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Concentration Models for Dissolved Nitrogen Nutrients from Non-point Sources in Potomac Estuary

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Multiple regression analysis and the hierarchical predictor selection method were used to formulate quantitative models for estimating concentrations of dissolved nitrite + nitrate nitrogen and total dissolved nitrogen from non-point sources in the Potomac estuary. The models of these nitrogen nutrients were respectively expressed by four and five predictors (simple, quadratic and interactive terms) of two independent variables, daily mean water flows and daily mean air temperatures. A bi-weekly sampling (26 observations per year) was recommended for model reparameterization.

Keywords: concentration models, dissolved nitrite–nitrate nitrogen, dissolved total nitrogen, non-point sources, estuarine system.

1. Introduction

In order to understand the impacts of nutrient loadings on the Potomac estuary ecosystem and to facilitate prudent management, it is essential to measure accurately the concentration and quantity of nutrients that flow into, and are transported through, the estuary (Callender *et al.*, 1984). Such measurements require a proper sampling method for water quality data and suitable models for quantitative estimates of nutrients.

Four linear regression models have been reported for estimating concentrations of nitrogen and phosphorous nutrients from non-point sources in the Potomac River water (Table 1). The Hydroscience (1976) model is statistically unacceptable because the coefficient of determination (r^2) is too low (Thomann and Fitzpatrick, 1982): 0·24 to 0·42 (Hydroscience Inc., 1976); 0·34 (Sullivan, 1980); less than 0·5 (U.S. Geological Survey,

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TABLE 1. Linear regession models for estimating nutrient concentrations from non-point sources in Potomac estuary reported in literature (C, nutrient concentration; N, nitrogen; P, phosphorus; Q, instantaneous water flow; a, constant; b, regression parameter)

Model	Formula	r^2	Source
$\ln C = a + b\ln Q$	$\ln CN = 0{\cdot}02 + 0{\cdot}44\ln Q$	0·42	Hydroscience (1976)
	$\ln CP = 0{\cdot}02 + 0{\cdot}18\ln Q$	0·24	-
$\ln C = a + b\ln Q$	$\ln CN = 0{\cdot}00001\ln Q$ when $Q < 283{\cdot}2$ m^3/s	–	Smith (1980)
	$\ln CN = 1{\cdot}11$ when $Q > 283{\cdot}2$ m^3/s	--	–
$\ln(C \times Q) = a + b\ln Q$	$\ln(CN \times Q) = 0{\cdot}01 + 1{\cdot}55\ln Q$	0·85	FWPCA (1969)
	$\ln(CP \times Q) = 0{\cdot}02 + 1{\cdot}19\ln Q$	0·93	--
$\ln(C/Q) = a + b\ln(1/Q)$	$\ln(CN/Q) = 0{\cdot}39 + 0{\cdot}86\ln(1/Q)$	0·80	Smullen *et al.* (1982)
	$\ln(CP/Q) = 1{\cdot}00 + 1{\cdot}33\ln(1/Q)$	0·72	–

1980). The Smith (1980) model is merely a variation of the Hydroscience Inc. (1976) model, where b [the regression parameter = 1 when water flow (Q) is less than 283·2 m^3/s, and $b=0$ when Q is greater than 283·2 m^3/s]. The loading-rate model of the Federal Water Pollution Control Administration (1969) and the "variance-establishing transformation model" of Smullen *et al.* (1982) represent an auto-correlation manipulation of the Hydroscience Inc. (1976) model by multiplying (the former) or dividing (the latter) by Q on the Hydroscience Inc. (1976) linear regression equation. Their models are no improvement over the Hydroscience model.

Blanchard and Hahl (1987) used the MAXR (maximum r^2 improvement technique) analysis, and attempted to establish a multiple regressive relationship between daily mean nutrient concentrations (dependent variable) and suspended sediment, pH, temperatures, dissolved oxygen contents (DO), and specific conductance (independent variables). They found that dissolved nitrite + nitrate nitrogen concentrations inversely correlate with water temperatures (T), while dissolved phosphorus concentrations correlate with pH and DO. Their analysis did not yield any relationship that could be used to determine daily nutrient concentrations. Instead, they estimated nutrient loadings by using the hydrograph method (Porterfield, 1972). In this method, the nutrient concentrations were estimated by continuously plotting the constituent nutrient concentrations and water flows. This method required a large amount of data sampled at short time intervals. It is complicated and time consuming.

In the absence of an adequate model, arithmetic means for baseflows and flow-weighted means for storm flows have been used to estimate nutrient loadings (Metropolitan Washington Council of Governments, 1984). This method raises a question as to the validity of the estimates of nutrient inputs that were made in the past or will be made in the future, and has severely limited our ability to estimate the non-point nutrient inputs that can best be controlled. Towards this end, statistic models that estimate concentrations of nutrient inputs from non-point sources to the Potomac estuary were pursued in this study, using dissolved nitrite + nitrate nitrogen ($DNO_{2,3}$) and total dissolved nitrogen (DN) as examples.

2. Data sources

There were two types of data available for this study: the instantaneous data and discrete data. Instantaneous data are those collected sporadically at unequal time intervals. During December 1977 to September 1981, U.S. Geological Survey (USGS) conducted the Potomac Estuary Study Program in which an intensive data collection was made at Chain Bridge (Blanchard and Hahl, 1981; Blanchard *et al.*, 1982; Blanchard, 1983). Water quality data also were collected at Chain Bridge as a part of other programs by USGS during the same period (U.S. Geological Survey, 1979–1982). These data were used in this study. The water discharge of the Potomac River at Chain Bridge is the largest contribution (about 88%) of freshwater to the Potomac estuary. The amount of nutrients measured at Chain Bridge dominates that from non-point sources that enters the estuary (Metropolitan Washington Council of Governments, 1984, 1987).

Discrete data are those collected systematically at constant intervals. USGS has continuously measured water flow at the Chain Bridge gauging station and reported it as daily mean flows (Q_m) in Water Resources Data–Maryland and Delaware (U.S. Geological Survey, 1979–1982). Also, Washington National Airport at Arlington, Virginia, has recorded daily mean air temperatures (T_a). The weather observations at the airport are considered to be representative of climatic conditions of the tidal freshwater zone of the Potomac estuary (Metropolitan Washington Council of Governments, 1984). The T_a data were obtained from the National Oceanic and Atmospheric Administration.

3. Modeling method

3.1. Instantaneous T, Q, pH and DO as independent variables

The data set of the 1979 water year which had the highest number of instantaneous observations on $DNO_{2,3}$ and DN concentrations and corresponding environmental variables, Q (m^3/s), T(^{0}C), pH and DO (mg/l) were used for modeling. The nutrient concentrations were plotted against each of the environmental variables and their relationships were examined. A correlation matrix was computed for environmental variables to assess any interdependency and multicollinearity. On the basis of these relationships, the potential independent (environmental) variables for the model were chosen. A multiple regression analysis was used to relate the nutrient concentrations to the potential independent variables including linear, quadratic and interactive terms (second-order model) as predictors.

In multiple regression analysis, multicollinearity creates analysis problem when independent variables are highly correlated with each other. This may cause the t_{b_j} statistics (b_j: the least square estimate of parameter B_j; t_{b_j}, the t value that tests the significant level of difference between parameter B_j and zero) for individual independent variables to look unimportant, even when they are important. When the correlation coefficient between two independent variables is greater than 0·9, the multicollinearity is severe (Bowerman and O'Connel, 1987). Whenever such correlation was noted among the variables used in this study, one of the two correlated variables was excluded as a potential variable.

To select significant predictors, the hierarchical predictor selection method proposed by Peixoto (1987) was used. Since powers or multiples of variables are always highly correlated to the variables themselves, multicollinearity may exist in a model which contains cross-products and other higher order predictors of independent variables (Neter and Wasserman, 1974). In such cases, a linear transformation (coding) of the form, X-$\bar{X}$, where $\bar{X}$ is the average of the independent variable X, was used to eliminate or to reduce the multicollinearity. However, t values for regression coefficients of lower-order predictors may change as a result of linear transformations (Griepentrog *et al.*, 1982), and thus a polynomial regression model should be tested by sequential sum of squares. That is, one should test only the highest-order predictor, retaining the lower-order predictors in the model regardless of their t values (Barr *et al.*, 1976). Peixoto's (1987) method takes into account the hierarchy of predictors and modifies existing stepwise regression and other related one-step procedures, such as backward elimination and forward selection, to restrict their search for a model that is hierarchically well-formulated. A parsimonious model that includes high-order predictors but excludes some of the lower-order predictors may be acceptable, if the model is to be used for prediction purposes only and no reparameterization is expected. If estimation and reparameterization are the intended uses of the model, as in the case of this study, a hierarchically well-formulated model is recommended (Griepentrog *et al.*, 1982; Peixoto, 1987). When the highest-order predictor was decided, the variables were then decoded and the final model was established by using the original variables.

The multiple regression procedure in the microcomputer package STATGRAPHICS was used to calculate the least square estimates of parameters. Outliers were excluded at the 99% confidence level. The adjusted coefficient of determination (r^2) and standard deviation (SD) were used to evaluate the fitness models. A model having a larger adjusted r^2 value and a smaller SD value is preferred.

3.2. DISCRETE T_a AND Q_m AS INDEPENDENT VARIABLES

Multiple regressive models were also formulated for $DNO_{2,3}$ and DN by using the instantaneous concentrations of the nitrogen nutrients as dependent variables and T_a (°C) and Q_m (m^3/s) as discrete independent variables. The procedure used was similar to that used for formulating the nutrient concentration models based on instantaneous independent variables. In order to compare the concentration models developed from T_a and Q_m with those formulated from instantaneous data, the data set of the 1979 water year was used. In addition, the data sets of the 1978 and 1980 water years which had respectively the highest number of observations of $DNO_{2,3}$ and DN concentrations were used. The 1978–1981 water years also were used in examining the consistency of the models.

4. Results

4.1. DISSOLVED NITRITE–NITRATE NITROGEN CONCENTRATION MODEL

4.1.1. *Instantaneous* T, *ln*Q, *pH and DO as independent variables*

The correlation matrix of four instantaneous environmental variables, ln$Q$, T, pH and DO for the 1979 water year is shown in Table 2. The correlation coefficient between T and DO was -0·94, indicating the presence of severe collinearity. Because T is easier to measure and more data are often available, DO was excluded as an independent variable. The other three variables ln$Q$, T and pH, were also significantly correlated with each other but not at an unacceptable level of severity ($r < 0{\cdot}90$), thus they were used in the modeling as independent variables.

Relationships between natural logarithms of $DNO_{2,3}$ and each of the three independent variables are shown in Figure 1 and regression statistics are present in Table 3.

TABLE 2. Correlation matrix among instantaneous environmental variables in Potomac estuary at Chain Bridge for the 1979 water year (Q, water flow; T, water temperatures; DO, dissolved oxygen content)

Variable	T	pH	DO
$\ln Q$	−0·35	−0·76	0·28
T	—	0·36	−0·94
pH	—	—	−0·29

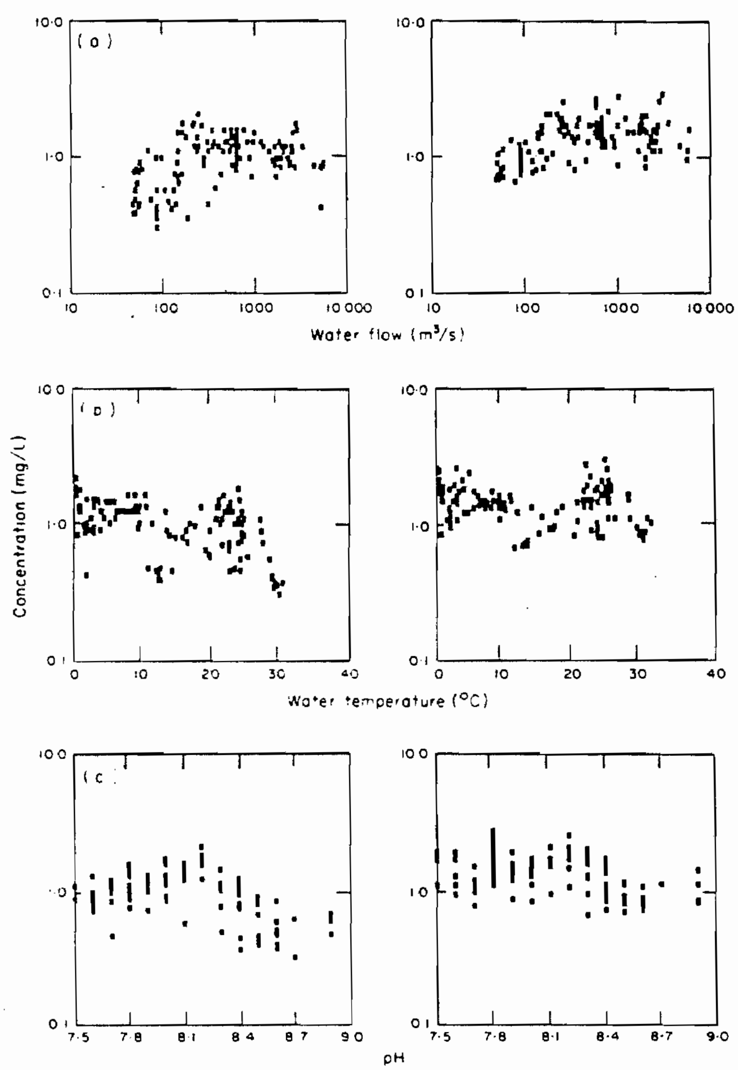


Figure 1. Plots of: (a) $DNO_{2,3}$ (left column) and DN (right column) concentrations against instantaneous water flows; (b) water temperatures; and (c) pH, in Potomac estuary at Chain Bridge, the 1979 water year.

TABLE 3. Linear and quadratic regression analyses for the logarithms of $DNO_{2,3}$ concentrations on the logarithms of water flows (ln$Q$), water temperatures (T) or pH for the 1979 water year (P, probability of type I error by t-test; n is the number of observations)

Independent variable	n	Regressor	Parameter estimates: Linear	Parameter estimates: Quadratic	$P<$	Statistics: Adj. r^2	Statistics: SD
lnQ	130	ln$Q$†	0·16	—	0·01	0·19	0·387
	130	(ln$Q$)^2	1·49	−0·11	0·01	0·39	0·332
T	130	T	−0·02	—	0·01	0·22	0·374
	130	T^2	−0·01	−0·01	0·22	0·22	0·374
pH	110	pH	−0·69	—	0·01	0·29	0·361
	110	(pH)^2	18·61	−1·18	0·01	0·41	0·332

† Hydroscience (1976) model.

ln$DNO_{2,3}$ was quadratically correlated to pH and ln$Q$ and negatively linearly correlated to T. Using the multiple regression analysis with linear transformation and the hierarchical predictor selection method, six predictors were identified, T, ln$Q$, pH, (ln$Q$)^2, (pH)^2 and $T \times \ln Q$. The r^2 value was 0·66, much higher than 0·19 of the Hydroscience Inc. (1976) linear model using the same data set. The SD value was 0·245. The variances of residuals of the model were fairly constant and independent from predicted values and independent variables. The general 6-predictor model for the $DNO_{2,3}$ is of the form (Table 4):

$$\ln DNO_{2,3} = a + b_1 T + b_2 \ln Q + b_3 \mathrm{pH} + b_4(\ln Q)^2 + b_5(\mathrm{pH})^2 + b_6 T \times \ln Q + e \qquad (1)$$

4.1.2. T_a *and* lnQ_m *as independent variables*

As in the case of the model identification based on the instantaneous data, ln$DNO_{2,3}$ was significantly quadratically correlated to lnQ_m for all three data sets (1979, 1980 and 1978–1981), significantly negatively linearly correlated to T_a for the 1979 water year, and quadratically correlated to T_a for 1980 and 1978–1981 (Table 5). Four predictors [T_a, lnQ_m, (lnQ_m)^2 and $T_a \times \ln Q_m$] for 1979 and 1978–1981 and five predictors [T_a, lnQ_m, (lnQ_m)^2, $T_a \times \ln Q_m$ and $T_a \times (\ln Q_m)^2$] for 1980 were identified (Table 6). For each of the three data sets, the 4-predictor model and the 5-predictor model were compared. There was no difference in the adjusted r^2 values (0·60–0·76) and SD values (0·05–0·09) between the two models for any time paired. Obviously, the presence of $T_a \times (\ln Q_m)^2$ in the model

TABLE 4. Regression parameter estimates and statistics of the $DNO_{2,3}$ concentration model developed from the 1979 water year instantaneous data

Predictor	Estimate	Standard error	$P<$
Intercept	−46·98	13·81	0·001
T	−0·10	0·02	0·001
ln$Q$	1·85	0·37	0·001
(ln$Q$)^2	−0·10	0·02	0·001
$T \times \ln Q$	0·01	0·01	0·001
pH	9·73	3·42	0·005
(pH)^2	−0·61	0·21	0·004
Adj. r^2 = 0·66		SD = 0·245	n = 110

TABLE 5. Linear and quadratic regression analysis for the logarithms of $DNO_{2,3}$ concentrations on the logarithms of daily mean flows ($\ln Q_m$) or the daily mean air temperatures (T_a) for the water years 1979, 1980 and 1978–1981

Water year	n	Regressor	Parameter estimates Linear	Quadratic	$P<$	Adj.r^2	SD
1979	130	$\ln Q_m$	0·138	—	0·001	0·16	0·387
		$(\ln Q_m)^2$	1·46	−0·111	0·001	0·36	0·337
		T_a	−0·0194	—	0·001	0·16	0·385
		T_a^2	−0·0375	0·000660	0·206	0·17	0·384
1980	138	$\ln Q_m$	0·311	—	0·001	0·45	0·352
		$(\ln Q_m)^2$	2·10	−0·157	0·001	0·60	0·303
		T_a	−0·0368	—	0·001	0·51	0·334
		T_a^2	0·0154	−0·00166	0·001	0·59	0·306
1978–1981	477	$\ln Q_m$	0·207	—	0·001	0·21	0·441
		$(\ln Q_m)^2$	1·37	−0·100	0·001	0·30	0·417
		T_a	−0·0323	—	0·001	0·39	0·388
		T_a^2	−0·0191	−0·000466	0·040	0·40	0·386

TABLE 6. Regression estimates and statistics for $DNO_{2,3}$ concentration models regressed on the daily mean air temperatures (T_a) and the logarithms of the daily mean water flows ($\ln Q_m$) for the water years 1979, 1980 and 1978–1981

Water year	n	Predictor	Estimate	SE	$P<$
1979	130	Intercept	−5·92	1·30	0·001
		T_a	0·129	0·0945	0·001
		$\ln Q_m$	2·11	0·424	0·001
		$(\ln Q_m)^2$	−0·174	0·0338	0·001
		$T_a \times \ln Q_m$	−0·0589	0·0319	0·061
		$T_a \times (\ln Q_m)^2$	0·00558	0·00265	0·038
			Adj. $r^2 = 0{\cdot}55$	SD = 0·281	
1980	130	Intercept	1·95	0·386	0·001
		T_a	−0·167	0·0187	0·001
		$\ln Q_m$	−0·268	0·0650	0·001
		$T_a \times \ln Q_m$	0·0259	0·00338	0·001
			Adj. $r^2 = 0{\cdot}76$	SD = 0·233	
1978–1981	477	Intercept	0·911	0·173	0·008
		T_a	−0·121	0·0104	0·001
		$L_n Q_m$	−0·0895	0·0294	0·001
		$T_a \times \ln Q_m$	0·0172	0·00188	0·001
			Adj. $r^2 = 0{\cdot}57$	SD = 0·326	

did not improve fitness and thus was excluded from the model. The general $DNO_{2,3}$ concentration model for the 4-predictor model for all three data sets is of the form:

$$\ln DNO_{2,3} = a + b_1 T_a + b_2 \ln Q_m + b_3 (\ln Q_m)^2 + b_4 T_a \times \ln Q_m + e \qquad (2)$$

The residuals were independent of the predicted values and each of the independent variables.

The two $DNO_{2,3}$ concentration model (1) formulated from T, Q and pH (Table 4) and model (2) from T_a and Q_m (Table 6) for 1979 were compared. Both models consisted of the same types of four predictors: (1) temperature; (2) flow; (3) the quadratic term of flow; and (4) the interactive term of temperature and flow. An exception was that model (1) had two more predictors, pH and $(pH)^2$. When pH was excluded as an independent variable in model (1), models (1) and (2) had fairly similar r^2 and SD values (Table 7).

There was a high correlation between T_a and T ($r = 0{\cdot}96$) and between Q_m and Q ($r = 0{\cdot}98$) (Figure 2). Because of such high correlation, T_a may represent T and Q_m may represent Q. There is no long-term record of pH and its contribution on predictability of the model seems to be limited. Therefore, model (2) using T_a and Q_m as independent variables is adequate for the estimation of the $DNO_{2,3}$ concentration.

4.2. TOTAL DISSOLVED NITROGEN CONCENTRATION MODEL

4.2.1. *Instantaneous* T, *ln*Q *and PH as independent variables*

As found in the $DNO_{2,3}$ model formulation, the natural logarithms of DN for 1979 were significantly, quadratically correlated with pH and $\ln Q$, and almost significantly negatively linearly correlated with T ($P < 0{\cdot}07$) (Figure 1, Table 8). In the multiple regression analysis with linear transformation and hierarchical predictor selection, four

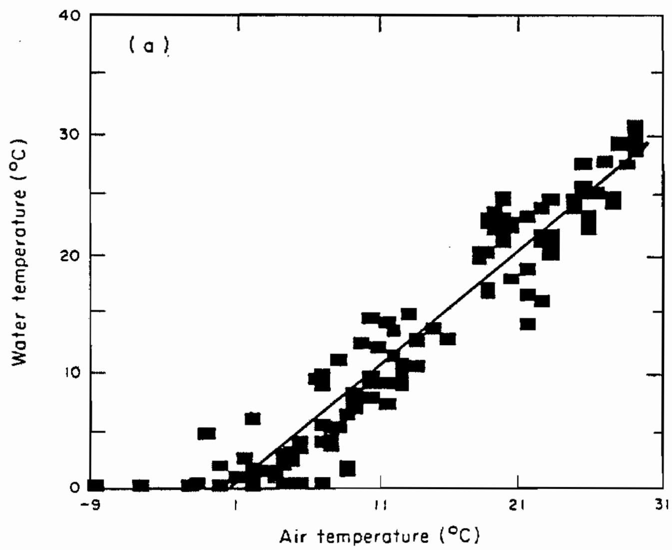
TABLE 7. A comparison of statistics between the $DNO_{2,3}$ concentration model identified from instantaneous flows (Q) and water temperatures (T) and that from daily mean flows (Q_m) and daily mean air temperatures (T_a) for the 1979 water year

Predictor	n	r^2	SD
T, $\ln Q$, $(\ln Q)^2$, $T \times \ln Q$	130	0·63	0·265
T_a, $\ln Q_m$, $(\ln Q_m)^2$, $T_a \times \ln Q_m$	130	0·60	0·265

TABLE 8. Linear and quadratic regression analyses for the logarithms of DN concentrations on the logarithms of water flows ($\ln Q$), water temperatures (T) or pH for the 1979 water year

Independent variable	n	Regressor	Parameter estimates: Linear	Parameter estimates: Quadratic	$P<$	Statistics: Adj. r^2	Statistics: SD
$\ln Q$	123	$\ln Q$†	0·11	–	0·01	0·17	0·283
	123	$(\ln Q)^2$	1·06	−0·08	0·01	0·34	0·265
T	122	T	−0·01	–	0·07	0·02	0·316
	122	T^2	−0·02	0·01	0·17	0·03	0·316
pH	104	pH	−0·42	–	0·01	0·19	0·283
	104	$(pH)^2$	6·94	−0·45	0·04	0·22	0·283

† Hydroscience (1976) model.



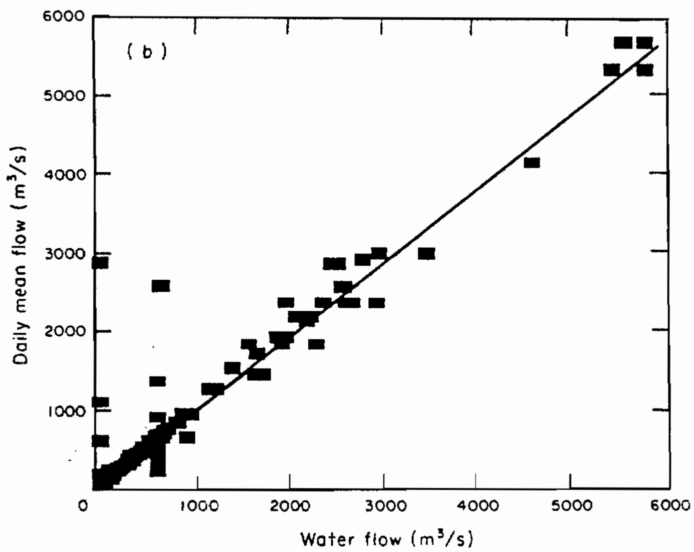


Figure 2. Relationships between: (a) instantaneous water temperatures in Potomac estuary at Chain Bridge and daily mean air temperatures at Washington National Airport, $T = -0{\cdot}25 + 0{\cdot}96T_a$, $r = 0{\cdot}95$, d.f. = 130, $P < 0{\cdot}01$; and (b) between daily mean water flows and instantaneous water flows in Potomac estuary at Chain Bridge, $Q_m = 36{\cdot}7 + 0{\cdot}96\ Q$, $r = 0{\cdot}98$, d.f. = 130, $P < 0{\cdot}06$.

predictors, T, $\ln Q$, $(\ln Q)^2$ and $T \times \ln Q$, were identified for the model. The pH and $(\mathrm{pH})^2$ parameters were not significantly different from zero. Table 10 shows the parameters statistics of the 4-predictor model. The adjusted r^2 value was 0·45 and the SD value was 0·245. The residuals were fairly independent of the predictor $\ln Q$, but were curvilinear with T (Figure 3). The latter indicated that T^2 should be included as a predictor in the model (Neter *et al.*, 1985).

The regression parameters of the 5-predictor mode are shown in Table 9. The adjusted r^2 value was 0·54, higher than 0·45 of the 4-predictor model and 0·17 of the Hydroscience Inc. (1976) linear model (Table 8). The SD value was 0·224. The residuals

TABLE 9. Regression parameter estimates and statistics of the 4-predictor and 5-predictor DN concentration models developed from the instantaneous data of the 1979 water year

Predictor	Parameter	Standard error	$P<$
		The 4-predictor model	
Intercept	−4·79	1·351	0·0006
T	−0·10	0·019	0·0001
$\ln Q$	1·11	0·271	0·0001
$(\ln Q)^2$	−0·06	0·014	0·0001
$T \times \ln Q$	0·01	0·002	0·0001
	Adj. $r^2 = 0·45$	SD = 0·239	$n = 122$
		The 5-predictor model	
Intercept	−3·53	1·270	0·0063
T	−0·18	0·025	0·0001
$\ln Q$	0·95	0·251	0·0002
$(\ln Q)^2$	−0·05	0·013	0·0001
$T \times \ln Q$	0·01	0·002	0·0001
T^2	0·01	0·001	0·0001
	Adj. $r^2 = 0·54$	SD = 0·219	$n = 122$

were fairly independent of the predicted values and any of the independent variables. The DN concentration model is of the form:

$$\ln \mathrm{DN} = a + b_1 T + b_2 \ln Q + b_3 (\ln Q)^2 + b_4 \mathrm{T} \times \ln Q + b_5 T^2 + \mathrm{e} \tag{3}$$

4.2.2. *Discrete* T_a *and* $\ln Q_m$ *as independent variables*

When T_a and Q_m were used as independent variables in modeling, lnDN was significantly quadratically correlated to $\ln Q_m$ for all three data sets and to T_a for 1979, but only

TABLE 10. Linear and quadratic regression analyses for the logarithms of DN concentrations on the logarithms of daily mean flows ($\ln Q_m$) or the daily mean air temperatures (T_a) for water years 1978, 1979 and 1978–1981

			Parameter estimates				
Water year	n	Regressor	Linear	Quadratic	$P<$	Adj. r^2	SD
1978	140	$\ln Q_m$	0·209	–	0·001	0·26	0·335
		$(\ln Q_m)^2$	1·474	−0·101	0·001	0·38	0·307
		T_a	−0·0276	–	0·001	0·57	0·257
		T_a^2	−0·0312	0·000137	0·614	0.56	0·258
1979	123	$\ln Q_m$	0·103	–	0·001	0·15	0·290
		$(\ln Q_m)^2$	1·14	−0·0860	0·001	0·36	0·251
		T_a	−0·00926		0·010	0·006	0·305
		T_a^2	−0·0432	−0·00125	0·001	0·14	0·291
1978–1981	478	$\ln Q_m$	0·170	–	0·001	0·23	0·341
		$(\ln Q_m)^2$	1·06	−0·0766	0·001	0·32	0·322
		T_a	−0·0243	–	0·001	0·36	0·310
		T_a^2	−0·0188	−0·000192	0·290	0·36	0·310

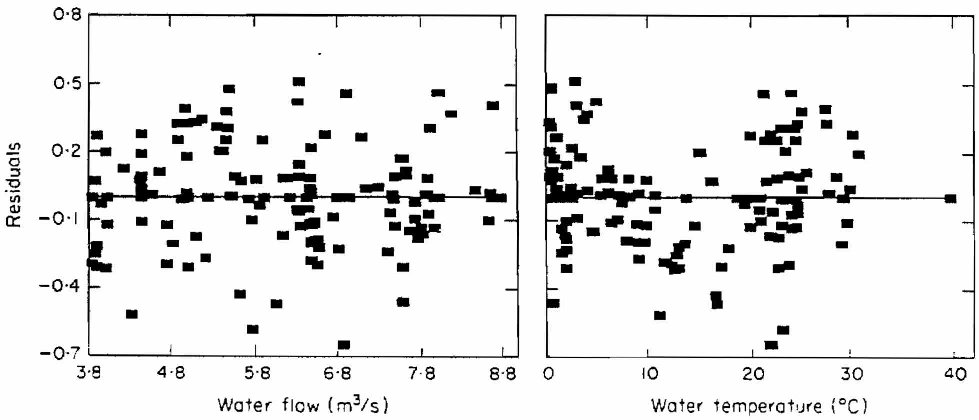


Figure 3. Residual plots against the two independent variables, water flows and water temperatures, for the 4-predictor DN, concentration model.

linearly correlated to T_a for 1978 and 1979–1981 (Table 10). Four predictors [T_a, $\ln Q_m$ $(\ln Q_m)^2$ and $T_a \times \ln Q_m$] for 1978 and 1978–1981, and five predictors [T_a, $\ln Q$m $(\ln Q_m)^2$, $(T_a)^2$ and $T_a \times \ln Q_m$] for 1979 were identified (Table 11). The 5-predictor model had higher adjusted r^2 value and lower SD value than those of the 4-predictor model for the 1978 and 1979 data sets, and had the same values for 1978–1981 data set (Table 12). The general DN concentration model is expressed by five predictors:

$$\ln DN = a + b_1 T_a + b_2 \ln Q_m + b_3(\ln Q_m)^2 + b_4 T_a \times \ln Q_m + b_5(T_a)^2 + e \tag{4}$$

TABLE 11. Regression estimates and statistics for lnDN concentration models regressed on the daily mean air temperatures (T_a) and the logarithms of the daily mean water flows ($\ln Q_m$) for the water years 1978, 1979 and 1978–1981

Water year	n	Parameter	Estimate	SE	$P<$
1978	140	Intercept	−1·48	0·949	0·001
		T_a	−0·0628	0·0181	0·001
		$\ln Q_m$	0·713	0·282	0·001
		$(\ln Q_m)^2$	−0·0586	0·0208	0·006
		$T_a \times \ln Q_m$	0·00708	0·00311	0·025
			Adj. $r^2 = 0·69$	SD = 0·217	
1979	123	Intercept	−2·05	0·645	0·001
		T_a	−0·0743	0·0202	0·010
		$\ln Q_m$	0·881	0·199	0·001
		T_a^2	0·00103	0·000323	0·002
		$(\ln Q_m)^2$	−0·0724	0·0153	0·001
		$T_a \times \ln Q_m$	0·00655	0·00286	0·025
			Adj. $r^2 = 0·48$	SD = 0·227	
1978–1981	477	Intercept	−1·38	0·355	0·001
		T_a	−0·0697	0·00826	0·001
		$\ln Q_m$	0·714	0·114	0·001
		$(\ln Q_m)^2$	−0·0622	0·00914	0·001
		$T_a \times \ln Q_m$	0·00908	0·00150	0·001
			Adj. $r^2 = 0·59$	SD = 0·249	

TABLE 12. A comparison of statistics between the 4-predictor model and 5-predictor model of DN concentrations for the 1978, 1979 and 1978–1981 water years

Water year	n	Model†	Adj. r^2	SD
1978	140	(1)	0·66	0·224
	140	(2)	0·69	0·200
1979	123	(1)	0·44	0·245
	123	(2)	0·51	0·224
1978–1981	478	(1)	0·57	0·245
	478	(2)	0·57	0·245

†(1) 4-predictors, T_a, $\ln Q_m$, $(\ln Q_m)^2$, $T_a \times \ln Q_m$. (2) 5-predictors, T_a, $\ln Q_m$, $(\ln Q_m)^2$, $T_a \times \ln Q_m$, T_a^2.

Model (3) formulated from T and Q and model (4) formulated from T_a and Q_m were similar in types of predictors. The r^2 and SD values for 1979 were also fairly similar (Tables 9 and 12). Therefore, model (4) was as good as model (3) and was selected as the DN concentration model.

5. Model evaluation and sample size requirement

Since the $DNO_{2,3}$ and DN concentration models (2) and (4) shared similar characteristics expressed by four and five predictors of the same two independent variables T_a and $\ln Q_m$, only the $DNO_{2,3}$ concentration model (2) evaluation is presented. To evaluate this model, for the 1979 water year, a resampling technique of the observed data was used. During the 1979 water year, data for all three variables was available on 100 observations distributed over 50 weeks. The first step was to "clone" these 100 observations several times. For example, a "cloned" data set of 6000 observations would be obtained by making 60 copies of the original 100 observations. The 6000 observations would then be randomly assigned to say, $N = 1000$ samples of $n = 6$ observations each. The parameters were than estimated for each of the 1000 samples. For each sample of size n, a predicted value of $\ln DNO_{2,3}$ and the deviation between the predicted and the observed was computed for each of the original 100 observations. The average squared deviation was computed for each sample and then the square root of the mean squared deviation (RMSD) was computed over the N samples.

Eleven different sample sizes ($n = 6$, 9, 12, 18, 24, 30, 36, 48, 60, 84 and 100) were evaluated with N equals 1000 to 5500 for different sample sizes. The smaller (N) number of samples (i.e. $N = 1000$) was used for those sample sizes (n) where it was quickly obvious that the RMSD was too large to be acceptable or for the largest sample size which was very near the standard deviation for model (2) on the original 100 observations (SD = 0·28).

The results of this model evaluation are reported in Table 13. The results for samples of size n equals 6 and 9 would certainly indicate that samples of this size could not provide reasonable daily predictions for the water year since their RMSD are more than 20-times greater than the standard deviation for the observed data. Samples sizes between $n = 18$ and 84 produced RMSD from 1·2 to two-times greater than that observed on the original data, except for the $n = 30$ samples which had a RMSD of 3·2. Examination of several sets of $N = 500$ samples of various samples sizes (n), indicated that it was not unusual to observe a large RMSD. For example; at $n = 12$, one 500

TABLE 13. Resampling results of model evaluation

Sample size (n)	Number of samples (N)	RMSD
6	1000	24·9
9	2500	6·6
12	5500	0·86
18	5000	0·57
24	5500	0·50
30	3000	3·2
36	4000	0·53
48	3500	0·38
60	2000	0·35
84	5500	0·57
100	1000	0·28

sample RMSD = 1–2, at $n = 30$ we observe both at 5·5 and a 3·2, and at $n = 84$, one 500 sample had a RMSD of 1·4. It is the opinion of the authors that such results, although distressing, would not be unexpected in environmental sampling. It is hope that someone trying to use a sample of data from a single water year to predict daily concentrations would recognize such outliers and would not use such data to estimate regression parameters. In practice, the occurrence of these unusual results may not be as frequent as observed in our simulations, since it would be expected that the actual data would be more uniformly distributed through out the water year, rather than randomly distributed as in our simulation. It is our recommendation that bi-weekly ($n = 26$) samples would provide adequate predictions of daily concentrations of $DNO_{2,3}$.

6. Discussion and conclusions

This study used the multiple regression analysis and the hierarchical predictor selection method (Peixoto, 1987) to formulate quantitative models for estimating nutrient concentrations from non-point sources in the Potomac estuary, using $DNO_{2,3}$ and DN as examples. Instantaneous water temperatures and dissolved oxygen contents showed severe collinearity, and thus the latter were excluded from the models. There is no discrete time series of pH data. Its contribution to the predictability of models was apparently limited.

Daily mean air temperatures and daily mean water flows were, respectively, highly correlated to instantaneous water temperatures and water flows. They were mutually representative and replaceable in the models. Therefore, the concentration models of $DNO_{2,3}$ and DN were expressed respectively by four and five predictors (simple, quadratic and interaction term) of two independent variables, daily mean water flows and daily mean air temperatures [models (2) and (4)]. The adjusted r^2 values of the models ranged between 0·53 and 0·76.

Blanchard and Hahl (1987) estimated nutrient concentrations and loadings for the Potomac River at Chain Bridge by using the hydrograph method (Porterfield, 1972). This was a direct and thus accurate computation of nutrient concentrations and loadings (Lang, 1982). When the monthly concentrations and loadings of $DNO_{2,3}$ and DN from 1978 to 1981 obtained in this study were compared to those obtained by the hydrograph method (Figure 4), there was no significant difference in the estimates between the two studies (paired t-test, $P > 0·05$). This indicates that the regression models established in

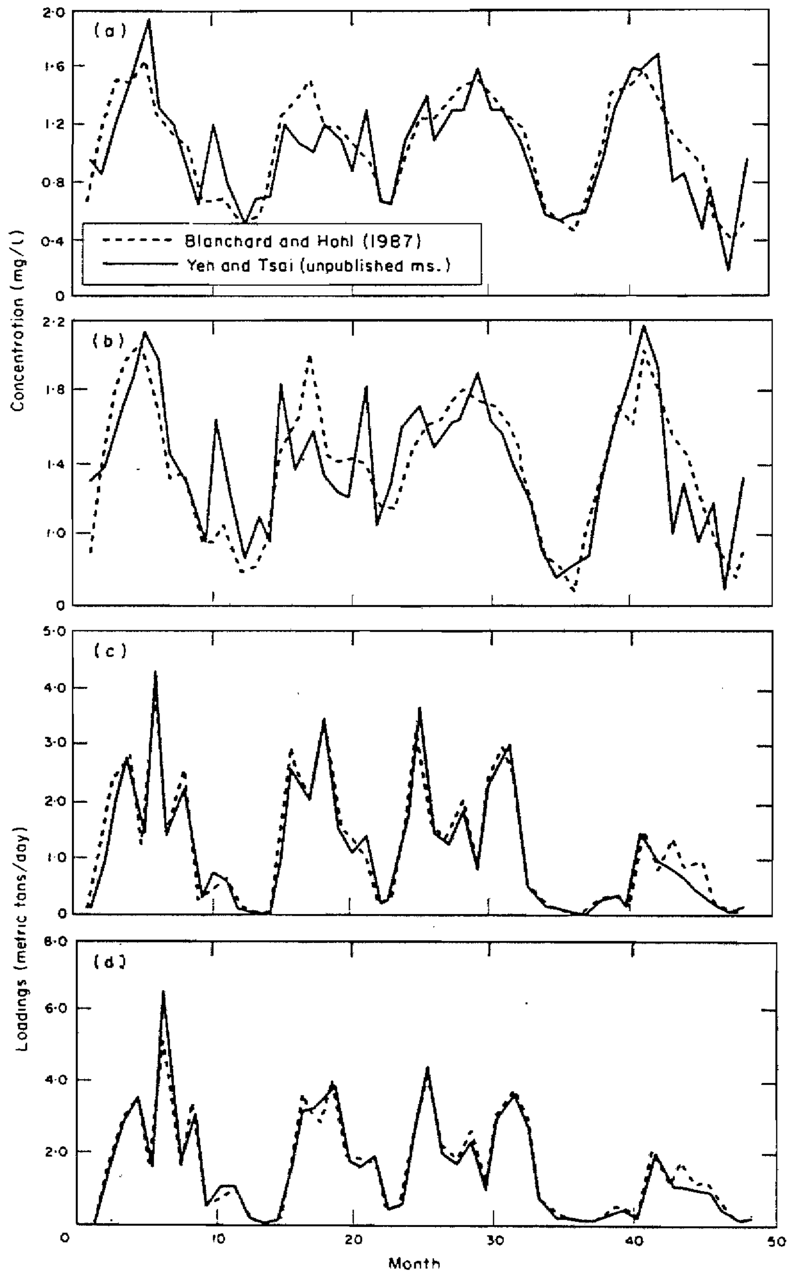


Figure 4. A comparison of: (a) estimated monthly mean DNO_3 concentrations; (b) monthly mean DN concentrations; (c) monthly total loadings of DNO_3; and (d) monthly total loadings of DN between this study and Blanchard and Hahl (1987). ---, Blanchard and Hahl (1987); ——, Yeh and Tsai (unpublished ms.).

this study estimated the nutrient concentrations and loadings as accurately as the hydrograph method.

The hydrograph method is complicated and requires frequent sampling at short intervals. The regression models established by this study are simple and easily conducted. The independent variables of the models are daily mean water flows and daily mean air temperatures. They have been measured by the U.S. Geological Survey and the Washington National Airport, respectively. Their discrete time series data are ready available. The only other data required for the estimation of model parameters are nutrient concentrations. Twenty six observations per year (bi-weekly sampling) were found to be adequate for model reparameterization.

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