# Spatiotemporal Variability of Water Quality and Stable Water Isotopes in an Intensively Managed Prairie Watershed

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## I Background

Eutrophication, has been identified as an important water quality issue for freshwater systems (Barlow, et al., 2004). Factors impacting watershed management in Prairie landscapes include extensive land drainage networks (Seine-Rat River Conservation District, 2009), non point source loading from land use practices (Kaste, et al., 2006), and lack of water quality data (Dawson, et al., 2012).

Studies indicate that watershed analysis and data collection can become less intensive and more reliable as stable water isotopic ratios offer high spatial and temporal resolution (Dawson, et al., 2012).

## II Objectives

The overall goal of this research was to examine the spatiotemporal variability and usefulness of stable water isotopes in a typical, intensively managed Prairie watershed by:

1. Assessing the differences in stable water isotopic ratios between natural waterways and artificial waterways such as drains and diversions
2. Quantifying the strength of the relationship between topographic and land use characteristics and stable water isotopic ratios
3. Predicting water quality ($PO_4$ concentrations) using stable water isotopic ratios.

## III Study area

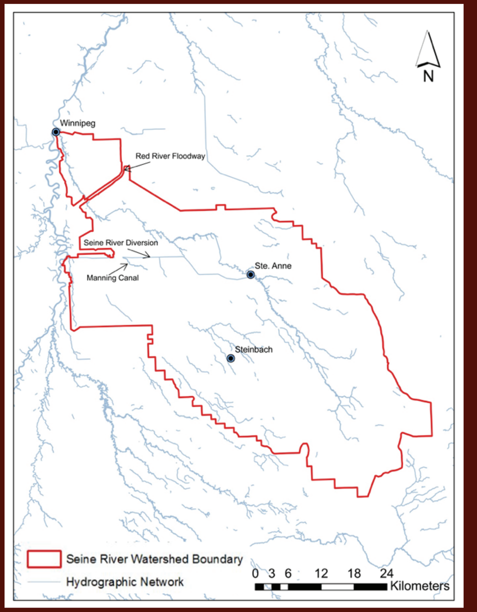


Figure 1 – Location and boundaries of the Seine River Watershed.

Seine River watershed:

- 2509 km$^2$ (Jones & Armstrong, 2001)
- Drains into the Red River and then Lake Winnipeg
- 87% land use is agricultural (Jones & Armstrong, 2001)
- 21% of Manitoba's hog population (Seine-Rat River Conservation District, 2009)
- Significant increases in nutrient loading between 1973 and 1999 (Seine-Rat River Conservation District, 2009)
  - o 188% for Total Phoshorus
  - o 75% for Total Nitrogen

(A) (B)

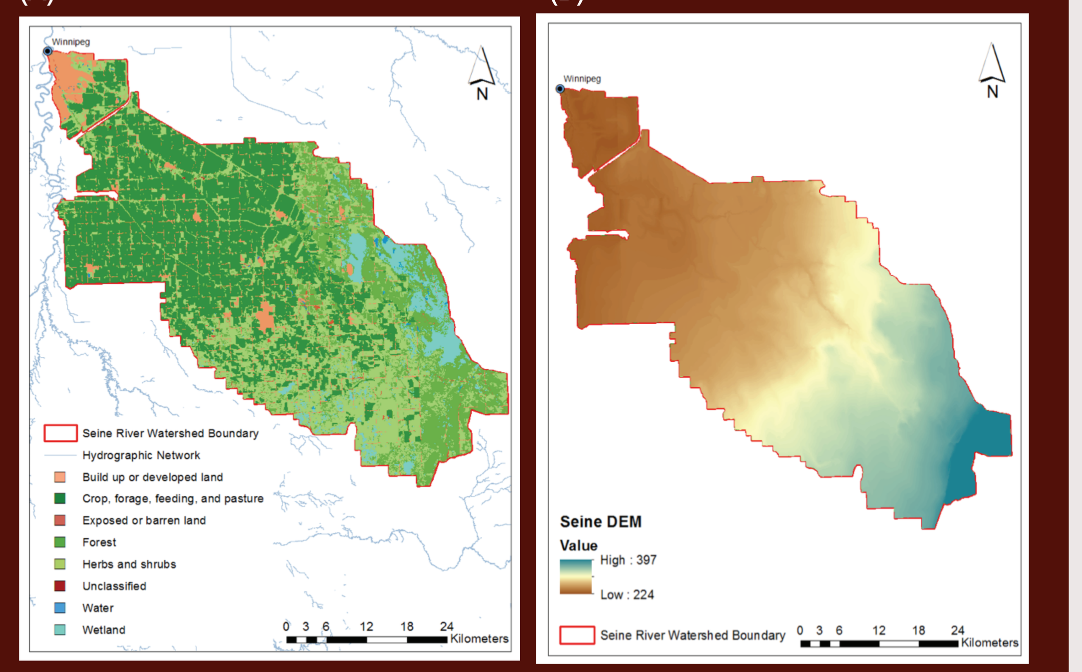


Figure 2– (A) Land use and land cover for the Seine River Watershed. Horizontal resolution=100m. (B) Digital elevation model (DEM) for the Seine River Watershed. Horizontal resolution=30m.

## IV Data collection

Weekly sampling between May 8 and June 18, 2013 (7 weeks in total)
3 precipitation collectors + 24 surface water-sampling sites:

- 17 on natural waterways
- 3 on drains
- 4 on the Seine River Diversion.

All samples tested for $\delta^{18}O$ and $\delta^2H$ (PicarroTM CRDS liquid water isotope) and $PO_4$ concentration (LamotteTM colorimeter after filtration)

(A) (B)

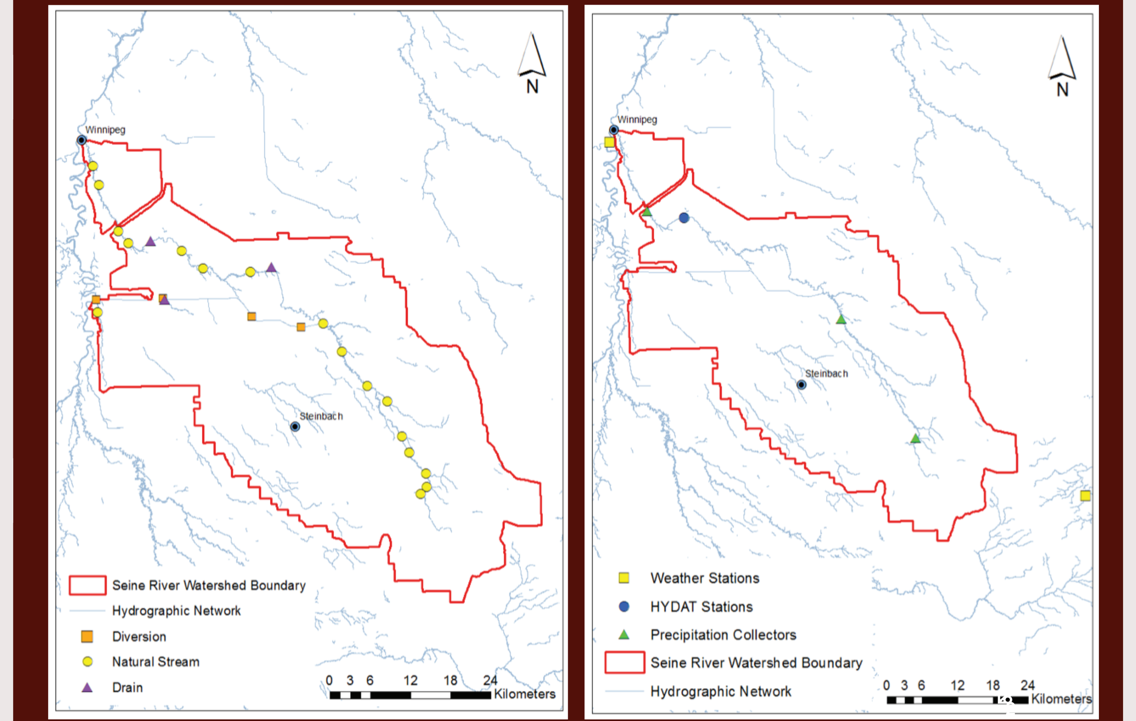


Figure 3 – (A) Surface-water sampling points. (B) Precipitation collectors throughout the watershed along with Environment Canada weather stations and hydrometric stations (HYDAT).

## V Data analysis

### i. To assess differences in stable water isotopic ratios between waterways: Kruskal-Wallis test

- Null hypothesis: precipitation and the three types of waterways show similar $\delta^{18}O$ and $\delta^2H$
- Alternative hypothesis: At least one type of waterway show different $\delta^{18}O$ and $\delta^2H$.

### ii. To quantify the strength of relationship between watershed characteristics and stable water isotopic ratios: Partial correlation analysis

- Sub-watersheds were delineated upstream of each surface water sampling point
- Topographical and land use characteristics were determined

Table 1 – Sub-watershed characteristics associated with each of the twenty-four surface-water sampling points

| Topographic variables | Land use and land cover |
|---|---|
| Gross drainage area | % Wetland |
| Mean slope | % Herbs and shrubs |
| Minimum slope | % Forest |
| Maximum slope | % Crop, and pasture |
| Standard deviation of slope | % Build up or developed land |
| Mean elevation | % Exposed and barren land |
| Minimum elevation | % Water |
| Maximum elevation | % Unclassified |
| Standard deviation of elevation | |

### iii. To predict $PO_4$ concentrations using stable water isotopic ratios: Regression analysis

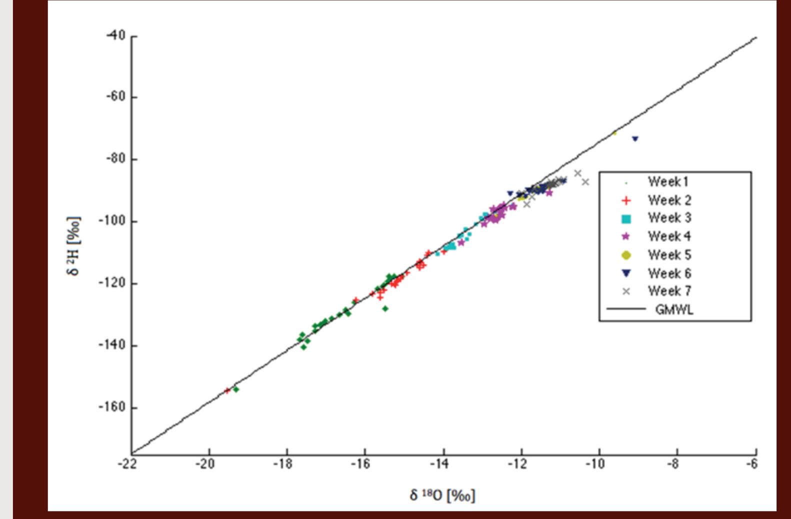
- Dependent variable: $PO_4$ concentrations
- Independent variable: $\delta^{18}O$ or $\delta^2H$
- Controlling variables: the effect of selected watershed characteristics on regression results was assessed.

## VI Results and discussion

### i. Sampling conditions

Table 2 – 7 day antecedent precipitation stations ( Environment Canada http://climate.weather.gc.ca/) and daily flow (http://www.wsc.ec.gc.ca/applications/H2O/index-eng.cfm) associated with each sampling date.

| Week | Sampling Date | 7-Day Total Precipitation [mm] | Daily Flow [m³/s] |
|---|---|---|---|
| 1 | May 8, 2013 | *125.6 (snowmelt) | 2.35 |
| 2 | May 14, 2013 | 0.65 | 1.53 |
| 3 | May 21, 2013 | 55.10 | 1.69 |
| 4 | May 28, 2013 | 0.20 | 1.74 |
| 5 | June 5, 2013 | 39.50 | 2.51 |
| 6 | June 11, 2013 | 29.30 | 2.49 |
| 7 | June 18, 2013 | 5.55 | 1.42 |



According to the global meteoric water line (GMWL), the Seine River Watershed is in non-equilibrium and surface water evaporation leads to depleted $\delta^2H$ and $\delta^{18}O$ values.

Figure 4 – Weekly $\delta^2H$ and $\delta^{18}O$ values in ‰ surface water samples compared to the Global Meteoric Water Line (GMWL).

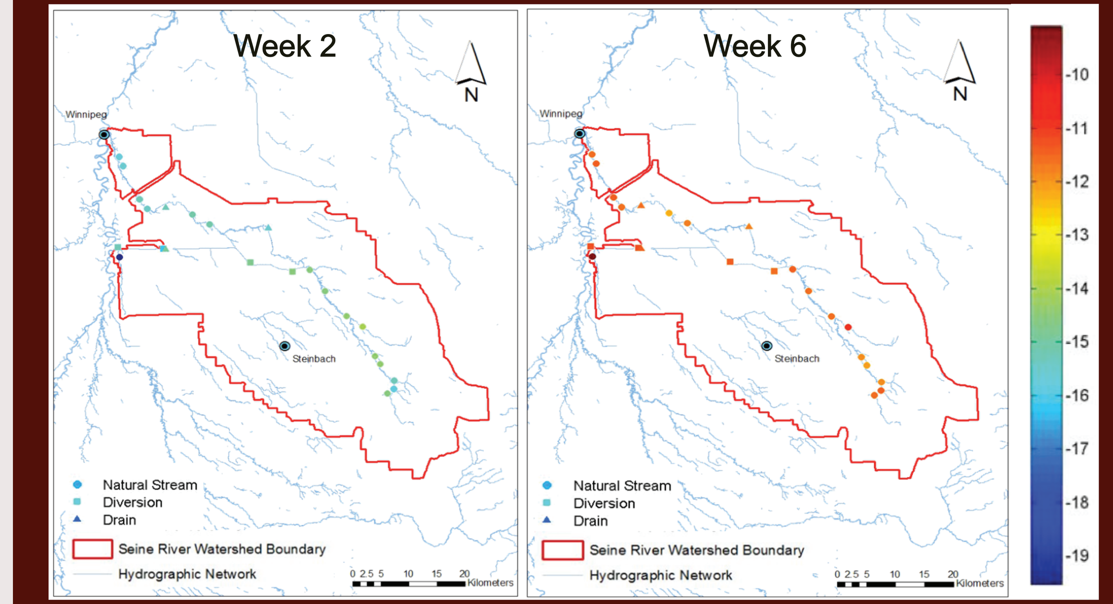


Figure 5 - Spatiotemporal variability of $\delta^{18}O$, in ‰, for selected sampling weeks.

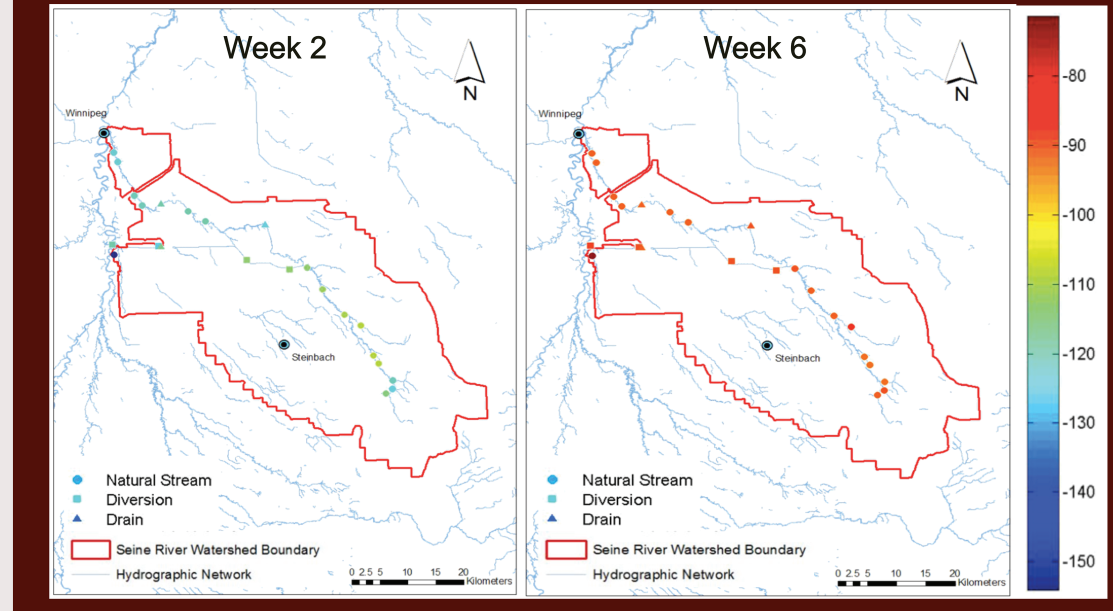


Figure 6 - Spatiotemporal variability of $\delta^2H$, in ‰, for all selected sampling weeks.

### ii. Differences between waterway types

A low p-value (<0.05) indicates a significant difference between precipitation and waterway types. Very few sampling weeks were associated with significant differences between waterway types

(A) (B)

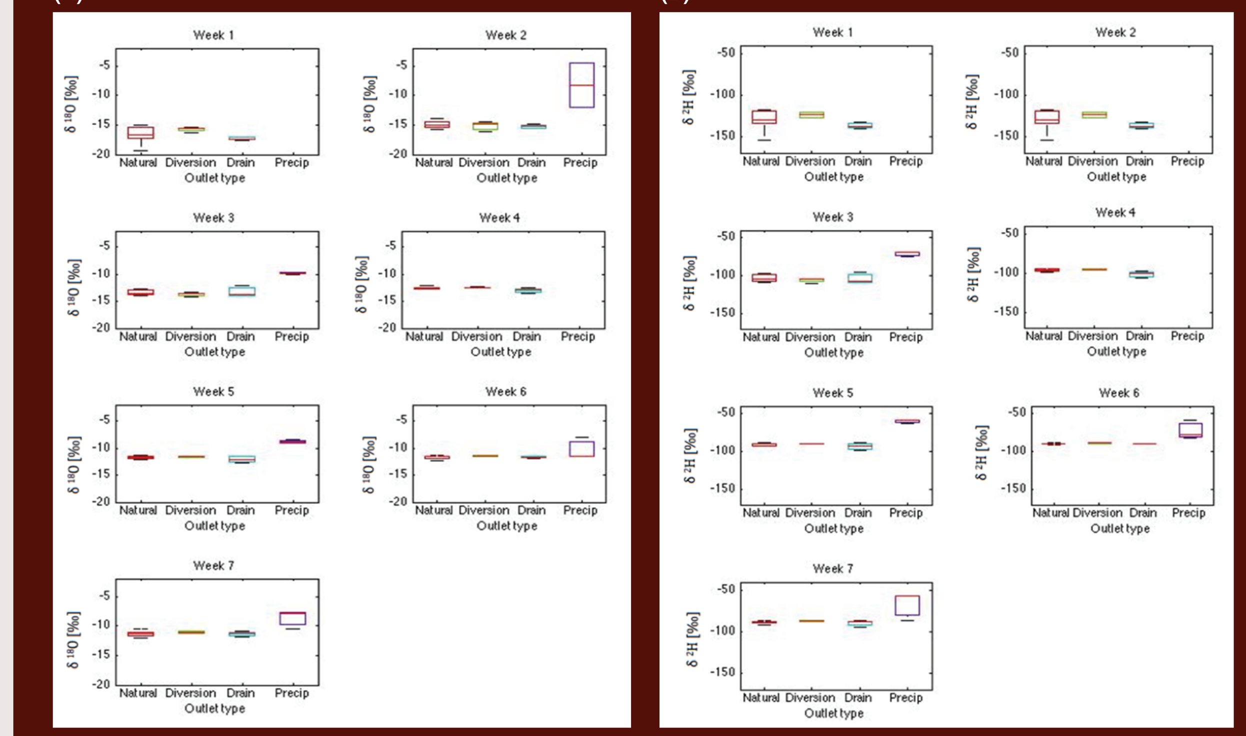


Figure 7 – Boxplots showing the differences in (A) $\delta^{18}O$, and (B) $\delta^2H$, in ‰, as a function of outlet type and for precipitation samples for all seven sampling weeks.

Table 3 – Probability of rejecting the null hypothesis associated with the Kruskal-Wallis test: p-values < 0.05 mean that there are significant statistical differences between the naturalized, drain, and diversion waterways.

| Parameter | p-values | | | | | | |
|---|---|---|---|---|---|---|---|
| | Week 1 | Week 2 | Week 3 | Week 4 | Week 5 | Week 6 | Week 7 |
| $\delta^{18}O$ | 0.14 | 0.13 | 0.04 | 0.06 | 0.02 | 0.10 | 0.02 |
| $\delta^2H$ | 0.08 | 0.11 | 0.04 | 0.06 | 0.03 | 0.01 | 0.04 |

The lack of variation in $\delta^{18}O$ and $\delta^2H$ between artificial and natural waterways may be due to the fact that:

- Diversions and drains were lined with vegetation, aiding in pollutant filtration, sediment and soil stabilization, and recycling of nutrients (Needelman, et al., 2008)
- Engineered hydraulic drop structures were constructed along the diversion create turbulence that mixes and dilutes pollutants, while aerating the water to create significant oxygen transfer (Mak, 1999)
- Channel stabilization techniques such as riprap were also used along the outside edge of unstable slopes to minimize soil erosion.

### iii. Correlation between watershed characteristics and stable water isotopic ratios

Partial correlations for stable water isotopic ratios, land use and topographical characteristics are displayed in the following tables. Blank cells correspond to correlations that were not statistically significant at the 95% level.

Table 4 – Selected partial Spearman rank correlation coefficients between stable water isotopic ratios and land use characteristics, with sub-watershed topographical characteristics held constant.

| Parameter | % Developed land | % Wetland | % Herbs and shrubs | % Forest | % Crop, and pasture |
|---|---|---|---|---|---|
| $\delta^{18}O$ Week 1 | 0.42 | 0.35 | 0.39 | | |
| $\delta^{18}O$ Week 2 | -0.43 | 0.51 | -0.48 | | |
| $\delta^{18}O$ Week 7 | | 0.66 | -0.48 | | |
| $\delta^2H$ Week 1 | 0.41 | | 0.55 | -0.31 | |
| $\delta^2H$ Week 2 | -0.40 | 0.54 | -0.47 | | |
| $\delta^2H$ Week 7 | | 0.64 | -0.32 | | |

Table 5 – Selected partial Spearman rank correlation coefficients between stable water isotopic ratios and sub-watershed topographical characteristics land use characteristics were held constant. STDEV = standard deviation.

| Parameter | Gross drainage area [km²] | Min elevation [m] | Max elevation [m] | Mean elevation [m] | STDEV elevation [m] | Max % slope | Mean % slope | STDEV % slope |
|---|---|---|---|---|---|---|---|---|
| $\delta^{18}O$ Week 4 | | | | 0.31 | | -0.40 | -0.34 | -0.54 |
| $\delta^{18}O$ Week 6 | | | | 0.35 | | -0.40 | | -0.42 |
| $\delta^{18}O$ Week 7 | -0.47 | 0.30 | -0.40 | | | -0.47 | | -0.36 |
| $\delta^2H$ Week 4 | | | | 0.33 | | -0.42 | | -0.51 |
| $\delta^2H$ Week 6 | -0.61 | 0.34 | -0.64 | | -0.37 | -0.65 | -0.50 | -0.50 |
| $\delta^2H$ Week 7 | -0.49 | 0.35 | -0.46 | | | -0.53 | -0.32 | -0.44 |

### iv. Predicting $PO_4$ concentrations using stable water isotopic ratios

Full regressions led to strong r-squared (>0.77) between $\delta^{18}O$ and $PO_4$ concentrations for week 2 while partial regressions led to quasi-perfect r-squared (0.93) between $\delta^2H$ and $PO_4$ concentrations.

Blank cells correspond to regressions not significant at a 95% level and incremental partial r-squared values should be interpreted as follows:

Partial r-squared = (Full r-squared) + (Incremental r-squared)

Table 6 – Full and partial regression analyses between $\delta^{18}O$ and $PO_4$ concentrations. For the partial regression analyses, selected controlling variables are held constant. STDEV = standard deviation.

| X | Y | R-squared of full regression analysis | Incremental r-squared of partial regression analyses using selected controlling variables | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Area | Mean % slope | Mean elevation | STDEV elevation | Crop | Forest | Herbs and shrubs |
| $\delta^{18}O$ Week 1 | $PO_4$ Week 1 | 0.30 | 0.01 | 0.02 | 0.03 | 0.02 | 0.05 | 0.08 | 0.01 |
| $\delta^{18}O$ Week 2 | $PO_4$ Week 2 | 0.77 | 0.06 | 0.01 | 0.00 | 0.06 | -0.02 | 0.01 | 0.01 |
| $\delta^{18}O$ Week 3 | $PO_4$ Week 3 | 0.24 | | 0.46 | 0.54 | 0.20 | 0.55 | 0.52 | 0.37 |
| $\delta^{18}O$ Week 4 | $PO_4$ Week 4 | 0.41 | 0.10 | 0.27 | 0.23 | 0.22 | 0.19 | 0.25 | 0.02 |
| $\delta^{18}O$ Week 5 | $PO_4$ Week 5 | 0.67 | 0.01 | 0.17 | 0.21 | 0.02 | 0.19 | 0.24 | 0.03 |
| $\delta^{18}O$ Week 6 | $PO_4$ Week 6 | 0.68 | 0.00 | 0.01 | 0.07 | 0.00 | 0.10 | 0.06 | 0.04 |
| $\delta^{18}O$ Week 7 | $PO_4$ Week 7 | 0.36 | 0.03 | 0.04 | 0.12 | 0.04 | 0.18 | 0.16 | 0.05 |

Table 7 – Full and partial regression analyses between $\delta^2H$ and $PO_4$ concentrations. For the partial regression analyses, selected controlling variables are held constant. STDEV = standard deviation.

| X | Y | R-squared of full regression analysis | Incremental r-squared of partial regression analyses using selected controlling variables | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Area | Mean % slope | Mean elevation | STDEV elevation | Crop | Forest | Herbs and shrubs |
| $\delta^2H$ Week 1 | $PO_4$ Week 1 | 0.42 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.03 | 0.00 |
| $\delta^2H$ Week 2 | $PO_4$ Week 2 | 0.75 | 0.07 | 0.00 | 0.00 | 0.05 | 0.02 | 0.01 | 0.01 |
| $\delta^2H$ Week 3 | $PO_4$ Week 3 | 0.20 | | 0.54 | 0.64 | 0.23 | 0.63 | 0.63 | 0.42 |
| $\delta^2H$ Week 4 | $PO_4$ Week 4 | 0.15 | | 0.42 | 0.48 | 0.26 | 0.40 | 0.45 | 0.08 |
| $\delta^2H$ Week 5 | $PO_4$ Week 5 | 0.72 | 0.00 | 0.17 | 0.20 | 0.03 | 0.16 | 0.21 | 0.01 |
| $\delta^2H$ Week 6 | $PO_4$ Week 6 | 0.81 | 0.00 | 0.01 | 0.05 | 0.00 | 0.08 | 0.06 | 0.02 |
| $\delta^2H$ Week 7 | $PO_4$ Week 7 | 0.05 | | 0.22 | 0.33 | | 0.40 | 0.39 | 0.14 |

Depleted isotopic ratios are significant because $\delta^{18}O$ and $\delta^2H$ are likely to bond, and remain bonded, with other elements (McGuire & McDonnell, 2007), leading to the belief that depleted stable water isotopic ratios can be used to predict PO concentrations in other watersheds.

## VII Conclusion and outlook

According to our study, $\delta^2H$ and $\delta^{18}O$ can be used to predict $PO_4$ concentrations. The Seine River Watershed was the focus of this study, but the methodology and results are potentially relevant on a much larger spatial scale.

Provided that it can be done in other watersheds, predicting $PO_4$ concentrations using $\delta^{18}O$ and $\delta^2H$ is a significant development for managing phosphorus loading because stable water isotopes offer high temporal resolution data that is affordable for studies over a large spatial scale.

## VIII References

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