Groundwater geochemistry: are wells unique? A case study from upstate New York

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T56. **Streams and Aquifers: Integrating the Physical and Chemical**
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Sunday, 27 October 2013, in Room 301, at 2:35 PM

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  - Fiona Lowry, at Public Health, U of MN Graduate School
  - Molly Reed, now at Plumley Engineering, P.C., Syracuse
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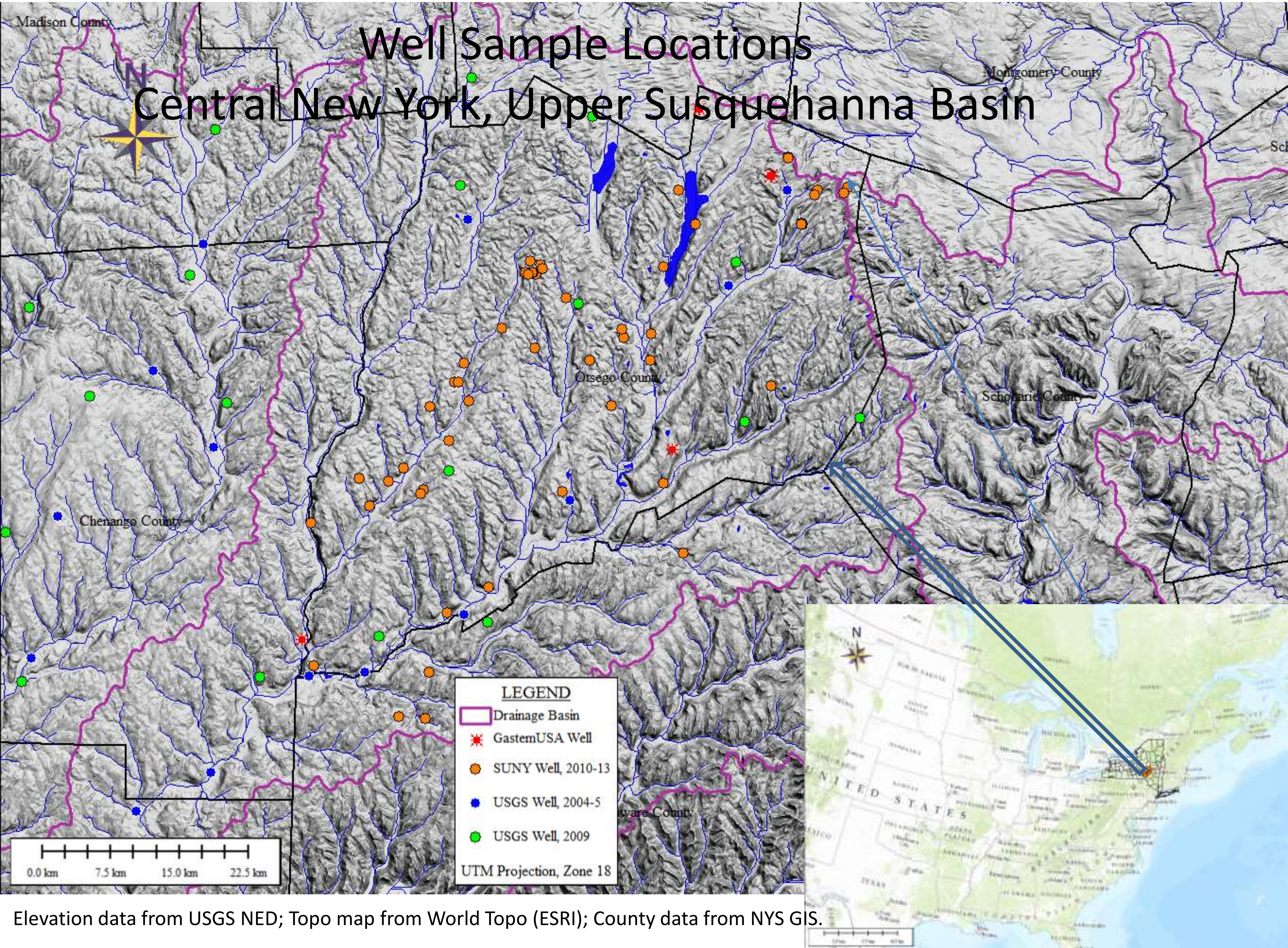
  - Ryan Pasternak, New York State Geological Survey
  - Devin Castendyk, Director of Water Resources program, SUNY Oneonta

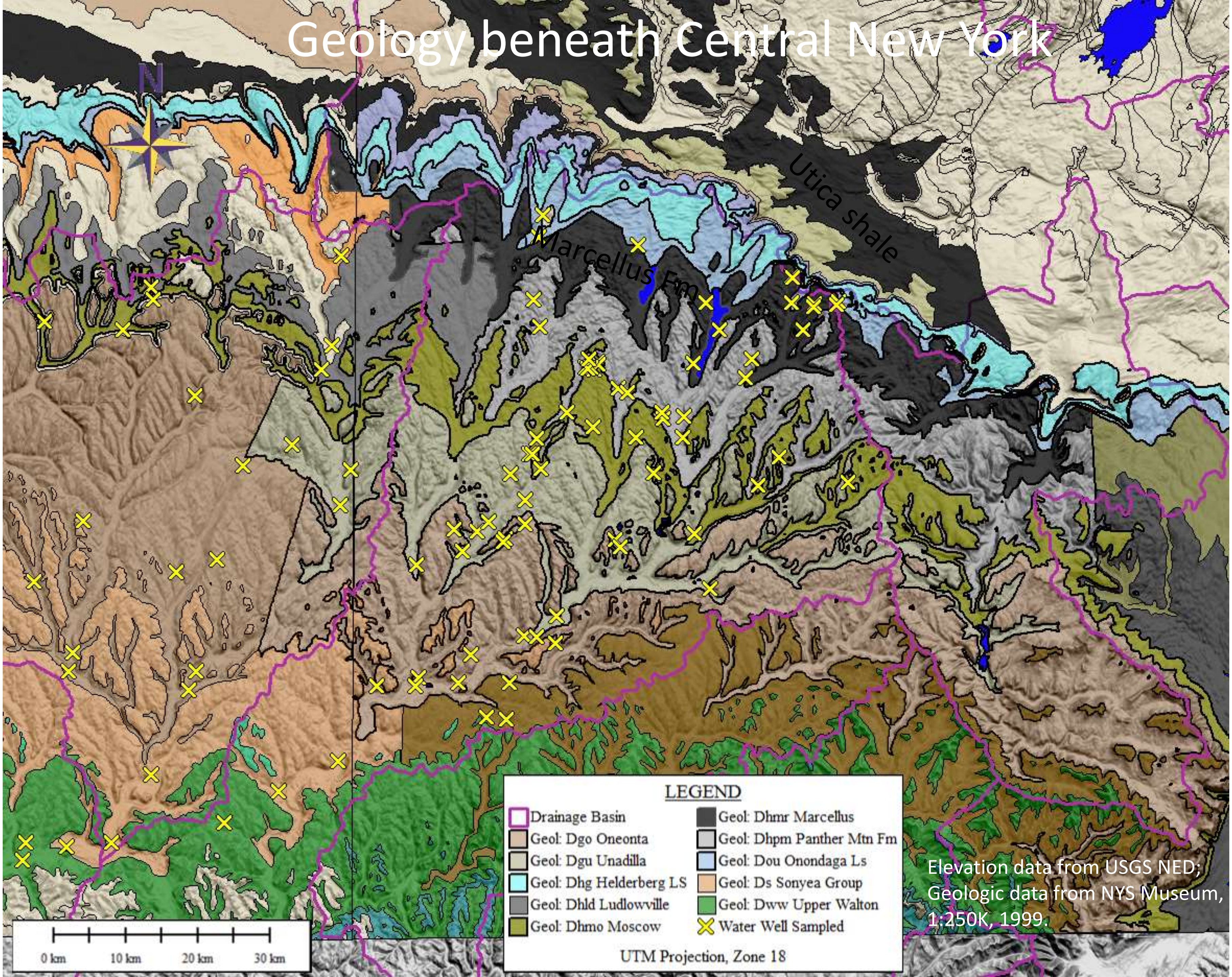
Well Sample Locations

Central New York, Upper Susquehanna Basin



Elevation data from USGS NED; Topo map from World Topo (ESRI); County data from NYS GIS.

Geology beneath Central New York



Elements we sampled for…

Na	Y	Dy	Zr	Ga
Ca	Cs	Ge	Tb	Pd
K	Br	Mo	Ho	Ag
Mg	Cu	Fe	Tl	Be
Si	Pb	Ni	Th	Bi
Mn	La	Cd	Sc	Hg
Zn	Li	Yb	Lu	In
Ba	Ce	Sm	Re	Nb
Sr	Nd	Er	Cr	Os
Rb	Eu	Al	V	Pt
Ti	W	Se	Au	Ru
U	Co	Sb	Tm	Sn
As	I	Pr	Hf	Ta
	Gd			Te

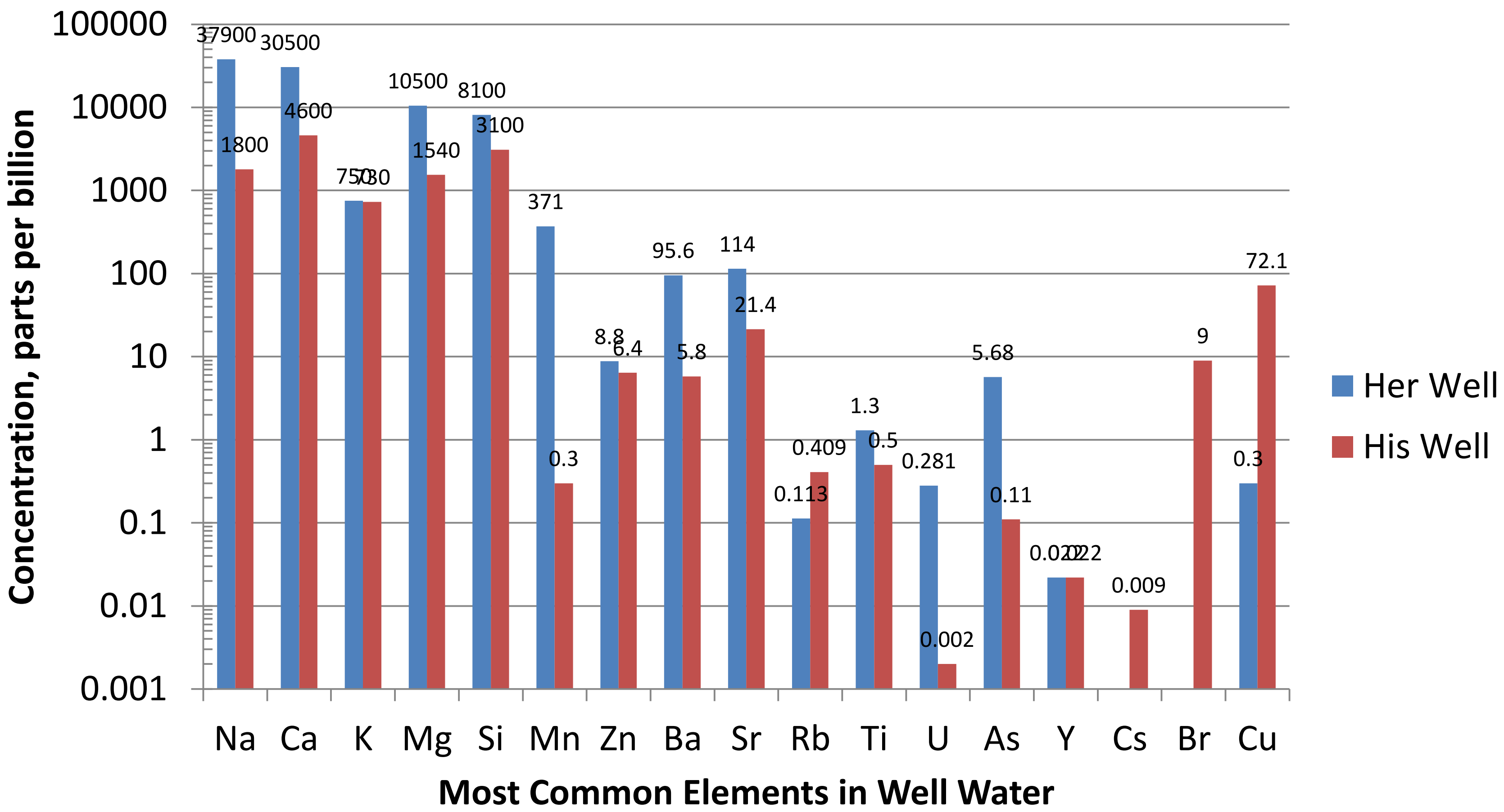
See http://www.ptable.com/ for more info on elements

Most common elements are in first column; least common are in far right column. Of these typically 33 are detected in a well (some have more, some less.)

Well Water Concentration Most Common Inorganic Elements…

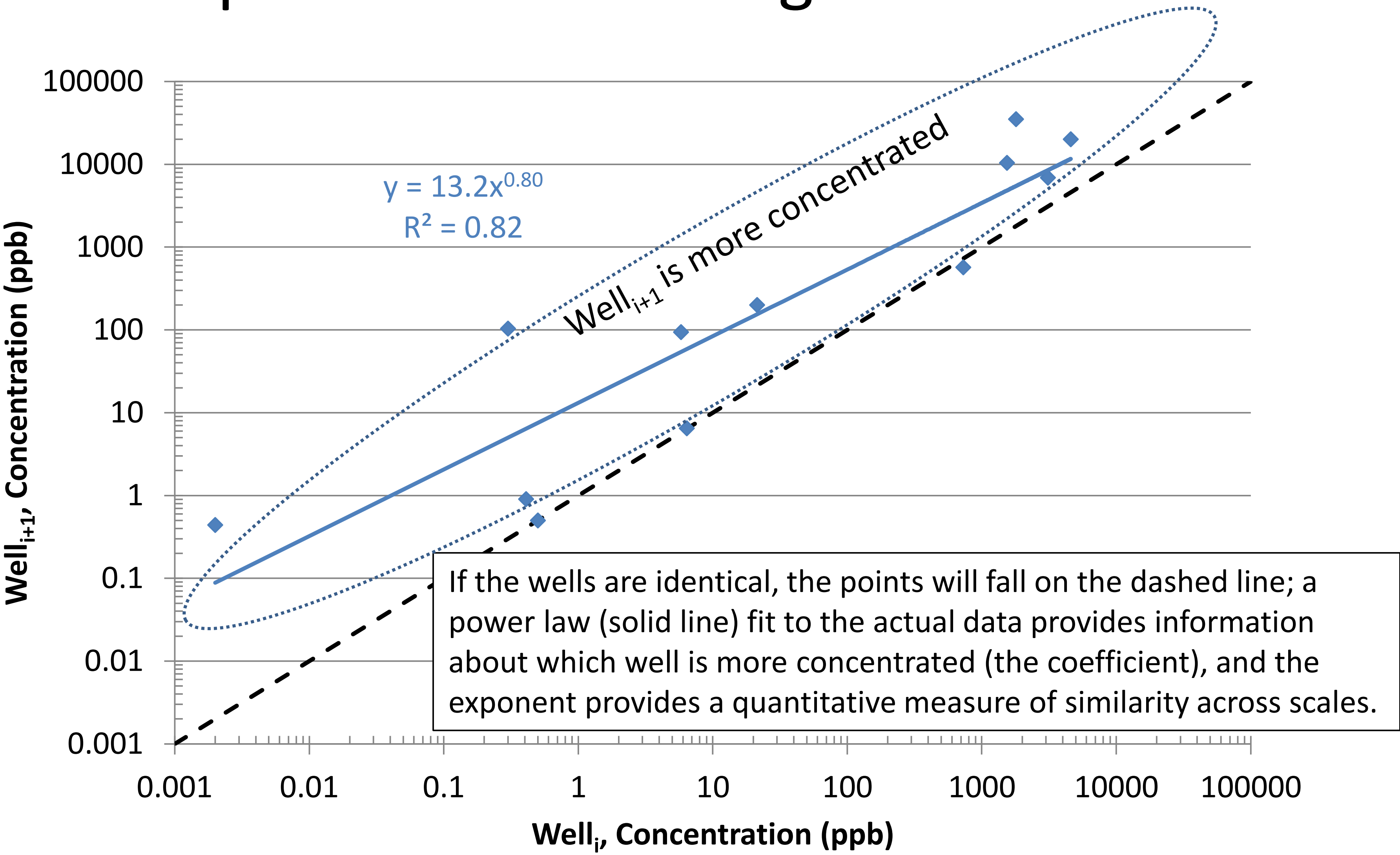
Analyte Symbol	Coefficient of Variation (std dev / ave)	Standard Deviation (μg/L)	Min (μg/L)	Max (μg/L)	Median (μg/L)	Average (μg/L)	# Wells with analyte present
Na	0.84	15617	1100	60900	15200	18689	47
Ca	0.87	15459	2100	89800	20000	17748	47
K	2.64	5702	180	35500	710	2157	47
Mg	0.73	3719	366	18100	4360	5114	47
Si	0.30	1445	2700	8800	4700	4838	47
Mn	1.40	79.90	0.3	371	20.9	57.06	47
Zn	1.47	38.85	1.5	228	12.9	26.34	47
Ba	0.89	65.29	1.6	217	55.8	73.57	47
Sr	1.38	225.93	12.8	1390	120	163.50	47
Rb	0.59	0.38	0.113	1.95	0.477	0.64	47
Ti	0.34	0.23	0.3	1.3	0.7	0.70	47
U	1.27	0.16	0.002	0.634	0.03	0.13	47
As	2.16	1.71	0.06	10.3	0.265	0.79	46
Y	1.49	0.06	0.004	0.37	0.0195	0.04	46
Cs	1.11	0.04	0.003	0.139	0.0155	0.03	46
Br	2.52	322.95	4	1800	22	128.09	45
Cu	1.43	65.95	0.3	200	5	46.17	45
Pb	1.40	0.71	0.02	3.46	0.22	0.51	43

Establishing a Baseline: Comparison between two wells

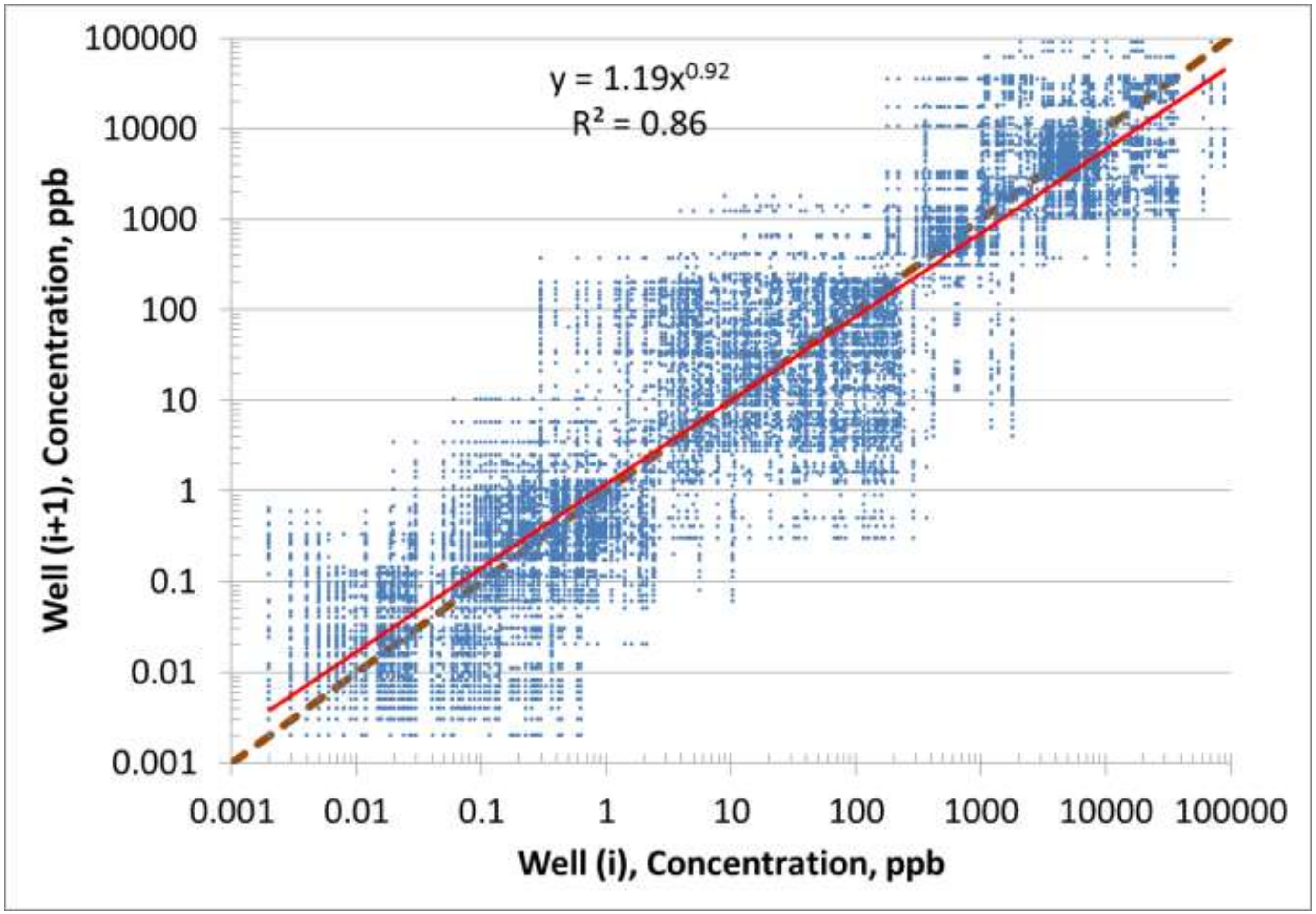


Note: Data are plotted on a logarithmic scale. In the example above, Her Well has much higher concentrations in Na, Ca, Mg, Mn, Ba, Sr, U, and As. His well has more Cs, Br, Cu.

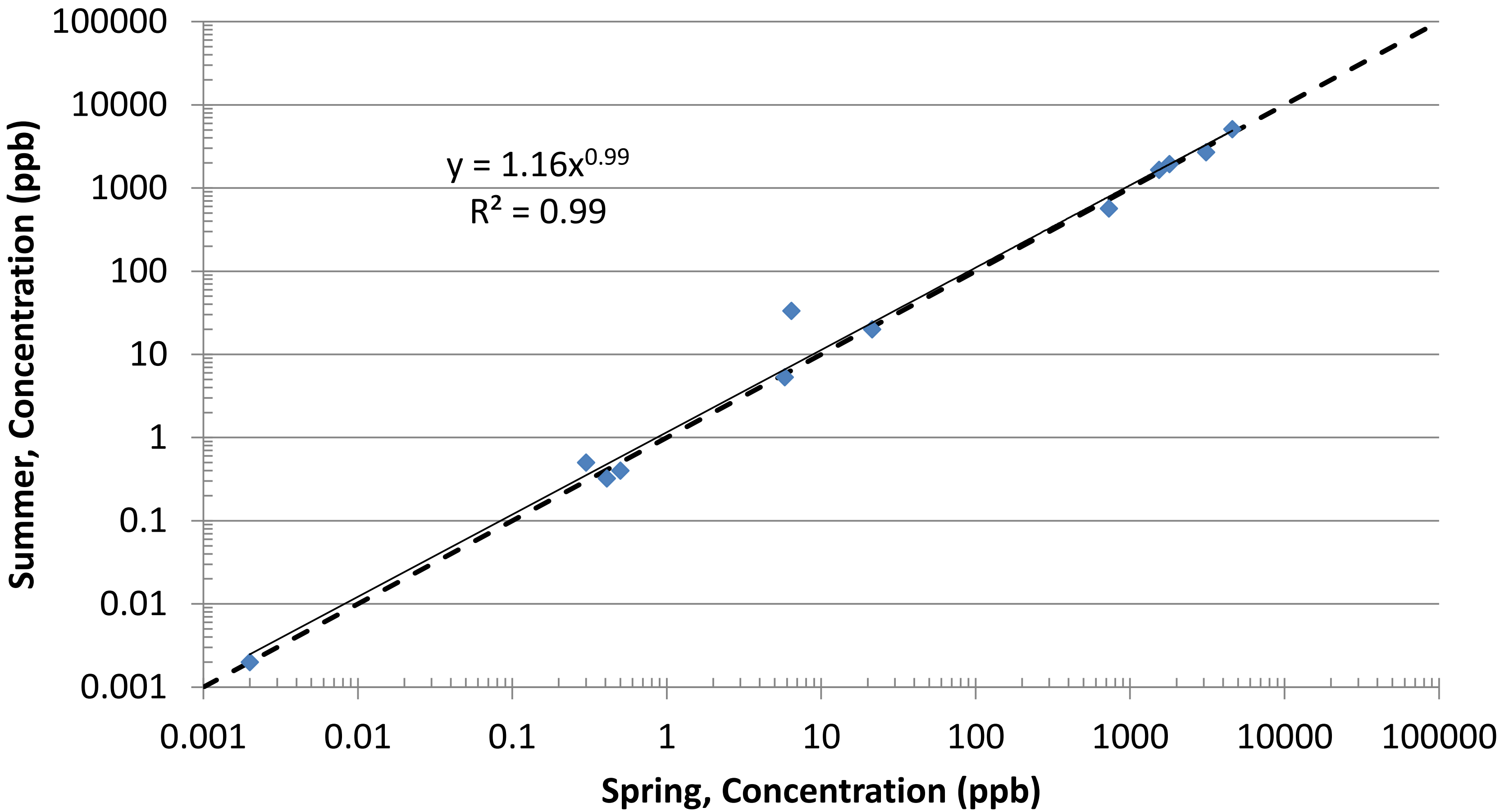
Comparison Between Wells
Scatter plot of two wells against each other



Plot of each well against every other well: Large variability in space

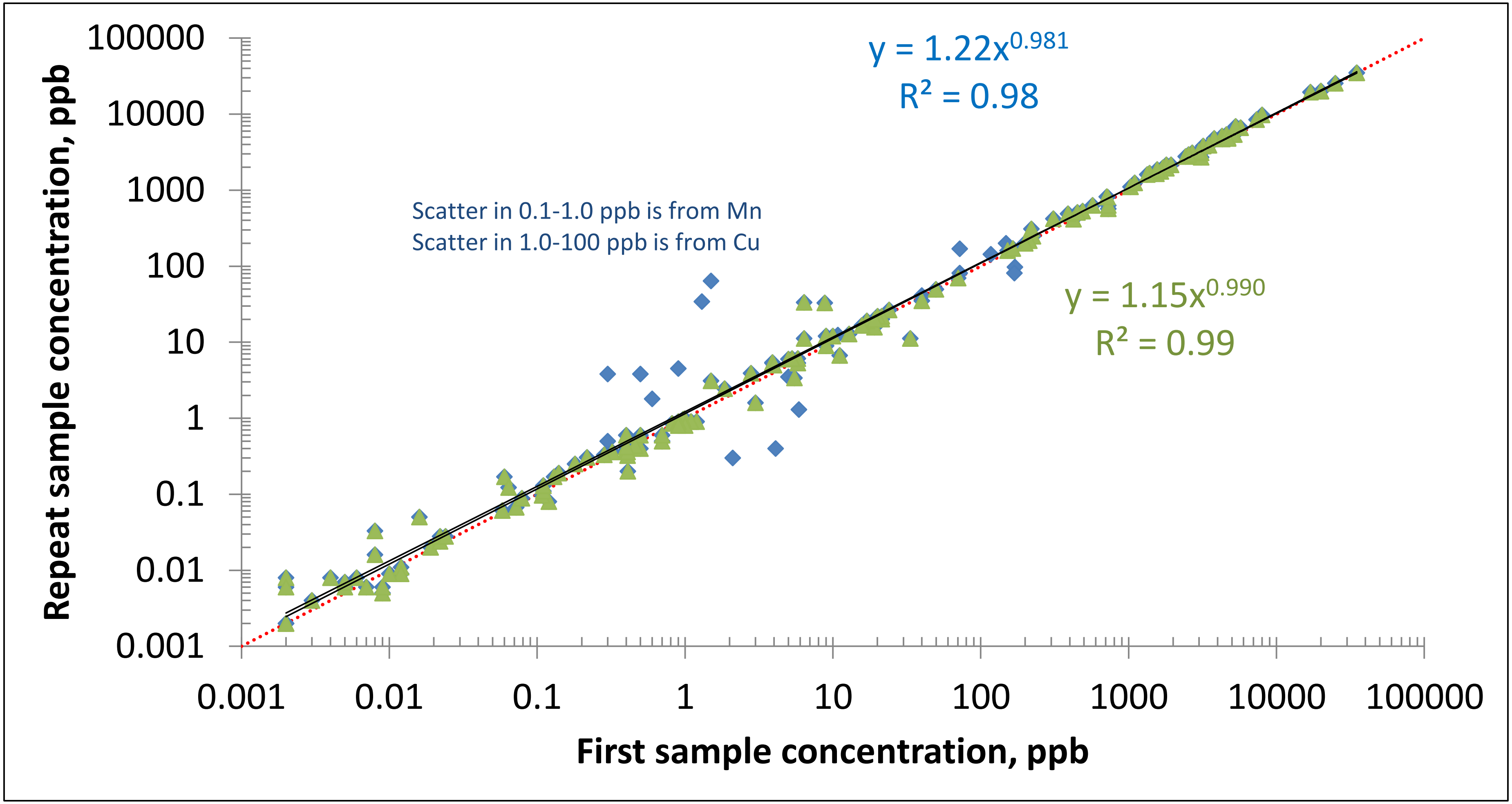


This well was sampled at two different times



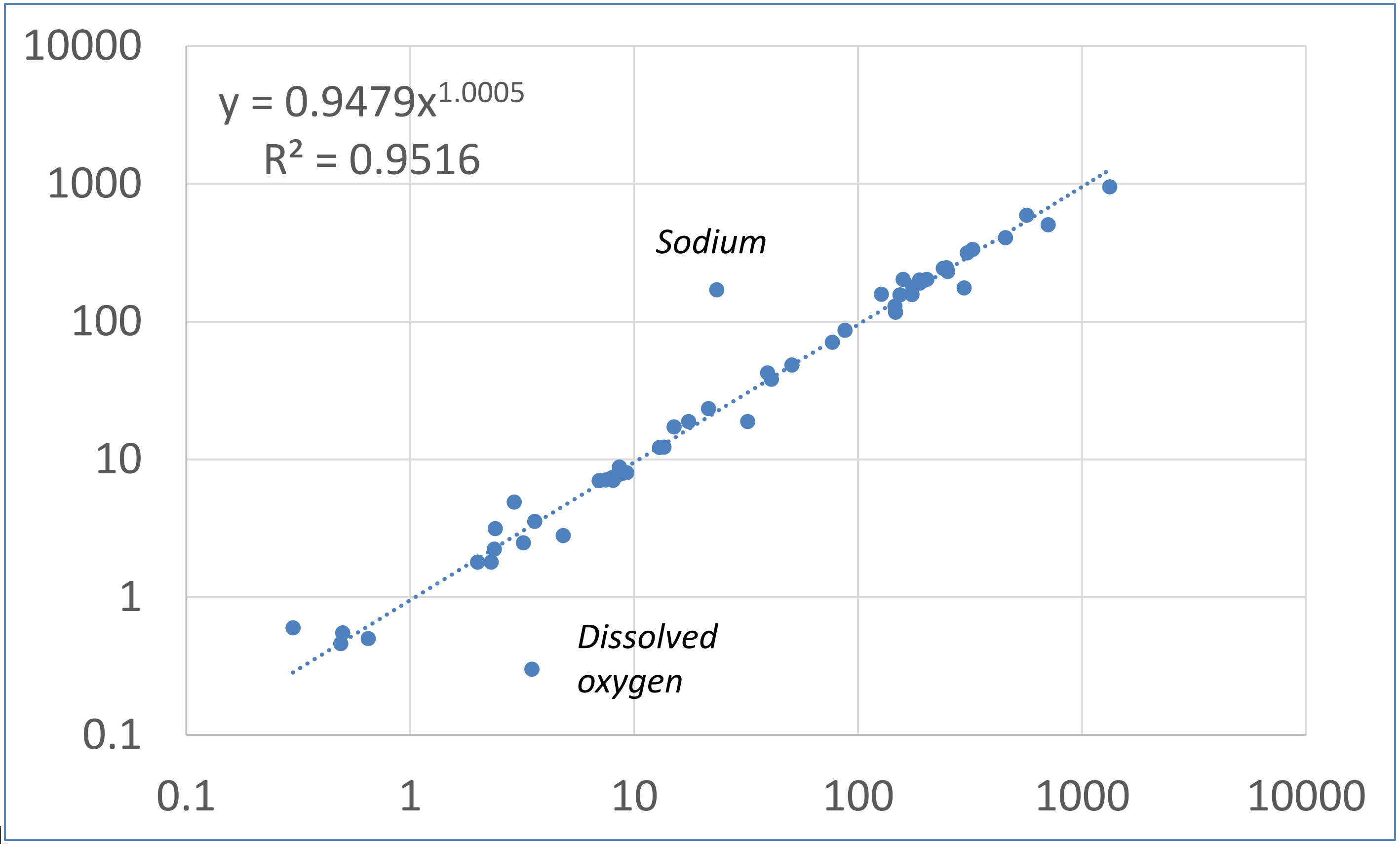
Note that the data pretty much fall on the dashed line, with slightly higher concentration in summer. The relation shows an individual well does vary, but the variability is far less than what we see between wells.

Ensemble of all wells sampled at two different times



Data from repeat sampled wells, SUNY Oneonta's sampling campaigns, 2010 to 2012

USGS Repeat Sampled Wells



Analytes
Dissolved oxygen, unfiltered, mg/L
pH, unfiltered
Specific conductance, unfiltered, uS/cm
Calcium, filtered, mg/L
Magnesium, filtered, mg/L
Potassium, filtered, mg/L
Sodium, filtered, mg/L
Acid neutralizing capacity, unfiltered, fixed endpoint, lab, mg/L as CaCO3
Alkalinity, filtered, fixed end point, laboratory, mg/L as CaCO3
Bicarbonate, filtered, fixed endpoint, laboratory, mg/L
Chloride, filtered, mg/L
Silica, filtered, mg/L
Sulfate, filtered, mg/L
Residue on evaporation @180C, filtered, mg/L

Hetcher-Aguila, K.K. and Eckhardt, D.A.V., 2006, Ground-water quality in the upper Susquehanna River Basin, New York, 2004-05: U.S. Geological Survey Open-File Report 2006-1161, 20 p., online only. http://ny.water.usgs.gov/pubs/of/of061161/

Reddy, J.E., and Risen, A.J., 2012, Groundwater quality in the Upper Susquehanna River Basin, New York, 2009: U.S. Geological Survey Open-File Report 2012–1045, 29 p., at http://pubs.usgs.gov/of/2012/1045/ .

Conclusions

- **10-20% variations in concentration are not uncommon at a single well**
- **Variations in concentration over space can range by a factor of 1000**
- **A power law is a useful comparative tool, and offers clues to whether waters are simple dilutions or more complex mixtures**

Here's to the samplers!
And to the good waters of New York








QUESTIONS?

Abstract as submitted

In advance of high volume hydraulic fracturing activities planned for central New York, we have initiated an inventory of groundwater chemistry in 53 separate wells. A few dozen of the wells were sampled repeatedly. Wells penetrate unconsolidated sand and gravel and Devonian age sedimentary strata, including the Marcellus shale. We find that deep wells are more concentrated, exhibit higher pH, and greater alkalinity. We could detect 30 to 45 elements in most wells and 15 major and minor elements were detected in all wells. We present a statistical summary of elemental concentrations for all of the wells we have sampled.

Well chemistry provides a baseline for detecting change in a well. We introduce a simple method for comparing wells against each other. The elemental concentrations in one well are plotted against another well, and a power law is fit to the data. The parameters (that is, the coefficient and the exponent) in the power law, along with a measure of the scatter, provide a powerful tool to characterize similarity and uniqueness. When the power law coefficient, correlation coefficient, and power law exponent approach unity, the samples approach identical concentrations. A high degree of similarity implies uniform dilution or concentration for all species being compared. When the exponent approaches unity, the coefficient indicates which sample is more or less concentrated than the other. When the exponent is greater than unity, major elements are more enriched in one well. The correlation coefficient (R^2, in this case) measures the scatter around the power law relation. As the correlation coefficient approaches 0, a wide scatter exists, even if the exponent indicates similarity. We apply this method to our wells and discover that individual wells look far more like themselves than any other well. One implication is that groundwater flow paths have characteristic chemical reactions with rocks along their path to the well, and reach a steady state concentration. Temporal variations amount to uniform changes in concentrations across all elements, such as might occur from mixing with very fresh water. Any mixing with non-identical water will yield either more scatter, or values for the power law parameters other than unity. We show that the elements commonly detected in all wells provide a local fingerprint of groundwater.

References

- **Hetcher-Aguila, K.K. and Eckhardt, D.A.V.**, 2006, Ground-water quality in the upper Susquehanna River Basin, New York, 2004-05: U.S. Geological Survey Open-File Report 2006-1161, 20 p., online only. http://ny.water.usgs.gov/pubs/of/of061161/
- **Reddy, J.E., and Risen, A.J.**, 2012, Groundwater quality in the Upper Susquehanna River Basin, New York, 2009: U.S. Geological Survey Open-File Report 2012–1045, 29 p., at http://pubs.usgs.gov/of/2012/1045/ .

- Online access to data presented in this presentation is available through the **Catskill Headwaters Research Institute's** site: http://www.oneonta.edu/academics/chresi/
- And as a Google Fusion table: https://www.google.com/fusiontables/DataSource?docid=1XVFFGVB2wgu_ICeDcS0XiXiWDoYpQETEnkZP1WQ