MATERIAL LOADING TO DEGRAY LAKE, ARKANSAS: PATTERNS AMONG VARIABLES AND SIGNIFICANCE OF STORM EVENT LOADING

by

Robert H. Montgomery
Department of Civil Engineering
Colorado State University
Fort Collins, CO 80523

INTRODUCTION

The physical, chemical, biological, and social characteristics of reservoir ecosystems are directly controlled by the input of material from external sources. Nutrients, such as phosphorus, nitrogen, carbon, and silica, control algal and macrophyte growth, which in turn affect the higher levels in the food chain (Wetzel, 1976). The link between the input of nutrients and reservoir productivity has resulted in efforts to relate nutrient loads to the level of lake eutrophication (e.g. Vollenweider, 1968; Rast and Lee, 1978).

The rate of allochthonous sediment input directly controls the rate of depletion of reservoir storage capacity (USDA, 1973). The chemical composition of input particulate matter affects lake sediment characteristics and water clarity which govern the benthic community, internal loading during periods of anoxia, and reservoir water quality (Thornton et al., 1981; Kennedy et al., 1983). Material loading may also cause longitudinal gradients in water quality and sediment characteristics (Kennedy et al., 1982; Gunkel et al., 1984). Since material loads have such a significant impact on reservoir systems, accurate quantification of material loads is essential.

Material loading to a lake can be estimated by four different types of estimators (Wu and Ahlert, 1978): 1) zero-order, 2) direct, 3) statistical, and 4) descriptive. The zero-order method utilizes loading estimates from either the same, or a similar, watershed obtained from a previous study or uses export coefficients as a function of land use (e.g. Reckhow et al., 1980). The zero-order methods are the most simplistic and least expensive. However, care must be taken when transferring data from different areas by evaluating the accuracy and reliability of previous sampling design programs.

The direct method uses routine water quality data and discrete or instantaneous flow data to calculate loads (e.g. Walker, 1981; Verhoff et al.,

1980). Direct methods are the most commonly used since routine water quality data is usually all that is available (i.e. no special studies on high flow or storm events).

Statistical methods use correlation and regression analyses to develop stochastic models for predicting concentration and/or load from a set of independent variables (e.g. Omernik, 1977; Jewell et al., 1980). These methods, while often providing good loading estimations, are extremely limited in their applicability to other watersheds, and require sufficient amounts of data (i.e. over the complete range of flow) and computational facilities.

Descriptive methods employ deterministic mathematical models of physical, chemical and hydrological processes (McElroy et al., 1976; Mills et al., 1982; Hydrocomp, 1980). The most common descriptive method employs the Universal Soil Loss Equation (USLE). While the USLE is widely used, and thus facilitates comparisons with other watersheds, it suffers from the same deficiencies as the zero-order method in that the model coefficients usually have to be obtained from the literature. Complex deterministic models are also used; however, these are usually expensive, have high data requirements, and usually have high level of total prediction uncertainty.

While numerous comparisons of material load estimation methods have been done, no one method has been shown to be acceptable for all application variables (Ongley et al., 1977; Smith and Stewart, 1977, Johnson, 1979; Jewell et al., 1980; Westerdahl et al. 1981; Dolan et al., 1981; Whitfield, 1982). Since significant differences exist between baseflow and storm events, the estimation of total annual load by any method is most appropriately done by estimating baseflow and storm load separately (Colston 1974; Stevens and Smith, 1978; Cahill, 1977), and in some cases, by further separating by season or month (Johnson, 1979).

The selection of an estimation method should involve examining the project objective, resources available, uncertainty acceptable, and possible inherent biases (Montgomery and Kennedy, 1986). The use of routine/surveil-lance data can create bias in annual loading estimations by over-estimating in dilution variables and under-estimation in flow-driven variables (Ongley et al., 1977, Johnson, 1979). This bias results because data from fixed interval sampling frequently contains only a few samples at high flows due to the infrequency of temporal occurrence of storm events. Thus, low (dilution) or high (flow-driven) concentrations that occur in storm events are not well

represented in the distribution of water quality variables and cause a bias in the loading estimate. The ideal temporal sampling scheme should be continuous and flow-proportional, but since this is usually not feasible, a discrete sampling program should sample each flow regime with a frequency proportional to the sum of discharges during that flow regime (Stevens and Smith, 1978). Johnson (1979) showed the effect of changing sample size in estimating loads using samples proportional to discharge and duration.

The purpose of this paper is to present a summary of the results obtained in estimating material loads to DeGray Lake, Arkansas. The objectives of the study were to calculate material load estimates for DeGray Lake via the Caddo River, examine patterns in water quality variables during baseflow and storm events, and examine significance of storm event loading.

The Caddo River arises in the Ouachita Mountains of south-central Arkansas and flows southeast for 126 km to its confluence with the Ouachita River (Figure 1). The river is impounded 12.7 km above this confluence to form DeGray Lake, a US Army Corps of Engineers reservoir providing flood control, hydropower, and recreation. The total drainage area of the river is 1269 km². In general, the watershed can be divided into two geographic regions: the Interior Highlands, which is part of the Novaculite Uplift (area northwest of Glenwood), and the Athens Piedmont Plateau (below Glenwood) (Perrier, 1977). Land uses in the Caddo River watershed include forest (68 percent), agriculture (30 percent), and urban (2 percent).

The climate of the watershed is generally mild with an average monthly temperature of 17°C (range of 6°C in January to 28°C in July). The average annual precipitation is 134 cm/year at Arkadelphia and 140 cm/year at Glenwood. Monthly precipatation is distributed fairly uniformly throughout the year, although the summer storms tend to be short and intense with long periods between events. Precipatation occurs approximately 20 percent of the time and is rarely distributed evenly over space in the watershed. The amount of precipatation that enters the Caddo River as runoff ranges from 15-90 percent and averages 43 percent (Perrier, 1977). The upper basin (west of Glenwood) contributes a larger portion of steamflow in late fall and winter while the lower basin contributes more in the late spring and summer. During periods of low precipatation groundwater may contribute significantly to streamflow. Snowfall occurs from one to four times per year but will usually melt immediately; hence, there is no major snow melt/runoff event in the spring.

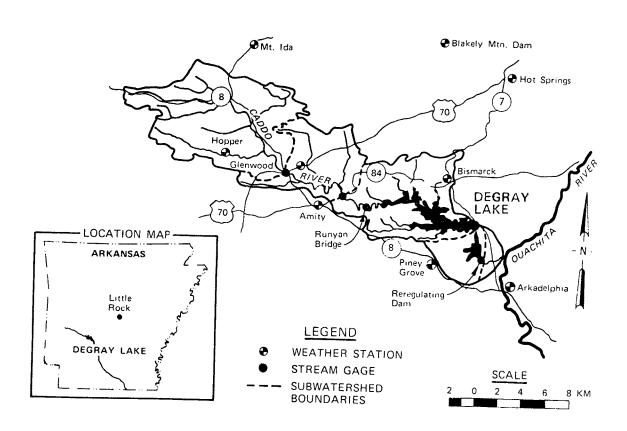


Figure 1. Watershed map of DeGray Lake, Arkansas.

METHODS

Water quality variables were sampled every two weeks from the Hwy 84 bridge on the Caddo River during the period 1 Jan 76 - 31 Dec 80. Samples were collected at midstream approximately 0.5 meter below the surface using a horizontal Van Dorn water sampler. Sample time was 10 a.m. for all samples. Presented in Table 1 are water quality variables and sample preparation, sample storage, and analytical methods used (see Glossary for variable definitions). Samples during storm events, which were defined as major rain events that generated a significant rise in the Caddo River, were collected approximately hourly until the rate of change in flow diminished. A minimum of 10 representative samples were maintained and analyzed. In general, at least four samples each on the rising and falling side of the hydrograph and two at the peak flow were analyzed. Sampling techniques and analytical methods were the same as for the routine samples. Sample collection and analysis were performed by the Water Chemistry Lab, Ouachita Baptist University, Arkansas.

A complete, bi-hourly flow record at the Highway 84 site for the years 1976 - 1980 was established by combining hourly stage measurements from the river gages located at Glenwood and Hwy 84 (Figure 2). For the years 1976, 1977, 1978 and 1980, missing values in the Hwy 84 flow record were calculated by linear interpolation between observed flow values. This was feasible since meteorologic records revealed no rainfall events during the periods of missing flow values. However, during early 1979 missing values occurred during periods of significant rainfall. For these values, a linear regression model of mean daily flows between Glenwood and Hwy 84 using data from the first half of 1979 was developed. This model accounted for travel time between stations and for conditions specific to 1979.

RESULTS

Summary statistics for water quality variables collected during the routine sampling program are presented in Table 2. Water quality relations under baseflow conditions and storm events were evaluated and modeled independently. Baseflow conditions were defined by comparing routinely collected water quality data with the continuous flow record. Samples not collected during or immediately after a storm event were subjectively

Table l Analytical Methods

Variable	Sample Preparation	Sample Preparation	Analytical Method	Reporting Units	References
Total Phosphorus	None	H ₂ SO ₄ to pH <2;	Acid-persulfate digestion; ascorbic acid-molybdate colorimetric reaction	mg P/l	Jeffries et al. 1979
Total Soluble Phosphorus	Filtration (0.45 µ)	H ₂ SO ₄ to pH <2;	Acid-persulfate digestion; ascorbid acid-molybdate colorimetric reaction	mg P/l	Jeffries et al. 1979
Soluble Reactive Phosphorus	Filtration (0.45 µ)	4°C; analysis within 24 hr	Ascorbic acid-molybdate colorimetric reaction	mg P/l	Skougstad et al. 1979
Particulate Phosphorus		Total Phos Total Soluble		mg P/L	
Soluble Unreactive Phosphorus		Total Soluble- Soluble Reactive		mg P/l	
Nitrate Nitrogen	Filtration (0.45μ)	HgCl ₂ 40 mg Hg/2)	Brucine-sulfanilic acid	mg N/R	Skougstad et al. 1979
Nitrate/Nitrite Nitrogen	Filtration (0.45 µ)	7°4	Cadmium reduction	%/8m	SMEWW, 1976
Ammonia Nitrogen	None	$H_2^{SO_4}$ (2m1/ ℓ);	Selective ion electrode	mg/k	SMEWW, 1976
Total Kjeldahl Nitrogen	None	$H_2^{SO_4}$ (2 m1/ ι)	Kjeldahl digestion and selective-ion probe	mg N/2	АРНА, 1980
Total Solids		7°4	Total residue at 105°C	ng/g	SMEWW, 1976

(Continued

Table 1 (Concluded)

Variable	Sample Preparation	Sample Preparation	Analytical Method	Reporting Units	References
Dissolved Solids		4°C	Filterable (standard glass fiber filter) residue at 105°C	mg/ k	SMEWW, 1976
Suspended Solids		Total - Dissolved		mg/gm	
Total Silica					
Dissolved Silica					
Total Magnesium, Calcium, Sodium, Potassium, Manganese, Iron	None	HNO ₃ (pH ≤2)	Atomic absorption	я (X) / д	АРНА, 1980
Dissolved Magnesium, Calcium	Filtration (0.45 µ)	HNO ₃ (pH <2)	Atomic absorption	mg (X)/ц	АРНА , 1980
Total Organic Carbon	None	H ₂ SO ₄ (pH ≤2); amber glass storage	Persulfate oxidation; infrared analysis	mg C/2	EPA, 1974
Dissolved Organic Carbon	Filtration (pre-combusted glass fiber)	H ₂ SO ₄ (pH ≤2); amber glass storage	Persulfate oxidation; infrared analysis	mg C/2	

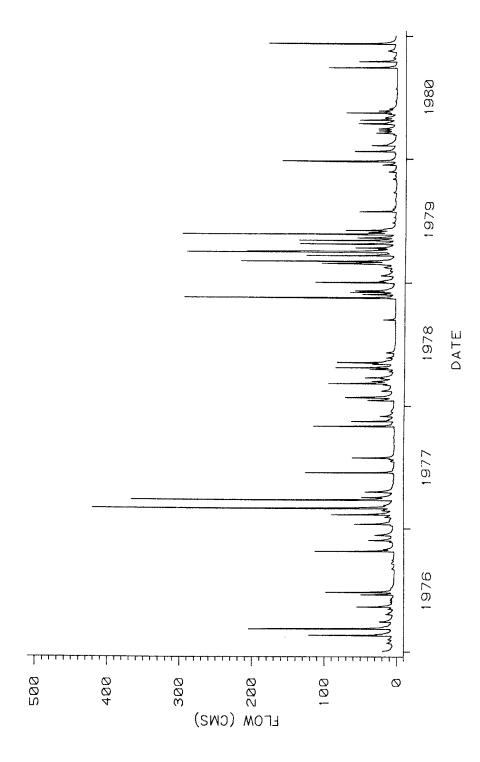


Figure 2. Mean-daily hydrograph for Caddo River at highway 84 bridge.

Table 2 Summary Statistics for Routine Water Quality Variables

Variable	Mean	Standard Deviation	Standard Error of Mean	Coefficient of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
TP	0.0304	0.0355	0.00252	116.601	6.11	45.48	900.0	0.340	0.0230	0.019
PP	0.0139	0.0314	0.00240	225.219	7.06	57.83	000.0	0.313	0.0070	0.005
SUP	0.0072		0.00051	87,482	1.59	3.08	000.0	0.034	0.0050	0.005
SRP	0.0136		0.00070	70.655	1.91	68.9	000.0	0.070	0.0120	0.012
NO3N	0.1541	0.1676	0.01720	108.775	3.88	22.95	000.0	1.300	0.1200	0.070
NHXN	0.0319		0.00309	130.769	2.12	5.42	000.0	0.220	0.0200	0.000
TKN	0.4312		0.02264	70.822	2.02	5,39	000.0	1.970	0.3895	0.400
TS	71.4663	7	3,51165	65.557	7.82	82.06	2,000	584.000	0000.99	000.69
DS	58,4689	19,1386	1,43854	32,733	0.19	0.01	11,000	113,000	58,0000	65.000
SS	17.5423		3,97538	270.046	8.62	86.63	000.0	513,000	8.0000	000.9
DSI	6.7301	1.8639	0.13416	27.695	-0.38	-0.24	2.100	11,000	0008.9	8.700
TMG	1.8753		0.04158	21.839	0.23	0.27	0.800	3.100	1.9000	1.600
TCA	11.4838		0.38818	33,633	0.26	-0.55	3.000	20.000	11,0000	16.000
TNA	2.0915		0.02382	16.066	-0.12	1.83	1,000	3.300	2,1000	2.000
TK	0.9297	0.3343	0.02412	35.954	2.05	7.46	0.200	2.700	0.9000	0.800
TMN	0.0489	0.0935	96600.0	191.262	2.06	3.91	000.0	0.400	000000	000.0
TFE	0.2953		0.04280	133,622	4.01	20.56	000.0	2.800	0.2000	0.200
TOC	3.6305	1,9912	0.15993	54.845	2.31	8.23	009.0	15.100	3.0000	2.400
DOC	3.4000		0.15251	54,383	1.65	3.21	0.500	10.700	2.8000	2.800

identified as occurring under baseflow conditions. Only water quality data specifically collected during storm events were used.

Long-term (i.e. annual) changes or trends in water quality may imply changing watershed or hydrologic conditions, which in turn can potentially affect the accuracy of nutrient load estimates. Therefore, time series plots of concentration for the period 1 Jan 76 - 31 Dec 80 were examined for each water quality variable. While such visual tests provide only qualitative results, they do provide a means for determining if the application of statistical tests is warranted. The time series plots exhibited no obvious trends in any of the water quality variables. Since these observations were consistent with the fact that there have been no significant land-use changes in the watershed, no statistical tests were conducted. Similar evaluations of possible seasonal water quality trends were performed by pooling data for all years, but were confounded by the existence of seasonal patterns in flow. However, since seasonal changes in water quality and flow were similar, both sources of variation were addressed by regressing concentration on flow.

Summary statistics for baseflow water quality variables which allowed identification of tendencies, variations, distributions, and possible outliers are presented in Table 3. Typical patterns between concentration and flow are shown in Figures 3 and 4. Mean concentrations in conjunction with flow are usually used to estimate nutrient loads. However, if non-normality is present in water quality variables more robust estimators are warranted. Based on the summary information, stem-leaf diagrams, Box plots, and normal probability plots, the following were chosen as the "best" measure of central tendency for water quality concentration:

Mean - TP, SRP, TKN, DSI, TMG, TCA, TNA, TK, TME, TFE, TS, DS

Median - SUP, PP, NO3N, NH4, TOC, DOC, SS

For SUP, PP, NO3N, NH4N, TOC, and DOC the mean tended to overestimate (skewed right distribution) while for SS the mean tended to underestimate (skewed left distribution), hence the use of the median as central tendency.

Summary statistics for the fractions (percentages of individual constituents) of phosphorus, carbon, and solids during baseflow conditions were also examined (Table 4). This information will be compared with fractions during storm events to examine possible changes in species composition resulting from increased flow. Associations between water quality variables during baseflow were analyzed by examining the correlation matrix and performing a factor

Table 3 Summary Statistics of Baseflow Water Quality Variables

			1	9 - 1 - 1 - 2 - 2						
Variable	Mean	Standard	Standard Error of Mean	Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
FLOW	5.01	2.43	0.220	48.41	1.19	1.69	2.09	15.26	7.34	3.42
TP	0.0221	0.0084	0.00078	38,15	0,40	80.0-	900.0	0.044	0.022	0.017
PP	0.0073	0.0057	0.00057	78.14	1,36	2.58	00000	0.030	900.0	0.002
DUP	0,0065	0.0054	0.00056	83,58	1.17	1.14	000.0	0.023	0.005	0.005
DRP	0.0117	0.0069	0.00065	59.07	0.77	0.49	000.0	0.033	0.011	0.011
NO 3 N	0.1082	0.0872	0.01176	80.64	1.31	2.19	000.0	0.410	00.00	0.070
N'ON	0.0324	0.0432	0.00418	133.32	2.20	5.75	000.0	0.220	0.220	000.0
TKN	0.3967	0.3107	0.03018	78.32	2.41	7.80	000.0	1.970	0.300	0.400
TS	71.6402	54.2693	5.34731	75.75	8.39	79.57	29,000	584,000	65,000	000.09
DS	60.2308	18.7349	1.83710	31.10	-0.01	90.0-	11,000	104.000	59.500	50.000
SS	16.6154	57,9781	6.56473	348.94	8.36	72.32	000.0	513.000	8.000	000.9
DSI	6.5106	1,9105	0.17972	29.34	-0.35	-0.21	2,100	10.800	009.9	6.800
TMG	1.9849	0,3427	0.04708	17.26	0.93	1.67	1.500	3,100	2,000	1.600
тсн	12.6909	3,2906	0.44371	25.92	0.44	-9.85	7.400	19,400	12,100	8.800
TNH	2.1209	0,3378	0.3150	15.92	-0.26	2.88	1,00	3,300	2.100	2.200
TK	0.8575	0.2199	0.02069	25.64	0.62	4.48	0.200	1.900	0.800	0.800
TMN	0.0589	0.1058	0.01414	179.52	1.85	2.76	000.0	0.400	00000	000.0
TFE	0.2000	0.1633	0.02202	81.65	2.27	09.6	000.0	1.000	0.200	0.200
TOC	3,2253	1.5577	0.16240	48.29	1.57	2.78	009.0	8.700	2.700	2.400
DOC	3.1092	1.5752	0.16888	50.66	1.49	2.60	0.500	8.600	2.700	2.200

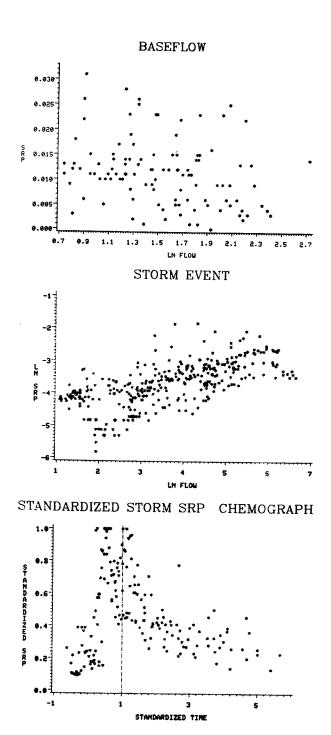
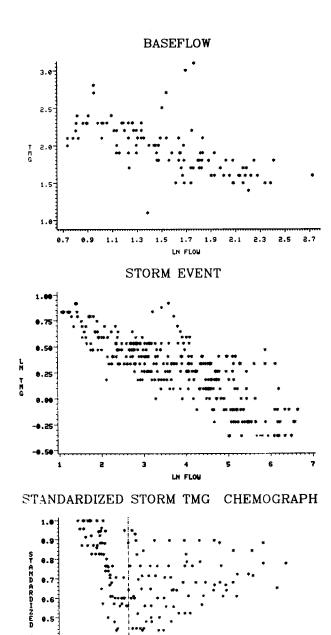
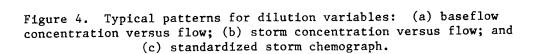


Figure 3. Typical patterns for flow concentrating variables: (a) baseflow concentration versus flow; (b) storm concentration versus flow; and (c) standardized storm chemograph.





STANDARDIZED TIME

Table 4
Summary Statistics of Percent Fractions During Baseflow

		Standard	Standard Error							
Variable	Mean	Deviation	of Mean		Skewness	Kurtosis	Minimum	Maximum	Median	Mode
P-PP	.311	.192	.019	61.68	.38	57	0	.812	.307	0
P-SUP	.304	.227	.024	74.49	69.	60.	0	.947	.263	0
P-SRP	.502	.228	.022	45.47	.12	59	0	1.0	.50	.33
P-SS	.145	.141	.016	97.61	2.12	5.16	0	.718	.109	0
P-DS	.855	.141	.016	16.50	-2.12	5.16	. 282	 i	.891	
P-DOC	.912	.107	.012	11.74	-2.75	8.91	7.0	1.0	7964	

analysis. The information generated can be used to reduce efforts on similar variables and concentrate on dissimilar variables. The factor analysis utilized an iterated principal axis factoring method, an equamax rotation method, and was limited to a maximum of five factors. While a few possible associations were identified there were no consist patterns between variables.

Based on the exploratory analyses, baseflow water quality concentrations for the entire baseflow period were predicted by either regressing concentration on natural loagarithm transformed flow (if the slope of the model was significant at 0.05 level) or the selected "best" measure of central tendency was used (Table 5).

Water quality data for the 16 storm events were subjectively screened for completeness and appropriateness. Eliminated from further consideration were storms with minimal peak discharges (maximum flow less than 15 cms) or incomplete water quality records on either the rising or falling limb of the hydrograph. Based on this screening, data for 14 storms were retained for analysis (Table 6). Both static storm variables (those in Table 6) and the non-static variables FLOW, TIMESSS (time since start of storm), and AQ (accumulated flow) were used as independent variables in developing statistical water quality models during storm events (see Glossary of Symbols for variables definitions).

Summary statistics for storm water quality variables and fractions of phosphorus, solids, and carbon are presented in Tables 7 and 8, respectively. The correlation matrix and factor analysis (same method as used for baseflow) of storm water quality variables suggested three groups:

Group 1 - TMG, TCA, TNA, TSI

Group 2 - TP, PP, SRP, TKN, SS, TK, TMN, TFE, TOC, DOC, TS, NH4N

Group 3 - SUP, NO3N, DS

Although TS and NH4N fall in group 2, both had some tendencies to associate with groups 1 and 3.

Concentration in storm events is usually most significantly affected by flow and often modeled as a function of flow only. Thus, plots of natural logarithm transformed concentration and flow were examined to suggest potential statistical models for predicting concentration (Figures 3-4). To show the typical pattern of concentration in a storm, concentration and time were standardized around the time of peak flow within a storm (Figures 3-4).

Table 5

Estimators for Water Quality Concentrations During Baseflow

		Ba	seflow	Vai	riables w	Ltl	h Si	lgnificant	Slope (Ln Flow		_
									Prob.	$\frac{R^2}{R^2}$	
	TP	=	.02959	-	.004989	*	Ln	Flow	.0039	.0713	
	PP	=	.01198	-	.0031269	*	Ln	Flow	.0129	.0614	
	SRP	22	.01801	-	.004187	*	Ln	Flow	.0035	.0751	
1	NO ₃ N	=	00132	+	.06759	*	Ln	Flow	.0102	.1182	
	TS	=	106.484	-	22.9290	*	Ln	Flow	.0514	.0374	
	DS	=	83.6667	-	15.3600	*	Ln	Flow	.0001	.1400	
	TMG	=	2.8128	_	.4996	*	Ln	Flow	.0001	.4128	
	TCA	=	22.4879	-	6.0200	*	Ln	Flow	.0001	.6743	
	TK	=	1.1844	-	.2149	*	Ln	Flow	.0001	.1959	

Variables with Non-significant Slopes, Best Measure of Central Tendency

Mean	Median
TKN	SUP
TNA	$_{ m NH}_{ m 4}$ N
TMN	SS
TFE	TOC
	DOC

Table 6 Hydrologic Characteristics of 14 Sampled Storms

Storm	Month	Day	Year	DURATION	TVOLUME	MAXQ	MEANQ	TTP	TLS	PQLS	MQL 10	MQL25	PQL10	PQL25
7610	10	24	9/	137.0	18287946	197.3	48.0	21.0	35.0	7.6	4.1	4.3	4.2	5.7
7702	2	က	77	53.5	2855223	17.1	14.2	21.5	21.0	78.5	9.6	13.9	10.9	78.5
7706	9	17	77	245	19132751	375.7	48.9	0.6	57.9	52.5	9.4	4.4	8.3	8.3
7711	11	_	77	37.5	18167157	471.87	139.0	9.5	93.2	136.3	4.0	3.5	5.2	5.2
7801	1	16	78	170	13257857	63.3	26.0	20.0	6.94	276	9.4	4.7	5.2	5.2
7803	8	9	78	73	16846569	114.2	6.79	17.0	3.7	20.4	12.6	12.5	20.4	26.3
7804	4	17	78	57	5729562	60.7	29.2	0.6	6.7	14.0	9.8	13.0	14.0	9.49
7811	11	15	78	167	44836291	510.7	103.6	17.5	63.1	22.1	2.9	2.8	2.9	2.9
7903	ო		79	55	41207508	758.7	223.9	14.0	7.6	296.2	32.9	20.7	296.2	296.2
7905	7	e	79	113	23853226	180.9	82.0	14.0	10.2	196.1	31.8	24.2	93.7	196.1
7907	7	27	79	95	8779433	112.8	29.7	11.0	32.6	11.0	3.7	4.2	9.4	11.0
8005	5	12	80	36	2291958	21.4	17.7	12.5	11.5	21.0	10.1	14.0	21.0	104.3
8005.5	5	15	80	36	8107362	103.4	62.8	13.0	3.4	21.4	9.2	13.9	21.4	104.3
8010	10	17	80	87	10118969	162.7	34.7	7.0	18.8	150.0	3.5	11.8	4.6	150.0

Table 7 Summary Statistics of Storm Water Quality Variables

		Standard	Standard Brror	Coefficient of						
Variable	Mean	Deviation	of Mean	Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
FLOW	6.99		3.50	148.3	3.40	14.09	5.15	758.7	26.7	10.8
TP	0.1094		0.0058	85.4	1,35	1.75	0.004	0.529	0.0795	0.034
PP	0.0696	0.0759	0.0048	109.0	1.48	2.06	0	0.394	0.047	0
SUP	0.0119		0.0007	86.5	1.19	1.07	0	0.051	0.008	0.008
SRP	0.0342		0.0014	68.2	2.00	6.16	0.005	0.157	0.029	0.02
NO ₃ N	0.288	0,183	0.0111	63.7	0.98	0.62	0.01	0.98	0.22	0.18
NH N	0.046		0.0041	148.4	2.96	13.10	0	0.53	0.02	0
TKN	0.860		0.0296	57.5	0.85	0.40	0.19	2.5	8.0	1
TS	134.3		6.92	85.0	2.63	8.59	31	817	94	58
DS	56.1		1.37	40.2	2.97	15.81	14	216	53	65
SS	81.1		6.70	133.7	2.88	10.47	0	757	43	12
TSI	5.94		0.129	36.6	-0.37	0.38	0.5	14.6	6.3	6.3
TMG	1.31	0.35	0.021	26.7	0.20	- 0.07	0.7	2,5	1.3	1.4
TCA	60.9		0.167	44.7	1.26	2.17	1.6	17	5.5	3.9
TNA	1.67		0.025	24.9	90.0	- 0.81	8.0	2.7	1.7	1.4
TK	1.52		0.042	44.5	1.91	5.49	9.0	5.2	1.4	6.0
TMN	0.136		0.0119	67.3	0.27	- 0.67	0	0.3	0.1	0.1
TFE	1.05		0.0894	66.1	0.94	0.59	0.2	3.2	0.85	0.5
TOC	9.18		0.308	53.2	1.22	2.01	8.0	30.5	8.1	7
DOC	7.06	3.64	0.256	51.6	0.56	0.11	0	19.2	6.35	5

Table 8 Summary Statistics of Percent Fractions During Storm Events

		Standard	Standard Error Coefficient	Coefficient						
Variable	Mean		of Mean	of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
P-PP	.473		.016	51.8	53	71	0	.864	.524	0
P-SWP	.160	.172	.012	107.4	1.88	3.97	0	1.0	.102	0
P-SRP	.419	.222	.014	53.0	76.	.28	.083	1.0	.367	1.0
P-SS	.454	. 238	.015	52.3	.02	-1.05	0	.938	.451	0
P-DS	.546	.238	.015	43.5	02	-1.05	.061	1.0	.599	1.0
P-DOC	.776	.193	.015	24.8	-2.20	90*9	0	1.0	.820	1.0

Standardized concentration is storm concentration divided by maximum storm concentration and standardized time is TIMESSS divided by time of peak flow. The standardized storm concentration plots allow for the visual determination of how concentration increases or decreases with increased flow and where concentration peaks occur in relation to flow.

A stepwise multiple regression technique, using Maximum R2 improvement, was performed to develop statistical models to predict storm water quality. The 11 static and 3 dynamic storm variables were used as potential dependent variables. All independent and dependent variables were transformed to natural logarithms to provide symmetric distributions. An a-priori criterion for all models was that at least one static and dynamic variable must be included. A "best" model (Table 9) was chosen by:

- 1. Examining the increase of R2 improvement as independent variables were added to fine asymptotic level.
- 2. Examining the decrease in model MSE as independent variables were added.
- 3. Significance of parameter and model estimates.
- 4. Examining changes in Type II SSi, f-ratio, and parameter estimates for possible multicollinearity.

The model variables are listed in order of significance. For each selected model, plots of residuals versus predicted and independent variables not used in the model were examined. All models except NH4N contained dynamic variables. For NH4N, the scatter plots of natural logarithm transformed concentration and flow during storms had no changing relations, thus only a static variable was used in the storm model. The storm models for TMG and TNA had multicollinearity arise when static variables were added. This suggests TMG and TNA can be modeled as a straight function of flow without static hydrologic variables. Summary statistics for the predicted storm water quality concentrations are presented in Table 10. An important note when comparing these statistics with those of the sampled storms is that the predicted set of storms (i.e., all storms during 1976-1980) contains many more storms of lower magnitude (Table 11 and 12). Thus, the water quality probability distributions and summary statistics would be shifted toward those concentrations associated with low magnitude storm events. For example, the mean flow and TP are smaller for predicted (all storms) than observed (14 storms).

Using the continuous (bi-hourly) flow record and estimators for water quality concentrations for baseflow and storm events a bi-hourly concentration

Table 9
Statistical Models for Storm Water Quality Variables

	_R ²
LOG TP = -0.5155 + 0.6854*LFLOW - 1.0875*LTTP - 0.1359*LAQ	.734
LOG PP = 0.0506 + 0.9505*LFLOW - 1.2861*LTTP - 0.2616*LAQ	.647
LOG SUP = -3.2533 - 1.509*LTTP - 0.4264*LTLS + 0.6304*LDUR + 0.1858*LFLOW	.374
LOG SRP = -4.6914 + 0.4312*LFLOW - 0.3197*LMQL10	.580
$log NO_3N = -3.3490 + 0.3772*LTLS + 0.2702*LAQ - 0.0080*TIMESSS - 0.1902*LTVOL$.422
$LOG NH_4N = -0.7945 - 0.4581*LTLS - 0.2465*LPQLS$.358
LOG TKN = -0.3271 + 0.4138*LFLOW - 0.0860*LAQ - 0.0996*LPQLS	.471
LOG TS = 4.9865 + 0.4850 * LFLOW - 0.1508 * LAQ	.672
LOG DS = $4.1666 + 0.1113*LFLOW -0.2441*LTTP$.198
LOS SS = 4.8168 + 0.8599*LFLOW - 0.3032*LAQ	.606
LOG TSI = 2.2793 - 0.1491*LFLOW	.112
LOG TMG = 0.9638 - 0.1799*LFLOW	.560
LOG TCA = 2.8819 - 0.2871*LFLOW	.605
LOG TNA = 0.9011 - 0.1573*LFLOW - 0.0827*LTLS + 0.1804*LTTP	.607
LOG TK = 1.8008 + 0.2405*LFLOW - 0.0967*LAQ - 0.1101*LPQL10 - 0.260*TTP	.567
LOG TMN = -2.1695 + 0.4191*LPQLS + 0.3440*LFLOW - 0.1799*LAQ	.617
$LOG\ TFE = 0.3295 + 0.5866*LFLOW - 0.2484*LAQ + 0.4577*LMQL25$.849
LOG TOC = 1.0228 + 0.3638*LFLOW - 0.1126*LPQLS	.570
LOG DOC = 1.9977 - 0.6419*LPQL10 + 0.2580*LFLOW	.552

Table 10 Summary Statistics of Predicted Storm Concentrations

		Standard	Standard Error	Coefficient of						
Variable	Mean	Deviation	of Mean	Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
FLOW	37.5706	58,3324	0.835969	155.261	5.9209	45.6416	12,0200	776.520	20.3500	12.9000
TP	0.0632		0.001588	175.349	4.1480	24.0831	0.0007	1.574	0.0270	0.3420
PP	0.0323	_	0.001140	246.021	6.1928	006.09	0.0001	1.574	0.0080	
SUP	0.0185		0.000500	187.632	3,6371	13.8259	0.0002	0.220	0.0077	
SRP	0.0187	0.0089	0.000128	47.618	3.1052	13,7160	0.0075	960.0	0.0163	
NO ₃ N	0.3068	0.1262	0.001816	41.153	1.0997	2,3583	0.0342	0.796	0.2913	0.1217
NO ₄ N	0.0571	0.0405	0.000583	70.924	3.4644	19,6453	0.0142	0.390	0.0460	0.437
TKN	0.4788	0.1932	0.002780	40.359	2.3754	8,5362	0.2269	1.924	2,4273	0.4161
TS	68.2157	33.6947	0.482883	46.394	2.4516	8.3098	30.0623	295.484	57.9670	90.1743
DS	47.0873	13.4269	0.192420	28.515	0.6493	0.5922	22.0086	100.227	46.5481	81,0979
SS	21.0959	23,2811	0,333645	110.359	3.9617	21.776	3.8458	238,309	13,4913	34.7242
ISI	6.0582	0.5924	0.008490	9.779	-1.3578	1.5711	3.6221	6.743	6.2342	
TMG	1.4747	0.1712	0.002453	11.608	-1,3006	1,3506	0.7918	1.676	1.5246	1,6519
TCA	7.1722	1.2587	0.018038	17.550	-1.1174	0.7089	2.6414	8.741	7.5140	8.5653
TNA	2.0973	0.5039	0.007249	24.024	0.6219	0.2286	0.9345	3.776	2.0270	3,0101
TK	0.9968	0,4460	0.006417	44.743	1.2500	2.4092	0.3070	3.959	0.9284	1.0329
TMN	0.1411	0.0950	0.001367	67.364	2.1689	7,1376	0.00374	0.816	0.1150	4.0818
TFE	0.6809	0.5122	0.007369	75.223	3,1900	14.8052	0.1209	4.788	0.5296	1.4064
TOC	5.8231	2.0244	0.029125	34.764	2,5085	9.3445	3,3165	21,541	5.2890	5.001
DOC	2.8346	2.0484	0.029471	72.266	1.8019	6.4826	0.2598	18.360	2.7512	

Summary Statistics for Static Storm Variables for all Storms in Continuous Flow Record (n=86) Table 11

		Standard	Standard Error	Coefficient						
Variable	Mean	Deviation	of Mean	of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
DURATION	111	101	11	91.249	1.64630	3.2044	0.0	486	76	126.0
TVOLUME	15315186	20078784	2165151	131.104	2.49124	7.0362	87212.3	107836992	8941211	87212.3
MAXQ	123	165	18	134.371	2.15146	4.2812	12.1	777	51	14.0
MEANQ	29	18	7	60.044	1.50495	2.2964	12.1	66	24	12.1
TTP	18	34	4	187,283	4.77735	27.9502	0.0	256	10	2.0
TLS	21	25	က	119,993	2.54422	6.5698	0.3	123	12	0.9
MQL 10	11	80	1	75.266	2.57584	9,6683	2.5	54	8	11.3
MQL25	13	6	1	68,649	1.55806	3,1974	2.4	51	11	20.4
PQL10	41	72	&	174.428	4.01527	20.3734	2.9	498	15	10.8
PQL25	116	161	17	139.198	2,28625	5.0729	2.9	777	53	115.5
PQLS	118	160	17	135,316	2,28556	5.1453	12.1	777	20	14.0

Table 12 Summary Statistics for Static Variables from Sampled Storms (n=14)

Variable	Mean	Standard	Standard Error of Mean	Coefficient of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
DURATION	97	63	17	64.323	1,13	0.79	36	245	80	36
TVOLUME	16676558	12906143	3449312	77,391	1.21	1.00	2291958	44836291	15052209	2291958
MAXQ	225	221	59	98.140	1.35	1.17	17	759	138	17
MEANQ	99	57	15	86.629	1.84	3.69	14	224	48	14
TTP	14	5	1	33,968	0.27	-1.15	7	22	14	6
TLS	30	27	7	91.374	1.15	0.76	Э	93	20	ю
MQL10	10	10	m	97.322	1.87	2.54	E .	33	7	'n
MQL25		7	2	64.107	0.56	-0.49	3	24	12	14
PQL10	37	78	21	213.670	3.26	11.05	3	296	10	5
PQL25	76	88	24	116.980	1.40	1.66	3	296	45	5
PQLS	75	88	23	116.227	1,55	1.84	∞	296	24	80

record was established for the period 1 Jan 76 - 31 Dec 80. A corresponding material load record was established by integrating the area under the material load curve. Summary statistics for predicted daily concentrations and load for all variables are shown in Tables 13 and 14, respectively.

DISCUSSION

Based on the information generated, three groups of water quality variables were identified based on characteristics during baseflow and storm events. The three groups were 1) flow concentrating, 2) flow dilution, and 3) no pattern. The characteristics of each group will be discussed separately and while there were definite patterns between groups, a continuum from one group to another was observed.

The flow concentrating group had a strong positive linear relation between concentration and flow having the same shape curve during storm events (Figure 3). The peak concentration occurred slightly in advanced of peak flow, especially as storm magnitude increased. The mean and standard deviation (std) of observed baseflow samples tended to be less than the mean and std from observed routine, suggesting the significance of storms (i.e., increased concentration and variation with increased flow). Observed baseflow concentrations usually had a negative relation with flow until approximately 12 cms, which probably arose due to dilution. At flows greater than 12 cms, the increased flow caused runoff and resuspension to occur and concentration to increase. The observed storm concentrations had means from 2-6 times larger than baseflow while coefficients of variation (cv) were smaller. Observed storm concentrations were strongly correlated with flow, hence flow was usually the most significant independent variable in the storm model. The mean of predicted storm concentrations were usually less than observed because of the higher percentage of low magnitude storms in the predicted storm set (all storms) in comparison to the set used to develop the storm models (14 storms). This occurred because the higher percentage of small storms caused lower predicted mean flows; therefore the predicted storm concentrations had smaller means and maximums. In comparison, the means and maximums of complete set of predictions (baseflow and storm) were smaller than observed routine conditions. The overall set of predictions also tended to have the same or larger maximum and range. The group consisted of (in order from most applicable to least):

Summary Statistics for Predicted Daily Water Quality Concentrations (1976-1980) Table 13

Variable	Меап	Standard	Standard Error	Coefficient of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
TP	0.0307	0.0463		150.695	7.51	72.74		0.728	0.0221	0.0234
PP	0.0126	0.0305	0.000714	242.094	8.79	99.43	0.0001	0.522	0.0072	0.0082
SUP	0.0080	0.0161	0.000377	201.759	8.21	77.43	0.0003	0.198	0.0050	0.0050
SRP	0.0128	0.0050	0.000118	39.167	4.11	27.97	0.0056	0.075	0.0120	0.0128
NO3N	0.1524	0.1024	0.002397	67.203	2,32	6.97	0.0528	0.779	0.1231	0.0818
NHXN	0.0282	0.0226	0.000530	80.326	5.12	41.53	0.0142	2,359	0.0200	0.0200
TKN	0.4148		0.001999	20.584	4.80	31.81	0.2346	1.418	0.3967	0.3967
TS	69.0161		0.385092	23.837	1.93	11.10	32,5810	215.550	88.8978	78.2843
DS	56.1396		0.231447	17.612	-0.65	0.74	22.4687	89.700	56,6805	64.7827
SS	10,9116	10,1771	0.238227	93.268	6.07	49.87	4.4398	148.165	8.0000	8,0000
TSI	6.4100		0.007337	4.889	-3.74	15.47	4.1344	6.673	6.5106	6.5108
TMG	1.8822		0.007112	16.143	-0.24	-0.64	0.9295	2,410	1.8797	2.1957
TCA	11.4822	3,3740	0.078979	29.385	0.02	-1.11	3,4252	17.671	11.2804	15.0876
TNA	2,1157	0.2243	0.005250	10.601	1,36	11.26	1.0978	3,667	2,1209	2.1209
TK	0.8706		0.004841	23.754	2.04	8.96	0,3195	2.370	0.8546	0.9202
TMN	0.0770	0.0517	0.001209	67.052	4.24	24.12	0.0396	0.657	0.0589	0.0589
TFE	0.3061		0.006531	91.148	69.4	31.72	0.1411	3,386	0.2000	0.2000
TOC	3,3889	1.5092	0.035328	44.534	2,95	11.14	2,7000	15.607	2,7000	2,7000
DOC	2,7297	0.9137	0.021387	33.472	3,92	40.86	0.2781	15.792	2.7000	2.7000

Table 14
Summary of Statistics for Predicted Daily Material Loads (1976-1980)

Variable	Mean	Standard Deviation	Standard Error of Mean	Coefficient of Variation	Skewness	Kurtosis	Minimum	Maximum	Median	Mode
TP	76168	405452	9491	532.316	11.30	155.26	1003	7441136	10778	6927
PP	42919	276743	6478	644.805	11.75	162.20	123	5004076	3298	2419
SUP	14002	56167	1315	401.140	9.68	119.78	330	896645	2582	1427
SRP	25572	114563	2682	448.008	12.07	183.36	2816	2125526	5689	3793
NO3N	268149	749819	17552	279.628	8.00	88.08	10156	12115757	70730	24178
NHYN	45880	129257	3026	281.728	9.32	139.20	3847	2783098	11272	5910
TKN	673131	2613702	61182	388.290	12.40	207.08	76304	60217665	223558	117220
TS	105124399	426510929	9983866	405.720	12.38	195.72	16951368	9142252474	35728688	23132080
DS	57500988	127073755	2974572	220.994	9.29	115.45	13729237	2245214700	30826080	19142512
SS	41189181	274841573	6433555	667.266	15.15	287.26	1538784	6771193003	4508639	2363903
TSI	6313394	9783503	229014	154.964	6.27	54.94	1252301	132689965	3667368	1923804
TMG	1631884	2195825	51400	134.558	6.14	52.39	463589	29347087	1052527	648795
TCA	8453993	8304427	194392	98.231	5.35	40.01	3399187	102570940	6920418	4458194
TNA	2148530	3581292	83832	166.686	6.50	57.59	407951	45374910	1190410	626700
TK	1166332	3598329	84321	308.517	10.51	144.13	194735	63843344	438940	271893
TMN	170135	816789	19120	480.083	16.41	380.10	11329	23026852	33195	17404
TFE	989392	5923407	138656	598.692	15.09	274.95	38470	126109281	112716	59098
TOC	7132624	29826444	698184	418.169	12.03	195.62	519340	675874164	1521665	797818
DOC	3766951	15273640	357529	405.464	15.77	336.54	384201	409259748	1443711	797818

PP, SS, TP, SRP, TFE, TOC, TKN, TS, NO3N, DS, DOC, TK, and TMN. All variables from PP to TKN were definite members of the group while the other variables had the following discrepancies: TS showed flow dilution until flows exceeded 12 cms; NO3N tended to asymptote out at flows greater than 50 cms; DS had a smaller percentage of storm load; DOC, TMN, and TK had larger variations in concentration at high flows.

In the dilution group, concentration had an inverse relation with flow and peaked simultaneously with flow (Figure 4). Mean observed baseflow concentrations were slightly larger than routine and had a very strong negative relation with flow. The observed mean storm concentration was less than baseflow and had an increase in cv and decrease in minimum and maximum. The storm model was usually a function of only flow with the addition of static variables usually causing multicollinearity. The predicted storm concentrations had a larger mean and smaller std and range than observed storm concentrations because the large percentage of small storms caused less dilution (increased mean), and less change in concentration (smaller std and ranges). The complete set of predictions (baseflow and storm) were very similar to the observed routine data because the biases in baseflow and storm predictions tended to cancel each other. The dilution group consisted of TCA, TMG, TNA, and TSI. Both TCA and TMG were strong members with TNA having larger variation in concentration at low flows and TSI having larger variations at low to medium flows.

Group 3, the no pattern or high variation group, showed very little pattern with flow during baseflow or storms (Figure 5). The lack of pattern may occur because the variables had characteristics of both group 1 and 2 combined or actually exhibit no consistent relationships at all. The observed baseflow concentrations were very similar to observed routine with both sets of data having large cv. The means of observed storm concentrations were slightly higher than those for baseflow. Since no strong influence was exerted by any dynamic independent variable, the peaks of predicted concentrations in storm events were flat. The group consisted of SUP and NH4N.

The contributions of storm event loads to the total monthly and annual loads are typified in Figures 6-7, respectively, with the annual percentages for all variables in Table 15. Before examining the water quality load plots, it is important to examine the amount of water load from baseflow and storm

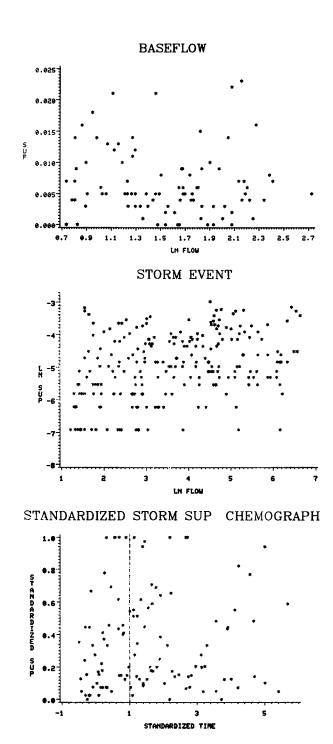
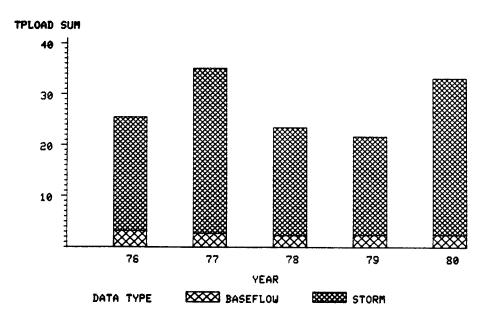


Figure 5. Typical patterns for no pattern variables: (a) baseflow concentration versus flow; (b) storm concentration versus flow; and (c) standardized storm chemograph.

ACCUMULATED LOAD BY YEAR



AVERAGE MONTHLY LOAD

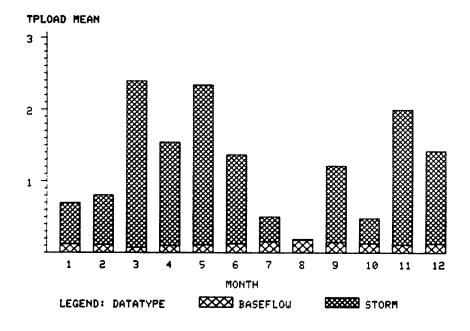
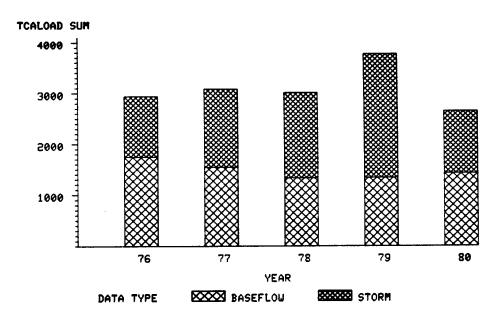


Figure 6. Typical patterns for flow concentrating variables: (a) annual load (separated into baseflow and storm) for 1976-1980; and (b) mean monthly load (separated into baseflow and storm).

ACCUMULATED LOAD BY YEAR



AVERAGE MONTHLY LOAD

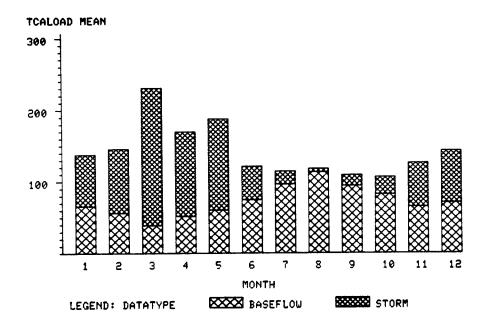


Figure 7. Typical patterns for dilution variables: (a) annual load (separated into baseflow and storm) for 1976-1980; and (b) mean monthly load (separated into baseflow and storm).

Table 15

Percentages and Coefficient of Variation of Total Annual Water Quality Load From Baseflow and Storm Events

ARIABLE	BASEFLOW Z	BASEFLOW CV	STORM Z	STORM CV	MEAN ANNUAL LOAD (GRAMS)	ANNUAL LOAI CV
FLOW	0.327	28.4	0.673	13.8	4819959388	24.1
TP	0.097	22.6	0.903	2.4	27801150	21.5
PP	0.056	29.0	0.944	1.7	15665417	29.4
SUP	0.130	27.4	0.870	4.1	5110697	29.3
SRP	0.154	36.1	0.846	6.5	9333684	30.5
NO3N	0.164	35.8	0.836	7.0	97874218	27.1
NH4N	0.163	39.9	0.837	7.8	16746252	28.2
TKN	0.220	35.9	0.780	10.1	245692908	31.7
TS	0.234	34.8	0.766	10.7	38370405731	33.2
DS	0.344	20.9	0.656	10.9	20987860603	15.7
SS	0.079	47.0	0.921	4.0	15034050985	45.5
TSI	0.367	25.5	0.633	14.8	2304388669	20.0
TMG	0.415	22.7	0.585	16.2	595637723	17.6
TCA	0.486	18.9	0.514	17.9	3085707310	13,4
TNA	0.363	32.1	0.637	18.3	784213572	29.1
IK	0.240	21.2	0.760	6.7	425711270	13.8
TMN	0.142	45.5	0.858	7.5	62099203	47.8
TFE	0.088	50.8	0.912	4.9	361128026	56.8
TOC	0.146	41.2	0.854	7.1	2603407712	37.8
DOC	0.250	21.8	0.750	7.3	1374937129	12.9

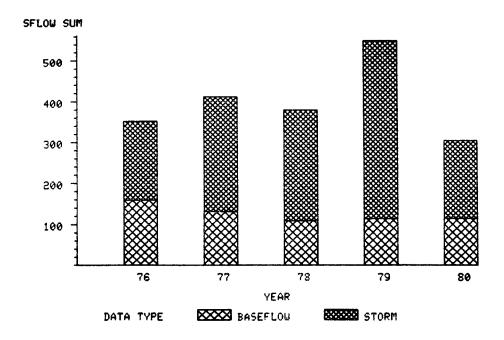
events (Figure 8), for if storm events have no effect on concentration during storms the percentages of water load and water quality load should be very similar. However, if increased flows caused increased concentrations, then storm events should contribute a higher percentage than water load; whereas if dilution of concentration occurred with increased flow, a decrease in storm load percentages should be expected. For concentration variables, storm events dominated the total load (94-98 percent) with medium to large cv's. In contrast, the percentage of storm event contribution to the total load for dilution variables was much smaller (51-64 percent).

A pattern that emerged within all variables was that as the percentage of storm event contribution increased, the cv decreased. This suggests that the variables that are significantly concentrated by flow do so in a consistent manner, while dilution variables have increased variation in storm event percentages in comparison to baseflow. However, this pattern must be viewed in the light that even though a smaller cv existed with variables having large storm loadings, a small variation at the higher percentage actually caused more change in loading than a larger variation at a lower percentage. Another important pattern was that even though dilution variables had high cv's of percentages during storm events, they had lower annual cv's because the lower percentage cv's during baseflow coupled with more baseflow loadings created lower annual variations.

Both baseflow and storm event material loading have seasonal patterns, exemplified in Figures 6-7 and Tables 16 and 17 for all variables, respectively. The total mean monthly loads for concentrating variables occurred on a definite seasonal basis: very high in spring, decreasing in summer and increasing in fall. For dilution variables, the total mean monthly loads were fairly uniform throughout the year. For all variables, the seasonality in storm loading was similar to patterns in water loading with the major peaks in the spring and slightly smaller ones in the fall. In comparison, baseflow material loads peaked in summer. In both storm and baseflow loadings, when the monthly percentage increased, the cv decreased, and may exhibit the same properties of changing percentages and cv as was examined for total annual loads.

The fact that material loads occur in a seasonal manner can have an important impact on the response of the system (lake or reservoir) based on the uneven impulse loading. Thus, even though annual estimates may predict

ACCUMULATED LOAD BY YEAR



AVERAGE MONTHLY LOAD

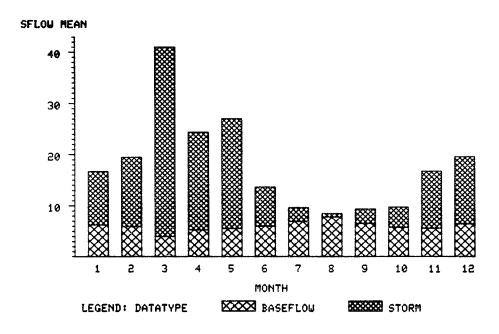


Figure 8. Baseflow and storm: (a) annual water load (1976-1980); and (b) mean monthly water load.

Table 16

Monthly Mean and Coefficient of Variation of Percent Baseflow Load

		AN	FE	D D	MA	p	AP	R	MA	Y	JU	N	J	UL	A	ÜĞ	S	EP	0	CT	NO		DE	
VARIABLE	<u>J</u>	SCV	S	SCV	S	SCV	S	SCV	S	scv	S	scv	S	scv										
FLOW	.589	33.1	.652	29.5	.874	11.3	.694	34.7	.619	61.1	.437	71.2	.198	140.8	.055	223.6	.204	116.2	.245	128.0	.517	59.3	.599	42.2
TP	.773	15.1	.722	29.9	.915	7.5	.822	24.7	.739	56.7	.659	60.0	.337	137.4	.043	223.6	.364	137.6	.409	105.0	.707	42.0	.795	24.1
PP	.816	13.9	.753	28.5	.929	7.8	.853	20.4	.767	56.l	.689	58.5	.363	137.2	.039	223.6	.380	137.1	.458	98.9	.764	35.1	.838	20.8
SUP	.587	26.8	.708	34.0	.866	10.3	.799	30.1	.756	56.3	.659	58.0	.252	143.0	.052	223.6	.309	141.9	.284	122.8	.610	54.4	.769	24.2
SRP	.711	32.1	.781	23.2	.941	8.0	.786	30.0	.687	57.9	.552	70.4	.276	137.3	.082	223.6	.262	153.9	.336	127.4	.629	53.4	.736	36.1
NO3N	.746	25.1	.760	19.2	.934	5.7	.775	26.0	.662	59.1	.563	70.7	.284	137.3	.076	223.6	.328	140.7	.373	113.8	.645	48.4	.720	32.9
NH4N	.672	30.7	.799	24.1	.935	6.1	.810	26.6	.736	56.4	.598	58.5	.245	159.8	.153	223.6	.213	156.0	.270	126.3	.666	36.7	.780	23.0
TKN	.636	31.6	.706	31.2	.914	9.5	.724	34.4	.658	59.0	.506	69.8	.238	141.3	.072	223.6	.244	156.7	.288	127.4	.580	56.6		41.8
TS	.635	30.8	.701	30.4	.914	10.7	.726	34.7	.651	59.9	.485	72.3	.230	139.0	.054	223.6	.220	162.7	.283	128.8	.562	61.6	-	44.2
DS	.576	27.6	.632	30.2	.862	11.6	.693	35.2	.616	60.7	.444	71.1	.187	139.2	.041	223.6	.211	159.3	.240	126.9	.513	63.4	.595	41.2
SS	.795	20.8	.816	22.0	.963	5.2	.820	27.1	.727	56.8	.615	64.9	.331	137.2	.095	223.6	.306	144.1	.382	120.4	.693	44.5		31.5
TKN	.571	34.2	.633	29.0	.853	11.9	.680	34.5	.605	61.6	.410	71.3	.184	141.5	.053	223.6	.191	160.5	.229	128.2	.497	58.3	.567	40.9
TMG	.541	36.2	.614	30.3	.836	13.6	.661	36.0	.589	62.5	.374	73.8	.159	142.3	.044	223.6	.160	163.7	.203	130.2	.465	61.1		42.2
TCA	.499	38.8	.586	31.6	.806	16.0	.634	37.7	.564	63.8	.325	77.1	.131	143.7	.034	223.6	.125	164.4	.170	131.3	.420	62.7		43.1
TNA	.570	36.9	.637	31.9	.858	13.1	.678	36.2	.606	62.7	.391	73.7	.180	147.1	.066	223.6	.157	166.3	.212	131.3	.479	57.9		43.9
TK	.652	28.0	.722	23.6	.908	7.9	.755	29.0	.660	58.5	.518	66.4	.246	137.3	.051	223.6	.268	147.7	.309	121.8	.604	52.3		33.0
TMN	.730	31.4	.765	16.7	.946	6.9	.815	24.7	.680	60.2	.557	69.5	.308	137.4	.059	223.6	.251	155.2	.363	119.5	.619	55.3		37.5
TFE	.761	26.2	.848	15.0	.965	5.0	.858	21.6	.732	57.0	.623	63.0	.303	137.7	.088	223.6	.272	149.4	.367	122.0	.676			25.7
TOC	.713	28.9	.785	24.3	.944	6.5	.789	29.4	.703	57.4	.574	67.6	.274	139.5	.101	223.6	.270	160.0	.325	126.0	.643	48.8		32.3
DOC	.665	28.8	.699	25.7	.895	11.1	.671	31.2	.559	62.0	.432	72.3	.236	137.8	.034	223.6	.283	147.0	.331	124.0	.591	56.1	.642	42.6

Table 17 Monthly Mean and Coefficient of Variation of Percent Storm Load

VARI-	1,	AN	E.	EB		MAR		APR		MAY		TIIN		1111	· ·	V110	100	5					ľ	
- 1	m	BCV	m	B BCV B BCV B	m	BCV	<u>~</u>	BCV	В	BCV	e e	BCV	m	BCV	m	BCV	8	BCV	B 8	BCV	B	BCV	B	BCV
FLOW .	411	.411 47.5 .348	.348	55.2	.126	77.8	306	78.6	.381	99.1	.563	55.3	.802	34.8	.945	13.0	.796	41.2	.755	41.6	.483	63.6	.401	63.0
TP .	.227	51.2		77.7	.085	81.6	.178	113.9	.261	160.1	.341	115.8	.663	7.69	.957	6.6	.636	78.6	.591	72.6	.293	101.4	. 205	93.5
PP .	184 (61.9	.247	87.1	.071	101.5	.147	117.9	.233	184.5	.311	129.8	.637	78.1	.961	9.1	.620	84.0	.542	83.5	.236	113.4	.162	107.9
sup.	.413	38.1	.292	82.3	.134	66.4	.201	119.9	.244	174.6	.341	112.0	.748	48.2	876.	12.3	169.	63.5	.716	48.7	.390	85.2	.231	80.4
SRP .	289	79.0	.219	82.7	.059	126.2	.214	110.2	.313	127.3	.448	86.8	.724	52.3	.918	20.02	.738	54.7	.664	4.49	.371	90.7	.264	100.5
NO3N	254	73.9	.240	61.1	990.	80.3	.225	89.5	.338	116.1	.437	6.06	.716	54.3	.924	18.3	.672	8.89	.627	9.19	.355	88.1	. 280	84.5
_	.328	67.9	.201	95.7	.065	87.9	.190	113.5	. 264	157.2	.402	87.2	.755	51.9	.847	40.5	.787	42.3	.730	46.7	.334	73.2	.220	81.7
	364		. 294	75.0	980.	100.5	.276	90.1	.342	113.7	765.	71.6	.762	44.2	.928	17.3	.756	50.5	.712	51.5	.420	78.2	.319	89.4
TS .	365		.299	71.3	980.	112.6	.274	92.2	.349	111.9	.515	68.2	.770	41.5	946	12.8	.780	46.0	7117.	50.8	.438	79.0	.334	88.1
DS.			.368	51.9	.138		.307	79.5	.384	97.6	.556	56.8	.813	32.0	.959	9.6	.789	42.5	.760	40.0	.487	6.99	.405	9.09
	.215		.184	97.3	.037	134.9	.180	123.9	.273	151.3	.385	103.7	699.	8.79	.905	23.4	769 .	63.6	.618	74.4	.307	100.4	.211	117.8
TSI.	429 4	45.5	.367	50.1	.147	4.69	.320	73.2	.395	94.1	.590	9.67	.816	31.8	.947	12.6	800	37.8	.771	38.0	. 503	57.5	.433	53.6
TMG .	459 4		.386	48.3	.164	9.69	.339	70.3	.411	89.5	.626	44.1	.841	26.9	.956	10.2	.840	31.2	797	33.1	.535	53.0	694.	47.9
TCA .	501 3	38.7	.414	44.8	.194	4.99	.366	65.3	.436	82.7	.675	37.1	.869	21.6	996.	7.9	.875	23.4	.830	26.9	.580	45.3	.524	39.2
TNA.	430 4		.363	26.0	.142	79.5	.322	76.2	.394	96.3	609.	47.3	.820	32.2	.934	15.7	.843	31.1	.788	35.2	.521	53.3	439	56.0
¥.	348 5		.278	61.3	.092	78.0	.245	89.4	.340	113.3	.482	71.4	.754	8.44	676.	12.0	.732	54.2	.691	54.6	.396	7.61	.310	73.5
THIN .	.270		.235	54.6	.054	122.2	.185	108.6	.320	127.8	.443	87.2	.692	61.1	.941	13.9	.749	52.1	.637	68.3	.381	89.8	. 289	92.2
TFE .				83.7	.035	137.6	.142	130.3	.268	155.9	.377	104.0	.697	8.69	.912	21.6	.728	55.9	.633	6.07	.324	6.46	. 192	108.3
TOC .	.287 7		.215	88.7	.056	109.7	.211	110.0	.297	136.0	.426	6.06	.726	52.6	.899	25.2	.730	55.9	.675	9.09	.357	88.0	.246	99.1
D00	.335 5	57.3	.301	59.7	. 105	6.46	.329	63.6	.441	78.5	.568	55.1	.764	42.7	996.	7.8	.717	57.9	699.	61.5	.409	81.1	.358	76.4

similar annual loads, by not incorporating the seasonal pattern in material loads, they have limited usefulness. Also, if annual input-output models are used, the fact that seasonal loading exists may have a significant impact on the coefficients used in the model. Another important aspect of spring seasonal loads is the possibility for the large amounts of material loads to be added either directly to the water or sediment and provide the spring starting point for water quality concentrations and an internal nutrient source to become available later in the year (Kennedy et al., 1983).

The change in chemical species composition between baseflow and storm event loadings was most pronounced in variables having dissolved and particulate fractions. The fraction of particulate or suspended material was much larger than dissolved during storm events (eg., PP to SUP and SS to DS). Thus, the variables consisting of a significant amount of both dissolved and suspended species and which have a large percentage of storm loadings may be comprised of many more particulates than reflected by the percentages calculated from using observed routine data and a direct loading estimator. For example, if storm events contribute 90 percent of the total load and 90 percent of storm loads are particulates, then out of 100 units a year, 81 are particulates. The importance of increased percentage of particulates is augmented by presence of seasonal loading, in that the spring load, high in particulates, may be deposited and utilized later during anoxic conditions. However, if no anoxic conditions occur, then the spring peaks high in particulates may overestimate the actual amount of phosphorus available, for the majority, when they would be deposited and lost to the system (i.e., sink). The increase in particulates may be of special importance in riverine or dendritic type reservoirs, where in the headwaters, or arms, flow may diminish enough to allow decomposition of material loads and thus change the species composition (i.e., particulates to dissolved). Hence, when high flows do occur, resuspension and scour could cause a large amount of internal loading.

REFERENCES

- Cahill, T. 1977. Forms and Sediment Association of Nutrients (C.N.&P)
 Pesticides and Metals, Introduction. In Proc. of Workshop on the Fluvial
 Transport of Sediment-Associated Nutrients and Contaminants, IJC Pluarg
 Report.
- Colston, N. V. 1974. Characterization and Treatment of Urban Land Runoff, EPA-670/2-74-096.
- Dolan, D. M., Yui, A. K., and R. D. Geist. 1981. Evaluation of River Load Estimation Methods for Total Phosphorus. JGLR 7(3):207-214.
- Gunkel R. C., et. al. 1984. A Comparative Study of Sediment Quality in Four Reservoirs. Technical Report E-84-2, USAE Waterways Experiment Station, Vicksburg, MS.
- Hydrocomp. 1980. Users Manual for Hydrologic Simulation Program Fortran (HSPF). Hydrocomp Inc., Mount View, CA. Prepared for USEPA Research Lab, Athens, GA.
- Jewell, T. K., Adrian, D. D., and F. A. DiGiuno. 1980. Urban Stormwater Pollutant Loadings. Pub. No. 113, Water Resources Center, U. of Mass. at Amherst, MA.
- Johnson, A. H. 1979. Estimating Solute Transport in Streams from Grab Samples. WRR 15(5)+1224-1228.
- Kennedy, R. H., Thornton, K. W., and R. C. Gunkel. 1982. The Establishment of Water Quality Gradients in Reservoirs. Prepared for Int. Sym. on Reservoir Ecology and Management, Quebec, Canada. June 1981.
- Kennedy, R. H., Montgomery, R. H., James, W. F., and J. Nix. 1983. Phosphorus Dynamics in an Arkansas Reservoir: The importance of seasonal loading and internal recycling. Miscellaneous Paper E-83-1. USAE Waterways Exp. Station, Vicksburg, MS.
- McElroy, A. D., et. al. 1976. Loading Functions for Assessment of Water Pollution from Nonpoint Sources. EPA-600/2-76-151.
- Mills, W. B., et. al. 1982. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants, Part I. EPA-600/6-82-004a.
- Montgomery, R. H., and R. H. Kennedy. 1986. Material loadings to DeGray Lake, Arkansas, via the Caddo River. Technical Report. USAE Waterways Exp. Station, Vicksburg, MS. (In prep.)
- Omernik, J. M. 1977. Nonpoint Source Stream Nutrient Level Relationships: A Nationwide Survey. EPA-600/3-77-105.
- Ongley, E. D., Ralston J. G., and R. L. Thomas. 1977. Sediment and Nutrient Loadings to Lake Ontario: Methodological Arguments. Can. J. Earth Sci. 14:1555-1565.
- Perrier, E. R., Ford, W. B., and J. Harris. 1977. An Evaluation of Several Deterministic Mathematical Watershed Models, Unpublished Report, USAE Waterways Exp. Station, Vicksburg, MS.
- Rast, W. and G. F. Lee. 1978. Summary Analysis of North American (US Portion) OECD Eutrophication Project: Nutrient Loading-Lake Response Relation-ships and Trophic State Indices. EPA-600/3-78-008.

- Reckhow, K. H., Beaulac, M. N., and J. T. Simpson. 1980. Modeling Phosphorus Loading and Lake Response under Uncertainty: A Manual and Compilation of Export Coefficients. EPA-440/5-80-011.
- Smith, R. V., and D. A. Stewart. 1977. Statistical Models of River Loadings of Nitrogen and Phosphorus in the Lough Neagh System. Water Res. 11:631-636.
- Stevens, R. J., and R. V. Smith. 1978. A Comparison of Discrete and Intensive Sampling for Measuring the Loads of Nitrogen and Phosphorus in the River Main, County Antrim. Water Res. 12:823-830.
- Thornton, K. H., et. al. 1981. Reservoir Sedimentation and Water Quality An Heuristic Model. In Proc. of the Symp. on Surface Water Impoundments,
 ASCE. NY.
- USDA, 1973. Summary of Reservoir Deposition Surveys made in the United States through 1970. Misc. Pub. 1266, Agricultural Research Service, Water Resources Council.
- Verhoff, F. H., Yaksich, S. M., and D. A. Melfi. 1980. River Nutrient and Chemical Transport Estimation. ASCE JEED(EE3):591-608.
- Vollenweider, R. A. 1968. Water Management Research: Scientific Fundamentals of Eutrophication of Lakes and Flowing Waters, with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication. Tech. Report DAS/CSI/68.27, OECD, Paris, France.
- Walker, W. W. 1981. Empirical Methods for Predicting Eutrophication in Impoundments: Phase I: Data Base Development. Technical Report E-81-9, USAE Waterways Exp. Station, Vicksburg, MS.
- Westerdahl, E. H., Ford, W. B., Harris, J., and C. R. Lee. 1981. Evaluation of Techniques to Estimate Annual Water Quality Loadings to Reservoirs. Technical Report E-81-1. USAE Waterways Exp. Station, Vicksburg, MS.
- Wetzel, R. G. 1976. Limnology. W. B. Sanders Co., Philadelphia, PA. 743 pp.
- Whitfield, P. H. 1982. Selecting a Method for Estimating Substance Loadings. WRB 18(2):203-210.
- Wu, J. S. and R. C. Ahlert. 1978. Assessment of Methods for Computing Storm Runoff Loads. WRB 14(2):429-439.

GLOSSARY OF SYMBOLS

A. Water Quality Variables

Symbol	Description
DOC	Dissolved organic carbon
DS	Dissolved solids
NH4N	Ammonia nitrogen
NO3N	Nitrate nitrogen
PP	Particulate phosphorus
SRP	Soluble phosphorus
SS	Suspended solids
SUP	Soluble unreactive phosphorus
TCA	Total calcium
TFE	Total iron
TK	Total potassium
TKN	Total Kjeldahl nitrogen
TMG	Total magnesium
TMN	Total manganese
TNA	Total sodium
TOC	Total organic carbon
TP	Total phosphorus
TS	Total solids
P-DOC	DOC/TOC
P-DS	DS/TS
P-PP	PP/TP
P-SRP	SRP/TP
P-SS	SS/TS
P-SUP	SUP/TP

B. Storm Model Independent Variables

Symbol	Description
AQ	Accumulated flow since start of storm (cubic meters)
DURATION	Duration of storm (hours)
FLOW	Flow (cms)
MAXO	Maximum flow of storm (cms)
MEANO	Mean flow of storm (cms)
MQL10	Mean flow last 10 days (cms)
MOL25	Mean flow last 25 days (cms)
PQLS	Peak flow last storm (cms)
PQL10	Peak flow last 10 days (cms)
PQL25	Peak flow last 25 days (cms)
TIMESSS	Time since start storm (hours)
TLS	Time since last storm (days)
TTP	Time to peak flow from start of storm (hours)
TVOLUME	Total volume of storm (cubic meters)