I intended this to be a short report on some changes that have been observed on the river as we reach the end of summer (regarding Labor Day as the traditional, if not the astronomical end). The included photos were taken during a trip by Diana and myself on Sept. 2, 2008 to find and sample the point at which upper watershed flow disappeared from the riverbed. That point proved to be a few hundred feet below the Robles Diversion. We decided to take additional samples some distance above the diversion (VR12.9) and below the downstream area where water re-appears (VR06.3). I've also thrown in photos from the September 6<sup>th</sup> Channelkeeper sampling to illustrate some interesting developments on the lower river.

However, as usual, I've gotten carried away and have also included some further discussion of the *algal intensity* parameter I proposed in my last report. This is in response to comments received from both Diana and Ron. And, if I don't run out of steam, some further expansion of the *acid neutralizing capacity* (ANC, or alkalinity)/*delta-pH* (mid-afternoon *p*H minus pre-dawn *p*H) connection I've discussed previously. I suggest casual recipients just read the first page or so and look over the pictures; those interested in my proposed measure of algal intensity can go further. Only gluttons for punishment should stick around for the section on ANC.

Figure 1 shows the development of a healthy enteromorpha crop, both benthic and floating, from above the San Antonio confluence (VR06.3) to below Foster Park (VR06). Enteromorpha has almost totally replaced the earlier cladophora bloom (although some surviving cladophora, along with strands of spirogyra can be found mixed within the benthic enteromorpha). But Figures 2 and 3 show the most interesting change: the beginning of a rather impressive spirogyra bloom above Matilija Dam (VR15). In the previous report I talked about how *delta-DO* values (mid-afternoon DO minus pre-dawn DO) have continually increased at this location, and a possible relationship to increased sunlight and water temperatures caused by arundo removal above the dam. This new development further reinforces that impression. Interestingly, conditions at VR14 (N. Fork Matilija) and VR12.9 (below the Matilija conjunction) have not changed.

My subjective opinion is that spirogyra thrives in low-nutrient and quiescent environments, but that doesn't mean it can't be found in riffles and in areas with higher nutrient concentrations (it's currently doing quite well at Foster Park, thank you). A further inference I've drawn from this summer is cladophora's liking for high nutrient environments – from its early appearance when nutrient concentrations were at their peak and the fact that it has endured longest in high-flux riffle situations. It's tempting to conclude that it's replacement by enteromorpha, late in the season, is due to a decrease in overall watershed nutrient concentrations.

But concentrations above Foster Park (at VR06.3) would seem to be still high enough to feed a continued or second bloom. Concentrations below the sewage treatment plant are still very high, actually much higher than earlier in the year (plant effluent currently making up more than 50 % of total flow at this point), but the abrupt demise of filamentous algae below the plant indicates factors other than algal succession may be at work (see my previous reports titled, *A July look at algae on the Ventura.pdf*, *Revisiting the lower Ventura in 2003.pdf*, and *Attack of the Killer Effluent.pdf*). Thus these lower reaches may not be typical, although I did see cladophora trying to make a comeback in August just below the treatment plant (at VR03.5).



**Figure 1.** VR06.3, just above the San Antonio confluence: upper - July 25<sup>th</sup>; lower - Sept. 2<sup>nd</sup>. During the latter part of August algae (in this case enteromorpha, floating and benthic, in place of the original cladophora bloom) have made a serious comeback above Foster Park. Unfortunately, I don't have two photos with the same view, but the arrows indicate the same point in each.



**Figure 2.** VR15, above Matilija Dam, looking downstream: upper – July 25<sup>th</sup>, lower – Sept. 2<sup>nd</sup>. Beginning some time in August, there has been a substantial spirogyra bloom at VR15. Nothing corresponding to this has occurred at the lower VR14 and 12.9 locations. I can't help thinking that increased sunlight and warmer temperatures are the underlying cause.



**Figure 3.** VR15, above Matilija Dam, looking upstream: upper – July 15<sup>th</sup>; lower – Sept. 2<sup>nd</sup>. Another view of the on-going spirogyra bloom. This marks the return of appreciable spirogyra to the upper watershed. Last year, spiro, not the cladophora we saw earlier this season, was the dominant alga in the upper river reaches.

If not nutrients, perhaps other factors such as current speed or water temperature determine which alga has a late-season competitive advantage. Or maybe cladophora had simply run out its string.

However, the most spectacular development on the river doesn't concern algae at all. It's the rapid expansion of *Ludwigia*, our handsome Bolivian invader, on the lower river. Most of the noticeable intrusion of this species into the waterway occurred during August (see Figures 4 and 5), until it now totally dominates the river from Main Street to Shell Road – and it is making inroads as far up as the Canada Larga confluence. In places the open waterway has been reduced to less than 20 % of what it was earlier this summer, leaving little un-shaded habitat for algal growth. At present, water still flows beneath most of the *Ludwigia*-covered areas, but its root system is such that, absent a winter storm severe enough to uproot the plants, it will rapidly accumulate enough sediment to leave these areas high and dry, and narrowly restrict river flow.

## The Algal Intensity Parameter:

To answer points raised by both Diana and Ron I want to look in some detail at the diel oxygen variation. Daytime algal photosynthesis adds oxygen to water; nighttime respiration removes it. For a given flow, greater algal density will produce a greater diel variation, but concentrations of dissolved oxygen are almost never stable – the river is constantly either losing oxygen to, or gaining oxygen from, the overlying air. As algal photosynthesis drives DO concentrations above saturation (the amount of oxygen that water in equilibrium with the overlying atmosphere can contain, i.e., losing and gaining oxygen at the same rate, thus maintaining a steady concentration at a given water temperature and air pressure) the river begins to leak oxygen into the air.

Stream turbulence (think rapids and riffles) and increasing water temperatures will increase the rate of oxygen *loss*, as will increasing the concentration of DO – anything that decreases the ability of water to hold oxygen in solution, or increases the concentration of DO above the equilibrium level, will increase the rate of loss. *Super-saturation*, water holding more than it's equilibrium amount of DO, means, almost by definition, the constant loss of oxygen to the air above.

Conversely, during the nighttime, as DO concentrations decrease below saturation, increasing turbulence or decreasing temperatures, or lower DO concentrations because of biotic respiration, or any combination of these and other factors will increase the rate of oxygen *gain* as oxygen moves into water from the overlying air in an attempt to reestablish equilibrium. *Under-saturation*, water holding less than it's equilibrium amount of DO, means continually gaining oxygen from the air.

Maximum and minimum DO concentrations do not occur at the points of peak algae photosynthetic production or maximum respiration, but simply represent the high and low points of numerous competing processes. The question then become one of magnitude and how rapidly each of these processes operate – if the biological processes of photosynthesis and respiration dominate then the countervailing physical processes become relatively unimportant. That the peaks and troughs of the diel oxygen variation are far removed from 100 % saturation shows this to be so.

However, at times photosynthetic oxygen production is too low to keep ahead of the various factors causing oxygen loss during the day. An example was July's measurement at VR14: where pre-dawn DO concentration was higher than that at mid-afternoon, i.e., algal oxygen production was unable to keep up with oxygen loss – mostly due to high day-time water temperatures although turbulence probably played a role. The conclusion: not enough algae present to seriously modify DO concentrations in the creek. (However, there were some algae, and they did somewhat modify the oxygen content – the diel variation, measured as percent saturation went from 96 to 106%.).

Given that DO concentrations are constantly being modified by processes and factors other than algal photosynthesis and respiration, does this make using the diel variation as a measure of algal density or productivity useless – a complete waste of time? No, it doesn't. It's important not to make the perfect the enemy of the good. As long as conditions on the various reaches are roughly similar, and – and this is the most important caveat – as long as algae are the dominant factor producing changes in dissolved oxygen, the diel variation, combined with flow, can be an important parameter in judging algal impact. Let me repeat this: As long as algal photosynthesis and respiration are the primary process controlling changes in dissolved oxygen, other loss or gain factors remain relatively unimportant. VR14 is the exception that proves the rule.

(I have generally used % DO saturation over 120 % as a good rule of thumb for algal dominance. A recent series of experiments conducted in my lab – otherwise known as the kitchen – showed that extreme aeration almost never raised oxygen concentrations above 104 %; but rapidly raising or lowering water temperature could produce % saturation changes in the range of 20-30 %. Since natural temperature variations rarely reach the extreme of putting a beaker of water into the freezer for an hour – which produced the 30 % change – I concluded that my 120 % rule might even be too conservative.)

Concluding that my algal intensity parameter remains valid doesn't mean it's without problems. Algae may not be the only primary producers active in a river reach. Given the recent dominance of Ludwigia on the lower river (Figure 5) there is no way to distinguish between the effects of algae vs. the submerged parts of photosynthesizing aquatic plants. There is also a seasonal bias in the parameter. As the dry-season progresses, flows, turbulence and water depths decrease, while temperatures increase. Given constant algal productivity, increasing temperatures, and decreasing flows and depths will produce greater daytime losses (by increasing % saturation) and nighttime gains; while decreasing turbulence has the opposite affect of reducing the rate of change. On balance, the general trend will be towards lower delta-DO values over time.

However, let's consider the alternative. Unlike algal intensity, derived from a measure of the algal *effect* on a stream (delta-DO), the current parameter of choice is algal density, the *amount* of algae in units of chlorophyll-a per square meter (chl-a/m<sup>2</sup>). The approved procedure, used by the current UCSB study, is to collect 3 samples across the width of a stream (in the center and a quarter of the way in from each bank) and to do this along 10 transects, each 10 meters apart (an imperfect analogy might be to think of the river as a football field, with samples taken at the center and quarter points of each 10-yard line). Each sample is collected with a 26mm diameter syringe, i.e., each sample is a circle of algae slightly more than an inch in diameter. A total of 30 samples are collected and analyzed, and the average chl-a/m<sup>2</sup> determined.

A typical 100 meter Ventura reach sampled this spring contained about 4 million syringe-areas of



**Figure 4.** VR02, looking downstream from the vicinity of Stanley Drain: above, on April 5<sup>th</sup>, below on May. 3<sup>rd</sup>. This figure, and the next, show the near incredible (to me at least) transformation of the lower river as aquatic plants replaced algae. In April and June cladophora was dominant.



**Figure 5.** VR02, same location as in Figure 4: above, on June 7<sup>th</sup> algae were still dominant but you can see Ludwigia growth encroaching into the river on both banks; below, by Sept. 6<sup>th</sup> only a narrow open channel remained Ludwigia-free. Absent a major winter storm, the still swampy areas of Ludwigia growth will trap enough sediment to and become dry .

of water. In other words, the 30 collected samples represent only 0.000025 % of the total area in a typical reach. Now 4,000,000 is about the number of voters who participate in Presidential elections in an above-average population state: Michigan is a good example. So ask yourself, if someone told you they polled 30 people in Michigan with results predicting McCain the winner with 53 % of the vote, how believable would that be? And what if they then told you the 30 people were not selected at random?

To be fair, the other side of the argument would state that if differences were huge then 30 samples should be enough to distinguish between sites with big algal problems and those with minor ones. For example, if 30 people were polled in Charleston, South Carolina, and another 30 in San Francisco, California, results predicting one city voting for McCain, but the other for Obama, might be more readily believed.

## The *p*H conundrum:

Throughout this year's series of diel measurements, variations in dissolved oxygen appeared to follow consistent patterns, patterns that matched observed changes in algal conditions on the river. However, pH did no such thing, and variations between sites, or from month-to-month at the same site, appeared to have neither rhyme nor reason. The following graph is an example of what I mean.



It shows delta-*p*H (the difference between mid-afternoon and pre-dawn *p*H) *if* delta-DO were held constant at 6 mg/L (measured delta-pH was simply multiplied by the same factor required to change delta-DO to 6 mg/L, e.g., if delta-DO was 9 mg/L, the measured delta-*p*H would be multiplied by 1.5 (9\*1.5 = 6) to obtain the value shown in the graph). Note that some sites are relatively consistent (e.g., VR07), but others vary widely (VR15), and there are large differences between locations. My question is a simple one: Why?

The explanation I've given in the past was that higher acid neutralizing capacity (ANC, or, as it used to be called, alkalinity) is moderating pH changes at locations with little pH variation (compared with rather large DO fluctuations), while low ANC sites have much larger variations. It turns out that I'm wrong – well, not completely wrong, but ANC is not the main reason.

ANC is a very conservative quantity, i.e., it has a great tendency to remain unchanged under normal conditions. There are a number of definitions we could use, but the one that best shows its conservative nature is that ANC is the difference between the concentrations of major cations and those of major anions: ANC =  $\Sigma$  cations –  $\Sigma$  anions. The major cations being calcium, magnesium, potassium and sodium, and the anions being sulfate, chloride and nitrate. ANC is measured in milli- or micro- equivalents per liter, i.e., it represents the net positive charge carried by the major ions dissolved in the water. Of course water is electrically neutral (otherwise surfing would be a *really, really* interesting activity) and the unreported negative charges are furnished mainly by various forms of dissolved carbon dioxide, aided, at times, by a miscellaneous bunch of weakly ionized organics and hydroxides. The point here being you can do a lot to water, adding and removing oxygen and carbon dioxide to your heart's content, and playing with it in a host of other ways, but as long as you don't modify its concentrations of major ions ANC remains the same. A further important point being that if you know the ANC of a water, *and* its *p*H, you can calculate its carbon dioxide content.



And that's what I've done here. The graph shows the relationship between pH and  $EpCO_2$ .  $EpCO_2$  is the excess partial pressure of carbon dioxide, i.e., the ratio of the actual pressure of carbon dioxide in the water to the equilibrium pressure (the 100 % saturation pressure) at a given temperature. For example, an  $EpCO_2$  of 6 indicates 6-times the equilibrium concentration of carbon dioxide (in terms of dissolved oxygen, this would be equivalent to 600 % of saturation).  $EpCO_2$  can be calculated from ANC and pH using a number of readily available formulas (different formulas offer various refinements and incorporate additional factors, but all return similar results for the range of values shown here; I'll be happy to provide these to anyone who requests it) and the graph show the results of these calculations for 4 assumed values of ANC.

The 4 values show the range of ANCs in the Ventura system (based on analyses I did in 2003): 3000  $\mu$ eq/L is roughly characteristic of the upper watershed and Matilija branches; 4500  $\mu$ eq/L for water at Foster Park; 5800  $\mu$ eq/L on the lower San Antonio and 7000  $\mu$ eq/L on Pirie Creek after it flows through Ojai. I've taken the high and low ANC ranges and shown the changes in EpCO<sub>2</sub> necessary to produce a change in pH from 8.5 to 7.5. Almost twice as much carbon dioxide must be added to the higher ANC water to produce the same pH change. So ANC does make a difference. The problem is that it doesn't make that much of a difference.



In the top graph I've plotted delta-DO and delta-*p*H for the July 25<sup>th</sup> diel sampling. On the bottom I've converted pre-dawn and mid-afternoon *p*H readings to delta-*p*CO<sub>2</sub> values, i.e., looking directly at changes in  $CO_2$  – not simply using pH as an indicator of them. There is probably some improvement in matching the changes in  $CO_2$  with variations in DO, but not much. (I have to confess that I don't *actually* know today's ANC values, I've simply assumed them to be similar to those measured in 2003. New samples are currently being analyzed.) While there is some improvement for high ANC waters (VR06.3 and VR07), other locations have been made worse (e.g., VR01). Something else is obviously going on.

It turns out that changes in  $EpCO_2$  (i.e., delta- $CO_2$ ) is not as important to the *p*H variation as are the absolute values of carbon dioxide in solution. In the graph that follows I've plotted two changes in delta- $CO_2$ , each increase in  $EpCO_2$  being equal to 23, but beginning at different partial pressures: the one in black begins at an  $EpCO_2$  of 2, while the change shown in red begins at 12.



Note that the first increase produced a *p*H change of 0.98, while the second produced one less than 1/3 the magnitude (0.31). So while the overall ANC of water plays a role, the initial magnitude of its carbon dioxide concentration is a more important determinant. We see much smaller changes in *p*H at VR07 and VR06.3 mostly because these are locations with high concentrations of dissolved CO<sub>2</sub>. But that still doesn't answer why certain locations have these higher concentrations. High carbon dioxide concentrations typically arise from appreciable bacteriological respiration. Possibly from high organic carbon content (lots of substrate for bacteria to work on) or possibly from aquifer confinement (lots of time for bacteria to work).

High CO<sub>2</sub> at VR06.3 might derive from surfacing groundwater above this location, but similar, and even higher values, on San Antonio presumably have a different source (VR09 and VR10 have had the highest  $EpCO_2$  values in the past). The question of what might be causing changing relationships between DO and *p*H at highly varying sites like VR06 and VR15 also remains open. Are differences between VR06 and VR06.3 caused by the reduction in high concentrations of CO<sub>2</sub> with downstream flow? Or are they related to different source waters supplying flow at each site? Are the changes at VR15 being caused by increasing ANC and CO<sub>2</sub> provided by deeper groundwaters as the season progresses, or by increased organic carbon content (possibly from the earlier algal bloom) and warmer temperatures? Obviously, there's a lot we still don't know. Stay tuned.

I did forewarn you about reading this section.