Potomac Aquifer Recharge Monitoring Laboratory (PARML)

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Analytical Determination of 1,4-Dioxane and Nitrosamines in Water

Currently two separate methods are utilized to measure these constituents:

- USEPA Method 521 – Nitrosamines
- USEPA Method 522 – 1,4 Dioxane

PARML Development of a Single (Combined) Method to Analyze both Nitrosamines and 1,4 Dioxane in a Single Analysis

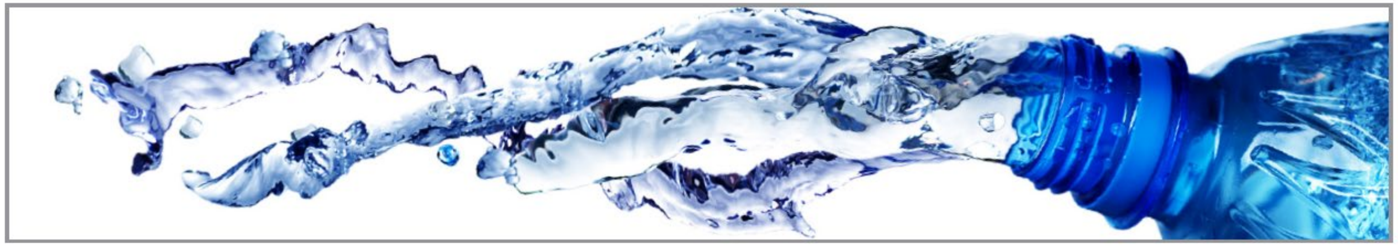
Benefits:

- Greater number of analyses per time
- Greater number of samples per time
- Increased productivity
- Reduced solvent use (less hazardous waste generation)

Requirements for a Combined Method

- Must be substantially robust/stable
- Must have detection limits comparable to individual approved EPA methods
- The method should follow well established analytical procedures and minutely detailed (described)
- The method should be published in the refereed literature

PARML is Not the First Laboratory to Explore a Combined Method



Combined Determination of 1,4-Dioxane and Nitrosamine Contaminants in Drinking Water

Using a Single SPE Cartridge and Concurrent Solvent Recondensation–Large Volume Splitless Injection (CSR-LVSI) With EI GC-MS

By Chris Rattray and Jack Cochran

Unpublished paper/ technical note on cartridge manufacturer's internet site

Some aspects of the analysis undefined

Requires large volume of sample to be extracted

https://www.restek.com/en/chromablography/chromablography/combine-epa-521-and-epa-522-into-a-single-analysis-using-a-very-large-volume-injection-with-an-agilent-style-splitsplitless-inlet/

Procedure

The method uses the same coconut charcoal sorbent solid phase extraction (SPE) cartridges and dichloromethane eluent recommended in EPA Methods 522 and 521 to concentrate 500 mL water samples to 10 mL extracts.

Samples are 50 times concentrated

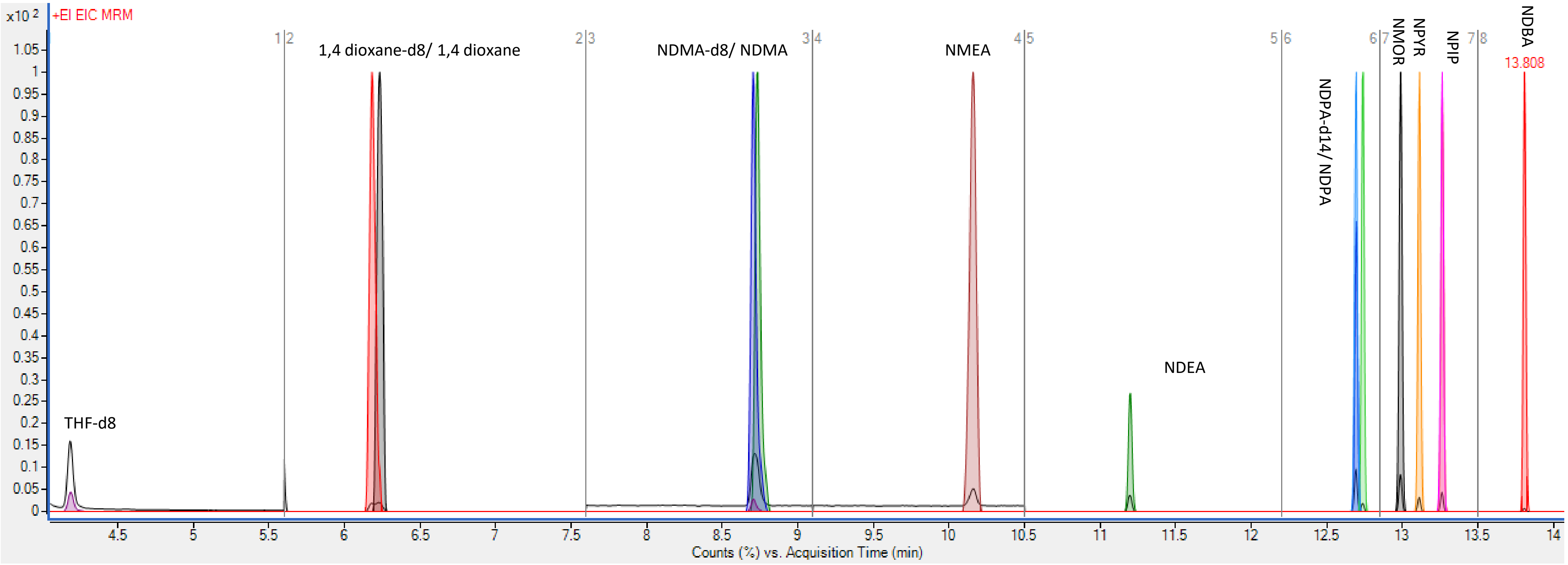
Calibration Curves For Quantitative Determination

(Selected Sample Concentrations (ng/L) in parenthesis)

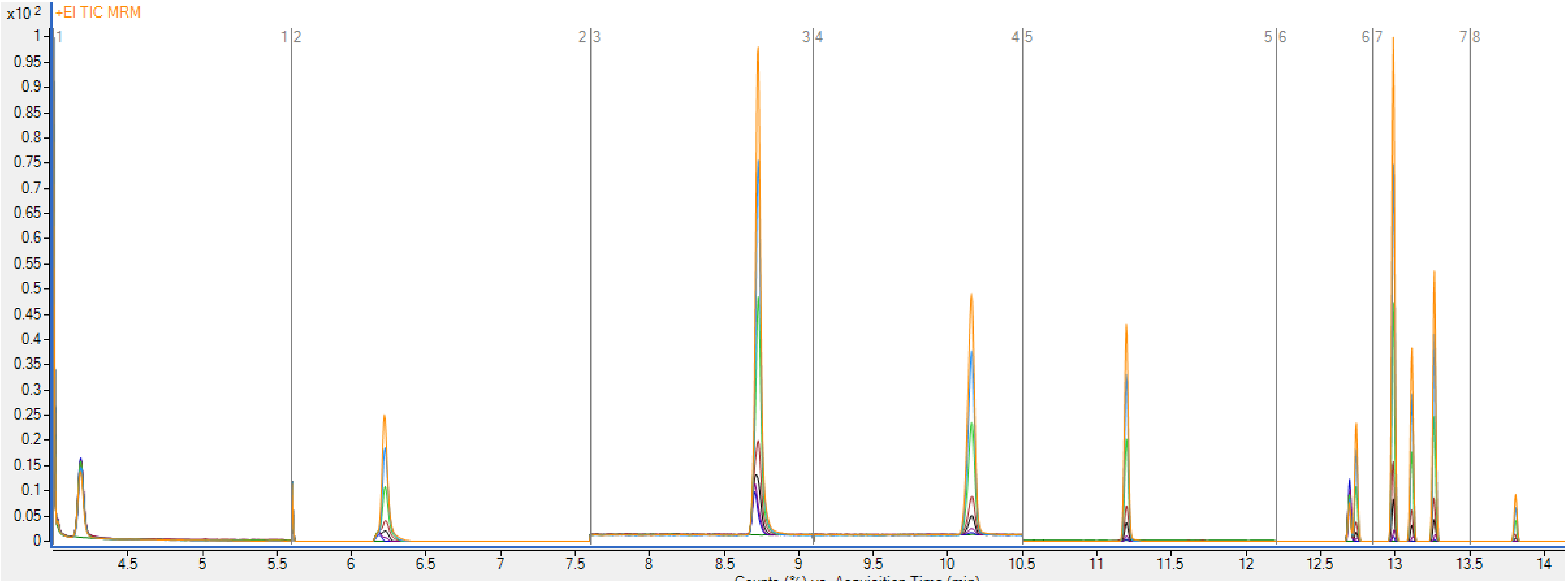
	L1 (ng/L)	L2	L3	L4	L5	L6	L7
1,4 Dioxane		200 (4ng/L)	500	1000	3000	5000	7000 (140 ng/L)
THF-d8 (IS)	1970	1970	1970	1970	1970	1970	1970
1,4 Dioxane-d8 (SUR)	2000	2000	2000	2000	2000	2000	2000
NDMA	100 (2 ng/L)	200	500	1000	2500	5000	7000
NDMA-d8 (SUR)	2000	2000	2000	2000	2000	2000	2000
NDPA-d14 (IS)	4000	4000	4000	4000	4000	4000	4000
NMEA	100	200	500	1000	3000	5000	7000
NDEA	100	200	500	1000	3000	5000	7000
NDPA	100	200	500	1000	3000	5000	7000
NPYR	100	200	500	1000	3000	5000	7000
NMOR	100	200	500	1000	3000	5000	7000
NPIP	100	200	500	1000	3000	5000	7000
NDBA	100	200	500	1000	3000	5000	7000

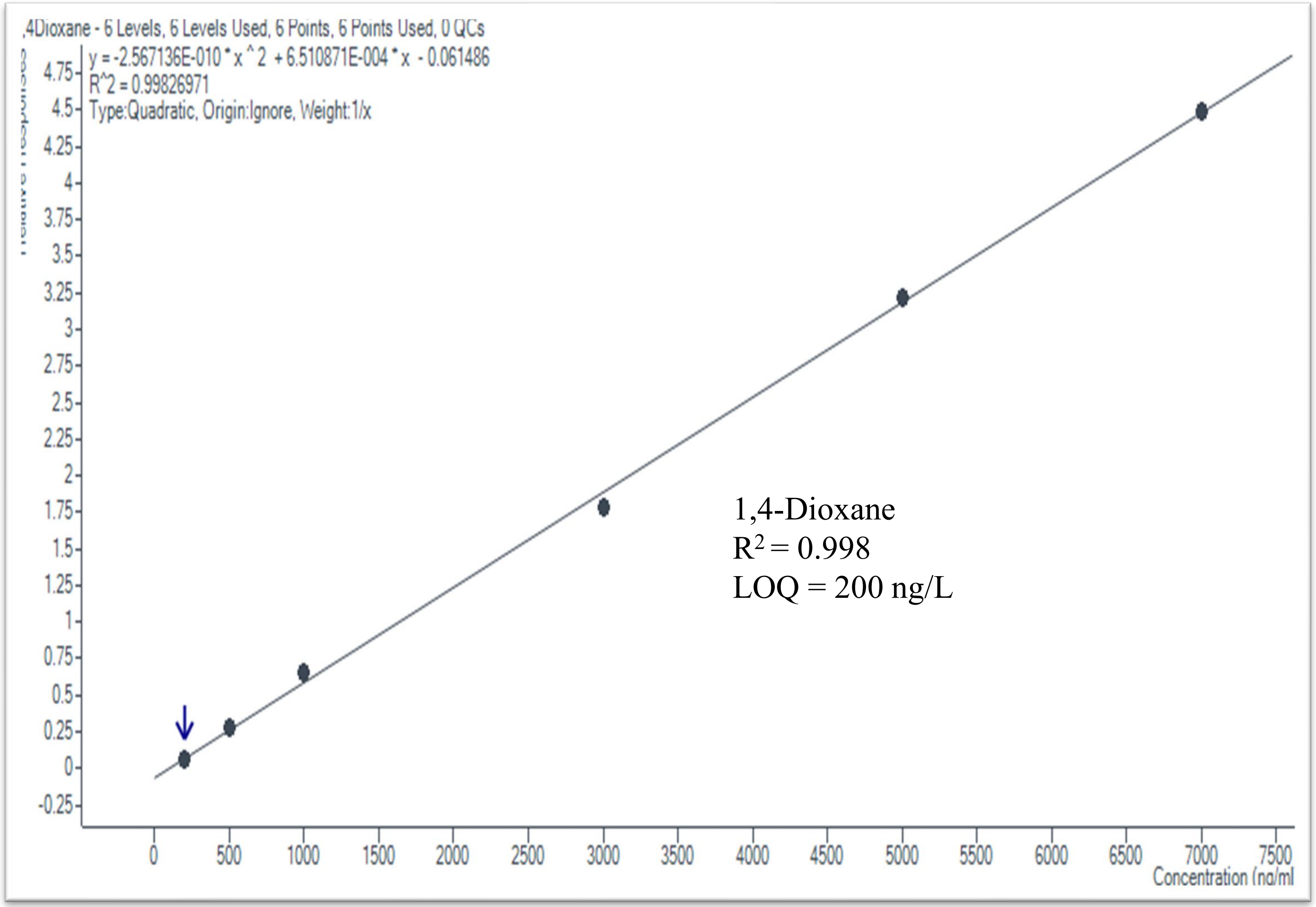
Preliminary Results

500 ng/L Nitrosamines Standard



Calibration curve (200 ng/L to 7000 ng/L)

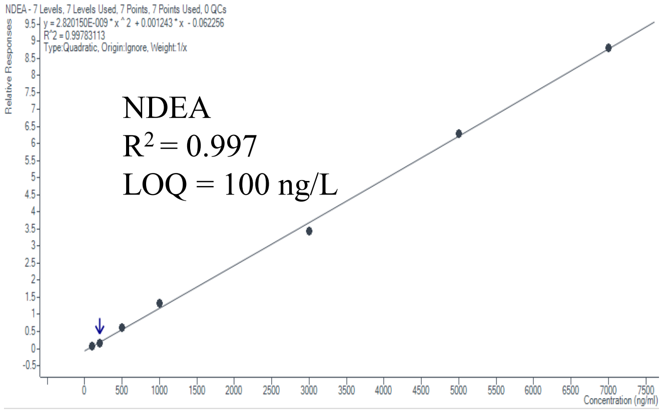


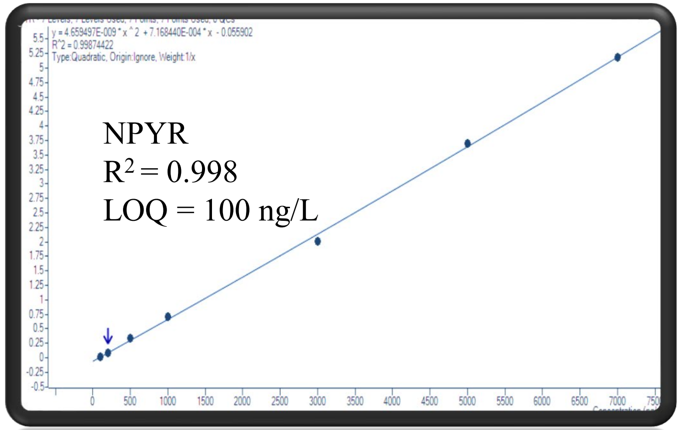


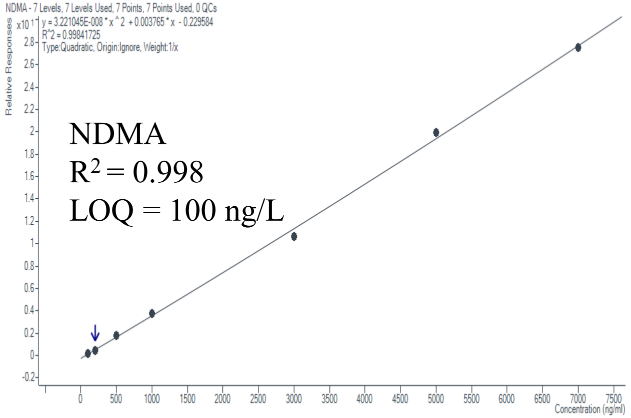
Calibration Curve for 1,4 Dioxane

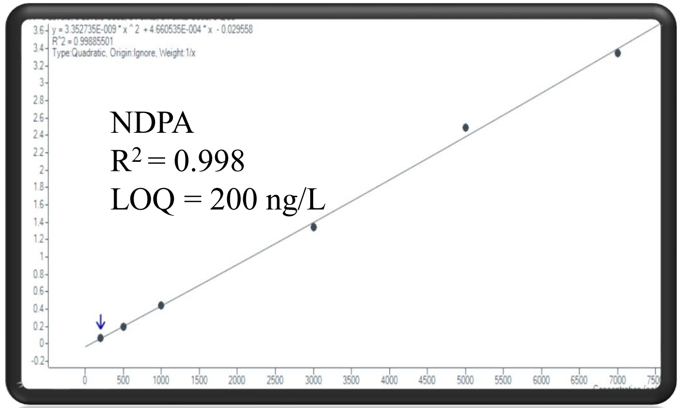
Quantitation limit for 500 mL sample (HRSD) = 0.06 µg/L
Quantitation limit for 500 mL sample (PARML in DI water) = 0.004 µg/L
Quantitation limit for 500 mL sample (Restek) = 0.010 µg/L

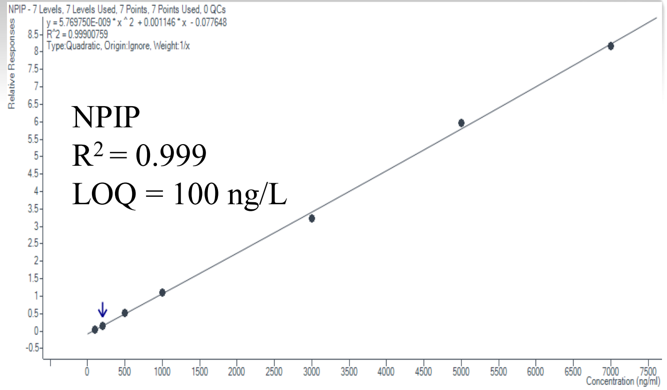
Calibration Curves for Eight Nitrosamines

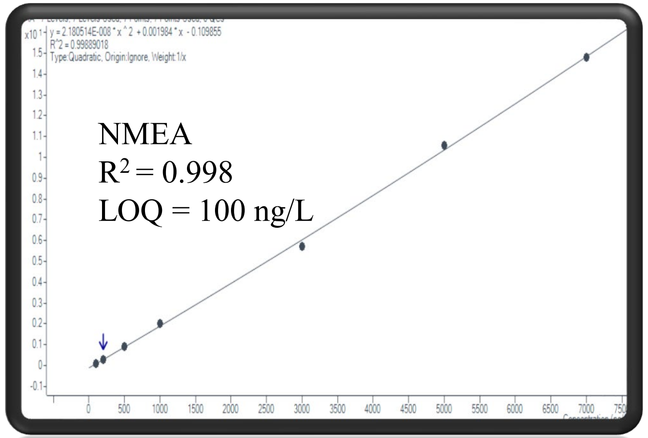


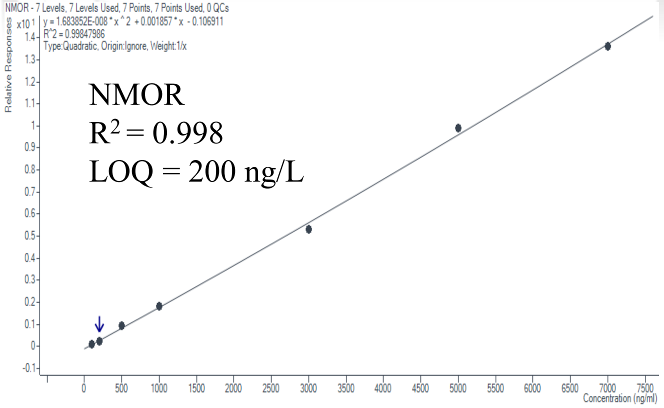


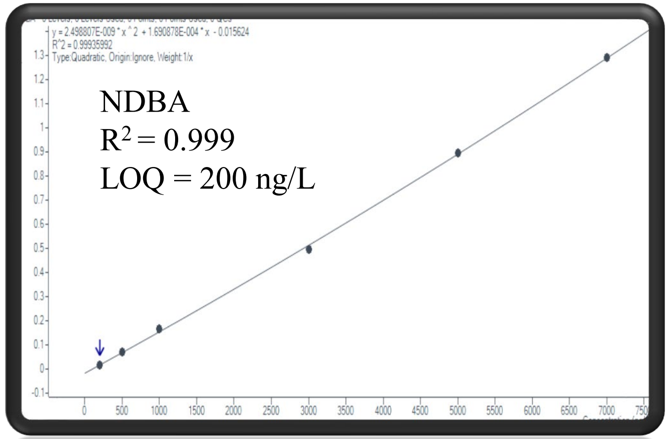












Evaluation of Analyte Recoveries from Solid Phase Extraction

Analyte Recoveries: Lab Fortified Samples (DI Water + Spiked Compound) were prepared to evaluate the recoveries. EPA considers 70 to 130% as acceptable.

Analytes	MQ Water	LFB (2ng/L)	Recover (%)	LFB (4 ng/L)	Recovery (%)
1,4 -Dioxane	4.282			7.64	84%
NDMA	0	2.308	115%		
NMEA	0	1.47	74%		
NDEA	0	1.714	86%		
NMOR	0	1.65	83%		

Surrogates	MQ Water	LFB (10ng/L)	Recover (%)	LFB (20 ng/L)	Recovery (%)
1,4 –Dioxane-d8	0			18.26	92%
NDMA-d8	0	7.23	72.3%		

LFB ≡ Lab-fortified blank

Summary

Standard curves, recoveries and detection limits all appear comparable or better than the two methods (EPA 521, 522) operated separately.

The combined method uses readily available materials under well defined conditions with an industry standard triple quad GC/MS.

Savings in analysis time has been identified without compromising the quality of the analyses

Next step is to challenge the analysis with more complex waters of varying TOC concentrations and ionic content to assess any aqueous matrix affects

Acknowledgment

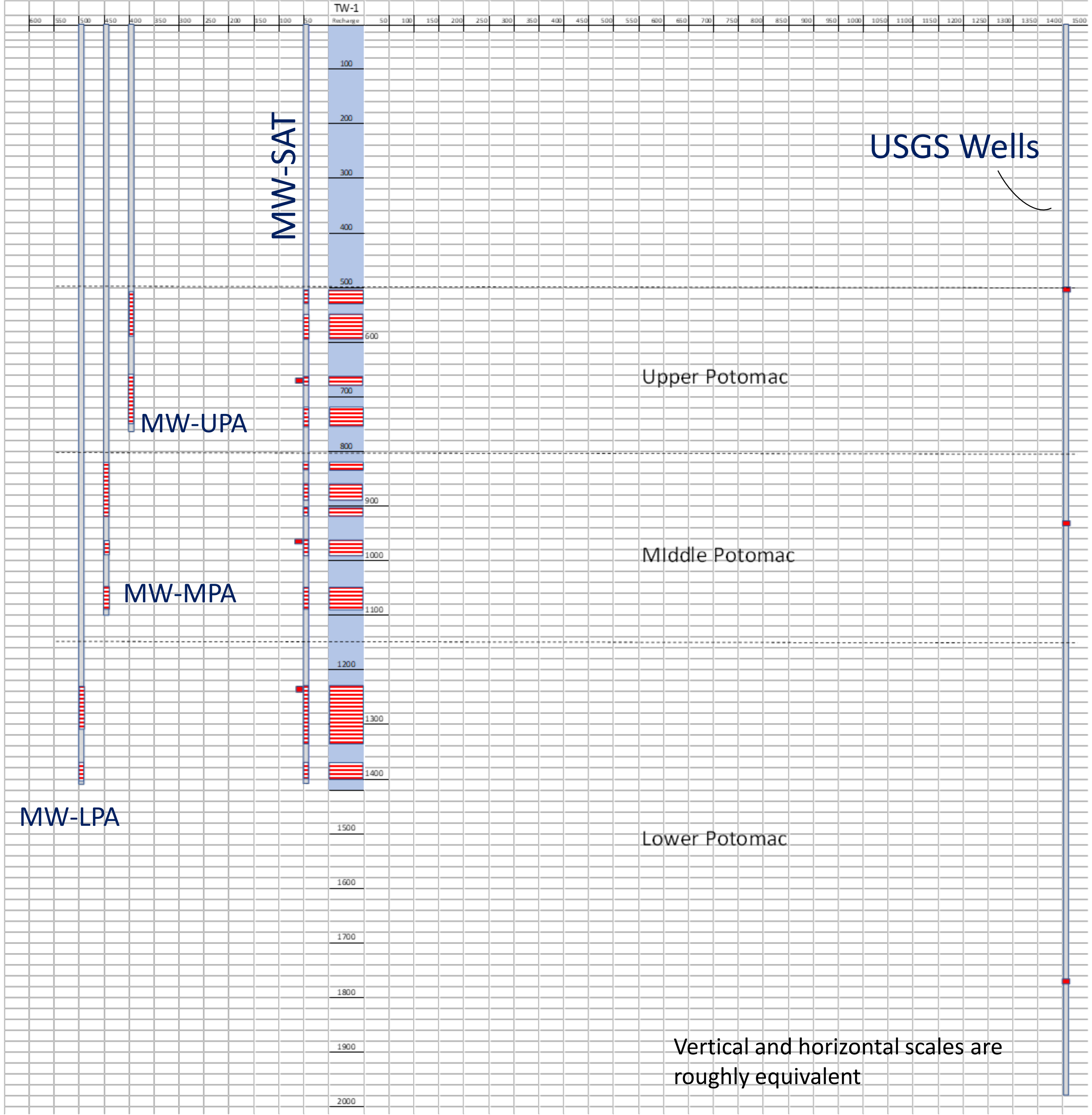
- Dr. Megan Pennington-Boggio
  HRSD Central Environmental Laboratory

Aquifer Isotope Ratio Monitoring

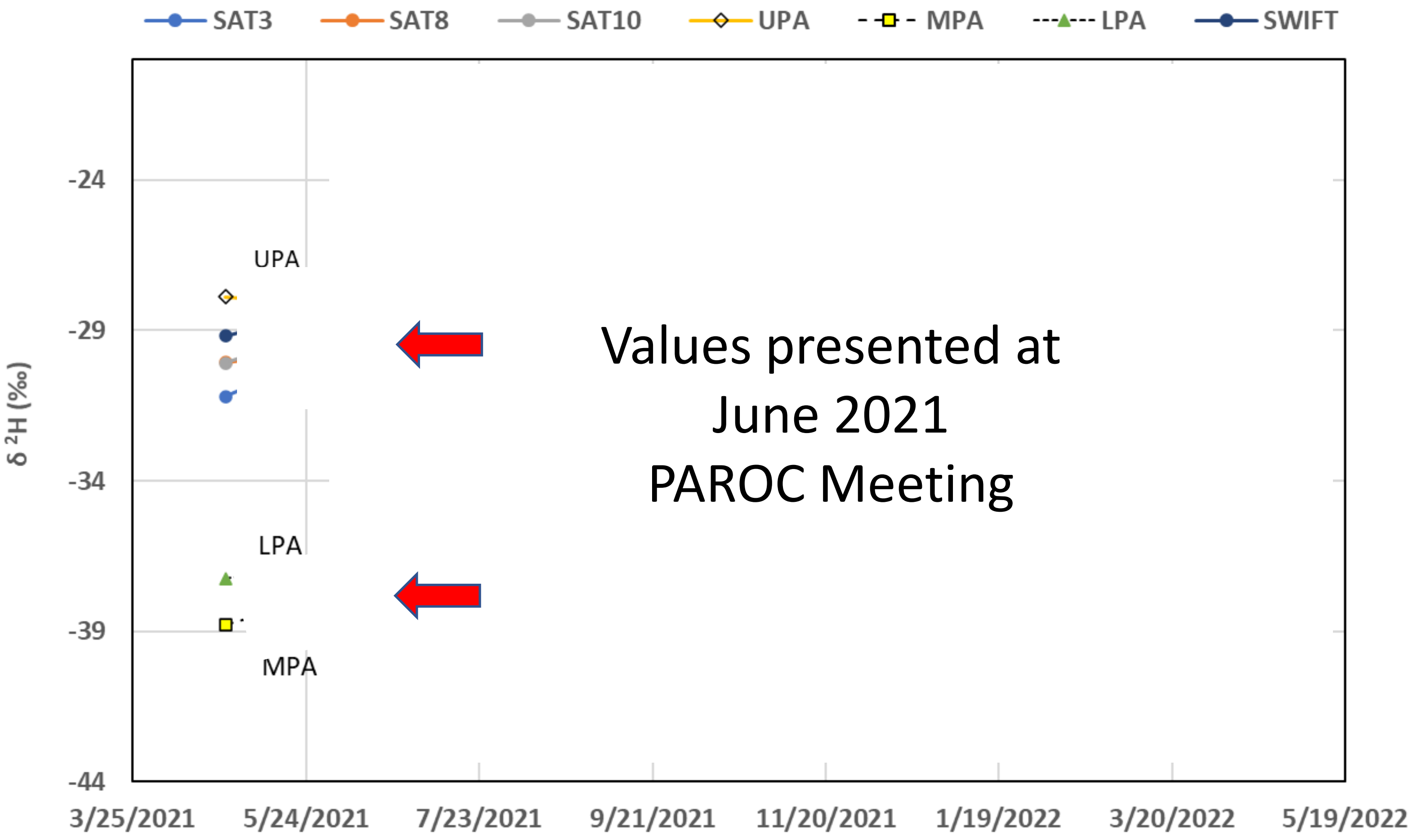
Examination of Isotopic Ratios of Oxygen ($^{18}O/^{16}O$) and Hydrogen ($^{2}H/^{1}H$) in Water Molecules to Potentially Serve as a Groundwater Tracer

- Isotope ratios of $^{18}O/^{16}O$ and $^{2}H/^{1}H$ in water can be measured
- Can be used as a natural tracer where waters of different isotopic signature are mixed
- Essentially unaffected by geochemical reactions on short time scales

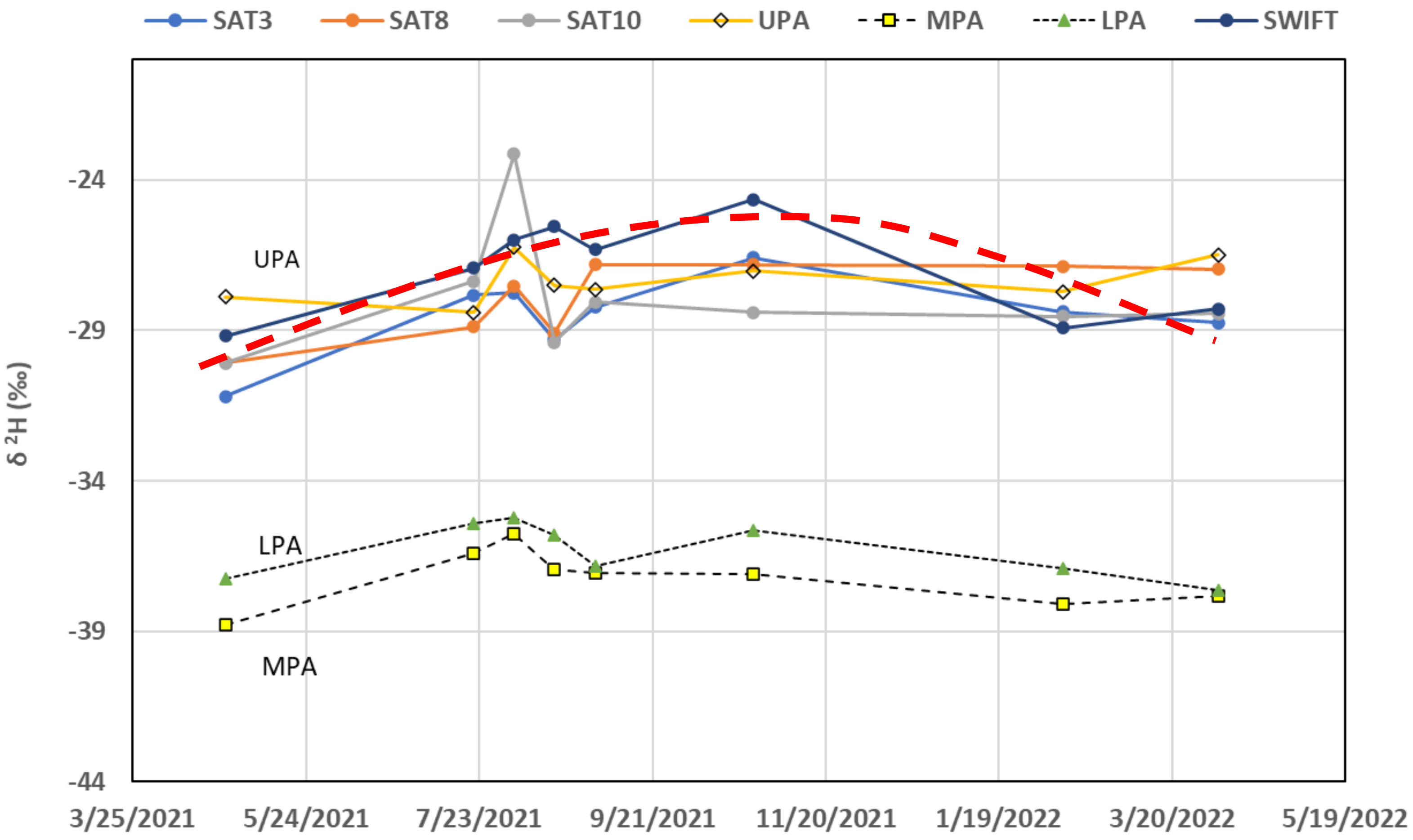
Recharge and Monitoring Wells at the SWIFT Research Center and USGS Wells



Isotope Ratio in SWIFT Water and in HRSD Monitoring Wells



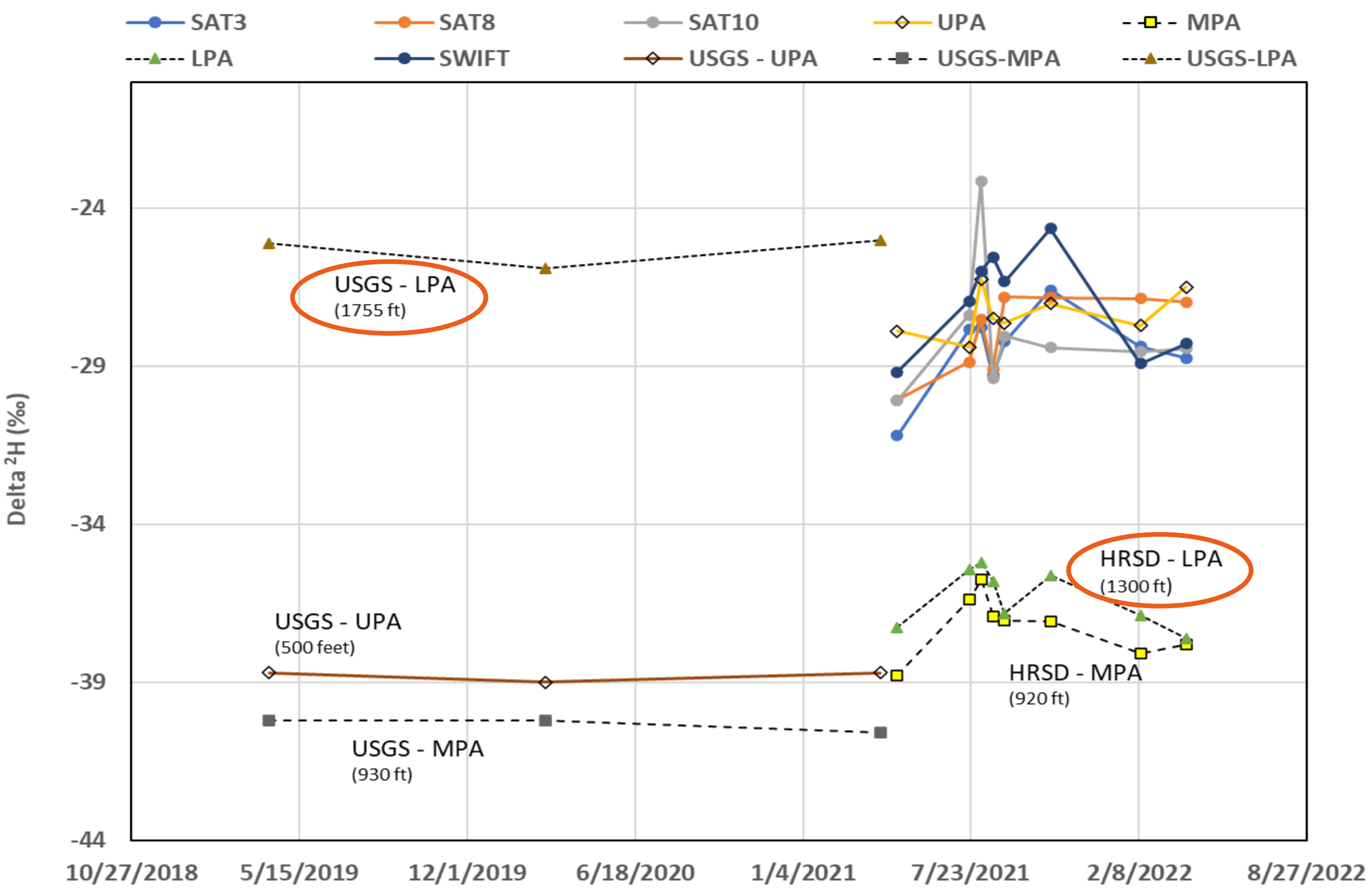
Isotope Ratio in SWIFT Water and in HRSD Monitoring Wells



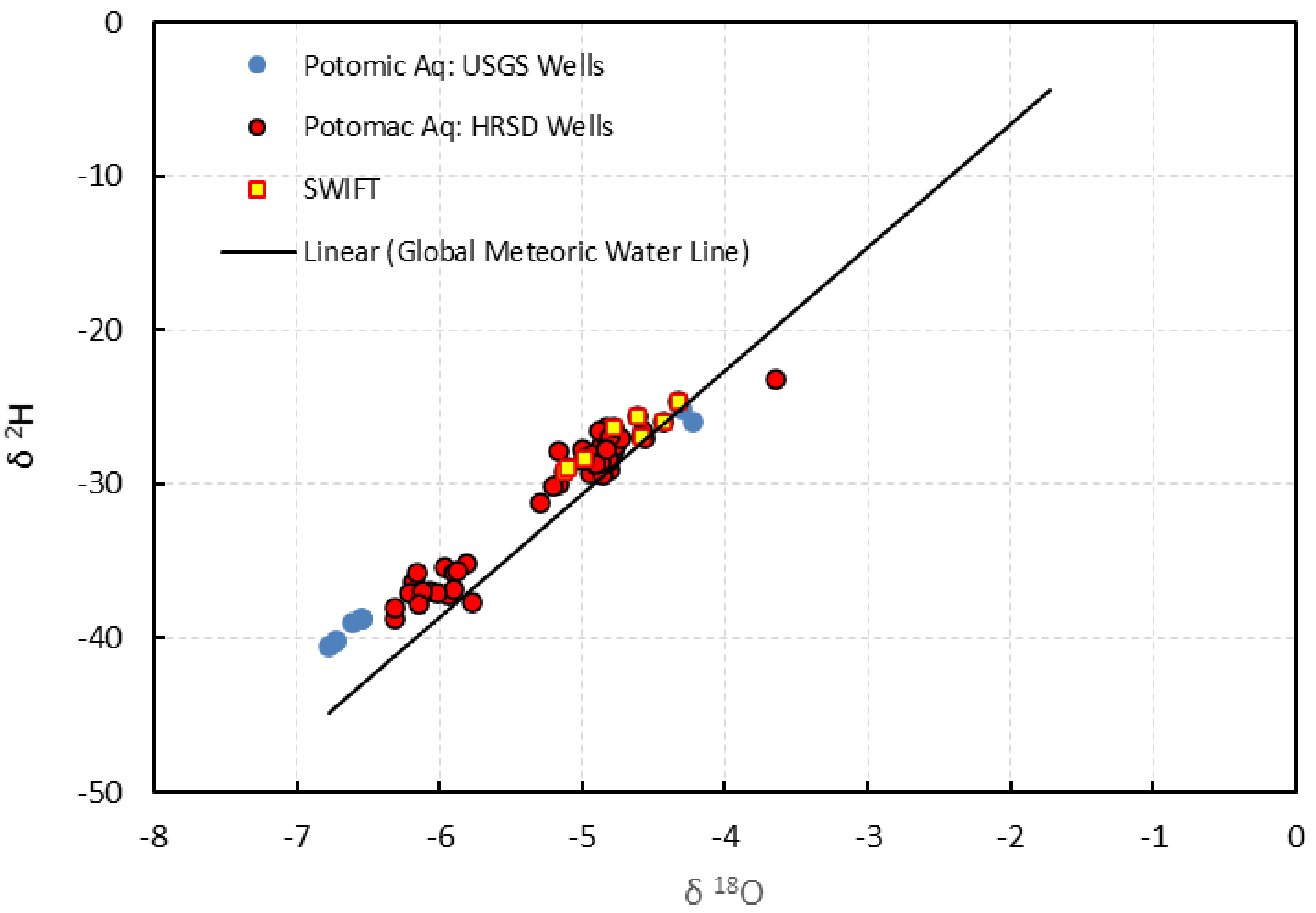
Seasonal isotopic signature of SWIFT water?

Variation in the potable isotopic ratio due to variation in proportions of GW:SW?

Isotope Ratio in SWIFT Water and in HRSD and USGS Monitoring Wells



Measured Isotopic Ratios of Water in the Potomac Aquifer & SWIFT



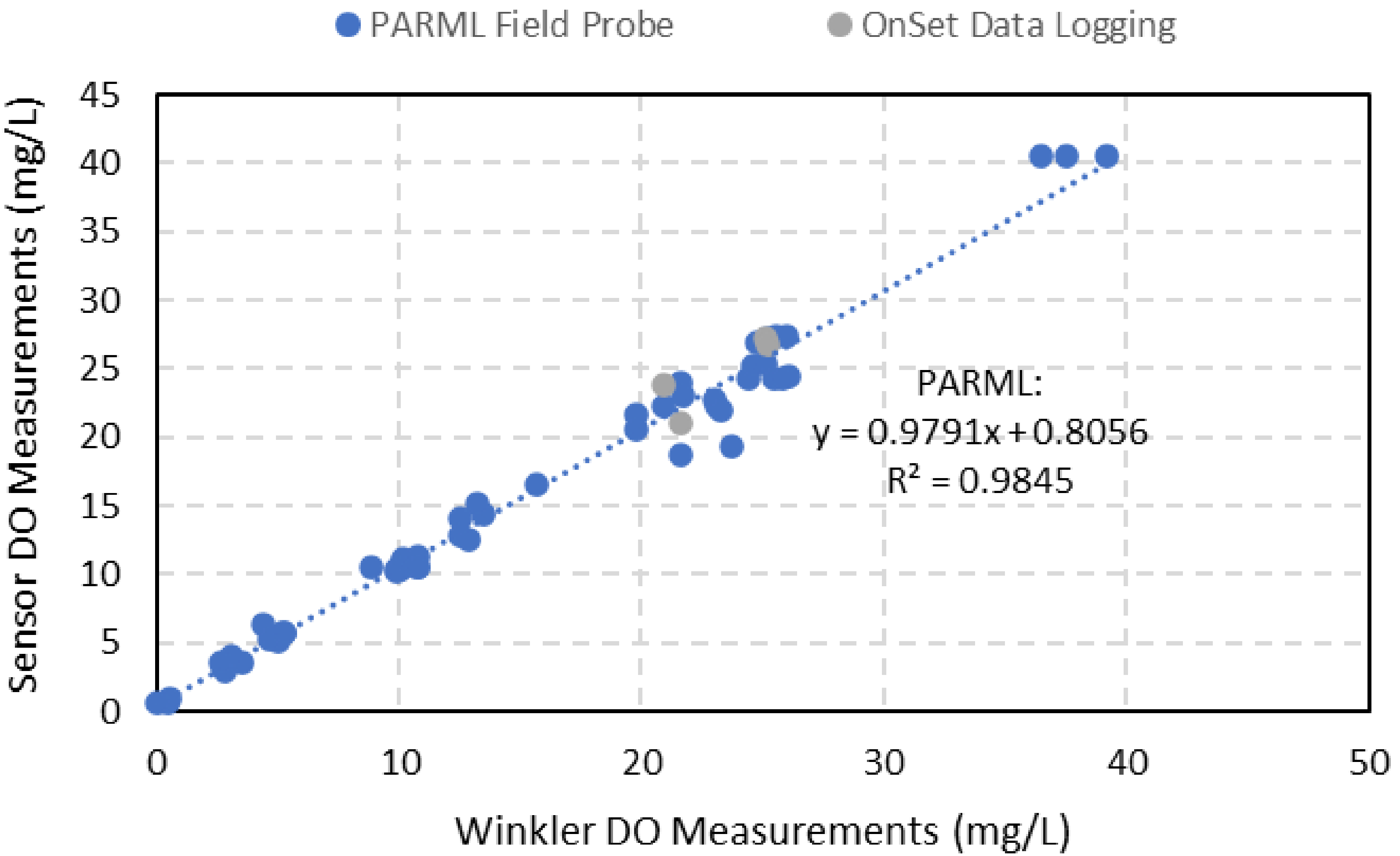
Fate of Dissolved Oxygen and DO Measurements Across SWIFT RC Process Train

Question: Are high DO values accurately read by RDO probes?

Compare probe DO values to Winkler DO measurements

Question: Following ozonation, are changes in DO values driven largely by equilibration with atmospheric oxygen (and where)?

Sensor versus Winkler DO Measurements



Sensor measurements taken at taps at SRC (primarily in laboratory), over filters, or PARML laboratory

Questions?