Before the Dawn's Early Light,
or
What Happens with Dissolved Oxygen and *p*H Overnight ?

During the dry-season, streams of the Goleta and Ventura watersheds are ideal for algae. Temperatures are warm, daylight abundant and nutrients in plentiful supply. This is particularly true following winters with exceptional amounts of rain – when local flooding has swept channels clear of plants and sediment, and opened them to greater amounts of sunlight. More winter rainfall means higher summer flows, elevated concentrations of nitrate and increased habitat for algae (see "What's All That Green Stuff in the Backcountry," Leydecker, 2005). The dry-season following a "big" rainfall winter is a season of increased algal growth and decay, and as such, introduces additional problems for monitoring water quality. 2005 is that kind of year, a year when rainfall was 200-250 % above average.

Regarded as unsightly and a nuisance, the real problem is that algae can transform the carbonate balance of a stream and drastically impact the amount of dissolved oxygen – and it does this over a daily cycle. With sunlight, algae photosynthesize, removing carbon dioxide from the water column and replacing it with oxygen. The process reverses at night, as oxygen is removed and carbon dioxide added (Carlsen, 1994; NM-SWQB, 2000). [I'm going to list references available over the web for those who would like more information.]

Figure 1. Algae on lower San Antonio Creek (VR07) in the summer of 2001. Ugly? Disgusting? One of nature's more exquisite art forms? Whatever. But too much algae is a major water quality problem.

Channelkeeper sampling takes place during daylight and we are used to seeing high concentrations of daytime oxygen and thinking, “all is well.” But high oxygen concentrations can also indicate an overabundance of algae. And those high levels can rapidly decrease after the sun sets. With heavy algal growth dissolved oxygen (DO) reaches a minimum just before sunrise – and it’s concentrations during this critical period that determine the threat to fish and other aquatic species, a threat we, and sad to say, most other sampling groups, usually don’t evaluate (Windel et al., 1987; Deas and Orlob, 1999; PIRSA, 1999).

As algae add oxygen during daylight they remove carbon dioxide. Removing carbon dioxide is the same as removing acidity (carbon dioxide in water forms carbonic acid – the stuff that gives soda its zip), thus increasing *p*H (PIRSA, 1999; NM-SWQB, 2000). Normally, absent this process, streams would show little change in *p*H; some of the same dissolved minerals that give our local streams high conductivity – carbonates of calcium and magnesium – also “buffer” them against large variations in *p*H. And large variations are dangerous, a change of more than two points on the *p*H scale can kill many species of fish. The EPA and Regional Water Quality Control Boards regard a *p*H change of more than 0.5 as harmful (SWQCB-LA, 1994; SWQCB-CC, 1994). Keep in mind that half a unit of *p*H is not a small thing, the scale is logarithmic and half a unit represents a 500 percent change.

Given this extraordinary year, Channelkeeper decided that early morning – very early morning, around 3-5 AM – oxygen concentrations and pH needed to be measured as part of this summer’s sampling program. We’ve now done four of these expeditions, two in Goleta (June 15 and July 8) and two in Ventura (June 2 and July 20), and this report discusses the results.

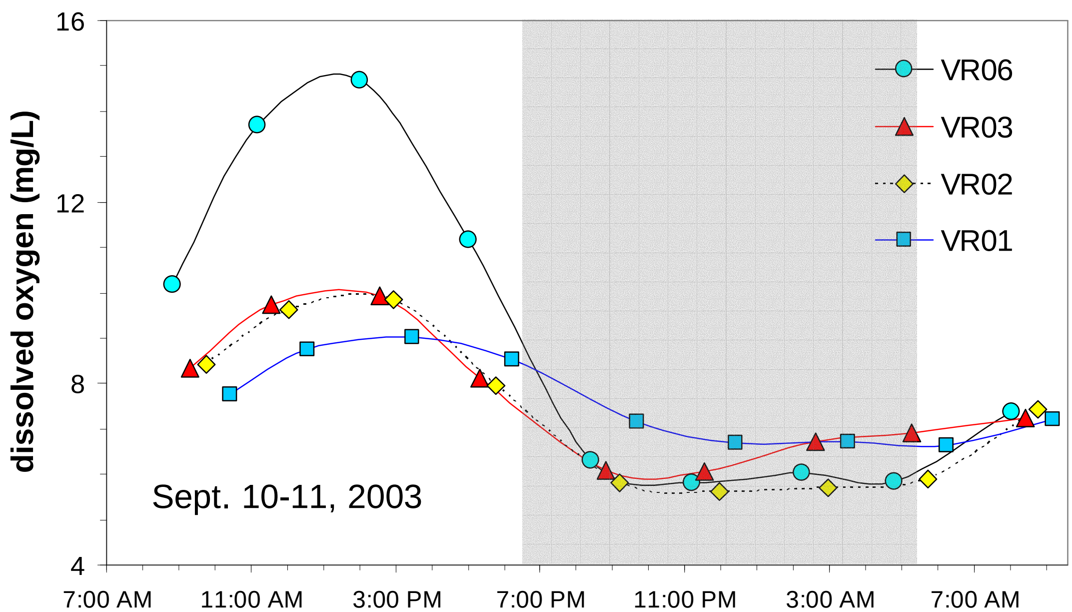


Figure 2. Changes in dissolved oxygen at four lower Ventura River locations over a 24 hour period on September 10-11, 2003.

First, let’s examine what we should be seeing. Figure 2 shows the changes in dissolved oxygen that occurred on the lower Ventura River on September 10-11, 2003. At this time the river at VR06 (Foster Park) was overgrown with algae and the graph shows what we might expect under similar circumstances elsewhere: oxygen varied over the 24 hour period from a high of 15 mg/L around 2 PM (170 % of saturation) to a low of 5.8 mg/L at 5 AM (60 % of saturation). Sampling locations further downstream, dominated by aquatic plants not algae, showed a more muted oxygen cycle: peaking at 9-10 mg/L between 2 and 3:30 PM (100-110 % of saturation) and declining to 6-7 mg/L before dawn. The take-home message is simple: the more algae, the deeper the cycle and the greater the difference between early afternoon and predawn oxygen concentrations.

However, the story was not text book perfect. Oxygen peaked at some locations later than at others. Why? Was it cloud, fog, the angle of sun and shade, or something else? Why did VR03 reach a minimum concentration around 9 PM and then increase? And why did oxygen levels at VR02 go as low as VR06, even though there appeared to be much less algae at that site?

Welcome to the messy, complicated world of environmental science. Aquatic plants usually cause lower oxygen depletion because their above water parts have an alternate reservoir from which to extract or expel carbon dioxide and oxygen – the atmosphere. But below water they play host to a wide range of epiphytic algae clinging to stalks and roots, and are a source of decaying matter that can also affect the oxygen balance. Physical processes add and remove oxygen and even mild turbulence enhances gas exchange at the water surface (see Figure 3).

Figure 3. At Atascadero at Patterson Avenue (AT2) a concrete and rock apron leading under the bridge acts as a weir and forms a long, narrow impoundment which can be seen in the middle of the photo. In summer, water trickles from the pond over the rock apron. At around 11 AM on August 2005 (the photo was taken in June) dissolved oxygen in the ponded water had a concentration of 4.6 mg/L; ten feet downstream the concentration had increased to 9.1 mg/L.

As almost everything else in nature, oxygen concentrations arise from complex interactions (the cycle of photosynthesis and respiration, bacterial decay, effects of temperature and turbulence, current velocity, water depth, etc.) and we shouldn't expect any simple explanation to be totally satisfactory. It shouldn't be surprising that surprise is nearly a constant in water sampling.

The variation in *p*H over the diurnal cycle for the four Ventura River locations on September 10-11, 2003, is shown in Figure 4.

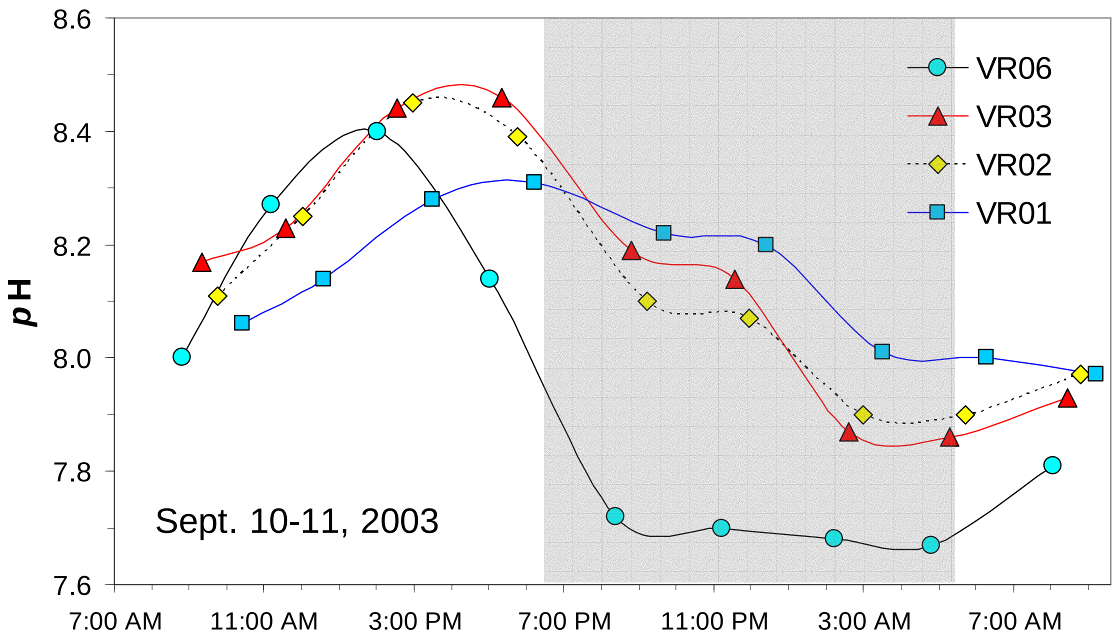


Figure 4. Changes in *p*H at four lower Ventura River locations over a 24 hour period on September 10-11, 2003.

The depressions in nighttime *p*H (as carbon dioxide accumulated and the water column became more acidic) mimic the dissolved oxygen results: pH and oxygen moving up and then down together. As might have been expected, the greatest change was produced by heavy algal growth at VR06, with VR02 and VR03 showing lesser, but still substantial, depressions and VR01 with the least. Again, there are mysteries. Why the step-like nighttime decrease at VR01, 02 and 03? Why is pH at VR06 so much lower at night, but not as high during the day? And why did *p*H peak much closer to sunset than dissolved oxygen?

Some of the answers lie in the change in water quality as effluent from the Ojai Sewage Treatment Plant is added to the river below VR06. By late summer, treated sewage effluent contributes most of the flow below this point and Ojai water (which is basically what the treatment plant discharges), with higher mineral content and conductivity, is better buffered against pH change. Plant output may also vary over the evening hours, both in quality and quantity: VR03, the sampling location closest to the plant, had the greatest "step-change" in pH – and a matching step-change in dissolved oxygen (Figure 2).

I've spent time on this old Ventura data because knowing what to expect is important in interpreting predawn efforts, and because they convey another critical lesson: expect the unexpected. This summer's results also presented a number of mysteries.

Goleta Data

Figure 5 shows the results of this year's early morning sampling compared with dissolved oxygen concentrations and pH measured on the nearest regular sampling day.

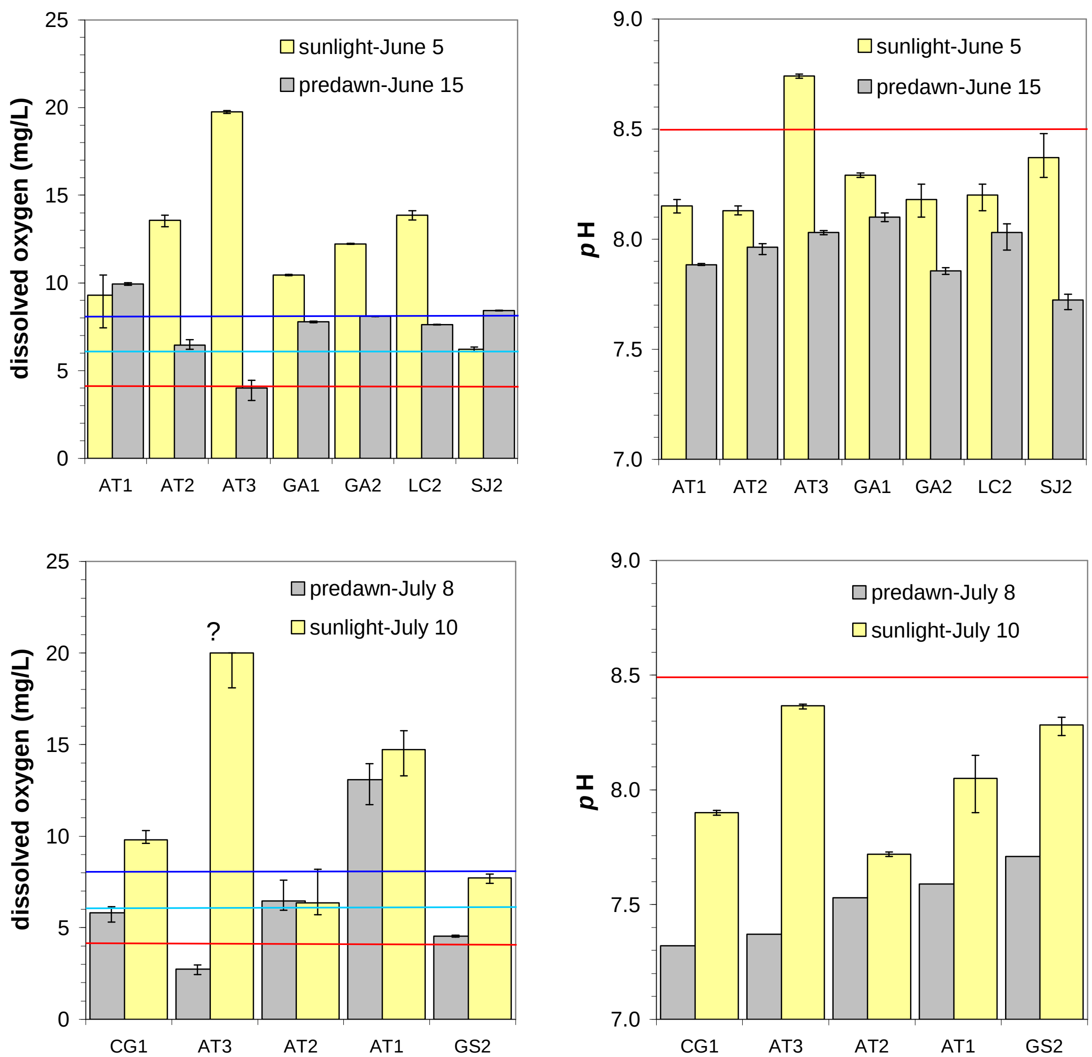


Figure 5. Predawn dissolved oxygen concentrations and pH at selected Goleta locations compared with values measured on the nearest regular sampling day. The horizontal lines mark important DO and *p*H milestones for steelhead. For oxygen: above 8 mg/L represents near ideal conditions; at 6 hypoxia begins and fish start to feel stress (but no lasting harm is done in the short term); and below 4 lies severe damage and death. For *p*H: 8.5 marks the upper limit set by the Regional Boards for Santa Barbara and Ventura Counties (the EPA recommends a range between 6.5 and 8 as preferable for aquatic life). The "error bars" represent the maximum and minimum values measured at the time of sampling and the question mark above AT3 indicates that some measurements exceeded the meter maximum of 20 mg/L.

While most locations showed a decrease in predawn dissolved oxygen concentrations, only AT3 (Atascadero at Puente Avenue) reached dangerously low levels (< 4 mg/L). AT3 is a strange location, a concrete channel where low flows weave in and out of dense algal mats. Flow here is very shallow, and shallow flows respond quickly to changes in gas concentration because they equilibrate rapidly with the atmosphere (lots of surface area, very little depth). The situation may have further deteriorated in August as an odor of rot was prevalent during the regular daylight sampling – it's probable that the now decaying algal mat is turning parts of the stream septic at night. We should also begin to worry about the Goleta Slough (GS2): a DO concentration of 4.5 mg/L on July 8 is not a good sign (fish kills due to low oxygen in the slough have happened in the past). However, predawn dissolved oxygen concentrations appeared to be adequate at all other locations.

Day-night *p*H changes at AT3 were equally dramatic, 0.7 units in June, 1.0 in July (a 10-fold increase in acidity when the sun went down). AT3 also exceeded the allowable 8.5 *p*H limit at the time of the regular June sampling. In addition to AT3, GS2 and Cieneguitas Creek (CG1) exceeded the maximum allowable 0.5 unit change in *p*H.

Figure 6. AT3 on June 5, 2005. A small storm pushed the old algal crop to the side and a new one was growing in the center if the channel.

There are no shortage of odd occurrences in the data. While all the *p*H measurements exhibited the expected nighttime decrease, oxygen actually increased or changed little at some locations (AT1 and SJ2 on June 15, AT1 and AT2 on July 8). While error is always a possibility, where measurements were taken may also make a difference (see Figure 3). Daylight measurements taken in a quiescent portion, compared with predawn riffle values, may well show the opposite of any expectations. Comparisons like this would be invalid, similar to comparing apples and oranges. Other differences may affect comparisons, for example, differences in sampling times or the presence of sun or shade. And since the June measurements were 10 days apart, stream conditions and algal populations could have varied in the interim.

However, rationalization aside, something strange is going on at AT1. Predawn measurements in June and July indicate highly saturated conditions (9.9 and 13.1 mg/L, 110 and 150 % of saturation, respectively). How could a stream remain supersaturated all night? What could possibly cause this?

At AT1 a large rock and concrete weir separates fresh water from the tidally influenced slough, forming a long skinny lake that backs water up almost to the Patterson Bridge. In summer, very low flows simply trickle over the weir (the situation is similar to that of Figure 3, but the ponded section is larger and deeper). A close look at the July data reveals that 2-3 DO measurements were taken in a quiescent section near the bank, and a single measurement closer to the center of the weir (where trickling outflows usually decrease supersaturated oxygen concentrations). Before dawn on July 8, oxygen was 13-14 mg/L in the quiet section, 12 mg/L nearer the center of the stream; in daylight, on July 10, measurements in roughly the same locations showed respective increases to 15-16 and 13 mg/L. It appears that concentrations had actually decreased overnight, but not by much.

My explanation for this very strange phenomena is that when flow slows to a trickle, deep and quiescent pools may need a lot more time than expected to equilibrate with in-stream biological processes – that nighttime dissolved oxygen concentrations may retain a daylight signature, and daytime concentrations nighttime effects. If mixing is slow and incomplete, and the water is deep, the sampling location may act more as a reservoir of past history than of current conditions – especially if most biological transformations occurred further upstream. At AT1, macroalgae form a mat on the surface which may help retard atmospheric surface exchange and delay loss of oxygen from the water column below.

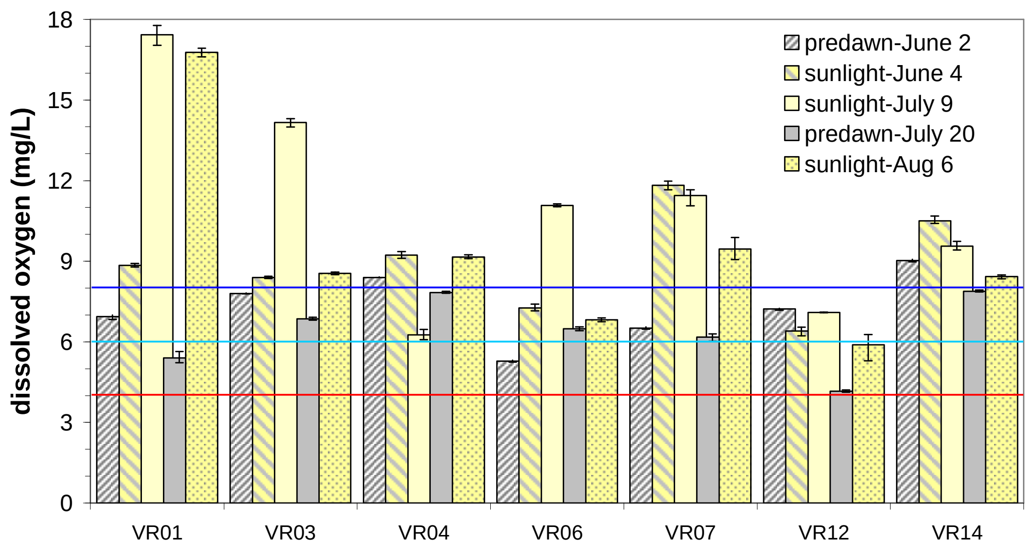
AT2, another location with higher predawn than daylight oxygen concentrations, also has a relatively quiet upstream pool (Figure 3), but here DO concentrations were much lower: 6.0-6.2 mg/L on July 8, 5.7-5.8 on July 10. In this well shaded area with low algal growth it's possible that we are simply seeing the normal variations that occur when measurements are taken by different people at different times with different instruments. However, this is an exceptional location. It can be considered the bottom end of a long, narrow swamp – a swamp about 4 to 10 foot wide and over a mile long. All the action takes place upstream, where the concrete canal is exposed to sunlight, and algae and plants grow in profusion. Water slowly trickles through this area and it's possible that upstream changes take a long time to become manifest at AT2. The low oxygen measured in daylight on July 10 may simply be late-arriving, nighttime influenced, flows.

A question I really don't want to ask but will is, if oxygen concentrations at AT1 and AT2 didn't show much day-night variation, why then did *p*H? If the data are correct (always a big "if" when *p*H is being considered), the combination implies that dissolved oxygen concentrations remained approximately the same while the amount of carbon dioxide in the water increased. A further implication is that a majority of the carbon dioxide cannot have come from the respiration of photosynthetic algae (which remove oxygen). In deep quiet pools, where algal growth is limited (AT2) or mainly confined to the surface (AT1), the processes of bacterial assimilation and decay in bottom sediments may provide this alternate source of carbon dioxide. Monitoring the daily change in pH and oxygen, by taking measurements every few hours, may provide additional insight and I hope to conduct this type of experiment in the future.

There are other puzzles. Why did nighttime pH decrease as water flowed from AT3 to AT1 on June 15, but increase on July 8 (Figure 5)? And what could have happened at upper San Jose Creek (SJ2)? But enough is enough; I did say we shouldn't be surprised to be surprised.

Ventura Data

Figure 6 shows the results of early morning Ventura sampling compared with dissolved oxygen concentrations and pH measured on recent regular sampling days. Only VR12 showed a decrease in oxygen (4.2 mg/L) close to the 4 mg/L danger zone. However the basin plan for the Ventura River calls for dissolved oxygen concentrations greater than 7 mg/L (SWQCB-LA, 1994) and only VR04 and VR14 consistently met this standard .



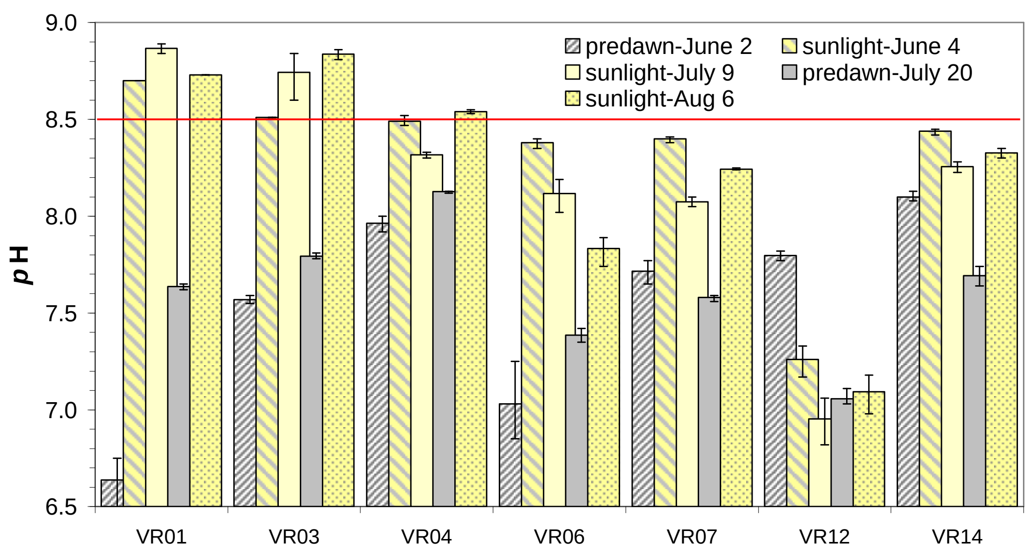


Figure 7. Predawn dissolved oxygen concentrations and pH at selected Ventura locations compared with values measured on regular sampling days. The horizontal lines mark important DO and pH milestones for steelhead (see Figure 5). The “error bars” represent the maximum and minimum values measured at the time of sampling.

[Since it's not regarded as a cold water stream, Canada Larga (VR04) only needs to meet a standard of > 6 mg/L. Sites not shown on Figure 7, VR09, 10 and 11, were also sampled predawn on June 2 and all met the 7 mg/L criterion.]

Predawn oxygen measurements on July 20 were in almost all cases lower than on June 2 (VR06 being the only exception). As flow decreases throughout the summer, algae can exert a greater influence – it's a matter of proportion, equal amounts of algal growth will have a greater effect on smaller quantities of water. Off setting this, we have some good news and some bad news. The good news is that the peak of the algal bloom occurred earlier, when water levels and flows were much higher, depressing oxygen concentrations less than we initially expected.

In Figure 8, I've shown some of the data from Figure 7 in a different format: as a line graph instead of bars so the progression of change in DO over time can be more easily visualized (the shaded portions represent predawn measurements).

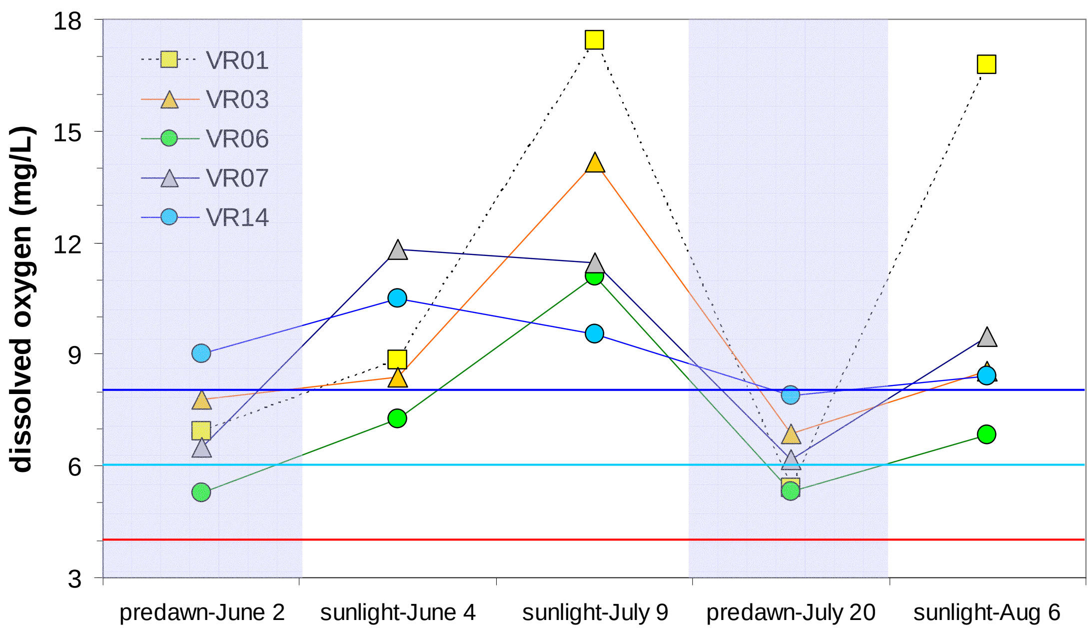


Figure 8. Dissolved oxygen at selected Ventura River locations: June 2 to August 6, 2005.

On the lower river (VR01, 03 and 06) the combination of algal density and river flow produced the highest daylight DO concentrations in early July, but on the North Fork of the Matilija (VR14) maximum DO occurred in June. This indicates the peak of the algal bloom either occurred earlier on the Matilija (and probably on San Antonio) or algal concentrations decreased more rapidly. Or both. Remember, it's the combined effect we are looking at – greater amounts of algae may have had a lesser impact when flows were higher. The lower daylight DO concentrations in August make it obvious that we were well past the algal bloom at all locations (except perhaps at VR01) at that time.

What's the bad news? The bad news is that *Chadophora*, the alga we've been seeing everywhere this year, can have two blooms – one in spring or early summer and another in the fall. The fall bloom, if it makes an appearance, will occur when flows are much lower than now, and the impact on dissolved oxygen may be far greater.

The progression of *p*H changes at the Figure 8 locations are shown in Figure 9. The day-night fluctuations are great, exceeding the maximum variation limit of 0.5 units in almost all cases (VR14 is the only possible exception). All sites show the expected nighttime decrease. However, the same peculiarity noticed in Goleta data can be seen on the lower river: why, if there were greater differences in day-night DO in July-August than in June, were the earlier *p*H differences greater (Figure 9)? If the *p*H data are accurate (again, that "if"), I can only think of one possibility. The predawn *p*H measurements were relatively far apart in time (a month and a half) and conditions on the river undoubtedly changed during that period. We know that flow from the upper Ventura River (from the Matilija and its tributaries) practically ceased during that time and conductivity increased (by 15-20 %). The change in *p*H that occurs when carbon dioxide is added to a stream is dependent on its acid neutralizing capacity (ANC) – or what used to be called "carbonate alkalinity."

Stay with me here, this is not exactly "rocket science." The greater the alkalinity – or as a rough approximation, think of it as more carbonates in the water – the less impact increased carbon dioxide will have on *p*H – that's what alkalinity or ANC measures, the ability to resist changes in *p*H. And if the carbonate concentration increased from June to mid-July, we just might have seen more of a fluctuation in pH earlier in the year.

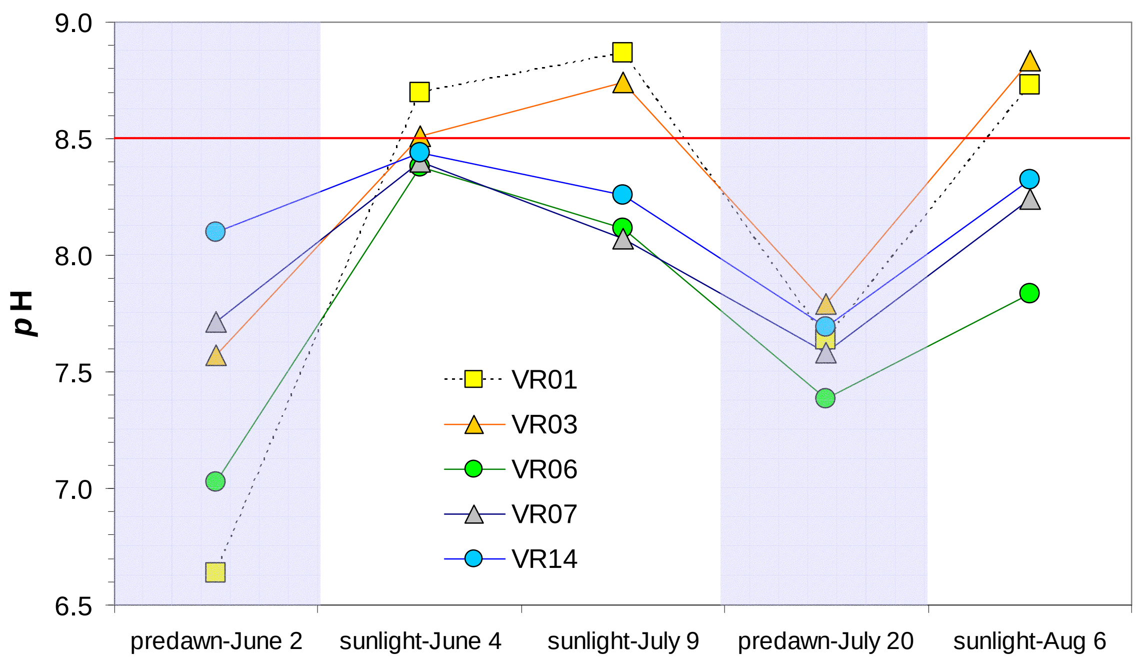


Figure 9. *p*H at selected Ventura River locations: June 2 to August 6, 2005.

Do I know that this actually happened? Well, no. We have no measurements of carbonate alkalinity (ANC) from this year. I did, however, measure ANC in 2003, and waters of the upper river (the Matilija) did have lower alkalinity than ANC in the lower section, and Ojai water (from San Antonio Creek and treatment plant effluent) had the highest of all. So a change in where flow is coming from *could* affect the magnitude of the *p*H variation. Could happen. Trust me. The check's in the mail.

[This effect could account for differences as great as 0.2-0.3 *p*H units, so it remains a possibility at VR03, but the 1 unit difference at VR01 is far too large and probably due to error. ANC differences between sampling events may also account for some of the odd occurrences in Goleta data. Measurements during the summer of 2003 indicate that it was not unusual to have ANC vary by up to 2000 µeq/L at a single site, or by up to 4000 µeq/L between sampling locations on a single day (on Atascadero Creek). When dealing with urban "nuisance flows," chemical variations along a stream or from day-to-day are common: it makes a difference whether "Harry" waters his lawn or "Jane" washes her car. Low flows, in particular, are subject to rapid chemical changes.]

Hunter S. Thompson famously said, "when the going gets tough, the tough get weird," and data from two of the Ventura sites are not only tough to interpret but downright weird (Figure 10). The locations are VR04 (lower Canada Large) and VR12 (on the upper Ventura River) and I've circled problem data points in the figure.

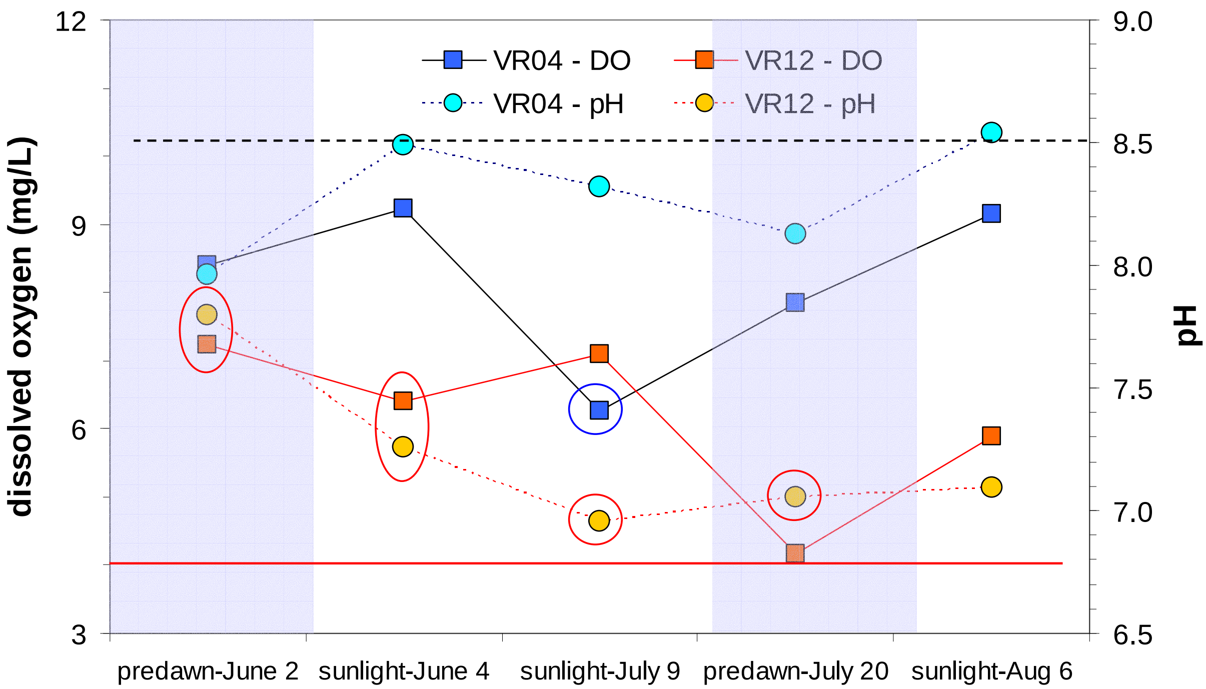


Figure 9. Dissolved oxygen and *p*H at VR04 and VR12: June 2 to August 6, 2005. Horizontal lines represent the minimum oxygen limit of 4 mg/L and the maximum pH limit of 8.5. Problem data are shown circled on the figure.

The variation in *p*H at VR04 is exactly what we might expect, but the low oxygen value of 6.3 mg/L measured on July 9 makes little sense when compared with nighttime oxygen concentrations or that day's *p*H measurement. I can only suggest a meter malfunction: all recorded measurements by that team on July 9 were unusually low: varying from 6.1 to 7.1, compared with an average measurement of 10.2 mg/L for the other three sampling groups.

However, it's VR12 that's particularly horrifying: nothing makes sense other than pH in July and August. Algal growth from May to July was extremely heavy at this location, yet there is no indication of this in any DO measurement other than before dawn on July 20. Things seemed fine in May: DO was 10.8 mg/L and pH was 8.3, not very different from conditions at adjacent sites, with all indicating appreciable algal growth. But from then on data from VR12 appeared to go berserk – low pH and low DO. The only possible explanation that occurs to me is that algal growth was so heavy that the bulk of the algae began to die and decompose in late May – a lush, green appearance on the surface, where sunlight and nutrients were still plentiful, disguising the carbon dioxide producing rot below. The only evidence I can offer to show that this might actually be the case is an increase in nitrate and dissolved organic nitrogen concentrations in July. If algae were healthily multiplying, the expectation is a nutrient shortage, and not a gain as river flows decreased. But as to very high predawn oxygen and pH on June 2? I don't have a clue.

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