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Daniel May

University of Wollongong, dbm05@uow.edu.au

Muttucumaru Sivakumar

University of Wollongong, siva@uow.edu.au

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Prediction of Nutrient Concentrations in Urban Storm Water

Daniel May¹ and Muttucumaru Sivakumar²

Abstract: Excessive quantities of nutrients in urban storm-water runoff can lead to problems such as eutrophication in receiving water bodies. Accurate process based models are difficult to construct due to the vast array of complex phenomena affecting nutrient concentrations. Furthermore, it is often impossible to successfully apply process based models to catchments with limited or no sampling. This has created the need for simple models capable of predicting nutrient concentrations at unmonitored catchments. In this study, simple statistical models were constructed to predict six different types of nutrients present in urban storm-water runoff: ammonia (NH₃), nitrogen oxides (NO_x), total Kjeldahl nitrogen, total nitrogen, dissolved phosphorus, and total phosphorus. Models were constructed using data from the United States, collected as a part of the Nationwide Urban Stormwater Program more than two decades ago. Comparison between the models revealed that regression models were generally more applicable than the simple estimates of mean concentration from homogeneous subsets, separated based upon land use or the metropolitan area. Regression models were generally more accurate and provided valuable insight into the most important processes influencing nutrient concentrations in urban storm-water runoff.

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CE Database subject headings: Nutrients; Urban areas; Runoff; Stormwater management; Water quality; Nitrogen; Phosphorus.

Introduction

Many surface waters throughout the world are adversely affected by eutrophication. This is a phenomenon which occurs when large nutrient loads are rapidly consumed by algae present in the receiving water, thereby causing an algal bloom. The nightly algal respiration reduces dissolved oxygen concentrations, sometimes resulting in mortality of aquatic organisms (Thomann and Mueller 1987). In addition, when the level of the limiting nutrients is used up, the algae can die off. The decay processes involved in the conversion of dead algae back to their basic constituents further depletes the level of oxygen in the water, resulting in the mortality of additional aquatic organisms. This may decrease the diversity of aquatic life, ultimately influencing the balance of the ecosystem (Burian et al. 2001).

To remediate or prevent problems associated with eutrophication, the levels of nutrients in storm-water runoff must be quantified. However, it is commonly known that storm-water monitoring programs are time consuming and expensive (Driver and Tasker 1990; Brezonik and Stadelmann 2002; Sliva and Williams 2001). This has created the need to forecast nutrient levels at catchments with limited or no sampling. Even though process based models are recognized as having wider domains of appli-

cability than statistical models, they often only provide crude representations of the complex environmental systems (Maier and Dandy 1996). Furthermore, essential data may not be available and important processes may be overlooked (Loke et al. 1999). This has created the demand for simplistic statistical models capable of making use of the available data.

Statistical models vary in complexity. The simplest model is the constant concentration model, which averages event mean concentration (EMC) data from catchments within a homogeneous domain to form a single representative estimate of the pollutant concentration. The specification of homogeneous domains may be based upon the catchments within common localities or some predefined characteristic such as land use. Previous studies by Duncan (1999) and Athayde et al. (1983) sought to define average pollutant concentrations within distinct land-use categories using a worldwide data set and the U.S. data set, respectively. However, the observed overlap of pollutant concentrations between land-use categories was perceived to limit the usefulness of such models. Another statistical technique used to predict urban storm-water quality is the regression model. Previous studies by Driver and Tasker (1990) and Brezonik and Stadelmann (2002) sought to use multiple linear regression models to predict storm-water concentrations at catchments within the United States and Minnesota, respectively. However, these studies made no comparison between regression and constant concentration models predicting water quality at unmonitored catchments.

Methods

The main goal of the current study was to compare the ability of simple statistical models to predict nutrient concentrations in urban storm-water runoff. Six of the most prevalent nutrient compounds found in urban storm water were analyzed: ammonia (NH₃), nitrogen oxides (NO_x), total Kjeldahl nitrogen (TKN), total nitrogen (TN), dissolved phosphorus (DP), and total phosphorus (TP). Water quality data were obtained from the U.S. metropolitan areas presented in Table 1. This data was initially

¹Graduate Student, Sustainable Water and Energy Research Group (SWERG), School of Civil, Mining, and Environmental Engineering, Faculty of Engineering, Univ. of Wollongong, New South Wales 2522, Australia.

²Associate Professor, Sustainable Water and Energy Research Group (SWERG), School of Civil, Mining, and Environmental Engineering, Faculty of Engineering, Univ. of Wollongong, New South Wales 2522, Australia (corresponding author). E-mail: siva@uow.edu.au

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Table 1. Locations of the Urban Areas Monitored in the Nationwide Urban Runoff Program

Metropolitan area	Metropolitan area
Baltimore, Md.	Long Island, N.Y.
Bellevue, Wash.	Miami, Fla.
Champaign-Urbana, Ill.	Milwaukee, Wis.
Columbus, Ohio	Portland, Ore.
Denver, Colo.	Rapid City, S.D.
Fresno, Calif.	Rochester, N.Y.
Glen Ellyn, Ill.	Salt Lake City, Utah
Houston, Tex.	St. Paul, Minn.
Kansas City, Mo.	Tampa, Fla.
Lansig, Mich.	Washington, D.C.
Little Rock, Ark.	Winston-Salem, N.C.

collected as part of the Nationwide Urban Runoff Program (NURP) by the U.S. Environmental Protection Agency and the U.S. Geological Survey in the late 1970s and early 1980s. It was then converted to an electronic format by the Cahaba/Warrior Student Chapter of the American Water Resources Association (University of Alabama) (1998) and used in the current study. In general, nutrient concentrations were not measured during every storm event. Table 2 summarizes how many storms, catchments, and metropolitan areas associated with each nutrient were monitored.

A number of explanatory variables were available in the NURP study. In total, 7 broad scale climatic variables, 23 catchment variables, and 19 storm variables were measured. However, only some of these variables were used in the final regression models developed in this study. These variables are presented in Table 3. In addition to the NURP variables, an additional six broad scale geographic and climatic variables obtained from other sources were also used in the study. These variables are presented in Table 4.

For the most part, the variables shown in Table 3 do not require explanation. However, three may possibly require clarification. The spatial arrangement of impervious surfaces within a catchment is often assumed to influence the quantity and quality of the runoff entering receiving waters. This gave rise to the development of a variable known as “effective impervious area” (EFFIA) or “directly connected impervious area.” Pandit and Gopalakrishnan (1997) defined it as the portion of impervious area (IA) that is connected directly to the drainage network. It is based upon the fundamental assumption that runoff from impervious surfaces that flows onto pervious areas infiltrates the soil medium in the same manner as rain falls onto these areas. The second variable requiring further explanation was the “seasonal coefficient” (VS), which was used to define seasonal trends in the data. It was derived using the following equation:

Table 2. Water Quality Constituents Analyzed

Water quality constituent	Acronym	Metropolitan areas	Catchments	Storms
Ammonia	NH ₃	8	33	247
Dissolved phosphorus	DP	8	33	307
Nitrogen oxides	NO _x	9	27	278
Total Kjeldahl nitrogen	TKN	14	53	559
Total nitrogen	TN	11	35	387
Total phosphorus	TP	22	79	956

Table 3. Explanatory Variables from the NURP Study Used in the Regression Models

Acronym	Variable	Units	Number of observations filled in
ABS	Average basin slope	%	337
DA	Drainage area	ha	0
DRN	Duration of rainfall	min	519
EFFIA	Effective impervious area	%	182
IA	Impervious area	%	7
LUR	Residential land use	%	0
MAR	Mean annual rainfall	mm	0
PIRN	Previous 1-day rainfall	mm	471
P3RN	Previous 3-day rainfall	mm	530
P7RN	Previous 7-day rainfall	mm	525
PD	Population density	people/ha	354
QMAX	Peak flowrate	m ³ /s	455
ROI	Average runoff intensity	mm/hr	442
SD	Street density	km/ha	610
TRN	Total event rainfall	mm	0
VS	Seasonal coefficient	N/A	0
SCGD	% of streets that have curb and gutter drainage	%	368

$$VS = \sin\left(2\pi \frac{j}{365}\right) \quad (1)$$

where j =the Julian day or the number of days that have passed in a year (Bastarache et al. 1997). The third variable requiring further explanation was “average runoff intensity” (ROI). It was derived using the following equation:

$$ROI = \frac{TRF}{DRF} \quad (2)$$

where TRF=the total storm runoff depth (mm) and DRF=the duration of runoff (h).

The initial stage of data preprocessing involved the removal of atypical catchments from the data set, using criteria specified in a previous study by May and Sivakumar (2003). These catchments were assumed to lie outside the domain of modeling. Catchments with large portions of agricultural land use were assumed to contain additional sources of nutrients, derived from fertilizer application and/or animal wastes. Therefore, catchments with portions of agricultural land use greater than 50% (LUAGR > 50%) were removed. Catchments with large portions of industrial land use were also assumed to contain increased sources of nutrients, depending upon the type of industry. For example, the increased nitrogen oxide emissions from vehicular sources in highly industrial areas were assumed to contribute to increased levels of nitrogen oxides in runoff. Therefore, catchments with portions of industrial land use in excess of 50% (LUI > 50%) were removed. Highly urbanized city catchments were also assumed to contain increased quantities of certain nutrients, predominantly derived from transport activities and sewerage. Hence, catchments with population densities (PDs) in excess of 130 people per ha (PD > 130 people/ha) were removed from the data set. Relatively low nutrient concentrations were assumed to be associated with very large catchments. This was assumed to be due to the increased portions of vegetated pervious surfaces capable of uptaking the nutrients. Furthermore, various forms of nitrogen may also be more readily oxidized within large drainage networks. There-

Table 4. Explanatory Variables Obtained from Other Sources

Acronym	Explanatory variable	Units	Source
AMRN	Average monthly rainfall	mm	Ward and Elliot (1995)
AMT	Average monthly temperature	°F	Ward and Elliot (1995)
KAVE	Average soil erodibility factor	N/A	Ward and Elliot (1995)
MAP	Mean annual precipitation	mm	National Atmospheric Deposition Program (1994)
NH4CR	Ammonium concentration in rain	mg/L	National Atmospheric Deposition Program (1994)
NO3CR	Nitrogen oxide concentration in rain	mg/L	National Atmospheric Deposition Program (1994)
RASEI	Regional average storm event intensity	mm/h	Athayde et al. (1983)

fore, catchments with drainage areas in excess of 3,000 ha (DA > 3,000 ha) were excluded from the data set. Finally, catchments containing large detention storages (DS's) were assumed to produce lower nutrient concentrations than other urban catchments. It was assumed that the DS's promoted the sedimentation of particulates and adsorbed nutrients. However, the location of the DS was considered to influence the extent of pollutant removal. Those located at the pour point of the catchment would treat all runoff from the catchment. Hence, these catchments were removed. Those located upstream of the pour point would not treat all runoff from the catchment. However, the exact location of these DS within the catchment was not provided. Therefore, the relative size of the DS was analyzed to estimate the extent of pollutant removal in these catchments. Catchments containing very large ratios between DS and drainage area (DS/DA > 20 mm) were assumed to treat a large portion of the runoff, hence, were removed from the data set.

The total number of atypical catchments removed is presented in Table 5 along with a summary of the criteria used to remove them. In addition, the characteristics of the remaining catchments used in subsequent analyses have been provided in Table 6. These characteristics indicate the domain on which the models were constructed, and ultimately, the domain which the models may be applied on in the future.

After the removal of atypical catchments from the data set, the missing values associated with the NURP explanatory variables were infilled. The total number of infilled values associated with each explanatory variable is presented in Table 3. In general, a combination of different methods was used to infill missing values for any given variable. They ranged in complexity from multiple linear regressions to simplistic average estimates. Due to the large number of variables requiring infilling, only two examples have been provided below.

The missing values associated with the duration of rainfall (DRN) variable were infilled using two models. The first model used the strong relationship between DRN and duration of runoff (DRF) to infill 323 missing values via the following equation:

$$\text{DRN} = -2.87 + 0.81 \times \text{DRF} \quad (3)$$

A total of 263 values were used to derive this linear regression, which had an associated coefficient of determination of 0.91. However, due to the absence of values of DRF, another model was required to infill the remaining 196 missing values of DRN. The second model was a multiple linear regression equation calibrated on logarithmically transformed data. The retransformed equation used to infill the remainder of missing values was

$$\text{DRN} = 10^{(2.2)} \times \text{AMT}^{(-1.04)} \times \text{RASEI}^{(-0.87)} \times \text{TRN}^{(0.72)} \quad (4)$$

where AMT=the average monthly temperature (°F); RASEI=the regional average storm event intensity (mm/h); and TRN=the total event rainfall depth (mm). A total of 756 values were used to derive the aforementioned regression, which had an associated coefficient of determination of 0.44 (calculated on logarithmically transformed data).

The missing values associated with EFFIA were infilled using a combination of simple linear regression equations. Catchments were initially separated into a number of categories based upon dominant land use. Linear regression equations between EFFIA and IA were then developed for each land-use category. It was assumed that the intercepts of the regression models were equal to zero, to minimize the total number of calibration coefficients, thereby reducing the potential for data overfitting. The regression equations are presented in Table 7 along with their associated coefficients of determination and the number of catchments used to derive them.

The regression equation predicting EFFIA in catchments with large portions of median density residential area initially produced a negative coefficient of determination. However, this was deemed to be due to a potentially outlying catchment, which had a very low value of EFFIA associated with a large value of IA. As a result, this catchment was removed and the regression model recalibrated.

Since each catchment requiring data infilling was typically made up of a combination of different types of land uses, the following equation based upon the single variable regressions presented in Table 7 was used to infill the missing values:

Table 5. Number of Atypical Catchments and the Criteria Used to Remove Them

Removal criteria	Number of catchments
LUAGR > 50%	4
LUI > 50%	2
PD > 130 people/ha	2
DA > 3,000 ha	7
DS at pour point	4
DS/DA > 20 mm	2

Table 6. Characteristics of the Catchments Used in Subsequent Analyses

Catchment characteristic	Minimum	Maximum	Average	Median
LUAGR (%)	0	17	0	0
LUI (%)	0	32	2	0
PD (people/ha)	0	79	17	13
DA	1	2131	103	31
DS/DA (mm)	0	17.6	0.5	0

Table 7. Summary of the Linear Regression Equations Predicting Effective Impervious Area Using Impervious Area

Model	Gradient	Intercept	Count	R ²
LUIC > 90%	0.98	0	7	1.00
LUHDR > 85%	0.74	0	6	0.39
LUMDR > 80%	0.57	0	8	0.57
LULDR > 60%	0.75	0	7	0.92
LUN > 50%	0.81	0	7	0.70

Note: LUIC=commercial and industrial land use; LUHDR=high density residential land use; LUMDR=median density residential land use; LULDR=low density residential land use; and LUN=nonurban land use.

$$\text{EFFIA} = (0.98 \times \text{LUIC} + 0.74 \times \text{LUHDR} + 0.57 \times \text{LUMDR} + 0.75 \times \text{LULDR} + 0.81 \times \text{LUN}) \times \left(\frac{\text{IA}}{100} \right) \quad (5)$$

An associated coefficient of determination of 0.65 was achieved when this equation was applied to the 24 catchments not used to calibrate the individual regression models. Overall, this technique infilled a total of 19 missing values of EFFIA.

Water quality constituents and explanatory variables were then logarithmically transformed and used to construct multiple linear regression models. In the current study, EMCs were modeled as opposed to event loads. This was in accordance with a previous study by May and Sivakumar (2003), which suggested that the known relationship between event load and runoff volume should not be modeled. This enabled considerably more priority to be placed upon modeling the unknown concentration variability, thereby ultimately allowing the identification of significant processes influencing urban storm-water quality. The following equation expresses the functional form of the regression model used to predict EMC:

$$\log(y) = \beta_0 + \sum_{i=1}^n \beta_i \log(X_i) \quad (6)$$

Where x_i =explanatory variable i ; y =response variable; β_i =regression coefficient associated with explanatory variable i ; β_0 =intercept calculated on logarithmically transformed data; and n =number of explanatory variables.

Stepwise regression procedures (Draper and Smith 1998) were used to initially select variables for the regression models. Variables were entered into the model if their p -values were less than 0.05 and removed if their p -value increased above 0.10. In addition, the signs of the regression coefficients were viewed to determine whether they were counterintuitive; then removed accordingly. Furthermore, the catchment and broad scale climatic variables were found to lack data independence. Therefore, excessive numbers of these types of variables were prevented from entering the model.

A number of urban land-use categories were then defined, as shown in Table 8. Geometric mean estimates of EMCs were calculated for each of these land-use categories. In addition, geometric mean estimates of EMCs were also derived for the individual sites, metropolitan areas, and the entire nation.

Following model construction, models were compared with one another to determine the optimum way of predicting nutrient concentrations in urban storm-water runoff. This was primarily achieved by using a series of leave one out analyses. Disjoint subsets of data were separated, containing data from an individual site or metropolitan area. In this manner, all EMCs were at some stage included in a disjoint subset. Each disjoint set was then

Table 8. Land-Use Categories

Land use	Domain
Commercial and industrial	LUIC > 66%
Residential	LUR > 66%
Nonurban	LUN > 50%
Mixed	LUM

sequentially used as a validation set with the remainder of the available data used to recalibrate the model. This process was repeated until each unique disjoint set had been used as a validation set. EMC predictions were thereby generated for each disjoint set. Average validation errors were then generated using these EMC predictions.

Mean metropolitan area concentration (MMC) models were validated using a series of leave one site out analyses. However, not all metropolitan areas contained sufficient numbers of catchments to do this. In situations where the total number of catchments in a given metropolitan area was less than two, a geometric mean estimate of the entire data set was used as an approximation of the MMC. Land-use models, on the other hand, were validated using leave one metropolitan area out analyses. This was to determine how well the models predicted EMCs at geographical areas outside the modeling domain. Regression models were validated using both leave one site out analyses and leave one metropolitan area out analyses. This was to enable direct comparison with both the MMC models and land-use models. Finally, calibration errors associated with site mean concentration (SMC) models and nationwide geometric means were calculated. These errors were assumed to provide a basis for comparison to the other models.

The accuracy of each of the constructed models was determined using a combination of error measures. The ability of models to estimate individual EMCs was gauged using two error measures; standard error of estimate (SEE) and average absolute percentage error (AAPE). The SEE was calculated using the following equation:

$$\text{SEE} = 100[e^{(\sigma^2 \times 5.302)} - 1]^{0.5} \quad (7)$$

where σ^2 =the mean square error in logarithm (base 10) units (Driver and Tasker 1990)

$$\sigma^2 = \frac{\sum_{i=1}^N [\log(y) - \log(\hat{y})]^2}{N} \quad (8)$$

where y =observed value; $\hat{y}$ =predicted value; and N =the number of data points. The functional form of the AAPE is presented in the following equation:

$$\text{AAPE} = 100 \frac{\sum_{i=1}^N \left(\frac{|Y_i - \hat{y}_i|}{Y_i} \right)}{N} \quad (9)$$

The AAPE was also used to gauge the ability of the models to estimate long term loads as well as EMCs. Observed and predicted event loads were first generated by multiplying the observed and predicted EMCs by the event runoff volumes. The observed long term load at a catchment was then calculated by summing all observed event loads at a catchment. Similarly, the predicted long term load at a catchment was calculated by summing all the predicted event loads at a catchment. These values

Table 9. Regression Coefficients for Regression Models Predicting Nutrient EMCs

Variable	Regression coefficients					
	NH ₃	DP	NO _x	TKN	TN	TP
β ₀	3.64	−3.07	−0.72	0.23	−0.03	1.28
AMRN	−0.54	—	—	—	—	—
AMT	—	1.13	—	—	—	—
DRN	—	—	—	—	—	−0.17
PIRN	−0.30	—	—	—	—	—
P3RN	—	−0.29	—	—	—	−0.19
P7RN	—	—	—	−0.18	−0.21	—
QMAX	—	—	—	0.20	0.35	—
ROI	—	—	—	−0.43	−0.66	—
TRND	−0.44	—	−0.21	—	—	—
VS	—	—	0.39	—	—	—
ABS	—	—	−0.14	—	—	—
DA	−0.35	—	—	—	—	—
EFFIA	—	—	—	0.14	—	0.09
IA	0.58	—	—	—	—	—
LUR	—	—	—	—	—	0.14
PD	—	0.22	0.19	—	0.14	—
SCGD	—	—	—	—	—	−0.17
SD	—	—	4.79	—	3.44	—
KAVE	—	—	—	—	—	0.48
MAP	—	—	—	—	—	−0.57
MARN	−1.16	—	—	—	—	—
NH4CR	—	—	—	0.29	—	—
NO3CR	—	—	0.82	—	0.54	—

where then entered into Eq. (9) to determine the AAPE associated with the prediction of long term load at a catchment.

Average long term load errors and average EMC errors were first calculated for each of the six constituents. These errors were then averaged to provide overall measures of accuracy for each model.

Results and Discussion

Various regression models were constructed to predict nutrient concentrations in urban storm water. The explanatory variables and their associated regression coefficients are presented in Table 9. In general, each of the regression models used a different set of explanatory variables. However, some general trends were observed.

The results indicated that rainfall depth variables were the most commonly used type of variable in the regression models. Rain falling during and prior to a storm event influenced nutrient concentrations, as did the average monthly and annual rainfall. The negative regression coefficients associated with all rainfall depth variables implied that nutrients were supply limited on the catchment surface and/or in the atmosphere. This observation was further supported by the fact that the DRN variable used in the TP model had a negative regression coefficient. It was assumed that long duration storms tended to produce more rainfall, which removed additional supply limited pollutants from the catchment surface. In addition, the longer duration storms also tended to have lower rainfall and runoff intensities. The decreased erosive power of such events was assumed to lead to decreased quantities of particulate phosphorus removed from the catchment.

Positive regression coefficients were observed for peak flow rate (QMAX), used in regression models predicting both total TKN and TN. Large peak flow rates may cause sewerage overflows and/or flush contaminants from the bed of the channel, thereby increasing TKN and TN concentrations in the runoff. However, both these models also used a variable defining the average runoff rate (ROI). The negative regression coefficient associated with this variable may be deemed counterintuitive and result from a correlation with peak flow rate. Alternatively, it may result from the fact that large portions of TKN and TN are present in the dissolved state. Storms with high values of average runoff intensity potentially reduce the contact time between the runoff and ground surface. This may decrease the dissolution of TKN and TN into the runoff, thereby reducing pollutant concentrations.

The importance of contact time with respect to dissolved contaminant concentrations was further supported by the inclusion of average basin slope (ABS) in the model predicting nitrogen oxide concentration. The negative regression coefficient suggested that nitrogen oxide concentrations were lower in steeply sloping catchments. This was assumed to be due to the faster runoff flowing from steep catchments, which decreased the contact time between runoff and pollutant on the catchment surface. This ultimately decreased the quantity of nitrogen oxides, which dissolved into the runoff.

The PD was used in three regression models. It was used in the prediction of TN, nitrogen oxides (NO_x), and DP. The positive regression coefficients suggest that additional sources such as sewerage and fertilizer cause increased nutrient levels exported from high density residential areas. Furthermore, catchments with increased PDs tended to have large portions of impervious surfaces, particularly roads. Such surfaces were more likely to contain traffic related pollutants, particularly nitrogen oxides from exhaust emissions. This was further supported by the positive regression coefficient associated with street density (SD) used in the models predicting TN and nitrogen oxide concentrations.

The average concentrations of nitrogen compounds in rainwater were used in the three models. The average nitrogen oxide concentration in rainwater (NO3CR) was used in the models predicting both TN and nitrogen oxide concentrations, whereas the average ammonia concentration in rainfall (NH4CR) was used in the regression model predicting TKN concentration though surprisingly not in the regression model predicting ammonia concentration. This may have been due to the strong correlation between mean annual rainfall and ammonium concentration in the rainfall.

Drainage area (DA) and IA were both used in the regression model predicting ammonia concentration. The negative regression coefficient associated with drainage area suggested that large catchments tended to produce lower ammonia concentrations. This was due to the fact that time dependent oxidation of ammonia was more likely to occur in large catchments. In contrast, the shorter travel time associated with small, highly impervious catchments essentially limits the conversion of ammonia to nitrogen oxides. This concept was further supported by the positive regression coefficient sign associated with EFFIA used in the model predicting TKN.

The EFFIA was also used in the model predicting TP concentration. The positive regression coefficient suggested the presence of additional phosphorus sources from catchments with large portions of EFFIA such as sewerage. In addition, larger portions of EFFIA may also cause additional erosion of particulate phosphorus through increases in the velocity of overland flow. The percentage of residential land use (LUR) was also used in the model predicting TP concentration. The positive regression coef-

ficient indicates that additional TP sources are present in the residential areas. These include sewerage, fertilizer, animal waste, and vegetation matter. The percentage of sewer drains, which are curbed and guttered (SCGD) was also used in the model predicting TP concentration. The negative regression coefficient suggested that there were higher TP concentrations within the swale and ditch drainage systems (SDSD), potentially due to the increased decaying vegetation matter in these systems. A factor representing the erodibility of soils (KAVE) was also used in the model predicting TP. The positive regression coefficient inferred that soils with higher erodibility led to increased concentrations of adsorbed TP in storm-water runoff.

Average monthly temperature (AMT) was used in the model predicting DP concentration. The positive regression coefficient suggested that the application of fertilizers during the warmer seasons could lead to increased DP concentrations. Another seasonal variable was used in the model predicting nitrogen oxide concentration. The negative sign of the regression coefficient associated with the seasonal variable termed VS suggested that high nitrogen oxide concentrations were observed in the spring. This may have resulted from the leaching of nitrogen oxides from the snow pack during the snowmelt phenomenon. Alternatively, the seasonal variable may represent the amount of accumulated pollutant on the catchment surface. For example, the low intensity drizzles occurring in the winter months are less likely to deplete the accumulated pollutants than the higher intensity summer storms. This essentially leads to high concentrations in the spring and low concentrations in the autumn.

An example of how to apply the regression models is presented next. A city engineer from Salt Lake City, Utah needs an estimate of ammonia EMC for a storm with a rainfall depth of 6.4 mm, preceded by two storms precipitating a total of 8 mm of rainfall on the previous day, in a month with an average rainfall totaling 34 mm. The urban catchment under analysis has a drainage area of 26 ha, an IA of 52% and a mean annual rainfall of 432 mm. Using the appropriate equation from Table 9, the ammonia EMC is calculated as follows:

$$\text{NH}_3 = (10)^{(3.64)} \times (34)^{(-0.54)} \times (8)^{(-0.30)} \times (6.4)^{(-0.44)} \times (26)^{(-0.35)} \\ \times (52)^{(0.58)} \times (432)^{(-1.16)}$$

$$\text{NH}_3 = 0.43 \text{ mg/L}$$

The regression models constructed in the current study were subject to a number of perceived limitations. In general, the data infilling process was assumed to reduce the confidence associated with the regression models. As a result, the application of these models on catchments outside the modeling domain may result in larger prediction errors. Despite this fact, the models were assumed to be significantly better than the models constructed using only variables with no missing values infilled. This is because the models constructed in the current study were assumed to better define the most important processes influencing nutrient concentrations. In addition, they identified a selection of important explanatory variables to be monitored in future studies.

The accuracy of the regression models was also assumed to be affected by the removal of atypical catchments during data preprocessing. If they were not removed, the calibration of the regression models would have been potentially biased by the predominantly larger EMCs associated with the atypical catchments. However, the use of logarithmically transformed data would have limited the influence of these values.

Table 10. Standard Errors of Estimate Associated with the Regression Models Developed by Driver and Tasker (1990) and Those Developed in the Current Study

Water quality constituent	SEE (%)		
	Driver and Tasker (1990)		Current study
	Event load	EMC	
DP	129	99	114
TKN	123	83	70
TN	124	74	64
TP	141	108	81

The use of simple stepwise regression procedures to construct regression models was perceived to be subject to a number of limitations. Foremost, problems associated with multicollinearity and a lack of data independence associated with many of the variables could result in the selection of spurious variables into the regression model. This problem was primarily minimized by viewing the signs of the regression coefficients and excluding potentially erroneous variables from the models. Furthermore, excessive numbers of catchment and broad scale climatic variables lacking data independence were prevented from entering the model. However, despite the precautions, it was possible that the "wrong" variable was entered into the model. This was due to the fact that many of the variables analyzed were surrogates for more important fundamental variables. This gave rise to a situation whereby a number of equally valid regression models may be constructed on the same data set.

The regression models developed in the current study were then compared to the regression models developed in a seminal study by Driver and Tasker (1990). The SEE associated with event load and EMC regression models were directly comparable, hence, this error measure was used for comparative purposes. However, the Driver and Tasker (1990) regression models were calibrated and verified on different domains of data than the regression models constructed in the current study. This meant that the errors were not directly comparable. Despite this fact, the various models are compared in Table 10. Overall, all regression models developed in the current study were significantly more accurate than the associated event load models developed by Driver and Tasker (1990). They were also more accurate than most of the EMC models constructed by Driver and Tasker (1990). The one exception was associated with the regression models predicting DP. It was assumed that the lack of explanatory variables used in the regression model predicting DP in the current study reduced the accuracy of this model. A major advantage of the regression models constructed in the current study was their ability to identify key processes influencing storm-water quality. Unlike the Driver and Tasker (1990) study, explanatory variables were entered into the regression models according to the strength of their correlation with EMC rather than the load. Furthermore, additional explanatory variables not used in the Driver and Tasker (1990) study were available for analysis. In particular, the use of additional storm variables allowed more efficient modeling of storm to storm variability at single catchments, previously unaccounted for by total event rainfall depth.

The land use based geometric means were then calculated and presented in Table 11 along with the nationwide geometric means. Furthermore, graphs were also generated to show the variation of EMCs within each land-use category. This was achieved by logarithmically transforming the data, then adding and subtracting the

Table 11. Land-Use-Based Geometric Means and Nationwide Geometric Means

Land-use category	Geometric mean concentration (mg/L)					
	DP	NH ₃	NO _x	TKN	TN	TP
LUR > 66%	0.10	0.26	0.64	1.93	2.99	0.31
LUIC > 66%	0.07	0.62	0.32	1.68	1.58	0.22
LUN > 50%	0.04	0.11	0.15	0.59	0.66	0.10
LUM	0.18	0.48	0.69	2.08	3.53	0.37
LUAGR > 50%	0.36	0.12	0.58	3.11	6.15	1.09
LUI > 50%	4.47	4.82	1.01	27.10	29.96	6.01
All	0.09	0.30	0.43	1.65	2.17	0.27

standard deviation from the mean. Figs. 1–6 present these ranges after the logarithmic values were raised to the power of ten. In general, catchments comprised of more than 50% industrial land use or more than 50% agricultural land use produced the largest geometric means. As mentioned previously, these catchments were assumed to contain additional sources of nutrients and therefore removed during data preprocessing. One notable exception to the general rule was the relatively low ammonium concentration associated with highly agricultural catchments. However, it was believed that the increased size of these catchments may have increased the portion of ammonium oxidized into other forms of nitrogen.

Catchments containing more than 50% nonurban land use typically had the lowest nutrient concentrations. However, these catchments were not removed from the data set during prepro-

Fig. 3. Nitrogen oxide EMC versus land use

cessing since it was deemed that there was sufficient data associated with this type of land use to analyze it further. The low concentrations in these catchments were assumed to arise from the decreased number of sources and increased portion of vegetation capable of uptaking nutrients. The overlap between the remainder of land-use categories was assumed to decrease the validity of using such segregations of data to define storm-water concentrations at unmonitored catchments. However, further comparative analyses were used to supplement this initial observation.

The accuracy of each of the constructed models was compared using a number of error measures. These values are presented in Table 12. The most accurate models for predicting nutrient con-

Fig. 1. DP EMC versus land use **Fig. 4.** TKN EMC versus land use **Fig. 2.** Ammonium EMC versus land use **Fig. 5.** TN EMC versus land use

Fig. 6. TP EMC versus land use

concentrations in urban storm-water runoff were the SMC models. In particular, these models were considerably more accurate than the remainder of the models at predicting long term loads. However, the main limitation of the SMC models was that they could not be used to predict urban storm-water quality at unmonitored catchments. Furthermore, the results were potentially biased since the models were not validated on independent data. This was to ensure that catchments with very few sampled storms did not produce non representative errors, which dominated the calculation of average errors associated with these models. As a result, the average errors associated with the SMC models were deemed to be a “lower limit” on which to compare the remainder of the models.

The second most accurate models were the multiple linear regression models. The main advantage of the regression models over the constant concentration models was their ability to model EMC variability at single catchments as well as between catchments. Furthermore, the regression models were able to identify the most significant processes governing nutrient generation and transport in urban areas. The models were also constructed using large domains of data, thereby increasing their statistical significance and ability to be applied at unmonitored catchments throughout the United States.

The MMC models were only slightly less accurate than the regression models at predicting long term loads. The accuracy of these estimates may have been greater if only metropolitan areas

with large numbers of sampled catchments were analyzed. It was assumed that the use of a geometric mean of the entire data set at metropolitan areas with less than two sampled catchments may have significantly biased the final accuracy of the models. However, the MMC models were subject to a number of limitations. Foremost, the significance of a number of catchment variables used in the regression models implied that the use of a single mean value is not going to adequately define all water quality variability at catchments in a given metropolitan area. Furthermore, the significance of a number of storm variables infers that poor estimates of MMC may arise in situations when very few storms are sampled at a metropolitan area. In general, the successful application of MMC models is perceived to be restricted by the lack of sampling at most metropolitan areas throughout the United States.

The land use based geometric means produced less accurate estimates of EMCs and long term loads than the nationwide geometric means. However, the nationwide geometric means were not validated using a leave one out analysis. Despite this fact, it was assumed that these models were not overfitted as a result of the large data sets used for model calibration. The results imply that common urban land-use categories should not be used to predict urban storm-water quality at unmonitored catchments or metropolitan areas. However, two important land-use categories (agricultural and industrial) were removed during the preprocessing of data. In addition, observation of Figs. 1–6 also infers that nutrient concentrations at nonurban catchments may be less than at typical urban catchments.

Conclusion

Various models were constructed to predict nutrient concentrations in urban storm-water runoff. The most accurate models were the SMC models. However, these models may not be used to predict nutrient concentrations at unmonitored catchments. The most accurate models for predicting nutrient concentrations at unmonitored catchments were the regression models. Regression models were also useful in identifying significant processes influencing nutrient concentrations in urban storm water. For example, the negative regression coefficients associated with all the rainfall depth variables inferred that nutrient loads on the catchment surface and/or in the atmosphere were supply limited. The second most accurate models predicting nutrient concentrations at unmonitored catchments were the MMC models. However, these models would have been more accurate if only well sampled metropolitan areas were analyzed. Coincidentally, the main limitation with these models was that they could not be successfully applied at metropolitan areas with little or no prior sampling. Land use based geometric means produced the least accurate predictions of water quality at unmonitored metropolitan areas. Surprisingly, nationwide geometric means were more accurate than the land use based geometric means.

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Table 12. Comparison between Models Predicting Nutrient EMCs

Model	SEE ^c (%) EMC	AAPE ^d (%) EMC	AAPE ^d (%) Long term load	Validation procedure
SMC ^a	80	80	14	Calibration set
Regression	94	94	47	Site leave one out Metropolitan area
Regression	99	108	50	Leave one out
MMC ^b	115	112	53	Site leave one out Metropolitan area
Land-use mean	157	192	83	Leave one out
Nationwide mean	140	156	71	Calibration set

^aSite mean concentration.

^bMean metropolitan area concentration.

^cStandard error of estimate.

^dAverage absolute percentage error.

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