**Figure 1 Supporting Information: Trends in Base Cation Mixtures in Fresh Waters**

 

Figure 1. [1](Antonopolis et.al. 2001), [2](Chapra et.al. 2012), [3](Dailey et.al. 2014), [4](Etchanchu and Probst, 1988), [5](Finnish Department of the Environment), [6](Kuzmin et.al., 2014), [7](Niazi et. al., 2014), [8](Kaushal et. al., 2018), [9](Rogora et. al. 2015), [10](Smeltzer et.al., 2012), [11](Van Der Weijden and Middelburg, 1989), [12](Cao et.al. 2015), [13](Aquilina et. al. 2012), [14](Dove 2009), [15](U.S. Army Corps of Engineers, Washington Aqueduct). Measurements pre 1970 may not be as accurate and precise as measurements post 2000. Improved methodology, sampling handling, and detection limits have changed dramatically for many analytes. This may be expected to cause variability in older data.

Table 1: Citations and characterization of datasets for above figure (and Figure 1 in main text) indicating long-term trends in base cations.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Paper/Data Source** | **Brief Description of Study** | **Cations Studied** | **Location of Study Sites** | **Name of Water Body Studied** | **Period of Sampling** | **Frequency of Sampling** | **Available Details on Analytical****Methods from Literature** |
| [1] V. Z. Antonopoulos, D. M. Papamichail, K. A. Mitsiou. Statistical and trend analysis of waterquality and quantity data for the Strymon River in Greece. Hydrology and Earth SystemSciences Discussions, European Geosciences Union, 2001, 5 (4), pp.679-692. | Examination of relationships between solute loads & concentrations and the discharge for the Strymon River in Greece | Na+, K+, Mg2+, Ca2+ | ~41°16’54.49”N~23°19’47.18”E | StrymonRiver | 1980-1997 | Monthly | Department of Irrigation at the Greek Ministry of Agriculture |
| [2] Chapra S. C., Dove A., Warren G. J. Long-term trends of Great Lakes major ion chemistry. 2012. Journal of Great Lakes Research 38 (2012) 550–560 | Comprehensive compilation of major ion chemistry in the Great Lakes | Na+, K+, Mg2+, Ca2+ | Dove, A., L'Italien, S., Gilroy, D., 2009. Great Lakes surveillance program field methods manual. Water Quality Monitoring and Surveillance, Environment Canada, Burlington, Ontario, Canada. Report No. WQMS09-001. | Lake Superior, Erie, Michigan, Ontario, and Huron | 1965-2009 | Spring (April/Early May) | GLNPO, 2010. Sampling and analytical procedures for GLNPO's open lake water quality survey of the Great Lakes. Prepared by U.S. Environmental Protection Agency. Great Lakes National Program Office, Chicago IL. EPA 905-R-05-001, March 2010 |
| [3] Dailey KR, Welch KA, Lyons WB. Evaluating the influence of road salt on water quality of Ohio rivers over time. 2014. Applied Geochemistry 47 (2014) 25–35 | Investigation of halite as the main chloride contributor into Ohio surface waters | Na+ | 39°44’25.93”N83°56’16.14”W | Little Miami Rivers (Milford, Ohio; USGS Gage 3245500) | 1965-1995 | Twice. Or once depending on accessibility | Ion Chromatography using a Dionex Ion Chromatograph (DX-120), and Picarro L1102-I water isotope analyzer |
| [4] D. ETCHANCHU & J. L. PROBST (1988) Evolution of the chemical composition of the Garonne River water during the period 1971–1984, Hydrological Sciences Journal, 33:3, 243-256, DOI: 10.1080/02626668809491246 | Presentation and analysis of chemical composition fluctuations in the Garonne River, France | Na+, K+, Mg2+, Ca2+ | ~44°31’23”N~0°02’14”E | Garonne River | 1971-1984 | Monthly | *Agence de Bassin Adour Garonne*, which is published in the *Annuaires de la Qualite des Eaux by the Minstere de l’Environment* |
| [5] Finnish Environment Institute | Study of base cation concentrations and exports out of unmanaged and undisturbed forest catchments | Na+, K+, Mg2+, Ca2+ | ~60°17’56.66”N~24°51’59.35”E | Vantaan-jokiRiver | 1978-Present | Between 12-32 times per year | Flame Atomic Absorption Spectrophotometry |
| [6] M.I. Kuzmin, E.N. Tarasova, E.A. Mamontova, A.A. Mamontov, E.V. Kerber, 2014, published in Geokhimiya, 2014, No. 7, pp. 579–589. | Study of trophic status and ionic compositional variations in Angara River headwaters | Na+, K+, Mg2+, Ca2+ | ~38°06’54.71”N~104°49/28.”E | Angara River | 1950-2010 | Monthly | 1) I. V. Glazunov, “Hydrochemical regime and chemical runoff of the Angara River,” Tr. LINa 3 (23), 57–94 (1963).2) E. N. Tarasova and A. I. Meshcheryakova, Modern State of the Hydrochemical Regime of Lake Baikal (Nauka, Novosibirsk, 1992) [in Russian].3) E. N. Tarasova, Organic Matter of Southern Baikal Waters (Nauka, Novosibirsk, 1975) [in Russian]. |
| [7] Niazi F, Mofid H, Modares NF. Trend Analysis of Temporal Changes of Discharge andWater Quality Parameters of Ajichay River in Four Recent Decades. Water Qual Expo Health (2014) 6:89–95 | Analysis of discharge trends and water quality of | Na+ | ~38°06”56.96”N~46°24’05.91”E | Aji Chay River at Vanyar Station | 1967-2007 | Monthly averages | Similar methods at Vanyar Station from their previous work. |
| [8] Kaushal SS, Likens GE, Pace ML et al. 2018 Freshwater salinization syndrome on a continental scale. Proc. Natl. Acad. Sci. USA. DOI 10.1073/pnas.1711234115. | Statistical Trend Analysis of US Geological Survey (1) sensor data of specific conductance and pH, and (2) grab sample data of cations. “All records were compiled from water quality measurements made by the USGS. Time series included in our analyses were based on at least 25 y of data…” | Na+, Mg2+, Ca2+ | 31°45'25" N, 88°07'30" W,35°15'28" N, 77°35'08" W,46°26'49" N, 97°40'44" W,35°28'13" N, 101°52'45" W, | Tombigbee River,Neuse River,Sheyenne River,Canadian River, | 1969-2001,1955-2001,1956-2010,1948-2011, | ~biweekly | US Geological Survey standardized analytical lab methods for grab samples for analyses of base cations |
| [9] Rogora M, Mosello R, Kamburska L, Salmaso N, Cerasino L, Leoni B, Garibaldi L, Soler V, Lepori F, Colombo L, Buzzi F. Recent trends in chloride and sodium concentrations in the deep subalpine lakes (Northern Italy). Environ Sci Pollut Res (2015) 22:19013–19026 | Identification and analysis of chloride and sodium ion trends and causes in the subalpine district of Italy | Na+, K+, Mg2+, Ca2+ | 45d°57”40.06”N8°38’42.33”E46°00’15.93”N9°01’48.91”E~46°00’17.86”N~9°15’47.83”E~45°43’51.82”N~10°45’19.37”E~45°43’47.83”N~10°04’39.55”E | Lakes Maggiore, Lugano, Como, Garda, Iseo | 1988-2012 | Yearly (late February-early March | Chemical analyses performed by the CNR ISE in Verbania Pallanza, Italy |
| [10] Smeltzer E, Shambaugh A, Stangel P. Environmental change in Lake Champlain revealed by long-term monitoring. Journal of Great Lakes Research 38 (2012) 6–18 | Analysis of long-term monitoring data for water quality and biological changes in Lake Champlain, Vermont | Na+, Ca2+ | 69 monitoring sitesDescribed in:Henson, E.B., Potash, M., 1966. A synoptic survey of Lake Champlain, Summer 1965. Univ. Michigan Great Lake Res. Div. Publ. No. 15, pp. 38–43.andHenson, E.B., Potash, M., 1987. Sampling strategies for detecting water quality trends in Lake Champlain. Completion Report to the U.S. Dept. Interior Office of Water Resources and Technology. Project No. 03. University of Vermont, Burlington15 monitoring sites described in:Vermont Department of Environmental Conservation and New York State Department of Environmental Conservation, 2010. Long-term water quality and biological monitoring project for Lake Champlain. Quality Assurance Project Plan. : Prep. For Lake Champlain Basin Program. Grand Isle, VT. | Lake Champlain | 1964-19741992-2009 | Variable (April to November)Bi-weekly (April-November) | Analytical methods are documented in Vermont Department of Environmental Conservation and New York State Department of Environmental Conservation, 2010. Long-term water quality and biological monitoring project for Lake Champlain. Quality Assurance Project Plan. : Prep. For Lake Champlain Basin Program. Grand Isle, VT. |
| [11] Van Der Weijden CH, Middelburg JJ. Hydrogeochemistry of the river Rhine: long term and seasonal variability, elemental budgets, base levels and pollution. Water Resources (1989) Vol. 23, No. 10, pp. 1247-1266 | Analysis of the relationships of the inorganic chemistry of the Rhine River, The Netherlands | Na+, K+, Mg2+, Ca2+ | ~51°50’54.08”N~6°08’19.47”E | Rhine River | 1974-1985 | Twice per month | Anon. (1975-1984) Investigations of the water quality in the public waterways. Quarterly Reports of DBW/RIZA, Lelystad, The Netherlands. |
| [12] Cao Y, Tang C, Song X, Liu C. Major ion chemistry, chemical weathering and CO2 consumption in the Songhua River basin, Northeast China Environ Earth Sci (2015) 73:7505–7516 | Examine the characteristics and mechanisms of major ion chemistry in the Songhua River basin | Na+, K+, Mg2+, Ca2+ | 56 stationsPlease see Fig. 1 of Cao et al. (2014) | Songhua River | 1962-1984 | Unspecified | EDTA titration, flame spectrometry |
| [13] Aquilina L, Poszwa A, Walter C, Vergnaud V, Pierson-Wickmann AC, Ruiz L. Long-Term Effects of High Nitrogen Loads on Cation and Carbon Riverine Export in Agricultural Catchments. Environ. Sci. Technol. 2012, 46, 9447−9455 | Investigation of cation concentration evolution in the Armorican crystalline shield | Na+, Mg2+, Ca2+ | Exact coordinates are unspecified | Aulne, Blavet, Oust, Arguenon, and Vilaine Rivers | 1970-2010 | Unspecified | Ion Chromatography |
| [14] Alice Dove (2009) Long-term trends in major ions and nutrients in Lake Ontario, Aquatic Ecosystem Health & Management, 12:3, 281-295, DOI:10.1080/14634980903136388 | Summarization of Lake Ontario’s Surveillance Program’s water quality results of major ions and nutrients | Na+, K+, Mg2+, Ca2+ | 95 stationsPlease see map in Dove et al. (2009) | Lake Ontario | 1969-19931966- 1993 [Except 1972, 1973, 1980, 1983, 1984]1998-2008 | Yearly (late March- early May)Yearly (Mid-August)Every other year (Summer) | National Laboratory for Environmental Testing (NLET), 1997. Manual of Analytical Methods, Major Ions and Nutrients, Volume 1. Environment Canada, Burlington, Ontario. |
| [15] U.S. Army Corps of Engineers, Washington Aqueduct | Routine monitoring of drinking water supply for Washington, D.C. | Na+, K+, Mg2+, Ca2+ | 38°56’11.72”N77°06’38.85”W | PotomacRiver | ~1962-present | Daily and Monthly | Flame Atomic Absorption Spectrophotometry |

**Figure 2 Supporting Information: High-Frequency Relationships between Specific Conductance, pH, and Nitrate**

Data collected from the US Geological Survey National Water Information System is usually collected *via* sensors at gaging stations at 15 minute intervals. Some of the most recent data used in this analysis is provisional as it can take a year or more for the US Geological Survey to ensure that instrument malfunctions or physical changes at the measurement site are not altering the data provided. Due to being located in different states, climates, and being installed / maintained at different intervals, the exact model of each sensor is not uniform across monitoring sites.

Mean specific conductance is measured as unfiltered, microsiemens per centimeter at 25 degrees Celsius. Median pH data is collected via a hydrogen ion electrode and is measured in standard units. Mean and Median Nitrate plus nitrite is measured in situ as milligrams per liter as nitrogen. Nitrate sensors use UV light at wavelengths less than 220 nm which is absorbed by nitrate ions. In field measurements are usually within 3 to 5 % of laboratory data. Mean turbidity is measured unfiltered in formazin nephelometric units (FNU) via monochrome near infra-red LED light, 780-900 nm, detection angle 90 +-2.5 degrees. Mean Discharge (Q) is measured in cubic feet per second

Turbidity, pH, specific conductance, and temperature are often measured via multiparameter sonde (a sensor probe). Discharge is often recorded by Water-stage recorder and crest-stage gages. Datasets ranged from a minimum of 137 days of data to a maximum of 10569 days. See; US Geological Survey Field Manual, Chapter 6 (<https://water.usgs.gov/owq/FieldManual/Chapter6/Archive/Section6.4.pdf>), US Geological Survey real-time nitrate summary (<https://water.usgs.gov/coop/features/real-time.nitrate.summary.pdf>), US Geological Survey Provisional Data Statement (<https://water.usgs.gov/data/provisional.html>), and National Water Information System data access portal (<https://waterdata.usgs.gov/nwis>).

Table 2. Regression analyses of specific conductance vs. turbidity, pH, and nitrate concentrations for high-frequency sensors maintained by the US Geological Survey from the Midwestern U.S. and Eastern U.S. Data analyzed from https://waterdata.usgs.gov/nwis

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Site | USGS site no. | Latitude | Longitude | Period of record | Days | P value (Turbidity / SC) | R2 (Turbidity / SC) | Slope (Turbidity / SC) |
| Midwest |   |   |   |   |   |   |   |   |
| EAST FORK WHITEWATER RIVER AT BROOKVILLE, IN | 3276000 | 39°26'02" | 85°00'12" | 02/10/2017 - 03/06/2018 | 384 | 0.000 | 0.056 | 0.286 |
| EAST FORK WHITEWATER RIVER AT RICHMOND, IN | 3275500 | 39°48'24" | 84°54'26" | 10/21/2017 - 03/06/2018 | 137 | 0.000 | 0.711 | -0.319 |
| MAUMEE RIVER AT TECUMSEH STREET AT FORT WAYNE, IN | 4182867 | 41°05'05.8" | 85°07'20.4" | 12/19/2014 - 12/09/2015 | 356 | 0.000 | 0.345 | -0.191 |
| ROUGH RIVER NEAR FALLS OF ROUGH AT DAM, KY | 3318010 | 37°37'19" | 86°30'15" | 01/29/2016 - 03/08/2018 | 770 | 0.223 | 0.006 | -0.011 |
| Mississippi River at Clinton, IA | 5420500 | 41°46'50" | 90°15'07" | 03/03/2015 - 03/08/2018 | 1102 | 0.000 | 0.261 | -0.195 |
| MISS R AT AUX LOCK 14 (DS) AT PLEASANT VALLEY, IA | 7080101 | 41°34'29.6" | 90°24'15.7 | 07/11/2017 - 03/08/2018 | 241 | x | x | x |
| Missouri River at Hermann, MO | 5420500 | 41°46'50" | 90°15'07" | 02/24/2006 - 03/08/2018 | 4396 | 0.000 | 0.413 | -0.757 |
| Mississippi River at Cape Girardeau, MO | 7020850 | 37°18'06.8" | 89°31'04.8" | 03/10/2015 - 03/08/2018 | 1095 | 0.000 | 0.334 | -0.666 |
| SUGAR CREEK NEAR CHATHAM, IL | 5576195 | 39°39'32.67" | 89°39'32.17" | 06/13/2015 - 03/14-2018 | 1006 | 0.000 | 0.145 | 0.000 |
| BIG MUDDY RIVER AT RTE 127 AT MURPHYSBORO, IL | 5599490 | 37°45'30" | 89°19'40" | 10/22/2015 - 03/15-2018 | 876 | 0.000 | 0.165 | -0.059 |
| KASKASKIA RIVER AT NEW ATHENS, IL | 5595000 | 38°19'11" | 89°53'19" | 09/22/2015 - 03/15-2018 | 906 | 0.000 | 0.668 | -0.322 |
| ILLINOIS RIVER AT FLORENCE, IL | 5586300 | 39°37'58" | 90°36'28" | 04/04/2012 - 03/15/2018 | 2172 | 0.000 | 0.104 | -0.166 |
| LICK CREEK NEAR WOODSIDE, IL | 7130007 | 39°42'55.94" | 89°42'08.8"  | 06/13/2015 - 03/15/2018 | 1007 | 0.000 | 0.126 | -0.039 |
| GREEN RIVER NEAR GENESEO, IL | 7090007 | 41°29'20" | 90°09'27" | 06/26/2015 - 03/15/2018 | 994 | 0.000 | 0.300 | 0.015 |
| ILLINOIS RIVER AT SENECA, IL | 5543010 | 41°17'59" | 88°36'51"  | 06/26/2013 - 03/28/2018 | 1737 | 0.000 | 0.091 | 0.013 |
| KANKAKEE RIVER AT SHELBY, IN | 5518000 | 41°10'58" | 87°20'25" | 12/05/2015 - 03/29/2018 | 846 | 0.000 | 0.152 | -0.209 |
| KANKAKEE RIVER AT DUNNS BRIDGE, IN | 5517500 | 41°13'12" | 86°58'06" | 04/09/2016 - 03-29-2018 | 720 | 0.000 | 0.373 | -0.046 |
| KANKAKEE RIVER AT DAVIS, IN | 5515500 | 41°23'22.7" | 86°42'22.2" | 12/05/2013 - 03/29/2018 | 1576 | 0.000 | 0.481 | -0.166 |
| IROQUOIS RIVER NEAR FORESMAN, IN | 5524500 | 40°52'14" | 87°18'24" | 03/20/2015 - 03/29/2018 | 1106 | 0.000 | 0.307 | -0.155 |
| BIG RACCOON CREEK AT FERNDALE, IN | 3340900 | 39°42'40.2" | 87°04'16.6" | 01/28/2017 - 03/29/2018 | 426 | 0.139 | 0.005 | -0.008 |
| East |   |   |   |   |   |   |   |   |
| OCONALUFTEE RIVER AT BIRDTOWN, NC | 3512000 | 35°27'41" | 83°21'13" | 10/03/2014 - 03/08/2018 | 1253 | 0.024 | 0.006 | -0.101 |
| CONNECTICUT RIVER AT MIDDLE HADDAM, CT | 1193050 | 41°32'30" | 72°33'13" | 12/16/2008 - 03/08/2018 | 3370 | 0.000 | 0.205 | -0.075 |
| POTOMAC RIVER NEAR WASH, DC | 1646500 | 38°56'59.2" | 77°07'39.5" | 12/03/2011 - 06/27/2018 | 2399 | 0.000 | 0.176 | -0.180 |
| Passaic River below Pompton Riv at Two Bridges NJ - Right Intake | 1389005 | 40°53'47" | 74°16'09" | 04/01/1989 - 03/08/2018 | 10569 | 0.000 | 0.093 | -0.004 |
| Toms River near Toms River NJ | 1408500 | 39°59'11" | 74°13'24" | 07/11/2012 - 09/30/2014 | 812 | 0.000 | 0.064 | -0.026 |
| Delaware River at Trenton NJ | 1463500 | 40°13'18" | 74°46'41" | 12/20/2017 - 06/27/2018 | 190 | 0.005 | 0.045 | -0.043 |
| SUSQUEHANNA RIVER NEAR DARLINGTON, MD | 1579550 | 39°37'33.8" | 76°09'27.9" | 07/11/2014 - 03/08/2018 | 1337 | 0.000 | 0.244 | -0.091 |
| DIFFICULT RUN NEAR GREAT FALLS, VA | 1646000 | 38°58'33" | 77°14'46" | 10/19/2012 - 06/28/2018 | 2079 | x | x | x |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Site | USGS site no. | Latitude | Longitude | Period of record | Days | P value (pH / SC) | R2 (pH / SC) | Slope (pH / SC) |
| Midwest |   |   |   |   |   |   |   |   |
| EAST FORK WHITEWATER RIVER AT BROOKVILLE, IN | 03276000 | 39°26'02" | 85°00'12" | 02/10/2017 - 03/06/2018 | 384 | 0.000 | 0.425 | 0.006 |
| EAST FORK WHITEWATER RIVER AT RICHMOND, IN | 3275500 | 39°48'24" | 84°54'26" | 10/21/2017 - 03/06/2018 | 137 | 0.000 | 0.137 | 0.001 |
| MAUMEE RIVER AT TECUMSEH STREET AT FORT WAYNE, IN | 4182867 | 41°05'05.8" | 85°07'20.4" | 12/19/2014 - 12/09/2015 | 356 | 0.000 | 0.334 | 0.001 |
| ROUGH RIVER NEAR FALLS OF ROUGH AT DAM, KY | 3318010 | 37°37'19" | 86°30'15" | 01/29/2016 - 03/08/2018 | 770 | 0.000 | 0.295 | 0.004 |
| Mississippi River at Clinton, IA | 5420500 | 41°46'50" | 90°15'07" | 03/03/2015 - 03/08/2018 | 1102 | 0.537 | 0.000 | 0.000 |
| MISS R AT AUX LOCK 14 (DS) AT PLEASANT VALLEY, IA | 7080101 | 41°34'29.6" | 90°24'15.7 | 07/11/2017 - 03/08/2018 | 241 | 0.000 | 0.078 | 0.001 |
| Missouri River at Hermann, MO | 5420500 | 41°46'50" | 90°15'07" | 02/24/2006 - 03/08/2018 | 4396 | 0.000 | 0.296 | 0.001 |
| Mississippi River at Cape Girardeau, MO | 7020850 | 37°18'06.8" | 89°31'04.8" | 03/10/2015 - 03/08/2018 | 1095 | 0.000 | 0.196 | 0.002 |
| SUGAR CREEK NEAR CHATHAM, IL | 5576195 | 39°39'32.67" | 89°39'32.17" | 06/13/2015 - 03/14-2018 | 1006 | 0.000 | 0.300 | 0.000 |
| BIG MUDDY RIVER AT RTE 127 AT MURPHYSBORO, IL | 5599490 | 37°45'30" | 89°19'40" | 10/22/2015 - 03/15-2018 | 876 | 0.000 | 0.593 | 0.001 |
| KASKASKIA RIVER AT NEW ATHENS, IL | 5595000 | 38°19'11" | 89°53'19" | 09/22/2015 - 03/15-2018 | 906 | 0.000 | 0.362 | 0.002 |
| ILLINOIS RIVER AT FLORENCE, IL | 5586300 | 39°37'58" | 90°36'28" | 04/04/2012 - 03/15/2018 | 2172 | 0.000 | 0.278 | -0.166 |
| LICK CREEK NEAR WOODSIDE, IL | 7130007 | 39°42'55.94" | 89°42'08.8"  | 06/13/2015 - 03/15/2018 | 1007 | 0.010 | 0.010 | 0.000 |
| GREEN RIVER NEAR GENESEO, IL | 7090007 | 41°29'20" | 90°09'27" | 06/26/2015 - 03/15/2018 | 994 | 0.000 | 0.122 | 0.001 |
| ILLINOIS RIVER AT SENECA, IL | 5543010 | 41°17'59" | 88°36'51"  | 06/26/2013 - 03/28/2018 | 1737 | 0.000 | 0.117 | 0.013 |
| KANKAKEE RIVER AT SHELBY, IN | 5518000 | 41°10'58" | 87°20'25" | 12/05/2015 - 03/29/2018 | 846 | 0.000 | 0.125 | 0.001 |
|  KANKAKEE RIVER AT DUNNS BRIDGE, IN | 5517500 | 41°13'12" | 86°58'06" | 04/09/2016 - 03-29-2018 | 720 | 0.000 | 0.141 | 0.001 |
| KANKAKEE RIVER AT DAVIS, IN | 5515500 | 41°23'22.7" | 86°42'22.2" | 12/05/2013 - 03/29/2018 | 1576 | 0.000 | 0.027 | 0.001 |
| IROQUOIS RIVER NEAR FORESMAN, IN | 5524500 | 40°52'14" | 87°18'24" | 03/20/2015 - 03/29/2018 | 1106 | 0.000 | 0.262 | 0.002 |
| BIG RACCOON CREEK AT FERNDALE, IN | 3340900 | 39°42'40.2" | 87°04'16.6" | 01/28/2017 - 03/29/2018 | 426 | 0.000 | 0.420 | 0.004 |
| East |   |   |   |   |   |   |   |   |
| OCONALUFTEE RIVER AT BIRDTOWN, NC | 3512000 | 35°27'41" | 83°21'13" | 10/03/2014 - 03/08/2018 | 1253 | 0.000 | 0.243 | 0.016 |
| CONNECTICUT RIVER AT MIDDLE HADDAM, CT | 1193050 | 41°32'30" | 72°33'13" | 12/16/2008 - 03/08/2018 | 3370 | x | x | x |
| POTOMAC RIVER NEAR WASH, DC | 1646500 | 38°56'59.2" | 77°07'39.5" | 12/03/2011 - 06/27/2018 | 2399 | 0.000 | 0.202 | 0.002 |
| Passaic River below Pompton Riv at Two Bridges NJ - Right Intake | 1389005 | 40°53'47" | 74°16'09" | 04/01/1989 - 03/08/2018 | 10569 | 0.000 | 0.210 | 0.000 |
| Toms River near Toms River NJ | 1408500 | 39°59'11" | 74°13'24" | 07/11/2012 - 09/30/2014 | 812 | 0.000 | 0.348 | 0.015 |
| Delaware River at Trenton NJ | 1463500 | 40°13'18" | 74°46'41" | 12/20/2017 - 06/27/2018 | 190 | 0.000 | 0.131 | 0.004 |
| SUSQUEHANNA RIVER NEAR DARLINGTON, MD | 1579550 | 39°37'33.8" | 76°09'27.9" | 07/11/2014 - 03/08/2018 | 1337 | x | x | x |
| DIFFICULT RUN NEAR GREAT FALLS, VA | 1646000 | 38°58'33" | 77°14'46" | 10/19/2012 - 06/28/2018 | 2079 | 0.000 | 0.006 | 0.000 |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Site | USGS site no. | Latitude | Longitude | Period of record | Days | P value (NO3 + NO2 / SC) | R2 (NO3 + NO2 / SC) | Slope (NO3 + NO2 / SC) |
| Midwest |   |   |   |   |   |   |   |   |
| EAST FORK WHITEWATER RIVER AT BROOKVILLE, IN | 3276000 | 39°26'02" | 85°00'12" | 02/10/2017 - 03/06/2018 | 384 | 0.000 | 0.425 | 0.010 |
| EAST FORK WHITEWATER RIVER AT RICHMOND, IN | 3275500 | 39°48'24" | 84°54'26" | 10/21/2017 - 03/06/2018 | 137 | 0.000 | 0.153 | -0.003 |
| MAUMEE RIVER AT TECUMSEH STREET AT FORT WAYNE, IN | 4182867 | 41°05'05.8" | 85°07'20.4" | 12/19/2014 - 12/09/2015 | 356 | 0.003 | 0.032 | -0.003 |
| ROUGH RIVER NEAR FALLS OF ROUGH AT DAM, KY | 3318010 | 37°37'19" | 86°30'15" | 01/29/2016 - 03/08/2018 | 770 | 0.000 | 0.236 | -0.006 |
| Mississippi River at Clinton, IA | 5420500 | 41°46'50" | 90°15'07" | 03/03/2015 - 03/08/2018 | 1102 | 0.000 | 0.498 | 0.017 |
| MISS R AT AUX LOCK 14 (DS) AT PLEASANT VALLEY, IA | 7080101 | 41°34'29.6" | 90°24'15.7 | 07/11/2017 - 03/08/2018 | 241 | x | x | X |
| Missouri River at Hermann, MO | 5420500 | 41°46'50" | 90°15'07" | 02/24/2006 - 03/08/2018 | 4396 | 0.001 | 0.014 | 0.001 |
| Mississippi River at Cape Girardeau, MO | 7020850 | 37°18'06.8" | 89°31'04.8" | 03/10/2015 - 03/08/2018 | 1095 | 0.808 | 0.000 | 0.000 |
| SUGAR CREEK NEAR CHATHAM, IL | 5576195 | 39°39'32.67" | 89°39'32.17" | 06/13/2015 - 03/14-2018 | 1006 | 0.000 | 0.161 | 0.015 |
| BIG MUDDY RIVER AT RTE 127 AT MURPHYSBORO, IL | 5599490 | 37°45'30" | 89°19'40" | 10/22/2015 - 03/15-2018 | 876 | 0.858 | 0.000 | 0.000 |
| KASKASKIA RIVER AT NEW ATHENS, IL | 5595000 | 38°19'11" | 89°53'19" | 09/22/2015 - 03/15-2018 | 906 | 0.000 | 0.096 | -0.003 |
| ILLINOIS RIVER AT FLORENCE, IL | 5586300 | 39°37'58" | 90°36'28" | 04/04/2012 - 03/15/2018 | 2172 | 0.004 | 0.004 | -0.001 |
| LICK CREEK NEAR WOODSIDE, IL | 7130007 | 39°42'55.94" | 89°42'08.8"  | 06/13/2015 - 03/15/2018 | 1007 | 0.629 | 0.000 | 0.000 |
| GREEN RIVER NEAR GENESEO, IL | 7090007 | 41°29'20" | 90°09'27" | 06/26/2015 - 03/15/2018 | 994 | 0.000 | 0.034 | -0.007 |
| ILLINOIS RIVER AT SENECA, IL | 5543010 | 41°17'59" | 88°36'51"  | 06/26/2013 - 03/28/2018 | 1737 | 0.000 | 0.014 | -0.001 |
| KANKAKEE RIVER AT SHELBY, IN | 5518000 | 41°10'58" | 87°20'25" | 12/05/2015 - 03/29/2018 | 846 | 0.000 | 0.255 | -0.009 |
|  KANKAKEE RIVER AT DUNNS BRIDGE, IN | 5517500 | 41°13'12" | 86°58'06" | 04/09/2016 - 03-29-2018 | 720 | 0.000 | 0.145 | -0.006 |
| KANKAKEE RIVER AT DAVIS, IN | 5515500 | 41°23'22.7" | 86°42'22.2" | 12/05/2013 - 03/29/2018 | 1576 | 0.000 | 0.199 | -0.004 |
| IROQUOIS RIVER NEAR FORESMAN, IN | 5524500 | 40°52'14" | 87°18'24" | 03/20/2015 - 03/29/2018 | 1106 | 0.000 | 0.110 | -0.007 |
| BIG RACCOON CREEK AT FERNDALE, IN | 3340900 | 39°42'40.2" | 87°04'16.6" | 01/28/2017 - 03/29/2018 | 426 | 0.000 | 0.148 | 0.008 |
| East |   |   |   |   |   |   |   |   |
| OCONALUFTEE RIVER AT BIRDTOWN, NC | 3512000 | 35°27'41" | 83°21'13" | 10/03/2014 - 03/08/2018 | 1253 | 0.000 | 0.396 | 0.014 |
| CONNECTICUT RIVER AT MIDDLE HADDAM, CT | 1193050 | 41°32'30" | 72°33'13" | 12/16/2008 - 03/08/2018 | 3370 | 0.000 | 0.130 | 0.001 |
| POTOMAC RIVER NEAR WASH, DC | 1646500 | 38°56'59.2" | 77°07'39.5" | 12/03/2011 - 06/27/2018 | 2399 | 0.000 | 0.016 | -0.001 |
| Passaic River below Pompton Riv at Two Bridges NJ - Right Intake | 1389005 | 40°53'47" | 74°16'09" | 04/01/1989 - 03/08/2018 | 10569 | 0.000 | 0.263 | 0.002 |
| Toms River near Toms River NJ | 1408500 | 39°59'11" | 74°13'24" | 07/11/2012 - 09/30/2014 | 812 | 0.000 | 0.477 | 0.010 |
| Delaware River at Trenton NJ | 1463500 | 40°13'18" | 74°46'41" | 12/20/2017 - 06/27/2018 | 190 | 0.000 | 0.478 | 0.004 |
| SUSQUEHANNA RIVER NEAR DARLINGTON, MD | 1579550 | 39°37'33.8" | 76°09'27.9" | 07/11/2014 - 03/08/2018 | 1337 | 0.000 | 0.014 | -0.001 |
| DIFFICULT RUN NEAR GREAT FALLS, VA | 1646000 | 38°58'33" | 77°14'46" | 10/19/2012 - 06/28/2018 | 2079 | x | x | x |



Figure 2. Examples of relationships between specific conductance and pH, nitrate, and turbidity using high-frequency USGS daily sensor data.

Figure 3. Examples of relationships between specific conductance and pH, nitrate, and turbidity using high-frequency daily USGS sensor data. Please note the bifurcated relationship between specific conductance and nitrate concentrations.

Figure 4. Examples of relationships between specific conductance and pH, nitrate, and turbidity using high-frequency USGS daily sensor data.

*Site description for Rock Creek, high-frequency sensor:*

Data from 1 high-frequency sensor site was deeply explored in this study on a storm event basis. The sensor is located in the Rock Creek stream, in the northern corner of Washington DC, and in close proximity to the Anacostia Watershed incubation sites (above). Rock Creek is a tributary of the Potomac River and the Chesapeake Bay. The sensor site was selected due to the availability of high-frequency nitrate measurements for multiple storm events over multiple years, and because of similarities in its discharge and watershed size to sites where experiment incubation were performed. Rock Creek has a watershed size of 16,600 ha and predominantly urban land cover throughout the watershed. However near the sensor, Rock Creek has a wide and undeveloped riparian zone consisting of hiking trails, recreational areas, and bands of intact forest with temperate deciduous trees. The Rock Creek sensor has 2 years of continuous high-frequency 15 minute interval measurements of specific conductance and nitrate. Previous studies have characterized nutrient loading and emerging contaminants in the Rock Creek watershed.

*In-situ high-frequency sensor, storm event response of specific conductance and nitrate:*

High-frequency sensor data from US Geological Survey station for Rock Creek (station 01648010) was analyzed to empirically characterize the in-situ relationships between salinity (represented as specific conductance) and nitrate during a road salting event. Specific conductance was measured using a submersible electrode sensor, calibrated to each site, and adjusted to represent the cross-sectional mean at the time of observation. Nitrate concentrations were measured using a Submersible Ultraviolet Nitrate Analyzer (SUNA, Sea-Bird Scientific, Bellevue, Washington, USA) with a 10 mm optical path length. The nitrate optical sensors were lab calibrated to grab samples from each site by the US Geological Survey, and the optics were corrected for temperature and turbidity. Although the optical sensor cannot distinguish between nitrate and nitrite, the measurement was assumed to be nitrate (as nitrite is negligible in these streams). Specific conductance and nitrate were measured by the sensors in 15 minute intervals.

Figure 5: Similar to Rock Creek (presented in the manuscript), there were similar cyclical relationships between nitrate concentrations and salinity (specific conductance) in the Potomac River (near Washington DC, USA) during a winter snow storm (road salt pulse). The left panel is the relationship during the entire storm event (1 week), while the right panel separates the response directly before, during, and after a winter snow event.



**Figure 3 Supporting Information: FSS Mobilizes Mixtures of Metals: Monitoring, Laboratory**

*Panel A:*

Throughout snowmelt samples were collected daily, and at peak snowmelt, samples were collected twice a day. Samples were acidified with 0.5% high-purity nitric acid and analyzed for dissolved base cation concentrations (sodium, calcium, magnesium) and trace metals (copper, manganese) in an acidified matrix on an ICP-OES (see methodology for chemical analyses below). Paint Branch, a tributary of the Anacostia River and the Chesapeake Bay, is located approximately 5 miles outside of Washington DC and has a drainage basin area of 30.5 square miles, basin slope of 0.0652 feet/foot, impevious surface land coverage of 31.7%, urban development land coverage of 67.5%, and forested land coverage of 25.4%. This sampling station is located near the University of Maryland Campus (38ᵒ 59’ 20.8” N, 76ᵒ56’07.23” W), and is further downstream then incubation site (below).

*Panel B:*

Dissolved metals concentrations in filtered and acidified water samples were analyzed by inductively coupled plasma – mass spectrometry (see chemical analyses below). The samples were acidified with nitric acid at time of collection. Reporting limits are 1 ug/L. Results were accurate +/- 1.7% for concentrations between 25 and 50 ug/L and SC below 2500 uS/cm. (Faires 1993, <https://pubs.usgs.gov/of/1992/0634/report.pdf>)

Specific conductance was measured with a battery powered Wheatstone bridge conductivity sensor with temperature range of -5 to 45 deg C with an accuracy of 5% under or equal to 100 uS/cm or 3% over 100 uS/cm that compensates value to 25 deg C. Measurements were done in situ for surface water and must be done every 10th sample. No daily averages reported (Radtke et al. 2005, <https://water.usgs.gov/owq/FieldManual/Chapter6/Final508Chapter6.3.pdf>)

Patterns in specific conductance and metals were shown for one stream represented in the main text of the paper – Rock Creek in Washington, DC. However, the same patterns were consistent with other urban streams in the region. For example, there were comparable sites with similar data during the same time frame in other nearby streams besides Rock Creek. Some information for Rock Creek and the other two sites is as follows: Rock Creek at Joyce RD – USGS 01648010 – drainage area 63.7 mi2 – land use: park/residential; Watts Branch at Washington DC – USGS 01651800 – drainage area 3.36 mi2 – land use: commercial/residential; Hickey Run at National Arboretum – USGS 01651770 – drainage area 0.99 mi2 – land use: park. Rock Creek is also described further below. Examples of similar patterns in metals and specific conductance are presented below for the other nearby streams.

Faires, Lynda M. (1993). Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory – determination of metals in water by inductively coupled plasma – mass spectrometry. U.S. Department of Interior

Radtke, D.B, Davis, J.V & Wilde, F.D. (2005). Specific Electrical Conductance. U.S. Geological Survey TWRI Book.

Figure 6: Similar patterns in watershed exports of metals (mass transport in streams per unit of watershed area) and specific conductance at nearby urban streams in Washington DC, USA, relative to Rock Creek (shown in main text).

*Panel C and D:*

Experimental salinization of a headwater suburban stream was conducted in summer 2017 in the Gywnns Falls watershed near Glyndon, MD (GFGL gage site, described below in table 3). 10 liters of stream water is collected into a bucket and 3,000g of NaCl is dissolved into the water [300g/L]. Stations are established every 10m along a 50m reach downstream from the release point. The salt mixture is poured into the center of flow ~10m upstream of the first station. Water samples are taken intermittently with a large syringe from the center of the channel at each station, immediately filtered through a Whatman GF/F glass fiber filter in a housing that attaches to the syringe and stored in bottles on ice until returned to the lab. In the laboratory samples are acidified and analyzed on a Shimadzu ICP-OES for element concentrations (see methodology and chemical analyses information below).

**Figure 4 Supporting Information: FSS Mobilizes Mixtures of Metals: Lab Experiments**

We conducted laboratory experiments from sediments collected at 10 sites across 2 metropolitan regions and analyzed high-frequency sensor data from 1 nearby site to characterize the potential relationships between salinization and solute concentrations during snowstorms in streams, and the potential release of base cations and trace metals from sediments to the overlying water column. Sediments, streamwater, and sodium chloride were incubated in a controlled lab environment to mimic post snowstorm conditions (i.e., high salinity runoff entering the stream). The methods for these incubations were previously described in Haq et al (2018) and Duan and Kaushal (2015).

*Site description for incubation experiments:*

Sediment and streamwater were incubated form 10 sites in the Baltimore-Washington Metropolitan Area in the Chesapeake Bay Watershed in the USA. Six of the stream sites are within the U.S. National Science Foundation (NSF) supported Baltimore Ecosystem Study Long Term Ecological Research Project (BES-LTER), and are long-term, routinely monitored, and well characterized sites. These 6 stream sites are located in Baltimore, Maryland, where they exhibit a land use gradient. These sites vary in drainage area (8 ha to 8,400 ha), percent of watershed area covered in impervious surfaces (0% to 62%), population density (0 people/ha to 20 people/ha), and dominant land use (undisturbed forest in a state park, suburban, agricultural, urban residential, and heavily urban commercial). All 6 of these sites are in close proximity and share the same hydrologic, geologic (piedmont), and biome (temperate deciduous/humid). Five of these 6 sites are collocated with US Geological Survey gaging stations, and all 6 sites are nested in the heavily modified suburban and urban Gwynns Falls Watershed, which drains 17,500 ha (and empties into the Patapsco River and then Chesapeake Bay) in Southern Baltimore County and Baltimore City.

The remaining 4 of the 10 incubation stream sites are from the heavily urbanized Anacostia watershed (46000 ha) in Southern Maryland, near Washington DC. The Anacostia is a major tributary of the tidal Potomac River and the Chesapeake Bay as described in Smith and Kaushal (2015). These 4 sites vary in both drainage area (200 ha to 18,800 ha) and impervious surface cover (25% to 41%) and offer a slightly different hydrology, geology (coastal plain), land use, and drainage infrastructure (less leaky, less old, and more green/Best Management Practices stormwater features) than the Baltimore LTER sites. Three of these 4 Anacostia watershed sites are collocated with US Geological Survey gaging stations.

*Sediment incubation across a range of salinization, experimental set-up:*

As described in Haq et al (2018), roughly 1 kg of sediment was collected from the streambed per site using a clean shovel and a new Ziploc bag during fall 2014. In order to achieve a representative sediment sample for each site, small amounts of sediment were gathered from 3 places (left bank, center, right bank) of 2 separate transects, roughly 20 meters apart. Two liters of streamwater were also collected (via acid-washed HPDE Nalgene bottles; no headspace). The sediment and streamwater were transported in a chilled cooler to a laboratory, and were kept cool and moist during the experiment set-up. In order to homogenize the sample for particle size, the sediment was sieved in the lab with a 2mm sieve and the fine fraction (<2mm) was used for the incubation. Sixty grams of homogenized sediment were added to each acid-washed glass Erlenmeyer flask along with 100 mL of unfiltered streamwater to simulate a vertical water column with a sediment-water interface. Sodium chloride was added to increase the salinity of the simulated stream columns at various treatments; 0, 0.5, 1, 2.5, 5, and 10 g/L. This is a plausible range of salinity (0 to 6 g/L chloride, 0 to 4 g/L of sodium), as long-term studies have reported elevated measurements of both chloride (e.g. 8 g/L) and sodium (e.g. 3 g/L) during winter months at the Baltimore sites; regression models have suggested even higher concentrations of salinity (e.g. 14,000 µS/cm) following road salt applications at the Anacostia sites.

In order to represent salt inputs to rivers (snowmelt with road salt), pure lab-grade sodium chloride was dissolved into 100 mL unfiltered streamwater in a separate volumetric flask before being pipetted onto sediment in the Erlenmeyer flask. We acknowledge that salinization can actually be a mixture of ions, but used sodium chloride because it is commonly used as a deicer. In order to isolate the sediment-water interaction, a control flask of just unfiltered streamwater was also incubated along with the treatment flasks. All experiments for each site were incubated together in duplicates within 12 hours of field collection. The flasks were capped loosely with aluminum foil to limit evaporation but allow for air exchange to simulate open system conditions. The flasks were incubated on a shaking table (slow mode) in the dark for 24 hours at room temperature (20 ᵒC). After the incubation, the water was immediately and carefully removed from the flask using a pipette as to avoid any disturbance to the sediment, and then filtered through a pre-combusted Whatman 0.7 micron glass fiber filter. The filtered post-incubation water was stored in a fridge at 4 ᵒC for water chemistry analysis (described below). An aliquot of the post-incubation filtered water was immediately acidified in a small acid-washed HDPE Nalgene bottle to contain 0.5% high-purity nitric acid for base cation analysis and was stored at room temperature for up to 12 months. For each site, the incubation experiments were conducted in duplicates (using the same sediments and streamwater grab samples), the resulting dissolved concentrations were averaged.

*Sediment incubations across a range of salinization, streamwater chemical analyses:*

Base cation (calcium, potassium, magnesium) and trace metals (manganese, zinc, strontium, copper) concentrations in the acidified water samples were measured within 12 months after the incubation via inductively coupled plasma optical emission spectrometry in an acidified (0.5% high-purity nitric acid) analytical matrix on a Shimadzu Elemental Spectrometer (ICPE-9800; Shimadzu, Columbia, Maryland, USA). For base cation measurements, the acidified sample was nebulized in radial mode (across plasma flame). For trace metals measurements, the acidified sample were nebulized in axial mode (down plasma flame). The instrument was calibrated to the range of trace metals that are commonly observed in urban streams in accordance to analytical guidelines for surface water analysis issued by the US Environmental Protection Agency.

Table 3: Characteristics of 10 sites for lab ecosystem incubation experiments, and 1 high-frequency sensor site for in-situ chemical response during a road salting event.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Site | Land Use Context | Drainage Area (ha) | Impervious Surface (%)  | USGS Gaging Station  | Metropolitan Area  | Purpose |
| MCDN | Forest/Agriculture | 8 | 0 | 01589238 | Baltimore, MD | Incubation Exp.  |
| GFGL | Suburban | 81 | 19 | 01589180 | Incubation & Field Exp.  |
| GFGB | Suburban | 1065 | 15 | 01589197 | Incubation Exp. |
| GFVN | Suburban  | 8349 | 17 | 01589300 |
| DRKR | Urban  | 1414 | 31 | 01589330 |
| GRGF | Urban  | 557 | 61 | NA |
| CC | Urban  | 178 | 27 | NA | Washington, DC |
| PB  | Urban  | 7925 | 32 | 01649190 |
| NERP | Urban  | 18777 | 29 | 01649500 |
| SLIG | Urban  | 1676 | 41 | 01650800 |
| Rock Creek | Urban | 16600 | 32 | 01648010 | High-Freq. Sensor |