Where Do the Nitrate Come From?
Part 2: Conductivity and Such

Conductivity

Water is one of the great solvents of the natural world, capable of dissolving a host of different solids. Many of these solids when put into solution carry an electrical charge. For example, chloride, nitrate and sulfate carry negative charges, while sodium, magnesium and calcium have positive charge. These dissolved substances increase water's *conductivity* – its ability to conduct electricity – so the conductivity of water indirectly measures the amount of dissolved solids (TDS) carried in solution. It's not a perfect measure because some dissolved substances, particularly organic compounds like alcohol or sugar, are very poor conductors.

Conductivity is measured in *siemens*: typically micro-siemens per centimeter (µS/cm) or milli-siemens per centimeter (mS/cm). Distilled water has a conductivity in the vicinity of 0.5 to 3 µS/cm; the conductivity of rivers in the United States generally ranges from 50 to 1500 µS/cm; and drinking water typically has to meet a standard of less than 1600 µS/cm – with a maximum total dissolved solids concentration of 1000 mg/L.

Conductivity in any particular stream can vary considerably, but it generally does so in a relatively predictable manner that, once established, can be used as a baseline for future comparisons. Conductivity typically decreases in winter when heavy rainfall and runoff increase the amount of fresh, lower-conductivity, water entering a stream: with greater flow mineral concentrations typically become more dilute. On the other hand, in late summer and fall, especially during periods of drought, dissolved solids become more concentrated (mostly because of increased evaporation), raising conductivity.

Conductivity in the Ventura watershed is relatively high; it is often above 1000 µS/cm because of high, and readily dissolvable, mineral content in the loosely consolidated marine sediments that form the coastal mountains of the upper watershed (and from the debris of these mountains that fills the basins). Generally, in Ventura streams, there is a trend of increasing conductivity during relatively dry years (years of below average rainfall) which is abruptly terminated – dropping to a much lower level – during a wet year. It's a pattern produced by the changing volume and age of groundwater inflows into those streams.

Figure 1 illustrates the pattern. The increasing trend on upper San Antonio Creek, from 2001 through 2004 and from 2005 until the present, was caused by a combination of factors: (1) aging and increasingly depleted groundwater inflows in the absence of a good runoff winter; (2) enhanced uptake by growing riparian vegetation in dry years, and (3) a relative increase in evaporation as dry-season flows diminished with the passage of time since the last big rainfall winter (i.e., the winters of 1997/98 and 2004/05). Conductivity in groundwater, everything else being equal, generally increases with age. The longer water is in contact with soil or geologic strata, the higher its conductivity: groundwater has higher conductivity than water in the soil, and older groundwater higher conductivity than younger.

The occasional sharp dip in the Figure 1 trend line indicates a sample taken during, or shortly after, a storm. Recent rain dramatically lowers conductivity; rainfall being about as young as water gets, with a conductivity in the Ventura area of around 20 µS/cm, and even though this increases as runoff moves by various pathways to the stream, conductivity still remains much

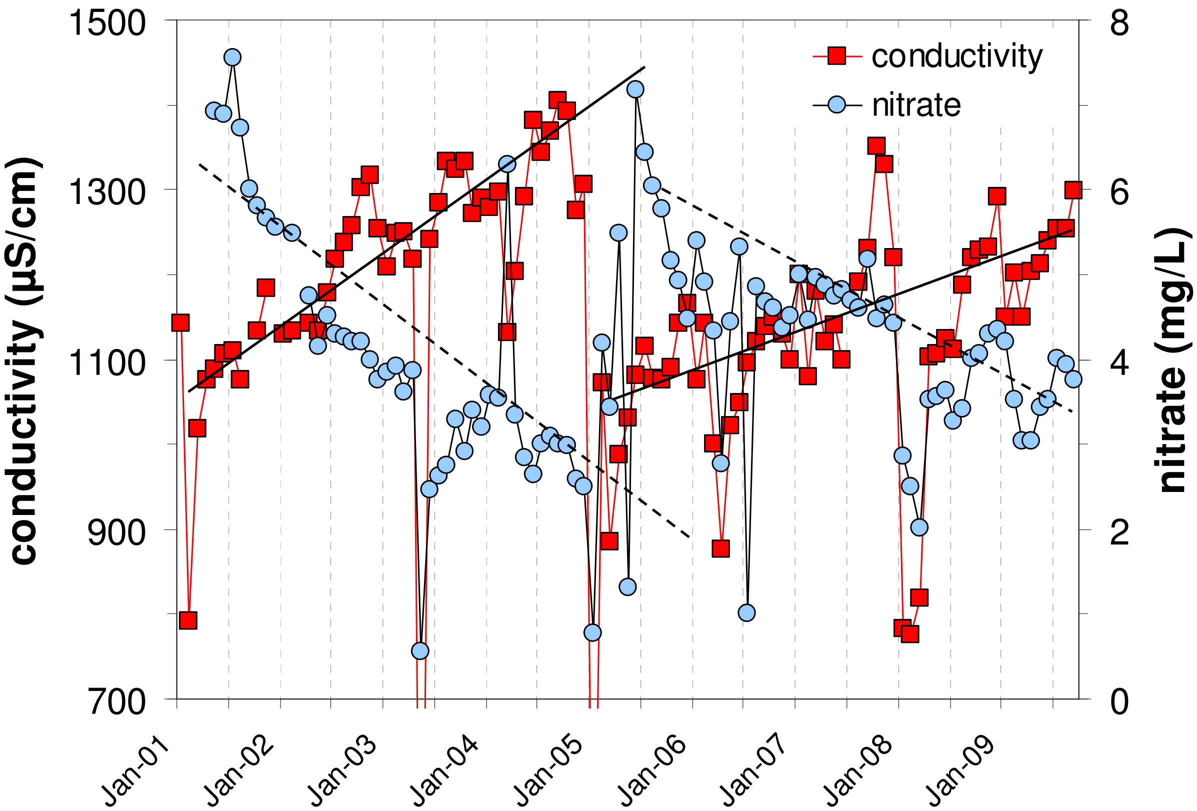

Figure 1. Monthly measurements of conductivity and nitrate concentration in upper San Antonio Creek: January 2001 through September 2008. The general conductivity pattern is one of continual increase during drier years, followed by an abrupt decrease during a big rainfall winter. The increase is caused by the gradual aging of the principal groundwater source feeding this stream, the sudden decrease by appreciable recharge by younger, lower-conductivity waters. Nitrate exhibits the opposite behavior: concentrations decreasing as groundwater ages, while newer recharge carries significantly higher nitrogen concentrations. (The lines on the graph are hand-drawn.)

lower during storms. The two measurements falling below the 700 µS/cm x-axis were made during the storms of May 3, 2003 (217 µS/cm) and January 8, 2005 (335). Sampling only once a month, Channelkeeper doesn't often manage to be out there during a storm, but it does occasionally happen. The other major deviation from the pattern is a gradual increase in conductivity during the last months of the dry-season, when evaporation has a greater than usual effect on very low flows. This is especially evident in years like 2002 and 2004 when winter rains came late, or barely came at all.

The graph also shows nitrate concentrations on upper San Antonio. They too exhibit a pattern, albeit a diametrically opposite one: nitrate decreasing as conductivity increases. But the cause is the same. Newly recharged groundwater, formed by recent rainfall moving vertically downward through soil, carrying along with it surface and near-surface deposits of nitrogen, is higher in nitrate than older water since, over time, nitrogen concentrations become biologically reduced – mostly uptaken or denitrified by bacteria.

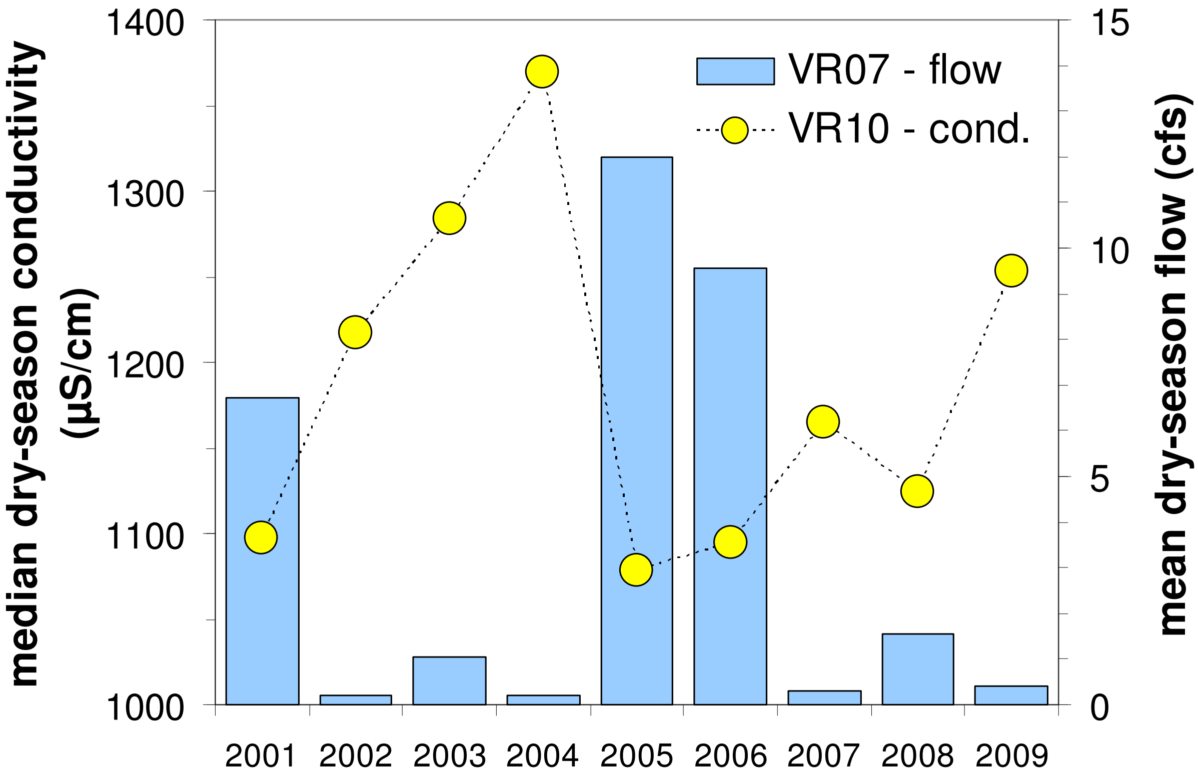

Figure 2. Median dry-season (May through September) standard conductivity on upper San Antonio Creek (VR10) are shown for 2001 through 2009 along with average dry-season flows measured at the County gauge (#605) on lower San Antonio Creek (the only gauged location on San Antonio Creek, SBCK sampling site VR07 is located just upstream).

Figure 2 makes the same point. Average dry-season data better show the pattern indicated by the hand-drawn lines in Figure 1 by smoothing out month-to-month variations and restricting conductivity measurements to the period when streamflow is dominated by inflowing groundwaters: conductivity increases in dry years (when low winter rainfall produces low dry-season flows) and decreases with significant increases in winter rainfall.

As mentioned earlier, this pattern is seen not only on the upper San Antonio but everywhere we find a clear groundwater signature in dry-season flow (the principal exceptions being locations where mixtures of waters from different origins occur, e.g., below the Ojai wastewater treatment plant). In Figure 3, I've added the annual variation in dry-season conductivity from both the North Fork (VR14) and mainstem (VR15) of Matilija Creek to that of upper San Antonio (VR10). If anything, the response in the upper Ventura watershed is even more sensitive to changes in flow, i.e., annual rainfall (exemplified here by flow measured at Foster Park – VR06). The Matilija exhibits an almost ideal correspondence between rainfall and conductivity: an increase in rainfall (i.e., reflected in increased summer flows) is followed by a decrease in conductivity (2003 & 2008), a lot more rainfall and the conductivity decrease is even greater (2001 & 2005).

So far, so good. Unfortunately, the correspondence between increasing conductivity and decreasing nitrogen is not as exact. In Figure 4, I've substituted nitrogen concentrations for the flow shown in

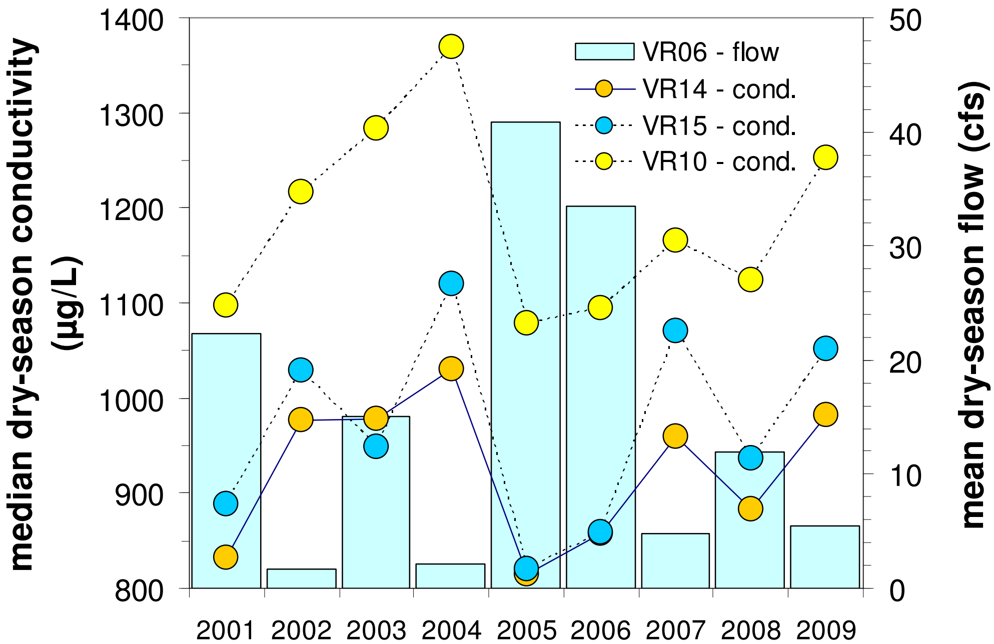

Figure 3. Median dry-season (May through September) standard conductivity on North Fork Matilija (VR14) and Matilija (VR15) creeks are added to that of upper San Antonio Creek (VR10): 2001 through 2009. Average dry-season flows were measured at the USGS Foster Park (VR06) gauge.

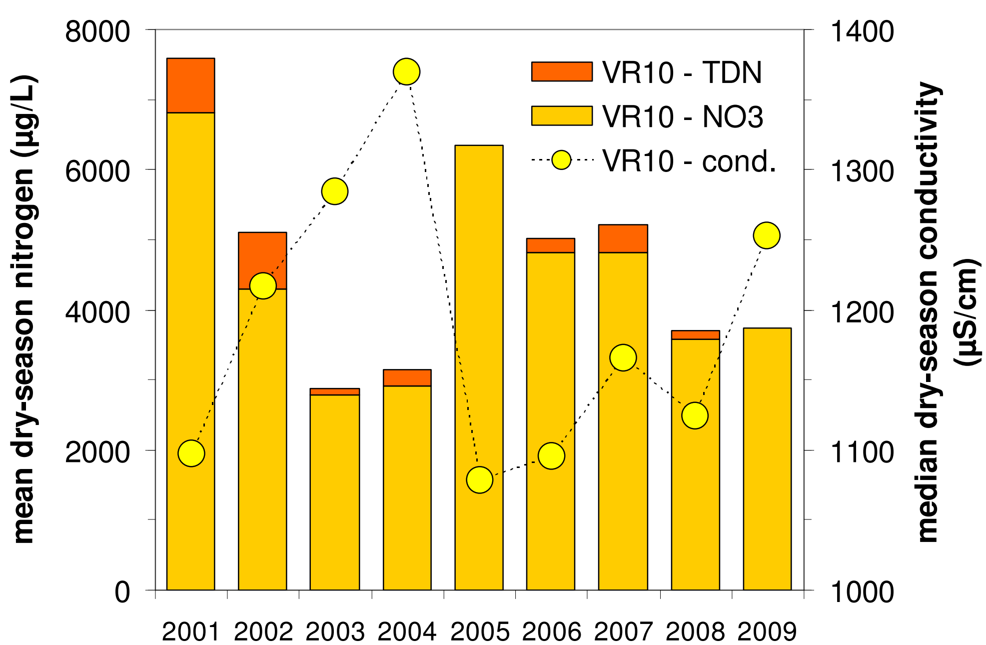

Figure 4. The annual variation in average dry-season nitrate and total dissolved nitrogen concentrations on upper San Antonio Creek are compared with median dry-season conductivity: 2001 through 2009. (TDN results are not yet available for 2009; in 2005 they were nearly identical with nitrate.) The expected annual variation is a decrease in nitrate as conductivity increases.

Figure 2. With increased rainfall and increased groundwater recharge we should see decreased conductivity and increased nitrogen concentrations in dry-season flows; in other words, an increase in conductivity from one year to the next should bring with it a decrease in nitrogen – as one goes up the other goes down. Figure 4 almost shows that, but not quite. The dry years of 2007 and 2009 showed no nitrogen decrease corresponding to the increase in conductivity. On the contrary, both years had higher than expected nitrogen concentrations. Similarly, nitrogen concentrations in 2003, a wetter year than either 2002 or 2004 (see Figure 3), appear to be abnormally low.

Nitrate and TDN are both shown in the graph to illustrate that nitrate is the dominant form of nitrogen at this location. (Assume that the red portion above each nitrate bar represents dissolved organic nitrogen (DON), the sum of nitrate and TDN being equal to TDN for purposes of this discussion. This is not exactly true since ammonium plays are role, but since ammonium concentrations on the Ventura are usually extremely low, the assumption is close enough.) As mentioned in Part I, nitrate in streamflow is continually being assimilated by plants, algae, and bacteria. which, in turn, release it back into the stream in the form of organic nitrogen when they senesce or die. TDN is therefore considered a better measure of available nitrogen than nitrate alone. However, different organisms turn over nitrogen at various rates – bacteria very rapidly, algae less so, and plants perhaps not until they are flushed downstream in winter storms – and appreciable available nitrogen may never be accounted for in measured concentrations.

At locations with high nitrate concentrations all this makes little difference, taking a little from a lot still leaves a lot. But at low-nitrate locations the difference between nitrate and TDN is often substantial, as is the amount of nitrogen being stored, albeit however temporarily, biologically. Since upper San Antonio Creek is a high-nitrate location with little algae (due to its narrow highly-shaded width) we must look elsewhere for a possible explanation of unexpectedly high nitrate in 2007 and 2009.

The most probable explanation is some relatively new, and recent, source of nitrate in the reach above the sampling point. That this anomaly was only noticeable in the two drought years since 2005, and was larger during the more severe drought of 2007, provides some evidence for this. Some leakage, either direct or via a shallow localized groundwater table, from over-irrigation of fertilized land – either agricultural or the upstream golf course – seems a logical source. On the other hand, with only five or less samples collected each dry-season, a single bad sample might be all the explanation required.

But back to my story: The upper graph in Figure 6 shows the same data as in Figure 5, but plotted as points on a semi-logarithmic graph. Yellow circles represent nitrate concentrations, but I've also shown TDN (as black dots) to demonstrate how little difference this measurement makes at a high nitrate site. The dashed regression line shows the expected variation ($R^2 = 0.68$): decreasing nitrate (or TDN) as conductivity increases. In the lower panel, I've added TDN data from N.F. Matilija Creek and Matilija Creek (above the dam). Note that the relationship is now contrary to expectation: nitrate is increasing with increasing conductivity.

So here's the case: We have an excellent relationship between conductivity and dry-season flow (or the previous winter's rainfall) for the two Matilija creeks. This indicates, among other things, a relatively small, shallow and responsive groundwater resource supplying flow to these streams. Dry seasons following wet winters should be characterized by large amounts of newly mobilized nitrogen – and, by and large, this is so, as evidenced by the extraordinary algal blooms of these years.

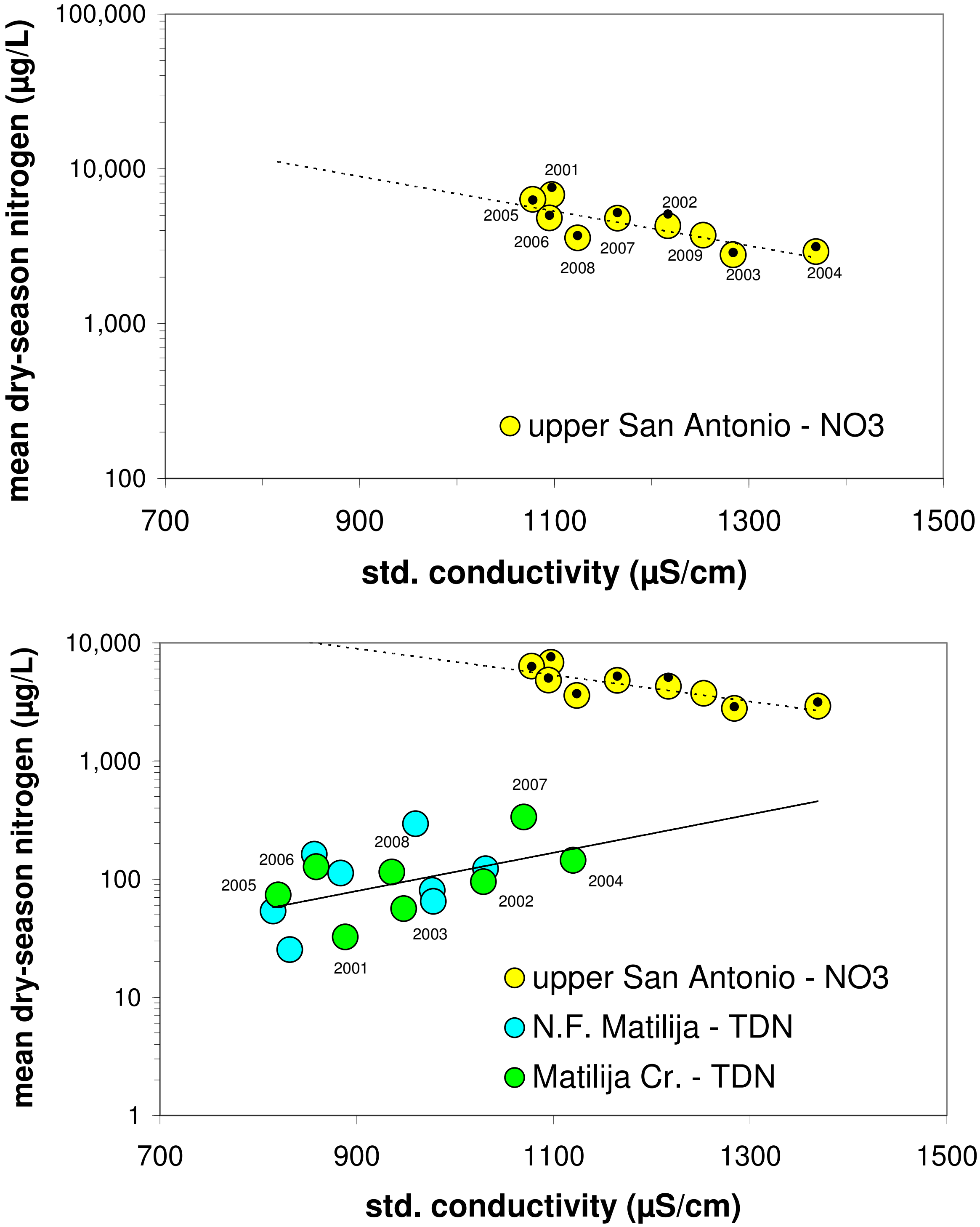

Figure 6. (upper) The annual variation in average dry-season nitrate (yellow circles) and total dissolved nitrogen (black dots) concentrations on upper San Antonio Creek are compared with median dry-season standard conductivity: 2001 through 2009. San Antonio exhibits the expected variation: a decrease in nitrate as conductivity increases. (lower) The same type data, but for Matilija and NF Matilija creeks, are added to the graph. Note how, contrary to expectation, TDN is increasing with increasing conductivity. Water-years for the respective data points are shown for San Antonio (top) and Matilija Creek (bottom)

However, in spite of this, TDN concentrations, averaged over the entire day-season, are actually higher in drought than in wet years. The explanation can only be the one given above for higher than expected nitrate in upper San Antonio Creek in the drought years of 2007 and 2009: there must be an additional source of nitrate beyond the normally expected wet-year groundwater pulse entering these streams. It's a small source (i.e., a small contribution), because it only becomes noticeable during the very low flows – and very low background nitrogen concentrations – of drought years, but a source nevertheless. In this case the additional nitrogen must be coming from the creek-side homes located along both streams. Probably from leach-field seepage, but fertilized landscaping remains an additional possibility. As Sherlock Holmes said, "Whenever you have eliminated the impossible, whatever remains, however improbable, must be the truth."

(Keep in mind, from Part I, the essential difference between concentration and flux: flux being the *amount* of nitrogen being supplied to a stream. It's high flux that grows algae. Drought year nitrogen concentrations on the Matilija may be higher than in wet years, but there is no such relationship between dry and wet year fluxes – flux being the product of concentration multiplied by flow. Quite the contrary, the wet-year flux on the Matilija being about 20-30 times what we see in a dry-year. Higher flow always means higher flux.)

Looking at Nitrogen and Phosphorus . . . Together

Examining both nutrients at the same time can provide insight into which land uses may be principal contributors to excessive concentrations seen on particular streams. What follows, however, is not rocket science. I will simply compare nutrient concentrations between sampling sites – some with well-defined upstream land uses, and others where the miscreants may be, as yet, unidentified – and draw some conclusions. The comparative data comes from both the Ventura and Goleta SBCK sampling programs, and a host of UCSB-LTER sampling sites monitored over the past ten years. LTER stands for Long Range Ecological Research and the project sampled, and continues to sample, nutrients – during storms and throughout the dry-season – on dozens of coastal streams between Gaviota Creek and the Ventura River.

In Figure 7, I've plotted average dry-season nutrient concentrations for 17 sampling sites on almost as many different streams. For some sampling locations, such as those in the SBCK Ventura program, we now have 10 years of data; for others, somewhat less (Bell Canyon – an agricultural stream flowing just east of the Bacara Resort in Goleta – has only 4 years of data; it's the only site shown with record this short). Thus the nitrogen values (nitrate and TDN) represent a mean dry-season concentration across a broad spectrum of years (i.e., 4 to 9 years) and annual rainfall differences. Phosphorus values (phosphate and TDP) only include data from 2005 to 2009 since results (samples are analyzed by the UCSB lab) prior to this time are unaccountably high (details are available in the UCSB-TMDL Report).

Sites in Figure 7 are arranged first in order of increasing total dissolved nitrogen (top) and then in order of increasing total dissolved phosphorus (bottom). For undeveloped, reasonably pristine, streams, total nitrogen is typically below 200 µg/L (0.2 mg/L); concentrations greater than 2000 µg/L (2 mg/L) usually indicate heavy agricultural use – row crops, orchards, grazing, etc. And anything over 10,000 µg/L (>10 mg/L), almost invariably, comes from intense commercial agriculture. Streams with nitrogen values between these limits – between 200 and 2,000 µg/L – are typically characterized by either urban, suburban or light agricultural development, or some mixture

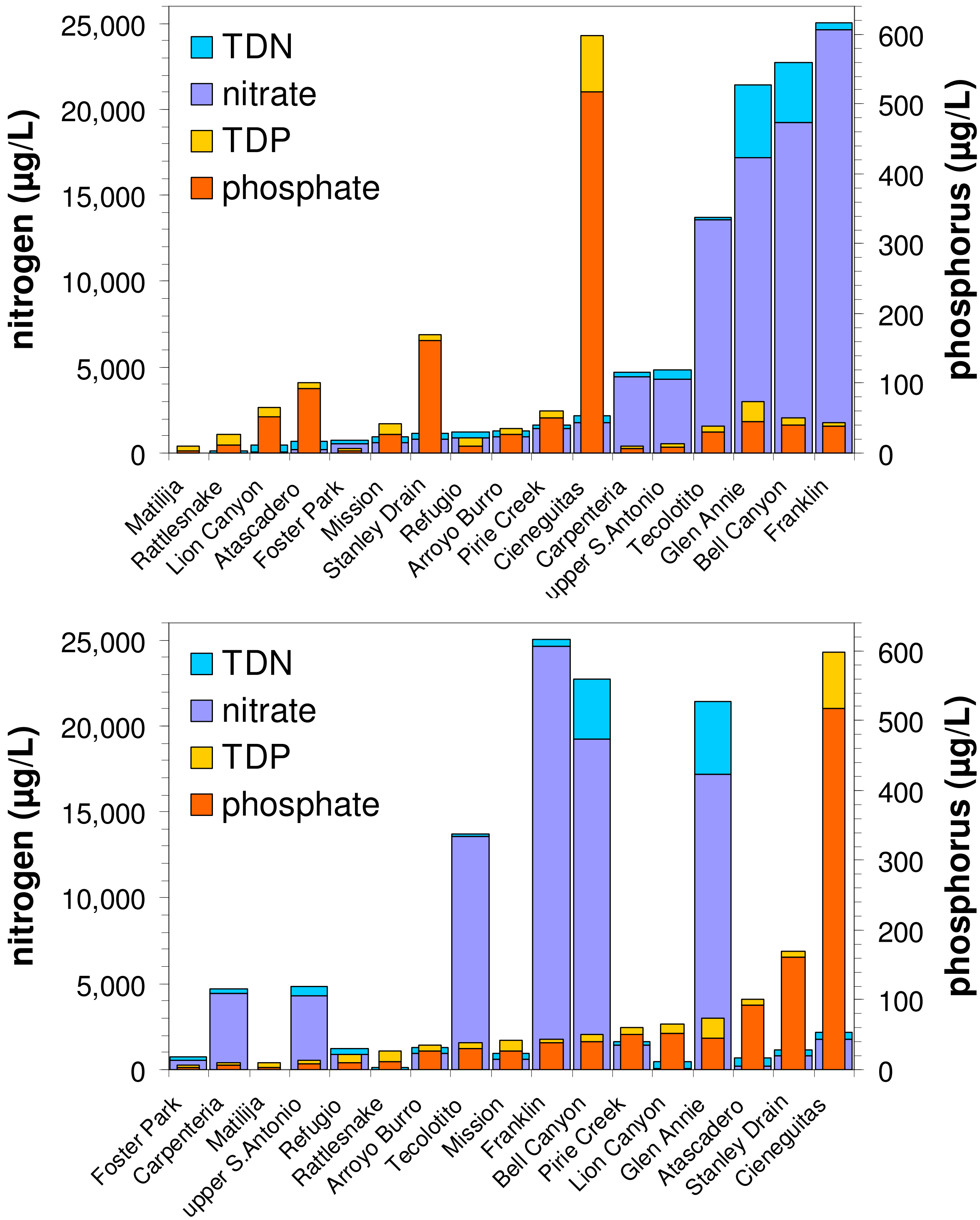

Figure 7. (upper) Average dry-season nutrient concentrations are shown for a wide assortment of SBCK and UCSB-LTER sampled streams. Data for each stream varies somewhat, but each was sampled for multiple years from 2001 through 2009. The nitrogen (TDN) excess over nitrate, and phosphorus (TDP) excess over phosphate, can be interpreted as the dissolved organic fractions. The steams are arranged in order of increasing nitrogen concentrations. (lower) Exactly the same data, but now arranged in order of increasing phosphorus concentration.

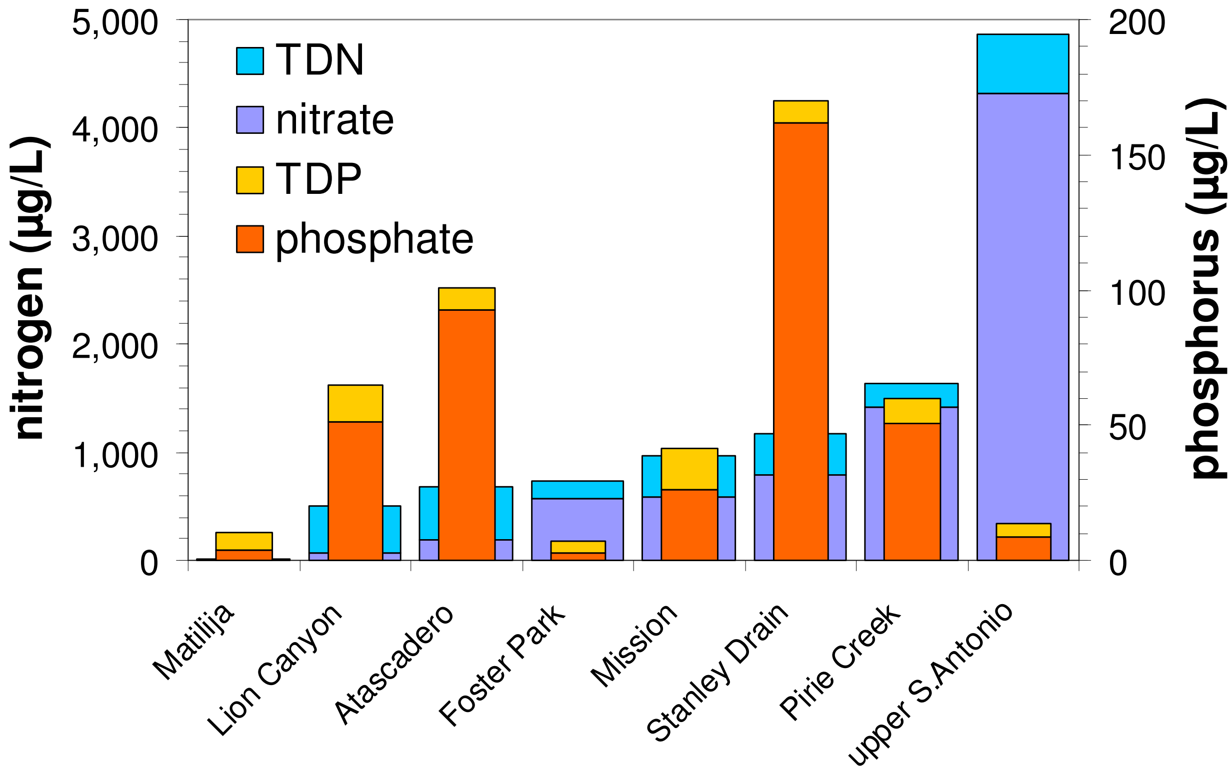

Figure 8. A subset of the streams shown in Figure 7, focused on San Antonio Creek sampling locations. Matilija Creek exemplifies an undeveloped, relatively pristine, Ventura watershed, whereas Foster Park resembles urban watersheds of Santa Barbara (e.g., Mission Creek) – except, perhaps, for relatively low phosphorus concentrations. Upper San Antonio Creek has a strong agricultural signature: very high nitrate but low phosphate concentrations. Pirie Creek, Lion Canyon and Atascadero Creek have notably higher phosphate. At Lion Canyon and Atascadero (and Cieneguitas in Figure 7) this is directly attributable to manure – horse or cattle manure – and we might reasonably assume that Pirie carries a similar signature. However, almost all mammalian excrement is high is phosphorus and high concentrations can also come from poorly performing septic tank leach fields – note the high phosphate concentrations from WWTP effluent at Stanley Drain, about 3 miles below the treatment plant (another example is Shell Road in Figure 7).

thereof.

The phosphorus story is not as clear-cut. We live in a region where local geology can contribute high phosphorus concentrations to local steams (much of our mountains consisting of recently piled-up seabed sediments, sediments relatively rich in this element). The difference between Rattlesnake and Matilija creeks, both relatively pristine watersheds, indicates a possible range of natural variation. On the other hand, extremely high phosphorus concentrations are predominately a product of manure or excrement. Cieneguitas, Atascadero and Lion Canyon have high phosphorus as a direct result of horse and cattle grazing (Lion) or horse corrals and stables (the other two).

Unlike nitrogen, there is typically a curious reversal between agricultural and urban/suburban land uses when it comes to phosphorus: streams dominated by commercial agriculture generally have much lower phosphate and phosphorus concentrations.

The reasons might be many (concentration of domestic animals for example), but it probably comes down to a more judicious choice of a suitable N/P/K ratio (with a focus on high nitrogen) and application rate on commercial agricultural land (for economic reasons; homeowners and hired gardeners tend to overuse the highest concentration, broad-spectrum, fertilizer they can find – cost being seldom a serious consideration). To me, a reasonable hierarchy of phosphorus contributions from various land uses would go something like this (from lowest to highest): undeveloped, commercial agricultural, urban/suburban and, finally, animal operations.

With both the nitrogen and phosphate hierarchical categorizations in mind, we can now take a look at the various San Antonio Creek sampling sites (Figure 8). Most easily seen is that upper San Antonio Creek bears a clear signature of agricultural land use: high nitrogen, especially nitrate (4,800 and 4,300 µg/L, respectively), and low phosphorus (14 µg/L, not all that different from Matilija Creek at 11 µg/L). Foster Park, although lower in both nitrogen and phosphorus (740 and 7 µg/L, respectively) also looks agricultural. The groundwater that gives Foster Park this dry-season character arises from an aquifer primarily located in western Ojai. Although concerns have been raised about possible pollution from cattle, horses, domestic animals, etc., along the middle Ventura, the nutrient chemistry at Foster Park (and above the San Antonio confluence) gives no indication of this. This doesn't mean that these uses don't contribute to the problem; it simply indicates that the agricultural signal is over-powering enough to overwhelm other contributions.

Figure 8 shows that Pirie Creek nutrient chemistry (sometimes called "Ojai Creek") is both different, and opposite, to that of upper San Antonio. It's high in phosphorus (60 µg/L) and high in nitrogen (1,640 µg/L), but not exceptionally so. To me, the phosphorus concentration is a clear sign of excrement. I'm calling it excrement instead of manure since it's not only animals that produce high phosphorus – lets not bandy words here – shit; humans do also. So while it could be animals it could also be also be domestic sewage from improperly sited or functioning septic tank/leach field systems. I've included dry-season concentrations from the Ventura River at Stanley Drain, located about 3 miles below the WWTP, in the figure to illustrate this point. During the summer, especially in dry years, treated effluent from the WWTP dominates the nutrient chemistry of the lower river and you can clearly see a high phosphate signal from what is mostly domestic sewage. Sewage treatment, even very effective sewage treatment, can only remove some of the incoming phosphorus.

High nitrate in Pirie may be coming from a number of possible sources. Urban and suburban gardening and landscaping being the most likely. However, it is possible that it may also be partly an artifact of a relative absence of algae. Atascadero, Cieneguitas and Lion Canyon, other streams mentioned earlier as bearing a dominant excrement signature (in their case, mostly from horse manure), nitrogen, and especially nitrate, concentrations are typically low because of open watersheds and low flow, i.e., lots of sunlight and warm water temperatures. Heavy algal growth frequently driving nitrate concentrations to zero. Pirie, in contrast, is a very shaded reach for quite some distance above the sampling point. Algal growth, even in what might be generally considered a very good algal year, is brief and never overwhelming. Less algae, i.e., less biological uptake, means more residual nitrogen remaining in the stream.

I did say this wasn't rocket science.

Finally, in answer to a request from Scott, I've included Figure 9 in which I've taken the TDN and TDP concentrations shown in Figure 7, converted them to µmoles and divided one by the other, and displayed the molar N:P ratio for each steam; I've done the same with nitrate and phosphate and have shown that as a nitrate:phosphate ratio.

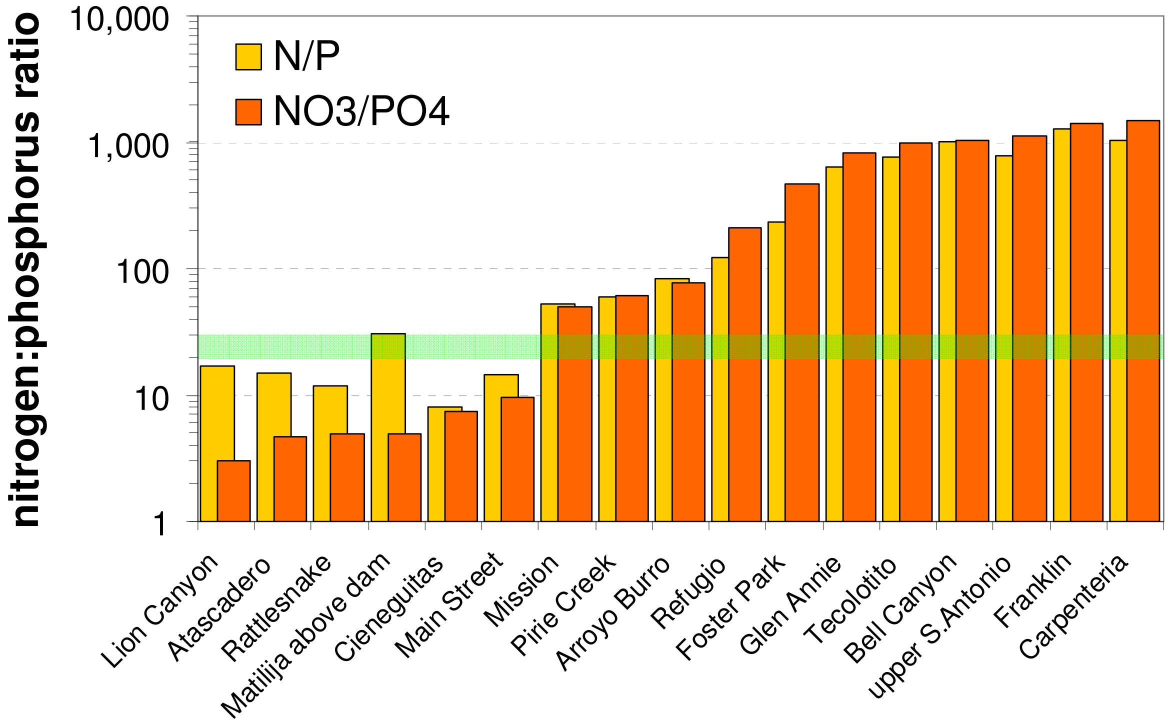

Figure 8. Dry-season molar N:P ratios for the streams shown in Figure 7 (expressed as both TDN/TDP and nitrate/phosphate). I've shown the ratios on a logarithmic scale since the range is so great. The green-band indicates ratios in the range of 20-30; ratios in this range are generally regarded a providing a balanced diet for primary producing freshwater organisms. This can be considered analogous to the 16:1 Redfield Ratio for oceanic phytoplankton. Ratios above this range indicate an excess of nitrogen over phosphorus, ratios below indicate the opposite

The green band on the chart indicates nutrient balance; streams with nutrient ratios in this range are offering a suitable mix for freshwater primary producers (analogous to the 16:1 Redfield Ratio for oceanic phytoplankton). Streams with excessive nitrogen fall above the band, those with excessive phosphorus fall below. These data can also be interpreted as indicating which nutrient potentially limits algal growth: phosphorus above the band, nitrogen below. The key word is "*potential*." *Potentially* limiting doesn't mean actually limiting. Actual concentrations may be high enough, as they are for almost all the agricultural streams shown on the chart, as to *never* limit growth. And algae need more than nutrients, they need sunlight and often some highly particular growing conditions. Things like water temperature and current speed and suitable substrate are important – and often limiting. Even the absence of things, like potential predators (or at least, low numbers of them) can be critical. Algae, like everything else in the biological universe, have enemies.

That said, we do see nutrient limitation in the Ventura watershed, mainly in the aforementioned open-to-sunlight, manure dominated, streams, and often on the lower Ventura at Main Street and on lower San Antonio Creek, where nitrate concentrations can be driven to zero for a month or so, usually during low-rainfall years.

I've been thinking about predation lately. My former research partner, Julie Simpson (we did an intensive algal study on the lower Ventura back in 2003) mentioned, at the start of the TMDL process

Figure 9. I was struck last Saturday by the relative absence of algae at Foster Park and the sites further below (at the Canada Larga confluence and Main Street). This is a photo montage of algal conditions during (or near) August in 2008, 2009 and 2010: (top), from left to right, July 25 and September 6, 2008; (middle) August 1, 2009; and (bottom) August 7, 2010. The left-hand photos show the view just upstream of the bridge, the right-hand photos show downstream conditions just below the bridge. What little algae were present consisted solely of small amounts of trapped Enteromorpha and some crustal critters. Most suprising was a total absence of Spirogyra, usually abundant below the bridge (e.g., in 2008 & 2009). Cladophora appeared to be totally absent. Conditions just above the Canada Larga confluence were almost exactly the same.

, that this might be an important consideration. And not to forget about it. We sometimes see sites, with seemingly good conditions for algal growth, having damn few algae. And this month I'm beginning to see a lot of them. I've included Figure 9 to show what I mean. In it are upstream and downstream photos of August (or reasonably close to August) algal conditions at Foster Park in 2008, 2009 and 2010.

Last Saturday (August 7) I could find no Cladophora and very little other algae, just some trapped Enteromorpha and – of all things – crustal algae growing on some cobbles. (Crustal algae are usually seen only at the very beginning of the algal season.) Cladophora are often still vibrant at this location until late in the season, and Spirogyra, usually coming into its own and making a big show at this time, also appeared to be totally absent. Even trapped Enteromorpha were few and far between. Similar conditions prevailed just above the Canada Larga confluence and at Main Street. I also saw no sign of dead Cladophora.

Sunshine, cobbles, warm temperatures, a variety of flow conditions, nutrients – but no algae. Something other than the Regional Water Quality Control Board must not like algae, or perhaps likes it far too much. The thought here being that predator populations (or since algae, if not plants, are plant-like, we might think "grazers," but then there are also various parasites and disease organisms) always start a step behind, but usually catch up and often cause a catastrophic crash in prey abundance, followed, of course, by a crash in their own numbers.

Storms in the winter of 2007-08 set the clock for the big algal season that followed. But the winter of 2008-09 was without a major storm and things picked up pretty much where they left off the year before. As discussed in the latest diel report, flows this summer are almost identical to those of 2008, but the storms of the past winter were much milder – the biggest storm of 2008 causing an average daily flow of 6,340 cfs vs. 687 cfs this year. It could be that predator populations, given two mild winters in a row, have had more than enough time to catch up. Meanwhile, up on the Matilija, the late season Mougeotia bloom has made it's usual appearance and is still going strong. But late winter stormflows in the upper watershed were considerably stronger than those experienced below.

It's worth thinking about.

Back in 2003, Julie and me thought the absence of late-season Cladophora at Shell Road, during an impressive second bloom at Foster Park, might be blamed on something untoward coming out of the treatment plant. I might need to apologize.