Within-Year Temporal Variability in Water Chemistry in EPA's National Aquatic Resource Surveys (2000-2014)

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Key Messages

- The objective of the National Aquatic Resource Surveys (NARS) is to determine the condition of the nation's waters at the national and large ecoregional scale. To meet this objective, the NARS sample a large number of randomly selected sites (lakes, coastal waters, rivers/streams, and wetlands) across the United States once per year.
- To assess the representativeness of the data collected from a single visit, ~10% of sites are revisited a second time within the index period of the same year. The water quality data (e.g., nutrients and ionic strength variables) collected from the revisit sites were analyzed to assess if individual site temporal variability influenced the ability to make accurate national spatial assessments.
- Analysis of signal to noise ratios and the standard deviation of water chemistry data from revisit sites indicates that the revisit (temporal and measurement) variability of water quality parameters at individual sites is small relative to the spatial variability observed nationwide.
- The fact that the difference in revisit data is small compared to the range of concentrations observed nationally means that even if a water chemistry variable concentration increases or decreases from visit one to visit two, the change is not large enough to significantly change the national assessment results. This low relative temporal variability signifies that NARS is able to effectively and efficiently assess the condition of the nation's waters using a single one-time sampling design.

Introduction

The EPA's National Aquatic Resource Surveys (NARS) were designed to estimate the condition of surface waters throughout the United States. To address this objective, a large number (~1000) of randomly selected lakes, streams, rivers, wetlands or near coastal sites are visited each year during a defined index period (e.g., summer baseflow for streams/rivers). A variety of ecological indicators are collected during a one-day sampling visit including a water sample for chemical analysis. To assess temporal variability, about 10% of the sites each year are randomly selected for a second visit within the sampling index period.

A commonly heard observation about the NARS approach to chemical sampling and resulting assessment is that "you can't say anything about the water chemistry at a site with just one sample." This concern is often connected to other statements about the variability that exists within a single waterbody and interests in evaluating temporal differences for local/watershed-scale objectives. However, the temporal and spatial sampling frequency that is required for a particular study is dependent on the scale and objective of the specific monitoring project.

Variability in water chemistry exists across space and time; both are of interest. Because resources are limited, monitoring programs must balance how intensively to sample both spatially and temporally based on their objectives. NARS, with the primary objective of assessing condition at the national and broad ecoregional scales, focuses its efforts on spatial differences by sampling a large number of sites once or twice that are located representatively across the United States. It is critical to note that the goal of NARS is not to provide assessments of individual waters but to characterize the condition of these waters as whole populations providing critical information about spatial patterns and changes over time. Other monitoring objectives require a different balance in the allocation of samples across space and time. For example, to address the question of temporal variability for selected parameters, frequent sampling may be needed. Resource limitations tend to require that such studies focus on only a small number of systems, however, thus limiting their ability to consider spatial variability. Both of these objectives address important questions, but that doesn't mean that the same frequency of sampling is required. The objective of this white paper is to evaluate whether the NARS approach is effectively addressing variability with respect to water chemistry parameters given

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its objective of large-scale national and ecoregional assessments by using the NARS spatial data along with the site revisit data.

Methodology

The NARS data that we analyzed consisted of measurements from the surveys in Table 1. All surveys measured pH, conductivity (or salinity), and nutrients (Total P, Total N, ammonium, nitrate, chlorophyll-a) with the exception of no chlorophyll-a measurements in stream/river water and no nitrate measurements in near coastal. Lakes and streams/rivers also measured base cations (Ca, Mg, Na, K), acid neutralizing capacity (ANC), sulfate, chloride, dissolved organic carbon (DOC), color, silica and turbidity. Note that near coastal sampling includes the freshwater Great Lakes near shore zone.

Resource	Number of	Number of Sites with Repeat Visits Within-	
	Sites	Year	Survey Years
Streams/Rivers	6,446	371	2000-2004, 2008-2009, 2013-2014
Lakes	2,482	192	2007, 2012
Wetlands	668	48	2011
Near Coastal	1,341	102	2010

Table 1. Sample size of NARS studies with water chemistry samples

Due to the extreme difference in the magnitude of concentration between freshwater and saline waters, we analyzed the ionic strength variables (Ca, Mg, Na, K, ANC, SO₄, Cl) in separate analyses for freshwater vs. saline sites. Similarly, conductivity was analyzed for freshwater site data and salinity for saline site data. To distinguish saline from freshwater sites, we used a conductivity above/below 2000 μ S criteria. There were very few revisit sites in saline lakes and streams/rivers so that data is not reported.

We quantified variability using two statistical approaches and one graphical approach. Graphically, we simply plotted visit 2 versus visit 1 data along with a 1:1 line for each resource type. In all 1:1 plots except for pH, DOC and Salinity, the plot axes are log(x+1) transformed due to the orders of magnitude variability in the data. Statistically, we calculated a signal:noise ratio and pooled standard deviation for each analyte in each survey.

Signal:Noise (S:N): is simply the ratio of the variance among all sites (the signal) to the variance within site from the revisits (the noise). Variances were calculated using a repeated measures analysis of variance model. Note that the noise variance includes measurement variance (e.g. laboratory and sampling variability) as well as temporal revisit variance.

At S:N=0, all the variance in water chemistry observed among sites in the survey can be attributed to "noise." In terms of its effect on making spatial assessments of chemical condition in survey data, Kaufmann et al. (2014) report that the adverse effects of noise variance are negligible when S:N >10, become minor as S:N decreases to 6, increase to moderate as S:N decreases to 2, and become severely limiting as S:N approaches 0.

S:N can be low due to either low signal and/or high noise. If all the data for metric X is between 0 and 2, the S:N is likely to be very low (no signal). If there is high diurnal variability relative to the range in the data, S:N will also be low. One may think an indicator is noisy relative to a restricted local range of data, but if there's a large national range in the data, the national S:N may be quite high.

Pooled Standard Deviation (SD): is the pooled standard deviation of the revisit samples (the square root of the repeat visit variance). As SD is proportional to absolute concentration, the overall SD across the multiple orders of magnitude range in concentrations across the U.S. is typically not that useful. Therefore, we arbitrarily divided the data into three concentration ranges (low, medium, high) for each analyte to make them more meaningful (e.g., a SD for total P for low, intermediate and high nutrient systems). The specific concentration ranges for each analyte were defined arbitrarily for interpretive ability and are given in each result table. There's no set standard defining what is noisy (high) or stable (low) variability. It depends on what the data are to be used for. The numbers presented in the tables here can be used to indicate typical repeat measurement variability in the three different concentration ranges.

Results

Example results are presented here for conductivity (Fig. 1, Table 2) in freshwater systems and total phosphorus (TP) in all systems (Fig. 2, Table 3). Results for all the remaining analytes are presented in Appendix 1. The wide range in concentrations observed across the U.S. are shown in the 1:1 plots for each analyte. They often span 3-4 orders of magnitude.

For conductivity, the S:N ranged from 20 in near coastal to 134 for lakes. Thus, variability in conductivity between visits is much smaller than the spatial variability in conductivity across U.S. surface waters as is also evident in Fig. 1. For low conductivity sites (0-100 μ S), the SD between sample visits ranged from 6-12 μ S among the NARS resource groups. Similarly, in medium conductivity systems (100-500 μ S), the SD between sample visits ranged from 21-42 μ S (Table 2). As a percentage, the SD between visits was typically ~5-10% of the observed conductivity range.

Variability of TP among sites was also much greater than between visits with S:N ratios between 10 and 19 for lakes, wetlands, and streams/rivers. For near coastal, the S:N was 3.3 mostly due to a smaller signal as the SD between visits for near coastal sites was similar to that seen in the other resource groups (Table 3). For oligotrophic systems (TP = 0-25 μ g/L) the SD between visits ranged between 4-7 μ g/L for all resource groups. For more mesotrophic systems (TP = 25-100 μ g/L), the SD between visits ranged from 16-26 μ g/L (Table 3). As a percentage, the SD between visits was typically ~15-30% of the observed TP range.

S:N, pooled SD, and 1:1 plots for all of the other NARS water chemistry analytes show these same basic patterns (Appendix 1). Ionic strength variable variability (i.e. Ca, Mg, Na, K, ANC, SO₄, Cl) followed the pattern shown by conductivity. Ionic strength variables tend to have higher S:N (> 10) and less revisit variability than nutrient variables. The variability in nutrient variables (i.e. total nitrogen, nitrate, DOC, color, silica, chlorophyll-a, turbidity) resembled the patterns shown by TP. It seems likely that the dominant processes driving nutrient concentrations (biogeochemical cycling, anthropogenic additions) are somewhat more temporally variable and/or have smaller natural ranges than the process driving ionic strength (weathering, soils, geology). The only chemical variable with a S:N below 2 is ammonium in lakes and near coastal and that's because ammonium concentrations are almost universally very low (no signal).



Figure 1. Visit 1 versus visit 2 plots for conductivity at freshwater sites (Near Coastal sites are all Great Lakes sites). The solid line is a 1:1 line and axes are log(x+1) transformed.

Table 2. Overall freshwater site signal:noise ratio (S:N) and pooled standard deviation (SD) in surface water conductivity within three conductivity range classes.

		SD Low	SD Med	SD High
Survey Resource	<u>S:N</u>	(0-100 uS)	(100-500 uS)	(500-2000 uS)
Streams/Rivers	31.4	8.76	41.6	116
Lakes	134	6.13	21.3	67
Wetlands	69.0	9.57	38.8	95.5
Near Coastal	19.8	12.3	27.3	



Figure 2. Visit 1 versus visit 2 plots for total phosphorus at all sites. The solid line is a 1:1 line and axes are log(x+1) transformed.

Table 3. Overall signal:noise ratio (S:N) and pooled standard deviation (SD) for surface water total phosphorus within three concentration range classes.

		SD Low	SD Med	SD High
Survey Resource	S:N	(0-25 ug/L)	(25-100 ug/L)	(>100 ug/L)
Streams/Rivers	10.2	6.39	25.5	225
Lakes	18.6	5.24	16.8	123
Wetlands	14.8	6.61	19.4	265
Near Coastal	3.29	4.18	16.4	64.1

<u>Summary</u>

The overall conclusion for almost all NARS water chemistry variables is that at the scale of the U.S., spatial variability is far greater than between visit temporal and measurement variability. The exception being nutrient variables (e.g., ammonium) that were universally very low across all sites in the survey. Therefore, results of assessments made at the national and large ecoregion scale would not significantly change with increased sampling frequency during the index period. In addition, the distribution of the data in the 1:1 plots (Figure 1, Figure 2, and Appendix 1) show that a one-time water sample does a good job of characterizing water chemistry at a site in terms of placing it along the spatial gradient of water chemistry observed in NARS. Thus, a one-time sample is sufficient to meet the NARS objectives of characterizing the status and extent of water chemistry in the surface water population of the U.S. However, it is important to note that for studies that seek to understand water chemistry parameters at different spatial and temporal scales, the revisit variability shown here needs to be evaluated in context of the specific monitoring objectives of the particular study.

References

For a more technical and in-depth discussion of signal to noise ratios, variability, and its effect on NARS assessments, see;

Kaufman, P.R., P. Levine, E.G. Robison, C. Seeliger, and D.V. Peck. 1999. Quantifying physical habitat in wadeable streams. Washington DC: U.S. Environmental Protection Agency, EPA/620/R-732 99/003.

Kaufmann, P.R., R.M. Hughes, J. Van Sickle, T.R. Whittier, C.W. Seeliger, and S.G. Paulsen. 2014. Lakeshore and littoral physical habitat structure: A field survey method and its precision. Lake and Reservoir Management, 30:157-176, dx.doi.org/10.1080/10402381.2013.877543.

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Appendix 1.

The appendix includes the results for all the other NARS chemical analytes. The plots show the relationship between visit 1 and visit 2, the line is a 1:1 line. In all cases except pH, DOC and Salinity, the plot axes are log(x+1) transformed. The table for each analyte shows the signal to noise ratio (S:N), and the pooled standard deviation of the visit 1-2 pairs broken down into three different concentration ranges (low, medium, high). Specific concentration ranges for the low, medium, and high groups are given in each table. For ionic strength variables (Ca, Mg, Na, K, ANC, SO4, Cl), only the freshwater (Conductivity < 2000 µS) site results are shown.



		SD Low	SD Medium	SD High
рН	S:N	(0-6)	(6-8)	(>8)
Stream	11.2	0.456	0.171	0.162
Lake	5.44	0.111	0.28	0.343
Wetland	7.04	0.387	0.284	0.621
Near Coastal	3.16		0.198	0.17

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Total Nitrogen



		SD Low	SD Medium	SD High
Total Nitrogen	S:N	(0-250 ug/L)	(250-1000 ug/L)	(>1000 ug/L)
Stream	12.3	44.9	188	1350
Lake	23.2	42.5	160	818
Wetland	25.2	54.9	207	1050
Near Coastal	3.76	32.2	138	402

Ammonium



		SD Low	SD Medium	SD High
Ammonium	S:N	(0-1 ueq/L)	(1-5 ueq/L)	(>5 ueq/L)
Stream	3.98	0.31	1.4	44.4
Lake	-0.381	0.363	1.61	41.2
Wetland	4.15	0.465	1.76	20.8
Near Coastal	0.537	0.336	2.64	6.92

Nitrate







		SD Low	SD Medium	SD High
Nitrate	S:N	(0-10 ueq/L)	(10-100 ueq/L)	(>100 ueq/L)
Stream	12.3	2.08	19.2	143
Lake	99.1	2.59	20.5	34.9
Wetland	2.00	2.18	32.8	

Dissolved Organic Carbon



Dissolved		SD Low	SD Medium	SD High
Organic Carbon	S:N	(0-5 mg/L)	(5-10 mg/L)	(>10 mg/L)
Stream	11.1	0.592	1.48	4.92
Lake	97.2	0.388	0.687	4.35

Color



Color	S:N	SD Low (0-10 PCU)	SD Medium (10-50 PCU)	SD High (>50 PCU)
Stream	4.52	4.04	7.77	59
Lake	8.2	4.32	5.9	40.1

Silica



Silica	S:N	SD Low (0-10 mg/L)	SD Medium (10-25 mg/L)	SD High (>25 mg/L)
Stream	9.93	1.44	3.59	7.28
Lake	28.4	1.71	5.37	11

Turbidity



Turbidity	S:N	SD Low (0-5 NTU)	SD Medium (5-25 NTU)	SD High (>25 NTU)
Stream	115	1.21	9.33	181
Lake	6.69	1.1	6.85	33.9

Chlorophyll-a



Visit 1 - Chlorophyll-a	(ug/L)
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		SD Low	SD Medium	SD High
Chlorophyll-a	S:N	(0-10 ug/L)	(10-50 ug/L)	(>50 ug/L)
Lake	3.85	2.47	16.9	63.6
Wetland	12.6	3.21	20.1	83.4
Near Coastal	3.22	2.06	11.2	

Acid Neutralizing Capacity – Freshwater Sites



Acid Neutralizing Capacity	S:N	SD Low (<500 ueq/L)	SD Medium (500-2500 ueq/L)	SD High (>2500 ueq/L)
Stream	39.2	44.8	236	440
Lake	98.3	28.9	153	309

Sulfate – Freshwater Sites



		SD Low	SD Medium	SD High
Sulfate	S:N	(0-250 ueq/L)	(250-1000 ueq/L)	(>1000 ueq/L)
Stream	24.9	23.2	103	1100
Lake	238	13.3	50.2	364

Chloride - Freshwater Sites



Chloride	S:N	SD Low (0-250 ueq/L)	SD Medium (250-1000 ueq/L)	SD High (>1000 ueq/L)
Stream	16.9	24.8	150	560
Lake	78.7	9.32	59.1	373

Calcium - Freshwater Sites



Calcium	S:N	SD Low (0-500 ueq/L)	SD Medium (500-2500 ueq/L)	SD High (>2500 ueq/L)
Stream	31.7	39.5	197	563
Lake	41.1	21.6	201	256

Magnesium - Freshwater Sites



Magnesium	S:N	SD Low (0-500 ueq/L)	SD Medium (500-2500 ueq/L)	SD High (>2500 ueq/L)
Stream	32.3	33.2	191	728
Lake	461	19.4	70.6	264

Sodium - Freshwater Sites



Sodium	S:N	SD Low (0-500 ueq/L)	SD Medium (500-2500 ueq/L)	SD High (>2500 ueq/L)
Stream	31.8	45.2	388	801
Lake	78.7	19.8	114	640

Potassium - Freshwater Sites



Potassium	S:N	SD Low (0-50 ueq/L)	SD Medium (50-250 ueq/L)	SD High (>250 ueq/L)
Stream	19.9	4.29	18.5	83.3
Lake	219	5.25	9.43	55.3

Salinity – Saline Sites



Salinity	S:N	SD (1-60 ppt)
Wetland*	4.91	4.66
Near Coastal	6.75	3.91

* conductivity was measured in wetlands and converted to salinity in saline sites for this analysis