WARMF model Calibration refinement for Nitrogen Compounds

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The original calibration of the WARMF model application for the Santa Clara River was presented in the Task 2 report prepared by Systech Engineering, Inc. The original calibration was generally based on standard rates of nitrification and denitrification in the various segments of the river. However, in some regions the apparent rate of disappearance of ammonia, nitrite and/or nitrate is faster or slower, based on an evaluation of the observed data. This could be due to additional assimilation of these nitrogen compounds by in-stream and riparian vegetation, increased volatilization of ammonia due to the relatively high surface area and mixing energy of the rocky river bottom, or slightly anoxic conditions which would reduce the rate of nitrification and increase denitrification in some regions. Given the length of the river segments, from a few hundred meters to several kilometers, it is not inconceivable that all of these processes can be taken place within a river segment. Thus, it seems appropriate to adjust the first-order rate constants for the rate of ammonia, nitrite and nitrate disappearance. After several iterations to minimize relative and absolute errors, a set of best fit rate constants were developed (Table 1).

Some of the guiding concepts in the calibration refinement were:

- Slightly overpredict concentrations relative to observed data, to provide a small additional margin of safety;
- Calibrate nitrate and nitrite together, given that any nitrite is likely to rapidly convert to nitrate, and that adjustment of nitrite concentrations alone is difficult given the dependence on both the rate of nitrification and denitrification;
- Consistently adjust rate constants throughout a region;
- For those segments where no observed data is available, adjust the rate constants by interpolating the values from segments where data is available.

The results of the calibration refinement are presented in the following figures for those river segments where there is adequate observed data. Tables 2 to 4 present the statistics of the calibration, in terms of concentrations at 50, 90, 95, 99 and 99.9 percentiles, as well as relative error (RE), absolute error (AE) and root mean square error (RMSE), as defined here:

$$RE = \frac{1}{n}\sum_{i=1}^{n}(x_i - c_i)$$

$$AE = \frac{1}{n}\sum_{i=1}^{n}\left|(x_i - c_i)\right|$$

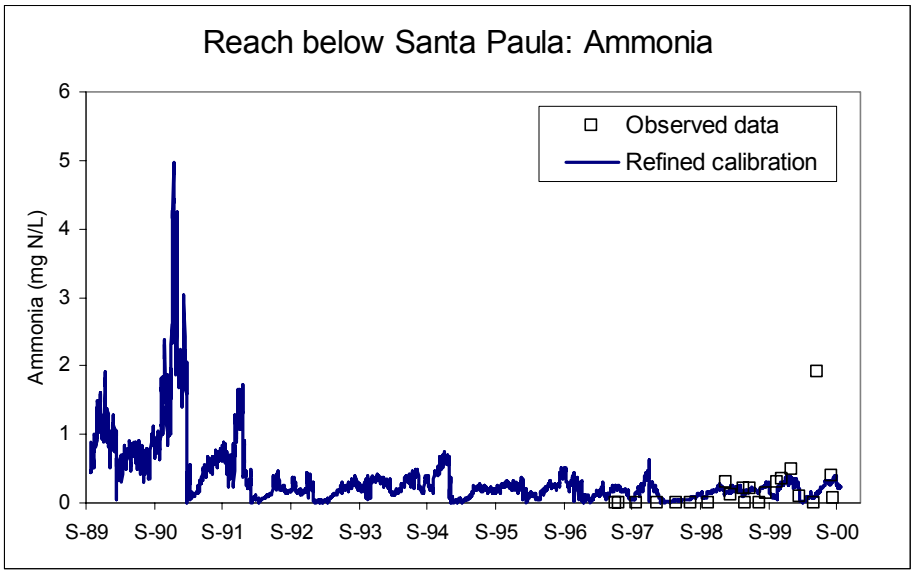
$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(x_i - c_i)^2}$$

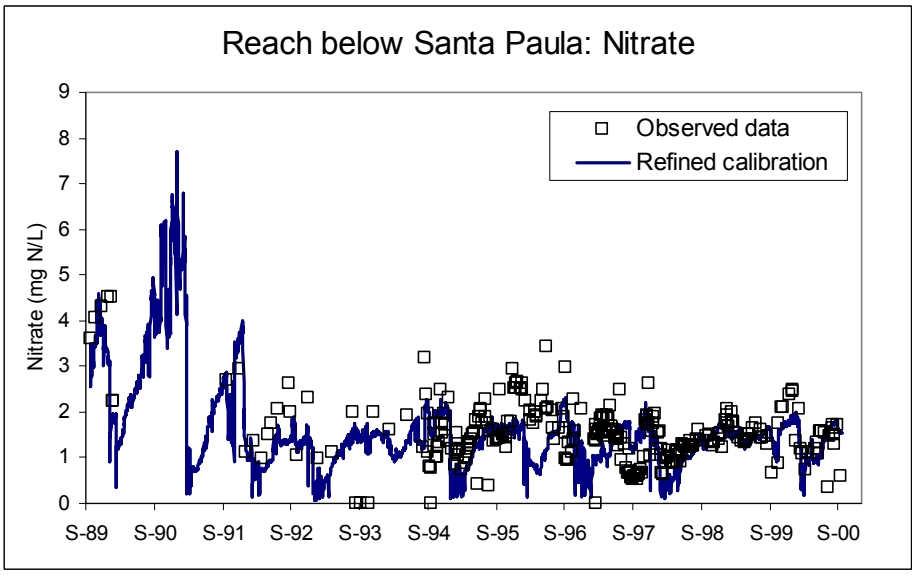
where x_i is the simulated value, c_i is the observed value and n is the number of observations. RE is the average of all errors over all time steps (11-year at a daily time step or 4018 time steps). It is a measure of model accuracy and any consistent bias. However, over-predictions can cancel out under-predictions. AE is the absolute value of the average of all errors over all time steps, and provides another measure of model accuracy, indicating whether the simulated values are generally close to the observed values. RMSE is a measure of model precision, and magnifies the effect of larger than average errors.

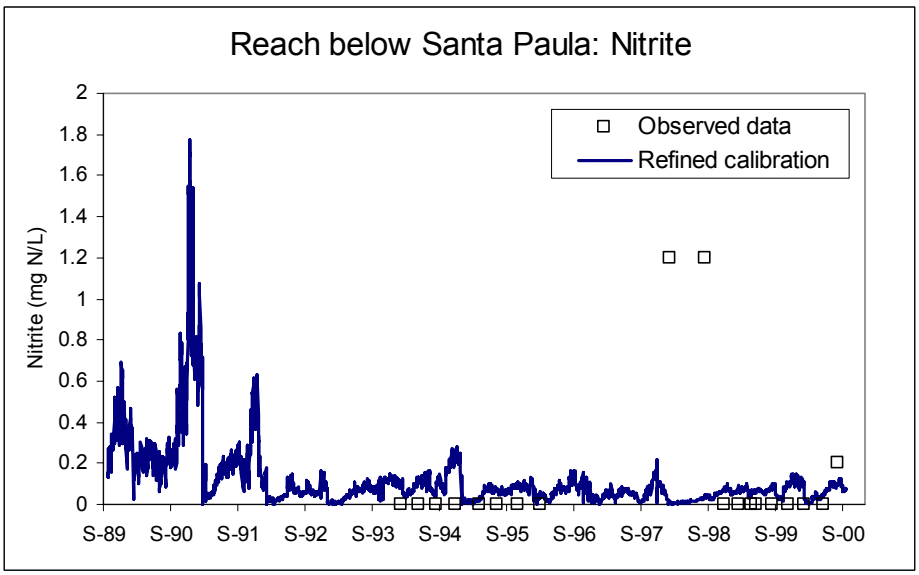
Table 1 Nitrification and denitrification rates (in day^{-1}) for the refined calibration. Segment Ids are presented from lower to upper watershed.

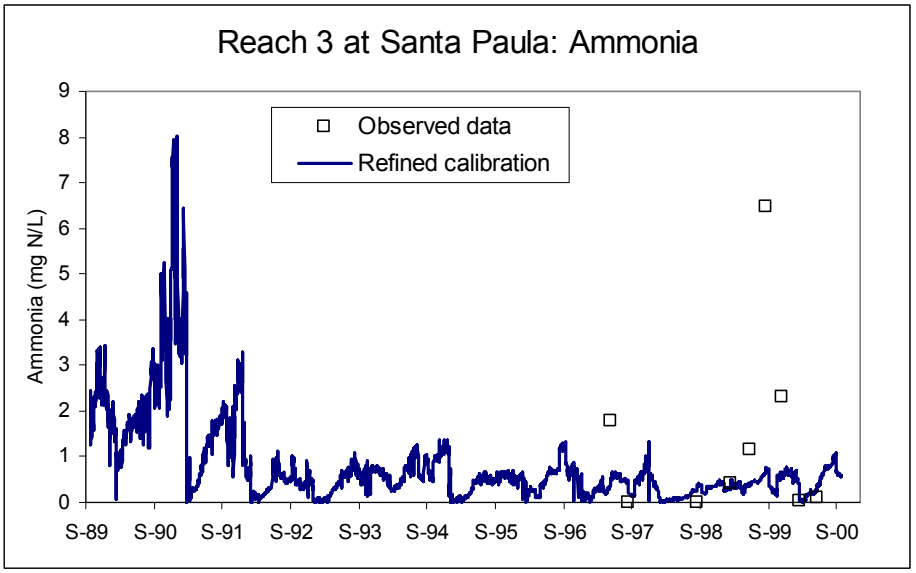
Reach	3	3	3	7	7	7	7	7	7	8	8	8	9
Segment ID	7	9	69	111	113	115	56	137	129	47	149	159	167
Nitrification rate	1.0	0.8	0.7	0.8	0.6	0.4	0.35	0.035	1.0	0.65	0.35	0.0	0.2
Denitrification rate	0.4	0.4	0.3	0.05	0.1	0.2	0.3	0.0	0.3	0.3	0.3	0.15	0.0

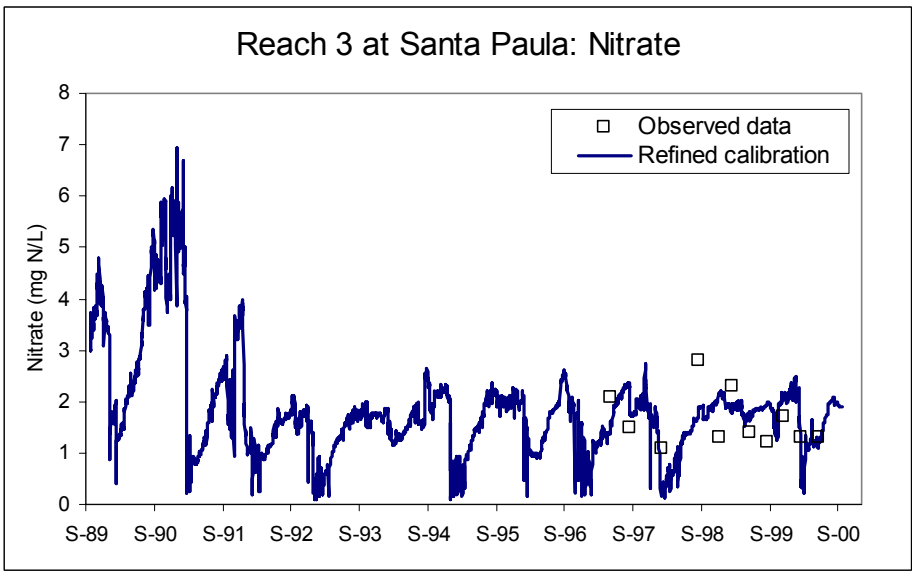
Note that common values for nitrification rates range from 0 to 1.0 day^{-1} and for denitrification from 0 to 0.5 day^{-1}, depending on redox conditions (aerobic or anaerobic).

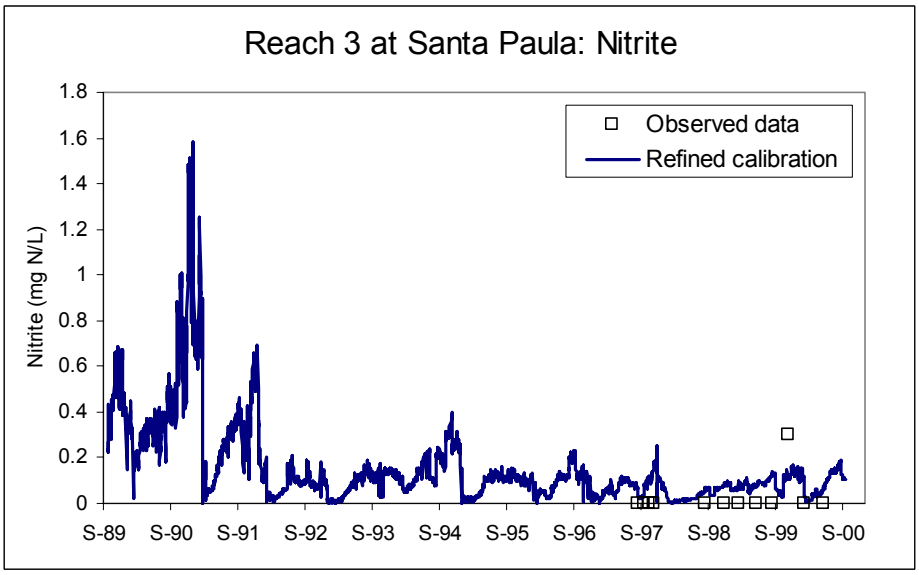

Reach below Santa Paula: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
1
2
3
4
5
6
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

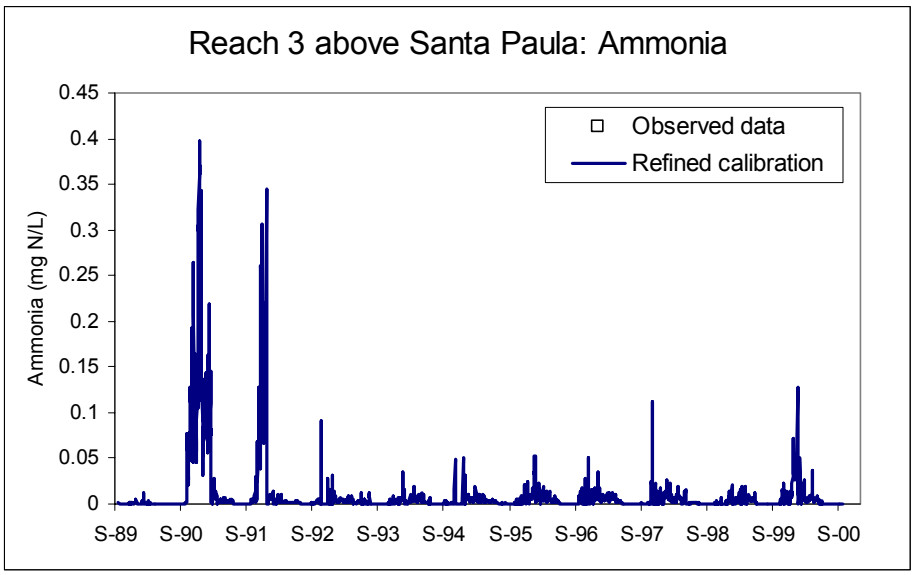

Reach below Santa Paula: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
1
2
3
4
5
6
7
8
9
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

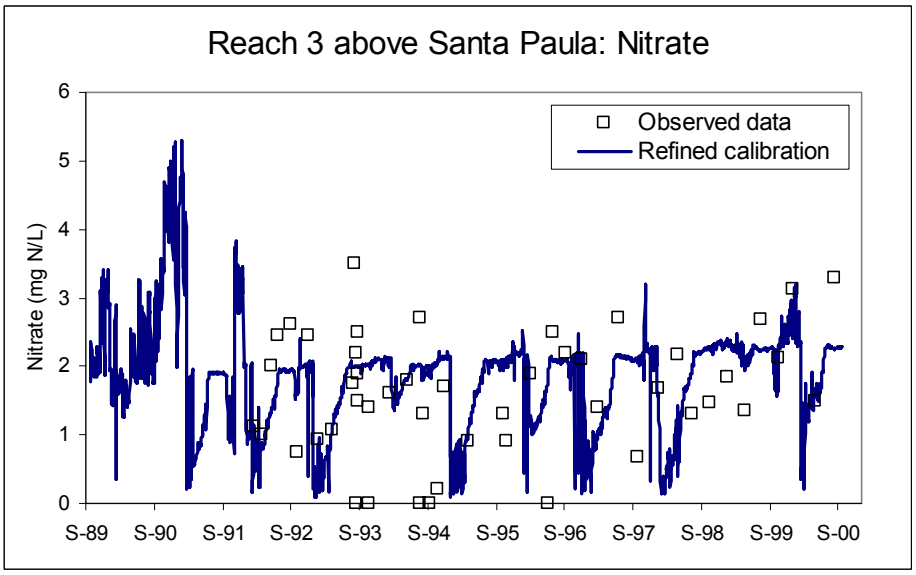

Reach below Santa Paula: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

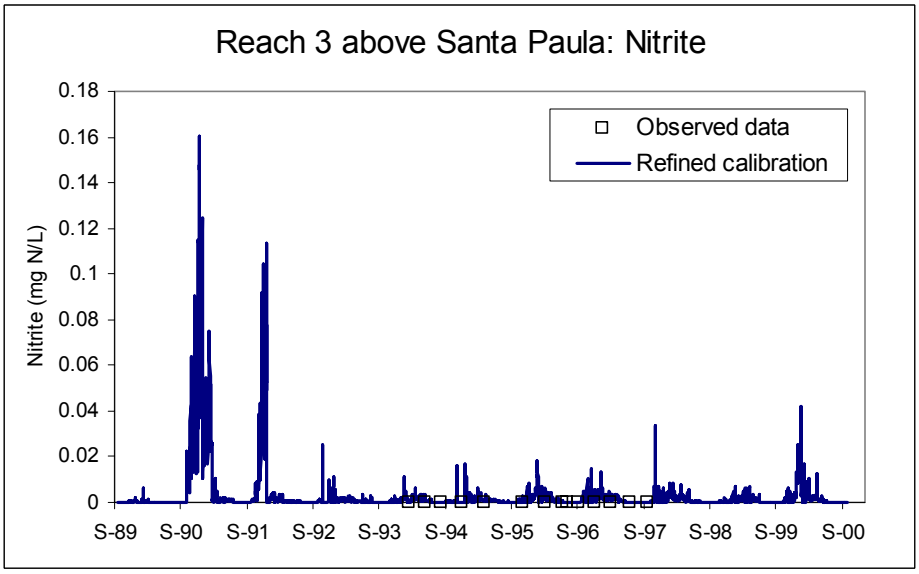

Reach 3 at Santa Paula: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
1
2
3
4
5
6
7
8
9
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

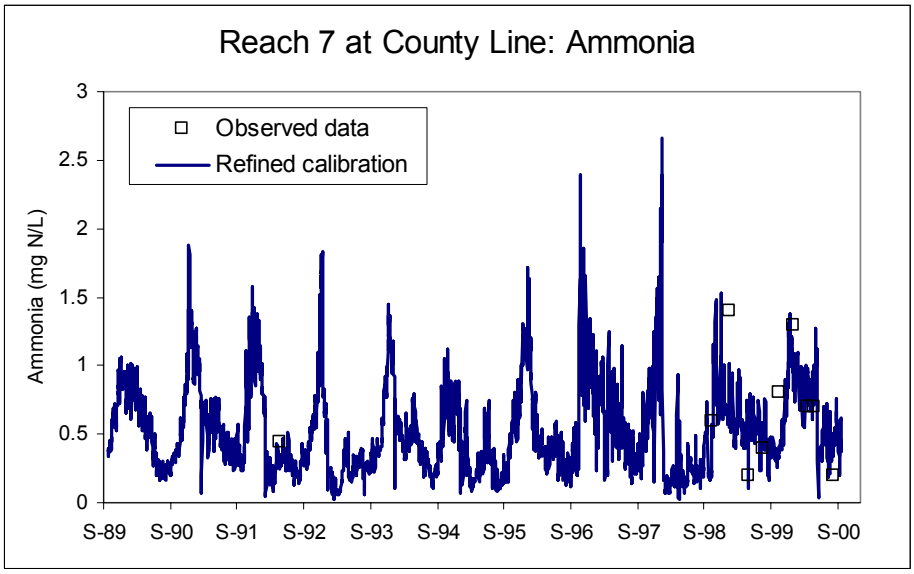

Reach 3 at Santa Paula: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
1
2
3
4
5
6
7
8
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

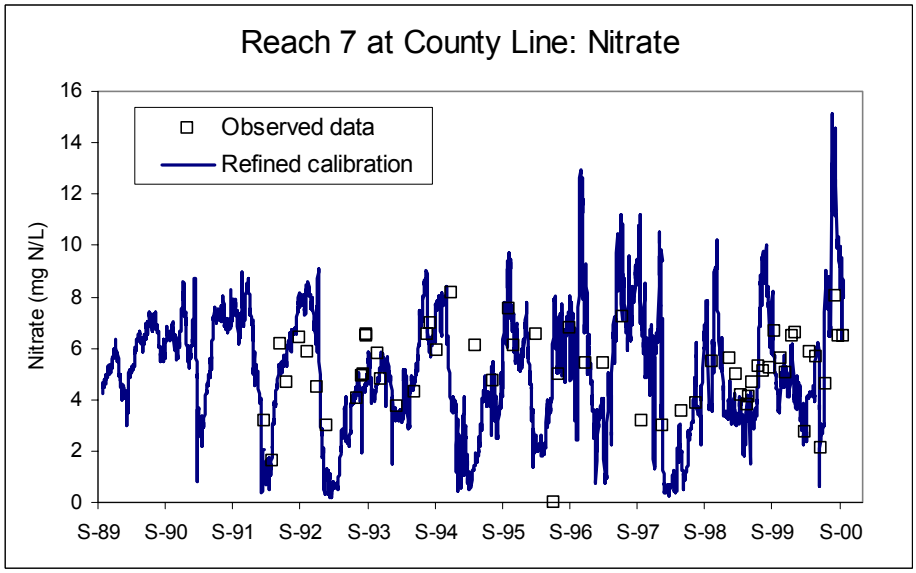

Reach 3 at Santa Paula: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

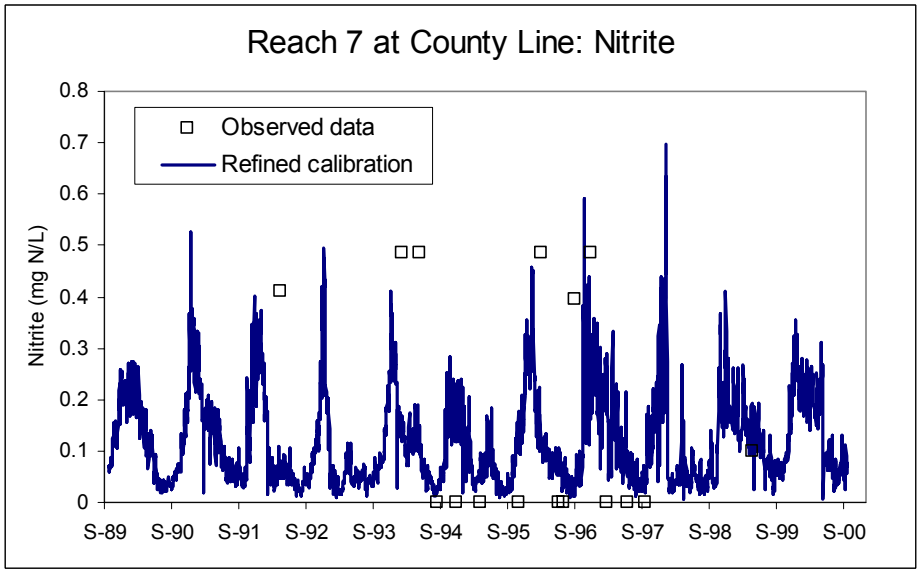

Reach 3 above Santa Paula: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

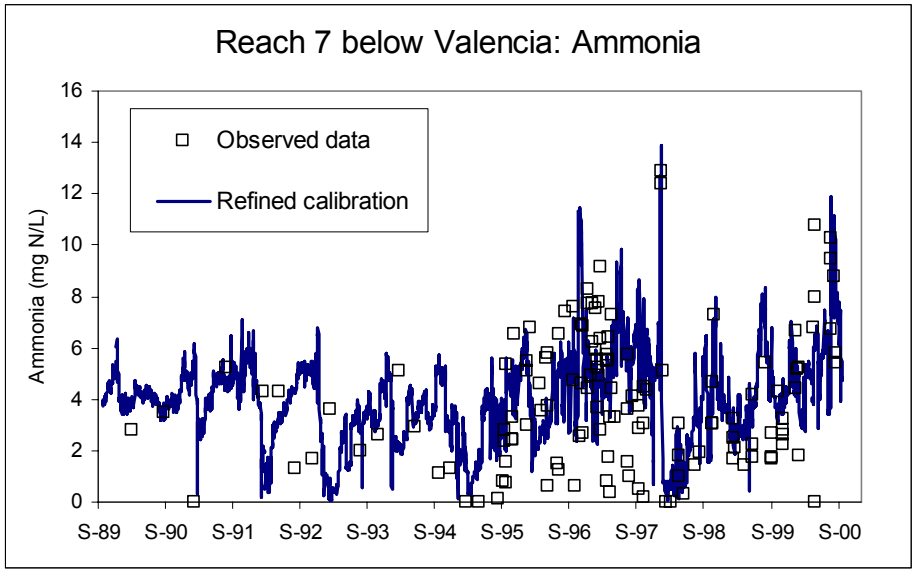

Reach 3 above Santa Paula: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
6
5
4
3
2
1
0
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

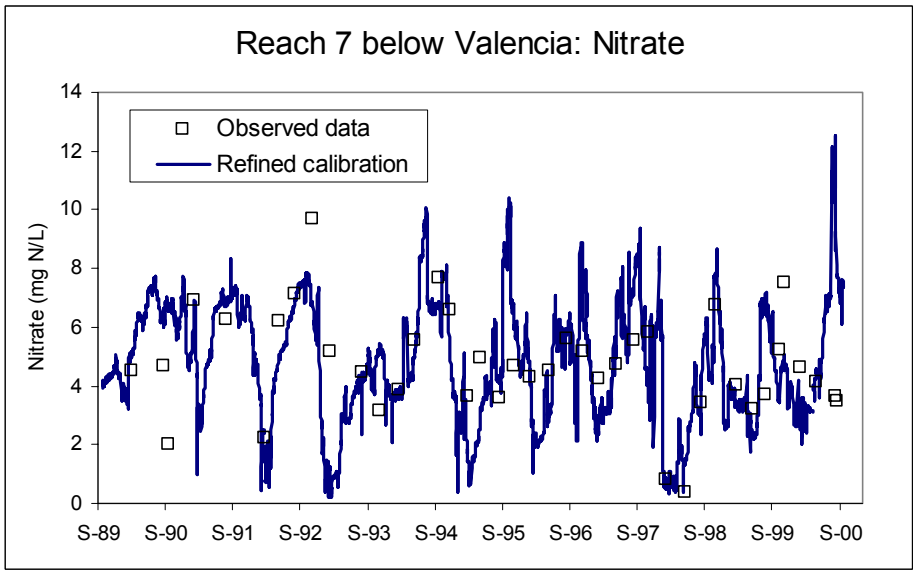

Reach 3 above Santa Paula: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

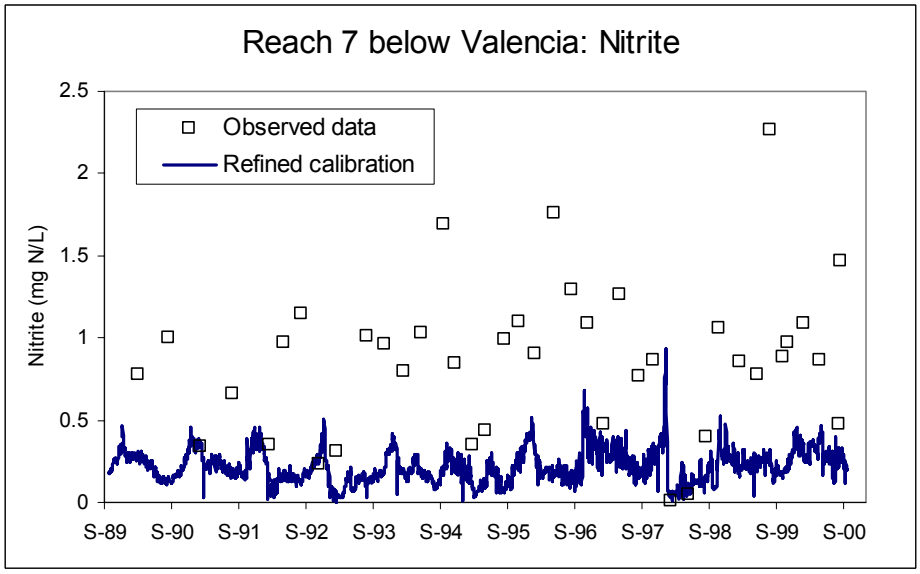

Reach 7 at County Line: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
0.5
1
1.5
2
2.5
3
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

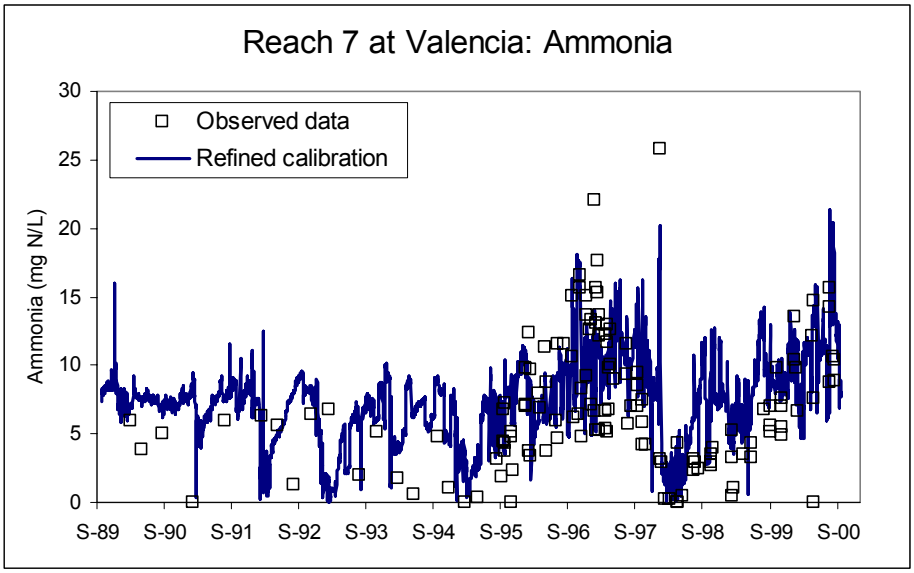

Reach 7 at County Line: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
2
4
6
8
10
12
14
16
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

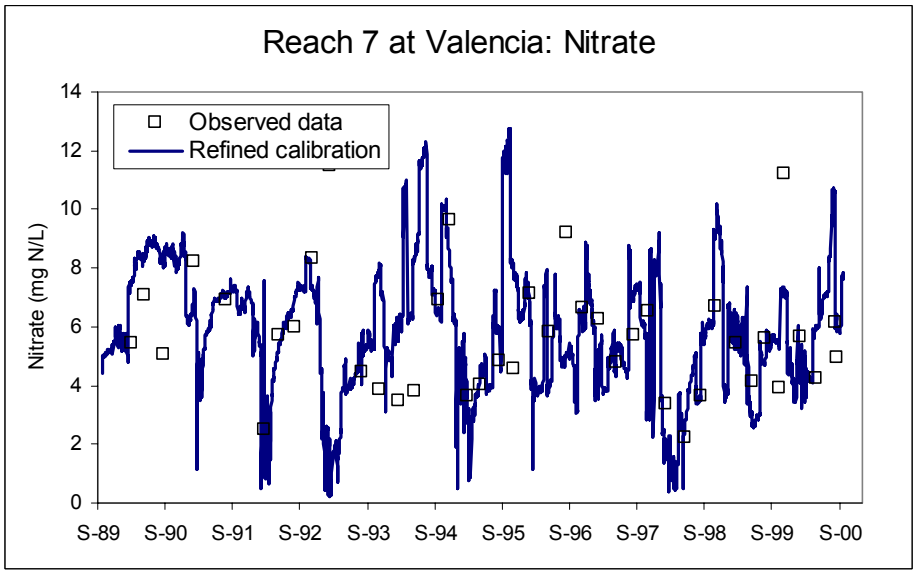

Reach 7 at County Line: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

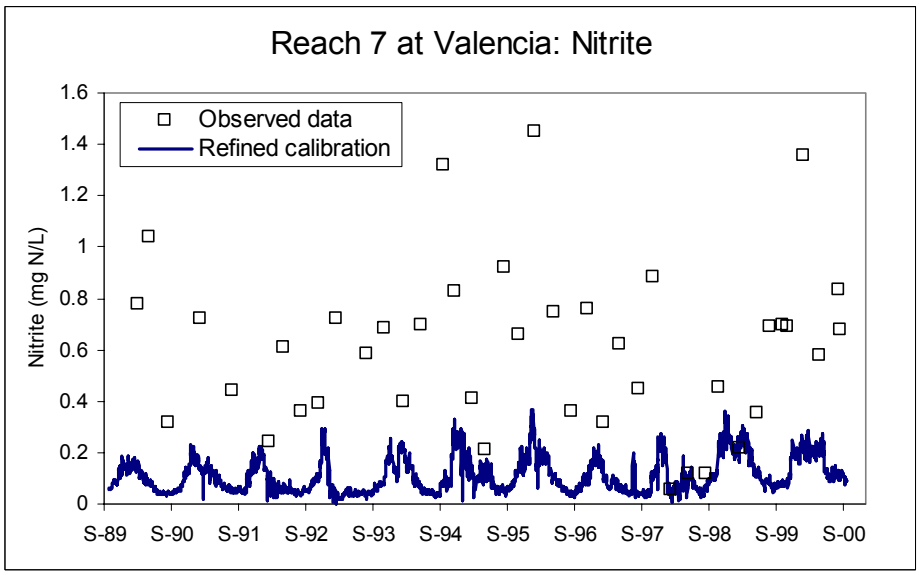

Reach 7 below Valencia: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
2
4
6
8
10
12
14
16
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

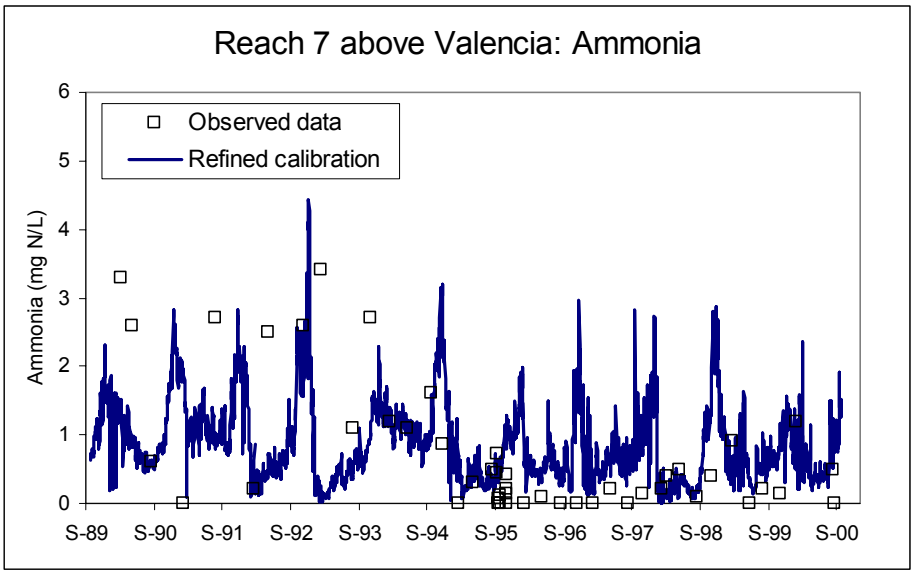

Reach 7 below Valencia: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
2
4
6
8
10
12
14
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

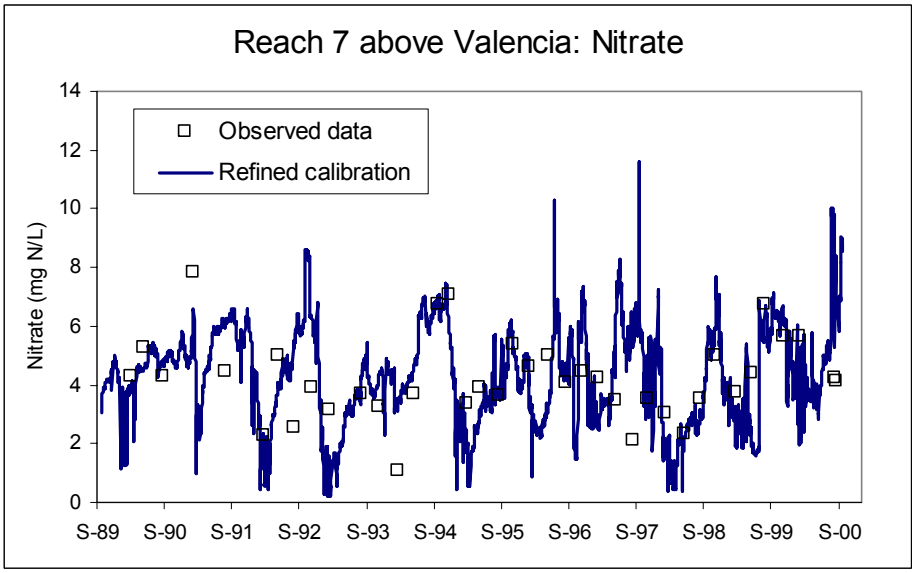

Reach 7 below Valencia: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.5
1
1.5
2
2.5
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

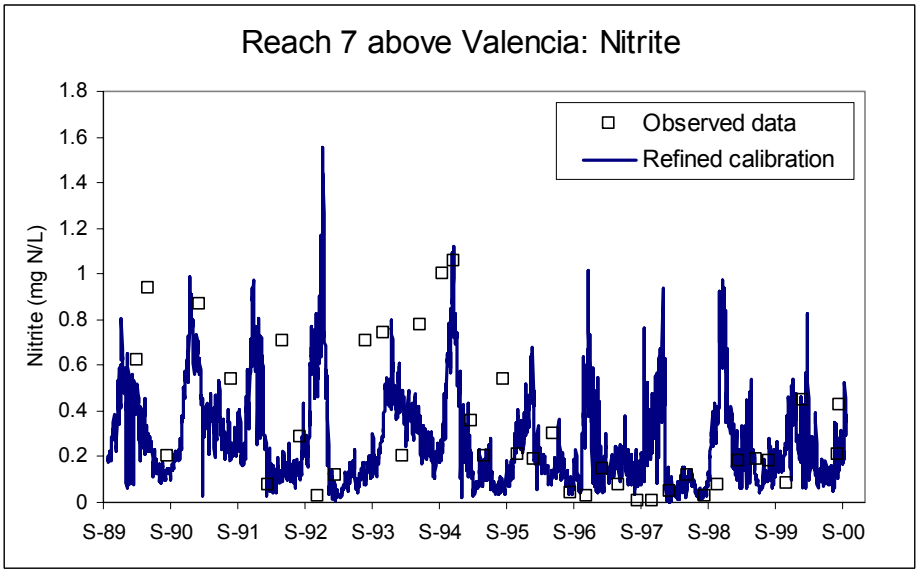

Reach 7 at Valencia: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
5
10
15
20
25
30
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

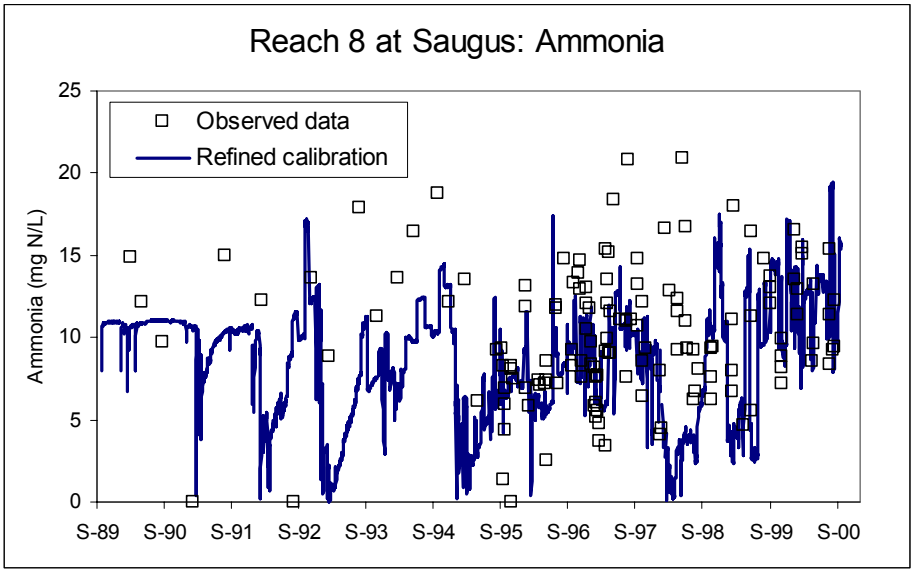

Reach 7 at Valencia: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
2
4
6
8
10
12
14
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

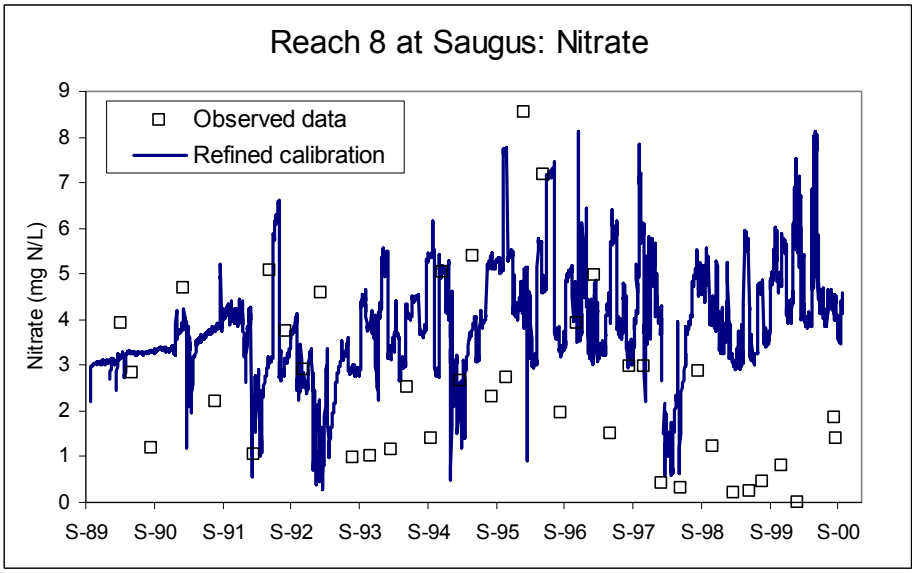

Reach 7 at Valencia: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00


Reach 7 above Valencia: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
1
2
3
4
5
6
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00


Reach 7 above Valencia: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
2
4
6
8
10
12
14
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00


Reach 7 above Valencia: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00


Reach 8 at Saugus: Ammonia
Observed data
Refined calibration
Ammonia (mg N/L)
0
5
10
15
20
25
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00


Reach 8 at Saugus: Nitrate
Observed data
Refined calibration
Nitrate (mg N/L)
0
1
2
3
4
5
6
7
8
9
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

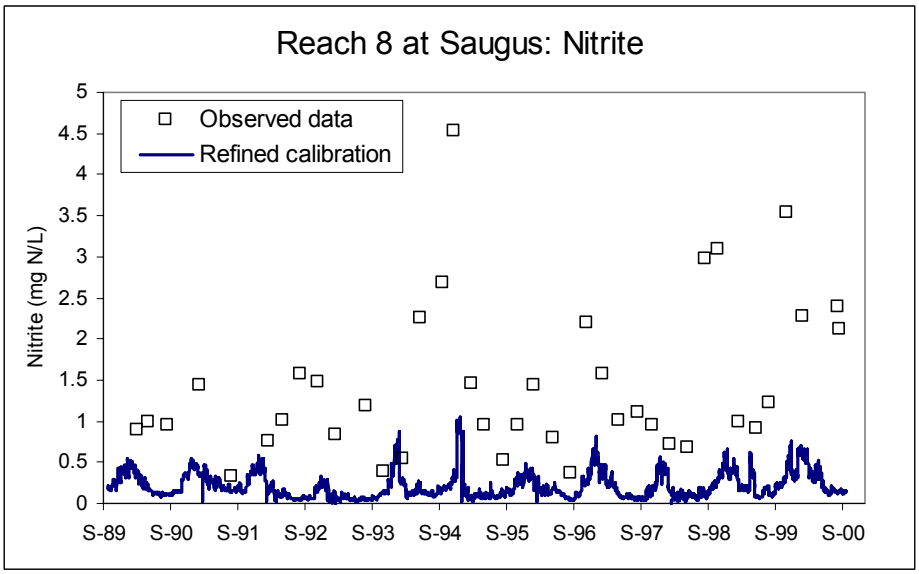

Reach 8 at Saugus: Nitrite
Observed data
Refined calibration
Nitrite (mg N/L)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
S-89
S-90
S-91
S-92
S-93
S-94
S-95
S-96
S-97
S-98
S-99
S-00

Table 2 Statistics of Ammonia calibration refinement

Reach ID	7	9	69	111	56	137	129	159
Number of Observations	22	9	0	10	136	138	50	138
Observed 50 percentile	0.08	0.43	N.D.	0.65	3.62	6.39	0.35	9.52
Observed 90 percentile	0.39	3.14	N.D.	1.31	7.46	13.56	2.70	15.40
Observed 95 percentile	0.50	4.81	N.D.	1.36	8.43	15.36	3.36	16.76
Observed 99 percentile	1.61	6.15	N.D.	1.39	11.84	20.44	10.05	20.86
Observed 99.9 percentile	1.88	6.46	N.D.	1.40	12.83	25.29	11.62	22.45
Simulated 50 percentile	0.22	0.52	0.00	0.46	4.00	7.42	0.75	9.56
Simulated 90 percentile	0.76	1.85	0.01	0.96	5.88	11.17	1.68	12.72
Simulated 95 percentile	1.11	2.67	0.04	1.14	6.75	12.36	2.04	14.13
Simulated 99 percentile	2.31	5.05	0.17	1.48	9.27	16.23	2.69	16.98
Simulated 99.9 percentile	4.39	7.44	0.36	2.08	12.59	18.93	4.12	19.22
Relative error	-0.020	-0.968	N.D.	-0.034	0.677	2.011	-0.338	-1.972
Absolute error	0.214	1.158	N.D.	0.281	1.938	3.367	1.071	3.618
Root mean square	0.404	2.068	N.D.	0.326	2.486	4.192	2.172	5.022

N.D. = No data

Table 3 Statistics of Nitrate calibration refinement

Reach ID	7	9	69	111	56	137	129	159
Number of Observations	276	11	48	58	41	41	39	38
Observed 50 percentile	1.51	1.40	1.73	5.26	4.61	5.59	4.15	2.32
Observed 90 percentile	2.39	2.30	2.70	6.67	6.90	8.33	5.90	5.05
Observed 95 percentile	2.64	2.55	3.07	7.25	7.54	9.62	6.78	5.58
Observed 99 percentile	4.13	2.75	3.41	8.06	8.88	11.38	7.56	8.02
Observed 99.9 percentile	4.52	2.80	3.49	8.12	9.62	11.49	7.82	8.48
Simulated 50 percentile	1.45	1.75	1.99	5.10	4.73	5.88	4.37	3.73
Simulated 90 percentile	2.71	2.85	2.36	7.98	7.25	8.53	6.33	5.38
Simulated 95 percentile	3.89	4.15	3.06	8.77	7.82	9.09	6.74	5.83
Simulated 99 percentile	5.74	5.54	4.60	11.24	9.77	11.79	8.55	7.63
Simulated 99.9 percentile	6.73	6.17	5.21	12.98	10.93	12.50	9.93	8.03
Relative error	-0.189	-0.025	0.104	0.29	0.128	0.0247	0.0393	1.331
Absolute error	0.491	0.488	0.566	1.65	1.503	1.722	1.262	2.105
Root mean square	0.621	0.589	0.728	2.162	1.987	2.429	1.509	2.543

Table 4 Statistics of Nitrite calibration refinement

Reach ID	7	9	69	111	56	137	129	159
Number Observations	19	12	14	16	40	41	39	38
Observed 50 percentile	0.00	0.00	0.00	0.00	0.88	0.62	0.21	1.02
Observed 90 percentile	0.40	0.00	0.00	0.49	1.31	0.92	0.80	2.74
Observed 95 percentile	1.20	0.14	0.00	0.49	1.69	1.32	0.95	3.14
Observed 99 percentile	1.20	0.27	0.00	0.49	2.07	1.41	1.04	4.16
Observed 99.9 percentile	1.20	0.30	0.00	0.49	2.25	1.45	1.06	4.50
Simulated 50 percentile	0.07	0.10	0.00	0.09	0.21	0.09	0.21	0.16
Simulated 90 percentile	0.25	0.35	0.00	0.24	0.35	0.21	0.56	0.43
Simulated 95 percentile	0.38	0.50	0.01	0.29	0.39	0.24	0.67	0.51
Simulated 99 percentile	0.81	0.97	0.06	0.39	0.48	0.29	0.91	0.72
Simulated 99.9 percentile	1.55	1.46	0.14	0.53	0.80	0.34	1.44	0.99
Relative error	-0.063	0.0624	0.0007	-0.069	-0.649	-0.497	-0.1	-1.251
Absolute error	0.195	0.0932	0.0007	0.183	0.655	0.497	0.228	1.27
Root mean square	0.393	0.105	0.0011	0.226	0.786	0.583	0.3	1.55