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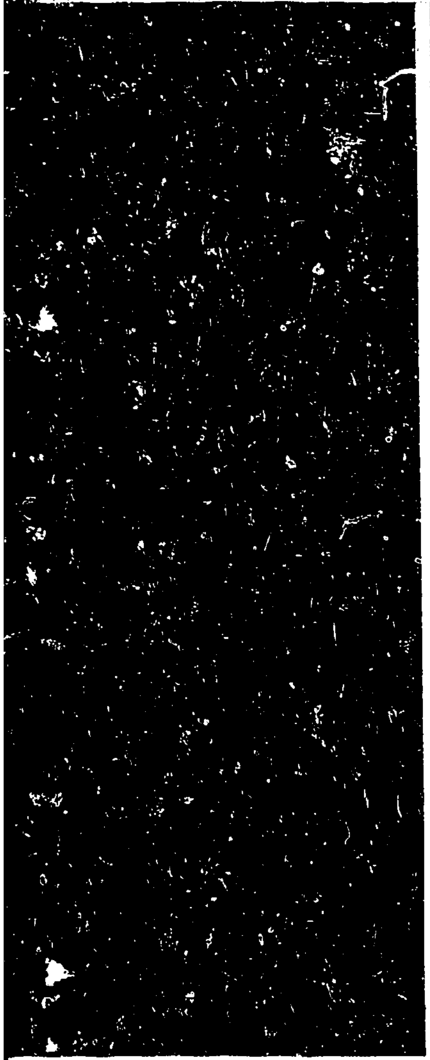
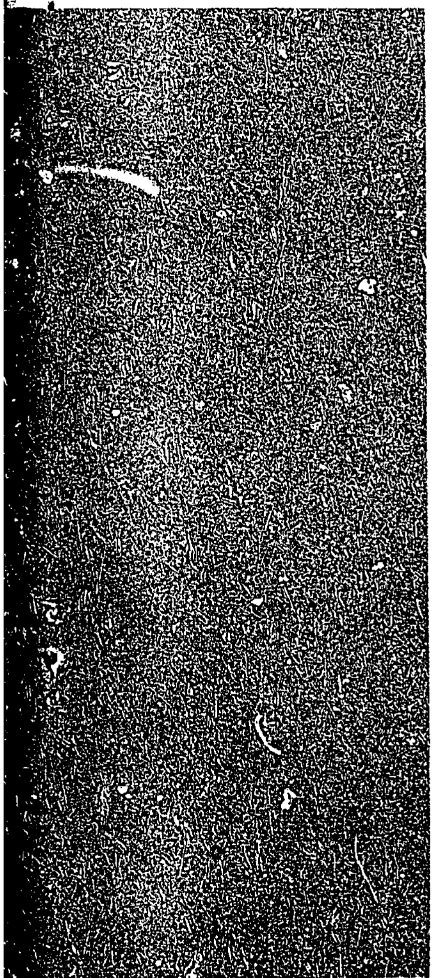


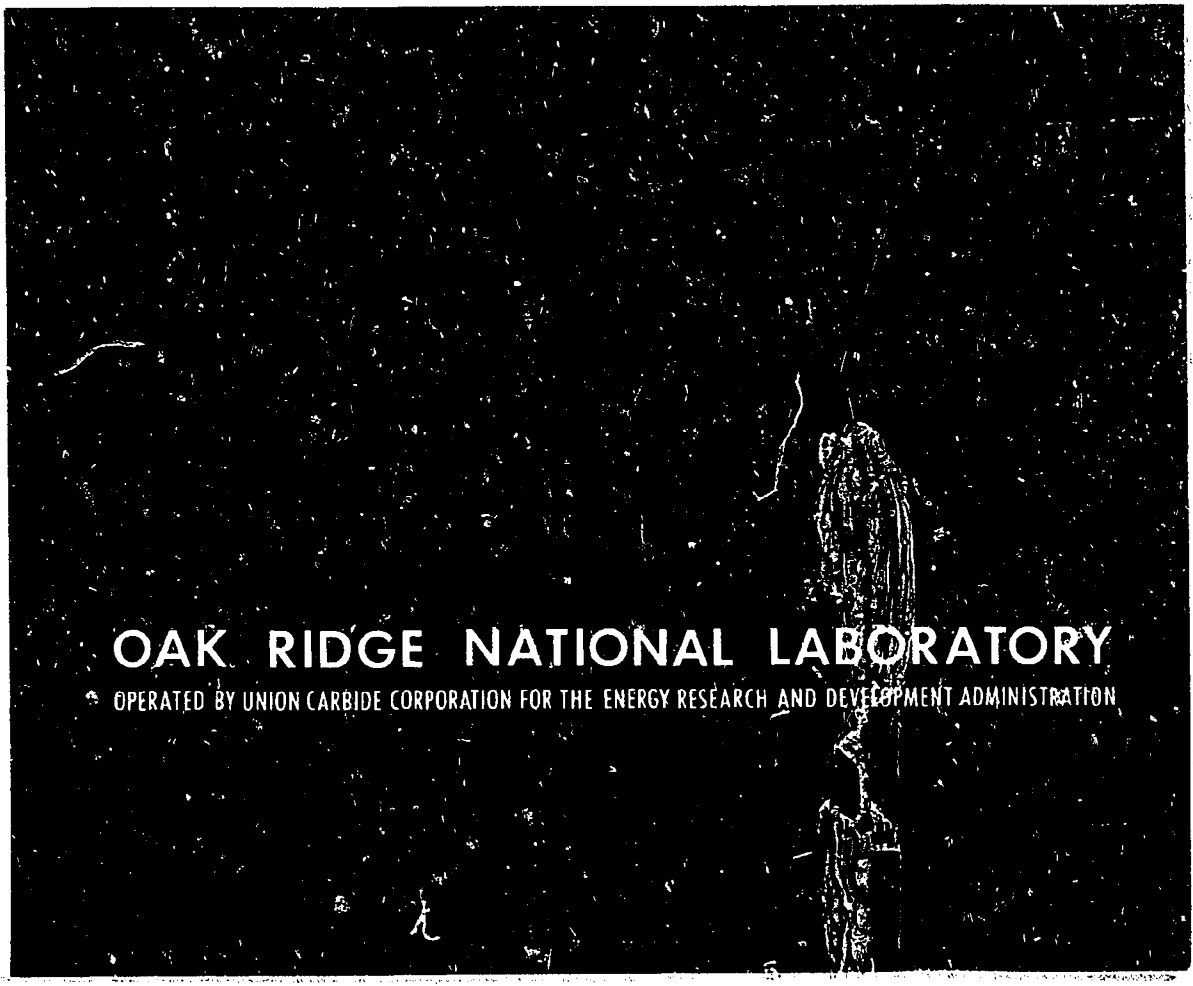
Studies of the Contributions of Nonpoint Terrestrial Sources to Mineral Water Quality

Dale D. Huff

MASTER

Environmental Sciences Division Publication No. 1046





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STUDIES OF THE CONTRIBUTIONS OF NONPOINT TERRESTRIAL SOURCES TO MINERAL WATER QUALITY[1,2]

Dale D. Huff

ENVIRONMENTAL SCIENCES DIVISION
Publication No. 1046

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[2] Originally presented at the December, 1974, meeting of the Joint National Research Council/The Institute of Ecology panel on Ecosystem Analysis, Austin, Texas.

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The author would like to thank Roger P. Betson for his help and cooperation in describing the TVA nonpoint source mineral quality model. I also wish to thank M. R. Patterson, J. K. Munro, and R. J. Raridon of the Computing Sciences Division, Oak Ridge National Laboratory, for their efforts in preparing trace metal simulations. S. E. Lindberg provided the most current data concerning atmospheric inputs of trace elements and their net accumulation at Walker Branch Watershed.

FOREWORD

The original motivation for assembling the material contained in the following pages was a presentation made by the author to the Joint National Research Council/The Institute of Ecology (NRC/TIE) Panel on Ecosystem Analysis. The materials were to be included in a workshop proceedings, however, those proceedings were not published. Because of current, ongoing interest in trace element transport and fate, the original manuscript was updated where appropriate and has been issued in its present form. A more detailed discussion of the ORNL Unified Transport model may be found in the October 1974 - December 1975 progress report of the Ecology and Analysis of Trace Contaminants project (ORNL/NSF/EATC-22, Ch. 3, February, 1976).

ABSTRACT

HUFF, D. D. 1977. Studies of the contributions of nonpoint terrestrial sources to mineral water quality. ORNL/TM-5876. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 35 pp.

The contributions of nonpoint sources of water quality constituents represent a background loading rate that will not be reduced easily. Consequently, those contributions may have a dominant effect on aquatic ecosystems once point sources have been controlled. Modeling studies conducted at the Tennessee Valley Authority and Oak Ridge National Laboratory represent contrasting approaches that highlight some of the possibilities for predicting nonpoint source inputs to aquatic systems.

The TVA model employs regression equations to empirically relate basin properties to concentrations of 15 water quality constitutents. In general, the model predictions are within plus or minus 50% of measured values for specific samples that represent conditions over the entire Tennessee Valley region. For impacted areas, where changes in concentration may span several orders of magnitude, the model may be used for estimating background levels, thus allowing quantitative assessments of incremental changes caused by watershed impacts.

At ORNL, a combined field research and modeling program has focused on heavy metals transport. Research has shown that metals such as Cd, Zn and Pb are accumulating in the study basin. To address questions related to long-term possible effects of such accumulation, a unified transport model has been developed. It is based on physical processes and has been designed to simulate atmospheric, terrestrial, and hydrologic processes important to transport and accumulation of trace elements. Application of the model to two different basins has shown its utility both for estimating transport and accumulation and for posing questions that guide field research.

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INTRODUCTION

Relationships between water quality and aquatic ecosystem response have often been studied to estimate the deleterious effects of increased point source inputs of pollutants. However, as point source inputs to water bodies are reduced in compliance with the Federal Water Pollution Control Act Amendments of 1972, Public Law 92-500 (also known as the Clean Water Act), we need to examine the extent to which aquatic ecosystems will recover. This is particularly important for comparing the benefits and costs resulting from Public Law 92-500.

It is beyond the scope of this paper to explore the interactions between water quality and ecosystem response. However, when the Clean Water Act is fully implemented, the nonpoint source component of water quality may have a dominant effect on aquatic ecosystem behavior. To predict that behavior, we must estimate the amounts of materials from nonpoint sources that are present in streamflow. Hence, the objective of the following discussion is to provide background information on how that can be done. The discussion is confined to examples of models used by the Tennessee Valley Authority and by Oak Ridge National Laboratory. Even though the examples are admittedly limited, they represent contrasting approaches that span a large part of the spectrum of modeling possibilities.

THE TVA NON-POINT SOURCE MINERAL WATER QUALITY MODEL

The work of Betson and McMaster (1974) is an empirical approach to the estimation of mineral water quality constituents from nonpoint input sources. For the sake of brevity, only highlights of the TVA model are presented here. The essence of the model is:

$$C_i = a_i \left[\frac{Q}{DA}\right]^{b_i} , \quad i = 1,n \qquad (1)$$

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where

C_i = concentration of water quality constituent i,
Q = stream discharge rate,
DA = drainage basin area above measurement point,
a_i, b_i = parameters characterizing constituent i, and
n = number of water quality constituents considered (Betson and McMaster used n = 15).

Equation (1) relates the concentration of water quality constituents and flow conditions at a particular point in a rural watershed. The coefficient a_i is the expected concentration of the i th mineral constituent when the stream discharge per unit area is unity. The coefficient b_i relates the expected concentration C_i to discharge per unit area. When b_i is greater than zero, concentration will increase with increasing flow rate; when b_i is less than zero, concentration is inversely related to discharge.

Model Application

Application of the TVA model to a watershed depends upon knowledge of the coefficients a_i and b_i in equation (1). Betson and McMaster (1974) have described a two-step method for estimating them. First, regional values of the coefficients must be determined from observed data. Betson and McMaster analyzed corresponding flow and concentration data for 15 water quality constituents for 66 different watersheds. In each basin, at least 10 separate sets of observations were available. They used a logarithmic transformation to linearize equation (1) and linear regression to determine the 15 sets of a_i and b_i coefficients for each basin. They found that the standard error of concentrations predicted by equation (1) averaged 46 ± 34% when the derived a_i and b_i coefficients were used.

Determination of Coefficients

The second part of the TVA method was to relate the a_i and b_i coefficients to measures of forest cover and geologic parent materials present in the study watersheds. Betson and McMaster found that they could use the equations represented by

$$a, b = N_1F + N_2C + N_3S + N_4I + N_5U \quad ,$$

where

a, b are the coefficients in Eq. 1 (for a given constituent),
$N_1 \ldots N_5$ are regression coefficients (for a given constituent),
F is the fraction of the watershed that is forested,
C is the drainage area fraction over carbonate rock,
S is the drainage area fraction over shale-sandstone rock,
I is the drainage area fraction over igneous rock, and
U is the drainage area fraction over unconsolidated rock.

Topographic and geologic maps contain enough information to define the variables F, C, S, I, and U for any basin of interest, thus the regression coefficients in equation (2) were determined using the data analyzed in the first step. Table 1 shows a few examples of the variability of basin factors within a physiographic province. These data help to explain the observed variation in water quality constituents between basins in close proximity. Table 2 contains examples of regression coefficients found to apply in the TVA region. The complete set of all 150 regression coefficients that define equation (2) can be found in the original reference (Betson and McMaster, 1974).

Results

The accuracy of the model was tested by its application to 12 watersheds that were not included in the original 66. The test

Table 1. Examples of measured basin factors from the valley and ridge physiographic province of the Tennessee Valley region

	Fraction of watershed attributed to factor[a]				
Watershed	Forest	C	S	I	U
Beech Creek at Kepler, TN	0.79	0.0	1.00	0	0
Little River at Wardell, VA	0.21	0.97	0.03	0	0
Reedy Creek at Orebank, TN	0.45	0.59	0.41	0	0

Adapted from Betson and McMaster (1974).

[a] C is the carbonate rock fraction
S is the shale-sandstone rock fraction
I is the igneous rock fraction
U is the unconsolidated rock fraction

Table 2. Examples of regression coefficients that relate forest and geology fractions to the TVA mineral quality model

Constituent	Concentration coefficient		Regression coefficient			
		N_1	N_2	N_3	N_4	N_5
Ca	a	-8.52	53.9	13.4	8.32	8.41
	b	0.064	-0.116	-0.203	-0.229	-0.005
HCO_3	a	-22.8	200	35.3	26.8	21.8
	b	0.110	-0.156	-0.294	-0.335	-0.139
SO_4	a	-7.41	9.15	12.5	7.90	9.56
	b	-0.302	0.103	0.155	0.272	0.592
TDS	a	-39.0	195.6	68.5	55.5	57.7
	b	0.016	-0.094	-0.146	-0.142	0
pH	a	-0.573	8.37	7.32	7.33	6.86
	b	-0.003	-0.010	-0.003	-0.013	-0.003

Adapted from Betson and McMaster (1974).

results were intended to be representative of the six physiographic provinces within the seven-state Tennessee Valley region. They consisted of predictions of concentrations of 15 mineral water quality constituents for specific points in space and time. In general, the standard errors averaged plus or minus 50%, with some larger scatter. Thus, the use of predicted values for the coefficients a_i and b_i of equation (1) produced results that were almost as good as those expected when a_i and b_i were derived directly from water quality data (50% vs 46%).

The results in Table 3 illustrate two aspects of model use. The data shown for White Creek (near Sharps Chapel, Tennessee) are generally representative of the correspondence between model predictions and observations for a rural or undisturbed basin. The maximum prediction error for the constituents shown is 65% (SO_4 concentration at high flow). Thus the model may be used to estimate certain aspects of water quality for rural basins where streamflow observations are available. In contrast, Betson and McMaster found discrepancies that exceeded an order of magnitude when they tried to simulate sulfur and bicarbonate concentrations for Crooked Fork watershed near Wartburg, Tennessee; however, there was active strip mining on the Crooked Fork basin when the observations on water quality were made. One may infer that the model estimated water quality that would exist in the absence of an impact, and that the differences were caused by strip mining activity. Thus, the TVA model may be useful for evaluating the impact of man's activities on watersheds where data were not obtained prior to disturbance and, similarly, to estimate the maximum improvement that could ever be achieved in some water quality parameters if one assumes that the undisturbed state represents the best water quality possible. The latter point is the main reason for presenting the work of Betson and McMaster here.

In addition, the TVA model parameters can be measured rather easily. That is very important to a potential user because it lends

Table 3. Example comparisons of observed concentrations of water quality constituents and those estimated using the TVA mineral quality model

Watershed	Date	Q (csm)		Ca (mg/l)	HCO_3 (mg/l)	SO_4 (mg/l)	TDS (mg/l)	pH
White Creek near Sharps Chapel, TN	3-72	4.10	obs.	28	137	3.7	135	7.8
			sim.	42	166	1.3	140	7.7
	12-71	0.735	obs.	39	178	4.5	145	8.0
			sim.	46	180	1.8	160	7.8
Crooked Fork Near Wartburg, TN	7-67	19.1	obs.	7.7	10	23	48	6.2
			sim.	4.2	9	5	25	6.7
	7-68	0.062	obs.	45	2	249	409	4.5
			sim.	10	30	8	54	7.0

Adapted from Betson and McMaster, 1974.

strength to the general utility of the model. Even though the approach is empirical and there are limits to the applicability of the results, the model may provide a useful method for estimating the best mineral water quality that can be expected as a result of the Clean Water Act.

THE RELATIONSHIP OF TVA AND ORNL MODELING APPROACHES

The TVA model has limited applicability because it does not deal explicitly with man's perturbations of the landscape. This capability is needed for estimating water quality in drainage basins that are being changed by man's activity. As experience and data are accumulated, models of the type developed by Betson and McMaster (1974) will become increasingly useful for dealing with perturbed basins. However, in the absence of extensive data, estimation of nonpoint source water quality must rely upon the assembly and linkage of the results from many independent studies that cover the spectrum of transport processes. For example, the evaluation of the transport and fate of anthropogenic elements and compounds is particularly important to those concerned with the development of energy facilities. Because of the chance for long-term build-up of some potentially toxic materials in the environment, a transport model must consider their input, disposition, and movement. I think that a more complex, mechanistic model is necessary to allow one to address that problem. Furthermore, I believe that atmospheric contaminants are closely linked to water pollution from nonpoint terrestrial sources. Therefore, I wish to highlight studies of trace element transport that are in progress at Oak Ridge National Laboratory. This work includes field studies and development and application of a Unified Transport Model (UTM) that comprises linked atmospheric, terrestrial, and aquatic processes (Patterson et al., 1974a).

ORNL STUDIES RELATED TO TRACE CONTAMINANT TRANSPORT

Oak Ridge, Tennessee, is surrounded by three separate coal-fired steam plants with a combined consumption of about [illegible]^6 tons of coal per year. Even with pollution control devices on the stacks, there can be significant discharges of trace materials to the atmosphere. Table 4 contains estimates of the minimum annual atmospheric discharge of selected elements from the steam plants in the Oak Ridge area. These values have been estimated from measured elemental discharges at the Allen Steam Plant in Memphis, Tennessee, adjusted for differences in coal consumption. For example, about 0.5 tons of mercury, 0.9 tons of lead, and more than 9 tons of zinc are released to the atmosphere annually. Our field studies are focused on the rates and amounts of deposition of these elements relative to their natural occurrence and cycling.

Field Studies

Preliminary data indicate that depositions of atmospheric inputs to Walker Branch Watershed, near Oak Ridge, Tennessee, occur primarily as wetfall for some elements (Cd, Pb and Zn), are equally divided between wetfall and impaction/sedimentation (SO_4-S), or are predominantly in the form of impaction/sedimentation (Mn) (Lindberg and Turner, 1977). Through a combination of modeling and empirical data it has been estimated that local coal-fired power plants can account for up to 20% of individual elements present in the air mass over the watershed. A similar fraction of the deposition thus results from these sources (Andren and Lindberg, 1977). The data presented in Table 5 show the approximate annual deposition of five trace constituents via precipitation and dry deposition for the Walker Branch Watershed study area (97.5 ha). The most interesting results (Lindberg and Turner, 1977) deal with the mass balance of selected trace elements (Table 6). The output of the more toxic trace metals is less than 10% of the input. Furthermore, element ratios indicate that the output of certain

Table 4. Estimated[a] minimum annual discharge of elements from the stacks of three (2630 Mw_e total) coal-fired steam plants near Oak Ridge, Tennessee

Element	Atmospheric discharge (tons/year)	Element	Atmospheric discharge (tons/year)
Al	142	Mn	0.95
As	0.95	Mo	0.35
Ba	1.4	Na	18.9
Br	23.6	Ni	0.028
Ca	47.3	Pb	0.95
Cd	0.09	Rb	0.33
Ce	0.19	Sb	0.95
Co	0.09	Sc	0.047
Cr	1.4	Se	1.89
Cs	0.05	Si	25.34
Cu	0.70	Sm	0.014
Eu	0.0024	Sr	0.032
Fe	284	Ta	0.0033
Ga	0.24	Th	0.047
Hf	0.0095	Ti	18.9
Hg	0.47	U	0.095
K	43	V	1.89
La	0.095	Zn	9.46
Mg	236		

[a] Based on atmospheric emission data for the Allen Steam Plant, Memphis, Tennessee.

From Andren *et al.* (1975).

Table 5. Element Deposition on Walker Branch Watershed, near Oak Ridge, Tennessee (Sept 75 - Aug 76) (g/ha/yr).

Element	Cd	Mn	Pb	Zn	SO_4-S
Deposition by wetfall	11.6	19.2	72.0	92.4	10.9×10^3
Deposition by impaction/sedimentation	0.14	420	22	29	8.7×10^3

From Lindberg and Turner, 1977

Table 6. Annual Net Retention of Trace Elements at Walker Branch Watershed, near Oak Ridge, Tennessee (9/75 - 8/76).

	Annual Net Watershed Retention (% of total atmospheric inputs)				
Element	Cd	Mn	Pb	Zn	SO_4-S
	99	56	98	90	54

Adapted from Lindberg and Turner, 1977.

metals from the basin is mainly derived from the soils rather than the anthropogenic aerosol inputs. Thus, one may conclude that the watershed is efficient in retaining metals such as Cd, Zn, and Pb (Lindberg and Turner, 1977). This conclusion raises important questions. For example, where are trace metals retained within a basin? Will concentrations eventually reach hazardous levels? Is a long-term water pollution problem being created?

Modeling

A unified transport model (Patterson et al., 1974a) has been developed at Oak Ridge National Laboratory to study those questions and others related to them. The models contained in the UTM have been described in detail elsewhere (Mills and Reeves, 1973; Patterson et al., 1974b), so I will simply highlight their operation here.

The structure of the UTM is represented schematically in Fig.1. The atmospheric component is the Atmospheric Transport Model (ATM) developed by Mills and Reeves (1973). The ATM is based upon a Gaussian plume model and calculates deposition rates of aerosols for any point within a watershed. Concentrations of airborne aerosols at ground level are also calculated. The model includes consideration of point, area, line, and windblown sources for air pollutants. Deposition occurs by fallout and washout caused by rain falling through the plume. Air concentrations depend upon source strength, atmospheric stability, and wind speed and direction patterns. The spatial resolution of the ATM is limited to a 50-km radius from any source because of inherent properties of the Gaussian plume model. One can use the model to simulate larger areas by constructing a mosaic of sub-area calculations. The deposition values calculated by the ATM are used for input to the terrestrial component of the UTM, which is the hydrologic transport model.

The basic assumption that underlies the hydrologic transport model is that water is one of the major carriers of materials through the terrestrial system. Thus, trace material transport can

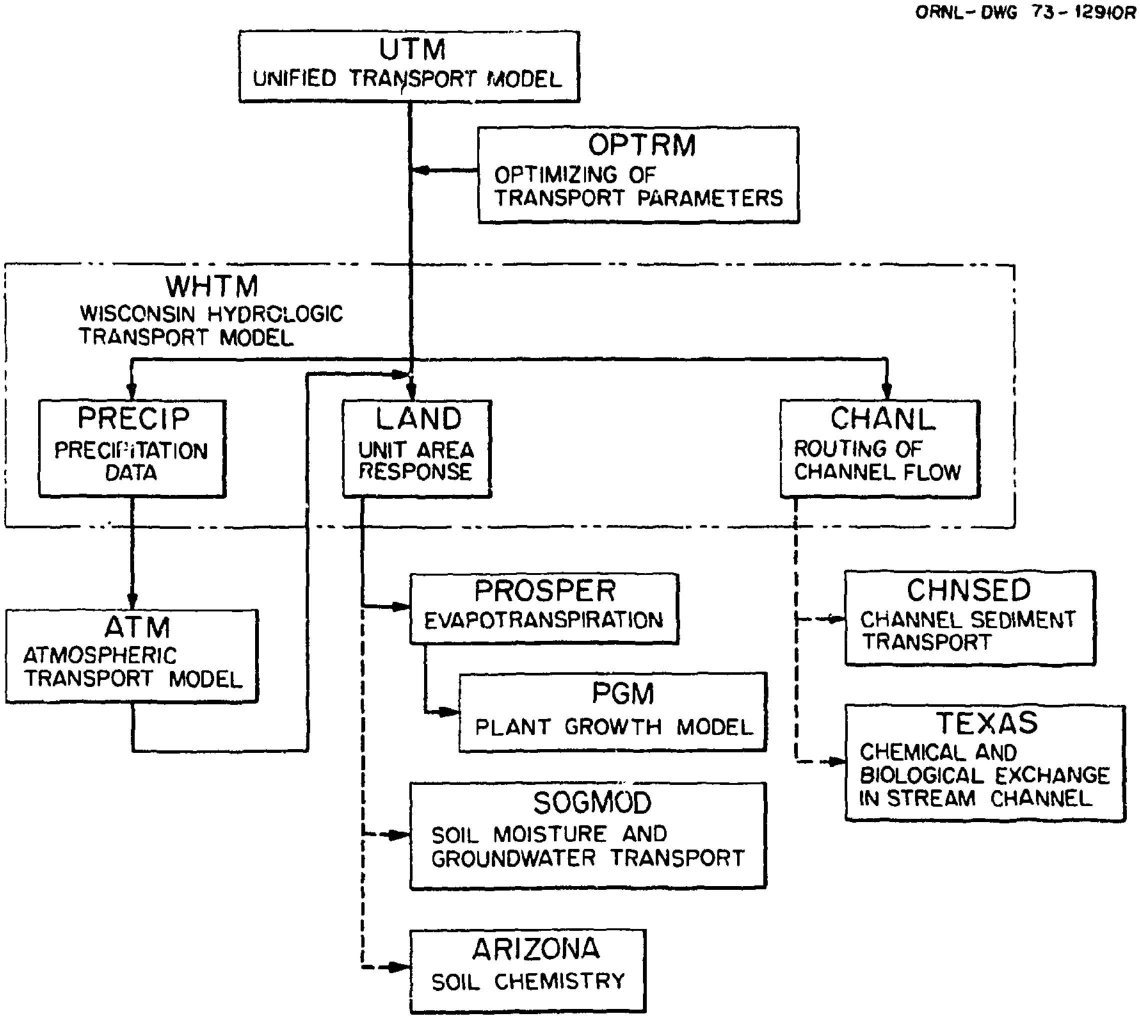

Fig. 1. The structure of the Unified Transport Model. From Patterson et al. (1974).

be modeled by combining hydrologic calculations with consideration of the chemistry of trace materials in aqueous media. Briefly, the hydrologic transport model is structured to receive atmospheric wet and dryfall input to the watershed canopy and then simulate its movement until it is discharged in streamflow. The model simulates the amount of material washed from the canopy to the land surface during rainfall and allows for the exchange and uptake or adsorption of materials on surface soil. Surface runoff and scour of soil particles are considered together with leaching of trace elements into the soil profile. An experimentally derived equilibrium distribution coefficient is used to estimate the concentration of contaminants in subsurface soil water. That concentration and the rate of soil water drainage are combined to estimate a subsurface input to the stream channel.

Finally, the outputs from the terrestrial component of the UTM enter the channel component, where flows are routed by a kinematic wave approximation. This portion of the program simulates transport of dissolved and particulate materials in streamflow. Suspended and bedload transport are considered by the model. Mixing and exchange between the aqueous and solid phases for the particular chemical species of concern are also simulated. However, thus far we have not emphasized the effects of biological processes on transport. I think that is one direction we must pursue.

At present, the UTM can be used to estimate concentrations of elements in streamflow and relate them to atmospheric inputs and basin properties. So far our research has focused on how well we can achieve that objective. Figure 2 illustrates the ability of the UTM to reproduce flow patterns and potassium transport for Walker Branch Watershed. The UTM parameters were held constant for the full four-year period simulated. In general, the model underestimates streamflow, especially during spring and early summer months. This may be the result of underestimating the extent of the groundwater reservoir that feeds Walker Branch. Field data to resolve the question are not yet available. Simulated potassium

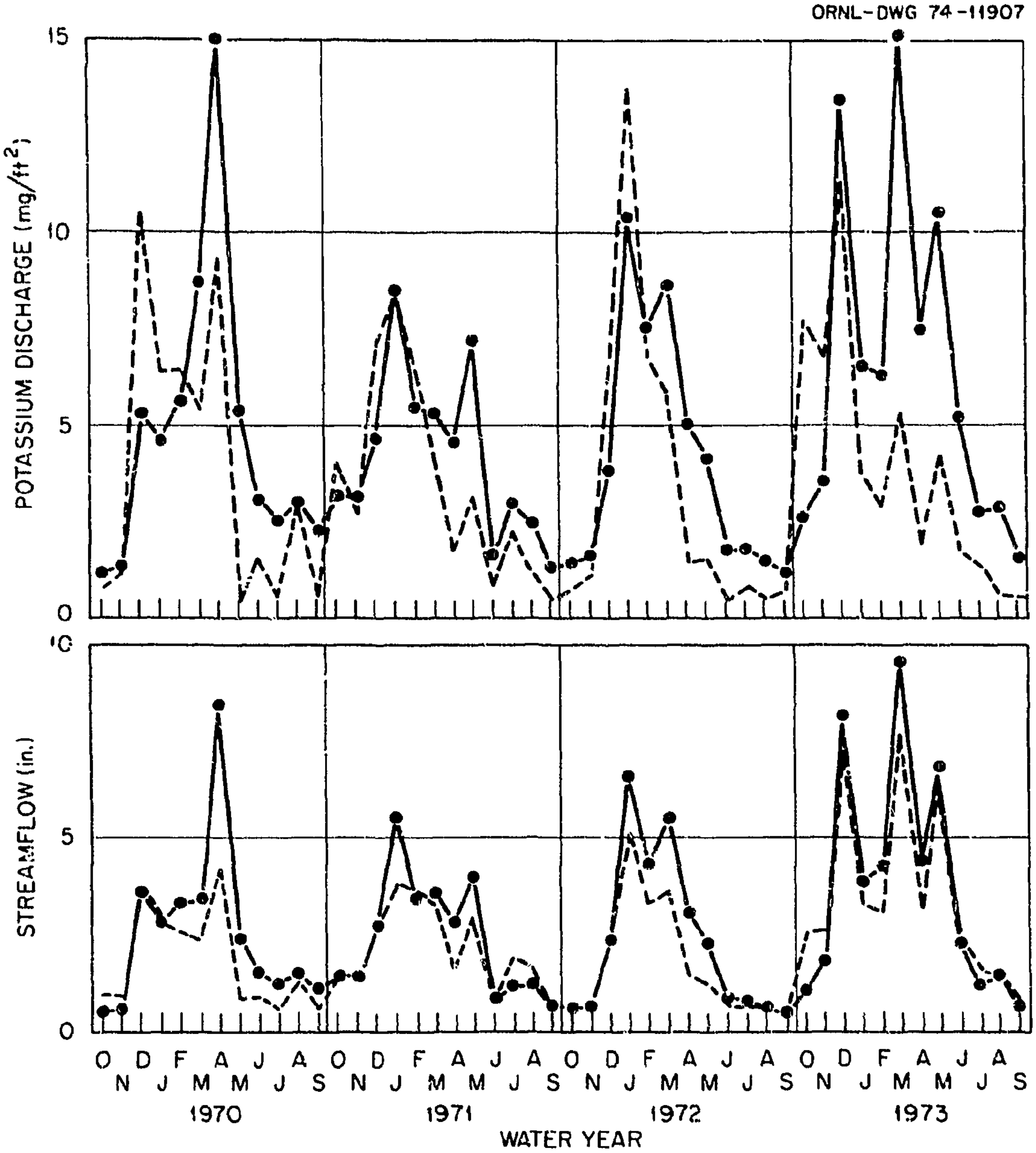

Fig. 2. Observed and simulated transport of water and potassium on Walker Branch Watershed near Oak Ridge, Tennessee. From Patterson et al. (1974).

transport shows poorer agreement with observed values than streamflow, although monthly flux estimates are generally within a factor of 2 of actual values.

Figure 3 illustrates observed and simulated streamflows for June to December 1973 on Walker Branch Watershed. Cadmium discharge was estimated for the same period, and the results are shown in Fig. 4. The simulation was based upon preliminary data, so the goodness of fit to the observed data should be interpreted cautiously. The point of the figure is the discrepancy in December. The overestimate resulted from simulation of large amounts of overland flow. The result highlights the importance of storm event runoff to trace metal transport. Our sampling program has not focused on storm events, although the model results indicate it should. In fact, we have already begun to change our sampling program to place primary emphasis on storm events.

CONCLUSIONS

On the basis of the results that we have obtained, I think it is fair to say that the UTM is capable of estimating trace metal transport through a watershed and predicting concentrations in streamflow. However, it is still very much a research tool, and we need to do more work before we can apply it with confidence for new situations. For example, we have used data that are relatively easy to measure when we have evaluated model results. As we use more detailed field results to refine and evaluate the UTM, our ability to answer questions about concentrations of elements within a basin will improve.

Meanwhile, the UTM is a tool that can be used now. For example, we have joined forces with staff at the University of Missouri at Rolla to study heavy metal export from a watershed adjacent to a mine and smelter in the "New Lead Belt" area. We are particularly interested in examining the effects of elevated heavy metal concentrations on the forest ecosystem there. (Subsequent work with a newer version of the UTM has been reported by Munro et al., 1977).

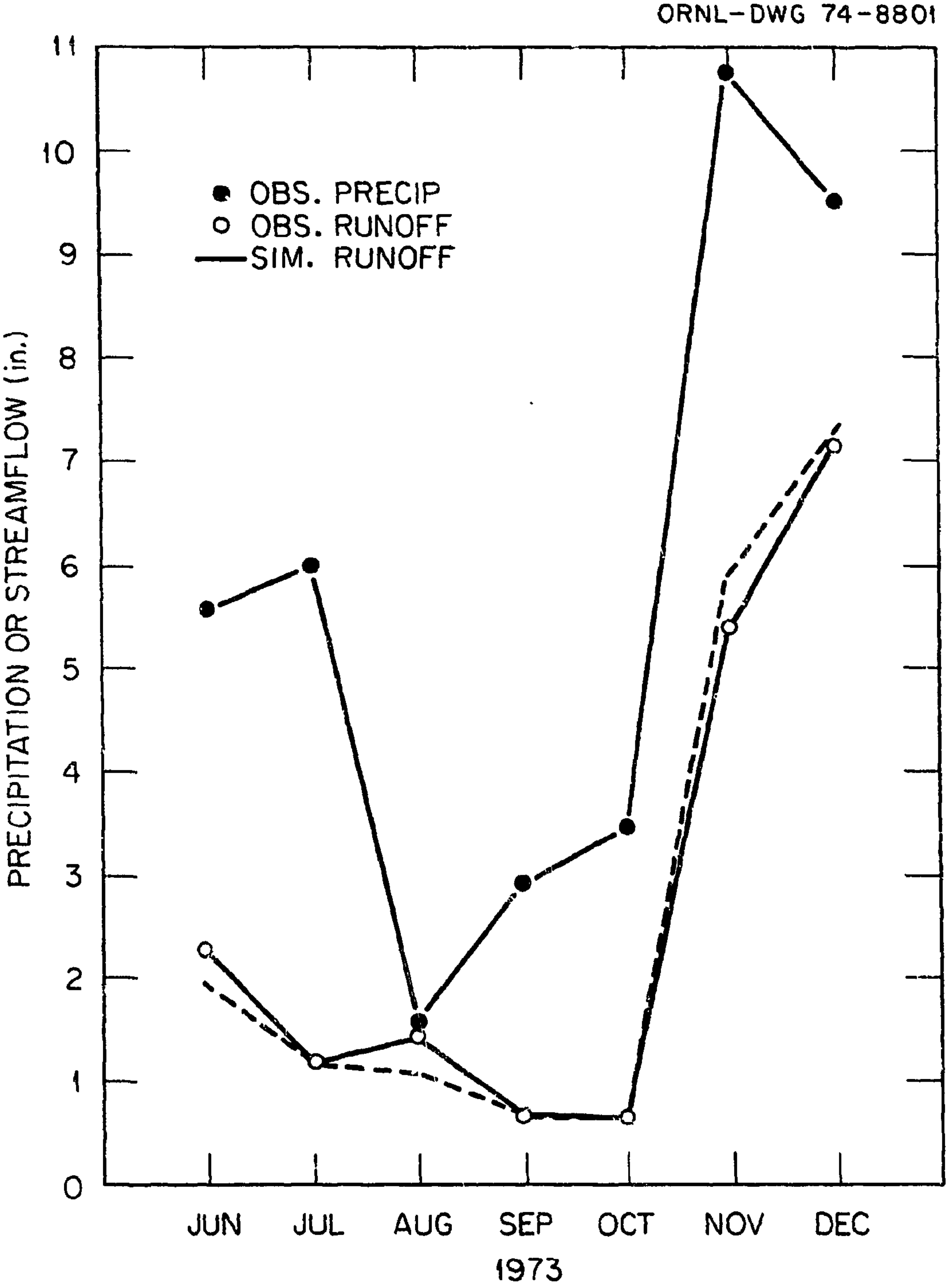

Fig. 3. Walker Branch Watershed water budget: June-December 1973. From Patterson et al. (1974).

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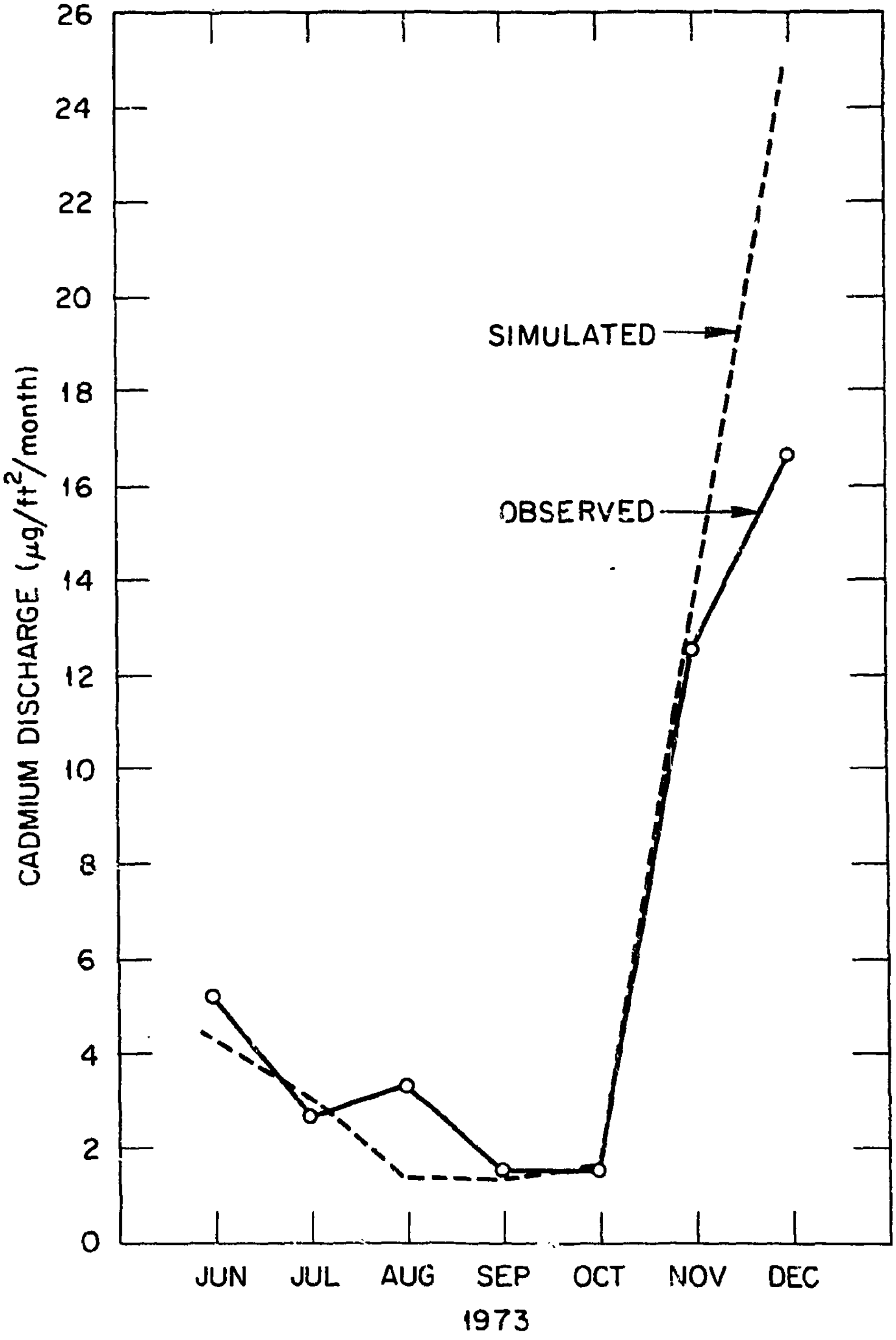

Fig. 4. Walker Branch Watershed cadmium discharge: June–December 1973. From Patterson et al. (1974).

Thus, with each new study we expect to improve the reliability of the UTM. We believe that continued application of the model will establish its usefulness for assessing the impact of man's activities on water yield and background water quality.

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