Synthesizing Data, Isotope Analyses and DSM2 Nutrient Model Output to Characterize Nutrient Transformations in the Delta

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- <u>Collaborators</u>:
 - <u>USGS</u>: Carol Kendall, Megan Young, Sara Peek
 - <u>SFEI</u>: Emily Novick, Rusty Holleman, Thomas Jabusch, Jennifer Sun, Phil Trowbridge and David Senn

"Synthesis" Project Objectives

- Analyze seasonal and spatial variability in nitrogen (N) forms and concentrations in the Delta
- Quantify the capacity of the Delta to transform
 N-species using a mass balance approach, relying
 on DWR-IEP historical nutrient data
- Use DSM2 model output, water quality and isotope data to form hypotheses on the dominant processes controlling nutrient fate: *i.e.*, transformation *vs*. uptake/burial *vs*. other loss processes



Selected Project Findings/Results:

- DSM2 nutrient model recalibration update (RMA)
- Mass balance calculations for N-species transformation and/or loss (SFEI)
- Isotope identification of N-transformations (USGS: C. Kendall, M. Young and S. Peek)
- DSM2 volumetric source water calculations and isotope analyses on the San Joaquin River (USGS: M. Young and C. Kendall)

RMA: DSM2 Nutrient Model Update & Recalibration

DSM2 QUAL Nutrient extended to 03/2012

- Hydrodynamics Boundary conditions (BCs) from DWR-DMS, effluent flows added by RMA
- Major update in QUAL's DICU nutrient and water temperature BCs by RMA
- Recalibrated water temperature and nutrient models 01/00 03/12:
 - New QUAL version
 - Updated and extended nutrient & effluent BCs
 - Nutrient calibration very difficult compared to previous efforts
 - Calibration of NH₃, NO₃+NO₂, Organic-N much harder
 - Several stations had poor calibration results
 - No DWR-IEP station data in South Delta during modeled time span
- DO calibration along SJR much improved



Stockton WTP Effluent Receiving Water Measurement & Model Calibration



Calibration parameters and categorical statistics used in residual analysis and model skill assessment

Performance Rating	RSR	NSE	PBIAS (%)	Categorical Rating
Very Good	$0.00 \le RSR \le 0.50$	$0.75 < NSE \le 1.00$	PBIAS < +/- 25	1
Good	$0.50 < RSR \le 0.60$	$0.65 < NSE \le 0.75$	$+/-25 \le PBIAS < +/-40$	2
Satisfactory	$0.60 < RSR \le 0.70$	$0.00 \le NSE \le 0.65$	$+/-40 \le PBIAS < +/-70$	3
Unsatisfactory	RSR > 0.7	NSE < 0.0	PBIAS ≥ +/- 70	4

All WYs - ALGAE	NSE	PBIAS	Bias	RSR									
C10-Vernalis	VG	VG	Underestimate	VG									
C3A-Hood	VG	VG	Underestimate	VG									
C7-Mossdale	G	VG	Underestimate	G						NH3	NSE	PBIAS	RSR
D10-RSAC075	S	VG	Underestimate	S	All WYs - NH3	NSE	PBIAS	Bias	RSR	C10	1	1	1
D12-Antioch	G	VG	Underestimate	G	C10-Vernalis	VG	VG	Underestimate	VG	C3A	1	1	1
D16-Twitchell	S	VG	Underestimate	U	C3A-Hood	VG	VG	Overestimate	VG	D19	1	1	1
D19-Russo	S	VG	Underestimate	S	D19-Russo	VG	VG	Underestimate	VG	D26	1	1	1
D22-Emmaton	S	VG	Underestimate	U	D26-Potato Point	VG	VG	Underestimate	VG	D28A	3	2	4
D24A-Rio Vista	VG	VG	Underestimate	VG	D28A-Old River RDR	S	G	Overestimate	U	D4	1	1	2
D26-Potato Point	S	VG	Underestimate	U	D4-Pt. Sacramento	VG	VG	Underestimate	G	D6	1	1	1
D28A-Old River RDR	S	VG	Underestimate	U	D6-Martinez	VG	VG	Underestimate	VG	D7	1	1	1
D4-Pt. Sacramento	G	VG	Underestimate	S	D7-Grizzly	VG	VG	Overestimate	VG	MD10	3	4	4
D6-Martinez	VG	VG	Underestimate	VG	MD10-Disappointment Sl.	S	U	Overestimate	U	P8	3	3	4
D7-Grizzly	S	VG	Overestimate	S	P8-Buckley Cove	S	S	Underestimate	U	MODEL	Good	Good	Good
MD10-Disappointment Sl.	S	U	Overestimate	\mathbf{U}			<u>!</u>		,	SKILL	2	2	2
NZ032-Montezuma Sl.	S	VG	Underestimate	\mathbf{U}								_	_
NZS42-Suisun Volanti	S	VG	Underestimate	U									
P8-Buckley Cove	S	G	Underestimate	U									

Challenge – Timing mismatch of data

- Most BC nutrient data is monthly or, rarely, 2x monthly
- Most in-Delta calibration data is also monthly
- But, the measurement dates don't relate to travel time
- Also grab samples are single sample, single site measures really need multiple samples to get a measure of local variability

Hypothetical Example: Nutrient measured as BC on 5th of the month at 3 PM



Nutrient measured downstream on 6th of the month at 10 AM Nutrient peak arrives downstream on 8th of the month at 11 AM

SFEI: Mass Balance Calculations

Seven regions defined to understand nutrient transformation, loss & exchange within the DSM2 model domain.

Using net monthly-average flows to/from each region, monthly-average nutrient loads calculated using QUAL output

NH₃ and Total-N load calculations by region include:

- Load in at inflow boundaries
- Effluent load in at each WTP location
- DICU load into the model domain
- DICU load out of the model using regional average concentration
- Load out at Martinez
- Load out at export locations



	NH4				TN			
	In	Out	Loss	In	Out	Loss		
North	12700	5000	61%	28500	25600	10%		
East	3400	1700	50%	11700	11300	3%		
Central	1600	700	56%	20800	15300	26%		
Confluence	2800	1700	39%	23700	23000	3%		
South	900	800	11%	20400	17800	13%		
San Joaquin	500	200	60%	13700	13500	1%		
Total Delta	13900	2300	85%	48800	36400	25%		

N-loads in/out of each Delta sub-region, and for the entire Delta for June-October of 2006-2011, and % loss within each region.

Some load exchanges within regions are internal. Units are kg-N/day.



Average N-loss within each Delta sub-region June-October of 2006-2011. Color indicates % loss in each region (note different scale for NH₄). Mass losses (text) in units of kg N/day.

Mass balance complications:

- N-constituents are incorporated in algae
- N-concentrations are reincorporated in QUAL via: algae -> organic-N -> NH₃
- NH₃ gained from the sediment
- Some N is lost from the model to the sediment from algal death & settling and organic-N settling

These mass exchanges are not quantified within DSM2-QUAL



Mass Balance Findings:

- Nutrient transformations/losses not uniform within Delta, due to site-specific or system characteristics
 - Tot-N losses highest in North, Central and South regions
 - USGS isotopic data confirm nitrification is occurring throughout Delta, but <u>not</u> uniformly
 - SJR region USGS isotopic analyses+ DSM2 source volumetric percentages confirm that physical processes (*i.e.* mixing) dominate over biological processes in determining the fate of N-constituents
- Tot-N loss in Delta occurred at a rate of 10,000 12,000 kg N/day; losses large relative to inputs (~30%), possibly by:
 - N lost through denitrification (conversion of NO₃ to N₂) literature data estimates show 25-30% of the estimated Tot-N loss could be *via* this route
 - Tot-N lost through storage (e.g., plants) or burial (sediments)

USGS: Isotopes Identify N-Transformations

Isotopes are atoms of the same element with the same numbers of protons & electrons but different numbers of neutrons.

N-14, or ¹⁴N, is one of two stable (non-radioactive) isotopes of N which comprise about 99.636% of naturally occurring nitrogen.

¹⁵N is a relatively rare stable isotope of nitrogen.

Organisms preferentially use the lighter isotopic species, ¹⁴N, because of lower energy "costs". Result: significant fractionations between the substrate (heavier) and the biologically-mediated product (lighter).

$\boldsymbol{\delta}$ values are calculated by:

(in ‰) = $(R_{sample}/R_{standard} - 1)1000$

where "R" is the ratio of the heavy to light isotope in the sample or standard.

Ref: http://wwwrcamnl.wr.usgs.gov/isoig/res/funda.html



Nitrification: Isotope ratios shift as bacteria convert NH_4 to NO_3 , using lighter N-isotopes first. Uptake: Algae have lighter $\delta^{15}N$ than their source. From: Kendall et al. (2015) online report: <u>http://dx.doi.org/10.5066/F7QJ7FCM</u>



Figure 1 - δ^{15} N values of NO₃ (blue/aqua) and NH₄ (pink/violet) of grab samples from Sacramento R. transects 2009-2011. Symbol shape identifies mainstem versus Cache/Yolo Complex slough locations.

Slough samples are plotted at RM14.1 as the sloughs sampled all drain into Cache Slough & RM14.1 is where Cache Slough converges with the mainstem Sacramento R.

Figure 2 – March 2009 transect data show the downstream trend of increasing NH_4 - $\delta^{15}N$ as an isotopically-light fraction of the NH_4 pool is preferentially converted to NO_3 (nitrification) *i.e.*, nitrification is the dominant process. Downstream of the SJR/Sac R. confluence, NO_3 - $\delta^{15}N$ increases as the "heavier" NH_4 is utilized.

USGS: Isotopes and Source Water Volumes on the San Joaquin River

Background:

- NO₃ concentrations and isotopic compositions in the Stockton Deep Water Ship Channel (SDWSC) on the SJR do not match those upstream at Mossdale and Vernalis.
- Instead, NO₃ concentrations and isotopic compositions more closely match those values in the Sacramento River at Rio Vista and downstream in Suisun Bay, suggesting significant influence from either biological processes or additional NO₃ sources.
- There are large temporal variations in the amount of mixing between SJR and Sacramento R. water. This mixing exerts significant control on the downstream distribution of SJR nutrients, particularly NO₃.

Main Finding:

 NO_3 isotope measurements and volumetric water source estimates from DSM2-QUAL show that the mixing of water sources, not biological processes, is the dominant control on NO_3 distribution in the SDWSC portion of the SJR.

DSM2 Volumetric calculations were used to interpret isotope data





Measured δ¹⁵N-NO₃ values during a single transect, location in the SDWSC (green triangles), and DSM2 volumetric percentages of Sacramento R. water (purple squares) and SJR water (red diamonds), shows the strong agreement between the modeled source water and the NO₃ derived from each river. From: Young *et al.*, 2016

For additional information:

DWR Contact for DSM2 model setup : Min Yu in DWR-Delta Modeling Section, <u>Min.Yu@water.ca.gov</u>

<u>FULL PROJECT REPORT:</u> <u>http://sfbaynutrients.sfei.org/books/dwr-contract-deliverable</u>