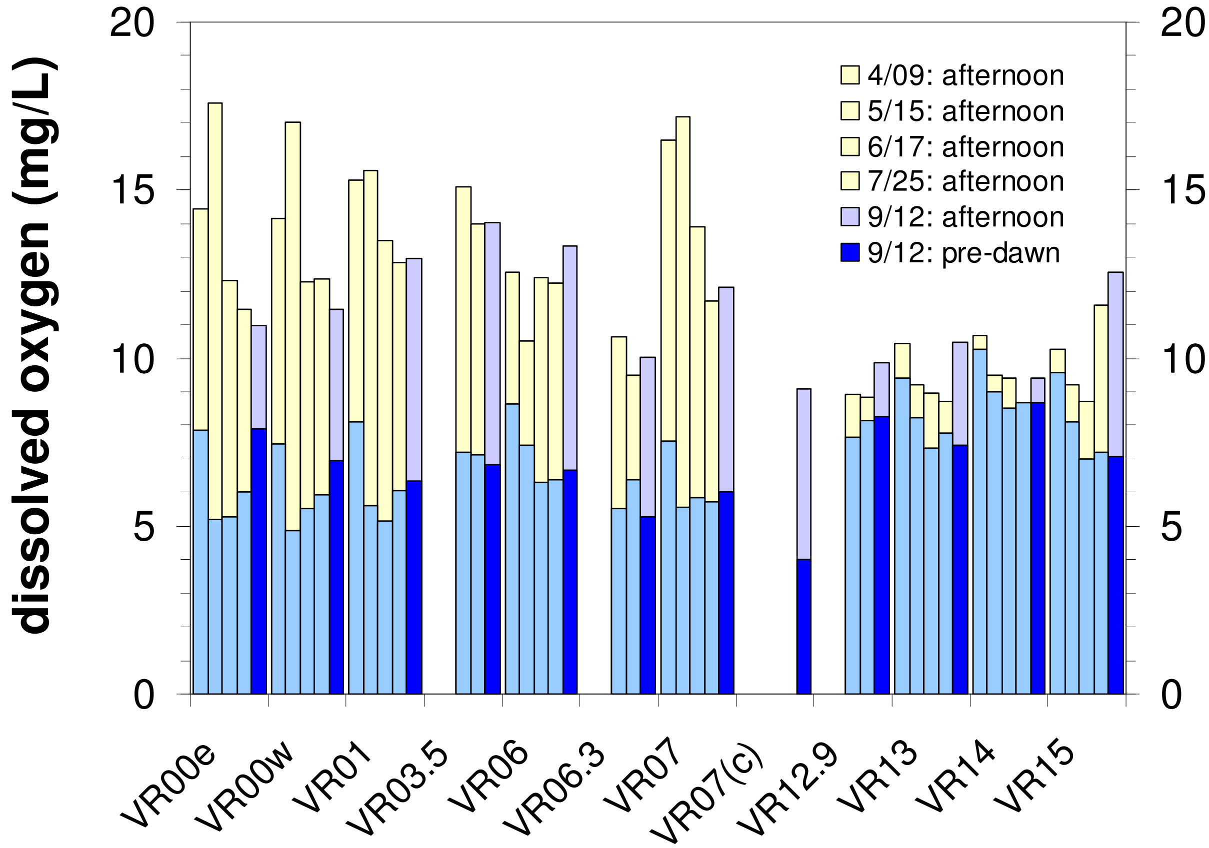


On September 12, 2008, Santa Barbara Channelkeeper completed a fifth, and probably last, round of diel measurements of dissolved oxygen (DO) and *p*H on the Ventura River. Pre-dawn measurements were made from 4:56 to 6:05 AM, afternoon measurements between 1:39 and 3:52 PM. We delayed the afternoon measurements a little longer than usual, awaiting the lifting of a persistent coastal fog and the clearing of overcast skies. (As a check on the possible effect of the overcast, especially at lower locations which never saw direct sunlight, measurements were repeated on Sunday, September 14. Differences between the two days were minor, and appeared to be more related to time-of-sampling than solar radiation.) The dissolved oxygen values recorded, along with differences between pre-dawn and mid-afternoon concentrations, are shown on the graph (in mg/L, i.e., ppm). Originally, back in April, we sampled 10 river locations and 2 sites in the lagoon. Since then the program has been somewhat modified: The same two lagoon locations are still being sampled, as well as 6 of the river locations (VR01, 06, 07, 13, 14 and 15), but three new sites (VR03.5, 06.3 and 12.9) were added in June. We also sampled an additional new location this month, VR07(c), lower San Antonio Creek at the Ventura River confluence. This site, which was included in the UCSB-TMDL algal survey, is located a half a mile below the lower San Antonio Creek Channelkeeper site (VR07) and is identified as VR07(c).

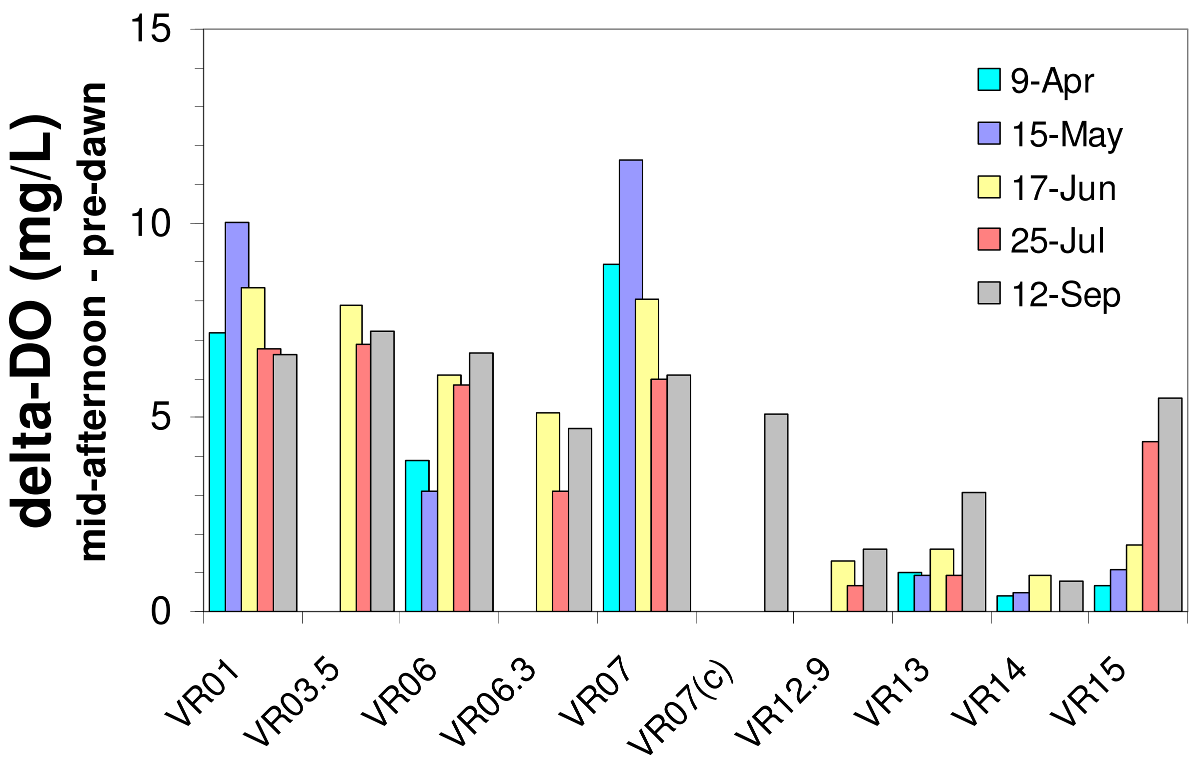
The chart shows September 12th results along with those from earlier diel measurements (April 9 & May 15, if available, June 17 and July 25) to illustrate changes throughout the entire algal season. The latest results are shown in darker shades of color to help them stand out.

Figure 1. VR15, looking upstream: above, on April 9th, 2008, during the height of the cladophora bloom; below, on Sept. 14th, just past the peak of the spirogyra bloom. Flow during this period has decreased from about 40 to 5 cfs.

Figure 2. VR15: above, on Sept. 2nd; below, on Sept. 14th. Approximately one week after the upper photo, the spirogyra bloom appeared to have passed its peak and had gone into rapid decline. The reasons for this remain a mystery. Temperatures have decreased, but not by much, and nutrient data is, as yet, unavailable.

Algal growth produces a daily cycle in both DO and *p*H: daylight photosynthesis adds oxygen while removing carbon dioxide; nighttime respiration reverses the process. DO concentrations in the surrounding water typically peak around mid-afternoon and decline to a minimum just before sunrise. The magnitude of the change in DO reflects (1) the abundance of algae, (2) the extent of their biological productivity, i.e., how hard they are working, and (3) the amount of water in which this change in DO is reflected. A fixed amount of algae will produce increasingly greater changes in DO as the volume (or flow) of water decreases.

The location with the greatest diel variation (delta-DO) in September was VR03.5, just below the Ojai Treatment Plant (from ~7.8 to 14.0 mg/L; from 77 % saturation to over 165 %). This represents little change from July 25th when the numbers here were roughly the same.



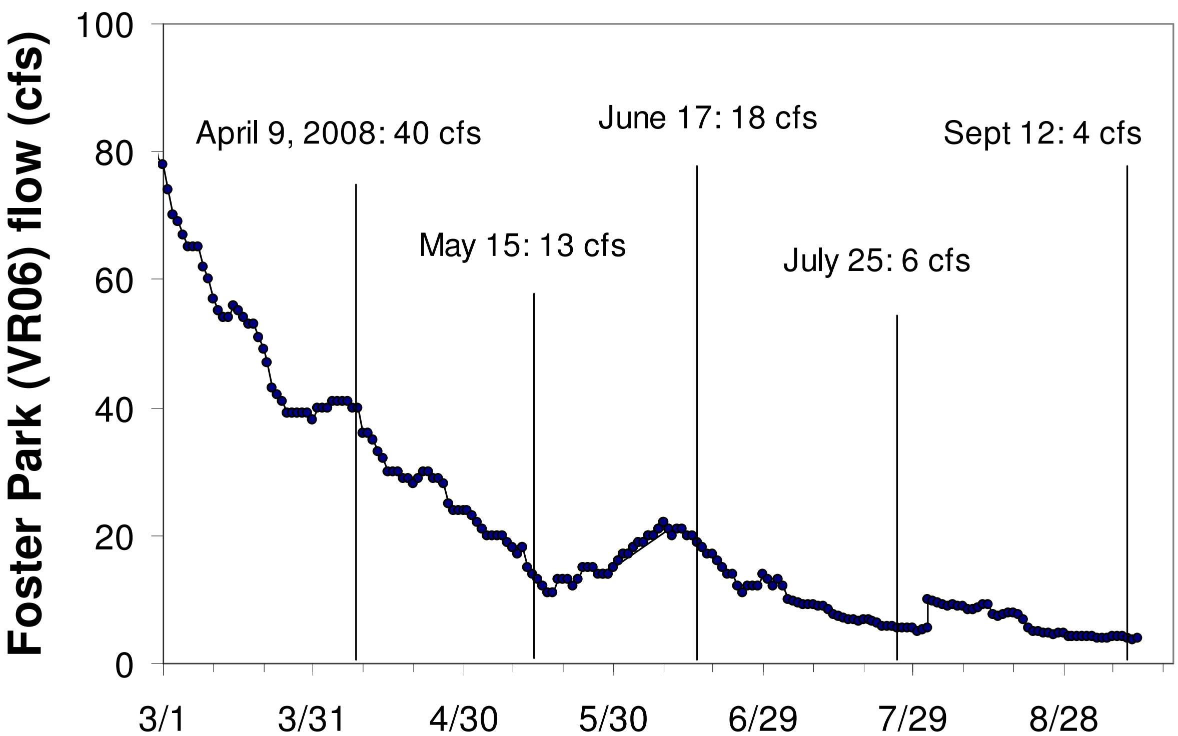
As the above graph of delta-DO values indicates, the September dissolved oxygen variation was only slightly less at VR01, VR06 and VR07; and at all these sites it remained virtually unchanged from that of late July. However, a number of locations did show a rise in delta-DO from the previous sampling: VR06.3 and the upper watershed sites, VR12.9, VR13 and VR15. Some of these increases can be accounted for by the resurgence of enteromorpha at VR06.3 and of spirogyra at VR15 documented in my last report (*We're Back . . . pdf*). But increases at VR12.9 and VR14 remain somewhat of a mystery since no readily visible changes have taken place at these locations.

It's interesting that the DO variation at VR07 was similar to that a half mile downstream (VR07(c)), but here the devil is in the details. Pre-dawn DO and *p*H at 07(c) were much lower, 4 mg/L and 7.1 vs. 6 mg/L and 7.4, respectively, indicating that decay was playing a much greater role downstream – producing greater over-night oxygen depression along with increased amounts of carbon dioxide. The downstream difference in delta-DO was 1 mg/L, or about 17 %, indicating some decrease in

Figure 3. VR12.9, looking downstream from the Camino Cielo low-water crossing: above, on April 10th, at the height of the cladophora bloom; below, on Sept. 14th. The little spirogyra found at this location during July and August also appears to have gone into a decline.

algal photosynthesis had occurred, but not much.

Lower on the river, at Main Street (VR01), similar delta-DO measurements in both July and September may also mask an appreciable change – the impressive growth of Ludwigia (water primrose) over the past month and a half. This aquatic plant now dominates the river from Main Street up to Shell Road, and is advancing into the river as far as the treatment plant (VR03.5). Since algae (mainly diatoms on the lower river) and the submerged green parts of Ludwigia both photosynthesize, we're unable to distinguish the principal agent responsible for the sizable continued DO cycle at Main Street .



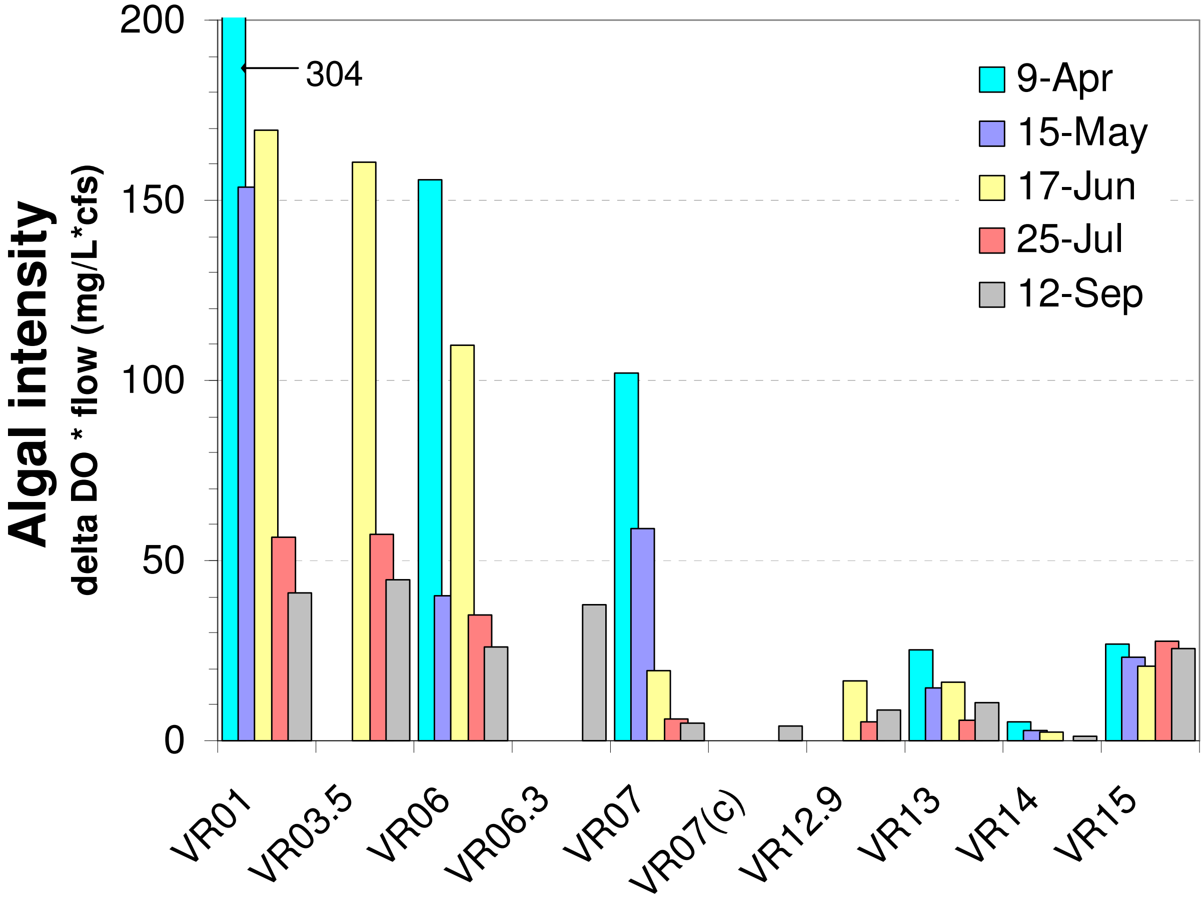
Flows in the watershed have further decreased since the July measurements, the Foster Park hydrograph, shown above, indicates flow on September 12th was about two-thirds that of July 25th; flows at VR07 and VR15 have similarly decreased. (The only exception to the general decrease in flow was VR14, where Channelkeeper's stream-team measured an increase from 1.3 to 1.8 cfs. Without personally having been there it's difficult to access whether the increase was real or simply an artifact of imprecision.) With decreasing flows, a stable or declining delta-DO can only have been caused by a reduction in overall photosynthetic productivity. Where declining flows are balanced by increases in the diel oxygen cycle, as at VR06.3 and VR15, determining if any change in productivity occurred requires further evaluation. If the measured flow increase at VR14 was real, the increase in September delta-DO marks a real, if puzzling, increase in productivity (but a very small one since the delta-DO value was only 0.8 mg/L).

The lagoon remains dominated by planktonic algae (a lovely green shade of color). The sand berm at the mouth was well breeched on September 12th, as it was on July 25th. It's probable that it has remained continually open since that time. As a result, September delta-DO values showed an

Figure 4. VR12.9, a little cascade just below the Camino Cielo low-water crossing: above, on July 15th, below, on Sept. 14th. This close-up shows the noticeable decrease in spirogyra mentioned in Figure 3. Spirogyra in this cascade has always been an exception to its seeming preference to quiet backwaters and pools.

appreciable decrease – oxygenated tidal inflows buffering the algal cycle. This tidal effect can be seen in the different DO readings shown for VR00e and VR00w in my opening chart: VR00e, closer to the ocean, showing greater tidal buffering than VR00w, further upstream and more heavily influenced by river flows (conductivity at VR00w was around 3,000 µS/cm lower than at VR00e during both morning and afternoon samplings).

In the photos included in this report I've departed from my regular format of showing changes between sampling events and chose instead, to compare September 12th photos with ones taken soon after the beginning of the algal season. My hope is that, in this final diel report, these will better convey the rather dramatic changes that have taken place during the course of the summer.



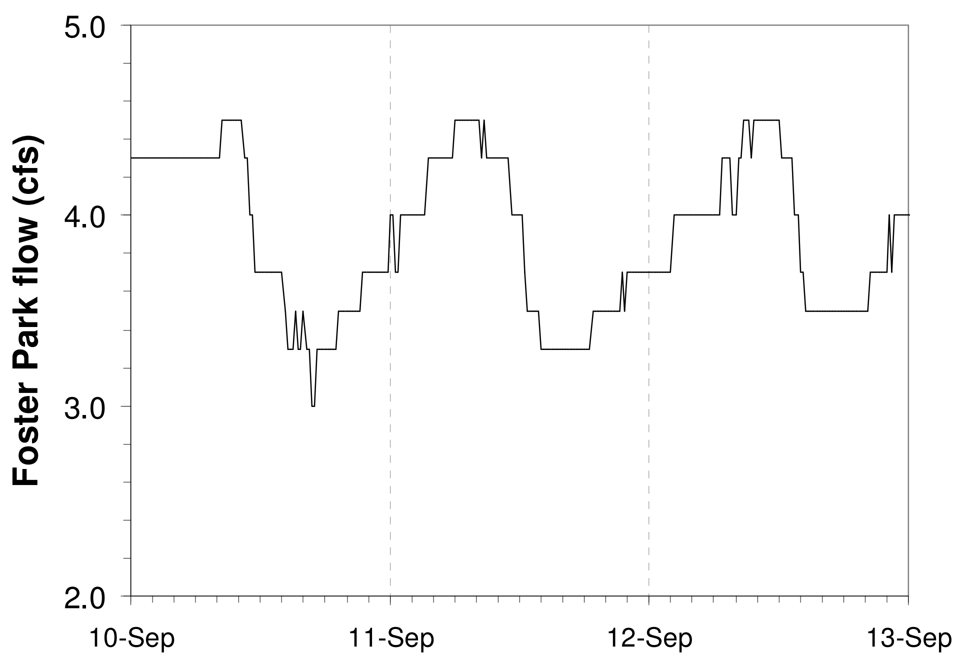
The above graph shows values of *Algal Intensity* for the sites monitored in September, along with values, when available, for previous monitoring events. I've been proposing Algal Intensity, a term introduced in previous reports, as a measure of algal productivity, i.e., the combined effect of the amount of algae and their photosynthetic activity. Algal Intensity (AI) is calculated by multiplying delta-DO by flow. If delta-DO is measured in mg/L and flow in cubic feet per sec (cfs), the resulting unit for Algal Intensity is mg/L*cfs. With appropriate conversion factors this could be reduced to mg of dissolved oxygen per sec, but the actual units of measure are, at this point, unimportant. The relationship between AI, flow (Q) and delta-DO can also be expressed as AI/Q = delta-DO. When algal productivity increases (either by an increase in algal biomass or photosynthetic activity or both) delta-DO increases; when flow increases, delta-DO decreases. What is important is the potential of converting an easily measured water quality parameter,

Figure 5. VR06.3, looking upstream above the S.Antonio confluence: above, on May 18th during the earlier cladophora bloom; below, on Sept. 14th when enteromorpha is still actively dominating the stream. Flow has appreciably decreased over this period, but by an unknown amount; nitrate concentrations have also decreased, from 74 µM at the time of the upper photo, to 32 µM at the beginning of August.

dissolved oxygen, one that directly measures the effect of algal growth on the stream, into a measure of algal activity simply by multiplying it by flow.

For September 12th flow I've used either the Foster Park gauge (adding average treatment plant output to this value to estimate flow at VR01 and 03.5) or Channelkeeper measurements from September 6th. AI results are in line with the previous narrative: a decrease in algal productivity at most sites, except for those in the upper watershed where small increases are shown. VR15, which showed no real change in AI from the July value, is a bit of a surprise. With a spirogyra bloom and an increase in delta-DO, I would have expected at least a modest increase – even though the bloom had past its peak by September 12th. There may well have been an increase, but inaccuracies in flow measurements may prevent us from seeing it. Channelkeeper flow measurements probably have an error of ± 20 % and this should be kept in mind when comparing month-to-month, or between-site, results.

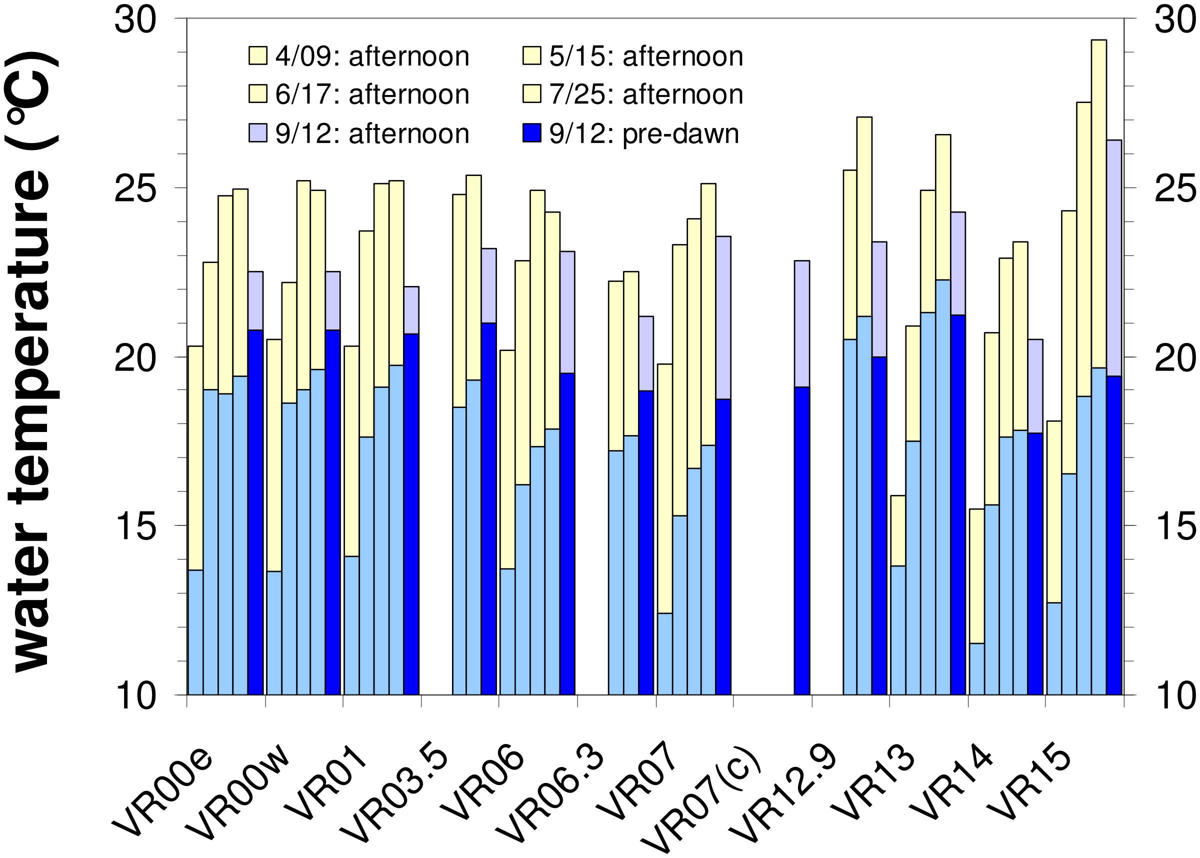
September was also the first occasion we've had to actually measure flow at VR06.3 (the reason only a single AI result is shown for this site). Measured flow was 8 cfs. My impression is that flows here were very much higher earlier in the summer, but, unfortunately, apart from visual changes in sequential photos, we have no direct evidence. Diana and I did try to make some rough approximations (using pacing for distance and floating twigs for velocity) on August 11th and got values between 20 and 30 cfs (the lower one taken further upstream). I regard our failure to monitor this location more closely this year as a lost opportunity.



While on the subject of flow, I did want to show what might be characterized as a normal daily dry-season fluctuation. The above graph shows three days of 15-min flow data from the USGS Foster Park gauge (the dashed lines mark midnight). In it you can see a daily fluctuation of slightly more that 1 cfs. Flow is peaking around 7:30 AM and reaches a minimum around 6:00 PM, the difference caused mainly by evapotranspiration – increased losses during daytime from *evapo*ration (higher temperatures and solar radiation) and plant uptake (during photosynthesis,

Figure 6. VR06.3, upstream approximately 100-200 m above the S.Antonio confluence: above, on May 18th, below on Sept. 14th. These photos show the difference in algal densities between the early cladophora bloom and the later enteromorpha one (some small percentage of spirogyra has been mixed in with the enteromorpha during the second bloom.

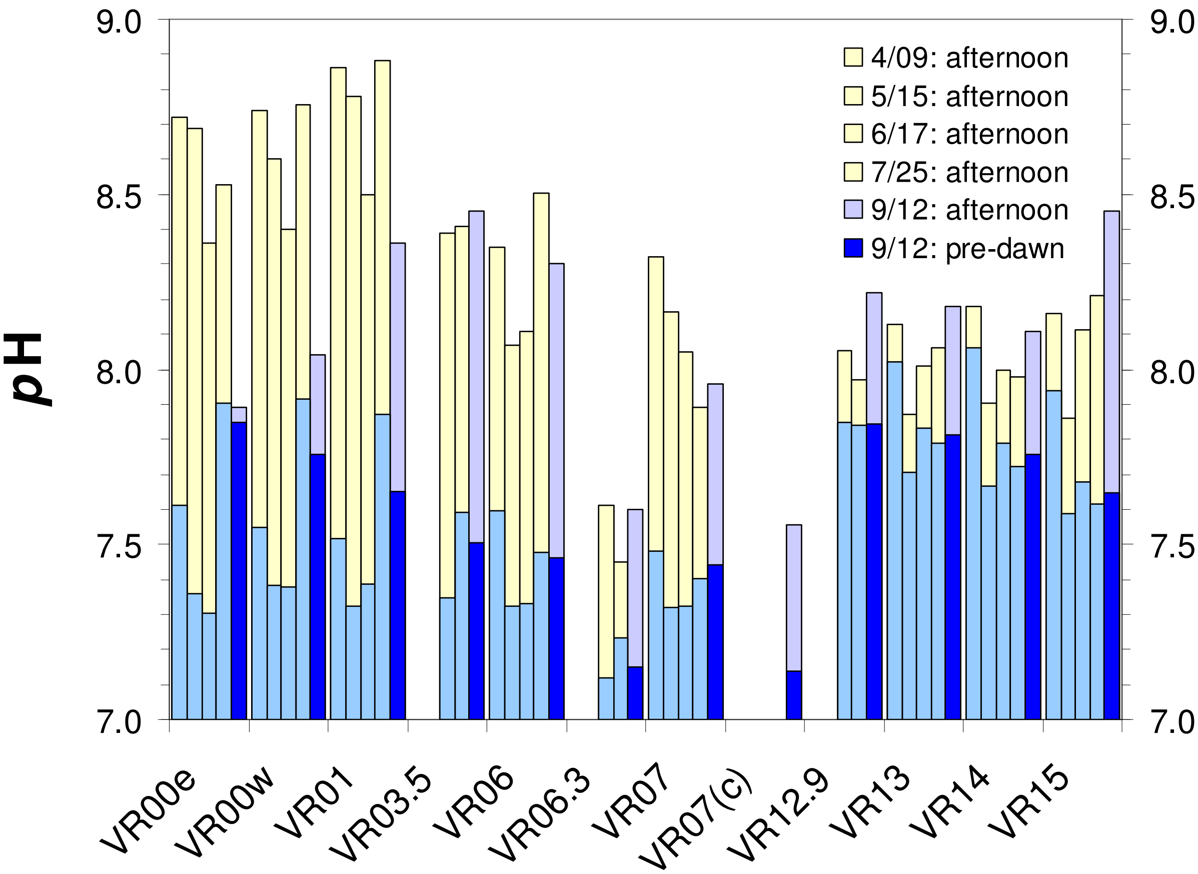
i.e., the *transpiration* part). As to why the graph appears so step-like? The gauge measures stage, i.e., water depth, with an ultrasonic sensor from the top of the bridge – and since the river is relatively wide at this location, and the gauge far above, the small changes in depth that occur are difficult to measure accurately.



The above chart is a plot of mid-afternoon and pre-dawn water temperatures taken during the five diel sampling events. September results are shown in darker shades of color. Mid-day temperatures in September appear to have finally passed their peak. (Although, as I write this, the region seems to have entered another heat wave.) Lower flows, now seen everywhere on the river, more readily reflect changes in air temperature. A quicker response to changes in local conditions would be my best guess as to why pre-dawn water temperatures in upper watershed locations exhibit the same pattern as those measured in mid-afternoon, a decrease from July 25th, while those on the lower river show an increase: colder waters due to clear skies and cooler nights at higher altitudes vs. warmer water temperatures from heat-retaining cloud cover at lower elevations. Note that the magnitude of the temperature cycle diminishes as we move down-river from Foster Park to Main Street – matching a probable trend of increasing coastal overcast. Temperature changes in the lagoon are, as was DO, buffered by tidal inflows.

I regard the failure to install a few, inexpensive (~$100) tidbit water temperature loggers at a number of the monitored sites over this past season as another lost opportunity. Had this been done, better track could have been kept of the extraordinarily high temperatures seen in the upper watershed, especially at VR15, and the potential problems this might cause steelhead evaluated. It would also have allowed a further look into the relationship between air and water temperatures, and helped to answer questions on the influence of flow and other factors.

Figure 7. VR06, looking downstream from the Foster Park Bridge: above, on April 9th during the peak of the cladophora bloom; below on Sept. 6th when spirogyra was the dominant alga below the bridge. This location makes the best case for the effects of flow and nutrients in determining which algal species will dominate: during the time between the two photos flow decreased from 40 to 4 cfs, and nitrate from 110 to 8 µM.



We now come to *p*H. September *p*H values, along with those of previous months, are shown in the graph. Both *p*H and DO have similar diel patterns: as photosynthesis removes carbon dioxide from water, i.e., removing acidity, and replaces it with oxygen, *p*H rises to an afternoon peak; it then declines to a pre-dawn minimum as night-time respiration restores carbon dioxide to the flow (making it more acidic). Aerobic decay, where oxygen fuels the breakdown of organic material and is converted to carbon dioxide (i.e., increasing acidity or lowering *p*H), is another process that should be kept in mind; as should decay within the increasing amounts of anaerobic sediments accumulating on the river bottom (think black and smelly). These processes generally result in an overall decrease in *p*H, since decay is no respecter of day-light, nor of much else. We are, however, more apt to notice a decay-produced lowering of *p*H in pre-dawn measurements since the addition of carbon dioxide at this time is not counteracted by algal photosynthesis.

In September, almost all locations showed little change in pre-dawn *p*H when compared with measurements in July, arguably due to a similarity of conditions during both months. However, *p*H may not be a reliable indicator at sites that also exhibit greater delta-DO. (Any increase in delta-DO will be accompanied by an increase in delta-*p*H. If we assume similar amounts of decay, pre-dawn *p*H would decrease while mid-afternoon pH increased – i.e., the increase and decrease would be roughly the same since both were caused by greater algal productivity. Less decay would shift both *p*H measurements upwards, a greater increase than decrease; more decay would shift them downwards, a greater decrease than increase. Clear? Can I sell you a bridge in San Francisco? Anyway, the diel *p*H variation at upper watershed locations has increased, like the DO variation – see my chart on the first page – but most of the *p*H increase occurred in the mid-afternoon measurement; signifying less decay.)

Main Street, with large reductions in both pre-dawn and mid-afternoon *p*H, would appear to be an exception to the general impression. It's possible that greater decay due to advancing Ludwigia is the cause (from increased sediment capture and the competitive displacement of algae, i.e., dead algae). September measurements of lagoon *p*H were also different than before, at least those in mid-afternoon. But lagoon pH, like lagoon DO and water temperature, is undoubtedly more dependent on tidal influences than either algae productivity or decay. Seawater is highly oxygenated and well buffered, and measurements near a high tide will be very different than those taken at low tide. Closeness of the sampling point to the lagoon mouth then becomes the principal reason for differences between the two sampling points: the eastern point, VR00e, is closest and shows the least variation in both DO and *p*H. Similarly, differences between measurements in July and September may simply result from how closely a measurement coincided with a high tide.

As I mentioned last month, explaining the ups-and-downs of *p*H variation has become so complicated that I may no longer even be convincing myself. But hey, that's this month's story and I'm sticking to it.

Back to Carbon Dioxide and ANC:

Finally, I want to return to the topic of what causes highly varying *p*H values and different magnitudes of delta-*p*H at sites with relatively similar changes in dissolved oxygen. Simply put, the *p*H variation is dependent on the acid neutralizing capacity (ANC) and carbon dioxide content of the water. And of the two, the carbon dioxide concentration is, by far, the most important. In my last report I defined ANC as the difference between the concentrations of major cations and those of major anions: ANC = Σ strong cations – Σ strong anions. The major cations being calcium, magnesium, potassium and sodium, and the anions being sulfate, chloride and nitrate. Another way of defining ANC is:

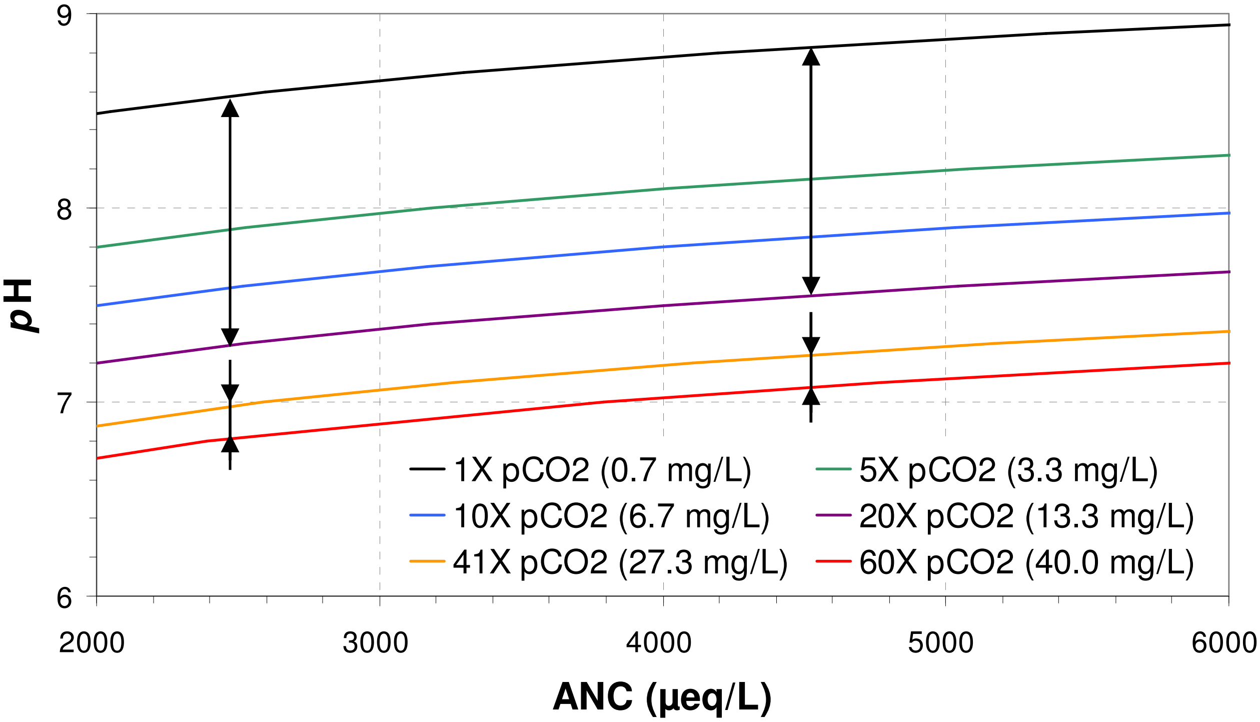
$$ANC = 2[CO_3^{=}] + [HCO_3^-] + [OH^-] - [H^+] + [\text{other bases of weak acids}]$$

Don't panic. At least, not yet. In words this equation would read: ANC is the sum of the negative charges found in water from carbonates (think washing soda), bicarbonates (think baking soda and upset stomach remedies), hydroxides (think lye) and other bases of weak acids, minus the hydrogen ion concentration (think *p*H). For most freshwaters, like the Ventura River, the negative charges from carbonates, hydroxides, hydrogen ions and bases from a host of weak acids are all negligible and can be ignored. And only thing that usually counts is bicarbonate ($[HCO_3^-]$); indeed the old term for ANC was "alkalinity" or "bicarbonate alkalinity" or even more simply, the *bicarbonate* concentration.

The important points to remember are, first, that ANC is conservative, meaning its value is not easily changed. You can do a lot to water, adding and removing oxygen and carbon dioxide, messing with it in a host of other ways, but as long as you don't change the concentrations of its major ions ANC will remain the same. And second, since ANC, *p*H and the inorganic carbon content of a water (carbonate, bicarbonate and carbon dioxide) are all related, if you know any two of these parameters you can calculate the third, e.g., if you know the ANC *and* the *p*H, the carbon dioxide content is easily calculated.

The chart that follows shows the relationship between these three terms. It was made by assuming a *p*H and a carbon dioxide concentration, then calculating the ANC necessary to achieve that

Figure 8. VR06, looking upstream from the Foster Park Bridge: above, on April 9th during the peak of the cladophora bloom; below on Sept. 6th. In September, enteromorpha (mixed with a healthy percentage of spirogyra – the darker spots in the lower photo) was dominant above the bridge. In between these two time periods, algal densities waxed and waned a number of times.

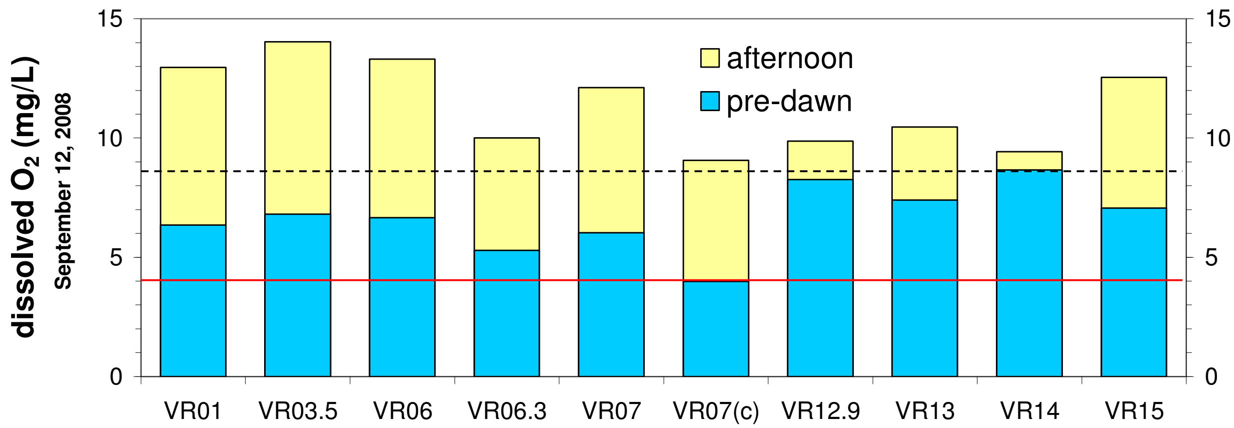


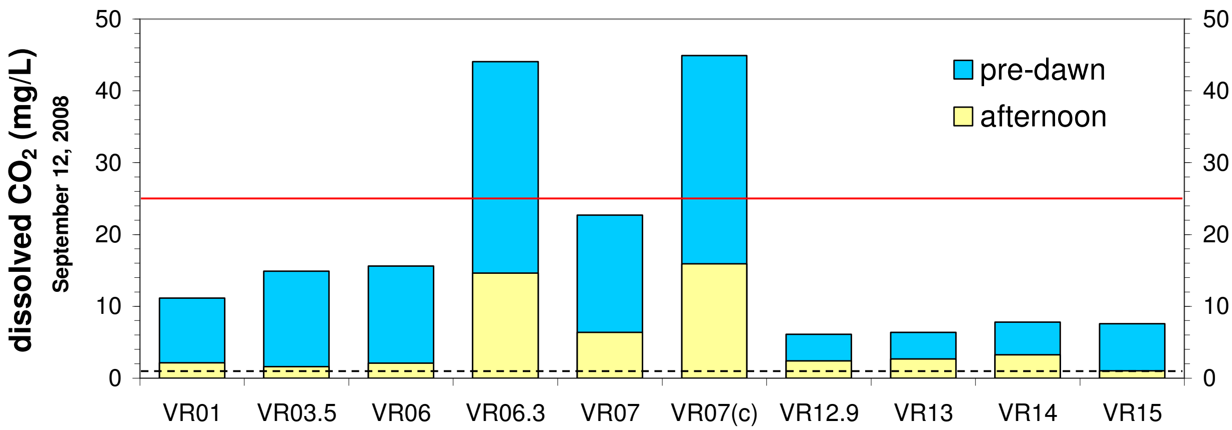
combination. I could have as easily started with any other two and calculated the third. Carbon dioxide concentrations in the chart are expressed as multiples of the *partial pressure of carbon dioxide in the atmosphere* (pCO2), e.g., 1X pCO2 indicates that carbon dioxide in the water is in equilibrium with the actual carbon dioxide concentration in the atmosphere (currently, pCO2 is 387 parts per million by volume, or ppmv); 5X pCO2 indicates a carbon dioxide value 5-times as high (one in equilibrium with an atmospheric pressure 5-times as high), 20X pCO2 is a carbon dioxide value 20-times as high, etc. If we were to discuss dissolved oxygen in the same way the equivalent terms would be 1X pO2 is equal to 100 % DO saturation in water, 5X pO2 is 500 % of saturation, and 20X pO2 represents 2,000 % of saturation. As we shall see, carbon dioxide concentrations in water vary much more drastically than do those of oxygen. To make it somewhat easier to understand, I've put the equivalent concentrations of carbon dioxide, in parenthesis, next to the pCO2 values; water in equilibrium with the atmosphere contains only around 0.5 mg of carbon dioxide per liter (the equivalent dissolved oxygen concentration at 100 % saturation is ~9 mg/L).

The chart shows the change in *p*H for an 2,500 µeq/L ANC water (think upper Matilija) if the carbon dioxide concentration changes from 20X pCO2 to 1X pCO2 during daytime photosynthesis, *p*H will increase from 7.29 to 8.58: an increase of 1.29 units. If the ANC was increased to 4,500 (think Foster Park) the total change in *p*H would remain about the same (1.28 units) but the actual range of *p*H variation would change considerably: increasing from 7.55 to 8.83. Both the maximum and minimum *p*H values will be higher as ANC increases.

However, if the same amount of change (a decrease from 20X pCO2 to 1X pCO2) were to be applied to a water containing much greater initial amounts of carbon dioxide, for example one at 60X pCO2 (the same change would decrease a concentration of 60X pCO2 to 41X pCO2), the *p*H change would be greatly reduced: to 0.17 units in both cases, from 7.07 to 7.24 in the 4,500 µeq/L water, and from 6.82 to 6.99 in the 2,500 ANC water. Again, the maximum and minimum values would be higher as ANC increased, but the amount of *p*H change is greatly reduced as initial carbon dioxide concentrations increase.

Figure 9. VR01, looking upstream from the Main Street Bridge: above, on April 9th during the peak of the cladophora bloom; below on Sept. 6th. As hard as it may be to believe, the arrows point to the same spot. Over the last month or so, Ludwigia have come to dominate the lower river, helping, in the process, to de-water over ¾ of the channel. In mid-July cladophora on the lower river practically disappeared, and was replaced by diatoms (note the dark-colored water in the lower photo.



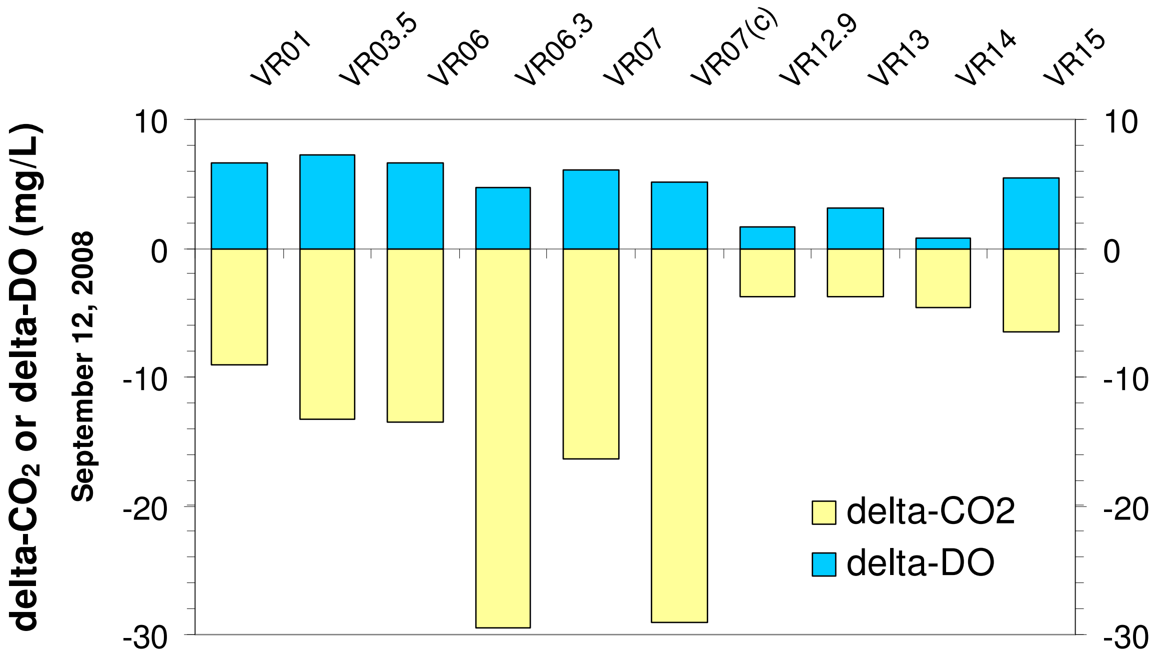


The DO measurements taken on September 12th are shown in the top part of the above graph, with calculated carbon dioxide concentrations below. (*I've decided it would be easier to illustrate these points by using carbon dioxide concentrations instead of the EpCO2 values used in the last report. As mentioned earlier, carbon dioxide concentrations can be calculated from pH and ANC, and there's the rub. I don't actually know the current ANC values for each of these sampling stations, but I do know what they were in 2003. I am in the process of having samples taken on September 14th analyzed, but in the interim I'm simply assuming the new results will not be far removed from the old. Should they differ greatly, I will modify these graphs in my next report.*) Note that the peak carbon dioxide values fall into a pattern (peak being pre-dawn values, before any daytime photosynthesis takes place): low in the upper watershed, moderate from Foster Park and below, and very high on the lower San Antonio and on the Ventura above this confluence.

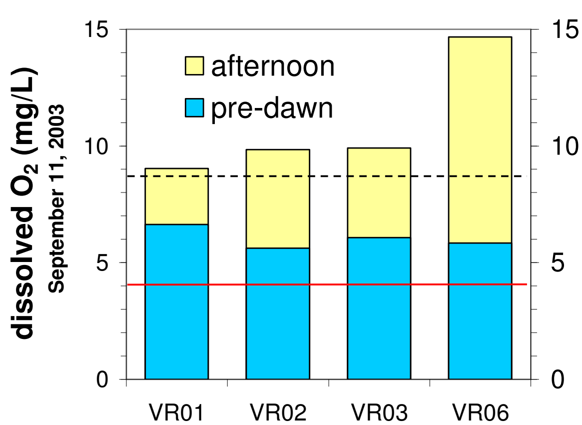
There are a couple of lines drawn on each graph: for DO the dashed line represents an average 100 % saturation value (~9 mg/L), and the red a generally accepted minimum limit of 4 mg/L; for carbon dioxide a 1X pCO2 concentration of ~0.5 mg/L (dashed) and a limit of 25 mg/L (red), generally regarded as the point at which high CO2 concentrations begin to present problems for fish. It's not unusual for streams and rivers to have carbon dioxide concentrations above atmospheric equilibrium; 2-5X pCO2 would seem to be a typical range. This is the general range of mid-afternoon measurements at all locations except VR06.3 and VR07. It's also not unusual for groundwaters (the main water source for all still-flowing late-summer Ventura locations) to have higher values. But still, those very high VR06.3 and VR07 values appear rather extraordinary.

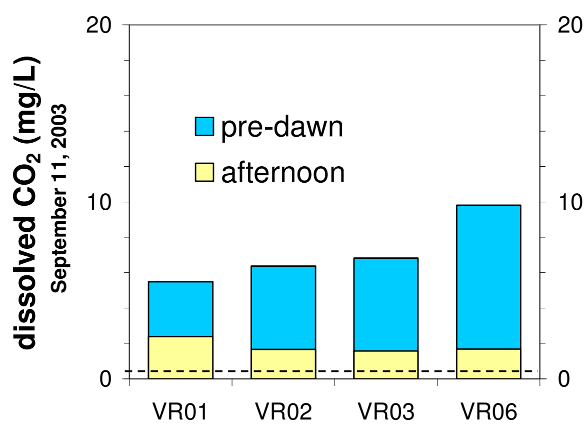
Figure 10. VR01, looking upstream from the Main Street Bridge: above, on April 5th; below on Sept. 6th. The arrows point to the same spot shown in Figure 9. This wider view better shows Ludwigia's progress. The east-side (on the right) of the river bed is now totally dry.

In contrast, the very low mid-afternoon value at VR15 (~2X pCO2) also strikes me as interesting. It gets me wondering if restrictions in the amount of available carbon dioxide might affect the maximum size of algal blooms on the upper Matilija. I'm also intrigued by the remarkable increase in CO2 between VR07 and VR07(c). Is this simply an artifact of increased decay, or could something else be going on?



Finally, I've convinced myself, no matter how intrinsically interesting these carbon dioxide concentrations may be, that there is absolutely no future in attempting to use *p*H variations in a way analogous to those of dissolved oxygen. And, as this plot of September 12th delta-CO2 and delta-DO values shows, there will also be no easy utilization of carbon dioxide concentrations (delta-CO2 is negative since mid-afternoon concentrations are lower than those of pre-dawn, the CO2 variation is exactly opposite that of DO).





Lastly, this plot, similar to the one on the previous page, shows the diel DO and carbon dioxide variations at Foster Park and 3 sites below the treatment plant, but in September 2003. Interestingly, they are not all that different than those of this year. Conditions on the lower river were similar, algae still doing well at Foster Park (VR06) while Ludwigia dominated below the treatment plant. Flows were almost identical, circa 4 cfs. The only major difference being that 2003 was the second year of Ludwigia dominance and flows were both deeper and more restricted, which probably accounts for a reduced DO cycle below the plant.

Photos taken on September 12 and 14 (and on other Channelkeeper sampling days) can be downloaded at:
http://sbc.lternet.edu/~leydecke/Al's_stuff/Recent%20Stream-Team%20Photos/

Photos of the initial UCSB-TMDL algal survey can be downloaded at:
http://sbc.lternet.edu/~leydecke/Al's_stuff/Ventura%20Nutrient%20TMDL/TMDL%20algal%20survey%20photos/

Posted PDF copies of all my previous Ventura Nutrient TMDL reports can be found at:
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