration of total atrazine in a typical one-liter cell of the reservoir by the day 18 May 1978 $+\, t$;

(ii) $m_2(t)$ is the mean of $C(t)$:

$$m_2(t) = e^{-bt}\left(C(0) + \frac{q_{\text{in}}}{V} \int_0^t c_{\text{in}}(x)\, dx \right);\qquad (4.1)$$

(iii) $C(0)$ is the initial concentration of total atrazine in a typical one-liter cell of the reservoir on 18 May 1978;

(iv) b is the mean daily fractional loss of total atrazine from a typical one-liter cell of the reservoir:

$$b = \frac{q_{\text{out}}}{V} + K\frac{1}{1 + k_p M}.$$

The quantity dV/dt is set equal to zero in the MR model by a previous assumption and does not appear in the expression for the coefficient b. The quantity $(k_s k_p M)/(1 + k_p M)$ is set equal to zero in both the state-variable (SV) and MR models, based upon analysis of the size of the particulate fraction [1]. Then

$$\text{Prob}\big(C_{\text{out}}(t) = C_{\text{out}} \big) = \frac{\left[m_3(t) \right]^{C_{\text{out}}}}{C_{\text{out}}!} e^{-m_3(t)}$$

$$(C_{\text{out}} = 0, 1, 2, \ldots, \quad 0 < t < 72),\qquad (5)$$

where:

(i) $C_{\text{out}}(t)$ is a Poisson-distributed random variable describing the cumulative discharge of total atrazine from a typical one-liter cell of the reservoir t days into the study period;

(ii) $m_3(t)$ is the mean of $C_{\text{out}}(t)$:

$$m_3(t) = m_1(t) - m_2(t) + C(0).$$

RESULTS AND DISCUSSION

The computations shown in Tables 3–7 are based upon a value of the reaction rate constant equal to 0.01, the same as used in the SV numerical modeling results shown in Table 1. The ratios q_{in}/V and q_{out}/V are both set equal to $1/162$. The two available records of inflow concentration were time-averaged so as to produce a piecewise constant estimate of $m_1(t)$ (Table 2). The coefficient b is estimated as $b = 1/61.8$.

Table 3 contains estimated mean concentrations $m_1(t)$, $m_2(t)$, and $m_3(t)$ for selected days throughout the study period. Substituting values from Table 3 into Equation (4), expected percentages of cells in the reservoir containing given concentrations of total atrazine ranging from 0 to 5 μg/liter are computed (Table 4). It is clearly shown that low mean concentrations can be accompanied by much higher concentrations in a significant percentage of

TABLE 2
ESTIMATED MEAN INPUT CONCENTRATION $m_1(t)$

Subinterval	$m_1(t)^a$
18 May–26 June	0.40
27 June–25 July	8.00
26 July–29 July	2.70

[a]Weighted average over subinterval.

TABLE 3
ESTIMATED MEAN CONCENTRATIONS ON SELECTED DAYS

Date	Mean accum. input $m_1(t)$	Mean conc. in typical cell, $m_2(t)$	Mean accum. conc. in discharge, $m_3(t)$
18 May	0	0.150	0
25 May	0.017	0.150	0.017
31 May	0.032	0.151	0.032
7 June	0.050	0.151	0.049
14 June	0.067	0.151	0.066
23 June	0.089	0.151	0.088
27 June	0.147	0.198	0.100
29 June	0.246	0.289	0.108
6 July	0.593	0.586	0.161
14 July	0.990	0.887	0.254
21 July	1.337	1.120	0.368
26 July	1.562	1.242	0.471
28 July	1.612	1.230	1.624

TABLE 4

EXPECTED PERCENTAGES OF CELLS IN RESERVOIR CONTAINING GIVEN CONCENTRATIONS
OF TOTAL ATRAZINE

Date	$m_2(t)$	Percentage of cells					
		Conc. = 0	1	2	3	4	5 μg/liter
20 May	0.15	86	13	1			
14 June	0.15	86	13	1			
7 July	0.60	55	33	10	2		
28 July	1.23	29	36	22	9	3	1

cells when inflows contain a completely random distribution of atrazine. The percentages in Table 4 translate directly into probabilities that randomly selected cells of reservoir water will contain given concentrations, and hence probabilities that given numbers of samples are required in order to obtain the first cell containing any given concentration. For instance, the MR model predicts that on 7 July, 55 percent of one-liter cells in the reservoir contain no detectable concentration of total atrazine. There is therefore a 45-percent chance that the first sample drawn at random will contain a concentration of at least 1 μg/liter. Table 5 illustrates the point further by giving probabilities that single samples of one liter each will contain concentrations in excess of the upper ends of the ranges indicated. During the month of July there is a highly significant chance that single samples will yield concentrations in excess of the indicated ranges, even though the measured mean concentrations all fall within the ranges. Table 6 shows the same probabilities computed for concentrations of total atrazine in the reservoir discharge. As in Table 5, there is a significant probability that single samples will produce concentrations in excess of the range limits for the month of July. Since only means of measured samples are available, it is unknown whether individual

TABLE 5

PROBABILITY THAT A 1-LITER CELL CONTAINS A CONCENTRATION EXCEEDING
UPPER LIMIT OF INDICATED RANGE

Date	Range (μg/liter)	Probability	Meas. conc. (μg/liter)
18 May	(0, 1.00)	0.010	0.13
14 June	(0, 2.00)	0.001	1.20
29 June	(0, 1.00)	0.035	0.65
14 July	(0, 1.00)	0.223	0.95
28 July	(0, 1.00)	0.349	0.65

TABLE 6

PROBABILITY THAT A 1-LITER CELL IN DISCHARGE CONTAINS A CONCENTRATION
EXCEEDING UPPER LIMIT OF INDICATED RANGE

Date	Range (μg/liter)	Probability	Meas. conc.
18 May	(0, 1.00)	0.010	0.13
31 May	(0, 1.00)	0.010	0.67
14 June	(0, 1.00)	0.010	0.82
29 June	(0, 2.00)	0.004	1.10
14 July	(0, 1.00)	0.223	0.67
28 July	(0, 1.00)	0.349	0.50

measurements fell outside the given ranges. Distributions of concentrations on given days provide evidence for or against the two hypotheses (i) completely random distribution of concentration in inflow and (ii) complete and instantaneous mixing in the reservoir. Further evaluation of the evidence depends upon sample sizes upon which published measured mean concentrations were based and the distributions of individual measurements of concentrations. As matters stand the model, under the two hypotheses (i) and (ii) above, predicts a relatively wide range of measured concentrations for the month of July. A small variance of measured concentrations in the reservoir water column, provided the sample size is sufficiently large, would refute either of the hypotheses (i) or (ii) or possibly both. Lack of evidence in support of (i) above implies alternatives such as a more regular distribution of input concentration which may incorporate unidentified sources of input of total atrazine to the reservoir.

Table 7 estimates probabilities of different magnitudes of runoff of total atrazine from the reservoir watershed during the period of the study. The conversion factor used is 746 pounds of total atrazine per microgram per liter of input of total atrazine during the study period. The Poisson distribution of the cumulative total input of total atrazine [Equation (3)], using an estimated mean of 1.61 μg/liter (Table 3), yields a range of probable values for the cumulative input of total atrazine to the reservoir. As shown in Table 7, the most probable cumulative amount is estimated to be about 1500 pounds, although the amount could be as high as approximately 4400 pounds.

Although a budget for the soil column in the watershed was not attempted by either Schnoor et al. or the author, a rough estimate of the quantity of atrazine discharged onto the watershed can be obtained using the calculations from Table 7. According to Schnoor et al. [1] the watershed contains 138,565 ha, devoted to row-crop agriculture and pasture. Atrazine is applied

TABLE 7

ESTIMATED RUNOFF OF TOTAL ATRAZINE INTO RESERVOIR
FOR PERIOD 18 MAY–28 JULY 1978

Quantity of total atrazine (lb)	Probability
746	0.200
1492	0.322
2238	0.259
2981	0.139
3727	0.056
4473	0.015

at 0.5–0.8 kg/ha per year on portions of the watershed. Assuming no retention of atrazine from one year to the next in that portion of the soil-vegetation column that releases the chemical to the water table, and assuming that the entire watershed receives an application, the percentage of atrazine that is applied to the watershed which reaches the lake water column ranges from 0.3 to 2.9. If only one-half of the watershed receives atrazine, the range of percentages doubles to 0.6–5.8. Laboratory and microcosm tests would be required to further refine these estimates.

It is clear that either the deterministic or MR models are capable of much greater detail in budgeting the transport and fate of atrazine than available data permit in the case considered. Out of a total of twelve possible compartments identified for inclusion in a numerical model, only two were selected. Due to the simplicity of the model structure, the only information supplied by the MR model that was not provided by the deterministic SV model was (i) the probability distributions of concentrations in the lake water column, (ii) the probability distributions of concentrations in the lake discharge, and (iii) the probability distribution of estimated atrazine loading into the lake water column. The computed concentration in the lake water column from the SV model coincided with the mean of the time-indexed distribution of concentration obtained from the MR model.

CONCLUSIONS

Markov-renewal models are feasible both theoretically and computationally for tracking the transport and fate of toxic chemicals in the environment for cases in which the kinetics of transport, decay, and transformation are no higher than first-order, as illustrated by the present study. Formal allowance for statistical variability in field-measured concentrations and for differences

between computed and measured concentrations provides for applications of tools of statistical inference. Hypothesis testing about model assumptions underlying the Markov-renewal model suggests where data need to be collected with certain ranges of frequencies. In the present study available data were not sufficient to either strongly support or refute the two underlying assumptions of completely random distribution of input of total concentration of atrazine and complete and instantaneous mixing within the reservoir.

REFERENCES

1   J. L. Schnoor, B. R. Narasinga, K. J. Cartwright, and R. M. Noll, Fate and transport modelling for toxic substances, in *Modelling the Fate of Chemicals in the Aquatic Environment* (K. L. Dickson, A. W. Maki, and J. Cairns, Eds.), Ann Arbor Science Publishers, 1982, Chapter 9.