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Abstract

The composition of main constituents in the natural
waters of remote catchments is usually difficult to determine.
A data base, however, is required to assess impact of intended
land use practices on upland areas which are the main source
of prime quality water. Relationships between water quality
and the readily available data on streamflow can provide the
required baselines for comparative purposes.

Dilution effects in the stream waters of Marmot Experimen-
tal Watershed were examined to investigate water quality and
quantity relationships. A number of mathematical models incor-
porating linear and nonlinear functional forms were hypothe-
sized. The model parameters were determined from 31 samples
collected and analyzed during 1971 and 1972. Calcium, Mg, Na,
K, HCO_3, SO_4, Cl, and SiO_2 were the main constituents of these
waters. Of the 28 postulated models, the regression models
incorporating current flow, specific conductance, and a lagged
variable of streamflow gave the best fit for most of the ana-
lyzed constituents. Other models based on the relationships
of the above mentioned constituents to the components of
streamflow (base flow and storm flow) are presently being
developed and tested.

The coefficients for all models were derived from the
collected data by the method of least squares. The models'
prediction capabilities were tested by comparison with actual
quality data acquired subsequently. The models are reassessed
on this basis and ranked according to the magnitude of the sum
of the squared deviations of observed values from those pre-
dicted by each model.

Introduction

The study of the composition and concentration of dis-
solved chemical constituents in natural waters is important in
assessing the environmental impacts of land use practices. The
laboratory analyses required for such determinations are costly

nd time-consuming. A simple scheme is needed for remote
atchments, where feasible, to predict the concentration of
ommonly occurring constituents from easily determined hydro-
ogic variables.

An obvious variable is streamflow. Johnson et al. (1969),
'inder and Jones (1969), Hall (1970, 1971), Pionke, Nicks
nd Schoof (1972), and Steele (1973, 1976) have shown how the
elationship between stream discharge and water chemistry can
e used as a predictive tool. The present study explores the
redictive feasibility of using the relationships of stream-
low and its components with the inorganic constituents in
he streams originating from upland mountain forest watersheds.

Water is the chief agent releasing and transporting
utrients in an ecosystem (Hewlett and Nutter, 1969). Rela-
ionships of chemical constituents with streamflow are thus
mportant for an understanding of the ecosystems in relation
o forestry practices causing changes in nutrient exports.

As Hem (1970) states, the streams having the most con-
istent relationship between water discharge and dissolved-
olids concentrations ought to be the streams that receive a
arge part of their mineral load from a relatively constant
ource upstream. The stream used in this study fulfills this
riterion, and thus further provides a basis for testing this
ypothesis.

Study area. The study was conducted in Marmot Creek
xperimental watershed, situated on the eastern slopes of the
ocky Mountains, about 80 km west of Calgary. It ranges in
levation from about 1500 m to 2750 m (mean elevation 2113 m)
nd represents spruce-fir [*Picea engelmanni* Parry, *P. glauca*
Moench) Voss, and *Abies lasiocarpa* (Hook.) Nutt.] vegetation
ypical of the Saskatchewan River headwaters. The watershed
as selected in 1962 as the first major research effort under
he Alberta Watershed Research Program. In 1974 a treatment
as applied on the Cabin subbasin to determine the effects of
ommercial logging on water yield, quality, and regime. The
reatment consisted of clear-cutting six blocks totalling
10 ha.

The geology, soils, and vegetation of the area are de-
cribed by Stevensen (1967), Beke (1969), and Kirby and
gilvie (1969), respectively. Jeffrey (1965), Golding (1970),
ingh and Kalra (1972), Singh (1976), and Telang et al. (1976)
ave described the hydrological and water quality aspects of
he research program in the watershed.

Methods

Collection of data. The water quality samples collected
from the permanent gaging site were analyzed at the Water
Quality Laboratory of Environment Canada, Calgary. Stream
discharge at the time of sampling was also determined from
the hydrograph. Samples were collected at least monthly when
the streamflow was nearly constant, as in the winter months,
and more frequently in other months when it showed greater
variation. Only samples collected from the Main Marmot Creek
prior to commercial logging were used in this study.

Modelling data. The 31 samples collected during the
2-year period (1971-1972) were used for model building. These
samples provided concentration data (mg/ℓ) for Ca, Mg, Na, K,
HCO_3, SO_4, SiO_2, Cl and total dissolved solids which were
treated as the variables to be predicted. The streamflow
data (ℓ/sec) and specific conductance (μS/cm) were the pre-
dictor variables.

Test data. The data collected during 1973 were used for
testing or validating the models. The same input data were
used for all models. As no data were available for SO_4, the
models for this constituent could not be tested for the pres-
ent. Further tests and updating of the models are planned for
future years when more data become available.

Modelling procedures. Stream discharge at the time of
sampling (X_1) was used to find linear and nonlinear relation-
ships with the concentration of each constituent. Another
variable, specific conductance (X_2), was included later to
improve the goodness of fit. In order to incorporate the
lagged effect, one more variable for the mean daily streamflow
on the previous day (X_3) was also included as a predictor
variable to further improve the fit.

All models were fitted to the data by the method of
least squares. In addition to the estimation of model parame-
ters, the correlation coefficient and the standard error of
estimate were also computed.

For validation, the estimated values from each model
were compared with the actual data. Each residual was listed
and used for determining sum of residuals, sum of the squared
deviations, mean square error, and standard error of estimate.

A computer program (Bathlahmy, 1972) was used on the
1973 data for determining the groundwater, interflow, and
rapid flow components of stream discharge. A model based on
three predictor variables (base flow, storm flow, and specific
conductance) was derived for each modelled constituent. The

model parameters, the correlation coefficient, and the standard error of estimate were also computed for this model by the method of least squares.

Results

The summary of modelling data is provided in Table 1. Table 2 gives a summary of the test data for comparative purposes.

Twenty-eight models were tried in all (Table 3). Of these, 12 had only one predictor variable, 12 had two predictor variables, and 4 had three predictor variables included.

Although outputs of model parameters and related statistics were obtained for all models, only results from I, XIII and XXV are listed in Tables 4, 5, and 6 and presented here. These tables summarize comparative statistics for the individual constituents Ca, Mg, Na, K, HCO_3, Cl, and SiO_2 and also for the total dissolved solids.

Table 7 gives the related information on model parameters and other statistics when two of the three predictor variables of model XXV are replaced by the variables containing information on current base flow (or groundwater flow) and storm flow.

Discussion

The dependence of the concentration of chemical constituents of stream waters on discharge is evident from the generally highly significant relationships listed in Table 4. Total dissolved solids and Ca^{2+} show the most significant relationship, whereas Cl^- relationship is the least, and statistically nonsignificant. The negative sign of the correlation coefficient shows dilution effects, i.e., the concentration of constituents become lower if streamflow increases.

The slope (b) representing change in concentration with unit change in streamflow is the highest for total dissolved solids and the lowest for K. From Table 4, the individual constituents can be ranked in order of the absolute value of b as $HCO_3^- > Ca^{2+} > Mg^{2+} > SiO_2 > Na^+ > K^+ > Cl^-$.

The relationships improve considerably when specific conductance is included as an additional variable in the prediction model. The use of specific conductance for estimating the concentration of total dissolved solutes has been tested earlier (Singh and Kalra, 1975). In this paper its use has been extended to other dissolved constituents. The results (Table 5) show improvements in all the tested constituents.

Table 1. Summary of Modelling Data, Marmot Creek

Variable	Mean	Standard Deviation	Minimum	Maximum	Coefficient of Variation
Ca^{2+} (mg/ℓ)	44.2	10.4	25.2	56.6	23.61
Mg^{2+} "	11.9	3.1	6.8	17.2	25.87
Na^+ "	1.1	0.6	0.4	2.5	51.90
K^+ "	0.5	0.1	0.3	0.7	21.09
HCO_3^- "	173.6	40.7	101.7	232.8	23.44
Cl^- "	0.2	0.1	0.1	0.3	41.45
SiO_2 "	4.5	0.8	2.9	5.5	18.48
Total dissolved solids "	164.4	42.1	83.0	226.5	25.58
Current streamflow (ℓ/sec)	279.7	388.2	11.6	1441.3	138.79
Specific conductance (μS/cm)	302.9	66.8	182.0	406.0	22.06
Streamflow previous day (ℓ/sec)	284.0	390.7	11.6	1452.6	137.54

Table 2. Summary of Test Data, Marmot Creek

Variable	Mean	Standard Deviation	Minimum	Maximum	Coefficient of Variation
Ca^{2+} (mg/ℓ)	41.8	10.1	28.2	62.6	24.09
Mg^{2+} "	10.5	2.6	3.4	16.7	24.72
Na^+ "	1.1	0.4	0.6	2.0	38.01
K^+ "	0.5	0.1	0.3	0.8	19.25
HCO_3^- "	161.9	34.0	115.0	230.0	21.01
Cl^- "	0.4	0.2	0.1	1.0	58.01
SiO_2 "	4.7	0.6	3.6	6.0	12.18
Total dissolved solids "	152.1	33.9	107.0	218.0	22.29
Current streamflow (ℓ/sec)	369.9	289.3	15.3	996.7	78.20
Specific conductance (μS/cm)	282.6	62.6	204.0	452.0	22.15
Streamflow previous day (ℓ/sec)	354.4	261.6	15.6	985.4	73.82

Table 3. Mathematical Models for Estimating Concentration (mg/ℓ) of Dissolved Constituents (Y); X_1 is Current Streamflow (ℓ/sec), X_2 is Specific Conductance (μS/cm), and X_3 is Mean Streamflow (ℓ/sec) on Previous Day

Code	Model
One predictor variable:	
I	$Y = a + bX_1$
II	$Y = a + bX_2$
III	$Y = a + bX_3$
IV	$Y = a + b (\ln X_1)$
V	$Y = a + b (\ln X_2)$
VI	$Y = a + b (\ln X_3)$
VII	$\ln Y = a + bX_1$
VIII	$\ln Y = a + bX_2$
IX	$\ln Y = a + bX_3$
X	$\ln Y = a + b (\ln X_1)$
XI	$\ln Y = a + b (\ln X_2)$
XII	$\ln Y = a + b (\ln X_3)$
Two predictor variables:	
XIII	$Y = a + bX_1 + cX_2$
XIV	$Y = a + bX_1 + cX_3$
XV	$Y = a + bX_2 + cX_3$
XVI	$Y = a + b (\ln X_1) + c (\ln X_2)$
XVII	$Y = a + b (\ln X_1) + c (\ln X_3)$
XVIII	$Y = a + b (\ln X_2) + c (\ln X_3)$
XIX	$\ln Y = a + bX_1 + cX_2$
XX	$\ln Y = a + bX_1 + cX_3$
XXI	$\ln Y = a + bX_2 + cX_3$
XXII	$\ln Y = a + b (\ln X_1) + c (\ln X_2)$
XXIII	$\ln Y = a + b (\ln X_1) + c (\ln X_3)$
XXIV	$\ln Y = a + b (\ln X_2) + c (\ln X_3)$
Three predictor variables:	
XXV	$Y = a + bX_1 + cX_2 + dX_3$
XXVI	$Y = a + b (\ln X_1) + c (\ln X_2) + d (\ln X_3)$
XXVII	$\ln Y = a + bX_1 + cX_2 + dX_3$
XXVIII	$\ln Y = a + b (\ln X_1) + c (\ln X_2) + d (\ln X_3)$

Table 4. Model Parameters and Related Statistics for Estimating Concentration (mg/ℓ) of Dissolved Constituents (Y) Using Current Streamflow (X_1, ℓ/sec) as Predictor Variable (Model: $Y = a + bX_1$)

| Constituent (mg/ℓ) | Model Parameters | | r* | S_E* | | Sum of prediction residuals |
	a	b		Model	Predicted	
Ca^{2+}	50.6317	-0.0229	-0.85	5.56	6.86	-10.23
Mg^{2+}	13.4855	-0.0057	-0.72	2.18	2.01	-27.70
Na^+	1.3937	-0.0016	-0.69	0.42	0.42	8.03
K^+	0.4913	-0.0001	-0.23	0.10	0.13	2.41
HCO_3^-	197.565	-0.0858	-0.82	23.74	22.08	-138.92
Cl^-	0.1864	-0.00003	-0.09	0.08	0.35	7.09
SiO_2	5.0612	-0.0027	-0.77	0.54	0.90	19.77
Total dissolved solids	190.179	-0.0920	-0.85	22.58	20.41	-122.03

* r is correlation coefficient and S_E is standard error of estimate.

Table 5. Model Parameters and Related Statistics for Estimating Concentration (mg/ℓ) of Dissolved Constituents (Y) Using Current Streamflow (X_1, ℓ/sec) and Specific Conductance (X_2, μS/cm) as Predictor Variables (Model: $Y = a + bX_1 + cX_2$)

| Constituent (mg/ℓ) | Model Parameters | | | R* | S_E* | | Sum of prediction residuals |
	a	b	c		Model data	Predicted data	
Ca^{2+}	3.7706	-0.0035	0.1368	0.984	1.94	3.46	20.09
Mg^{2+}	-3.4576	0.0013	0.0494	0.94	1.10	2.20	-15.59
Na^+	-1.5724	0.0002	0.0084	0.85	0.31	0.28	6.20
K^+	0.5393	-0.0001	-0.0001	0.24	0.10	0.13	2.39
HCO_3^-	-5.2898	-0.0016	0.5920	0.985	7.33	8.23	5.72
Cl^-	0.1035	0.00002	0.0002	0.14	0.08	0.37	6.91
SiO_2	1.9047	-0.0008	0.0089	0.85	0.46	0.84	17.26
Total dissolved solids	4.8911	-0.0151	0.5407	0.977	9.27	7.72	2.14

* R is multiple correlation coefficient and S_E is standard error of estimate.

Table 6. Model Parameters and Related Statistics for Estimating Concentration (mg/ℓ) of Dissolved Constituents (Y) Using Current Streamflow (X_1, ℓ/sec), Specific Conductance (X_2, μS/cm), and Mean Streamflow on the Previous Day (X_3, ℓ/sec) as Predictor Variables (Model: $Y = a + bX_1 + cX_2 + dX_3$)

Constituent (mg/ℓ)	Model parameters				R*	S_E*
	a	b	c	d		
Ca^{2+}	-6.0787	-0.00003	0.00014	0.1739	0.95	2.93
Mg^{2+}	3.5253	0.00001	-0.00009	0.0271	0.78	1.54
Na^+	-0.9534	-0.000002	-0.000004	0.0071	0.93	0.13
K^+	0.1487	-0.0000007	-0.000002	0.0014	0.53	0.10
HCO_3^-	4.7719	-0.00007	-0.00002	0.5680	0.986	4.67
Cl^-	0.2865	-0.000006	0.000002	0.0013	0.68	0.19
SiO_2	3.8966	-0.000007	-0.000003	0.0039	0.62	0.46
Total dissolved solids	-0.6559	-0.00015	0.00007	0.5635	0.990	4.19

* R is multiple correlation coefficient and S_E is standard error of estimate.

Table 7. Model Parameters and Related Statistics for Estimating Dissolved Constituents Using Components of Hydrograph. X_1 is Base Flow (ℓ/sec), X_2 is Storm Flow (ℓ/sec), and X_3 is Specific Conductance (μS/cm) (Model: $Y = a + bX_1 + cX_2 + dX_3$)

Constituent (mg/ℓ)	Model parameters				R*	S_E*		Sum of prediction residuals
	a	b	c	d		Model data	Predicted data	
Ca^{2+}	3.4044	-0.0090	0.1378	0.0056	0.984	1.97	3.71	23.62
Mg^{2+}	-3.3459	0.0030	0.0491	-0.0017	0.94	1.12	2.29	-16.67
Na^+	-1.7233	-0.0009	0.0088	0.0012	0.85	0.31	0.32	6.68
K^+	0.5626	0.00004	-0.0002	-0.0002	0.25	0.10	0.14	2.31
HCO_3^-	-5.0626	0.0018	0.5914	-0.0035	0.985	7.46	8.41	4.56
Cl^-	0.1904	0.0005	0.000004	-0.0005	0.26	0.08	0.37	6.77
SiO_2	1.9188	-0.0007	0.0089	-0.0001	0.85	0.47	0.85	17.22
Total dissolved solids	4.5247	-0.0206	0.5417	0.0056	0.977	9.44	8.01	5.67

* R is multiple correlation coefficient and S_E is standard error of estimate.

The inclusion of mean streamflow on the previous day as yet another variable produced a slight improvement in the fit, as indicated by the R and S_E values in Table 6. These improvements occurred primarily in K^+ and Cl^-, as shown by the R values and the sum of prediction residuals for these constituents.

The models incorporating logarithmic transformation showed slightly higher R values in some cases, but were not preferred over those presented here. The slightly higher R values may be due to the slightly lesser deviations in the transformed data, rather than actual data (Brownlee, 1953). It was therefore decided to use models incorporating untransformed data only.

The use of the components of streamflow in deriving model equations for the 1973 data shows the best overall fit for all constituents. The R values for the modelled constituents range from 0.53 to 0.990 (Table 7). The R values for the model XXV in Table 6 had a range of 0.25 to 0.985.

The models based on the components of streamflow and specific conductance can therefore provide the most accurate estimates. Further work along these lines is in progress and consists of testing nonlinear predictive models for constituents which have multiple correlation coefficients lower than 0.90.

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