6. RESULTS

According to the methodology described in Section 4 and the procedures discussed in Section 5, the models of the agrichemical concentrations in the Midwest rivers are developed in two steps. First, the seasonal components are estimated, one for the nitrate plus nitrite as nitrogen concentration and the other for the atrazine concentration. The seasonal changes of the concentrations are discussed in Section 6.1. The second step of the model development estimates a regression equation that explains the average annual concentration in the sampled rivers. The process of representing the deseasonalized agrichemical concentration by such explanatory variables as chemical application, watershed morphometry, and climatologic parameters is presented in Section 6.2. Section 6.3 discusses the differences between the modeled concentrations and the measured ones. The statistical models of agrichemical concentrations have been developed utilizing data that characterize the Upper Mississippi-Missouri and the Ohio River basins.

The precision of the spatial redistribution of the monthly flow record is tested in Section 6.4. The flow measured in the USGS stations distributed over the Iowa-Cedar River watersheds is utilized in that portion of the study. Section 6.5 describes the application of the statistical models that are incorporated into the GIS - ArcView to predict atrazine and nitrate plus nitrite concentrations as well as the chemical loads in the Iowa River, the Cedar River and in their tributaries.

For the clarity of presentation, some information from Section 4 and Section 5 is repeated here.

6.1 Seasonal variation of agrichemicals in the Midwest streams

All seasonal models assume each station to have an annual average concentration represented by a constant around which the amount of agrichemical oscillates seasonally. By utilizing dummy variables, created by the S-plus function `factor(),` the regression equation describes the mean annual concentration by constants that are different for each site and by a set of sine-cosine functions describing monthly variation that are common for all sampling sites. Equation 6.1 (presented in Section 4.3.6 as Eq. 4.12) represents the regression model utilized to estimate the seasonal variations of the atrazine concentration as well as the nitrate plus nitrite as nitrogen concentration. The model that includes the flow rate as an explanatory variable is described by the Equation 6.2 (Eq. 4.13).

$$\ln\left[c(j,d)\right] = w_j + \sum_{k=1}^{5}\left(a_k \sin(2k\pi m/12) + b_k \sin(2k\pi m/12)\right) \tag{6.1}$$

and

$$\ln\left[c(j,d)\right] = w_j + a_0 \ln\left[Q(j,d)\right] + \sum_{k=1}^{5}\left(a_k \sin(2k\pi m/12) + b_k \sin(2k\pi m/12)\right) \tag{6.2}$$

where:

ln[...] = natural logarithm;

c(j,d) = concentration measured at site *j* on day *d* (μg/l or mg/l);

Q(j,d) = flow rate measured at site *j* on day *d* (m^3/s);

w_j = intersect specific for the *j*-th sampled watershed;

a_0, a_k and b_k = coefficients;

j = index of the sampling site;

d = day of sample collection;

k = harmonics number;

m = month of the year.

6.1.1 Seasonal variation of the atrazine concentration

The following listing shows an example of the S-plus regression model specification for seasonal variation of the atrazine concentrations in surface waters of the Mississippi-Missouri River and the Ohio River basins.

Listing 6.1 The S-plus session for estimation of the model of seasonal atrazine variation. Model does not contain the flow rate component.

```
a4si _ lm ( log(Concmgm3) ~ factor(Id)
+   + sin(2*pi*Month/12) + cos(2*pi*Month/12)
+   + sin(4*pi*Month/12) + cos(4*pi*Month/12)
+   + sin(6*pi*Month/12) + cos(6*pi*Month/12)
+   + sin(8*pi*Month/12) + cos(8*pi*Month/12)
+   + sin(10*pi*Month/12) + cos(10*pi*Month/12) , data = atra7)
```

In Listing 6.1 the results of the least square calculations are stored in an S-plus object that is named by the user `a4si`. The natural logarithm of the atrazine concentration `Concmgm3` is the dependent variable. Column `Concmgm3` in the data frame `atra7` contains concentrations in µg/L. The independent variables are trigonometric functions and the factorized variable `Id`. `Id` is the name of a column in the data frame `atra7` that contains sampling site identification numbers. Function `factor` tells the least square procedure `lm` to treat the variable as a factor that has p = 151 levels (the number of distinct `Id` values). The p-1 columns are added to the model matrix, and then the procedure `lm` estimates a value (intercept) for each `Id` category.

Table 6.1 shows selected results of the regression analysis of the atrazine concentration in the Midwest rivers. Since only the seasonal component is important in the analysis, Table 6.1 does not contain the 151 intercept terms.

Table 6.1 Selected coefficients of the regression analysis of the atrazine concentration in the Midwest rivers. Seasonal variation is explained only by the sine-cosine harmonics. Coefficients related to the dummy variables are not shown.

Explanatory variable	Value	Std. Error	t value	Pr(>|t|)
sin((2 * pi * Month)/12)	-0.1174	0.0975	-1.2040	0.2289
cos((2 * pi * Month)/12)	-1.5085	0.1256	-12.0105	0.0000
sin((4 * pi * Month)/12)	-0.1655	0.1085	-1.5261	0.1274
cos((4 * pi * Month)/12)	0.7244	0.1191	6.0829	0.0000
sin((6 * pi * Month)/12)	0.0397	0.1018	0.3903	0.6964
cos((6 * pi * Month)/12)	-0.2813	0.1128	-2.4933	0.0129
sin((8 * pi * Month)/12)	-0.3014	0.0871	-3.4594	0.0006
cos((8 * pi * Month)/12)	-0.0256	0.1153	-0.2218	0.8245
sin((10 * pi * Month)/12)	0.1521	0.1003	1.5167	0.1297
cos((10 * pi * Month)/12)	0.0700	0.0795	0.8809	0.3787
Residual standard error: 1.021 on 772 degrees of freedom				
Multiple R-Squared: 0.7555				
F-statistic: 14.91 on 160 and 772 degrees of freedom				

Table 6.2 presents the regression coefficients of the seasonal model that contains the flow rate. A similar S-plus dialog has been used to the one presented in Listing 6.1, except the independent variable `log(Flowm3s)`-- the natural logarithm of the flow rate in m^3/s -- has been added to the model specification. Listing 6.2 shows this dialog.

Listing 6.2 The S-plus session for estimation of the model of seasonal atrazine variation. Model contains the flow rate component.

```
1: a4siq _ lm ( log(Concmgm3) ~ factor(Id) + log(Flowm3s)
2: +   + sin(2*pi*Month/12) + cos(2*pi*Month/12)
```

```
3: +   + sin(4*pi*Month/12) + cos(4*pi*Month/12)
4: +   + sin(6*pi*Month/12) + cos(6*pi*Month/12)
5: +   + sin(8*pi*Month/12) + cos(8*pi*Month/12)
6: +   + sin(10*pi*Month/12) + cos(10*pi*Month/12) , data = atra7)
```

Table 6.2 Selected coefficients of the regression analysis of the atrazine concentration in the Midwest rivers. Seasonal variation is explained by the sine-cosine harmonics and by the flow rate. Coefficients related to the dummy variables are not shown.

Explanatory variable	Value	Std. Error	t value	Pr(>|t|)
log(Flowm3s)	0.2899	0.0297	9.7696	0.0000
sin((2 * pi * Month)/12)	-0.4237	0.0972	-4.3589	0.0000
cos((2 * pi * Month)/12)	-1.3266	0.1200	-11.0542	0.0000
sin((4 * pi * Month)/12)	-0.1536	0.1024	-1.5002	0.1340
cos((4 * pi * Month)/12)	0.5409	0.1140	4.7457	0.0000
sin((6 * pi * Month)/12)	0.0401	0.0960	0.4174	0.6765
cos((6 * pi * Month)/12)	-0.2170	0.1067	-2.0337	0.0423
sin((8 * pi * Month)/12)	-0.3110	0.0823	-3.7814	0.0002
cos((8 * pi * Month)/12)	0.0200	0.1089	0.1832	0.8547
sin((10 * pi * Month)/12)	0.1359	0.0947	1.4352	0.1516
cos((10 * pi * Month)/12)	0.0970	0.0751	1.2920	0.1967
Residual standard error: 0.9638 on 771 degrees of freedom				
Multiple R-Squared: 0.7825				
F-statistic: 17.23 on 161 and 771 degrees of freedom				

Regardless of the statistical significance, all harmonics have been utilized to determine the monthly seasonal factors of atrazine concentration. The seasonal factors *S(m)* have been calculated by the following formula (Eq. 4.11) that ensures that the average of 12 seasonal factors equals one:

$$S(m) = \frac{\exp(\sum_{k=1}^{5}\left(a_k \sin(2k\pi m/12) + b_k \sin(2k\pi m/12)\right)}{\sum_{i=1}^{12}\exp(\sum_{k=1}^{5}\left(a_k \sin(2k\pi i/12) + b_k \sin(2k\pi i/12)\right)} \qquad (6.3)$$

where:

S(m) = the seasonal factor of month *m*;

i = index of the month (i = 1, 2, ... 12);

k = index of the harmonics;

a_k and b_k = regression coefficients from Table 6.1 or Table 6.2.

Table 6.3 shows non-normalized seasonal factors (described by the numerator of right hand side of Equation 6.3) as well as the normalized seasonal factors *S(m)* in the way that the average value over a year is equal to one (Eq. 6.3).

Table 6.3 Seasonal factors of atrazine concentrations in the Midwest rivers estimated by the regression analysis with and without flow rate record.

Month	Not-normalized		Normalized	
	without flow	with flow	without flow	with flow
1	0.26	0.23	0.11	0.12
2	0.41	0.36	0.17	0.19
3	0.47	0.43	0.19	0.22
4	0.77	0.60	0.32	0.31
5	9.06	6.00	3.72	3.13
6	11.23	7.44	4.61	3.88
7	3.60	3.30	1.48	1.72
8	1.55	2.09	0.64	1.09
9	0.47	0.82	0.20	0.43
10	0.51	0.72	0.21	0.37
11	0.52	0.63	0.22	0.33
12	0.36	0.41	0.15	0.21
Average	2.43	1.92	1.00	1.00

Seasonal factors of the atrazine concentration are also presented in Figure 6.1. Some trace amount of atrazine exists in the rivers throughout the year. The major transport occurs after chemical application on the field, in May and in June. The average monthly concentration in late Spring and early Summer is about 20 times higher then the average concentration in the months from September to April.

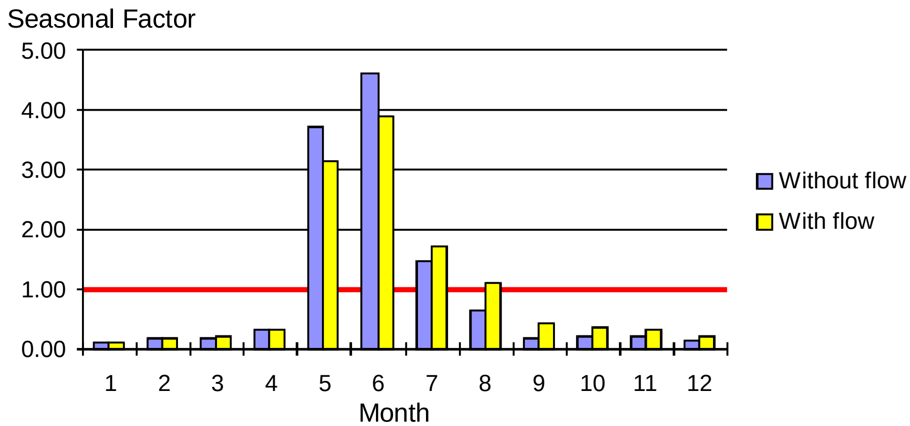


Figure 6.1 Seasonal factors of atrazine concentrations in the Midwest rivers estimated by the regression analysis with and without flow rate record.

The seasonal factors estimated without utilizing the flow rate have slightly higher amplitude than the ones that have been calculated by the regression model with the flow rate. This indicates, that the seasonally varying flow rate is correlated with the atrazine concentration. The flow coefficient listed in Table 6.2 describes a positive relationship between the atrazine concentration and the flow rate: $c = \ \ldots Q^{0.2899}$. It represents not only the relationship between flow and concentration at an individual site, but also reflects the “spatial” relationship of concentrations in rivers of different sizes.

6.1.2 Seasonal variation of the nitrate plus nitrite as nitrogen concentration

Listing 6.3 presents the S-plus dialog which has been applied to estimate the seasonal variations of the nitrate plus nitrite as nitrogen. The nitrate concentrations (mg/L) are stored in the in the column `Concgm3` of the S-plus data frame `nitr7.` The results of the least square procedure `lm` are written to the S-plus object `n4si`.

Listing 6.3 The S-plus session for estimation of the model of seasonal nitrate variation. Model does not contain the flow rate component.

```
n4si _ lm ( log(Concgm3) ~ factor(Id)
+   + sin(2*pi*Month/12) + cos(2*pi*Month/12)
+   + sin(4*pi*Month/12) + cos(4*pi*Month/12)
+   + sin(6*pi*Month/12) + cos(6*pi*Month/12)
+   + sin(8*pi*Month/12) + cos(8*pi*Month/12)
+   + sin(10*pi*Month/12) + cos(10*pi*Month/12) , data = nitr7)
```

Table 6.4 shows selected results of the regression analysis of seasonal nitrate concentration changes in the Midwest rivers. The coefficients related to the `factor(Id)` (150 coefficients plus one intercept) are not shown.

Table 6.4 Selected coefficients of the regression analysis of the nitrate concentration in the Midwest rivers. Seasonal variation is explained only by the sine-cosine harmonics.

Explanatory variable	Value	Std. Error	t value	Pr(>|t|)
sin((2 * pi * Month)/12)	0.8789	0.0871	10.0874	0.0000
cos((2 * pi * Month)/12)	0.0892	0.1095	0.8147	0.4154
sin((4 * pi * Month)/12)	0.1397	0.0964	1.4495	0.1475
cos((4 * pi * Month)/12)	0.6929	0.1040	6.6653	0.0000
sin((6 * pi * Month)/12)	-0.3028	0.0873	-3.4706	0.0005
cos((6 * pi * Month)/12)	-0.0526	0.0974	-0.5407	0.5889
sin((8 * pi * Month)/12)	-0.0318	0.0755	-0.4215	0.6735
cos((8 * pi * Month)/12)	-0.2373	0.1010	-2.3494	0.0190
sin((10* pi * Month)/12)	0.2794	0.0888	3.1445	0.0017
cos((10* pi * Month)/12)	-0.0878	0.0628	-1.3986	0.1622
Residual standard error: 0.948 on 1147 degrees of freedom				
Multiple R-Squared: 0.6803				
F-statistic: 15.26 on 160 and 1147 degrees of freedom				

Nitrate plus nitrite as nitrogen model specification is displayed in Listing 6.4. The natural logarithm of the flow rate `log(Flowm3s)`, has been added to the model determined in Listing 6.3. The results are stored in the object `n4siq`. Estimated model parameters, excluding coefficients related to the `factor(Id),` are displayed in Table 6.5.

Listing 6.4 The S-plus specification of the seasonal nitrate model. The model contains the flow rate component.

```
n4siq _ lm ( log(Concgm3) ~ factor(Id) + log(Flowm3s)
+   + sin(2*pi*Month/12) + cos(2*pi*Month/12)
+   + sin(4*pi*Month/12) + cos(4*pi*Month/12)
+   + sin(6*pi*Month/12) + cos(6*pi*Month/12)
+   + sin(8*pi*Month/12) + cos(8*pi*Month/12)
+   + sin(10*pi*Month/12) + cos(10*pi*Month/12) , data = nitr7)
```

Table 6.5 Selected coefficients of the regression analysis of the nitrate concentration in the Midwest rivers. Seasonal variations are explained by the sine-cosine harmonics as well as the flow record. Coefficients related to the dummy variables are not shown.

Explanatory variable	Value	Std. Error	t value	Pr(>|t|)
log(Flowm3s)	0.3432	0.0213	16.1054	0.0000
sin((2 * pi * Month)/12)	0.5789	0.0809	7.1570	0.0000
cos((2 * pi * Month)/12)	0.3487	0.1003	3.4776	0.0005
sin((4 * pi * Month)/12)	0.1035	0.0871	1.1882	0.2350
cos((4 * pi * Month)/12)	0.5066	0.0946	5.3546	0.0000
sin((6 * pi * Month)/12)	-0.2964	0.0788	-3.7596	0.0002
cos((6 * pi * Month)/12)	-0.0136	0.0880	-0.1550	0.8769
sin((8 * pi * Month)/12)	-0.0290	0.0682	-0.4255	0.6706
cos((8 * pi * Month)/12)	-0.1488	0.0914	-1.6275	0.1039
sin((10* pi * Month)/12)	0.2397	0.0803	2.9851	0.0029
cos((10* pi * Month)/12)	-0.0326	0.0568	-0.5733	0.5666

Residual standard error: 0.8565 on 1146 degrees of freedom
Multiple R-Squared: 0.7393
F-statistic: 20.19 on 161 and 1146 degrees of freedom

All sine-cosine terms have been used to calculate the seasonal factors. Likewise for the atrazine model (Eq. 6.1), the exponent of the sum of harmonics, non-normalized seasonal factors, has been normalized to make the average of the seasonal factors equal one. Table 6.6 compares the seasonal factors for two models, one without flow rate and the other with the flow rate.

Table 6.6 Seasonal factors of the nitrate plus nitrite as nitrogen concentrations in the Midwest rivers estimated by the regression analysis with and without flow rate.

Month	Not-normalized		Normalized	
	without flow	with flow	without flow	with flow
1	2.69	2.31	2.10	1.94
2	1.64	1.49	1.28	1.26
3	1.70	1.58	1.33	1.33
4	1.09	0.84	0.85	0.71
5	1.64	1.05	1.28	0.88
6	1.66	1.06	1.30	0.89
7	1.14	0.95	0.89	0.80
8	0.52	0.59	0.41	0.50
9	0.09	0.17	0.07	0.14
10	0.43	0.66	0.34	0.56
11	1.28	1.62	1.00	1.36
12	1.50	1.94	1.17	1.63
Average	1.28	1.19	1.00	1.00

The seasonal variations of the nitrate plus nitrite as nitrogen in the Midwest rivers are also visualized in Figure 6.2. The variations of nitrate exhibit a different pattern than do the variations of atrazine. The amplitude of nitrate oscillations is much smaller than the one for atrazine. For the nitrate, the range of seasonal factors varies between 0.1 and 2.1, whereas the range of atrazine factors is from 0.1 to 4.6.

For the months from February to June, nitrate concentrations fluctuate very little around the annual average value. From June the concentration level decreases reaching the minimum in September (about 10% of the annual average). Then nitrate concentration increases to a maximum value, 200% of annual average, in January. The variations of the nitrate plus nitrite concentration evaluated from the reduced model generally agree with the published patterns (for example, for Great Britain: Jones and Burt, 1993, for Slovakia: Mendel and Repa, 1994), except for April, when the concentrations are lower then the ones estimated for May, June and July. The high May - July concentrations can be explained by the late Spring (May) application of fertilizers.

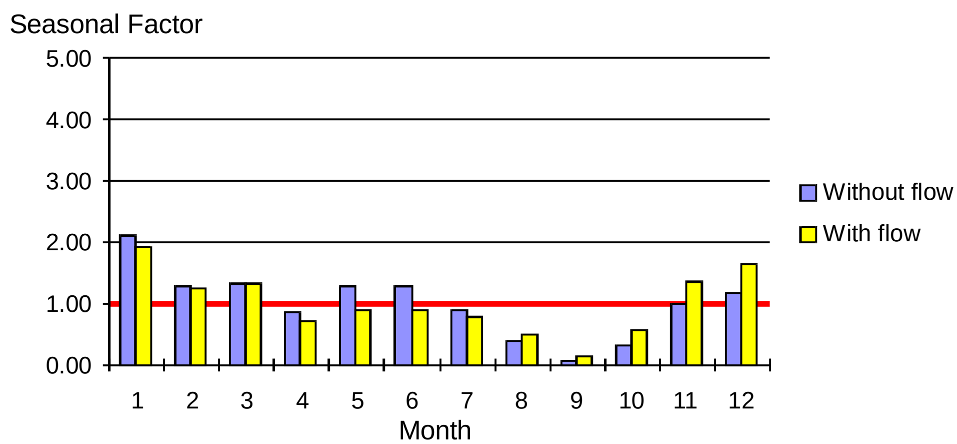


Figure 6.2 Seasonal factors of the nitrate plus nitrite as nitrogen concentrations in the Midwest rivers estimated by the regression analysis with and without flow rate included as an explanatory variable.

6.2 Average annual agrichemical concentration in the Midwest streams

One hundred fifty one average concentration levels, each for one sampling site, have been assumed to calculate seasonal changes of the agrichemicals. This section presents the results of the regression analysis of deseasonalized concentration data. The seasonal component has been removed from the concentration measurements $c(j,d)$ by dividing the concentrations by the respective seasonal factor $S(m)$:

$$c_{ns}(j,d) = \frac{c(j,d)}{S(m)} \tag{6.4}$$

where:

$c_{ns}(j,d)$ = deseasonalized agrichemical concentration;

$c(j,d)$ = observed concentration at site j on day d;

j = sample site indicator;

m = month of the year when the sample was collected;

$S(m)$ = seasonal factor;

A second set of the deseasonalized concentration measurements has been calculated by removing from the data a component that is explained by both the flow rate Q and the seasonal factor $S_q(m)$. The process of preparing agrichemical concentration observations for further analysis is described by the Eq. 6.5.

$$c_{nsq}(j,d) = \frac{c(j,d)}{S_q(m)Q(j,d)^a} \tag{6.5}$$

where:

$c_{nsq}(j,d)$ = concentration with removed seasonal and flow components;

$Q(j,d)$ = observed flow rate at j-th site, on day d;

$S_q(m)$ = seasonal factor estimated from a model that includes flow rate;

a = a coefficient estimated by the regression during seasonal changes of concentration analysis;

$d, m, j, c(j,d)$ = same as in Eq (6.4)

The deseasonalized observations have been utilized to determine the model that relates the average annual concentration level at a given location to the annual agrichemical application rate, parameters that describe the watershed upstream to that location, and to selected climatologic variables. A linear form was assumed to model the average annual atrazine and nitrate concentrations (Eq. 6.6):

$$c_{ns}(j,d) = a + bX(j) \tag{6.6}$$

where:

$c_{ns}(j,d)$ = observed, deseasonalized concentration at site j on day d (for the seasonal model with the flow rate this dependent variable is $c_{nsq}(j,d)$);

a = intercept;

b = vector of regression coefficients;

$X(j)$ = vector of explanatory variables.

Table 6.7 Explanatory variables used to in the analysis of the deseasonalized atrazine and nitrate plus nitrite as nitrogen concentrations in the Midwest rivers.

Variable description	Symbol	S-plus var.	Units
Agrichemical total application	U	`Use`	kg/yr
Agrichemical application rate	A_p	`Appl`	kg/km^2/yr
“Decayed” stream network length	E_S	`Decstr`	$e^{(-100km)}$
Average slope of the streams	S_S	`Slpstr`	-
Average travel distance from the field to the closest stream	L_L	`Alflgkm`	km
Land slope	L_S	`Slplnd`	-
Drainage area	A	`Area`	km^2
Average annual temperature at sampled site	T	`Tc`	°C
Average annual temperature over sampled watershed	T_{avg}	`Tcavg`	°C
Annual precipitation depth at sampled site	P	`Pmm`	mm
Annual precipitation depth over sampled watershed	P_{avg}	`Pmmavg`	mm

Table 6.7 shows the explanatory variables used to develop these models. The notation of the predictor variables shown in column “Symbol” is compatible with the notation that has been introduced in Section 4, whereas the column “S-plus var.” contains names of variables used in S-plus sessions.

The following Section 6.2.1 discusses selected models of the deseasonalized (average annual) atrazine concentrations whereas Section 6.2.2 presents models of the deseasonalized nitrate concentrations.

6.2.1 Average annual atrazine concentration in the Midwest rivers

The following S-plus stepwise variable selection procedure has been used to determine the variables and their coefficients to explain the average annual atrazine concentration in rivers studied:

```
stepcs1 _ step ( csnq.lm, ~ Area + Appl + Flowm3s + Decstr + Slpstr
+               + Slplnd + Alflgkm + Tc + Tcavg + Pmm + Pmmavg )
```

where: `stepcs1` is the object in which the results are stored and `step` is the S-plus stepwise regression procedure. The object `csnq.lm` contains results of the least squares analysis of the simplest model (the simplest model is composed only of an intercept). It is created by the following command:

```
csnq.lm _ lm ( csnq ~ 1, data = atra8)
```

Selected explanatory variables, the regression coefficients as well as their significance are presented in Table 6.8.

Table 6.8 Results of the stepwise regression analysis of average annual atrazine concentration in the Midwest rivers (Data = atrazine concentration with removed seasonal component).

Variable	Value	Std. Error	t value	Pr(>|t|)
(Intercept)	-1.5575	1.2660	-1.2303	0.2189
Appl	0.0260	0.0120	2.1785	0.0296
Alflgkm	0.7998	0.2651	3.0171	0.0026
Tcavg	0.4559	0.1166	3.9093	0.0001
Pmmavg	-0.0048	0.0014	-3.3401	0.0009

Residual standard error: 4.002 on 928 deg. of freedom
Multiple R-Squared: 0.04599
F-statistic: 11.18 on 4 and 928 degrees of freedom

The model has a very low R^2 which raises questions about the application of the regression equation to explain the average concentration. The low R^2 is partially a result of applying daily deseasonalized concentrations to estimate the annual average concentration. Even after the seasonal component was removed, the deseasonalized daily concentration varies significantly, for example, the deseasonalized concentrations in the Sangamon River at Monticello, Illinois, vary from 0.2 μg/L to 19 μg/L (mean =1.8, standard deviation = 2.7), or those in the West Fork Big Blue River near Dorchester, Nebraska, vary from 0.08 μg/L to 8.7 μg/L (mean =3.2 , st. dev. = 2.0),

The other reason for the low variance explained is that only 5 stations have data available for period longer than 3 months. The majority of Midwest rivers (94%) were sampled on average three times per year, a number too small to construct a statistically sound spatial model of the average annual concentration. It must be noted, that although the reconnaissance samples were collected by depth integrating techniques at three to five locations across each stream (Thurman, et al., 1992, work cited by Scribner, et al., 1993) they represent the conditions of the stream only at the time the sample was taken. The herbicide concentration in a river after application during runoff can change significantly in a short period of time. For example, the atrazine concentration in the Old Mans Creek, Iowa, increased during one day 05/16/1996, from 0.57 μg/L (Q = 256 cfs, time = 00:15) to 6.2 μg/L (Q = 307 cfs, time = 6:15), and then to 47 μg/L (Q = 304 cfs, time =22:15) (Scribner, et al., 1993). Thus, characterizing the average annual river conditions by three samples can not be supported by a good summary statistics.

Despite the low R^2 the model is further analyzed. The coefficients have expected signs. Increase in atrazine application causes an increase of the atrazine concentration in rivers. The longer the average distance of the overland flow, the less dense river network is, and the higher are the concentrations in rivers. This is a result of atrazine accumulation when it travels from a field to the surface water.

The positive coefficient for temperature indicates that in "warmer" regions, where more agricultural activity is performed, the rivers are more polluted. Thus, in such regions higher river pollution may be expected than in colder watersheds.

The negative relationship between atrazine concentration and the annual precipitation depth suggests, that considering average annual conditions, the rainfall "dilutes" polluted water. Regions that have smaller annual precipitation tend to have higher atrazine concentrations. On the other hand, if a single event is considered, the rainfalls that occur in a short time after atrazine application cause a positive relationship between the river flow rate and the atrazine concentrations, which is indicated by the regression analysis of seasonal variations discussed in Section 6.1.1.

A similar analysis to the one presented above has been performed for the atrazine concentrations with the seasonal cycle removed as well as the flow related components. The atrazine application rate, despite its statistical insignificance, was forced into the equation selected by the stepwise regression analysis. The coefficients of the final model are listed in Table 6.9.

Table 6.9 Results of the regression analysis of average annual atrazine concentrations in the Midwest rivers (Data = atrazine concentration with removed component explained by the seasonal factor and the flow rate).

Variable	Value	Std. Error	t value	Pr(>|t|)
(Intercept)	-0.8142	0.9148	-0.8901	0.3737
Appl	0.0133	0.0087	1.5353	0.1251
Slplnd	38.8804	16.8116	2.3127	0.0210
Alflgkm	0.3346	0.1751	1.9109	0.0563
Tcavg	0.2732	0.0736	3.7131	0.0002
Pmmavg	-0.0029	0.0009	-3.1999	0.0014

Residual standard error: 2.516 on 927 deg. of freedom
Multiple R-Squared: 0.03118
F-statistic: 5.966 on 5 and 927 degrees of freedom

The regression included the average slope of the watershed into the model. This suggests, that the watershed slope has influence on the concentration. Indeed, it is easier to mobilize and transport agrichemical in steep slope-watersheds than in flat-watersheds.

Table 6.10 Quartiles of the explanatory variables selected by the regression analysis of the deseasonalized agrichemical concentrations.

Statistics Statistics	Area	Appl atrazine	Appl nitrogen	Slplnd	Alflgkm	Tcavg	Pmmavg
	km^2	$kg/km^2/yr$	$kg/km^2/yr$	-	km	°C	mm
Minimum	173	1.00	482	0.001	2.4	5.0	487
First quartile	961	18.08	4544	0.005	3.1	9.4	759
Median	1425	25.32	6034	0.006	3.3	10.4	886
Third quartile	3521	34.18	7372	0.011	3.5	10.7	921
Maximum	2335354	50.55	9481	0.045	5.5	13.5	1148
Average	19109	26.66	5878	0.009	3.4	10.0	848

Figure 6.3 and Figure 6.4 show the influence of the selected explanatory variables on the average concentration represented by the model described in Table 6.7 and Table 6.8, respectively. The change in concentration is related to the change in each variable assuming the minimum, first quartile (25th percentile), median (50th

percentile), third quartile (75th percentile), and maximum value. The values of the quartiles are listed in Table 6.10.

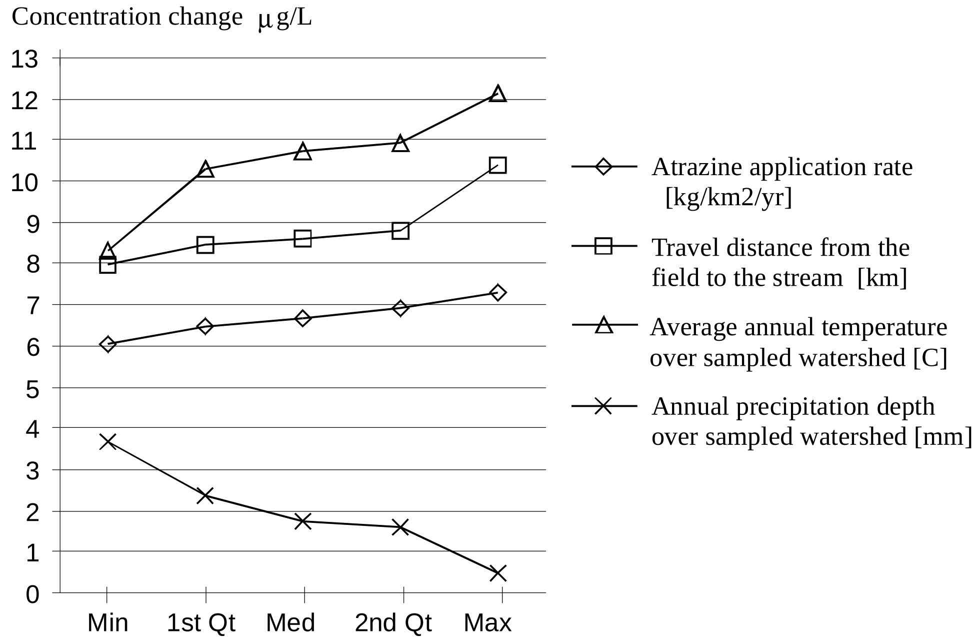


Figure 6.3 Influence of the explanatory variables on the average atrazine concentration (μg/L). Model without the flow rate (Table 6.7).

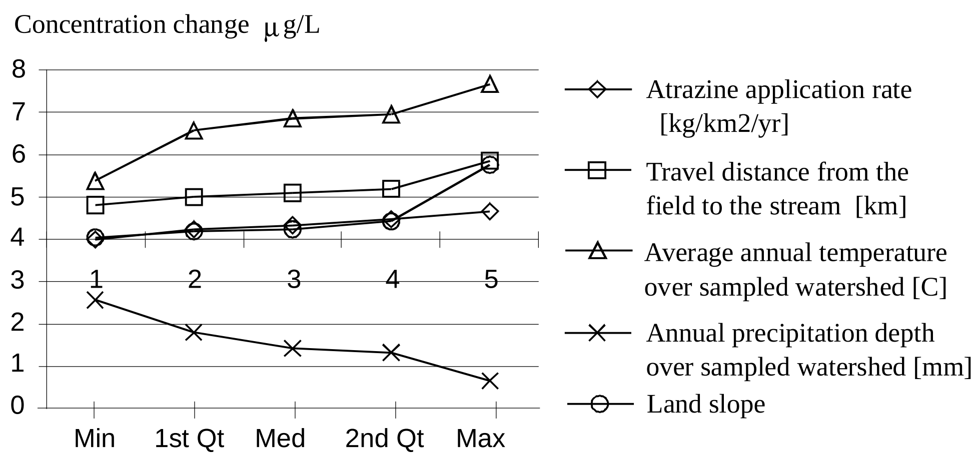


Figure 6.4 Influence of the explanatory variables on the average atrazine concentration (μg/L). Model with the flow rate (Table 6.8).

6.2.2 Average annual nitrate plus nitrite as nitrogen concentration

Parallel to the analysis of the atrazine concentrations, an analysis of the deseasonalized nitrate plus nitrite as nitrogen concentration has been conducted. The investigation was initiated by the model selected by the following S-plus stepwise regression procedure:

```
stepcs1 _ step ( csnq.lm, ~ Area + Appl + Flowm3s + Decstr + Slpstr
+           + Slplnd + Alflgkm + Tc + Tcavg + Pmm + Pmmavg )
```

where `scnq.lm` is an object that contains results of the simplest regression model

```
csnq.lm _ lm(ncsnq ~ 1 , data = n8v1).
```

The final model `atcs1` of the average annual nitrate concentration is presented in Table 6.11.

Table 6.11 Results of the regression analysis of average annual nitrate plus nitrite as nitrogen concentrations in the Midwest rivers (Data = nitrate concentration with removed seasonal component).

Variable	Value	Std. Error	t value	Pr(>|t|)
(Intercept)	-7.424541	0.8887	-8.3541	0.0000
Appl	0.001062	0.0001	17.7787	0.0000
Tcavg	-1.033063	0.0855	-12.0820	0.0000
Pmmavg	0.019339	0.0012	16.3178	0.0000

Residual standard error: 3.862 on 1304 deg. of freedom
Multiple R-Squared: 0.3025
F-statistic: 188.5 on 3 and 1304 degrees of freedom

The nitrate model has much better statistics than the analogous atrazine model. The coefficients for the climate variables have opposite signs to the respective coefficients in the atrazine equation. This proves that nitrate transport proceeds quite differently than atrazine transport does. The estimated inverse relationship between nitrate concentration and the temperature shows that higher temperature enhances microbial activity and the vegetation uptake, which affects the nitrate concentration not only seasonally but also spatially (due to the climatic differences).

Tisdale, et al., (1993) pointed out that because of nitrogen mobility in soils, the greater the surplus rainfall, the greater the possibility of loss of nitrogen through leaching. This association is supported here by the estimated positive relationship between annual precipitation and the deseasonalized nitrate plus nitrite as nitrogen concentration in the Midwest rivers.

Regions with higher rainfall have greater surface runoff and greater leaching through the soil. Both, the surface flow and the groundwater transport atrazine and nitrate. Since atrazine decays, and since the groundwater transport takes months or years, the atrazine concentration in the surface waters is mainly related to surface runoff events that occur after atrazine application on the field in late spring and early summer. Thus for a single event that occurs after atrazine application, the expected relationship between precipitation and concentration is positive (except for extremely large rainfalls). But for the long period of time this relationship becomes an opposite one, since a large fraction of the river flow is from groundwater (e.g., groundwater constitutes 80% of the flow in the Cedar River, Iowa) and a high portion of the annual precipitation occurs before atrazine use. Thus, for regions with higher annual precipitation depth the lower average annual atrazine concentration can be expected if other explanatory variables are constant.

Nitrate is very a persistent chemical. It enters the river not only with the surface runoff but also it is transported by the subsurface flows that supply the river with nitrate all year around. The long-term average of the annual precipitation depth is an indicator of the magnitude of agrichemical transport by the leaching and groundwater flow.

Table 6.12 shows selected variables and coefficients estimated for the model of the nitrite and nitrate as nitrogen concentration without the seasonal part and without the component explained by the measured flow rate.

Table 6.12 Results of the regression analysis of average annual nitrate concentrations in the Midwest rivers (Data = nitrate plus nitrite as nitrogen concentrations with removed component explained by the seasonal factor and the flow rate).

Variable	Value	Std. Error	t value	Pr(>|t|)
(Intercept)	-7.57848	1.0244	-7.3977	0.0000
Appl	0.00064886	0.0001	11.5591	0.0000
Tcavg	-0.520245	0.0643	-8.0874	0.0000
Pmmavg	0.0088545	0.0009	9.7573	0.0000
Slplnd	173.6409	18.3246	9.4758	0.0000
Alflgkm	0.776683	0.1674	4.6390	0.0000

Residual standard error: 2.879 on 1302 degrees of freedom
Multiple R-Squared: 0.1636
F-statistic: 50.95 on 5 and 1302 degrees of freedom

Figure 6.5 and Figure 6.6 show the range of the influence of the selected explanatory variables on the average concentration represented by the model described in Table 6.11 and Table 6.12, respectively. The change in concentration is related to the change in each variable assuming the minimum, first quartile (25th percentile), median (50th percentile), third quartile (75th percentile), and maximum value. The values of the quartiles are listed in Table 6.10 (Section 6.2.1). The slope of lines between first and third quartiles (Fig. 6.11 and Fig.6.12) indicates that the nitrate fertilizer application rate has relatively high influence on the nitrate concentration in the Midwest rivers.

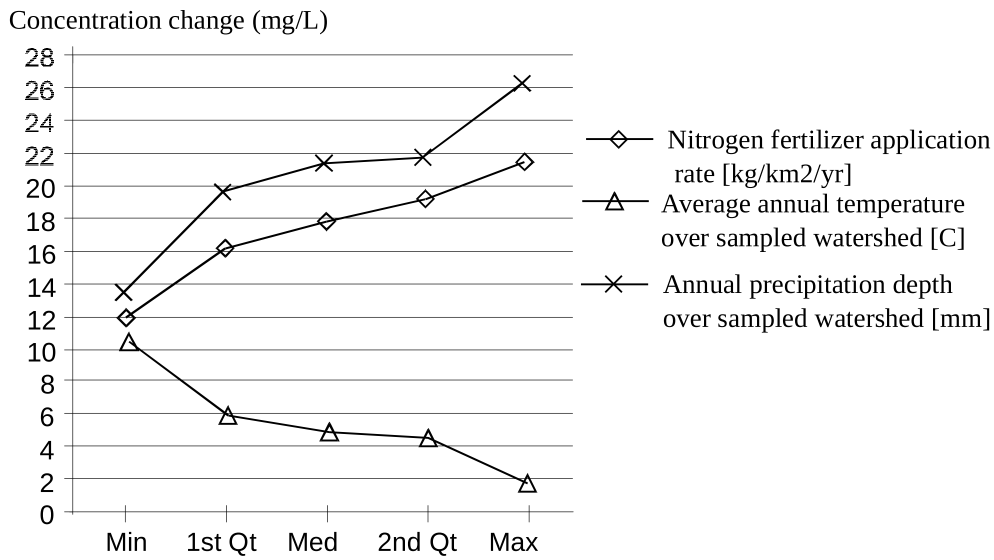


Figure 6.5 Influence of the explanatory variables on the average nitrate plus nitrite as nitrogen concentration (mg/L). Model without the flow rate (Table 6.11).

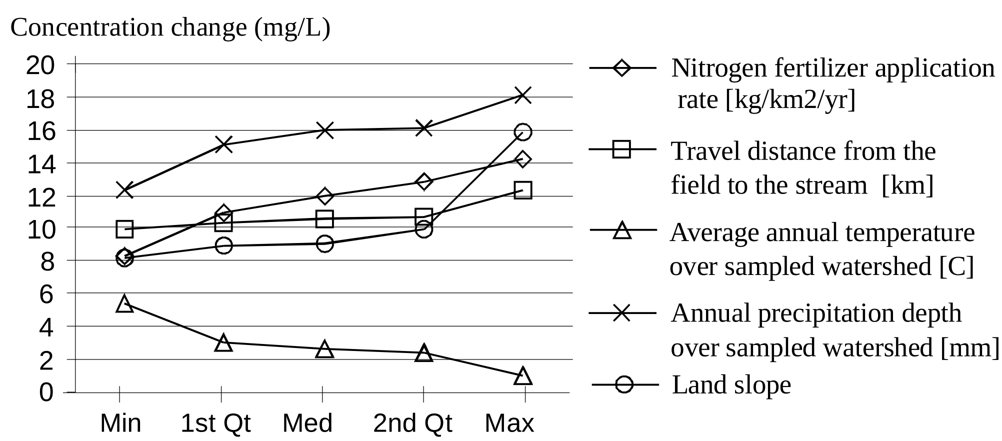


Figure 6.6 Influence of the explanatory variables on the average atrazine concentration (mg/L). Model with the flow rate (Table 6.12).

6.3 Error of model predictions

The mean squared error (*MSE*) of the estimate for the agrichemical concentrations about the model is calculated from the following equation:

$$MSE = \sqrt{\frac{\sum (c - \hat{c})^2}{n}} \qquad (6.7)$$

where:

c = measured agrichemical concentration;

$\hat{c}$ = modeled concentration;

n = sample size.

Figure 6.7 shows the difference between measured atrazine concentrations and the predicted ones by two models: one developed without utilizing flow rate as an independent variable, and the other one calculated utilizing recorded flow rate. Since the atrazine concentrations are high in May and the June, the prediction errors are also much higher in these month than the errors in the other months of the year. Thus two standard errors have been calculated for each model. One MSE for May and June and the other for July - April. Table 6.13 summarizes the results:

Table 6.13. Mean Standard Errors for the atrazine concentration models (μg/L).

Model	Mean Squared Error	
	May, June	July-April
Model 1(no flow)	14.23	1.34
Model 2 (with flow)	16.55	1.92
Sample size	442	491

The relatively high error for the period from late summer to early spring is due to the high variability of measured concentrations in June (10% of sample) that often are larger than 3 μg/L, and some as large as 16 μg/L observations in March. For example, the concentration measured in the Auglaize River near Fort Jennings, Ohio on 03/14/89 was 15 μg/L and on 03/21/90 was 16 μg/L. (Scribner, et al., 1993).

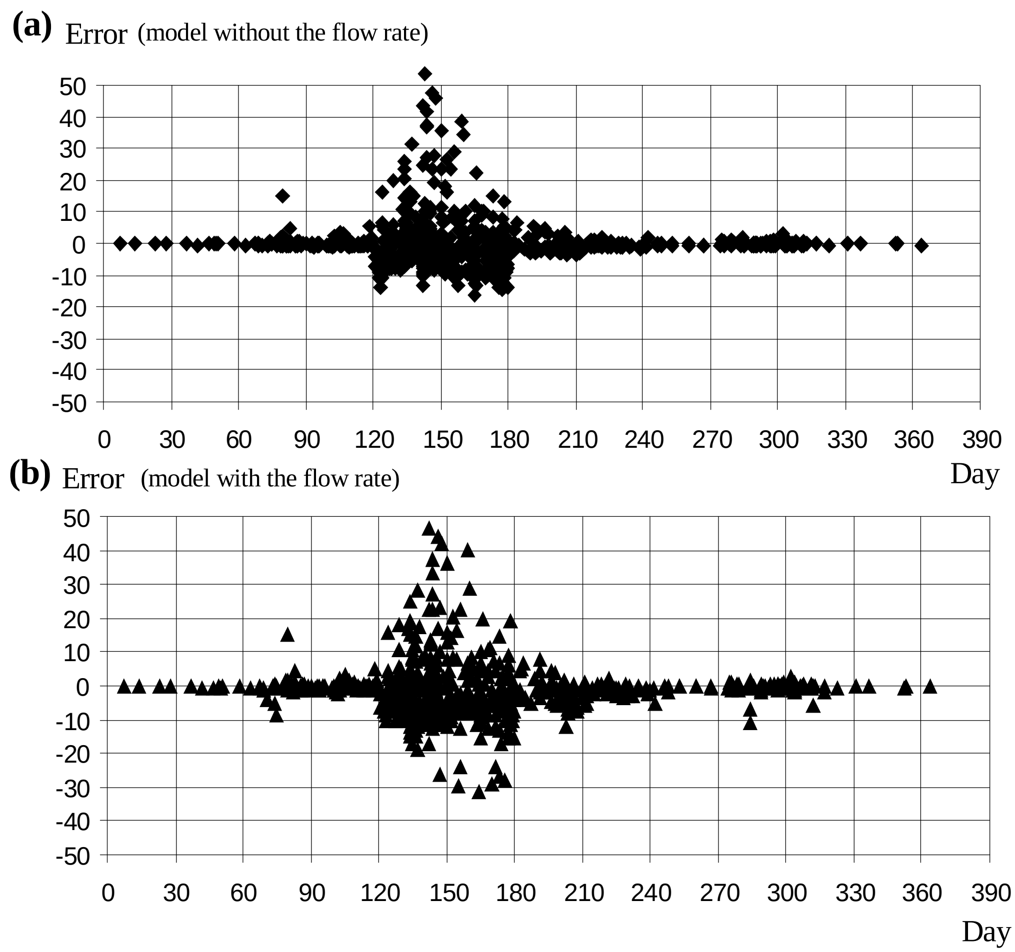


Figure 6.7 Difference between measured atrazine concentrations and predicted concentrations in the Midwest rivers:
a) model without the flow rate;
b) model with flow rate included as an explanatory variable.

Figure 6.8 presents the difference between measured nitrate concentrations and the predicted ones. The differences do not exhibit clear seasonal variations as was the case for the atrazine models. Therefore, just one mean squared error has been calculated for each model. The errors are listed in Table 6.14.

Table 6.14. Mean Standard Errors for the nitrate plus nitrite as nitrogen concentration models (mg/L).

Model	Mean Squared Error
Model 1(no flow)	4.04
Model 2 (with flow)	13.43
Sample size	1308

Both Figure 6.8 and Table 6.14 indicate that the model that uses the flow rate for predictions overestimates the concentrations for high discharges. It is clearly visible for rivers with the extremely high flow events. For example, the flow of 20,500 m^3/s (721,000 cfs) was recorded in the Ohio River near Grand Chain. Illinois, on 3/16/1989 and almost 9,000 m^3/s (309,000 cfs) on 6/11/89. The model predicted an unrealistic concentration of 310 mg/L and 200 mg/L respectively, whereas the observed levels were less than the reporting limit of 0.1 mg/L.

It must be noted that the standard errors are estimated using daily observations and daily predictions. The models are not intended to calculate the agrichemical in the surface waters on a daily basis but they are designed to estimate average monthly conditions. Thus such a very high flow rates as the one recorded for the Ohio River near Grand Chain on 3/16/1989 can not be used as a representation of the mean monthly flow. The errors discussed in this section serve only as a rough model verification and as an indicator of how the daily concentrations scatter around the mean monthly prediction.

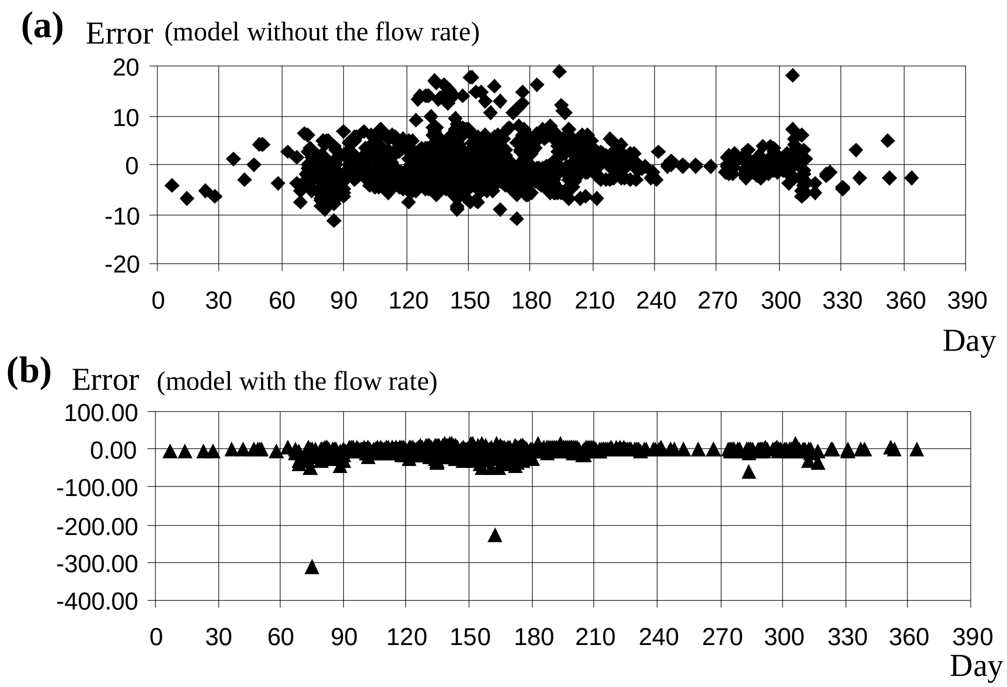
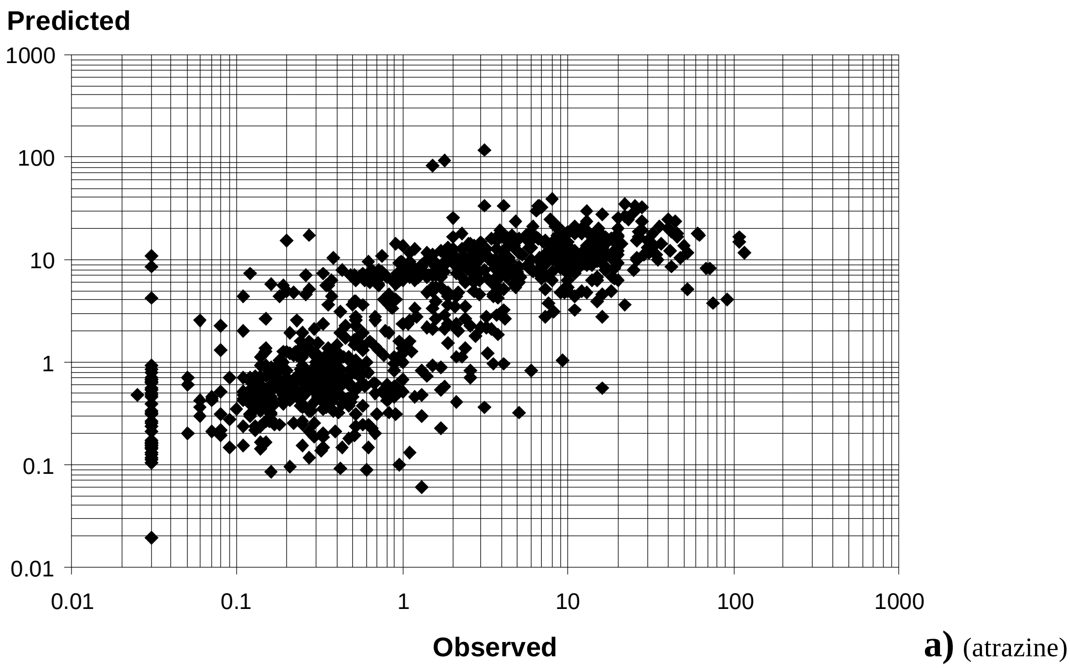


Figure 6.8 Difference between measured nitrate concentrations and predicted concentrations in the Midwest rivers:
a) model without the flow rate;
b) model with flow rate included as an explanatory variable.

The observed atrazine concentrations and the observed nitrate concentrations are compared to the predicted values by the model with the flow rate in Figure 6.9a and Figure 6.9b respectively. The plot of observed values vs. predicted concentrations by the model without the flow rate exhibits a similar pattern to the one shown in Figure 6.9.



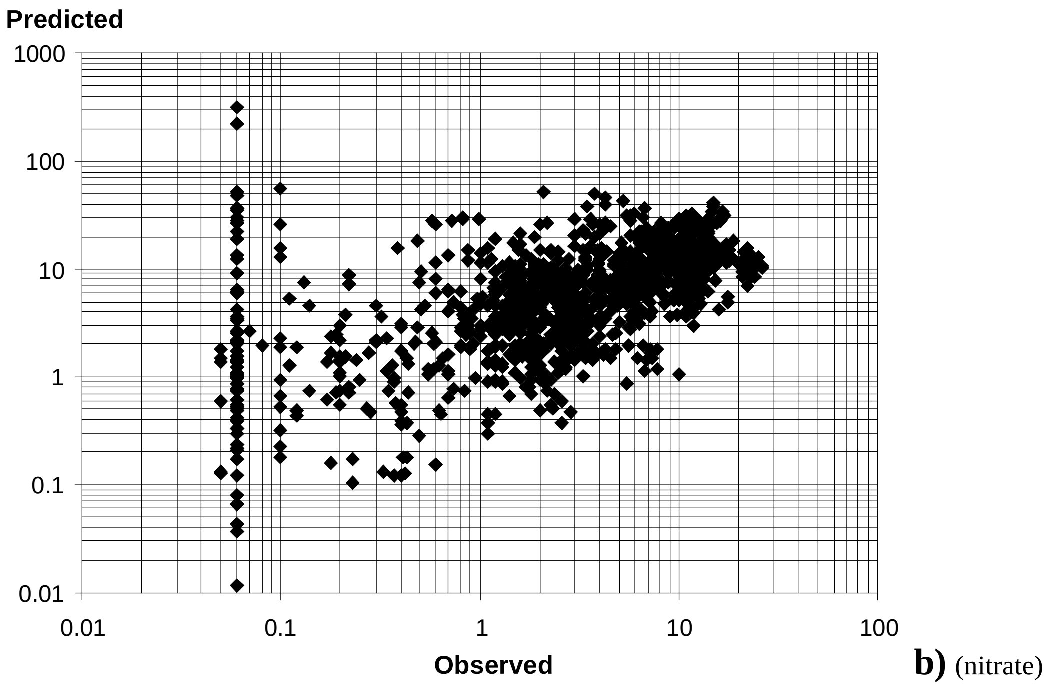


Figure 6.9 Observed vs. predicted agrichemical concentrations in the Midwest rivers (model with the flow rate): a) atrazine in μg/L; b) nitrate plus nitrite as nitrogen in mg/L.

6.4 Comparison of predicted flow with observed one

Verification of the method of spatial redistribution of the recorded flow rate is performed within the Iowa-Cedar River basin. Three USGS gauging stations: (a) Shell Rock R. near Northwood, IA (5459000) (b) Fourmile Cr. near Traer, IA (5464137); and (c) Prairie Cr. at Fairfax, IA (5464640) has not been utilized in redistribution process. Figure 6.10 shows location of these gauging stations as well as the location of selected USGS stations whose record have been used in the flow rate estimations. Table 6.15 compares the predicted flow with the observed values.

Table 6.15 Comparison of predicted and observed flow rate (m^3/s) for three USGS gauging stations.

	Sample 1	Sample 2	Sample 3
USGS station ID	5459000	5464137	5464640
Modeling unit ID	71	388	486
Time period	1960/01-1986/09	1962/10-1980/12	1966/10-1982/9
Sample size	321.00	209.00	192.00
Mean predicted	5.37	0.48	3.66
Mean measured	5.33	0.33	3.78
Std. dev. of predicted	5.23	0.54	3.86
Std. dev. of measured	6.24	0.42	4.45
Mean difference	-0.05	-0.15	0.12
Std. dev. of difference	3.48	0.29	1.88

Although, the normality of the error has not been verified, the following normal deviates of difference between observed and estimated flow have been estimated (as an approximation of the valid statistical indicator), Sample1: $z_1 = 0.24$, Sample2: $z_2 = -7.5$, and Sample 3: $z_3 = 0.89$. The error is significant for Sample2. This comparison shows that the inaccuracy in predicted flow is larger for units located farther from gauging stations that the error for units that are closer to a measurement point.

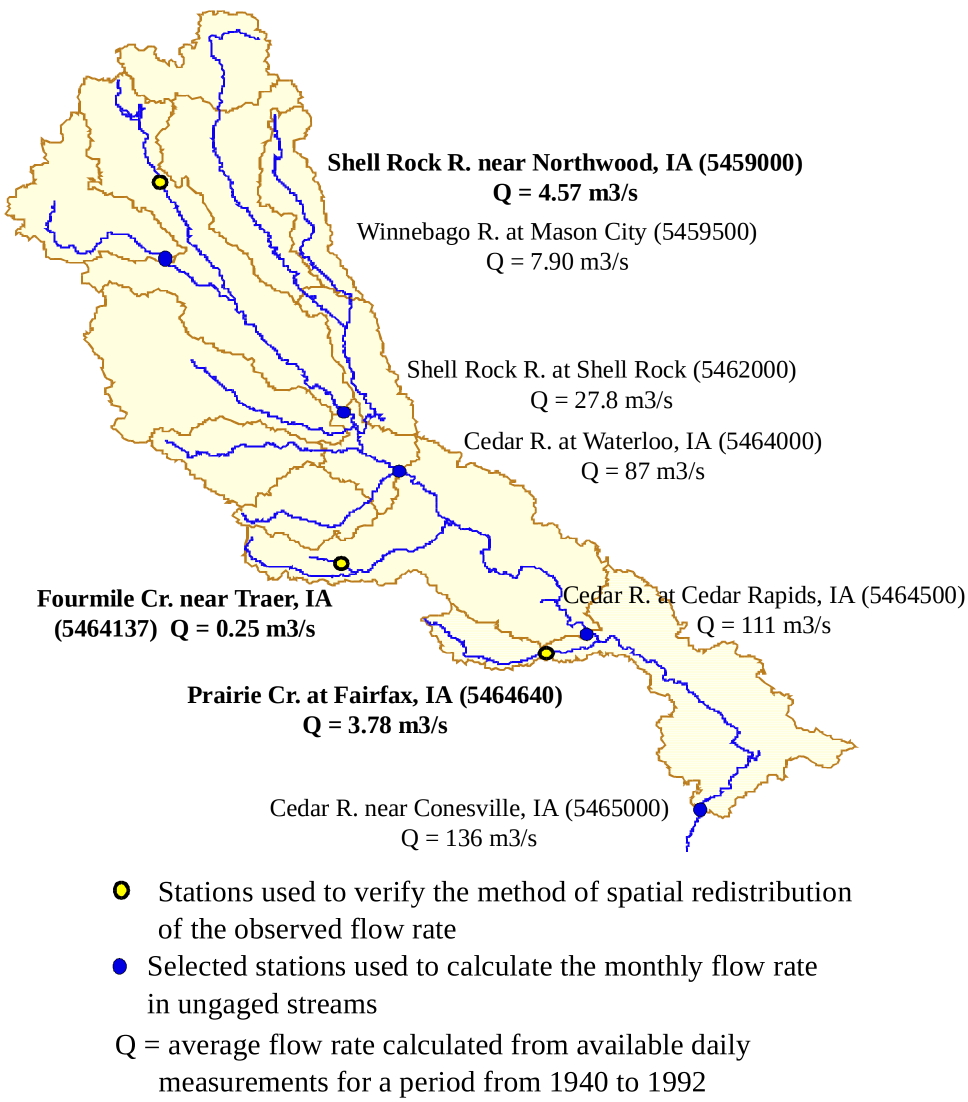


Figure 6.10 Location of the USGS gauging stations to verify method of spatial redistribution of the observed flow rate.

Figure 6.11 presents the time series of the observed and predicted flow rate in three selected streams of the Cedar River basin. Although the flow redistribution method is a very simple one, estimated monthly flow rates in ungauged streams are very close to the true values.

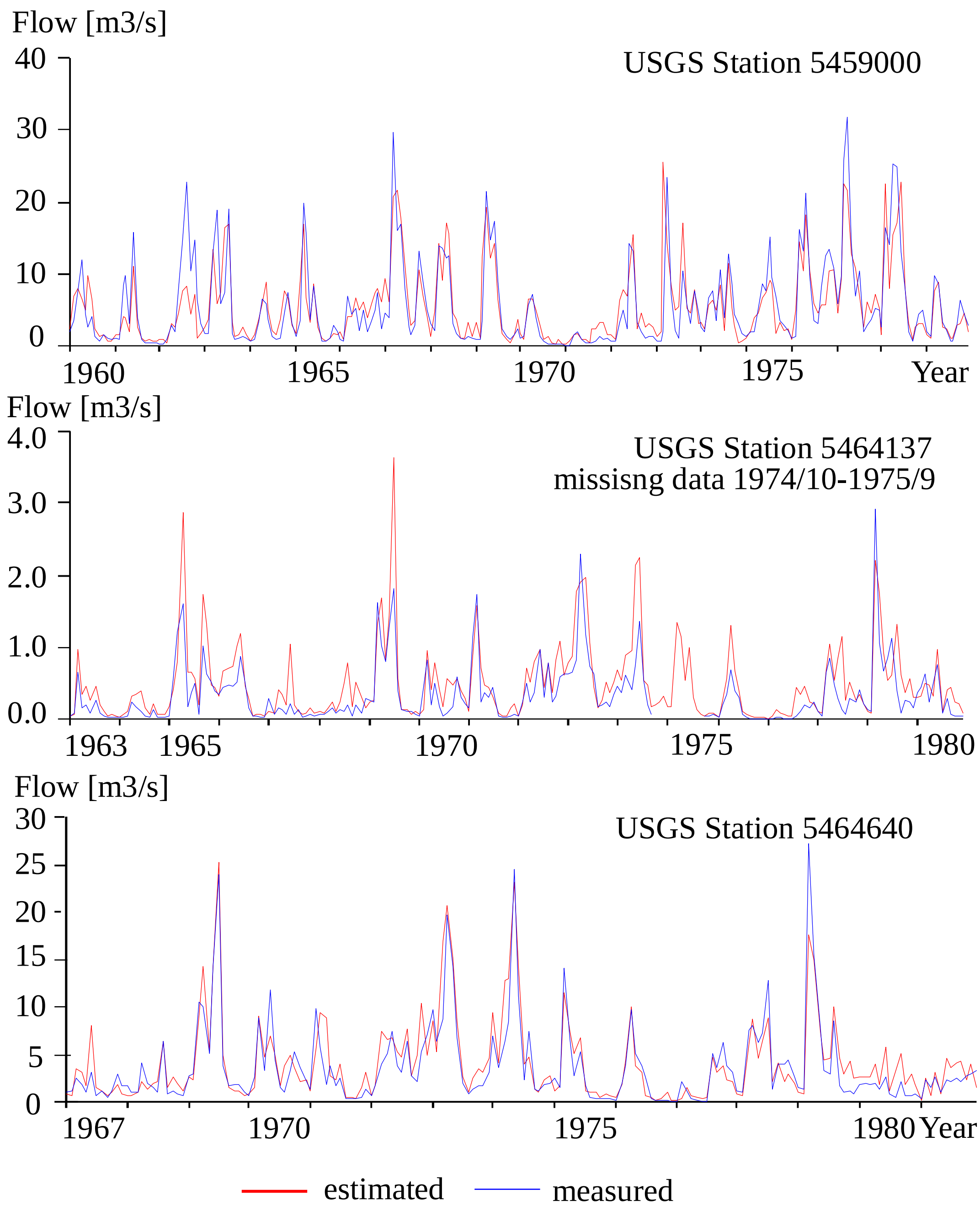


Figure 6.11 Observed and predicted flow rate in selected streams of the Cedar River basin.

The method of spatial redistribution of the measured flow has a potential application in estimation of water losses and identification of modeling units that do not contribute to the flow in rivers. In addition, the information about the difference between outflow and inflow for each individual modeling watershed can be used to model the transport of agrichemicals between a field and the stream network. Negative balance, i.e. inflow into an unit is greater than the outflow from the unit, means water losses, occurs mainly in regions where lakes exist. It also may indicate groundwater recharge zones. Since the unit with a negative surface water balance do not contribute to the flow in the river, it is unlikely that such a unit significantly contributes to the river pollution.

On the other hand, the high positive surface water balance indicates a big contribution of the unit surface and subsurface flow to the river flow, and thus a large agrichemical contribution may be expected.

Figure 6.12 shows the estimated surface water balance for each modeling unit of the Iowa-Cedar River basin in June 1990. The ArcView script `decom2` has been applied to calculate the difference between the cumulative flow at the unit outlet and the sum of the cumulative inflows which enter the unit. The spatially distributed flow in rivers in the Iowa - Cedar River, in June 1990 (Figure 5.7), has been utilized.

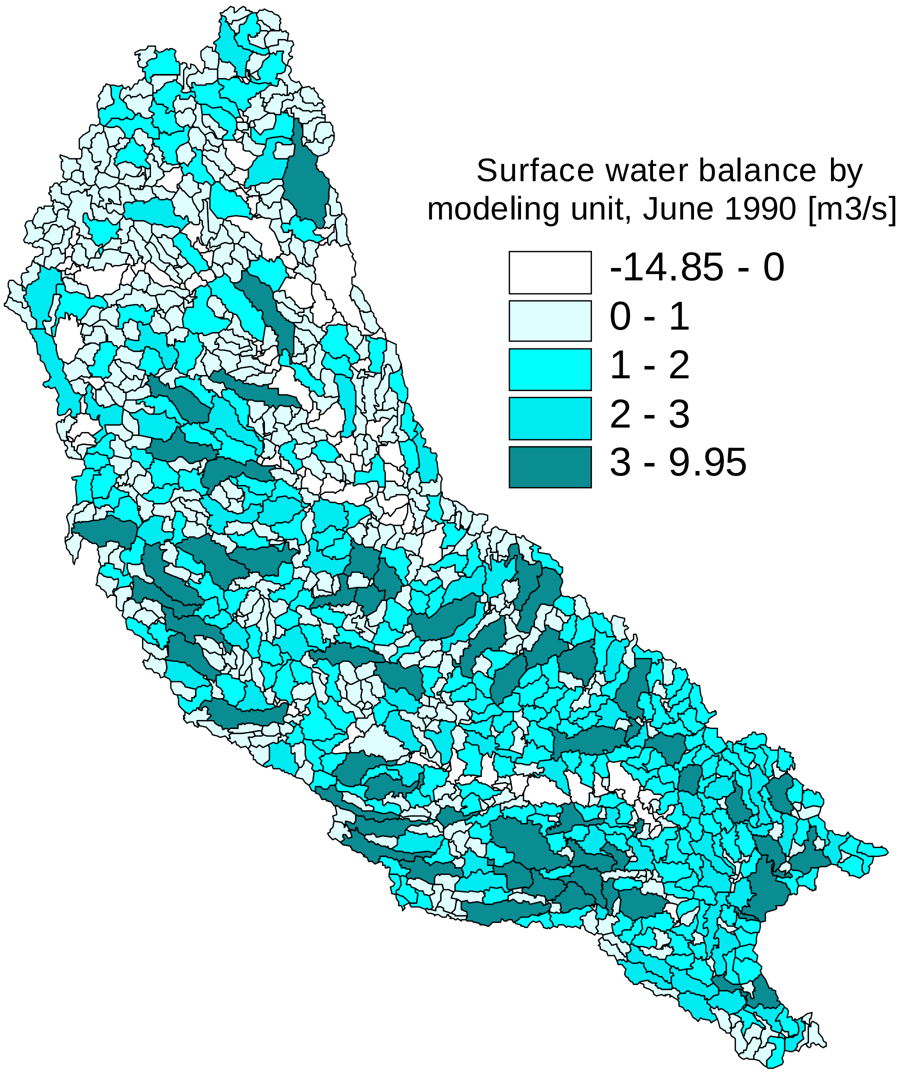


Figure 6.12 Spatial distribution of the surface water balance for the modeling units. Estimated from recorded flow rate, precipitation depth and selected unit features, the Iowa-Cedar River basin, June 1990.

6.5 Agrichemical concentrations in the Cedar River basin

This section presents the application of the methodology developed in this dissertation to estimate the agrichemical concentrations in the Iowa-Cedar River basin. The regression equations that describe the atrazine and nitrate concentration in the midwest rivers have been derived from the data gathered in more that 150 sampling points scattered over the Upper Mississippi-Missouri River and the Ohio River basins. Therefore the models reflect the regional average conditions in the rivers, and for a specific watershed, the model results may be considerably different from the available measurements.

The monthly flow rate for the year 1990, as well as the annual nitrogen fertilizer use in 1990 have been extracted from the GIS database for the Iowa-Cedar Basins. After the Arc/View model performed calculations, the results for two units that represent Old Mans Creek at Iowa City (unit_ID = 5455100) and the Cedar River at Palisades (unit_ID = 475) have been extracted for further analysis. Figure 6.13 compares calculated concentrations of nitrate plus nitrite as nitrogen in the selected locations with the values published by the USGS (Scribner, et al., 1994). The predictions are much lower than the observations, except for the Cedar River in April and the Old Mans Creek in June, when the estimated nitrate concentrations are close to the measured ones. The plot of the measurements shows a significant increase of agrichemical at the end of April-beginning of May: from about 2 mg/L (April) to as high as 13 mg/L (May) in the Cedar River at Palisades, and from about 10 mg/L (April) to as high as 25 mg/L (May) in the Old Mans Creek near Iowa City. Most likely the jump in the concentration level was caused by the late Spring application of nitrogen fertilizers..

Modeling nitrogen in the surface waters is a very difficult task. Even such advanced model as GRASS-SWAT-QUAL2E has difficulties to make predictions that agree with the measurements. “Researchers agree that modeling nitrogen is one of the most challenging tasks even at field scale.” (Ramanarayanan, et al., 1996)

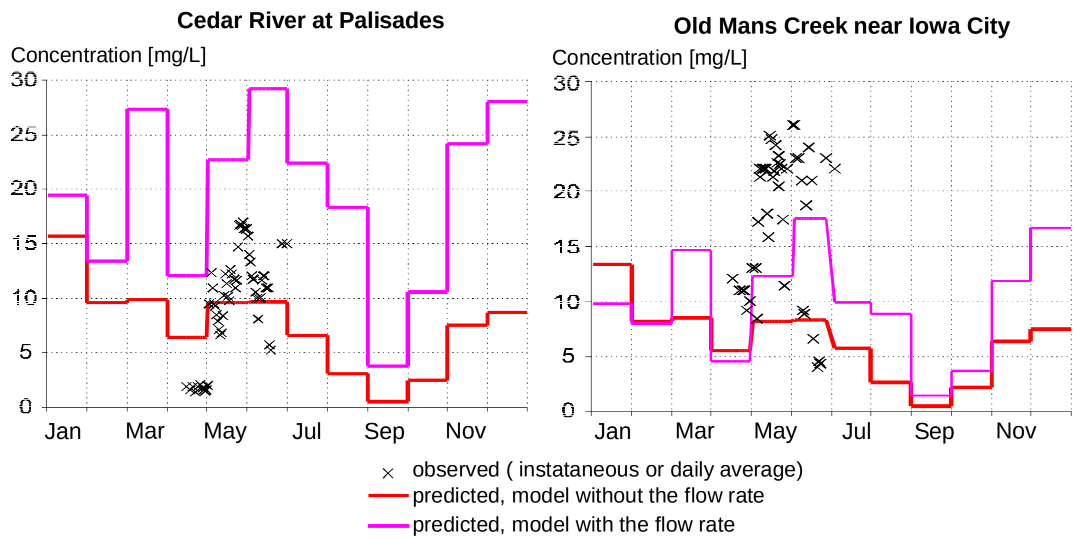


Figure 6.13 Comparison of the predicted and observed concentrations of nitrate plus nitrite as nitrogen in the Cedar River at Palisades, Iowa and the Old Mans Creek at Iowa City, Iowa, in 1990.

An exercise similar to the one for nitrate plus nitrogen has been performed for the atrazine. Since no herbicide usage has been available for 1990, the values estimated for the 1989 have been applied in the calculations. Figure 6.14 shows the predicted values of the atrazine concentration in the Cedar River at Palisades and in Old Mans Creek near Iowa City. The estimated values are compared with the measured concentrations in 1990 (Scribner, et al., 1994). Unlike the nitrate, the predictions of the atrazine are within the range of the observed values.

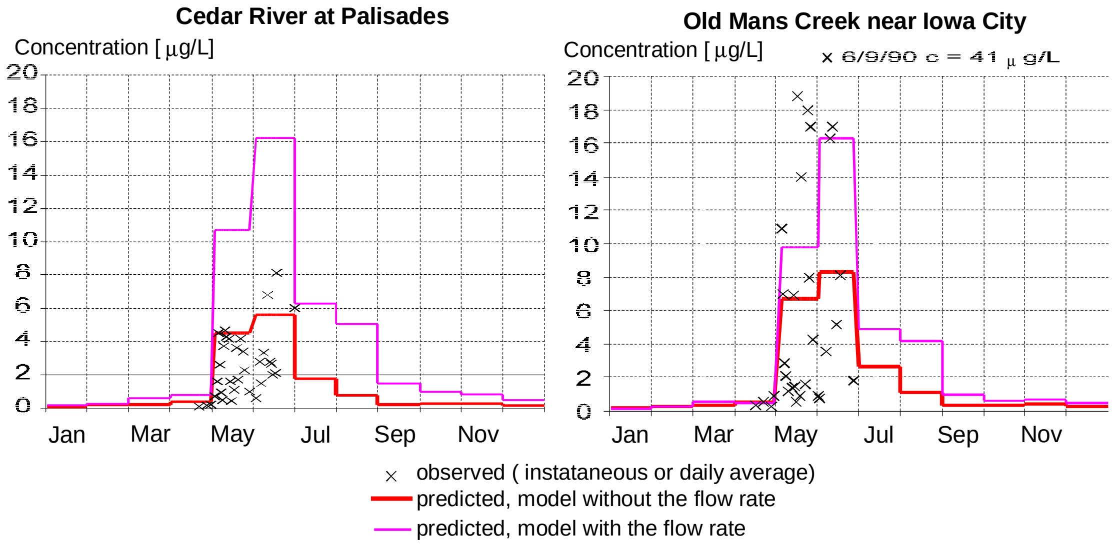


Figure 6.14 Comparison of the predicted atrazine concentrations in the Cedar River at Palisades, Iowa and the Old Mans Creek at Iowa City, Iowa, in 1989 with the observed concentrations in 1990.

The ArcView model of the agrichemical transport in surface waters has very versatile tools to create profiles along a selected flow path. Figure 6.15 presents such profiles of the atrazine application and the atrazine concentration in the Cedar River estimated for June 1989. For selected unit watersheds that represent the Cedar River, three items have been extracted from the attribute table:

- calculated concentration for June 1989;
- annual atrazine application; and
- length of the flow path.

Moving downstream, the average increase of the herbicide mass applied to the field is about 1.25 t/km of the Cedar River (if major tributaries such as the Iowa River and the Rock Shell River are excluded from calculations, the increase of atrazine application is

400 kg/km). The concentration in the upper portion of the river under study increases going downstream, with the rate of 1.0 µg/L/100 km. In the downstream portion of the river, the rate decreases to 0.3 µg/L/100 km.

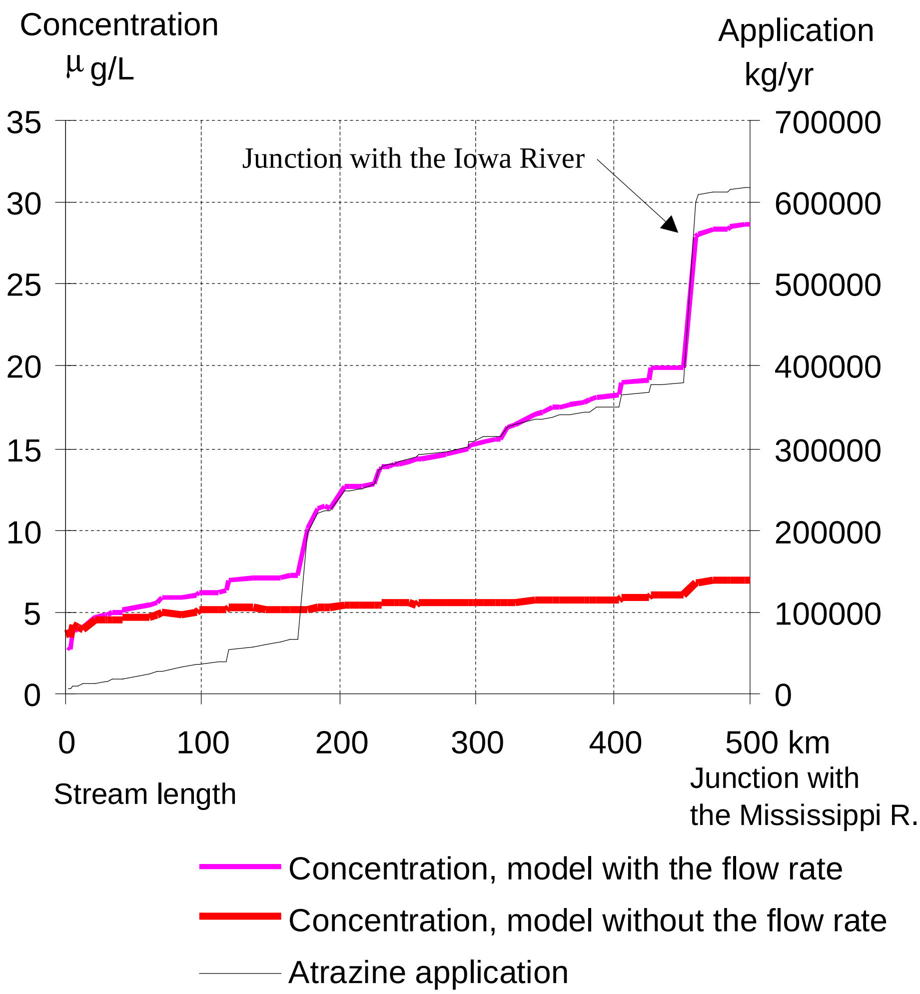


Figure 6.15 Profiles of the predicted atrazine concentrations in the Cedar River for June 1989 and the annual atrazine application (based on the results of the ArcView model).

The model estimates the concentrations based on the agrichemical application in the upstream drainage area, and the selected parameters of the watershed. To check if the mass balance at river junctions is reasonable, i.e., if the amount of the atrazine in the Iowa River is high enough to create in the Cedar River an increase in concentration of about 0.8 µg/L (Figure 6.15), the bar charts of the concentration for units close to the junction have been drawn utilizing the model tools (Figure 6.16). Indeed, the concentration in the Iowa River exceeds 8 µg/L, a value that is high enough to produce concentration of 6.8 µg/L after water from Iowa River mixes with the Cedar River.

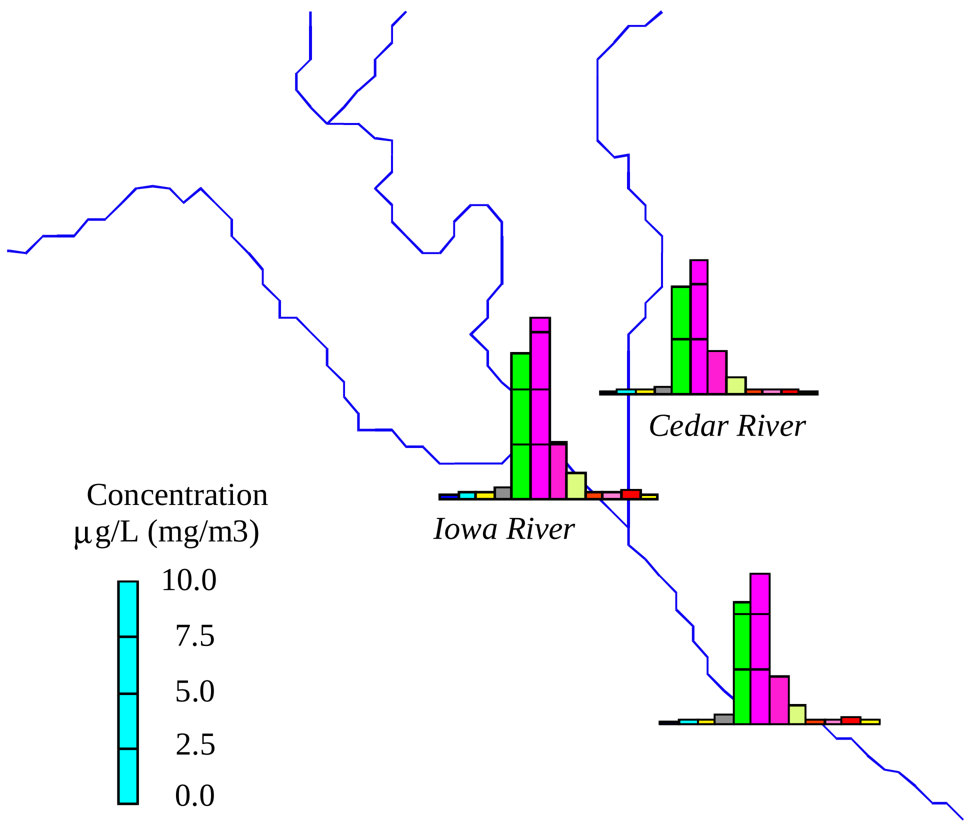


Figure 6.16 Predicted atrazine concentrations (mg/m3 = µg/L) at the Iowa River and the Cedar River junction (June 1990).

Table 6.16 shows estimated values of atrazine concentration, load and the flow rate in the modeling units that represent the confluence of the Iowa River with the Cedar River.

Table 6.16 Atrazine concentration, load and the flow rate in modeling units that represent the confluence of the Iowa River with the Cedar River estimated for June 1990.

Parameter	Units	Unit 677 (Iowa River)	Unit 665 (Cedar River)	Unit 680 (Iowa R + Cedar R)
Concentration	μg/L	8.2	6.0	6.8
Flow rate	m^3/s	301	496	800
Load	kg/month	6,375	7,764	14,143
Drainage Area	km^2	11,500	20,146	31,637
Application	t/yr	222.4	379.0	601.4
Applic. rate	$kg/km^2/yr$	19.335	18.812	19.000

Further analysis has been performed to verify if the models (with and without flow rate) can be used for making predictions of total annual chemical transport in the midwest rivers. The annual load has been calculated for two Iowa rivers, the Cedar river at Palisades and the Old Mans Creek at Iowa City. The atrazine application rate in 1989 was extracted from the USGS maps (Battaglin and Goolsby, 1995 a, b). The 1990 monthly flow rate was used to predict concentrations and loads. The calculations have been performed by the ArcView agrichemical transport model. The selected results have been extracted from the polygon attribute table of the map of modeling units and they are presented in Table 6.17.

Table 6.17 Relation of the atrazine application to the atrazine load in two Iowa rivers: the Cedar River at Palisades and the Old Mans Creek at Iowa City (Chemical application for year 1989, flow data for 1990).

Sampling site	Application kg/yr	Model with flow rate	Estimated load kg/yr	Load as a fraction of application %
Cedar River at Palisades	325416	no	9639	3.0
		yes	31456	9.7
Old Mans Creek at Iowa City	9440	no	845	8.9
		yes	1660	17.6

The model that applies flow rate to evaluate atrazine concentration, predicts high atrazine loads: the predicted annual load for the Old Mans Creek is as high as 18% of total atrazine application and in the Cedar River it is about 10 % of herbicide use.

The model that does not utilize flow rate to calculate chemical concentrations gives smaller load estimates, 3% and 9% for the Old Mans Creek and the Cedar River respectively. These results are very close to the published agrichemical runoff from the field: Squillace and Engberg (1988) estimated that 1.5% - 4% of atrazine applied, depending on the assumed rate of chemical application, was transported by the Cedar River, Iowa in 1985. Two - three percent applied atrazine was carried by the Wye River, Maryland when substantial runoff occurred within two weeks of application (Wu, et al., 1983, cited by Squillace and Engberg, 1988). Based on the extensive review of literature on pesticides losses in runoff waters Wauchope (1978) stated that losses as high as 5 % can be expected for pesticides formulated as wettable powders (atrazine is such a pesticide), and, in addition, losses may be three times higher if a large runoff occurs about 2 weeks of application. The estimated transport of atrazine in the Mississippi River and its four tributaries (from 04/1991 to 03/1992) varied from 0.58% of use for Platte River at Louisville, Nebraska, to 1.83% in Illinois River at Valley City, Illinois (Battaglin, et al., 1993).

Figure 6.17 shows the monthly distribution of the loads, represented as a fraction of the annual load, in the sites under investigation. These bar charts indicate that the seasonal variation of atrazine loads is very realistic, about 70% of total atrazine load in the Cedar River at Palisades and about 80% of total load in the Old Mans Creek have occurred in May and June (average for 1990).

Squillace and Engberg (1988) estimated that 70% of the annual chemical load in the Cedar River, calculated for period from May 1984 through November 1885, occurred in June 1984. Thus, the models give realistic temporal distribution of the atrazine loads in the rivers of the Iowa-Cedar Basin.

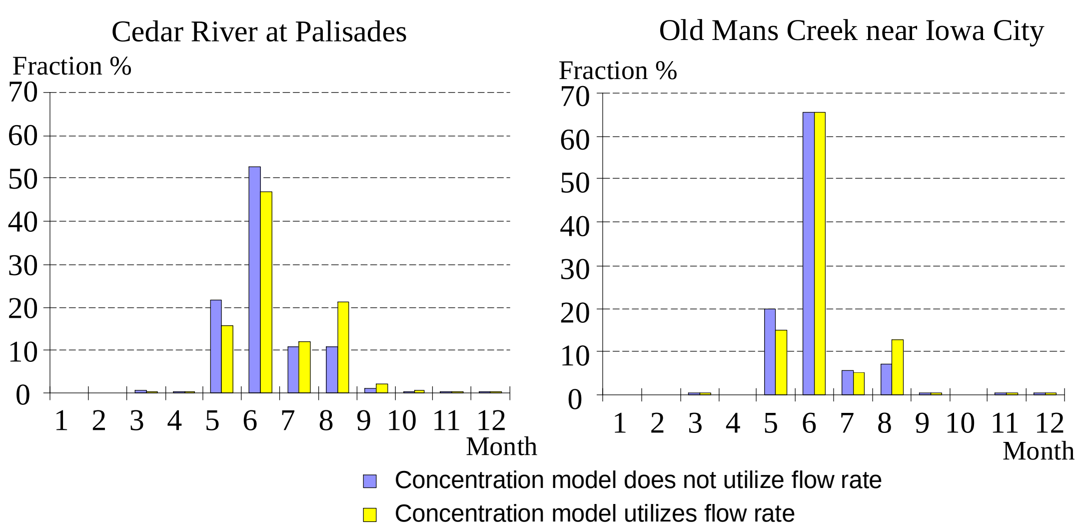


Figure 6.17 Estimated monthly fractions of the annual atrazine load in the Cedar River at Palisades and the Old Mans Creek near Iowa City, Iowa for year 1990.

The spatially distributed atrazine loads in the rivers of the Iowa-Cedar Basin in June 1990 are presented in Figure 6.18. The concentration were evaluated by the “without-flow” model.

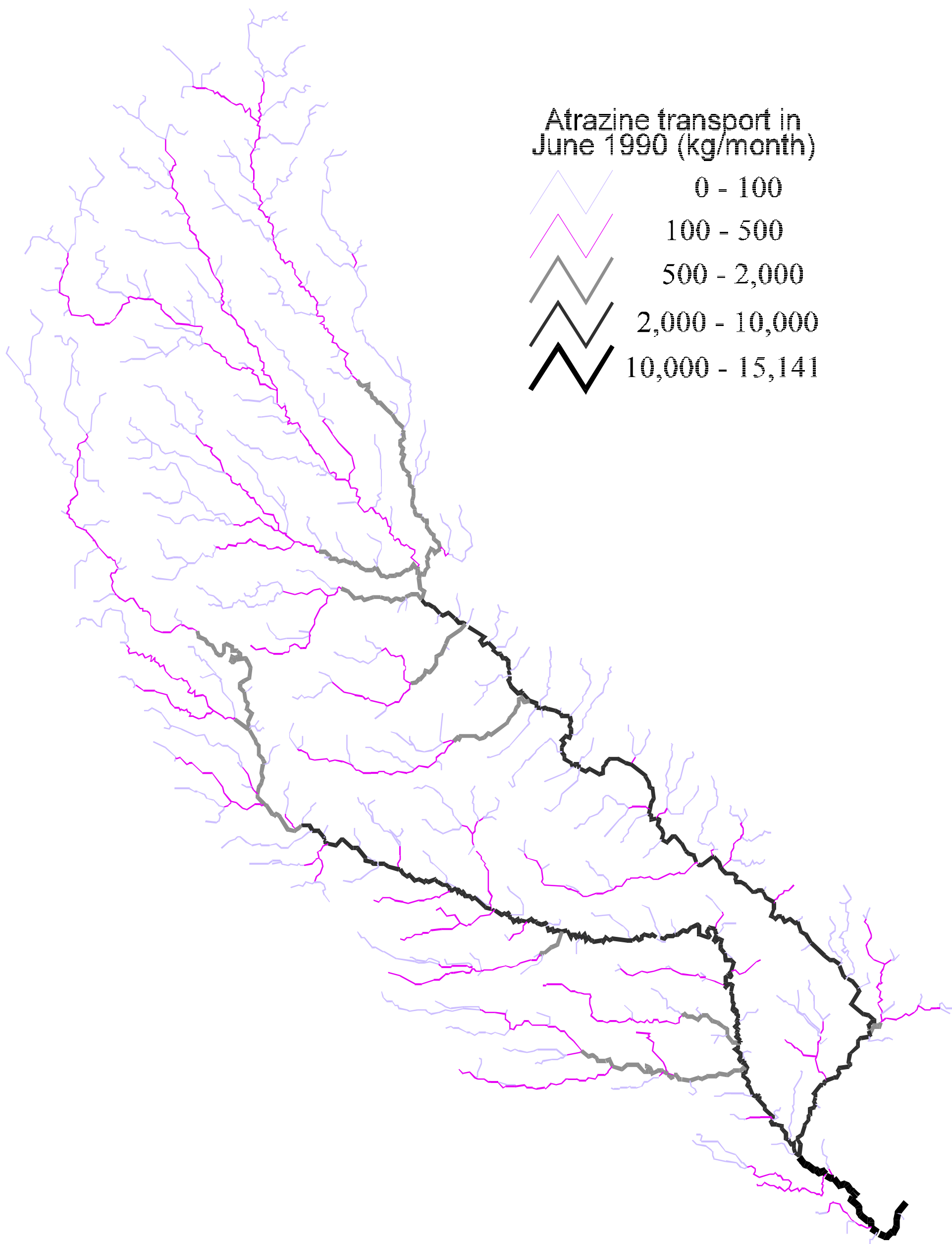


Figure 6.18 Estimated atrazine load in the rivers of the Iowa-Cedar Basin in June 1990.

The nitrate plus nitrite as nitrogen loads were calculated for the same rivers as were the atrazine loads. The 1990 nitrogen fertilizer application has been extracted from the USGS maps of the annual nitrogen fertilizers sales in US counties (Battaglin and Golsby, 1995a). Table 6.18 presents selected results of the calculations made by the ArcView agrichemical transport models.

Table 6.18 Relation of the nitrogen fertilizer application to the nitrate plus nitrite as nitrogen load in two Iowa rivers: the Cedar River at Palisades and the Old Mans Creek at Iowa City (Chemical application and flow rate represent year 1990).

Sampling site	Application t/yr	Model with flow rate	Estimated load t/yr	Load as a fraction of N application %
Cedar River at	123651	no	28234	22.8
Palisades		yes	95221	77.0
Old Mans Creek at	3165	no	1267	40.0
Iowa City		yes	2589	81.8

The nitrogen loads constitute large portion of the nitrogen fertilizers application. The model that utilizes the flow rate to estimate the concentrations forecasts relatively large loads. However, as shown in Figure 6.13, the model "without flow rate" predicts concentrations that are in agreement with the observed values (Cedar River at Palisades) or are lower than the observed ones (Old Mans Creek near Iowa City). Thus the estimated fractions of total chemical use are realistic. For comparison, the average transport of nitrate in the Mississippi River and its four tributaries (from 04/1991 to 03/1992) was about 15.5% of use (Battaglin, et al., 1993). It must be noted that the nitrate plus nitrite as nitrogen in Midwest rivers is not only a result of the nitrogen fertilizer application but it is also related to other sources of the nitrogen such as discharge from municipal treatment plants and manure nitrogen inputs. For example, Coote, et al., 1978 explained 92% of the nitrate variability in the Canadian Great Lakes Basin rivers by row crops and manure nitrogen inputs.

The monthly fractions of the annual nitrate loads are shown in Figure 6.19

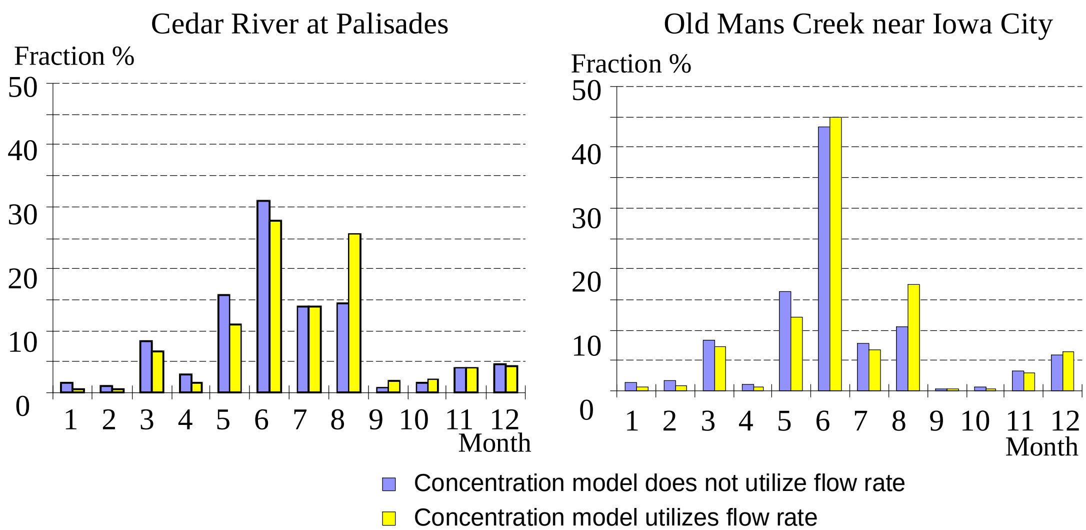


Figure 6.19 Estimated monthly fractions of the annual nitrate load in the Cedar River at Palisades and the Old Mans Creek near Iowa City, Iowa for year 1990.

Although the seasonal pattern of the nitrate plus nitrite as nitrogen concentration in the midwest rivers differs from the atrazine concentration variations, the seasonal pattern of the nitrate load shown in Figure 6.19 is similar to the atrazine one. The high transport in Summer months is due to high flow rate that is recorded in the Iowa-Cedar Rivers, especially in June, July, and August.