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The Supplementary Material contains three sections. We tabulate some data characteristics in the first section. The bootstrap method for computing confidence intervals of state-wide mean (median) annual rate of change in nitrate-nitrogen concentration is given in the second section. The final section contains detailed model fits for the 60 ambient time series.

S1 Data Characteristics

Table S1 summarizes some pertinent data characteristics site by site, including the beginning monitoring date, the end date, the length of study period (in months), and the number of months with observations (effective sample size) which is generally smaller than the length of the study period, owing to the presence of missing data.
Table S1: Data characteristics.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>ID No.</th>
<th>Beginning date</th>
<th>Ending date</th>
<th>length of study period (in months)</th>
<th># of months with observations (sample size)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Iowa River near Dorchester</td>
<td>10030001</td>
<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>158</td>
</tr>
<tr>
<td>West Fork Cedar River at Frackford</td>
<td>10070003</td>
<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>158</td>
</tr>
<tr>
<td>South Raccoon River near Redfield</td>
<td>10250001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>147</td>
</tr>
<tr>
<td>Boone River near Stratford</td>
<td>10400001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>147</td>
</tr>
<tr>
<td>Maquoketa River at Maquoketa</td>
<td>10490001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>152</td>
<td>125</td>
</tr>
<tr>
<td>West Nishabotna River near Malvern</td>
<td>10650001</td>
<td>11/1998</td>
<td>6/2012</td>
<td>164</td>
<td>150</td>
</tr>
<tr>
<td>Floyd River near Sioux City</td>
<td>10750001</td>
<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>158</td>
</tr>
<tr>
<td>South River near Akrweth</td>
<td>10910003</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>147</td>
</tr>
<tr>
<td>English River at Riverside</td>
<td>10920001</td>
<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>159</td>
</tr>
<tr>
<td>Yellow River near Volney</td>
<td>10030002</td>
<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>151</td>
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<td>Chariton River near Centerville</td>
<td>10040001</td>
<td>10/1999</td>
<td>6/2012</td>
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<td>10/1998</td>
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<td>165</td>
<td>151</td>
</tr>
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<td>Shell Rock River at Shell Rock</td>
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<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
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<td>10180001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
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<td>10220001</td>
<td>10/1999</td>
<td>6/2012</td>
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<td>165</td>
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<td>6/2012</td>
<td>165</td>
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<td>10270001</td>
<td>10/1999</td>
<td>6/2012</td>
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<td>Little Sioux River near Milford</td>
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<td>10/1999</td>
<td>6/2012</td>
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<tr>
<td>Iowa River near Gifford</td>
<td>10420001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>146</td>
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<td>Boyer River near Missouri Valley</td>
<td>10430001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>146</td>
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<td>Soldier River near Pisgah</td>
<td>10430002</td>
<td>10/1998</td>
<td>6/2012</td>
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<td>Cedar Creek near Oakland Mills</td>
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<td>10/1998</td>
<td>6/2012</td>
<td>164</td>
<td>158</td>
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<td>West Fork Des Moines River near Humboldt</td>
<td>10460001</td>
<td>11/1998</td>
<td>6/2012</td>
<td>164</td>
<td>150</td>
</tr>
<tr>
<td>Indian Creek near Colfax</td>
<td>10500001</td>
<td>10/1999</td>
<td>6/2012</td>
<td>153</td>
<td>146</td>
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<tr>
<td>Old Maas Creek near Iowa City</td>
<td>10520001</td>
<td>5/2000</td>
<td>6/2012</td>
<td>146</td>
<td>139</td>
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<td>North Skunk River</td>
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<td>10/1998</td>
<td>6/2012</td>
<td>165</td>
<td>151</td>
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<tr>
<td>South Skunk River near Oskaloosa</td>
<td>10620001</td>
<td>10/1999</td>
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<td>10/1999</td>
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<td>Cedar Creek near Buxey</td>
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<td>10/1999</td>
<td>6/2012</td>
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<td>10/1999</td>
<td>6/2012</td>
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<td>Cedar River near Conwayville</td>
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<td>6/2012</td>
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<td>6/2012</td>
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<td>6/2012</td>
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<td>10770001</td>
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<td>10/1998</td>
<td>6/2012</td>
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<td>10/1998</td>
<td>6/2012</td>
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<td>Little Sioux River near Smithland</td>
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<td>6/2012</td>
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<td>10/2000</td>
<td>6/2012</td>
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<td>Cedar River at Cedar Bluff</td>
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<td>10/1999</td>
<td>7/2006</td>
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<td>Des Moines River near Keokuk</td>
<td>10560001</td>
<td>10/1999</td>
<td>11/2006</td>
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<td>Iowa River at Columbus Junction</td>
<td>10580001</td>
<td>10/1998</td>
<td>8/2006</td>
<td>95</td>
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<td>Iowa River near Lone Tree</td>
<td>10580002</td>
<td>9/2006</td>
<td>6/2012</td>
<td>70</td>
<td>64</td>
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<td>Whitebreast Creek near Dallas</td>
<td>10630003</td>
<td>4/2010</td>
<td>6/2012</td>
<td>27</td>
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<tr>
<td>Iowa River near Rowan</td>
<td>10990001</td>
<td>10/2000</td>
<td>11/2006</td>
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<td>Winnebago River at Mason City</td>
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<td>10/1999</td>
<td>9/2000</td>
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<td>Flood Creek at Greene</td>
<td>10340002</td>
<td>10/2000</td>
<td>9/2006</td>
<td>72</td>
<td>39</td>
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<tr>
<td>Des Moines River at Ottumwa</td>
<td>10900001</td>
<td>10/1999</td>
<td>9/2000</td>
<td>12</td>
<td>12</td>
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</tbody>
</table>
S2 Bootstrap Procedure for Computing the 95% Confidence Intervals

A measure of the uncertainty in the mean or median annual rate of change (in nitrate-nitrogen concentration) may be obtained by the method of bootstrapping, see Wu (1986). The estimates from the 46 sites are, however, spatially correlated, as depicted by their semivariogram shown in the upper panel of Fig. S1. Thus, we use the following bootstrapping method which accounts for the spatial correlation by first fitting the following spatial regression model:

\[ 12\beta_1 = s(\text{longitude}, \text{latitude}) + \epsilon, \]

where \( s(\text{longitude}, \text{latitude}) \) is a smooth function estimated from the data using the gam function of the R package mgcv. The regression errors are no longer spatially correlated, as confirmed by the residual semivariogram displayed in the lower panel of Fig. S1. We then (i) bootstrapped data by adding the randomly signed residuals to the fitted values, (ii) compute the overall mean (median) bootstrapped annual rate of change, and (iii) repeat steps (i) and (ii) 10,000 times to get 10,000 bootstrapped overall mean (median) annual rate of change. The 95% bootstrap confidence interval of the overall mean (median) annual rate of change is given by the 2.5 to 97.5 percentiles of the 10,000 bootstrap overall mean (median) annual rate of change.

Figure S1: The semivariogram of the annual rates of change (upper panel) and the residuals \( \epsilon \) (lower panel).
S3 Detailed Time-Series Analysis for 60 Ambient Iowa Sites

S3.1 Upper Iowa River near Dorchester

The monthly (mean nitrate-nitrogen concentration) data and its sample autocorrelation function (ACF) are shown in Figure S2.

Figure S2: The monthly data and its ACF for Upper Iowa River near Dorchester. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t-4.9216 - 0.0008t) = \varepsilon_t, \quad t = 1, ..., 165,
$$

$$(0.8770) (0.0091)$$

where

$$
\phi(B) = 1-0.5270B - 0.1395B^5 - 0.1431B^9 + 0.3259B^{10} - 0.2770B^{11},
$$

$$(0.0640) (0.0665) (0.0763) (0.0812) (0.0752)$$

the estimated variance of $\varepsilon_t$ is 2.127, and the AIC (of the fitted model) is 586.68. The trend coefficient is not significant, suggesting constant mean nitrate-nitrogen concentration over the study period. An outlier is detected and marked in Figure S2. (And the outlier is accounted...
Nitrate Concentration Trends in Iowa’s Rivers

for in the model.) Figure S3 shows the model diagnostics, including the the time plot of the standardized residuals (upper diagram) with its sample ACF (middle diagram) and the Box-Ljung tests (lower diagram). The model diagnostics show a good fit to the data.

Figure S3: The diagnostic checking for Upper Iowa River near Dorchester.

S3.2 West Fork Cedar River at Finchford

The monthly data with its (sample) ACF are shown in Figure S4.
The fitted model is

\[ \phi(B)(y_t - 7.2684 + 0.0082t) = \varepsilon_t, \quad t = 1, \ldots, 165, \]

\[
(1.1248) (0.0118)
\]

where

\[ \phi(B) = 1 - 0.5733B - 0.1121B^2 + 0.1587B^3 + 0.1223B^6 - 0.3320B^{11} + 0.1673B^{12} + 0.1777B^{13}, \]

\[
(0.0768) (0.0894) (0.0696) (0.0563) (0.0741) (0.0921) (0.0803)
\]

the estimated variance of \( \varepsilon_t \) is 4.555, and the AIC is 711.31. The trend coefficient is not significant. There are no outliers. The model diagnostics are shown in Figure S5 showing a good fit.
S3.3 South Raccoon River near Redfield

The monthly data and its ACFs are shown in Figure S6.

Figure S6: The monthly data and its ACF for South Raccoon River near Redfield.
The fitted model is

\[(y_t - 4.8837 - 0.0068t) = \varepsilon_t, \quad t = 1, \ldots, 153,\]

\[(0.9621) (0.0108)\]

where

\[\phi(B) = 1 - 0.8093B + 0.1623B^2 + 0.1402B^3 - 0.3316B^4 + 0.1370B^5,\]

\[(0.0749) (0.0733) (0.0560) (0.0592) (0.0623)\]

the estimated variance of \(\varepsilon_t\) is 3.499, and the AIC is 619.59. The trend coefficient is not significant. There are no outliers. The model diagnostics are shown in Figure S7, suggesting a good fit.

Figure S7: The diagnostic checking for South Raccoon River near Redfield.

S3.4 North Raccoon River near Jefferson

The monthly data and its ACFs are shown in Figure SS.
Figure S8: The monthly data and its ACF for North Raccoon River near Jefferson.

The fitted model is

\[ \phi(B)(y_t - 5.0019 - 0.0673 t) = \varepsilon_t, \quad t = 1, \ldots, 86, \]

\[ (3.0441) \quad (0.0483) \]

where

\[ \phi(B) = 1 - 0.6355B + 0.2868B^3 - 0.1580B^4 - 0.3735B^{11}, \]

\[ (0.0755) \quad (0.0943) \quad (0.0882) \quad (0.0707) \]

the estimated variance of \( \varepsilon_t \) is 9.694, and the AIC is 455.29. The trend coefficient is not significant. There are no outliers. The model diagnostics are given in Figure S9, indicating a good fit.
Figure S9: The diagnostic checking for North Raccoon River near Jefferson.
S3.5  Boone River near Stratford

The monthly data and its ACF are shown in Figure S10.

![Boone River near Stratford](image)

Figure S10: The monthly data and its ACF for Boone River near Stratford. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$
\phi(B)(yt-7.0075 + 0.0013t) = \varepsilon_t, \quad t = 1, \ldots, 153,
$$

$$(2.2651) \ (0.0234)$$

where

$$
\phi(B) = 1 - 0.5823B + 0.1376B^3 - 0.0940B^5,
$$

$$(0.0652) \ (0.0673) \ (0.0645)$$

$$
+ 0.1649B^7 - 0.1683B^9 - 0.2217B^{11}
$$

$$(0.0822) \ (0.0992) \ (0.0876)$$

the estimated variance of $\varepsilon_t$ is 14.48, and the AIC is 831.49. The trend coefficient is not significant. An outlier is detected and marked in Figure S10. The model diagnostics are given in Figure S11, suggesting a good fit.
Figure S11: The diagnostic checking for Boone River near Stratford.
S3.6 Maquoketa River at Maquoketa

The monthly data and its ACF are shown in Figure S12.

\[ \phi(B)(y_t - 6.7225 - 0.0004t) = \varepsilon_t, \quad t = 1, \ldots, 132, \]
\[ (0.7270) (0.0094) \]

where

\[ \phi(B) = 1 - 0.5911B + 0.1965B^2 - 0.2287B^5 + 0.1315B^6 - 0.1288B^{11}, \]
\[ (0.0868) (0.0846) (0.0829) (0.0867) (0.0778) \]

the estimated variance of \( \varepsilon_t \) is 2.958, and the AIC is 507.97. The trend coefficient is not significant. An outlier is detected and then marked in Figure S12. The model diagnostics given in Figure S13 indicate a good fit.
Figure S13: The diagnostic checking for Maquoketa River at Maquoketa.

S3.7 West Nishnabotna River near Malvern

The monthly data and its ACF are shown in Figure S14.
The fitted model is

\[
\phi(B)(y_t - 5.4775 - 0.0049t) = \varepsilon_t, \quad t = 1, \ldots, 164, \\
(1.1965) \quad (0.0122)
\]

where

\[
\phi(B) = 1 - 0.7480B + 0.2089B^2 - 0.2556B^3 + 0.1499B^4, \\
(0.0605) \quad (0.0859) \quad (0.1021) \quad (0.1004) \\
-0.1254B^5 + 0.1620B^8 - 0.2043B^{11} \\
(0.0842) \quad (0.0612) \quad (0.0575)
\]

the estimated variance of \(\varepsilon_t\) is 2.263, and the AIC is 574.06. The trend coefficient is not significant. The model diagnostics are given in Figure S15 indicating an adequate fit, although there is some evidence in the time plot of the residuals that the variance of the residuals became much smaller after 2010.
Figure S15: The diagnostic checking for West Nishabotna River near Malvern.

S3.8 Floyd River near Sioux City

The monthly data and its ACF are shown in Figure S16.
The fitted model is

$$\phi(B)(y_t-8.2992 - 0.0243t) = \varepsilon_t, \quad t = 1, \ldots, 165,$$

$$(0.5322) \quad (0.0059)$$

where

$$\phi(B) = 1-0.5344B + 0.1685B^{10} - 0.1473B^{11} - 0.1952B^{12},$$

$$(0.0603) \quad (0.0739) \quad (0.0870) \quad (0.0864)$$

$$+0.1870B^{13} + 0.2795B^{15} - 0.1236B^{18} + 0.2430B^{19}$$

$$(0.0763) \quad (0.0629) \quad (0.0723) \quad (0.0693)$$

the estimated variance of $\varepsilon_t$ is 6.469, and the AIC is 771.06. The trend coefficient is significant at 5% level. The model diagnostics are displayed in Figure S17, suggesting a good fit.
S3.9 South River near Ackworth

The monthly data and its ACF are shown in Figure S18.
Figure S18: The monthly data and its ACF for South River near Ackworth. The red
points and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

\[
\phi(B)(y_t-0.6601-0.0011t) = \varepsilon_t, \quad t = 1, \ldots, 153, \\
(0.1906) (0.0021)
\]

where

\[
\phi(B) = 1-0.2986B + 0.1257B^{10} - 0.3138B^{11}, \\
(0.0757) (0.0793) (0.0788)
\]

the estimated variance of \(\varepsilon_t\) is 0.4211, and the AIC is 305.94. The trend coefficient is not
significant. Two outliers are detected and then marked in Figure S18. The model diagnostics
shown in Figure S19 indicates a good fit.
S3.10 English River at Riverside

The monthly data and its ACF are shown in Figure S20.
Figure S20: The monthly data and its ACF for English River at Riverside. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t - 4.3285 - 0.0022t) = \varepsilon_t, \quad t = 1, \ldots, 165,
$$

$$(0.5626) \quad (0.0060)
$$

where

$$
\phi(B) = 1 - 0.6679B + 0.0889B^2 + 0.2149B^3
$$

$$(0.0748) \quad (0.0730) \quad (0.0679)
$$

$$
-0.1872B^{10} - 0.1443B^{12} + 0.2648B^{15},
$$

$$(0.0725) \quad (0.0582) \quad (0.0557)
$$

the estimated variance of $\varepsilon_t$ is 3.702, and the AIC is 682.37. The trend coefficient is not significant. An outlier is detected and then marked in Figure S20. The model diagnostics given in Figure S21 indicates an adequate fit although there is some evidence that the noise variance was much smaller after 2010.
S3.11 Yellow River near Volney

The monthly data and its ACF are shown in Figure S22.
Figure S22: The monthly data and its ACF for Yellow River near Volney. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

\[(1-0.7035B)(y_t - 4.9566 - 0.0050t) = \varepsilon_t, \quad t = 1, ..., 165,\]
\[(0.0582) \quad (0.5343) \quad (0.0055)\]

where the estimated variance of \(\varepsilon_t\) is 1.076, and the AIC is 459.06. The trend coefficient is not significant. Five outliers are detected and then marked in Figure S22. The model diagnostics shown in Figure S23 indicates a good fit.
S3.12 Chariton River near Centerville

The monthly data and its ACF are shown in Figure S24.
Figure S24: The monthly data and its ACF for Chariton River near Centerville. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

\[(1-0.6854B)(y_t - 0.4171 - 0.0015t) = \varepsilon_t, \quad t = 1, \ldots, 165,\]

\[
(0.0570) \quad (0.1189) \quad (0.0012)
\]

where the estimated variance of \(\varepsilon_t\) is 0.0609, and the AIC is 31.46. The trend coefficient is not significant. Nine outliers are detected and then marked in Figure S24. The model diagnostics shown in Figure S25 indicates an adequate fit, although the time plot of the residuals suggests volatility clustering in the data, i.e. there were alternating periods of lower variance followed by higher variance. The large number of outliers also indicates larger percent of atypical nitrate-nitrogen fluctuation.
S3.13  Beaver Creek near Cedar Falls

The monthly data and its ACF are shown in Figure S26.
Figure S26: The monthly data and its ACF for Beaver Creek near Cedar Falls. The blue line (in the upper panel) is the trend.

The fitted model is

\[ \phi(B)(y_t - 8.6933 + 0.0101t) = \varepsilon_t, \quad t = 1, \ldots, 165, \]

\[ (1.3232) \quad (0.0134) \]

where

\[ \phi(B) = 1 - 0.5959B + 0.2462B^4 - 0.1984B^5 + 0.1164B^8 - 0.3418B^{11}, \]

\[ (0.0538) \quad (0.0701) \quad (0.0687) \quad (0.0525) \quad (0.0539) \]

where the estimated variance of \( \varepsilon_t \) is 4.919, and the AIC is 688.97. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S27 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
Figure S27: The diagnostic checking for Beaver Creek near Cedar Falls.

S3.14 Wolf Creek at La Porte City

The monthly data and its ACF are shown in Figure S28.
Figure S28: The monthly data and its ACF for Wolf Creek at La Porte City. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 8.1527 - 0.0061t) = \varepsilon_t, \quad t = 1, ..., 153,$$

$$(0.7254) (0.0083)$$

where

$$\phi(B) = 1 - 0.6258B + 0.1602B^2 - 0.1796B^{11} - 0.1379B^{12}$$

$$(0.0789) (0.0759) (0.0687) (0.0731)$$

$$+ 0.2347B^{15} - 0.1195B^{16} + 0.1477B^{20}$$

$$(0.0773) (0.0758) (0.0553)$$

where the estimated variance of $\varepsilon_t$ is 4.36, and the AIC is 657.18. The trend coefficient is not significant. Two outliers are detected and then marked in Figure S28. The model diagnostics shown in Figure S29 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
S3.15 Black Hawk Creek at Waterloo

The monthly data and its ACF are shown in Figure S30.
Figure S30: The monthly data and its ACF for Black Hawk Creek at Waterloo. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

\[ \phi(B)(y_t - 8.5582 - 2.1 \times 10^{-5} t) = \varepsilon_t, \quad t = 1, \ldots, 153, \]

\[ (1.1243) \quad (0.0122) \]

where

\[ \phi(B) = 1 - 0.6044B + 0.1964B^3 - 0.2007B^6 + 0.1872B^7 - 0.2986B^{11} \]

\[ (0.0582) \quad (0.0588) \quad (0.0673) \quad (0.0706) \quad (0.0589) \]

where the estimated variance of \( \varepsilon_t \) is 5.192, and the AIC is 681.45. The trend coefficient is not significant. Two outliers are detected and then marked in Figure S30. The model diagnostics shown in Figure S31 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
Figure S31: The diagnostic checking for Black Hawk Creek at Waterloo.

S3.16 Cedar River near Janesville

The monthly data and its ACF are shown in Figure S32.
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Figure S32: The monthly data and its ACF for Cedar River near Janesville. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

\[ \phi(B)(y_t - 5.5051 - 0.0069t) = \varepsilon_t, \quad t = 1, \ldots, 153, \]

\[ (0.5919) \quad (0.0061) \]

where

\[ \phi(B) = 1 - 0.3180B + 0.1261B^{10} - 0.1376B^{11} - 0.1758B^{13} \]

\[ (0.0748) \quad (0.0785) \quad (0.0735) \quad (0.0761) \]

\[ + 0.1446B^{14} + 0.1217B^{15} + 0.1599B^{22} - 0.3651B^{23}, \]

\[ (0.0794) \quad (0.0736) \quad (0.0785) \quad (0.0750) \]

where the estimated variance of \( \varepsilon_t \) is 4.355, and the AIC is 681.7. The trend coefficient is not significant. Two outliers are detected and then marked in Figure S32. The model diagnostics shown in Figure S33 indicates a good fit.
Figure S33: The diagnostic checking for Cedar River near Janesville.

S3.17 Shell Rock River at Shell Rock

The monthly data and its ACF are shown in Figure S34.
Figure S34: The monthly data and its ACF for Shell Rock River at Shell Rock. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 5.0667 + 0.0027t) = \varepsilon_t, \quad t = 1, \ldots, 153,$$

(0.7701) (0.0081)

where

$$\phi(B) = 1 - 0.3688B - 0.1419B^{11} - 0.1045B^{13} + 0.2190B^{15}$$

(0.0690) (0.0706) (0.0733) (0.0643)

$$- 0.1830B^{18} + 0.1460B^{19} - 0.1363B^{23} - 0.1735B^{24},$$

(0.0653) (0.0737) (0.0765) (0.0840)

where the estimated variance of \(\varepsilon_t\) is 3.158, and the AIC is 613.04. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S35 indicates a good fit.
Figure S35: The diagnostic checking for Shell Rock River at Shell Rock.

S3.18 Cedar River at Cedar Bluff

The monthly data and its ACF are shown in Figure S36.
Figure S36: The monthly data and its ACF for Cedar River at Cedar Bluff. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t-4.3795-0.0233t) = \varepsilon_t, \quad t = 1, \ldots, 82,
$$

$$(0.8803) \quad (0.0174)$$

where

$$
\phi(B) = 1-0.4961B + 0.2029B^2 - 0.3304B^{11}
$$

$$(0.0990) \quad (0.1010) \quad (0.0912)$$

where the estimated variance of $\varepsilon_t$ is 3.654, and the AIC is 352.94. The trend coefficient is not significant. An outlier is detected and then marked in Figure S36. The model diagnostics shown in Figure S37 indicates a good fit.
S3.19 Little Sioux River near Larrabee

The monthly data and its ACF are shown in Figure S38.
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The fitted model is

$$\phi(B)(y_t - 3.6438 - 0.0150t) = \varepsilon_t, \quad t = 1, \ldots, 153,$$

$$(0.9564) (0.0104)$$

where

$$\phi(B) = 1 - 0.5791B + 0.2723B^3 - 0.2244B^4 + 0.1705B^9 - 0.2777B^{11},$$

$$(0.0650) \quad (0.0765) \quad (0.0758) \quad (0.0647) \quad (0.0648)$$

the estimated variance of $\varepsilon_t$ is 5.227, and the AIC is 673.4. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S39 indicates a good fit.
Figure S39: The diagnostic checking for Little Sioux River near Larrabee.

S3.20  Turkey River near Garber

The monthly data and its ACF are shown in Figure S40.
Figure S40: The monthly data and its ACF for Turkey River near Garber. The blue line (in the upper panel) is the trend.

The fitted model is

\[ \phi(B)(y_t-5.6599 - 0.0065t) = \varepsilon_t, \quad t = 1, \ldots, 153, \]

\[ (0.5229) (0.0058) \]

where

\[ \phi(B) = 1-0.2469B - 0.1193B^2 + 0.1739B^3 - 0.1760B^4, \]

\[ (0.0789) (0.0789) (0.0788) (0.0778) \]

\[ -0.1234B^5 + 0.2042B^6 - 0.2337B^7, \]

\[ (0.0767) (0.0773) (0.0776) \]

the estimated variance of \( \varepsilon_t \) is 2.82, and the AIC is 585.88. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S41 indicates a good fit.
Figure S41: The diagnostic checking for Turkey River near Garber.

S3.21 Volga River near Elkport

The monthly data and its ACF are shown in Figure S42.
Figure S42: The monthly data and its ACF for Volga River near Elkport. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 4.5584 - 0.0031t) = \varepsilon_t, \quad t = 1, \ldots, 165,$$

$$\begin{align*}
(0.4212) & \quad (0.0044)
\end{align*}$$

where

$$\phi(B) = 1 - 0.2508B - 0.1273B^2 + 0.1405B^3 - 0.1334B^4,$$

$$\begin{align*}
(0.0742) & \quad (0.0768) & \quad (0.0770) & \quad (0.0716)
\end{align*}$$

$$-0.2825B^{12} + 0.1063B^{14} + 0.1701B^{15}$$

$$\begin{align*}
(0.0712) & \quad (0.0777) & \quad (0.0778)
\end{align*}$$

the estimated variance of $\varepsilon_t$ is 2.789, and the AIC is 631.72. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S43 indicates a good fit.
Figure S43: The diagnostic checking for Volga River near Elkport.

S3.22  Bloody Run Creek Site #1 (BR01)

The monthly data and its ACF are shown in Figure S44.
Figure S44: The monthly data and its ACF for Bloody Run Creek Site #1 (BR01). The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 4.8343 - 0.0069t) = \varepsilon_t, \quad t = 1, \ldots, 257,$$

$$(0.6918) \ (0.0045)$$

where

$$\phi(B) = 1 - 0.6814B - 0.1198B^2 + 0.1113B^4 - 0.1414B^5,$$

$$(0.0659) \ (0.0746) \ (0.0741) \ (0.0738)$$

$$-0.1053B^7 + 0.105B^{10} - 0.0715B^{11}$$

$$(0.0636) \ (0.072) \ (0.0678)$$

the estimated variance of $\varepsilon_t$ is 0.3674, and the AIC is 484.45. The trend coefficient is not significant. Three outliers are detected and then marked in Figure S44. The model diagnostics shown in Figure S45 indicates a good fit.
To compare with other sites, we re-do the analysis for the sub-series over the time window from October 1998 to June 2012. Its sample ACF is shown in Figure S46.
Figure S46: The monthly data and its ACF for Bloody Run Creek Site #1 (BR01). The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t - 6.2751 + 0.0030t) = \varepsilon_t, \quad t = 1, \ldots, 165,
$$

$$
(0.6980) (0.0072)
$$

where

$$
\phi(B) = 1 - 0.8892B,
$$

$$
(0.0347)
$$

the estimated variance of $\varepsilon_t$ is 0.3039, and the AIC is 277.18. The trend coefficient is not significant. Four outliers are detected and then marked in Figure S46. The model diagnostics shown in Figure S47 indicates a good fit.
S3.23 Thompson Fork-Grand River at Davis City

The monthly data and its ACF are shown in Figure S48.
The fitted model is

$$\phi(B)(y_t - 0.7494 - 0.0041t) = \varepsilon_t, \quad t = 1, ..., 153,$$

$$(0.2197) \quad (0.0025)$$

where

$$\phi(B) = 1 - 0.4665B + 0.1934B^{10} - 0.3947B^{11} + 0.0981B^{15} + 0.1537B^{16},$$

$$(0.0636) \quad (0.0703) \quad (0.0714) \quad (0.0718) \quad (0.0757)$$

the estimated variance of $\varepsilon_t$ is 0.5813, and the AIC is 362.14. The trend coefficient is not significant. Three outliers are detected and then marked in Figure S48. The model diagnostics shown in Figure S49 indicates a good fit.
Figure S49: The diagnostic checking for Thompson Fork-Grand River at Davis City.

S3.24 Little Sioux River near Milford

The monthly data and its ACF are shown in Figure S50.
Figure S50: The monthly data and its ACF for Little Sioux River near Milford. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 3.7758 - 0.0143t) = \varepsilon_t, \quad t = 1, ..., 153,$$

$$(0.6313) (0.0073)$$

where

$$\phi(B) = 1 - 0.4392B - 0.1846B^5 + 0.0922B^7 + 0.1147B^9,$$

$$(0.0644) (0.0675) (0.0654) (0.0658)$$

$$-0.2888B^{11} + 0.2270B^{16} + 0.1491B^{21},$$

$$(0.0647) (0.0787) (0.0752)$$

the estimated variance of $\varepsilon_t$ is 5.441, and the AIC is 691.11. The trend coefficient is not significant. Three outliers are detected and then marked in Figure S50. The model diagnostics shown in Figure S51 indicates a good fit.
Figure S51: The diagnostic checking for Little Sioux River near Milford.

S3.25 Iowa River near Gifford

The monthly data and its ACF are shown in Figure S52.
Figure S52: The monthly data and its ACF for Iowa River near Gifford. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t-5.8781 + 0.0010t) = \varepsilon_t, \quad t = 1, ..., 153,$$

$$(1.7993) (0.0186)$$

where

$$\phi(B) = 1-0.4873B + 0.1394B^3 - 0.0967B^5 - 0.3511B^{11},$$

$$(0.0645) (0.0656) (0.0636) (0.0675)$$

the estimated variance of $\varepsilon_t$ is 8.897, and the AIC is 749.22. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S53 indicates a good fit.
S3.26  Boyer River near Missouri Valley

The monthly data and its ACF are shown in Figure S54.
Figure S54: The monthly data and its ACF for Boyer River near Missouri Valley. The blue line (in the upper panel) is the trend.

The fitted model is

\[ \phi(B)(y_t - 6.1096 - 0.0132t) = \varepsilon_t, \quad t = 1, \ldots, 153, \]

\[ (0.5380) \quad (0.0060) \]

where

\[ \phi(B) = 1 - 0.3532B - 0.1216B^2 + 0.2096B^3 - 0.1826B^{11}, \]

\[ (0.0788) \quad (0.0842) \quad (0.0799) \quad (0.0784) \]

the estimated variance of \( \varepsilon_t \) is 3.737, and the AIC is 620.07. The trend coefficient is significant at the 5% level. No outliers are detected. The model diagnostics shown in Figure S55 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after 2008.
Figure S55: The diagnostic checking for Boyer River near Missouri Valley.

S3.27 Soldier River near Pisgah

The monthly data and its ACF are shown in Figure S56.
Figure S56: The monthly data and its ACF for Soldier River near Pisgah. The blue line (in the upper panel) is the trend.

The fitted model is

\[ \phi(B)(y_t-5.1659 - 0.0029t) = \varepsilon_t, \quad t = 1, ..., 165, \]

\[ (1.4308) \quad (0.0143) \]

where

\[ \phi(B) = 1-0.6693B - 0.2252B^5, \]

\[ (0.0555) \quad (0.0579) \]

the estimated variance of \( \varepsilon_t \) is 1.303, and the AIC is 500.65. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S57 indicates a good fit.
Figure S57: The diagnostic checking for Soldier River near Pisgah.

S3.28 Cedar Creek near Oakland Mills

The monthly data and its ACF are shown in Figure S58.
Figure S58: The monthly data and its ACF for Cedar Creek near Oakland Mills. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 4.1266 + 0.0068t) = \varepsilon_t, \quad t = 1, ..., 164,$$

(1.0460) (0.0109)

where

$$\phi(B) = 1 - 0.4802B - 0.1551B^{11},$$

(0.0685) (0.0701)

the estimated variance of $\varepsilon_t$ is 6.818, and the AIC is 762.72. The trend coefficient is not significant. An outlier is detected and then marked in Figure S58. The model diagnostics shown in Figure S59 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
S3.29  West Fork Des Moines River near Humboldt

The monthly data and its ACF are shown in Figure S60.
Figure S60: The monthly data and its ACF for West Fork Des Moines River near Humboldt. The blue line (in the upper panel) is the trend.

The fitted model is

\[
\phi(B)(y_t - 4.7201 - 0.0009t) = \varepsilon_t, \quad t = 1, \ldots, 164, \\
(0.7465) \quad (0.0080)
\]

where

\[
\phi(B) = 1 - 0.5173B - 0.1414B^4 + 0.1054B^6 + 0.1940B^{10} \\
(0.0641) \quad (0.0666) \quad (0.0662) \quad (0.0749) \\
-0.3315B^{11} + 0.2361B^{15}, \\
(0.0745) \quad (0.0680)
\]

the estimated variance of \( \varepsilon_t \) is 5.629, and the AIC is 706.33. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S61 indicates a good fit.
Figure S61: The diagnostic checking for West Fork Des Moines River near Humboldt.

S3.30 North Fork Maquoketa River near Hurstville

The monthly data and its ACF are shown in Figure S62.
Figure S62: The monthly data and its ACF for North Fork Maquoketa River near Hurstville. The blue line (in the upper panel) is the trend.

The fitted model is

$$
\phi(B)(y_t - 6.9149 - 0.0015t) = \varepsilon_t, \quad t = 1, \ldots, 165,
$$

$$(0.4260) (0.0045)$$

where

$$
\phi(B) = 1 - 0.2938B - 0.2270B^5 - 0.1580B^7 + 0.1903B^8,
$$

$$(0.0723) (0.0706) (0.0749) (0.0757)$$

the estimated variance of $\varepsilon_t$ is 2.053, and the AIC is 575.59. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S63 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance beginning in 2009.
Figure S63: The diagnostic checking for North Fork Maquoketa River near Hurstville.

S3.31 Indian Creek near Colfax

The monthly data and its ACF are shown in Figure S64.
Figure S64: The monthly data and its ACF for Indian Creek near Colfax. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t-5.5959+0.0036t) = \varepsilon_t, \quad t = 1, ..., 153,$$

where

$$\phi(B) = 1-0.5681B + 0.1808B^2 - 0.1861B^3 - 0.1248B^5 - 0.3306B^{12} + 0.2395B^{13}$$

$$+0.3013B^{17} - 0.1891B^{18} + 0.2050B^{19} - 0.1939B^{23} - 0.1588B^{25},$$

the estimated variance of $\varepsilon_t$ is 6.783, and the AIC is 729.02. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S65 indicates a good fit.
S3.32 Old Mans Creek near Iowa City

The monthly data and its ACF are shown in Figure S66.
Figure S66: The monthly data and its ACF for Old Mans Creek near Iowa City. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 6.3718 + 0.0055t) = \varepsilon_t, \quad t = 1, ..., 146,$$

$$(1.5069) \quad (0.0171)$$

where

$$\phi(B) = 1 - 0.6383B + 0.1474B^2 - 0.2592B^{11},$$

$$(0.0794) \quad (0.0792) \quad (0.0637)$$

the estimated variance of $\varepsilon_t$ is 7.506, and the AIC is 687.57. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S67 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance beginning in 2009.
Figure S67: The diagnostic checking for Old Mans Creek near Iowa City.

S3.33 Wapsipinicon River near Olin

The monthly data and its ACF are shown in Figure S68.
Figure S68: The monthly data and its ACF for Wapsipinicon River near Olin. The blue line (in the upper panel) is the trend.

The fitted model is

$$
\phi(B)(y_t - 4.9471 - 0.0112t) = \varepsilon_t, \quad t = 1, \ldots, 86,
$$

$$(0.9614) (0.0190)$$

where

$$
\phi(B) = 1 - 0.4691B + 0.1229B^2 + 0.2725B^8 - 0.1772B^9 - 0.2088B^{11},
$$

$$(0.1017) (0.0977) (0.1018) (0.1071) (0.0983)$$

the estimated variance of $\varepsilon_t$ is 6.804, and the AIC is 424.71. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S69 indicates a good fit.
Figure S69: The diagnostic checking for Wapsipinicon River near Olin.

S3.34 North Skunk River

The monthly data and its ACF are shown in Figure S70.
Figure S70: The monthly data and its ACF for North Skunk River. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

\[ \phi(B)(y_t - 5.1486 + 0.0001t) = \varepsilon_t, \quad t = 1, \ldots, 165, \]

where

\[ \phi(B) = 1 - 0.6104B + 0.2135B^2 - 0.2060B^4 - 0.1175B^{11}, \]

\[ (0.0669) \quad (0.0775) \quad (0.0755) \quad (0.0715) \]

\[ -0.2034B^{12} + 0.1646B^{13} + 0.1459B^{16} \]

\[ (0.0777) \quad (0.0669) \quad (0.0698) \]

the estimated variance of \( \varepsilon_t \) is 3.661, and the AIC is 653. The trend coefficient is not significant.

Two outliers are detected and then marked in Figure S70. The model diagnostics shown in Figure S71 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
S3.35 East Fork of The Des Moines River near St. Joseph

The monthly data and its ACF are shown in Figure S72.
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The fitted model is

$$\phi(B)(y_t-6.9599 + 0.0022t) = \varepsilon_t, \quad t = 1, \ldots, 165,$$

$$(0.7178) (0.0080)$$

where

$$\phi(B) = 1-0.5743B + 0.1556B^3 - 0.1700B^4 + 0.1661B^6$$

$$(0.0635) (0.0780) (0.0804) (0.0650)$$

$$+0.1411B^9 - 0.1844B^{11} - 0.0678B^{14} - 0.0794B^{17}$$

$$(0.0653) (0.0659) (0.0678) (0.0794)$$

$$-0.1695B^{18} + 0.1131B^{20} - 0.2121B^{25} + 0.2339B^{26}$$

$$(0.0786) (0.0672) (0.0768) (0.0793)$$

the estimated variance of $\varepsilon_t$ is 10.05, and the AIC is 847.66. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S73 indicates a good fit.
Figure S73: The diagnostic checking for East Fork of The Des Moines River near St. Joseph.

S3.36 Des Moines River near Keokuk

The monthly data and its ACF are shown in Figure S74.
Figure S74: The monthly data and its ACF for Des Moines River near Keokuk. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 1.9632 - 0.0426t) = \varepsilon_t, \quad t = 1, ..., 86,$$

$$\quad (1.2408) (0.0228)$$

where

$$\phi(B) = 1 - 0.7016B + 0.2292B^2 - 0.2811B^{11},$$

$$\quad (0.0980) \quad (0.0978) \quad (0.0797)$$

the estimated variance of $\varepsilon_t$ is 3.658, and the AIC is 367.68. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S75 indicates a good fit.
Figure S75: The diagnostic checking for Des Moines River near Keokuk.

S3.37 Iowa River at Columbus Junction

The monthly data and its ACF are shown in Figure S76.
Figure S76: The monthly data and its ACF for Iowa River at Columbus Junction. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 4.5407 - 0.0101t) = \varepsilon_t, \quad t = 1, \ldots, 95,$$

$$(0.3570) (0.0065)$$

where

$$\phi(B) = 1 - 0.3452B - 0.1699B^2 + 0.1676B^3 + 0.1188B^5 + 0.1316B^7 + 0.1358B^{10},$$

$$(0.0844) (0.0926) (0.0831) (0.0766) (0.0813) (0.0855)$$

$$- 0.1705B^{11} + 0.1329B^{12} + 0.1946B^{15} + 0.2772B^{21} - 0.4047B^{23}$$

$$(0.0864) (0.0884) (0.0841) (0.0861) (0.0874)$$

the estimated variance of $\varepsilon_t$ is 2.781, and the AIC is 402.01. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S77 indicates a good fit.
Figure S77: The diagnostic checking for Iowa River at Columbus Junction.

S3.38 Iowa River near Lone Tree

The monthly data and its ACF are shown in Figure S78.
The monthly data and its ACF for Iowa River near Lone Tree. The blue line (in the upper panel) is the trend.

The fitted model is

\[
\phi(B)(y_t - 6.6798 + 0.0406t) = \varepsilon_t, \quad t = 1, \ldots, 70,
\]

\[
(0.4933) \quad (0.0117)
\]

where

\[
\phi(B) = 1 - 0.4789B + 0.2020B^3 + 0.3471B^8,
\]

\[
(0.1052) \quad (0.1064) \quad (0.1086)
\]

the estimated variance of \(\varepsilon_t\) is 3.267, and the AIC is 270.32. The trend coefficient is significant at the 5% level, which might be caused by small sample size. No outliers are detected. The model diagnostics shown in Figure S79 indicates a good fit.
Figure S79: The diagnostic checking for Iowa River near Lone Tree.

S3.39 South Skunk River near Oskaloosa

The monthly data and its ACF are shown in Figure S80.
Figure S80: The monthly data and its ACF for South Skunk River near Oskaloosa. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 4.854 - 0.0026t) = \varepsilon_t, \quad t = 1, \ldots, 153,$$

(2.242) (0.0217)

where

$$\phi(B) = 1 - 0.5595B + 0.1729B^3 - 0.1022B^5 - 0.2174B^{11} - 0.1460B^{12},$$

(0.0666) (0.0618) (0.0580) (0.0713) (0.0786)

the estimated variance of $\varepsilon_t$ is 8.18, and the AIC is 743.83. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S81 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
Figure S81: The diagnostic checking for South Skunk River near Oskaloosa.

S3.40 Whitebreast Creek near Knoxville

The monthly data and its ACF are shown in Figure S82.
Figure S82: The monthly data and its ACF for Whitebreast Creek near Knoxville. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

\[ \phi(B)(y_t - 0.7219 - 0.0023t) = \epsilon_t, \quad t = 1, \ldots, 126, \]

\[ (0.1615) \quad (0.0023) \]

where

\[ \phi(B) = 1 - 0.1600B + 0.1943B^6 - 0.2478B^{11}, \]

\[ (0.0899) \quad (0.0907) \quad (0.0899) \]

the estimated variance of \( \epsilon_t \) is 0.5348, and the AIC is 279.1. The trend coefficient is not significant. An outlier is detected and then marked in Figure S82. The model diagnostics shown in Figure S83 indicates a good fit.
Figure S83: The diagnostic checking for Whitebreast Creek near Knoxville.

S3.41 Cedar Creek near Bussey

The monthly data and its ACF are shown in Figure S84.
Figure S84: The monthly data and its ACF for Cedar Creek near Bussey. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t - 0.4615 - 0.0007t) = \varepsilon_t, \quad t = 1, ..., 153,
$$

(0.1018) (0.0011)

where

$$
\phi(B) = 1 - 0.2239B - 0.1482B^2 + 0.2103B^6 - 0.2595B^{11},
$$

(0.0783) (0.0770) (0.0821) (0.0776)

the estimated variance of $\varepsilon_t$ is 0.1464, and the AIC is 160.84. The trend coefficient is not significant. Five outliers are detected and then marked in Figure S84. The model diagnostics shown in Figure S85 indicates a good fit.
S3.42 Whitebreast Creek near Dallas

The monthly data and its ACF are shown in Figure S86.
Figure S86: The monthly data and its ACF for Whitebreast Creek near Dallas. The blue line (in the upper panel) is the trend.

The fitted model is

\[ y_t - 0.7170 - 0.0062t = \varepsilon_t, \quad t = 1, \ldots, 27, \]

\( (0.1821) (0.0114) \)

where the estimated variance of \( \varepsilon_t \) is 0.2116, and the AIC is 38.68. The trend coefficient is not significant. No outliers are detected. Actually, the sample size is only 27 so that we cannot find any mechanism of the change of the N-N content. The model diagnostics shown in Figure S87 indicates that this data is a white noise after detrending.
Figure S87: The diagnostic checking for Whitebreast Creek near Dallas.

S3.43 Maple River near Mapleton

The monthly data and its ACF are shown in Figure S88.
Figure S88: The monthly data and its ACF for Maple River near Mapleton. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 7.3742 - 0.0139t) = \varepsilon_t, \quad t = 1, \ldots, 153,$$

$$(0.8632) \; (0.0098)$$

where

$$\phi(B) = 1 - 0.5223B - 0.2508B^2 + 0.3246B^3 - 0.2108B^5 + 0.1919B^7 - 0.1715B^9$$

$$(0.0742) \; (0.0806) \; (0.0757) \; (0.0738) \; (0.0688) \; (0.0672)$$

$$- 0.2490B^{12} + 0.1791B^{13} + 0.2303B^{16} - 0.1718B^{17} + 0.1967B^{20},$$

$$(0.0741) \; (0.0765) \; (0.0776) \; (0.0825) \; (0.0729)$$

where the estimated variance of $\varepsilon_t$ is 2.942, and the AIC is 606.88. The trend coefficient is not significant. An outlier is detected and then marked in Figure S88. The model diagnostics shown in Figure S89 indicates a good fit.
Figure S89: The diagnostic checking for Maple River near Mapleton.

S3.44 Cedar River near Conesville

The monthly data and its ACF are shown in Figure S90.
Nitrate Concentration Trends in Iowa’s Rivers

Figure S90: The monthly data and its ACF for Cedar River near Conesville. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t-4.8213-0.0053t) = \epsilon_t, \quad t = 1, \ldots, 153,$$

$$\begin{align*}
\phi(B) &= 1-0.4173B + 0.1305B^2 - 0.1809B^6 + 0.1114B^7 - 0.210B^{11}, \\
&\quad (0.0597) \quad (0.0718) \quad (0.0767) \quad (0.0725) \quad (0.068) \\
&+0.1669B^{17} - 0.1824B^{18} + 0.1260B^{20} + 0.1504B^{21} - 0.3988B^{23}, \\
&\quad (0.0788) \quad (0.0791) \quad (0.0717) \quad (0.0763) \quad (0.0749)
\end{align*}$$

where the estimated variance of $\epsilon_t$ is 3.566, and the AIC is 637.01. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S91 indicates a good fit.
Figure S91: The diagnostic checking for Cedar River near Conesville.

S3.45 West Nodaway River near Shambaugh

The monthly data and its ACF are shown in Figure S92.
Figure S92: The monthly data and its ACF for West Nodaway River near Shambaugh. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 2.1289 - 0.0144t) = \varepsilon_t, \quad t = 1, \ldots, 153,$$

$$(0.5977) \quad (0.0068)$$

where

$$\phi(B) = 1 - 0.6418B + 0.0873B^2 + 0.2794B^3 - 0.4933B^4 + 0.1853B^5$$

$$(0.0650) \quad (0.0608) \quad (0.0719) \quad (0.0746) \quad (0.0664)$$

where the estimated variance of $\varepsilon_t$ is 2.458, and the AIC is 570.98. The trend coefficient is not significant. Three outliers are detected and then marked in Figure S92. The model diagnostics shown in Figure S93 indicates an adequate fit, although the time plot of the residuals suggests volatility clustering.
Figure S93: The diagnostic checking for West Nodaway River near Shambaugh.

S3.46 East Nodaway River near Clarinda

The monthly data and its ACF are shown in Figure S94.
Figure S94: The monthly data and its ACF for East Nodaway River near Clarinda. The blue line (in the upper panel) is the trend.

The fitted model is

\[ \phi(B)(y_t - 1.7922 - 0.0136 t) = \varepsilon_t, \quad t = 1, \ldots, 153, \]

\[ (0.7594) (0.0084) \]

where

\[ \phi(B) = 1 - 0.3888B - 0.1500B^2 + 0.2050B^3 + 0.1461B^{10} \]

\[ (0.0798) (0.0848) (0.0717) (0.0733) \]

\[ -0.3735B^{11} - 0.1770B^{12} + 0.1489B^{13} \]

\[ (0.0807) (0.0873) (0.0851) \]

where the estimated variance of \( \varepsilon_t \) is 4.544, and the AIC is 657.94. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S95 indicates an adequate fit, although the time plot of the residuals suggests volatility clustering.
Figure S95: The diagnostic checking for East Nodaway River near Clarinda.

S3.47 Beaver Creek near Grimes

The monthly data and its ACF are shown in Figure S96.
Figure S96: The monthly data and its ACF for Beaver Creek near Grimes. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 6.2537 - 0.0094t) = \varepsilon_t, \quad t = 1, ..., 153,$$

(1.5343) (0.0168)

where

$$\phi(B) = 1 - 0.5079B - 0.0879B^{11} - 0.3932B^{12} + 0.1133B^{13} + 0.1683B^{15}$$

(0.0509) (0.0376) (0.0570) (0.0477) (0.0366)

where the estimated variance of $\varepsilon_t$ is 9.443, and the AIC is 766.89. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S97 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
S3.48 Wapsipinicon River at De Witt

The monthly data and its ACF are shown in Figure S98.
Figure S98: The monthly data and its ACF for Wapsipinicon River at De Witt. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

\[
\phi(B)(y_t - 4.6030 - 0.0092t) = \varepsilon_t, \quad t = 1, \ldots, 153,
\]

\[
(0.9656) (0.0102)
\]

where

\[
\phi(B) = 1 - 0.4468B + 0.1659B^2 - 0.2254B^11 - 0.2180B^12
\]

\[
(0.0789) (0.0735) (0.0743) (0.0811)
\]

where the estimated variance of \(\varepsilon_t\) is 4.507, and the AIC is 651.82. The trend coefficient is not significant. An outlier is detected and then marked in Figure S98. The model diagnostics shown in Figure S99 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after end of 2007.
Figure S99: The diagnostic checking for Wapsipinicon River at De Witt.

S3.49 Rock River near Hawarden

The monthly data and its ACF are shown in Figure S100
Figure S100: The monthly data and its ACF for Rock River near Hawarden. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 5.2736 - 0.0274t) = \varepsilon_t, \quad t = 1, ..., 153, $$

$$(0.7642) (0.0088)$$

where

$$\phi(B) = 1 - 0.7117B + 0.2481B^3 - 0.1633B^4 + 0.2155B^{10}$$

$$(0.0620) (0.0705) (0.0693) (0.0708)$$

$$- 0.2565B^{11} - 0.2946B^{12} + 0.3822B^{13}$$

$$(0.0857) (0.0849) (0.0730)$$

where the estimated variance of $\varepsilon_t$ is 3.839, and the AIC is 637.21. The trend coefficient is significant at 5% level. No outliers are detected. The model diagnostics shown in Figure S101 indicates an adequate fit, although the time plot of the residuals suggests a smaller noise variance after 2008.
Figure S101: The diagnostic checking for Rock River near Hawarden.

S3.50 Middle River near Indianola

The monthly data and its ACF are shown in Figure S102.
Figure S102: The monthly data and its ACF for Middle River near Indianola. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t-1.8993 - 0.0030t) = \varepsilon_t, \quad t = 1, \ldots, 165,$$

$$(0.4378) (0.0046)$$

where

$$\phi(B) = 1 - 0.6771B + 0.2356B^3 - 0.2622B^4 + 0.1470B^6$$

$$(0.0630) (0.0827) (0.0829) (0.0639)$$

$$- 0.1692B^{11} + 0.1063B^{14} + 0.1302B^{16}$$

$$(0.0594) (0.0651) (0.0657)$$

where the estimated variance of $\varepsilon_t$ is 1.726, and the AIC is 534.56. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S103 indicates a good fit.
Figure S103: The diagnostic checking for Middle River near Indianola.

S3.51 North River near Norwalk

The monthly data and its ACF are shown in Figure S104
Figure S104: The monthly data and its ACF for North River near Norwalk. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 4.1824 - 2.272 \times 10^{-5}t) = \varepsilon_t, \quad t = 1, \ldots, 165,$$

$$(0.8014) \quad (0.0084)$$

where

$$\phi(B) = 1 - 0.6066B - 0.1199B^{12} + 0.2033B^{14} - 0.1778B^{15} + 0.1797B^{16}$$

$$(0.0605) \quad (0.0594) \quad (0.0750) \quad (0.0842) \quad (0.0705)$$

$$+ 0.1316B^{21} - 0.1887B^{23} - 0.2035B^{24} + 0.1796B^{25}$$

$$(0.0584) \quad (0.0755) \quad (0.0889) \quad (0.0763)$$

where the estimated variance of $\varepsilon_t$ is 4.282, and the AIC is 711.69. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S105 indicates an adequate fit.
Figure S105: The diagnostic checking for North River near Norwalk.

S3.52  Little Sioux River near Smithland

The monthly data and its ACF are shown in Figure S106.
Figure S106: The monthly data and its ACF for Little Sioux River near Smithland. The red point and the blue line (in the upper panel) are the outlier and the trend, respectively.

The fitted model is

$$\phi(B)(y_t - 5.3231 - 0.0024t) = \epsilon_t, \quad t = 1, \ldots, 165,$$

$$(0.7235) (0.0076)$$

where

$$\phi(B) = 1 - 0.6777B - 0.1245B^{11} + 0.1986B^{14} + 0.1853B^{17} - 0.2782B^{18}$$

$$(0.0496) (0.0524) (0.0481) (0.0683) (0.0862)$$

$$+ 0.1356B^{19} + 0.1488B^{20} + 0.0952B^{22} - 0.3207B^{24}$$

$$(0.0885) (0.0755) (0.0753) (0.0707)$$

where the estimated variance of $\epsilon_t$ is 2.573, and the AIC is 604.64. The trend coefficient is not significant. An outlier is detected and then marked in Figure S106. The model diagnostics shown in Figure S107 indicates an adequate fit.
Figure S107: The diagnostic checking for Little Sioux River near Smithland.

S3.53 West Fork Ditch at Hornick

The monthly data and its ACF are shown in Figure S108
Figure S108: The monthly data and its ACF for West Fork Ditch at Hornick. The red points and the blue line (in the upper panel) are the outliers and the trend, respectively.

The fitted model is

$$
\phi(B)(y_t-8.1491-0.0126t) = \varepsilon_t, \quad t = 1, \ldots, 141,
$$

$$
(0.5142) \quad (0.0064)
$$

where

$$
\phi(B) = 1-0.5987B + 0.2019B^3 + 0.1848B^8 - 0.1140B^{11}
$$

$$
(0.0692) \quad (0.0746) \quad (0.0739) \quad (0.0775)
$$

where the estimated variance of $\varepsilon_t$ is 4.065, and the AIC is 586.36. The trend coefficient is significant at 5% level. Two outliers are detected and then marked in Figure S108. The model diagnostics shown in Figure S109 indicates a good fit.
S3.54 Iowa River near Rowan

The monthly data and its ACF are shown in Figure S110.
Figure S110: The monthly data and its ACF for Iowa River near Rowan. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 6.7844 - 0.00196t) = \varepsilon_t, \quad t = 1, \ldots, 74,$$

$$\text{(0.8128) (0.0190)}$$

where

$$\phi(B) = 1 - 0.4975B + 0.2790B^3 + 0.1967B^7,$$

$$\text{(0.0983) (0.1028) (0.1055)}$$

where the estimated variance of $\varepsilon_t$ is 10.11, and the AIC is 392.05. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S111 indicates a good fit.
S3.55 Other sites

There are 6 sites with inadequate data, see Table S2. Nonetheless, we still perform the model-based analysis.

Table S2: The names with ID No. and the No. of observations of 6 sites.

<table>
<thead>
<tr>
<th>Site Name</th>
<th>ID No.</th>
<th>No. of observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winnebago River at Mason City</td>
<td>10170001</td>
<td>12</td>
</tr>
<tr>
<td>Flood Creek at Greene</td>
<td>10340002</td>
<td>39</td>
</tr>
<tr>
<td>Iowa River near Marshalltown</td>
<td>10640001</td>
<td>12</td>
</tr>
<tr>
<td>Monona-Harrison Ditch</td>
<td>10670001</td>
<td>12</td>
</tr>
<tr>
<td>South Skunk River near Ames</td>
<td>10850001</td>
<td>16</td>
</tr>
<tr>
<td>Des Moines River at Ottumwa</td>
<td>10990001</td>
<td>12</td>
</tr>
</tbody>
</table>

Winnebago River at Mason City

The monthly data and its ACF are shown in Figure S112.
Figure S112: The monthly data and its ACF for Winnebago River at Mason City. The blue line (in the upper panel) is the trend.

The fitted model is

$$y_t - 2.9682 - 0.2280t = \varepsilon_t, \quad t = 1, \ldots, 12,$$

$$\text{(1.4730)} \text{ (0.2001)}$$

where the estimated variance of $\varepsilon_t$ is 5.728, and the AIC is 59. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S115 indicates a good fit.
Figure S113: The diagnostic checking for Winnebago River at Mason City.

Flood Creek at Greene

The monthly data and its ACF are shown in Figure S114.
Figure S114: The monthly data and its ACF for Flood Creek at Greene. The blue line (in the upper panel) is the trend.

The fitted model is

\[
\phi(B)(y_t - 8.7497 - 0.0517t) = \varepsilon_t, \quad t = 1, ..., 72,
\]

\[(1.0321) \quad (0.0195)\]

where

\[
\phi(B) = 1 - 0.2612B + 0.4889B^5,
\]

\[(0.1299) \quad (0.1371)\]

where the estimated variance of \(\varepsilon_t\) is 5.788, and the AIC is 193.88. The trend coefficient is significant at the 5% level. No outliers are detected. The model diagnostics shown in Figure S115 indicates a good fit.
Figure S115: The diagnostic checking for Flood Creek at Greene.

Iowa River near Marshalltown

The monthly data and its ACF are shown in Figure S118
Figure S116: The monthly data and its ACF for Iowa River near Marshalltown. The blue line (in the upper panel) is the trend.

The fitted model is

$$\phi(B)(y_t - 0.4254 - 0.5898t) = \varepsilon_t, \quad t = 1, \ldots, 12,$$

(1.4615) (0.2076)

where

$$\phi(B) = 1 + 0.5864B^2,$$

(0.2446)

where the estimated variance of $\varepsilon_t$ is 9.665, and the AIC is 68.12. The trend coefficient is significant at the 5% level. No outliers are detected. The model diagnostics shown in Figure S119 indicates a good fit.
Monona-Harrison Ditch

The monthly data and its ACF are shown in Figure S118.
Figure S118: The monthly data and its ACF for Monona-Harrison Ditch. The blue line (in the upper panel) is the trend.

The fitted model is

$$
\phi(B)(y_t - 7.5648 + 0.5388t) = \varepsilon_t, \quad t = 1, \ldots, 12,
$$

$$(1.4615) \quad (0.2076)$$

where

$$\phi(B) = 1 - 0.5308B,$$

$$\quad (0.2497)$$

where the estimated variance of $\varepsilon_t$ is 0.7318, and the AIC is 36.64. The trend coefficient is significant at the 5% level. No outliers are detected. The model diagnostics shown in Figure S119 indicates a good fit.
South Skunk River near Ames

The monthly data and its ACF are shown in Figure S120.
Figure S120: The monthly data and its ACF for South Skunk River near Ames. The blue line (in the upper panel) is the trend.

The fitted model is

$$
\phi(B)(y_t - 11.7858 + 0.4528t) = \epsilon_t, \quad t = 1, ..., 12,
$$

$$(3.2700) (0.2167)$$

where

$$
\phi(B) = 1 - 0.5491B,
$$

$$(0.2142)$$

where the estimated variance of $\epsilon_t$ is 13.67, and the AIC is 94.93. The trend coefficient is significant at the 5% level. No outliers are detected. The model diagnostics shown in Figure S121 indicates a good fit.
Figure S121: The diagnostic checking for South Skunk River near Ames.

Des Moines River at Ottumwa

The monthly data and its ACF are shown in Figure S122
Figure S122: The monthly data and its ACF for Des Moines River at Ottumwa. The blue line (in the upper panel) is the trend.

The fitted model is

\[ y_t - 1.9530 - 0.0752t = \varepsilon_t, \quad t = 1, ..., 12, \]

\[ (0.7129) (0.0969) \]

where the estimated variance of \( \varepsilon_t \) is 1.342, and the AIC is 41.58. The trend coefficient is not significant. No outliers are detected. The model diagnostics shown in Figure S123 indicates a good fit.
Figure S123: The diagnostic checking for Des Moines River at Ottumwa.

Reference