

Dead Fish Talking?



All slides produced by Anke Mueller-Solger, CA DWR, Oct./Nov. 2007

Thanks to the IEP EMP, Steve Gittings and Larry Huber, City of Stockton, Inge Werner, UCD-ATL, and Dave Vogel, NRS, for providing data and information.

The 2007 VAMP salmon kill near Stockton: What killed these fish?



This is really from the 2002 Klamath salmon kill...

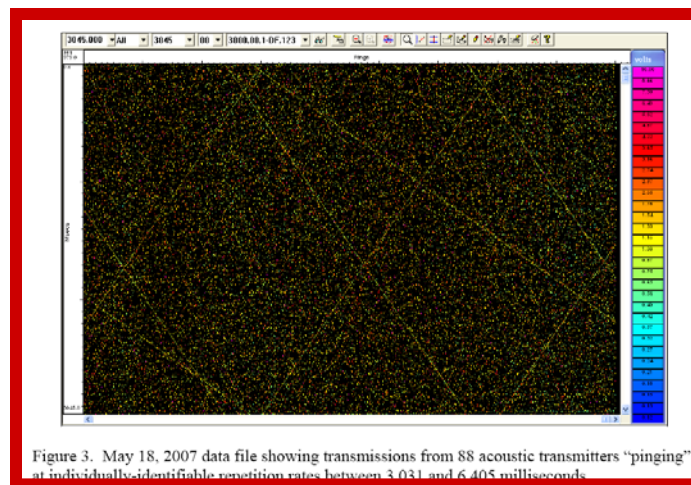


Figure 3. May 18, 2007 data file showing transmissions from 88 acoustic transmitters "pinging" at individually-identifiable repetition rates between 3.031 and 6.405 milliseconds.

Figure from
report by
Dave Vogel,
May 20, 2007

Who am I?

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EDUCATION

1998: Ph.D. (Ecology), University of California, Davis, USA

1994: M.S. (Biology), Georg-August-University, Goettingen, Germany

PROFESSIONAL EXPERIENCE

2000 - Present: DWR-DES Environmental Specialist/Staff Environmental Scientist

1998 - 2005: Postdoctoral Scientist & Staff Research Associate, UC Davis

1993-1997: Field Director, UC Davis Castle Lake Limnological Research Laboratory

RESPONSIBILITIES

IEP: Scientist with Environmental Monitoring Program / Estuarine Studies Branch responsible for monitoring design and data analysis

Member, IEP POD Study Management Team & IEP Management Team

CALFED: Calfed Science Conferences 2003-2008,

P.I. & collaborator in CALFED studies

Agency mentor and supervisor for several Calfed Science Fellows/Postdocs

SOME PUBLICATIONS

Jassby, A.D., A. B. Müller-Solger, and Marc Vayssières. 2005. Subregions of the Sacramento-San Joaquin Delta: identification and use. Spring 2005 IEP Newsletter

Müller-Solger, A. B., A. D. Jassby, and D. C. Müller-Navarra. 2002. Nutritional quality of food resources for zooplankton (*Daphnia*) in a tidal freshwater system (Sacramento-San Joaquin River Delta, USA). *Limnology and Oceanography* 47:1468-1476.

Sobczak, W. V., J. E. Cloern, A. D. Jassby, and A. B. Müller-Solger. 2002. Bioavailability of organic matter in a highly disturbed estuary: The role of detrital and algal resources. *Proceedings of the National Academy of Sciences* 99: 8101-8105. (Received ASLO Lindeman Award)



The 2007 VAMP salmon kill near Stockton: What killed these fish?

Outline

1. The 2007 VAMP Salmon Kill
2. The Stockton Wastewater Treatment Plant (WWTP)
3. The Stockton WWTP Receiving Water Monitoring Program
4. Stockton WWTP Nitrogen Discharge
5. Ammonia & fish – a brief review
6. Ammonia near Stockton, Jan – July 2007
7. Some more questions:
 - A. Does the ammonia really come from the WWTP?
 - B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?
 - C. What about D.O.?
8. Conclusions
9. VAMP monitoring recommendations for 2008

1. The 2007 VAMP Salmon Kill:

May 17 and 18, 2007: 116 VAMP salmon acoustic tags detected by the Stockton Wastewater Treatment Plant (WWTP) outfall and a railroad bridge.

What killed these fish?

1. WWTP effluent?
2. Predators?
3. Or something else?, e.g. low D.O.? Other toxicants?

Late last week, while performing mobile telemetry monitoring in the San Joaquin River near Stockton, I located a high number of acoustic transmitters at a very small, localized site approximately 0.75 miles downstream of the Highway 4 bridge, 1.7 miles upstream of the Stockton Deep Water Ship Channel, and adjacent to a railroad bridge and the Stockton waste water treatment facilities (Figure 2).



Figure and text from report by Dave Vogel, May 20, 2007

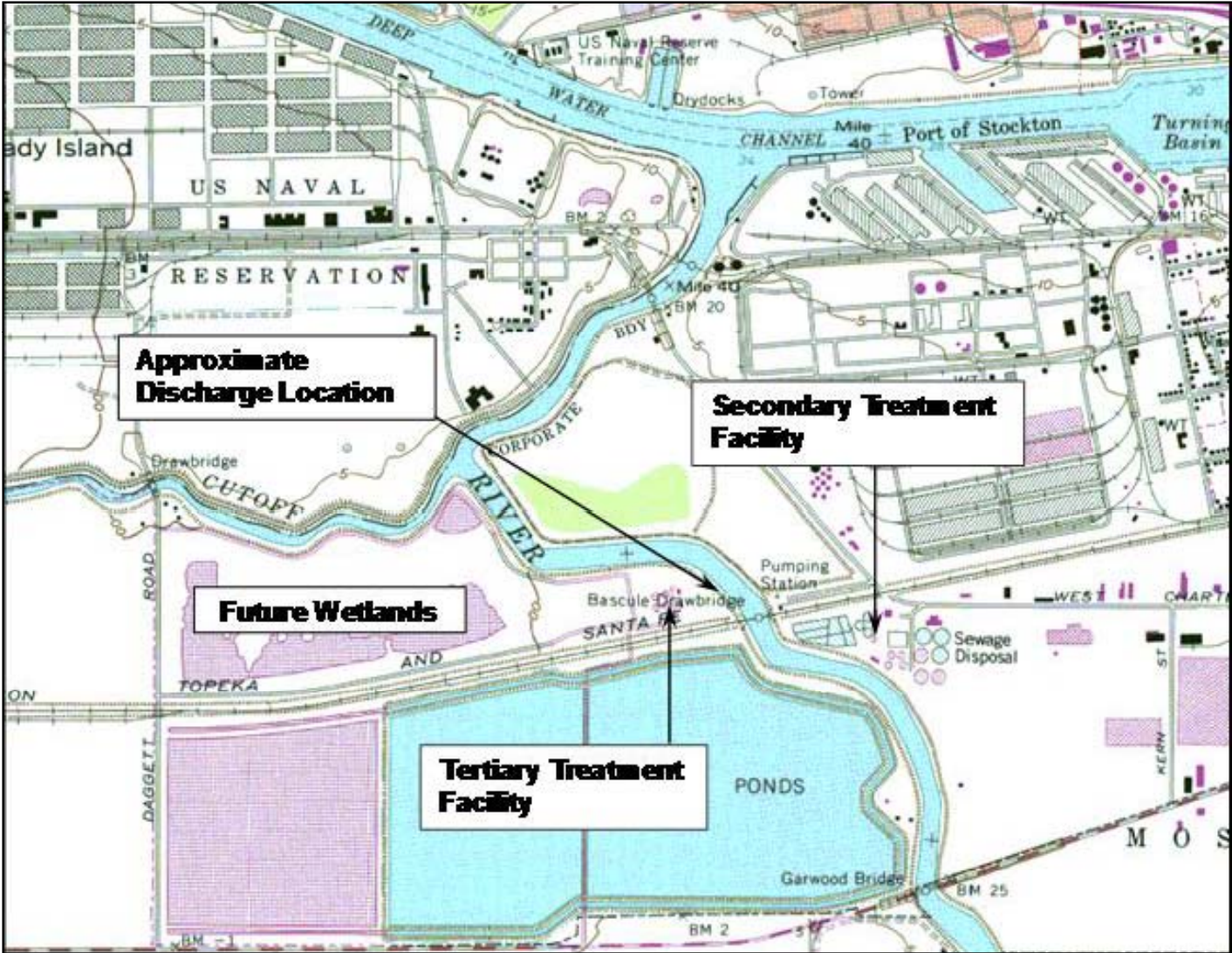
Figure 2. Location of high mortality among juvenile acoustic-tagged Chinook salmon.

My main conclusions up front:

1. The 2007 VAMP salmon **MAY** have been killed by toxic ammonia originating from the Stockton WWTP, but this is **not conclusive** due to lack of data (& in my view inadequate water quality criteria)
2. In the San Joaquin River near Stockton, fish get (or got) hit by a “1-2 punch”:
 - Punch 1: WWTP discharge & river algae/elevated pH produce toxic ammonia levels;
 - Punch 2: More river algae & environmental conditions produce critically low dissolved oxygen in the DWSC
3. The new improved treatment at the Stockton WWTP may help improve this situation, but **water quality monitoring & fish assays should be added to VAMP**

2. The Stockton Wastewater Treatment Plant (WWTP)

(Image from Larry Huber, City of Stockton)

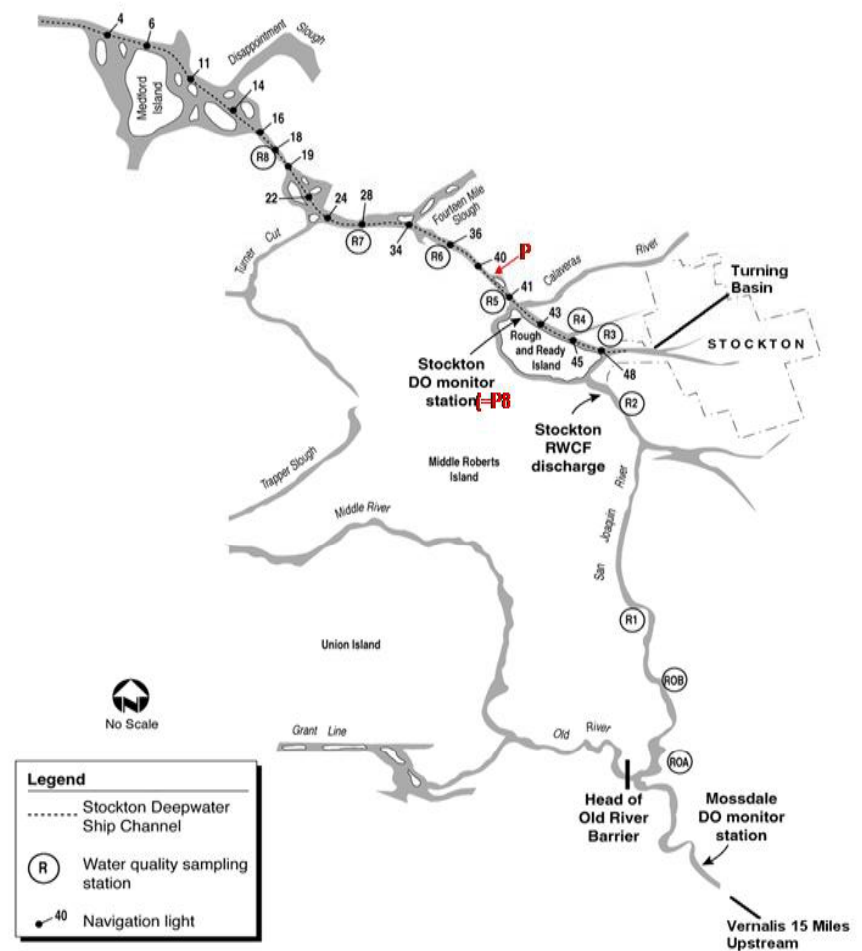


3. The Stockton WWTP RECEIVING WATER MONITORING PROGRAM

Most analyses in this presentation were conducted with data from this monitoring program!

“All receiving water samples shall be grab samples, collected at mid-depth, in mid-stream of the river. Receiving water sampling may be postponed or eliminated if hazardous weather and/or river flow conditions prevent safe access to sampling location.”

(Information provided by Steve Gittings and Larry Huber, City of Stockton)



Station	Description/Location
R-1	San Joaquin River @ Bowman Road, 8.0 miles south of outfall
R-2	San Joaquin River @ Highway 4, 0.5 miles south of outfall
R-2A	San Joaquin River @ Burns Cutoff, 0.5 miles north of outfall
R-3	San Joaquin River @ Deep Water Channel, 1.5 miles north of outfall
R-4	San Joaquin River @ Light 45, 2.5 miles north of outfall
R-5	San Joaquin River @ Light 41, 3.5 miles north of outfall
R-6	San Joaquin River @ Light 36, 5.0 miles north of outfall
R-7	San Joaquin River @ Light 24, 7.3 miles north of outfall
R-8	San Joaquin River @ Light 18, 9.0 miles north of outfall

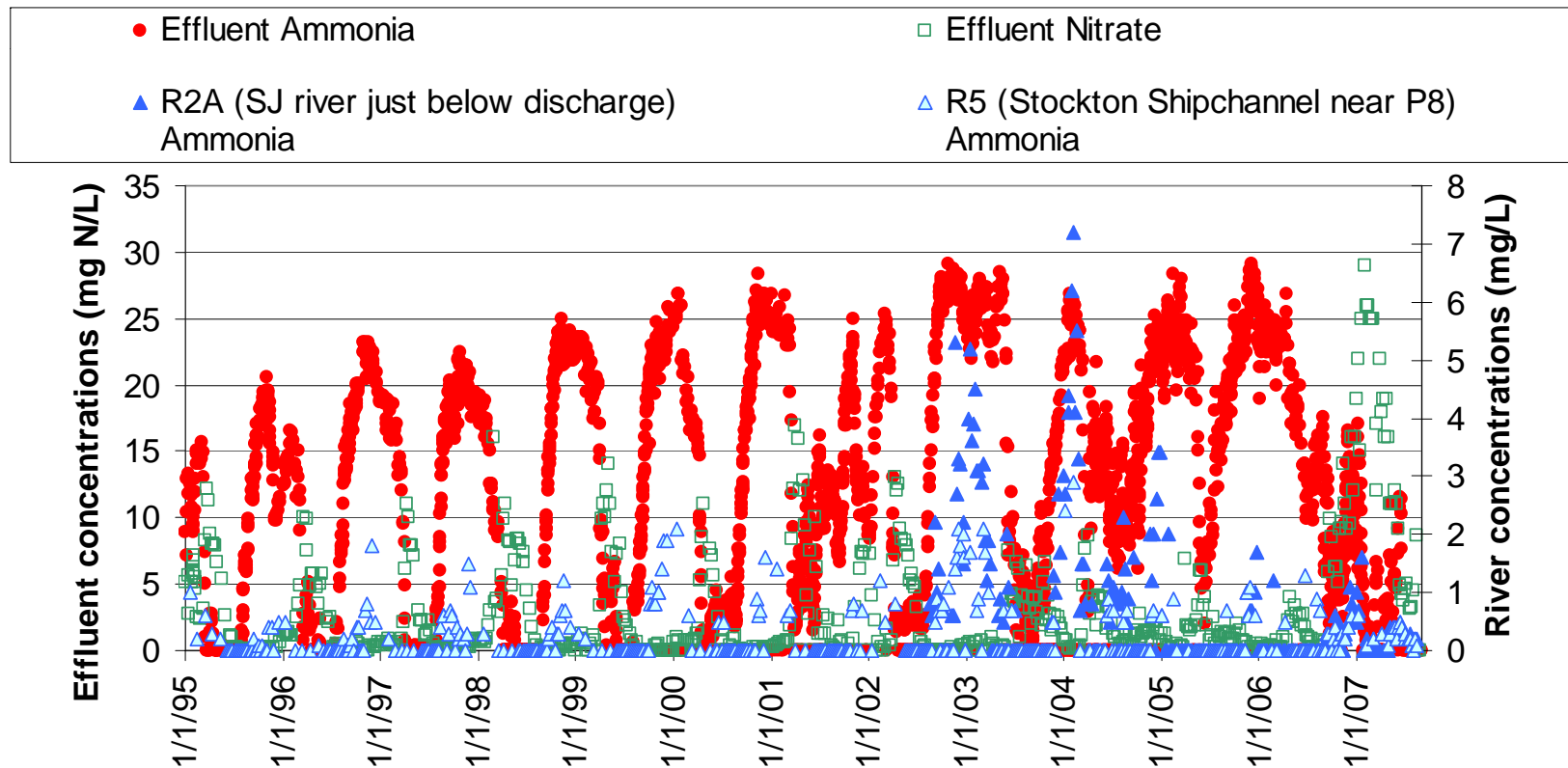
4. Stockton WWTP Nitrogen Discharge:

Very Seasonal

Since October 2006: less ammonia, more nitrate

Stockton Wastewater Treatment Plant and nearby River Ammonia & Nitrate concentrations

Data provided by Steve Gittings, City of Stockton



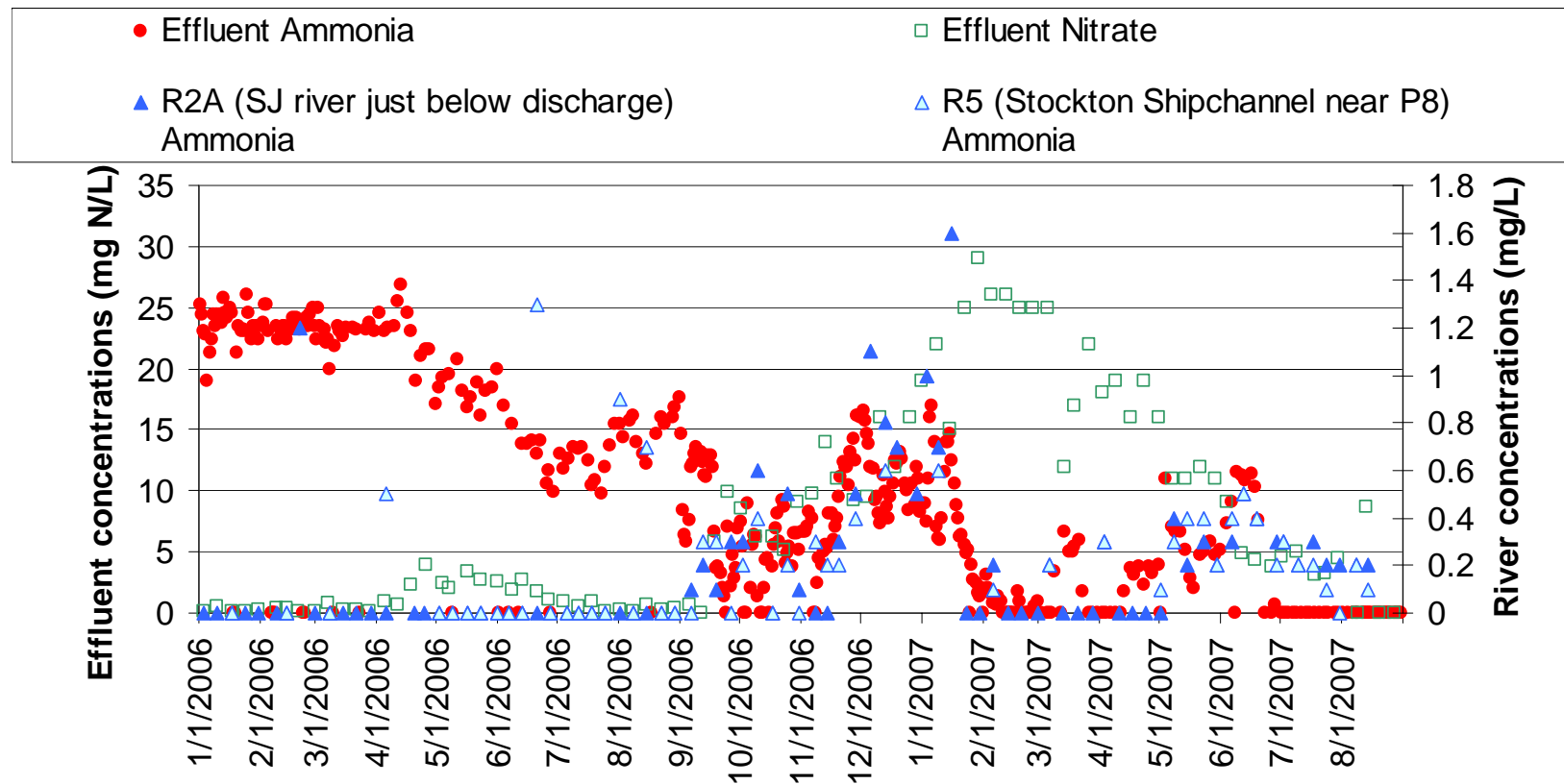
Zooming in:

... But effluent and river total ammonia levels were still quite high in Dec 06/Jan 07 and in May/Jun 07.

Could ammonia toxicity have killed the VAMP salmon?

Stockton Wastewater Treatment Plant and nearby River Ammonia & Nitrate concentrations, Jan-2006 to Aug-2007

Data provided by Steve Gittings, City of Stockton



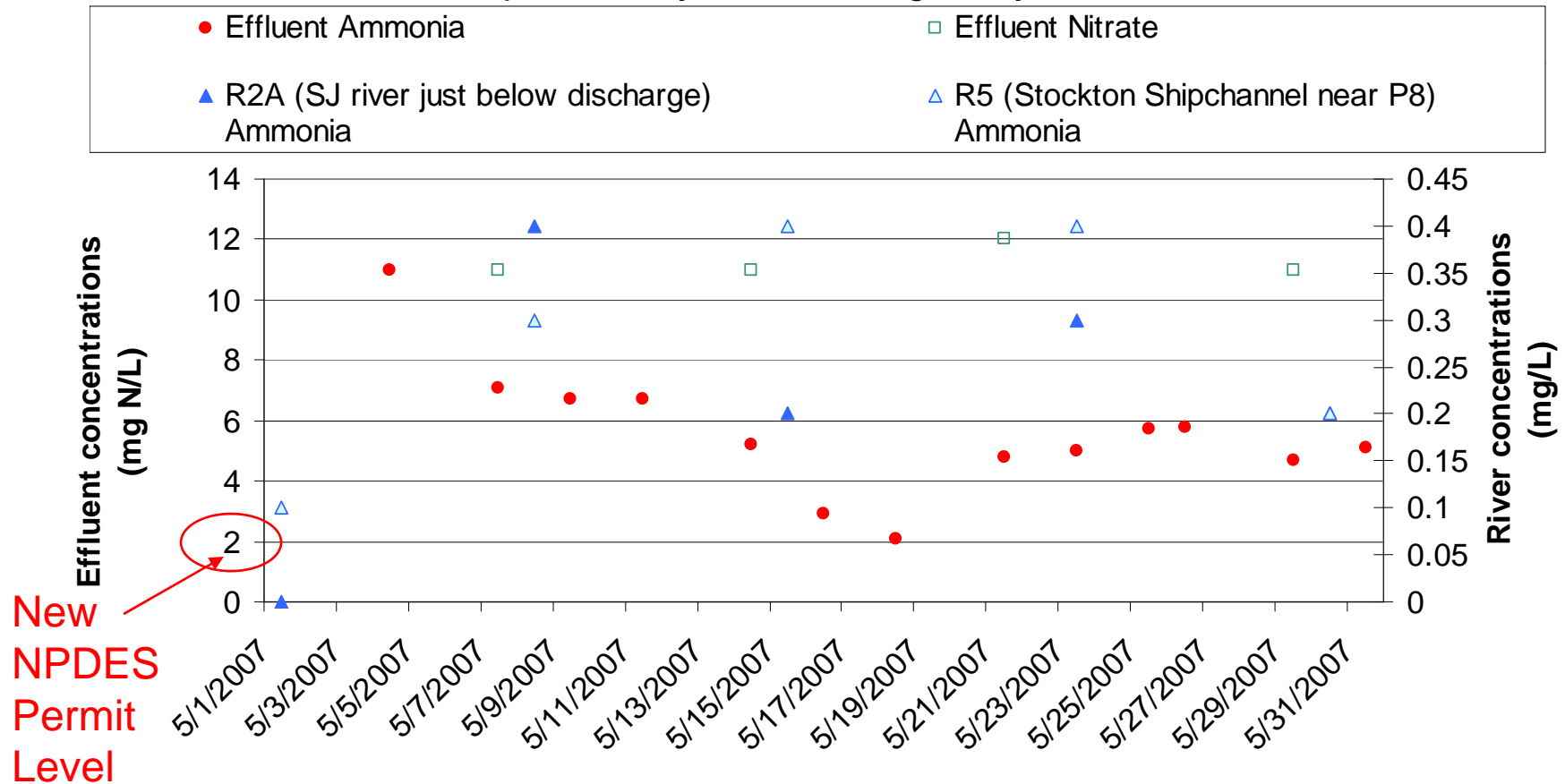
Zooming in even more:

May 2007:

- Ammonia fairly stable, much below previous peak levels
- Effluent ammonia above new NPDES permit level (not yet in effect)

Stockton Wastewater Treatment Plant and nearby River Ammonia & Nitrate concentrations, May 2007

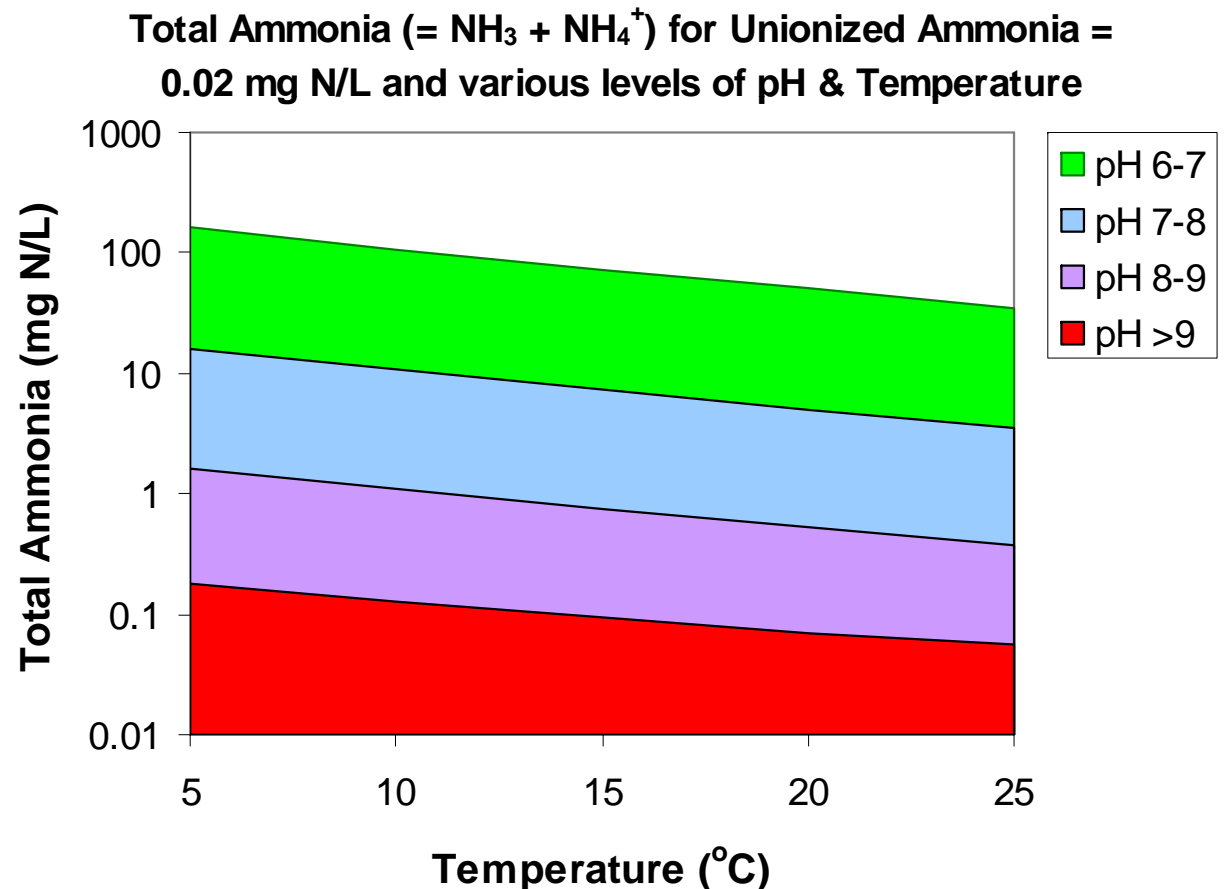
Data provided by Steve Gittings, City of Stockton



5. Ammonia & fish – a brief review:

- Total ammonia = unionized ammonia (NH_3) + ammonium ion (NH_4^+).
- NH_3 & NH_4^+ concentrations depend mostly on **pH**
- **Unionized ammonia tends to be more toxic to fish**
- Old EPA “red book” (1976) fish protection criterion: 0.02 mg/L

- 1-fold pH difference
~> 10-fold unionized
 NH_3 difference
- At pH>8: < 1 mg/L
total ammonia
produces unionized
 NH_3 levels >0.02
mg/L
- In the San Joaquin
River, pH>8 is not
uncommon

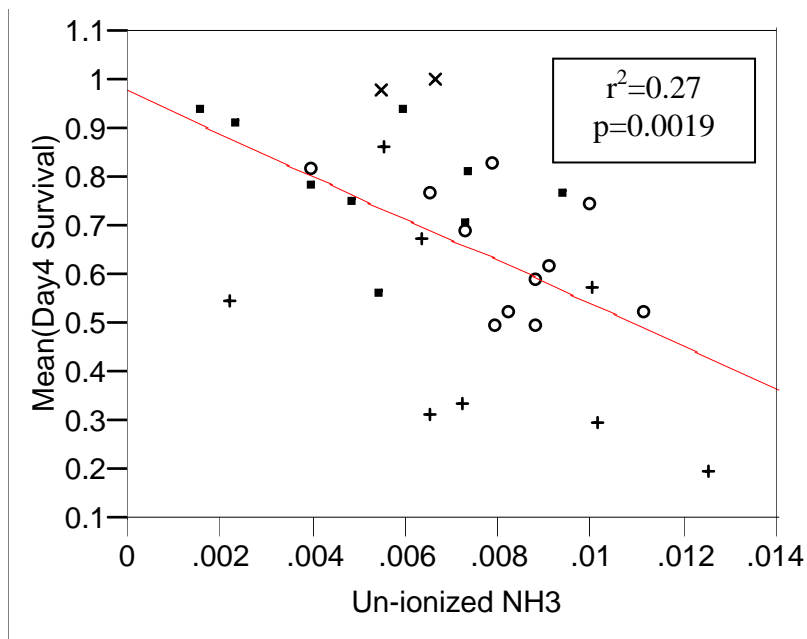


- **Salmonids are known to be particularly sensitive to unionized ammonia.**
- As an aside: Delta smelt MAY be as or even more sensitive – more tests to be conducted this year

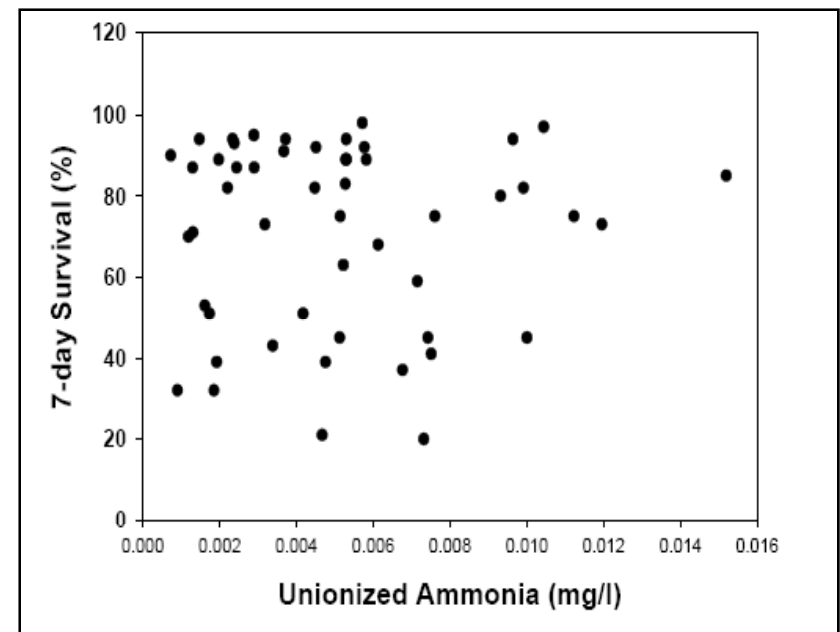
Delta smelt survival versus un-ionized ammonia (mg/L) in ambient Delta water samples and control water

Graphs provided by Dr. Inge Werner, UCD-ATL

2006



2007



And some more on EPA ammonia criteria:

Before 1998, the ammonia criterion was simple:

EPA Red Book 1976, page 16:

Criterion: 0.02 mg/L as unionized ammonia for freshwater aquatic life.

The 0.02 mg/L criterion is set as 1/10th of the lowest toxic level found [which was for trout] to provide a safety margin before toxicity = mortality occurs and also for untested organisms.

A similar standard has been adopted in many other areas/states/countries.

SF Bay Basin Plan: “Annual Median Limit” = 0.025 mg unionized ammonia/L

In 1998 & 1999 EPA updates, this became **MUCH** more complicated:

The one-hour average concentration of **total ammonia** nitrogen (in mg N/L) does not exceed, more than once every three years on the average, the **CMC** (criterion maximum concentration; **acute criterion**) calculated using [separate] equations when salmonid fish are present or absent.

The thirty-day average concentration of total ammonia nitrogen (in mg N/L) does not exceed, more than once every three years on the average, the **CCC** (criterion continuous concentration; **chronic criterion**) calculated using [separate] equations when fish early life stages are present or absent.

In addition, the highest four-day average within the 30-day period should not exceed 2.5 times the CCC.

Problems with the 1998/99 EPA ammonia criteria (in my opinion):

They are based on studies of acute or chronic toxicity of

- ammonia alone
- administered continuously
- without other stressors present
- using healthy, unstressed, resting fish

For VAMP salmon in the polluted San Joaquin, this is not realistic!

Several review papers call new criteria “unprotective.”

Just one example: LC50 for resting trout was 6.5 times higher than for swimming trout in Randall & Tsui, 2002

Old standard = 0.02 mg/L unionized ammonia seems like a more protective benchmark!

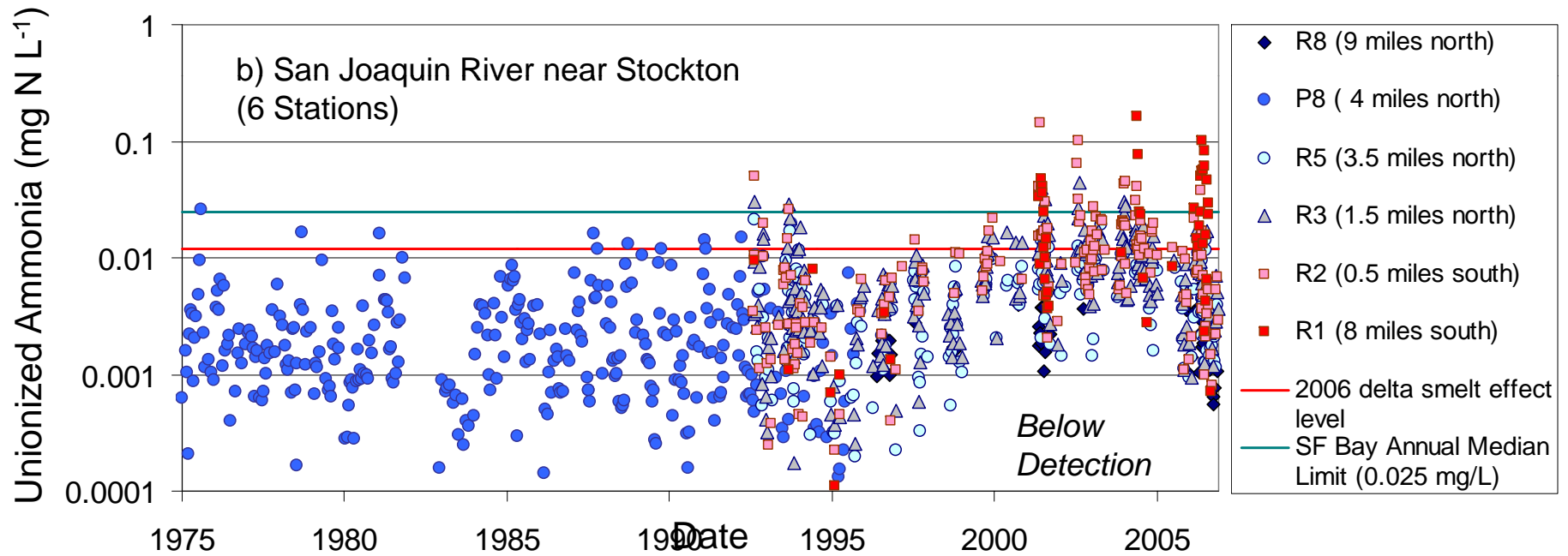
Following slides:

6. a) Unionized ammonia in the SJ River

6. b) Total ammonia in the effluent & the river compared to calculated CMCs & CCCs

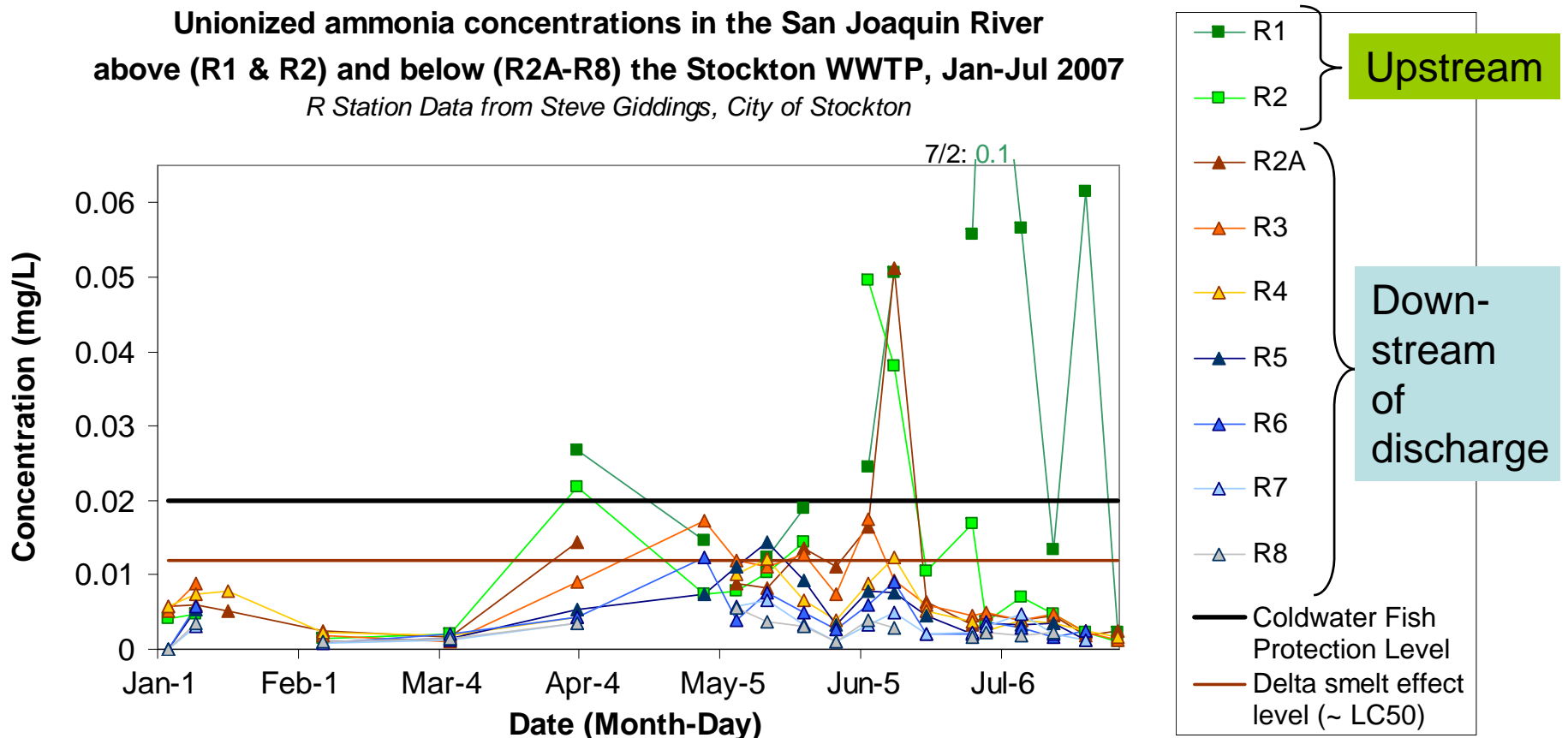
6. a) Unionized ammonia in the SJ River, 1975-2006

- up to > 0.1 mg NH₃-N/L (at stations ≥ 0.5 miles away from WWTP discharge)



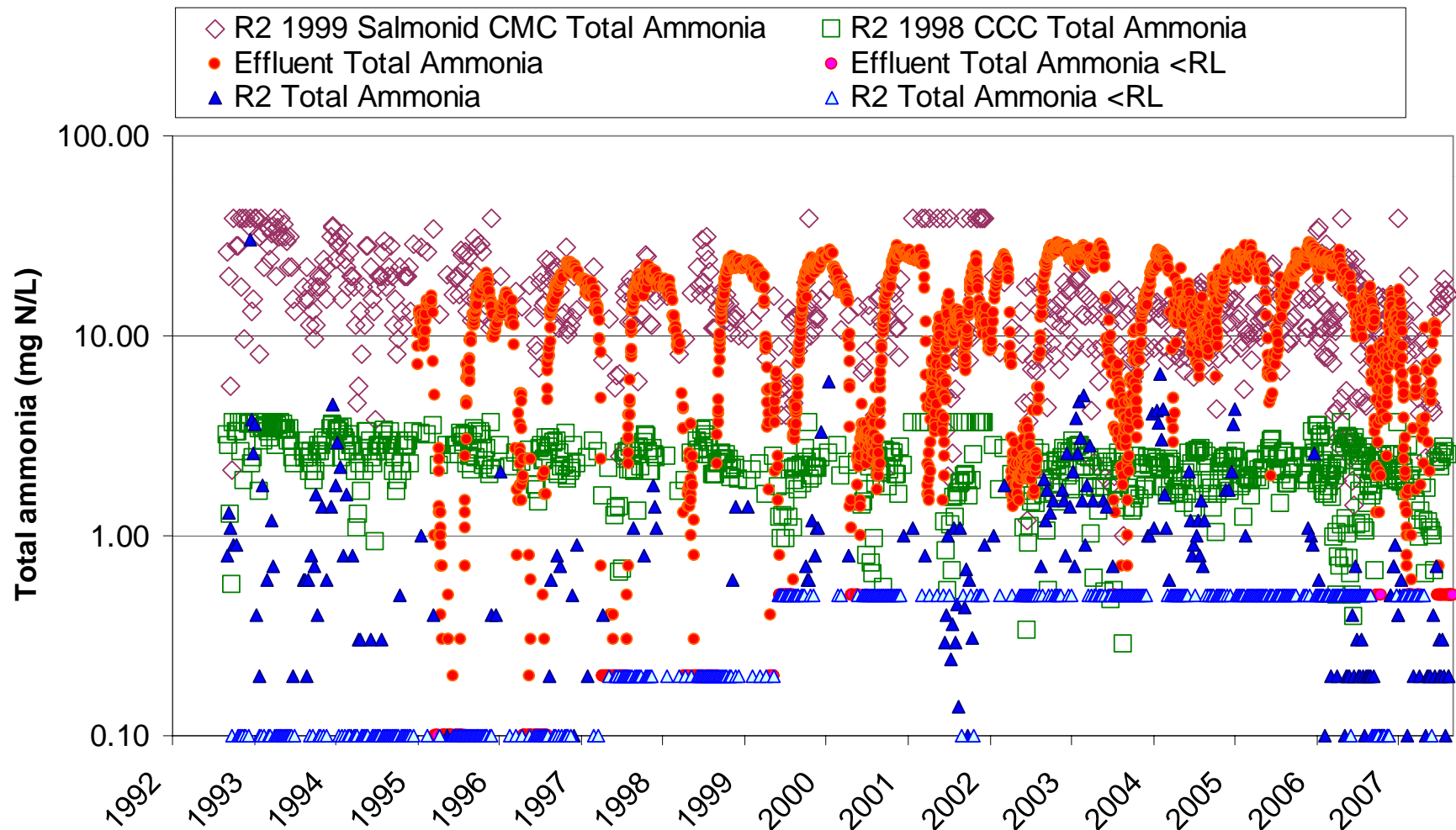
2007: Unionized ammonia in the SJ River, Jan – July 2007

- Highest at upstream sites
- In May, below 0.02 mg/L



6. b) 1998/9 EPA ammonia CMCs & CCCs

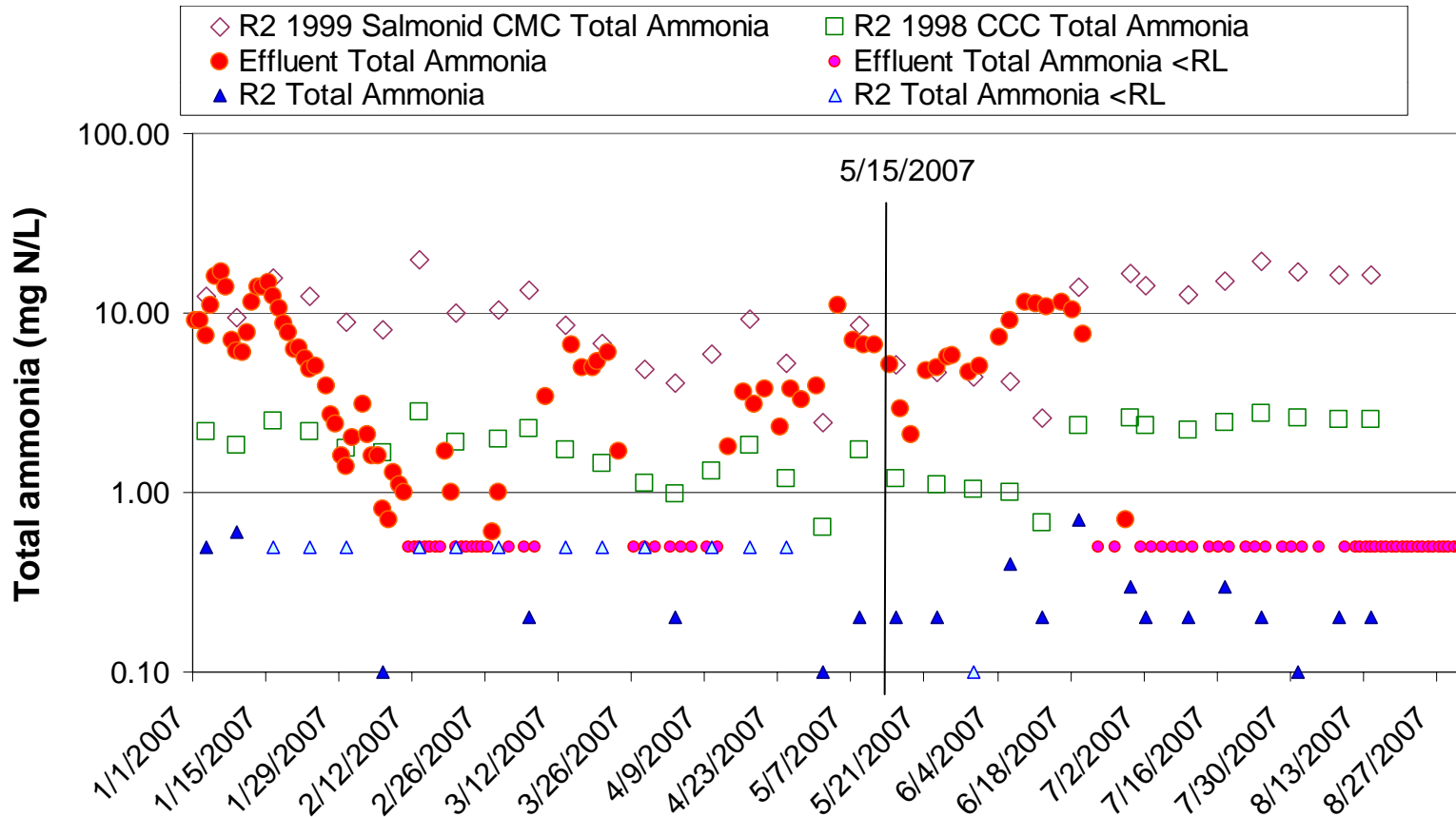
- Effluent: Many exceedances since 1992 (at river pH (R2))
- River 0.5 miles upstream of discharge (R2): CCC & some CMC exceedances esp. after 2000



6. b) CMCs & CCCs

Zooming in on May 2007:

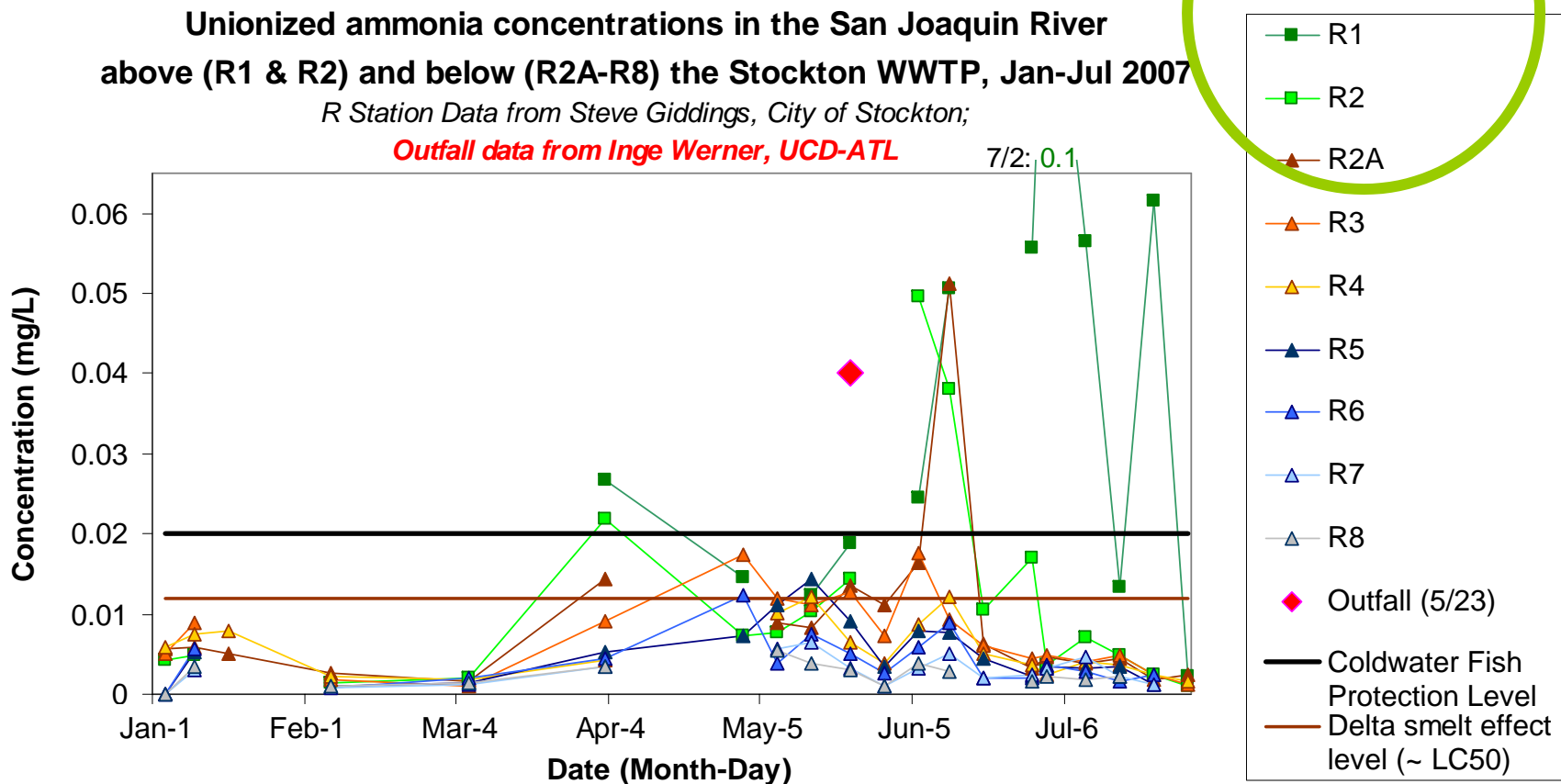
- Effluent ammonia > CCC, ~ CMC (at river pH)
- River ammonia 0.5 miles upstream < CCC & CMC



But no, I'm not done...

7. Some more questions:

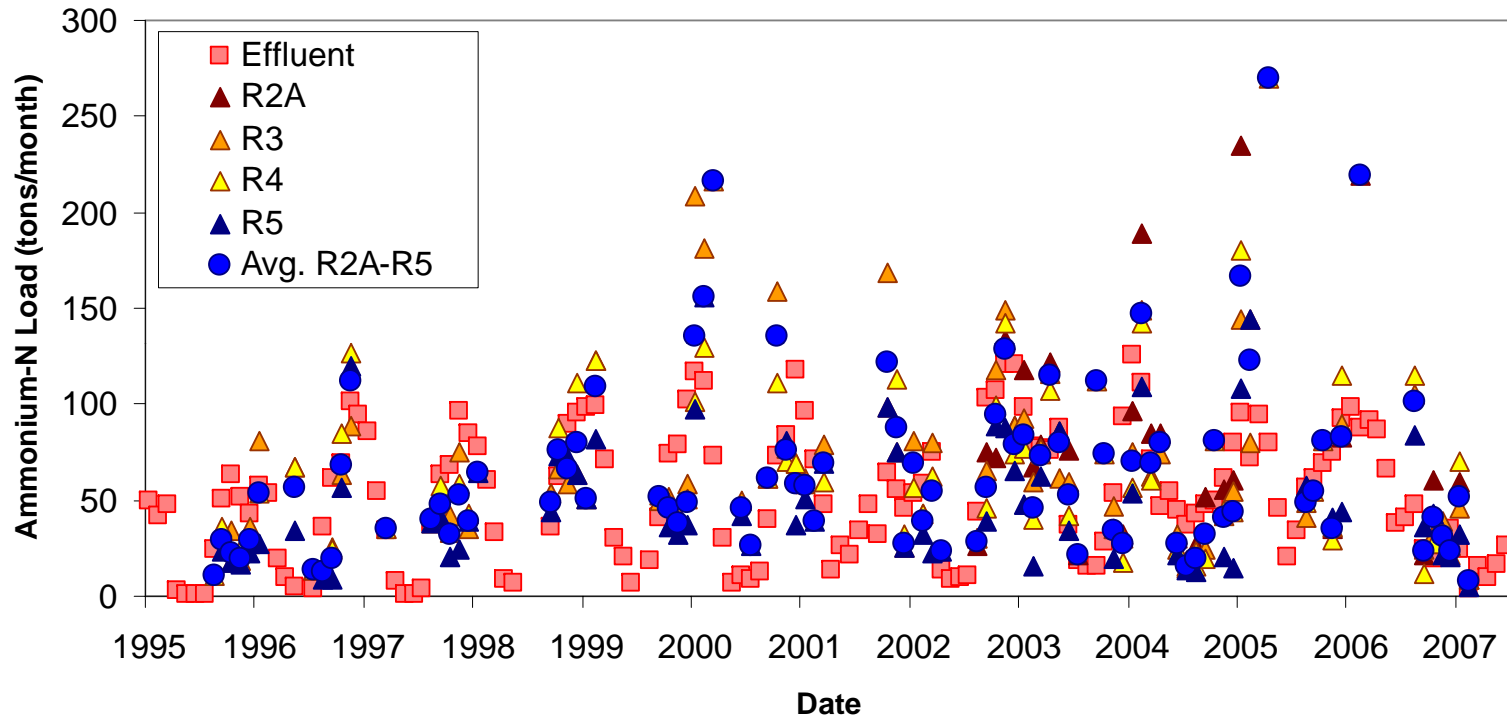
- A. Does the ammonia really come from the WWTP?
- B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?
- C. What about D.O.?



A. Does the ammonia really come from the WWTP?

Stockton WWTP Effluent vs. SJ River Ammonia Loads

Monthly Total Ammonia Loads in the San Joaquin River below the Stockton WWTP and in Effluent from the Stockton WWTP



Median effluent contribution to monthly NH_4 -Loads at R2A: **107%**
(Spearman correlation coefficient = 0.74, $p < 0.001$)

Median effluent contribution to monthly NH_4 -Loads at R2A-R5 (averaged): **110%**
(Spearman correlation coefficient = 0.56, $p < 0.001$)

On an annual basis: Median effluent contributions to NH_4 -Loads at R2A to R5: **77-118%**

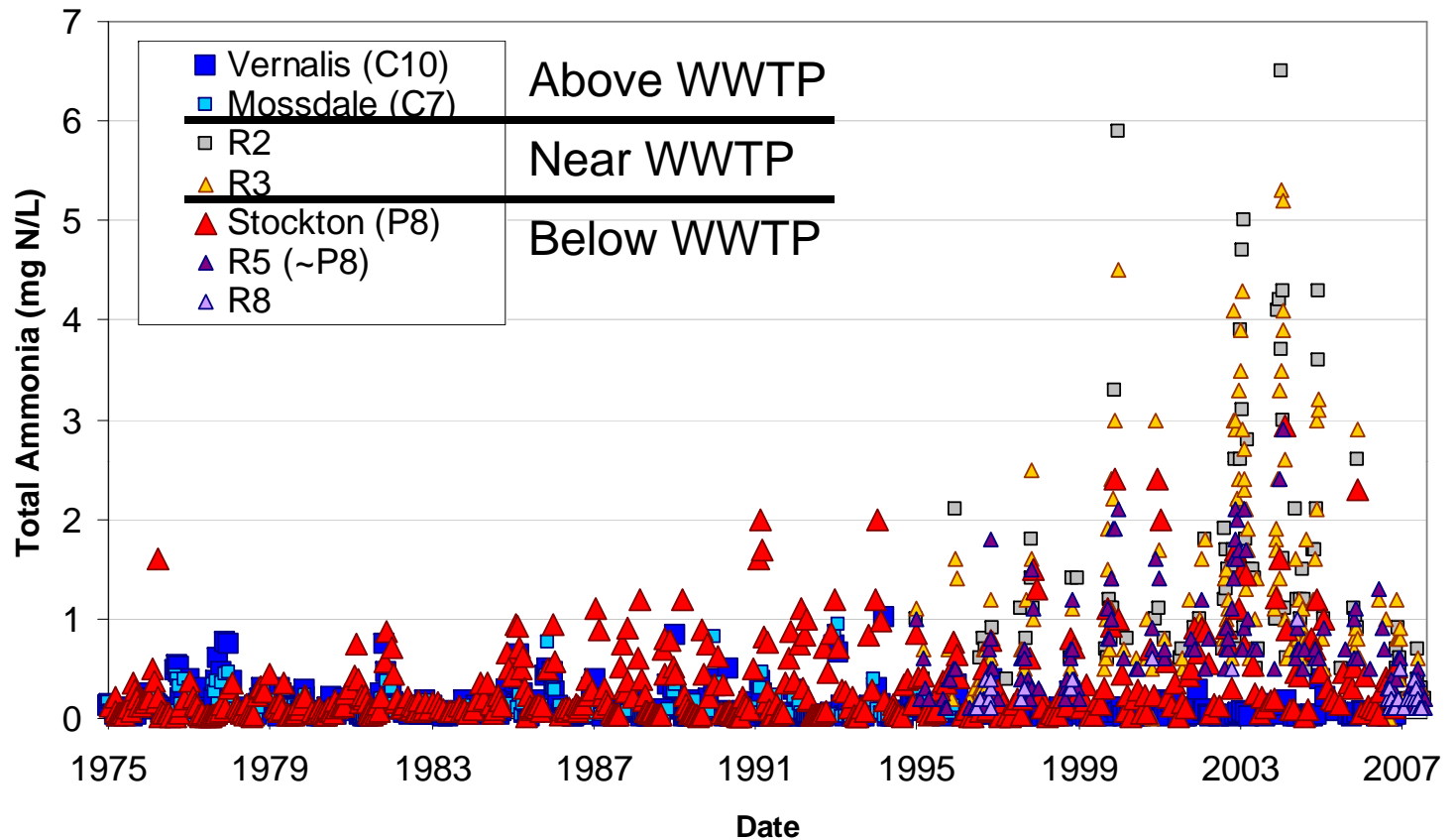
Since 1995, ~ all of the ammonium-N in the SJ River near Stockton comes from the WWTP!

A. Cont. Does the ammonia really come from the WWTP?

Total Ammonia-N Concentrations

**Above, near,
& Below the
Stockton
WWTP**

*Tertiary
treatment
started in
October 2006*



- Upstream input was important ammonia source to San Joaquin River near Stockton until mid-90s;
- **Since mid-90s, Stockton WWTP appears to be the most important ammonia source**
- New improved treatment may change this

7. Some more questions:

A. Does the ammonia really come from the WWTP?



B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?

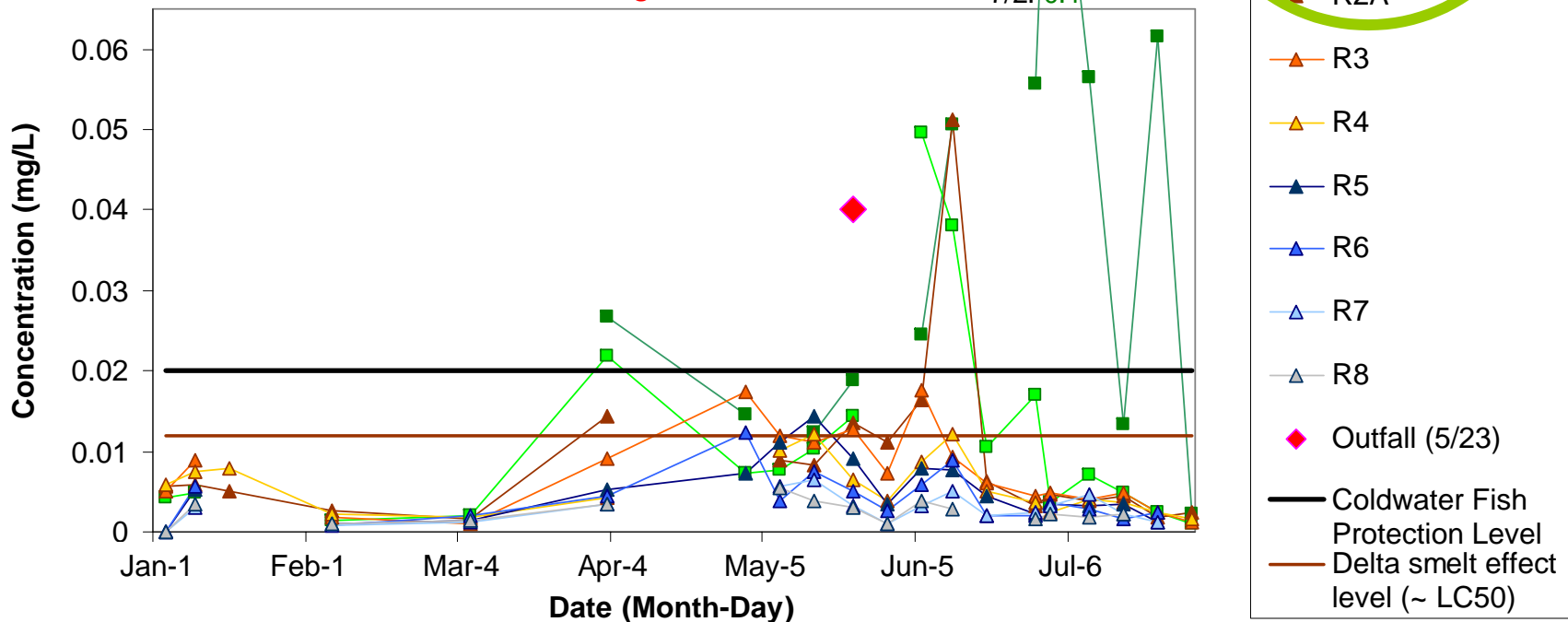
C. What about D.O.?

Upstream & Near WWTP

Unionized ammonia concentrations in the San Joaquin River
above (R1 & R2) and below (R2A-R8) the Stockton WWTP, Jan-Jul 2007

R Station Data from Steve Giddings, City of Stockton;

Outfall data from Inge Werner, UCD-ATL

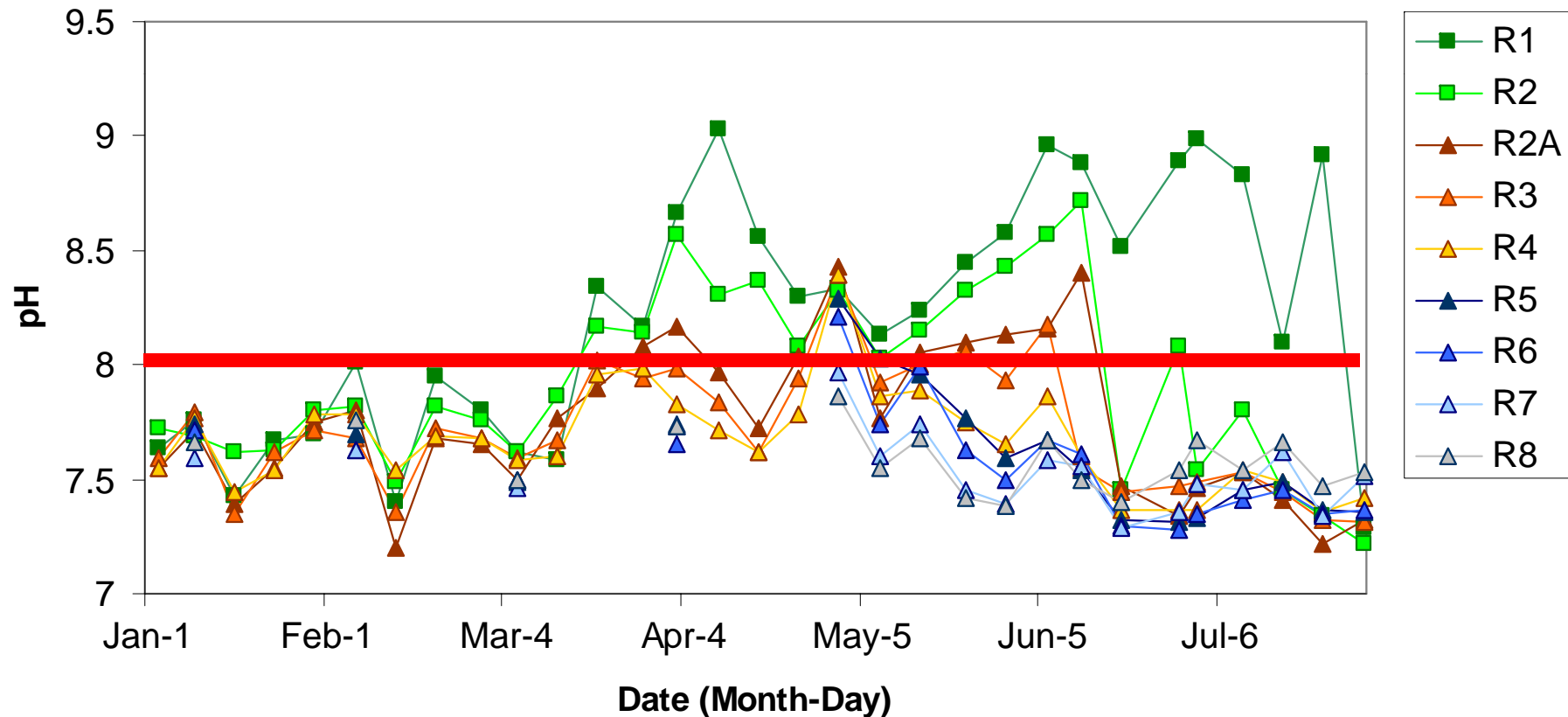


B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?

Starting in April, upstream pH is much higher!

pH in the San Joaquin River above (R1 & R2) and below (R2A-R8) the Stockton WWTP

Data from Steve Giddings, City of Stockton

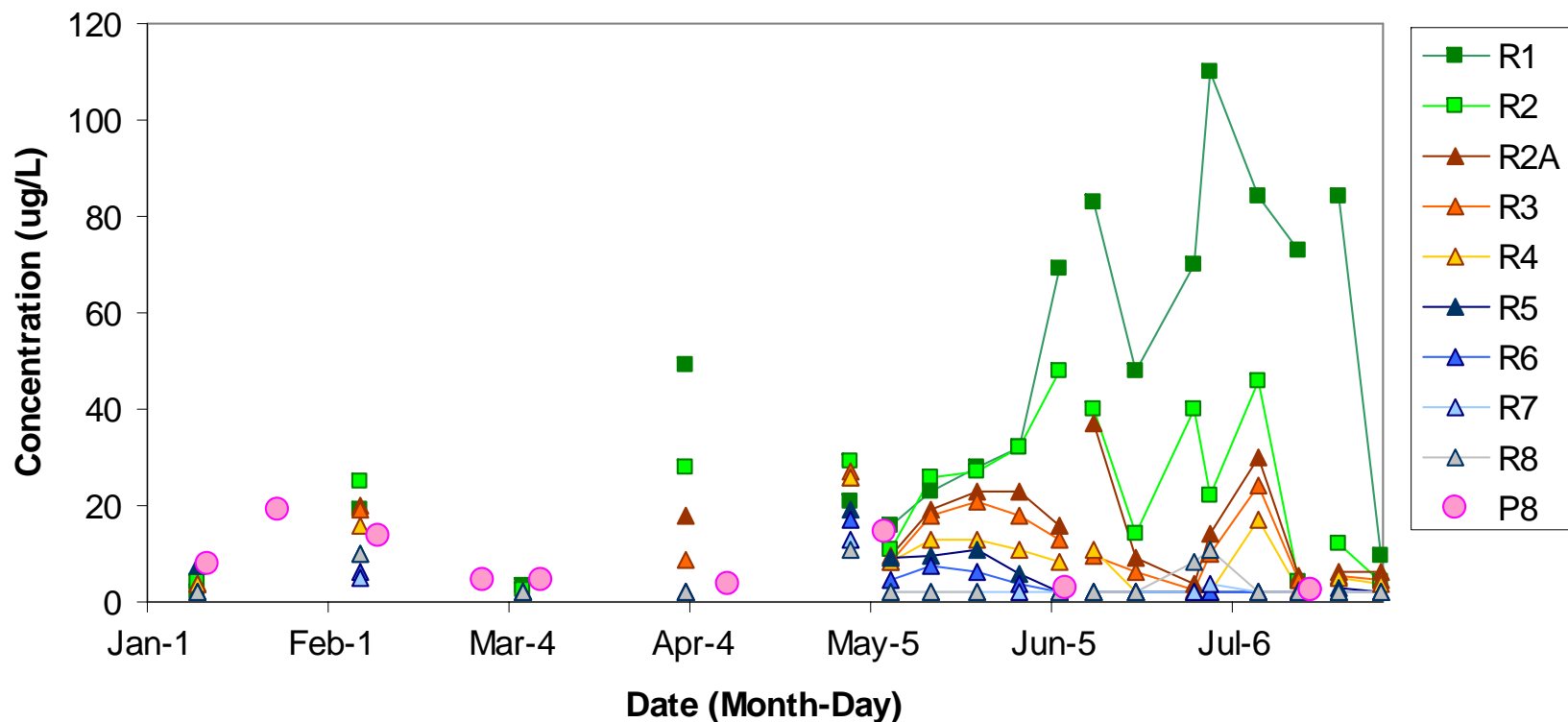


B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?

... because of more algae / primary production
(primary production elevates pH)

Chlorophyll *a* concentrations in the San Joaquin River above (R1 & R2) and below (R2A-R8, P8) the Stockton WWTP

Data from Steve Giddings, City of Stockton; P8 data: IEP EMP; RL=2 ug/L

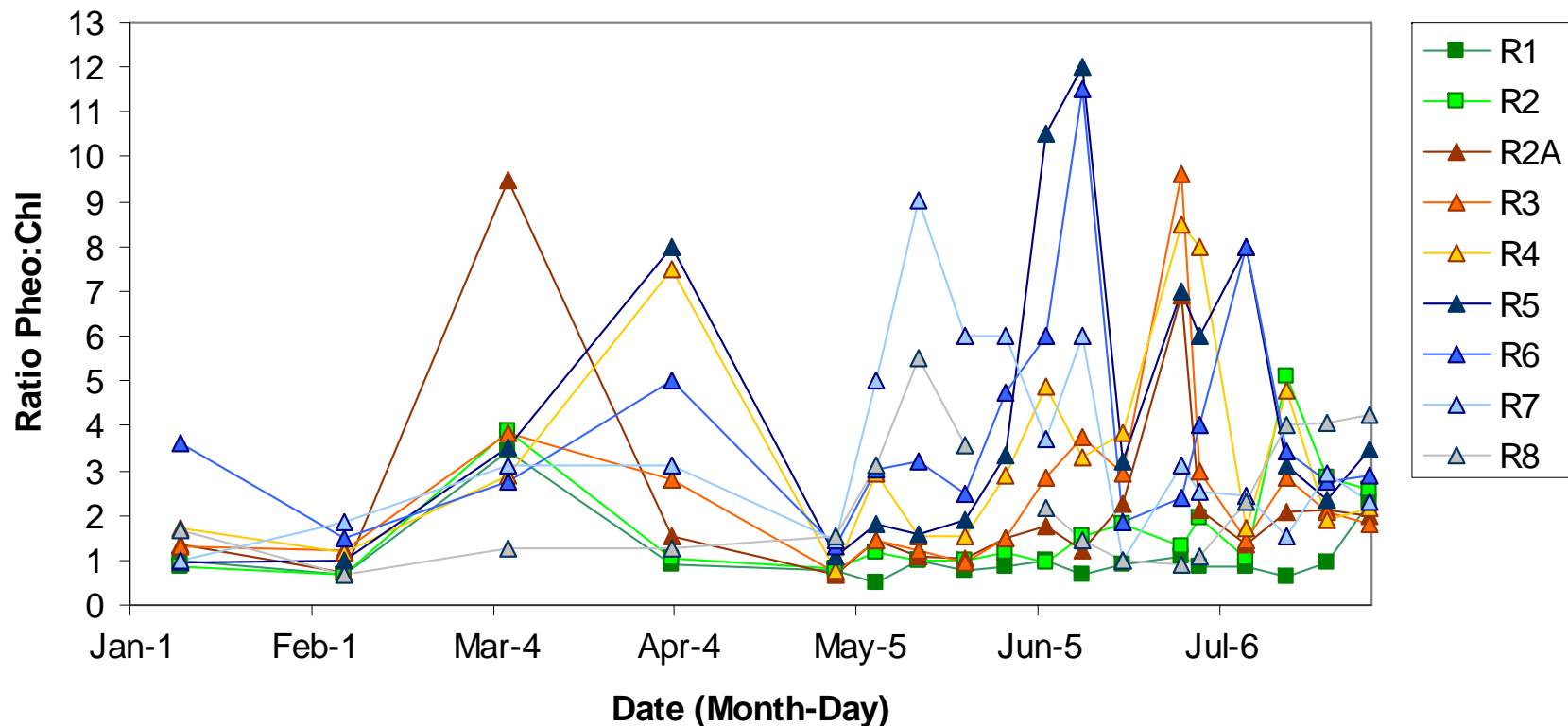


B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?

At & below the WWTP / in the DWSC, river algae **die** (more pheophytin/chlorophyll) and/or **produce less**.
This lowers the pH.

Pheophytin : Chlorophyll a Ratios in the San Joaquin River above (R1 & R2) and below (R2A-R8) the Stockton WWTP

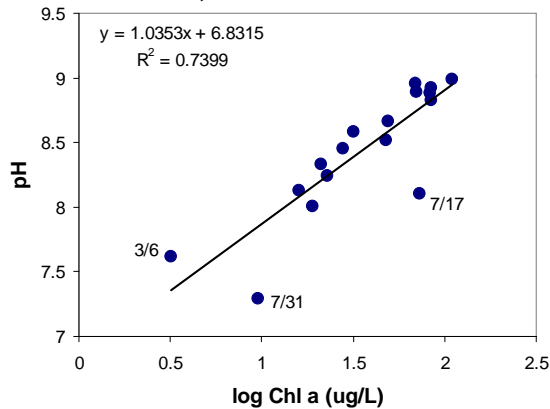
Data from Steve Giddings, City of Stockton



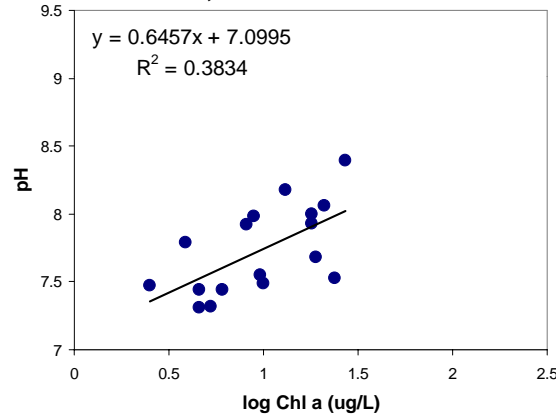
B. Why are unionized ammonia levels higher UPSTREAM OF & closest to the WWTP than farther downstream?

Relationship between chlorophyll *a* and pH, Jan – Jul 2007

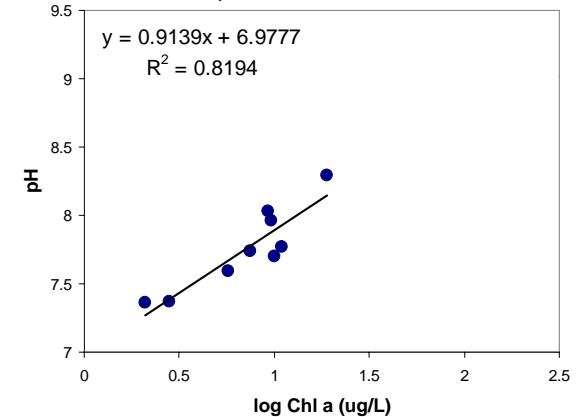
8 mi upstream
of WWTP
R1, Jan-Jul 2007



1.5 mi downstream
of WWTP
R3, Jan-Jul 2007



3.5 mi downstream
of WWTP
R5, Jan-Jul 2007



- Chlorophyll *a* concentrations & pH are positively correlated
- The relationship changes from upstream to downstream
- Above the WWTP: lots of healthy, productive river algae
- Just below the WWTP: fewer healthy & more dead/dying algae
- Farther downstream: fewer, but more healthy estuarine algae

7. Some more questions:

A. Does the ammonia really come from the WWTP?

B. Why are unionized ammonia levels higher UPSTREAM OF
& closest to the WWTP than farther downstream?

C.What about D.O.?

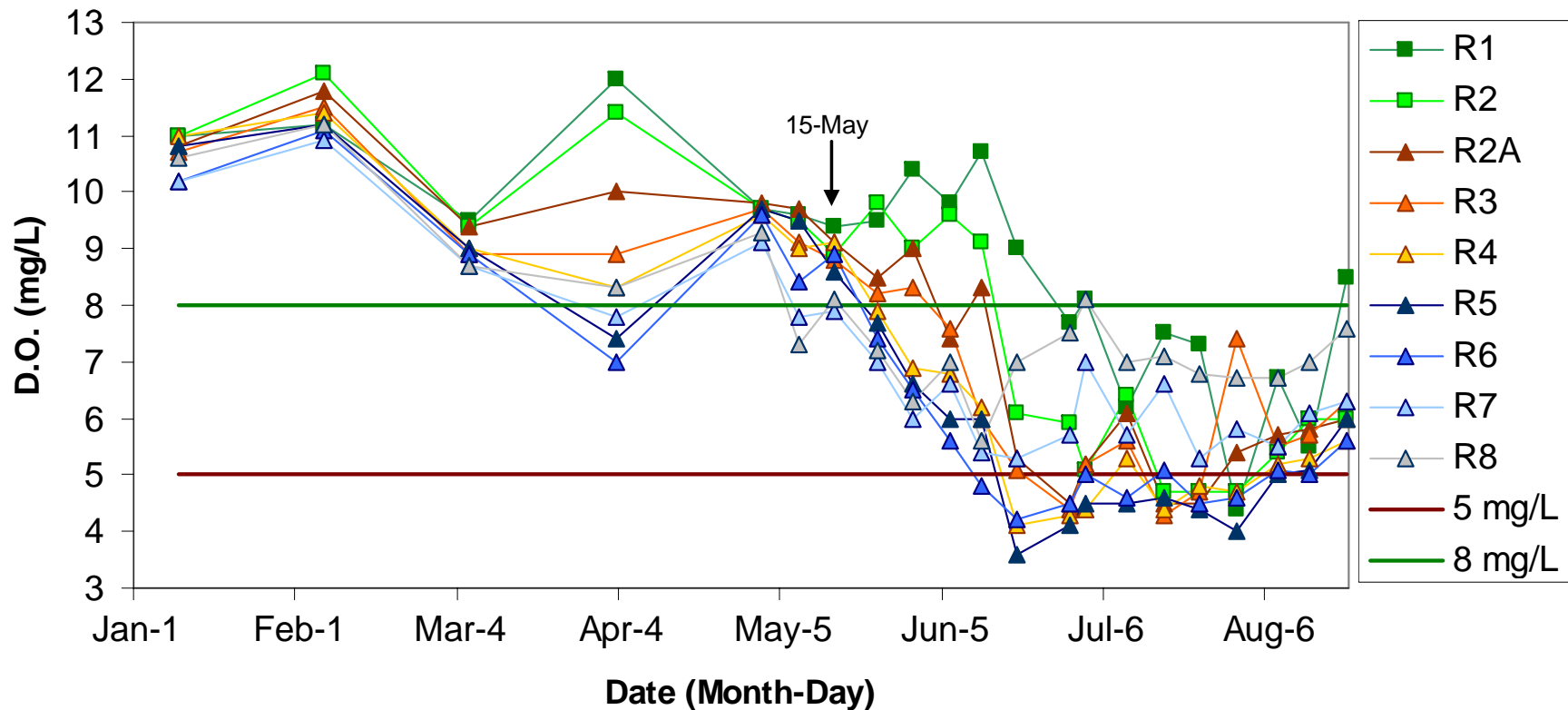
C. What about Dissolved Oxygen?

In 2007 (at mid-depth)

- D.O. levels started dropping early (mid May)
- But **remained above 5 mg/L** throughout May
- Critically low levels were reached by mid-June
- In July, D.O. was very low even at the most upstream station (R1).

Mid-depth D. O. in the San Joaquin River above (R1 & R2) and below (R2A-R8) the Stockton WWTP

Data from Steve Giddings, City of Stockton

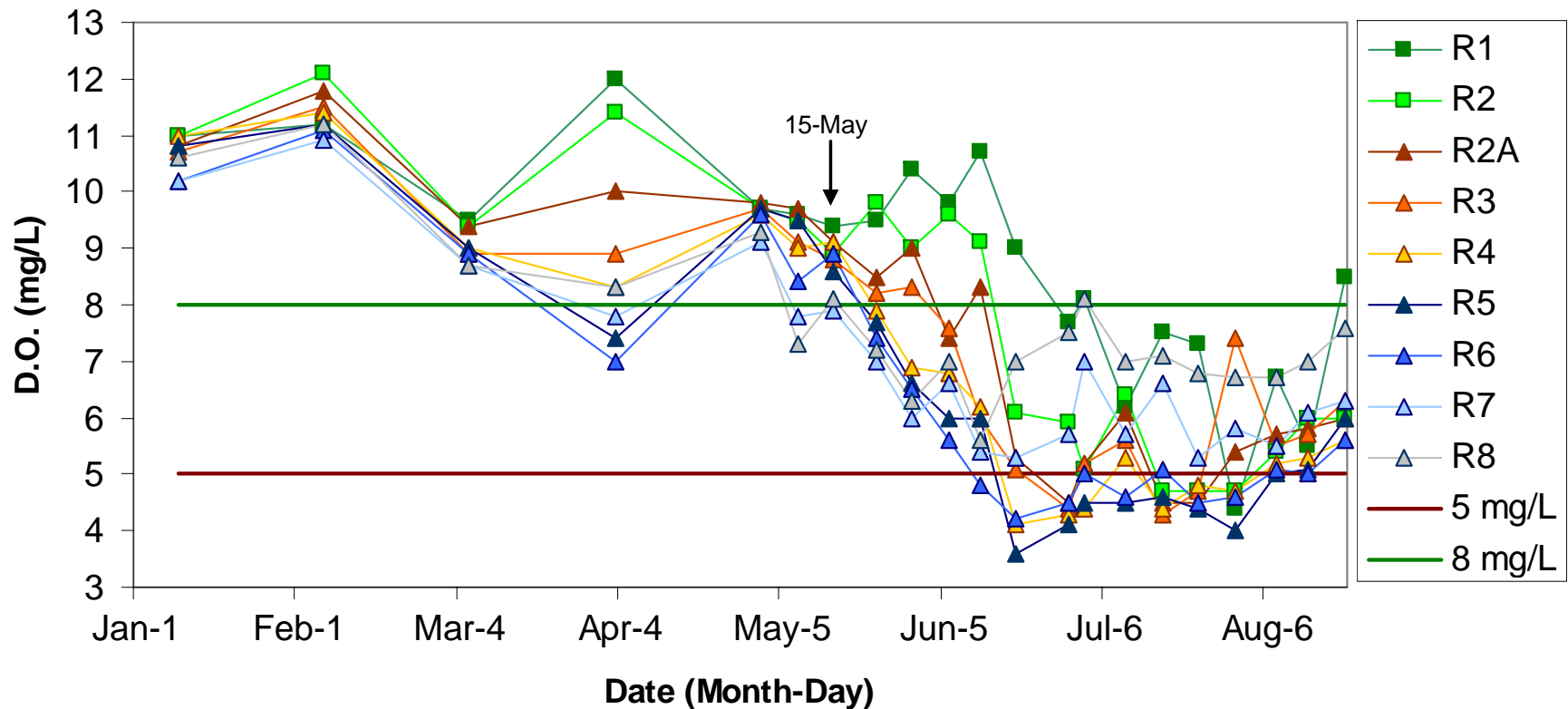


C. What about Dissolved Oxygen?

... Low D.O. did likely NOT kill the salmon in May 2007, but may have killed fish starting in June (but salmon were then gone).

Mid-depth D. O. in the San Joaquin River above (R1 & R2) and below (R2A-R8) the Stockton WWTP

Data from Steve Giddings, City of Stockton



8. Conclusions:

1. What killed the VAMP salmon?

- Toxic ammonia originating from the Stockton WWTP could have killed the VAMP salmon in May - by itself or with other toxicants/stressors.
- This is not conclusive because of a lack of data from the immediate vicinity of the salmon kill site / WWTP discharge – dead fish *not* talking...
- More water quality monitoring & fish testing should take place WITHIN a one-mile radius of the discharge (the closer the better!).

8. Conclusions, cont.:

2. Could this have happened before?

- Yes – high unionized ammonia levels, CCC & CMC exceedances (especially in (& near???) discharge)

3. Will this happen again?

- The new improved nitrification treatment should help prevent this from happening again – but at $\text{pH} > 8$, not much ammonia discharge is needed to kill sensitive fish... Is new 2 mg/L discharge permit level low enough?

AMMONIA MODELING FOR ASSESSING POTENTIAL TOXICITY TO FISH SPECIES IN THE RIO GRANDE, 1989–2002

HOWARD D. PASSELL,^{1,4} CLIFFORD N. DAHM,² AND EDWARD J. BEDRICK³

“results [...] suggest that NH₃ toxicity [from sewage treatment plants] may have played some role in the disappearance of [minnow species in the Rio Grande].”

“Ammonia toxicity [...] likely had **direct negative effects** [on the minnows] through chronic or acute toxicity.”

“In addition to direct effects, NH₃ toxicity downstream of the SSWRP may have **fragmented fish habitat** in the Rio Grande by creating an NH₃ barrier through which migrating fish would not pass.”

AMMONIA MODELING FOR ASSESSING POTENTIAL TOXICITY TO FISH SPECIES IN THE RIO GRANDE, 1989–2002

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“Additional toxicants could act **synergistically** with NH₃ to raise toxicity.”

“[A] mixture of toxicants* produced a toxicity that was more toxic to both the silvery minnow and the fathead minnow than any of the five chemicals tested alone.”

(*NH₃, arsenic, copper, and nitrate)

“Although individual toxicant concentrations in rivers are regulated, **site-specific mixtures** of toxicants are not. [...]

Synergistic effects of multiple toxicants in the Rio Grande may make **site specific acute and chronic values** for the endangered silvery minnow more appropriate than national or statewide values.”

“An appropriate chronic criterion for silvery minnow in the Rio Grande could be **as low as 0.001 mg/L N-NH₃**.”

8. Conclusions, cont.:

4. A “1-2 punch” by WWTP discharge & river algae

Punch 1: Ammonia is (was) discharged Oct-May

- SJ River algae production increases starting in March/April, increasing pH above the WWTP
- Together, this creates toxic unionized ammonia levels near the WWTP discharge in spring
- *fish die!*

Punch 2: Algal production increases in/after April

- With increasing upstream river algae production & loading into the deep & dark & (nutrient etc.-) polluted Stockton ship channel, dead (river algae etc. -) biomass accumulates & microbes go to work.
- D.O. levels reach critically low levels starting in early summer. Hard-working estuarine algae (flagellates) cannot produce enough oxygen to balance microbial respiration near the turning basin.
- *fish die!* (although VAMP salmon have already passed through by this time)

The new improved WW treatment should greatly lessen at least punch 1...

9. VAMP monitoring recommendations for 2008:

- COLLECT MORE water quality DATA in close proximity (+/- 100 m) to the WWTP discharge (as well as at the more distant sites)
- Conduct salmonid toxicity assays with water from the discharge area
- Work toward site-specific toxicant criteria
- Closely work/coordinate with EMP, Stockton WWTP, and UCD/POD water quality and fish toxicity work
- Find smiling salmon!





Questions?

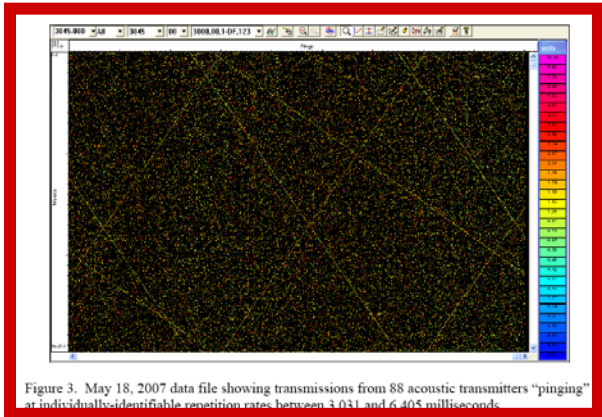


Figure 3. May 18, 2007 data file showing transmissions from 88 acoustic transmitters "pinging" at individually identifiable repetition rates between 3.031 and 6.405 milliseconds.



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